accompanied the weights and cylinders, guaranteeing an accuracy of one part in 10,000 in the measurement of pressure.

Over-All Accuracy

When one combines the errors in the measurement of temperature and volume, a conservative estimate of the probable over-all accuracy of measurement may be placed at 4 parts in 10,000, which assures four significant figures in specific volume. [Statistical analyses of the data on two compounds, *n*-heptane 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 $(vol\ ^P_T)/(vol^{\circ}_T)$, 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 eight *n*-alkanes, from 7 to 40 carbons, were measured by Simon and Cornish at a number of temperatures from 20° to 300°C. and over a range of pressures from 0 to 4,000 kg./sq. cm., with the apparatus and method described in the prior paper (*10*). This method has the advantage of very high accuracy in the measurement of volumes under pressure, but it does not afford equivalent accuracy in the direct measurement of the weight of the material whose volume is being measured. It is therefore necessary to resort to indirect means of determining the sample weight.

Also this procedure measures volumes very accurately under high pressure, but somewhat less accurately at low pressures. Therefore, to realize the full advantage of the method it is necessary to establish the values of the zero-pressure volumes with more certainty than is possible by extrapolating the lower pressure values alone.

A procedure was devised for making an indirect extrapolation to zero pressure of the volumes measured at higher pressures which gives values fully as accurate as the measurements. When applied to the Simon and Cornish data, this procedure permits the results to be reported as compressions or ratios of the volume at the pressure of measurement to the zero-pressure volume $(vol^P_T)/(vol^{\circ}_T)$.

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*):

$$\ln \frac{P\,(vol^P_T)^{2/3}}{(vol^{\circ}_T)^{1/3} - (vol^P_T)^{1/3}} = C_1 + C_2[\,(vol^{\circ}_T)^{1/3} - (vol^P_T)^{1/3}]$$

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 $(vol^{\circ}_T)^{1/3}$ and the denominator becomes vanishingly small. A slight error in $(vol^{\circ}_T)^{1/3}$ 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 $(vol^{\circ}_T)^{1/3}$. 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 $(vol^{\circ}_T)^{1/3}$ 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°_T) were determined for each compound at all temperatures of measurements, thereby enabling the compressions to be calcu-

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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.

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 $C_2 = B/w^{1/3}$. Therefore when comparing Hudleston parameters one must deal with the same quantity of sample.

The zero-pressure specific volumes 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

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* 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.

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

Ref.	t., °C.	A (From velocity of sound)	A (From compressions)	B	$(v^0_T)^{1/3}$
19	0	10.254	10.25	13.2	1.1259
20	0	10.254	10.25	12.9	1.1259
21	4.44	10.221	10.22	13.2	1.1280
22	25	10.005	10.12	12.3	1.1375
20	25	10.065	10.06	12.9	1.1375
24	30	10.026	10.023	13.18	1.1398
23	30	10.026			
21	37.78	9.964	9.95	13.2	1.1435
20	40	9.945	9.94	12.8	1.1447
24	50	9.862	9.854	13.16	1.1495
19	50	9.862	9.80	13.3	1.1492
20	60	9.776	9.77	12.8	1.1548
21	71.11	9.675	9.67	13.2	1.1608
19	95	9.441	9.43	13.2	1.1745
24	100	9.388	9.365	13.18	1.1776
23	100	9.388			
21	104.44	9.341	9.32	13.2	1.1810
21	137.78		8.86	12.7	1.2055
24	150		8.694	13.27	1.2149
23	150		8.72	13.5	1.2133
21	171.11		8.40	13.0	1.2327
24	200		7.566	13.65	1.2756
23	200		7.64	13.9	1.2713
21	204.44		7.44	13.9	1.2800
21	237.78		5.86	14.5	1.3625
24	250		4.752	14.25	1.4300
23	250		4.90	13.5	1.4300
24	300		—17.79	15.60	2.7531

Values of A in column 4 that are carried to three decimal places were calculated from data of Simon and Cornish by the method of least squares. All others were obtained graphically. Data of reference 23 do not extend to high enough pressures to determine the Hudleston line accurately at 30° and 100°C. Column 3 gives the values of A calculated from velocity-of-sound data as explained in the text.

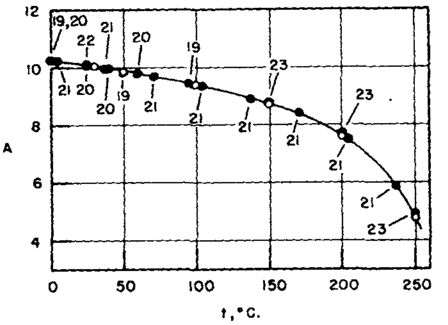

Fig. 5. n-Heptane. [Numbers refer to literature. Open circles are data of Simon and Cornish (*24*)].

observed specific volumes for n-heptane was shown by a machine calculation made on the IBM-650 computer. Temperatures and pressures were chosen for the calculations that exactly duplicated certain Simon and Cornish measurements, and so deviations of the calculated from the measured values could be observed directly. Calculations at each of the following pressures: 116.1, 214.2, 312.3, 508.5, 1,051, 1,577, 2,089, and 3,011 bars were made at each of the following temperatures: 30°, 50°, 100°, 150°, 200°, 250°, and 300°C. (IBM run 5).

The SPE of the deviations calculated from the measured specific volumes are given in Table 3. It will be noted that at 30°, 50°, and 100°C. (up to approximately the normal boiling point) the Hudleston equation duplicates the specific volumes fully as accurately as the values themselves were measured at these three temperatures, whereas above 100° the agreement, while good, diminishes as the temperature of the measurement increases. The SPE for the entire spread of temperatures and pressures for 55 points (weighted in accordance with the number of measurements at each temperature) 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.

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 approximately 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^P_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 6. HUDLESTON PARAMETERS, *n*-EICOSANE, CONSTANT *B*

Temperature, °C.	*A*	*B*	$(v^0_T)^{1/3}$*
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

* From reference *12*.

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