

Water-hydrogen fluoride mixtures also present unusual properties for study through this means.

The assumption of an equilibrium of a series of chain-like polymers has not yet given us an adequate explanation of the apparent approach of the molecular weight of the gas to the value 120 as the temperature is lowered. The viscous behavior of the liquid is also difficult to understand. On the one hand, since the experimental heat of activation for viscous flow for many normal liquids is in the neighborhood of a third or fourth of the heat of vaporization,²² one would expect hydrogen fluoride to have a considerably greater fluidity than does water. On the other hand, the chain lengths are estimated to be much longer in the former than in the latter substance and hence the viscosity should be correspondingly greater for hydrogen fluoride. Although no measurements have been made, qualitative observations indicate that the viscosity must be low.

The structure of hydrogen fluoride is of considerable interest; infrared and Raman spectra might be used to test the correctness of the model suggested in this paper.

Summary

An electron diffraction study of gaseous hydrogen fluoride resulted in patterns which are incom-

(22) J. Hirschfelder, D. Stevenson and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

patible with a hexagonal structure wherein the fluorine atoms are at the corners and the hydrogen atoms at any position along the sides; agreement between observed and calculated intensity curves was found, however, when a zig-zag chain configuration was assumed. The fuzziness of the rings strongly supports the view that a number of different polymers are present.

Best values for the interatomic distances are:

F-H	1.00 ± 0.06 Å.
F---H	1.55 ± .06 Å.
F-H---F	2.55 ± .03 Å.

The average FFF angle is $140 \pm 5^\circ$, and the hydrogen atoms are on line with the fluorine atoms ($\pm 15^\circ$).

The possibility that the saturated vapor consists of the monomer and a chain or ring hexamer which dissociates into various chain-like fragments before the photographs are taken, when the vapor suddenly is allowed to expand into the evacuated chamber, has not been eliminated definitely; but this appears unlikely for there are a sufficient number of collisions in the gas nozzle for the gas to reach its equilibrium composition. Several of the properties of liquid hydrogen fluoride have been correlated on the basis of a continued equilibrium between chain polymers, and the difficulties of this assumption are also indicated.

PRINCETON, N. J.

RECEIVED OCTOBER 11, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 410]

The Vapor Pressure and Critical Constants of Normal Butane

BY JAMES A. BEATTIE, GERALD L. SIMARD AND GOUQ-JEN SU

In the course of a study of the compressibility of normal butane, we measured the vapor pressure of butane at several temperatures and investigated several isotherms in the critical region thereby locating the critical point. The method of procedure has been described elsewhere¹ and is the same as that used to locate the critical points of propane² and normal heptane,³ the bomb with the glass liner being used for normal butane.

The *n*-butane was obtained from the Buffalo Laboratory of The Linde Air Products Company

(1) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

(2) J. A. Beattie, N. Poffenberger and C. Hadlock, *J. Chem. Phys.*, **3**, 96 (1935).

(3) J. A. Beattie and W. C. Kay, *THIS JOURNAL*, **59**, 1586 (1937).

through the courtesy of Dr. L. I. Dana. It was fractionated by us five times, mainly for the purpose of removing permanent gases. Two separate loadings of the compressibility bomb were made: the vapor pressure at 75, 100, 125 and 150° and the isotherms in the critical region were investigated before the compressibility runs were made with the first loading; and the vapor pressure at 150° and the critical isotherm were measured with the second loading.

Results

Vapor Pressure.—The vapor pressures of normal butane are given in Table I. At each

TABLE I
VAPOR PRESSURE OF NORMAL BUTANE (C₄H₁₀)

Temp., °C. (Int.)	Vapor vol., cc.	Vapor press., normal atm.	Vapor vol., cc.	Vapor press., normal atm.	True vapor press., normal atm.
75	63	8.962	0.5	8.981	8.96 ± 0.02
100	52	15.087	3.5	15.111	15.09 ± .02
125	22	23.889	0.1	23.912	23.89 ± .02
150 ^a	7	36.262	.4	36.283	36.26 ± .02
150 ^b	9	36.245	.2	36.257	
150 ^c	9	36.246	.2	36.252	

^a First loading. ^b Second loading (before compressibility runs). ^c Second loading (after compressibility runs).

temperature the vapor pressure was determined at about 7 different vapor volumes. In Table I are given the values for the largest and smallest vapor volume, and the true vapor pressure. In each case the vapor pressure increased 0.01 to 0.02 atm., an amount greater than the experimental error in the determination of relative values of pressure at the same temperature. This indicates the presence of a small amount of some impurity, probably isobutane, but in insufficient

agreement with that obtained by extrapolation of the data of Dana, Jenkins, Burdick, and Timm⁴

