

We are much indebted to Prof. J. S. Fruton of Yale for supplying us with all the leucine containing peptides (except poly-L-leucine). These peptides had been chromatographically purified.

The poly-L-leucine was prepared in our laboratory by Dr. M. S. Muthana by the polymerization of the corresponding N-carboxy anhydride in benzene solution.

Calcd. for  $(C_6H_{11}ON)_n$ : C, 63.7; H, 9.8. Found: C, 64.0; H, 9.8.

It is a pleasure to acknowledge the technical assistance of Misses A. Asadourian, A. O'Rourke and A. Sutton in the spectroscopic work.

BOSTON, MASSACHUSETTS RECEIVED SEPTEMBER 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY OF THE UNIVERSITY OF TEXAS]

## The Pressure-Volume-Temperature Relations of 3-Methylpentane

BY H. O. DAY WITH W. A. FELSING

The vapor pressures of 3-methylpentane have been determined for the temperature range of 150 to 231.2°. Equations representing these data are presented and a comparison with previously reported data is made. Compressibility data on the liquid in the range from 80 to 275° are presented tabularly. Calculated values of molar heats of vaporization are also given in tabular form.

### Introduction

The research program devoted to the determination of the thermodynamic properties of hydrocarbons has been in progress for a number of years. The properties determined have included compressibilities, heat capacities, heats of vaporization and vapor pressure.<sup>1</sup> A particular objective of this program has been the determination of the compressibilities of the isomeric hexanes; thus Kelso and Felsing<sup>2</sup> determined the pressure-volume-temperature relations for *n*-hexane, 2-methylpentane and 2,3-dimethylbutane, whereas Felsing and Watson<sup>3</sup> reported on 2,2-diethylbutane. The purpose of this investigation was the determination of the compressibilities and the vapor pressures of 3-methylpentane, thereby completing the *p-v-T* data for the five hexanes.

### Previous Investigations

The only recorded *p-v-T* data for 3-methylpentane within the temperature range of the present investigation are those due to Kay.<sup>4</sup> Kay determined the vapor pressures, the critical constants, and the orthobaric densities of all five of the isomeric hexanes.

**Method and Apparatus.**—The apparatus used in this investigation has been patterned after that described by Beattie<sup>5</sup> and previously discussed by Kelso and Felsing.<sup>2</sup> Bath temperatures were held constant to  $\pm 0.005^\circ$  by means of a platinum resistance thermometer in conjunction with a Mueller bridge and a photoelectric cell relay. The regulating platinum resistance thermometer, calibrated by the National Bureau of Standards, also determined the thermostat temperature. Samples of liquid 3-methylpentane of various sizes were introduced into the glass liner (for the pressure bomb) in the usual manner of distillation under a vacuum; these liners containing the samples were introduced into the pressure bomb as previously described.<sup>2</sup>

(1) (a) W. A. Felsing, A. M. Cuellar and W. M. Newton, *THIS JOURNAL*, **69**, 1972 (1947); W. A. Felsing and G. M. Watson, *ibid.*, **64**, 1822 (1942), and **65**, 780 (1943); (b) D. H. Templeton and D. D. Davies with W. A. Felsing, *ibid.*, **66**, 2033 (1944); B. P. Dailey with W. A. Felsing, *ibid.*, **65**, 42 (1943); (c) J. F. Lemons with W. A. Felsing, *ibid.*, **66**, 46 (1943); and (d) H. O. Day and D. E. Nicholson with W. A. Felsing, *ibid.*, **70**, 1784 (1948).

(2) E. A. Kelso with W. A. Felsing, *ibid.*, **62**, 3132 (1940), and *Ind. Eng. Chem.*, **34**, 161 (1942).

(3) W. A. Felsing and G. M. Watson, *THIS JOURNAL*, **65**, 1889 (1943).

(4) W. B. Kay, *ibid.*, **68**, 1336 (1946).

