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

The Vapor Pressure of Liquid Nitrogen

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Introduction

Many investigations of the vapor pressure of nitrogen have been carried out, but only Crommelin at Leiden[1] and Dodge and Davis[2] in this country have measured the vapor pressure above one atmosphere. The vapor pressure of nitrogen from the boiling point to the critical point has been redetermined at this Laboratory in connection with general investigation of data of state for nitrogen.

Experimental Techniques and Results

The vapor pressure cryostat and the experimental techniques used in this investigation are the same as those previously used for the determination of the vapor pressure of hydrogen.[3] An M.I.T.-type dead weight gage[4] was used to measure pressures above two and a half atmospheres, and a constant volume manometer was used for the lower pressure readings. The temperatures were determined by means of two standard copper–constantan thermocouples, using a White double potentiometer. The nitrogen used was supplied by Linde Air Products and contained less than one-hundreth mole per cent. impurities.

The vapor pressures obtained are presented in Table I. They can be adequately expressed by the equation

$$\log P_{\text{atm.}} = a + b/T + cT \qquad (1)$$

TABLE I

Run	Temp., °K.	P, atm. Obsd.	P, atm. Calcd.	ΔP (obsd. − calcd.)	ΔT (obsd. − calcd.)
1	77.86	1.0527	1.0612	−0.0085	+0.07
2	83.66	1.9771	1.9661	.0110	− .05
3	86.85	2.67498	2.6653	.00968	− .04
4	90.90	3.82872	3.8094	.01932	− .06
5	95.05	5.35056	5.3276	.02296	− .05
6	98.96	7.13564	7.1213	.01434	− .03
7	102.02	8.81269	8.8079	.00479	− .01
8	104.55	10.3930	10.4008	− .0078	+ .01
9	106.71	11.9082	11.9189	− .0107	+ .01
10	109.09	13.7321	13.7688	− .0367	+ .04
11	110.85	15.2048	15.2597	− .0549	+ .06
12	114.16	18.2853	18.3587	− .0734	+ .06
13	116.27	20.4631	20.5404	− .0773	+ .06
14	117.95	22.3496	22.4135	− .0639	+ .05
15	120.14	24.9755	25.0085	− .0330	+ .02
16	121.57	26.8225	26.8207	.0018	.00
17	123.14	28.9509	28.8944	.0565	− .04
18	124.50	30.9120	30.7803	.1317	− .08
19	125.53	32.3477	32.2589	.0888	− .05

(1) Crommelin, *Leiden Comm.*, No. 145d (1914).

(2) B. F. Dodge and H. N. Davis, THIS JOURNAL, **49**, 610 (1927).

(3) D. White, A. S. Friedman and H. L. Johnston, *ibid.*, **72**, 3565 (1950).

(4) F. C. Keyes, *Ind. Eng. Chem.*, **23**, 1375 (1931).

where the constants are a, 3.720822; b, −293.94358; c, 10.31993×10^{-4}. The vapor pressure equation determined above is applicable for temperatures from the critical point to a few degrees below the boiling point, but deviations become significant in the neighborhood of the triple point. A convenient equation which would fit the data from the critical point to the boiling point within experimental error could not be obtained.

Table I also shows the deviation of the experimental points from this equation, in the columns headed "observed minus calculated." The normal boiling point of nitrogen, calculated from the equation, is 77.34°K. This value is in reasonable agreement with the generally accepted value of 77.36°K.[5,6]

Table II compares our data with equation (1) and with equations obtained by previous investigators.

TABLE II

Run	Temp., °K.	Pressure, atm.	ΔP (obsd. − calcd.) Eqn. (1)	Leiden eqn.[a]	D. & D. eqn.[b]
1	77.86	1.0527	−0.0085	+0.0699	−0.0103
4	90.90	3.8287	+ .0193	+ .0273	+ .0137
7	102.02	8.8127	+ .0048	+ .0629	+ .0159
10	109.09	13.7321	− .0367	+ .0904	− .0486
13	116.27	20.4631	− .0773	+ .0368	− .1707
16	121.57	26.8225	+ .0018	− .0545	− .2588
19	125.53	32.3477	+ .0888	− .2532	− .3879

[a] $\log P = 5.76381 - 853.522/T + 54372.3/T^2 - 1783500/T^3$. [b] $\log P = 4.47582 - 316.824/T - 0.0071701T + 2.940 \times 10^{-5}T^2$.

The vapor pressure curve is plotted in Fig. 1.

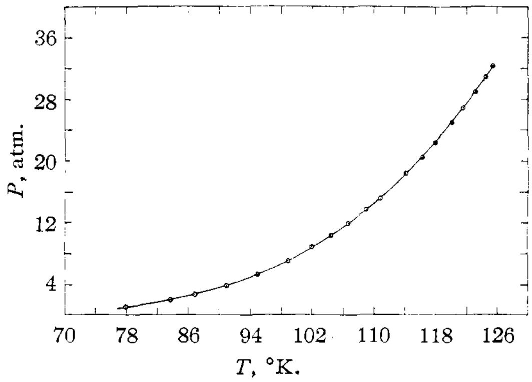

Fig. 1.—The vapor pressure of nitrogen.

