EQUILIBRIUM IN BINARY SYSTEMS UNDER PRESSURE. III. THE INFLUENCE OF PRESSURE ON THE SOLUBILITY OF AMMONIUM NITRATE IN WATER AT 25°

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It has been shown[1] that it is possible to calculate without any approximate assumptions the influence of high pressure on the solubilities of the pure solid components in a binary system, if the requisite simple thermodynamic data at all pressures are available. Furthermore, methods were described in detail whereby the data peculiar to changes under pressure might be obtained with a high degree of precision. The application of these principles and methods to the influence of pressure on two-phase equilibria in the system, NH_4NO_3–H_2O, at 25° has brought to light results of considerable interest. The solubility of ammonium nitrate is very greatly altered by the application of hydrostatic pressure; indeed, we have found that one hundred grams of water which dissolves 208.9 grams of ammonium nitrate at atmospheric pressure will only dissolve 42.25 grams of the salt when the pressure on the system is 10 kilobars.[2] The impression is still prevalent that hydrostatic pressure has but little effect on equilibria in condensed systems. We quote from Rothmund[3] the following passage which has in different versions been repeated from time to time: "Die nicht sehr zahlreichen Beobachtungen, welche über den Einfluss des Druckes auf die Löslichkeit vorliegen, bestätigen, dass dieser Einfluss ein sehr geringer ist, was ja auch von vornherein erwartet werden kann, da das Volumen und die sonstigen Eigenschaften bei festen und flüssigen Stoffen sich mit dem Drucke nur wenig ändern." (The few observations that have been made on the influence of pressure on solubility indicate strongly that this influence is a very small one, a conclusion that might certainly have been expected, as the volume and other properties of solid and liquid substances vary only slightly with pressure.) Since this statement was written, Cohen[4] and his school have brought forward several examples of systems where large changes of solubility have resulted from relatively small changes of pressure, and, in fact, as each new system is investigated, it becomes more and more apparent that any general statements about the effect of pressure on condensed systems are rather apt to be misleading. The data are still inadequate to support a generalization.

[1] L. H. Adams, THIS JOURNAL, (a) 53, 3769 (1931); (b) 54, 2229 (1932).

[2] 1 kilobar = 1000 bars or approx. 1000 atm.

[3] V. Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung," Leipzig, 1907, p. 81.

[4] See especially E. Cohen and A. L. Th. Moesveld, Z. physik. Chem., 93, 385 (1919); E. Cohen, W. de Meester, and A. L. Th. Moesveld, ibid., 114, 321 (1924).

In this paper we shall present the experimental data and the calculations necessary for the determination of the solubility curves of NH_4NO_3 IV[5] and ice$_{VI}$ under pressure at 25°, and thence construct the pressure–concentration diagram, which we shall check at certain points by direct measurements of phase changes under pressure.

Experimental

Specific Volumes of Ammonium Nitrate Solutions at Atmospheric Pressure.—Of all the thermodynamic data necessary for our calculations none are more important than the partial volumes of the components in the solutions at atmospheric pressure. These are derived directly from the specific volumes of solutions of different concentrations. The values of the densities or specific volumes of solutions of ammonium nitrate which are summarized in the "International Critical Tables"[6] were hardly of sufficient accuracy for our work, so a series of determinations at 25° was made with the apparatus and procedure which have already been frequently used and described.[7] The experimental results are recorded in Table I, the temperature of the thermostat being 25 ± 0.003° and the volume of the pycnometer being taken as 55.0368 ml. The values at even concentrations, obtained by interpolation from a plot of the first differences against the concentration,

TABLE I

SPECIFIC VOLUMES OF SOLUTIONS OF AMMONIUM NITRATE AS DETERMINED
EXPERIMENTALLY AT 25°

Corrected weight Salt	Solution	Weight fraction of salt, x_2	Weight of soln. in pycnometer	Specific volume ml./g., v
0	0	0		1.002932
0.9983	99.8842	0.009995	55.0981	0.998887
4.9477	99.0136	.049970	55.9886	.983000
7.9591	80.2827	.099138	57.1017	.963838
11.9318	79.4705	.150141	58.2849	.944272
17.9221	89.5478	.200140	59.4743	.925388
21.8358	87.3707	.249921	60.6916	.906828
22.7062	90.8086	.250045	60.6941	.906790
31.9456	91.2455	.350106	63.2391	.870297
43.7932	97.9445	.447123	65.8417	.835896
49.3806	89.8086	.549843	68.7554	.800472
60.2629	100.4476	.599944	70.2415	.783537
58.1451	89.5440	.649347	71.7538	.767023
64.8719	99.5058	.651941	71.8341	.766163
66.6345	98.3358	.677622	72.6417	.757647

[5] NH_4NO_3 IV is the orthorhombic form of solid ammonium nitrate which is stable at atmospheric pressure between −18 and 32.3°. The effect of pressure is to increase in both directions the temperature range over which the modification IV is stable.

[6] "I. C. T.," Vol. III, p. 59.

[7] R. E. Hall, *J. Wash. Acad. Sci.*, **14**, 167 (1924); R. E. Gibson, *J. Phys. Chem.*, **31**, 496 (1927); *ibid.*, **55**, 690 (1931).

are given in Table II. In each case the interpolation interval was so small that no appreciable error was introduced.

<div align="center">TABLE II</div>

THE SPECIFIC VOLUMES OF AMMONIUM NITRATE SOLUTIONS, THE APPARENT VOLUME OF THE SALT, AND THE PARTIAL VOLUMES OF THE SALT AND WATER AT EVEN INTERVALS OF CONCENTRATION

x_2	v	ϕ	$\dfrac{\phi_{obs.} - \phi_{calcd.}}{\times 10^5}$	$\bar{v}_2$	$\bar{v}_1$
0	1.002932	(0.5932)		0.5932	1.002932
.01	0.998885	.5981	-38	.6005	1.00291
.05	.982989	.60404	-2	.6090	1.00267
.10	.963513	.60872	22	.6157	1.00216
.15	.944326	.61222	9	.6207	1.00145
.20	.925440	.615465	9	.6252	1.00050
.25	.906807	.618404	0	.6293	0.99930
	.906799				
.30	(.88843)	(.62127)	(-1)	.6332	.99782
.35	.870335	.624080	2	.6367	.99608
.375	(.86138)	(.62546)	(3)	.6383	.99523
.40	(.85249)	(.62682)	(4)	.6398	.99428
.45	.834890	.629502	5	.6426	.99222
.50	(.81753)	(.63212)	(4)	.6451	.98995
.525	(.80893)	(.63341)	(2)	.6463	.98868
.55	.800404	.634698	0	.6474	.98741
.60	.783519	.637242	(-6)	.6491	.98515
.65	.766808	.639662	(-23)	.6504	.98299
	.766806				
.68	.756860	.641060	(-38)	.6510	....
.6763	....	....	....	.6509	....

