oxalate ion. The $K_4$ in the table is the instability constant of this ion calculated from the solubility data, with the assumption that zinc sulfate is incompletely dissociated and its ionization constant[4] is 0.0054.

Recalculation of the data on the oxalatozincate ion $Zn(C_2O_4)_2^=$ in the same manner as for the oxalatocadmiate ion gives the results in Table VII. To the data of Clayton and Vosburgh have been added some experimental data of Metler and Vosburgh[7] and some of Kunschert.[8] The first three values for $K_5$ from the data of Metler and Vosburgh are probably too high; the analysis for zinc gave somewhat low results and the error was probably largest in the most dilute solutions. It may be concluded that in the more dilute solutions the complex ion $Zn(C_2O_4)_2^=$ is formed, but all three sets of results are in agreement in showing that at a molality of between 0.05 and 0.1 the value of $K_5$ begins a rapid decrease. The significance of this is discussed by Clayton and Vosburgh.

TABLE VII

INSTABILITY CONSTANT OF THE OXALATOZINCATE ION

| Oxalate total $m \times 10^3$ | $ZnC_2O_4$ total $m \times 10^3$ | $C_2O_4^=$ $m \times 10^3$ | $Zn(C_2O_4)_2^=$ $m \times 10^3$ | $K_5$ |
|---|---|---|---|---|
| | A. Clayton and Vosburgh | | | |
| 10.00 | 0.460 | 9.21 | 0.331 | 0.0036 |
| 27.45 | 1.030 | 25.52 | .901 | .0037 |
| 48.44 | 1.803 | 44.97 | 1.674 | .0035 |
| 111.6 | 6.48 | 98.77 | 6.35 | .0020 |
| | B. Metler and Vosburgh | | | |
| 12.2 | 0.43 | 11.5 | 0.30 | 0.0049 |
| 12.7 | .45 | 11.9 | .32 | .0048 |
| 25.9 | .85 | 24.3 | .72 | .0043 |
| 52.1 | 1.9 | 48.4 | 1.77 | .0035 |
| 51.6 | 1.8 | 48.1 | 1.67 | .0037 |
| 108.7 | 5.8 | 98.2 | 5.67 | .0022 |
| 224.7 | 19.4 | 186.0 | 19.3 | .0012 |
| 262.0 | 25.4 | 211.3 | 25.3 | .0011 |
| C. Kunschert (concentrations in moles per liter) | | | | |
| 52.2 | 2.2 | 47.9 | 2.1 | 0.0029 |
| 105.5 | 5.5 | 94.6 | 5.4 | .0023 |
| 160.6 | 10.55 | 140 | 10.4 | .0017 |
| 217.3 | 17.4 | 183 | 17.3 | .0014 |
| 275.7 | 25.7 | 224 | 25.6 | .0011 |

## Summary

The solubility of cadmium oxalate in solutions of potassium and cadmium perchlorates and potassium sulfate has been measured.

The increase in solubility with concentration in solutions of potassium and cadmium sulfates and cadmium perchlorate, and the constancy in potassium perchlorate solutions, can be explained if the existence of the ions $CdC_2O_4 \cdot Cd^{++}$ and $CdC_2O_4 \cdot SO_4^=$ is postulated and cadmium sulfate regarded as incompletely dissociated.

The solubility of zinc oxalate in zinc sulfate solutions can be explained similarly if the ion $ZnC_2O_4 \cdot Zn^{++}$ is postulated.

The instability constants of the ions $Cd(C_2O_4)_2^=$ and $Zn(C_2O_4)_2^=$ have been recalculated.

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[7] Metler and Vosburgh, THIS JOURNAL, **59**, 2421 (1937).

[8] Kunschert, *Z. anorg. Chem.*, **41**, 339 (1904).

DURHAM, NORTH CAROLINA RECEIVED JANUARY 19, 1940

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

# Ternary Systems. XXV. Solid Solutions of Some Picromerites at 25°

BY ARTHUR E. HILL,* GEORGE S. DURHAM** AND JOHN E. RICCI

In continuation of the project undertaken in this Laboratory, of collecting reliable equilibrium data on the distribution of isomorphous salts between liquid and conjugate solid solutions, a series of ternary systems consisting of water and a pair of double sulfates of the picromerite series, has been investigated, at the temperature of 25°. The purpose of these measurements is ultimately to relate if possible the distribution ratio of these salts between liquid and solid phases, with certain properties of the individual salts such as their aqueous solubilities. With the necessity in mind of having as nearly as possible ideal conditions for the interpretation of solution relationships, pairs of salts were chosen for this work which because of their very close similarity in formula and in other properties would be expected to form very nearly ideal solid solutions in their mixed crystals. Reports already have been published on a number of alum pairs,[1,2] as also on some picromerite systems.[3] The present report covers

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* This paper is being published, following the death of Professor Hill, by his collaborators.

