

A VSE Equation of State for Liquids. VI.

Polymethylene 450–650 K

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Synopsis

This is the sixth and final paper in the series under the above title. In prior papers, a VSE equation of state was proposed and applied to a variety of liquids at ambient pressure, but over broad ranges of temperature. Comparisons of thermodynamic quantities calculated from the equation were made with published measured values. In the present paper v , α , s , γ , c_v , and c_p are calculated for polymethylene from our equations between 450 and 650 K, but extensive corresponding values have not been measured on polymethylene at these temperatures. One approximate value of c_p and one value of γ , measured on high-density polyethylene, show that our predicted values for polymethylene must be of the correct order of magnitude. Several characteristics of the liquid state, observed during the progress of this study (1954–1979), are listed and discussed.

INTRODUCTION

This is the sixth and final paper in the present series. The purpose of the investigation, which has been continuously pursued since 1954, is to gain a better understanding of the nature of the liquid state. It was considered that the appropriate way in which to carry out this inquiry was to devise a VSE equation of state for liquids, because only a VSE equation of state can be "fundamental." All other equations of state can be derived from a VSE equation, but the inverse of this statement is not true.¹

The VSE equation of state proposed by us² is of the following form:

$$\epsilon = f_1 s^{f_2} + f_3 \quad (1)$$

where ϵ = specific energy, J/g; s = specific entropy at saturation pressure, J/g deg; and f_1 , f_2 , and f_3 are abbreviations for $f_1(u)$, $f_2(u)$, and $f_3(u)$ in which

$$u^{-1} = v^{1/3} - v_0^{1/3} \quad (2)$$

where v = specific volume at T and v_0 = "occupied" volume, or $v_{T=0}$. This equation is applicable, without the use of any corrections, in what we call the "region of regular performance." In this region, the volume-dependent functions are defined as follows:

$$\left. \begin{aligned} f_1 &= c_1 + c_2 u \\ f_2 &= c_3 \end{aligned} \right\} \text{(exact relations)} \quad (3)$$

$$\ln f_3 = c_4 + c_5 \ln u \quad \text{(approximation)} \quad (4)$$

An exact relation defining f_3 is given in ref. 1, but this involves a double integration and several additional constants, hence it is not practical to use. Values of f_3' and f_3'' may be obtained experimentally, if required. [See eqs. (15) and (16) of ref. 3.]

The region of regular performance in any liquid is that region in which the average separation of the molecules exceeds $1/ud$. For the family of n -alkanes this is $0 > u \leq 10$ (see Table I).

PROCEDURE FOLLOWED IN STUDYING POLYMETHYLENE

The value of ud for polymethylene corresponds to about 450 K. Therefore, we chose to explore the range 450–650 K. Our procedure in verifying the applicability of our equation to various liquids has been to calculate a number of thermodynamic quantities pertaining to each liquid and compare them with published measured values.

In the case of polymethylene, no extensive accurate calorimetric measurements are known to us in the range of 450–650 K. Wunderlich and Dole⁴ measured c_p at 453.16 K, whereas Orwoll and Flory⁷ measured γ at 465.04 K (see Table II). Wunderlich and Dole gave an equation applicable from 413.16 to 453.16 K, which comprises the region of "irregular" performance of polymethylene.

The melting temperature of polymethylene is given⁴ as 134.85°C, or 408.01 K, at which temperature c_p is very much greater than it is at 140°C,⁴ whence eq. (1) of ref. 4 gives values of c_p that do not increase rapidly enough as the temperature rises. In other words, their eq. (1) cannot be safely extrapolated above 180°C (453.16 K), which is just at the beginning of the regular region. For this reason, it is useless to compare c_p values calculated from our equation with corresponding values calculated from eq. (1) of Wunderlich and Dole.⁴ Since the various thermodynamic quantities are calculated from c_p (and other quantities), all thermodynamic quantities calculated from erroneous values of c_p will also be in error. We therefore have chosen to present our results without comparison with any experimental values except the two mentioned above.

CALCULATIONS

To apply our VSE equation of state to any liquid, it is necessary to have two kinds of information: (1) the equation parameters and (2) the specific volumes and temperatures at which the desired thermodynamic quantities should be calculated.