The partial or fictive volumes of the salt ($\bar{v}_2$) and of the water ($\bar{v}_1$) in the solutions were calculated with the help of the intermediate quantity ϕ, the "apparent volume" of one gram of ammonium nitrate in a solution, which is defined by the equation

$$v = x_2\phi + x_1 v_w \tag{1}$$

where v_w is the specific volume of pure water. Several investigators[3] have recently confirmed the opinion that ϕ, or its analog the apparent molal volume, is a linear function of the square root of the volume concentration over a considerable range which appears to extend down to infinitely dilute solutions. We found that a slightly different form of equation, namely

$$\phi = 0.59318 + 0.049161 x_2^{1/2} \tag{2}$$

fitted our results from 1 to 15% within the experimental error, even though the concentration was expressed as the weight fraction. This equation was used in the estimation of ϕ at zero concentration and in the calculation of the fictive volumes in solutions containing from zero to 10% of ammonium nitrate. A second equation

[3] See Adams, Ref. 1b, Footnote on p. 2233.

$$\phi = 0.594118 + 0.043431x_2^{1/2} + 0.020524x_2^{3/2} \tag{3}$$

represented the data moderately well above 10%, as will be seen in column 4 of Table II which gives the difference between the values of ϕ as observed and as calculated by equation (3). It might be remarked that equation (3) fitted the results even better than a four constant power series in $(x_2/x_1)^{1/2}$. The interpolated values of v, enclosed in parentheses in Table II, were obtained from values of ϕ calculated by equation (3) and corrected from a deviation curve. In this way a table of x_2 at even intervals of 0.05 and of ϕ was constructed. The first divided differences, $\Delta\phi/\Delta x_2$, which were taken as giving the mean values of $d\phi/dx_2$ at the intermediate concentrations, were plotted against x_2. From this curve were read the mean values of $d\phi/dx_2$ corresponding to the concentrations listed in Table II. By this simple procedure all the data necessary for computing the partial volumes of the salt, $\bar{v}_2$, were made available and substituted in the formula

$$\bar{v}_2 = x_1 x_2 \frac{d\phi}{dx_2} + \phi \tag{4}$$

The resulting values of $\bar{v}_2$ are given in the fifth column of Table II. These figures were carefully compared with values of $\bar{v}_2$ as calculated directly from equation (3) together with the slopes of the deviation curve. The agreement was excellent at all concentrations above $x_2 = 0.10$, showing that the method of tabular differences was very satisfactory. The relation

$$v = x_1\bar{v}_1 + x_2\bar{v}_2 \tag{5}$$

was used to calculate $\bar{v}_1$, the fictive volumes of the water in the various solutions.

Changes in the Total and Partial Volumes under Pressure.—By the piston-displacement method[9] the *compressions* of the solutions produced by a rise of pressure from 2 to P kilobars were compared directly with the *compressions* of pure water produced by the same increase of pressure. To remind the reader of our nomenclature we may add that k represents the total *compression* or relative volume change per cc. at 1 atm., when the pressure is raised a definite amount from atmospheric pressure, and that k' stands for the same quantity when the upper limit of the pressure is fixed at 2 kilobars. Thus directly from the experimental observations we obtain the difference between $(k - k')$ for water and $(k - k')$ for the solution. This quantity we call $(\Delta k - \Delta k')$. The glass piezometer method[10] was used in the determination of k', which, together with the known values of the compressions of water,[11] led to an estimate of the compressions k of the various solutions. The product of k and the specific volume of the solution at 1 bar gave $\Delta_P v$, the increase in the specific volume of the solution pro-

[9] Adams, Ref. 1a, pp. 3773–3780.
[10] Adams, Ref. 1a, p. 3773.
[11] Summarized by Adams, Ref. 1a, Table II.

duced by the corresponding increase of pressure. Now it will readily be seen that equations (1), (4) and (5) may be written in the forms[12]

$$\Delta_P v = x_2 \Delta_P \phi + x_1 \Delta_P v_w \tag{1'}$$

$$\Delta_P \bar{v}_2 = x_1 x_2 \frac{d}{dx_2} \Delta_P \phi + \Delta_P \phi \tag{4'}$$

$$\Delta_P v = x_1 \Delta_P \bar{v}_1 + x_2 \Delta_P \bar{v}_2 \tag{5'}$$

The change in the apparent volume of the salt $\Delta_P \phi$ was computed by equation (1'), and the values obtained were found, within the scope of our measurements, to be linear functions of x_2. The constant slopes, $\frac{d}{dx_2} \Delta_P \phi$, at the different pressures are given in the last column of Table V. Tables III, IV and V record, respectively, the values of k, $\Delta_P v$ and $\Delta_P \phi$ at different pressures in solutions of different concentrations. The values of $\Delta_P \bar{v}_2$ recorded in Table VI represent a weighted mean of the values calculated from $\Delta_P \phi$ by equation (4'), and of a series computed directly from the slopes of $(\Delta k - \Delta k')$ with respect to x_2, taken as smoothed func-

TABLE III

EXPERIMENTAL VALUES OF $10^4 k$ FOR AMMONIUM NITRATE SOLUTIONS AT HIGH PRESSURES

P in kilobars x_2....0	0.15	0.30	0.375	0.45	0.525
0.001	0	0	0	0	0	0
1.0	393	351	309	289	270	250
2.0	699	626	556	524	490	467
3.0	945	850	762	719	677	667
4.0	1152	1039	935	891	840	
5.0	1330	1205	1087	1039	1001	
6.0	1485	1349	1222	1174	1151	
7.0	1622	1478	1344	1300		
8.0	1746	1592	1451			
9.0	1858	1701	1553			
10.0	1964	1802	1650			

