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CALCIUM NITRATE. I. THE TEMPERATURE-COMPOSITION RELATIONS OF THE BINARY SYSTEM CALCIUM NITRATE–WATER

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Calcium nitrate crystallizes from water solutions, forming crystals of tetrahydrate, trihydrate, dihydrate or anhydride. If the solution is seeded with a crystal of cadmium nitrate tetrahydrate, a β form of the tetrahydrate may be obtained.

Bassett and Taylor[1] and Taylor and Henderson[2] have investigated the temperature-composition relations of this system by means of the solubility method. They find that the tetrahydrate melts at 42.7°, the β-tetrahydrate at 39.6° and the trihydrate at 51.1°, and that the dihydrate crystals are in stable equilibrium with the saturated solution only between 48.4° and 51.3°. At this latter temperature a transition takes place, the anhydride and water being formed. They also report a cryohydric temperature at —28.7° and eutectic formation between the tetra-trihydrates and the tri-dihydrates. They remark that the freezing-point method gives anomalous results.

In some work on the vapor pressure of this same system one of the authors[3] found, when crystals of the tetrahydrate are dehydrated in a vacuum at 35°, that they did not pass into the lower hydrated or anhydride crystalline forms, but that a solution phase began to appear. This behavior could not be explained by the then existing temperature-composition diagram. The following investigation was undertaken to complete the diagram. We have verified the data of the above investigators, except in the region of the dihydrate curve, and have extended the diagram into the metastable region. The freezing-point method has been used throughout.

Experimental Method

The calcium nitrate used and the method of analysis were the same as described in our vapor-pressure investigation.[3] Crystals of tetrahydrate were made by drying the moist crystals over 60 per cent. sulfuric acid in a vacuum desiccator to constant weight. The anhydride was prepared in a similar manner, using phosphorus pentoxide as the drying agent. The various concentrations were made by mixing either water and tetrahydrate, or anhydride and tetrahydrate. By heating the latter mixture

[1] Bassett and Taylor, *J. Chem. Soc.*, **101**, 576 (1912).

[2] Taylor and Henderson, THIS JOURNAL, **37**, 1688 (1915).

[3] Ewing, THIS JOURNAL, **49**, 1963 (1927).

to 70° and stirring for some time, the anhydride could be brought into solution. All mixtures were analyzed after their freezing points had been determined.

The method of determining the freezing point of the solutions was essentially that of Lidbury,[4] who has recommended a modification of the usual procedure for viscous solutions, in which equilibrium is attained slowly and in which, therefore, there is a considerable change in concentration before equilibrium is reached. He insulated the freezing tube with thick layers of cotton after crystallization had started, in order to prevent loss of heat to the surroundings.

The authors accomplished this same result by having the bath of the ordinary Beckmann apparatus consist of a vacuum tube with dilute sul-

Table I

Temperature-Composition Relations

$Ca(NO_3)_2$, %[a]	Temp., °C.	Solid phase
12.5	— 4.7	Ice
22.9	— 9.0	Ice
33.2	—16.1	Ice
46.2	—15.3	Tetrahydrate
52.0	+7.4	Tetrahydrate
59.9	30.2	Tetrahydrate
62.2	35.0	Tetrahydrate
66.2	40.5	Tetrahydrate
68.3	42.4	Tetrahydrate
69.5	42.7	α-Tetrahydrate (F. p. of compound)
69.5	39.7	β-Tetrahydrate (F. p. of compound)
69.8	42.7	Tetrahydrate
70.7	42.4	Tetrahydrate
Eutectic	42.6	Tetra-Trihydrate
71.3	42.5	Tetrahydrate
71.8	42.2	Tetrahydrate
73.4	40.9	Tetrahydrate
Eutectic	39.6	Tetra-Dihydrate
75.25	51.1	Trihydrate (F. p. of compound)
76.0	51.1	Trihydrate
76.0	48.1	Dihydrate
76.3	36.4	Tetrahydrate
76.3	50.8	Trihydrate
76.7	35.6	Tetrahydrate
76.7	49.8	Dihydrate
76.7	50.8	Trihydrate
Eutectic	50.6	Tri-Dihydrate
Transition	51.6	Di-Anhydride
Eutectic	32.7	Tetra-Anhydride
Eutectic	49.8	Tri-Anhydride

[a] % = g. $Ca(NO_3)_2$ per 100 g. of solution.

