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PVT Properties of Liquid n-Octane

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The PVT properties of liquid n-octane are presented for six isotherms: −15.00, 5.00, 25.00, 45.00, 65.00, and 85.00° C. The pressure ranged from atmospheric to near freezing at each temperature. The accuracy is estimated at ±0.0006 cm³/cm³. The data were fitted to the Tait equation of state at each temperature. The data were also used to obtain the Tait parameters L and J as functions of temperature. The error introduced by the temperature fitting averaged 0.041%. The worst error introduced was 0.0017 cm³/cm³.

The *PVT* data for liquid *n*-octane, as reported in the literature, are inconsistent. Furthermore, the more accurate data do not extend over a large enough range of pressure and temperature to allow the differentiation necessary to calculate accurately thermal properties.

Previous data taken in this laboratory on C_{10} to C_{16} normal alkanes showed the sylphon-bellows technique sufficiently accurate to be used for calculating properties requiring two differentiations of the data (*14*). In this work, *n*-octane is examined from −15° to 85° C at pressures from atmospheric to near freezing.

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EXPERIMENTAL

Apparatus. The operation of the *PVT* cell can be described with the aid of Figure 1. The two main components of the *PVT* cell are the bellows, marked *B* on the drawing, and the slide wire, *S*. The slide wire is a section of Karma wire approximately 1 inch in length and 0.010 inch in diameter. Karma is a trademark of the Driver-Harris Co., Harrison, N. J., and is an alloy of nickel, chromium, and aluminum. Karma wire was used as the slide wire because of its low temperature coefficient of resistivity (0 ± 10 ppm/°C), its precision drawn diameter, and its highly uniform linear conductivity (experimentally determined as
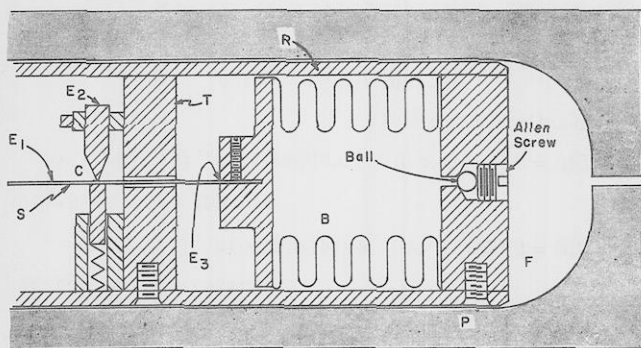
Figure 1. Detail of bellows–slide wire arrangement

3.87800 ± 0.00002 cm/ohm for the 0.010-inch diameter Karma wire) (13). There are three electrical contacts, labeled E_1, E_2, and E_3 on Figure 1, made to the Karma slide wire. The slide wire is held against the edge of contact C by a Teflon plunger-spring arrangement. Contact C is a piece of 0.010-inch diameter Karma wire soldered to a brass plate. The retainer, R, supports the bellows and the associated electrical components. The bellows is held in the retainer by three screws, marked P on the drawing.

As the bellows and sample compress longitudinally under hydrostatic load, the Karma slide wire is drawn past the fixed contact C of Figure 1. The change in length of the bellows is calculated from the change in electrical resistance across E_1, E_2, and E_3 after thermal equilibrium is attained.

A Leeds and Northrup Model G-2 Mueller bridge and a Model 2284d galvanometer and scale were used in conjunction with a four-position mercury contact commutator to make the necessary resistance measurements. The bridge had been calibrated by Leeds and Northrup using National Bureau of Standards calibrated reference resistors, and a set of correctional constants was provided with the bridge. The measuring circuit was wired to eliminate lead wire and contact resistance (13).