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

Four separate samples of 3-methylpentane were subjected to both vapor pressure and compressibility measurements. The vapor pressures were determined at different relative values of liquid and vapor volume; they were found to be independent of volume over a large range, which behavior is indicative of high purity.

At higher temperatures (200° and above), the imposition of high pressures caused a slight decomposition of the 3-methylpentane. This resulted in an increase in the vapor pressure and, also, the vapor pressure was no longer independent of the volume (increased as the specific volume decreased). If high pressures were avoided, the decomposition was extremely slow and, hence, vapor pressure measurements on a given sample were always completed before the compressibility runs were made.

**The Material Used.**—The 3-methylpentane was part of a 100-g. sample of research grade 3-methylpentane produced by the Phillips Petroleum Company. The stated purity of the product was given as 99.80 mole per cent., a value determined by an infrared scanning comparison with a National Bureau of Standards product of known purity.

This hexane was distilled into a glass reservoir, discarding the first and last portions. All distillation was done under a vacuum at very low temperatures. It was then distilled under a vacuum into the various calibrated glass liners used in the pressure bomb.

**The Experimental Data.**—The vapor pressures are presented in Table I, and the compressibilities in Table II.

TABLE I

EXPERIMENTAL VAPOR PRESSURES OF 3-METHYLPENTANE					
Temp., °C.	150	175	200	225	231.2°
Vapor press., atm.	8.197	12.868	19.286	27.983	30.616

<sup>a</sup> Critical point according to Kay.<sup>4</sup>

**Treatment of Data and Discussion.**—Two equations were found to express the relationship of vapor pressure to temperature, each covering a definite temperature range:

$$\begin{aligned} \text{Range } 150\text{--}200^\circ: \log_{10} p(\text{mm.}) &= 7.310661 - 1487.9519/T \\ \text{Range } 200\text{--}231.2^\circ: \log_{10} p(\text{mm.}) &= 3.728948 - 636.3719/T \\ &\quad + 0.00376627T \end{aligned}$$

$T = t(^{\circ}\text{C.}) + 273.16^{\circ}$ . At the higher temperatures, Kay's values<sup>4</sup> differ considerably from the values found in this investigation even after an error<sup>6</sup> in one of Kay's deviation charts has been taken into account; no explanation can be offered at present for the differences.

Kay<sup>4</sup> compared his experimental vapor pressures of *n*-hexane and 2,3-dimethylbutane with those of

(6) Private communication from Professor W. B. Kay.

