the assumption that the carbon chain of the lower acids tends to have a ring rather than a straight chain structure.

BETHLEHEM, PENNA.

The Heats of Solution and of Dilution of the Binary Systems Zinc Nitrate–Water and Cadmium Nitrate–Water

BY WARREN W. EWING, JOHN D. BRANDNER AND WALTER R. F. GUYER

This article, which presents calorimetric data for the binary systems zinc nitrate–water and cadmium nitrate–water, is a continuation of a series of studies made on the nitrates of certain bivalent metals. Vapor pressure studies of these two systems already have been published.[1,2] These two systems are excellent for these studies since the salts form several hydrates which melt not far above room temperature, their anhydrides are extremely soluble, and the solutions can be supercooled.

Solubility studies[3–5] show that zinc nitrate crystallizes in five hydrated forms, 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. $55.4°$), and $Zn(NO_3)_2 \cdot H_2O$ (m. p. $73.9°$). Zinc nitrate anhydride has also been prepared as will be shown later in this article. Likewise, cadmium nitrate[2,6,7] exists as the anhydride and forms three hydrates, namely, $Cd(NO_3)_2 \cdot 9H_2O$ (T. P. $+3.5°$), $Cd(NO_3)_2 \cdot 4H_2O$ (m. p. $59.5°$) and $Cd(NO_3)_2 \cdot 2H_2O$ (m. p. $56.8°$).

The stable saturated solution of the monohydrate of zinc nitrate has a concentration of 86.2% at 51.8° and the anhydride of cadmium nitrate, 86.0% at 56.8°. Since solutions of these salts can be supercooled to room temperature, this means that calorimetric measurements can be obtained at 25° through extremely large concentration ranges: up to 35 molal for zinc nitrate and up to 21 molal for cadmium nitrate. The zinc nitrate solutions decompose slowly at the very high concentrations but suitable precautions enable measurements to be made with a reasonable degree of accuracy. The calorimetric data presented consist of heats of solution of the various hydrates and the anhydrides and heats of

dilution of solutions of various concentrations. These data were obtained by sealing the various samples in small bulbs and then breaking the bulbs under water in an adiabatic calorimeter, to yield dilute solutions.

Preparation of Materials

Zinc nitrate hexahydrate was prepared by recrystallizing the c. p. salt three times from a slightly acidified solution. The moist product was dried in a stream of air on a day when the humidity was low. The tetrahydrate, dihydrate and monohydrate were prepared by melting the purified hexahydrate and evaporating to the required concentration. The solution was then slightly acidified, the desired crystallization was carried out, and the hydrates were filtered on sintered glass filters at temperatures slightly above the respective eutectic temperatures. The excess of nitric acid was removed by evaporation in a vacuum and the final drying carried out in vacuum desiccators over the proper drying agents, viz., 65% sulfuric acid for the tetrahydrate, 78% sulfuric acid for the dihydrate and phosphorus pentoxide for the monohydrate.

The preparation of anhydrous zinc nitrate offered extreme difficulties. The dehydration of the monohydrate either by heating or by continuous evacuation by means of a mercury diffusion vacuum pump at room temperatures resulted in a decomposition of the nitrate. An insoluble product was formed probably consisting of various basic zinc nitrates.[8,9] Success was finally attained by the reaction of nitrogen pentoxide on U. S. P. zinc oxide. Ozone was used to inhibit the slow decomposition of the nitrogen pentoxide.[10,11] The apparatus consisted of an all-glass system in which the gases were circulated by means of a pump in a cyclic manner. The successive parts of the cycle consisted of the nitrogen pentoxide generator, phosphorus pentoxide drying tube, eight zinc oxide reaction bulbs, phosphorus pentoxide drying tube cold trap, pump, ozonizer, nitrogen pentoxide generator, etc. The zinc oxide bulbs were blown in such a manner that the two arms were above the axis of the bulb so that the nitrogen pentoxide could circulate over the surface of the zinc oxide. The bulbs were of such a size that they could be sealed and used in the calorimeter.

