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# Study of the Compressions of Several High Molecular Weight Hydrocarbons

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Isothermal compressions were measured for thirteen high-purity liquid hydrocarbons and two binary mixtures of liquid hydrocarbons. These hydrocarbons have a molecular weight range of 170 to 351 and included normal paraffins, cycloparaffins, aromatics, and fused ring compounds. The pressure range for these measurements was from atmospheric to as high as 10 000 bars, being limited to lower values for some compounds to avoid possible solidification of the liquid. The volume changes due to pressure were measured at six temperatures spaced about equally in the range 37.8°C to 135.0°C. The volume changes and pressures were measured by methods similar to those of P. W. Bridgman.

Pressure-volume isotherms can be described adequately by the Tait equation, $v_0 - v = C \log(1 + P/B)$, or for pressures above a certain minimum, whose value depends on the compound, by the Hudleston equation

$$\log[v^{2/3}P/(v_0^{1/3} - v^{1/3})] = A + B(v_0^{1/3} - v^{1/3}).$$

For the Tait equation the parameter $C$ can be predicted for hydrocarbon liquids from the relation $C = 0.2058 \, v_0$.

Compressibility for a given hydrocarbon decreases with increasing pressure at constant temperature and increases with increasing temperature at constant pressure. The compression, and the compressibility, of liquid hydrocarbons are strongly dependent on molecular structure. Cyclization introduces a rigidity of molecular shape which decreases the compressibility markedly. Furthermore, fused ring cyclization as exemplified by naphthyl and decalyl structures has a considerably greater effect in decreasing compressibility than cyclization to nonfused rings such as cyclopentyl, cyclohexyl, or phenyl, even at equivalent carbon atom in ring percentages.

Isobars and isochores were drawn and studied over the full range of temperature and pressure. The coefficient of thermal expansion, $(1/v_0)(\delta v/\delta T)_P$, for a given hydrocarbon, decreases with increasing pressure at constant temperature. $(\delta^2 v/\delta T^2)_P$ undergoes a sign change at a certain pressure, whose value depends on the compound; $(\delta v/\delta T)_P$ increases with increasing temperature below this pressure and decreases with increasing temperature above this pressure. The pressure coefficient, $(\delta P/\delta T)_v$, is not a function of volume alone but is also dependent on the temperature and pressure. $(\delta E/\delta v)_T$ and $(\delta E/\delta P)_T$ go to zero and then reverse sign for compounds that can be studied to sufficiently high pressures.

## INTRODUCTION

ALTHOUGH the study of liquid compressibility dates back to the English scientist, John Canton, in the eighteenth century only a relatively few experimenters[1–4] have gathered data on liquid of high molecular weight.

Since 1947 the High Pressure Laboratory and the Hydrocarbon Laboratory at The Pennsylvania State University have cooperated[5] in the study of the effect of hydrocarbon structure on physical properties. Under the direction of R. W. Schiessler and F. C. Whitmore[6–10] over 230 high-purity hydrocarbons have been produced synthetically. These hydrocarbons range in number of carbon atoms from 10 to 50 and present a wide variety of molecular structure. Atmospheric pressure values of the density, viscosity, index of refraction, and melting point of each of these compounds were also available, having been determined by the Hydrocarbon Laboratory as a part of the study of the physical properties. It was logical continuation of the research activity to seek data on the physical behavior of certain of these hydrocarbons under high pressure.

The hydrocarbons selected for the study reported herein are listed in Table I.

Two binary mixtures of pure hydrocarbons were also studied. Each mixture had an average molecular weight and average molecular structure equivalent to one of the other pure compounds available. The mixtures used were as follows (the subscript indicates the number of moles of each constituent in the physical mixture):

$$PSU25_1 + PSU113_2$$

$$PSU25_1 + PSU90_2.^{11}$$
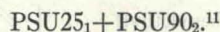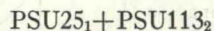
The first of the mixtures is equivalent to PSU 111 and the second mixture is equivalent to PSU 19, in

[1] Bradbury, Mark, and Kleinschmidt, Trans. Am. Soc. Mech. Engrs. 73, 667 (1951).
[2] Am. Soc. Mech. Engrs. Research Publication, *Pressure-Viscosity Report* (American Society of Mechanical Engineers, New York 1953, Vol. I and II.
[3] R. H. McMickle, Ph.D. dissertation, The Pennsylvania State University (1952).
[4] W. G. Cutler, Ph.D. dissertation, The Pennsylvania State University (1955).
[5] This work is partly supported by the American Petroleum Institute and known as American Petroleum Institute Research Project 42.
[6] R. W. Schiessler and F. C. Whitmore, Ind. Eng. Chem. 47, 1660 (1955).
[7] J. N. Cosby, and L. H. Sutherland, Proc. Am. Petrol. Inst. Sec. III 22 13 (1941).
[8] Schiessler, Cosby, Clarke, Rowland, Sloatman, and Herr, Am. Petrol. Inst. Sec. III Proc. 23 15 (1942).
[9] Schiessler, Clarke, Rowland, Sloatman, and Herr, Prod. Am. Petrol. Inst. Sec. III 24 49 (1943).
[10] Schiessler, Herr, Rytina, Weisel, Fischl, McLaughlin, and Kuehner, Proc. Am. Petrol. Inst. Sec. III 26 254 (1946).
[11] PSU 90 is 1,5-dicyclohexyl-3(2-ethylhexyl)pentane.
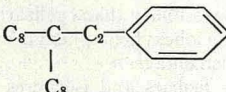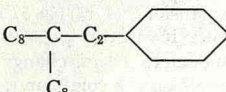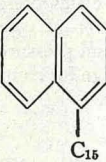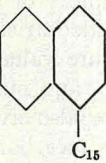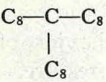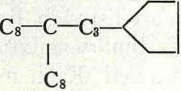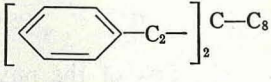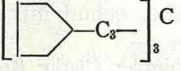
TABLE I. Atmospheric pressure physical properties of the hydrocarbons.

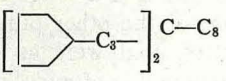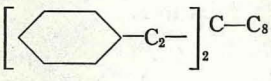| PSU[a] No. | Name | Structure [b] | Molecular weight | Melting point | Boiling point at 1 mm (°C) | Refraction index at 40°C | Viscosity at 98.9°C (cp) |
|---|---|---|---|---|---|---|---|
| 528 | n-Dodecane | $n\text{-}C_{12}$ | 170.3 | −5.5 | 104.0 (20 mm) | 1.4134 | 0.5172 |
| 532 | n-Pentadecane | $n\text{-}C_{15}$ | 212.4 | 9.9 | 91.5 | 1.4238 | 0.7984 |
| 537 | n-Octadecane | $n\text{-}C_{18}$ | 254.5 | 27.8 | 128.0 | 1.4314 | 1.154 |
| 87 | 9(2-Phenylethyl)heptadecane | $C_8\text{—}C\text{—}C_2\text{—}$⟨phenyl⟩ with $C_8$ below | 344.6 | −26.7 | 175.5 | 1.4729 | 2.03 |
| 88 | 9(2-Cyclohexylethyl)heptadecane | $C_8\text{—}C\text{—}C_2\text{—}$⟨cyclohexyl⟩ with $C_8$ below | 350.6 | Glasses | 188.5 | 1.4539 | 2.57 |
| 174 | 1-alpha-Naphthylpentadecane | ⟨naphthyl⟩—$C_{15}$ | 338.7 | 41.6 | 215.0 | 1.5215[c] | 2.891 |
| 175 | 1-alpha-Decalylpentadecane | ⟨decalyl⟩—$C_{15}$ | 348.6 | Up to 30.9 | 204.5 | 1.4694 | 3.547 |
| 25 | 9-n-Octylheptadecane | $C_8\text{—}C\text{—}C_8$ with $C_8$ below | 352.7 | −13.8 | 184.0 | 1.4412 | 1.87 |
| 110 | 9(3-Cyclopentylpropyl)heptadecane | $C_8\text{—}C\text{—}C_3\text{—}$⟨cyclopentyl⟩ with $C_8$ below | 350.7 | −20.6 | 188.0 | 1.4515 | 2.26 |
| 111 | 1-Cyclopentyl-4(3-cyclopentylpropyl)dodecane | $[$⟨cyclopentyl⟩—$C_3\text{—}]_2$ $C\text{—}C_8$ | 348.6 | Approx. −40 | 193.0 | 1.4630 | 2.88 |
| 19 | 1-Cyclohexyl-3(2-cyclohexylethyl)hendecane | $[$⟨cyclohexyl⟩—$C_2\text{—}]_2$ $C\text{—}C_8$ | 348.6 | Glasses −40 | 194.5 | 1.4683 | 4.06 |
| 18 | 1-Phenyl-3(2-phenylethyl)-hendecane | $[$⟨phenyl⟩—$C_2\text{—}]_2$ $C\text{—}C_8$ | 336.5 | Liquid at −60 | 197.0 | 1.5116 | 2.50 |
| 113 | 1,7-Dicyclopentyl-4(3-cyclopentylpropyl)heptane | $[$⟨cyclopentyl⟩—$C_3\text{—}]_3$ $C$ | 346.6 | −23.7 | 198.0 | 1.4754 | 3.88 |

[a] Assigned for identification purposes only.

[b] $C_n$ refers to an unbranched, saturated chain of $n$ carbon atoms with the substituent hydrogens.

[c] Measured on supercooled sample.

the sense defined above. For an earlier study of these mixtures at atmospheric pressure see reference 10.

In selecting these hydrocarbons particular attention was given to structural relationships. Because of the structural variations among the compounds selected definite variations in compression with structure were expected. PSU 528, 532, and 537 represent an extension of Bridgman's work on the normal paraffins, his work having extended through $n$-decane.[12]

PSU 25, 87, 18, 88, 19, 110, 111, and 113 all have the same basic symmetry, three groups of eight carbon atoms each, arranged about a central carbon atom. The differences in structure were such that a study could be made of the effect of changing from straight chain groups to one, two, or three cyclopentyl groups, and from straight chain groups to one or two phenyl groups, or one or two cyclohexyl groups. PSU 174 and 175 were included to bring fused ring compounds into the structural study.

The compounds selected cover a molecular weight range of 170 to 351. This represents a fairly wide range over which to study such empirical relationships as the Tait and Hudleston equations and such thermodynamic quantities as $(\delta v/\delta T)_P$, $(\delta P/\delta T)_v$, $(\delta v/\delta P)_T$, $(\delta^2 v/\delta T^2)_P$, $(\delta E/\delta P)_T$, and $(\delta E/\delta v)_T$. Since there is no generally accepted equation of state for liquids involving the three variables, pressure, volume, and temperature, the quantities mentioned previously are important in that their observed behavior should shed light on the validity of any equation of state that might be proposed.

## EXPERIMENTAL METHODS AND PROCEDURES

The methods used in this study to measure volume changes and pressures were similar to those employed by Bridgman.[12,13] Bridgman utilized a flexible bellows with attached slide-wire for measurement of volume changes and the changes in the resistance of a coil of manganin wire for measurement of pressure changes.