TABLE II

COMPRESSIBILITY OF LIQUID AND GASEOUS 3-METHYLPENTANE

Spec. vol., ml./g.	Pressure, atm.	Spec. vol., ml./g.	Pressure, atm.	Spec. vol., ml./g.	Pressure, atm.
150.00°		100.00°		125.00°	
1.6469	5.597	1.7058	5.591	1.7944	5.592
1.6435	13.499	1.7002	13.493	1.7846	13.494
1.6395	21.396	1.6955	21.390	1.7766	21.391
1.6342	31.900	1.6890	31.894	1.7682	31.895
1.6266	49.007	1.6791	49.000	1.7525	49.002
1.6046	101.511	1.6519	101.504	1.7183	101.505
1.5863	154.058	1.6294	154.051	1.6880	154.052
1.5702	206.689	1.6101	206.682	1.6633	206.682
1.5559	259.356	1.5932	259.349	1.6420	259.349
1.5432	311.798	1.5784	311.791	1.6236	311.791
150.00°		175.00°		200.00°	
1.9080	8.509	2.0558	13.472	2.2838	20.062
1.9075	8.733	2.0469	16.100	2.2711	21.382
1.9059	9.522	2.0295	21.393	2.1980	31.884
1.9030	10.842	1.9993	31.897	2.1208	48.989
1.8980	13.478	1.9618	49.003	2.0436	75.230
1.8842	21.399	1.8815	101.502	1.9890	101.489
1.8682	31.902	1.8268	154.047	1.9116	154.034
1.8470	49.009	1.7853	206.677	1.8567	206.663
1.7941	101.513	1.7522	259.344	1.8140	259.330
1.7550	154.058	1.7242	311.786	1.7788	311.770
1.7233	206.690	250.00°		275.00°	
1.6962	259.354	3.6002	41.078	3.6002	55.770
1.6733	311.797	3.5059	41.532	3.5054	56.864
225.00°		3.4116	42.095	3.4107	58.188
2.8254	28.440	3.3176	42.767	3.3163	59.732
2.7277	29.757	3.2234	43.608	3.2219	61.548
2.6393	31.860	3.1292	44.673	3.1277	63.726
2.5129	37.165	3.0350	46.034	3.0333	66.410
2.4358	42.424	2.9410	47.834	2.9368	69.763
2.3680	48.960	2.8941	48.929	2.8194	75.080
2.2914	59.378	2.8083	51.460	2.7311	80.339
2.2109	75.200	2.6818	56.718	2.6292	88.233
2.1211	101.458	2.5931	61.979	2.5085	101.330
2.0105	154.001	2.4489	75.163	2.3545	127.594
1.9376	206.629	2.2905	101.420	2.2545	153.868
1.8842	259.296	2.1927	127.686	2.1239	206.492
1.8411	311.735	2.1237	153.961	2.0365	259.154
		2.0262	206.586	1.9742	311.591
		1.9583	259.252		
		1.9056	311.689		

Young<sup>7</sup>: his values for these two isomeric hexanes are higher than Young's values by about the same amount that his values for 3-methylpentane are higher than found in this investigation.

The critical temperature according to Kay is 231.2°. A compressibility isotherm was determined at this temperature; the experimental data are presented in Table III. A graph of specific volume *versus* pressure has a *flat* segment, indicating that 231.2° is actually lower than the true critical temperature.

Since 3-methylpentane decomposes slowly under the conditions of the critical point, it would have required a half-dozen sample loadings to determine the critical constants with the accuracy of which the compressibility method is capable. Unfortunately, a lack of time prevented this scheme. It is *estimated*, therefore, that the critical temperature is

(7) S. Young, *Sci. Proc. Roy. Soc. (Dublin)*, **12**, 374 (1910).

TABLE III

COMPRESSIBILITY ISOTHERM OF 3-METHYLPENTANE AT 231.2°

Specific volume, ml./g.	Pressure, atm.	Specific volume, ml./g.	Pressure, atm.
4.6727	30.602	3.8670	30.624
4.4041	30.613	3.7327	30.635
4.2698	30.616	3.5985	30.650
4.1355	30.616	3.3302	30.757
4.0012	30.620		

about 231.5° and the critical pressure 30.75 atm. This latter value was obtained by substituting the estimated critical temperature into the vapor pressure equation.

The compressibility values are believed to be accurate to within 0.1 to 0.2%. The decomposition of 3-methylpentane proceeded slowly enough even at the highest temperatures to provide accurate *p-v-T* data; vapor pressure values are changed more by a slight decomposition than are compressibility values.

**Calculated Heats of Vaporization.**—Molar heats of vaporization were calculated by four methods. The first method employed the Clapeyron equation  $dp/dT = \Delta H^v/T(v_g - v_l)$ . Use was made of the compressibility data of this investigation to evaluate the molar volume of the liquid,  $v_l$ ; the Berthelot equation was employed to evaluate the molar volumes of the saturated vapors, using  $t_c = 231.5^\circ$  and  $p_c = 30.75$  atmospheres; and the two equations for vapor pressures yielded values for  $dp/dT$ . The second method made use of compressibility factor charts,<sup>8</sup> instead of the Berthelot equation, to evaluate the molar volume of the saturated vapor. The third method was based upon the experimental values of Kay<sup>4</sup> for liquid and vapor densities and the vapor pressure data of this investigation. The fourth method was that of Watson,<sup>9</sup> using the equation

$$\Delta H^v = 0.95 RB \left( \frac{T_B}{T_B - 43} \right)^2 \times \left( \frac{1 - T_r}{1 - T_{rB}} \right)^{0.35}$$

where

$$B = \frac{\ln p_c/p_B}{\left( \frac{1}{T_B - 43} \right) - \left( \frac{1}{T_c - 43} \right)}$$

