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Compressions of Liquids

This three-part paper reports on the first step of a study of the liquid state initiated in 1954 by Union Carbide Chemicals Company. The ultimate objectives of this program are to elucidate the mechanism of the flow process and to write an equation of state that is valid continuously from the melting point through the ideal-gas region.

Only the compressions of the *n*-alkanes (ratios of the volumes under the pressures of measurement to the volume under the initial pressure at the same temperature) are here considered. An accuracy of four significant figures in the measurement was sought to enable the subsequent calculation of the thermodynamic properties of these liquids to be made with equivalent accuracy.

I. Apparatus and Method of Measurement

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A novel type of piezometer used to measure the compressions of liquids from 20° to 300°C. and from 1 to 4,000 kg./sq. cm. is described. The accuracy anticipated is 4 parts in 10,000.

The four essential operations involved in the determination of the compressions of liquids are measurements of volume, pressure, temperature, and mass of the sample. Of these the determination of volume with an accuracy better than one part in 10,000 under pressures up to 4,000 kg./sq. cm. and temperatures up to 300°C. was the most difficult problem experimentally. Several known methods of measurement were considered and rejected. For example the method of Beattie (*1*), which depends upon the accuracy of the calibrated mercury injector and the sample bulb, was not applicable beyond the pressure range of 0 to 500 kg./sq. cm. The piston-displacement method of Bridgman (*2*) has limited accuracy in the lower pressure range because of friction and is not easily adapted for temperatures higher than 100°C. The accuracy of the method of metallic bellows (*3*) suffers from the inelastic hysteresis of the bellows. The glass piezometer of Adams and Gibson (*4*) allows determination of only one volume at one filling and therefore is too slow. The glass piezometer with sealed-in contacts used extensively by Michels (*5*) and his co-workers has high accuracy but is not operable above 200°C. because the mercury dissolves the platinum contacts at the higher temperatures. Since none of these and other known methods were entirely satisfactory for the purpose of this investigation, a novel type of piezometer was developed.

Although the piezometer is the most critical part of the apparatus, the other components such as the pressure plant, the pressure gauge, and the temperature control will also be described because they are all functionally interconnected.

APPARATUS

The piezometers to be described were based on the idea that the displacement of a small iron core could be measured from the outside of a pressure container made of an austenitic, nonmagnetic steel by means of a linear differential transformer (*6*). The iron core floated on the surface of mercury enclosing the liquid under test.

The piezometers were made of lengths (about 19 in.) of precision-drawn, thin-walled stainless steel (type 321) tubing (0.097-in. O.D., 0.005-in. wall) terminated by screw closures at the top and mercury valves at the bottom. During measurements the piezometer was positioned in a pressure container consisting of thick-walled, high-pressure stainless steel (type 316) tubing (0.375-in. O.D., 0.125-in. I.D.) which was filled with light mineral oil as a pressure-transmitting medium. The pressure was transmitted to the sample via a column of mercury which communicated with the oil medium in the mercury cup at the bottom of the apparatus (Figure 1).

The construction of the piezometer is shown in detail in Figure 2. The top, which was silver-soldered to the stainless steel piezometer tube, was provided with a closure consisting of a steel socket set screw (No. 2-56, ½ in. long) fitting into a cone seat with a 60 deg. angle. The sample, introduced into the piezometer through the top with a long hypodermic syringe, filled it to the cone seat. Then the socket screw was put in and tightened with a miniature wrench. Repeated tests with a helium-leak detector proved that this seal remained completely tight over the whole temperature range.

The small lateral dimensions of the piezometer resulted in a considerable saving on the volume of sample and in a great reduction of the thermal capacity of the entire apparatus. The length of the sample column was sufficient to allow accurate determination of the compression; in a typical arrangement the sample column was approximately 100 mm. long, its length being determined by readings on the external micrometer directly to 0.01 mm. (Five microns can be estimated on the dial.)

Volume Measurement

The volume of the sample in the piezometer was essentially the volume between the electromagnetic centers of the plug at the top and the float that rode on the mercury column.

These electromagnetic centers were located from without the apparatus by means of two small linear differential transformers, which slid with small clearance over the surface of the pressure vessel. These two coils were mounted securely on a stainless steel rod so that their distance apart was fixed (*a* in Figure 1). An Invar wire passing over a pulley connected the coil suspension with a precision micrometer slide. It was necessary to use two coils because the micrometer slide commercially available did not have a span large enough to cover the whole length of the sample column directly.

The transformers were connected to an A.C. 1,000 cycles/sec. bridge with a vacuum-tube voltmeter as a null indicator (*7*). Either coil might be switched into this circuit at will. To balance the bridge one of the coils was moved until either the plug or the float, depending on which coil was moved, lay in the exact electromagnetic center of that coil. This position, indicated by a very sharp minimum deflection of the voltmeter, could be located easily to within 5 μ on the dial scale of the micrometer. Manipulation of the dial thus permitted one to center the top coil on the plug and the bottom coil on the float.

The difference between these two readings x established the distance

tween the float and the plug. Thus a was the difference between two ls and x the difference between the readings of the micrometer, the th of sample in the piezometer ld be $X = x + a$. The volume of ple contained in the instrument the temperature and pressure of surement could then be determined m the length X, the cross-sectional A of the piezometer, and the ini- volume.

easurement of Mass

The mass of the sample contained the piezometer was measured by ect weighing of the piezometer be- and after filling it with the sample. simple plug valve at the bottom of the zometer made it possible to introduce predetermined amount of mercury; n the piezometer was weighed before ng filled with sample, as described above. ter the two weights had been obtained, valve was opened by rotating it with key until a small inner hole lined up h a similar hole in the wall of the meter. This was done with the piezo- er dipping into the mercury reservoir the base of the apparatus (Figure 1). The weight of the sample was also ked by weighing the filling pipette podermic syringe) before and after sample was transferred to the piezo- er. By either method the mass could weighed to 0.2 or 0.3 mg, but on a sample weight of 0.3 g. this represented accuracy of only one part in 1,000, which is at least an order of magnitude less than the accuracy attainable in the measurements of pressure, volume, and temperature. For this and other reasons the mass of sample was determined by indirect methods, as described in a companion paper (*8*).

Temperature Control and Measurement

Because the steel piezometer with its surrounding pressure vessel represented a relatively small mass of low heat capacity, the temperature control was simplified with respect to both changing from one temperature to another and maintaining a fixed temperature accurately during a set of volume measurements at various pressures.

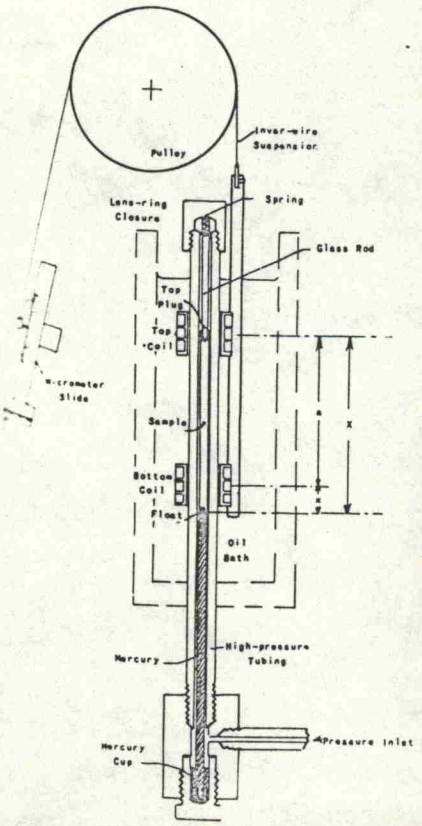
The pressure vessel containing the piezometer and surrounded by the two differential transformer coils was immersed in an oil bath 3 in. in diameter and extending approximately 8 in. above and 5 in. below the sample. The bath was insulated with magnesia-pipe insulation and asbestos soaked with water glass. Two heaters were employed; one, an electric heating tape, was wound spirally around the outside of the oil bath container, and the other was an immersion heater inside the oil bath. Dow-Corning No. 710 fluid was used as the heat transfer medium, and a small electric stirrer provided adequate circulation. The external heater was controlled manually by a variac; the immersion heater was connected to a thyratron controller, but it was found that even better temperature control could be maintained during the period of a run by manual operation of the variac. The vertical temperature gradients were checked by means of three thermocouples attached to the steel tube containing the piezometer, and the variations never exceeded a few hundredths of a degree. The temperature was maintained uniform to within $\pm 0.1°C.$, but the actual temperature was measured to five significant figures at the moment of each measurement of volume. Temperatures were measured with a platinum resistance thermometer and Mueller resistance bridge.

Pressure Measurement

The dead-weight or free-piston gauge was chosen for the measurement of high pressures because of its accuracy and its ability to maintain the pressure constant during operation. In such a gauge the internal pressure in a system is balanced by the force of a known weight acting upon a piston of known area. Two conditions must be satisfied for the practical application of this principle: first, there must be negligible friction between the piston and the cylinder walls, and, second, there must be little leak of the pressure-transmitting oil. These conditions are resolved by the rotation of the piston above the critical velocity so that a continuous film of oil is maintained.

The Michels dead-weight gauge, or pressure balance, which became available shortly after this project was started, consists essentially of a differential piston moving in a cylinder that contains two coaxial bores. The cylinder is mounted in a frame, and the piston is connected to a weight-carrying shaft at the bottom and a pointer arm at the top. The assembled pressure balance, as made by the 'T Hart Company, is shown in Figure 3.

