

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

On the Equation of State of Oligomer and Polymer Liquids¹

BY ROBERT SIMHA AND A. J. HAVLIK

RECEIVED JUNE 18, 1963

By examining published volume-temperature data at atmospheric pressure for several series of oligomer and high polymer liquids, the principle of corresponding states is shown to be valid over the whole range available, namely up to reduced volumes \bar{V} of about 1.6. Such diverse structures as the polymethylenes, polyoxyethylenes, and phosphonitrilic fluorides are included. For $\bar{V} \geq 1.1$, the theoretical equation of state, based on the application of cell theory in its simplest form to chain liquids, is obeyed for oligomers and high polymers. Computed thermal expansivities are in satisfactory agreement with experimental results for the high polymer liquids. By means of an additional experimental quantity, chosen here to be the low temperature enthalpy of vaporization or the cohesive energy density, we derive numerical values of the characteristic volume, energy, and flexibility parameters for the methylene, styrene, dimethylsiloxane, and perfluoromethylene series. Similarities and differences in respect to molecular flexibility are discussed.

I. Introduction

Some years ago an equation of state for liquids of chain molecules was developed.² This equation was shown to describe quite successfully the dependence of volume on chain length for normal paraffins³ and other hydrocarbons^{4a,b} and to provide a theoretical basis for previous empirical relations.^{3,4a} An investigation of the pressure-volume-temperature relations for oligomer and polymer liquids of different structures is desirable, just as in liquids of spherical molecules, in order to evaluate the range of validity and the generality of the theoretical equation of state, to provide a guide for improved theory, and to make quantitative comparisons between different systems in terms of the molecular parameters entering into the theory. This enables us to predict quantities such as specific volume, thermal expansivities, and compressibilities, which are not readily and accurately available for the amorphous high polymer, from experimental data for corresponding oligomers. Finally a knowledge of the parameters for the liquid polymer is important for the interpretation and characterization of the glass transition of the polymer.⁵

The equation of state is derived from the cell theory of liquids with additional assumptions arising from the chain-like nature of the constituent molecules.² As a consequence of these assumptions, the theory is inadequate when applied to sufficiently wide ranges of temperature and pressure.³ The characteristic volume and energy parameters, which by assumption are constants of the system, must be readjusted and become slowly varying functions of temperature and pressure, in order to maintain formal agreement with experimental volumes at a given temperature. However, no range of validity of the theory for chain liquids has been quantitatively defined so far.

The equation of Prigogine, Trappeniers, and Mathot² satisfies the theorem of corresponding states. The reduced variables may be written as

$$\bar{p} = pV^*/(qze^*); \quad \bar{V} = V/V^* = v/v^*; \quad \bar{T} = Tck/(qze^*) \quad (1)$$

In eq. 1 $qz = s(z - 2) + 2$ represents the number of nearest neighbors of a given chain, subdivided into s units, where z is the coordination number of the lattice defining the average positions of the chain segments; $v = \bar{V}/s$ is the volume per chain segment, and $3c$ the number of external or volume dependent degrees of freedom of the molecule. Hence c may be regarded

as a measure of chain flexibility. For a nearly rigid molecule c is of the order of unity, whereas for a flexible chain it is of the order of s . However, the characterization of flexibility in terms of the parameter c does not necessarily parallel the measure of flexibility in terms of the root mean square radius of gyration of the unperturbed chain. First, c is determined by the relative importance of inter- and intramolecular interactions. Secondly, a rigid backbone with relatively flexible or highly structured substituents results in a relatively large c , whereas the average dimensions reflect rigidity. This point will be illustrated later by a comparison of polystyrene and polydimethylsiloxane which possess considerably different molecular dimensions. Finally ϵ^* represents the minimum of the spherically symmetrical intermolecular potential and $(v^*)^{1/3}\gamma$ is the corresponding distance between a segment pair, where γ depends on the lattice type and will be set equal to $2^{1/6}$. In eq. 2 to follow, the potential is assumed to be 6-12. Consequently $(v^*)^{1/3}$ is the distance at which the potential changes sign and may be regarded as the collision diameter of the segment. In eq. 1 the difference between the terminal and interior segments is disregarded. This results in somewhat different parameter values for the lowest members in a homologous series^{6,7} (see section III).

The general conditions for the existence of a theorem of corresponding states for spherically symmetrical molecules have been formulated and do not depend on the functional form of the equation of state, but are based on a universality of the intermolecular force law. More recently the conditions for the validity of the theorem in systems of chain molecules have been discussed.⁶ In terms of the variables in eq. 1 it has been verified for the series of n -paraffins, mainly by studying the volume-temperature-molecular weight relations at atmospheric pressure.^{6,7} Corresponding state relations for a series of liquids, including chain compounds, have been investigated by Bondi.⁸

The purpose of this paper is first to examine the range of validity of the statistical mechanical equation of state 2 and second to establish the general validity of the principle of corresponding states. Such a principle, in turn, yields an explicit form of the p - V - T function, inviting further theoretical development. The discussion (section II) is based on published volume-temperature data at atmospheric pressure, elevated pressures being the subject of a future communication. The results obtained permit the evaluation of the characteristic parameters ϵ^* , v^* , and c in eq. 1 and 2. The procedure used here involves additionally experimental enthalpies of vaporization at low temperatures

(1) This work was supported by Research Grant NsG-343 of the National Aeronautics and Space Administration to the University of Southern California.

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

(3) R. Simha and S. T. Hadden, *J. Chem. Phys.*, **25**, 702 (1956).

(4) (a) S. T. Hadden and R. Simha, *ibid.*, **36**, 1104 (1962); (b) *J. Chem. Eng. Data*, **7**, 444 (1962).

(5) R. Simha and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).

(6) J. Hijmans, *Physica*, **27**, 433 (1961).

(7) I. Prigogine, A. Bellemans, and C. Naar-Colin, *J. Chem. Phys.*, **26**, 751 (1957).

(8) A. Bondi, *A.I.Ch.E. J.*, **6**, 191 (1960).

