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

Some Further Solid Solutions of Picromerites, at 25°[1]

BY ARTHUR E. HILL, GLENN C. SOTH AND JOHN E. RICCI

In continuation of the study, through equilibrium solubility measurements, of the distribution of isomorphous salts between liquid phases and saturating solid solutions, a further series of ternary systems consisting of water and a pair of double salts of the picromerite series has been investigated, at the temperature of 25°. The data so obtained are being used to test the applicability of thermodynamic relationships to the distribution ratio of these salts between liquid and solid phases. The general purpose and the experimental procedure involved have been discussed in preceding articles, reporting similar studies on a number of alum pairs,[2] which form very nearly ideal solid solutions in their mixed crystals, and also on a number of picromerite systems.[3] As in these preceding investigations, careful attention was given to the question of attainment of complete equilibrium. Wherever solubility determinations involved the formation of a solid solution of two salts, A and B, as saturating phase, the final equilibrium was obtained from two directions, two complexes of the same total composition being prepared in each case, one starting with excess of salt A, the other with salt B, as the initial solid phase. Agreement between the two complexes, in respect to both liquid and solid compositions, proves the attainment of equilibrium.

The present report covers the experimental investigation of the equilibrium relations of four pairs of picromerites studied as ternary systems with water at 25°. The picromerites, like the alums, offer the possibility of variation in respect to both cations and anions. This series of isomorphous salts takes its name from the naturally occurring salt $MgK_2(SO_4)_2 \cdot 6H_2O$ which is known as "picromerite" and less frequently as "schoenite." Although the name "picromerite" is usually restricted to the monoclinic hexahydrated double sulfates (Winchell[4]), it seems allowable to use the name for the isomorphous and analogous chromates and selenates. The general formula for the picromerite type would seem to be, then, $M^{++}N^{+}_2(RO_4^{=})_2 \cdot 6H_2O$, in which M^{++} may be Mg, Mn, Ni, Co, Fe (-ous), Cu, Zn or Cd, N^+ may be K, Rb, Cs, Tl or NH_4, and R may be S, Se, Te or Cr, although by no means all the possible combinations are actually known. The present study covers three systems in which the anion was varied: I, $Mg(NH_4)_2(CrO_4)_2$–$Mg(NH_4)_2(SO_4)_2$–H_2O; II, $Mg(NH_4)_2(SO_4)_2$–$Mg(NH_4)_2(SeO_4)_2$–H_2O; III, $Mg(NH_4)_2(CrO_4)_2$–$Mg(NH_4)_2(SeO_4)_2$–H_2O; and one system involving a pair of selenates in which the univalent cation was varied: IV, $Mg(NH_4)_2(SeO_4)_2$–$MgK_2(SeO_4)_2$–H_2O. Complete miscibility of the two picromerites in the solid state, at 25°, was found in every case. In connection with the preparation of two of these picromerites, the ternary systems $MgCrO_4$–$(NH_4)_2CrO_4$–H_2O and $MgSeO_4$–K_2SeO_4–H_2O were also investigated, at 25°, to determine the relationships involved in the formation and crystallization of the double salts.

The determinations involved in all cases the preparation of complexes of known, exact composition, rotation in a thermostat, for periods of one to six weeks, to allow the attainment of equilibrium, and analysis, at equilibrium, of the filtered liquid phase. In the two systems involving simply the formation of a double salt, the solid phase was not directly analyzed, but was determined by the method of algebraic extrapolation of tie-lines through the total compositions (complexes) and the compositions of the liquid solutions.[5] In the systems involving formation of solid solutions, the solid phases were all analyzed completely, after centrifuging and air-drying (since the salts involved in the systems are all known to be stable in air at room temperature); the only error in this analysis was a very slight one resulting from crystallization of salts from traces of residual mother liquor. In addition the consistency and accuracy of the work were checked by comparing the compositions of solid phases derived by analysis, with the course of the tie-lines involved, calculated by algebraic extrapolation.

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[1] This paper is being published, following the death of Professor Hill, by his collaborators. The material of the paper is taken from part of a thesis presented for the degree of Doctor of Philosophy at New York University, June, 1940, by G. C. Soth.

[2] (a) Hill and Kaplan, THIS JOURNAL, **60**, 550 (1938); (b) Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).

[3] (a) Hill and Taylor, *ibid.*, **60**, 1099 (1938); (b) Hill, Durham and Ricci, *ibid.*, **62**, 1031 (1940).

