Equation-of-State Parameters for Normal Alkanes. Correlation with Chain Length

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Abstract: Inconsistencies among existing equation-of-state data for *n*-alkanes have been resolved by careful determinations of thermal expansion coefficients, α, and thermal pressure coefficients, γ, for hydrocarbons $H(CH_2)_nH$ with $n = 6$, 8, 16, 22, 36, and ∞ (linear polymethylene) over ranges of temperature and at zero pressure. These experimental results in conjunction with selected data from the literature for other hydrocarbons are compared with the reduced equation of state specified by the partition function proposed recently (Flory, Orwoll, and Vrij) for chain molecule liquids. Excellent correlations over the entire range $n = 6$ to ∞ are obtained using the same set of parameters for all homologs. Isotherms are well reproduced, but parameters of the reduced equation of state change somewhat with temperature, as previously noted. These results provide a basis for interpreting the thermodynamic properties of *n*-alkane mixtures.

A partition function, which is of such simplicity as to permit its ready application to liquids and liquid mixtures consisting of nonspherical molecules, has been formulated recently for the express purpose of comprehending those equilibrium properties of mixtures which elude conventional theories.[1-3] Analysis of thermodynamic data for mixtures of small molecules met with encouraging success, particularly with respect to the correlation of excess volumes and excess enthalpies.[4] The similar treatment of polymer solutions promises to resolve long-standing discrepancies between theory and experiment.[5]

The partition function and the equation of state derived from it are adaptable also to the representation of homologous chain molecules. A previous attempt[1] to apply the theory to *n*-alkanes ranging from *n*-hexane to polymethylene was hampered by inadequate accuracy of some of the existing equation-of-state data. Reliable values for the thermal pressure coefficients, $\gamma = (\partial p/\partial T)_V$, have been determined for only a few of the homologs; even the thermal expansion coefficients, $\alpha = (1/V)(\partial V/\partial T)_p$, are not known with sufficient accuracy in some instances.

We have accordingly undertaken to determine α and γ for five *n*-alkanes and for linear polymethylene. The results of these measurements are here presented and compared with selected data from the literature for these hydrocarbons and other homologs. The equation-of-state parameters for this important homologous series of chain molecules are correlated with the theory cited above.

Experimental Section

***n*-Hexane and *n*-Octane.** Chromatoquality grade *n*-C_6H_{14} and *n*-C_8H_{18}, purchased from Matheson Coleman and Bell, were used without further purification. According to gas chromatographic analyses by the supplier, the former contained 0.5 mole % of methylcyclopentane and 0.08 mole % of methylpentane, and the latter about 0.3 mole % of unspecified impurities.

Thermal expansion coefficients of *n*-C_6H_{14} and *n*-C_8H_{18} were measured using the Pyrex dilatometer represented in Figure 1. Because of the length (72 cm) of capillary A, the alkanes were subjected to a pressure of nearly 2 atm, making expansion measurements possible above their normal boiling points. The volume of capillary A and reservoir B up to capillary C and the total volume of the dilatometer were carefully determined. About 30 g of the alkane liquid was then introduced into the cell. After the hydrocarbon had been thoroughly degassed, the remainder of the dilatometer was filled with mercury, care being taken to prevent the mercury from overflowing into the lower section of reservoir D. Reservoirs B and D were immersed in a constant-temperature bath, and the volume change of the hydrocarbon accompanying a temperature change, ΔT (1.5 to 4°), was determined from the mass of mercury drawn into the dilatometer from the weighing bottle E if the alkane contracted, or from the mass expelled into E if the alkane expanded.

Since the temperature intervals were small, the expansion of the hydrocarbon, $(\partial V/\partial T)_p$, was calculated as the sum of the observed expansion $(\Delta m_{Hg}/\Delta T)/\rho_{Hg}$ and the expansion of the glass dilatometer minus the expansion of the mercury, *i.e.*

$$(\partial V/\partial T)_p \cong (\Delta m_{Hg}/\Delta T)/\rho_{Hg} + V_g\alpha_g - V_{Hg}\alpha_{Hg} \quad (1)$$

The volume V_{Hg} of mercury present in the dilatometer at any temperature was determined from the total volume of the dilatometer V_g, from the temperature t_0 at which the mercury–alkane interface was at the fiducial point in C (*i.e.*, at exact filling of the calibrated volume by mercury), and from the density–temperature data of Young[6] for *n*-C_6H_{14} and *n*-C_8H_{18}. Values used for the thermal expansion coefficients of mercury and of Pyrex glass, α_{Hg} and α_g, are as follows[7] (in deg^{-1}): $\alpha_{Hg} = 1.82 \times 10^{-4}$ ($t \leqslant 10°$), 1.81×10^{-4} ($10° < t \leqslant 40°$), 1.80×10^{-4} ($40° < t \leqslant 100°$), and 1.79×10^{-4} ($100° < t$); $\alpha_g = 9.9 \times 10^{-6}$.

The values of $(\partial V/\partial T)_p$ thus found were fitted by the method of least squares to a polynomial equation, cubic in temperature, which was integrated to give the volume of the hydrocarbon as a function of temperature

$$V = \int_{t_0}^{t} (A + Bt' + Ct'^2 + Dt'^3)\mathrm{d}t' + V_0 \quad (2)$$

where V_0 is the volume of *n*-alkane at t_0. Equations 1 and 2 were used to compute α and V for *n*-C_6H_{14} and *n*-C_8H_{18}.

The thermal pressure coefficients of these two *n*-alkanes were measured according to the procedures of Westwater, Frantz, and Hildebrand[8] and of Allen, Gee, Mangaraj, Sims, and Wilson.[9] The degassed liquid sample (*ca.* 20 cm^3) was contained in a Pyrex cell in-

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(1) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).

(2) P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3515 (1964).

(3) P. J. Flory, *ibid.*, **87**, 1833 (1965).

(4) A. Abe and P. J. Flory, *ibid.*, **87**, 1838 (1965).

(5) B. E. Eichinger and P. J. Flory, in preparation.

(6) S. Young, recorded by J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Vol. I, Elsevier Publishing Co., New York, N. Y., 1950.

(7) "Handbook of Chemistry and Physics," 39th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1957.

(8) W. Westwater, H. W. Frantz, and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928).

(9) G. Allen, G. Gee, D. Mangaraj, D. Sims, and G. J. Wilson, *Polymer*, **1**, 467 (1960).

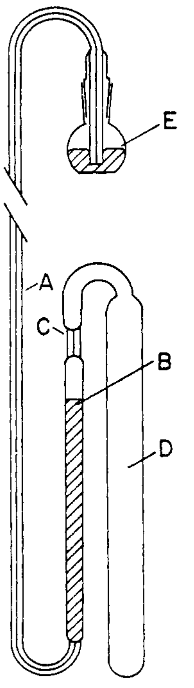

Figure 1. Dilatometer for expansion measurements on *n*-hexane and *n*-octane.

verted over mercury in a pressure bomb. As the contents of the pressure bomb were compressed isothermally, mercury was forced up a 2-mm capillary, the only opening in the cell. Part way up the capillary the mercury made contact with a fine, pointed platinum wire positioned along the capillary axis. This completed an electrical circuit and activated a relay which signaled the circuit closure. The pressure required to maintain the mercury–alkane interface at the end of the platinum wire was plotted as a function of temperature. The isochore was linear within limits of experimental precision throughout the pressure range of the measurements, *i.e.*, 0–40 bars; the observed thermal pressure coefficient, γ_{obsd}, for $p = 0$ was taken as the slope of the linear least-squares line passing through at least three and usually five p, T data points. Equation 3[8] was used to correct γ_{obsd} for the thermal expansion and the compression of the Pyrex cell, where $\kappa_g = 2.96 \times 10^{-6}$ bar^{-1}.[9,10]

$$\gamma = \gamma_{obsd}\alpha/(\alpha + \gamma_{obsd}\kappa_g - \alpha_g) \qquad (3)$$

***n*-Hexadecane.** Superior grade *n*-$C_{16}H_{34}$, supplied by Matheson Coleman and Bell, was purified by crystallization three times from 30–35 wt % solutions in toluene, and finally by distillation under reduced pressure. Analysis by gas chromatography did not reveal the presence of any impurities in the distillate. The melting point of the sample was 18.14–18.22° (lit.[11] 18.11–18.25°).