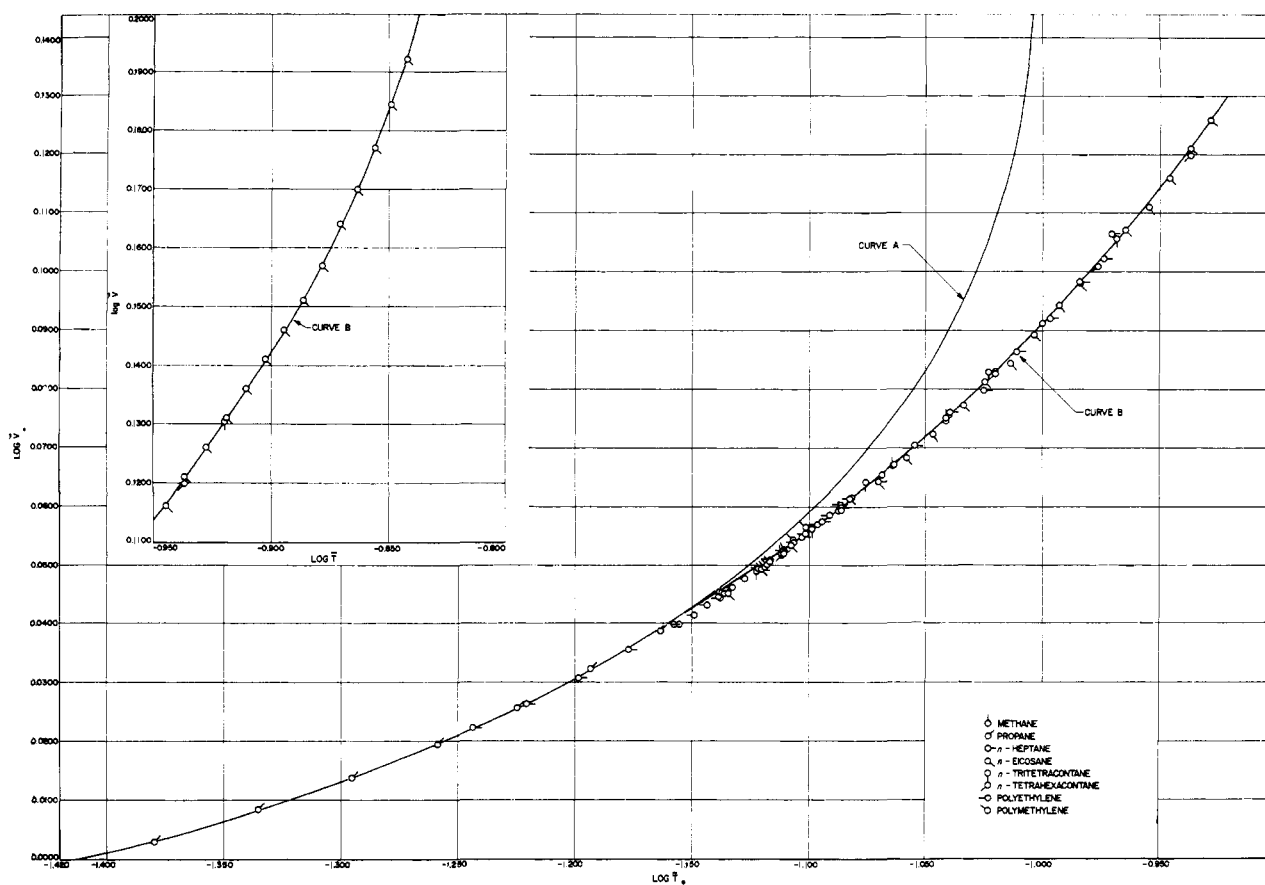


Fig. 1.—Reduced volumes of *n*-paraffins, polyethylene, and polymethylene as a function of the reduced temperature; substances illustrated: methane, propane, *n*-heptane, and *n*-eicosane⁹; *n*-tritetracontane¹⁰; *n*-tetrahexacontane¹¹; polyethylene¹²; polymethylene.¹³ Line A, eq. 2; line B, eq. 3 and 5.

or cohesive energy densities. In section III numerical values of the parameters are obtained and compared for several series in the oligomer and high polymer range of molecular weights. With the aid of these and the reduced equation of state, thermal expansivities can be computed.

II. General Discussion

The equation of state under discussion is²

$$\bar{p}\bar{V}/\bar{T} = 6 + (1 - 2^{-1/6}\bar{V}^{-1/3})^{-1} + 7.227(1.011\bar{V}^{-2} - 2.409)^{-1} + (2/\bar{T})\bar{V}^{-2}(1.011\bar{V}^{-2} - 1.2045) \quad (2)$$

At atmospheric pressure the left-hand side may be equated to zero. We note that for $\bar{V} = 0.916$, all but the second term on the right-hand side of eq. 2 vanish. However, for $\bar{V} \geq 0.92$, it is legitimate to set $\bar{p} = 0$, because of the rapid variations of the third and fourth terms on the right. In practice this represents no limitation. For example, results to be derived later yield a temperature $T = 10^\circ\text{K}$. for polymethylene in this limit of \bar{V} . The discontinuity in the second right hand term for $\bar{V} = 0.707$ is irrelevant. Figures 1 through 4 show the reduced volume-temperature curves, respectively, for the normal paraffins and the polymers polymethylene and polyethylene; some styrene oligomers and polymers as well as toluene; polyoxyethylenes and polydimethylsiloxanes; and finally some perfluorinated hydrocarbons as well as two phosphonitrilic fluorides. In each of these figures, eq.

2 appears as upper curve A. By the application of appropriate ordinate and abscissa shifts to the experimental $V-T$ data for different molecular weights in the different series, we obtain superposition over a certain range of \bar{V} and \bar{T} values upon the curve represented by eq. 2. As \bar{T} increases, eq. 2 deviates increasingly from the experimental values and the representative points proceed to define a lower curve B.

From the results summarized in Fig. 1-4 we conclude first that the theoretical equation of state 2 is valid at atmospheric pressure up to a reduced volume \bar{V} equal to 1.1 for oligomers as well as high polymers. At this point, the average distance between segment pairs is 3% larger than that corresponding to the potential minimum. The increasing departures from experiment occurring for larger \bar{V} are anticipated and in the expected direction.^{2,3,7} In the derivation of eq. 2, a uniform lattice, *i.e.*, the equality of inter- and intramolecular distances between segments is assumed, the distortion of the quasi-lattice with increasing temperature and lattice imperfections being neglected. Formal agreement with eq. 2 for larger reduced volumes would be maintained only by increasing the effective size of the segment and hence v^* and more markedly ϵ^* .³ The validity of eq. 2 supports the original assumption² that the degrees of freedom of a molecule in the liquid can be separated in the evaluation of the partition function into internal and external ones by means of an assignment which is temperature independent over a considerable range. The high temperature deviations observed here can be related to a temperature dependence of c only by requiring a decrease of c with increasing temperature.

We find secondly that the theorem of corresponding states (1) is valid over the whole range of reduced

(9) American Petroleum Institute, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(10) G. W. Nederbragt and J. W. M. Boelhouwer, *Physica*, **13**, 305 (1947).

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

(12) M. G. Gubler and A. J. Kovacs, *J. Polymer Sci.*, **34**, 551 (1959).

(13) L. Mandelkern, M. Hellmann, D. W. Brown, D. E. Roberts, and F. A. Quinn, Jr., *J. Am. Chem. Soc.*, **75**, 4093 (1953).