The zinc oxide was first dried by passing oxygen through the system for several hours. Even this treatment does

(1) Ewing and Fisher, THIS JOURNAL, **59**, 1046 (1937).
(2) Ewing and Guyer, ibid., **60**, 2707 (1938).
(3) Ewing, McGovern and Mathews, ibid., **55**, 4827 (1933).
(4) Ewing, Ricards, Taylor and Winkler, ibid., **55**, 4830 (1933).
(5) Sieverts and Petzold, Z. anorg. allgem. Chem., **212**, 52 (1933).
(6) Sieverts and Petzold, ibid., **212**, 56 (1933).
(7) Malquori, Gazz. chim. ital., **58**, 206 (1928).

(8) Marketos, Compt. rend. seances l'acad. sci. chim. min., **155**, 210 (1912).
(9) Dubsky and Nevralova, Chem. Listy, **25**, 373 (1931).
(10) Daniels and Bright, THIS JOURNAL, **42**, 1131 (1920).
(11) Wulf, Daniels and Karrer, ibid., **44**, 2398 (1922).

not remove the last trace of the adsorbed water. The nitrogen pentoxide generator, containing a paste of anhydrous nitric acid and phosphorus pentoxide, was sealed in place and the pump and ozonizer started. Crystals forming in the cold trap, chilled with a dry ice–alcohol mixture, indicated that nitrogen pentoxide was circulating. Each sample of zinc oxide was then successively chilled with the cooling mixture until considerable nitrogen pentoxide crystals had collected. After the chilling mixture was removed, the temperature of the bulbs and the change in appearance of the zinc oxide indicated that a reaction was proceeding. The appearance of a light brown color in the system and the appearance of a trace of liquid in the chilled portions of the apparatus indicated that the ozone did not eliminate entirely the decomposition of the nitrogen pentoxide. Finally the generator was replaced by an empty flask and the system cut between the pump and the ozonizer and a stream of oxygen introduced at this point to sweep out all excess fumes. The sample bulbs were then sealed off and the heats of solution were determined.

After the calorimetric determination of the heat of solution of the anhydrous salt considerable unreacted zinc oxide remained in the solution. The solution was analyzed for soluble zinc, for nitrate and for nitrite. The zinc was determined by evaporation to dryness and igniting to the oxide. Nitrite was determined by titration with potassium permanganate. Nitrate was determined by reducing with an excess of ferrous ammonium sulfate and back-titrating with potassium dichromate by a modification of the method of Kolthoff, Sandell and Moscovitz.[12] The analytical results indicated that the soluble product consisted of 90% zinc nitrate and 10% zinc nitrite. The calorimetric heats gave a satisfactory check when calculated from analytical results, assuming that the heats of solution of zinc nitrate and of zinc nitrite were the same.[13]

Cadmium nitrate tetrahydrate was prepared by recrystallizing the C. P. salt twice and drying in a vacuum over 55% sulfuric acid. The anhydride was formed when the tetrahydrate was placed in a vacuum over concentrated sulfuric acid. The dihydrate was prepared by dehydrating the tetrahydrate in a vacuum using a large excess of the anhydrous salt as the drying agent.

The hexahydrate of zinc nitrate and the tetrahydrate of cadmium nitrate were dissolved in enough water to form the various solutions up to the concentration of the hydrates themselves. For the more concentrated solutions these hydrates were melted and the required amount of water was removed by evaporation. In the case of the zinc nitrate, which decomposes slowly in hot concentrated solutions, it was necessary to add anhydrous nitric acid to reform the pure zinc nitrate solution.