** The material of this article is taken from a thesis presented by G. S. Durham for the Degree of Doctor of Philosophy at New York University, June, 1939.

[1] Hill and Kaplan, THIS JOURNAL, **60**, 550 (1938).

[2] Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).

[3] Hill and Taylor, *ibid.*, **60**, 1099 (1938).

the experimental investigation of the equilibrium relations of six pairs of picromerites studied as ternary systems with water at 25°; the picromerites, or schoenites, are a series of isomorphous monoclinic hexahydrated double sulfates of univalent and divalent bases, of which Mohr salt, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, is a familiar example. *In* all the systems of the present study complete miscibility of the two picromerites in the solid state was found, at the temperature of the determinations.

The experimental procedure in these measurements is marked, as in the preceding papers of this series, by particular attention to the establishment of equilibrium both in respect to the solid–liquid relations and as to the equilibrium within the mixed crystals themselves, in order to leave no question as to the validity of the results for any possible theoretical interpretation. The procedure was therefore that already described, in which the solid solution equilibrium was approached, for every determination, from two opposite directions. Every complex was prepared in exact duplicate (Tubes A and B of the Tables). In Tube A one of the salts was dissolved completely in the water, and the second solid then added as the initial solid phase; this order was then reversed for Tube B of the same complex. If the two tubes give the same results for both liquid and solid compositions, equilibrium is proved. Although the attainment of this kind of solid solution equilibrium is in general very slow, it was found that by enclosing two glass marbles in each complex during the rotation, which by their motion kept the solid phase finely ground, a week was sufficient for the purpose.

The determinations involved the preparation, as described, of complexes of known composition, and analysis, at equilibrium, of both the liquid and the solid phases, the former after adequate filtration, the latter after centrifuging and air-drying; all the double salts of the systems studied are stable, as hexahydrates, exposed to ordinary air, so that this latter procedure involved no error except for the crystallization of salts from traces of residual mother liquor. In addition the algebraic extrapolation[4] of the tie-lines through the total compositions (complexes) and the compositions of the liquid solutions, was used as a check on the consistency and accuracy of the work, by comparing the extrapolated composition of the solid phase with the observed.

**System I. Magnesium Ammonium Sulfate–Copper Ammonium Sulfate–Water, at 25°.**—Both of the double salts forming the solid components of this system are congruently soluble at room temperature. While the magnesium salt is known to remain so up to the boiling point,[5] the copper salt has not been studied at temperatures above 61°[6,7]; nevertheless it can be prepared successfully by crystallization from boiling solution of the simple sulfates of copper and ammonium, followed by prolonged cooling and stirring.[3] This method was used for both the magnesium ammonium and the copper ammonium double sulfates for the present investigation. Their composition, checked by analyses both for the metal and for the ammonium radical, was found to agree with the theoretical formulas within experimental error. The ammonium was determined by distillation into standard acid and subsequent titration, with an accuracy of 1/500. The liquids and solids of the ternary system were analyzed by determination of magnesium and of copper. Magnesium was determined following the procedure given by Kolthoff and Furman,[8] by precipitation as ortho-hydroxyquinolate and titration of the precipitated quinolate with standard potassium bromate (Berg's method[9]), the end-point being fixed by spot-tests with potassium iodide–starch paper. In the presence of copper the magnesium was precipitated after addition of excess of potassium cyanide, which avoided the necessity of previous removal of the copper. This determination likewise had an accuracy of 1/500. Copper was determined electrolytically, the analysis being exact to 1/1000.

