[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

CALCIUM NITRATE. II. THE VAPOR PRESSURE-TEMPERATURE RELATIONS OF THE BINARY SYSTEM CALCIUM NITRATE–WATER

BY WARREN W. EWING

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In recent years considerable work has been published on the vapor pressures of hydrated inorganic salts. Three general methods have been used in obtaining the data. Washburn and Heuse[1] have published a critical study of the dynamic method as applied to the vapor pressure lowering of solutions. Baxter and Lansing[2] have applied this method in a study of the vapor pressures of crystals, obtaining accurate results. The procedure is to pass a known volume of dry air over the mixture of crystals and to analyze for its acquired water content. Carpenter and Jette[3] have made, recently, a critical study of the static method and have applied it in determining the vapor pressures of hydrated crystals of various sulfates. In this method the substance is confined over one arm of a manometer and its pressure is compared with that of some known reference material.

Early measurements by these two methods gave conflicting results, but Menzies[4] has made a critical comparison of the two, using cupric sulfate, and has pointed out that if proper precautions are observed they give concordant results.

Indirect methods have been investigated by Wilson[5] and by Noyes and Westbrook.[6] These consist in establishing vapor distribution equilibrium between the hydrates and some reference material; in establishing water distribution equilibrium between the hydrates and some liquid in which the salt is insoluble; and of various other ingenious devices.

The method used in this investigation was the so-called dynamic method developed by Smith and Menzies.[7] It seems to be rather a static method since the substance is maintained at equilibrium pressure over a confining liquid and the vapor pressure is read from a manometer under static conditions. Derby and Yngve[8] and Edgar and Swan[9] have recently used this

[1] Washburn and Heuse, THIS JOURNAL, **37**, 309 (1915).

[2] Baxter and Lansing, *ibid.*, **42**, 419 (1920).

[3] Carpenter and Jette, *ibid.*, **45**, 578 (1923).

[4] Menzies, *ibid.*, **42**, 1951 (1920).

[5] Wilson, *ibid.*, **43**, 704 (1921).

[6] Noyes and Westbrook, *ibid.*, **43**, 726 (1921).

[7] Smith and Menzies, *ibid.*, **32**, 1448 (1910).

[8] Derby and Yngve, *ibid.*, **38**, 1439 (1916).

[9] Edgar and Swan, *ibid.*, **44**, 570 (1922).

method with excellent results. A voluminous bibliography is contained in the references mentioned above.

Although extensive investigation has been carried out in this field, a rather limited amount of reliable data has accumulated, due largely to the fact that most of the recent work has been concerned primarily with a study of methods. In the data available the vapor pressures of most systems are given at only one temperature, usually in the neighborhood of 25°. Vapor pressure-temperature relations have been investigated for only a few systems. These are either of simple type or for systems having such high melting or transition temperatures that only the partial vapor pressure-temperature diagrams have been investigated. The calcium nitrate–water system lends itself admirably to a complete investigation for the following reasons:

The complete temperature-composition diagram[10] has been worked out. The lowest temperature of this system is the cryohydric temperature at —28.7°. The vapor pressure of this point is the same as the known vapor pressure of ice at that temperature. Three hydrates and an anhydride exist. The tetrahydrate melts at 42.7° and the trihydrate at 51.1°. The dihydrate has a transition temperature at 51.6°. There are five eutectics, the lowest being at 32.7°. Complete vapor-pressure data can, therefore, be obtained for all mixtures of crystal systems and for all saturated solutions of the hydrates by making measurements through the temperature range 20 to 60°. Calcium nitrate is very soluble in water, 77.3% at 25° and 79% at its boiling point, 151°. The anhydride is the solid phase at these concentrations. All of the concentrated solutions can be supercooled to very low temperatures. Complete vapor-pressure-temperature data for solutions up to 79% can thus be obtained by measuring the vapor pressures between 20 and 60° and by determining the boiling points of the solutions. The vapor pressure-temperature relations for the three types of systems: mixtures of hydrated crystals, saturated solutions and solutions of various concentrations, give a complete equilibrium diagram for the binary system calcium nitrate–water.