The concentration of saturated zinc nitrate hexahydrate and of saturated cadmium nitrate tetrahydrate are, respectively, 55 and 61.3% at 25°. All solutions which were more concentrated than these values were in the supersaturated state of aggregation. These supersaturated solutions were prepared by melting the mixtures, filtering

hot through sintered glass filters, and cooling. These solutions were then carefully transferred to the small bulbs and sealed off. Comparatively little difficulty was encountered except with the 65.1, the 71.5 and the 75.9% zinc nitrate solutions. These three supersaturated solutions were stabilized sufficiently to withstand the subsequent experimental manipulation only after heating the sealed bulbs in an oven for several days at temperatures 15° above their melting points. In general, it seemed that with all these nitrates, supercooling was attained more easily in the very concentrated and the more dilute ranges than in the intermediate ranges. (It is of interest to mention that some calcium nitrate solutions prepared seven years ago are still in the supersaturated condition. Meanwhile, these highly viscous liquids have experienced the temperature variations of the laboratory and have been handled occasionally for demonstration purposes.)

All compositions were determined by evaporation to dryness and igniting to the oxide.

Experimental

For the zinc nitrate (except for the heats of dilution of the 65.1, the 71.5 and the 75.9% solutions and for the heat of solution of the anhydride) experiments the adiabatic calorimeter was the same as previously described.[14,15] For the remainder of this work some modifications were made. The heater-stirrer was replaced by two separate units. The new heater, which was used to determine the heat capacity of the system after each calorimetric measurement, consisted of a constantan wire (B. & S. no. 28; 375 cm.; 19.13282 ohms) in a gold-plated silver tube. The tube was wrapped in a spiral around the breaking device tubes. The new stirrer consisted of a downward thrust propeller 3.7 cm. in diameter which revolved in a cylinder 7 cm. tall. It was driven by an 80 r. p. m. synchronous motor. The outside of the calorimeter can was plated with bright chromium and the one centimeter air space between this can and the outer jacket was maintained by means of conical synthetic resin spacers. The Type K potentiometer and the Mueller temperature bridge were recalibrated.

The experimental procedure consisted of introducing 1 liter of water and the bulbs containing the crystals or the solutions into the calorimeter at 25°, obtaining the initial temperature rating period, breaking the bulbs, obtaining a second rating period, introducing a measured input of electrical energy and finally obtaining a third rating period.

Results

All the experimental heats were to finite dilutions, the final concentrations ranging from 0.01 to 0.08 molal. It was necessary to correct these heats to infinite dilution in order to put all results on a comparable basis for calculating other data. Our calorimeter was not adapted to measuring heats of dilution of very dilute solutions to infinite dilution and these data do not appear in the literature. These heats are surprisingly large in the very dilute range. For magnesium nitrate the molal heats of dilution to infinite dilu-

(12) Kolthoff, Sandell and Moscovitz, THIS JOURNAL, **55**, 1454 (1933).

(13) Charles F. Glick assisted in the preparation and analysis of the anhydrous zinc nitrate, this being his research problem requirement for the degree B.S. in *Chem. Eng.*

(14) Ewing and Rogers, THIS JOURNAL, **55**, 3603 (1933).

(15) Ewing, Rogers, Miller and McGovern, *ibid.*, **54**, 1335 (1932).

tion of 0.040 and 0.100 molal solutions are, respectively, $\Delta H = -1250$ and $\Delta H = -1600$ j. per mole of salt.[16] In these calculations it was assumed that these values hold also for zinc nitrate and for cadmium nitrate. This assumption was justified by plotting comparable values of heats of dilution *versus* molality from 1 to 4 molal for these three salts. All the values fell on a single curve, within experimental error. The calorimetric determinations usually varied from 25° by a fraction of a degree. The heats, therefore, were corrected to 25° by means of the Kirchhoff equation.

Table I presents the heats absorbed when the various salts are dissolved in water. Column 2 gives the heat absorbed, when one mole of the salt is dissolved in sufficient water to give the concentrations tabulated in column 1. The corrections to infinite dilution in column 3 are calculated on the assumptions explained in the preceding paragraph. Column 4 contains the heat absorbed when one mole of salt is dissolved in sufficient water that further dilution involves no heat effect. The percentage deviation of the individual readings from the average is given in column 5. The probable error of the average is also estimated.