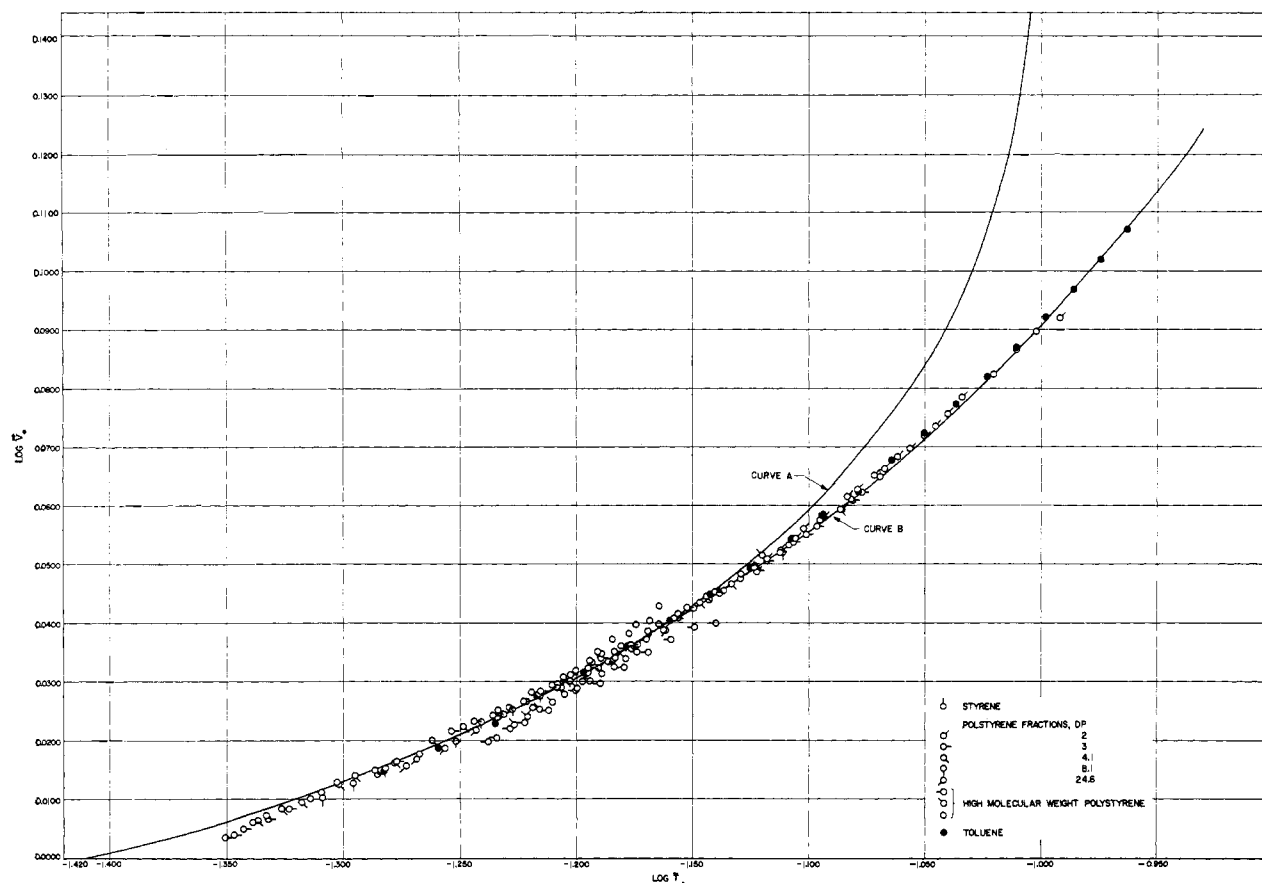


Fig. 2.—Reduced volumes of styrene, polystyrene oligomer fractions, high molecular weight polystyrene, and toluene as a function of the reduced temperature; substances illustrated: styrene, polystyrene with degrees of polymerization 2, 3, 4.1, 8.1, and 24.6¹⁴; high molecular weight polystyrene from ref. 14 (—O), 15 (○), and 16 (○); and toluene.⁹ Line A, eq. 2; line B, eq. 3 and 5.

volumes which extends here to about 1.6, and for both high and low molecular weights. Now, as is understandable on theoretical grounds, the principle is not obeyed in liquids of small polar molecules. The polymers investigated here are nonpolar, with the exception of the polyoxyethylene glycols and the phosphonitrilic fluorides. These, nonetheless, can be placed on the master curve (see also section III).

The results obtained enable us to compute the reduced thermal expansivity

$$\bar{\alpha} = (1/\bar{V})(\partial\bar{V}/\partial T)_{\bar{p}}$$

and ultimately the actual expansivities and the temperature coefficients of the specific volume. These quantities have been determined experimentally for some of the polymers considered here, at least over a limited range of temperatures. In this manner an additional comparison between experiment and theory is provided. More importantly, we can calculate these derivatives over a wide range, where experimental information is lacking or involves extrapolations below the melting range in partially crystalline polymers or even below the glass temperature of amorphous systems.

The calculation of $\bar{\alpha}$ from eq. 2 is, of course, straightforward, although cumbersome, and will not be reproduced. For numerical estimates it is convenient to use the expanded form of eq. 2 for $p = 0$ and $\bar{V} \rightarrow 1$. Neglecting terms of order $(\bar{V} - 1)^2$, the result is

$$T = 0.3948\bar{V} - 0.3560 \quad (2a)$$

When $\bar{V} = 1.05$, eq. 2a yields $\bar{T} = 0.0585$, compared with the exact value of 0.0563, a difference of 4%. The reduced thermal expansivity from 2a is 2.533. For $\bar{V} = 1.05$, the exact result is 3.060, indicating an error of 17%.

For $\bar{T} > 0.07$, the portion B, Fig. 1–4, of the $\bar{V}-\bar{T}$ function is pertinent and the slopes must be either determined numerically or, preferably, by means of an analytical representation of the function. Application of a least square polynomial is immediately suggested. For this purpose the large scale plot was used, which had been constructed originally by means of the n -paraffin data for the superposition of the other experimental data. Selecting equally spaced points, a least square quartic was derived,^{16a} resulting in deviations of, at most, 1%. The result is

$$y = 16.058 + 58.494x + 81.615x^2 + 51.210x^3 + 12.121x^4; \quad -1.120 \leq x \leq -0.840 \quad (3)$$

with $x = \log \bar{T}$, $y = \log \bar{V}$, and

$$\bar{\alpha} = (1/\bar{T})dy/dx; \quad \alpha = (1/T)dy/dx = (\bar{T}/T)\bar{\alpha} \quad (4)$$

It will be noted that the ranges of applicability of eq. 3 and 2 do not overlap. This could have been avoided by the use of a higher order polynomial, which is laborious. Moreover, since we are primarily concerned with the accuracy of the derivatives rather than of the function values, the gap between eq. 2 and 3 is bridged by the equation

$$y = 2.3027 + 5.0419x + 3.8584x^2 + 1.0288x^3; \quad -1.206 \leq x \leq -1.026 \quad (5)$$

(14) K. Ueberreiter and G. Kanig, *Z. Naturforsch.*, **6a**, 551 (1951).

(15) T. G. Fox, Jr., and P. J. Flory, *J. Polymer Sci.*, **14**, 315 (1954); *J. Appl. Phys.*, **21**, 581 (1950).

(16) G. M. Martin, S. S. Rogers, and L. Mandelkern, *J. Polymer Sci.*, **20**, 579 (1956).

(16a) M. Sasuly, "Trend Analysis in Statistics," Brookings Institution, Washington, D. C., 1934, p. 42.