Degassed *n*-$C_{16}H_{34}$ was contained over mercury in the dilatometer illustrated in Figure 2. The masses of alkane and mercury in the dilatometer at one temperature, t_0, were determined from the known volume of the dilatometer, the densities of the alkane and mercury at t_0, and the sum of the masses of the two liquids filling the dilatometer. The mass of mercury m_{Hg} remaining in the cell after the temperature was adjusted from t_0 to t was ascertained by subtracting the change in mass of the weighing bottle from the mass of mercury in the cell at t_0. The volume V of the *n*-$C_{16}H_{34}$ at t was calculated from

$$V = V_g[1 + \alpha_g(t - t_0)] - m_{Hg}/\rho_{Hg} \qquad (4)$$

where V_g is the volume of the dilatometer at t_0. A quartic equation, with coefficients determined by the method of least squares, was used to express V as a function of t. The thermal expansion coefficient was determined from this expression and its temperature derivative.

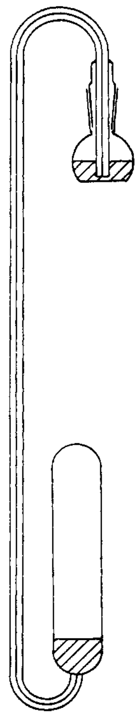

Figure 2. Dilatometer for expansion measurements on *n*-hexadecane.

The thermal pressure coefficient of *n*-$C_{16}H_{34}$ was determined by the same procedure as for *n*-C_6H_{14} and *n*-C_8H_{18}.

***n*-Docosane, *n*-Hexatriacontane, and Polymethylene.** Superior grade *n*-$C_{22}H_{46}$ (Matheson Coleman and Bell) and *n*-$C_{36}H_{74}$ (Humphrey Chemical Co.) were recrystallized three times from dilute toluene solutions. No impurities in the *n*-$C_{22}H_{46}$ were detected by gas chromatographic analysis. The *n*-$C_{22}H_{46}$ and *n*-$C_{36}H_{74}$ melted at 43.61–43.94° (lit.[12] 43–45°) and 75.78–75.92° (lit.[13] 75.73°), respectively. Marlex-50 polymethylene, produced by the Phillips Petroleum Co., was used without fractionation. A number-average molecular weight of 10^4 was estimated from its dilute solution viscosity in conjunction with Chiang's[14] analysis of the molecular weight distribution in Marlex-50. A second linear polymethylene, designated Marlex-6050, was a fractionated sample having a molecular weight of 180,000 as determined from viscosity measurements by the supplier, Phillips Petroleum Co. This specially prepared sample, which contained very little low molecular weight polymethylene, was stabilized with 2,6-di-*t*-butyl-*p*-cresol.

Thermal expansion coefficients of these higher homologs were measured in dilatometers similar to the one shown in Figure 2. The most satisfactory design incorporated some of the features necessary for a thermal pressure cell, illustrated in Figure 3. Once filled with hydrocarbon and mercury, this dilatometer could be converted to a cell for measuring γ by replacing the long capillary characteristic of the dilatometers in Figures 1 and 2 with a short tube (A in Figure 3) equipped with an electrical contact within the capillary section. The ground-glass joint B permitted interchange of the two components. The cells were charged with weighed quantities of alkane through openings in the tops of the sample reservoirs which were then sealed off. Mercury was introduced into the evacuated cells after the samples had been thoroughly degassed. Thermal expansion measurements on *n*-$C_{22}H_{46}$, *n*-$C_{36}H_{74}$, Marlex-50, and Marlex-6050 were carried out by the same procedure as was used for *n*-$C_{16}H_{34}$.

The thermal pressure cell represented in Figure 3 is a slightly modified version of one described by Allen and his co-workers.[9]

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(13) A. K. Doolittle and R. H. Peterson, *J. Am. Chem. Soc.*, 73, 2145 (1951).

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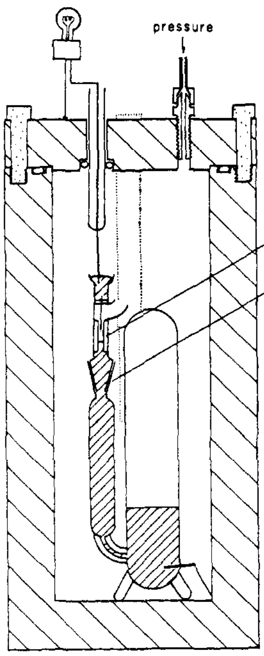

Figure 3. Pressure bomb and cell for measuring thermal pressure coefficients of n-docosane, n-hexatriacontane, and polymethylene. The dashed lines locate the thermometer well behind the sample cell.

A tungsten wire[15] with a sharpened tip was centered in the 1.5-mm capillary in A. The volume of the cell was 40–50 cm^3. The measurements of γ for n-$C_{22}H_{46}$, n-$C_{36}H_{74}$, and polymethylene were carried out by procedures essentially duplicating those described above for the lower homologs. The thermal pressure coefficients were calculated from γ_{obsd} using the equation[9,16]

$$\gamma = \gamma_{obsd}\alpha V/[\alpha V + (\alpha_{Hg} - \gamma_{obsd}\kappa_{Hg})V_{Hg} - (\alpha_g - \gamma_{obsd}\kappa_g)V_g] \quad (5)$$

where κ_{Hg} is represented as a function of the centigrade temperature by the equation[17]

$$\kappa_{Hg} = 3.921 \times 10^{-6} + 4.7 \times 10^{-9}t + 3.5 \times 10^{-14}t^3 \text{ bar}^{-1}$$

Thermometers. Temperature changes in the determinations of α for n-C_6H_{14} and n-C_8H_{18} were measured with a Beckmann thermometer which had been calibrated over a wide range of temperature using a platinum resistance thermometer (Rosemount Engineering Co., Model 104BW) in conjunction with a Leeds and Northrup G-1 Mueller bridge and a Medistor Instrument Co. A-60C microvoltmeter. For all other determinations of α, temperature intervals were measured using either the platinum resistance thermometer or a Hewlett-Packard DY-2801A quartz crystal thermometer. The latter instrument is capable of measuring temperatures with a precision of ±0.0001°.

The platinum resistance thermometer was used for all measurements of the thermal pressure coefficient γ. The temperature probe was inserted in a copper well in the cover of the bomb, so that the sensing element was situated very close to the liquid sample.

Pressure Gauges. In some of the determinations of γ, pressures were measured with a dead-weight pressure gauge (Ruska Instrument Corp., Model 2400.6), which generated pressures from 1.4 to 44.3 bars and measured them to ±0.007 bar.

A fused quartz, bourdon-type pressure gauge (Texas Instruments, Model 140A) was used in the remaining experiments. Pressures between 1.0 and 35.5 bars were measured with a precision of ±0.002 bar. The gauge was calibrated with the dead-weight instrument. Pressures were generated by compressing oil in a cylinder connected in series with the pressure bomb and with the fused quartz gauge. A manually operated piston developed the approximate required pressure, and a smaller motor-driven piston provided the fine pressure control. The direction of the reversible motor was determined by the same relay which responded to the mercury contact with the wire in the capillary. The motor, operating continuously, maintained the mercury–alkane interface in the immediate vicinity of the tip of the wire contact in the capillary. The adiabatic temperature changes which would have resulted from intermittent adjustments of pressure were thus avoided, and attainment of equilibrium was expedited.