Table II presents heats of dilution and of solution for zinc nitrate and for cadmium nitrate at 25°. These data are all the average values of several calorimetric experiments. The number of individual experiments for each initial concentration is given in column 1. The weights of sample for each experiment were adjusted so that there was seldom a greater than one gram deviation from the average. A notable exception was the 71.54% zinc nitrate where the weights were 5.9761 and 21.5452 g. in the two experiments. Column 6 gives the heats of dilution per mole of anhydrous salt calculated from the experimental heats obtained when the weight of solution, column 4, of initial concentration, columns 2 and 3, reacts with 995.94 g. (1 liter) of water to yield a solution of the final molal concentration indicated in column 5. The correction to infinite dilution is given in column 7; column 8 gives corrected heats of dilution to infinite dilution with the average deviation from the mean value of the individual experiments. These heats of dilution when enough solution of concentration *m*, column 3, to contain one mole

(16) Lange and Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

TABLE I

HEATS OF SOLUTION OF SALTS AT 25°, IN JOULES PER MOLE

1 Final concn. in molality	2 ΔH to final concn.	3 Corrn. to infinite dilution	4 ΔH to infinite dilution	5 Deviation, %
$Zn(NO_3)_2$				
0.011	−83,740	−835	−84,575	−0.2
.010	−84,096	−775	−84,871	+ .2
		Average	−84,723 ± 100	
$Zn(NO_3)_2 \cdot H_2O$				
0.036	−48,357	−1,220	−49,577	+0.3
.039	−48,246	−1,255	−49,501	+ .1
.042	−47,800	−1,260	−49,060	− .8
.039	−48,061	−1,255	−49,316	− .3
.056	−48,348	−1,380	−49,728	+ .6
		Average	−49,440 ± 80	
$Zn(NO_3)_2 \cdot 2H_2O$				
0.022	−28,672	−1,050	−29,722	−0.2
.023	−28,792	−1,055	−29,847	+ .2
		Average	−29,780 ± 40	
$Zn(NO_3)_2 \cdot 4H_2O$				
0.050	−11,315	−1,320	−12,635	+0.3
.050	−11,290	−1,320	−12,610	+ .1
.050	−11,255	−1,320	−12,575	− .1
.050	−11,235	−1,320	−12,555	− .3
		Average	−12,595 ± 20	
$Zn(NO_3)_2 \cdot 6H_2O$				
0.017	+24,533	−925	+23,608	+0.9
.026	+24,300	−1,105	+23,195	− .9
.026	+24,503	−1,100	+23,403	± .0
		Average	+23,400 ± 80	
$Cd(NO_3)_2$				
0.073	−32,730	−1,130	−33,860	−0.4
.073	−32,679	−1,130	−33,809	− .2
.073	−32,404	−1,130	−33,534	+ .6
		Average	−33,735 ± 70	
$Cd(NO_3)_2 \cdot 2H_2O$				
0.089	−5,018	−1,240	−6,258	−0.8
.089	−5,023	−1,240	−6,263	− .9
.089	−4,866	−1,240	−6,106	+1.7
		Average	−6,210 ± 35	
$Cd(NO_3)_2 \cdot 4H_2O$				
0.077	+20,455	−1,160	+19,295	−2.2
.077	+21,085	−1,160	+19,925	+1.0
.077	+21,182	−1,160	+20,022	+1.5
.077	+20,895	−1,160	+19,735	+0.0
.077	+20,837	−1,160	+19,677	− .3
		Average	+19,730 ± 60	

of anhydride is diluted with an infinitely large quantity of water are plotted as curves II in Figs. 1 and 2.

