[Contribution from the Departments of Chemical Engineering and of Chemistry of The University of Texas]

The Pressure–Volume–Temperature Relations of 2,2,3,3-Tetramethylbutane

By W. A. Felsing, A. M. Cuellar and W. M. Newton

Introduction.—There have appeared from this Laboratory a series of reports[1] on the determination of certain physical properties, such as liquid compressibilities, heat capacities, and heats of evaporation for certain pure hydrocarbons. This program, interrupted by the War, has again been instituted by this investigation. The compressibilities of two other octanes, *n*-octane and 2,2,4-trimethylpentane (*i*-octane), have been reported[1c]; this investigation on 2,2,3,3-tetramethylbutane (hexamethylethane) completes our octane investigations, since these three represent molecules of progressively increasing compactness.

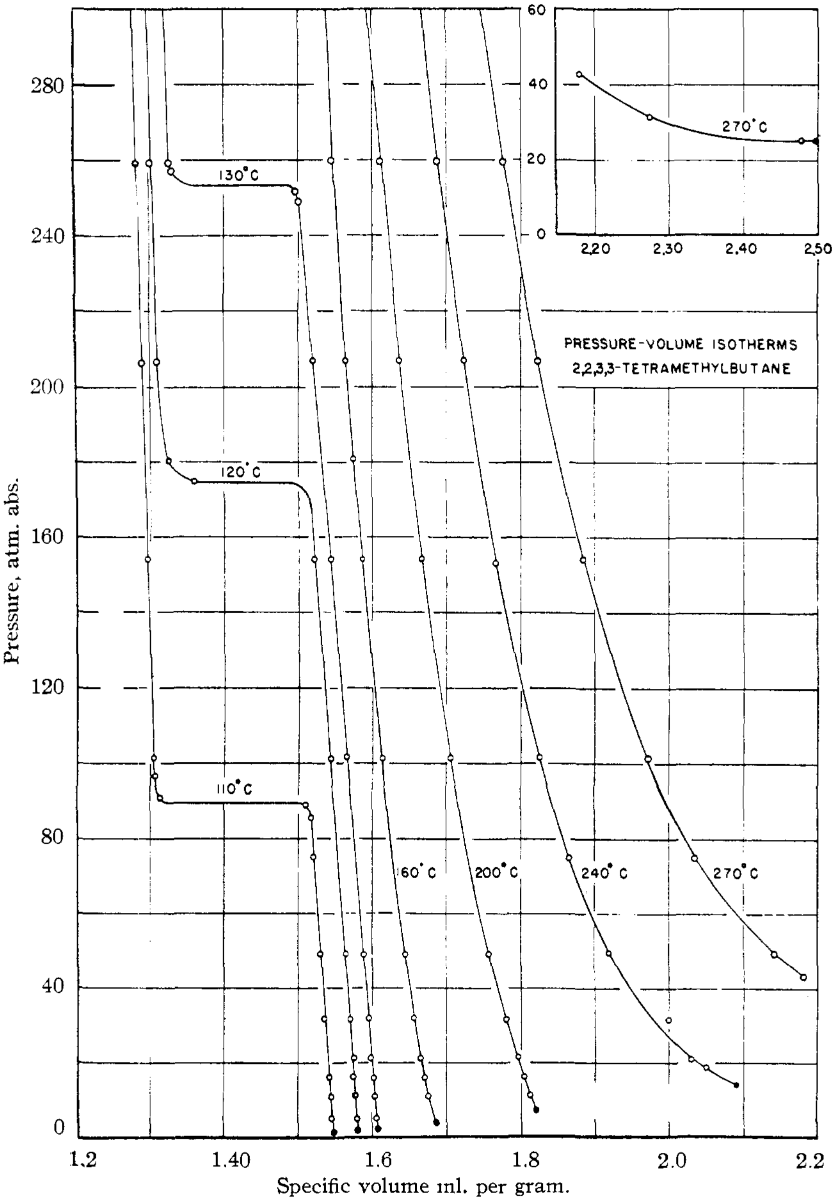

Fig. 1.