The solubilities of the two double salts of this system, here reported, were determined with very close agreement, from both under- and super-saturation, and are based on analysis for both of the positive radicals of each salt; the values found, 16.61% for the magnesium salt and 18.60% for the copper salt, are in close agreement with recent determinations appearing in the literature.[10,11]

The results for the ternary system are given in Table I, which includes the data for the remaining systems discussed below; the table is self-explanatory. The solubilities of the pure double salts have been omitted from this table and are collected, together with density measurements, in a subsequent table (II). The usual triangular diagrams for the graphical representation of the equilibria in the ternary systems are not shown; their appearance and the general disposition of the tie-lines involved are very similar to the diagrams for the related picromerite systems reported by Hill and Taylor.[3] The composition of the solid phase was checked by algebraic extrapolation of tie-lines passing through the compositions of original complex and of liquid solution, to the straight line joining the compositions of the two picro-

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

[5] Benrath and Thiemann, *Z. anorg. Chem.*, **208**, 179 (1932).

[6] Schreinemakers, *Z. physik. Chem.*, **66**, 687 (1909).

[7] Caven and Mitchell, *J. Chem. Soc.*, **125**, 1428 (1924).

[8] Kolthoff and Furman, "Volumetric Analysis," Vol. II, John Wiley and Sons, Inc., New York. N. Y., 1929, p. 483.

[9] Berg, *Z. anal. Chem.*, **71**, 23 (1927).

[10] For $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$: (a) Benrath and Thiemann, ref. 5 above, report 15.9%; (b) Porlezza, *Atti accad. Lincei*, [2] **23**, 596 (1914): 16.5%; (c) Locke, *Am. Chem. J.*, **27**, 455 (1902): 16.6%.

[11] For $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$: (a) Hill and Taylor, ref. 3, above; (b) Caven and Mitchell, ref. 7, above.

merites, on which all the solid solutions should lie; the average absolute deviation, in per cent. of $Mg(NH_4)_2(SO_4)_2$, between the observed and the extrapolated compositions, was only 0.30%. In connection with the magnitude of this deviation, it is to be noted that since the composition of the complex is usually quite near that of the resulting liquid solution, any analytical error in the composition of either will be multiplied by a factor of from ten to twenty in the extrapolation.