## Pressure System

The pressure generating equipment consisted of a hand operated hydraulic pump, capable of generating a pressure of 1380 bars (approximately 20 000 psi) and two intensifiers. The intensifiers, each of which consisted of a floating piston having a different cross-sectional area at each end, provided multiplication of the pump pressure by theoretical ratios of 4:1 and 9.5:1, respectively.

In operation, the pressure cylinders were preloaded to 1380 bars (20 000 psi) by direct use of the hydraulic pump. Further preloading to 3450 bars (50 000 psi) was carried out using the 4:1 intensifier. Pressures above 3450 bars were produced by driving the high-

pressure piston inward, thus compressing the hydraulic fluid in the pressure vessel.

A maximum limit of 10 000 bars was set, although this was not the theoretical limit, to reduce the possibility of equipment trouble and speed the production of data.

## Pressure Measurement

Pressures were measured by observing the changes in electrical resistance of a coil of manganin wire. Bridgman has examined the pressure-resistance characteristics of manganin and found its behavior to be linear to 13 000 atmospheres.[14,15] The manganin coil used in this study was wound from B. and S. 40 gauge double silk covered manganin wire, and had an atmospheric pressure resistance of about 120 ohms.

The manganin coil is a secondary pressure gauge and, therefore, required calibration against a standard. The manganin coil used was calibrated against a dead-weight gauge. In this calibration resistances were measured to the nearest 0.001 ohm by use of a Mueller bridge to 3450 bars at 345-bar intervals. The best value of the slope of the straight line relationship between resistance and pressure was obtained by a least squares calculation.

The resistance changes of the manganin coil during pressure run were measured using a slide-wire Wheatstone bridge. A potentiometric calibration of the slide wire was made to minimize errors arising from the nonlinearity of the slide-wire resistance.

## Temperature Regulation and Measurement

The piezometer containing the hydrocarbon under study was immersed in an oil bath whose temperature was regulated to ±0.1°C of the desired temperature. The bath temperature was measured with a mercury-in-glass thermometer calibrated by the National Bureau of Standards.

## Detection and Measurement of Volume Change

The technique used for detection and measurement of the volume change was a modification of the Bridgman[12] bellows technique. Figure 1 is an exploded view showing internal construction of the instrument,[16] hereafter called the piezometer. The piezometer held approximately five cubic centimeters of the hydrocarbon being studied. Although a much larger sample would have been advantageous in volume change determinations, the small sample size was dictated by the scarcity and value of the hydrocarbon samples and by the possibility of sample contamination in a pressure run.

The hydrocarbon to be studied was admitted to the

[12] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1949).

[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **66**, 185 (1931).

[14] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **47**, 321 (1911).

[15] P. W. Bridgman, Proc. Roy. Soc. (London) **A203**, 1 (1950).

[16] The flexible bellows used in this instrument is a product of the Fulton Sylphon Division of the Robertshaw-Fulton Controls Company Knoxville, Tennessee.
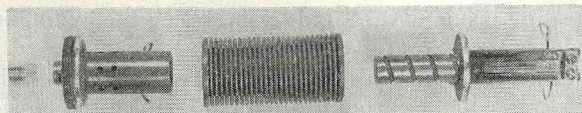
FIG. 1. Piezometer. Exploded view to show internal construction.

flexible brass bellows after the piezometer had been washed, dried, and weighed. The filling operation took place in a large glass tube, evacuated to a pressure of about $10^{-3}$ mm of mercury in order that the liquid hydrocarbon be freed of dissolved gases and that no gas bubbles be trapped in the bellows. After being filled the piezometer was removed from the vacuum system and sealed with a set screw. The loaded piezometer was again washed externally, dried and weighed to ascertain the mass of the sample. The loaded piezometer was then inserted into a brass container and the slide-wire contact was mounted in the container so as to bear on the slide wire.

Application of hydrostatic pressure produced a compression of the bellows and movement of the attached slide wire under the slide wire contact. Since the bellows compressed without change in cross-sectional area, except for small variations due to compressibility and thermal expansion of the brass, the change in bellows length is proportional to the volume change of the enclosed liquid.

A potentiometric method was used for measuring change in bellows length. The piezometer slide wire carried a constant current. Potential leads, which were separate from current leads, were arranged to measure the potential drop over the total length of the wire and the potential drop from one end of the wire to the sliding contactor. The change in the ratio of these two potential drops is proportional to the change in bellows length. This ratio is independent of changes in resistance per unit length of the slide wire with pressure.

Two calibrations were required to convert changes in the ratio of potential drops to changes in volume. The first of these determined the change in length of the bellows for a given change in ratio of potential drops. For this the piezometer was held in a special rig and the bellows compressed known amounts by a micrometer screw which could be read to 0.0001 in. Potential drop ratios were determined for each micrometer setting. The second calibration determined the change in bellows volume per unit change in bellows length. The bellows was loaded with *n*-hexadecane and arranged in the rig so that when the bellows was compressed with the micrometer screw the liquid was forced up a precision bore glass tube of known cross-sectional area.

The volume changes computed from changes in ratio were corrected for the volume effects arising from the thermal expansion and the compressibility of

brass. It was also necessary to take account of the change in compressibility of brass with pressure.

The observed data consist of a series of values for the potential ratio with the corresponding pressures under isothermal conditions. Values of the volume change were computed from the observed changes in the potential ratio. Values of the volume change were ascertained at both ascending and descending pressure, with an observation of the volume change being made at least every 175 bars.

The volume changes computed from the observed data were plotted against pressure to large scale and then smoothed by drawing the best possible curve through the plotted points with a flexible ruler. Volume changes were read from the curve at 345-bar intervals and these volume changes were fully corrected for the thermal expansion and compressibility of brass. The correction for the compressibility of the brass in the piezometer was laborious in that it involved two quantities that were pressure functions, the compressibility of the brass and the volume of the liquid sample. Therefore, only smooth curve values of the volume change at regular pressure intervals were corrected instead of correcting all observations. It is emphasized that the smoothing operation described involved no major numerical change in the data, the smoothing process being largely a matter of mathematical convenience.

## EXPERIMENTAL RESULTS

The atmospheric pressure properties of the high-purity liquid hydrocarbons used are listed in Table I. The changes in specific volume with pressure are compiled in Table II. The data in Table II are the fully corrected, smoothed data. Volume changes were measured at six temperatures, 37.8°, 60.0°, 79.4°, 98.9°, 115.0°, and 135°C, except where necessary to omit the lower temperature because of proximity to the melting point. A maximum pressure of 10 000 bars was reached where possible but some of the work was limited to lower pressures to avoid solidification of the sample or because of extreme viscosity of the sample.

An examination of the volume changes determined in this study in regard to deviation of points from the smooth curves gave an average deviation of 0.0003 cc/g. In addition to the uncertainty in a reported volume change because of the average deviation from the smooth curves, the calibration constants have a possible cumulative error of ±0.3%. The total uncertainty in the reported volume change depends on the magnitude of the volume change which is dependent, in turn, on the sample being studied and the pressure. The total uncertainty in the reported volume changes ranged at the worst, from ±1.6% at 345 bars to ±0.4% at 10 000 bars. The effect of this uncertainty on the accuracy of the density values obtained

TABLE II. Smooth curve specific volume.

### PSU 25, 9-n-octylheptadecane

| Pressure (bars)[a,b] | Specific volume cc/g | | | | | |
|---|---|---|---|---|---|---|
| | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
| atmospheric | 1.2650 | 1.2885 | 1.3099 | 1.3321 | 1.3510 | 1.3751 |
| 344.6 | 1.2344 | 1.2542 | 1.2722 | 1.2898 | 1.3051 | 1.3224 |
| 689.1 | 1.2110 | 1.2281 | 1.2432 | 1.2586 | 1.2727 | 1.2852 |
| 1033.6 | 1.1919 | 1.2075 | 1.2201 | 1.2333 | 1.2468 | 1.2571 |
| 1378.2 | 1.1750 | 1.1903 | 1.2016 | 1.2135 | 1.2254 | 1.2348 |
| 1722.8 | 1.1604 | 1.1745 | 1.1855 | 1.1961 | 1.2069 | 1.2157 |
| 2067.3 | 1.1475 | 1.1611 | 1.1712 | 1.1807 | 1.1907 | 1.1990 |
| 2411.8 | 1.1360 | 1.1484 | 1.1585 | 1.1672 | 1.1770 | 1.1838 |
| 2756.4 | 1.1256 | 1.1377 | 1.1467 | 1.1551 | 1.1643 | 1.1709 |
| 3101.0 | 1.1157 | 1.1273 | 1.1354 | 1.1440 | 1.1531 | 1.1588 |
| 3445.5 | 1.1064 | 1.1178 | 1.1256 | 1.1339 | 1.1426 | 1.1480 |
| 3790.0 | 1.0980 | 1.1088 | 1.1166 | 1.1243 | 1.1330 | 1.1382 |
| 4134.6 | 1.0899 | 1.1006 | 1.1084 | 1.1156 | 1.1237 | 1.1286 |
| 4479.2 | 1.0820 | 1.0925 | 1.1003 | 1.1072 | 1.1153 | 1.1199 |
| 4823.7 | | 1.0852 | 1.0927 | 1.0993 | 1.1072 | 1.1118 |
| 5168.2 | | 1.0781 | 1.0856 | 1.0917 | 1.0996 | 1.1041 |
| 5512.8 | | 1.0717 | 1.0786 | 1.0847 | 1.0928 | 1.0968 |
| 5857.4 | | 1.0655 | 1.0722 | 1.0778 | 1.0861 | 1.0897 |
| 6201.9 | | | 1.0663 | 1.0714 | 1.0795 | 1.0838 |
| 6546.4 | | | 1.0609 | 1.0656 | 1.0736 | 1.0776 |
| 6891.0 | | | 1.0553 | 1.0596 | 1.0677 | 1.0717 |
| 7235.6 | | | | 1.0546 | 1.0624 | 1.0661 |
| 7580.1 | | | | 1.0496 | 1.0570 | 1.0608 |
| 7924.6 | | | | 1.0445 | 1.0522 | 1.0553 |
| 8269.2 | | | | 1.0397 | 1.0475 | 1.0500 |
| 8613.8 | | | | 1.0352 | 1.0427 | 1.0455 |
| 8958.3 | | | | 1.0310 | 1.0382 | 1.0407 |
| 9302.8 | | | | 1.0265 | 1.0337 | 1.0365 |
| 9647.4 | | | | 1.0220 | 1.0295 | 1.0323 |
| 9992.0 | | | | 1.0178 | 1.0251 | 1.0281 |
| 10336.5 | | | | 1.0136 | 1.0209 | 1.0244 |

