

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

The System Calcium Selenate-Ammonium Selenate-Water at 30°¹

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In a previous communication, the isotherm at 30° for the system $(\text{NH}_4)_2\text{SeO}_4$ - MgSeO_4 - H_2O was reported.² Continuing the study of systems of the type selenate-selenate-water, it was the purpose of this investigation to study the system CaSeO_4 - $(\text{NH}_4)_2\text{SeO}_4$ - H_2O . Solubility data in this system appear to be entirely lacking.

Experimental

Materials and Apparatus.—The preparations of selenic acid and ammonium selenate have been reported in previous papers.^{3,4} Calcium selenate was prepared by adding a slight excess of selenic acid to purified calcium carbonate and recrystallizing the salt. Since calcium selenate shows a retrograde solubility, crystallization was effected from hot solution.

An electrically controlled thermostat, which maintained the temperature at $30 \pm 0.05^\circ$, was employed.

Method of Procedure.—The method of preparation of the solutions and the separation of solid and liquid phases has been described previously.² In order to ensure equilibrium, samples of the solutions were removed at intervals and analyzed. Equilibrium was found to be reached within forty-eight hours; however, the stirring was continued for three days as a rule and sometimes as long as seven days.

Methods of Analyses.—The ammonium selenate was determined by adding an excess of sodium hydroxide and distilling the evolved ammonia into an excess of standard acid; the excess acid was determined by titration with a standard alkali. The calcium selenate was determined by precipitating the calcium as calcium oxalate, dissolving the precipitate in sulfuric acid, and titrating the liberated oxalate ion with standard potassium permanganate solution.

Results

The compositions of solutions and wet residues are shown in Table I and are represented graphically in Fig. 1. The composition of the solid phases was determined by the method of Schreinemakers.⁵

At 30° two solid phases, $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SeO}_4$, exist. From 0 to 53.74% ammonium selenate, the solid phase in equilibrium with the solutions is $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$; from 53.74 to 55.18% ammonium selenate, the solid phase is $(\text{NH}_4)_2\text{SeO}_4$.

(1) A portion of a thesis presented by Ralph C. Welton in partial fulfillment of the requirements for the degree of Master of Science at The State College of Washington.

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

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

(4) King, *J. Phys. Chem.*, **41**, 797 (1937).

(5) Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

TABLE I
THE SYSTEM CaSeO_4 - $(\text{NH}_4)_2\text{SeO}_4$ - H_2O AT 30°

Solution		Residue		Solid phase
$(\text{NH}_4)_2\text{SeO}_4$ wt. %	CaSeO_4 wt. %	$(\text{NH}_4)_2\text{SeO}_4$ wt. %	CaSeO_4 wt. %	
0.0	6.84	C ^a
4.59	6.70	2.61	40.52	C
10.45	6.26	5.21	47.68	C
12.89	6.17	7.61	38.23	C
16.50	5.83	10.14	34.60	C
20.64	5.51	9.44	47.03	C
25.09	5.22	7.66	59.60	C
28.07	4.94	12.87	47.74	C
34.51	4.14	15.62	47.36	C
39.89	3.53	15.41	54.35	C
45.21	2.95	13.69	58.70	C
49.17	2.74	17.04	56.73	C
50.99	2.37	26.77	40.84	C
52.31	2.28	25.08	44.77	C
53.72	2.04	51.10	26.60	C + A
53.70	2.15	60.10	9.12	C + A
53.81	2.10	58.90	23.00	C + A
Av. 53.74	2.10	C + A
54.47	1.06	90.41	0.40	A
54.69	0.36	88.19	.10	A
55.18	0.0	A

^a C = $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$. A = $(\text{NH}_4)_2\text{SeO}_4$.

The average of three determinations gave 53.74% ammonium selenate and 2.10% calcium selenate as the composition of the eutectic mixture.