[4] Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, New York, N. Y., 1931, p. 239.

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

Formation of the Double Salt $Mg(NH_4)_2(CrO_4)_2 \cdot 6H_2O$: System $MgCrO_4$–$(NH_4)_2CrO_4$–H_2O at 25°.—The double salt $Mg(NH_4)_2(CrO_4)_2 \cdot 6H_2O$ had been prepared by several investigators,[6] but the ternary system for the relations of the double salt to its components had not previously been studied. The 25° isotherm was therefore determined, for the solubility and the limits of formation of the double salt. The preparation and purification of the salts $MgCrO_4$ and $(NH_4)_2CrO_4$ required for the study have been described in connection with the study of the binary systems involving these separate salts and water.[7] The ternary solutions in the present work were analyzed for total chromate and ammonia, the former by the usual iodometric method, the latter by distillation into standard acid and titration of the excess acid. The solid phases were not analyzed, but the composition of the double salt is very easily established by the tie-lines on the isothermal ternary diagram; the accuracy of the total procedure, and the attainment of equilibrium, were checked by the algebraic extrapolation of tie-lines to the composition of the double salt, which gave an average error, based on the extrapolations, of only 0.52% in respect to $(NH_4)_2CrO_4$.

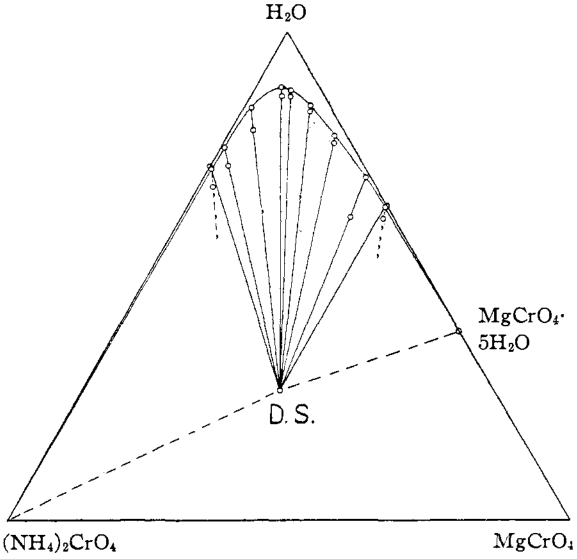

Fig. 1.—System $MgCrO_4$–$(NH_4)_2CrO_4$–H_2O at 25°; D. S. = $Mg(NH_4)_2(CrO_4)_2 \cdot 6H_2O$.

TABLE I

SYSTEM $MgCrO_4$–$(NH_4)_2CrO_4$–H_2O AT 25°

Original complex, wt. %		Liquid phase, wt. %		Solid phase
$MgCrO_4$	$(NH_4)_2$-CrO_4	$MgCrO_4$	$(NH_4)_2$-CrO_4	
0.00	...	0.00	27.02	$(NH_4)_2CrO_4$
2.53	28.99	.36	27.02	$(NH_4)_2CrO_4$ + D. S.[a]
3.17	24.03	.53	22.81	D. S.
3.96	15.93	1.25	14.02	D. S.
5.50	7.50	4.62	6.64	D. S.
7.10	6.02	6.52	5.31	D. S.
12.13	3.99	11.71	3.39	D. S.
19.70	3.07	19.21	1.95	D. S.
29.97	7.55	28.81	0.85	D. S.
35.92	2.00	35.20	0.41	D. S. + $MgCrO_4 \cdot 5H_2O$
...	0.00	35.39	0.00	$MgCrO_4 \cdot 5H_2O$

[a] D. S. = $Mg(NH_4)_2(CrO_4)_2 \cdot 6H_2O$.

The results are given in Table I and shown in the usual triangular diagram in Fig. 1. The double salt is congruently soluble at this temperature, and is formed as solid phase over almost the whole range of concentration. The solubility curves for the single components are too small for actual representation, but the solid phases involved are known from actual analysis and from related studies to be $MgCrO_4 \cdot 5H_2O$[7] and anhydrous $(NH_4)_2CrO_4$.[8] Separate determinations were made for the solubility of the double salt, by using the pure double salt itself as the starting material. Equilibrium was assured by approach from both super- and undersaturation. The result averaged from both directions was 11.50 wt. per cent. of anhydrous salt; density of the saturated solution, 1.088; molar solubility, 0.4279; no other determinations are found in the literature for comparison with this value. The salt used for the determination was prepared by precipitation from a mixture of hot saturated solutions of the component salts and cooling to room temperature, with continuous stirring. The stirring was maintained for eighteen hours to ensure complete hydration of the solid phase. The crystals, separated by suction, centrifuged, and air-dried for forty-eight hours, were kept in a desiccator over some partly dehydrated salt. Analysis based on both chromate and ammonia determinations showed a purity of 100.0 ± 0.1% calculated as the hexahydrated double salt.