The pressure generating system consisted of three hydraulic handjacks and a piston intensifier. The system is capable of pressures to 200,000 psi with a maximum temperature limit on the PVT cell of 150°C. Two Heise gages, one 0- to 1500-psi gage and one 0- to 50,000-psi gage, were used for pressure measurements below 50,000 psi. These were temperature compensated and accurate to 0.1% of full scale. The two Heise gages were calibrated by the Heise Bourdon Tube Co. using a National Bureau of Standards approved dead weight tester. A report of the calibration was supplied with each gage. In addition, the calibration of the two gages was rechecked in this laboratory using a Ruska dead weight tester for the 0- to 1500-psi gage and an Aminco 100,000-psi dead weight tester for the 0- to 50,000-psi gage. For pressures above 50,000 psi, a Manganin cell pressure transducer was used in conjunction with the Mueller G-2 bridge. The Manganin cell, calibrated at 25.00°C using the Aminco 100,000-psi dead weight tester, was maintained at 25.00° ± 0.01°C during each isotherm by an Aminco constant temperature bath.

A Hallikainen constant temperature bath and Hallikainen Thermitrol controller were used to control the temperature of the PVT cell. A Sola constant voltage transformer was used as the Thermitrol's power supply. The temperature of the bath was measured to ±0.01°C with a platinum resistance thermometer previously calibrated by the National Bureau of Standards on the 1948 International Practical Temperature Scale. All isotherms were run at the set point temperature with measured variations of ±0.003°C about the set point.

Data Reduction. The change in volume of the sample in the bellows relative to the volume at atmospheric pressure

as pressure is applied to the system as a function of the following: the vacuum corrected weight of the sample in the bellows, W_{vc}, the atmospheric pressure density of the sample, $\rho_{o,T}$, the temperature and pressure corrected cross-sectional area of the bellows, $A_{P,T}$, and the change in length of the bellows with pressure, ΔL_B. Appropriate temperature and pressure corrections were applied to ΔL_B and $A_{P,T}$ to obtain the true compression of the sample as represented by Equation 1.

$$(v_o - v_i)/v_o = (\Delta L_B \cdot A_{P,T} \cdot \rho_{o,T})/W_{vc} \tag{1}$$

The quantity $(v_o - v_i)/v_o$ is the compression of the sample where v_i is the specific volume at temperature T and pressure P_i and v_o is the specific volume at temperature T and atmospheric pressure P_o.

With the exception of the atmospheric pressure density, $\rho_{o,T}$, all terms on the right-hand side of Equation 1 were obtained during the course of this study. The atmospheric pressure density, $\rho_{o,T}$, was determined by Chappelow to ±1 × 10^{-5} g/cm^3 using a hydrostatic weighing technique (4). Standard mean ocean water was used to establish the volume of his plummet at 3.98°C where the density of degassed water is 1.00000 g/ml as defined by the International Bureau of Weights and Measures. The density of degassed n-octane was then determined from −27.63 to 122.57°C.

An error analysis technique used by the National Bureau of Standards, and detailed by Mickley (10), indicates that the errors in the PVT measurements made with this system are no greater than 0.0006 cm^3/cm^3.

Materials. The research grade n-octane used to conduct this study was donated by the Phillips Petroleum Co. The n-octane was 99.92 mol % pure as stated by Phillips and no further purification was attempted. The more probable impurities were other normal paraffins and isoparaffins in the same boiling range. The sample was degassed before the bellows was filled.

RESULTS AND DISCUSSION

Experimental Data. The compression and relative volume for n-octane as a function of pressure for the −15.00°C isotherm are presented in Table I herewith. The compression is defined by Equation 1. The relative volume, V_i, is defined as $1.0000 - (v_o - v_i)/v_o$. The compression and relative volume as a function of pressure for the 5.00, 25.00, 45.00, 65.00, and 85.00°C isotherms have been deposited with the ACS Primary Publications Microfilm Depository Service (1a). No smoothing of the data has been done in Table I or in the material deposited with the Depository Service.

Representation of Experimental Data by the Tait Equation. The Tait equation has been used to represent the PVT behavior for a number of liquids (5–9, 11–14, 16). The differential form of the Tait equation is written as

$$-(\partial v_i/\partial P_i)_{T,N_j} = J/(P_i + L) \tag{2}$$

where J and L, the two Tait parameters, are functions of temperature but not pressure (13). Eduljee et al. (6) have stated that the Tait parameter, J, is independent of temperature; however, this was recently shown not to be the case for high-accuracy PVT measurements (13).

