

the tube containing the solid phase was then cut off and the crystals analyzed. Analysis showed 90.3% manganous nitrate. Theoretically, the monohydrate contains 90.86% manganous nitrate.

It is estimated that the results are accurate to 0.1% up to concentration of about 78%. For concentrations higher than this the accuracy is not quite so good since these very concentrated solutions decompose slowly at their melting points.

The sesquihydrate and the hemihydrate which appear as stable forms in the ternary system manganous nitrate-nitric acid-water at 20°⁴ do not appear in the binary system. Existence of stable hydrates in equilibrium with concentrated nitric acid solutions does not indicate that they are in stable equilibrium with their saturated water solutions. Also the data for the ternary system were at 20°, and the sesquihydrate curve, if this hydrate were in stable equilibrium with its saturated water solution, would be in the 35° temperature region and similarly the hemihydrate curve somewhere around 75°. This latter temperature is in the range where manganous nitrate is decomposing quite rapidly. However, it is not even necessary that a stable form appear in both sys-

tems. The anhydride appeared in neither system. It was prepared only by dehydrating the dry solid hydrates in vacuum. It should be possible to prepare the sesquihydrate and the hemihydrate in a similar manner, taking due precaution to keep the vapor pressure above the salt in the equilibrium pressure range corresponding to the hydrate desired. The trihydrate reported by Funk³ failed to appear in the binary system in any of the three methods used, solubility, freezing point, or vapor pressure, nor did it appear in the ternary system.

Summary

The solubility temperature relations for the system manganous nitrate-water over the temperature range 5 to 75° and the concentration range 50 to 84% have been investigated.

The existence of the hexahydrate, the tetrahydrate, the dihydrate, and the monohydrate in equilibrium with water solutions has been established.

No evidence of the existence of the trihydrate, which is reported in the literature, has been found.

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

Vapor Pressure-Temperature Relations and Heats of Solution and Dilution of the Binary System Manganous Nitrate-Water

BY WARREN W. EWING, CHARLES F. GLICK AND HERBERT E. RASMUSSEN

The manganous nitrate-water system is well adapted to a physical chemical study of concentrated solutions because its anhydride is very soluble in water and the concentrated solutions can be supercooled to room temperatures. Solutions up to 24 *m* can thus be obtained. These desirable characteristics are counterbalanced to some extent by the tendency for the solute to decompose slowly, especially in the concentrated range at higher temperatures.

Vapor pressure data from 20 to 40° and from 5 to 24 *m* for solutions, saturated solutions, and supersaturated solutions and calorimetric data on heats of solution and dilution of the anhydride are reported in this article. Only fragmentary data on these systems are found in the literature.

Vapor Pressure Part.—The methods used in preparing and analyzing the materials have been

reported¹ and the apparatus and technique for measuring vapor pressures have been described² previously.

In Table I are tabulated vapor pressure data of the solution phase for the temperature range 20 to 40°. The measured data have been corrected to whole degrees by means of the equation

$$\ln p = A/T + B \quad (1)$$

The constants *A* and *B* were determined for each solution by the method of least squares. The temperature correction was never more than 0.1°.

The difficulty experienced in supercooling the 66.18% solution was overcome by filtering the melted solution through sintered glass and warming to 60° to destroy any crystalline nuclei present.

(1) Ewing and Glick, *THIS JOURNAL*, **62**, 2174 (1940).

(2) Ewing and Fisher, *ibid.*, **59**, 1046 (1937).

With solutions more concentrated than this, satisfactory supercooling could not be obtained. On melting these mixtures (combination of hydrates to give desired concentration) a slow decomposition took place, forming a faint cloud of minute, dark-colored particles which apparently served as nuclei for crystallization, thus preventing supercooling. On these more concentrated solutions, vapor pressures were measured only at 40°. The observed vapor pressures of these solutions gradually rose due to decomposition, and the true vapor pressure was obtained by taking measurements over a period of forty-eight hours and extrapolating back to the time at which evacuation was completed.