TABLE IV

VALUES OF $10^4 \Delta_P v$ FOR AMMONIUM NITRATE SOLUTIONS AT HIGH PRESSURES

P x_2....0	0.15	0.30	0.375	0.45	0.525
0.001	0	0	0	0	0	0
1.0	− 394	− 332	− 275	− 249	−225	−202
2.0	− 701	− 591	− 494	− 452	−409	−378
3.0	− 948	− 803	− 677	− 620	−565	−540
4.0	−1155	− 981	− 831	− 768	−701	
5.0	−1334	−1138	− 966	− 895	−836	
6.0	−1489	−1274	−1086	−1012		
7.0	−1627	−1396	−1194	−1120		
8.0	−1751	−1503	−1290			
9.0	−1863	−1606	−1380			
10.0	−1970	−1702	−1466			

[12] The operator Δ_P indicates the finite change in the particular quantity produced by a finite change of pressure, the other variables, T and x, being kept constant.

TABLE V

VALUES OF $10^4 \Delta_p\phi$ FOR SOLUTIONS OF AMMONIUM NITRATE AT DIFFERENT PRESSURES AND VALUES OF $\dfrac{d}{dx_2} \Delta_p\phi$

P	$x_2\ldots 0.15$	0.30	0.375	0.45	0.525	$\dfrac{d}{dx_2} \Delta_p\phi$ $\times 10^3$
0.001	0	0	0	0	0	
1.0	20	3	− 8	− 18	− 29	−13
2.0	33	− 10	− 37	− 51	− 86	−29
3.0	20	− 43	− 72	− 98	−171	−39
4.0	6	− 80	−123	−147		−52
5.0	− 27	−107	−163	−227		−60
6.0	− 53	−147	−216	−316		−63
7.0	− 87	−183	−275			−64
8.0	−100	−213				−75
9.0	−153	−253				−68
10.0	−180	−290				−73

TABLE VI

CHANGES IN THE PARTIAL VOLUMES OF AMMONIUM NITRATE IN VARIOUS SOLUTIONS UNDER PRESSURE. WEIGHTED MEAN OF $10^3 \Delta_p\bar{v}_2$

P	$x_2\ldots 0$ 0.15	0.30	0.375	0.45	0.525
0.001	0	0	0	0	0
1.0	0.6	− 2.6	− 4	− 5	− 6
2.0	− 0.5	− 6.9	−10	−12	−15
3.0	− 3.1	−11.6	−15	−19	−24
4.0	− 6.0	−17.0	−21	−24	
5.0	−10.0	−21.4	−26		
6.0	−13.2	−25.8	−31		
7.0	−16.7	−29.8	−35		
8.0	−19.8	−34.5			
9.0	−23.6	−37.6			
10.0	−27.1	−42.0			

TABLE VII

CHANGES IN THE PARTIAL VOLUMES OF WATER IN SOLUTIONS OF AMMONIUM NITRATE UNDER PRESSURE. $10^3 \Delta_p\bar{v}_1$

P	$x_2\ldots 0$ 0.15	0.30	0.375	0.45	0.525
0.001	0	0	0	0	0
1.0	− 39.1	− 38.1	− 37.4	− 36.4	−35.8
2.0	− 69.4	− 67.3	− 66.2	− 64.7	−62.9
3.0	− 93.9	− 91.7	− 90.2	− 88.0	−87.1
4.0	−114.3	−111.4	−110.2	−107.5	
5.0	−132.1	−128.9	−127.5		
6.0	−147.5	−144.3	−143.4		
7.0	−161.3	−157.9	−158.2		
8.0	−173.3	−169.4			
9.0	−184.8	−181.0			
10.0	−195.4	−191.4			

tions of the pressure. Equation (5′) was used to calculate Table VII directly from Table VI.

We have plotted the values of the partial volumes of ammonium nitrate in solutions of different concentrations against the pressure in Fig. 1. The dotted curve shows the specific volume of solid ammonium nitrate as a function of the pressure. This diagram shows a marked contrast to the similar one for sodium chloride or for potassium sulfate. While the partial volumes of ammonium nitrate decrease as the pressure increases, except in the dilute solutions (15% or below) at low pressures, the partial volumes of the sodium chloride or potassium sulfate increase rapidly with pressure
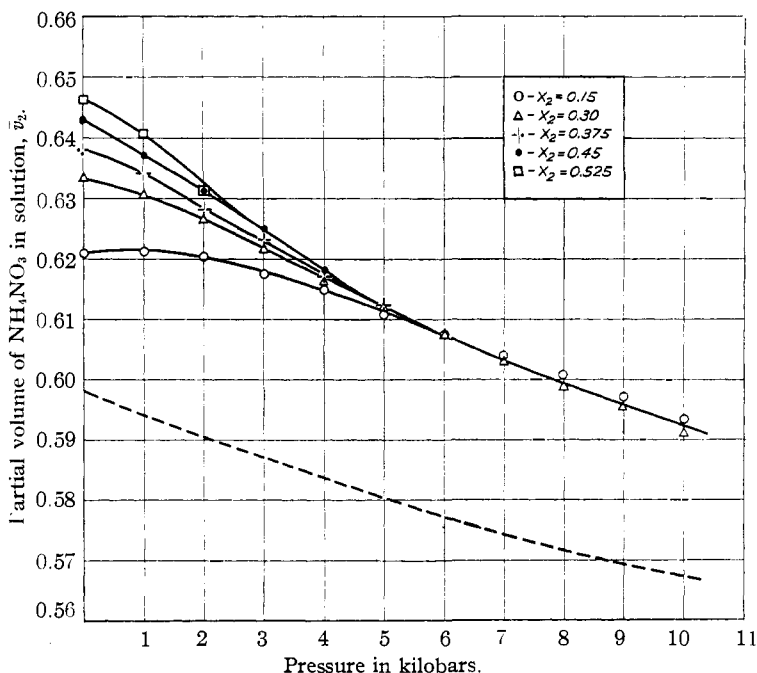
Fig. 1.—The partial volumes, $\bar{v}_2$, of ammonium nitrate in different solutions as a function of the pressure. The dotted curve shows the specific volume of the solid salt at different pressures.

except at the highest pressures in the most concentrated solutions. Furthermore, within the error of experiment our values of the partial volumes in different solutions seem to merge into one curve at the higher pressures, a curve whose slope is not very different from the slope of the volume–pressure curve of the solid salt. In other words, it seems that in aqueous solutions containing 15% or more ammonium nitrate the partial volumes of the salt are independent of the concentration above 5 kilobars and that. the partial compressibility of the salt differs only slightly from the compressibility of the solid salt above this pressure. Ammonium nitrate adds another striking example in support of the supposition that at high pres-

sures and high concentrations aqueous salt solutions behave more and more like ideal solutions, at least in respect to volume changes.

