is found to account satisfactorily for the X-ray data. This structure is closely related to that of $(NH_4)_3AlF_6$; the $[AlF_6]^{\equiv}$ complex ions are replaced by $[ZrF_7]^{\equiv}$ complex ions in which zirconium has coördination number seven. Potassium heptafluozirconate is found to have a similar structure, with $a_0 = 8.95$ Å.

PASADENA, CALIF. RECEIVED SEPTEMBER 6, 1938

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

The Binary System Cadmium Nitrate–Water: Vapor Pressure–Temperature Relations

BY WARREN W. EWING AND WALTER R. F. GUYER

This article presents the vapor pressure data for the binary system cadmium nitrate–water, and is a continuation of the series of studies being made on the alkaline earth nitrates in this Laboratory. Results for calcium nitrate, magnesium nitrate, and zinc nitrate already have been published. The alkaline earth nitrates are a particularly fruitful group for these investigations for several reasons: the water–nitrate system is quite stable; various hydrates exist, making crystalline mixture studies possible. The salts are very soluble in water, yielding solutions which can be supercooled. Vapor pressures have been obtained for a concentration as high as 86% cadmium nitrate (26 molal).

In addition to the anhydride, three hydrates of cadmium nitrate are mentioned in the literature: the dihydrate, which melts incongruently at 56.8°; the tetrahydrate, which melts congruently at 59.5°; and the enneahydrate which melts incongruently at 3.5°. Although the tetrahydrate was observed as early as 1855, by v. Hauer,[1] the existence of the dihydrate was not satisfactorily demonstrated until the work of G. Malquori[2] was published.

Sieverts and Petzold,[3] in their work on the nitrates of the second group in the periodic system, recently determined the solubility curve of the cadmium nitrate–water system. In the "I. C. T." very fragmentary data of vapor pressure for cadmium nitrate are found.

Preparation of Materials.—C. P. cadmium nitrate tetrahydrate was recrystallized three times as the tetrahydrate. The tetrahydrate was dried by putting it over 55% sulfuric acid in a vacuum desiccator. The single phase solutions were analyzed after the vapor pressure had been determined by ignition in porcelain crucibles to the oxide at 600° for two hours. These solutions had been concentrated almost to dryness in a rapid drier before ignition.

Experimental.—The vapor pressure measurements were made in the modified Smith–Menzies apparatus.[4–6] The dibutyl phthalate trap, having two capillaries, introduced by Ewing and Fisher in their work on zinc nitrate,[7] was used for all of the vapor pressure measurements.

TABLE I

THE VAPOR PRESSURES OF SATURATED SOLUTIONS OF CADMIUM NITRATE (m = metastable)

Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.
Solid phase: Tetrahydrate		Solid phase: Dihydrate	
0.00	2.93	30.00	5.26m
4.99	4.09	40.03	7.95m
9.97	5.56	49.02	10.59
15.00	7.34	49.93	10.81
19.94	9.81	51.04	11.05
24.88	12.76	52.00	11.26
29.87	16.36	52.42	11.33
35.03	20.68	53.04	11.31
40.18	25.77	54.02	11.48
45.18	30.95	55.03	11.34
50.03	36.09	55.91	11.20
55.06	39.97	56.02	11.00
56.13	40.22	56.60	10.92
57.13	40.14	Solid phase: Anhydride	
58.00	39.39	20.01	1.18m
58.96	32.88	25.00	1.56m
58.00	27.91	30.00	2.13m
57.75	26.10	35.00	2.84m
55.01	18.73	39.98	3.71m
54.86	18.56	50.03	6.45m
49.99	11.58	55.02	8.35m
44.98	7.42m	60.00	10.86
44.62	7.42m	61.43	11.58
39.97	4.80m	61.60	11.70
34.98	3.06m	70.13	17.37

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[1] v. Hauer, *Ber. Wien. Akad.*, **15**, 30 (1855).

[2] Malquori, *Gazz. chim. ital.*, **58**, 206 (1928).

[3] Sieverts and Petzold, *Z. anorg. allgem. Chem.*, **212**, 49 (1933).

[4] Smith and Menzies, THIS JOURNAL, **32**, 1448 (1910).

[5] Ewing, *ibid.*, **49**, 1963 (1927).

[6] Ewing, Klinger and Brandner, *ibid.*, **56**, 1053 (1934).