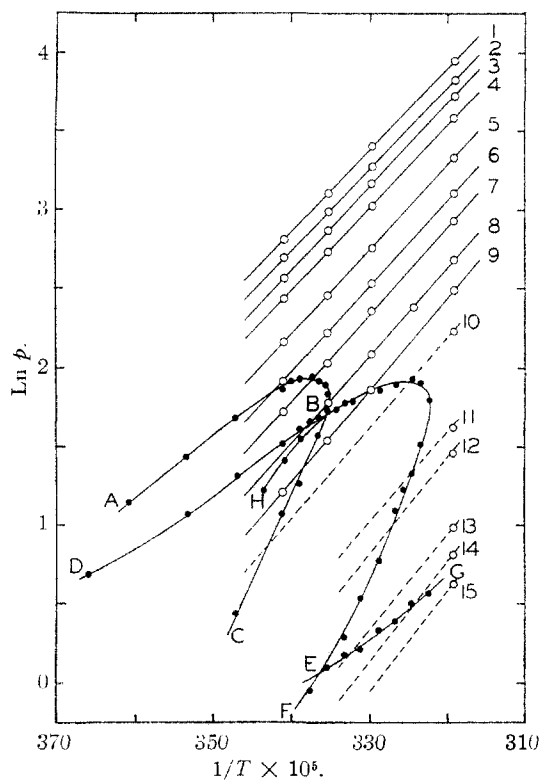


Fig. 1.

Table II contains vapor pressure data on the saturated solutions and on a mixture of hexahydrate and tetrahydrate crystals. The mixture of crystals was made by completely freezing the metastable saturated solution of hexahydrate by surrounding it with ice until seeds of the tetrahydrate had formed, whereupon a stable mixture of the two crystalline phases resulted. Slow decomposition again caused trouble in the measurements on the more concentrated solutions in equilibrium with the lower hydrates. Here the

true vapor pressure was estimated by the extrapolation method mentioned above.

Figure 1 includes the $\ln p$ vs. $1/T$ plot of the vapor pressure data for the system. The applicability of Eq. 1 is illustrated by the straight lines obtained for solutions 1 to 9. In passing, it may be noted that as in other systems studied² the lines so obtained are not parallel but they increase in negative slope with increasing concentration. This point was discussed in connection with Babo's law in a previous article.³

$\ln p$ vs. $1/T$ for the saturated solutions is also plotted in Fig. 1. Curve ABC represents solutions saturated with the hexahydrate, BC being a metastable region. DBEF represents solutions saturated with the tetrahydrate, DB and EF being metastable regions. EG represents solutions saturated with the dihydrate. B and E are the eutectic points for the hexa-tetrahydrates and the tetra-dihydrates, respectively. BH represents a mixture of hexahydrate and tetrahydrate crystals. The intersection of a single phase solution line with the saturated solution curve gives the freezing point of that single phase solution. Freezing points obtained in this way are plotted as solid circles on the phase diagram in the preceding article.⁴

The data for the first nine solutions (16 to 66%) tabulated in Table I are estimated to be accurate to ± 0.05 mm. Solutions more concentrated than 66% decompose slowly with the appearance of a faint brown cloudiness (mentioned

TABLE I

VAPOR PRESSURES OF SOLUTIONS OF MANGANOUS NITRATE

The values in parenthesis are calculated from heat data as described later.

Soln.	Concn., % Mn(NO ₃) ₂	Molality	Pressure, mm.			
			20°	25°	30°	40°
1	16.89	1.14	16.66	22.43	30.00	52.03
2	31.17	2.53	14.90	19.96	26.47	45.94
3	37.18	3.31	13.07	17.75	23.92	41.49
4	43.70	4.34	11.51	15.51	20.65	36.28
5	51.61	5.96	8.68	11.71	15.85	28.04
6	56.91	7.38	6.83	9.24	12.61	22.38
7	59.93	8.36	5.61	7.71	10.59	18.87
8	63.55	9.74	...	5.96	8.09	14.60
9	66.18	10.94	3.39	4.70	6.47	12.42
10	68.28	12.03	...	(3.69)	...	9.39
11	74.04	15.93	...	(1.92)	...	5.10
12	74.19	16.94	...	(1.61)	...	4.32
13	77.53	19.28	...	(0.98)	...	2.69
14	79.27	21.37	...	(0.81)	...	2.26
15	80.32	22.81	...	(0.68)	...	1.90

(3) Ewing and Guyer, *THIS JOURNAL*, **60**, 2707 (1938).(4) Ewing and Rasmussen, *ibid.*, **64**, 1443 (1942).

previously) and the evolution of a gas. The fine solid does not affect the vapor pressure of the solution since it is insoluble and present only in very small amounts. The gas evolved does affect the vapor pressure readings and corrections are necessary. Data thus affected (solutions 68 to 80%) are estimated to be accurate to ± 0.1 mm.

