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

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

Since the Hudleston (*15*) equation has been shown (*8*, *14*) to represent pressure-volume data on liquids at constant temperature with high accuracy, it seemed desirable to investigate the temperature-dependent parameters of this equation so that it could be used as an equation of state for the purpose of making certain liquid-state thermodynamic calculations.

To permit the calculation of compressions for all members of the *n*-alkane family, empirical equations for the molecular-weight dependence of all parameters involved were determined. These are applicable to the *n*-alkanes only. With all variables defined as functions of temperature and molecular weight, a trial-and-error solution of the Hudleston equation was programed for the IBM-650 computer, and a set of tables was listed giving the specific volumes of all the *n*-alkanes studied at their temperatures of measurement but at even pressures.

The purpose of carrying out this empirical study was twofold: to determine the nature of the variation, particularly that of the temperature dependence, as a step toward a better understanding of the liquid state and to provide a body of compression data at even pressures for use in subsequent calculations involving the behavior of liquids.

The apparatus and method used by Simon and Cornish to measure the volumes of liquids under pressure have been described (*10*), and their data on eight *n*-alkanes of 7 to 40 carbons has been evaluated (*8*). It has been shown that the data for *n*-heptane and *n*-eicosane are very well represented by the Hudleston (*15*) equation. This paper considers all the Simon and Cornish data and the *n*-alkane data of other investigators for the purpose of establishing the temperature and molecular-weight dependence of the parameters of the Hudleston equation.

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

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

The constant B is substantially independent of temperature except in the neighborhood of the critical point, but A_T and v^o_T are temperature dependent. In addition, v^o_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^o_T

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

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

The values of ln (v^o_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^o_T at temperatures from the melting point to within 30 to 50 centigrade degrees of the normal boiling point. Trial values of v^o_o were calculated from ln $(v^o_o) = 10/m$ (25). The quantity y in Equation (2) may be expressed as

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

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 $(v^o_o) = 10/m$ did not provide zero intercepts (or more exactly intercepts $< \mp 0.0001$), trial calculations were continued until a value of ln (v^o_o) was found for which the intercept was $< \mp 0.0001$. This gave twenty pairs of parameters ln (v^o_o) and k. It is interesting to note that in an earlier publication (*6*), it was stated that ln (v^o_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_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_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^o_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.

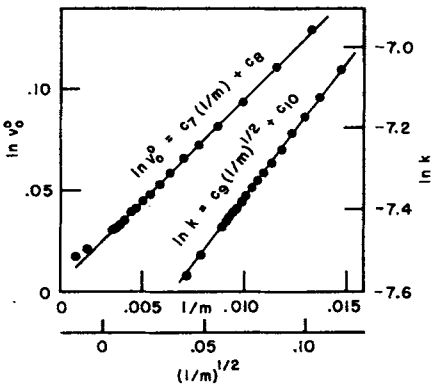

Fig. 6. n-Alkanes. Parameters of the relationship defining the dependence of specific volume on temperature.

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^o_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 $(v^o_T)^{1/3}$ 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:

$$\left.\begin{aligned} e^{A/2} &= c_3\left(1 - \frac{T}{c_4}\right) \\ \text{or} \\ A &= 2\ln\left[c_3\left(1 - \frac{T}{c_4}\right)\right] \end{aligned}\right\} \quad (4)$$

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-triacontane 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	$(v^o_T)^{1/3}$ 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

Ref.	t, °C	A	B	$(v^o_T)^{1/3}$ from IBM 7 *
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

represents the values of B over the entire range with an SPE of 2.5%. Practically all this error occurs in the B's for the two highest molecular-weight compounds.

Parameters of Equations (2) and (3)

The parameters of Equations (2) and (3) that are molecular-weight dependent are v°_o, k, and c_2. The following equations express these relationships:

Table 8.