[7] Ewing and Fisher, *ibid.*, **59**, 1046 (1937).

TABLE II

THE VAPOR PRESSURE OF SOLUTIONS OF CADMIUM NITRATE (m = METASTABLE)

Soln., no.	% $Cd(NO_3)_2$	Molality		Temperature °C.						
				20	30	40	50	60	70	
1	10.900	0.517	P	17.05	31.03	54.01	90.61	146.42		
			P/P_0	0.9727	0.9751	0.9761	0.9772	0.9802		
2	23.358	1.289	P	16.26	29.60	51.56	86.64	139.86		
			P/P_0	0.9283	0.9302	0.9320	0.9365	0.9360		
3	28.908	1.720	P	15.75	28.69	50.00	83.72	135.78		
			P/P_0	0.8981	0.9014	0.9038	0.9050	0.9089		
4	43.935	3.315	P	13.78			73.82	119.92		
			P/P_0	0.7858			0.7979	0.8050		
5	49.615	4.165	P	12.71	23.14	40.62	68.28	111.26		
			P/P_0	0.7248	0.7276	0.7340	0.7382	0.7447		
6	61.701	6.814	P	9.28	17.18	30.39	51.51	84.55		
			P/P_0	0.5287	0.5400	0.5492	0.5569	0.5661		
7	65.357	7.980	P	8.09m	14.98m	26.40	44.88	74.17		
			P/P_0	0.4610	0.4709	0.4774	0.4851	0.4965		
8	69.823	9.786	P		12.02m	21.22m	36.21	60.12		
			P/P_0		0.3777	0.3839	0.3914	0.4025		
9	73.501	11.731	P		9.15m	16.25m	28.04m	47.41	76.29	
			P/P_0		0.2875	0.2938	0.3031	0.3173	0.3265	
10	78.710	15.637	P		5.70m	10.29m	18.14m	30.39	49.56	
			P/P_0		0.1791	0.1859	0.1961	0.2034	0.2121	
11	81.218	18.290	P		4.00m	7.38m	13.20m	22.45	37.25	
			P/P_0		0.1257	0.1336	0.1427	0.1502	0.1596	
12	83.132	20.845	P			6.05m	10.58m	18.23	30.36	
			P/P_0			0.1094	0.1144	0.1221	0.1315	
13	85.176	24.303	P			4.41m	7.90m	13.77	22.91	
			P/P_0			0.0797	0.0855	0.0921	0.0982	
				40	50	55	60	65	70	75
14	86.075	25.886	P	3.88m	6.99m	9.21m	12.13	15.69	20.17	25.85
			P/P_0	0.0701	0.0756	0.0781	0.0812	0.0838	0.0864	0.0894

Vapor pressure measurements were made for the following systems: (1) the metastable anhydride–tetrahydrate mixture of crystals from the eutectic melting point, 33°, to 15° (Table III); (2) the dihydrate–tetrahydrate from the eutectic melting point, 49°, to 20° (Table III); (3) the dihydrate–anhydride from the transition temperature, 56.8°, to 40° (Table III); (4) saturated solutions of the tetrahydrate, the dihydrate and the anhydride in the stable and the metastable regions (Table I); (5) fourteen solutions ranging in concentration from 10 to 86% in various temperature ranges (Table II). Table II also presents the relative humidity, P/P_0 (Babo's constant), for the fourteen solutions.

The data for the saturated solutions (Table I) are the experimental data. The data for the fourteen solutions (Table III) are tabulated for whole degrees, having been extrapolated over a short range, usually less than 0.05°, but occasionally as much as 0.10°. by obtaining the best equation of the form $\ln p = A/T + B$ for the solutions (and this was done for the crystalline

TABLE III

VAPOR PRESSURES OF MIXTURES OF CRYSTALS

Temp., °C.	V. p., mm.
(1) Anhydride–Dihydrate	
40	2.93
45	4.14
50	5.86
55	8.17
(2) Anhydride–Tetrahydrate	
15	0.70
20	1.00
25	1.45
30	1.89
(3) Dihydrate–Tetrahydrate	
20	1.48
25	2.11
30	3.04
35	4.31
40	5.94
45	8.24

mixtures also), and then calculating the change in ln/p for the temperature increment. The data are estimated to be accurate to ±0.03 mm.