### PSU 18, 1-phenyl-3(2-phenylethyl)hendecane

| Pressure (bars)[a] | Specific volume cc/g | | | | | |
|---|---|---|---|---|---|---|
| | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
| atmospheric | 1.0996 | 1.1174 | 1.1334 | 1.1507 | 1.1648 | 1.1832 |
| 344.6 | 1.0799 | 1.0956 | 1.1090 | 1.1223 | 1.1320 | 1.1485 |
| 689.1 | 1.0626 | 1.0769 | 1.0887 | 1.0998 | 1.1068 | 1.1221 |
| 1033.6 | 1.0480 | 1.0610 | 1.0716 | 1.0812 | 1.0878 | 1.1000 |
| 1378.2 | 1.0352 | 1.0471 | 1.0568 | 1.0660 | 1.0722 | 1.0818 |
| 1722.8 | 1.0244 | 1.0350 | 1.0440 | 1.0526 | 1.0582 | 1.0667 |
| 2067.3 | 1.0144 | 1.0243 | 1.0327 | 1.0403 | 1.0465 | 1.0537 |
| 2411.8 | 1.0054 | 1.0145 | 1.0226 | 1.0296 | 1.0350 | 1.0422 |
| 2756.4 | 0.9971 | 1.0056 | 1.0135 | 1.0199 | 1.0247 | 1.0316 |
| 3101.0 | 0.9891 | 0.9974 | 1.0050 | 1.0110 | 1.0154 | 1.0224 |
| 3445.5 | 0.9814 | 0.9896 | 0.9971 | 1.0029 | 1.0065 | 1.0138 |
| 3790.0 | | 0.9826 | 0.9898 | 0.9950 | 0.9984 | 1.0057 |
| 4134.6 | | | 0.9828 | 0.9876 | 0.9910 | 0.9977 |
| 4479.2 | | | 0.9764 | 0.9803 | 0.9841 | 0.9903 |
| 4823.7 | | | 0.9700 | 0.9739 | 0.9773 | 0.9832 |
| 5168.2 | | | 0.9642 | 0.9679 | 0.9708 | 0.9768 |
| 5512.8 | | | 0.9586 | 0.9621 | 0.9647 | 0.9704 |
| 5857.4 | | | 0.9533 | 0.9565 | 0.9587 | 0.9646 |
| 6201.9 | | | 0.9482 | 0.9513 | 0.9534 | 0.9591 |
| 6546.4 | | | 0.9429 | 0.9463 | 0.9485 | 0.9540 |
| 6891.0 | | | 0.9380 | 0.9415 | 0.9437 | 0.9489 |
| 7235.6 | | | | 0.9371 | 0.9391 | 0.9441 |
| 7580.1 | | | | 0.9325 | 0.9345 | 0.9395 |
| 7924.6 | | | | 0.9284 | 0.9302 | 0.9352 |
| 8269.2 | | | | 0.9243 | 0.9261 | 0.9309 |
| 8613.8 | | | | 0.9203 | 0.9221 | 0.9267 |
| 8958.3 | | | | 0.9165 | 0.9183 | 0.9229 |
| 9302.8 | | | | 0.9128 | 0.9147 | 0.9192 |
| 9647.4 | | | | | 0.9111 | 0.9158 |
| 9992.0 | | | | | 0.9079 | 0.9122 |
| 10336.5 | | | | | 0.9046 | 0.9093 |

### PSU 19, 1-cyclohexyl-3(2-cyclohexylethyl)hendecane

| Pressure (bars)[a] | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
|---|---|---|---|---|---|---|
| atmospheric | 1.1699 | 1.1898 | 1.2070 | 1.2258 | 1.2415 | 1.2614 |
| 344.6 | 1.1467 | 1.1643 | 1.1777 | 1.1937 | 1.2054 | 1.2218 |
| 689.1 | 1.1273 | 1.1429 | 1.1554 | 1.1703 | 1.1784 | 1.1929 |
| 1033.6 | 1.1112 | 1.1258 | 1.1367 | 1.1507 | 1.1575 | 1.1709 |
| 1378.2 | 1.0977 | 1.1106 | 1.1209 | 1.1341 | 1.1405 | 1.1530 |
| 1722.8 | 1.0857 | 1.0976 | 1.1072 | 1.1198 | 1.1257 | 1.1370 |
| 2067.3 | 1.0745 | 1.0861 | 1.0954 | 1.1065 | 1.1117 | 1.1223 |
| 2411.8 | 1.0648 | 1.0752 | 1.0842 | 1.0945 | 1.0995 | 1.1093 |
| 2756.4 | 1.0559 | 1.0657 | 1.0742 | 1.0840 | 1.0887 | 1.0978 |
| 3101.0 | | 1.0570 | 1.0651 | 1.0743 | 1.0787 | 1.0874 |
| 3445.5 | | 1.0491 | 1.0564 | 1.0654 | 1.0693 | 1.0778 |
| 3790.0 | | 1.0412 | 1.0484 | 1.0572 | 1.0608 | 1.0689 |
| 4134.6 | | 1.0336 | 1.0412 | 1.0496 | 1.0532 | 1.0607 |
| 4479.2 | | | 1.0341 | 1.0426 | 1.0458 | 1.0528 |
| 4823.7 | | | 1.0277 | 1.0357 | 1.0389 | 1.0457 |
| 5168.2 | | | 1.0216 | 1.0288 | 1.0319 | 1.0387 |
| 5512.8 | | | 1.0160 | 1.0227 | 1.0255 | 1.0318 |
| 5857.4 | | | | 1.0173 | 1.0197 | 1.0254 |
| 6201.9 | | | | 1.0120 | 1.0138 | 1.0198 |
| 6546.4 | | | | | 1.0082 | 1.0142 |
| 6891.0 | | | | | 1.0028 | 1.0086 |
| 7235.6 | | | | | 0.9975 | 1.0035 |
| 7580.1 | | | | | 0.9924 | 0.9986 |
| 7924.6 | | | | | 0.9875 | 0.9942 |
| 8269.2 | | | | | | 0.9896 |
| 8613.8 | | | | | | 0.9853 |
| 8958.3 | | | | | | 0.9812 |

### PSU 110, 9(3-cyclopentylpropyl)heptadecane

| Pressure (bars)[a] | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
|---|---|---|---|---|---|---|
| atmospheric | 1.2228 | 1.2455 | 1.2655 | 1.2862 | 1.3034 | 1.3264 |
| 344.6 | 1.1947 | 1.2138 | 1.2313 | 1.2470 | 1.2622 | 1.2796 |
| 689.1 | 1.1730 | 1.1903 | 1.2059 | 1.2192 | 1.2323 | 1.2460 |
| 1033.6 | 1.1551 | 1.1712 | 1.1852 | 1.1980 | 1.2074 | 1.2192 |
| 1378.2 | 1.1396 | 1.1545 | 1.1679 | 1.1796 | 1.1878 | 1.1992 |
| 1722.8 | 1.1260 | 1.1399 | 1.1525 | 1.1637 | 1.1709 | 1.1818 |
| 2067.3 | 1.1138 | 1.1272 | 1.1382 | 1.1491 | 1.1561 | 1.1670 |
| 2411.8 | 1.1023 | 1.1152 | 1.1260 | 1.1364 | 1.1427 | 1.1526 |
| 2756.4 | 1.0921 | 1.1047 | 1.1149 | 1.1246 | 1.1307 | 1.1398 |
| 3101.0 | 1.0829 | 1.0950 | 1.1047 | 1.1141 | 1.1200 | 1.1286 |
| 3445.5 | 1.0747 | 1.0855 | 1.0955 | 1.1046 | 1.1103 | 1.1181 |
| 3790.0 | 1.0665 | 1.0774 | 1.0871 | 1.0957 | 1.1011 | 1.1082 |
| 4134.6 | 1.0591 | 1.0700 | 1.0791 | 1.0872 | 1.0928 | 1.0989 |
| 4479.2 | 1.0522 | 1.0633 | 1.0715 | 1.0793 | 1.0852 | 1.0907 |
| 4823.7 | | 1.0564 | 1.0646 | 1.0719 | 1.0778 | 1.0831 |
| 5168.2 | | 1.0501 | 1.0580 | 1.0650 | 1.0706 | 1.0757 |
| 5512.8 | | 1.0442 | 1.0521 | 1.0586 | 1.0635 | 1.0688 |
| 5857.4 | | | 1.0462 | 1.0528 | 1.0568 | 1.0626 |
| 6201.9 | | | 1.0403 | 1.0469 | 1.0510 | 1.0568 |
| 6546.4 | | | 1.0350 | 1.0415 | 1.0453 | 1.0508 |
| 6891.0 | | | 1.0294 | 1.0359 | 1.0402 | 1.0452 |

TABLE II.—Continued.

### PSU 110, 9(3-cyclopentylpropyl)heptadecane

| Pressure (bars)[a] | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
|---|---|---|---|---|---|---|
| 7235.6 | | | | 1.0308 | 1.0348 | 1.0398 |
| 7580.1 | | | | 1.0256 | 1.0297 | 1.0344 |
| 7924.6 | | | | 1.0207 | 1.0248 | 1.0293 |
| 8269.2 | | | | 1.0161 | 1.0200 | 1.0245 |
| 8613.8 | | | | 1.0113 | 1.0154 | 1.0199 |
| 8958.3 | | | | 1.0070 | 1.0108 | 1.0150 |
| 9302.8 | | | | 1.0029 | 1.0064 | 1.0104 |
| 9647.4 | | | | 0.9990 | 1.0023 | 1.0057 |
| 9992.0 | | | | 0.9952 | 0.9980 | 1.0017 |
| 10336.5 | | | | 0.9916 | 0.9937 | 0.9976 |

### PSU 111, 1-cyclopentyl-4(3-cyclopentylpropyl)dodecane

| Pressure (bars)[a] | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
|---|---|---|---|---|---|---|
| atmospheric | 1.1808 | 1.2013 | 1.2207 | 1.2399 | 1.2563 | 1.2771 |
| 344.6 | 1.1554 | 1.1719 | 1.1898 | 1.2052 | 1.2169 | 1.2356 |
| 689.1 | 1.1365 | 1.1506 | 1.1665 | 1.1797 | 1.1892 | 1.2057 |
| 1033.6 | 1.1214 | 1.1331 | 1.1474 | 1.1591 | 1.1669 | 1.1816 |
| 1378.2 | 1.1073 | 1.1181 | 1.1316 | 1.1422 | 1.1489 | 1.1630 |
| 1722.8 | 1.0949 | 1.1050 | 1.1179 | 1.1273 | 1.1336 | 1.1464 |
| 2067.3 | 1.0834 | 1.0933 | 1.1060 | 1.1145 | 1.1199 | 1.1320 |
| 2411.8 | 1.0726 | 1.0825 | 1.0949 | 1.1033 | 1.1079 | 1.1191 |
| 2756.4 | 1.0628 | 1.0724 | 1.0847 | 1.0925 | 1.0971 | 1.1073 |
| 3101.0 | 1.0537 | 1.0631 | 1.0751 | 1.0829 | 1.0873 | 1.0965 |
| 3445.5 | 1.0453 | 1.0545 | 1.0661 | 1.0736 | 1.0775 | 1.0864 |
| 3790.0 | 1.0379 | 1.0463 | 1.0575 | 1.0645 | 1.0688 | 1.0776 |
| 4134.6 | 1.0310 | 1.0382 | 1.0499 | 1.0561 | 1.0605 | 1.0690 |
| 4479.2 | 1.0245 | 1.0313 | 1.0427 | 1.0484 | 1.0526 | 1.0613 |
| 4823.7 | 1.0183 | 1.0248 | 1.0357 | 1.0412 | 1.0453 | 1.0538 |
| 5168.2 | 1.0125 | 1.0188 | 1.0286 | 1.0347 | 1.0383 | 1.0468 |
| 5512.8 | 1.0068 | 1.0131 | 1.0223 | 1.0287 | 1.0321 | 1.0399 |
| 5857.4 | | 1.0078 | 1.0166 | 1.0228 | 1.0259 | 1.0339 |
| 6201.9 | | 1.0028 | 1.0113 | 1.0168 | 1.0202 | 1.0284 |
| 6546.4 | | 0.9980 | 1.0063 | 1.0115 | 1.0149 | 1.0229 |
| 6891.0 | | 0.9930 | 1.0013 | 1.0065 | 1.0099 | 1.0172 |
| 7235.6 | | 0.9884 | 0.9967 | 1.0017 | 1.0051 | 1.0119 |
| 7580.1 | | | 0.9922 | 0.9969 | 0.9998 | 1.0071 |
| 7924.6 | | | | 0.9924 | 0.9948 | 1.0022 |
| 8269.2 | | | | 0.9877 | 0.9901 | 0.9977 |
| 8613.8 | | | | 0.9835 | 0.9857 | 0.9931 |
| 8958.3 | | | | 0.9793 | 0.9810 | 0.9891 |
| 9302.8 | | | | 0.9753 | 0.9767 | 0.9850 |
| 9647.4 | | | | 0.9712 | 0.9724 | 0.9812 |
| 9992.0 | | | | 0.9674 | 0.9685 | 0.9776 |
| 10336.5 | | | | 0.9635 | 0.9644 | 0.9740 |

