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

The System Ammonium Selenate–Magnesium Selenate–Water at 30°[1]

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Relatively few ternary systems of the type selenate–selenate–water have been investigated. Meyer and Aulich[2] studied the following systems at 25°: Na_2SeO_4–$MgSeO_4$–H_2O; K_2SeO_4–$MgSeO_4$–H_2O; K_2SeO_4–$CaSeO_4$–H_2O; Na_2SeO_4–$CaSeO_4$–H_2O; and K_2SeO_4–Na_2SeO_4–H_2O. It was of interest to study further salt pairs of this type and to compare these with the corresponding sulfate systems. The purpose of the present investigation was to study solubility relationships in the system $(NH_4)_2SeO_4$–$MgSeO_4$–H_2O. Although the double salt $(NH_4)_2SeO_4 \cdot MgSeO_4 \cdot 6H_2O$ has been reported, solubility data in this system appear to be entirely lacking.

Experimental

Materials and Apparatus.—The preparations of selenic acid and ammonium selenate have been described previously.[3] Magnesium selenate was prepared by dissolving magnesium carbonate in selenic acid and recrystallizing the salt.

An electrically controlled thermostat was employed, allowing the temperature to be maintained at 30 ± 0.05°.

Methods of Analyses.—The ammonium selenate was determined by distilling the ammonia from an alkaline solution into standard acid and the excess acid determined by titration with sodium hydroxide. The magnesium selenate was determined by precipitation of the magnesium as magnesium ammonium phosphate and subsequent ignition to the pyrophosphate. Both determinations were checked by using samples of known magnesium and ammonium content. Water was determined by difference. The results of duplicate determinations varied no more than three parts in one thousand.

Solubility Determinations.—Various mixtures of ammonium selenate, magnesium selenate hexahydrate, and water were weighed out approximately and placed in 6-inch (15 cm.) Pyrex test-tubes. Each of these tubes was closed by a cork through the center of which passed a glass stirrer, surmounted by a small air turbine. None of the samples were dissolved by heating because of the danger of hydrolysis of ammonium selenate.

The tube contents were stirred continuously for at least twelve hours before samples were taken for analysis. In order to ensure equilibrium, samples of the solutions were removed at intervals and analyzed. Analysis showed that in all cases equilibrium conditions were reached in less than twelve hours.

Samples were removed from the solution by means of a small pipet equipped with a cotton filter, the pipet being pre-heated to slightly above the temperature of the thermostat. The solutions were weighed in glass-stoppered bottles. The tube and its content of wet residue was stoppered, the outside of the tube dried, and the tube and wet residue weighed. The residue was then transferred to a 100-ml. volumetric flask. Aliquot portions were taken for analysis.

The solubility of magnesium selenate was determined by removing samples at intervals of four hours until concordant results were obtained. A similar procedure was followed for ammonium selenate. Solubility determinations of samples of pure magnesium selenate made up at different times by different individuals gave concordant results. The same is true for ammonium selenate.

Results

The compositions of solutions and residues are given in Table I and are shown graphically in Fig. 1. Solid phases were determined by the method of Schreinemakers.[4]

TABLE I

THE SYSTEM $(NH_4)_2SeO_4$–$MgSeO_4$–H_2O AT 30°

Solution		Residue		
$(NH_4)_2SeO_4$ wt. %	$MgSeO_4$ wt. %	$(NH_4)_2SeO_4$ wt. %	$MgSeO_4$ wt. %	Solid phase
	36.60			M[a]
1.25	36.66	0.43	54.40	M
2.24	36.74	8.45	49.79	M + D
2.29	36.76	12.61	40.00	M + D
2.25	36.78	5.16	48.05	M + D
Av. 2.26	36.76			M + D
2.53	36.08	17.52	36.35	D
5.03	27.60	28.33	34.00	D
9.73	17.48	27.92	29.23	D
16.60	8.95	33.37	29.90	D
20.24	5.63	33.28	27.03	D
26.20	3.24	35.63	28.05	D
33.60	1.55	37.57	27.46	D
36.40	1.17			D
40.50	0.70	39.60	26.90	D
52.26	.22	45.24	20.77	D
55.13	.18	82.31	3.53	D + A
55.17	.22	75.07	9.11	D + A
55.15	.22	70.30	7.34	D + A
Av. 55.15	.21			D + A
54.16				A

[a] M = $MgSeO_4 \cdot 6H_2O$. D = $(NH_4)_2SeO_4 \cdot MgSeO_4 \cdot 6H_2O$. A = $(NH_4)_2SeO_4$

At 30° three solid phases: $MgSeO_4 \cdot 6H_2O$, $MgSeO_4 \cdot (NH_4)_2SeO_4 \cdot 6H_2O$, and $(NH_4)_2SeO_4$ exist. The double salt exists over almost the entire range

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(1) Part of a thesis presented by R. W. Lawrence in partial fulfilment of the requirements for the degree of Master of Science at the State College of Washington.

