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Summary

1. Previous data in the literature have been reviewed and shown to lend little support to the generally accepted formula for hydrated aluminum sulfate, namely, $Al_2(SO_4)_3 \cdot 18H_2O$.

2. Parts of ternary systems have been repeated at 25° and evidence presented which indicates that the heptadecahydrate is the stable form of aluminum sulfate in equilibrium with its saturated aqueous solution at this temperature.

3. Part of the solubility curve of $Al_2(SO_4)_3 \cdot 17H_2O$ in the system $NiSO_4$–$Al_2(SO_4)_3$–H_2O at 25° has been determined.

4. A substance of composition corresponding to the formula $Al_2(SO_4)_3 \cdot 17H_2O$ has been prepared by crystallization at a low temperature.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE SCHOOL OF APPLIED SCIENCE]

Thermodynamic Properties of Nitrogen at High Pressures as Analytic Functions of Temperature and Pressure

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Introduction

Accurate P–V–T data for nitrogen were determined by Bartlett and co-workers[1] in 1928 over the temperature range −70 to 600° and up to pressures of 1000 atmospheres. Utilizing these data, Deming and Shupe[2] evaluated Beattie–Bridgeman constants which, in conjunction with the Beattie–Bridgeman equation of state, reproduced the P–V–T relations of this gas with an accuracy of 2% down to volumes of 84 cc. per mole. At the lowest temperature, −70°, this volume corresponds to a pressure of about 200 atmospheres, while at the highest temperature, 600°, about 1000 atmospheres. Later, employing graphical methods, Deming and Shupe[3] evaluated from these same data a number of the thermodynamic properties of nitrogen at various temperatures and pressures, but made no attempt to express these properties as analytic functions of temperature and pressure.

The Beattie–Bridgeman equation of state, as ordinarily formulated, gives the pressure as an explicit function of volume and temperature. In order to obtain the thermodynamic properties as functions of pressure and temperature, it is convenient to have the volume as an explicit function of these two variables. By setting the actual volume equal to the ideal in all terms of the Beattie–Bridgeman equation beyond the first, Beattie[4] was able to formulate an equation explicit in volume, still retaining the ordinary constants. In preceding papers[5] the authors tested this modified Beattie–Bridgeman equation by calculating the activity coefficients (*i. e.*, ratios of fugacity to pressure) of nitrogen, and showed that the equation yields satisfactory results up to pressures of 300 to 500 atmospheres over the entire temperature range, but is not satisfactory for pressures higher than these. They also went on to show[6] how it is possible, knowing the Beattie–Bridgeman constants for nitrogen, to evaluate from these the Beattie–Bridgeman constants for any other gas.

Since the treatment employed in these papers is not limited to the equation used, but should be applicable to any equation of state explicit in volume, it should be possible to extend the pressure range of the analytic equations for the thermodynamic properties of a gas as soon as an equation of state of some gas is available which is more accurate at the high pressures than the modified Beattie–Bridgeman equation. It is the purpose of this paper (1) to present an equation of state for nitrogen explicit in volume and covering the temperature range −70 to 600° up to 1000 atmospheres pressure; (2) to deduce from this equation analytic expressions for the thermodynamic properties of the gas at high pressures; (3) to compare the quantities calculated from these

(1) Bartlett, Cupples and Tremearne, THIS JOURNAL, **50**, 1275 (1928).

(2) Deming and Shupe, *ibid.*, **52**, 1382 (1930).

(3) Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931); **45**, 111 (1934); **48**, 448 (1935).

(4) Beattie, *Proc. Natl. Acad. Sci.*, **16**, 14 (1930).

(5) Maron and Turnbull, *Ind. Eng. Chem.*, **33**, 69 (1941); **33**, 246 (1941).

(6) Maron and Turnbull, *ibid.*, **33**, 408 (1941).

equations with the results obtained graphically by Deming and Shupe. The manner in which this equation can be employed for other gases will be the subject of a subsequent paper.