The piston is a tight fit in the cylinder until pressure is applied, the hydraulic pressure causing a slight expansion in the



Schematic diagram of steel piezometer measuring assembly (not a scale drawing; mechanical details omitted).

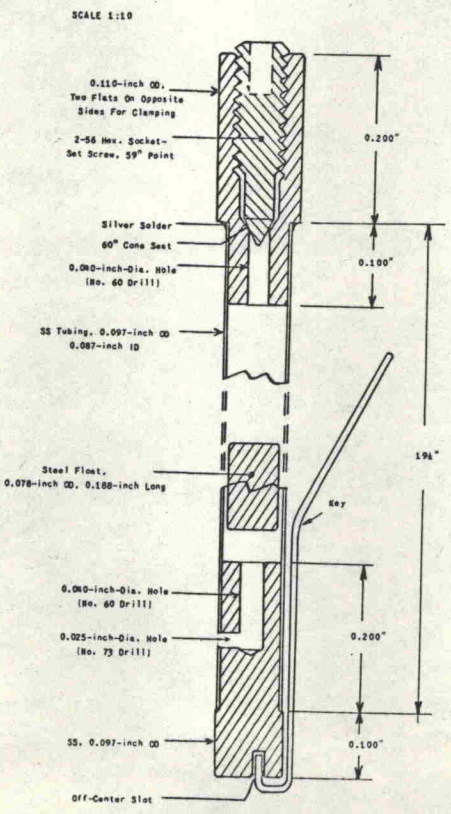


Fig. 2. Steel piezometer.

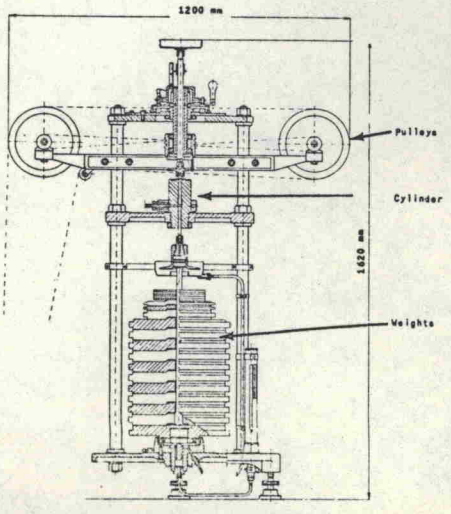


Fig. 3. Michels pressure balance.

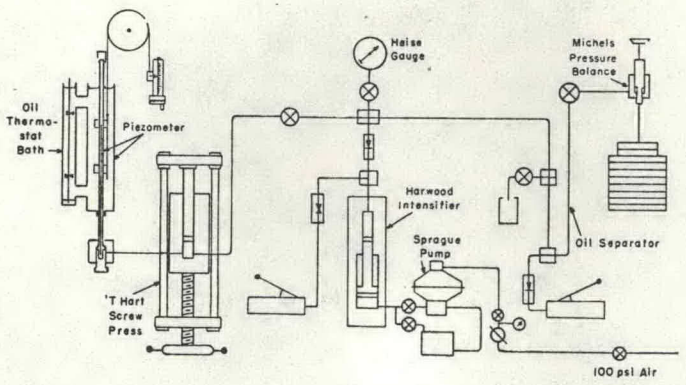


Fig. 4. Pressure plant.

cylinder walls and also a slight decrease in the area of the piston. Under these conditions the piston can rotate freely, and there is sufficient leakage to ensure continuous oil-film lubrication. A motor-driven pulley system rotates the piston and the column of weights above the critical velocity of about 50 to 60 rev./min. At the time of measurement a clutch is disengaged, and the piston and weights can therefore rotate freely by their own momentum. A mixture of 75% Shell Talpa 30 and 25% Shell Diala AX (by volume), having a viscosity of approximately 80 centipoises at 25°C., was found to be satisfactory. Under pressure the piston and weights can fall through 2 cm. of free travel. With an oil of proper viscosity a good cylinder with piston and weights rotating freely takes 5 to 10 min. to fall this 2 cm.

The Michels pressure balance has a series of six measuring cylinders that cover a range from 118 to 4,000 kg./sq. cm. There are twelve 50-kg., one 10-kg., two 5-kg., and five 1-kg. weights, all calibrated to 0.1 g.

For low pressures a Bourdon-tube gauge was employed which, over the range of 0 to 250 kg./sq. cm., had an accuracy of better than 1 part in 1,000, as demonstrated repeatedly by checks against the Michels pressure balance.

Pressure Plant

The diagram of the pressure plant is shown in Figure 4. Pressures up to 8,000 kg./sq. cm. can be generated by means of a Harwood intensifier operated by a 1,500-kg./sq. cm. Sprague air/oil booster pump or by a Blackhawk hand pump. A screw press allows fine adjustments of volume and pressure directly on the high-pressure side (up to 4,000 kg./sq. cm.).

The high-pressure vessel consists of a vertical section of ⅜-in. O.D. by ⅛-in. I.D. cold-drawn stainless steel tubing, approximately 40 in. long, connected to the various components of the system through 5/16-in. O.D. by 1/16-in. I.D. cold-drawn stainless steel (type 316) tubing which was proof tested by the supplier at 130,000 lb./sq. in. The rupture pressure is 20,000 to 40,000 lb./sq. in. above the proof test. Harwood series 5 M fittings, designed for service to 100,000 lb./sq. in., are used for connecting the various components.

The pressure-transmitting fluid is Shell Diala AX, which has a viscosity of approximately 30 centipoises at 25°C. and can withstand the maximum operating temperature (300°C.) without excessive decomposition. Its viscosity rises rather rapidly with pressure. Thus in the upper limit of the working range (4,000 kg./sq. cm.) the time necessary to reach equilibrium between the pressure gauge and the pressure vessel may be a minute or more, which makes it difficult to obtain pressure equalization throughout the system in the time allowed for the piston to sink freely on the leaking oil film.

Since the pressure balance requires a different type of oil for satisfactory operation, a fluid separator, consisting of a 4-ft. vertical section of the same ⅜-in. O.D. by ⅛-in. I.D. high-pressure tubing, was inserted. A second Blackhawk pump supplied fresh balance oil from a reservoir through a high-pressure check valve.

CALIBRATION

Volume-Measuring Instrument

The cross-sectional areas of the piezometers were determined at atmospheric pressure by weighing small increments of mercury released from the instrument and observing the corresponding drop in the level of the steel float by means of the sensing coil. From the density of mercury the volume of mercury released is computed. This volume divided by the corresponding difference in level is equal to the area of cross section. The precision-drawn polished stainless steel tubing was found to be uniform to better than ± 0.05% in cross section over the length used.

The setting constant a, which represents essentially the distance between the electromagnetic centers of the two sensing coils, can be determined by filling the sample space with a known volume of liquid. The difference between the top and bottom coil readings added to the length of the column of liquid is equal to the setting constant. As long as the distance between the coils is mechanically fixed, and if the float and the plug are not changed, the value of the setting constant is fix except for the change resulting fr the thermal expansion of the apparat The accuracy of the measurements, duced as explained in the succeedi papers, does not depend on the curacy of the setting constant, sin the extrapolated zero-pressure volum are shown to be far more accurate th the initial volumes computed from lo pressure measurements by use of t setting constant.

The change in the cross-sectio area of the piezometer as a result the thermal expansion of the me must be taken into account, but a change in the length of the piezomet or in the column of mercury inside it immaterial, since the length of t column of sample is measured ind pendently of its surroundings.

The temperature dependence of t setting constant results from the lin expansion of the section of the stainl steel suspension rod between the sen ing coils; the value of $1.62 \cdot 10^{-5}$ deg. was used for the thermal expansion c efficient of the steel used (type 321 Similarly the thermal expansion caus an increase of the cross-sectional ar of the piezometer at a rate of 3.24 10^{-5} deg.$^{-1}$

Hydrostatic pressure decreases t cross-sectional area of the piezomet tubing by a factor of approximatel $(1 - 3.9 \cdot 10^{-7} p)$, where p is in kg. sq. cm. A series of test runs with pu water up to pressures of 3,000 kg./s cm. indicated that the compression actually smaller than the value est mated from the formula above a below the limits of observational a curacy.

The combined experimental erro involved allowed the measurements volume to be made with an accura of one part in 10,000 at all temper tures and at all pressures except tho in the neighborhood of 1 atm. T loss of accuracy at very low pressur is presumably occasioned by a chan in the shape of the meniscus at t mercury-sample interface.

Temperature-Measuring Instrument

The platinum resistance thermomet was calibrated by the manufacturer comparison with a platinum resistan thermometer certified by the Natio Bureau of Standards. One check of t resistance at the ice point agreed e actly with the manufacturer's calib tion; which assures an accuracy in t measurement of temperature of at le one part in 10,000.

Pressure-Measuring Instrument

The calibration of the dead-weig gauge was supplied by the ma facturer. Certificates of calibration The Netherlands Bureau of Standa

ompanied the weights and cylinders, aranteeing an accuracy of one part 10,000 in the measurement of pres-

Over-All Accuracy

When one combines the errors in measurement of temperature and ume, a conservative estimate of the bable over-all accuracy of meas-ment may be placed at 4 parts in 000, which assures four significant res in specific volume. [Statistical lyses of the data on two compounds, ptane and *n*-eicosane, described in a companion paper (*8*), indicate that the over-all accuracy for the entire range of temperatures and pressures is more likely to be of the order of 3 parts in 10,000.]