A comparison of the heats of vaporization calculated by these four methods is presented in Table V.

TABLE IV

CALCULATED MOLAR HEATS OF VAPORIZATION

Temperature, °C.	Method 1	Method 2	Method 3	Method 4
150	5397	5317	5156	5198
175	4893	4512	4503	4523
200	4260	3552	3559	3622
225	3552	2216	1919	1988

The results of method 1 show the inadequacy of the Berthelot equation at the higher pressures. In general, when no accurate vapor and liquid volume data are available, Watson's method (method 4) is perhaps the most reliable.

**Acknowledgment.**—This work was made pos-

(8) O. A. Hougen and K. M. Watson, "Chemical Process Principles Charts," John Wiley and Sons, Inc., New York, N. Y., 1946.

(9) K. M. Watson, *Ind. Eng. Chem.*, **23**, 360 (1931).

sible, in part, by a grant from the Defense Research Laboratory, The University of Texas, under the sponsorship of the Bureau of Ordnance, Navy De-

partment, Contract NOrd-9195. The authors express their gratitude.

AUSTIN, TEXAS

RECEIVED OCTOBER 9, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF PORTLAND]

## Dissociation Constants of Some Substituted Propylpyridonium Picrates in Ethanol; Correlation with Structural Effects<sup>1</sup>

BY EUGENE L. COLICHMAN, WILLIAM R. VANDERZANDEN<sup>2</sup> AND SHIH KUNG LIU

Previously unreported halogen and hydroxyl substituted propylpyridonium picrates were prepared and used in studying the effect of structure on ion-pair dissociation in ethanol. The Fuoss and Kraus conductance method was employed in evaluating the corresponding dissociation constants. Ethanol proved to be a satisfactory solvent for the study of structural variations. The dissociation constants were correlated with structure.

It has been clearly demonstrated by Kraus<sup>3</sup> and his many co-workers that if structural differences in ions are to be studied, solvents of sufficiently low dielectric constants must be employed. Under these conditions, ion-pair dissociation constant measurements yield information about ionic structure. The most commonly used solvent for these studies has been ethylene chloride<sup>3</sup> ( $D = 10.2$  at  $25^\circ$ ). Benzene<sup>3</sup> ( $D = 2.2$  at  $25^\circ$ ) has been used occasionally; however, very low salt solubilities and low conductances enhance random errors. Other non-aqueous solvents, such as for example, liquid ammonia<sup>4,5</sup> ( $D = 22.4$  at about  $-33$  to  $-40^\circ$ ) and nitrobenzene<sup>6,7</sup> ( $D = 34.5$  at  $25^\circ$ ), have been widely used. Previously, very few dissociation constant measurements have been reported in ethanol. Goldschmidt and Dahll<sup>8</sup> determined the dissociation constants of the halogen acids. Hartley and associates<sup>9,10</sup> studied the conductance of uni-univalent inorganic salts in ethyl alcohol. A few conductance measurements on common inorganic salts have been made in ethanol-water mixtures.<sup>11-13</sup> Specific influences and anomalies are seen in these results. Presumably, ethanol has been avoided in previous work because solvation might complicate the conductance studies, and also, the higher dielectric constant ( $D = 24.3$  at  $25^\circ$ ) might not allow full realization of the influence of structural effects on the dissociation process. Re-

cent results by Bezman and Verhoek<sup>14</sup> using modern techniques and theories show the importance of knowing precisely the water content in conductance work in alcohol-water mixtures. Relatively small changes in water concentration can greatly influence the dissociation process of electrolytes.