Experimental determinations of compressibility were made at seven temperatures, beginning at 110° and including 270°. No data over any portion of this temperature range were found in the literature. Accurate vapor pressures from 3.3 to 110° on a very pure sample have been reported by Calingaert and his co-workers,[2] who reviewed all previous pertinent data in their paper.

Method and Apparatus.—All compressibility measurements were made in the usual manner and with the usual precautions by means of a dead-weight piston gage and accessories; these and the method of operation have been described elsewhere.[3,4]

Materials Used.—Two samples of 2,2,3,3-tetramethylbutane were used in this investigation. This material was furnished the authors through the courtesy of Dr. George Calingaert and it was labelled "415-XP-6, Fractions 3 and 4." Both samples had a stated purity of 99.96 ± 0.04 mole per cent. and their identical characteristic constants were determined[2] to be f. p. = 100.69 ± 0.03°; b. p. (normal) = 106.30 ± 0.02°; d. (solid; g./cc. at 20°) = 0.823 and n^{20}_{D} (solid) = 1.4695.

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[1] (a) Kelso and Felsing, This Journal, **62**, 3132 (1940); (b) Kelso and Felsing, *Ind. Eng. Chem.*, **34**, 161 (1942); (c) Felsing and Watson, This Journal, **64**, 1822 (1942); *ibid.*, **65**, 780 (1943); (d) Dailey and Felsing, *ibid.*, **65**, 42 (1943); *ibid.*, **65**, 44 (1943), and (e) Lemons and Felsing, *ibid.*, **65**, 46 (1943).

[2] Calingaert, Soroos, Hnizda and Shapiro, *ibid.*, **66**, 1389 (1944).

[3] Kelso and Felsing, *ibid.*, **62**, 3132 (1940).

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

The Data Obtained.—The experimental results are presented graphically in Fig. 1, in which the specific volumes (ml./g.) are related to the pressure (atm.) at different temperatures. The actual experimental points have been plotted. From such large-scale graphs, the specific volumes at each temperature were read off at rounded pressures; these values are shown in Table I. In Table II are shown the actual values for 110, 120 and 130° of the pressures just above and below the transition of the solid into the liquid state. In Table III are presented vapor pressures calculated from the data of Calingaert[2] by the method of Othmer[5]; these values are shown as solid circles in Fig. 1 (with the exception of the last point of the 270° curve, which was an experimental point). It should be noted that these values fit in excellently into the extensions of the p–v curves of this investigation.

TABLE I

COMPRESSIBILITY OF 2,2,3,3-TETRAMETHYLBUTANE

Molecular weight 114.224; pressures in normal atmospheres and temperatures are on the International temperature scale.

Press., atm.	Specific volumes, milliliters per gram at 110°	120°	130°	160°	200°	240°	270°
10	1.546	1.573	1.604	1.676	1.815		
20	1.542	1.568	1.600	1.666	1.798	2.039	
40	1.535	1.559	1.593	1.651	1.769	1.946	2.196
75	1.522	1.544	1.579	1.628	1.731	1.866	2.040
100	1.305	1.535	1.568	1.614	1.709	1.829	1.976
150	1.297	1.518	1.546	1.590	1.671	1.772	1.892
200	1.289	1.312	1.524	1.569	1.642	1.730	1.832
250	1.284	1.303	1.500	1.551	1.616	1.696	1.786
300	1.279	1.296	1.321	1.535	1.596	1.667	1.752

TABLE II

COMPRESSIBILITY OF 2,2,3;3-TETRAMETHYLBUTANE AT 110, 120 AND 130 ABOVE AND BELOW THE SOLID–LIQUID TRANSITION

Temp., °C.	Pressure, atm.	Specific vol., ml./g.
110	85.81	1.518
	88.44	1.512
	91.07	1.313
	96.34	1.307
120	154.11	1.516
	175.08	1.360
	180.35	1.325
130	248.85	1.501
	251.47	1.498
	256.73	1.331
	259.37	1.327

