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

Studies on the Vapor Pressure–Temperature Relations of the Binary System Zinc Nitrate–Water

BY WARREN W. EWING AND H. M. FISHER

Vapor pressure data on the binary system zinc nitrate–water are presented in this article, which is a continuation of a series of similar studies being carried on in this Laboratory. Reports on the calcium nitrate system and the magnesium nitrate system have been published. The cadmium nitrate system is now being investigated. These systems are particularly suitable for these types of studies since, in general, they are quite stable over ordinary temperature ranges, they form various hydrates, they are quite soluble and the solutions can be supercooled readily, especially in the concentrated ranges. Due to this supercooling, vapor pressures can be measured on very concentrated solutions; up to 82% on the zinc nitrate system.

According to solubility studies,[1-3] zinc nitrate crystallizes with varying amounts of water, namely, $Zn(NO_3)_2 \cdot 9H_2O$ (T. P. = −17.6°), $Zn(NO_3)_2 \cdot 6H_2O$ (m. p. = 36.1°), $Zn(NO_3)_2 \cdot 4H_2O$ (m. p. 44.7°), $Zn(NO_3)_2 \cdot 2H_2O$ (m. p. 55.4°), $Zn(NO_3)_2 \cdot H_2O$ (m. p. 73.9°). Probably the anhydride also exists.[4] In this investigation, vapor pressures of two-phase systems (unsaturated and supersaturated solutions plus vapor), and the three-phase systems hydrated salt-saturated solution–vapor (in the stable and the metastable regions) and mixtures of two hydrated salts–vapor have been measured over the temperature range 20 to 60°.

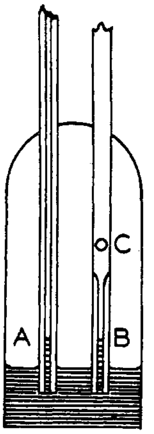

Fig. 1.—Tensimeter trap.

Preparation of Materials.—A C. P. grade of zinc nitrate was purified by three recrystallizations, first as tetrahydrate and subsequently twice as hexahydrate, from solutions containing a little nitric acid. The hexahydrate crystals were freed from excess water and nitric acid by continuous evacuation.

The unsaturated solutions for the vapor pressure experiments were made by dissolving the hexahydrate. The more concentrated solutions were made by evaporating the molten hexahydrate crystals at 80°. This resulted in some decomposition of zinc nitrate. Consequently, all solutions were adjusted to neutrality, where necessary, with 100% nitric acid, using brom thymol blue indicator.

Experimental

The vapor pressure measurements were made in a modified Smith–Menzies apparatus which was described in the magnesium nitrate article.[5]

The only alteration was the redesign of the dibutyl phthalate trap. The new design is illustrated in Fig. 1. A and B are two capillary tubes of identical bore. Consequently, when the pressures on the two sides of the dibutyl phthalate are the same, the liquid rises in A to the same height that it does in B due to capillary attraction. This makes the measuring of the difference from the true equilibrium height much easier. C is an opening through which air and vapor can pass. This arrangement also has an advantage in the measurement of pressures below one millimeter. In this low range the errors in measuring the difference in heights of two mercury columns are a large percentage of the total pressure. When the external system is evacuated completely, the dibutyl phthalate trap then serves as a manometer which is about thirteen times as sensitive as a mercury manometer, due to the different densities of the two liquids. This sensitivity is diminished somewhat due to the greater difficulty in measuring the exact position of the meniscus of dibutyl phthalate.

Vapor pressure studies were made on the following systems: (1) a mixture of hexahydrate and tetrahydrate crystals from below the eutectic temperature down to 10° (Table I); (2) a mixture of tetrahydrate and dihydrate crystals from the eutectic temperature down to 20° (Table II); (3) saturated solutions over the range from a saturated solution of hexahydrate at 10° to a saturated solution of dihydrate at 55° (Table III); (4) solutions ranging in concentration from 10 to 57% from 20 to 50°; solutions from 63 to 72% from 30 to 60°; and two solutions 80 and 82% from 35 to 60° (Table IV).

TABLE I

THE VAPOR PRESSURE OF A MIXTURE OF HEXAHYDRATE AND TETRAHYDRATE CRYSTALS

Temp., °C.	V. p., mm.
34	7.54
30	5.95
25	4.15
20	2.92
15	2.00
10	1.36

TABLE II

THE VAPOR PRESSURE OF A MIXTURE OF TETRAHYDRATE AND DIHYDRATE CRYSTALS

Temp., °C.	V. p., mm.
39	2.42
38	2.25
37	1.80
35	1.25
30	0.65
25	.27
20	.08

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[1] Ewing, McGovern and Mathews, THIS JOURNAL, **55**, 4827 (1933).

[2] Ewing, Ricards, Taylor and Winkler, *ibid.*, **55**, 4830 (1933).

[3] Sieverts and Petzold, *Z. anorg. allgem. Chem.*, **212**, 52 (1933).

[4] Marketos, *Compt. rend.*, **155**, 210 (1912).