TABLE I

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

| No. | Original complex % A[a] | % B[b] | Liquid phase % A | % B | Solid phase % A | % B |
|---|---|---|---|---|---|---|
| I. Magnesium Ammonium Sulfate (A)–Copper Ammonium Sulfate (B)–Water | | | | | | |
| 1 A | 15.68 | 4.00 | 13.69 | 3.46 | 55.80 | 14.85 |
| B | 15.68 | 4.00 | 13.76 | 3.46 | 55.84 | 14.90 |
| 2 A | 14.55 | 9.00 | 11.20 | 6.42 | 42.67 | 28.49 |
| B | 14.55 | 9.00 | 11.08 | 6.51 | 42.41 | 28.84 |
| 3 A | 13.40 | 14.00 | 9.15 | 8.66 | 33.17 | 38.52 |
| B | 13.40 | 14.00 | 9.17 | 8.64 | 33.14 | 38.54 |
| 4 A | 7.00 | 16.74 | 5.77 | 12.43 | 18.28 | 53.91 |
| B | 7.00 | 16.74 | 5.74 | 12.44 | 18.29 | 53.97 |
| 5 A | 2.75 | 17.87 | 2.65 | 15.87 | 6.99 | 65.23 |
| B | 2.75 | 17.87 | 2.61 | 15.88 | 6.63 | 65.27 |
| II. Copper Potassium Sulfate (A)–Nickel Potassium Sulfate (B)–Water | | | | | | |
| 1 A | 12.50 | 1.50 | 9.25 | 0.72 | 61.77 | 13.86 |
| B | 12.50 | 1.50 | 9.26 | .69 | 61.76 | 13.85 |
| 2 A | 11.00 | 4.00 | 7.84 | 1.505 | 44.92 | 30.50 |
| B | 11.00 | 4.00 | 7.84 | 1.508 | 44.89 | 30.52 |
| 3 A | 9.00 | 6.00 | 6.56 | 2.221 | 33.16 | 42.23 |
| B | 9.00 | 6.00 | 6.55 | 2.218 | 33.06 | 42.30 |
| 4 A | 6.50 | 7.50 | 5.07 | 3.084 | 22.23 | 53.24 |
| B | 6.50 | 7.50 | 5.06 | 3.080 | 22.25 | 53.15 |
| 5 A | 3.50 | 8.50 | 2.980 | 4.33 | 10.75 | 64.52 |
| B | 3.50 | 8.50 | 2.981 | 4.34 | 10.86 | 64.46 |
| III. Cobalt Potassium Sulfate (A)–Copper Potassium Sulfate (B)–Water | | | | | | |
| 1 A | 15.00 | 2.00 | 11.74 | 1.312 | 63.17 | 12.19 |
| B | 15.00 | 2.00 | 11.71 | 1.323 | 63.08 | 12.07 |
| 2 A | 13.00 | 5.00 | 9.72 | 2.961 | 48.30 | 27.09 |
| B | 13.00 | 5.00 | 9.71 | 2.965 | 48.61 | 26.83 |
| 3 A | 10.50 | 8.50 | 7.63 | 4.60 | 34.40 | 41.08 |
| B | 10.50 | 8.50 | 7.60 | 4.61 | 34.40 | 40.92 |
| 4 A | 7.00 | 11.00 | 5.39 | 6.28 | 21.79 | 53.67 |
| B | 7.00 | 11.00 | 5.37 | 6.30 | 21.90 | 53.62 |
| 5 A | 3.50 | 13.00 | 2.918 | 8.20 | 10.04 | 65.45 |
| B | 3.50 | 13.00 | 2.915 | 8.21 | 10.10 | 65.50 |
| IV. Zinc Potassium Sulfate (A)–Copper Potassium Sulfate (B)–Water | | | | | | |
| 1 A | 15.00 | 2.00 | 10.36 | 1.305 | 66.11 | 9.61 |
| B | 15.00 | 2.00 | 10.38 | 1.302 | 66.23 | 9.60 |
| 2 A | 13.00 | 5.00 | 8.54 | 3.012 | 52.96 | 22.66 |
| B | 13.00 | 5.00 | 8.52 | 3.008 | 52.78 | 22.70 |
| 3 A | 10.50 | 8.50 | 6.63 | 4.74 | 39.20 | 36.30 |
| B | 10.50 | 8.50 | 6.65 | 4.74 | 39.24 | 36.29 |
| 4 A | 7.00 | 11.00 | 4.74 | 6.41 | 26.16 | 49.43 |
| B | 7.00 | 11.00 | 4.73 | 6.43 | 26.00 | 49.45 |
| 5 A | 3.50 | 13.00 | 2.617 | 8.22 | 12.72 | 62.79 |
| B | 3.50 | 13.00 | 2.616 | 8.22 | 12.64 | 62.83 |
| V. Zinc Potassium Sulfate (A)–Nickel Potassium Sulfate (B)–Water | | | | | | |
| 1 A | 15.50 | 1.50 | 10.64 | 0.457 | 63.81 | 11.75 |
| B | 15.50 | 1.50 | 10.64 | .454 | 63.85 | 11.68 |
| 2 A | 13.50 | 3.50 | 9.35 | 1.026 | 50.21 | 25.33 |
| B | 13.50 | 3.50 | 9.36 | 1.036 | 50.23 | 25.31 |
| 3 A | 11.00 | 5.50 | 7.91 | 1.697 | 37.90 | 37.54 |
| B | 11.00 | 5.50 | 7.91 | 1.692 | 37.68 | 37.75 |
| 4 A | 8.00 | 8.00 | 6.01 | 2.657 | 24.46 | 51.04 |
| B | 8.00 | 8.00 | 6.01 | 2.662 | 24.52 | 50.90 |
| 5 A | 5.00 | 10.00 | 3.99 | 3.78 | 13.64 | 61.66 |
| B | 5.00 | 10.00 | .... | .. | 13.62 | 61.70 |
| VI. Copper Ammonium Sulfate (A)–Copper Potassium Sulfate (B)–Water | | | | | | |
| 1 A | 17.86 | 3.00 | 15.44 | 2.03 | 56.92 | 16.46 |
| B | 17.86 | 3.00 | ... | .. | 57.11 | 16.24 |
| 2 A | 17.12 | 6.00 | 13.47 | 3.30 | 47.03 | 26.82 |
| B | 17.12 | 6.00 | 13.50 | 3.25 | 46.81 | 26.98 |
| 3 A | 12.00 | 8.65 | 10.04 | 5.45 | 31.68 | 42.80 |
| B | 12.00 | 8.65 | ... | .. | 31.55 | 42.76 |
| 4 A | 8.00 | 9.22 | 7.35 | 6.85 | 20.40 | 54.51 |
| B | 8.00 | 9.22 | 7.35 | 6.89 | 20.79 | 54.10 |
| 5 A | 4.00 | 9.78 | 3.90 | 8.55 | 8.99 | 66.13 |
| A | 4.00 | 9.78 | 3.91 | 8.52 | .. | ... |
| B | 4.00 | 9.78 | 3.87 | 8.58 | 9.03 | 66.11 |
| B | 4.00 | 9.78 | 3.89 | 8.55 | .. | ... |