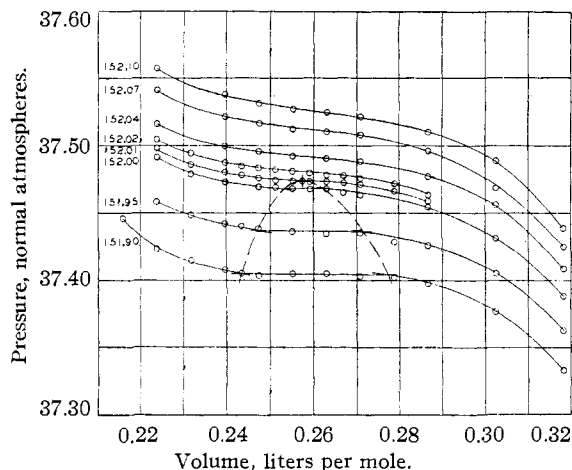


Fig. 1.—Isotherms of normal butane in the critical region. The radius of each circle is 0.002 atm.

which extend from -18 to $+60^{\circ}$; and our values at 75, 100 and 125° are in satisfactory agreement

TABLE II
ISOTHERMS OF NORMAL BUTANE (C₄H₁₀) IN THE CRITICAL REGION
Molecular weight, 58.077

Temp., °C. (Int.)	Density, moles/liter	Volume, liters/mole	Pressure, normal atmospheres									
			151.900	151.950	152.000	152.010	152.020	152.040	152.070	152.100		
2.860		0.3497			37.2195							
2.994		.3340			37.3400							
3.142		.3183	37.3340	37.3630	37.3885			37.4090	37.4255	37.4395		
3.305		.3026	37.3770	37.4055	37.4315			37.4565	37.4690	37.4895		
3.486		.2869	37.3985	37.4260	37.4550	37.4595	37.4640	37.4775	37.4965	37.5105		
3.583		.2791	37.4025	37.4285		37.4670	37.4720					
3.687		.2712	37.4035	37.4355	37.4635	37.4715	37.4760	37.4885	37.5085	37.5220		
3.741		.2673			37.4655	37.4730	37.4780					
3.797		.2634	37.4055	37.4350	37.4685	37.4740	37.4785	37.4905	37.5110	37.5250		
3.855		.2594			37.4680	37.4735	37.4800					
3.914		.2555	37.4055	37.4370	37.4685	37.4740	37.4815	37.4935	37.5125	37.5275		
3.975		.2516			37.4690	37.4745	37.4825					
4.039		.2476	37.4035	37.4390	37.4695	37.4765	37.4835	37.4960	37.5170	37.5315		
4.103		.2437	37.4055	37.4405		37.4785	37.4845					
4.170		.2398	37.4085	37.4420	37.4730	37.4800	37.4875	37.5000	37.5220	37.5380		
4.310		.2320	37.4150	37.4490	37.4790	37.4860	37.4945					
4.462		.2241	37.4235	37.4590	37.4915	37.4980	37.5045	37.5165	37.5415	37.5580		
4.625		.2162	37.4460									
4.798		.2084			37.5875						37.7375	

Critical point from Fig. 1: $t_c = 152.01 \pm 0.01^{\circ}$ (Int.), $p_c = 37.47 \pm 0.02$ normal atm., $v_c = 0.258$ liter per mole (4.44 cc. per gram), $d_c = 3.88$ moles per liter (0.225 gram per cc.). The uncertainty in the critical volume and density is 1%.

quantity to affect the compressibility data appreciably. The last two entries in the table show that in the second compressibility run, during which the sample was at 250 to 300° for thirty-six hours, no perceptible decomposition took place.

Our value of the vapor pressure at 75° is in good

with those of Sage, Webster and Lacey⁵ (20 to 120°). The vapor pressures of Seibert and Burrell⁶

(4) L. I. Dana, A. C. Jenkins, J. N. Burdick and R. C. Timm, *Refriger. Eng.*, **12**, 387 (1926).

(5) B. H. Sage, D. C. Webster and W. N. Lacey, *Ind. Eng. Chem.*, **29**, 1188 (1937).

(6) F. M. Seibert and G. A. Burrell, *THIS JOURNAL*, **37**, 2683 (1915).

(0 to 130°) are somewhat higher than the values given in Table I.