TABLE II

THE VAPOR PRESSURES OF SATURATED SOLUTIONS OF MANGANOUS NITRATE (m = METASTABLE)

Temp., °C.	V. p., mm.	Temp., °C.	V. p., mm.
Solid phase: hexahydrate			
4.01	3.12	25.41	5.68
9.90	4.16	25.90	5.72
15.00	5.36	26.89	5.93
20.04	6.45	27.89	6.03
21.00	6.74	29.87	6.25
21.98	6.88	30.87	6.43
23.32	7.01	32.88	6.67
24.04	6.84	35.89	6.70
24.86	6.64	36.90	6.04
24.87	5.68	35.89	4.57
24.00	4.83m	34.89	3.77
21.96	3.61m	33.89	3.43
19.98	2.91m	32.88	3.00
15.00	1.56m	30.87	2.16
Solid phase: tetrahydrate			
0.00	2.00m	28.88	1.71
9.91	2.92m	26.89	1.34
15.00	3.69m	24.90	1.10
19.94	4.60m	22.91	0.95m
21.91	5.06m	Solid phase: dihydrate	
22.91	5.21m	26.89	1.20
23.91	5.39m	28.88	1.23
24.91	5.67m	30.87	1.39
24.91	5.60	32.88	1.48
		34.89	1.66

The vapor pressures of a mixture of hexahydrate and tetrahydrate

Temp., °C.	V. p., mm.
18.00	3.36
20.00	4.02
22.00	4.70
24.00	5.29

Calorimetric Part.—The calorimeter used has been described.^{5,6} A few changes were made. The complicated vacuum tube and telegraph relay assembly was replaced by an electronic relay designed and built by Earl J. Serfass.⁷ The bank of storage cells supplying the 8-volt potential drop for the electrical heater was replaced by a bank of air cells. The latter gave a more constant voltage drop across the heater and required less time for polarization.

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

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

(7) Serfass, *Ind. Eng. Chem., Anal. Ed.*, **13**, 262 (1941).

Table III contains the data of the calorimetric measurements of heats of dilution and Table IV of heats of solution of the anhydride. The data in Table III are all the average values of several runs. The experimental heats were obtained when the weight of solution (column 2) of initial concentration (column 1) reacts with 995.94 g. (1 liter) of water to yield a solution of final concentration (column 3). Column 4 gives the heats of dilution per mole of anhydrous salt obtained by dividing the experimental heats by the final concentrations (column 3). These heats of dilution, when enough solution of concentration m (column 1) to contain one mole of anhydride is diluted with an amount of water to give the final concentration (column 3) are plotted as Curve I, Fig. 2.

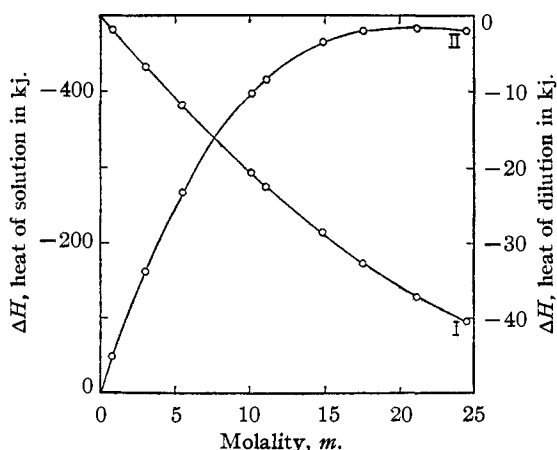


Fig. 2.—Heat of dilution, curve I, and heat of solution, curve II, of manganous nitrate.

The calorimeter used was not adaptable to measuring heats of dilution of very dilute solutions to infinite dilution, and these data for manganous nitrate do not appear in the literature. The heats of dilution, therefore, could not be corrected to infinite dilution. An attempt was made to put all the data on a comparable basis by correcting to one final concentration (experimental final concentrations range in value from about 0.02 to 0.13 m as shown in Table III). After a careful study of the data, however, it was concluded that such corrections would not be justified since the magnitude of the corrections probably would be less than the experimental error. Final concentrations of the samples are included in the table so that if heats of dilution of dilute solutions ever become available, corrections to infinite dilution can readily be made.