[4] Lidbury, *Z. physik. Chem.*, **39**, 453 (1902).

furic acid for the liquid. Electrodes consisting of loops of copper wire were placed at the top and the bottom. When crystallization started, the bath could be quickly raised, by means of the 110-volt alternating current, to within one degree of the temperature of the melt and could be maintained there. This gave almost adiabatic freezing conditions, and assured a maximum freezing temperature with a minimum change in concentration.

Freezing points and eutectic temperatures were determined by plotting time-temperature cooling curves.

The data obtained are tabulated in Table I.

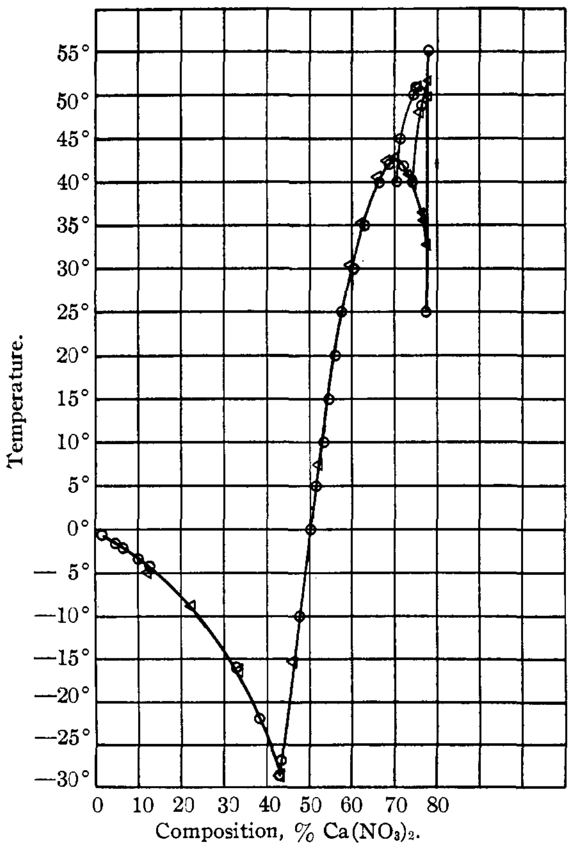

Fig. 1.—Freezing point-composition diagram of the system calcium nitrate–water.

Discussion of Results

The results are also expressed graphically in Figs. 1 and 2. For purpose of comparison, the results of Bassett and Taylor are included in these diagrams. The metastable region is plotted on a large scale in Fig. 2 for the sake of clearness, and to facilitate discussion.

Ice Curve.—For saturated solutions containing up to 44% of calcium nitrate, ice is the solid phase.

Tetrahydrate Curve.—For saturated solutions more concentrated than the cryohydric composition, calcium nitrate tetrahydrate is the solid phase. These equilibria are illustrated by curve A,B,C,D (Fig. 2). For concentrations higher than the tetra-tri eutectic the solid phase is in a metastable condition. Between B and C the solution is supersaturated with respect to the trihydrate, and between C and D with respect to both the tri- and the dihydrates. From vapor-pressure data we have found that this curve extends beyond D, in which region it is supersaturated with respect to the tri- and dihydrates and the anhydride.

