[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Vapor Pressure, Orthobaric Densities and Critical Constants of 2,2,4-Trimethylpentane

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In previous publications[1] determinations of the vapor pressures, critical constants, and compressibility from the critical temperature to about 300° of a number of hydrocarbons have been given. Isoöctane (2,2,4-trimethylpentane) is a hydrocarbon of considerable industrial interest because of its anti-knock properties. It decomposes rather rapidly at and above the critical temperature so that measurement of its compressibility over an extended temperature range is not possible.

However, when the critical constants of a substance are known we can obtain a fair estimate of its volumetric behavior on application of the law of corresponding states. Extensive application[2] of the law to the graphical determination of compressibility and fugacity has been given as well as the use[3] of the law for computing the constants of the Beattie–Bridgeman equation of state from the critical pressure and temperature alone.

The freezing point, density, index of refraction and boiling point of isoöctane have been determined by Brooks and co-workers,[4] and by Rossini and co-workers,[4] the vapor pressure to 130° was measured by Smith and Matheson,[5] and the compressibility of the liquid from 100 to 275° and to 300 atmospheres was measured by Felsing and Watson.[6] Our preliminary value of the critical constants has been quoted by Gilliland and Parekh.[7] It was at the request of Dr. Gilliland that we determined the critical constants of isoöctane.

The method of determining vapor pressures and compressibilities in the critical region has been published elsewhere.[8] The bomb with the glass liner was used. We removed the permanent gases from the isoöctane during the process of loading into the glass liner but did not attempt to fractionate the sample, which was obtained from the U. S. National Bureau of Standards through the courtesy of Dr. E. R. Smith and Dr. D. B. Brooks. In a letter dated June 5, 1940, Dr. Smith writes: "Batch 25 [prepared by the Röhm and Haas Company, Inc.] showed a freezing point of −107.38° as compared with −107.31° for pure isoöctane, and this batch is the best that has been received. One gallon of this batch was distilled in the 150 bubble cap column of about 100 theoretical plates, described by Brooks, Howard and Crafton, Jr., in *J. Research Nat. Bur. Stds.*, **24**, 33 (1940), RP 1271. The material was collected in 52 fractions and the sample which you will receive is composed of the center fractions 25 and 26. For pure isoöctane $n^{20}\text{D}$ 1.39147 and for fractions 25 and 26 the values measured by Brooks and Howard were $n^{19.98}\text{D}$ 1.39145 and $n^{19.98}\text{D}$ 1.39147, respectively. The two fractions were combined to make the sample of about 100 ml." The value of $n^{20}\text{D}$ given for pure isoöctane is the 1938 value; that published by Brooks[4] in 1940 is 1.39146. Rossini and co-workers[4] (1946) give −107.365 ± 0.013 for the freezing point of pure isoöctane.

The measured vapor pressures of isoöctane from 150 to 250° are listed in Table I as well as the measured saturation liquid densities and estimated saturation vapor densities. At each temperature the vapor volume was varied through a wide range as indicated in the table. The increase of vapor pressure with decreasing vapor volume, although somewhat greater than that found for some of the hydrocarbon samples previously investigated, is sufficiently small to indicate that the sample received from the National Bureau of Standards was of a high degree of purity.

Our observed vapor pressures from 150 to 250° and those computed from the formula of Smith[5] for 100 and 125° were fitted by the equation[9]

$$\log_{10} p(\text{atm.}) = 4.43444 - (1650.17/T) \quad (T = t\ ^\circ\text{C. (Int.)} + 273.13^\circ)$$

with the deviations given in Table II.

The orthobaric liquid densities were determined at each temperature by locating the break on the liquid end of a plot of pressure *versus* volume for

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(1) For the last reports on this work see J. A. Beattie, H. G. Ingersoll and W. H. Stockmayer, THIS JOURNAL, **64**, 546, 548 (1942).

(2) J. Q. Cope, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931); W. K. Lewis and C. D. Luke, *Trans. Am. Soc. Mech. Engrs.*, **54**, PME-8, 55 (1932); G. G. Brown, M. Souders, Jr., and R. L. Smith, *Ind. Eng. Chem.*, **24**, 513 (1932); C. W. Selheimer, M. Souders, Jr., L. R. Smith and G. G. Brown, *ibid.*, **24**, 515 (1932); R. H. Newton, *ibid.*, **27**, 302 (1935); W. B. Kay, *ibid.*, **28**, 1014 (1936).

(3) F. G. Keyes, THIS JOURNAL, **60**, 1761 (1938); S. H. Maron and D. Turnbull, *Ind. Eng. Chem.*, **33**, 69, 246, 408 (1941); F. W. Brown, *ibid.*, **33**, 1536 (1941); J. Corner, *Trans. Faraday Soc.*, **37**, 358 (1941); S. H. Maron and D. Turnbull, *Ind. Eng. Chem.*, **34**, 544 (1942); THIS JOURNAL, **64**, 44, 2195 (1942); G.-J. Su and C.-H. Chang, *ibid.*, **68**, 1080 (1946); *Ind. Eng. Chem.*, **38**, 802 (1946).