### PSU 113, 1,7-dicyclopentyl-4(3-cyclopentylpropyl)heptane

| Pressure (bars)[a] | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
|---|---|---|---|---|---|---|
| atmospheric | 1.1397 | 1.1581 | 1.1758 | 1.1934 | 1.2084 | 1.2277 |
| 344.6 | 1.1178 | 1.1331 | 1.1477 | 1.1610 | 1.1748 | 1.1899 |
| 689.1 | 1.0999 | 1.1140 | 1.1272 | 1.1377 | 1.1489 | 1.1623 |
| 1033.6 | 1.0849 | 1.0983 | 1.1099 | 1.1189 | 1.1287 | 1.1407 |
| 1378.2 | 1.0710 | 1.0840 | 1.0949 | 1.1032 | 1.1124 | 1.1238 |
| 1722.8 | 1.0591 | 1.0713 | 1.0818 | 1.0891 | 1.0976 | 1.1085 |
| 2067.3 | 1.0484 | 1.0598 | 1.0696 | 1.0769 | 1.0845 | 1.0948 |
| 2411.8 | 1.0386 | 1.0495 | 1.0586 | 1.0654 | 1.0730 | 1.0822 |
| 2756.4 | 1.0298 | 1.0405 | 1.0491 | 1.0552 | 1.0625 | 1.0708 |
| 3101.0 | | 1.0319 | 1.0398 | 1.0459 | 1.0527 | 1.0607 |
| 3445.5 | | 1.0235 | 1.0317 | 1.0378 | 1.0441 | 1.0521 |
| 3790.0 | | 1.0161 | 1.0242 | 1.0301 | 1.0355 | 1.0437 |
| 4134.6 | | | 1.0175 | 1.0227 | 1.0281 | 1.0358 |
| 4479.2 | | | 1.0109 | 1.0158 | 1.0209 | 1.0285 |
| 4823.7 | | | 1.0044 | 1.0094 | 1.0143 | 1.0213 |
| 5168.2 | | | 0.9982 | 1.0033 | 1.0081 | 1.0146 |
| 5512.8 | | | 0.9923 | 0.9974 | 1.0023 | 1.0087 |
| 5857.4 | | | 0.9868 | 0.9919 | 0.9966 | 1.0028 |
| 6201.9 | | | | 0.9864 | 0.9910 | 0.9974 |
| 6546.4 | | | | 0.9814 | 0.9856 | 0.9921 |
| 6891.0 | | | | 0.9766 | 0.9805 | 0.9874 |
| 7235.6 | | | | 0.9718 | 0.9755 | 0.9826 |
| 7580.1 | | | | 0.9671 | 0.9708 | 0.9781 |
| 7924.6 | | | | | 0.9662 | 0.9738 |
| 8269.2 | | | | | 0.9617 | 0.9692 |
| 8613.8 | | | | | 0.9574 | 0.9647 |
| 8958.3 | | | | | | 0.9603 |
| 9302.8 | | | | | | 0.9563 |
| 9647.4 | | | | | | 0.9522 |
| 9992.0 | | | | | | 0.9481 |
| 10336.5 | | | | | | 0.9443 |

### PSU 528, n-dodecane

| Pressure (bars)[a] | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
|---|---|---|---|---|---|---|
| atmospheric | 1.3587 | 1.3900 | 1.4180 | 1.4478 | 1.4745 | 1.5103 |
| 344.6 | 1.3160 | 1.3430 | 1.3632 | 1.3861 | 1.4072 | 1.4318 |
| 689.1 | 1.2858 | 1.3102 | 1.3273 | 1.3484 | 1.3675 | 1.3860 |
| 1033.6 | 1.2619 | 1.2833 | 1.2995 | 1.3184 | 1.3361 | 1.3525 |
| 1378.2 | 1.2425 | 1.2617 | 1.2767 | 1.2933 | 1.3102 | 1.3257 |
| 1722.8 | | 1.2436 | 1.2573 | 1.2726 | 1.2883 | 1.3032 |
| 2067.3 | | 1.2280 | 1.2403 | 1.2556 | 1.2699 | 1.2847 |
| 2411.8 | | 1.2139 | 1.2256 | 1.2406 | 1.2539 | 1.2685 |
| 2756.4 | | | 1.2125 | 1.2269 | 1.2397 | 1.2539 |
| 3101.0 | | | 1.2006 | 1.2142 | 1.2272 | 1.2404 |
| 3445.5 | | | 1.1894 | 1.2027 | 1.2160 | 1.2283 |
| 3790.0 | | | | 1.1922 | 1.2054 | 1.2174 |
| 4134.6 | | | | 1.1827 | 1.1952 | 1.2072 |
| 4479.0 | | | | 1.1738 | 1.1856 | 1.1975 |
| 4823.7 | | | | 1.1655 | 1.1769 | 1.1883 |
| 5168.2 | | | | | 1.1686 | 1.1799 |
| 5512.8 | | | | | 1.1606 | 1.1720 |
| 5857.4 | | | | | 1.1528 | 1.1648 |
| 6201.9 | | | | | | 1.1579 |
| 6546.4 | | | | | | 1.1513 |
| 6891.0 | | | | | | 1.1449 |

### PSU 532, n-pentadecane

| Pressure (bars)[a] | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
|---|---|---|---|---|---|---|
| atmospheric | 1.3224 | 1.3499 | 1.3751 | 1.4015 | 1.4263 | 1.4575 |
| 344.6 | 1.2872 | 1.3098 | 1.3289 | 1.3488 | 1.3678 | 1.3906 |
| 689.1 | 1.2594 | 1.2803 | 1.2961 | 1.3132 | 1.3295 | 1.3484 |
| 1033.6 | | 1.2560 | 1.2703 | 1.2854 | 1.2997 | 1.3158 |
| 1378.2 | | 1.2360 | 1.2487 | 1.2626 | 1.2754 | 1.2894 |
| 1722.8 | | 1.2185 | 1.2298 | 1.2429 | 1.2550 | 1.2677 |
| 2067.3 | | | 1.2138 | 1.2260 | 1.2375 | 1.2496 |
| 2411.8 | | | 1.1996 | 1.2112 | 1.2219 | 1.2341 |
| 2756.4 | | | 1.1873 | 1.1983 | 1.2082 | 1.2202 |
| 3101.0 | | | | 1.1866 | 1.1962 | 1.2077 |
| 3445.5 | | | | 1.1757 | 1.1853 | 1.1961 |

TABLE II.—*Continued.*

| Pressure (bars)[a] | Specific volume cc/g | | | | | |
|---|---|---|---|---|---|---|
| | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
| **PSU 532, n-pentadecane** | | | | | | |
| 3790.0 | | | | 1.1655 | 1.1746 | 1.1854 |
| 4134.6 | | | | 1.1559 | 1.1647 | 1.1754 |
| 4479.2 | | | | 1.1469 | 1.1555 | 1.1661 |
| 4823.7 | | | | | 1.1469 | 1.1571 |
| 5168.2 | | | | | 1.1390 | 1.1489 |
| 5512.8 | | | | | 1.1316 | 1.1413 |
| 5857.4 | | | | | | 1.1338 |
| 6201.9 | | | | | | 1.1266 |
| 6546.4 | | | | | | 1.1196 |
| **PSU 537, n-octadecane** | | | | | | |
| atmospheric | | 1.3231 | 1.3468 | 1.3714 | 1.3941 | 1.4215 |
| 344.6 | | 1.2855 | 1.3049 | 1.3233 | 1.3392 | 1.3598 |
| 689.1 | | 1.2572 | 1.2741 | 1.2905 | 1.3043 | 1.3216 |
| 1033.6 | | 1.2344 | 1.2494 | 1.2638 | 1.2767 | 1.2919 |
| 1378.2 | | | 1.2287 | 1.2417 | 1.2539 | 1.2678 |
| 1722.8 | | | 1.2113 | 1.2227 | 1.2340 | 1.2472 |
| 2067.3 | | | 1.1960 | 1.2068 | 1.2171 | 1.2298 |
| 2411.8 | | | | 1.1929 | 1.2026 | 1.2143 |
| 2756.4 | | | | 1.1809 | 1.1900 | 1.2007 |
| 3101.0 | | | | 1.1698 | 1.1782 | 1.1886 |
| 3445.5 | | | | 1.1591 | 1.1674 | 1.1774 |
| 3790.0 | | | | | 1.1573 | 1.1668 |
| 4134.6 | | | | | 1.1478 | 1.1573 |
| 4479.2 | | | | | 1.1384 | 1.1482 |
| 4823.7 | | | | | | 1.1396 |
| 5168.2 | | | | | | 1.1316 |
| 5512.8 | | | | | | 1.1239 |
| **PSU 87, 9(2-phenylethyl)heptadecane** | | | | | | |
| atmospheric | 1.1847 | 1.2054 | 1.2243 | 1.2438 | 1.2626 | 1.2854 |
| 344.6 | 1.1608 | 1.1779 | 1.1933 | 1.2090 | 1.2247 | 1.2400 |
| 689.1 | 1.1403 | 1.1555 | 1.1694 | 1.1828 | 1.1963 | 1.2093 |
| 1033.6 | 1.1233 | 1.1373 | 1.1497 | 1.1619 | 1.1738 | 1.1856 |
| 1378.2 | 1.1089 | 1.1218 | 1.1334 | 1.1447 | 1.1554 | 1.1660 |
| 1722.8 | 1.0961 | 1.1081 | 1.1189 | 1.1293 | 1.1397 | 1.1491 |
| 2067.3 | 1.0849 | 1.0960 | 1.1061 | 1.1157 | 1.1255 | 1.1339 |
| 2411.8 | 1.0747 | 1.0851 | 1.0948 | 1.1037 | 1.1126 | 1.1203 |
| 2756.4 | 1.0653 | 1.0753 | 1.0845 | 1.0930 | 1.1010 | 1.1086 |
| 3101.0 | 1.0567 | 1.0662 | 1.0748 | 1.0828 | 1.0905 | 1.0981 |
| 3445.5 | 1.0487 | 1.0578 | 1.0659 | 1.0736 | 1.0812 | 1.0822 |
| 3970.0 | 1.0409 | 1.0500 | 1.0578 | 1.0648 | 1.0727 | 1.0791 |
| 4134.6 | 1.0339 | 1.0426 | 1.0501 | 1.0570 | 1.0648 | 1.0709 |
| 4479.2 | | 1.0357 | 1.0427 | 1.0498 | 1.0572 | 1.0633 |
| 4823.7 | | 1.0294 | 1.0358 | 1.0432 | 1.0502 | 1.0565 |
| 5168.2 | | 1.0232 | 1.0294 | 1.0366 | 1.0435 | 1.0499 |
| 5512.8 | | 1.0173 | 1.0234 | 1.0303 | 1.0371 | 1.0435 |
| 5857.4 | | | 1.0175 | 1.0241 | 1.0311 | 1.0372 |
| 6201.9 | | | 1.0119 | 1.0183 | 1.0254 | 1.0312 |
| 6546.4 | | | 1.0065 | 1.0128 | 1.0198 | 1.0255 |
| 6891.0 | | | 1.0017 | 1.0076 | 1.0143 | 1.0201 |
| 7235.6 | | | | 1.0027 | 1.0090 | 1.0149 |
| 7580.1 | | | | 0.9981 | 1.0041 | 1.0099 |
| 7924.6 | | | | 0.9937 | 0.9993 | 1.0052 |
| 8269.2 | | | | 0.9894 | 0.9948 | 1.0007 |
| 8613.8 | | | | | 0.9905 | 0.9961 |