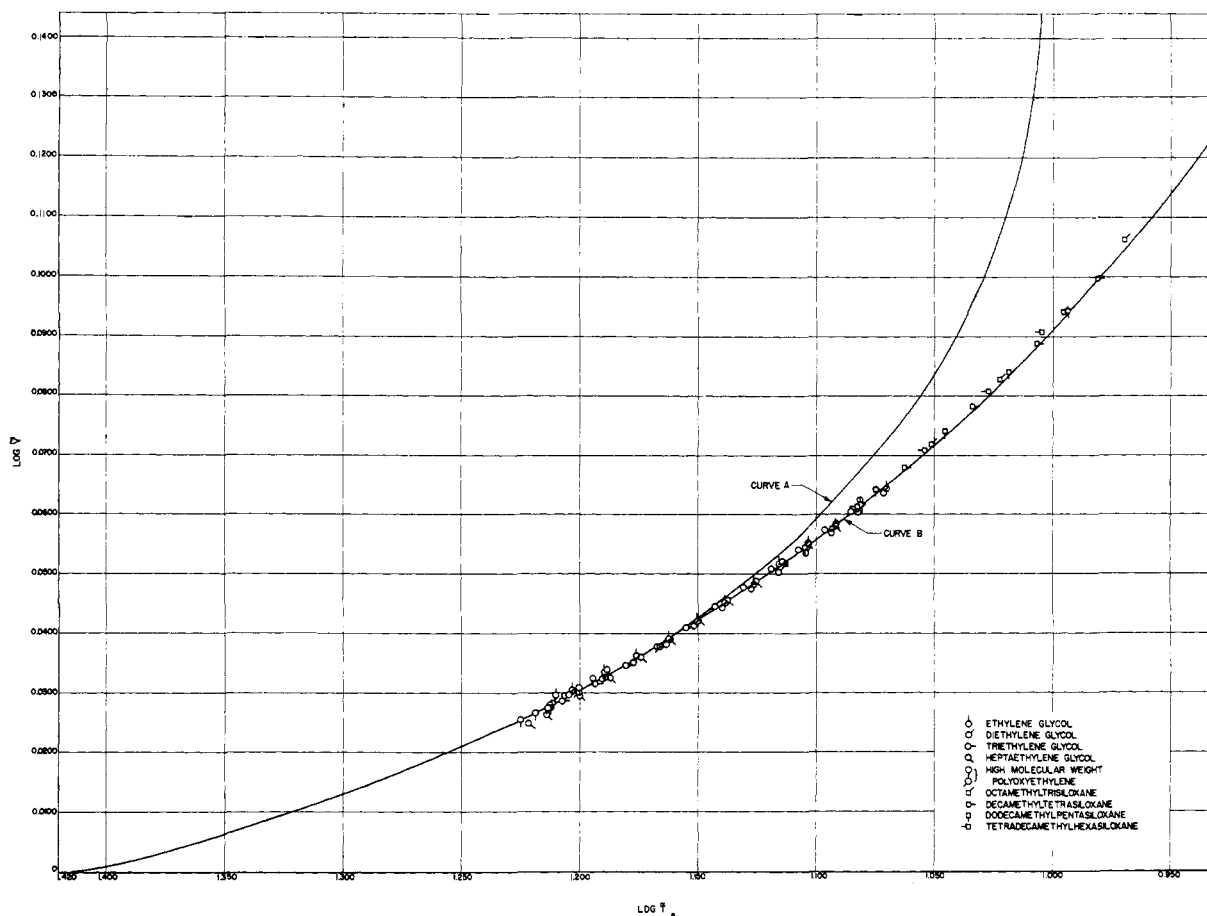


Fig. 3.—Reduced volumes of ethylene glycol, polyoxyethylene glycols, and polydimethylsiloxanes as a function of the reduced temperature; substances illustrated: ethylene, diethylene, triethylene, and heptaethylene glycols¹⁷; high molecular weight polyoxyethylene from ref. 18 (○) and 19 (○); and octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, and tetradecamethylhexasiloxane.^{20–22} Line A, eq. 2; line B, eq. 3 and 5.

Curve B, Fig. 1–4, actually represents eq. 3 and 5. A plateau region in $\bar{\alpha}$, with $\bar{\alpha} \approx 3.5$ is observed to extend from $x = -1.18$ to -1.12 , corresponding to $0.066 \leq \bar{T} \leq 0.076$. Outside this region, however, α is a slowly increasing function of T which can be approximated by a constant with an error of 10% over a range of not more than fifty degrees. These conclusions agree with the results of computing the derivatives directly from the original graph by the method of moving arcs.^{16a}

The characteristic volume $V^* = V/\bar{V}$ per mole and the temperature shift factor T/\bar{T} are obtained as functions of n , the number of backbone atoms in the chain, by the superposition of the experimental volume-temperature data of a particular polymer series on the master curve. The relationship is determined by the dependence of s , the number of segments per chain, which span the lattice, and of c , a function of s , on n . It is certainly reasonable to write in general s as a linear function of n . The quantity c should be linear in s and hence in n . For sufficiently high molecular weights, simple proportionalities will result. In respect to c this will be true for any molecule, which is not completely rigid. We assume therefore

$$s = (n + A)/B; \quad c = (n + C)/D \quad (6)$$

(17) A. F. Gallagher and H. Hibbert, *J. Am. Chem. Soc.*, **59**, 2514 (1937).

(18) T. P. Yin, S. E. Lovell, and J. D. Ferry, *J. Phys. Chem.*, **65**, 534 (1961); J. D. Ferry, private communication.

(19) J. A. Faucher, private communication, Union Carbide Chemicals Co., South Charleston, W. Va.

(20) W. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

(21) C. B. Hurd, *ibid.*, **68**, 364 (1946).

(22) D. W. McCall, E. W. Anderson, and C. M. Huggins, *J. Chem. Phys.*, **34**, 804 (1961).

and from eq. 1 and $z = 12$

$$\begin{aligned} T/\bar{T} &= (T/\bar{T})_{\infty} [1 - (C - A - B/5)/(n + C)] \\ V^* &= N_A v^*(n + A)/B \\ (T/\bar{T})_{\infty} &= 10\epsilon^*D/(kB) = 10(\epsilon^*/k)(s/c)_{\infty} \end{aligned} \quad (7)$$

A complete characterization of a given polymer series requires six parameters. From the volume shift it is possible to deduce the quantity v^*/B and, if low molecular weight data are available, also A . Hence B and v^* are determined with the aid of the first of eq. 7. This is essentially the procedure of Hijmans⁶ used in the analysis of the n -paraffin series. When volume-temperature data in the high polymer range of molecular weights are also available, the linear plot of the ratio

$$(T/\bar{T})_{\infty} / [(T/\bar{T})_{\infty} - T/\bar{T}]$$

vs. n will conveniently yield C and $A + B/5$ from slope and intercept. If data on oligomers only are given, algebraic solution for the three unknowns in the equation for T/\bar{T} is necessary. Lastly the product ϵ^*D follows from $(T/\bar{T})_{\infty}$. To separate these two factors, we take recourse to the enthalpy of vaporization or, in the case of the high polymer species, to cohesive energy densities estimated in the literature.^{22a}

For the region in which eq. 2 is valid, we have²

$$\Delta H_{\text{vap}} - RT = N_A q_2 \epsilon^* / (2.409 \bar{V}^{-2} - 1.011 \bar{V}^{-4} - 3\bar{T}) \quad (8)$$

Therefrom the cohesive energy density (c.e.d.) is obtained on dividing by $V = \bar{V}V^*$. Provided the temperature is specified at which the c.e.d. has been calcu-

(22a) See H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York, N. Y., 1950, p. 263; A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 65.