Experimental Methods

Materials.—The calcium nitrate was prepared by treating a high grade of calcium carbonate with nitric acid and was subsequently crystallized out. This material was recrystallized as tetrahydrate, eight times, from water.

Apparatus.—The apparatus used was essentially the isoteniscope of Smith and Menzies,[11] with the following modifications. The bulb for the material had a volume of about 25 cc. To insure concentration equilibrium in the solutions an electromagnetic stirrer was enclosed. The bulb also had a side tube for ease in filling and in sealing it on to the isoteniscope. Cottonseed oil was used as the confining liquid. It is superior to a mineral oil in that it wets glass better than water does. The water vapor bubbling

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[10] Ewing, Krey, Law and Lang, THIS JOURNAL, 49, 1958 (1927).

[11] Smith and Menzies, *ibid.*, 32, 1448 (1910).

through the oil had no tendency to condense on the glass in the capillary tube, whereas when a mineral oil was used drops of water frequently formed on the walls of the glass capillary and blocked it up. The large vacuum and air reservoirs were eliminated.

In securing pressure equilibrium small quantities of air were admitted by means of a straight stopcock with a solid core. This core had a small cavity which carried air from the atmosphere side to the vacuum side. The pressure in the system could be lessened in small increments by quickly turning the stopcock between the system and the Cenco Hyvac pump.

Pressure was measured by comparing the mercury level in the manometer tube with that in a barometer tube of the same diameter (1 cm.). Both tubes were connected with the same mercury reservoir at their lower ends. A complete vacuum was assured above the barometer liquid by having it attached to a McLeod gage which registered a pressure of 0.018 mm. of mercury. The difference in heights between the manometer and the barometer mercury was read by means of an accurately graduated brass cathetometer with a vernier reading to 0.05 mm. Readings were corrected to zero degrees. A mercury trap was used instead of a stopcock between the isoteniscope and the remainder of the system. This insured against leakage of air through periods of a month, which was the time required to complete the measurements for some of the systems.

The electrically controlled thermostat could be regulated to ±0.05°. All temperature measurements were made with mercury in glass thermometers which were compared with a thermometer calibrated by the Bureau of Standards.

Analysis of Samples.—The samples were analyzed by placing them in weighing bottles overnight in an electric oven at 70°, which dried them to about 75% calcium nitrate. They were then cooled, seeded, crystallized and dried over phosphorus pentoxide in a vacuum desiccator, forming the anhydride. Constant weight was usually attained in five days. They were then dried for two weeks longer and check weighings made. All samples were analyzed in duplicate. This method was checked by means of the oxalate method and concordant results were obtained.

Procedure.—The usual procedure was followed in making the readings. Since the two most common criticisms of this method are that adsorbed air is not entirely removed and that equilibrium is difficult to obtain, these two points will be discussed.

When a solid phase is present in work of this type, a large amount of air is adsorbed on the surface. The finer the crystals, the greater is the surface, and consequently a larger amount of air is adsorbed. Most workers have assumed that the evaporation of water of crystallization from hydrated crystals effectually removes this adsorbed gas. Menzies,[4] however, has demonstrated with cupric sulfate that there is a residual gas which is slowly evolved and that its pressure may amount to as much as 0.3 mm. In this work this adsorbed gas was eliminated by the initial treatment of the sample. The correct amounts of materials were placed in the tensimeter so that, at the lowest temperature measured, the system would be practically all crystalline with not more than one mm. of supernatant saturated solution. This was necessary in order to obtain concentration equilibrium quickly, since it was not possible to stir the contents. The temperature was then raised until but a few small crystals remained. While in this condition the tensimeter was evacuated, intermittently, until a large volume of water vapor had been removed. The temperature was then lowered and the mass crystallized in contact only with solution and water vapor. This effectually eliminated adsorbed air. As conditions of greater solubility were reached in determining the vapor pressure-temperature curve of the saturated solutions, more water vapor was removed in order to maintain the above-mentioned relations between volumes of solid and saturated solutions. Finally, when proper concentrations existed, eutectic crystallization was induced, still in the presence only of solution and water vapor, and the vapor pressure-temperature curve for these mixtures of crystals was determined. In one case, that of the dihydrate-anhydride, measurements were made on an intimate mixture of dry crystals after they had been thoroughly evacuated to remove adsorbed air and the results checked those obtained by the above-mentioned preparation.