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

**System II. Copper Potassium Sulfate–Nickel Potassium Sulfate–Water, at 25°.**—The nickel potassium sulfate, being congruently soluble up to the boiling point,[12] was prepared in the manner described for the salts of System I. The copper potassium double sulfate was prepared from solutions of the simple sulfates at temperatures not above 55°, to avoid precipitation of basic salt.[7,13] The purity of the double salts was checked by analysis for copper and nickel, respectively. The analytical method for this ternary system involved the consecutive electrolytic determination of these metals, the nickel after deposition and removal of the copper. The analysis is judged to be accurate to 1/1000. The solubility of the copper potassium double sulfate, 10.35% from both under- and super-saturation, is in fair agreement with published results: 10.47 (Locke[10c]), 10.46 (Caven and Mitchell[7]), and 10.02 (Trevor[14]). That of the nickel potassium double salt, 6.33%, also both from under- and from super-saturation, may be compared with Locke's value, 6.43%.[10c]

Again complete miscibility is observed between the two solid picromerites at this temperature. The average

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(12) Benrath, *Z. anorg. Chem.*, **208**, 169 (1932).

(13) Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans, Green and Co., London, 1923, p. 259.

(14) Trevor, *Z. physik. Chem.*, **7**, 468 (1891).

absolute deviation, in per cent. $CuK_2(SO_4)_2$, between the observed and the extrapolated compositions of the solid phase, was 0.49% for this system.

**System III. Cobalt Potassium Sulfate–Copper Potassium Sulfate–Water, at 25°.**—These salts were already known to form a complete series of solid solutions, the system having been studied at 0 and 7.8°, by Ploin.[15] The 25° isotherm was determined for the purpose of comparison with the other related systems. The cobalt potassium double sulfate, becoming incongruently soluble at 78° and ceasing to exist at 90°,[12] was prepared at temperatures not higher than 75°. Its purity was checked by determination of cobalt. The analytical method for the ternary system, involving the consecutive electrolytic determination of copper and cobalt, was accurate to 1/1000. The solubility here reported for the cobalt potassium double sulfate, 13.65% from both under- and supersaturation, differs widely from the older literature values, namely, 11.41% reported by Locke[10c] and 15.60% by Benrath.[12] The great difference is probably due to the difficulty of establishing true equilibrium between the various isomeric forms of hydrated cobaltic salts both in solution and in the crystalline state. The agreement between the two approaches to equilibrium both for the solubility of the cobalt potassium double sulfate itself and for the ternary complexes, does not, even in the present work, constitute absolute proof of the establishment of all the possible equilibria involved.

The average absolute deviation between extrapolated and observed percentage of $CoK_2(SO_4)_2$ in the solid phase, is very small (0.08%), indicating the high precision and the consistency, at any rate, of the various analytical steps involved.

**System IV. Zinc Potassium Sulfate–Copper Potassium Sulfate–Water, at 25°.**—This system also has been studied by Ploin, at 8°, showing similarly, at that temperature, complete miscibility of the two double salts.[15] The zinc potassium double sulfate was prepared at 85°, as it becomes incongruently soluble at 88° and above.[16] The purity of the salt so prepared was verified by analysis for zinc. The analytical procedure for the ternary system involved again the consecutive electrolytic deposition of copper followed by the deposition of the more active metal, in this case, zinc; the analysis was accurate to 1/1000. The solubility of the zinc potassium double sulfate, found to be 11.72% from both under- and super-saturation, was determined by direct evaporation to the anhydrous sulfates, a very accurate procedure. The result is in fair agreement with the value reported by Locke, 11.65%.[10c]

The analytical precision can be judged by the small average absolute deviation (0.08%) between extrapolated and observed compositions (as % $ZnK_2(SO_4)_2$) for the solid phase.

**System V. Zinc Potassium Sulfate–Nickel Potassium Sulfate–Water, at 25°.**—In this system the percentage of total solids was determined by evaporation, nickel was determined gravimetrically by precipitation with dimethylglyoxime, with an accuracy of 1/1000, and the zinc salt was then calculated by difference.