Column 9 gives the heats of solution when one mole of the anhydrous salt is dissolved in the amounts of water required to give the concen-

TABLE II

a. HEATS OF DILUTION AND INTEGRAL HEATS OF SOLUTION OF ZINC NITRATE ANHYDRIDE AT 25°, IN JOULES

Expt. 1	Initial concn. % 2	Molal, m 3	Sample, g. 4	Final concn., molal 5	Heat of diln. to final concn. 6	Correction to infinite diln. 7	Corrected heat of diln. 8	Heat per mole of salt in req. H₂O 9	ΔH for m moles per 1000 g. of H₂O 10
4	20.78	1.385	20.1365	0.0218	−935	−1,029	−1,960 ± 110	−84,720	−114,600
4	24.39	1.703	22.5415	.0286	−848	−1,118	−1,970 ± 100	−82,760	−140,900
4	30.67	2.336	22.1547	.0355	−1,025	−1,204	−2,230 ± 30	−82,490	−192,700
4	34.30	2.757	25.3558	.0453	−1,377	−869	−2,240 ± 70	−82,480	−227,400
4	40.23	3.554	25.5236	.0535	−2,093	−1,366	−3,460 ± 90	−81,260	−288,800
4	45.52	4.411	21.7498	.0520	−3,931	−1,345	−5,280 ± 60	−79,440	−350,400
4	49.89	5.257	21.4483	.0562	−5,629	−1,396	−7,110 ± 30	−77,710	−408,500
2	53.50	6.077	16.4324	.0464	−7,826	−1,305	−9,130 ± 50	−75,590	−459,400
3	53.60	6.099	27.6141	.0774	−8,031	−1,508	−9,540 ± 30	−75,180	−458,500
3	55.27	6.524	25.6449	.0734	−8,785	−1,503	−10,290 ± 110	−74,430	−485,600
3	65.11	9.853	17.0840	.0583	−20,855	−1,396	−21,920 ± 470	−62,800	−618,800
2	71.54	13.270	13.7606	.0520	−29,966	−1,293	−31,260 ± 120	−53,460	−709,400
2	75.90	16.628	9.7877	.0395	−38,215	−1,245	−39,460 ± 30	−45,260	−752,600
5	80.31	21.54	9.2517	.0393	−47,253	−1,151	−48,400 ± 200	−36,320	−782,300
2	82.31	24.57	7.1788	.0313	−50,406	−1,155	−51,560 ± 40	−33,160	−814,700
6	82.56	25.00	9.6380	.0421	−50,741	−1,271	−52,000 ± 100	−32,720	−818,000
4	83.75	27.21	8.9347	.0396	−52,904	−1,246	−54,150 ± 100	−30,570	−831,800
3	86.52	33.89	14.3940	.0658	−58,450	−1,427	−59,880 ± 150	−24,840	−841,800
4	86.60	34.15	12.2752	.0561	−59,253	−1,374	−60,630 ± 60	−24,090	−822,700
1	86.83	34.81	19.4812	.0899	−58,518	−1,560	−60,080	−24,640	−857,700

b. HEATS OF DILUTION AND INTEGRAL HEATS OF SOLUTION OF CADMIUM NITRATE ANHYDRIDE AT 25°, IN JOULES

Expt. 1	Initial concn. % 2	Molal, m 3	Sample, g. 4	Final concn., molal 5	Heat of diln. to final concn. 6	Correction to infinite diln. 7	Corrected heat of diln. 8	Heat per mole of salt in req. H₂O 9	ΔH for m moles per 1000 g. of H₂O 10
2	20.09	1.063	21.4887	0.0180	−587	−941	−1,530 ± 150	−32,200	−34,200
3	29.85	1.799	23.0663	.0288	−1,067	−1,150	−2,220 ± 230	−31,520	−56,700
5	40.01	2.821	24.2925	.0406	−1,188	−1,258	−2,445 ± 300	−31,290	−88,300
3	50.12	4.251	27.7772	.0584	−2,717	−1,382	−4,100 ± 170	−29,640	−126,000
3	60.10	6.372	30.8781	.0780	−4,856	−1,508	−6,365 ± 100	−27,370	−174,400
3	70.17	9.949	27.3758	.0809	−9,237	−1,530	−10,770 ± 90	−22,970	−228,500
2	71.06	10.383	14.8855	.0447	−10,437	−1,289	−11,725 ± 450	−22,010	−228,500
3	76.12	13.482	17.5326	.0564	−13,408	−1,379	−14,790 ± 140	−18,950	−255,500
2	79.91	16.826	14.7400	.0498	−16,973	−1,340	−18,315 ± 00	−15,420	−259,500
2	83.27	21.048	13.2958	.0469	−20,509	−1,320	−21,890 ± 50	−11,850	−249,400