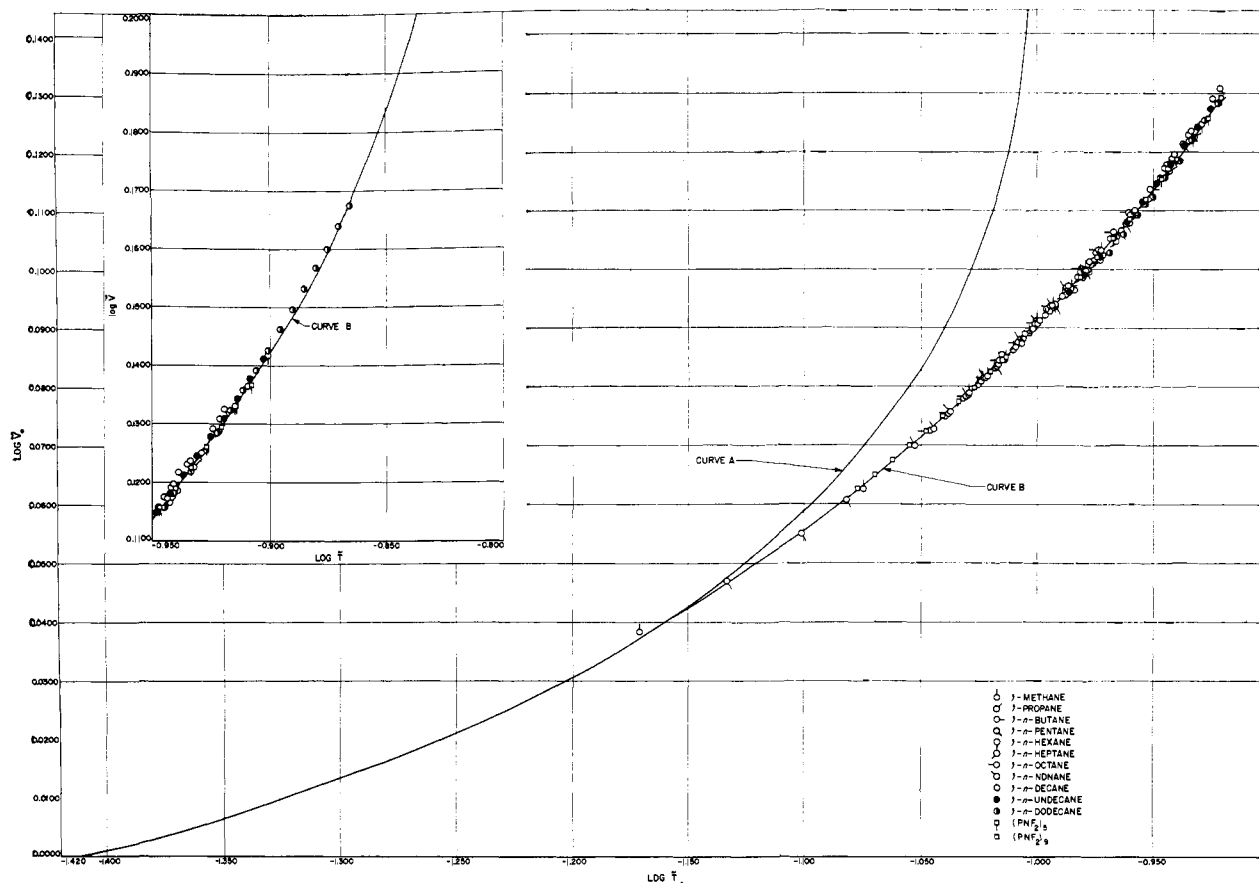


Fig. 4.—Reduced volumes of perfluorinated *n*-paraffins and the cyclic phosphonitrilic fluorides as a function of the reduced temperature. Substances illustrated: f-methane^{23,24}; f-propane^{25,26}; f-*n*-butane^{27,28}; f-*n*-pentane^{28,29}; f-*n*-hexane^{30,31}; f-*n*-heptane, octane, nonane, decane, undecane, and dodecane³²; octane³³; pentameric and nonameric cyclic phosphonitrilic fluorides.^{34,35} Line A, eq. 2; line B, eq. 3 and 5.

lated from thermodynamic solution or swelling data,^{22a} the quantity qze^* can be computed. Writing

$$\text{c.e.d.} = N_A q z e^* f(\bar{V}) / (2V^*) \quad (8a)$$

we note as an example that according to eq. 2 and 8 $f(\bar{V})$ varies between 1.28 and 0.99, as \bar{V} varies between 1 and 1.1. The numerical values of e^* , given in what follows, are based on $z = 12$.

If the melting points in a series are corresponding temperatures, the first of eq. 7 will describe the dependence of the melting temperature on chain length. The numerical values for the *n*-paraffin series, to be discussed, indicate that this is roughly true.

III. Relations for Special Systems

A. Polymethylenes.—For the series of *n*-paraffins starting with methane and including polymethylenes and polyethylenes, described in Fig. 1, the procedure indicated in connection with eq. 7 yields

$$T/\bar{T} = 5402[1 - 5.33/(n + 6.34)]; n \geq 1$$

(23) N. C. S. Chari, *Dissertation Abstr.*, **21**, 2220 (1961).

(24) Bulletin T-14, "Preliminary Thermodynamic Properties of Freon-14," "Freon" Products Division, Organic Chemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., 1961.

(25) J. A. Brown, *J. Chem. Eng. Data*, **8**, 106 (1963).

(26) T. J. Brice, private communication, Minnesota Mining and Manufacturing Co., St. Paul, Minn.

(27) J. A. Brown and W. H. Mears, *J. Phys. Chem.*, **62**, 960 (1958).

(28) J. H. Simons and T. J. Brice, "Fluorine Chemistry," J. H. Simons, Editor, Academic Press, Inc., New York, N. Y., 1954, Chapter 6.

(29) L. L. Burger and G. H. Cady, *J. Am. Chem. Soc.*, **73**, 4245 (1951).

(30) V. E. Stiles and G. H. Cady, *ibid.*, **74**, 3771 (1952).

(31) R. D. Dunlap, C. J. Murphy, and R. G. Bedford, *ibid.*, **80**, 83 (1958).

(32) R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 603 (1951).

(33) A. Kreglewski, *Bull. Acad. Polon., Ser. Sci. Chim.*, **10**, 629 (1962).

(34) A. C. Chapman, N. L. Paddock, D. H. Pain, H. T. Searle, and D. R. Smith, *J. Chem. Soc.*, 3608 (1960).

(35) N. L. Paddock, private communication.

However, in conjunction with the molecular weight dependence of V^* , given below, this expression leads to $B < 1$, which is a physically inadmissible result. The definitions used here refer to polymeric species. Exclusion of methane and ethane gives the expression

$$T/\bar{T} = 5402[1 - 5.36/(n + 6.48)]; n \geq 3 \quad (9)$$

Arguing that end effects have not been explicitly included in the definitions² of the reduced variables, we obtain alternatively

$$T/\bar{T} = 5402[1 - 5.6/(n + 7)]; n \geq 8 \quad (9a)$$

Actually the difference between eq. 9 and 9a, arising from the difference between terminal and other segments, is minor; namely 1% for $n = 3$ and 0.5% for $n = 8$. The limiting value for $n \rightarrow \infty$ is, of course, common to the three expressions, since it derives from the high polymer data.