The average absolute deviation, in respect to per cent. of $ZnK_2(SO_4)_2$, between the extrapolated and observed compositions of the solid phase, was only 0.17%.

**System VI. Copper Ammonium Sulfate–Copper Potassium Sulfate–Water, at 25°.**—This system differs from the preceding five combinations in that here the univalent rather than the divalent cation of the picromerite is being varied. For the analysis the total copper was determined by electrolysis. The copper ammonium double salt was determined by distillation of ammonia, with an accuracy of 1/500, and the copper potassium double salt was then calculated by difference.

The deviation in this system between extrapolated and observed per cent. $Cu(NH_4)_2(SO_4)_2$ for the solid phase was 0.68%.

To permit the calculation of the molar solubilities of the various double salts involved, the densities of their pure saturated solutions at 25° were determined together with their weight per cent. solubility. These densities were determined with only moderate accuracy, by means of calibrated pipets fitted with proper filter paper to separate the liquid phase from excess of solid.

TABLE II

SOLUBILITIES OF SOME PICROMERITES AT 25°

| Salt | Solubility, wt. % anhydrous salt | Density of saturated solution | Molar solubility |
|---|---|---|---|
| $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ | 16.61 | 1.090 | 0.7176 |
| $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ | 18.60 | 1.160 | .7399 |
| $CuK_2(SO_4)_2 \cdot 6H_2O$ | 10.35 | 1.094 | .3392 |
| $NiK_2(SO_4)_2 \cdot 6H_2O$ | 6.33 | 1.056 | .2032 |
| $CoK_2(SO_4)_2 \cdot 6H_2O$ | 13.65 | 1.128 | .4679 |
| $ZnK_2(SO_4)_2 \cdot 6H_2O$ | 11.72 | 1.109 | .3873 |
| $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ | 12.24[3] | 1.103 | .4601 |
| $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$ | 7.09[3] | 1.057 | .2614 |

**Distribution between Liquid Solution and Solid Solution.**—The distribution of the picromerites here studied, between the equilibrium liquid and solid phases, may be considered from the point of view of Roozeboom's[17] classification of such binary solid solutions occurring in ternary systems of water and two salts. In order to interpret the above data in terms of this classification the concentrations have been recalculated into mole fractions of the two picromerites, disregarding water, in the two phases. The results, giving for each system the mole fraction of the more soluble picromerite (more soluble in molar units), are shown in Table III, and are plotted in Figs. 1 and 2, in which the curves I–VI represent, respectively, the six combinations studied; in the table and figures, the $Y$ values represent the mole fraction of the more soluble picromerite in the liquid phase and $X$ its mole fraction in the solid phase.

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[15] Ploin, *Roczniki Chem.*, **6**, 690 (1926); *cf. C. A.*, **21**, 3503 (1927).

[16] Benrath and Cremers, *Z. anorg. Chem.*, **189**, 88 (1930).

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

Table III

Distribution of Picromerites between Liquid and Solid Phases

| System | Mole fraction of salt A |  |
|---|---|---|
|  | $Y$, in dissolved salts | $X$, in solid solution |
| I. A: $Mg(NH_4)_2(SO_4)_2$<br>B: $Cu(NH_4)_2(SO_4)_2$ | 0.000 | 0.000 |
|  | .161 | .108 |
|  | .349 | .282 |
|  | .550 | .499 |
|  | .666 | .632 |
|  | .821 | .813 |
|  | 1.000 | 1.000 |
| II. A: $CuK_2(SO_4)_2$<br>B: $NiK_2(SO_4)_2$ | 0.404 | 0.142 |
|  | .619 | .292 |
|  | .744 | .436 |
|  | .837 | .592 |
|  | .928 | .815 |
| III. A: $CoK_2(SO_4)_2$<br>B: $CuK_2(SO_4)_2$ | .265 | .136 |
|  | .464 | .292 |
|  | .628 | .460 |
|  | .769 | .646 |
|  | .900 | .841 |
| IV. A: $ZnK_2(SO_4)_2$<br>B: $CuK_2(SO_4)_2$ | .241 | .167 |
|  | .423 | .344 |
|  | .582 | .518 |
|  | .738 | .699 |
|  | .888 | .873 |
| V. A: $ZnK_2(SO_4)_2$<br>B: $NiK_2(SO_4)_2$ | .508 | .178 |
|  | .689 | .320 |
|  | .821 | .496 |
|  | .899 | .660 |
|  | .958 | .842 |
| VI. A: $Cu(NH_4)_2(SO_4)_2$<br>B: $CuK_2(SO_4)_2$ | .342 | .135 |
|  | .550 | .303 |
|  | .678 | .458 |
|  | .825 | .666 |
|  | .897 | .800 |