Changes of the Chemical Potentials μ_1 and μ_2 in Solutions of Ammonium Nitrate.—Measurements made recently in this Laboratory show that the vapor pressures of solutions of ammonium nitrate may be expressed as a function of concentration within the error of experiment by the following simple equation

$$\log \frac{p}{p_0 X_1'} = 0.00093 + 0.31317\, X_2'^{3/2} - 0.1580\, X_2'^{5/2} \qquad (6)$$

The equation, which is valid over a range from 15 to 65% of ammonium nitrate, contains the quantities, p/p_0, the relative vapor pressure of the solution, X_2', the mole fraction of the ammonium nitrate calculated on the basis of the molecular weight being one-half of the usual formula weight, and X_1', which is equal to $(1 - X_2')$. This relation will be discussed in detail elsewhere—in this paper it is used to calculate $(\mu_1 - \mu_w)$, the difference between the chemical potential of water in any solution of ammonium nitrate and that of pure water at the same pressure and temperature.

At the low vapor pressures at which p/p_0 was determined, the chemical potential difference was given with sufficient accuracy by the equation

$$\begin{aligned}\mu_1 - \mu_w &= \frac{2.303RT}{M_1} \log \frac{p}{p_0} \\ &= \frac{2.303RT}{M_1} \left\{ \log X_1' + 0.00093 + 0.31317\, X_2'^{3/2} - 0.1580\, X_2'^{5/2} \right\} \qquad (7)\end{aligned}$$

The difference between the chemical potential of the salt in any solution, μ_2, and in the saturated solution at 25°, $\mu_{satd.}$, was computed from the foregoing with the aid of Gibbs' equation (97), which for a binary system at constant temperature and pressure assumes the form

$$x_1 d\mu_1 = -x_2 d\mu_2 \qquad (8)$$

From equations (7) and (8) it follows that

$$\mu_2 = \frac{2.303RT}{M_2'} \left\{ \log X_2' - 0.93951\, X_2'^{1/2} + 0.57649\, X_2'^{3/2} - 0.1580\, X_2'^{5/2} \right\} + const. \qquad (9)$$

The value of μ_2 at the mole fraction corresponding to $x_2 = 0.6763$, the concentration of the saturated solution at 25°,[13] was taken as zero and hence $(\mu_2 - \mu_{satd.})$ was computed.

In order to bring these chemical potential differences from 20 to 25°, the partial enthalpy differences $(\bar{h}_1 - \bar{h}_w)$ and $(\bar{h}_2 - \bar{h}_{satd.})$ at the various concentrations were derived from the data of Cohen and Helderman[14] on the heats of solution of ammonium nitrate at 32.4° and brought to 22.5° by the heat capacity data of Cohen, Helderman and Moesveld.[15]

[13] E. Cohen and H. L. Bredée, *Z. physik. Chem.*, **117**, 148 (1925).

[14] E. Cohen and W. D. Helderman, *ibid.*, **113**, 154 (1924).

[15] E. Cohen, W. D. Helderman, and A. L. Th. Moesveld, *ibid.*, **112**, 139 (1924).

Equation (10) gives the exact formula for changing μ_2 from one temperature T_0 to another temperature T

$$(\mu_2 - \mu_{satd.})_T = \frac{T}{T_0}(\mu_2 - \mu_{satd.})_{T_0} - \frac{T - T_0}{T_0}(\bar{h}_2 - \bar{h}_{satd.})_{T_0} - \int_{T_0}^T \int_{T_0}^T \frac{\Delta \bar{c}_p}{T}\, dT dT \quad (10)$$

but by taking the value of $(\bar{h}_2 - \bar{h}_{satd.})$ at the intermediate temperature we avoided the necessity of using the last term.

In Table VIII we have incorporated values of the chemical potential differences in joules per gram at 20° as calculated by equations (7) and (9), and such values of these quantities at 25° as were necessary for this investigation.

<div align="center">

TABLE VIII

CHEMICAL POTENTIAL DIFFERENCES AT 20 AND 25°. JOULES PER GRAM

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x_2	$(\mu_1 - \mu_w)_{20}$	$(\mu_1 - \mu_w)_{25}$	$(\mu_2 - \mu_{satd.})_{20}$	$(\mu_1 - \mu_{satd.})_{25}$
0	0	0	∞	∞
0.10	(− 5.33)			
.15	− 8.18	− 8.39	−78.1	−81.3
.20	−11.16		−66.77	−69.35
.25	−14.34		−55.81	−57.96
.30	−17.76	−18.33	−46.76	−48.54
.35	−21.50		−38.98	−40.44
.40	−25.67		−32.03	−33.20
.45	−30.38		−25.67	−26.58
.50	−35.78		−19.71	−20.39
.55	−42.10		−13.97	−14.54
.60	−49.65		− 8.40	− 8.66
.65	−58.84		− 2.89	− 2.98
.6763	−64.56		0	0

The changes in the chemical potentials produced by a given rise in pressure at constant concentration are given by the general relation

$$\mu = (\mu)_0 + \int_0^P \bar{v}\, dP \quad (11)$$

where the subscript zero outside the parentheses, as always in this paper, means zero pressure. Terms of this nature will be introduced as required.