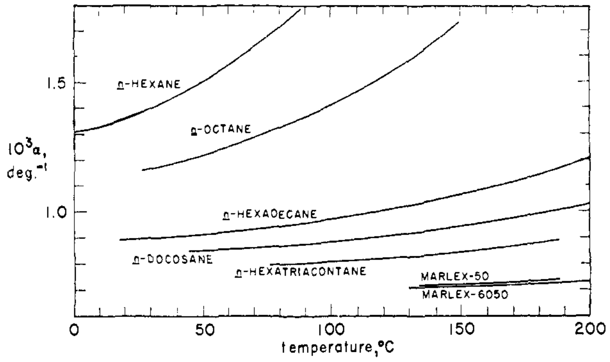

Figure 4. Thermal expansion coefficients of n-hexane, n-octane, n-hexadecane, n-docosane, n-hexatriacontane, and polymethylene plotted against temperature.

Results

Thermal Expansion Coefficients. Densities and thermal expansion coefficients are given by the polynomials in powers of temperature in Table I. Estimated ranges of error in ρ were ±0.0002 g cm^{-3} for n-C_6H_{14}, n-C_8H_{18}, and n-$C_{16}H_{34}$; they were ±0.0006 g cm^{-3} for the remaining four alkanes. The direct measurements of α for n-C_6H_{14} and n-C_8H_{18} rarely deviated by more than 1% from the least-squares curves drawn through the experimental points. The averages of the absolute deviations from the least-squares lines for the volumes of n-$C_{16}H_{34}$, n-$C_{22}H_{46}$, n-$C_{36}H_{74}$, Marlex-50, and Marlex-6050 were less than 0.002% of the respective volumes. Although relatively large uncertainties apply to the absolute values of the densities of these higher alkanes, such errors remained constant over the entire temperature ranges and therefore did not affect the values computed for α. Thermal expansion coefficients calculated from the equations in Table I are accurate to ±0.5%. The temperatures over which the measurements were conducted and the number of observations are denoted in the final two columns of Table I.

The thermal expansion coefficients reported above are presented graphically as functions of temperature in Figure 4. The values of α for n-C_6H_{14}, n-C_8H_{18}, n-$C_{16}H_{34}$, and Marlex-50 polymethylene are compared in Table II with the results determined from densities previously reported from other sources.[6,18,19]

Thermal Pressure Coefficients. Results are presented in Table III. The mean values of the absolute deviations of the individual measurements of γ from the least-squares lines were 0.003 bar deg^{-1} for both n-C_6H_{14} and n-C_8H_{18}; for other hydrocarbons they were 0.031 (n-$C_{16}H_{34}$), 0.023 (n-$C_{22}H_{46}$), and 0.053 bar deg^{-1} (n-

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(15) Tungsten provides a more satisfactory contact with mercury than does platinum.

(16) R. D. Dunlap and R. L. Scott, *J. Phys. Chem.*, 66, 631 (1962).

(17) K. E. Bett, K. E. Weale, and D. M. Newitt, *Brit. J. Appl. Phys.*, 5, 243 (1954).

(18) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

(19) Unpublished data of D. T. F. Pals; private communication from A. Bondi.

Table I. Densities and Thermal Expansion Coefficients

n-Alkane	ρ, g cm^{-3}, and α, deg^{-1}	Temp range, °C	No. of observns
n-C_6H_{14}	$\rho = 0.6773 - 0.08914 \times 10^{-2}t - 0.00086 \times 10^{-4}t^2 - 0.00652 \times 10^{-6}t^3$ $\alpha = 1.315 \times 10^{-3} + 0.171 \times 10^{-5}t + 0.4498 \times 10^{-7}t^2 - 0.0487 \times 10^{-9}t^3$	−15–89	67
n-C_8H_{18}	$\rho = 0.7185 - 0.08075 \times 10^{-2}t + 0.00001 \times 10^{-4}t^2 - 0.00313 \times 10^{-6}t^3$ $\alpha = 1.095 \times 10^{-3} + 0.256 \times 10^{-5}t - 0.0327 \times 10^{-7}t^2 + 0.0999 \times 10^{-9}t^3$	26–145	58
n-$C_{16}H_{34}$	$\rho = 0.7871 - 0.07003 \times 10^{-2}t + 0.00185 \times 10^{-4}t^2 - 0.00134 \times 10^{-6}t^3 + 0.000045 \times 10^{-8}t^4$ $\alpha = 0.889 \times 10^{-3} + 0.035 \times 10^{-5}t + 0.0472 \times 10^{-7}t^2 + 0.0064 \times 10^{-9}t^3$	18–207	84
n-$C_{22}H_{46}$	$\rho = 0.8091 - 0.06760 \times 10^{-2}t + 0.00187 \times 10^{-4}t^2 - 0.00082 \times 10^{-6}t^3$ $\alpha = 0.835 \times 10^{-3} + 0.027 \times 10^{-5}t + 0.0262 \times 10^{-7}t^2 + 0.0054 \times 10^{-9}t^3$	44–201	62
n-$C_{36}H_{74}$	$\rho = 0.8317 - 0.06642 \times 10^{-2}t + 0.00338 \times 10^{-4}t^2 - 0.00094 \times 10^{-6}t^3$ $\alpha = 0.797 \times 10^{-3} - 0.013 \times 10^{-5}t + 0.0253 \times 10^{-7}t^2 + 0.0050 \times 10^{-9}t^3$	76–188	49
Marlex-50 polymethylene	$\rho = 0.8689 - 0.06823 \times 10^{-2}t + 0.00721 \times 10^{-4}t^2 - 0.00142 \times 10^{-6}t^3$ $\alpha = 0.783 \times 10^{-3} - 0.100 \times 10^{-5}t + 0.0310 \times 10^{-7}t^2 + 0.0056 \times 10^{-9}t^3$	134–188	16
Marlex-6050 polymethylene	$\rho = 0.8674 - 0.06313 \times 10^{-2}t + 0.00367 \times 10^{-4}t^2 - 0.00055 \times 10^{-6}t^3$ $\alpha = 0.727 \times 10^{-3} - 0.030 \times 10^{-5}t + 0.0120 \times 10^{-7}t^2 + 0.0021 \times 10^{-9}t^3$	130–207	30

Table II. Comparison of Thermal Expansion Coefficients

Temp, °C	$\alpha \times 10^3$, deg^{-1}							
	n-$C_{16}H_{14}$		n-C_8H_{18}		n-$C_{16}H_{34}$		Marlex-50	
	This work	Young[8]	This work	Young[6]	This work	API[18]	This work	Pals[19]
0	1.315							
20	1.367	1.364	1.146	1.151	0.897			
40	1.452	1.465	1.199	1.205	0.911	0.902		
60	1.569	1.563	1.259	1.259	0.929	0.929		
80	1.715	1.684	1.330	1.320	0.951	0.957		
100			1.418	1.398	0.978	0.987		
120			1.528	1.502	1.010	1.020		
140			1.664	1.640	1.048	1.055	0.720	0.722
160					1.092	1.092	0.726	0.732
180					1.143	1.132	0.737	
200					1.200	1.176		

$C_{36}H_{74}$). Only five of the 43 measurements listed in Table III deviated from the least-squares expressions by more than 1% in γ; of these five, four were for n-$C_{36}H_{74}$.