The integrated form of Equation 2 may be written in terms of the relative volume, V_i, as

$$V_i = V_o - J \ln \left[(P_i + L)/(P_o + L)\right] \tag{3}$$

where V_i is the relative volume at pressure P_i and V_o is the relative volume at pressure P_o.

The two Tait parameters were evaluated from the experimental PVT data on n-octane for each of the six isotherms by a least-squares regression technique (1). Table II is a summary of the results. In addition to the Tait

Table I. PVT Properties of n-Octane at −15.00° C

$(\rho_{c,T} = 0.73059 \text{ g/cm}^3)$

Press., atm	Compression, cm³	Relative vol, cm³	Press., atm	Compression, cm³	Relative vol, cm³
1.0	0.0000	1.0000	303.8	0.0247	0.9753
4.1	0.0001	0.9999	339.9	0.0270	0.9730
9.3	0.0003	0.9997	384.8	0.0303	0.9697
12.6	0.0006	0.9994	409.3	0.0321	0.9679
15.4	0.0008	0.9992	447.4	0.0347	0.9653
21.1	0.0013	0.9987	476.6	0.0362	0.9638
21.3	0.0014	0.9986	515.4	0.0392	0.9608
27.4	0.0030	0.9970	545.4	0.0407	0.9593
31.4	0.0035	0.9965	580.1	0.0428	0.9572
33.3	0.0037	0.9963	617.5	0.0450	0.9550
35.7	0.0033	0.9967	649.5	0.0468	0.9532
38.8	0.0034	0.9966	682.1	0.0484	0.9516
42.2	0.0034	0.9966	716.8	0.0507	0.9493
43.2	0.0036	0.9964	748.8	0.0520	0.9480
45.5	0.0033	0.9967	786.9	0.0539	0.9461
49.2	0.0051	0.9949	814.1	0.0551	0.9449
51.7	0.0051	0.9949	853.6	0.0570	0.9430
52.7	0.0052	0.9948	886.3	0.0586	0.9414
59.4	0.0059	0.9941	921.0	0.0603	0.9397
62.1	0.0063	0.9937	950.9	0.0619	0.9381
65.8	0.0061	0.9939	988.3	0.0635	0.9365
71.9	0.0067	0.9933	1027.1	0.0651	0.9349
72.0	0.0065	0.9935	1058.4	0.0664	0.9336
76.3	0.0074	0.9926	1089.7	0.0675	0.9325
79.7	0.0076	0.9924	1124.4	0.0697	0.9303
85.8	0.0081	0.9919	1160.5	0.0708	0.9292
86.8	0.0079	0.9921	1192.5	0.0723	0.9277
89.7	0.0081	0.9919	1229.9	0.0742	0.9258
93.5	0.0080	0.9920	1261.2	0.0753	0.9247
98.6	0.0083	0.9917	1286.4	0.0763	0.9237
105.8	0.0095	0.9905	1329.9	0.0778	0.9222
138.5	0.0122	0.9878	1364.6	0.0798	0.9202
171.1	0.0151	0.9849	1397.3	0.0804	0.9196
208.5	0.0178	0.9822	1435.4	0.0821	0.9179
237.8	0.0202	0.9798	1464.7	0.0831	0.9169
273.9	0.0225	0.9775			

Table II. Tait Parameters L and J for n-Octane

t, °C	L, atm	J, cm³/cm³	σ,[a] cm³/cm³
−15.00	904.78	0.086294	2.96×10^{-4}
5.00	780.97	0.086567	2.53×10^{-4}
25.00	674.64	0.087298	3.09×10^{-4}
45.00	576.65	0.087745	3.19×10^{-4}
65.00	486.01	0.087554	3.00×10^{-4}
85.00	413.65	0.089318	2.46×10^{-4}