Pressure equilibrium between mixtures of hydrated crystals and water vapor is attained quickly or slowly according to some specific nature of the substance. By grinding the crystals together to form an intimate mixture equilibrium is hastened. Some hydrated crystals can be kept an indefinite length of time under conditions at which they would be expected to dehydrate. In this metastable condition a scratch will start dehydration. In our vapor-pressure measurements on the mixtures of crystals of the tetra- and dihydrates and of the tetrahydrate and the anhydride, the tetrahydrate was apparently in such a metastable condition. The above-described method of forming a mixture of the crystals by eutectic formation gives a very intimate mixture of the crystals. Pressure equilibrium was established within four hours. However, the final measurement was made only after 24 hours. The saturated solution required about the same time interval. Solutions, when only one phase was present, came to equilibrium in a half hour, but two hours were allowed before making the final measurement. Two points on each solution curve represent overnight time intervals.

Accuracy of Results.—The difference in heights of the mercury columns could be read to within 0.05 mm. of mercury. A variation of 0.05° in temperature at 60° gives, for the most dilute solution, a change in pressure of 0.3 mm., and for the most concentrated solution, a pressure change of 0.05 mm. At 20° these changes are respectively, 0.07 mm. and 0.01 mm. For mixtures of crystals and for saturated solutions the maximum variation, per change of 0.05°, is 0.05 mm. at the higher temperatures, and 0.01 mm. at 20°. Therefore, the change in pressure, due to variation in the temperature of the thermostat, is negligible except in the case of the dilute solutions at the higher temperatures. At these higher temperatures the most probable vapor pressures were determined by following the change in vapor pressure with the change in temperature as the heaters of the thermostat went on and off. The error here is probably as great as 0.1 mm. The accuracy of the results is further attested by the fact that with but a half-dozen exceptions all points fall within 0.1 mm. of the plotted curves.

A preliminary test of the apparatus was made using cupric sulfate. The vapor pressure of $CuSO_4.5H_2O$-$CuSO_4.3H_2O$ was found to be 7.8 mm. Menzies[4] finds 7.80 mm. by the dynamic method and 7.74 mm. by the static method, while Wilson[5] obtains 7.80 by an indirect method. Other investigators find values scattered from 7.0 to 8.5 mm.

A final check was made by determining the vapor pressure of water at 20, 30, 40, 50 and 60°. The results are within 0.1 mm. of those of Scheel and Heuse.

From the above considerations the author estimates a maximum error of 0.1 mm. in the results presented.

Boiling Points of Solutions.—The boiling points of the solutions were determined by the bulblet method of Smith and Menzies.[12] The bulb had a volume of 10 cc. and 3 to 5g. samples were taken. These samples were analyzed in the usual manner after the runs. Paraffin wax having a melting point of about 55° was used as the confining liquid. This was a convenient liquid because in removing the bulb from the bath some of the bath liquid always sucked back into it. This solidified and so permitted the removal of the uncontaminated solution for analysis. The temperature was maintained constant to within 0.1° by means of an electric coil and vigorous stirring.

The following boiling points for the various concentrations were obtained: 21.5% $Ca(NO_3)_2$, 102.1°C.; 32.1%, 104.1°; 51.1%, 111.8°; 60.5%, 119.6°; 69.9%, 132.0°; 75.0%, 142.8°; 77.4%, 147.3°. By plotting these data, boiling points for any concentration may be obtained. This gives the following boiling points for the concentrations for which solution vapor pressures were measured: 20.2%, 102°; 30.6%, 104°; 49.6%, 111°; 59.1%, 118.3°; 66.6%, 126.7°; 72.2%, 136.0°; 74.2%, 140.5°; 74.7%, 141.5°; 76.3%, 145.0°; 76.9%, 146.4°; 77.4%, 147.5°. At these temperatures the vapor pressures of these various solutions are 760 mm.