Figure 2 is a plot of the reciprocal temperature *versus* the logarithm of the pressure. Observe that, unlike the curve for hydrogen, this curve is

(5) F. Henning and J. Otto, *Physik. Z.*, **37**, 639 (1936).

(6) W. H. Keesom and A. Bijl, *Leiden Comm.*, No. 217a (1931).

practically linear, and hence it can be shown that

$$\Delta H/\Delta V \approx 2.303P \log (P_0/P) \quad (2)$$

where P_0 is the pressure obtained by extrapolating the straight line curve to $1/T = 0$.

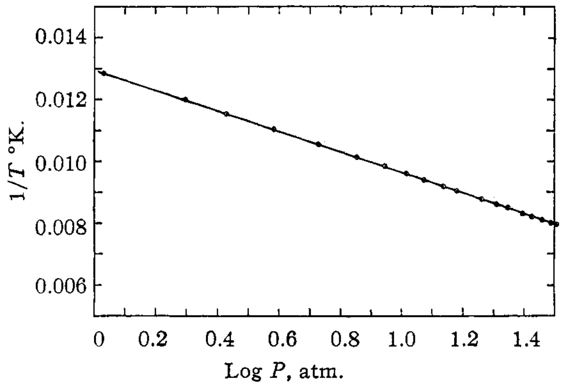

Fig. 2.—The vapor pressure of nitrogen.

Molal Heat of Vaporization.—The heat of vaporization, in calories per mole, is given by the equation

$$\Delta H = 0.05578P(V_g - V_l)(293.94358/T + 0.0010319937) \quad (3)$$

where P is in atmospheres, V in cc. per mole, and T in °K. The data obtained by Mathias, Onnes and Crommelin[7] on the rectilinear diameter of nitrogen have been used to get the molal volume of the liquid as a function of temperature and pressure. The gas density data of the Leiden Laboratories, which agree with data obtained in this Laboratory, were used to obtain the molal volume of the vapor as a function of temperature and pressure.

Molal heats of vaporization, computed from equation (3), are listed in Table III and are shown graphically in Fig. 3. The heat of vaporization at the normal boiling point is 1320 cal./mole. This result compares with the more accurate calorimetric values of 1332.9 obtained by Giauque and Clayton[8] and 1337 obtained by Dana.[9]

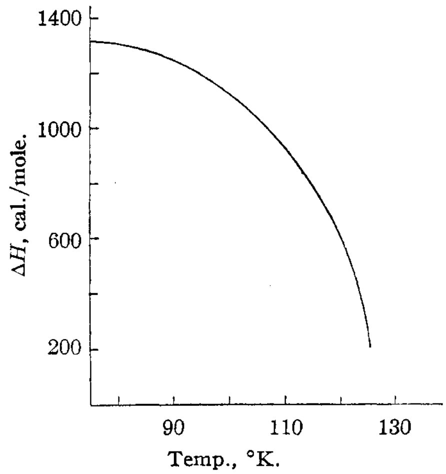

Fig. 3.—Heat of vaporization of nitrogen.

Table III

Temp., °K.	ΔH, cal./mole	Temp., °K.	ΔH, cal./mole
77.34	1320	112	872
80	1308	114	814
85	1283	116	750
90	1246	118	678
95	1194	120	599
100	1124	121	553
102	1092	122	502
104	1054	123	442
106	1015	124	373
108	970	125	280
110	923		

Discussion

The data of this research are more adequately fitted to an empiric equation than those of Leiden or of Dodge and Davis. All three sets of data lead to different critical constants for nitrogen. Using a critical temperature of 125.96°K. Leiden obtains a critical pressure of 33.490 atmospheres. Using a critical temperature of 126.00°K. Dodge and Davis obtain a critical pressure of 33.284 atmospheres. Using the above two critical temperatures, we obtain from our vapor pressure equation values of 32.900 and 32.958 atmospheres, respectively.

Extrapolation of $P-V$ isotherms determined in this Laboratory[10] lead to an estimated critical temperature of 126.1 to 126.2°K. Using a value of 126.15°K. in our vapor pressure equation, a value for the critical pressure of 33.181 atmospheres is obtained.

Summary

The vapor pressure of nitrogen from the boiling point to the critical point has been determined and can be accurately represented by the equation $\log P_{\text{atm.}} = 3.720822 - 293.94358/T + 10.31993 \times 10^{-4}\, T$.

The calculated boiling point of nitrogen from this equation is 77.34°K., and the molal heat of vaporization at the boiling point is 1320 cal./mole.

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(7) Mathias, Onnes and Crommelin, *Leiden Comm.*, No. 145c (1914).

(8) W. F. Giauque and J. Clayton, This Journal, **55**, 4875 (1933).

(9) L. Dana, *Proc. Am. Acad. Arts Sci.*, **160**, 241 (1925).

(10) The $P-V$ isotherms for nitrogen in the neighborhood of the critical point, as well as the direct determination of the critical constants for nitrogen which is now being attempted, will be reported on in a future publication.