Equation of State for Nitrogen

The equation of state for this gas was developed empirically by fitting several assumed relations to the experimental data. The first equation tried was

$$PV = RT + \alpha_1 P + \alpha_2' P^2 + \alpha_3' P^3 \qquad (1)$$

where α_1, α_2' and α_3' are virial coefficients dependent on temperature only. The virials were evaluated by least squares for each isotherm from the smoothed data of Bartlett and co-workers as tabulated by Deming and Shupe.[2] It was found that eq. (1) reproduced the compressibility data with satisfactory accuracy at temperatures above $-25°$ up to 1000 atmospheres, but did not work so well below this temperature. To permit the extension of the equation to $-70°$, another term was added, yielding

$$PV = RT + \alpha_1 P + \alpha_2 P^2 + \alpha_3 P^3 + \alpha_4 P^4 \qquad (2)$$

Retaining the values of α_1 obtained for eq. (1), the remaining virials in eq. (2) were again calculated by least squares. The new virials in conjunction with eq. (2) reproduced Bartlett's data much more closely than eq. (1).

To obtain the dependence of the virials on temperature, plots of α_1, α_2, α_3 and α_4 against $1/T$ were prepared. By trial of various functions, the following equations were found to fit the plots best

$$\alpha_1 = a_1 + \frac{a_2}{T} + \frac{a_3}{T^3} \qquad (3)$$

$$\alpha_2 = \frac{b_1}{T^2} + \frac{b_2}{T^4} + \frac{b_3}{T^6} \qquad (4)$$

$$\alpha_3 = \frac{c_1}{T^2} + \frac{c_2}{T^4} + \frac{c_3}{T^6} \qquad (5)$$

$$\alpha_4 = \frac{d_1}{T^2} + \frac{d_2}{T^4} + \frac{d_3}{T^6} \qquad (6)$$

a_1, a_2, . . . , b_1, b_2, . . ., etc., are constants independent of temperature and pressure. They were evaluated from the calculated virials by the method of least squares and are summarized in Table I. Through eq. (3) to (6) they yield the virials for eq. (2). The units employed were liters for volume, atmospheres for pressure, $T = 273.18 + t°$, and R was taken as 0.08206 liter-atmosphere per degree per mole.

The test of eq. (2) is summarized in columns 2 and 3 of Table II, where the average and maximum per cent. deviations of the calculated volumes from the observed are listed at the various temperatures. The pressures extend in all cases up to 1000 atmospheres. As may be seen from the table, eq. (2) reproduces the experimental P–V–T data for nitrogen from -70 to 600° and up to 1000 atmospheres pressure with an average deviation of 1.11% or less throughout, and a maximum percentage deviation no greater than 2.82 at the lowest temperature. Considering the wide temperature and pressure intervals covered by this equation, the agreement is as good as can be expected with the use of four virial coefficients.

Equation (2) meets also some of the conditions demanded for gas behavior at lower pressures. As P approaches zero, PV becomes equal to RT. Again, at low pressures the higher terms are negligible, and PV reduces to a linear function of P, a fact in accord with observation. It is of interest to point out that the equation gives for the standard density of nitrogen at 0° 1.2507 g. per liter as against the generally accepted value of 1.2506. In view of this, considerable reliance can be placed upon the equation for extrapolation to low pressures.

TABLE I

CONSTANTS FOR EQUATIONS (3) TO (6)

a_1 =	3.835×10^{-2}	c_1 =	-6.660×10^{-3}
a_2 =	-10.07	c_2 =	3.920×10^{2}
a_3 =	-2.449×10^{5}	c_3 =	-2.089×10^{7}
b_1 =	6.594	d_1 =	2.703×10^{-6}
b_2 =	-1.217×10^{5}	d_2 =	-0.2829
b_3 =	8.217×10^{9}	d_3 =	1.314×10^{4}

Calculation of Thermodynamic Properties.—In order to ascertain the applicability of eq. (2) for the calculation of the thermodynamic properties of nitrogen at high pressures, expressions were derived for the activity coefficient, entropy, heat and heat capacity of compression and the Joule–Thomson coefficients as functions of the temperature and pressure. The activity coefficient of the gas, γ, can be shown from eq. (2) to be given by

$$\ln \gamma = \frac{1}{RT}\left[\alpha_1 P + \left(\frac{\alpha_2}{2}\right) P^2 + \left(\frac{\alpha_3}{3}\right) P^3 + \left(\frac{\alpha_4}{4}\right) P^4\right] \qquad (7)$$

Furthermore, assuming that the activity coefficient of the gas is essentially unity at one atmosphere pressure, it can be shown that the expressions for ΔH, ΔS, ΔC_p and μ as functions of P and T follow from eq. (2) as

