TABLE II

ISOTHERMS OF NORMAL HEPTANE (C_7H_{16}) IN THE CRITICAL REGION

Molecular weight, 100.1248

Temp., °C. (Int.)		266.850	266.950	267.000	267.020	267.050
Density, moles/liter	Volume, liters/mole	Pressure, normal atmospheres				
2.138	0.4677	26.920		26.988		
2.229	.4486	26.934	26.975	26.993	27.001	27.010
2.328	.4296		26.977		27.004	27.013
2.338	.4277	26.932				
2.354	.4248		26.980			
2.381	.4200	26.932	26.979	26.996	27.005	27.016
2.419	.4134	26.932				
2.459	.4067	26.935	26.980	26.996	27.008	27.017
2.494	.4010		26.979			
2.555	.3914	26.932	26.983	27.001	27.013	27.025
2.619	.3818			27.007		
2.686	.3723	26.944	26.992	27.013	27.026	27.037
2.831	.3532	26.995				
2.993	.3341	27.150				

Critical point from Fig. 1: t_c = 267.01 ± 0.02° (International); p_c = 27.00 ± 0.02 normal atmospheres; v_c = 0.416 liter per mole (4.15 cc. per gram); d_c = 2.40 moles per liter (0.241 gram per cc.). The uncertainty in the critical volume and density is 1%.

Summary

The boiling point of normal heptane is 98.52 ± 0.01° (Int.) at 760.0 mm. pressure. The critical constants of normal heptane (C_7H_{16}, mol. wt. 100.1248) are t_c = 267.01 ± 0.02° (Int.), p_c = 27.00 ± 0.02 normal atmosphere, v_c = 0.416 liter per mole (4.15 cc. per gram), d_c = 2.40 moles per liter (0.241 gram per cc.). The uncertainty in the critical volume and density is 1%.

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The Compressibilities of Liquid and Gaseous Normal Heptane and an Equation of State for Gaseous Normal Heptane

BY LEIGHTON B. SMITH, JAMES A. BEATTIE AND WILLIAM C. KAY

We have studied the compressibility of liquid normal heptane from 30 to 250° and to pressures of 350 atmospheres, and the compressibility of gaseous normal heptane from 275 to 350° and from a density 1.0 to 5.0 moles per liter. The apparatus, method, and reduction of the observation have been described elsewhere[1] and are the same as those used for measurements of the compressibility of gaseous ethane[2] except that in the case of heptane the substance was contained in a Pyrex glass vessel enclosed in a chrome-vanadium steel bomb.[1] Two complete runs with different loadings of heptane were made on the gas phase.

At each temperature the procedure was to measure the pressures from the smallest to the largest densities and to repeat some of the measurements for the smaller densities, always repeating that for a density of 1 mole per liter. The time required for investigating a complete isotherm was about six hours. Decomposition of the heptane is indicated by an increase in pressure. At 325° the pressure at 1.0 mole per liter—32 atm.—increased during the six-hour period 0.003 atm. in run I and 0.008 atm. in run II; at 350° the pressure at 1.0 mole per liter—35 atm.—increased 0.040 atm. in run I and 0.045

TABLE I

COMPRESSIBILITY OF LIQUID NORMAL HEPTANE (C_7H_{16})

Molecular weight, 100.1248. Pressures are in normal atmospheres. Temperatures are on the International Temperature Scale.

Moles/liter	Cm.³/g.	Press., atm.
	30°	
6.7515	1.4793	7.12
6.7685	1.4756	19.08
6.7836	1.4723	31.04
6.7942	1.4700	43.00
6.8067	1.4673	52.31
6.8347	1.4613	82.20
6.8638	1.4551	112.10
6.9116	1.4440	171.89
6.9702	1.4329	231.68
7.0182	1.4231	291.46
7.0668	1.4133	351.25
	100°	
6.1394	1.6268	7.12
6.1690	1.6190	19.08
6.2000	1.6109	37.02
6.2449	1.5994	66.91
6.2700	1.5930	82.20
6.3120	1.5824	112.10
6.3912	1.5627	171.89
6.4598	1.5461	231.68
6.5244	1.5308	291.46
6.5824	1.5174	351.25
	150°	
5.6047	1.7820	7.37
5.6526	1.7669	19.33
5.7052	1.7506	37.26
5.7456	1.7383	52.55
5.8138	1.7179	82.44
5.8778	1.6992	112.34
5.9910	1.6671	172.13
6.0874	1.6407	231.91
6.1743	1.6176	291.70
6.2442	1.5995	351.49
	200°	
5.0078	1.9944	19.34
5.1124	1.9536	37.27
5.1859	1.9260	52.56
5.3074	1.8819	82.45
5.4098	1.8462	112.35
5.5718	1.7926	172.14
5.7029	1.7514	231.92
5.8145	1.7177	291.71
5.9094	1.6902	351.50
	250°	
4.0000	2.4970	24.38
4.5000	2.2195	54.84
5.0000	1.9976	135.97
5.3179	1.8781	231.80
5.5000	1.8160	310.83
5.5831	1.7889	351.36