Formation of the Double Salt $MgK_2(SeO_4)_2 \cdot 6H_2O$: System $MgSeO_4$–K_2SeO_4–H_2O at 25°.—A study of this system at 25° was made by Meyer and Aulich.[9] Their results, however, appeared to be incomplete and inconsistent, both internally and in comparison with the work of others on

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[6] (a) Porter, *Proc. Roy. Soc.* (London), **109A**, 78 (1925); (b) Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., London, 1923, p. 275.

[7] Hill, Soth and Ricci, THIS JOURNAL, **62**, 2131 (1940).

[8] Schreinemakers, *Z. physik. Chem.*, **55**, 71 (1906).

[9] Meyer and Aulich, *Z. anorg. Chem.*, **172**, 321 (1928).

related systems of selenates. No proof was given for the attainment of equilibrium, and, without the compositions for the total complexes, a check on accuracy and equilibrium through algebraic extrapolation of tie-lines was not possible. While they reported the double salt to be incongruently soluble, no mention of incongruent solubility was made by Tutton,[10] who also prepared this double salt. The solubility curve appeared further to be anomalous in several respects, and finally the solubility reported by these authors for magnesium selenate at various temperatures seemed to be in grave disagreement with the value obtained by Lawrence and King at 30°.[11] A repetition of the 25° isotherm was therefore necessary, for accurate information.

The starting material for the preparation of the selenates required both for this system and for the system involving solid solutions, was powdered metallic selenium. The element was converted to selenic acid according to the method of Gilbertson and King,[12] which involves oxidation to selenious acid by solution in concentrated nitric acid, sublimation of the selenium dioxide from the residue after evaporation to dryness, and finally oxidation to selenic acid with 30% hydrogen peroxide, the final solution being concentrated to a moderate extent by evaporation of water under reduced pressure. Although selenium dioxide is a relatively common reagent and its purification by sublimation is often mentioned in the literature, no description of a procedure for the effective purification of considerable amounts was found. A simple method[13] is here described therefore which may be used to prepare sublimed selenium dioxide in relatively large quantities.

A nitric acid solution of selenium containing about 150 g. of dissolved selenium is placed in a deep liter casserole and covered with a watch glass, convex side up. The solution is evaporated to dryness, leaving the selenium dioxide in the form of a hard cake. As the heating is continued, on a small flame, the selenium dioxide sublimes from the lower side of the cake onto the sides of the casserole and the upper part of the cake. Most of the material is deposited as needle-like crystals on the upper surface of the cake, very little of it appearing on the sides of the casserole and scarcely any on the watch glass. When a reasonable amount of sublimate has been formed, the casserole is allowed to cool and the sublimed product scraped off, care being taken not to disturb the residual underlying cake. A further crop can be obtained by adding a little nitric acid to the residue and repeating the process. The best results are obtained when about one-half of the selenium dioxide is sublimed at a time. Unless more nitric acid is then added to the residue before repeating the process, the sublimate becomes pink, indicating some decomposition to elementary selenium.

Magnesium selenate was prepared by neutralization of the prepared selenic acid with magnesium oxide, concentration of the filtered, slightly acid solution to saturation, by boiling, cooling to room temperature with continuous stirring, filtering and centrifuging of the crystals. The product was recrystallized from hot solution, centrifuged again and air-dried; kept over partly dehydrated material, the salt proved on analysis to be pure hexahydrated magnesium selenate (100.0 ± 0.1% by determination for both magnesium and selenate).

Potassium selenate was prepared by a similar procedure, except that the selenic acid was neutralized with potassium hydroxide pellets, and the salt was crystallized from a slightly basic solution. The final pure anhydrous potassium selenate was preserved in a desiccator over solid potassium hydroxide.