Over 4,000 measurements of volume under pressure were made in the course of this program. The presentation and complete evaluation of these and other liquid *n*-alkane data is the subject of the companion papers (*8*, *9*).

ACKNOWLEDGMENT

J. A. Beattie of the Massachusetts Institute of Technology and A. Michels of the University of Amsterdam served as consultants on the experimental phases of this project and contributed to its successful outcome in many ways. R. W. Zwanzig of Johns Hopkins University and J. C. Poirier of Duke University were retained as consultants on other phases of the project. The experimental work was carried out at Ohio State Research Foundation, Columbus, Ohio (preparation of *n*-triacontane and *n*-tetracontane) and at Arthur D. Little, Inc., Acorn Park, Cambridge, Massachusetts (measurements of volume under pressure), under contracts with Union Carbide Chemicals Company.

II. Critical Evaluation of New *n*-Alkane Data: *n*-Heptane to *n*-Tetracontane

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New measurements of the volumes of liquid *n*-alkanes of 7, 9, 11, 13, 17, 20, 30, and 40 carbon atoms over a range of temperatures from 20° to 300°C. and pressures from 0 to 4,000 kg./sq. cm. have been made. These volume measurements are here reduced to compressions $(vol^p_T)/(vol^o_T)$, and the accuracy of the measurements has been determined. Analysis of the data for *n*-heptane and *n*-eicosane shows that the order of accuracy of the compressions of each of these compounds appears to be approximately 3 parts in 10,000. Evaluation of random multiple measurements on the remaining six compounds indicates that their over-all accuracy is likewise of this same order.

The volumes of small samples of *n*-alkanes, from 7 to 40 carbons, were measured by Simon and Cornish number of temperatures from 20° 300°C. and over a range of pressures from 0 to 4,000 kg./sq. cm., with apparatus and method described in prior paper (*10*). This method has advantage of very high accuracy the measurement of volumes under sure, but it does not afford equivaaccuracy in the direct measureof the weight of the material volume is being measured. It therefore necessary to resort to inmeans of determining the sample ght.

Also this procedure measures volvery accurately under high pres- but somewhat less accurately at pressures. Therefore, to realize the advantage of the method it is nec- to establish the values of the pressure volumes with more cer- than is possible by extrapolating wer pressure values alone.

procedure was devised for making direct extrapolation to zero pres- the volumes measured at higher es which gives values fully as te as the measurements. When d to the Simon and Cornish data, rocedure permits the results to be d as compressions or ratios of lume at the pressure of measurement to the zero-pressure volume $(vol^p_T)/(vol^o_T)$.

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PURITY OF SAMPLES

The preparation and characterization of the samples of *n*-heptane, *n*-nonane, *n*-undecane, *n*-tridecane, and *n*-heptadecane used in this study have been described elsewhere (*11*). The remaining pure compound *n*-eicosane, was synthesized as follows. Decanol-1, was purified and brominated with anhydrous hydrogen bromide at 100°C. The purified 1-bromodecane was converted to *n*-eicosane by a Wurtz reaction with sodium. The crude distilled product was hydrogenated and fractionated, the fractions of common density being combined. The composite had a freezing point of 36.51°C.; the freezing point of pure *n*-eicosane is reported (*12*) to be 36.8°C.

The other two samples were characterized as follows: *n*-tricontane freezing point 65.512°C., purity (*13*) 99.48%; *n*-tetracontane freezing point 81.030°C., purity 98.6%.

DETERMINATION OF ZERO-PRESSURE VOLUME

Linear extrapolation of the volumes of sample under pressure is satisfactory at temperatures well below the normal boiling point of the substance being measured, but this method fails in the neighborhood of the normal boiling point and is obviously inapplicable above this temperature. An indirect extrapolation procedure was therefore devised which makes use of a pressure-volume relationship that has so far received very little attention in this country. This relationship used by Bett, Weale, and Newitt (*14*) for evaluating data on the compression of liquids, was originally proposed by Hudleston (*15*):

$$\ln \frac{P(vol^p_T)^{2/3}}{(vol^o_T)^{1/3}-(vol^p_T)^{1/3}} = C_1 + C_2[(vol^o_T)^{1/3}-(vol^p_T)^{1/3}]$$

One of the features of the Hudleston equation is that at low pressures the left-hand member of the equation is very sensitive to small changes in the zero-pressure volume. As the pressure is reduced in the low-pressure region, $(vol^p_T)^{1/3}$ approaches $(vol^o_T)^{1/3}$ and the denominator becomes vanishingly small. A slight error in $(vol^o_T)^{1/3}$ therefore makes a large difference in the quotient at the limit. Since the fit of data to the Hudleston equation is determined principally by the higher pressure points, deviations of the lower pressure points generally suggest an error in the value assigned to $(vol^o_T)^{1/3}$. This feature of the Hudleston equation makes it ideal for the indirect extrapolation of the volumes to the zero-pressure value, as it involves simply trying different values of $(vol^o_T)^{1/3}$ until a value is found that provides the best fit of the lower pressure points to the line determined by the higher pressure points. In this way the best fitting values of (vol^o_T) were determined for each compound at all temperatures of measurements, thereby enabling the compressions to be calcu-

Table 2. Precision of Measurements, *n*-Heptane Deviations in Specific Volume from the Mean of Duplicate Measurements

Temperature, °C.	Pressure range, bars	No. of duplicate measurements	SPE, %
30	116.1 to 3011	18	0.006
50	98.1 to 3011	20	0.006
100	116.1 to 3011	19	0.013
150	39.2 to 1866	17	0.053
200	116.1 to 1577	18	0.012
250	312.3 to 1015	11	0.046
300	508.5 to 1015	6	0.068
		109	

lated with an accuracy as good as the volume measurements themselves.

TYPICAL DATA

As it will be shown in the succeeding paper (9) that the compressions can be reproduced from equations with an accuracy equal in most cases to that of the measurements, only a few typical results for each compound will be given. These data have been chosen to cover the pressure range of the measurements, the points being selected at identical pressures wherever possible.*

PRECISION AND ACCURACY OF MEASUREMENTS

General Considerations

It was first necessary to establish the validity of the extrapolation to the zero-pressure volume by means of the Hudleston equation. The approximately 700 measurements made on *n*-heptane and *n*-eicosane were selected for this purpose for several reasons. *n*-Heptane is the lowest molecular weight compound measured by Simon and Cornish, whereas *n*-eicosane is the lowest molecular weight compound of the group measured which had a normal boiling point substantially above the highest temperature of measurement. Thus the maximum molecular weight and temperature ranges that it is practical to deal with are encompassed by these two compounds. Two independent runs were made with *n*-heptane, in each of which the initial sample filling was used at all temperatures of measurement. This coincidence enabled calculation of the specific volumes of *n*-heptane under pressure at all temperatures, which was desirable because, *n*-heptane having been extensively studied by others, comparisons were possible. With *n*-eicosane specific volumes under pressure could be calculated at all temperatures, since atmospheric-pressure densities were available over the entire range of temperatures.

* Data have been deposited as Table 1, document 6127, with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

PRECISION OF THE MEASUREMENTS ON N-HEPTANE

The zero-pressure volume is actually the volume of a hypothetical liquid of zero vapor pressure. At temperatures well below the normal boiling point the density of such a liquid should not differ appreciably from the atmospheric-pressure density of a real liquid. Validation of the Hudleston equation for *n*-heptane was therefore carried out in two parallel runs. In each case the weight of the sample in the piezometer was measured (independently of any Hudleston equation calculation) at each of two temperatures. The results were as follows:

Temperature, °C.	Measured weight, run A, g.	Avg., g.	Measured weight, run B, g.	Avg., g.
30	0.30934	0.30948	0.29943	0.29924
50	0.30961		0.29905	

The volumes in the piezometer were measured over a considerable range of pressures at each of these two temperatures and were converted to specific volumes by dividing each by the average measured weight for each of the two runs. A statistical analysis of the differences between the two runs at identical pressures and temperatures showed the root-mean-square deviation from the mean (standard percentage error, or SPE) for both 18 points at 30°C. and 20 points at 50°C. to be 0.006%.

Since the specific volumes from both runs were practically identical, all the values at each temperature were thrown together and fitted to a single Hudleston plot. The value of v°_T giving the best fit to the Hudleston line was then determined at each temperature. The results were as follow:

Temperature, °C.	Calculated v°_T	$1/\rho^\circ_T$ from reference 12
30	1.4807	1.4808
50	1.5191	1.5191

The agreement is one part in 14,808 for 30° and exact for 50°, which establishes the fact that the extrapolation of higher pressure volumes to atmospheric pressure by the Hudleston equation is valid for *n*-heptane.

The measured volumes for each run were converted to specific volumes by dividing them by the corresponding average of the sample weights computed at 30° and 50°C. The fractional deviation from the mean was calculated for each pair of points, and the SPE was determined with the results shown in Table 2. The over-all SPE in specific volume for 109 duplicate points was 0.031%.