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

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

TABLE II

VALUES OF THE CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION OF STATE FOR GASEOUS NORMAL HEPTANE (C_7H_{16})

$$p = [RT(1 - \epsilon)/V^2][V + B] - A/V^2$$
$$A = A_0(1 - a/V)$$
$$B = B_0(1 - b/V)$$
$$\epsilon = c/VT^3$$

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

$R = 0.08206$ $b = 0.19179$
$A_0 = 54.520$ $c = 400 \times 10^4$
$a = 0.20066$ Mol. wt. $= 100.1248$
$B_0 = 0.70816$

TABLE III

COMPARISON OF THE PRESSURES CALCULATED FROM THE EQUATION OF STATE WITH THE OBSERVED PRESSURES FOR GASEOUS NORMAL HEPTANE (C_7H_{16})

For each temperature the first line gives the observed pressure and the second line gives the observed minus the calculated pressure. The calculated pressures are computed from the equation given in Table II. The critical constants of normal heptane are: t_c = 267.01° (Int.); p_c = 27.00 normal atmospheres; d_c = 2.40 moles per liter; v_c = 0.416 liter per mole.[3]

Density, mole/liter Temp., °C.(Int.)		1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
							Pressure, normal atmospheres			
275	obsd.	25.19	28.55	29.72	30.38	31.70	36.62	53.17	97.49	196.15
	obsd.-calcd.	−0.24	+0.10	−0.03						
300	obsd.	28.68	34.43	38.08	41.29	46.65	57.67	83.40	140.51	255.67
	obsd.-calcd.	−0.12	+0.20	−0.06						
325	obsd.	32.03	40.12	46.38	52.89	62.30	79.57	114.24	183.67	315.73
	obsd.-calcd.	−0.12	+0.16	−0.05						
350	obsd.	35.34	45.74	54.63	64.58	78.53	102.18	145.88	227.88	
	obsd.-calcd.	−0.15	+0.09	−0.03						
Av. dev., atm.		.158	.138	.043						
Av. % dev.		.540	.383	.105						

Total average deviation (atm.), 0.113; total average % deviation, 0.343.

atm. in run II during the six-hour period. Thus, when confined by mercury in a glass vessel normal heptane decomposes very slowly at 325° but at an appreciable rate at 350°. The data were not corrected for this decomposition.

Purity of the Heptane.—The method of purification of the heptane is given in a paper on the critical constants.[3] That the sample was of exceptional purity is indicated by the constancy of the boiling point, the constancy of vapor pressure at 250° during a variation in vapor volume of from 60 to 1 cc., and the behavior of the sample in the critical region.

Accuracy of the Results.—High precision is attained in the measurement of temperature, pressure, and mass. The uncertainty in the reproduction of the International Temperature Scale is 0.01 to 0.02°, the uncertainty in the measurement of pressures in normal atmospheres is less than 0.03%, and that in the determination of mass is less than 0.01%. The greatest uncertainties lie in the measurement of volume which may be in error by as much as 0.1%.[1] At 325° and to a greater extent at 350° the assumption[1] that the mercury vapor acts quite independently of the gaseous heptane introduces an error of unknown amount, which, however, is probably not over 0.01 to 0.02 atmosphere.

It is believed that for the data on liquid heptane, the densities are not in error by as much as 0.3%; for the data on gaseous heptane the pressures are not in error by more than 0.3% up to a density of 2.5 moles per liter and by 0.6% above 2.5 moles per liter.

In run I an error of absolute amount (not a percentage effect) was made in the "zero-set" volume.[1] For this reason the data of run I are not reported. The pressures for gaseous heptane observed in run I were higher than those of run II by 0.1% at 1 mole per liter, 0.5% at 2.5 moles per liter, and 1.5% at 5 moles per liter.