The ternary solutions were analyzed by determination of magnesium and of selenate. Magnesium was determined by Berg's method, using the procedure of Kolthoff and Furman[14]: precipitation with 8-hydroxyquinoline and titration of the precipitate with standard potassium bromate solution, using indigo sulfonic acid as indicator. The analytical method used for the determination of selenate has been described elsewhere, being an improvement of the volumetric method first suggested by Pettersson and extensively studied by Gooch.[15] It involves reduction of the selenate to selenite by means of hydrogen bromide, distillation of the liberated bromine into excess of potassium iodide solution, and titration of the equivalent iodine with standard sodium thiosulfate solution.

TABLE II

SYSTEM $MgSeO_4$–K_2SeO_4–H_2O AT 25°

No.	Original complex, wt. % $MgSeO_4$	Original complex, wt. % K_2SeO_4	Liquid phase, wt. % $MgSeO_4$	Liquid phase, wt. % K_2SeO_4	Solid phase
1	0.00	...	0.00	53.26	K_2SeO_4
2	2.98	59.96	.191	52.82	K_2SeO_4 + D. S.[a]
3	6.98	51.95	.191	52.94	K_2SeO_4 + D. S.
4	4.6	50.0	.35	50.48	D. S.
5	6.00	41.99	1.52	41.54	D. S.
6	9.97	31.92	5.68	29.55	D. S.
7	16.99	22.45	13.91	18.30	D. S.
8	21.80	16.86	20.04	12.76	D. S.
9	25.04	14.02	24.08	9.79	D. S.
10	31.07	5.99	31.11	5.77	D. S.
11	37.30	11.02	34.33	3.52	D. S. + $MgSeO_4 \cdot 6H_2O$
12	40.30	7.05	34.42	3.63	D. S. + $MgSeO_4 \cdot 6H_2O$
13	...	0.00	35.74	...	$MgSeO_4 \cdot 6H_2O$

[a] D. S. = $MgK_2(SeO_4)_2 \cdot 6H_2O$.

The results of the measurements in the ternary system are given in Table II and Fig. 2. The simple component salts of this system are known to be anhydrous K_2SeO_4 and the hydrate $MgSeO_4 \cdot$

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(10) Tutton, *Trans. Roy. Soc.* (London), **A197**, 255 (1901).

(11) Lawrence and King, THIS JOURNAL, **60**, 1987 (1938).

(12) Gilbertson and King, *ibid.*, **58**, 180 (1936).

(13) This is a slight modification of Lenher's procedure, *ibid.*, **20**, 559 (1898), which has since been re-described in "Inorganic Syntheses," H. S. Booth, Editor, Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 120.

(14) Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1929, p. 483.

(15) Soth and Ricci, *Ind. Eng. Chem., Anal. Ed.*, **12**, 328 (1940).

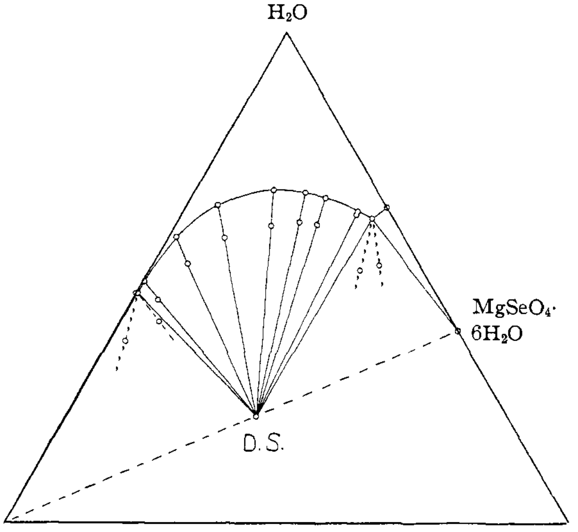

Fig. 2.—System $MgSeO_4$–K_2SeO_4–H_2O at 25°; D. S. = $MgK_2(SeO_4)_2\cdot 6H_2O$.

$6H_2O$. The curve for the solubility of the double salt covers almost the entire diagram, as is characteristic for most of the picromerite double salts. Again the composition of the double salt is evident from the diagram; algebraic extrapolation of the tie-lines to the point representing the composition of the double salt gives an average error of 0.46% in respect to K_2SeO_4.

The solubility of the picromerite, which is congruently soluble, is given by complex no. 7, which was made up exactly for the composition of the double salt: 32.21% by weight of anhydrous double salt; density of saturated solution, 1.319; molar solubility, 1.094. No other determination is found in the literature for comparison.

