fraction gratings, one may observe scattering at arbitrarily small angles or even at zero angle which is, of course, impossible for ordinary scattering.

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Statistical Thermodynamics of Chain Molecule Liquids. I. An Equation of State for Normal Paraffin Hydrocarbons[1]

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A partition function is formulated for chain molecule liquids using a model consisting of a linear sequence of segments endowed with hard sphere type repulsive potentials and soft attractions of unspecified character. The intermolecular energy is represented as varying inversely with the volume over the comparatively small range of volume of the liquid. Account is taken of intermolecular constraints on the segments by expressing the number of external degrees of freedom per segment as $3c$ where c (<1) enters as a parameter. In this respect the formulation follows recent treatments based on the cell model, use of which is avoided. A reduced equation of state $\tilde{p} = \tilde{p}(\tilde{T}, \tilde{v})$ is derived, with reduced variables defined by three primary parameters, namely, a segment net volume v^*, a quantity $s\eta$ characterizing the interaction per segment, and c. These can be evaluated from the volume, thermal expansion coefficient, and compressibility, for example. Data for the n-paraffin hydrocarbons from C_6 to C_∞ are very well represented in this manner. The values of the parameters are slightly dependent, however, on the temperatures to which the experimental data refer.

Introduction

Initiation of the investigations reported in this series of papers was motivated by the need for a basis on which to interpret and correlate the properties of macromolecular liquids and their solutions. Comprehension of the connection between molecular characteristics and thermodynamic properties of such liquids is an obvious prerequisite for interpretation of melting and glass transitions, for example. It has long been apparent also that the major discrepancies between theory and experiment on macromolecular solutions can only be resolved by treating these systems in some more satisfactory fashion than is possible within the strictures of the lattice model. By its disregard of changes in volume and local disorder with composition, this model fails to reflect changes in liquid structure, account of which is necessary for realizing an adequate grasp of solution properties.

Treatment of liquids consisting of nonspherical polyatomic molecules by methods which join rigor with tractability of result is an objective for which there is as yet small hope of fulfillment. In this paper we sacrifice rigor in favor of simplicity by resorting to a low order of approximation in formulating a partition function for chain liquids. While the level of refinement may leave much to be desired, the relationships derived are manageable, and the correlation with experiment is not altogether disappointing.

The subject is by no means new. Prigogine and co-workers[2-4] have adapted the cell model to chain molecule liquids. Equations of state thus derived have proved of little value.[2,5,6] The difficulty unquestionably is related to the unsatisfactory representation of the intermolecular energy and its dependence

on volume afforded by the cell model. As Hildebrand and Scott[7] have emphasized, this model, by fixing nearest neighbors of a given molecule (or segment) exactly at their mean positions, suppresses the randomness which is a foremost characteristic of the liquid state. Irregularity in the distribution of molecules about one another, as expressed by the radial distribution function for a liquid, is artificially suppressed by the assumed quasi-crystalline order. The intermolecular energy for a molecule moving in a cage provided by neighbors fixed in regular array may readily be seen to be unrepresentative of the energy for a molecule surrounded by molecules irregularly placed.

Prigogine and co-workers in later papers[2,4] formulated a law of corresponding states for chain molecules, and this has met with noteworthy success. Demonstration of a law of corresponding states embracing virtually the entire range of n-paraffin hydrocarbons[2,4,8] encourages the search for a partition function for chain liquids by means of which to rationalize an extensive body of experimental results. An analytical expression for the partition function and the equation of state derived from it are much to be preferred over the graphical–empirical methods of application of a law of corresponding states.

Our partition function is patterned after that introduced for simple liquids by Eyring and Hirschfelder[9,10] a number of years ago. With them, we assume the intermolecular energy to depend only on the volume, and a hard sphere repulsive potential is adopted for segments of the chain. The number of external degrees of freedom is introduced as a parameter on the premise that the corresponding modes can be separated unambiguously from the internal degrees of freedom of the molecule. In this respect we follow the procedure elaborated by Prigogine and co-workers.[2-4]

(1) Presented before the Division of Physical Chemistry of the American Chemical Society, Denver, Colo., Jan. 22, 1964.

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

(3) I. Prigogine, N. Trappeniers, and V. Mathot, *Discussions Faraday Soc.*, **15**, 93 (1953); *J. Chem. Phys.*, **21**, 559, 560 (1953).