(4) D. B. Brooks, *J. Research Natl. Bur. Standards*, **21**, 847 (1938); D. B. Brooks, F. L. Howard and H. C. Crafton, Jr., *ibid.*, **24**, 33 (1940); A. R. Glasgow, Jr., E. T. Murphy, C. B. Willingham and F. D. Rossini, *ibid.*, **37**, 141 (1946).

(5) E. R. Smith and H. Matheson, *ibid.*, **20**, 641 (1938); E. R. Smith, *ibid.*, **24**, 229 (1940).

(6) W. A. Felsing and G. M. Watson, THIS JOURNAL, **65**, 780 (1943).

(7) E. R. Gilliland and M. D. Parekh, *Ind. Eng. Chem.*, **34**, 360 (1942).

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

(9) In the earlier work of this Laboratory on the equation of state and other thermodynamic properties of gases the value of the ice-point on the Kelvin scale was taken to be $T_0 = 273.13°$. For consistency this value is retained although the best value seems to be 273.16° and the International Conference on Weights and Measures has recently adopted 273.15° as a compromise. In the temperature range for which the vapor pressure equation is valid, a change of T_0 would not affect the fit of the experimental results although it would require slightly different values of the constants.

TABLE I

VAPOR PRESSURES AND ORTHOBARIC DENSITIES OF 2,2,4-TRIMETHYLPENTANE

Temp., °C. (Int.)	Largest and smallest vapor volumes, ml.		Increase in vapor pressure, atm.	Vapor pressure normal, atm.	Orthobaric densities Liquid, g./ml.	Orthobaric densities Vapor (estimated), g./ml.
150	97	0.05	0.020	3.418	0.567	0.0105
175	98	.15	.023	5.650	.540	.0178
200	80	.50	.028	8.869	.507	.0287
225	82	.01	.040	13.211	.466	.0479
250	57	.47	.037	19.026	.407	.0793

TABLE II

COMPARISON OF CALCULATED WITH OBSERVED VAPOR PRESSURES OF 2,2,4-TRIMETHYLPENTANE

$\log_{10} p(\text{calcd.}) = 4.43444 - 1650.17/T \ (T = t° + 273.13)$

Temp., °C. (Int.)	Vapor pressure normal atm.	Obsd.-calcd. vapor pressure, atm.
100	1.0219[a]	−0.0060
125	1.964[a]	+ .016
150	3.418	− .006
175	5.650	− .001
200	8.869	+ .025
225	13.211	− .024
250	19.026	− .030

[a] E. R. Smith, Ref. 5.

each isotherm. The sample of isoöctane used weighed about 6.5 g. so that the total liquid volume in the bomb was of the order of 10 to 15 ml. We could determine this with sufficient accuracy so that the uncertainty in the density is 0.001 g. per ml. The measurements of Felsing and Watson did not extend to the saturation pressure, but extrapolation of their results to our vapor pressures indicated that our orthobaric liquid densities are lower by about 0.003 g./ml. than those derived by the extrapolation.

The orthobaric vapor densities were estimated from the following considerations. The critical temperature of isoöctane is 4° higher than that of normal heptane and its critical density (g./ml.) about 2% less. Comparison of the orthobaric liquid and vapor densities of normal heptane measured by Young[10] and our measured orthobaric liquid densities for isoöctane indicate that a displacement of +7° of the normal heptane curve will make it coincide on the liquid side with the isoöctane curve. The law of rectilinear diameters would indicate that this same displacement should cause the vapor densities to coincide. The tabulated values for the orthobaric vapor densities are those given by Young for normal heptane at a temperature 7° above the temperature listed in Table I.

The rapidity with which isoöctane decomposes at the higher temperatures necessitated two loadings of the bomb in order to complete the measurement of the vapor pressures and the compressibilities in the critical region. With the first we

TABLE III

ISOTHERMS OF 2,2,4-TRIMETHYLPENTANE IN THE CRITICAL REGION

Molecular Weight, 114.1386

Temp., °C. (Int.) →		270.80	270.90	270.96	271.00	271.10	271.12	271.14	271.16
Density, moles/liter	Volume, liters/mole	Pressure, normal atmospheres							
1.693	0.591	25.318			25.377				
1.721	.581		25.361	25.382		25.424			
1.770	.565	25.339			25.402				
1.798	.556		25.380	25.402		25.444			
1.856	.539	25.354			25.420				
1.883	.531		25.392	25.412		25.458	25.459	25.466	25.476
1.901	.526	25.355							
1.929	.518		25.393	25.417		25.460	25.467	25.473	25.480
1.951	.513	25.359			25.426	25.462	25.468	24.478	25.482
1.976	.506		25.395	25.418		25.462	25.470	25.477	25.483
2.001	.500	25.361				25.464	25.469	25.481	25.486
2.027	.493		25.395	25.420		25.463	25.472	25.478	25.487
2.053	.487	25.362			25.430	25.465	25.474	25.483	25.490
2.080	.481		25.396	25.419		25.467	25.470	25.483	25.491
2.107	.475	25.362				25.468	25.474	25.485	25.492
2.135	.468		25.397	25.420		25.470	25.477	25.487	25.495
2.169	.461	25.363			25.433				
2.194	.456		25.400	25.421		25.471	25.480		
2.232	.448	25.365							
2.256	.443		25.402	25.423		25.475			
2.299	.435	25.366			25.436				
2.322	.431		25.403	25.427					
2.370	.422	25.369							
2.391	.418		25.410	25.442		25.488			
2.445	.409	25.380			25.460				
2.465	.406		25.431	25.457					