The solubility of magnesium selenate in water was determined by both selenate and magnesium analysis, and from both directions of approach toward equilibrium. The average obtained from all determinations, as given in the accompanying summary, is quite different from the figure given by Meyer and Aulich.[9] The value at 30°, reported by Lawrence and King,[11] also differs considerably from the figure of Meyer and Aulich at that temperature. It appears that the entire study by Meyer and Aulich of the solubility of magnesium selenate in water from 0 to 75° may be incorrect, possibly due to the use of an impure salt.

Temp., °C.		Solubility, wt. % $MgSeO_4$ Supersatn.	Undersatn.	Av.
25	Selenate determination	35.73	35.56	
	Mg determination	35.76	35.74	35.70
	Meyer and Aulich[9]			27.5
30	Lawrence and King[11]			36.60
	Meyer and Aulich[9]			31.2

The solubility of potassium selenate, on the other hand, 53.26%, averaged from the values 53.23 and 53.29% from super- and undersaturation, respectively, is in good agreement with the determination of Meyer and Aulich, 53.3%.

System I. Magnesium Ammonium Chromate–Magnesium Ammonium Sulfate–Water, at 25°.—Both of the salts forming the solid components of this system are congruently soluble in water at room temperature. The double chromate was prepared as described above under the system magnesium chromate–ammonium chromate–water. The double sulfate was prepared as described in previous publications,[3b] from "analyzed" grade ammonium sulfate and heptahydrated magnesium sulfate and purified by recrystallization.

The only study of this system found in the literature is that of Porter,[6a] involving an examination of the change in the optical properties of the solid solutions formed as a function of the composition. The distribution reported for the components between the liquid and solid phases, presumably at room temperature, appeared however to be inaccurate, and there was no evidence of equilibrium. As already stated, exact complexes were made in duplicate, for the present study, to ensure equilibrium and to allow a check on the general accuracy by means of algebraic extrapolation. The analysis of the liquid and solid phases at equilibrium was made by determination of total ammonia and of chromate. The results are given in Table III, which includes the data for the remaining systems discussed below; the table is self-explanatory. Continuous solid solution is found over the whole range of compositions. The average deviation between the observed and extrapolated compositions of the solid phase was 0.50%, in terms of the chromate. The solubility of the double sulfate, $Mg(NH_4)_2(SO_4)_2\cdot 6H_2O$, 16.58%, averaged from the values 16.59 from supersaturation and 16.57 from undersaturation, is based on determination of ammonia, and agrees well with recent values.[3b]

System II. Magnesium Ammonium Sulfate–Magnesium Ammonium Selenate–Water at 25°.—Although the two components of this system have been reported by Tutton[10] to be isomorphous as the hexahydrates, there has been no study of the extent of solid solution formation between them. On the basis of the study by Lawrence and King[11] of the system magnesium selenate–ammonium selenate–water at 30 and 60°, indicating congruent solubility for the double selenate at both temperatures, the double salt was prepared in the usual manner, by combining hot saturated solutions of the simple salts and cooling to room temperature to precipitate the picromerite, as described above for magnesium ammonium chromate; the salt was finally preserved in a desiccator over partly dehydrated salt.

The equilibrium liquid and solid phases of the ternary system were analyzed by determination of total ammonia and of selenate by the methods already stated. The results are given in Table III. The average error, in respect to the selenate double salt, between the composition of the solid phases as determined by analysis, and the algebraic extrapolation of the tie-lines, was 0.40% in this system.

The solubility of the double selenate, $Mg(NH_4)_2(SeO_4)_2 \cdot 6H_2O$ at 25° was found to be 23.31% $Mg(NH_4)_2(SeO_4)_2$, by ammonia determination, from both super- and undersaturation; density, 1.202; molar solubility, 0.8278. The only figure in the literature, for comparison, is one at 30°, interpolated from the data of Lawrence and King,[11] of about 24%.

System III. Magnesium Ammonium Chromate–Magnesium Ammonium Selenate–Water at 25°.—No previous study of this system is to be found in the literature. The analytical method used for both liquid and solid phases at equilibrium was the determination of total ammonia and of chromate. It was found that the presence of selenate does not interfere with the iodometric determination of chromate under the experimental conditions used. The data for the system are given in Table III; the average extrapolation error was found to be 0.51% in respect to $Mg(NH_4)_2(CrO_4)_2$, in the solid phase.