Critical Constants.—In Table II are given the compressibility data in the critical region, and these values are plotted in Fig. 1. The pressures are given to 0.0005 atm. since relative values are consistent to about 0.001 atm. The critical data resulting from our measurements are given at the bottom of Table II. Germann and Pickering⁷ select $t_c = 153^\circ$, $p_c = 36$ atm., which are the values obtained by Seibert and Burrell.⁶

The critical isotherm, 152.01°, was reinvestigated with the second loading of the bomb. The pressures so measured were uniformly 0.02

(7) "International Critical Tables," Vol. III, 1928, p. 248.

atm. lower than the values listed in Table I.

Summary

The vapor pressure of normal butane has been measured from 75 to 150° by 25° intervals.

Normal butane confined in a glass vessel by means of mercury does not decompose perceptibly at temperatures up to 300°.

The critical constants of normal butane (C_4H_{10} , mol. wt. 58.077) are: $t_c = 152.01 \pm 0.01^\circ$ (Int.), $p_c = 37.47 \pm 0.02$ normal atm., $v_c = 0.258$ liter per mole (4.44 cc. per gram), $d_c = 3.88$ moles per liter (0.225 gram per cc.). The uncertainty in the critical volume and density is 1%.

CAMBRIDGE, MASS.

RECEIVED OCTOBER 18, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 411]

The Compressibility of and an Equation of State for Gaseous Normal Butane

BY JAMES A. BEATTIE, GERALD L. SIMARD AND GOUQ-JEN SU

The compressibilities of gaseous methane,¹ ethane,² propane,³ and heptane⁴ have been measured and the equation of state constants for these gases determined. We have measured the compressibility of gaseous normal butane. The most extensive series of measurements on the compressibility of normal butane at present are those of Sage, Webster and Lacey⁵ from 20 to 120°. Our method of procedure has been described elsewhere,⁶ and is the same as that used for ethane, propane and heptane. For normal butane the bomb with the glass liner was used.

Two loadings of the bomb were made: the low pressure loading was used to study the compressibility from 0.5 to 5.0 moles per liter; and the high pressure loading, from 4.0 to 8.5 moles per liter. The *n*-butane was obtained from the Buffalo Laboratory of The Linde Air Products Company through the courtesy of Dr. L. I. Dana, and was the same as that used by us for the determination of vapor pressures and critical constants.⁷ The behavior of the sample in the critical region, and the con-

stancy of vapor pressure with decrease in vapor volume indicate that the sample was of satisfactory purity. The fact that for the high pressure loading the vapor pressure at 150° was the same within the experimental error after the compressibility runs as it was before the runs indicates that the *n*-butane did not decompose during our measurements.

Results

The compressibility data below the critical density are given in Table II, and those above the critical density, in Table III. The constants of the Beattie-Bridgeman equation of state were determined from the data below the critical density ($d_c = 3.88$ moles per liter) and are given in Table I. The comparison of the pressures computed from the equation with the observed pressures is given in Table II. The agreement is about the same as for the other hydrocarbons.

TABLE I

VALUES OF THE CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION OF STATE FOR GASEOUS NORMAL BUTANE (C_4H_{10})

$$p = [RT(1 - \epsilon)/V^2][V + B] - A/V^2$$

$$A = A_0(1 - a/V)$$

$$B = B_0(1 - b/V)$$

$$\epsilon = c/VT^3$$

Units: normal atmospheres, liters per mole, °K. ($T^\circ K. = t^\circ C. + 273.13^\circ$).

$$R = 0.08206$$

$$A_0 = 17.7940$$

$$a = 0.12161$$

$$B_0 = .24620$$

$$b = 0.09423$$

$$c = 350 \times 10^4$$

$$\text{Mol. wt.} = 58.077$$

(1) F. G. Keyes and H. G. Burks, *THIS JOURNAL*, **49**, 1403 (1927).

(2) J. A. Beattie, C. Hadlock and N. Poffenberger, *J. Chem. Phys.*, **3**, 93 (1935).

(3) J. A. Beattie, W. C. Kay and J. Kaminsky, *THIS JOURNAL*, **59**, 1589 (1937).

(4) L. B. Smith, J. A. Beattie and W. C. Kay, *ibid.*, **59**, 1587 (1937).

(5) B. H. Sage, D. C. Webster and W. N. Lacey, *Ind. Eng. Chem.*, **29**, 1188 (1937).

(6) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

(7) J. A. Beattie, G. L. Simard and G.-J. Su, *THIS JOURNAL*, **60**, 24 (1938).