trations in column 3. These values are obtained by subtracting the heats of dilution to infinite dilution of the solutions of m molality, column 8, from the heat of solution to infinite dilution of the anhydrous salts.
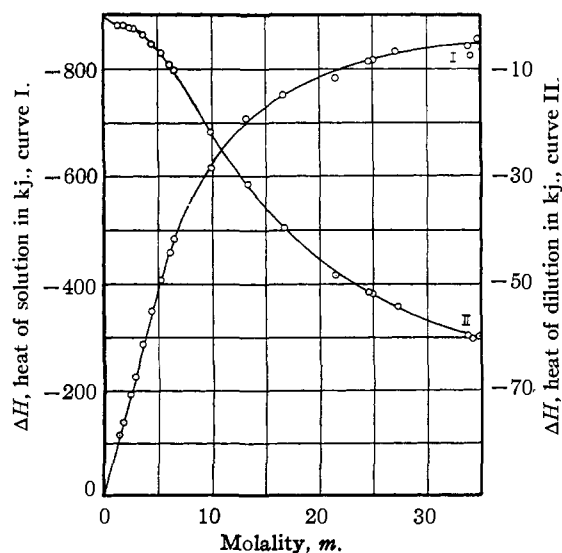
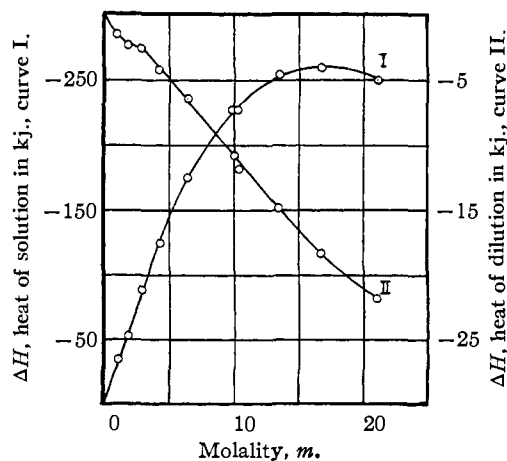

Fig. 1.—Zinc nitrate in water.

Fig. 2.—Cadmium nitrate in water.

Column 10 gives the heats of solution when m moles of anhydrous salt are dissolved in 1000 g. of water giving the molal concentration in column 3. These values are obtained by multiplying the concentration values, m, by the heat values in column 9. These heat changes in column 10 are the total or integral heats of solution and are plotted against the molality in curves I in Figs. 1 and 2.

The slopes of these latter curves give the partial molal heats of solution of the anhydrous salts, $d(\Delta H)/dm = \bar{H}_2 - H_2(c) = \Delta H_2$. The partial molal heats of solution of water, $\bar{H}_1 - H_1 = \Delta H_1$, are then obtained by the equation $\Delta H = n_1(\bar{H}_1 - H_1) + n_2(\bar{H}_2 - H_2 (c))$. H_1 and $\bar{H}_1$ are, respectively, the heat contents of one mole of pure water and one mole of water in the solution and $H_2(c)$ and $\bar{H}_2$ are, respectively, the heat contents of one mole of the anhydrous salt in the crystalline condition and in the solution. These partial molal heats of solution are further defined as the amount of heat absorbed when one mole of salt or one mole of water, respectively, is dissolved in a sufficiently large quantity of solution that the concentration is not changed.