Dunlap and Scott[16] also determined γ for n-C_6H_{14} by direct measurement. Their results above 20° and ours are in good agreement, as shown in Table IV. Boelhouwer[20] evaluated the coefficients of compressibility for n-C_8H_{18} and n-$C_{16}H_{34}$ by fitting his p, V measurements at 30, 60, 90, and 120° to the Tait equation. Values $\gamma = \alpha/\kappa$ calculated from his compressibilities at zero pressure and from the thermal expansion coefficients in Table I are 2–5% larger than the coefficients given in Table III. These differences can be attributed to errors in the compressibility measurements and to inadequacy of the Tait equation in representing the curvature of the isotherm at low pressures. Thermal pressure coefficients deduced from published equation-of-state data for low-pressure polyethylene[21–23] are not of the accuracy required for present purposes.

The thermal pressure coefficients reported in Table III are plotted against temperature in Figure 5. Results reported by other investigators for n-C_6H_{14}, n-C_7H_{16}, and n-$C_{14}H_{30}$, which likewise were obtained from direct measurements of γ,[8,9,16,24] are included also. The lines drawn through the data points represent least-squares equations. Values of γ computed from κ have not been included in Figure 5 because of large uncertainties in compression measurements (±2–5%) compared with those affecting direct determinations of γ (±0.5–1.5%).

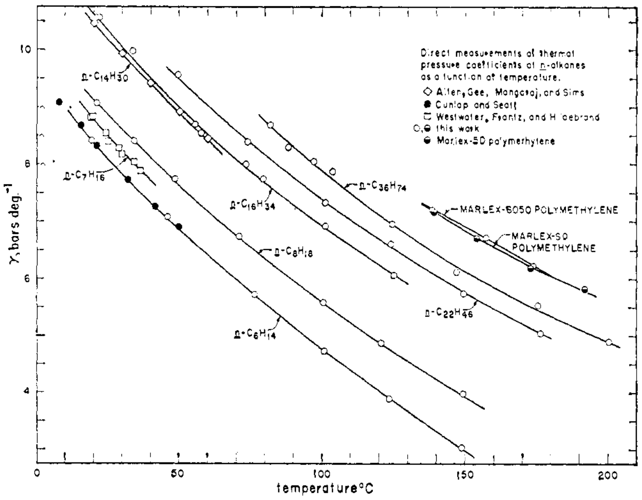

Figure 5. Thermal pressure coefficients plotted against temperature for n-hexane, n-heptane,[8,24] n-octane, n-tetradecane,[9] n-hexadecane, n-docosane, n-hexatriacontane, and polymethylene. Filled circles represent data of Dunlap and Scott[16] for n-hexane. Data for Marlex-6050 are represented by open circles, those for Marlex-50 by half-filled circles.

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(22) M. M. Martynyuk and V. K. Semenchenko, *Colloid J.* (USSR), **25**, 163 (1963).

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Table III. Thermal Pressure Coefficients

Temp, °C	γ, bars deg^{-1}	$(\gamma - \gamma_{eq})$, bars deg^{-1}
n-C_6H_{14}		
$\gamma = 9.595 - 6.220 \times 10^{-2}t + 1.732 \times 10^{-4}t^2 - 0.339 \times 10^{-8}t^3$		
19.34	8.453	−0.002
45.99	7.073	0.005
76.54	5.690	−0.007
100.53	4.753	0.004
123.46	3.920	0.001
149.02	3.052	−0.001
n-C_8H_{18}		
$\gamma = 10.255 - 5.822 \times 10^{-2}t + 1.330 \times 10^{-4}t^2 - 0.166 \times 10^{-6}t^3$		
20.90	9.094	−0.001
34.00	8.428	0.005
48.48	7.719	−0.008
70.99	6.738	0.005
100.62	5.574	−0.001
120.80	4.870	0.000
149.25	3.978	0.000
n-$C_{16}H_{34}$		
$\gamma = 11.876 - 6.744 \times 10^{-2}t + 2.292 \times 10^{-4}t^2 - 0.477 \times 10^{-6}t^3$		
20.39	10.556	−0.036
20.95	10.557	−0.002
33.40	9.946	0.086
55.81	8.748	0.005
57.42	8.571	−0.098
73.36	8.002	0.029
79.41	7.745	0.018
101.10	6.909	0.002
125.23	6.085	−0.004
n-$C_{22}H_{46}$		
$\gamma = 12.050 - 5.536 \times 10^{-2}t + 0.892 \times 10^{-4}t^2$		
49.85	9.532	0.020
73.77	8.425	−0.027
101.00	7.338	−0.030
124.19	6.595	0.045
149.83	5.761	0.003
177.21	5.030	−0.011
n-$C_{36}H_{74}$		
$\gamma = 13.168 - 6.424 \times 10^{-2}t + 1.153 \times 10^{-4}t^2$		
81.86	8.697	0.015
88.20	8.312	−0.088
97.11	8.045	0.028
103.71	7.844	0.098
124.41	6.937	−0.024
147.25	6.129	−0.080
175.38	5.521	0.071
200.81	4.899	−0.020
Marlex-50 Polymethylene		
$\gamma = 13.218 - 5.580 \times 10^{-2}t + 0.896 \times 10^{-4}t^2$		
139.42	7.177	−0.005
154.30	6.755	0.012
173.52	6.224	−0.010
191.88	5.815	0.004
Marlex-6050 Polymethylene		
$\gamma = 9.018 - 0.033 \times 10^{-2}t - 0.899 \times 10^{-4}t^2$		
139.17	7.231	...
157.57	6.733	...
173.02	6.269	...

Thermal Expansion Coefficients from Published Density Measurements. Reliable density measurements which accurately define the isobars for n-alkanes above $n = 5$ are presented in Table V in the form of least-squares equations. Densities computed from these expressions rarely differ from the experimental values by more than 0.0002 g cm^{-3}. Thermal expansion coefficients, derived from these density equations and presented in Table V, are accurate to ±1%, in general, except at the extremities of the temperature ranges where the curvature in the isobar is more sensitive to small errors in ρ.

Theoretical Relationships. Pursuant to application to chain molecules of the theory cited in the introductory section,[1-3] it is expedient to subdivide the molecule into segments, arbitrary in number and correspondingly in size. Let the n-alkane molecule comprise r such segments, each having a "hard core" volume v^*. Then $\mathrm{v}^* = rv^*$ is the hard-core volume of the molecule. Adopting a device introduced by Prigogine,[25,26] we let $3c$ be the number of intermolecular degrees of freedom per segment, averaged over all segments of the chain molecule. The partition function is then formulated[1,3] from the result obtained by Tonks[27] for the configuration integral for a one-dimensional system of hard lines (spheres), this being used in conjunction with a smoothed average energy for the liquid, which is expressed by

$$E_0 = -Nrs\eta/2v \tag{6}$$

where N is the number of molecules (or moles), v is the volume per segment (or per mole of segments), rs is the number of interaction sites per molecule, and $-\eta/v$ represents the average energy of interaction for a pair of adjacent sites of neighboring molecules. Thus, the average energy is taken to vary inversely as the volume and to be directly related to the number of contacts between first neighbors.

The reduced equation of state derived from the resulting partition function[1,3]

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T} \tag{7}$$

is of the same form as was introduced some years ago by Eyring and Hirschfelder.[28] The reduced quantities $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ are defined differently, however. They are given by[1,3]

$$\tilde{p} = p/p^* = 2pv^{*2}/s\eta \tag{8}$$

$$\tilde{T} = T/T^* = 2v^*cRT/s\eta \tag{9}$$

$$\tilde{v} = v/v^* = \mathrm{v}/\mathrm{v}^* \tag{10}$$

where $\mathrm{v} = rv$ is the molar volume. The isobar at zero pressure is

$$T^* = T\tilde{v}^{4/3}/(\tilde{v}^{1/3} - 1) \tag{11}$$

From eq 11

$$\tilde{v}^{1/3} = \alpha T/3(1 + \alpha T) + 1 \tag{12}$$

The temperature derivative of eq 7 at constant volume evaluated for $p = 0$ gives

$$p^* = \gamma T\tilde{v}^2 \tag{13}$$

The quantities T^*, p^*, and v^* can be computed from α, γ, and v as prescribed by eq 9–13. This set of three parameters suffices to characterize the p, v, T relationship for each n-alkane liquid, according to the equations given above.