Figure 1 is a plot of the complete vapor pressure data for this system over the range covered in this work. Curve AKBC is the saturated tetrahydrate curve; BC is the metastable saturated tetrahydrate curve and is supersaturated with respect to dihydrate. Curve GBH is the saturated dihydrate curve, and GB is supersaturated with respect to tetrahydrate. Curve JHCE is the anhydride saturated curve; curve HC is supersaturated with respect to dihydrate and CE is supersaturated with respect to both tetrahydrate and dihydrate.

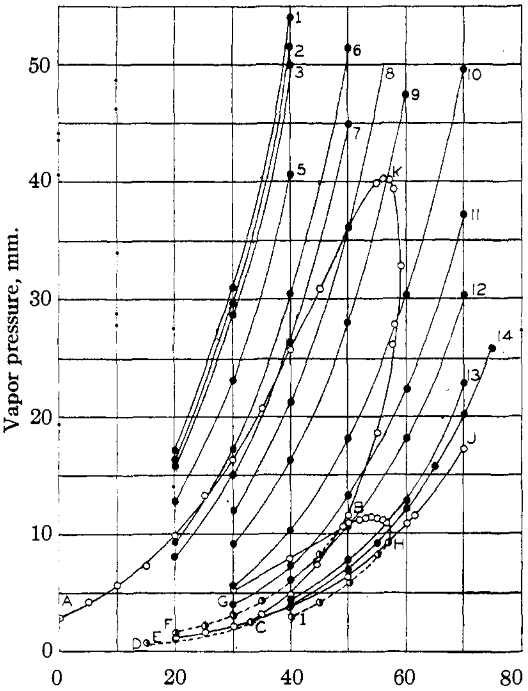

Fig. 1.—●, solution; ◑, crystalline mixture - - -; ○, saturated solution.

The tetrahydrate–dihydrate curve is FB; the anhydride–tetrahydrate, DC; and the dihydrate–anhydride, IH. (In order to avoid confusion in the curves, some of the individual points for these mixtures of crystals are not indicated, but they fall nicely on the curves.)

Solutions are numbered 1 to 14 in accordance with Table II (curve 4 is not plotted because it nearly coincides with curve 3) and are represented in the metastable regions also. The intersections of these solution curves with the saturated solution curves give the freezing points of the solutions of the respective concentrations. The freezing points obtained in this manner are plotted in Fig. 3, along with data of Sieverts and Petzold,[3] for concentrations above 50% $Cd(NO_3)_2$. The vapor pressure method confirms their data obtained by the freezing point method and extends the diagram into the metastable region.

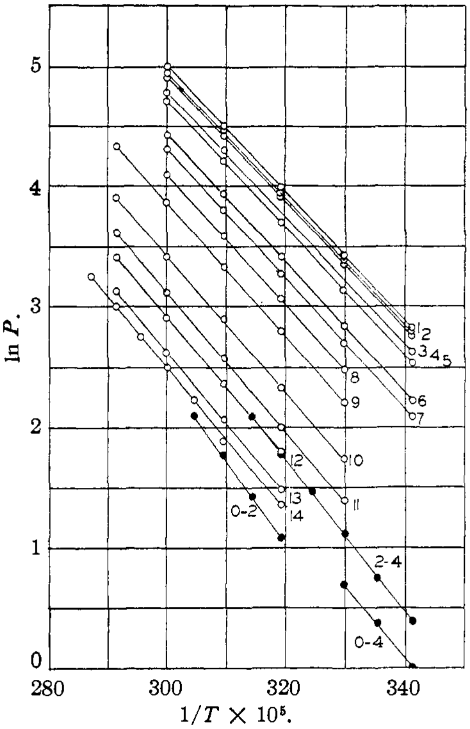

Fig. 2.