From the tabulation and the two figures, as also from a consideration of the disposition of the tie-lines in the triangular isothermal diagrams for the systems (not shown), it appears that these systems would all fall into Type I of Roozeboom's classification, systems in which there is complete miscibility between the two solid components and in which the proportion of one of these components is higher in the liquid than in the corresponding solid phase throughout the whole series of concentrations. We again note, as has been reported in connection with recent similar studies on a series of alum systems,[2] that the component present in greater concentration in the liquid than in the solid has the higher aqueous molar solubility. It must be observed of course at this point that the data are not sufficient to rule out the possibility that the curves of Figs. 1 and 2 may cross the diagonal near the extremities of the diagrams; in the case of the picromerites here reported, it appears, on the basis of further theoretical considerations not yet published, that this may actually be the case, and that these systems consequently would then fall into Type *II* of Roozeboom's classification, in which, starting from zero concentration of one component, the proportion of that component in the liquid phase ($Y$) is greater than its proportion in the solid phase ($X$) up to a certain point, then becoming smaller than $X$ up to a mole fraction of one for the component. In continuation of the suggestion made in a previous article of this series, in

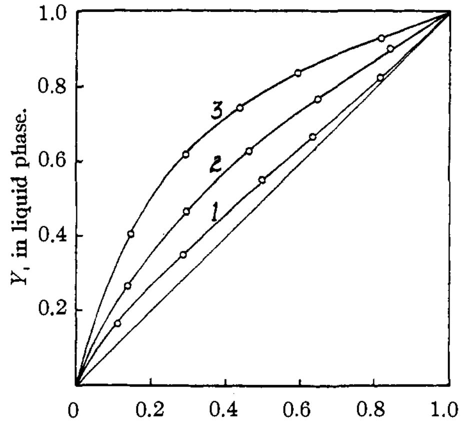

Fig. 1.—Distribution of picromerites between aqueous solution and solid solution at 25°: (1) $Mg(NH_4)_2(SO_4)_2$ in $Mg(NH_4)_2(SO_4)_2$–$Cu(NH_4)_2(SO_4)_2$; (2) $CuK_2(SO_4)_2$ in $CuK_2(SO_4)_2$–$NiK_2(SO_4)_2$; (3) $CoK_2(SO_4)_2$ in $CoK_2(SO_4)_2$–$CuK_2(SO_4)_2$.

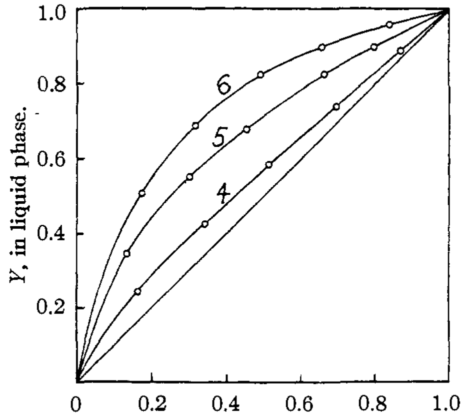

Fig. 2.—Distribution of picromerites between aqueous solution and solid solution at 25°: (4) $ZnK_2(SO_4)_2$ in $ZnK_2(SO_4)_2$–$CuK_2(SO_4)_2$; (5) $ZnK_2(SO_4)_2$ in $ZnK_2(SO_4)_2$–$NiK_2(SO_4)_2$; (6) $Cu(NH_4)_2(SO_4)_2$ in $Cu(NH_4)_2(SO_4)_2$–$CuK_2(SO_4)_2$.

which the empirical equation $X = Y^m$ was advanced, these measurements, together with similar studies from this Laboratory, will be considered, in a subsequent publication, for the purpose of deriving some generalization relating the distribution ratio of these isomorphous salts between liquid and solid phases, to the molar solubilities of the individual salts in the pure solvent.