(4) I. Prigogine, A. Bellemans, and C. Naar-Colin, *ibid.*, **26**, 751 (1957).

(5) R. Simha and S. T. Hadden, *ibid.*, **25**, 702 (1956); **26**, 425 (1957).

(6) R. Simha and A. J. Havlik, *J. Am. Chem. Soc.*, **86**, 197 (1964).

(7) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, pp. 49-65.

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

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

(10) J. O. Hirschfelder, *J. Chem. Educ.*, **16**, 540 (1939).

The Partition Function

Consider a linear chain molecule, e.g., $H-(CH_2)_n-H$, consisting of a succession of n repeating units and bounded by terminal groups of specified character. The terminal groups may exert intermolecular forces differing from those of the mid-chain repeating units. The chain molecule is assumed to be endowed with flexibility to the extent that it is capable of assuming a variety of spatial configurations. We imagine the chain to be subdivided into x segments. The segment is not explicitly defined; its definition may be adapted to circumstances. In general, the segment will not correspond to the repeating unit; i.e., $x \neq n$. We specify, however, that x shall be linear with n for homologous members of the series. More particularly, x will be taken proportional to the "hard core" molecular volume v^*, or, net volume, and we shall assume these volumes for homologs of the series to be linear in n; thus $v^* = xv^*$ where v^* is the net volume of a segment. Otherwise, the definition of x is left open.

Resort to a lattice model, where required, would predicate an isometric segment. Implicitly or otherwise, the segment should then be so defined as to have a length equal to the diameter of the chain if commitment to a lattice model is essential. Often this stipulation may be ignored without effect on the form of the results. In the treatment of solutions of chain polymers in monomeric solvents, for example, it is expedient to so define the segment as to render its volume, or its net volume, equal to that of the solvent, in which case x becomes the ratio of molecular volumes. These considerations may be ignored within the scope of the present paper; hence, the definition of the segment can be quite arbitrary.

Let s represent the mean number of external contact sites per segment of the molecule. Specifically, we take

$$xs = xs_m + s_e \qquad (1)$$

where s_m is the number of contacts for an internal segment and s_e is the added number for the chain ends.[11] Thus, xs may be regarded as a measure of molecular surface.

Following Prigogine, Trappeniers, and Mathot,[2,3] we assume that the normal oscillatory modes of the isolated chain molecule can be separated unambiguously into two categories, namely, internal (i.e., intramolecular) and external (i.e., intermolecular). The former, comprising modes of higher frequency, are considered to be inappreciably affected by neighbors in the liquid. The latter, comprising the lower frequency modes of the isolated molecule, are subject to much weaker intramolecular restraining potentials and therefore experience greater perturbation by interactions with neighbors. It is assumed that the intramolecular potentials associated with these latter modes can be disregarded altogether and, hence, that they may be treated as

translational (external) motions. Add to them the three degrees of freedom of the molecular center of gravity and the total number of intermolecular degrees of freedom is

$$3xc = 3(xc_m + c_e) \qquad (2)$$

per molecule; i.e., we take the number of degrees of freedom to be linear in x, and therefore in n also.[12] We shall assume c to be independent of temperature and volume over the range of application of the equations to be set down.

Assuming hard sphere repulsion between segments, we take the "free length" associated with each intermolecular degree of freedom to be of the familiar form

$$\gamma^{1/3}(v^{1/3} - v^{*1/3})$$

where $v = V/xN$ is the volume per segment, V being the volume of the system and N the number of x-meric (or n-meric) molecules; v^* is the net volume per segment, and γ is a geometric constant. This expression is usually identified with the cell model. It is given also by treatment of a hard sphere liquid in one dimension according to the method of Tonks.[13] On the basis of these concepts, the configuration partition function of the liquid may be written

$$Z = Z^\dagger [\gamma(v^{1/3} - v^{*1/3})^3]^{xNc} \exp(-E_0/kT) \qquad (3)$$

where E_0 is the intermolecular energy, the $Z^\dagger$ is the "combinatorial factor" having to do with the gross disposition of segments among one another in space. In terms of a lattice model, $Z^\dagger$ expresses the number of ways of arranging the segments of N molecules over a spatial array of xN sites. Specification of $Z^\dagger$ is not required in the present paper; it suffices here to assume it to be independent of volume and temperature. Equation 3 is identical in form with the partition function introduced by Prigogine, Trappeniers, and Mathot.[2,3] Our treatment of E_0 is at variance with theirs, however.