The Pressure–Solubility Curve of NH_4NO_3 IV.—If, at a given pressure P, a solution of ammonium nitrate of concentration x_2 is in equilibrium with solid NH_4NO_3 IV, whose chemical potential at that pressure may be written $(\mu_s)_P$, then according to Gibbs' fundamental equations

$$(\mu_2)_P = (\mu_s)_P \quad (12)$$

Now $\quad (\mu_2)_P = (\mu_2)_0 + \int_0^P \bar{v}_2\, dP$

and $\quad (\mu_s)_P = (\mu_s)_0 + \int_0^P v_s\, dP$

$\therefore \quad (\mu_2 - \mu_s)_0 = -\int_0^P (\bar{v}_2 - v_s)\, dP$, if $(\mu_2)_P - (\mu_s)_P = 0 \quad (13)$

i. e., $\quad (\mu_2 - \mu_{satd.})_0 = -\int_0^P (\bar{v}_2 - v_s)\, dP$, at the equilibrium concentration, $x_2 \quad (14)$

Hence, as $(\mu_2 - \mu_{satd.})$ at atmospheric pressure is a function of x_2, say $F(x_2)$, and as $-\int_0^P (\bar{v}_2 - v_s)\mathrm{d}P$ is another function of x_2, say $f(x_2)$, the problem of finding the equilibrium concentration at the pressure P resolves itself into determining a value of x_2 which satisfies the equation $F(x_2) = f(x_2)$ when the upper limit of the pressure is P. Graphically the problem may be solved by plotting $(\mu_2 - \mu_{satd.})_0$ and, for each pressure, $-\int_0^P (\bar{v}_2 - v_s)\mathrm{d}P$ in the same units against the weight fraction and reading the concentration at which these two curves intersect, as is done in Fig. 2.
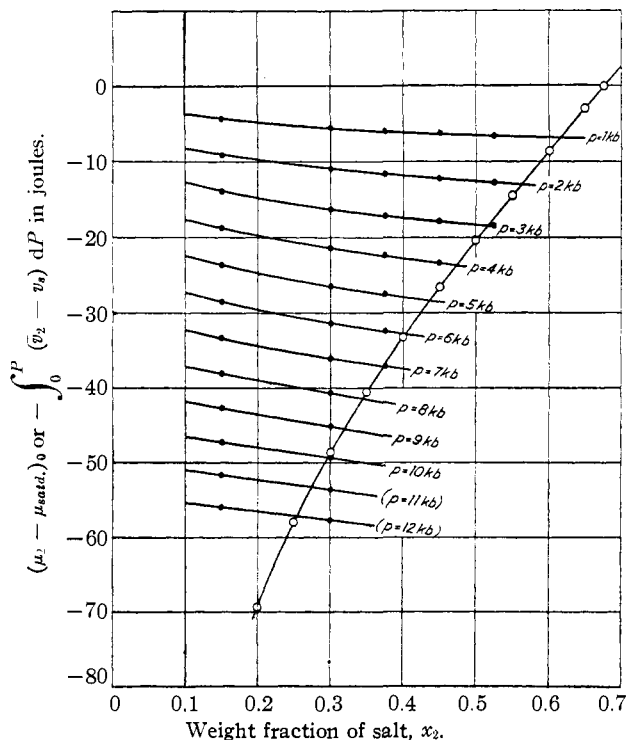
Fig. 2.—The curve with the open circles gives the chemical potential difference between ammonium nitrate in solutions of different concentration and ammonium nitrate in saturated solution, $(\mu_2 - \mu_{satd.})_0$, at 1 atmosphere and 25°. The other curves give the values of $-\int_0^P (\bar{v}_2 - v_s)\mathrm{d}P$ at even kilobars as a function of the concentration. The abscissas of intersections of this family of curves with the curve of $(\mu_2 - \mu_{satd.})_0$ are the equilibrium concentrations at the various pressures.

For convenience in calculation, equation (14) was modified to equation (15)

$$(\mu_2 - \mu_{satd.})_0 = -[(\bar{v}_2)_0 - (v_s)_0]P - \int_0^P (\Delta_P\bar{v}_2 - \Delta_Pv_s)dP \qquad (15)$$

where the terms to be integrated are much smaller; indeed, the second term on the right-hand side of equation (15) is very significant only at the high pressures, and graphical integration was found to be more than adequate in accuracy. The specific volume of NH_4NO_3 IV at atmospheric pressure $(v_s)_0$ was taken as 0.5797 and Δ_Pv_s was computed from the equation[16]

$$-\Delta_Pv_s = 0.5797k = (668.9P - 13.86P^2)0.5797 \times 10^{-5} \qquad (16)$$

while $\bar{v}_2$ and $\Delta_P\bar{v}_2$ were taken from Tables II and VI, respectively.

TABLE IX

VALUES IN JOULES OF $-\int_0^P (\bar{v}_2 - v_s)dP$ FOR DIFFERENT SOLUTIONS OF AMMONIUM NITRATE

P	x_2....0.15	0.30	0.375	0.45	0.525
0.001	0	0	0	0	0
1.0	− 4.35	− 5.43	− 5.90	− 6.2	− 6.53
2.0	− 9.03	−10.88	−11.62	−12.22	−12.71
3.0	−13.87	−16.23	−17.12	−17.97	−18.34
4.0	−18.78	−21.42	−22.40	−23.40	
5.0	−23.68	−26.44	−27.47		
6.0	−28.54	−31.30	−32.36		
7.0	−33.34	−36.01	−37.10		
8.0	−38.05	−40.58			
9.0	−42.67	−45.03			
10.0	−47.19	−49.34			
11.0	(−51.6)	(−53.5)			
12.0	(−55.9)	(−57.6)			

TABLE X

SOLUBILITY OF AMMONIUM NITRATE UNDER PRESSURE AT 25°

P	x_2
0	0.6763
1	.616
2	.563
3	.516
4	.473
5	.436
6	.403
7	.373
8	.345
9	.319
10	.297
11	(.275)
12	(.254)

Values in joules of the integral on the right-hand side of equation (14) are collected together in Table IX, and plotted against concentration for each value of the upper limit of pressure in Fig. 2. The original diagram on a large scale was used for the actual determination of the values of the equilibrium concentrations at each pressure which are summarized in Table X.

In effect we find for a given P the value of x_2 at which the μ of the solid salt is equal to that of the salt in solution. The same result may be obtained by finding, for a specified x_2, the value of P at which the μ's become equal, as was done in the previous investigations for determining the freezing-pressure curve of ice$_{VI}$. This would be accomplished by calcu-

[16] L. H. Adams and R. E. Gibson, *J. Wash. Acad. Sci.*, **21**, 388 (1931).