[a] Standard deviation of the fit of the Tait equation to experimental PVT data on n-octane as defined by Equation 4.
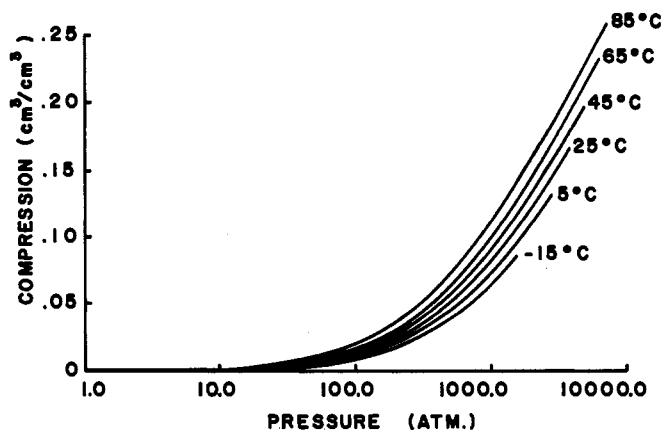

Figure 2. Smoothed compression data for liquid n-octane

Table III. Temperature Correlated Tait Parameters L and J for n-Octane

Polynomial Coefficients: t, °C

$$L(t) = 0.229609 \times 10^{-4} - 0.610650 \times 10^{-1} (t + 273.16)^2 +$$
$$0.228861 \times 10^{-2} (t + 273.16)^2$$
$$J(t) = 0.175930 \times 10^{-1} + 0.418642 \times 10^{-3} (t + 273.16) -$$
$$0.618762 \times 10^{-6} (t + 273.16)^2$$

t, °C	σ,[a] cm³/cm³
−15.00	3.75×10^{-4}
5.00	3.03×10^{-4}
25.00	4.12×10^{-4}
45.00	4.25×10^{-4}
65.00	5.53×10^{-4}
85.00	5.09×10^{-4}

[a] Standard deviation of fit of the temperature-correlated Tait parameters to experimental PVT data.

Table IV. Standard Deviation of Literature PVT Data on n-Octane as Compared with n-Octane PVT Data from This Study

Investigator	t, °C	Standard deviation,[a] cm³/cm³
Bridgman (3)	0.0	1.69×10^{-3}
	50.0	3.18×10^{-3}
Eduljee et al. (6)	0.0	1.18×10^{-3}
	25.0	3.42×10^{-3}
	40.0	1.55×10^{-3}
	60.0	1.38×10^{-3}
Boelhouwer (2)	30.0	5.65×10^{-4}
	60.0	2.84×10^{-4}

[a] Standard deviation of the fit of literature PVT data on n-octane to calculations made with temperature-correlated parameters L and J.

parameters, the standard deviation of the fit of the Tait equation to the experimental PVT data is also reported in Table II. The standard deviation of the fit of the Tait equation to the experimental data is defined as (10)

$$\sigma = \left[1/(n-1) \sum_{i=1}^{n} (d_i - \bar{d})^2 \right]^{1/2} \qquad (4)$$

where

$$d_i = V_i - V_{i_{calcd}}$$

$$\bar{d} = \left(\sum_{i=1}^{n} d_i \right) / n$$

n = number of data points

The worst deviation of any data point from the smooth curve was 0.00098 cm³/cm³.

Figure 2 represents the smoothed compression data for n-octane for the six isotherms. In order to see the difference in the fit of the Tait equation to the experimental n-octane PVT data, it was necessary to plot differences in compression as a function of pressure at constant temperature. Figure 3 is representative of the differences in raw and smoothed compression data as a function of pressure for n-octane. Figure 3 is for n-octane at 5.00° C.