System IV. Magnesium Ammonium Selenate–Magnesium Potassium Selenate–Water at 25°.—In this system the univalent cation is being interchanged in the formation of the mixed crystals. The preparation of the salts involved already has been described. The composition of the equilibrium phases was determined by analysis for total selenate and for ammonia. The data appear in Table III; the average error of extrapolation was 0.75%, in terms of $MgK_2(SeO_4)_2$.

Distribution between Liquid Solution and Solid Solution.—The data for the above systems involving solid solutions have been recalculated in terms of the mole fractions of the two component salts in the liquid and solid phases, omitting the water in each, for the purpose of classification of the systems on the basis of Roozeboom's types of solid solutions.[16] Representing by Y the mole fraction of the more soluble picromerite in the liquid phase and by X its mole fraction in the solid phase, and plotting Y against X, gives the usual Roozeboom type of rectangular diagram for the distribution. The values of X and Y for the present systems are listed in Table IV, and the resulting curves are shown in Fig. 3. When Y is always greater than X, the system belongs to Type I of Roozeboom's classification; when Y is greater than X for part of the range and becomes smaller than X as both X and Y approach 1, as is apparently the case for the first two systems here reported, the distribution is that of Roozeboom's Type II. While only the curve of System II (magnesium ammonium sulfate and selenate) definitely crosses the diagonal of the diagram, indicating unquestionably Type II for

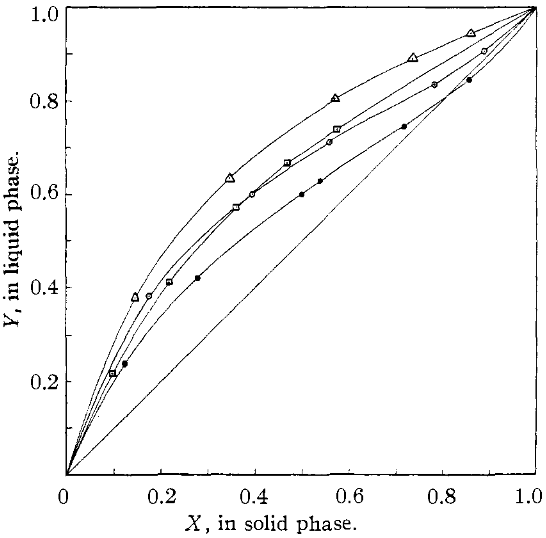

Fig. 3.—Distribution of picromerites between aqueous solution and solid solution at 25°: System 1 (○), $Mg(NH_4)_2(SO_4)_2$ in $Mg(NH_4)_2(CrO_4)_2$–$Mg(NH_4)_2(SO_4)_2$; System II (●), $Mg(NH_4)_2(SeO_4)_2$ in $Mg(NH_4)_2(SeO_4)_2$–$Mg(NH_4)_2(SO_4)_2$; System III (△), $Mg(NH_4)_2(SeO_4)_2$ in $Mg(NH_4)_2(SeO_4)_2$–$Mg(NH_4)_2(CrO_4)_2$; System IV (□), $MgK_2(SeO_4)_2$ in $MgK_2(SeO_4)_2$–$Mg(NH_4)_2(SeO_4)_2$.

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[16] Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

the system, it must be noted that the data are not sufficiently exhaustive to rule out the possibility of all the curves crossing the diagonal near the extremities of the figure. Systems of Type I require the formation of ideal solid solutions between the component isomorphous salts. The change to Types II and III occurs with increasing tendency to non-ideality in the solid phase. Systems in which the two salts have a tendency toward incomplete miscibility, *i. e.*, show positive deviations from ideal behavior or from Raoult's law, in the solid state, would exhibit curves of Type II, in which we see the tendency toward the formation of an isothermally invariant liquid in equilibrium with a varying solid. On the other hand, pairs of salts which would tend to form definite compounds, *i. e.*, show negative deviations from ideality in the solid state, would show distribution curves of Roozeboom's Type III, revealing the tendency for the formation of an isothermally invariant solid in equilibrium with a varying liquid.

On the basis of further theoretical considerations, soon to be published, of the data of these

TABLE III

TERNARY SYSTEMS OF PICROMERITES WITH WATER AT 25°, IN WEIGHT PER CENT.