| Pressure (bars)[a] | Specific volume cc/g | | | | | |
|---|---|---|---|---|---|---|
| | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
| **PSU 87, 9(2-phenylethyl)heptadecane** | | | | | | |
| 8958.3 | | | | | 0.9865 | 0.9917 |
| 9302.8 | | | | | | 0.9873 |
| 9647.4 | | | | | | 0.9830 |
| **PSU 88, 9(2-cyclohexylethyl)heptadecane** | | | | | | |
| atmospheric | 1.2171 | 1.2395 | 1.2585 | 1.2788 | 1.2974 | 1.3203 |
| 344.6 | 1.1909 | 1.2111 | 1.2251 | 1.2407 | 1.2557 | 1.2741 |
| 689.1 | 1.1701 | 1.1878 | 1.2006 | 1.2142 | 1.2265 | 1.2419 |
| 1033.6 | 1.1524 | 1.1685 | 1.1803 | 1.1920 | 1.2035 | 1.2167 |
| 1378.2 | 1.1373 | 1.1519 | 1.1627 | 1.1736 | 1.1842 | 1.1970 |
| 1722.8 | 1.1241 | 1.1375 | 1.1470 | 1.1574 | 1.1675 | 1.1792 |
| 2067.3 | 1.1123 | 1.1248 | 1.1333 | 1.1431 | 1.1529 | 1.1633 |
| 2411.8 | 1.1014 | 1.1135 | 1.1213 | 1.1303 | 1.1400 | 1.1496 |
| 2756.4 | 1.0917 | 1.1032 | 1.1109 | 1.1191 | 1.1283 | 1.1372 |
| 3101.0 | 1.0829 | 1.0938 | 1.1013 | 1.1089 | 1.1176 | 1.1259 |
| 3445.5 | 1.0748 | 1.0853 | 1.0924 | 1.0996 | 1.1078 | 1.1156 |
| 3790.0 | 1.0674 | 1.0774 | 1.0842 | 1.0909 | 1.0988 | 1.1061 |
| 4134.6 | | 1.0701 | 1.0767 | 1.0829 | 1.0908 | 1.0975 |
| 4479.2 | | 1.0630 | 1.0695 | 1.0752 | 1.0832 | 1.0900 |
| 4823.7 | | 1.0563 | 1.0626 | 1.0683 | 1.0760 | 1.0828 |
| 5168.2 | | 1.0498 | 1.0558 | 1.0618 | 1.0690 | 1.0758 |
| 5512.8 | | | 1.0496 | 1.0556 | 1.0622 | 1.0689 |
| 5857.4 | | | 1.0437 | 1.0497 | 1.0559 | 1.0625 |
| 6201.9 | | | 1.0381 | 1.0440 | 1.0502 | 1.0565 |
| 6546.4 | | | | 1.0385 | 1.0447 | 1.0507 |
| 6891.0 | | | | 1.0331 | 1.0397 | 1.0451 |
| 7235.6 | | | | 1.0280 | 1.0347 | 1.0397 |
| 7580.1 | | | | 1.0232 | 1.0297 | 1.0345 |
| 7924.6 | | | | 1.0185 | 1.0248 | 1.0296 |
| 8269.2 | | | | 1.0138 | 1.0198 | 1.0247 |
| 8613.8 | | | | | 1.0153 | 1.0201 |
| 8958.3 | | | | | 1.0110 | 1.0156 |
| 9302.8 | | | | | 1.0069 | 1.0111 |
| 9647.4 | | | | | 1.0027 | 1.0068 |
| 9992.0 | | | | | | 1.0027 |
| 10336.5 | | | | | | 0.9987 |
| **PSU 174, 1-alpha-naphthylpentadecane** | | | | | | |
| atmospheric | | 1.1255 | 1.1418 | 1.1586 | 1.1740 | 1.1927 |
| 344.6 | | 1.1030 | 1.1171 | 1.1314 | 1.1440 | 1.1599 |
| 689.1 | | 1.0847 | 1.0974 | 1.1100 | 1.1210 | 1.1354 |
| 1033.6 | | | 1.0808 | 1.0923 | 1.1025 | 1.1157 |
| 1378.2 | | | 1.0666 | 1.0774 | 1.0870 | 1.0988 |
| 1722.8 | | | 1.0541 | 1.0644 | 1.0730 | 1.0842 |
| 2067.3 | | | | 1.0529 | 1.0606 | 1.0715 |
| 2411.8 | | | | 1.0422 | 1.0496 | 1.0600 |
| 2756.4 | | | | 1.0327 | 1.0397 | 1.0498 |
| 3101.0 | | | | | 1.0307 | 1.0403 |
| 3445.5 | | | | | 1.0223 | 1.0317 |
| 3790.0 | | | | | 1.0145 | 1.0237 |
| 4134.6 | | | | | 1.0072 | 1.0163 |
| 4479.2 | | | | | | 1.0092 |
| 4823.7 | | | | | | 1.0028 |
| 5168.2 | | | | | | 0.9967 |
| 5512.8 | | | | | | 0.9908 |

TABLE II.—*Continued.*

| Pressure (bars)[a] | Specific volume cc/g | | | | | |
|---|---|---|---|---|---|---|
| | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
| | PSU 175, 1-alpha-decalylpentadecane | | | | | |
| atmospheric | | 1.1864 | 1.2039 | 1.2219 | 1.2384 | 1.2587 |
| 344.6 | | 1.1617 | 1.1758 | 1.1907 | 1.2051 | 1.2213 |
| 689.1 | | 1.1413 | 1.1537 | 1.1671 | 1.1789 | 1.1936 |
| 1033.6 | | 1.1245 | 1.1355 | 1.1479 | 1.1581 | 1.1718 |
| 1378.2 | | | 1.1206 | 1.1319 | 1.1407 | 1.1531 |
| 1722.8 | | | 1.1074 | 1.1177 | 1.1260 | 1.1377 |
| 2067.3 | | | 1.0955 | 1.1055 | 1.1132 | 1.1243 |
| 2411.8 | | | 1.0943 | 1.1017 | 1.1120 | |
| 2756.4 | | | 1.0844 | 1.0913 | 1.1010 | |

| Pressure (bars)[a] | Specific volume cc/g | | | | | |
|---|---|---|---|---|---|---|
| | 37.8°C | 60.0° | 79.4° | 98.9° | 115.0° | 135.0° |
| | PSU, 175 1-alpha-decalylpentadecane | | | | | |
| 3101.0 | | | | 1.0755 | 1.0818 | 1.0908 |
| 3445.5 | | | | 1.0672 | 1.0729 | 1.0815 |
| 3790.0 | | | | | 1.0646 | 1.0726 |
| 4134.6 | | | | | 1.0570 | 1.0646 |
| 4479.2 | | | | | 1.0495 | 1.0571 |
| 4823.7 | | | | | | 1.0501 |
| 5168.2 | | | | | | 1.0436 |
| 5512.8 | | | | | | 1.0375 |
| 5857.4 | | | | | | 1.0317 |

[a] The 345-bar pressure interval used in presentation of these data corresponds to 5000 psi. Corrections for the compressibility of the brass piezometer were originally worked out for 5000 psi

[b] The pressure should be rounded off to the nearest bar.

intervals. The temperatures 37.8°C, 60°C, 79.4°C, 98.9°C, 115°C, and 135°C correspond to 100°F, 140°F, 175°F, 210°F, 239°F, and 275°F, respectively.

varies from compound to compound. The worst effects these uncertainities had on the density ranged from approximately ±0.10% at 345 bars to ±0.14% at 10 000 bars.

Checks on sample mass, index of refraction, and

where necessary, density, were performed before and after obtaining pressure data to make certain that contamination of the sample did not occur.

An indication of the validity of the data reported here can be obtained by comparison with similar data

TABLE III. Comparison of relative volumes for "chemical" and physical mixtures as a function of pressure.

| Pressure (bars) | 60°C | | | 135°C | | |
|---|---|---|---|---|---|---|
| | Relative volume | | | Relative volume | | |
| | 19 | Mixture 25₁+90₂ | Ratio c/p | 19 | Mixture 25₁+90₂ | Ratio c/o |
| atmos | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 344.6 | 0.9786 | 0.9790 | 0.9996 | 0.9686 | 0.9670 | 1.0017 |
| 689.1 | 0.9606 | 0.9616 | 0.9990 | 0.9457 | 0.9434 | 1.0024 |
| 1033.6 | 0.9462 | 0.9466 | 0.9996 | 0.9283 | 0.9257 | 1.0028 |
| 1378.2 | 0.9336 | 0.9342 | 0.9994 | 0.9142 | 0.9108 | 1.0037 |
| 1722.8 | 0.9227 | 0.9232 | 0.9995 | 0.9014 | 0.8978 | 1.0040 |
| 2067.3 | 0.9130 | 0.9136 | 0.9993 | 0.8899 | 0.8869 | 1.0034 |
| 2411.8 | 0.9038 | 0.9053 | 0.9983 | 0.8796 | 0.8769 | 1.0031 |
| 2756.4 | 0.8959 | 0.8973 | 0.9984 | 0.8705 | 0.8684 | 1.0024 |
| 3101.0 | | | | 0.8622 | 0.8601 | 1.0024 |
| 3445.5 | | | | 0.8547 | 0.8525 | 1.0026 |
| 3790.0 | | | | 0.8476 | 0.8456 | 1.0024 |
| 4134.6 | | | | 0.8411 | 0.8388 | 1.0027 |
| 4479.2 | | | | 0.8348 | 0.8327 | 1.0025 |
| 4823.7 | | | | 0.8292 | 0.8271 | 1.0025 |
| 5168.2 | | | | 0.8237 | 0.8216 | 1.0026 |
| 5512.8 | | | | 0.8182 | 0.8161 | 1.0026 |
| 5857.4 | | | | 0.8132 | 0.8112 | 1.0025 |
| 6201.9 | | | | 0.8087 | 0.8069 | 1.0022 |
| 6546.4 | | | | 0.8043 | 0.8028 | 1.0019 |
| 6891.0 | | | | 0.7998 | 0.7986 | 1.0015 |
| 7235.6 | | | | 0.7958 | 0.7950 | 1.0010 |
| 7580.1 | | | | 0.7919 | 0.7914 | 1.0006 |