[5] Ewing, Klinger and Brandner, THIS JOURNAL, **56**, 1053 (1934).

TABLE III

THE VAPOR PRESSURE OF SATURATED SOLUTIONS

Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.
Solid phase $Zn(NO_3)_2 \cdot 6H_2O$		Solid phase $Zn(NO_3)_2 \cdot 4H_2O$		Solid phase $Zn(NO_3)_2 \cdot 2H_2O$	
10	4.25	34	7.54	37	1.80
20	7.27	35	7.95	38	2.00
25	9.01	36	8.36	39	2.15
30	10.76	38	8.74	40	2.24
33	11.45	40	9.18	42	2.36
34	11.55	42	9.14	45	2.48
35	11.42	43	9.02	50	2.44
36	10.55	44	8.56	55	2.06
36	9.66	44	5.73	$Zn(NO_3)_2 \cdot 2H_2O$ Metastable	
35	8.15	43	4.21	35	1.57
34	7.54	41	3.43	30	1.15
		39	2.42	25	0.55
		38	2.25	20	.42

These data are shown in Fig. 2. Curve ABC represents the vapor pressure–temperature relations of saturated solutions of hexahydrate. Curve CEF represents saturated solutions of tetrahydrate, while FI represents saturated solutions of dihydrate. Curve FH represents saturated solutions of dihydrate in a metastable region. Curves CD and FG are, respectively, the mixtures of hexahydrate–tetrahydrate crystals, and tetrahydrate–dihydrate crystals. The remaining curves, numbers 1 to 15, represent vapor pressure–temperature relations of the solutions designated in Table IV. The points at which these curves cross ABC, CEF, and FI, are the freezing points of the various solutions. Supersaturation was obtained in a few cases, more easily for solutions supersaturated with respect to tetrahydrate than with the other hydrates.

TABLE IV

THE VAPOR PRESSURE OF SOLUTIONS OF ZINC NITRATE

Solution	Concn., %	M	Temp., °C.					
			20	30	40	50	60	
1	10.258	0.603	16.78	30.41	53.04	88.97		
2	18.466	1.196	15.99	29.24	51.00	85.62		
3	25.577	1.815	15.60	28.31	49.70	82.55		
4	26.434	1.897	15.12	27.31	48.34	80.24		
5	32.354	2.525	14.25	25.31	45.21	75.01		
6	34.618	2.796	13.62	25.17	44.07	72.60		
7	35.079	2.853	13.37	23.33	42.42	71.63		
8	44.045	4.156	11.05	19.98	35.19	59.49		
9	53.236	6.011	8.04	14.85	26.25	43.16		
10	57.362	7.103	6.30	11.45	20.32	35.55		
11	63.150	9.048		7.76	13.91	24.05	40.96	
12	67.514	10.973		4.75	8.74	15.17	26.21	
13	72.713	14.070		2.46	8.42	8.42	14.74	
			35	40	45	50	55	60
14	80.177	21.355	1.77	2.38	3.20	4.21	5.65	7.11
15	82.375	24.677	1.02	1.45	1.87	2.48	3.28	4.33

Solution 15 20° 0.37 25° 0.53 30° 0.75

The method of least squares was used on an equation of the form, $\ln p = A/T + BT + C$ to coördinate the data on the fifteen solutions in Table IV. The pressures were calculated at each temperature and usually showed less deviation than the probable errors computed for each set of readings at one temperature. After a consideration of all errors, it may be said that the data presented is accurate to 0.2%.

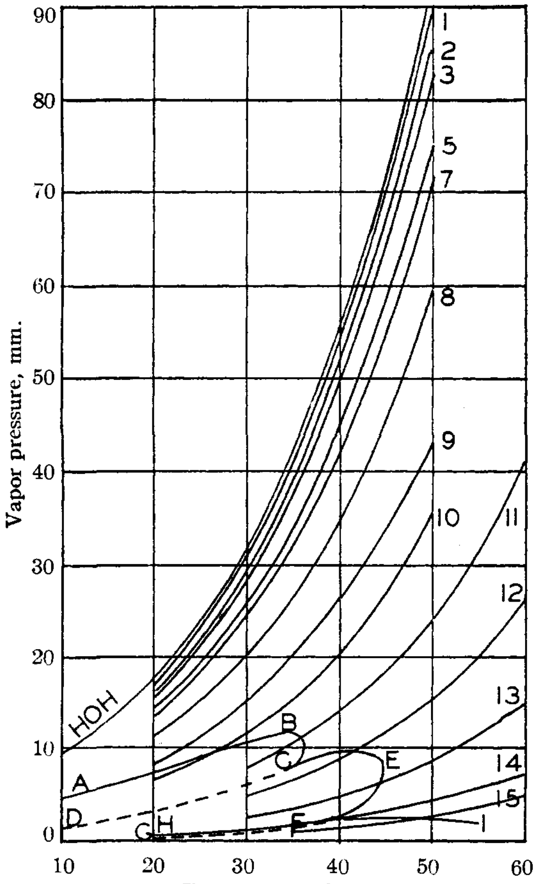

Fig. 2.