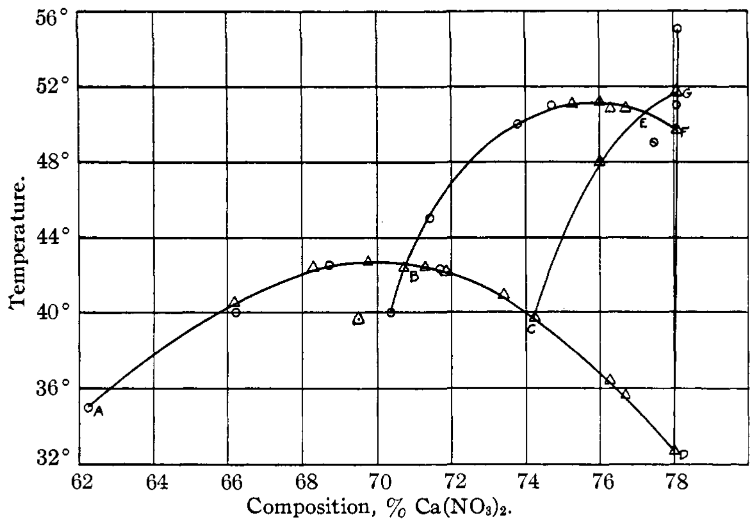

Fig. 2.—Detail of the freezing point-composition diagram of the system calcium nitrate-water. O Bassett and Taylor; △ Ewing, Krey, Law and Lang.

Trihydrate Curve.—B,E,F is the curve for a saturated solution of calcium nitrate in equilibrium with solid calcium nitrate trihydrate. Below B it is supersaturated with respect to the tetrahydrate and between E and F with respect to the dihydrate.

Dihydrate Curve.—C,E,G is the curve for a saturated solution in equilibrium with solid calcium nitrate dihydrate crystals. The reaction $Ca(NO_3)_2.2H_2O \rightleftarrows Ca(NO_3)_2 + 2H_2O$ represents the transition taking place at G (51.6°). Between E and C the solution is supersaturated with respect to the trihydrate. Vapor-pressure data show that this curve extends below C, in which region the solution is supersaturated with respect to both the tetra- and the trihydrates.

Anhydride Curve.—D,F,G is the saturated solution curve for the anhydride. It extends from below 25° up to its boiling point, 151°, at which temperature its concentration is 79% of calcium nitrate. The anhydride is in a metastable condition below the transition temperature, G.

β $Ca(NO_3)_2 \cdot 4H_2O$.—We have confirmed the existence of the metastable beta modification of the tetrahydrate by seeding a melt of tetrahydrate composition with a crystal of cadmium nitrate tetrahydrate. This gave a freezing point at 39.6°.

Types of Cooling Curves.—For any of the solutions having concentrations between about 70 and 78% several different time-temperature cooling curves are possible. Taking the 76% concentration as an example, four different curves have been obtained. They are as follows:

	F. p.	Solid phase	Eutectic	Solid phases
(1)	51.1°	$Ca(NO_3)_2 \cdot 3H_2O$	50.6°	$Ca(NO_3)_2 \cdot 3H_2O$-$Ca(NO_3)_2 \cdot 2H_2O$
(2)	51.1°	$Ca(NO_3)_2 \cdot 3H_2O$	49.8°	$Ca(NO_3)_2 \cdot 3H_2O$-$Ca(NO_3)_2$
(3)	48°	$Ca(NO_3)_2 \cdot 2H_2O$	39.6°	$Ca(NO_3)_2 \cdot 4H_2O$-$Ca(NO_3)_2 \cdot 2H_2O$
(4)	36.8°	$Ca(NO_3)_2 \cdot 4H_2O$	32.7°	$Ca(NO_3)_2 \cdot 4H_2O$-$Ca(NO_3)_2$.

Which of the four possible curves will be obtained depends upon some undetermined factor. Seeding with carefully prepared crystals apparently had little effect, sometimes one modification being obtained, sometimes another. Frequently, while one of the lower crystalline hydrates was crystallizing out in the metastable state, the temperature would suddenly rise, indicating a transformation to the stable modification. This usually occurred when the melt was nearly solid and was probably due to scratching the crystals with the stirrer.

Summary

1. The freezing-point method has been applied to determine the temperature-composition diagram of the binary system calcium nitrate–water.

2. A metastable region has been found and investigated. It lies between the concentrations of about 70 and 78% and between temperatures of 20 and 51°. In this region there are metastable eutectic mixtures containing tetra- and dihydrates, tetrahydrate and anhydride, and trihydrate and anhydride. The saturated solutions in this region are supersaturated with respect to various modifications and their solid constituents are in metastable conditions.

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