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

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

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

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

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) for molecular weights below n-octane and above n-nonadecane are not well represented by Equation (6). Since time was not

Table 7. *(continued)*

Ref.	t, °C	A	B	$(v_T^o)^{1/3}$ from IBM 7
C_8, mp -56.80°C; bp 125.66°C.				
3	0	10.35	13.3	1.1162
20	0	10.40	12.9	1.1162
22	25	10.24	12.6	1.1269
20	25	10.23	12.8	1.1269
20	40	10.12	12.8	1.1336
3	50	10.01	13.1	1.1382
20	60	9.97	12.9	1.1429
3	95	9.58	13.6	1.1602
30	100	----	----	1.1629
30	150	9.00	11.6	1.1925
30	200	8.37	11.1	1.2332
30	250	6.84	18.4	1.3126
Values Calculated from Velocity of Sound				
	0	10.33	----	------
	25	10.16	----	------
33,17,18	40	10.05	----	------
	50	9.98	----	------
	60	9.90	----	------
C_9, mp -53.52°C; bp 150.80°C.				
24	30	10.238	13.24	1.1210
31	37.78	------	-----	1.1243
24	50	10.073	13.36	1.1295
24	100	9.677	13.26	1.1524
31	104.44	9.63	13.0	1.1546
24	150	9.152	13.50	1.1790
31	171.11	8.92	13.0	1.1919
24	200	8.486	13.64	1.2125
31	237.78	7.66	13.9	1.2497
24	250	7.32	14.0	1.2666
24	300	2.64	15.7	1.4098
C_{10}, mp -29.66°C; bp 174.12°C.				
22	25	10.38	12.50	1.1125
32	37.78	-----	-----	1.1176
32	104.44	-----	-----	1.1463
32	171.11	-----	-----	1.1803
C_{11}, mp -25.59°C; bp 195.89°C.				
24	50	10.160	14.2	1.1169
24	100	9.828	14.0	1.1376
24	150	9.408	13.9	1.1606
24	200	8.918	13.6	1.1874
24	250	8.062	14.2	1.2220
24	300	6.03	15.7	1.2811
C_{13}, mp -5.39°C; bp 235.44°C.				
24	30	10.405	14.97	1.1009
24	50	10.254	14.97	1.1081
24	100	9.947	14.14	1.1274
24	150	9.593	13.74	1.1485
24	200	9.13	13.7	1.1720
24	250	8.49	14.1	1.1999
24	300	7.29	14.9	1.2375

Table 7. *(continued)*

Ref.	t, °C	A	B	$(v_T^o)^{1/3}$ from IBM 7
C_{17}, mp 21.98°C; bp 301.82°C.				
24	50	10.42	14.2	1.0966
24	100	10.13	13.8	1.1140
24	150	9.77	14.0	1.1330
24	200	9.40	13.9	1.1537
24	250	8.94	13.9	1.1763
24	300	8.35	13.9	1.2022
C_{20}, mp 36.8°C; bp 342.7°C				*
24	50	10.482	14.12	1.0914
24	100	10.206	14.12	1.1079
24	150	9.869	14.12	1.1258
24	200	9.509	14.12	1.1452
24	250	9.109	14.12	1.1665
24	300	8.579	14.12	1.1896
C_{30}, mp 65.8°C; bp 446.4°C.				*
24	100	10.34	15.8	1.0959
24	150	10.05	13.2	1.1117
24	200	9.75	13.3	1.1288
24	250	9.41	13.2	1.1474
24	300	9.01	13.2	1.1674
C_{40}, mp 81.5°C; bp 520°C.				*
24	150	10.12	13.9	1.1044
24	200	9.86	13.5	1.1202
24	250	9.57	13.3	1.1374
24	300	9.19	13.4	1.1559

* IBM Run 7 $(v_T^o)^{1/3}$ 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 $(v^\circ_T)^{1/2}$ 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_4, which is a number nearly but not exactly equal to the critical temperature. Its dependence on molecular weight is given by

$$c_4 = 10^2 (c_{13} \ln m + c_{14})^{1/2} \qquad (9)$$

Equations (4) and (9) represent the observed A's with an SPE of 0.16% The constants involved in all the equations discussed above are given in Table 8.

OVER-ALL EVALUATION

The Hudleston equation, Equation

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%.

(1) with auxiliary Equations (2) to (4), defines completely the PvT relations of liquids over its range of validity. By further relating all parameters to the molecular weight of the *n*-alkanes in Equations (5) to (9), one can make a general calculation giving the compressions of any of the *n*-alkanes at any temperature and pressure, in which the only independent variable is molecular weight. 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_o 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_o 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°_T = zero-pressure volume of sample at temperature T
v^p_T = specific volume of sample at temperature T and pressure P
v°_T = zero-pressure specific volume of sample at temperature T
v°_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

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