TABLE XI

THE FREEZING PRESSURES AT 25° OF ICE$_{VI}$ AND THE FREEZING TEMPERATURES AT ATMOSPHERIC PRESSURE OF ICE$_1$ IN CONTACT WITH SOLUTIONS OF AMMONIUM NITRATE. THE RATIO OF THE TEMPERATURE LOWERING TO THE PRESSURE ELEVATION IS GIVEN IN THE LAST COLUMN

x_2	P	$P - P_0$ (ice$_{VI}$)	$t_0 - t$ (ice$_1$)	$\frac{t_0 - t}{P - P_0} \times 10^2$
0	9,630	0	0	$(0.53)^a$
0.15	10,930	1300	5.79	.44
.30	12,700	3070	11.35	.37

^{a} Theoretical value calculated from dilute solution law.

lating $\mu_2 - (\mu_2)_r$ from $\bar{v}_2 - (\bar{v}_2)_r$ for each concentration (the subscript r denoting a reference concentration, say 15%) and determining from a plot the intersection of each curve with the curve for $\mu_s - (\mu_2)_r$. As a check on the computations, the solubility curve of ammonium nitrate was determined also by this method, with substantially the same results as those given by the first method, which, it may be noted, appears to be more convenient in the present instance.

The Solubility Curve of Ice$_{VI}$.—Pure water and ice$_{VI}$ coexist at equilibrium at 25° under a pressure of 9630 bars. Our problem was to find the pressures under which ice$_{VI}$ and a 15 or a 30% solution of ammonium nitrate are in equilibrium at this temperature. The chemical potential difference between water and ice$_{VI}$, $i.\ e.$, $(\mu_{VI} - \mu_w)$ has already been given as a function of the pressure,[17] and the chemical potential difference $(\mu_1 - \mu_w)$ for a given solution may be determined at any pressure by the relation

$$(\mu_1 - \mu_w)_P = (\mu_1 - \mu_w)_0 + \int_0^P (\bar{v}_1 - v_w)\mathrm{d}P \qquad (17)$$

The terms in this equation are all known; $(\mu_1 - \mu_w)$ is given in Table VIII, $\bar{v}_1$ may be written as a tabular function of P from Tables II and VII, and v_w at different pressures is given in a previous paper.[18] In Fig. 3 $(\mu_{VI} - \mu_w)$ and $(\mu_1 - \mu_w)$ for 15 and 30% solutions of ammonium nitrate were plotted against the pressure. The abscissas corresponding to the intersections of the curves represented the pressures at which ice$_{VI}$ is in equilibrium with these solutions. It was found that ice$_{VI}$ is in equilibrium with a 15% solution of ammonium nitrate at 10,930 bars and with a 30% solution at 12,700 bars. The solubility of the salt was so diminished by pressure that only these two of the solutions studied were available for the construction of the solubility curve of ice$_{VI}$.

The Equilibrium Diagram

The two solubility curves when plotted on the same system of coördinates give the simple pressure–composition diagram shown in Fig. 4. The curves

[17] Adams, Ref. 1a, Table X.
[18] Adams, Ref. 1a, Table II.

divide the diagram into fields in which the phases noted coexist when the system is in equilibrium and they intersect at the point $x_2 = 0.253$, $P = 12.100$ kb. This point is the *pressure eutectic* for the system, NH_4NO_3–H_2O, at 298.1°K., and its coördinates give the only pressure and concentration at which NH_4NO_3 IV, ice$_{VI}$, and liquid solution may coexist in stable equilibrium at this temperature.
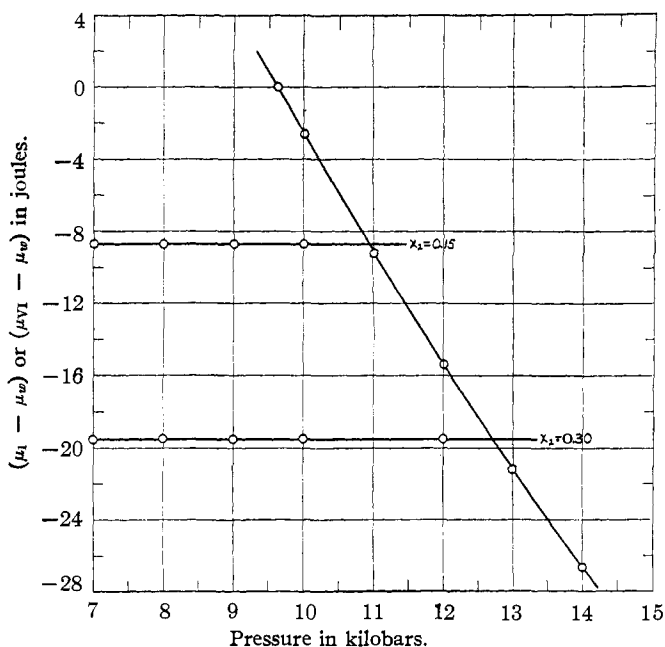

Fig. 3.—The differences between the chemical potential of water in 15 and 30% solutions of ammonium nitrate and of pure water are plotted as functions of the pressure. The abscissas of the intersections of these curves with the chemical potential–pressure curve of ice$_{VI}$ represent the pressures at which ice$_{VI}$ is in equilibrium with these two solutions.

This system differs in several respects from the systems $NaCl$–H_2O or K_2SO_4–H_2O, which are the subjects of the first two papers in this series. The solubility of ammonium nitrate at 25° diminishes continuously with increase of pressure, whereas the solubilities of the other two salts at first increase, then pass through a maximum and finally decrease as the pressure is raised. From this point of view the ammonium nitrate solutions behave more like ideal solutions. If we define an ideal solution as one which obeys Raoult's law in the generalized form

$$(\mu_2 - \mu_l) = \frac{RT}{M_2} \ln X_2 \tag{18}$$

at all pressures at any temperature, it may be shown that $\bar{v}_2 = v_l$ at all

concentrations at that temperature.   The reference state indicated by the subscript l is of necessity the pure liquefied component at the temperature and pressure of the experiment and M_2 is the effective molecular weight of that component.   The initial slope of the pressure–solubility curve is given in general by the equation

$$\frac{dx_2}{dP} = -\frac{(\bar{v}_2 - v_s)}{\left(\dfrac{d\mu_2}{dx_2}\right)_P} \tag{19}$$

which for an ideal solution becomes

$$\frac{dx_2}{dP} = -\frac{\Delta v}{\left(\dfrac{d\mu_2}{dx_2}\right)_P} \tag{20}$$