TABLE II

COMPARISON OF CALCULATED THERMODYNAMIC PROPERTIES OF NITROGEN WITH OBSERVED AND GRAPHICALLY ESTIMATED VALUES

Pressure range up to 1000 atmospheres except as indicated

	V		γ		ΔS		C_p[a]		μ[b]		ΔH	
t, °C.	% ± Dev., av.	% Dev., max.	% ± Dev., av.	% Dev., max.	% ± Dev., av.	% Dev., max.	% ± Dev., av.	% Dev., max.	Av. ± dev., °/atm.	Max. dev., °/atm.	Av. ± dev., cal./mole	Max. dev., cal./mole
− 70	1.11	−2.82	0.77	−1.85	1.62	−3.30	4.85	12.37	0.04	0.06	54	−103
− 50	0.89	−2.44	.98	−1.92	0.35	0.91	4.41	− 8.83	...	...	15	38
− 25	.55	1.26	..	..	..	..	..	..	...	...	..	...
0	.44	1.29	.33	1.08	.44	−0.86	2.89	9.59	.006	.013	11	− 24
100	.20	0.48	.58	1.00	.41	−1.42	2.24	− 4.82	.004	− .008	30	84
200	.22	− .92	.16	−0.77	..	..	0.71	− 3.33	.004	− .010	..	...
400	.11	.54	..	..	.07	0.20	..	..	...	...	10	− 27
600	.15	.51	..	..	.22	−0.46	.17	− 0.67	.007	− .010	..	...

[a] Pressure ranges covered: at −70° up to 100 atm.; −50° up to 300 atm.; at 0° up to 500 atm. All others up to 1000 atmospheres. [b] Pressure ranges covered: at −70° up to 300 atmospheres; all others up to 1000 atmospheres.

$$\Delta H = \left[a_1 + \frac{2a_2}{T} + \frac{4a_3}{T^3}\right]P + {}^1/_2\left[\frac{3b_1}{T^2} + \frac{5b_2}{T^4} + \frac{7b_3}{T^6}\right]P^2 + {}^1/_3\left[\frac{3c_1}{T^2} + \frac{5c_2}{T^4} + \frac{7c_3}{T^6}\right]P^3 + {}^1/_4\left[\frac{3d_1}{T^2} + \frac{5d_2}{T^4} + \frac{7d_3}{T^6}\right]P^4 \quad (8)$$

$$\Delta S = -R \ln P + \left[\frac{a_2}{T^2} + \frac{3a_3}{T^4}\right]P + \left[\frac{b_1}{T^3} + \frac{2b_2}{T^5} + \frac{3b_3}{T^7}\right]P^2 + {}^1/_3\left[\frac{2c_1}{T^3} + \frac{4c_2}{T^5} + \frac{6c_3}{T^7}\right]P^3 + {}^1/_2\left[\frac{d_1}{T^3} + \frac{2d_2}{T^5} + \frac{3d_3}{T^7}\right]P^4 \quad (9)$$

$$\Delta C_p = C_p - C_p^0 = -\left[\frac{2a_2}{T^2} + \frac{12a_3}{T^4}\right]P - \left[\frac{3b_1}{T^3} + \frac{10b_2}{T^5} + \frac{21b_3}{T^7}\right]P^2 - {}^1/_3\left[\frac{6c_1}{T^3} + \frac{20c_2}{T^5} + \frac{42c_3}{T^7}\right]P^3 - {}^1/_2\left[\frac{3d_1}{T^3} + \frac{10d_2}{T^5} + \frac{21d_3}{T^7}\right]P^4 \quad (10)$$

$$\mu = -\frac{1}{C_p}\left[\left(a_1 + \frac{2a_2}{T} + \frac{4a_3}{T^3}\right) + \left(\frac{3b_1}{T^2} + \frac{5b_2}{T^4} + \frac{7b_3}{T^6}\right)P + \left(\frac{3c_1}{T^2} + \frac{5c_2}{T^4} + \frac{7c_3}{T^6}\right)P^2 + \left(\frac{3d_1}{T^2} + \frac{5c_2}{T^4} + \frac{7d_3}{T^6}\right)P^3\right] \quad (11)$$

ΔH, ΔS and ΔC_p are the heat content, entropy and heat capacity changes accompanying the compression of the gas from one atmosphere to any pressure P, while μ is the Joule–Thomson coefficient. Since the constants of the equation of state were evaluated for P in atmospheres and V in liters per mole, eq. (8) yields ΔH in liter-atmospheres per mole, while eqs. (9) and (10) yield ΔS and ΔC_p in liter-atmospheres per mole per degree. μ, as usual, follows in degrees per atmosphere.