The first kind of information required is easily obtained in this case because polymethylene is simply a very high molecular weight n -alkane. It was shown in the prior paper⁵ on poly(tetrafluoroethylene) that our equation is applicable to liquids heterogeneous with respect to molecular weight. A weight-average molecular weight for polymethylene should therefore give the same values as

TABLE I
Values of ud

	ud
n -Alkanes (including polymethylene)	10.0
Benzene	12.31
Mercury	35.73
Water	9.72
Sodium	4.2
Poly(tetrafluoroethylene)	2.15

TABLE II
Calculation of v , α , u , F , f_1 , s , c_p , γ , c_p , and ϵ at Ambient Pressure

T, K	v , ml/g	$10^3\alpha$, deg $^{-1}$	u , cm $^{-1}$	F , dimensionless	f_1 , cm $^{-1}$	s , J/g deg	c_p , J/g deg	γ , (bars/10)/deg	c_p calc, J/g deg	$Tv\alpha\gamma$, J/g deg	ϵ , J/g
413.16	1.3077	0.64945	9.618396	25.787660	38.944777	3.0238	2.2254	0.552324	2.5954 ^a	0.1938	—
450	1.2977	0.64958	9.884074	27.371661	39.044361	3.2140	2.3653	0.621523	2.6011	0.2358 ^b	862.21
453.16	1.3004	0.64960	9.810769	26.929825	39.016882	3.2323	2.3788	0.615399	2.6855 ^a	0.2356	—
465.04	1.3105	0.64964	9.541779	25.368870	38.917934	3.3006	2.4290	0.593485 ^c	—	—	—
500	1.3406	0.64974	8.844682	21.447516	38.654774	3.4988	2.5750	0.535512	2.8082	0.2332	997.26
550	1.3849	0.65002	7.995111	17.149393	38.336339	3.7760	2.7789	0.465951	3.0096	0.2307	1142.21
600	1.4306	0.65030	7.288379	13.946391	38.071442	4.0463	2.9779	0.408875	3.2061	0.2282	1296.74
650	1.4779	0.65061	6.889474	11.496509	37.846960	4.3106	3.1723	0.361191	3.3980	0.2257	1458.92

^a These values of c_p obs are from eq. (1) of ref. 4.

^b c_p obs = c_p obs - $Tv\alpha\gamma$ = 3.4495.

^c Only two experimental points are compared with calculated points in this paper (see text). These are Wunderlich and Dole's⁴ c_p at 453.16 (2.6855 versus our 2.6134) and Orwoll and Flory's⁷ γ at 465.04 (0.5813 versus our 0.5935).

would be obtained with a homogeneous liquid of the same molecular weight. We arbitrarily assigned a weight-average molecular weight of 75,000 to our hypothetical liquid polymer.

In ref. 3, the values of our parameters for *n*-alkanes of 5, 6, 7, 9, and 17 carbons are listed. Figure 1 shows that $\ln c_1$ and c_2 , c_3 , and c_5 are linear with reciprocal molecular weight; whereas c_4 is a constant. The values for $M = 75,000$ are: $c_1 = 35.339610$, $c_2 = 0.374820$, $c_3 = 2.358789$, $c_4 = 6.054653$, $c_5 = -0.234402$. The value of $v_0^{1/3}$, which is a physical constant = 0.989576, is determined in the next section.

The second kind of information, density or specific volume ($1/\rho$), required additional investigation, which was carried out in this study.

The API 44 tables⁶ give picnometer values of the *n*-alkanes up to their boiling points. Above these temperatures, weighings of the picnometer are complicated by the boiling sample, so other devices must be employed for the higher temperatures. Some experimenters⁷ have devised dilatometers to enable filling of the picnometer in a closed system; others have attacked the problem in different ways.

We first solved the problem in 1951 by dealing with the family of *n*-alkanes simultaneously and plotting lines instead of points.⁸ Thus, we found that $\ln v$ versus $1/M$ was linear at each temperature. At temperatures above the boiling points of the low molecular weight members of the family, the lines were determined by measurements on the high molecular weight compounds. Hence, all picnometer measurements were made below the boiling points of the compounds. Unfortunately, when this work was done, desk calculators had not yet been introduced, and our eqs. (8)–(10) of ref. 8 were obtained graphically. The original data, however, (Table I of ref. 8) were very accurate, and the molecular weights involved were from 72.15 (C_5) to 899.68 (C_{64}).