Table 3. Precision of Measurements, *n*-Heptane, 0 to 3,000 Bars. Deviations of Calculated from Observed Values of Specific Volume, (IBM Run 5)

Temperature, °C.	No. of points	SPE, %
30	9	0.015
50	9	0.004
100	9	0.011
150	9	0.018
200	9	0.046
250	6*	0.052
300	4*	0.053
	55	

* At temperatures in the neighborhood of and above the critical temperature the lower pressure points lie above the line determined by the higher pressure points, because the zero-pressure volume may equal or exceed the volume at the critical temperature and pressure. Thus at 250°C. it was necessary to reject values through 214.2 bars and at 300°C. values through 508.5 bars.

CALCULATION OF SPECIFIC VOLUME BY HUDLESTON EQUATION

For a single substance the values of C_1 and C_2 of the Hudleston equation are somewhat dependent on the quantity of sample taken, since if $C_1 = A$ and $C_2 = B$ when the sample is 1 g. for any other weight of sample w, $C_1 = A + \ln w^{1/3}$ and $C_2 = B/w$. Therefore when comparing Hudleston parameters one must deal with the same quantity of sample.

The zero-pressure specific volume for *n*-heptane at the various temperatures of measurement were calculated by dividing the extrapolated zero-pressure volumes by the average of the 30° and 50°C. sample weights. The values of *A* and *B* were calculated from the data by the method of least squares.

The extreme accuracy with which the Hudleston equation, with the parameters referred to, reproduces the

Table 4. Hudleston Parameters for *n*-Heptane, Melting Point, −90.61°; Boiling Point 98.43°C.

t., °C.	*A* (From velocity of sound)	*A* (From compressions)	*B*	$(v^0_T)^{1/3}$
0	10.254	10.25	13.2	1.1259
0	10.254	10.25	12.9	1.1259
4.44	10.221	10.22	13.2	1.1280
25	10.005	10.12	12.3	1.1375
25	10.065	10.06	12.9	1.1375
30	10.026	10.023	13.18	1.1398
30	10.026			
37.78	9.964	9.95	13.2	1.1435
40	9.945	9.94	12.8	1.1447
50	9.862	9.854	13.16	1.1495
50	9.862	9.80	13.3	1.1492
60	9.776	9.77	12.8	1.1548
71.11	9.675	9.67	13.2	1.1608
95	9.441	9.43	13.2	1.1745
100	9.388	9.365	13.18	1.1776
100	9.388			
104.44	9.341	9.32	13.2	1.1810
137.78		8.86	12.7	1.2055
150		8.694	13.27	1.2149
150		8.72	13.5	1.2133
171.11		8.40	13.0	1.2327
200		7.566	13.65	1.2756
200		7.64	13.9	1.2713
204.44		7.44	13.9	1.2800
237.78		5.86	14.5	1.3625
250		4.752	14.25	1.4300
250		4.90	13.5	1.4300
300		−17.79	15.60	2.7531

[illegible] of A in column 4 that are carried to three decimal places were calculated from data of [illegible] and Cornish by the method of least squares. All others were obtained graphically. Data of [illegible] 23 do not extend to high enough pressures to determine the Hudleston line accurately at [illegible] 100°C. Column 3 gives the values of A calculated from velocity-of-sound data as explained [illegible] text.

[illegible]ved specific volumes for *n*-heptane [illegible]shown by a machine calculation [illegible] on the IBM-650 computer. Tem[illegible]tures and pressures were chosen [illegible] calculations that exactly dupli[illegible] certain Simon and Cornish meas[illegible]nts, and so deviations of the cal[illegible]ted from the measured values [illegible] be observed directly. Calcula[illegible]t each of the following pressures: [illegible] 214.2, 312.3, 508.5, 1,051, [illegible] 2,089, and 3,011 bars were [illegible]t each of the following tempera[illegible]30°, 50°, 100°, 150°, 200°, [illegible]nd 300°C. (IBM run 5).

[illegible] SPE of the deviations calcu[illegible]rom the measured specific vol[illegible]are given in Table 3. It will be [illegible]hat at 30°, 50°, and 100°C. (up [illegible]roximately the normal boiling [illegible]the Hudleston equation dupli[illegible]the specific volumes fully as ac[illegible]as the values themselves were [illegible]nd at these three temperatures, [illegible]s above 100° the agreement, [illegible]ood, diminishes as the tempera[illegible]the measurement increases. The [illegible]the entire spread of tempera[illegible]pressures for 55 points [illegible] in accordance with the [illegible]f measurements at each tem[illegible]) is 0.025%.

INDEPENDENT CHECK OF HUDLESTON INTERCEPTS

Bett, Weale, and Newitt (*14*) point out that the intercepts of the Hudleston lines can be checked independently of compression measurements if data on the velocity of sound, specific heat, coefficient of expansion at 1 atm., and liquid density are available at the temperatures of interest. Such data were available on *n*-heptane (*16*) up to 50°C. and were extrapolated up to 100°C. (*17, 18*). The results of these calculations are shown in column 3 of Table 4. The agreement of the Hudleston *A*'s calculated from velocity of sound data with those calculated from the authors' compression data is excellent.

COMPARISON WITH DATA OF OTHERS

For a further check on the Simon and Cornish data, calculations of the best values of the Hudleston parameters were made on published *n*-heptane data of other investigators. These results are shown in columns 4 and 5 of Table 4. The values of *A* from these and other sources are shown on Figure 5. It will be observed that the Hudleston *A*'s calculated from the authors' compressions (open circles) fall on the smooth curve running through most of the *A*'s calculated from the data of other investigators.

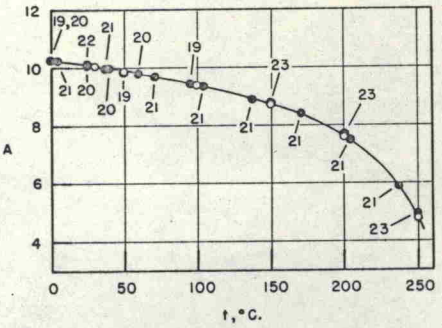


Fig. 5. *n*-Heptane. [Numbers refer to literature. Open circles are data of Simon and Cornish (*24*)].

ESTIMATE OF THE ACCURACY OF THE *N*-HEPTANE DATA

The following factors have been weighed in arriving at an estimate of the accuracy of the *n*-heptane data.

1. The root-mean-square percentage deviation from the mean of duplicate measurements of specific volume at 109 different temperatures and/or pressures was 0.031%.

2. Values of specific volume calculated from the Hudleston equation differed from the observed average specific volumes at 55 points with an SPE of 0.025%.

3. Since the sample weight is the product of the atmospheric-pressure density and the extrapolated zero-pressure volume at temperatures well below the normal boiling point, the Pv isotherms must extrapolate to $1/\rho$, at these temperatures.

4. The Hudleston *A*'s calculated from the Simon and Cornish data agree well with the corresponding parameters calculated from the data of most other investigators whose results have been examined and with values of *A* calculated from velocity-of-sound data.

The agreement of two independent runs at 109 identical temperatures and pressures establishes the precision of the measurements. This coincidence taken in conjunction with the agreement of the extrapolated specific volumes with $1/\rho$ and of the Hudleston *A*'s with those based on the work of other investigators may be taken as evidence of accuracy as well as precision. It is very unlikely that any systematic error could be common to both independent runs and still achieve the conformity indicated by the other criteria. It is therefore concluded that the over-all accuracy is of the same order as the over-all precision or ap-

proximately three parts in 10,000 for the entire spread of the measurements on *n*-heptane.

PRECISION OF THE *N*-EICOSANE MEASUREMENTS

Duplicate runs at identical temperatures and pressures were not made with *n*-eicosane, so the method of analysis that was used with *n*-heptane was not applicable. However with *n*-eicosane the normal boiling point (342.7°C.) is well above the highest temperature of measurement; therefore the published densities could be used to convert the measured compressions to specific volumes at all temperatures.

The measured compressions were obtained as follows. The volumes of sample in the piezometer over a range of pressures at constant temperature were fitted to the Hudleston equation, and the zero-pressure volume giving the best fit of the points to the line was calculated. Since the volumes were of the order of 0.5 ml., the zero-pressure volume was not a specific volume. However these measurements were converted to compressions by dividing each measured volume by the extrapolated zero-pressure volume. The multiplication of each value of compression by $1/\rho$ converts these numbers into specific volumes, and of course the zero pressure number is $1/\rho$ itself.

The establishment of the validity of the Hudleston extrapolation was done in the next step. (It is to be clearly understood that all that had been done so far was to multiply each measured volume by a constant.)

The specific volumes were next fitted to the Hudleston equation, and the value of the zero-pressure specific volume that gave the best fit of the points to the line was calculated for each temperature.

The results were as follow:

Temperature, °C.	Calculated v°_T	$1/\rho^{\circ}_T$ from reference 12
50	1.3007	1.3007
100	1.3598	1.3598
150	1.4267	1.4267
200	1.5013	1.5013
250	1.5876	1.5876
300	1.6926	1.6926

Since the agreement was perfect at all temperatures, it is established that the extrapolation of higher pressure volumes to atmospheric pressure by the Hudleston equation is likewise valid for *n*-eicosane.

For the purpose of making a statistical analysis of the precision of the measurements, a large number of points (163) were taken. Table 5 gives the Hudleston parameters resulting from these calculations.