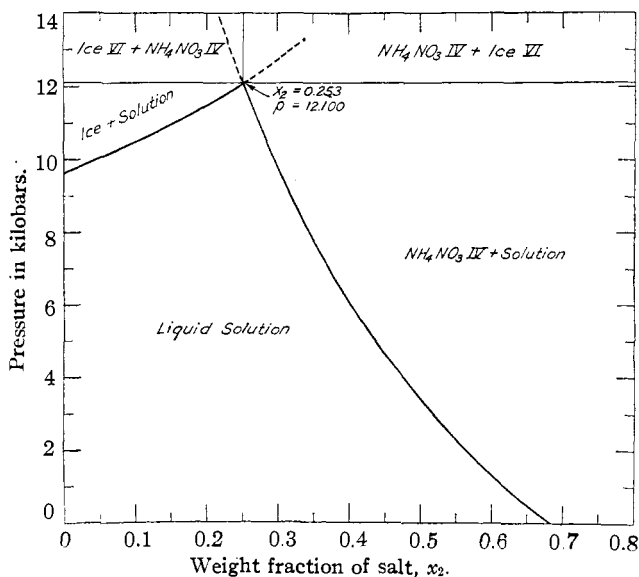where $\Delta v = v_l - v_s$, the volume change on melting of the pure solid.

Fig. 4.—The pressure–concentration equilibrium diagram for the system, NH_4NO_3–H_2O, at $25°$.

As the chemical potential μ_2 is always an increasing function of x_2 in a phase stable to continuous changes,[19] $(d\mu_2/dx_2)_{P,T}$ is always positive and the sign of the initial slope of the concentration–pressure curve therefore depends on the sign of Δv, the volume change on melting of the solid phase, being negative if Δv is positive and *vice versa*.   Except in very rare cases solids expand on melting so that in general increase of pressure should decrease the solubility of a solid in an ideal solution.   It should be remarked that the succeeding course of the pressure–solubility curve depends on the relative compressibilities of the solid and liquid forms of the com-

[19] J. Willard Gibbs, "Collected Works," Vol. I, p. 110, eqn. 171.

ponent—quantities that must be observed experimentally—they cannot be predicted from thermodynamics alone.

For purposes of comparison we have collected together in Table XII the data available on the initial values of dx_2/dP for different solutions. For most salts in aqueous solution this quantity is small and positive, whereas in the two solutions of organic solutes and solvents it is comparatively large and negative. The change in solubility of the ammonium nitrate resembles that of the organic compounds in that it is a relatively large decrease with increase of pressure, but it must be added that this decrease is not by any means as great numerically as in the case of the organic solutions. There seems to be little doubt but that aqueous solutions of ammonium nitrate behave more like ideal solutions over the whole range of pressure and concentration than do solutions of sodium chloride or of potassium sulfate.

TABLE XII

THE INITIAL SLOPES OF THE PRESSURE–SOLUBILITY CURVES OF DIFFERENT SOLUTES

Temp., °C.	Solute	Solvent	Soly. at 1 bar, g. per 100 g. soln.	Increase of soly. per 100 bars increase of pressure	Reference
25	NaCl	H_2O	26.42	0.083	Adams
25	K_2SO_4	H_2O	10.76	0.39	Adams
30	Tl_2SO_4	H_2O	5.80	0.33	I. C. T.[a]
25	$CdSO_4$	H_2O	43.44	0.088	I. C. T.[a]
25	$Ba(OH)_2$	H_2O	8.28	0.22	I. C. T.[a]
24	Mannitol	H_2O	17.11	0.072	I. C. T.[a]
25	$ZnSO_4$	H_2O	36.69	−0.013	I. C. T.[a]
30	CdI_2	H_2O	46.79	−0.38	I. C. T.[a]
30	$m\text{-}C_6H_4(NO_2)_2$	$CH_3COOC_2H_5$	34.44	−1.14	I. C. T.[a]
30	$C_{10}H_8$	$C_2H_2Cl_4$	35.08	−1.92	I. C. T.[a]
25	NH_4NO_3	H_2O	67.63	−0.63	Adams and Gibson

[a] "International Critical Tables," Vol. IV, p. 265.

Direct Determination of Equilibria

In the foregoing we have been able from the thermodynamic data to construct an equilibrium diagram for the system, NH_4NO_3–H_2O, on the assumption that the phases of the system were NH_4NO_3 IV, ice$_{VI}$, and liquid solution. The method we employed is based on exact thermodynamic principles and is as sound and trustworthy as direct observations themselves. However, the possibility that phases other than those assumed, for example a hydrate, might be formed under pressure must not be overlooked and the opportunity of making direct observations of pressures and concentrations on the equilibrium curves was welcomed as an important check on the validity of our assumptions about the phases. We were able to determine directly (a) the freezing pressure of the 15% solution, (b) the eutectic pressure, and (c) the solubility of NH_4NO_3 IV

at approximately 12,000 bars. The freezing pressure of the 15% solution was measured by a method which has already been described[20] and consists essentially of finding the intersection of the pressure piston-displacement curves for the solution alone and for an equilibrium mixture of ice and solution. The intersection of the "after melting" curve and the freezing curve (triangles) is shown in Fig. 5 at a pressure of 10,984 bars. The average of two determinations which differed by 40 bars gave 10,965 bars for the freezing pressure of the 15% solution of ammonium nitrate. This agrees well with 10,930 bars, the value of the freezing pressure of this solution as calculated from the thermodynamic data.
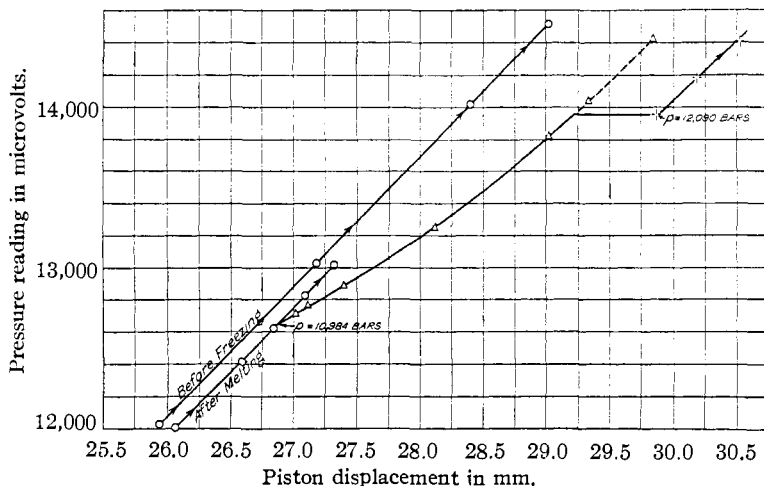