was found to fit the cadmium nitrate data. ΔH is the integral heat of solution, m is the molality, $a(-33,050)$, $b(+1023)$ and $C(\text{zero})$ for $Cd(NO_3)_2$ are constants, and $m/55.51 \equiv n_2/n_1$. Differentiating equation (1) with respect to m gave (2) $d(\Delta H)/dm = a + 2 \times 55.51\,b(n_2/n_1) = \bar{H}_2 - H_2(c)$. $\bar{H}_1 - H_1$ was then obtained from the equation (3) $\Delta H = n_1(\bar{H}_1 - H_1) + n_2(\bar{H}_2 - H_2 (c))$ which can be simplified by substituting for ΔH from equation (1) giving the equation (4)

$$\bar{H}_1 - H_1 = -55.51\,b(n_2/n_1)^2 + (C/55.51)$$

For zinc nitrate the same type equations, 1 to 4, apply, but for this salt the curve for ΔH had to be broken into two portions. For the first portion, from 0 to 10 molality (n_2/n_1 from 0 to 0.2, about) the constants were $a = -92,406$, $b = +2933$ and $c = 0$. For the second portion, from about 6.5 to 35 molality, the constants were: $a = -26,703$, $b = +413.5$, and $c = -410,896$. The partial molal heats so obtained are plotted as curves without experimental points in Figs. 3 and 4. For zinc nitrate the use of two equations results in an indeterminate region which is illustrated by the dotted lines.

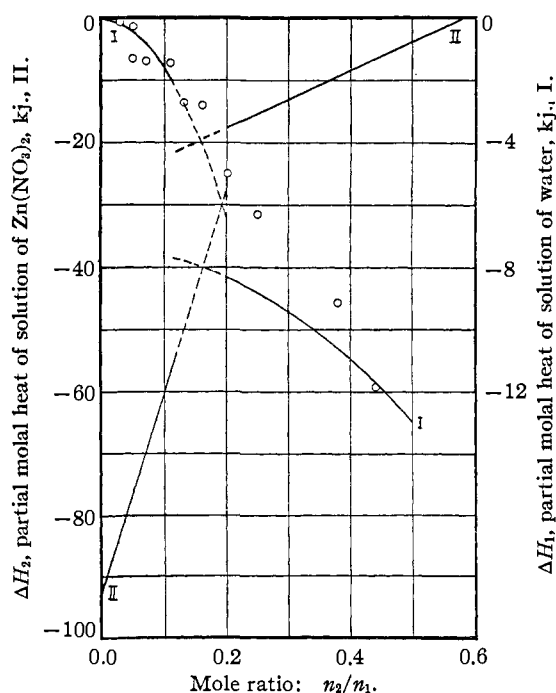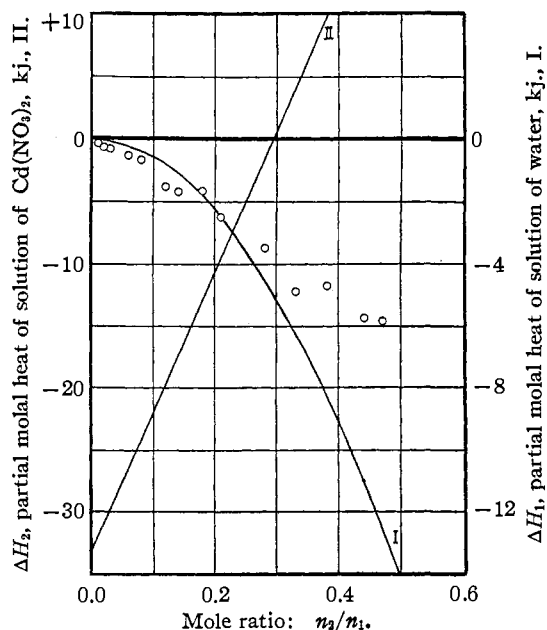

Fig. 4.—Cadmium nitrate in water.

Fig. 3.—Zinc nitrate in water.

The partial molal heats were obtained by mathematical methods. By the method of least squares, the equation (1) $\Delta H = am + bm^2 + C$

The partial molal heats of solution of water in the solutions can also be calculated from the vapor pressure data which have appeared in previous papers.[1,2] The methods of calculation have also been discussed previously.[14,17] The

(17) Ewing, Klinger and Brandner, THIS JOURNAL, 56, 1053 (1934).