In 1964, we published tables of specific volumes of *n*-alkanes from C_7 to C_{40}

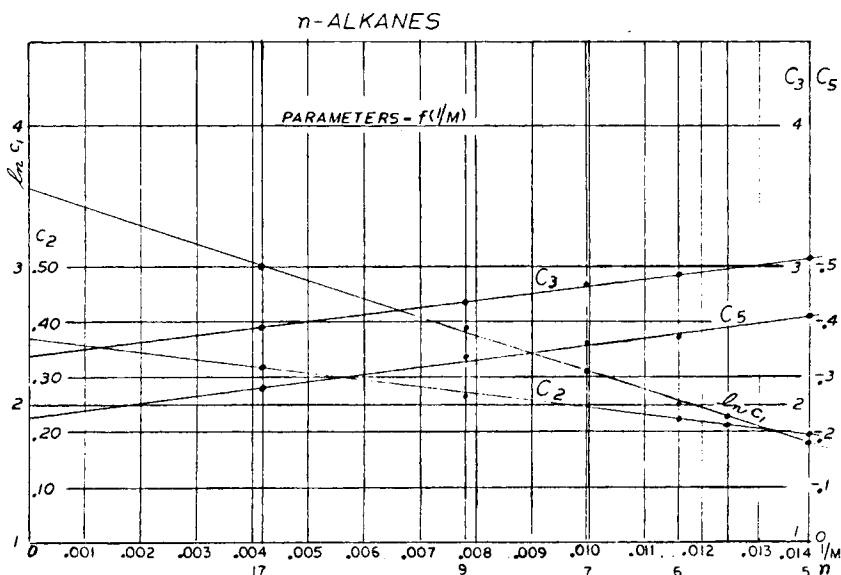


Fig. 1. Dependence of the equation parameters of the *n*-alkanes on reciprocal molecular weight. Note: $C_4 = \text{constant } 6.054653$.

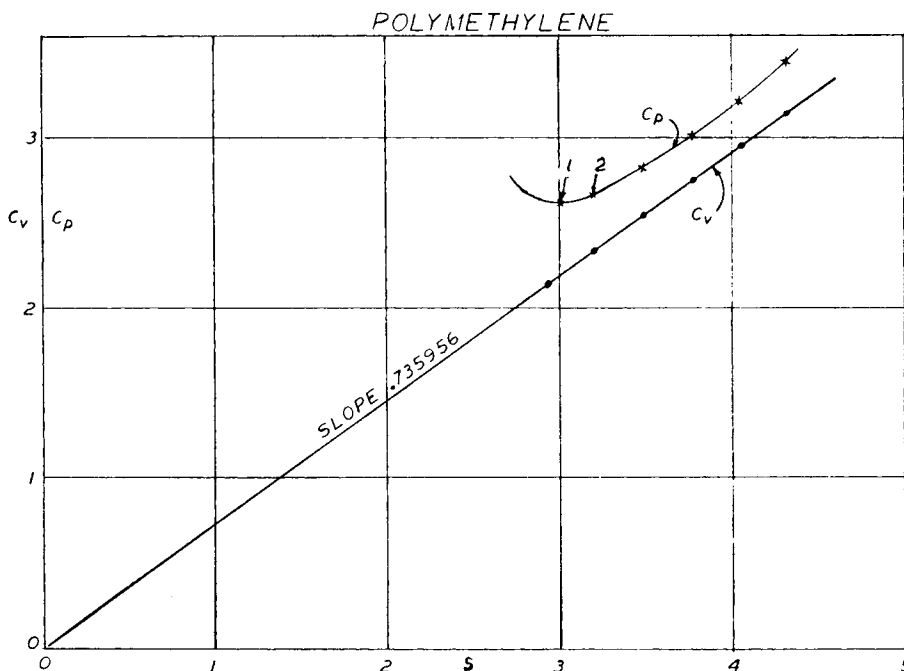


Fig. 2. Relation between c_v and s for polymethylene. Calculated c_p is plotted on the same graph. Points 1 and 2 are from eq. (1) from ref. 4.

over the range of 30 to 300°C and from ambient to 5000 bars of pressure.⁹ The zero-pressure values in these tables were obtained by a method first published by us in 1963.¹⁰ In this method, the Hudleston equation was used as a tool to correct the low-pressure points. This method is explained in detail in ref. 11. While the values of specific volumes at ambient pressure were very accurate in ref. 9, and were used in all of our prior work on equation of state,³ the equations used then could not be employed in the present case, because the factor K , first introduced in eq. (2) of ref. 11, cannot be extrapolated beyond C_{40} . Therefore, attention was again turned to our earlier work.⁸