The experimental PVT data for n-octane were also correlated as a function of temperature. This was done by allowing the PVT behavior to be represented by second-degree polynomials of L and J as a function of temperature. The entire data set of 461 points was correlated as a function of temperature by allowing the three variables P_i, V_i, and T to determine the six polynomial coefficient parameters

Figure 3. Difference in raw and smoothed compression data as function of pressure for *n*-octane at 5°C
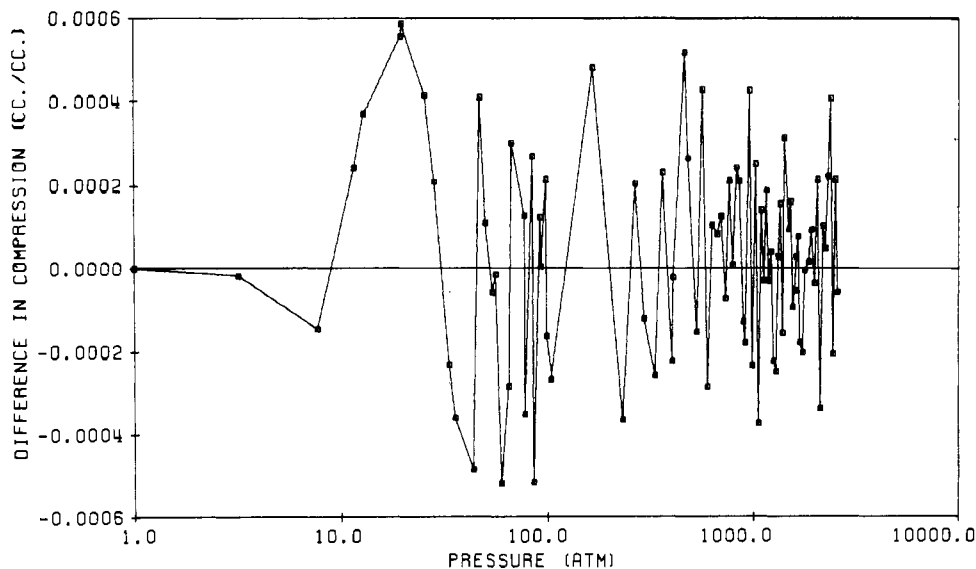
by a least-squares regression technique. Table III is a summary of the results of the temperature regression analysis. The second-degree polynomial coefficients for L and J as a function of temperature are reported in Table III. Also included in Table III are the standard deviations of the fit of the Tait equation to the experimental PVT data using the temperature correlated parameters L and J. The largest deviation of the data from these smoothed curves was $0.0017 \text{ cm}^3/\text{cm}^3$.

Comparison of Experimental *PVT* Data on *n*-Octane with Literature Data. There are three sources of PVT data for liquid *n*-octane in the literature (2, 3, 6). A comparison was made between each set of literature PVT data and the temperature correlated Tait equation calculations. A summary of the results is contained in Table IV.

The standard deviations of the fit of the PVT data from previous investigations to the Tait equation calculations, using the temperature correlated parameters, is within the estimated accuracy of the earlier investigations (1). The largest deviation was from the data set of Bridgman and was $-0.0084 \text{ cm}^3/\text{cm}^3$. The data Bridgman reports were derived from a graphical representation of the compression as a function of pressure. In the case of Eduljee et al. and Boelhouwer, smoothed data were reported in the literature. The data of Eduljee et al. were smoothed using the Tait equation; however, J was assumed independent of temperature. The data that Boelhouwer reports were apparently smoothed using the Hudleston equation.

ACKNOWLEDGMENT

NOMENCLATURE

$A_{P,T}$ = cross-sectional area of the sylphon-bellows, cm^2
J = Tait coefficient, cm^3/cm^3
L = Tait coefficient, atm
ΔL_B = change in length of the sylphon-bellows as a function of P and T, cm
P_o = atmospheric pressure, atm
P_i = pressure, atm
t = temperature, °C
T = temperature, °K
v_o = atmospheric pressure specific volume, cm^3/g
v_i = specific volume at ith pressure, cm^3/g
V_o = atmospheric pressure relative volume, cm^3/cm^3
V_i = relative volume at ith pressure, cm^3/cm^3

V_{calcd}^i = relative volume at ith pressure calculated from Tait equation, cm^3/cm^3
W_{uc} = vacuum corrected weight of sample in bellows, gram
σ = standard deviation, cm^3/cm^3
$\rho_{o,T}$ = atmospheric pressure density at tempeeature T, g/cm^3

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