Gerlach[13] gives results uniformly lower than these for concentrations above 50%. His results are evidently in error since he obtains the boiling point of 152° for a saturated solution containing 82% of calcium nitrate.

Discussion of Results

The vapor-pressure data obtained are tabulated in Tables I, II and III. For clearness of presentation and to facilitate discussion, the data are also plotted in the various curves. The reader should also refer to the temperature-composition diagram in the preceding article.

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[12] Smith and Menzies, THIS JOURNAL, **32**, 897 (1910).

[13] Gerlach, *Z. anal. Chem.*, **26**, 413 (1887).

TABLE I

TEMPERATURE-VAPOR PRESSURE RELATIONS OF THE SYSTEMS, CRYSTALS–SATURATED SOLUTION–WATER VAPOR

I. Crystal Phase, $Ca(NO_3)_2.4H_2O$

Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
0	2.7	39	19.5	38	8.6
5	3.9	40	19.7	37	7.75
10	5.2	41	19.7	36	7.0
15	6.9	42	19.3	35	6.4
20	9.4	42.5	19.0	34	5.75
25	12.0	42.5	15.5	32	4.7
30	14.9	42	13.8	30	3.9
35	17.7	41	12.25	25	2.4
36	18.2	40	10.9	20	1.5
37	18.9	39	9.5	15	1.15
38	19.3				

II. Crystal Phase, $Ca(NO_3)_2.3H_2O$

Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
35	13.3	46	19.8	51	19.4
40	16.2	47	20.2	51	16.8
42	17.8	48	20.5	50.5	15.4
43	18.3	49	20.6	50	14.4
44	18.8	50	20.5	49	13.3
45	19.3	50.5	20.2		

III. Crystal Phase, $Ca(NO_3)_2.2H_2O$

Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
20	4.25	45	13.2	50	15.3
30	7.1	48	14.4	51	15.6
40	11.1	49	15	51.5	15.8

IV. Crystal Phase, $Ca(NO_3)_2$

Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg.	Temp., °C.	V. p., mm. Hg
30	4.2	50	14.6	54	18.1
35	5.9	51	15.3	55	19.0
40	8.0	52	16.1	57	21.2
45	10.8	53	17.2	60	24.9
48	12.8				

TABLE II

TEMPERATURE-VAPOR PRESSURE RELATIONS OF THE SYSTEMS, MIXTURES OF CRYSTALS–WATER VAPOR

I. Crystalline Phases, $Ca(NO_3)_2.4H_2O$-$Ca(NO_3)_2.3H_2O$

Temp., °C.	V. p., min. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
20	3.0	37	11.7	40	14.8
25	4.5	38	12.5	41	15.8
30	6.8	39	13.7	42	16.9
35	10.0				

II. Crystalline Phases, $Ca(NO_3)_2.4H_2O$-$Ca(NO_3)_2.2H_2O$

20	2.8	35	8.0	38	9.8
25	4.0	36	8.6	39	10.6
30	5.7	37	9.2		

TABLE II (*Concluded*)

Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg	Temp., °C.	V. p., mm. Hg
III. Crystalline Phases, $Ca(NO_3)_2.4H_2O$-$Ca(NO_3)_2$					
20	2.0	25	3.0	30	4.1
IV. Crystalline Phases, $Ca(NO_3)_2.3H_2O$-$Ca(NO_3)_2.2H_2O$					
20	1.8	35	5.7	45	10.8
25	2.65	40	7.8	50.5	15.6
30	3.8				
V. Crystalline Phases, $Ca(NO_3)_2.2H_2O$-$Ca(NO_3)_2$					
20	1.5	38	6.2	48	12.4
25	2.2	40	7.1	50	14.4
30	3.3	45	10.1	51	15.3
35	4.9				