Equations (7) through (11) were used to calculate γ, ΔH, ΔS, C_p, and μ, and the calculated quantities were compared in turn with the values estimated graphically by Deming and Shupe[3] from Bartlett's data. The results of the comparison are summarized in Table II, where the average and maximum percentages deviation of calculated from graphically estimated values are listed for γ, ΔS and C_p, and the average and maximum deviations for ΔH and μ. In calculating C_p from eq. (10), the values of C_p^0 used at the various temperatures were those given by Deming and Shupe.[7] Since Deming and Shupe did not report ΔH, we evaluated this quantity from their γ and ΔS values. Due attention was given to the conversion of liter-atmospheres to calories wherever necessary.

Discussion

Inspection of Table II shows that the concordance between the calculated and graphically estimated activity coefficients of nitrogen is very good, the deviation being no greater than 2% in any case. With the exception of the results above 500 atmospheres at −70°, the same is true for ΔS. Above 500 atmospheres at −70° the deviation in ΔS is somewhat greater, rising to a maximum of 3.30% at 800 atmospheres.

The calculated heat capacities are in fairly good agreement with those of Deming and Shupe over the entire pressure range only at temperatures of 100° and higher. At the lower temperatures the two sets of values begin to deviate appreciably at considerably lower pressures, and for this reason the comparisons at these temperatures were not carried beyond the pressures indicated in the table. We are inclined to believe that at these temperatures the heat capacities given by Deming and Shupe are more nearly correct than

(7) Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931).

our own, and to ascribe the discrepancies to the fact that the evaluation of ΔC_p involves essentially a double differentiation of the equation of state. Because of this double differentiation, no equation of state can be expected to yield accurate values of C_p unless the equation of state can reproduce the P–V–T relations of a gas with an accuracy of 0.5% or better. However, whether the actual discrepancies are as large as found is not certain. It is of interest to point out in this connection that experimentally determined values of C_p for nitrogen reported by Mackey and Krase[8] at 100° and at pressures of 100–600 atmospheres are throughout closer to the values calculated from eq. (10) than to those estimated graphically by Deming and Shupe. To what extent this may be true at lower temperatures cannot be decided without further direct measurements.

Because of the small magnitude of the quantities involved, the comparisons for μ and ΔH are given in terms of actual deviations rather than percentages. As may be seen, the Joule–Thomson coefficients for nitrogen agree satisfactorily with those of Deming and Shupe over the entire pressure range at 0° and above. At −70° the agreement extends only up to 300 atmospheres. In calculating μ the values of C_p used were those evaluated from eq. (10), and since these deviate appreciably from those of Deming and Shupe at the higher pressures at the low temperatures, the same may be expected for the μ's under identical conditions.

On a percentage basis the concordance between calculated and graphically estimated ΔH values is not very good. When it is remembered, however, that ΔH involves an effect which amounts to only several hundred calories, then the deviation in calories rather than the percentage is of significance. The maximum discrepancy observed between any two values of calculated and graphically estimated ΔH's over the entire temperature and pressure range is 103 calories, and this only at −70°. In all other instances the deviations are considerably less. Deviations of this order are of relatively little consequence in most thermochemical calculations. Moreover, since ΔH is obtained as the difference of two large quantities, ΔF and $T\Delta S$, any errors in these are bound to appear magnified in ΔH, and a better agreement can hardly be anticipated.

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Summary

1. An equation of state for nitrogen is presented which reproduces the P–V–T behavior of the gas up to 1000 atmospheres from −70 to 600°.

2. From this equation are deduced analytic functions of temperature and pressure for the activity coefficients, heats, entropies, heat capacities of compression and the Joule–Thomson coefficients of the gas.

3. Comparisons are made between the quantities calculated by these relations and the thermodynamic properties of nitrogen as evaluated graphically by Deming and Shupe. It is shown that these equations reproduce satisfactorily the activity coefficients, entropies, and heats of compression over the entire temperature and pressure range, and the heat capacities and Joule–Thomson coefficients over most of the range.

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(8) Mackey and Krase, *Ind. Eng. Chem.*, **22**, 1060 (1930).