

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Systems $\text{Ag}_2\text{SO}_4\text{-BeSO}_4\text{-H}_2\text{O}$ and $\text{Ag}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ at 35°

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The systems silver sulfate-beryllium sulfate-water and silver sulfate-magnesium sulfate-water have been studied at 35°. The only solid phases observed were the pure salts silver sulfate, beryllium sulfate tetrahydrate and magnesium sulfate heptahydrate.

In two previous papers¹ the equilibrium relations in aqueous systems involving silver sulfate and the alkali sulfates have been reported. The solubility measurements here described have been made as an extension of this study to include the soluble sulfates of Group II.

Materials.—C.P. grade silver sulfate was further purified by recrystallization from concentrated sulfuric acid.² C.P. grade beryllium sulfate tetrahydrate was dehydrated to the anhydrous salt by heating for an hour and a half at 400–420°. C.P. grade magnesium sulfate heptahydrate was recrystallized³ and dehydrated to the monohydrate by heating for 24 hours at 130–140°. All salts were stored in glass-stoppered weighing bottles in a calcium chloride desiccator.

Solubility Determinations.—Complexes of known composition were made up by weight in stoppered test-tubes which were then tumbled end over end for several days in a constant temperature water-bath at $34.95 \pm 0.05^\circ$. To prevent photochemical decomposition of the silver sulfate, the solubility tubes were wrapped in aluminum foil. Samples for analysis were taken in the usual way by means of pipets fitted with filter paper tips.

In all cases two analytical samples were taken. The silver sulfate concentration was determined in one by titration with ammonium thiocyanate, using the Volhard indicator. In the beryllium sulfate system, the silver ion was precipitated from the second sample with hydrochloric acid, and a gravimetric sulfate determination run on the filtrate. To avoid contamination of the barium sulfate with nitrate the silver chloride precipitate was washed with 0.01 M hydrochloric acid instead of nitric acid. In the magnesium sulfate system, the second sample was evaporated to dryness by heating overnight at 110° followed by 24 hours at 130–140°. The resulting solid was a mixture of silver sulfate and magnesium sulfate monohydrate.

Results.—The data (in weight per cent.) are shown in Table I. Both systems are simple, the only solid phases being the pure salts, silver sulfate, beryllium sulfate tetrahydrate and magnesium sulfate heptahydrate, as determined by the algebraic extrapolation⁴ of the tie lines through the original complexes. The extrapolation errors

averaged 0.21 and 0.27% for the beryllium and magnesium systems, respectively. The compositions of the hydrates were determined by direct analysis after they had been filtered and freed from saturated solution by washing with petroleum ether.

TABLE I

SYSTEMS $\text{Ag}_2\text{SO}_4\text{-H}_2\text{O}$ AND BeSO_4 OR MgSO_4 AT 35°

| Liquid solution | | Original complex | | Solid phase ^a |
|--------------------------------|-----------------------|--------------------------------|-----------------------|--------------------------|
| Wt. % Ag_2SO_4 | Wt. % BeSO_4 | Wt. % Ag_2SO_4 | Wt. % BeSO_4 | |
| (1) BeSO_4 | | | | |
| 0.929 | | | | A |
| .892 | 2.48 | 9.63 | 2.26 | A |
| .935 | 6.17 | 9.57 | 5.63 | A |
| .945 | 11.05 | 9.83 | 10.08 | A |
| .900 | 16.95 | 10.00 | 15.38 | A |
| .792 | 22.25 | 9.95 | 20.14 | A |
| .661 | 27.31 | 9.98 | 24.77 | A |
| .601 | 29.91 | 9.84 | 29.49 | A + B |
| .596 | 30.00 | 7.30 | 32.58 | A + B |
| .600 | 29.95 | 5.08 | 35.21 | A + B |
| .601 | 29.87 | 0.53 | 35.25 | A + B |
| .599 | 29.93 | Average | | A + B |
| .247 | 30.02 | Unknown | | B |
| | 30.15 | | | B |
| (2) MgSO_4 | | | | |
| | Wt. % MgSO_4 | | Wt. % MgSO_4 | |
| 0.929 | | | | A |
| .906 | .320 | 14.03 | 2.75 | A |
| .952 | 5.44 | 15.38 | 4.70 | A |
| 1.050 | 11.64 | 14.97 | 9.93 | A |
| 1.065 | 14.50 | 14.68 | 12.46 | A |
| 1.052 | 18.63 | 14.86 | 16.05 | A |
| 0.99 | 24.06 | 14.99 | 20.66 | A |
| .837 | 29.35 | 7.42 | 32.53 | A + C |
| .840 | 29.33 | 5.02 | 35.07 | A + C |
| .842 | 29.31 | 2.98 | 37.02 | A + C |
| .840 | 29.33 | Average | | A + C |
| .633 | 29.35 | 0.54 | 35.00 | C |
| | 29.77 | | | C |

^a A = Ag_2SO_4 , B = $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, C = $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

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(1) E. L. Simons and J. E. Ricci, *THIS JOURNAL*, **68**, 2194 (1946); W. C. von Dohlen and E. L. Simons, *ibid.*, **73**, 461 (1951).

(2) E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 66.

(3) Ref. 2, p. 91.

(4) A. E. Hill and J. E. Ricci, *THIS JOURNAL*, **53**, 4306 (1931).