## Summary

1. The following ternary systems have been studied at 25°

$Mg(NH_4)_2(SO_4)_2-Cu(NH_4)_2(SO_4)_2-H_2O$
$CuK_2(SO_4)_2-NiK_2(SO_4)_2-H_2O$
$CoK_2(SO_4)_2-CuK_2(SO_4)_2-H_2O$
$ZnK_2(SO_4)_2-CuK_2(SO_4)_2-H_2O$
$ZnK_2(SO_4)_2-NiK_2(SO_4)_2-H_2O$
$Cu(NH_4)_2(SO_4)_2-CuK_2(SO_4)_2-H_2O$

2. Continuous series of solid solutions were found in each case.

3. The results, considered from the point of view of Roozeboom's classifications of solid solutions, show all these systems to belong apparently to Type I of that classification.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

# Freezing Point and Solubility Data for the System Chlorine Monoxide–Water

BY C. H. SECOY AND G. H. CADY

It is known that chlorine monoxide dissolves in water to give hypochlorous acid but no previous study has been made of the possible existence of hydrates of this acid nor have highly concentrated solutions of the acid been prepared and studied. In this work freezing point and solubility data have been obtained for the system chlorine monoxide–water. The only pertinent data found in the literature were the freezing point of pure chlorine monoxide, reported by Goodeve[1] to be −116°, and the freezing points of very dilute solutions of hypochlorous acid.[2]

## Experimental

**Preparation of Chlorine Monoxide and Hypochlorous Acid.**—Chlorine monoxide was prepared by passing a stream of dry chlorine mixed with air up through a column of yellow mercuric oxide.[3] A 35-mm. glass tube, one meter long, was filled with mercuric oxide with a sufficient quantity of porcelain chips added to prevent packing. The top of this tube was sealed to 8-mm. glass tubing leading to a 24 mm. × 30 cm. test-tube fitted with a stirrer and a thermocouple well. Other workers[3] have stated that the mercuric oxide previously should be heated to 400°, for a period of an hour or longer. This treatment, however, was not used since it has been found that it is neither necessary nor helpful.[4] The spent mercuric oxide was recovered by precipitation in the cold with sodium hydroxide, washed free of sodium hydroxide, and dried at 120°.[4] The air and chlorine were dried by bubbling through sulfuric acid and passed through a T-tube into the mercuric oxide. The rate of flow of the air was about twice that of the chlorine. The air prevented any noticeable heating effect from the reaction.

The chlorine monoxide was condensed by means of a dry-ice–alcohol cooling mixture, and hypochlorous acid of the desired concentration was then obtained by adding the required amount of water and stirring until equilibrium had been reached. Chlorine monoxide and strong hypochlorous acid were found to be stable over a period of a week if kept at a temperature below −20°. However, some free chlorine invariably was formed if the solution was allowed to stand for a few hours at a higher temperature.

**Temperature Measurements.**—Freezing point data were obtained by thermal analysis. Temperatures were measured by a copper–constantan thermocouple calibrated at the ice-point, the dry-ice point, and the boiling point of oxygen. The conversion table reported by Giauque, Buffington, and Schulze[5] was used after applying a constant factor, characteristic of the thermocouple used, to the e. m. f. readings. The use of this factor allowed points at the calibration temperatures to fall within 0.02° of Giauque's curve. The e. m. f. was measured with a Leeds and Northrup Type K potentiometer using a voltage-sensitive galvanometer. Readings were made to the nearest tenth of a microvolt and temperatures obtained were believed to be accurate to 0.1°. The warm junction of the thermocouple was kept at the temperature of melting ice.

**Method of Analysis.**—The method reported by Spinks[6] was used to determine both free chlorine and available chlorine in the form of chlorine monoxide and/or hypochlorous acid. The sample, from 0.2 to 0.5 g., was transferred by means of a pipet to a weighed flask containing a

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[1] Goodeve, *J. Chem. Soc.*, 2733 (1930).

[2] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

[3] "Gmelins Handbuch der anorganischen Chemie," 8th Ed., Vol. 6, "Chlor," Verlag Chemie, Berlin (1927), p. 228; Balard, *Ann. chim. phys.*, [2] **57**, 225 (1834); *Taylors Scientific Memoirs*, **1**, 269 (1837); Pelouze, *Ann. chim. phys.*, [3] **7**, 176 (1843).

[4] Muskat and Cady, U. S. Patent 2,155,281 (1939).

[5] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

[6] Spinks, *ibid.*, **53**, 3015 (1931).