Results

The data on the compressibility of liquid normal heptane are given in Table I; those on the compressibility of the gas phase in Table III. The constants of the Beattie–Bridgeman equation of state[4] were determined for the gas and their values are listed in Table II. Since the equation does not hold above the critical density (2.40 moles per liter), we have available only three isometrics for determination of the values of the constants. The comparison of the calculated with the observed pressures is given in Table III. The agreement, though fairly good, is not so satisfactory as for the other hydrocarbons.

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

[4] J. A. Beattie and O. C. Bridgeman, *Proc. Am. Acad. Arts Sci.* **63**, 229 (1928).

Substitution of the critical temperature (267.01°) and volume (0.416 liter per mole) into the equation gives a calculated pressure of 28.75 atm. The observed pressure is 27.00 atm.; and the error of extrapolation from 2 to 2.40 moles per liter is 6.5%.

Summary

Measurements are reported on the compressibility of liquid normal heptane over the temperature range from 30 to 250° and to 350 atmospheres, and on the compressibility of the gas phase from 275 to 350° and from a density of 1.0 to 5.0 moles per liter.

The constants of an equation of state for the gas phase are determined from the data for densities less than the critical.

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The Compressibility of and an Equation of State for Gaseous Propane

BY JAMES A. BEATTIE, WILLIAM C. KAY AND JOSEPH KAMINSKY

The critical constants and the compressibilities of liquid and gaseous propane from 70 to 220°K. and to 200 atmospheres have been studied by Sage, Schaafsma and Lacey.[1] They obtain for the values of the critical constants: t_c = 100.1°C., p_c = 43.77 atm., v_c = 4.31 cc. per gram. The critical constants determined in our apparatus are:[2] t_c = 96.81 ± 0.01°C. (Int.), p_c = 42.01 ± 0.02 normal atm., v_c = 4.43 cc. per gram (uncertainty in v_c is 1%). The agreement especially in the location of the critical temperature is not good.

TABLE I

VALUES OF THE CONSTANTS OF THE BEATTIE–BRIDGEMAN EQUATION OF STATE FOR PROPANE (C_3H_8)

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

$$A = A_0(1 - a/v) \qquad B = B_0(1 - b/v) \qquad \epsilon = c/VT^3$$

R	A_0	a	B_0	b	c	Mol. wt.
Units: normal atmospheres, liters per mole, °K. (T°K. = t°C. + 273.13).						
0.08206	11.9200	0.07321	0.18100	0.04293	120×10^4	44.0616
Amagat units: normal atmospheres, V = 1 at 0°C. and 1 atm., °K.						
3.73059×10^{-3}	24.6359×10^{-3}	3.3283×10^{-3}	8.2286×10^{-3}	1.9517×10^{-3}	54.554×10^3	44.0616
Berlin units: meters of mercury, V = 1 at 0°C. and 1 meter of mercury, °K.						
3.75354×10^{-3}	32.8158×10^{-3}	4.4062×10^{-3}	10.8937×10^{-3}	2.5838×10^{-3}	72.223×10^3	44.0616

We have measured the compressibility of gaseous propane over the temperature range 96.81 to 275°C. and the density range 1 to 10 moles per liter. Our data barely overlap those of Sage, Schaafsma and Lacey. We used the same method employed in studying the compressibilities of ethane[3] and normal heptane,[4] and the critical regions of propane[2] and heptane.[5] The apparatus has been described elsewhere.[6]

The propane was obtained from the Research Laboratories of the Linde Air Products Company at Buffalo and was of exceptional purity.[2]

Two complete sets of runs were made. In the first run the bomb was used immediately after the study of the compressibility of ethane. The bomb was heated to 400° and evacuated for one week. When the measurements were made, decomposition of the propane began at 200°. The measurements were discontinued and the bomb taken apart and all carbon thoroughly removed by means of fine emery paper. The series of measurements reported in the present paper was then made. No perceptible decomposition took place at 250° during a period of six hours, and the decomposition at 275° during a period of six hours was sufficient to affect the pressure at the lower density (41 atm.) by 0.015 atm. The pressures of run one were lower than those of run two by 0.02% at the critical temperature and at 100°,

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(1) B. H. Sage, J. G. Schaafsma, and W. N. Lacey, *Ind. Eng. Chem.*, **26**, 1218 (1934).

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

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

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

(5) J. A. Beattie and W. C. Kay, *ibid.*, **59**, 1586 (1937).

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