TABLE III

VAPOR PRESSURES CALCULATED BY MEANS OF THE OTHMER[5] RELATION

Temp., °C.	Vapor pressure, atm.
110	1.11
120	1.45
130	1.89
160	3.62
200	7.62
240	14.2

TABLE IV

CALCULATED AND OBSERVED DENSITIES OF LIQUID 2,2,3,3-TETRAMETHYLBUTANE

$P_c = 24.5$ atm.; $t_c = 270.8°$

Red. temp.	Densities in ml./g. $P_R = 2$ Calcd.	Obs.	$P_R = 4$ Calcd.	Obs.	$P_R = 6$ Calcd.	Obs.
0.796	0.6063	0.6080	0.6214	0.6192	0.6333	0.6281
.870	.5620	.5690	.5878	.5845	.6013	.5977
.943	.5031	.5210	.5418	.5460	.5631	.5634

Discussion of Results.—Figure 1 clearly shows the effect of pressure upon the solid–liquid equilibrium at the various temperatures; thus, at 110, 120 and 130° there is a considerable change in specific volume occurring under respective constant pressures of 89.5, 174.5 and 253.5 atmospheres. The freezing point of the hexamethylethane has, accordingly, been raised from 100.69° at one atmosphere to 110° at 89.5 atmospheres, etc.; this behavior is characteristic of hydrocarbons, since they exhibit a decrease in volume upon freezing.

Watson,[6] on the basis of a modified application of the theorem of corresponding states, has presented new methods of predicting certain thermodynamic properties of liquids, such as thermal expansion and compressibility, pressure correction to enthalpy, heat of vaporization, etc. Like all applications of this theorem, the relations obtained by Watson do not yield rigorously accurate

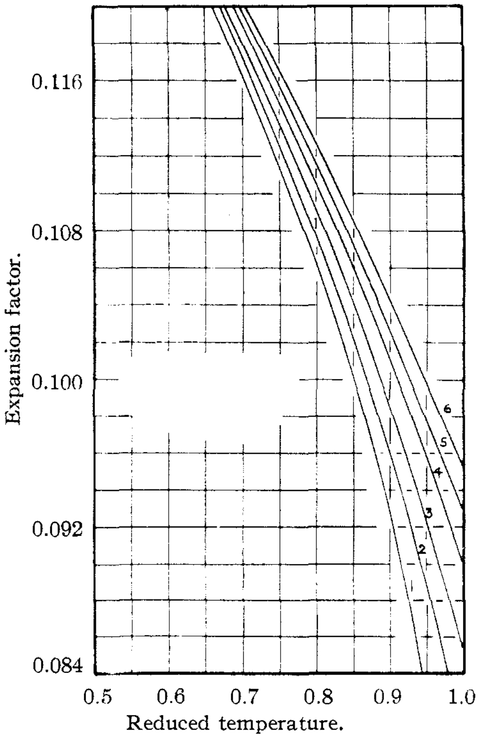

Fig. 2.—Thermal expansion and compressibility of liquids.

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(5) Othmer, *Ind. Eng. Chem.*, **32**, 841 (1940); *ibid.*, **34**, 1072 (1942).

(6) Watson, *ibid.*, **35**, 398 (1943).

values. However, the deviations from experimental values are sufficiently small to warrant the use of the method for many chemical engineering process calculations for which reliable data over a range are not available. As an example, the expansion factor[7] of Watson's correlations is closely related to the compressibilities measured in this investigation. In Fig. 2 are plotted values of W for various reduced conditions of pressure and temperature, using the data[8] of 2,2,4-trimethylpentane as the reference liquid. Using this chart, values of the expansion factor W for a liquid of unknown density may be then evaluated by means of the relation ρ (density of unknown) = $(\rho_1/W_1)W$, where ρ_1 and W_1 are single, experimental values of the liquid density and the expansion factor for the unknown liquid. Table IV gives a comparison of experimental and calculated density values for hexamethylethane; the agreement is satisfactory enough for many engineering calculations.