Over a relatively limited range of temperature Bett, Weale, and Newitt (*14*) concluded that the slope of *B* of the Hudleston lines was a constant for a given liquid. The Simon and Cornish data, over a considerably greater range, confirm this observation except at temperatures somewhat above the normal boiling point where the *B*'s are observed to increase. Since the Hudleston equation fails at the critical point, where v°_T may exceed v°_T, there is some uncertainty about the highest temperature at which the equation can be used with confidence. Therefore the observed increase in *B* as the critical temperature is approached may not be significant.

In the case of *n*-eicosane all temperatures of measurement were substantially below the normal boiling point, and so the *B*'s may be presumed to be constant. The actual values obtained were therefore averaged and the *A*'s adjusted accordingly. The parameters used in the Hudleston equation calculations are given in Table 6.

The differences between the calculated and the observed specific volumes gave a standard percentage error for the 163 points of 0.033%.

ESTIMATE OF THE ACCURACY OF THE *N*-EICOSANE DATA

The above calculation establishes the degree of precision attained in these measurements. However the Hudleston equation has been found to represent correctly the dependence of the volume of liquids on pressure at constant temperature by others (*14*) as well as the authors, and so the curvature of the *Pv* isotherms is presumed to be correct. Therefore since the extrapolated zero-pressure volumes correspond in all cases to $1/\rho$, it follows that the accuracy must again be substantially equivalent to the precision or an over-all SPE for the 163 points of the order of 0.03%.

ACCURACY OF OTHER SIMON AND CORNISH *N*-ALKANE MEASUREMENTS

Since the order of accuracy of the Simon and Cornish measurements was sufficiently well established by the analyses of the *n*-heptane and *n*-eicosane data, it was not considered necessary to go into such detail with the remaining six compounds (*n*-alkanes of 9, 11, 13, 17, 30, and 40 carbons). However an indication that these measurements are of the same order of accuracy may be taken from the observation that the root-mean-square percentage deviation from the mean volume for each of 190 random multiple points (458 measurements at identical temperatures and pressures) was 0.035%. These random points represent all the instances in which multiple measurements were made at identical temperatures and pressures on these six compounds. Although the agreement of multiple measurements at identical temperatures and pressures is a measure only of precision, other criteria lead the authors to believe that the accuracies are again of the same order as the precisions, except for *n*-tetracontane, which contained 1.4% impurity.

SUMMARY

The compressions of eight pure liquid *n*-alkanes have been calculated from new measurements of volumes under pressure at a series of temperatures. The zero-pressure volumes used for the calculation of the compressions were obtained by extrapolation of the measurements of the volumes under pressure.

Analyses of the data for *n*-heptane and *n*-eicosane indicate that the over-all accuracy of the compressions for each of these compounds appears to be of the order of 3 parts in 10,000. Less comprehensive analysis of the data for the other six compounds indicates an accuracy of approximately the same order.

TABLE 5. HUDLESTON PARAMETERS, *n*-EICOSANE

Temperature, °C.	Pressure range, bars	No. of measurements	*A*	*B*
50	165.2 to 557.6	9	10.483	14.186
100	165.2 to 3292	25	10.185	14.754
150	116.1 to 2534	32	9.865	14.216
200	116.1 to 3932	37	9.522	13.876
250	116.1 to 4007	30	9.124	13.872
300	116.1 to 3456	30	8.581	14.094

TABLE 6. HUDLESTON PARAMETERS, *n*-EICOSANE, CONSTANT *B*

Temperature, °C.	*A*	*B*	$(v^{0}_T)^{1/3}$ [a]
50	10.482	14.118	1.0916
100	10.206	14.118	1.1079
150	9.869	14.118	1.1258
200	9.509	14.118	1.1450
250	9.109	14.118	1.1666
300	8.579	14.118	1.1917

[a] From reference *12*.

III. Temperature and Molecular Weight Dependence of the Hudleston Parameters for the *n*-Alkanes

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...eral equations for the temperature dependence of the parameters of the Hudleston ...on are given which were deduced from a study of *n*-alkane compression data. Empirical ...ssions for the molecular-weight dependence of the constants of these equations are like- ... given which are applicable only to *n*-alkanes. By use of these relations in the Hudleston ...on the compressions of the family of liquid *n*-alkanes over ranges of *T*, *P*, and *m* were cal- ...ed on an IBM-650 computer. The over-all standard percentage error (SPE) of the computer ...ations for *n*-alkanes of 7 to 20 carbons up to temperatures not exceeding their normal ... points was 0.10%. The over-all SPE for *n*-alkanes of 7 to 40 carbons up to temperatures ...tially above their normal boiling points (but not exceeding 300°C.) was 0.21%.

...nce the Hudleston (*15*) equation ...been shown (*8, 14*) to represent ...ure-volume data on liquids at ...ant temperature with high accu- ...it seemed desirable to investigate ...temperature-dependent parameters ...s equation so that it could be used ...equation of state for the purpose ...aking certain liquid-state thermo- ...mic calculations.

...o permit the calculation of com- ...sions for all members of the *n*-al- ...family, empirical equations for ...olecular-weight dependence of all ...meters involved were determined. ...e are applicable to the *n*-alkanes ...With all variables defined as ...tions of temperature and molecular ...ht, a trial-and-error solution of the ...leston equation was programed for ...IBM-650 computer, and a set of ... was listed giving the specific ...es of all the *n*-alkanes studied at ...temperatures of measurement but ...n pressures.

...e purpose of carrying out this em- ...l study was twofold: to determine ...ature of the variation, particularly ...the temperature dependence, as ...p toward a better understanding ...liquid state and to provide a ...of compression data at even pres- ...for use in subsequent calculations ...ng the behavior of liquids.

...apparatus and method used by ... and Cornish to measure the vol- ...of liquids under pressure have ...described (*10*), and their data on ...n-alkanes of 7 to 40 carbons has ...valuated (*8*). It has been shown ...the data for *n*-heptane and *n*-eico- ...are very well represented by the ...ion (*15*) equation. This paper ...rs all the Simon and Cornish ...d the *n*-alkane data of other ...tors for the purpose of estab- ...the temperature and molecular- ...pendence of the parameters ...Hudleston equation.

...B. Doolittle is at the West Virginia In- ...Technology, Montgomery, West Virginia.

The Hudleston equation for a sample weight of 1 g. may be written as

$$\ln \frac{P(v^p_T)^{2/3}}{(v^\circ_T)^{1/3} - (v^p_T)^{1/3}} = A_T + B[(v^\circ_T)^{1/3} - (v^p_T)^{1/3}] \quad (1)$$

The constant B is substantially independent of temperature except in the neighborhood of the critical point, but A_T and v°_T are temperature dependent. In addition, v°_T, A_T, and B depend on the nature of the substance; thus when only the *n*-alkanes are considered, they depend on the molecular weight.

TEMPERATURE DEPENDENCE

The Parameter v°_T

To explore $v^\circ = f(T)$ a study of *n*-alkane liquid-density data (*12*) was made which yielded the following relationship:

$$\left.\begin{aligned} \ln \frac{(v^\circ_T)}{(v^\circ_o)} &= e^z - 1 \\ z &= e^y - 1 \\ y &= k\,(T + \Delta) \end{aligned}\right\} \quad (2)$$

The values of ln (v°_o) and k were determined for each of the twenty *n*-alkanes (methane to *n*-eicosane) in the following manner. Specific volumes from A.P.I.-44 density data (*12*) were assumed to be identical with v°_T at temperatures from the melting point to within 30 to 50 centigrade degrees of the normal boiling point. Trial values of v°_o were calculated from ln $(v^\circ_o) = 10/m$ (*25*). The quantity y in Equation (2) may be expressed as

$$y = \ln\left\{ \ln\left[\ln \frac{(v^\circ_T)}{(v^\circ_o)} + 1 \right] + 1 \right\} \quad (2a)$$

At temperatures well below the normal boiling point no correction Δ is necessary. Hence over the range specified, a series of values of y from Equation (2*a*) was calculated for each compound at intervals of 20 centigrade degrees. Values thus calculated plotted as straight lines, and their slopes and intercepts were determined by least-squares calculations. In accordance with Equation (2), the intercepts of these lines should be zero in all cases. Since calculation from ln $(v^\circ_o) = 10/m$ did not provide zero intercepts (or more exactly intercepts $< \pm 0.0001$), trial calculations were continued until a value of ln (v°_o) was found for which the intercept was $< \pm 0.0001$. This gave twenty pairs of parameters ln (v°_o) and k. It is interesting to note that in an earlier publication (*6*), it was stated that ln (v°_o) could have been read as $(10/m) - 0.005$, but the value $10/m$ was used for simplicity. The method here employed in Equation (2) gives values of ln (v°_o) almost exactly $= (10/m) - 0.005$, and these values are used here since more precise quantities are dealt with in this paper.

Calculations were made (IBM run 4) of the specific volumes of the *n*-alkanes with the twenty pairs of parameters, ln (v°_o) and k. For sixteen *n*-alkanes, *n*-pentane to *n*-eicosane, over a temperature range from the melting to within 30 to 50 centigrade degrees of the normal boiling temperature (309 points), the SPE of the calculated specific volumes was 0.05%. At temperatures in the neighborhood of the normal boiling point (and at higher temperatures) data on liquid density obtained at atmospheric pressure cannot be used to check values calculated from Equation (2). Another method was therefore used. It has been mentioned (*8*) that the Hudleston equation is an excellent device for extrapolating accurate measurements of volume under pressure to the zero-pressure volume. With *n*-heptane, accurate measurements of the specific volumes under pressure over a wide range of temperatures have been made by a number of investigators, including Simon and Cornish (*8*). Application of the Hudleston equation to these data therefore enabled the zero-pressure specific volumes of *n*-heptane to be calculated at temperatures beyond the

range of the atmospheric-pressure densities.