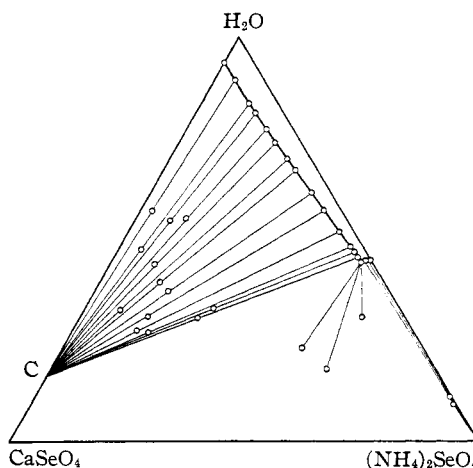


Fig. 1.—The isotherm at 30°: C represents $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$.

The most striking feature of the graph is that the solubility curve designating solutions in equilibrium with $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ is convex toward

the solid phase, whereas in most ternary systems of this type the solubility curves are concave. This indicates that the rate of decrease in solubility of calcium selenate increases with the addition of ammonium selenate. This may be due to a greater selenate ion activity in the solutions of low ammonium selenate concentration. However, the solubility of calcium selenate continuously decreases with increasing concentration of ammonium selenate, which would be expected from the common ion effect.

The corresponding sulfate system has been investigated thoroughly by Hill and Yanick.⁶ Isotherms at 25, 50, 75, and 100° were studied and results obtained by earlier investigators were shown to be incomplete in that several solid phases were not found because of their metastable nature. The solid phases were found to "differ from each other greatly in their rapidity of formation and in the time required to reach equilibrium," this time varying from a few minutes to several weeks. Hill and Yanick have pointed out that the formation of certain phases is very slow, particularly at the lower temperatures, which frequently makes it impossible to attain equilibrium.

If the sulfate and selenate systems be analogous, the eutectic mixture found in the present investigation would be in a metastable condition. It is

(6) Hill and Yanick, *THIS JOURNAL*, **57**, 645 (1935).

conceivable that because of persistence of metastable phases or because of lack of proper crystal nuclei, other solid phases may have been missed. However, samples which had been shaken occasionally over a period of three weeks and others which had been stirred continuously for as long as seven days showed no evidence of change in phase. Not a single instance was found in which a tie-line fell in the region of double salt formation except at the eutectic point. In view of this it would seem that analogous selenate solid phases are not formed at the temperature of this isotherm. However, correlation of the selenate and sulfate systems might be found at higher temperatures, although a few solubility determinations carried out at approximately 60° did not indicate such.

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Summary

1. The isotherm for the system calcium selenate–ammonium selenate–water has been determined at 30°.
2. Two solid phases, $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SeO}_4$, are present at this temperature.

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Structures of Complex Fluorides.¹ Potassium Heptafluocolumbate and Potassium Heptafluotantalate. The Configuration of the Heptafluocolumbate and Heptafluotantalate Ions

BY J. L. HOARD

Complex fluorides of quinquevalent tantalum of formulas RTaF_6 , R_2TaF_7 , and R_3TaF_8 have been described in the literature; those in which the atomic ratio of fluorine to tantalum is seven to one form the commonest and most characteristic class.² Columbium forms an extensive series of the type R_2CbF_7 , but, to a greater extent than tantalum, tends to form oxyfluorides such as $\text{K}_2\text{-CbOF}_5 \cdot \text{H}_2\text{O}$. The frequent occurrence of the seven to one ratio in the empirical formulas of so

(1) Studies of the structures of complex fluorides of tantalum, silicon, germanium, and other metals will be reported shortly from this Laboratory.

(2) Cf. Marks in J. N. Friend, "A Textbook of Inorganic Chemistry," J. B. Lippincott Co., Philadelphia, Pa., Vol. VI, Part III, p. 188.

many of these complex fluorides suggests strongly that TaF_7 and CbF_7 are stable coordination groups. It has been of interest to confirm this hypothesis through X-ray analysis of the structure of the isomorphous pair of crystals, potassium heptafluocolumbate and potassium heptafluotantalate, and to determine the configuration of the anions.

Recently published work³ indicates that ammonium and potassium heptafluozirconates contain ZrF_7 groups. As will be shown later, the configuration of ZrF_7^- is very different from that

(3) G. C. Hampson and I. Pauling, *THIS JOURNAL*, **60**, 2702 (1938).