(2) Meyer and Aulich, *Z. anorg. allgem. Chem.*, **172**, 321 (1928).

(3) Gilbertson and King, THIS JOURNAL, **58**, 180 (1936); King, *J. Phys. Chem.*, **41**, 797 (1937).

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

of concentrations. The solubility curve for $(NH_4)_2SeO_4$ was not experimentally realizable.

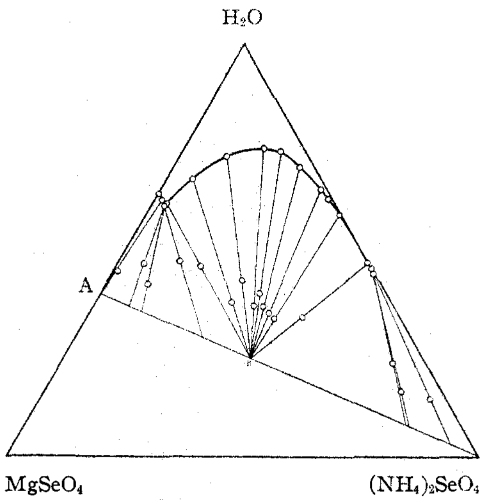

Fig. 1.—The isotherm at 30°: A represents $MgSeO_4 \cdot 6H_2O$; B represents $MgSeO_4 \cdot (NH_4)_2SeO_4 \cdot 6H_2O$.

Weston[5] investigated the corresponding sulfate system and found that the solubility curves of both $MgSO_4 \cdot 7H_2O$ and $(NH_4)_2SO_4$ could not be realized. The selenate and sulfate systems are analogous in nearly every respect.

It should be noted that the solubilities given here for both magnesium selenate and for ammonium selenate do not agree with previous determinations.[2,6] For the former, Meyer and Aulich give 31.2 wt. per cent. and for the latter, Tutton gives 57.9 wt. per cent. Tutton does not state his method for determining the solubility.

Approximate solubility determinations at 60° have been made. It was found that the same phases are present at that temperature as at 30°, the solubility of each phase increasing with increased temperature.

Acknowledgment.—Hydrogen peroxide used in the preparation of selenate salts was furnished by E. I. du Pont de Nemours and Company. This kindness is gratefully acknowledged.

Summary

1. The solubility relations in the system ammonium selenate–magnesium selenate–water have been determined at 30°.

2. The system is analogous to the corresponding sulfate system.

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(5) Weston, *J. Chem. Soc.*, **121**, 1223 (1922).

(6) A. E. H. Tutton, *ibid.*, **89**, 1071 (1906).

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Maleic Acid Production—Vapor Phase Oxidation of Five-Carbon Olefinic Acids[1]

By W. L. Faith and M. F. Yantzi

It has been shown that maleic acid may be produced by the catalytic oxidation of crotonic acid, or the corresponding aldehyde.[2,3] The purpose of the present work was to study the catalytic vapor phase oxidation of several five-carbon olefinic acids under similar conditions. The major objective of the study was to determine whether the chief product of such oxidation would be maleic acid or a five-carbon unsaturated dicarboxylic acid.

Three acids were chosen for the work: 2-pentenoic acid, $CH_3CH_2CH{=}CHCOOH$; 3-pentenoic acid, $CH_3CH{=}CHCH_2COOH$; tiglic acid, $CH_3CH{=}C(CH_3)COOH$.

It was felt that the results of the study might aid research on the catalytic vapor phase oxidation of olefin hydrocarbons.

Preparation of the Acids.—The 2-pentenoic acid was prepared by the method of Boxer and Linstead.[4] The acid boiled at 103–111° under 19 mm. pressure.

The 3-pentenoic acid was prepared by the method of Linstead, Noble and Boorman.[5] This acid boiled at 90–92° under 10 mm. pressure.

Tiglic acid was prepared by the method of Michael and Ross.[6] The crystals melted at 64°.

Method and Apparatus.—The apparatus used for the oxidation of the 2- and 3-pentenoic acids was essentially the same as that previously described.[3] In the oxidation of the tiglic acid, a preheater for the primary air was added to prevent deposition of tiglic acid crystals in the tube leading from the vaporizer to the catalyst chamber.

The bath surrounding the vaporizer was maintained at

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(1) The experimental work reported here is a part of Project No. 137 of the Kansas State College Engineering Experiment Station.

(2) Otto Drossbach, U. S. Patent 1,880,991 (Oct. 4, 1932).

(3) W. L. Faith and A. M. Schaible, This Journal, **60**, 52 (1938).

(4) S. E. Boxer and R. P. Linstead, *J. Chem. Soc.*, 740–751 (1931).

(5) R. P. Linstead, E. G. Noble and E. J. Boorman, *ibid.*, 557–561 (1933).

(6) A. Michael and J. Ross, This Journal, **55**, 3684 (1933).