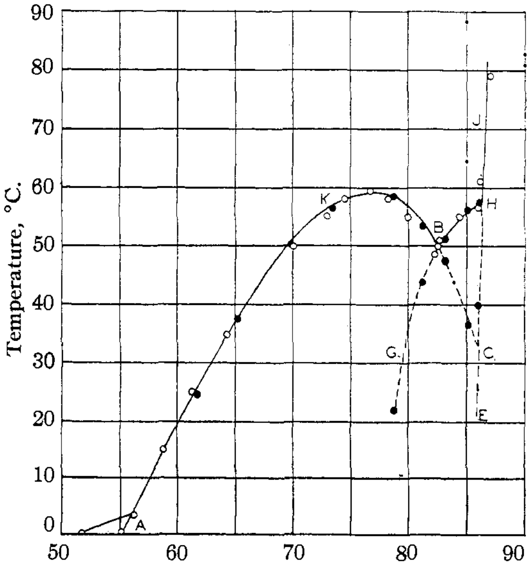

Fig. 3.—○, Sieverts, Petzold; ●, Ewing, Guyer (vapor pressure).

The equation $\ln p = A/T + B$ applies to the single phase solutions and to the mixtures of crystals, as is shown in Fig. 2, which is a plot of $\ln p$ versus $1/T \times 10^5$ for the fourteen solutions and three crystalline mixtures. Straight lines result in each case.

This equation is applicable to water also in the temperature range 0 to 60° within the error in plotting on ordinary semi-log paper, but above 60° a third term has to be added to the equation. This condition also applies to our dilute solutions. For the more concentrated solutions the two term equation fits the data even more closely than it does the water data, or the dilute solution data.

Discussion

The vapor pressure measurements are considered of sufficient accuracy to study the variation of Babo's constant, P/P_0 (relative humidity), with temperature. In general, the data available up to this paper indicate that this value is constant within the experimental accuracy. Leopold and Johnston[8] stated that there would be a slight increase in relative humidity with increase of temperature for accurate measurements. Table II confirms this statement; there is a definite rise in Babo's constant with rise in temperature. This trend was found for all of the experimental data except the 20° readings for the two most dilute solutions. Duplicate determinations of these two values, however, fell in the general trend. This trend obtained regardless of the order in which the vapor pressure readings were taken for the various temperatures. This same trend has been obtained in general in all of the measurements on the nitrates in this series of studies.

Quite serious errors would arise in measuring the vapor pressure for a solution at one temperature, and then calculating the vapor pressure at another temperature, far removed, by assuming that P/P_0 is constant. For solution 6 [61.70% $Cd(NO_3)_2$], which may be considered typical, determining P/P_0 at 30° (0.5385) and then calculating the vapor pressure at 60° ($P/P_0 = 0.5661$ actually) would cause an error of 4.61%. This is an error of 3.90 mm. for the vapor pressure at this temperature.

Summary

Complete vapor pressure data for the system cadmium nitrate–water are given from 0 to 86% concentration and for the temperature range 20–60°. These vapor pressures are for the unsaturated, saturated, and supersaturated solutions, and for the mixtures of crystals.

Babo's constant (P/P_0) is shown to increase appreciably with temperature for the binary system cadmium nitrate–water.

BETHLEHEM, PENNA. RECEIVED SEPTEMBER 9, 1938

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[8] Leopold and Johnston, THIS JOURNAL, 49, 1974 (1927).

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGY, YALE UNIVERSITY SCHOOL OF MEDICINE]

The Standardization of Hydrogen Ion Determinations. II. A Standardization of the *p*H Scale at 38°

BY DAVID I. HITCHCOCK AND ALICE C. TAYLOR[1]

In a recent paper[2] a revision of the *p*H scale was proposed, as a result of hydrogen electrode measurements made with buffer solutions at 25°, in cells including a stationary liquid junction with saturated potassium chloride solution. This revision involved the use of the thermodynamic dissociation constants of the buffer acids together with an extrapolation based, in part, on the Debye–Hückel theory. A consistent scale was obtained for solutions of about *p*H 4 to 9. Since this range includes that part of the *p*H scale which is of primary importance in physiology and biochemistry, it seemed worth while to extend the work by making similar measurements at 38°, a temperature which is close to that of physiological fluids.

Experimental

The materials, apparatus and technique were practically the same as in the earlier work.[2] The concentrations of the solutions were expressed, as before, in moles per liter of solution at room temperature, 21–23°. The series of buffer solutions was extended by preparing mixtures of hydrochloric acid with sodium or potassium acetate or disodium hydrogen phosphate, in such proportions as to yield 1:1 buffers.

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[1] This work was aided by a grant from the Fluid Research Funds of the Yale University School of Medicine.

[2] Hitchcock and Taylor, THIS JOURNAL, 59, 1812 (1937).