The dependences of p^*, T^*, and v^* on chain length may be interpreted in terms of two kinds of segments:

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(25) I. Prigogine, N. Trappeniers, and V. Mathot, *Discussions Faraday Soc.*, **15**, 93 (1953).

(26) I. Prigogine, "The Molecular Theory of Solutions," Interscience Publishers, Inc., New York, N. Y., 1957, Chapter XVI.

(27) L. Tonks, *Phys. Rev.*, **50**, 955 (1936).

(28) H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937); J. O. Hirschfelder, D. Stevenson, and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

Table IV. Comparison of Thermal Pressure Coefficients

Temp, °C	$-\gamma_{C_6H_{14}}$, bars deg^{-1} This work	$-\gamma_{C_6H_{14}}$, bars deg^{-1} Dunlap and Scott[16]	Temp, °C	$-\gamma_{C_8H_{18}}$, bars deg^{-1} This work	$-\gamma_{C_8H_{18}}$, bars deg^{-1} Boelhouwer[20]	Temp, °C	$-\gamma_{C_{16}H_{34}}$, bars deg^{-1} This work	$-\gamma_{C_{16}H_{34}}$, bars deg^{-1} Boelhouwer[20]
21.91[a]	8.31	8.26	30	8.62	8.95	30	10.05	10.27
32.13[a]	7.76	7.73	60	7.20	7.49	60	8.55	8.84
41.50[a]	7.29	7.26	90	5.97	6.18	90	7.32	7.53
50.18[a]	6.87	6.84	120	4.90	5.03	120	6.26	6.47

[a] For each isochore, the temperatures $t_{p=1\text{ atm}}$ given by Dunlap and Scott[16] have been recalculated for $t_{p=0}$.

Table V. Densities and Thermal Expansion Coefficients from the Literature

n-Alkane	ρ, g cm^{-3}, and α, deg^{-1}	Temp range, °C	Ref
n-C_6H_{14}	$\rho = 0.6769 - 0.08419 \times 10^{-2}t - 0.01558 \times 10^{-4}t^2 + 0.00934 \times 10^{-8}t^3 - 0.005201 \times 10^{-8}t^4$ $\alpha = 1.233 \times 10^{-3} + 0.772 \times 10^{-5}t - 0.6974 \times 10^{-7}t^2 + 0.5454 \times 10^{-9}t^3$	0–170	6
n-C_7H_{16}	$\rho = 0.7005 - 0.08498 \times 10^{-2}t + 0.00185 \times 10^{-4}t^2 - 0.00470 \times 10^{-6}t^3 - 0.000281 \times 10^{-8}t^4$ $\alpha = 1.210 \times 10^{-3} + 0.137 \times 10^{-5}t + 0.1117 \times 10^{-7}t^2 + 0.1157 \times 10^{-9}t^3$	0–180	6
n-C_8H_{18}	$\rho = 0.7183 - 0.07873 \times 10^{-2}t - 0.00506 \times 10^{-4}t^2 + 0.00198 \times 10^{-6}t^3 - 0.001545 \times 10^{-8}t^4$ $\alpha = 1.086 \times 10^{-3} + 0.363 \times 10^{-5}t - 0.2371 \times 10^{-7}t^2 + 0.1861 \times 10^{-9}t^3$	0–220	6
n-C_9H_{20}	$\rho = 0.7334 - 0.07892 \times 10^{-2}t + 0.00457 \times 10^{-4}t^2 - 0.00676 \times 10^{-6}t^3 + 0.001269 \times 10^{-8}t^4$ $\alpha = 1.076 \times 10^{-3} - 0.010 \times 10^{-5}t + 0.2778 \times 10^{-7}t^2 - 0.0434 \times 10^{-9}t^3$	−20–150	18
n-$C_{10}H_{22}$	$\rho = 0.7454 - 0.07674 \times 10^{-2}t + 0.00188 \times 10^{-4}t^2 - 0.00204 \times 10^{-6}t^3 - 0.000335 \times 10^{-8}t^4$ $\alpha = 1.030 \times 10^{-3} + 0.059 \times 10^{-5}t + 0.0677 \times 10^{-7}t^2 + 0.0470 \times 10^{-9}t^3$	−20–170	18
n-$C_{11}H_{24}$	$\rho = 0.7552 - 0.07498 \times 10^{-2}t + 0.00189 \times 10^{-6}t^2 - 0.00202 \times 10^{-6}t^3 - 0.000129 \times 10^{-8}t^4$ $\alpha = 0.993 \times 10^{-3} + 0.052 \times 10^{-5}t + 0.0679 \times 10^{-7}t^2 + 0.0297 \times 10^{-9}t^3$	−20–190	18
n-$C_{12}H_{26}$[a]	$\rho = 0.7635 - 0.07257 \times 10^{-2}t - 0.00089 \times 10^{-4}t^2 + 0.00052 \times 10^{-6}t^3 - 0.000683 \times 10^{-8}t^4$ $\alpha = 0.949 \times 10^{-3} + 0.135 \times 10^{-5}t - 0.0530 \times 10^{-7}t^2 + 0.0628 \times 10^{-9}t^3$	0–210	18
n-$C_{14}H_{30}$	$\rho = 0.7766 - 0.06881 \times 10^{-2}t - 0.00245 \times 10^{-4}t^2 + 0.00078 \times 10^{-6}t^3 - 0.000385 \times 10^{-8}t^4$ $\alpha = 0.884 \times 10^{-3} + 0.154 \times 10^{-5}t - 0.0376 \times 10^{-7}t^2 + 0.0317 \times 10^{-9}t^3$	10–210	18
n-$C_{15}H_{32}$	$\rho = 0.7823 - 0.06892 \times 10^{-2}t - 0.00052 \times 10^{-4}t^2 - 0.00065 \times 10^{-6}t^3 + 0.000026 \times 10^{-8}t^4$ $\alpha = 0.881 \times 10^{-3} + 0.093 \times 10^{-5}t + 0.0297 \times 10^{-7}t^2 + 0.0046 \times 10^{-9}t^3$	10–210	18
n-$C_{16}H_{34}$	$\rho = 0.7868 - 0.06719 \times 10^{-2}t - 0.00158 \times 10^{-4}t^2 - 0.00016 \times 10^{-6}t^3 - 0.000011 \times 10^{-8}t^4$ $\alpha = 0.854 \times 10^{-3} + 0.115 \times 10^{-5}t + 0.0140 \times 10^{-7}t^2 + 0.0044 \times 10^{-9}t^3$	20–210	18
n-$C_{17}H_{36}$	$\rho = 0.7907 - 0.06476 \times 10^{-2}t - 0.00390 \times 10^{-4}t^2 + 0.00108 \times 10^{-6}t^3 - 0.000208 \times 10^{-8}t^4$ $\alpha = 0.817 \times 10^{-3} + 0.173 \times 10^{-5}t - 0.0338 \times 10^{-7}t^2 + 0.0136 \times 10^{-9}t^3$	30–210	18
n-$C_{18}H_{38}$	$\rho = 0.7950 - 0.06598 \times 10^{-2}t - 0.00097 \times 10^{-4}t^2 - 0.00068 \times 10^{-6}t^3 + 0.000176 \times 10^{-8}t^4$ $\alpha = 0.831 \times 10^{-3} + 0.088 \times 10^{-5}t + 0.0412 \times 10^{-7}t^2 - 0.0089 \times 10^{-9}t^3$	30–210	18
n-$C_{19}H_{40}$	$\rho = 0.7973 - 0.06101 \times 10^{-2}t - 0.00664 \times 10^{-4}t^2 + 0.00232 \times 10^{-6}t^3 - 0.000358 \times 10^{-8}t^4$ $\alpha = 0.763 \times 10^{-3} + 0.236 \times 10^{-5}t - 0.0778 \times 10^{-7}t^2 + 0.0191 \times 10^{-9}t^3$	40–210	18
n-$C_{20}H_{42}$	$\rho = 0.8013 - 0.06432 \times 10^{-2}t - 0.00129 \times 10^{-4}t^2 - 0.00065 \times 10^{-6}t^3 + 0.000226 \times 10^{-8}t^4$ $\alpha = 0.805 \times 10^{-3} + 0.088 \times 10^{-5}t + 0.0448 \times 10^{-7}t^2 - 0.0136 \times 10^{-9}t^3$	40–210	18
n-$C_{26}H_{54}$	$\rho = 0.7847 + 0.00978 \times 10^{-2}t - 0.05875 \times 10^{-4}t^2 + 0.01515 \times 10^{-6}t^3$ $\alpha = -0.076 \times 10^{-3} + 1.316 \times 10^{-5}t - 0.3401 \times 10^{-7}t^2 - 0.0707 \times 10^{-9}t^3$	90–160	*b*
Marlex-50 polymethylene	$\rho = 0.8263 + 0.01619 \times 10^{-2}t - 0.04875 \times 10^{-4}t^2 + 0.01085 \times 10^{-6}t^3$ $\alpha = -0.143 \times 10^{-3} + 1.022 \times 10^{-5}t - 0.232 \times 10^{-7}t^2 - 0.0406 \times 10^{-9}t^3$	130–180	19