The accuracy of the observed compressibility data of this investigation on 2,2,3,3-tetramethylbutane is the same as that claimed[8] for 2,2,4-trimethylpentane, *viz.*, 0.2%.

Acknowledgment.—The authors wish to thank Dr. George Calingaert of the Ethyl Gasoline Corporation for the donation of the samples of hexamethylethane used in this investigation.

Summary

1. The compressibility of highly purified 2,2,-3,3-tetramethylbutane has been determined from 110 to 270° at pressures ranging from approximately 5 to 300 atmospheres.

2. The pressures at the solid–liquid transition were determined at three temperatures, 110, 120 and 130°.

3. The method of correlating liquid densities, as proposed by Watson, has been applied to the data of this investigation and the results were quite satisfactory.

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[7] $\rho(\text{density}) = \frac{PM}{ZRT} = \frac{P_R}{ZRT}\frac{P_cM}{T_c} = W\frac{P_cM}{T_c}$.

[8] Felsing and Watson, THIS JOURNAL, **65**, 780 (1943).

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Ionization of Ethyl Nitrate in Sulfuric Acid

BY LESTER P. KUHN

As part of our program for studying the chemistry of nitrate esters, we have investigated the behavior of ethyl nitrate in sulfuric acid. We have found interesting similarities between this system and the system nitric acid or nitric anhydride–sulfuric acid. A knowledge of these systems is essential for understanding the mechanism of nitration with mixed acids. Because of the current interest evinced in this problem by recent publications[1,2,3] we are publishing our results at this time. These recent papers give convincing evidence that nitric acid and nitric anhydride yield NO_2^+ ions in sulfuric acid. On the basis of spectroscopic and cryoscopic evidence and chemical reactivity, it can be shown that ethyl nitrate also yields NO_2^+ ions in sulfuric acid.

Spectroscopic Evidence.—Like nitric acid, ethyl nitrate shows an ultraviolet absorption spectrum in sulfuric acid which is different from that of its solution in an inert solvent such as chloroform as shown in Fig. 1. Furthermore, the spectra of sulfuric acid solutions of ethyl nitrate and nitric acid are almost identical.

Cryoscopic Evidence.—From freezing point depression measurements of the sulfuric acid solutions we have obtained "*i*" values of 3.97 for nitric acid, 4.95 for ethyl nitrate, and 5.50 for nitric anhydride. The "*i*" value tells how many particles are obtained from each molecule of solute. Our values are in good agreement with those obtained by Ingold and co-workers, 3.82 for nitric acid and 5.85 for nitric anhydride, which appeared in the literature[3] after our measurements were made. Hantzsch,[4] in his classical work on solutions in sulfuric acid, obtained "*i*" values of 2–3 for nitric acid and 3–4 for ethyl nitrate. As explained by Hammett,[5] the sulfuric acid for freezing point depression measurements must contain a small amount of water to yield the proper "*i*" values. Since Hantzsch used 100% sulfuric acid it is to be expected that his values be low.

Most organic acids and esters act like bases in sulfuric acid and ionize according to the equation

$$RCOOR' + H_2SO_4 = RCOOR'H^+ + HSO_4^-$$

giving an "*i*" value of 2. The high "*i*" values of nitric acid and its ester are strongly reminiscent of the complex ionization which Treffers and Hammett[6] discovered to be exhibited by certain sterically hindered aromatic acids such as mesitoic acid and its esters which have "*i*" values of 4 and 5, respectively. The complex ionization is be-

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[1] Bennett, Brand and Williams, *J. Chem. Soc.*, 869, 875, 880 (1946).

[2] Westheimer and Kharasch, THIS JOURNAL, **68**, 1871 (1946).

[3] Ingold, *et al.*, *Nature*, **158**, 448, 480 (1946).

[4] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); **62**, 626 (1907); **65**, 40 (1908).

[5] Hammett, "Physical Organic Chemistry," McGraw-Hill, Book Co., New York, N. Y., 1940.

[6] Treffers and Hammett, THIS JOURNAL ,**59**, 1708 (1937).