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[10] S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

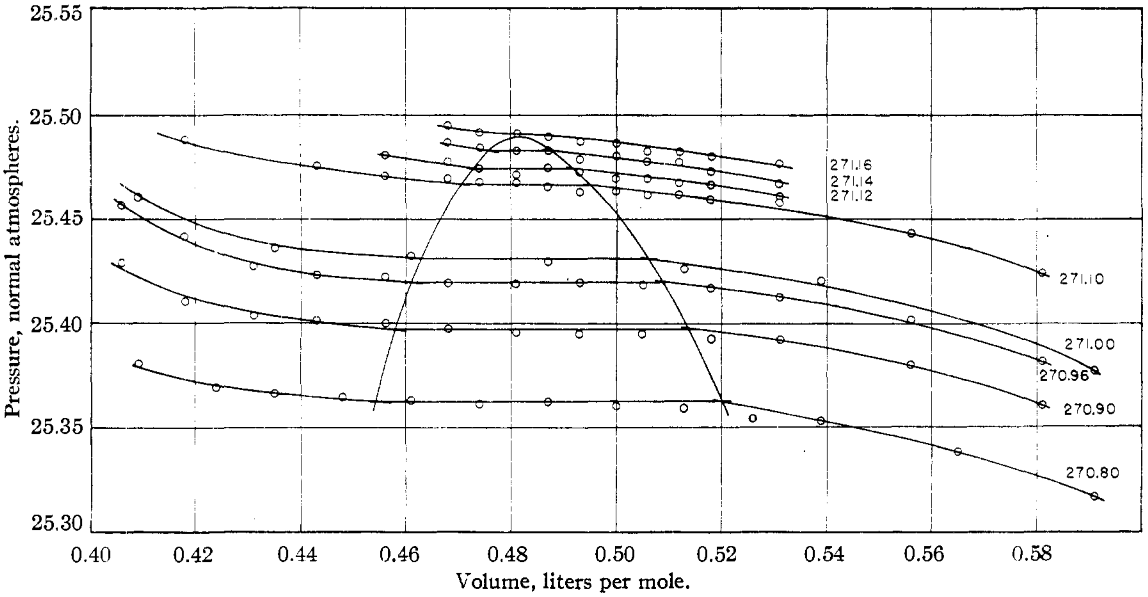

Fig. 1.—Critical region of isoöctane.

studied the vapor pressures and the compressibilities of 270.80° and 271.00°, with the second the other isotherms in the critical region were studied. At the end of each set of measurements there was a slight deposit of gum in the glass liner of the bomb indicating that appreciable decomposition had occurred.

The compressibility measurements in the critical region are listed in Table III and are plotted in Fig. 1. It will be noted that the pressures in the two-phase region decrease perceptibly with increasing volume, indicating that the sample was not pure. This is presumably not due to impurities in the original sample since the vapor pressures at lower temperatures show little change with large variation in vapor volume, but was caused by decomposition. From the plot we find for the critical point:

t_c = 271.15 ± 0.10° (International), p_c = 25.50 ± 0.10 normal atmospheres, v_c = 0.482 liters per mole (4.22 ml. per g.), d_c = 2.07 moles per liter (0.237 g. per ml.)

The uncertainty in the critical volume and density is 3%. These rather large uncertainties are our estimate of the probable effect of impurities and not the limit of accuracy of the method or the apparatus.

We are glad to thank Dr. Walter H. Stockmayer for his help in taking the measurements.

Summary

The vapor pressures and orthobaric densities of 2,2,4-trimethylpentane have been determined from 150 to 250°. These vapor pressures and those of E. R. Smith for 100 and 125° are fitted by the equation $\log_{10} p(\text{atm}) = 4.43444 - 1650.17/T$.

The critical constants of 2,2,4-trimethylpentane have been determined by the compressibility method. The constants are: t_c = 271.15 ± 0.10 (Int.), p_c = 25.50 ± 0.10 normal atmospheres, v_c = 0.482 liters per mole (4.22 ml. per g.), d_c = 2.07 moles per liter (0.237 g. per ml.). The uncertainty in the critical volume or density is 3%. These rather large uncertainties are due to the rapidity with which this substance decomposes with tar formation in the critical region.

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