When the values of y for n-heptane were calculated from these data according to Equation (2), the linear relationship was observed to hold up to approximately 0.6 T_c or 324°K. Above this temperature the observed values of y were greater than kT. The nature of the deviation was exponential and took the following form:

$$\Delta = \frac{y - kT}{k}$$

$$= [\exp c_1 (T - c_2 T_c)] - 1 \quad (3)$$

It was anticipated that $c_2 = 0.6$ would apply to all members of the n-alkane series, but a trial calculation with n-eicosane showed that the correction was applied at too low a temperature with the higher molecular-weight compound. This parameter was therefore made molecular-weight dependent.

The Parameter A

With the dependence of v°_T on T established, attention was directed to the other temperature-dependent parameter of the Hudleston equation. Bett, Weale, and Newitt (*14*), from a study of data extending over a rather limited range of temperatures, suggested that perhaps the Hudleston A was linear with temperature. Figure 1 of a prior paper (*8*) indicates however, that this linearity does not extend to the higher temperatures.

To explore $A_T = f(T)$, n-alkane compression data of a number of investigators were analyzed according to the Hudleston equation, and thus values of A were provided at a variety of molecular weights and temperatures. The published data have frequently been reported as specific volumes or have been given in a form that can be converted to specific volumes. Such data were extrapolated to zero pressure by use of the trial-and-error procedure described in the prior paper (*8*). In the few instances where the available data (well below the normal boiling point) did not extrapolate to $1/\rho$ [ρ = A.P.I.-44 liquid density (*12*)], such data were not included in this study.

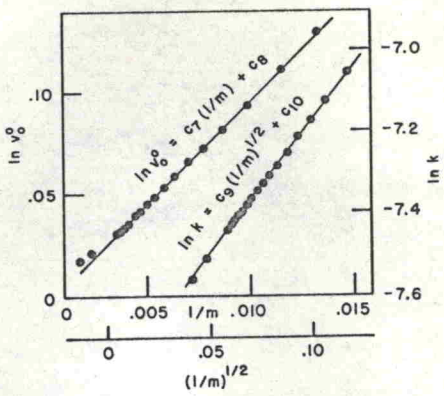


Fig. 6. n-Alkanes. Parameters of the relationship defining the dependence of specific volume on temperature.

The Simon and Cornish data and those of some other investigators are reported as compressions. These were converted to specific volumes by multiplying by v°_T calculated from Equation (2). With the authors' data the intercepts A and slopes B of the Hudleston lines were generally calculated by the method of least squares. Graphical determinations of the A's and B's were made in all other instances except n-octane, where several values calculated from velocity of sound data seemed more reliable. Table 7 presents the results of these calculations and lists the values of A, B, and $(v^\circ_T)^{1/3}$ for all compounds and temperatures involved.

Study of $A = f(T)$ with these extensive data led to the following relationship for the temperature dependence of the Hudleston A's:

$$e^{A/2} = c_3 \left(1 - \frac{T}{c_4}\right)$$

or

$$A = 2 \ln \left[c_3 \left(1 - \frac{T}{c_4}\right)\right] \quad (4)$$

The degree of fit of the observed values to the lines determined by Equation (4) is discussed in a later section.

MOLECULAR-WEIGHT DEPENDENCE

The Parameter B

Definition of B as a function of molecular weight was complicated by the fact that the values of B for n-tricontane and n-tetracontane appear to be less than for n-eicosane. Since confidence in the results for the highest molecular weight n-alkanes is less than for the lower members of the series, a compromise was made by choosing a function, Equation (5), that well represents the B's for the lower molecular weight n-alkanes but continues to increase slowly as the molecular weight increases. This function

$$\ln B = c_5 \left(\frac{1}{m}\right) + c_6 \quad (5$$

Table 7. Hudleston Parameters

Ref.	t, °C	A	B	$(v^\circ_T)^{1/3}$ from IBM 7 *
C_5, mp -129.72°C; bp 36.074°C.				
3	0	9.834	12.8	1.1576
26	37.78	9.610	12.8	1.1805
3	50	9.340	12.8	1.1886
26	71.11	9.126	12.8	1.2038
3	95	8.746	12.8	1.2239
26	104.44	8.606	12.8	1.2330
26	137.78	7.798	12.8	1.2748
26	171.11	6.19	12.8	1.3493
26	204.44	0.64	12.8	1.5325
C_6, mp -95.35°C; bp 68.74°C.				
3	0	10.13	13.2	1.1390
20	0	10.13	13.0	1.1390
20	25	9.93	13.0	1.1516
27	37.78	9.81	10.8	1.1584
20	40	9.82	12.8	1.1597
3	50	9.70	13.2	1.1653
20	60	9.63	12.7	1.1711
27	71.11	9.40	12.8	1.1779
3	95	9.18	13.3	1.1937
28	100	9.10	13.0	1.1973
27	104.44	9.00	12.8	1.2006
27	137.78	8.47	13.2	1.2292
28	150	8.25	13.2	1.2424
27	171.11	7.80	13.0	1.2713
28	200	6.60	13.0	1.3351
27	204.44	6.52	13.2	1.3493
27	237.78	4.21	13.6	1.5507
C_7, mp -90.61°C; bp 98.43°C.				
3	0	10.25	13.2	1.1259
20	0	10.25	12.9	1.1259
29	4.44	10.22	13.2	1.1279
22	25	10.12	12.3	1.1375
20	25	10.06	12.9	1.1375
24	30	10.023	13.18	1.1399
23	30	-----	-----	1.1399
29	37.78	9.95	13.2	1.1436
20	40	9.94	12.8	1.1447
24	50	9.854	13.16	1.1497
3	50	9.80	13.3	1.1497
20	60	9.77	12.8	1.1548
29	71.11	9.67	13.2	1.1608
3	95	9.43	13.2	1.1743
24	100	9.365	13.18	1.1774
23	100	-----	-----	1.1774
29	104.44	9.32	13.2	1.1801
29	137.78	8.86	12.7	1.2029
24	150	8.694	13.27	1.2126
23	150	8.72	13.5	1.2126
29	171.11	8.40	13.0	1.2325
24	200	7.566	13.65	1.2705
23	200	7.64	13.9	1.2705
29	204.44	7.44	13.9	1.2781
29	237.78	5.86	14.5	1.3684
24	250	4.752	14.25	1.4289
23	250	4.90	13.5	1.4289
24	300	-17.79	15.60	2.7478

nts the values of B over the en- ge with an SPE of 2.5%. Prac- all this error occurs in the B's two highest molecular-weight nds.

ters of Equations (2) and (3)

parameters of Equations (2) that are molecular-weight de- are v^o_o, k, and c_2. The follow- uations express these relation-

Table 8.

$c_1 = 0.02536$	$c_9 = 6.65397$
$c_3 = 335$	$c_{10} = -7.838779$
$c_5 = -9.3000$	$c_{11} = 0.000835$
$c_6 = 2.6720$	$c_{12} = 0.52$
$c_7 = 9.911902$	$c_{13} = 22.040$
$c_8 = -0.0057157$	$c_{14} = -71.428$

$$\ln (v^o_o) = c_7\left(\frac{1}{m}\right) + c_8 \qquad (6)$$

$$\ln k = c_9\left(\frac{1}{m}\right)^{1/2} + c_{10} \qquad (7)$$

$$c_2 = c_{11} \cdot m + c_{12} \qquad (8)$$

The conformity of the data to lines representing Equations (6) and (7) is shown on Figure 6. It will be observed that the values of ln (v^o_o) for molecular weights below n-octane and above n-nonadecane are not well represented by Equation (6). Since time was not

Table 7. *(continued)*

t, °C	A	B	$(v^o_T)^{1/3}$ from IBM 7	Ref.	t, °C	A	B	$(v^o_T)^{1/3}$ from IBM 7
mp -56.80°C; bp 125.66°C.				C_{10}, mp -29.66°C; bp 174.12°C.				
0	10.35	13.3	1.1162	22	25	10.38	12.50	1.1125
0	10.40	12.9	1.1162	32	37.78	-----	-----	1.1176
25	10.24	12.6	1.1269	32	104.44	-----	-----	1.1463
25	10.23	12.8	1.1269	32	171.11	-----	-----	1.1803
40	10.12	12.8	1.1336					
50	10.01	13.1	1.1382					
60	9.97	12.9	1.1429					
95	9.58	13.6	1.1602					
100	----	----	1.1629	C_{11}, mp -25.59°C; bp 195.89°C.				
150	9.00	11.6	1.1925	24	50	10.160	14.2	1.1169
200	8.37	11.1	1.2332	24	100	9.828	14.0	1.1376
250	6.84	18.4	1.3126	24	150	9.408	13.9	1.1606
				24	200	8.918	13.6	1.1874
Values Calculated from Velocity of Sound				24	250	8.062	14.2	1.2220
0	10.33	----	------	24	300	6.03	15.7	1.2811
25	10.16	----	------					
40	10.05	----	------					
50	9.98	----	------					
60	9.90	----	------					
mp -53.52°C; bp 150.80°C.				C_{13}, mp -5.39°C; bp 235.44°C.				
30	10.238	13.24	1.1210	24	30	10.405	14.97	1.1009
37.78	------	-----	1.1243	24	50	10.254	14.97	1.1081
50	10.073	13.36	1.1295	24	100	9.947	14.14	1.1274
100	9.677	13.26	1.1524	24	150	9.593	13.74	1.1485
104.44	9.63	13.0	1.1546	24	200	9.13	13.7	1.1720
150	9.152	13.50	1.1790	24	250	8.49	14.1	1.1999
171.11	8.92	13.0	1.1919	24	300	7.29	14.9	1.2375
200	8.486	13.64	1.2125					
237.78	7.66	13.9	1.2497					
250	7.32	14.0	1.2666					
300	2.64	15.7	1.4098					