Equation 9a is formally consistent with the earlier assignment used in the discussion of the *n*-paraffin series,² *viz.*, $A = 1$, $B = 2$, $C = 7$, to which may be added the statement $D = 6$. That is, the isolated polymethylene molecule is replaced by a chain of freely rotating segments, each equivalent to a methane or, for $n \rightarrow \infty$, two methylene units. Indeed, if we accept these assignments and combine them with eq. 9a or 9 for $n \rightarrow \infty$, it results in a value of $e^* = 249 \times 10^{-16}$ erg/segment, for $n \geq 5$. This is about 18% lower than was previously estimated from the molecular weight dependence of the density at 38°. The difference arises from the fact that at this temperature and for the compounds used, eq. 3 and 5 rather than eq. 2 must be used.

However, the dependence of V^* on n , derived from Fig. 1, requires a modification of the numerical values

for A and B indicated above. A least square analysis of V^* yields

$$V^* = 13.70 + 15.749n; 1 \leq n \leq 64 \quad (10)$$

$$V^* = 13.55 + 15.754n; 8 \leq n \leq 64$$

From these practically identical expressions one obtains $A = 0.870$ and 0.860 , respectively, and from eq. 9 and 9a, respectively, $B = 1.25$ and 2.70 . From eq. 10 $N_{Av^*}/B = 15.75$; this is the quantity which together with the c.e.d. determines the important parameter D , eq. 6. Similarly, there is no ambiguity in the subsequent evaluation of α and dv_{sp}/dT for the high polymer. However, we have the two alternatives $N_{Av^*} = 19.7$ and 42.5 cc./mole, depending upon whether 1.25 or 2.7 methylene units comprise the segment. The value per methylene unit, viz. 15.75 cc./mole, may be compared with $32.4/2 = 16.2$ previously² obtained. We observe from eq. 7 that the temperature shift factor approaches its limiting value the more rapidly with increasing n , the larger C and the larger A and B . In the polymethylene series 95% of the limit is reached for $n \approx 105$.

We may use the "assigned" parameter values to calculate a c.e.d. which can be compared with the value of 62 cal./cc. reported to apply at 20° ³⁶ or, from eq. 9, $T = 0.05424$, $\bar{V} = 1.044$. Hence eq. 8 is applicable and (8a) reduces to

$$\text{c.e.d.} = 5\epsilon^* \times 1.15/v^* = 65 \text{ cal./cc.}$$

if $B = 2$.³ To be sure, the use of swelling measurements, particularly with semicrystalline polymers, is subject to some doubt and here as well as for the subsequent discussion of other polymer systems, low temperature enthalpies of vaporization for oligomers are the desirable quantities. In the absence of such information for all polymer types to be investigated, we shall continue to use c.e.d.'s. We may say then that the assignments made and parameter values derived for the polymethylene series are consistent with estimates of the c.e.d.

However, in order to make a consistent comparison between all polymers we shall use the identical procedure, i.e., the energy parameter and D will be derived from the reported c.e.d. In the case of polymethylene, of course, the results will not differ much from those derived by means of the previous assignments. From eq. 8a and 7 we have

$$(T/\bar{T})_\infty = \text{c.e.d.}/f(\bar{V})(N_{Av^*}/B) \times 1.006D$$

$$\epsilon^*/B = \text{c.e.d.}/[5f(\bar{V})](N_{Av^*}/B) \times 0.694 \times 10^{-16} \text{ erg/molecule} \quad (8b)$$

and find for polymethylene with $\bar{T} = 0.05424$, $D = 6.3$, $\epsilon^*/B = 118.2 \times 10^{-16}$ as compared with the "assigned" $D = 6.0$ and $\epsilon^*/B = 124.5$. A consistent description of liquid polymethylene thus results.

Table I displays thermal expansivities α computed from eq. 4 and the derivative $dv_{sp}/dT = \alpha \bar{V} N_{Av^*} s/M$, where M is the molecular weight. The temperatures selected range from about twenty degrees above the glass transition temperature to about one hundred degrees above the melting temperature. The last two values in the third column agree well with those quoted in the literature from a variety of sources for the amorphous polymer. A comparison of calculated and observed (amorphous) expansivities for semicrystalline polymers involves, of course, the assumption that our results can be applied to the supercooled liquid fraction in the presence of the crystalline portion.

B. Polystyrenes.—Here the density values of different authors in the high polymer range differ somewhat.

(36) R. B. Richards, *Trans. Faraday Soc.*, **42**, 10 (1946).

TABLE I

THERMAL EXPANSIVITIES, EQ. 2, 3, AND 5, FOR LIQUID POLYMETHYLENE

$T, ^\circ\text{K.}$	$\alpha \times 10^4/\text{degree}$	$dv_{sp}/dT \times 10^4, \text{cc./g./degree}$
210	4.69	5.57
304	5.66	6.68
378	6.52	8.07
419	6.81	8.65
516	7.40	10.06

Upon averaging the temperature shift factors resulting from these data we find by an appropriate least square calculation

$$T/\bar{T} = 6450[1 - 2.06/(n + 3.81)]; 2 \leq n \leq \infty \quad (11)$$

and T/\bar{T} reaches 95% of its limit for $n \rightarrow \infty$, when $n = 37$. The volume shifts deduced from Fig. 2 show again fluctuations in N_{Av^*} . Whereas for the monomer N_{Av^*}/B is 50.6 cc./mole,³⁷ for the oligomers it is approximately 47, and the high polymers average to about 48. In order to obtain A and B , eq. 7, a least square analysis of the volume shifts for $4 \leq n \leq 49$ was performed with the result $A = -0.027 \approx 0$ and $N_{Av^*}/B = 46.8$. From eq. 7 and 11 we have therefore $C = 3.81$, $B = 8.9 \approx 9.0$. That is, 4.5 styrene units comprise the segment, which is assumed in the derivation of eq. 2 to equalize inter- and intramolecular distances between segments. While this number may reflect the approximations inherent in the lattice model, it is not unreasonable, considering the size of the phenyl ring. The volume parameter N_{Av^*} equals 421.5 cc./mole. It must be realized in interpreting this number that the actual force field between two segments has been approximated by a spherically symmetrical pair potential. Moreover, we are essentially treating a copolymer as a homopolymer.

In order to complete the analysis, we make use of the cohesive energy density which is 82 cal./cc.^{32a,38} at 296°K. or $\bar{T} = 0.0459$ and, from eq. 2a and 8, $\bar{V} = 1.02$, $f(\bar{V}) = 1.217$. Application of eq. 8a and 11 to the high polymer then yields $\epsilon^* = 3944 \times 10^{-16}$ erg/molecule or 5.68 kcal./mole. Thus per monostyrene unit this amounts to a value 3.7 times as large as for polymethylene. From eq. 7 we derive finally $D = 2.0$ and hence

$$c = (n + 3.81)/2 \approx (9s + 3.81)/2 \quad (12)$$

as compared with $c = (n + 7)/6$ or $(n + 6.48)/6.3$ for polymethylene. Thus in the high polymer the number of external degrees of freedom per backbone atom is three times as large in polystyrene as in polymethylene. This difference must be associated with motions of the phenyl ring.