The factor $c < 1$ is supposed to take into account the restrictions on the precise location of a given segment by its neighbors in the same chain. The distance between adjoining segments of the same chain may be presumed to be narrowly defined by bond lengths and angles; lateral displacements may also be restricted in some degree by structural connections. The former restraint may be considered to reduce the number of external degrees of freedom for a segment from three to two. Further reduction may be expected from lateral restraints. The description is over-simplified, of course. In any case, suppression of the number of degrees of freedom in the manner expressed in eq. 3 in order to account for actual restraints on the segment configuration imposed by their connections one to another is intuitive. Rigorous justification for this step is lacking.

Also to be noted is the omission of a factor for communal entropy. Its absence should not be construed as commitment to a cell model, which by its nature suppresses communal entropy. Rather, we incline to the view that full realization of communal entropy is approached for all of the liquids, and their mixtures,

(11) We deliberately avoid specification of the number of intermolecular contacts in terms of the liquid coordination number z by rejecting the widely used formula, $qz = x(z - 2) + 2$, where qz/x, the average number of contacts per segment, corresponds to our s. The assertion, implicit in this equation, that an end segment makes just one more contact than a mid-chain segment is artificial. Error can be avoided only by suitably defining x or by adjusting z. Either the desired arbitrariness in x or the definition of z as the coordination number of the liquid must be sacrificed. We prefer a more straightforward scheme which avoids injecting the coordination number z into equations where it is not relevant.

(12) Our xc corresponds to the c (alias c_r) used by Prigogine[2] and Hijmans.[8]
(13) L. Tonks, Phys. Rev., 50, 955 (1936).

with which we shall deal. Hence, its omission will be inconsequential.

As pointed out in the introductory remarks, we reject the cell model as a basis for expressing the intermolecular energy E_0. The energy of interaction between a pair of molecules is a sensitive function of intermolecular distance, and relegation of all members of the first shell to the same distance introduces a considerable error in the energy and in its dependence on the mean distance (*i.e.*, on volume).[7,13] Irrespective of the density of packing, and of the displacement of a given molecule from its mean position as well, one or more of its neighbors is likely to be in proximity to the distance of closest approach. The contribution of just these molecules to the energy is most important. The error is enhanced by ignoring the acentric nature of the forces operative between polyatomic molecules.

Such considerations serve to emphasize the intimate connection between the radial distribution function and the energy. If the energy is pairwise additive in intermolecular segment pairs, then in the approximation that the familiar correlation function $g^{(2)}(r_{12})$ is independent of the volume, the intermolecular energy must be proportional to the density ρ, as Hildebrand and Scott have stressed.[14] In this approximation, the mean intermolecular energy per contact pair is expressed as

$$\bar{\epsilon} = -\eta/v \qquad (4)$$

where η characterizes the mean interaction between a segment pair in the liquid of x-meric chains. Whereas η will be treated as a constant for a given chain homolog, allowance will be made for its dependence on x to the extent that interactions of end segments differ from those within the chain (see below).
It follows that

$$E_0 = -xNs\eta/2v \qquad (5)$$

Expression of the intermolecular energy in a form resembling eq. 5, namely

$$E_0 = -\text{constant}/V^m$$

where m is a power near unity, has been advocated by Hildebrand[7,14] and by Frank.[15] Hildebrand has successfully correlated energies of vaporization and $(\partial E/\partial V)_T$ for nonpolar simple liquids on this basis. A relation of this form is thus implied to hold for the entire range of densities from liquid to vapor. Present requirements are much less demanding; it suffices for eq. 4 and 5 to hold over a comparatively small range of volume. Specifically, the traditional quest for an all-embracing equation of state, applicable to vapor and liquid alike, is not an objective of the present development. In fact, the assumption of a fixed number $3xc$ of intermolecular degrees of freedom restricts the range of densities over which the treatment may be applied; since $xc > 1$, the vapor obviously is excluded from consideration.

On the supposition that terminal segments offer different forces of attraction to neighbors than do the mid-

(14) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corporation, New York, N. Y., 1950, p. 92 ff.