| Pressure (bars) | Relative volume | | | Relative volume | | |
|---|---|---|---|---|---|---|
| | 111 | Mixture 25₁+113₂ | Ratio c/p | 111 | Mixture 25₁+113₂ | Ratio c/p |
| atmos | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 344.6 | 0.9754 | 0.9753 | 1.0001 | 0.9676 | 0.9672 | 1.0004 |
| 689.1 | 0.9577 | 0.9574 | 1.0003 | 0.9442 | 0.9432 | 1.0011 |
| 1033.6 | 0.9431 | 0.9426 | 1.0005 | 0.9255 | 0.9245 | 1.0011 |
| 1378.2 | 0.9308 | 0.9299 | 1.0009 | 0.9109 | 0.9095 | 1.0015 |
| 1722.8 | 0.9198 | 0.9185 | 1.0014 | 0.8980 | 0.8965 | 1.0017 |
| 2067.3 | 0.9101 | 0.9084 | 1.0019 | 0.8867 | 0.8851 | 1.0018 |
| 2411.8 | 0.9011 | 0.8992 | 1.0021 | 0.8766 | 0.8752 | 1.0016 |
| 2756.4 | 0.8927 | 0.8910 | 1.0019 | 0.8675 | 0.8664 | 1.0013 |
| 3101.0 | 0.8849 | 0.8834 | 1.0017 | 0.8590 | 0.8580 | 1.0012 |
| 3445.5 | 0.8778 | 0.8762 | 1.0018 | 0.8512 | 0.8504 | 1.0009 |
| 3790.0 | 0.8710 | 0.8692 | 1.0021 | 0.8443 | 0.8433 | 1.0012 |
| 4134.6 | 0.8642 | 0.8627 | 1.0017 | 0.8375 | 0.8367 | 1.0010 |
| 4479.3 | 0.8585 | 0.8567 | 1.0021 | 0.8315 | 0.8305 | 1.0012 |
| 4823.7 | | | | 0.8256 | 0.8246 | 1.0012 |
| 5168.2 | | | | 0.8203 | 0.8189 | 1.0017 |
| 5512.8 | | | | 0.8149 | 0.8136 | 1.0016 |
| 5857.4 | | | | 0.8102 | 0.8086 | 1.0020 |
| 6201.9 | | | | 0.8059 | 0.8037 | 1.0027 |
| 6546.4 | | | | 0.8016 | 0.7991 | 1.0031 |
| 6891.0 | | | | 0.7971 | 0.7947 | 1.0030 |
| 7580.1 | | | | 0.7893 | 0.7868 | 1.0032 |
| 8269.2 | | | | 0.7820 | 0.7795 | 1.0032 |
| 8958.3 | | | | 0.7752 | 0.7731 | 1.0027 |
| 9647.4 | | | | 0.7692 | 0.7668 | 1.0031 |
| 10336.5 | | | | 0.7634 | 0.7610 | 1.0032 |

TABLE IV. Tait equation parameters.

| PSU No. | Temperature | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 37.8°C | | 60.0° | | 79.4° | | 98.9° | | 115.0° | | 135.0° | |
| | $C$ cc/gm | $B$ bars | $C$ | $B$ | $C$ | $B$ | $C$ | $B$ | $C$ | $B$ | $C$ | $B$ |
| 174 | | | 0.2316 | 1378 | 0.2350 | 1264 | 0.2384 | 1160 | 0.2416 | 1061 | 0.2455 | 976.4 |
| 87 | 0.2438 | 1315 | 0.2481 | 1170 | 0.2520 | 1048 | 0.2560 | 941.3 | 0.2598 | 857.9 | 0.2645 | 756.6 |
| 88 | 0.2505 | 1275 | 0.2551 | 1140 | 0.2590 | 1019 | 0.2632 | 907.6 | 0.2670 | 831.7 | 0.2717 | 736.0 |
| 532 | 0.2721 | 983.3 | 0.2778 | 876.5 | 0.2830 | 762.8 | 0.2884 | 676.7 | 0.2935 | 607.8 | 0.3000 | 532.0 |

of other observers. In a separate PVT study Bradbury[17] examined samples of PSU 25, 111, and 19 at 37.8° and 98.9°C. The average percent difference, without regard to sign, between Bradbury's data and the data of this study is 0.6%.

Table III presents data for the two mixtures studied. For these mixtures the equivalence of average molecular structure and molecular weight for the physical mixture with that for a certain pure chemical compound, termed "chemical" mixture, has been shown by previous work of Schiessler and co-workers[10] to produce also an equivalence in such atmospheric pressure physical properties as density, viscosity, and refractive index. Griest[18] has shown that the viscosity for three physical mixtures was identical (within 3%) to that for the corresponding "chemical" mixture for pressures to 3450 bars. In Table III relative volumes (relative volume=volume at a given pressure/volume at atmospheric pressure) for the physical and "chemical" mixtures studied by the present authors are compared. This comparison is made by listing the magnitude of the quantity $c/p$, which was the ratio of the value of the relative volume for the "chemical" mixture to the value of the relative volume for the physical mixture. The agreement over the full pressure range indicates that compression is determined by the coexistence in proper ratio of units smaller in size than the molecule itself.

### DISCUSSION AND ANALYSIS OF RESULTS

#### Tait Equation

Although no attempt was made in this study to develop a three-dimensional equation of state for the liquid hydrocarbons, considerable effort was devoted to attempts to express the pressure-volume isotherms analytically. Of chief interest in this connection was the Tait equation.[19]

The form of the Tait equation used in this study was

$$v_0 - v = C \log(1 + P/B),$$

where $v_0$ is the specific volume at atmospheric pressure, $v$ is the specific volume at pressure $P$, and $C$ and $B$ are constants. The data used to determine $C$ and $B$, were obtained from the smoothed volume-pressure isotherms. The initial values of $C$ and $B$ were determined by a method suggested by Wohl.[20]

A number of investigators[20-27] have observed that $C/v_0$ was a constant independent of temperature. The value of $C/v_0$ was evaluated for 20 hydrocarbons from this study and a study by Spencer,[28] using data from 103 isotherms. The average value obtained for $C/v_0$ was 0.2058, the standard deviation being 0.0045. The 20 hydrocarbons used in this evaluation cover a molecular weight range of 170 to 535 and included paraffinic, isoparaffinic, cycloparaffinic, aromatic, and fused ring compounds. It is believed that this is the widest range, both in respect to molecular weight and hydrocarbon structure, over which the constancy of $C/v_0$ has been ascertained.

Using the expression $C = 0.2058 \, v_0$, a value of $C$ was calculated for each isotherm and a corresponding value of $B$ was computed by a least-squares procedure. Representative values of $C$ and $B$ appear in Table IV.

A comparison between observed values of the specific volume change and the specific volume change computed from the Tait equation was made. The average percent of difference, without regard to sign, was 0.45%. The largest differences were at low pressures, this being particularly true for the normal paraffins.

An examination of the data showed that the temperature dependence of $B$ was adequately described by a quadratic about 79.4°C. Representative values

[17] D. Bradbury, D.Sc. dissertation, Harvard University (1950).
[18] Griest, Webb, and Schiessler, J. Chem. Phys. **29**, 711 (1958), this issue.
[19] P. G. Tait, *Physics and Chemistry of the Voyage of H. M. S. Challenger*, Vol. II, Part IV, S. P. LXI (1888).

[20] A. Wohl, Z. physik. Chem. **99**, 234 (1921).
[21] H. Carl, Z. physik. Chem. **101**, 238 (1922).
[22] R. E. Gibson, and J. F. Kincaid, J. Am. Chem. Soc. **60**, 511 (1938).
[23] R. E. Gibson, and O. H. Loeffler, J. Am. Chem. Soc. **61**, 2877 (1939), **61**, 2515 (1939).
[24] R. E. Gibson and O. H. Loeffler, J. Phys. Chem. **43**, 207 (1939).
[25] R. E. Gibson and O. H. Loeffler, J. Am. Chem. Soc. **63**, 898 (1941).
[26] Eduljee, Newitt, and Weale, J. Chem. Soc. (London), Part IV, 3086 (1951).
[27] D. M. Newitt, and K. E. Weale, J. Chem. Soc. (London), Part IV, 3092 (1951).
[28] J. W. Spencer, Ph.D. dissertation, The Pennsylvania State University (1952).

TABLE V. Temperature dependence of the Tait equation parameter "B", $B_t = B_{79.4} + a(t-79.4°) + b(t-79.4°)^2$.

| PSU No | $B_{79.4}$ bars | $a$ bars/°C | $b$ bars/(°C)$^2$ |
|--------|-----------------|-------------|-------------------|
| 174 | 1264 | −5.698 | 0.0094 |
| 87 | 1048 | −5.916 | 0.0121 |
| 88 | 1019 | −5.690 | 0.0107 |
| 532 | 762.8 | −4.805 | 0.0116 |

of the coefficients of the equations of the form

$$B_t = B_{79.4} + a(t-79.4) + b(t-79.4)^2$$

are given in Table V.

## Hudleston Equation

Hudleston[29] proposed an intermolecular force law of the form

$$f = a(l-l_0) \exp b(l_0-l),$$

where $f$ is the force between molecules, $l$ is the distance between molecular centers, $l_0$ is the distance at which molecules have no effect on each other, and $a$ and $b$ are empirical constants. If the distance between force centers is written as $v^{1/3}$ and the force as $v^{2/3}P$ the preceding equation can be put in the form

$$\log[v^{2/3}P/(v_0^{1/3}-v^{1/3})] = A + B(v_0^{1/3}-v^{1/3}),$$

where $v_0$ is the specific volume at atmospheric pressure, $v$ is the specific volume at pressure $P$, and $A$ and $B$ are constants.

To check the Hudleston equation with the data obtained in this study $\log[v^{2/3}P/(v_0^{1/3}-v^{1/3})]$ was plotted against $(v_0^{1/3}-v^{1/3})$. If the Hudleston equation is valid the locus of the points plotted should be a straight line having slope $B$ and intercept $A$. For the compounds checked straight lines did result except for some deviations at pressures of 700 bars or lower. These deviations are to be expected, because the mathematical form of the Hudleston equation is such
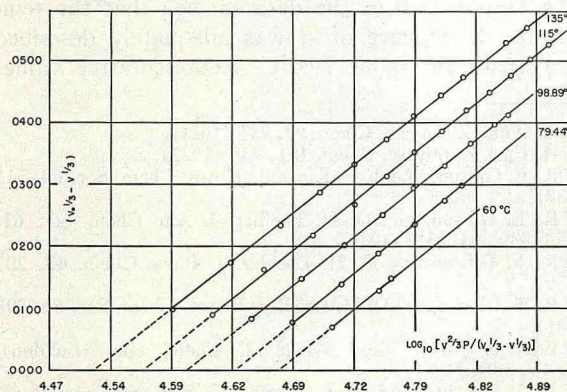


FIG. 2. The Hudleston relation for 1-alpha-naphtylpentadecane.