No.	Original complex, % A	Original complex, % B	Liquid phase, % A	Liquid phase, % B	Solid phase, % A	Solid phase, % B
I. Magnesium Ammonium Sulfate (A)–Magnesium Ammonium Chromate (B)–Water						
1	0.00	...	0.00	11.50	0.00	73.00
2A[a]	5.01	11.01	4.69	8.83	11.33	61.24
B[b]	5.01	11.01	4.81	8.83	10.94	61.42
3A	9.99	10.01	8.60	6.60	25.74	45.90
B	9.99	10.01	8.62	6.60	25.82	45.99
4A	14.51	9.00	10.87	5.08	37.49	34.23
B	14.51	9.00	10.90	5.08	37.34	33.48
5A	17.45	4.50	13.42	3.05	53.70	17.28
B	17.45	4.50	13.46	3.05	53.09	17.26
6A	21.52	2.80	15.15	1.77	61.63	8.89
B	21.52	2.80	14.78	1.77	61.15	8.90
7	...	0.00	16.58	0.00	70.02	0.00
II. Magnesium Ammonium Selenate (A)–Magnesium Ammonium Sulfate (B)–Water						
1	0.00	...	0.00	16.58	0.00	70.02
2A	6.61	21.00	5.67	13.33	11.57	59.59
B	6.61	21.00	5.68	13.31	11.32	59.82
3A	12.30	14.99	10.40	10.37	24.72	47.35
B	12.30	14.99	10.37	10.40	25.09	47.05
4A	20.52	10.24	15.65	6.66	45.23	28.44
B	20.52	11.98	14.98	7.19	42.53	30.98
5A	22.92	6.01	18.25	4.59	58.10	16.75
B	22.92	6.01	18.31	4.54	57.73	17.00
6A	27.00	3.51	20.14	2.72	67.56	8.27
B	27.00	3.51	20.10	2.64	67.49	8.33
7	...	0.00	23.31	0.00	76.21	0.00
III. Magnesium Ammonium Selenate (A)–Magnesium Ammonium Chromate (B)–Water						
1	0.00	...	0.00	11.50	0.00	73.00
2A	6.67	14.60	6.11	8.41	12.26	61.41
B	6.67	14.60	6.03	8.44	12.19	61.45
3A	14.00	11.00	11.75	5.62	28.75	45.68
B	14.00	11.00	11.94	5.63	28.64	45.75
4A	21.89	8.29	16.60	3.40	45.74	29.31
B	21.89	8.29	16.58	3.40	45.85	29.30
5A	24.78	4.31	19.36	2.04	57.93	17.70
B	24.78	4.31	19.38	2.03	57.95	17.66
6A	28.94	2.49	21.25	1.08	66.79	9.23
B	28.94	2.49	21.30	1.09	66.76	9.24
7	...	0.00	23.31	0.00	76.21	0.00
IV. Magnesium Potassium Selenate (A)–Magnesium Ammonium Selenate (B)–Water						
1	0.00	...	0.00	23.31	0.00	76.27
2A	6.68	30.21	5.92	19.01	8.15	67.86
B	6.68	30.21	5.99	19.00	8.21	68.10
3A	13.21	24.75	11.83	15.06	18.41	58.11
B	13.21	24.75	11.96	15.08	17.90	58.33
4A	20.20	20.20	17.10	11.44	29.58	47.27
B	20.20	20.20	17.21	11.39	29.64	47.18
5A	24.01	15.35	20.32	8.98	38.57	38.67
B	24.01	15.35	20.67	9.16	37.94	38.94
6A	26.55	10.98	23.03	7.25	46.58	30.68
B	26.55	10.98	22.91	7.33	46.64	30.49
7	...	0.00	32.15	0.00	78.23	0.00

[a] A: Initial solid phase = Salt A. [b] B: Initial solid phase = Salt B.

TABLE IV

DISTRIBUTION OF PICROMERITES BETWEEN LIQUID AND SOLID PHASES

System		Mole fraction of salt A, *Y*, in dissolved salts	Mole fraction of salt A, *X*, in solid solution
I.	A: $Mg(NH_4)_2(SO_4)_2$	0.000	0.000
	B: $Mg(NH_4)_2(CrO_4)_2$	.384	.174
		.602	.394
		.713	.561
		.836	.782
		.907	.889
		1.000	1.000
II.	A: $Mg(NH_4)_2(SeO_4)_2$	0.237	0.123
	B: $Mg(NH_4)_2(SO_4)_2$	.422	.278
		.603	.500
		.632	.537
		.745	.715
		.845	.856
III.	A: $Mg(NH_4)_2(SeO_4)_2$	.379	.144
	B: $Mg(NH_4)_2(CrO_4)_2$	.635	.346
		.805	.569
		.889	.734
		.944	.859
IV.	A: $MgK_2(SeO_4)_2$	.218	.097
	B: $Mg(NH_4)_2(SeO_4)_2$	.413	.218
		.573	.359
		.668	.468
		.738	.576