TABLE III

TEMPERATURE-VAPOR PRESSURE RELATIONS OF THE SYSTEMS, SOLUTIONS OF $Ca(NO_3)_2$ IN WATER–WATER VAPOR

Temp., °C.	V. p., mm. Hg										
	20.2%[a]	30.6%	49.7%	59.1%	66.6%	72.2%	74.2%	74.7%	76.3%	76.9%	77.4%
20	16.4	15.3	11.3	8.2	5.4	3.7	3.2	(3.05)	2.5	2.35	2.3
30	29.9	27.6	20.6	15.1	10.4	6.9	6.0	5.8	4.9	4.6	4.5
40	52.6	48.0	36.1	26.6	18.7	12.7	10.7	10.4	9.2	8.6	8.4
50	86.8	80.2	61.3	45.3	31.6	21.9	18.9	18.0	16.2	15.1	14.8
60	140.6	130.5	99.7	75.0	52.7	36.8	31.9	(30.0)	27.5	25.5	25.0

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

Saturated Solution Curves.—In Fig. 1, A,A,A is the vapor pressure-temperature curve for a saturated solution in contact with crystals of the tetrahydrate; B,B,B the trihydrate; C,C,C the dihydrate; and D,D,D the anhydride. In each of these saturated solutions the same supersaturated conditions for the solutions and the same metastable conditions for the crystals prevail as described in the composition-temperature discussion in the preceding article.

On the curve for the saturated solution in contact with crystals of the tetrahydrate the vapor pressure rises rapidly with the temperature up to about 37°. At this temperature the rate of increase slows down, with rise in temperature, due to the increased solubility becoming the predominating factor. At 41° the vapor pressure even begins to decrease with rise in temperature until the melting point, 42.7°, of the tetrahydrate is reached. The reflex portion of the curve represents the saturated solution in unstable equilibrium with respect to the other crystalline forms. The initial region of this curve may be extrapolated to meet the vapor pressure of ice, 0.321 mm., at the cryohydric temperature, —28.7°. This is permissible because at this condition ice, tetrahydrate, saturated solution and water vapor are in equilibrium and, therefore, the vapor pressure of the system is the same as the vapor pressure of any of the constituents. The curve for the trihydrate is similar to that for the tetrahydrate. The dihydrate and the anhydride curves do not show a region of decrease in vapor pressure with increase in temperature. This is because the dihydrate reaches its transition temperature before its melting point is reached, and the saturated solution boils (151°) below the melting point of the anhydride. The vapor pressure of water above this solution should approach zero as the composition of the saturated solution approaches pure anhydride and the temperature approaches the melting point of the anhydride.

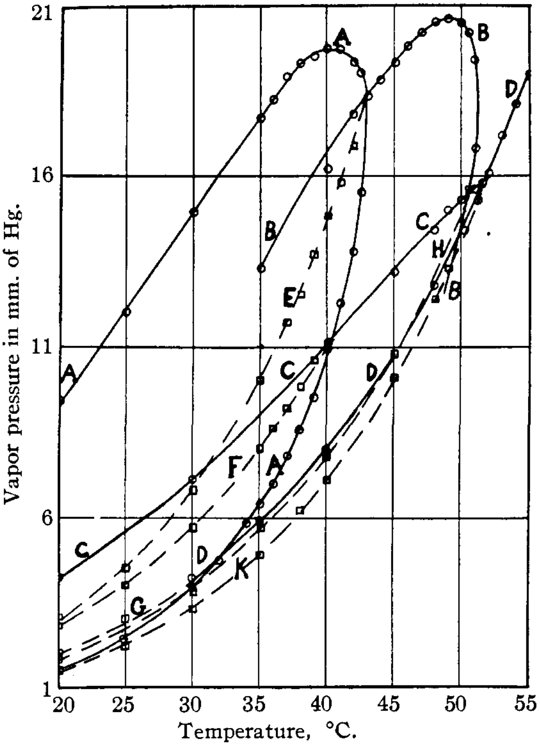

Fig. 1.—Vapor pressure-temperature relations for saturated solutions and for mixtures of hydrates of calcium nitrate.