TABLE III

PARTIAL MOLAL HEATS OF SOLUTION OF WATER AT 25°, IN JOULES PER MOLE

(a)

%Zn(NO₃)₂	Molality	n_2/n_1	$\bar{H}_1 - H_1$
10.258	0.603	0.0109	−101
18.466	1.196	.0216	−254
25.577	1.815	.0327	−135
26.434	1.897	.0342	−132
32.354	2.525	.0455	−245
34.618	2.796	.0504	−282
35.079	2.853	.0514	−1,302
44.045	4.156	.0749	−1,417
53.236	6.011	.1083	−1,448
57.362	7.103	.1280	−2,660
63.150	9.048	.1630	−2,806
67.514	10.973	.1977	−4,979
72.713	14.070	.2535	−6,278
80.177	21.353	.3847	−9,172
82.375	24.677	.4446	−11,811

(b)

%Cd(NO₃)₂	Molality	n_2/n_1	$\bar{H}_1 - H_1$
10.900	0.517	0.0093	−206
23.356	1.289	.0232	−271
28.908	1.720	.0310	−385
43.935	3.315	.0597	−592
49.615	4.165	.0750	−745
61.701	6.814	.1227	−1,548
65.357	7.980	.1438	−1,659
69.823	9.786	.1763	−1,615
73.501	11.731	.2113	−2,541
78.710	15.637	.2816	−3,442
81.218	18.290	.3295	−4,873
83.132	20.845	.3755	−4,711
85.176	24.303	.4378	−5,748
86.075	25.886	.4664	−5,803

partial molal heats of solution of water from vapor pressure data are tabulated in Table III for the concentrations on which vapor pressure measurements were made. These values are indicated by circles in Figs. 3 and 4 for sake of comparison with the calorimetric data.

The accuracy of the data presented is estimated to be about the same as that in the previous work which already has been discussed,[15,16,18] except for data involving the heat of solution of the anhydrous zinc nitrate. Due to the uncertainty as to the purity of this salt, the authors are unable to estimate the accuracy of its heat of solution.

Summary

A method for the preparation of anhydrous zinc nitrate has been devised.

The heats of solution of zinc nitrate and cadmium nitrate and their various hydrates have been measured.

Heats of dilution of the solutions of these two salts have been measured. The concentration range of these solutions extends into the extremely concentrated, and consequently supersaturated, range.

Certain thermodynamic quantities have been calculated from these data and comparisons made with values from vapor pressure data.

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A Critical Study of the Thiosulfate Titration of Chlorine

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The iodine–thiosulfate reaction is one of the most widely used in analytical chemistry. A strongly acid system is usually employed, but titration at the pH of the sample, possibly either neutral or slightly alkaline, has been suggested in the appendix of "Standard Methods for the Examination of Water and Sewage,"[1] with an expressed hope that further study would be stimulated. The use of such systems has been reported elsewhere in the literature[2,3] as a means of estimating effective chlorine bactericidal agents and of reducing interference by other compounds possibly present in natural waters. However, not only the oxidizing agents in the sample but the titration system itself are affected by pH change through varying proportion of thiosulfate conversion to tetrathionate ion and sulfate ion. Kolthoff and Furman[4] discuss some previous investigations which, however, were directed chiefly to the exploration of suitable ranges of hydrion concentration and other conditions separately, without any extensive consideration of the peculiarities of their interdependence. The object of the present communication is to present the results of a study of some of these relations which should be

(1) American Public Health Association, "Standard Methods for the Examination of Water and Sewage," American Public Health Association, New York, 1936, 309 pp.

(2) B. A. Skopintzew and F. J. Warfolomejewa, Z. anal. Chem., 88–89, 97–107 (1932).

(3) M. L. Koshkin. J. Am. Water Works Assoc., 29, 1761–1774 (1937).

(4) I. M. Kolthoff and N. H. Furman, "Volumetric Analysis," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1929, 552 pp.