and related systems involving alums and picromerites, it will be shown that all the picromerite systems so far studied are probably of Type II, showing to some degree a tendency toward positive deviations from ideality in the solid state. In this respect the picromerites of the present report, involving chromates and selenates besides sulfates, show, as expected, the most pronounced deviations and the greatest disagreement between the observed and the calculated distribution ratios.

Summary

1. The ternary systems $MgCrO_4$–$(NH_4)_2CrO_4$–H_2O and $MgSeO_4$–K_2SeO_4–H_2O, involving, respectively, the formation of the double salts $Mg(NH_4)_2(CrO_4)_2 \cdot 6H_2O$ and $MgK_2(SeO_4)_2 \cdot 6H_2O$, were studied at 25°.

2. The following ternary systems were also studied at 25°: $Mg(NH_4)_2(CrO_4)_2$–$Mg(NH_4)_2(SO_4)_2$–H_2O, $Mg(NH_4)_2(SO_4)_2$–$Mg(NH_4)_2(SeO_4)_2$–H_2O, $Mg(NH_4)_2(CrO_4)_2$–$Mg(NH_4)_2(SeO_4)_2$–H_2O, $Mg(NH_4)_2(SeO_4)_2$–$MgK_2(SeO_4)_2$–H_2O.

Continuous series of solid solutions were found in each case.

3. The results are considered from the point of view of the Roozeboom classification of solid solutions.

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Distribution of Isomorphous Salts in Solubility Equilibrium between Liquid and Solid Phases

BY ARTHUR E. HILL,[1] GEORGE S. DURHAM[2] AND JOHN E. RICCI

Several reports already have been published from this Laboratory on the experimental investigation of the equilibrium relations between solid solutions of isomorphous salts and their saturated aqueous solutions. The cases studied cover a number of pairs of alums,[3,4] in which one of the cations was varied, and a number of pairs of picromerites[5,6,7] (or schoenites), hexahydrated double sulfates, selenates or chromates of a univalent and a bivalent cation, in which again one of the ions was varied, to produce mixed crystals. The distribution of the isomorphous salts between liquid and solid phases in these systems was also studied for the purpose of assigning them to the proper type of solid solutions in the Roozeboom classification.[8] The present report is an attempt to account theoretically for the observed distribution, and to correlate this distribution quantitatively to some extent with the aqueous molar solubilities of the individual salts. The relations derived have been tested on what are believed to be probably the best data available on the equilibrium relations between solid solutions of isomorphous salts and their saturated aqueous solutions.[3–7] These measurements are in general quite reliable not only in respect to the precision and accuracy of the determinations, but also in respect to the question of the attainment of equilibrium, for which a special technique was used. It is felt therefore that whatever regularities can be shown to exist on the basis of these experimental observations, must have some significance which must be worth the attempt at interpretation.

The Roozeboom Classification

Roozeboom[8] classified systems of two isomorphous salts, A and B, varying in respect to only one ion so that with water they constitute ternary systems, and forming between themselves continuous solid solutions, into three types, depending on the relative distribution of the salts between liquid and solid phases. Calculating concentrations, whether in the liquid or in the solid phase, on the basis of the total salts present in the phase, disregarding the water, Roozeboom plotted the mole fraction of one salt, A, in the liquid phase, as y, against its mole fraction in the solid phase, as x, using the familiar type of rectangular diagram introduced by him. If the mole fraction of one of the salts, let us say A, is always greater in the liquid than in the solid phase, over the entire

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(1) This paper is being published, following the death of Professor Hill, by his collaborators; although originally submitted for publication March 18, 1940, it was rewritten to include the newer data of Ref. 7.

(2) The material of this article is taken (in part) from a thesis presented by G. S. Durham for the degree of Doctor of Philosophy at New York University, June, 1939.

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

(4) Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).

(5) Hill and Taylor, *ibid.*, **60**, 1099 (1938).

(6) Hill, Durham and Ricci, *ibid.*, **62**, 1031 (1940).

(7) Hill, Soth and Ricci, *ibid.*, **62**, 2717 (1940).

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