Table 7. *(continued)*

t, °C	A	B	$(v^o_T)^{1/3}$ from IBM 7	Ref.	t, °C	A	B	$(v^o_T)^{1/3}$ from IBM 7
mp 21.98°C; bp 301.82°C.				C_{40}, mp 81.5°C; bp 520°C.				*
50	10.42	14.2	1.0966	24	150	10.12	13.9	1.1044
100	10.13	13.8	1.1140	24	200	9.86	13.5	1.1202
150	9.77	14.0	1.1330	24	250	9.57	13.3	1.1374
200	9.40	13.9	1.1537	24	300	9.19	13.4	1.1559
250	8.94	13.9	1.1763					
300	8.35	13.9	1.2022					
mp 36.8°C; bp 342.7°C								
			*					
50	10.482	14.12	1.0914					
100	10.206	14.12	1.1079					
150	9.869	14.12	1.1258					
200	9.509	14.12	1.1452					
250	9.109	14.12	1.1665					
300	8.579	14.12	1.1896					
mp 65.8°C; bp 446.4°C.								
			*					
100	10.34	15.8	1.0959					
150	10.05	13.2	1.1117					
200	9.75	13.3	1.1288					
250	9.41	13.2	1.1474					
300	9.01	13.2	1.1674					

* $(v^o_T)^{1/3}$ values corrected by using observed ln (v^o_o) values instead of those calculated from Equation (6).

TABLE 9. MACHINE CALCULATION OF COMPRESSIONS, IBM RUN 9

t, °C	30	50	100	150	200	250	300
C_7, mp -90.61°C; bp 98.43°C; T_c 540.2°K.							
P, bars							
0	1.0000	1.0000	1.0000	1.0000	1.0000		
50	.9927	.9914	.9859	.9738	.9402		
100	.9860	.9836	.9739	.9540	.9059		
200	.9740	.9698	.9540	.9244	.8623		
300	.9635	.9579	.9378	.9023	.8333		
500	.9455	.9381	.9122	.8698	.7940		
1000	.9119	.9018	.8688	.8189	.7374		
1500	.8874	.8759	.8393	.7863	.7033		
2000	.8679	.8555	.8170	.7624	.6788		
3000	.8380	.8246	.7839	.7278	.6444		
5000	.7969	.7827	.7403	.6834	.6013		
SPE, %	0.019	0.008	0.035	0.193	0.457		
Range, bars	0-3000	0-3000	0-3000	0-3000	0-3000		
C_9, mp -53.52°C; bp 150.80°C; T_c 595°K.							
P, bars							
0	1.0000	1.0000	1.0000	1.0000	1.0000		
50	.9940	.9931	.9897	.9832	.9690		
100	.9884	.9867	.9805	.9693	.9465		
200	.9783	.9753	.9647	.9468	.9141		
300	.9692	.9651	.9514	.9290	.8905		
500	.9534	.9479	.9296	.9016	.8566		
1000	.9230	.9153	.8909	.8561	.8044		
1500	.9003	.8913	.8637	.8259	.7716		
2000	.8820	.8723	.8428	.8032	.7475		
3000	.8536	.8429	.8112	.7698	.7131		
5000	.8140	.8025	.7689	.7268	.6690		
SPE,%	0.113	0.031	0.036	0.065	0.262		
Range, bars	0-3000	0-3000	0-3000	0-3000	0-3000		

TABLE 9. *(continued)*

t, °C	50	100	150	200	250	300
C_{11}, mp -25.59°C; bp 195.89°C; T_c 640°K.						
P, bars						
0	1.0000	1.0000	1.0000	1.0000		
50	.9940	.9914	.9869	.9781		
100	.9883	.9836	.9756	.9609		
200	.9781	.9699	.9568	.9345		
300	.9690	.9581	.9414	.9142		
500	.9532	.9385	.9169	.8840		
1000	.9228	.9026	.8749	.8356		
1500	.9001	.8770	.8463	.8042		
2000	.8818	.8570	.8246	.7809		
3000	.8535	.8265	.7922	.7471		
5000	.8141	.7852	.7494	.7034		
SPE, %	0.065	0.020	0.063	0.367		
Range, bars	0-3000	0-3000	0-3000	0-3000		
C_{13}, mp -5.39°C; bp 235.44°C; T_c 677°K.						
P, Bars						
0	1.0000	1.0000	1.0000	1.0000	1.0000	
50	.9951	.9924	.9889	.9825	.9694	
100	.9893	.9854	.9791	.9681	.9473	
200	.9799	.9730	.9624	.9452	.9153	
300	.9714	.9622	.9485	.9271	.8921	
500	.9565	.9439	.9260	.8994	.8585	
1000	.9276	.9101	.8864	.8538	.8069	
1500	.9058	.8855	.8590	.8237	.7743	
2000	.8881	.8661	.8380	.8011	.7505	
3000	----	.8364	.8064	.7679	.7163	
5000	----	.7958	.7642	.7246	.6727	
SPE, %	0.057	0.045	0.090	0.108	0.391	
Range, bars	0-2000	0-3000	0-3000	0-3000	0-3000	

available to make further refinements, a run was made on the IBM computer (run 7) in which Equation (6) was used only for *n*-alkanes *n*-heptane to *n*-eicosane. Observed values of v°_o were used for *n*-alkanes below and above these limits. Equation (7) was satisfactory for defining k over the entire range. IBM run 7 duplicated the specific volumes of the *n*-alkanes *n*-pentane to *n*-tetracontane over the range from the melting point to within a few degrees of the normal boiling point with an SPE of 0.05%. Values of $(v^\circ_T)^{1/3}$ from IBM run 7 are listed in Table 7 for the various temperatures of interest.

Parameters of Equation (4)

The only molecular-weight–dependent parameter of Equation (4) is c_i, which is a number nearly but not exactly equal to the critical temperature. Its dependence on molecular weight is given by

$$c_i = 10^2 (c_{13} \ln m + c_{14})^{1/2}$$

Equations (4) and (9) represent observed A's with an SPE of 0. The constants involved in all the tions discussed above are giv Table 8.

OVER-ALL EVALUATION

The Hudleston equation, Eq

TABLE 9. *(continued)*

t, °C	50	100	150	200	250	300
C_{17}, mp 21.98°C; bp 301.82°C; T_c 735°K.						
P, bars						
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
50	.9951	.9935	.9910	.9867	.9790	.9649
100	.9905	.9875	.9828	.9754	.9624	.9373
200	.9820	.9766	.9686	.9564	.9367	.9009
300	.9743	.9670	.9565	.9410	.9170	.8767
500	.9606	.9504	.9364	.9165	.8874	.8436
1000	.9336	.9191	.9001	.8747	.8398	.7940
1500	----	.8959	.8742	.8462	.8089	.7627
2000	----	.8774	.8542	.8246	.7859	.7372
3000	----	.8488	.8237	.7925	.7525	.6992
5000	----	.8093	.7825	.7500	.7091	.6567
SPE, %	0.096	0.047	0.038	0.046	0.313	0.675
Range, bars	0-1000	0-3000	0-3000	0-3000	0-3000	0-3000
C_{20}, mp 36.8°C; bp 342.7°C; T_c 775°K.						
P, bars						
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
50	.9954	.9940	.9918	.9884	.9824	.9709
100	.9911	.9884	.9844	.9782	.9680	.9496
200	.9830	.9782	.9713	.9611	.9450	.9186
300	.9756	.9691	.9600	.9468	.9270	.8959
500	.9626	.9534	.9411	.9239	.8993	.8630
1000	----	.9233	.9063	.8840	.8540	.8121
1500	----	.9008	.8813	.8565	.8240	.7800
2000	----	.8828	.8618	.8354	.8015	.7564
3000	----	.8548	.8319	.8038	.7686	.7225
5000	----	.8158	.7913	.7618	.7256	.6791
SPE, %	0.060	0.156	0.053	0.091	0.198	0.483
Range, bars	0-500	0-3000	0-2000	0-3000	0-3000	0-3000