[29] L. J. Hudleston, Trans. Faraday Soc. 33, 97 (1937).

TABLE VI. PSU 88, 135°C.

| $P$ (bars) | $k$ (bar)$^{-1}$ |
|------------|------------------|
| Atmospheric | $12.1 \times 10^{-5}$ |
| 689 | 6.27 |
| 1378 | 4.22 |
| 3446 | 2.13 |
| 6891 | 1.18 |
| 10 336 | 0.81 |

that it could not hold as atmospheric pressure is approached.

For a given compound the plots of the Hudleston equation at a series of temperatures proved to be a family of approximately parallel lines, indicating that $B$ is constant for a given compound. The intercept $A$ approximates a linearly decreasing function of the temperature. Using the relations discovered for $A$ and $B$ it was possible to write a general Hudleston equation for each compound. Figure 2 is a representative plot of the Hudleston equation for one hydrocarbon.

## Compressibility

Compressibility is defined as $-(1/v_0)(\delta v/\delta P)_T$. Since the Tait equation analytically expressed most of the pressure-volume isotherms to within the experimental accuracy of the data, it was deemed adequate to differentiate the Tait equation to get values for the compressibilities. Using the fact that $C=0.2058v_0$, the following expression for $k$, the compressibility, is reached:

$$k = (0.08936)/(B+P).$$

An examination of the compressibilities of the hydrocarbons studied led to a number of general conclusions. For a given compound and temperature the compressibility decreases with increasing pressure, the rate of decrease becoming smaller at higher pressures, as Table VI shows. For a given structure and pressure the compressibility increases with increasing temperature. However, this increase is less marked at higher pressures as Table VII illustrates.

Pronounced structural dependence is apparent in the values of the compressibility (the effect of structure will be discussed in detail later). The effect of structure, however, tends to disappear as the pressure increases as shown in Table VIII. The disappearance of structural dependence of the compressibility can be explained by

TABLE VII. PSU 88.

| $P$ (bars) | $k$ (37.8°C) | $k$ (135°C) |
|------------|--------------|-------------|
| Atmospheric | $7.01 \times 10^{-5}$ | $12.1 \times 10^{-5}$ (bar)$^{-1}$ |
| 3446 | 1.89 | 2.13 |

considering compressibility from a molecular viewpoint. At low pressures molecules fit loosely together with a considerable amount of free space between them. The amount of free space depends upon the molecular shape and how well the molecules pack together. At low pressures the major part of the compressibility arises from crowding the molecules together, thus restricting any free rotation around C—C bonds. As higher pressures are approached this source of compressibility gradually disappears and the remaining compressibility probably is determined largely by the intermolecular repulsive forces. Since the only atoms in the compounds studied were hydrogen and carbon

TABLE VIII. Compressibility (bar)$^{-1}$

| P (bars) | 135°C | | |
|---|---|---|---|
| | PSU 174 | PSU 87 | PSU 528 |
| Atmospheric | $9.14 \times 10^{-5}$ | $11.8 \times 10^{-5}$ | $18.3 \times 10^{-5}$ |
| 3446 | 2.02 | 2.13 | 2.28 |
| 6891 | | 1.18 | 1.21 |

it is not surprising that the ultimate compressibilities approach the same value for all compounds studied.

### Effect of Structure on Compression

To examine the effect of molecular structure on volume behavior the compression was plotted against pressure. Compression, which is defined as the change in volume per unit initial volume, was determined by dividing the fully corrected changes in specific volume by the atmospheric pressure value of the volume. In Fig. 3 the compressions of PSU 174
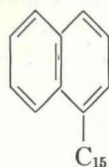
and 175
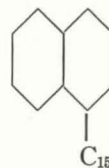
at 135°C are shown. The data at 135°C were selected to give the widest possible pressure range for the compression study. The comparative results at 135°C are in no way unique. PSU 174 and 175 differ in structure in that 174 consists of a naphtyl group with an attached chain of 15 carbon atoms whereas 175 is made up of a decalyl group with the same attached chain. The decalyl group proved to be the more com-
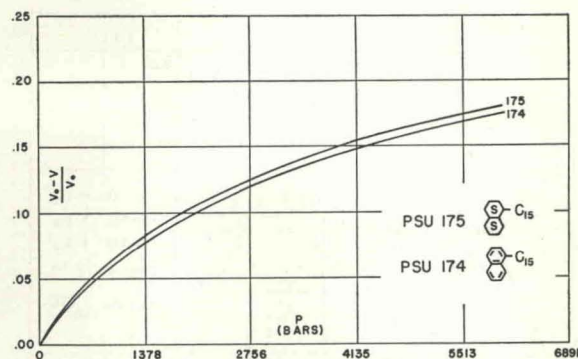
FIG. 3. Compression $(v_0-v)/v_0$ versus pressure for 1-alpha-naphtylpentadecane (PSU 174) and 1-alpha-decalylpentadecane (PSU 175) at 135°C.

pressible of the two structures. Although the difference in compression between these two compounds is small, less than 1% at 5500 bars and 135°C, the data consistently show PSU 175 to be the more compressible.

In Fig. 4 are shown the compressions of five more hydrocarbons with molecular structure such that the effect on compression of changing from straight chain groups to one or two cyclohexyl groups or one or two phenyl groups is revealed. A structural change from a straight chain to a cyclohexyl group decreases the compression, and a change from two straight chain groups to two cyclohexyl groups further reduces the value of the compression. The same sort of behavior is displayed in changing from straight chain groups to phenyl groups. Comparison of the data for PSU 88 and 87 and PSU 18 and 19 shows that the cyclohexyl compounds are more compressible than the corresponding benzenoid compounds. Again these differences are small but they occur without exception over the whole pressure and temperature range.

Figure 5 shows, first of all, the effect of increasing the length of straight chains in normal paraffins is to decrease the compression. Also shown in Fig. 5 for comparison purposes are compression data on two other
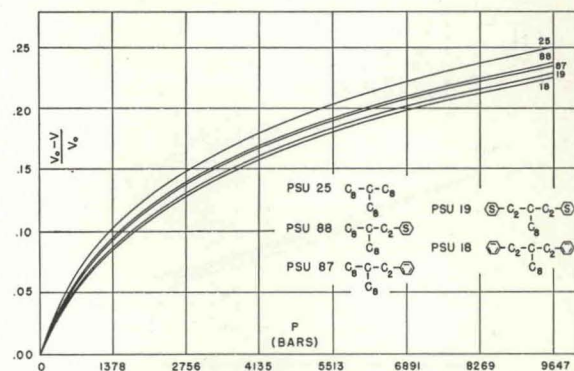
FIG. 4. Compression $(v_0-v)/v_0$ versus pressure for 9-$n$-octylheptadecane (PSU 25), 9(2-phenylethyl)heptadecane (PSU 87), 1-phenyl-3(2-phenylethyl)hendecane (PSU 18), 9(2-cyclohexylethyl)heptadecane (PSU 88), and 1-cyclohexyl-3(2-cyclohexylethyl)hendecane (PSU 19), at 135°C.

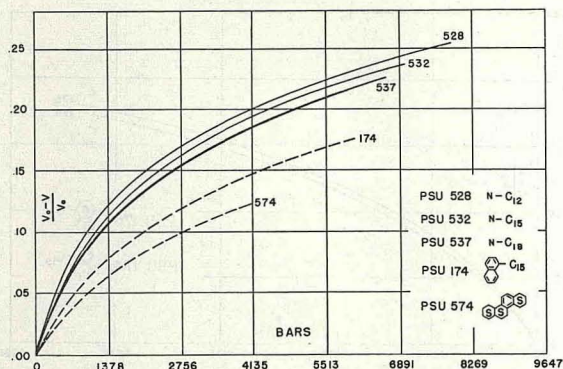FIG. 5. Compression $(v_0-v)/v_0$ versus pressure for n-dodecane (PSU 528), n-pentadecane (PSU 532), n-octadecane (PSU 537), 1-alpha-naphthylpentadecane (PSU 174), and 1, 2, 3, 4, 5, 6, 7, 8, 13, 14, 15, 16-dodecahydrochrysene (PSU 574) at 135°C.

hydrocarbons, PSU 174 and 574. PSU 174 and 528 were, respectively, the least and most compressible compounds in this present study and serve to illustrate the range of compression found in this study. PSU 574, a fused ring compound (whose PVT data were obtained by Lowitz[30] as part of a study of viscosity-temperature-pressure surfaces) proved to be even more incompressible.

Compression data for ten compounds are summarized in Fig. 6. All ten of these hydrocarbons contain 25 carbon atoms per molecule and are, therefore, of approximately the same molecular weight. From an examination of Fig. 6 one can obtain the effect of
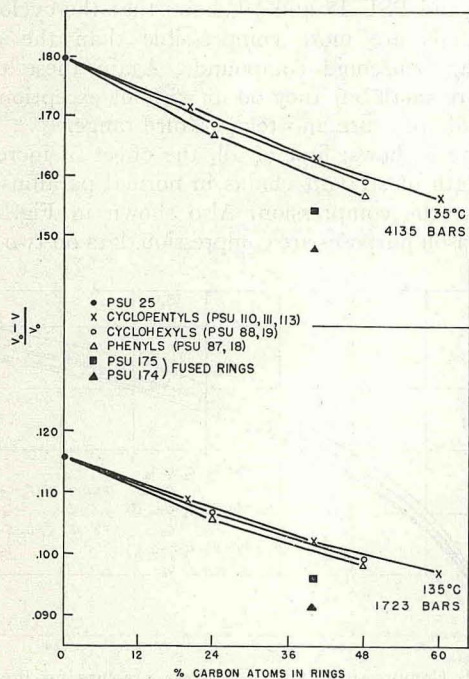


FIG. 6. Compression versus percent carbon atoms in rings.

[30] D. A. Lowitz, Ph.D. dissertation, The Pennsylvania State University (1955).

progressive cyclization on the compression. Increasing cyclization decreases the compression. The decrease in compression is a function, not only of the percent carbon atoms in rings, but of the type of rings as well. Fused ring cyclization, as exemplified by naphthyl and decalyl structures, produced the greatest decrease in the compression. The next most effective structural change in decreasing the compression was cyclization to phenyl rings followed in order by cyclization to cyclohexyl rings and cyclization to cyclopentyl rings.

The compression and the percent carbon atoms in rings form an almost linear relationship in the case of the cyclopentyls. The relationships for the other types of rings are not as well defined because these studies were not extended to the same number of compounds as in the case of the cyclopentyls. Nevertheless, the trend of decrease in compression with increasing cyclization is definitely established for the phenyl and cyclohexyl groups.
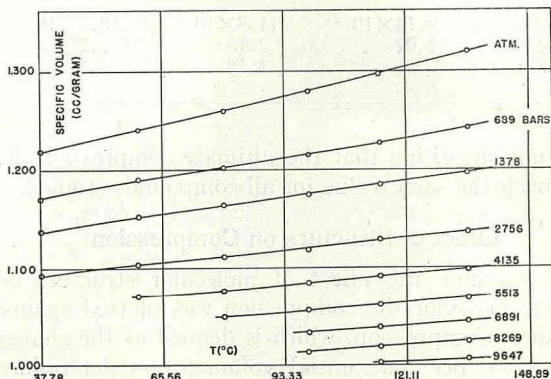


FIG. 7. Isobars for 9(2-cyclohexylethyl)heptadecane.