[a] The unpublished results of dilatometric measurements of α for *n*-$C_{12}H_{26}$ carried out in these laboratories by P. G. Barber differ by <0.5% from those computed here. Barber found $\alpha = 0.974 \times 10^{-3}$ deg^{-1} at 20°, 1.014×10^{-3} deg^{-1} at 50°, 1.098×10^{-3} deg at 100°, and 1.248×10^{-3} deg^{-1} at 150°. [b] R. Schenck and M. Kintzinger, *Rec. Trav. Chim.*, **42**, 759 (1923).

midchain and terminal.[1] Let s_m and s_e represent the contributions to rs from middle and terminal segments, respectively; that is

$$rs = rs_m + s_e \tag{14}$$

Three different interactions—midchain with midchain, midchain with terminal, and terminal with terminal—are characterized by η_m, η_{em}, and η_e, respectively. For segments randomly dispersed throughout the liquid

$$rs\eta = (rs_m^2/s)\eta_m + 2(s_e s_m/s)\eta_{em} + (s_e^2/rs)\eta_e \tag{15}$$

where s_e is taken as the number of sites on terminal segments whose interactions with other segments differ from the interactions of midchain segments. Account is taken of the number of external degrees of freedom associated with midchain and terminal segments in the equation

$$3rc = 3(rc_m + c_e) \tag{16}$$

By substitution of eq 15 and 16 in eq 8 and 9

$$p^* = p_\infty^*[1 + 2(s_e\eta_{em}/s_m\eta_m)/r + (s_e^2\eta_e/s_m^2\eta_m)/r^2]/[1 + (s_e/s_m)/r] \tag{17}$$

$$T^* = T_\infty^*[1 + 2(s_e\eta_{em}/s_m\eta_m)/r + (s_e^2\eta_e/s_m^2\eta_m)/r^2]/[1 + (s_e/s_m)/r][1 + (c_e/c_m)/r] \tag{18}$$

where

$$p_\infty^* = s_m\eta_m/2v^{*2}$$

$$T_\infty^* = s_m\eta_m/2Rv^*c_m$$

The definition of segment being arbitrary, it is convenient to assign it the same size v^* for all *n*-alkanes. We assume that v* can be written as a linear function of the number *n* of carbon atoms per molecule; *i.e.*

$$\text{v}^* = v^*(n + n_e) \tag{19}$$

Since $\text{v}^* = rv^*$

$$r = n + n_e \tag{20}$$

Discussion of Results and Comparison with Theory.

Table VI. Coefficients for the Equations for v*, T^*, and p^*

Temp, °C	v^*, cm^3 mole^{-1}	n_e	c_e/c_m	T_∞^*, °K	$2s_e\eta_{em}/s_m\eta_m$	$s_e{}^2\eta_e/s_m{}^2\eta_m$	p_∞^*, cal cm^{-3}	Range
20	13.989	1.119	1.772	6415	−0.180	−1.76	116.5	$6 \leq n \leq 16$
30	14.039	1.112	1.803	6570	−0.362	−1.14	117.1	$6 \leq n \leq 16$
40	14.073	1.112	1.826	6584	−0.186	−2.15	115.4	$6 \leq n \leq 16$
50	14.071	1.141	1.896	6658	−0.139	−2.48	115.0	$6 \leq n \leq 22$
60	14.114	1.130	1.931	6743	−0.188	−2.38	114.4	$6 \leq n \leq 22$
70	14.140	1.132	1.991	6766	−0.044	−3.15	112.5	$6 \leq n \leq 22$
80	14.135	1.163	1.781	6839	−0.341	−2.49	114.1	$6 \leq n \leq 36$
90	14.176	1.150	1.804	6915	−0.423	−2.17	113.2	$6 \leq n \leq 36$
100	14.206	1.153	1.644	7011	−0.773	−0.86	113.4	$7 \leq n \leq 36$
110	14.260	1.129	1.714	7106	−0.859	−0.43	112.4	$7 \leq n \leq 36$
120	14.288	1.127	1.743	7138	−0.789	−1.02	110.6	$7 \leq n \leq 36$
130	14.289	1.163	1.657	7219	−0.997	−0.38	110.6	$7 \leq n$
140	14.330	1.158	1.612	7294	−1.122	−0.14	109.9	$7 \leq n$
150	14.368	1.151	1.332	7363	−1.472	+0.63	109.5	$7 \leq n$
160	14.404	1.156	1.332	7426	−1.530	+0.82	108.5	$7 \leq n$
170	14.436	1.168	1.418	7477	−1.319	−1.85	107.3	$11 \leq n$
180	14.466	1.187	1.018	7529	−1.686	−1.78	107.0	$12 \leq n$

The parameters T^* and v* = rv^* have been evaluated on the basis of eq 9–12 from the equations for ρ and α in Tables I and V. Values of ρ and α for the compounds which appear in both tables have been computed according to the empirical equations in Table I. Thermal expansion coefficients calculated from the equations in Table V for the alkanes $7 \leqslant n \leqslant 26$ at temperatures within 20° of the extremities of the temperature ranges cited in the penultimate column of the table have not been used because of their diminished accuracy. The characteristic pressures p^* have been calculated according to eq 13 for n-C_6H_{14}, n-C_8H_{18}, n-$C_{16}H_{34}$, n-$C_{22}H_{46}$, n-$C_{36}H_{74}$, and the two polymethylenes using the least-squares polynomials for γ in Table III; values of p^* for n-C_7H_{16} and for n-$C_{14}H_{30}$ were calculated from results for γ presented in ref 8 and 9.