TABLE 9. *(continued)*

t, °C	100	150	200	250	300
C_{30}, mp 65.8°C; bp 446.4°C					
P, bars					
0	1.0000	1.0000	1.0000	1.0000	1.0000
50	.9949	.9933	.9910	.9874	.9813
100	.9900	.9872	.9830	.9765	.9661
200	.9811	.9761	.9689	.9583	.9422
300	.9731	.9663	.9568	.9434	.9237
500	.9590	.9495	.9369	.9196	.8954
1000	----	.9179	.9008	.8787	.8495
1500	----	----	.8752	.8508	.8193
2000	----	----	.8553	.8295	.7968
3000	----	----	.8251	.7978	.7638
5000	----	----	.7843	.7558	.7210
SPE, %	0.039	0.205	0.311	0.321	0.256
Range, bars	0-500	0-1000	0-1000	0-1000	0-1000
C_{40}, mp 815°C; bp 520°C					
P, bars					
0		1.0000	1.0000	1.0000	1.0000
50		.9940	.9922	.9894	.9850
100		.9885	.9851	.9801	.9724
200		.9783	.9725	.9641	.9519
300		.9693	.9615	.9507	.9355
500		.9537	.9431	.9290	.9098
1000		.9238	.9092	.8906	.8667
1500		.9015	.8847	.8639	.8378
2000		.8836	.8655	.8434	.8160
3000		.8558	.8361	.8125	.7838
5000		.8171	.7959	.7711	.7414
SPE, %		0.479	0.605	0.664	0.869
Range, bars		0-3000*	0-3000	0-3000	0-3000

*NOTE: Sample did not freeze under 3000 bars. Presumably because of impurity of 1.4%.

ith auxiliary Equations (2) to fines completely the PvT rela- liquids over its range of valid- further relating all parameters olecular weight of the *n*-alkanes ions (5) to (9), one can make l calculation giving the com- of any of the *n*-alkanes at any re and pressure, in which the pendent variable is molecular Such a calculation, which evaluates the combined accuracy of all the empirical equations, was made (IBM run 9). The compressions were computed for all compounds studied at all temperatures of interest and at the following even pressures: 0, 50, 100, 200, 300, 500, 1,000, 1,500 2,000, 3,000, and 5,000 bars. At the same time the compressions were likewise listed at 0, 116.1, 214.2, 312.3, 508.5, 1,015, 1,577, 2,089, and 3,011 bars so that the experimental values might be compared with the machine calculations. The even-pressure values for *n*-alkanes 7 to 40 carbons are presented in Table 9, and the fit of the Simon and Cornish data to the equation over the indicated pressure ranges is shown for each compound.

This comparison indicates that over a pressure range of 0 to 3,000 bars the over-all SPE of the computed values

for n-alkanes of 7 to 20 carbons at all temperatures from 30°C. to somewhat below the normal boiling temperature is 0.10%. The over-all SPE for the entire range of molecular weights and pressures and over a range of temperatures extending considerably above the normal boiling point (but not exceeding 300°C.) is 0.21%.

At temperatures considerably above the normal boiling temperatures for all compounds, and for n-triacontane and n-tetracontane at all temperatures, the agreement of the calculated with the observed values is not so good as elsewhere. The discrepancies at these extremes of temperature and molecular weight are due principally to slight disagreement between the calculated and observed values of the Hudleston paameters A and B at the upper limits of these ranges.

The relatively poor agreement of n-tetracontane may be due in part to the lower purity of this sample compared with the other compounds (8). The observed Hudleston A's for n-tetracontane (Table 6) are somewhat less than those calculated from Equation (4), whereas those for n-triacontane are well represented by the calculation. With both these compounds the observed Hudleston B's are less than those for the preceding members of the series and are therefore not properly represented by Equation (5).

SUMMARY

1. Equation (1) with one physical constant v°_T and two arbitrary constants A and B defines completely the Pv relations of a single liquid at a single temperature (substantially below the critical temperature).

2. Equations (1), (2), and (4) with one extrapolated physical constant v°_o and four arbitrary constants k, B, c_3, c_4 define completely the PvT relations of a single liquid n-alkane at all temperatures substantially below the normal boiling temperature.

3. Equations (1), (2), (3), and (4) with two physical constants v°_o and T_c and six arbitrary constants k, B, c_1, c_2, c_3, c_4 define completely the PvT relations of a single liquid n-alkane up to temperatures substantially above the normal boiling temperature.

4. The PvT relations of the family of liquid n-alkanes from 7 to 40 carbons may be completely defined by nine equations involving one physical constant T_c and twelve arbitrary constants up to temperatures substantially above the normal boiling temperature.

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NOTATION

A = Hudleston intercept for sample weight of 1 g.

a = setting constant

B = Hudleston slope for sample weight of 1 g.

C_1 = Hudleston intercept for any sample weight

C_2 = Hudleston slope for any sample weight

c_1 = numerical constant

c_2 = molecular - weight – dependent constant in Equation (3)
$= c_{11}\, m + c_{12}$

c_3 = numerical constant

c_4 = molecular - weight – dependent constant in Equation (4), nearly but not exactly equal to the critical temperature
$= 10^2\,(c_{13} \ln m + c_{14})^{1/2}$

c_5 to c_{14} = numerical constants

k = molecular - weight – dependent constant in Equation (2)
$= \exp\left[c_9 \left(\frac{1}{m}\right)^{1/2} + c_{10}\right]$

P = external pressure, bars

T = absolute temperature, °K.

T_c = absolute critical temperature, °K.

$vol^p{}_T$ = volume of sample at temperature T and pressure P

$vol^\circ{}_T$ = zero-pressure volume of sample at temperature T

$v^p{}_T$ = specific volume of sample at temperature T and pressure P

$v^\circ{}_T$ = zero-pressure specific volume of sample at temperature T

$v^\circ{}_o$ = limiting specific volume at zero pressure and zero temperature (See reference 34.)

y = variable in Equation (2)
$= k\,(T + \Delta)$

z = variable in Equation (2)
$= (\exp y) - 1$

Δ = variable in Equation (2)
$= [\exp c_1\,(T - c_2 T_c)] - 1$

ρ = liquid density

LITERATURE CITED

1. Beattie, J. A., *Proc. Am. Acad. Arts Sci.*, 69, 389 (1934).
2. Bridgman, P. W., *ibid.*, 77, 129 (1949).
3. ———, "The Physics of High Pressure." 2 ed., p. 126, G. Bell, Lon... England (1949).
4. Adams, L. H., and R. E. Gibson, *Am. Chem. Soc.*, 53, 3769 (1931).
5. Michels, A., *Proc. Roy. Soc.* (*Lond...* A160, 358 (1937).
6. Reitzel, J., I. Simon, and J. A. Wa... *Rev. Sci. Instr.*, 28, 828 (1957).
7. Bridgman, P. W., *Proc. Am. A... Arts Sci.*, 77, 214 (1949).
8. Doolittle, A. K., and D. B. Dooli... Paper II of this series.
9. ———, Paper III of this series.
10. Doolittle, A. K., Ivan Simon, and... K. Cornish, Paper I of this series.
11. Doolittle, A. K., and R. H. Peter... *J. Am. Chem. Soc.*, 73, 2145 (19...
12. Rossini, F. D., *et al.*, "Selected Va... of Physical and Thermodynamic P... erties of Hydrocarbons and Rel... Compounds," API Research Project... Carnegie Press, Pittsburgh (1953).
13. Glasgow, A. R., Jr., A. J. Strieff, ... F. D. Rossini, *J. Research Natl. B... Standards*, 35, 355 (1945).
14. Bett, K. E., K. E. Weale, and D. ... Newitt, *Brit. J. Appl. Phys.*, 5, ... (1954).
15. Hudleston, L. J., *Trans. Faraday S...* 33, 97 (1937).
16. Freyer, E. B., J. C. Hubbard, ... D. H. Andrews, *J. Am. Chem. S...* 51, 759 (1929).
17. Rao, M. R., *J. Chem. Phys.*, 9, ... (1941).
18. Osborne, N. S., and D. C. Ginni... *J. Research Natl. Bur. Standards*, ... 453 (1947).
19. Reference 3, p. 129.
20. Eduljee, H. E., D M. Newitt, ... K. E. Weale, *J. Chem. Soc.* (*Lond...* 3086 (1951).
21. Nichols, W. B., H. H. Reamer, ... B. H. Sage, *Ind. Eng. Chem.*, ... 2219 (1955).
22. Bridgman, P. W., *Proc. Am. A... Arts Sci.*, 77, 117 (1949).
23. Smith, L. B., J. A. Beattie, and W. ... Kay, *J. Am. Chem. Soc.*, 59, ... (1937).
24. Calculated from data of Simon ... Cornish in reference 8.
25. Doolittle, A. K., *J. Appl. Phys.*, ... 1471 (1951).
26. Sage, B. H., and W. N. Lacey, *I... Eng. Chem.*, 34, 730 (1942).
27. Stewart, D. E., B. H. Sage, and W. ... Lacey, *ibid.*, 46, 2529 (1954).
28. Kelso, E. A., and W. A. Felsing, *Am. Chem. Soc.*, 62, 3132 (1940).
29. Nichols, W. B., H. H. Reamer, ... B. H. Sage, *Ind. Eng. Chem.*, 47, ... (1955).
30. Felsing, W. A., and G. M. Watson, *Am. Chem. Soc.*, 64, 1822 (1942).
31. Carmichael, L. T., B. H. Sage, ... W. N. Lacey, *Ind. Eng. Chem.*, ... 2697 (1953).
32. Sage, B. H., and W. N. L... "Thermodynamic Properties of Hy... carbons," p. 83, API (1950).
33. Freyer, E. B., J. C. Hubbard, ... D. H. Andrews, *J. Am. Chem. S...* 51, 759 (1929).
34. Doolittle, A. K., and D. B. Dooli... *J. Appl. Phys.*, 28, 901 (1957).

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