As shown previously,<sup>15</sup> isomeric salts are desirable when making a systematic study of the effect of structure on ion-pair dissociation processes. Kraus' results<sup>16</sup> on phenylpyridonium picrate in ethylene chloride showed that unsymmetrically coordinated "onium" salts show unique conductance properties in non-aqueous solutions. Thus, it was anticipated that a series of isomeric pyridonium picrates would show considerable variation in their dissociation constants in ethanol.  $\beta$ - and  $\gamma$ -substituted propylpyridonium picrates (previously unreported) were synthesized and used in the present conductance study.

### Experimental

**Preparation of Salts.**—The *n*-propyl-, *i*-propyl- and  $\gamma$ -hydroxypropylpyridonium halides were prepared by accepted procedure<sup>17,18</sup> using Eastman Kodak Co. White Label chemicals. The  $\gamma$ -chloro-,  $\gamma$ -bromo- and  $\gamma$ -iodo-substituted salts were prepared by heating equimolar quantities of the corresponding 1,3-dihalopropanes (Eastman Kodak Co. White Label) and C.P. pyridine (J. T. Baker Co.) in sealed tubes at  $45-50^\circ$  for one to two days. The  $\gamma$ -bromo- and  $\gamma$ -iodopyridonium halides were obtained in substantially 100% yields. About a 70% yield of the  $\gamma$ -chloro-salt was obtained by freeing the reaction mixture of the unreacted pyridine and trimethylene chloride by several washes with C.P. ethyl acetate.

Equimolar quantities of propylene bromohydrin (Eastman Kodak Co. White Label, purified by vacuum distillation) and C.P. pyridine were heated in a sealed tube as described above to give approximately a 100% yield of  $\beta$ -hydroxypropylpyridonium bromide.

The  $\beta$ -chloropropylpyridonium bromide was prepared by mixing 0.0057 mole of C.P. thionyl chloride (Eastman Kodak Co. White Label) with 0.01 mole of  $\beta$ -hydroxypropylpyridonium bromide and heating at  $40^\circ$  for a period of five hours. The yield of the  $\beta$ -chloro-salt by this procedure was 97.5%. Before deciding upon these conditions, several others were tried and found to be less satisfactory.  $\beta$ -Hydroxypropylpyridonium bromide was maintained at 0.01 mole and various quantities of thionyl chloride were tried.

(1) Supported in part by a grant-in-aid from the Research Corporation.

(2) Part of the work described herein was included in a thesis submitted by W. R. Vanderzanden to the University of Portland in partial fulfillment of the requirements for the Degree of Master of Science.

(3) For summaries of early results see C. A. Kraus, *Trans. Electrochem. Soc.*, **66**, 179 (1934); *J. Franklin Inst.*, **225**, 687 (1938); *Science*, **90**, 281 (1939). Many later investigations, too numerous to mention, have been published in the last four or five years in THIS JOURNAL.

(4) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 1019 (1933).

(5) C. A. Kraus, *et al.*, *ibid.*, **55**, 2776, 3542 (1933); **71**, 1565 (1949).

(6) C. A. Kraus, *et al.*, *ibid.*, **69**, 1731, 2472 (1947); **70**, 1707 (1948); **71**, 1455, 2695, 3288 (1949).

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(14) I. I. Bezman and F. H. Verhoek, *THIS JOURNAL*, **67**, 1330 (1945).

(15) J. B. Ramsey and E. L. Colichman, *ibid.*, **69**, 3041 (1947).

(16) L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947).

(17) F. Krollpfeiffer and E. Braun, *Ber.*, **69B**, 2523 (1936).

(18) O. A. Barnes and R. Adams, *THIS JOURNAL*, **49**, 1307 (1927).