Fig. 5.—Graphical illustration of the direct determination of the freezing pressure of a 15% solution of ammonium nitrate and of the eutectic pressure in the system, NH_4NO_3–H_2O, at 25°.

The procedure for measuring directly the eutectic pressure has already been detailed.[21] The pressure is raised until so much ice has frozen out that the solution becomes sufficiently concentrated for the salt to separate— a super pressure of several hundred atmospheres often being needed. As long as three phases in equilibrium are present the pressure remains constant even though the piston displacement is changed.

Two direct determinations of this constant pressure gave as a mean 12,125 bars, the difference being 70 bars. The agreement between this figure and 12,100 bars, the pressure at which the two calculated solubility curves intersect, is most satisfactory.

In estimating the solubility of ammonium nitrate under pressure we placed a 30% solution in a cylindrical capsule and subjected it to a pressure

[20] Adams, Ref. 1a, p. 3811.
[21] Adams, Ref. 1b, p. 2241.

of approximately 12 kilobars. Although the solution was strongly super-saturated under these conditions, it did not usually begin to deposit salt until at least half an hour had elapsed. This delay in crystallization is in sharp contrast with the promptness with which crystals appear in a solution of ammonium nitrate which is only slightly supersaturated at atmospheric pressure. The solution was kept at high pressure for several hours. After the greater part of the crystallization (as judged by the fall in pressure) had taken place, the pressure was lowered by several hundred bars for a few minutes and then restored to the maximum value. We suspected that the salt might crystallize as long needles which might presumably grow to the top of the capsule. By lowering the pressure we hoped to dissolve these crystals partially and cause them to sink to the bottom of the capsule, where the small amount dissolved would also recrystallize when the system was again subjected to the highest pressure. After the capsule had been removed from the bomb a few cc. of solution was carefully withdrawn from the top layer and analyzed in a Rayleigh–Zeiss interferometer. In one experiment the uppermost layer of solution was found to contain 24.37% NH_4NO_3, while a sample drawn from immediately below it contained 24.40%. This convinced us that mixing had not proceeded to any appreciable extent and that in all probability the composition of the upper layer represented the composition of the solution which was in equilibrium with the solid salt at the maximum pressure. The method is not extremely precise but the results enable us to state with confidence as a result of several experiments that at 12,300 bars the solubility of ammonium nitrate is 24.9 ± 0.5 g. of salt per 100 g. of solution. The extrapolated solubility curve gives 24.8 as the value of this quantity.

The three direct determinations of the equilibrium pressures and concentrations are, therefore, in very good, one might say surprisingly good, agreement with the results of the thermodynamic calculations and confirm our confidence in the correctness of Fig. 4. It is, however, not impossible that the phases marked in this diagram are metastable and that other phases which exhibit extreme reluctance to appear are actually the stable ones, but, as far as our knowledge goes, none such are known or even suspected. Furthermore, as aqueous solutions of ammonium nitrate show small but positive departures from the Law of Ideal Solutions, and as the solid salt expands on dissolving, compound formation between these two components would not be expected.[22]

Summary

From new experimental data on the specific volumes of solutions of ammonium nitrate over the whole range of concentrations at 25° and 1

[22] See Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 72.

atm. pressure, and from direct measurements of the compressions of these solutions, we have calculated the partial volumes of ammonium nitrate and of water in different solutions under pressure from atmospheric to 10 kilobars. The partial volumes of the salt do not exhibit the large increases with rising pressure that were observed in solutions of sodium chloride or potassium sulfate except in the case of the 15% solutions where a small increase is observed at low pressures. Indications are that above 5 kilobars the partial volume of the salt in solutions containing more than 15% of ammonium nitrate is independent of the concentration.

From these data, together with the values of the chemical potential of the salt and water in the solutions at room temperature and pressure, we have calculated exactly the solubility curve of ammonium nitrate and the freezing curve of ice$_{VI}$ up to a pressure of 12 kb. and have constructed an equilibrium diagram for the system, NH_4NO_3–H_2O, under pressure. The solubility of ammonium nitrate decreases continuously as the pressure is raised, diminishing from 67.6% at atmospheric pressure to 43.6% at 5 kilobars, 29.7% at 10 kilobars, and 25.3% at 12.1 kilobars, the eutectic pressure. At three points, namely, the freezing pressure of a 15% solution, the pressure eutectic at 25°, and the concentration of the solution in equilibrium with NH_4NO_3 IV at 12,300 bars, we have checked the diagram by direct observations of equilibria and found very satisfactory agreement.

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THE SYSTEM LEAD ACETATE, ACETIC ACID, WATER[1]

BY GRADY TARBUTTON AND WARREN C. VOSBURGH

In connection with the study of certain voltaic cells it was found desirable to have further information concerning the system lead acetate, acetic acid, water. Sandved[2] found that the solubility of lead acetate trihydrate in mixtures of acetic acid and water increases with the proportion of acetic acid. He found a transition point at which the percentage of lead acetate was 67.90. Beyond this transition point the solubility data were somewhat uncertain, but he considered that anhydrous lead acetate was the stable solid form. He pointed out, however, that his data do not prove the non-existence of acid lead acetates.

Davidson and McAllister[3] studied the system lead acetate–acetic acid by the freezing point method. They obtained no evidence of solvates of lead

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[1] Part of a thesis presented by Grady Tarbutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

[2] Sandved, *J. Chem. Soc.*, 2971 (1927).

[3] Davidson and McAllister, THIS JOURNAL, **52**, 512 (1930).