The quantities v^* and n_e, which are listed in the second and third columns of Table VI for temperatures taken at 10° intervals between 20 and 180°, have been determined from a linear least-squares plot of v^* *vs.* n (see eq. 19). Both v^* and n_e gradually increase with temperature. The difference n_e between r and n (see eq 20) is between 1.1 and 1.2. With an error whose effect is negligible, we let $r = n + 1$ in all calculations which follow.

The parameters p_∞^*, T_∞^*, s_e/s_m, c_e/c_m, $2s_e\eta_{em}/s_m\eta_m$, and $s_e{}^2\eta_e/s_m{}^2\eta_m$, in the expressions relating p^* and T^* to r (eq 17 and 18) have been evaluated according to the following scheme.

(i) The quantity s_e/s_m was estimated from an analysis of a molecular model constructed using the crystallographic dimensions of the orthorhombic forms of several higher homologs.[29] It was taken arbitrarily to be the quotient of the intercept and slope in the expression of the molecular surface area as a linear function of r. In effect, those sites in excess of the number ascribable to r midchain segments are designated as terminal sites. The artificiality of this assignment will be reflected in the values found for η_{em}/η_m and η_e/η_m; it has no effect on the form of the relationships, however. The value of the ratio thus obtained is 0.6, which was used throughout. Since s_e/s_m assumes a minor role, this estimate suffices; possible errors arising from its inaccuracy are inconsequential.

(ii) The ratio c_e/c_m was determined from the slope and intercept of a plot of p^*/T^* *vs.* $1/(n + 1)$

$$p^*/T^* = (p_\infty^*/T_\infty^*)[1 + (c_e/c_m)/(n + 1)] \quad (21)$$

which follows from division of eq 17 by 18 and the stipulation $r = n + 1$.

(iii) Values for T_∞^*, $2s_e\eta_{em}/s_m\eta_m$, and $s_e{}^2\eta_e/s_m{}^2\eta_m$ were calculated as the coefficients of the terms in the least-squares expression, quadratic in $1/r = 1/(n + 1)$, for $T^*[1 + (c_e/c_m)/(n + 1)][1 + (s_e/s_m)/(n + 1)]$ (see eq 18).

(iv) The constant p_∞^* was obtained as the product of T_∞^* and the intercept of a plot of p^*/T^* *vs.* $1/(n + 1)$, as follows from eq 21.

The quantities c_e/c_m, T_∞^*, $2s_e\eta_{em}/s_m\eta_m$, $s_e{}^2\eta_e/s_m{}^2\eta_m$, and p_∞^* are given in columns 4–8 of Table VI. Values for the ratio c_e/c_m are between 1 and 2. Both T_∞^* and p_∞^* are temperature dependent, the former increasing and the latter decreasing with increasing temperature. The quantity $2s_e\eta_{em}/s_m\eta_m$ is small and negative; its temperature coefficient is negative. The term in eq 17 and 18 which is proportional to $1/(n + 1)^2$ is small; its coefficient, $s_e{}^2\eta_e/s_m{}^2\eta_m$, consequently is subject to large relative fluctuations.

The negative values of η_{em}/η_m and η_e/η_m (see Table VI) do not imply that interactions of terminal groups are repulsive. Rather, they are a consequence of our having placed the entire burden of the lower intermolecular energies for terminal methyl groups on only $s_e = 0.6s_m$ sites, a number which is probably too small by a factor of at least 5. A realistic account of the deficit of interactions of terminal groups would require specification of the number of sites on these groups, and this would entail a degree of arbitrariness that we prefer to avoid. As may readily be shown, such revision would easily render $0 < \eta_e/\eta_m < \eta_{em}/\eta_m < 1$ in accordance with expectation. The form of the equations would not be affected, however, as we have pointed out above.

Figures 6 and 7 illustrate the dependence of T^* and p^* on $1/(n + 1)$ at several temperatures. Equations 17 and 18, represented by the solid lines in the figures, yield values of p^* and T^* which generally are within ±0.6 cal cm^{-3} and ±15°K, respectively, of those obtained directly from the experimental values of γ and α for individual alkanes. These deviations in p^* and T^*

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(29) A. E. Smith, *J. Chem. Phys.*, 21, 2229 (1953).

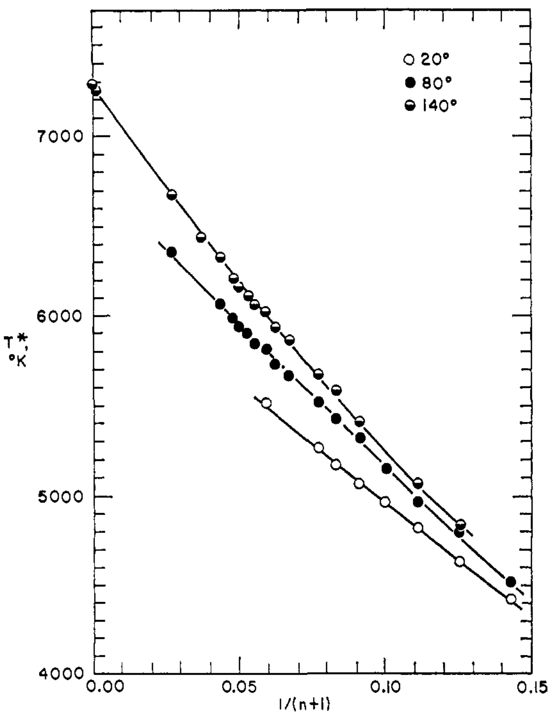

Figure 6. Characteristic temperatures plotted against $1/(n + 1)$ for 20, 80, and 140°. The solid lines have been drawn according to eq 18.

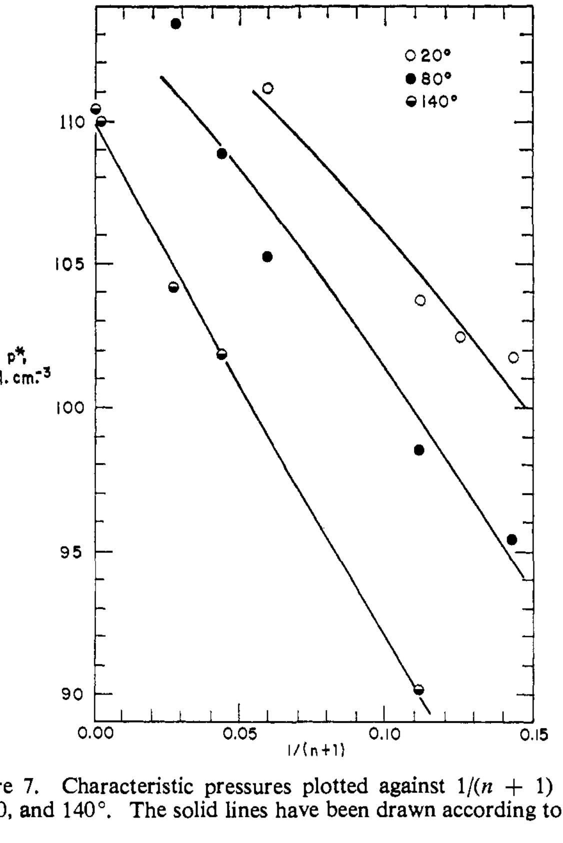

Figure 7. Characteristic pressures plotted against $1/(n + 1)$ for 20, 80, and 140°. The solid lines have been drawn according to eq 17.

correspond to discrepancies in γ and α of 0.6 and <0.5%, respectively.

For the hydrocarbons studied, p^* decreases 0.5 to 1.5% and T^* increases 0.2 to 1.0% over a 10° interval of temperature. The change of v* with temperature is functionally related to the change of T^*, as we have pointed out previously;[1] its magnitude represented by $d \ln v^*/dT$ ranges from 1×10^{-4} to 3×10^{-4} deg^{-1}. This dependence of the parameters on temperature limits the utility of the theory as applied to properties of a given hydrocarbon over a range of temperatures. Similar limitations are manifested in the corresponding treatment of other liquids.[4] The properties of the complete homologous series ($n > 5$) at any given temperature are very well reproduced by the theory, however, provided merely that the parameters applicable at that temperature are used.