Mixtures of Crystals.—At the temperatures at which the saturated solution curves meet, the pressure is the vapor pressure of the eutectic equilibrium for the four phases crystal + crystal + saturated solution + water vapor, except in the case of the dihydrate and the anhydride saturated solutions, where it is the vapor pressure of the transition equilibrium $Ca(NO_3)_2 . 2H_2O \rightleftarrows Ca(NO_3)_2 + 2H_2O$. Here, too, the same four phases are present. At lower temperatures the saturated solution phase disappears and the vapor pressure is that of the mixture of two crystalline forms.

These conditions are represented by curve E, Fig. 1, for a mixture of tetra- and trihydrates; F for tetra-di-; G for tetra-anhydride; H for tri-di-; and K for di-anhydride. The curve for the trihydrate-anhydride mixture was not determined. It would lie about 0.2 mm. above that for the dihydrate-anhydride. This is but slightly greater than the experimental error of measurement.

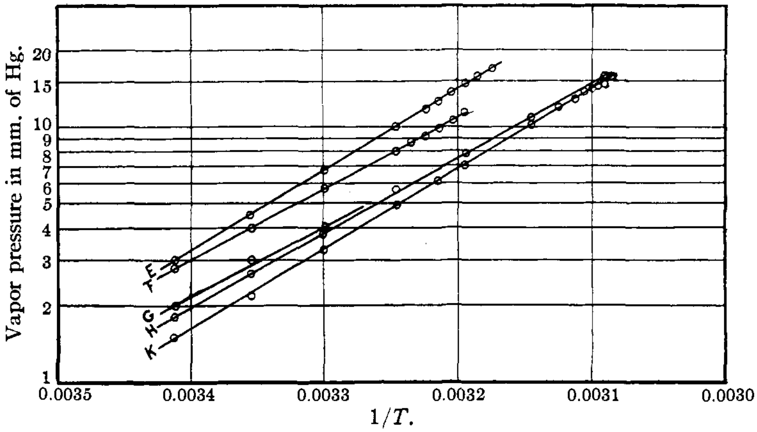

Fig. 2.—Mixture of crystals.

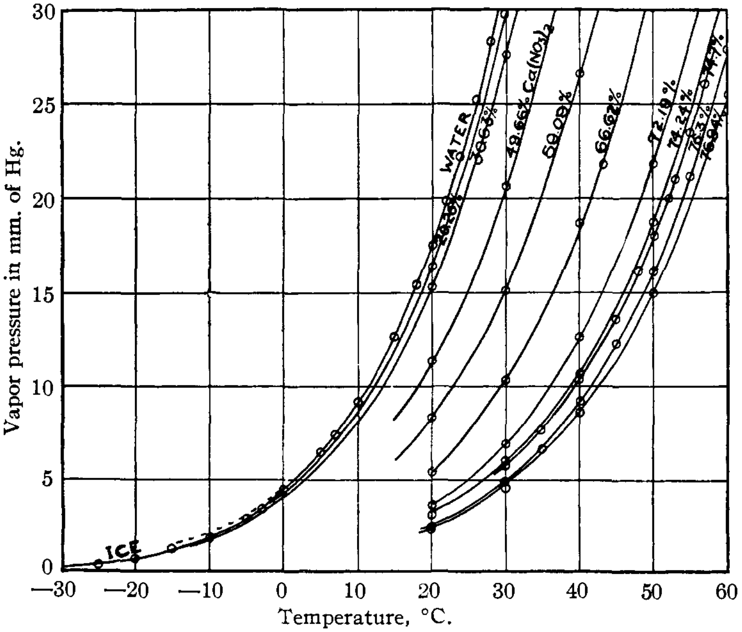

Fig. 3.—Vapor pressures of solutions of calcium nitrate in water.

In Fig. 2, the vapor pressure of these mixtures is plotted against the inverse of the absolute temperature, on a logarithmic scale for the pressure, the letters E, F, G, H and K having the same significance as above. Except for one point on the tetra-anhydride curve, all experimental values fall upon the straight lines. This is in agreement with the results of other investigators on this type of system.

