[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 387]

The Normal Boiling Point and Critical Constants of Normal Heptane

BY JAMES A. BEATTIE AND WILLIAM C. KAY

In the course of a study of the compressibility of normal heptane we investigated several isotherms in the critical region and located the critical point. The apparatus, the method of making the measurements, and the corrections of the observations have been described in detail.[1] The general procedure for the location of the critical point was the same as that used in the case of propane[2] except that for heptane we used a bomb with a glass liner[1] of about 125-cc. inside volume.

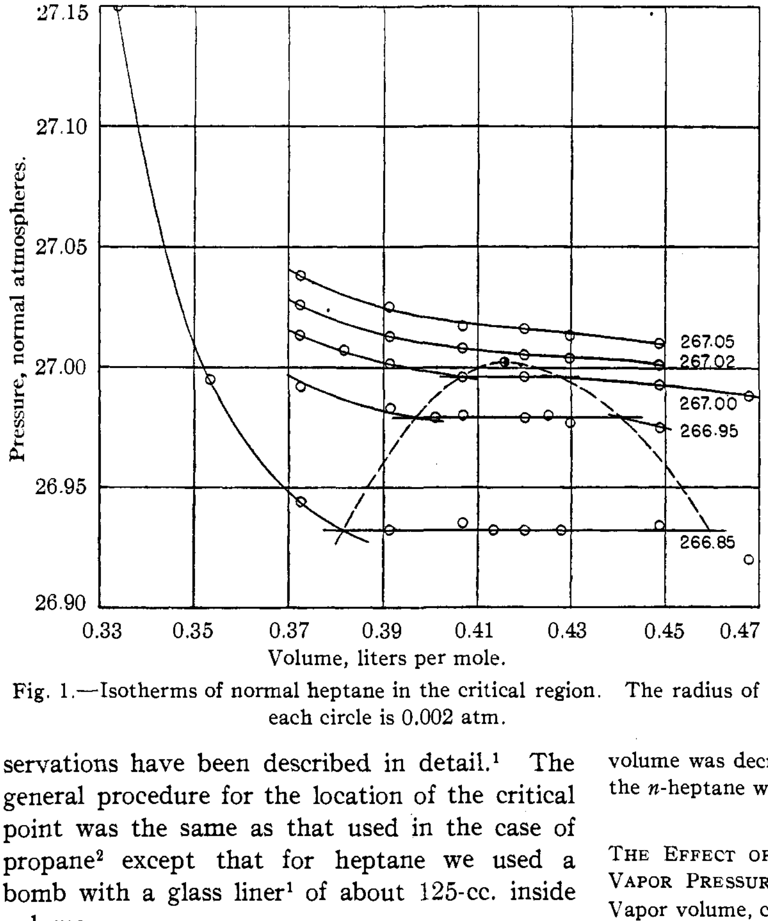

Fig. 1.—Isotherms of normal heptane in the critical region. The radius of each circle is 0.002 atm.

Purification of the Normal Heptane.—The *n*-heptane was obtained from the Eastman Kodak Company, who prepared it from Jeffrey pine oil.[3] The Eastman product was washed first with concentrated sulfuric acid, then with distilled water, and was finally refluxed over sodium–potassium amalgam. The liquid was then distilled in a Podbielniak fractionating column provided with a platinum resistance thermometer opposite the side-arm outlet. The wire of the resistance thermometer was wound in the form of a helix and the helix wound on a mica-cross frame, the over-all length of the winding of the thermometer being 6.35 mm. and its resistance at 0° about 5 ohms. A middle portion of heptane boiling over a temperature range of 0.01° was collected and distilled a second time. The liquid was transferred to an all glass system containing no stopcocks and deaerated by repeated distillation, freezing by means of liquid air, and pumping by means of a diffusion pump. The liquid was then condensed into a weighing bomb,[1] and finally transferred by distillation to the glass liner which had been evacuated for several days while at a temperature of 550°. The weighings were made against an almost identical tare, and vacuum corrections were applied.

Boiling Point of Normal Heptane.—During the second distillation of heptane the corrected barometer stood at 760.0 mm. The temperature indicated by the platinum resistance thermometer was 98.523 ± 0.005° (Int.) throughout the distillation. The normal boiling point of *n*-heptane is therefore 98.52 ± 0.01° (Int.). The values given in the literature are 98.4°,[4] 98.56–98.57°,[5] and 98.38°.[6]

Purity of the Sample.—As a test of the purity of the sample the vapor pressure was measured at 250° at several different vapor volumes. The results are given in Table I. Although the pressures are not as constant as they should be, there is no definite indication of an increase in vapor pressure as the vapor volume was decreased from 60 to 1 cc. This shows that the *n*-heptane was of satisfactory purity.

TABLE I

THE EFFECT OF VARYING THE VAPOR VOLUME ON THE VAPOR PRESSURE OF NORMAL HEPTANE AT 250° (Int.)

Vapor volume, cc.	60	20	5	1
V. p., normal atm.	21.175	21.190	21.192	21.184

Results

In Table II are given the compressibility data in the critical region. These values are plotted in Fig. 1. The critical data resulting from our measurements are given at the bottom of Table II. Germann and Pickering[7] select $t_c = 266.8°$, $p_c = 26.8$ atm., $d_c = 0.234$ g. per cc.

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[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] E. Kremers, *J. Am. Pharm. Soc.*, **9**, 857 (1920).

[4] "International Critical Tables," Vol. I, p. 215 (1926); G. Edgar, G. Calingaert and R. E. Marker, THIS JOURNAL, **51**, 1483 (1929).

[5] J. H. Mathews, *ibid.*, **48**, 562 (1926).

[6] B. J. Mair, *Bur. Standards J. Research*, **9**, 457 (1932).

[7] "International Critical Tables," Vol. III, 1928, p. 249.

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).