Column 5 gives the heats of solution when one

TABLE III

HEATS OF DILUTION AND INTEGRAL HEATS OF SOLUTION OF MANGANOUS NITRATE ANHYDRIDE AT 25°, IN JOULES

Initial concn., m_1 1	Sample, g. 2	Final concn., m_2 3	Heat of diln., m_1 to m_2 4	Integral heat of solution	
				Heat per mole of salt in req. H_2O 5	Heat for m moles per 1000 g. H_2O 6
0.815	19.856	0.0139	-1,940	-58,100	-47,400
3.006	19.115	.0371	-6,830	-53,200	-159,900
5.500	17.865	.0493	-11,900	-48,200	-264,800
10.14	28.349	.1015	-20,900	-39,200	-396,900
11.10	32.342	.1194	-22,700	-37,300	-414,600
14.84	32.207	.1301	-28,800	-31,300	-463,800
17.63	31.413	.1329	-32,900	-27,200	-478,700
21.20	23.402	.1034	-37,200	-22,800	-484,400
24.62	22.691	.1033	-40,500	-19,600	-481,300

mole of the anhydrous salt is dissolved in enough water to give the concentration in column 1. These values are obtained by subtracting the heats of dilution of the solutions of m concentration (column 4) from the heat of solution of the anhydrous salt (60,050 j.) given in Table IV.

TABLE IV

HEAT OF SOLUTION OF MANGANOUS NITRATE ANHYDRIDE

Run	Sample, g.	Final concn., m	ΔH per mole, j.
1	6.5458	0.03673	-60,030
2	5.3899	.03024	60,100
3	5.8340	.03273	60,290
4	5.2716	.02959	60,120
5	3.0796	.01728	60,270
6	3.9264	.02203	59,510
7	4.3023	.02414	60,060

Column 6 gives the heats of solution when m moles of the anhydrous salt is dissolved in 1000 g. of water, giving the molal concentration in col-

umn 1 and are obtained by multiplying the initial concentration m (column 1) by the values in column 5. These heats are the total or integral heats of solution and are plotted against molality as Curve II, Fig. 2.

The slope of the curve (II, Fig. 2.) at any point gives the partial molal heat of solution of the anhydrous salt at that point. The slope can be obtained by mathematical methods. By the method of least squares, the equation $\Delta H = am + bm^2 + cm^3 + d$, was found to fit the data, where ΔH is the integral heat of solution, m the molality, and $a(-60,420)$, $b(2,419.4)$, $c(-30.68)$, $d(\text{zero})$ are constants. Differentiating this equation with respect to m gives $d(\Delta H)/dm = a + 2bm + 3cm^2 = \Delta H_2$. Then from the well-known relation $\Delta H = n_1\Delta H_1 + n_2\Delta H_2$, where ΔH_1 and ΔH_2 are the partial molal heats of solution of solute and solvent, respectively, ΔH_1 can be calculated. These quantities, ΔH_1 and ΔH_2 , are plotted against mole ratio in Fig. 3. Calculated points lie on the mathematical curves and hence are not indicated.

ΔH_1 can also be calculated from vapor pressure data by means of thermodynamic relations. The process of dissolving one mole of water in a large enough body of solution so as to give no change in concentration can be considered to take place in three isothermal steps: (1) one mole of water vapor is evaporated at its own vapor pressure; (2) the vapor is expanded from the vapor pressure of water to the vapor pressure of the solution ($\Delta H = 0$); (3) the vapor is condensed into an infinite quantity of solution. The Clapeyron-Clausius equation with the usual assumptions, $L = -RT^2 d \ln p/dT$, applies to steps (1) and (3). The sum of the three steps gives $\Delta H_1 = L_W - L_S$. L_W and L_S , the latent heats of vaporization of water and solution, can be evaluated by differentiating Eq. 1 with respect to T , giving

$$d \ln p/dT = -A/T^2 \quad (2)$$

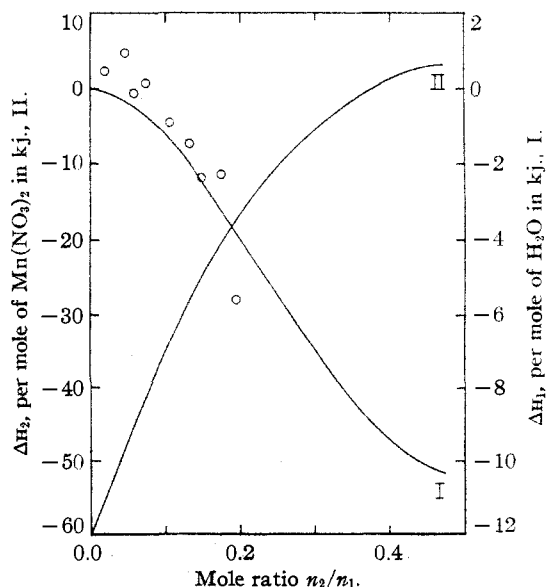


Fig. 3.—Partial molal heats of solution of water, curve I, and manganous nitrate, curve II.