Vapor pressure measurements were not made at concentrations higher than 82%, which is the concentration of the saturated dihydrate solution at 50° (see Fig. 2), because at higher concentrations than this the zinc nitrate decomposed to such an extent that the data obtained were not reliable enough to warrant publication. This decomposition became noticeable at the higher temperatures above 82% concentrations. Consequently, the complete data for the dihydrate curve and the data on the monohydrate saturated solutions are not given.

Summary

Complete vapor pressure data on the system zinc nitrate–water from 0 to 82% concentration and from 10 to 60° are given. This includes vapor pressures for unsaturated, saturated and supersaturated solutions and for eutectic mixtures of crystals.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Ionization Constant of α-Crotonic Acid at 25° from Conductance Measurements[1]

BY BLAIR SAXTON[2] AND GEORGE W. WATERS

A general outline of the experimental technique and method of calculation employed in this study can be found in previous communications[3,4] from this Laboratory. Measurements of the conductance of α-crotonic acid ($CH_3CH{=}CHCOOH$) at concentrations above 0.002 demal, and of its sodium salt at all concentrations, were made in a cell of Type B described by Saxton and Langer.[3] The cell constant was 3.7261 estimated on the basis of a 0.1 demal potassium chloride solution according to Jones and Bradshaw.[5] Measurements on the acid at concentrations below 0.002 demal were performed in a silica cell similar to that of Saxton and Meier,[4] and of cell constant, 1.0830 based upon the 0.01 demal solution of Jones and Bradshaw.[5] The bridge was built by Leeds and Northrup according to the description of Dike,[6] and the source of power was a Leeds and Northrup Audio Frequency Oscillator No. 9842 operating at 1000 cycles.

Preparation of Materials

The α-crotonic acid was a commercial product subjected to five recrystallizations from carefully purified petroleum ether, and slowly sublimed. The white crystalline product was almost odorless, and melted between 71.5 and 71.7° according to measurements made in a simple Thiele tube with a recently calibrated thermometer. The value 71.4° was previously obtained in this Laboratory[7] from cooling curves with acid from the same source. The acid was stored in a vacuum desiccator over calcium chloride and suffered no appreciable change in melting point during the course of the conductance measurements.

The sodium salt was prepared from sodium carbonate (*ex* bicarbonate) and α-crotonic acid in sufficient excess to bring the resulting solutions to a *p*H of 6.7 to 7.0 on the basis of Lamotte standard buffers and brom thymol blue. Conductivities of these solutions were corrected[8] for the effect of the excess acid.

The experimental results, $\Lambda_{(\text{obsd.})}$, for sodium α-crotonate are recorded in Table I along with values derived from the semi-empirical equation[9]

$$\Lambda_{(C_4H_5O_2Na)} = 83.30 - 78.84\sqrt{c} + 97.27c(1 - 0.2276\sqrt{c}) \qquad (1)$$

TABLE I

SODIUM α-CROTONATE

$c \times 10^3$	$\Lambda_{(\text{obsd.})}$	$\Lambda_{(\text{Eq. 1})}$
0.18773	82.13	82.24
.75176	81.19	81.21
1.6436	80.23	80.29
2.6083	79.45	79.52
2.8315	79.38	79.38
3.9861	78.68	78.71
4.5069	78.48	78.44
5.6194	77.95	77.93
7.2425	77.31	77.28
9.8864	76.46	76.40
14.735	75.19	75.12
20.222	74.04	73.99
23.334	73.49	73.45
29.457	72.48	72.52
32.616	72.08	72.10

The parameters of this equation were adjusted to fit the data by the method of least squares. Assuming the validity of the Kohlrausch principle, equation (1) may be combined with the expressions

$$\Lambda_{HCl} = 426.28 - 156.84\sqrt{c} + 169.7c(1 - 0.2276\sqrt{c}) \qquad (2)$$

$$\Lambda_{NaCl} = 126.47 - 88.65\sqrt{c} + 94.8c(1 - 0.2276\sqrt{c}) \qquad (3)$$

previously obtained in this Laboratory[10] to yield the relation

$$\Lambda_{C_4H_5O_2H} = 383.11 - 147.03\sqrt{c_i} + 172.2c_i(1 - 0.2276\sqrt{c_i}) \qquad (4)$$

for the hypothetical completely dissociated α-crotonic acid at an ion concentration c_i.

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[1] This communication embodies part of the experimental material to be presented by George W. Waters to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] After Professor Saxton's death, June 16, 1936, this work was continued under the direction of Professor Benton B. Owen.

[3] Saxton and Langer, THIS JOURNAL, **55**, 3638 (1933).

[4] Saxton and Meier, *ibid.*, **56**, 1918 (1934).

[5] Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

[6] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[7] Saxton and Skau, THIS JOURNAL, **52**, 335 (1930).

[8] MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[9] Shedlovsky, *ibid.*, **54**, 1405 (1932).

[10] The values of the characteristic parameters determined by Saxton and Langer (ref. 3) have been altered slightly to conform to present cell constants; *cf.* ref. 5.