We may use the reported enthalpies of vaporization for monostyrene³⁷ to obtain the corresponding c -value. At $T = 291^\circ\text{K.}$ or, from eq. 11, $\bar{T} \approx 0.070$, $\Delta H_{vap} - RT = 10,213$ cal./mole, or $qz\epsilon^*/2 = 1.29 \times 10^{-12}$ erg/molecule. Therefrom $c = qz\epsilon^*/(kT/\bar{T}) = 2.25$ compared with an extrapolated value of 2.9 from eq. 12. Thus in addition to the six degrees of freedom arising from translation and rotation in the gas phase there are effectively about one to two further volume-dependent degrees of freedom in the monomer.

Table II exhibits the thermal expansivities in the range between about 15 and 200 degrees above the glass transition temperature of the infinite polymer.

(37) The experimental results of D. R. Stull, "Styrene," ACS Monograph 115, R. H. Boundy and R. F. Boyer, Editors, Reinhold Publishing Corp., New York, N. Y., 1952, p. 55, lead to $T/\bar{T} = 3888$ as compared with 4046 from eq. 11, and $N_{Av^*}/B = 51.2$.

(38) R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **3**, 97 (1948).

TABLE II
THERMAL EXPANSIVITIES, EQ. 2, 3, AND 5, FOR LIQUID
POLYSTYRENE

$T, ^\circ\text{K.}$	$\alpha \times 10^4/\text{degree}$	$dv_{sp}/dT \times 10^4,$ cc./g./degree
388	5.01	4.80
478	5.46	5.46
575	6.11	6.49

Our results are in good agreement with literature values and illustrate once more the temperature dependence of α .

C. Polydimethylsiloxanes.—The temperature shifts for $n = 7, 9, 11,$ and 13 are available. Utilizing the last three, we find

$$T/\bar{T} = 4004[1 - 1.85/(n + 3.0)] \quad (13)$$

Equation 13 yields a value of 3263 for $n = 7$, compared with 3293 deduced from Fig. 3. The least square analysis of the volume shift factors results in $N_{Av}^*/B = 33.8, A = 0.218$. Therefore $C = 3, B = 4.7, N_{Av}^* = 158.2$ cc./mole. Two to three Si-O groups comprise the unit in the high polymer. The temperature shift factor reaches 95% of its limiting value for $n = 34$. Support for the numerical values pertaining to the high polymer and derived from oligomer data comes from reported densities of siloxane polymers at 25° .³⁹ We calculate 0.980 g./cc. compared with 0.973 and 0.974 measured by hydrostatic weighing.

Cohesive energy density values have been discussed by several authors.^{22a,40} They range from about 53 to 58 and will be averaged here to 56.3 cal./cc. at 25° . For the infinite polymer, eq. 8a is not applicable above 7° . Assuming the temperature correction in the c.e.d. above and below the latter temperature to be identical in this narrow temperature interval, we arrive at c.e.d. = 58.50. Then $\bar{V} = 1.1, f(\bar{V}) = 0.991$ and $\epsilon^* = 1297 \times 10^{-16}$ erg/molecule or 1.87 kcal./mole, about 2.4 times as large per monomer unit as for polymethylene. Finally $D = 1.99 \approx 2.0$ and

$$c = (n + 3)/2 \approx (4.7s + 3.78)/2 \quad (14)$$

The number of external degrees of freedom per backbone atom is identical in polystyrene and polydimethylsiloxane, although in the latter polymer it must be the main chain motions which principally contribute to the large value of c . However, for completely unrestricted bond rotation in the backbone skeleton $c = n/3$ and eq. 14 would appear to yield too large a value. It must be remembered that $(T/\bar{T})_\infty$ which determines D , eq. 7, was derived here from an extrapolation of oligomer data. This circumstance combined with the use of a c.e.d. derived from solution and swelling data, can to some extent affect the numerical value of D in eq. 14. On the other hand, the result may be indicative of additional low frequency motions.⁴¹

TABLE III
THERMAL EXPANSIVITIES, EQ. 2, 3, AND 5, FOR LIQUID
POLYDIMETHYLSILOXANE

$T, ^\circ\text{K.}$	$\alpha \times 10^4/\text{degree}^{-1}$	$dv_{sp}/dT \times 10^4,$ cc./g./degree
159	6.39	5.85
253	8.44	8.27
349	9.79	10.47
460	11.61	13.94

(39) C. E. Weir, W. H. Leser, and L. A. Wood, *J. Research Natl. Bur. Standards*, **44**, 367 (1950).

(40) R. L. Hauser, C. A. Walker, and F. L. Kilbourne, Jr., *Ind. Eng. Chem.*, **48**, 1202 (1956).

(41) H. Kusumoto, I. J. Lawrensen, and H. S. Gutowsky, *J. Chem. Phys.*, **32**, 724 (1960).

Table III shows computed thermal expansivities for the polymer in the range from about 10 to 300 degrees above the glass transition. For a shock-cooled sample of siloxane polymer between 153 and 173°K. , $\alpha = 5.4 \times 10^{-4}$ is found experimentally.³⁹ Corrections necessitated by crystallinity would reduce the difference between the predicted and observed values. In the range from 238 to 273°K. , $\alpha(\text{exptl.}) = 11.7 \times 10^{-4}$ has been reported.³⁹

D. Perfluorinated Polymethylenes.—In the oligomer range temperature shifts between $n = 1$ and $n = 12$ are available. Considerable scatter is observed, but eq. 7 can be shown to be applicable. However, the parameter B turns out to be less than unity. On the other hand, we can use an empirical equation of state by Lupton⁴² for polytetrafluoroethylene of high molecular weight above the melting range, to obtain $(T/\bar{T})_\infty = 4791$. Consideration of the oligomers alone yields 4524. The final result is

$$T/\bar{T} = 4791[1 - 5.91/(n + 7.34)]; 1 \leq n \leq \infty \quad (15)$$

The present data do not permit us to make the distinctions indicated by eq. 9, 9a, and 10 for the polymethylenes. For $n = 111$, T/\bar{T} reaches 95% of $(T/\bar{T})_\infty$. The volume shifts observed can be accurately described by a straight line which leads to $N_{Av}^*/B = 22.4, A = 0.928$, and $C = 7.34, B = 2.50, N_{Av}^* = 55.9$ cc./mole. Thus about one monomer represents the unit.

An estimate of the c.e.d. for polytetrafluoroethylene has been offered some time ago by Scott,⁴³ namely 36 cal./cc. at 298°K. , resulting in $\bar{V} = 1.07, f(\bar{V}) = 1.075$. Therefrom $\epsilon^* = 260 \times 10^{-16}$ erg/segment or 0.37 kcal./mole/segment, i.e., 88% of the corresponding value for polymethylene. Finally $D = 6.4$ and

$$c = (n + 7.34)/6.4 \approx (2.50s + 6.41)/6.35 \quad (16)$$

Thus the number of external degrees of freedom per carbon atom is about the same or slightly lower than in polymethylene.

It is apparent from the foregoing discussion that additional experimental investigations in the oligomer as well as the high polymer range are required for more reliable numerical values for the parameters and for a more adequate basis of comparison with nonfluorinated systems.

Finally, Table IV presents thermal expansivities over a wide range of temperatures extending from the lowest glass temperature reported to about 100 degrees above the melting point.