The slopes and intercepts of the lines $\ln v$ versus $1/M$, determined by the data of Table I, ref. 8, were obtained by least-squares calculations, giving a pair of values for each temperature of measurement. Of these, the intercepts were observed to be linear with temperature, whereas the slopes followed an exponential curve. The equations follow:

$$\text{intercepts} = -0.0315646 + 0.00064825T \quad (6)$$

range 223.2–523.2 K, SPE₉ = 0.8050%, and

$$\text{slopes} = 9.707270 e^{0.00285355T} \quad (7)$$

range 183.2–523.2 K, SPE₁₀ = 0.3905%.

From the equations, the intercept and slope of the line $\ln v$ versus $1/M$ can be calculated at any temperature. Thus, the values listed in Table II were determined for $M = 75,000$ at 450, 500, 550, 600, and 650 K. The value of $\ln v_0 = (9.707270/75000) - 0.0315646 = -0.03143513$, and $v_0^{1/3}$ for polymethylene of MW 75,000 = 0.989576, which is a physical constant.

Values of

$$\alpha = \left(\frac{\partial \ln v}{\partial T} \right)_P \quad (8)$$

were obtained by differentiation. The result is

$$\alpha = 0.00064825 - 0.00000037 e^{0.00285356T} \quad (9)$$

Calculation of Values Listed in Table II

Using the values of v and α calculated for the temperatures of interest in the regular range, and calculating u and f_1 values from eqs. (2) and (3), respectively, the remaining columns of Table II were calculated from the equations:

$$F = (u/v^{1/3})^2/3 \quad (10)$$

$$\ln s = \frac{\ln T - \ln f_1 - \ln c_3}{c_3 - 1} \quad (11)$$

$$c_{v \text{ calc}} = \frac{s}{c_3 - 1} \quad (12)$$

$$\gamma = F \cdot c_v (c_2/f_1) \quad (13)$$

$$c_{p \text{ calc}} = c_{v \text{ calc}} + Tv\alpha\gamma \quad (14)$$

$$c_{v \text{ obs}} = c_{p \text{ obs}} - Tv\alpha\gamma \quad (15)$$

Only two values of $c_{p \text{ obs}}$ are listed. These are obtained from eq. (1) of ref. 4, which is

$$c_{p \text{ obs}} = 4.184 (0.545 + 0.000538t) \text{ J/g}$$

where t is in °C. These are points 1 and 2 on Figure 2.

As mentioned earlier, this equation was not extrapolated to temperatures higher than 180°C (453.16 K) because it was derived from data taken in the irregular region and gives erroneous values at higher temperatures.

CONCLUSIONS

Since this is the final paper contemplated for this series, it may be well to recapitulate briefly what has been learned from this study about the nature of the liquid state.

1. All liquids have a region of regular performance that is defined by the average distance of separation of the molecules. If this average distance is represented by $1/u$, given by eq. (6), then the regular regions lie between values of u from 0 to u_d . In the irregular region the simple equations for f_1 , f_2 , and f_3 , eqs. (3)–(5), fail, so a correction must be applied. The form of this correction is the same for all liquids examined [eqs. (6)–(8) of ref. 3], but the agreement in the irregular region of calculated with experimental values is not as good with highly polar liquids (such as water and mercury) as it is with the other liquids studied by us. This suggests that, in the neighborhood of the melting point, certain cohesive forces come into play that are greater with highly polar liquids than with nonpolar liquids.

2. In the regular region, the fractional change in entropy is directly proportional to the fractional change in temperature just as it is in gases. The only difference is that in gases one deals with entropy at constant volume, whereas with liquids one uses saturation pressure. The proportionality constants are not the same for both phases.

3. A van der Waals-type PVT equation of state applies to liquid polymers in the regular region.

4. Volume, entropy, and energy are all substantially linear with absolute temperature in the regular region, as is the case with gases.

5. The point at which deviation from regular behavior begins is clearly evident visually in polyethylene. This suggests that u_d corresponds to the temperature at which all crystallites have melted. In liquids of lower molecular weight, these crystallites are not visible, but there is no reason to suppose that they do not exist and become more dense as the freezing temperature of the liquid is approached. This phenomenon could also contribute to the failure of uncorrected calculated thermophysical quantities to correspond to the observed values in the irregular region.

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