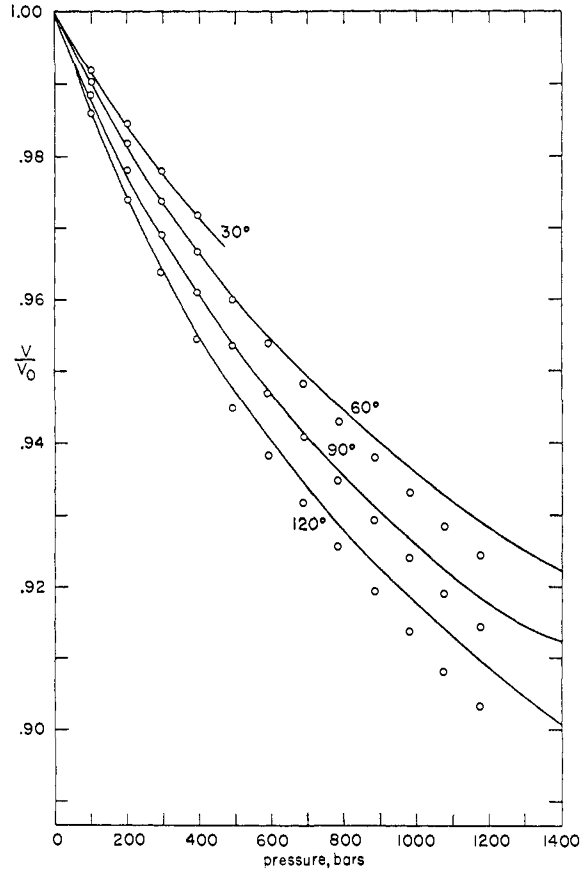

Figure 8. Ratio of the volume of *n*-hexadecane as a function of pressure to the volume at zero pressure, plotted against pressure for 30, 60, and 120°. The circles represent compression measurements of Boelhouwer;[20] the lines have been calculated from the equation of state using values for p^* and T^* derived from thermal pressure and thermal expansion coefficients measured at the stated temperatures.

Expressions for the primary parameters c and $s\eta$ can be written according to eq 8 and 9 as

$$c = p^*v^*/RT^* \qquad (22)$$

$$s\eta = 2p^*v^{*2} \qquad (23)$$

Values of c for hydrocarbons lie between 0.10 and 0.17; they decrease with increasing temperature and with increasing n. The parameter $s\eta$ varies from 3.8×10^4 to 4.6×10^4 cal cm^3 mole^{-2}; it decreases with increasing temperature and with decreasing n.

Thermal expansion coefficients and thermal pressure coefficients for all normal paraffins listed in the final column of Table VI can be calculated from values of p^* and T^* interpolated according to eq 17 and 18. Equations 11 and 12 relate T^* to α. Thermal pressure coefficients can be calculated by substitution in eq 13 of p^*

from eq 17 and of $\tilde{v}$ calculated from T^* or α according to eq 11 or 12. Error limits from values of α calculated on the basis of this scheme for a given temperature are $\pm 1.0\%$; for γ, $\pm 1.5\%$.

The results of compression measurements on n-$C_{16}H_{34}$ made by Boelhouwer[20] are compared with theoretical isotherms in Figure 8. At 1000 bars the calculated compressions underestimate the measured values by 6, 4, and 6% at 60, 90, and 120°, respectively.

Differentiation of eq 12 with respect to temperature at zero pressure and substitution of $\alpha = (1/\tilde{v})(\partial\tilde{v}/\partial T)_p$ yields[1]

$$(\partial\alpha/\partial T)_{p=0} = (7 + 4\alpha T)\alpha^2/3 \qquad (24)$$

The observed values of $(\partial\alpha/\partial T)_p$ for the alkanes listed in Table VI are 0.1×10^{-6} to 14×10^{-6} deg^{-2}. In most instances these are 0.5×10^{-6} to 2.5×10^{-6} deg^{-2} less than $(\partial\alpha/\partial T)_p$ calculated on the basis of eq 24. Thus, the theory correctly predicts a positive coefficient $(\partial\alpha/\partial T)_p$ but is quantitatively inaccurate in its estimate of the magnitude of this quantity. This is a further manifestation of the limitation of the treatment with respect to the dependence of properties on temperature.[1,4]

The temperature derivative of γ for $p = 0$ is given by

$$(T/\gamma)(\partial\gamma/\partial T)_{p=0} = (1 + 2\alpha T) \qquad (25)$$

Measured values of the dimensionless quantity $(T/\gamma)\cdot(\partial\gamma/\partial T))_{p=0}$ range from -4.6 to -1.5. Those calculated from α on the basis of eq 25 are also negative but are 0 to 30% smaller in magnitude.

The thermodynamic properties of binary mixtures of the n-alkanes are treated in the following paper with the aid of the results which have been presented here.

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Thermodynamic Properties of Binary Mixtures of *n*-Alkanes

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Abstract: The excess thermodynamic properties of mixtures of normal paraffin hydrocarbons are interpreted according to statistical mechanical theory developed earlier. The comprehensive equation-of-state data of the preceding paper are used to characterize the pure components, as required by the theory referred to. Effects of intrinsic properties of the components, ignored in conventional treatments of solutions, are large for these systems. A single arbitrary parameter, reflecting the differences of the interactions involving terminal (methyl) as compared to internal (methylene) groups, suffices to reproduce the excess volumes, excess thermal expansion coefficients, excess compressibilities, and excess enthalpies, ΔH_M, for all mixtures of normal paraffins, C_nH_{2n+2}, $n > 5$, for which data are available. The decrease in ΔH_M with temperature and the reversal of its sign at elevated temperatures, observed for several systems, are predicted, but the magnitude of the change with temperature is underestimated. Precise agreement of calculated excess chemical potentials with those observed for the several systems investigated experimentally is achieved through introduction of an additional parameter to represent the entropy associated with interactions between terminal and midchain groups; the same value is assigned to this parameter for all systems and temperatures. The theoretical equations, in conjunction with the equation-of-state information and the two parameters cited, correctly predict the occurrence of lower critical miscibility for solutions of polymethylene in the n-alkanes. Calculated critical temperatures approximate those found by experiment for n-C_6H_{14}, n-C_7H_{16}, and n-C_8H_{18}.

In earlier papers[1-4] we have called attention to the contributions of the characteristic properties of the pure liquid components to the excess thermodynamic properties of liquid mixtures. The conventional formulation of the free energy of mixing from a combinatory entropy and an interaction energy (*e.g.*, of the van Laar form) attributable to contacts between neighboring molecules does not afford an adequate representation of the thermodynamic functions of typical solutions. For the express purpose of taking account of the effects of the liquid-state properties peculiar to the components, a simple statistical mechanical theory was developed which admits of application to mixtures as well as to pure liquids.[1-3] The properties of component i of the solution are represented by a characteristic molar volume v_i^*, a characteristic temperature T_i^*, and a characteristic pressure p_i^*. These parameters may be evaluated from the molar volume v_i, the thermal expansion coefficient α_i, and the thermal pressure coefficient γ_i in the manner set forth in the preceding paper.[5] One additional pa-

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(1) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).

(2) P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3515 (1964).

(3) P. J. Flory, *ibid.*, **87**, 1833 (1965).

(4) A. Abe and P. J. Flory, *ibid.*, **87**, 1838 (1965).

(5) R. A. Orwoll and P. J. Flory, *ibid.*, **89**, 6814 (1967).