TABLE IV
THERMAL EXPANSIVITIES, EQ. 2, 3, AND 5, FOR LIQUID
POLYTETRAFLUOROETHYLENE

$T, ^\circ\text{K.}$	$\alpha \times 10^4/\text{degree}^{-1}$	$dv_{sp}/dT \times 10^4,$ cc./g./degree
166	5.12	2.27
398	8.06	4.16
603	11.33	7.04
693	15.07	10.56

The large difference between the second and third columns results from the comparatively large density of the fluorocarbons. Since Table IV refers to the amorphous polymer, it should prove interesting to compare experimental expansivities for partially crystalline systems with our results. Above the melting range, the calculated and observed values are in reasonable agreement.

Table V shows a comparison of the characteristic quantities in the limit of $n \rightarrow \infty$. The volume, energy, and flexibility parameters are given per backbone atom.

(42) See C. A. Sperati and H. W. Starkweather, Jr., *Fortschr. Hochpolym. Forsch.*, **2**, 465 (1961).

(43) R. L. Scott, *J. Am. Chem. Soc.*, **70**, 4090 (1948).

TABLE V
CHARACTERISTIC PARAMETERS FOR HIGH POLYMERS

	T/\bar{T}	$N_{Av}v^*/n$, cc./mole	$N_A\epsilon^*/n$, kcal./mole	n/s	$3c/n$
Polymethylene	5402	15.8	0.17	2.7	3/6.3
Polytetrafluoroethylene	4791	22.4	.15	2.5	3/6.4
Polystyrene	6450	46.8	.64	8.9	3/2.0
Polydimethylsiloxane	4004	33.8	.40	4.7	3/2.0

The relative magnitudes of the van der Waals volumes v^* are as expected. From Table V we conclude, for example, that 5 CH_2^- units are approximately equal in size to one $\text{CH}-\text{C}_6\text{H}_5^-$ unit. Similarly, the maximum energies of attraction represented by column 4 indicate that about 6.5 CH_2^- units are equivalent to one $\text{CH}-\text{C}_6\text{H}_5^-$ unit. Also, the position of the fluorocarbons is expected. The difference between dimethylsiloxane and methylene is consistent with the somewhat lower observed c.e.d. and considerably larger V^* for the former. The values in column 5 which are the result of equating intra- and intermolecular distances between segments on the effective lattice are reasonable.

The differences and similarities in the last column are noteworthy. We have previously commented on the reasons for the large values for polystyrene and polydimethylsiloxane. It is, furthermore, interesting to note the similarity between polymethylene and polyperfluoromethylene, which is contrary to the common characterization of the latter as more rigid. An interpretation of fluorine nuclear spin resonance experiments on perfluorocyclohexane, however, suggests⁴⁴ that conformational isomerizations in noncyclic fluorocarbons above C_2F_6 are facilitated by a 1,3-F-F interaction which would manifest itself in an increased c -value

(44) G. V. D. Tiers, *Proc. Chem. Soc.*, 389 (1960).

Moreover, we are comparing here frequencies of small amplitude oscillations rather than rotation barriers. The c -values for polymethylene are in approximate accord with deductions from root-mean-square chain dimensions.⁴⁵

It will be seen in Fig. 4 that the phosphonitrilic fluorides satisfy the principle of corresponding states obeyed by the other systems in spite of their markedly different structure. Their detailed characterization must await data on the high polymer and additional oligomers. Similarly, in Fig. 3 the polyoxyethylenes do not appear different from the other series. The volume shifts are, as always, linear in n and yield the least square result $N_{Av}v^*/B = 12.02$, $A = 0.409$. The temperature shifts, however, vary but slightly with n . For $n = 4$, $T/\bar{T} = 4855$ and for $n = 10$, $T/\bar{T} = 4903$, and finally $(T/\bar{T})_\infty = 5760$. While it is formally possible to represent these results by eq. 7, the parameter values obtained are meaningless in terms of the underlying lattice model. It is suggestive to ascribe this behavior to hydrogen bond formation between terminal hydroxyl groups, which must be particularly important in the low molecular weight range. Two factors are significant. First, the actual and apparent molecular weight, resulting from association, differ significantly. Second, copolymeric structures are formed, which change composition with increasing molecular weight. These effects can be eliminated by means of volume-temperature data for the methylated oligomers in combination with results for the high polymer.

Acknowledgment.—A. J. H. wishes to express his appreciation to the Jet Propulsion Laboratory, California Institute of Technology, for leave to pursue this investigation at the University of Southern California.

(45) W. J. Taylor, *J. Chem. Phys.*, **16**, 257 (1948).

[CONTRIBUTION FROM THE RENSSELAER POLYTECHNIC INSTITUTE, TROY, N. Y.]

Ortho- and Paratritium¹

BY E. W. ALBERS, P. HARTECK, AND R. R. REEVES

RECEIVED JUNE 26, 1963

The conversion of ortho-paratritium in the homogeneous gas and solid phases has been studied. The extent of conversion was measured by a heat conductivity cell cooled with liquid neon to 27.2°K. The gas phase conversion was observed at 27.2°K., at which temperature the equilibrium concentration is approximately one part ortho- to one part paratritium. The role of an ion mechanism in this conversion is discussed. In the solid phase, the rate of conversion of tritium exceeds that of hydrogen by two orders of magnitude. Consideration of the kinetic data for hydrogen, deuterium, and tritium in the solid phase and adsorbed phase indicates that a more favorable energy transfer process may be operative for tritium and deuterium.

Introduction

Because of the existence of the ortho and para modifications of hydrogen, not only the different physical properties of these modifications but also their interconversion reactions by the atomic mechanism $\text{H} + \text{H}_2(\text{para}) \rightarrow \text{H} + \text{H}_2(\text{ortho})$ ^{2,3} and by ionizing radiation^{4,5} became available for study. After the discovery of deuterium,⁶ in addition to the ortho-paradeuterium

(1) The research reported in this paper has been sponsored by the National Aeronautics and Space Administration, Washington, D. C. Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1963.

(2) (a) K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B4**, 113 (1929); (b) A. Farkas, *Z. Elektrochem.*, **36**, 782 (1930); *Z. physik. Chem.*, **B10**, 419 (1930).

(3) K. H. Geib and P. Harteck, *ibid.*, *Bodensteinband*, 849 (1931).

(4) P. C. Capron, *Ann. soc. sci. Bruxelles*, **55**, 222 (1935).

(5) H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, **4**, 479, 570 (1936).

(6) H. C. Urey, F. G. Brickwedde, and G. M. Murphy, *Phys. Rev.*, **39**, 164, 864 (1932).

system, the chemical exchange between hydrogen and deuterium could be studied. At first glance, one might be therefore lead to believe that very little new or basic knowledge could be acquired by investigating the ortho-paratritium system. Actually it appears that refined kinetic understanding may be achieved by the investigation of the ortho-paratritium system and mixtures of tritium with hydrogen and deuterium which could not be accomplished with hydrogen and deuterium alone.

In an earlier paper⁷ the conversion of normal tritium into paratritium was reported using a coconut charcoal as a catalyst. The conversion of the normal tritium (three parts ortho- and one part paratritium) was made at liquid neon temperature (27.2°K.), obtaining the equilibrium concentration of approximately 50% paratritium. By cooling the charcoal with liquid

(7) E. W. Albers, P. Harteck, and R. R. Reeves, *Z. Naturforsch.*, **18a**, 197 (1963).