Solution Curves.—Fig. 3 gives the vapor pressure-temperature relations of solutions of calcium nitrate in water for various concentrations from 20 to 77%. A solution of calcium nitrate saturated with the anhydride at 25° contains 77.3% of calcium nitrate. The vapor pressure data for water and ice are those of Scheel and Heuse.[14]

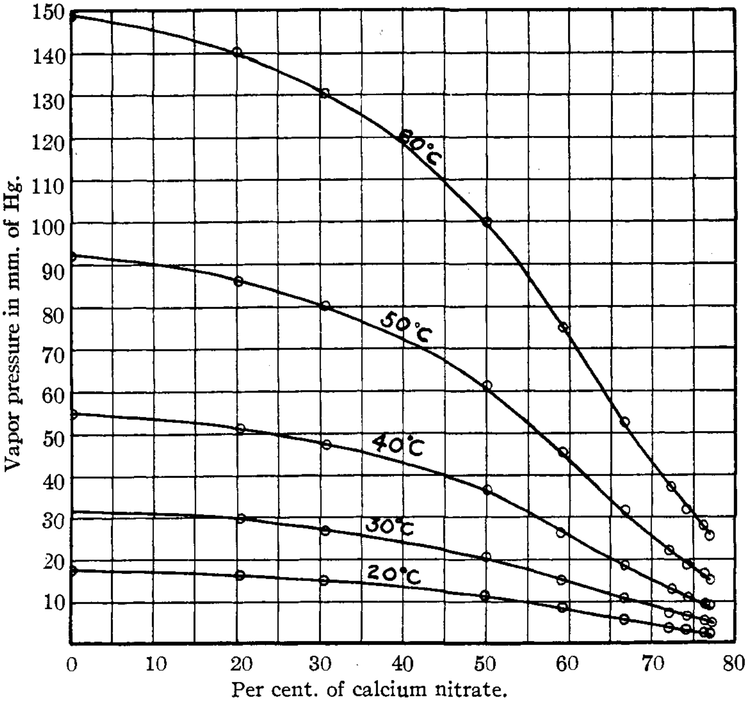

Fig. 4.—Vapor pressure-composition isotherms for calcium nitrate solutions.

The 20.2% and the 30.6% curves have been extrapolated to meet the ice curve at the temperatures at which they are in equilibrium with ice. If these data are plotted with the logarithm of the pressure against the inverse of the temperature as coördinates, apparently straight lines are obtained for temperatures up to 60°. The same holds for water. These lines are not parallel but converge in the direction of the higher temperatures. Above 60°, however, the value of ln P for water falls below

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[14] Scheel and Heuse, *Ann. Physik* [4] **29,** 723 (1909); [4] **31,** 715 (1910).

the straight line, the divergence increasing steadily up to its critical temperature. If values of the vapor pressure (760 mm.) at the boiling temperatures of these various solutions are plotted on this same diagram, these curves also show a change in slope similar to that of water.

Temperature-Composition Diagrams from Vapor-Pressure Data.—Fig. 4 contains vapor pressure-composition isotherms plotted from the solution data in Table III. From these curves it is possible to plot any number of additional vapor pressure-temperature curves for solutions. If a sufficient number of such curves are superimposed upon the saturated solution curves in Fig. 1, it is possible to obtain data for a complete temperature-composition diagram, at the vapor pressures of the systems, for this system. The point at which any given solution curve crosses any given saturated solution curve gives the composition and temperature data for that solution. Data obtained in this manner give a temperature-composition diagram which is, within experimental error, the same as Fig. 2 in the preceding article, with the additions that the unstable saturated solution curves extend beyond the various eutectics.

Thermal data for these systems are being measured in this Laboratory. Thermal data calculated from these vapor-pressure measurements will be presented when this work is completed.

Summary

Complete vapor-pressure-temperature relations of the binary system calcium nitrate–water have been determined. This involved measurements at various temperatures from 20° to the boiling points of the solutions, and for various concentrations from 20% to the saturated solution of the anhydride. The systems in this region contain dilute solutions and supersaturated solutions, stable and unstable saturated solutions, and stable and metastable mixtures of crystals.

In the mixtures of crystals, $\ln P$ is proportional to $1/T$. Solutions apparently obey the same law up to temperatures of about 60°.

Temperature-composition diagrams can be constructed from vapor pressure-temperature data.

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