Substituting this in the Clapeyron-Clausius equation gives $L = RA$ and

$$\Delta H_1 = R(A_w - A_s) \quad (3)$$

ΔH_1 values obtained from this equation appear as circles in Fig. 3 for the sake of comparison with calorimetric data. Table V contains the ΔH_1 values calculated from calorimetric data, column 4, and from vapor pressure data, column 3, for the solutions on which vapor pressure measurements were made (see Table I).

TABLE V

PARTIAL MOLAL HEATS OF SOLUTION OF WATER IN MANGANOUS NITRATE SOLUTIONS, IN JOULES

Soln.	Concn., <i>m</i>	ΔH_1 from v. p.	ΔH_1 from heat data
1	1.14	+ 480	- 55
2	2.53	+ 993	- 274
3	3.51	- 107	- 436
4	4.34	+ 173	- 730
5	5.96	- 849	-1314
6	7.38	-1453	-1930
7	8.36	-2356	-2399
8	9.74	-2230	-3115
9	10.94	-5604	-3766

The discordance in ΔH_1 is explained by the large change in slope of the $\ln p$ vs. $1/T$ line resulting from a small error in vapor pressure measurement. Assuming that the 40° measurement is most accurate, an error of 0.1 mm. at 25° for the most dilute solution changes the calculated ΔH_1 by about 1000 j. For this reason the ΔH_1 values from calorimetric data are much more reliable.

Vapor pressure data at 25° , tabulated in parentheses in Table I, were calculated by means of Eqs. 2 and 3, making use of ΔH_1 from calorimetric

data and the measured vapor pressures at 40° . Thus the slopes of the $\ln p$ vs. $1/T$ lines (plotted as broken lines in Fig. 1) for these solutions were fixed. Freezing points obtained from the intersection of these broken lines with the saturated solution curves fall nicely on the freezing point-composition curves obtained experimentally.⁴

The relative error in calorimetric measurements is about the same as in previous work.^{5,6} The absolute error may be slightly greater because of the inability to apply heat corrections to infinite dilution. On the basis of work done with other systems, this correction is estimated to be of the order of 1 kj. In the thermodynamic calculations, however, the difference between two experimentally determined values are involved in each case; hence, since final concentrations do not vary greatly (0.02 to 0.12 *M*) this very nearly constant error cancels out to a large extent.

Summary

Vapor pressure data for the system manganous nitrate-water are given for concentrations up to 24 *m*. They include vapor pressures for the unsaturated, saturated, and supersaturated solutions and for mixtures of the crystals of two hydrates.

The heat of solution of manganous nitrate anhydride has been measured, and the heats of dilution of solutions of the salt have been measured for concentrations up to 24 *m*.

Certain thermodynamic properties have been calculated for these two sets of data and comparison of the results made.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Optically Active Vasopressor Amines

BY WALLACE R. BRODE AND MAYNARD S. RAASCH¹

Two amines have been resolved for the purpose of comparing the pharmacological action of their optical antipodes. These compounds are β -phenyl-*n*-propylamine² and *N*-methyl- β -phenyl-*n*-propylamine.³

Experimental⁴

Resolution of β -Phenyl-*n*-propylamine.—Seventy-two grams of β -phenyl-*n*-propylamine, supplied by the Wm. S.

Merrell Co., and 36 g. of *l*-malic acid (mole ratio, 2:1) reacted in 200 ml. of absolute alcohol and the mixture was allowed to stand in ice for several hours. Fifty-one grams of the salt crystallized and was filtered. This was divided in halves and one-half was recrystallized four times from 90–95% alcohol. It had then reached its maximum rotation. The recrystallization liquors were used in recrystallizing the second half. The quantity of pure dextro β -phenyl-*n*-propylamine neutral *l*-malate obtained was 27.5 g., a yield of 51%; m. p. $182-4^\circ$; $[\alpha]^{25}_D$ 21.9° (*c*, 4; water).

Twenty-four grams of the levo amine recovered from the resolution mother liquors was treated in absolute alcohol with 12 g. of *d*-malic acid prepared by the procedure of

(1) Wm. S. Merrell Fellow.

(2) Hartung and Munch, *THIS JOURNAL*, **53**, 1875 (1931).

(3) Woodruff, Lambooy and Burt, *ibid.*, **62**, 923 (1940).

(4) The melting and boiling points reported are not corrected.