The most compressible compounds found in the studies of the higher molecular weight hydrocarbons possess the straight chain structure. The rotational freedom characteristic of straight chains results in a flexible, or nonrigid, structure that is relatively easy to compress. Next in order of compressibility come the branched chains. The branched chain is also a relatively nonrigid structure but has lost some of the flexibility of the straight chain structure. In going from the chain structures into ring structures the compression decreases and the key factor in this decrease is the rigidity of shape that comes with loss of rotational freedom. The fused ring compounds possess this rigidity of shape to an even higher degree than the nonfused aromatics and cycloalkanes, and proved to be decidedly less compressible than the nonfused compounds. In comparing the aromatics with the corresponding cycloalkanes it was noted that the aromatics, at atmospheric pressure and under similar temperature conditions, were always more dense. Therefore the aromatic molecules pack more closely at atmospheric pressure than do the molecules of the cycloalkanes.

This better packing results in less free space between molecules and reduces the compressibility of the aromatics as compared with the corresponding saturated hydrocarbons.

## Isobars

The isobars with specific volume as a function of temperature were plotted for each compound at 345-bar intervals. The isobars for each hydrocarbon had the same general form and were almost linear. Representative isobars are shown in Fig. 7.

The slopes of the isobars were determined from large-scale graphical plots by the use of a tangentometer. These slopes revealed a change in sign of $(\delta^2 v/\delta T^2)_P$ at elevated pressures, a phenomenon previously noted by Bridgman.[12,13] This effect is observed by noting that at lower pressures the magnitude of the slope of the isobar, $(\delta v/\delta T)_P$, increases with increasing temperature but above a certain pressure, the value of $(\delta v/\delta T)_P$ decreases with increasing temperature. Bridgman reported this sign reversal of $(\delta^2 v/\delta T^2)_P$ in the range 3100–4100 bars and also reported that the pressure of reversal appeared to decrease with increasing molecular weight. Representative values of the pressure range in which the sign reversal of $(\delta^2 v/\delta T^2)_P$ has been observed in the present study are as follows:

PSU 174    1030–1380 bars,
PSU 87     1030–1380 bars,
PSU 528    2410–2760 bars,
PSU 532    1720–2070 bars.

It was difficult to ascertain accurately the pressure of reversal for $(\delta^2 v/\delta T^2)_P$ because of scatter inherent in the isobars and the small magnitude of $(\delta^2 v/\delta T^2)_P$.

The sign reversal of $(\delta^2 v/\delta T^2)_P$ may be attributed to nonlinearity in the intermolecular forces. Large thermal expansion accompanies departure from linearity in the intermolecular forces. Or in other words, thermal expansion depends upon the anharmonic terms in the potential energy.[31] At high pressures and low temperatures the molecules may be so crowded together that the departure from linear intermolecular forces is greater than at high temperature and the same pressure. This would be consistent with a decrease in the thermal expansion as the temperature increased.

It was also noted for a given compound and temperature that the coefficient of thermal expansion, $1/v_0 (\delta v/\delta T)_P$, decreases with increasing pressure. This decrease is as much as a factor of 3 or 4 for a pressure range of 6900 bars. For example, for PSU 88 at 110°C the coefficient of thermal expansion at atmospheric pressure is $9.20 \times 10^{-4}/°C$. while at 6890 bars it is $2.63 \times 10^{-4}/°C$.
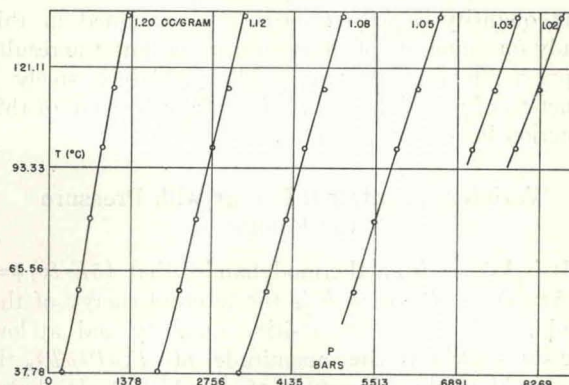


FIG. 8. Isochores for 9(2-cyclohexylethyl)heptadecane.

## Isochores

Isochores (curves of constant specific volume) were drawn over the entire range of temperature and pressure for all of the hydrocarbons studied. Isochores were drawn at intervals of 0.01 cc/g with the required pressures having been read from the pressure-volume isotherms. The isochores for various compounds all have the same general form. Representative isochores are illustrated in Fig. 8.

The slopes of the isochores were read with a tangentometer. It was especially noted that the isochores are not straight lines but that the slope of a given isochore decreases with increasing pressure and temperature. Furthermore, the slope of the isochore or pressure coefficient, $(\delta P/\delta T)_v$, for a given temperature, increases with increasing pressure as the volume decreases.

Since the isochores are not straight lines, one can state that $(\delta P/\delta T)_v$ is not a function of the volume alone. If $(\delta P/\delta T)_v$ were a function of volume alone, then $(\delta P/\delta T)_v = f_1(v)$ which could be integrated to give $P = f_1(v) T + f_2(v)$. Van der Waals' equation of state is a special case of the preceding equation. The physical interpretation of $P = f_1(v) T + f_2(v)$ is that pressure can be thought of as resulting from two mechanisms—one a function of volume alone, which at constant volume would be the same for all temperatures, and the other arising from a kinetic mechanism and dependent on the temperature. An equation of the van der Waals type did not hold for the liquids studied here (and probably will not hold for liquids in general) since $(\delta P/\delta T)_v$ is not a function of volume alone, but is dependent on the pressure and temperature. This must mean that the two pressure mechanisms interact. Bridgman[12] stated that this interaction would be expected if one considered molecules themselves to be compressible.

Gibson[23,32] has examined the quantity $T(\delta P/\delta T)_v + B$, where $B$ is the Tait equation parameter $B$, and has found this quantity to be a function of volume alone.

[31] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York 1953).

[32] R. E. Gibson and O. H. Loeffler, Ann. N. Y. Acad. Sci. **51**, 727 (1948).

The quantity $T(\delta P/\delta T)_v + B$ was examined in this study for a number of the hydrocarbons and the results support the finding that $T(\delta P/\delta T)_v + B$ is solely a function of volume. Details of the investigation of this function have been reported.[33]

## Variation of Internal Energy with Pressure and Volume

It is known from thermodynamics that $(\delta E/\delta v)_T = T(\delta P/\delta T)_v - P$ where $E$ is the internal energy of the liquid. $(\delta P/\delta T)_v$ is a positive quantity and at low pressures, where the magnitude of $T(\delta P/\delta T)_v$ is greater than the magnitude of $P$, $(\delta E/\delta v)_T$ is, therefore, positive. That is, as the volume is initially decreased under pressure, the internal energy decreases also. However, when the pressure becomes great enough that its magnitude exceeds $T(\delta P/\delta T)_v$, $(\delta E/\delta v)_T$ becomes negative and the internal energy increases with decreasing volume.

A similar analysis results when one considers the variation of internal energy with pressure. It is known that $(\delta E/\delta P)_T = -T(\delta v/\delta T)_P - P(\delta v/\delta P)_T$ and since $(\delta v/\delta T)_P$ is positive and $(\delta v/\delta P)_T$ is negative, the two terms in the right-hand member of this equation are opposite in sign. At lower pressures $T(\delta v/\delta T)_P$ is greater in magnitude than $P(\delta v/\delta P)_T$ and $(\delta E/\delta P)_T$ is negative; that is, the internal energy decreases with increasing pressure. However, the magnitude of $P(\delta v/\delta P)_T$ becomes increasingly great as the pressure increases and eventually makes $(\delta E/\delta P)_T$ positive and the internal energy then increases with increasing pressure.

The physical interpretation, in terms of molecular forces, of the phenomena described above is as follows. The resultant forces under low-pressure conditions are attractive and as the volume decreases the potential energy of mutual forces decreases. When the volume has undergone a sufficient decrease the repulsive forces become preponderant and further decreases in the volume increase the internal energy of the liquid.

It can be shown that both $(\delta E/\delta P)_T$ and $(\delta E/\delta v)_T$ change sign when the pressure exceeds the magnitude of $T(\delta P/\delta T)_v$. From the slopes of the isochores the pressure for which $P = T(\delta P/\delta T)_v$ can be found if it is within the experimental range. For example, for PSU 88 this pressure was 7240 bars at 135°C and 8270 bars at 115°C and for PSU 87 was 9100 bars at 135°C.

Bridgman[12] and Hildebrand[34] have speculated that since $(\delta E/\delta P)_T = (\delta E/\delta v)_T = 0$, when $P = T(\delta P/\delta T)_v$,

[33] Cutler, Webb, and Schiessler, J. Chem. Phys. **23**, 2466 (1955).
[34] J. H. Hildebrand, *Solubility of Non-Electrolytes* (Reinhold Publishing Corporation, New York, 1936), Chap. V.

giving a minimum energy for the liquid, that the volume of the liquid at this pressure should correspond to the volume of the liquid at 0°K. The following comparison was made for PSU 87 and 88. PSU 87; specific volume at 135°C and 9100 bars, 0.99 cc/gram, specific volume at 0°K (extrapolated linearly from known densities) 0.96 cc/gram. PSU 88; specific volume at 135°C and 7240 bars, 1.04 cc/gram, at 115°C and 8270 bars 1.02 cc/gram, and at 0°K 0.98 cc/gram.

## SUMMARY

Experimental evidence has been presented to establish the following characteristics of the volumetric behavior of liquid hydrocarbons of high molecular weight.

1. Pressure-volume isotherms can be described adequately by either the Tait equation or, for pressures above a certain minimum, whose value depends on the compound, by the Hudleston equation.

2. For the Tait equation the parameter $C$ can be predicted, for hydrocarbon liquids, from the relation $C = 0.2058v_0$.

3. Compressibility, for a given hydrocarbon, decreases with increasing pressure at constant temperature and increases with increasing temperature at constant pressure.

4. The compression, and compressibility, of the liquid hydrocarbons are strongly dependent on molecular structure. Cyclization, which decreases the rotational freedom characteristic of open chain hydrocarbons, introduces a rigidity of molecular shape which decreases the compressibility markedly. Furthermore, fused ring cyclization as exemplified by naphthyl and decalyl structures has a considerably greater effect in decreasing compressibility than cyclization to nonfused rings such as cyclopentyl, cyclohexyl, or phenyl, even at equivalent carbon atom in ring percentages.

5. The coefficient of thermal expansion, $1/v_0(\delta v/\delta T)_P$, for a given hydrocarbon, decreases with increasing pressure at constant temperature.

6. $(\delta^2 v/\delta T^2)_P$ undergoes a sign change at a certain pressure, whose value depends on the compound; $(\delta v/\delta T)_P$ increases with increasing temperature below this pressure and decreases with increasing temperature above this pressure.

7. The pressure coefficient, $(\delta P/\delta T)_v$, is not a function of volume alone but is also dependent on the temperature and pressure.

8. $T(\delta P/\delta T)_v + B$ evidently is solely a function of volume.

9. The pressure for which $(\delta E/\delta v)_T$ and $(\delta E/\delta P)_T$ are zero can be observed experimentally for compounds that can be studied to sufficiently high pressures.