(15) H. S. Frank, *J. Chem. Phys.*, **13**, 478, 493 (1945).

chain segments present in preponderance, the intermolecular energy can be written

$$E_0 = -(1/v)(N_m\eta_m + N_{em}\eta_{em} + N_e\eta_e) \qquad (6)$$

where η_m, η_{em}, and η_e characterize interactions between sites on two neighboring mid-chain segments, between a mid-chain and a terminal segment site, and between two terminal sites, respectively. The N's denote the numbers of neighbor pairs in the respective categories. We shall assume these numbers to equal those for random mixing of sites. For simplicity, we take the number of terminal sites having atypical interactions to be just s_e, the excess number of sites for the two end groups as required by eq. 1. Obviously, the number of atypical terminal sites cannot in general be identified with the s_e defined by eq. 1. It will be readily apparent, however, that a fictitious counting of these sites can always be rectified by modifying the η's without affecting appreciably the form of the result.

On this basis

$$E_0 = -(xN/2vs)[s_m^2\eta_m + 2(s_ms_e/x)\eta_{em} + (s_e^2/x^2)\eta_e]$$

which by comparison with eq. 5 defines η as

$$\eta = (s_m^2/s^2)\eta_m + 2(s_ms_e/s^2x)\eta_{em} + (s_e^2/s^2x^2)\eta_e \qquad (7)$$

In the familiar approximation

$$\eta_{em} \cong (\eta_e\eta_m)^{1/2} \qquad (8)$$

appropriate for dispersion interactions

$$\eta \cong (s_m/s)^2\eta_m[1 + (s_e\eta_e^{1/2}/s_m\eta_m^{1/2})/x]^2 \qquad (9)$$

The artificial designation of terminal sites introduced above invalidates literal adoption of this approximation in the form of eq. 8 and 9.

Upon substituting eq. 5 in eq. 3 and introducing reduced variables as

$$\tilde{v} = v/v^* \qquad (10)$$

$$\tilde{T} = T/T^* = 2v^*ckT/s\eta \qquad (11)$$

we obtain

$$Z = Z^\dagger(\gamma v^*)^{xNc}(\tilde{v}^{1/3} - 1)^{3xNc} \exp(xNc/\tilde{v}\tilde{T}) \qquad (12)$$

The Equation of State

The equation of state obtained from eq. 12 and expressed in reduced form is

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/(\tilde{v}\tilde{T}) \qquad (13)$$

with the reduced pressure $\tilde{p}$ defined by

$$\tilde{p} = p/p^* = 2pv^{*2}/s\eta \qquad (14)$$

or

$$\tilde{p} = pv^*/ckT^* \qquad (14')$$

Equation 13 corresponds to the reduced equation of state of Hirschfelder and Eyring.[9] The parameters differ, however, through the introduction of c; these differences vanish, of course, for $c = 1$. The reduced equation of state may be expressed alternatively as

$$\tilde{p}/\tilde{\rho}^2 = \tilde{T}/\tilde{\rho}(1 - \tilde{\rho}^{1/3}) - 1 \qquad (13')$$

where $\tilde{\rho} = 1/\tilde{v}$ is the reduced density.

Three parameters, namely, v^*, c, and the product $s\eta$, serve to characterize the chain molecule according to

TABLE I

PRIMARY DATA AND PARAMETERS FOR n-PARAFFIN HYDROCARBONS

n	ρ, g. cm.⁻³ [a]	$10^3\alpha$, deg.⁻¹	$\bar{v}$	v^*, cc. mole⁻¹	$\tilde{v}^* = v^*/(n+1)$	T^*, °K.	$\gamma \times 10^3$, cal. cc.⁻¹ deg.⁻¹	p^*, cal. cc.⁻¹
				Temp. = 20.00°				
5	0.62624	1.565[c,d]	1.3485	85.38	14.23	4170		
6	.65937	1.36[c-f]	1.3129	99.48	14.21	4420	211,[n] 200[l]	107, 101
7	.68376	1.23[b-f]	1.2886	113.65	14.21	4670	212(±3)[l,n,o,q,s]	103(±1)
8	.70252	1.14[c-e]	1.2716	127.89	14.21	4850	217,[l] 240[o]	103, 114
9	.71763	1.07[c,d]	1.2587	142.0	14.20	5000	226,[l] 234[n]	105, 109
10	.73005	1.02[c,d]	1.2485	156.1	14.19	5130		
11	.74017	0.98[c,d]	1.2402	170.3	14.19	5240		
12	.74869	.95[b-d]	1.2336	184.3	14.18	5350	239[l]	107
13	.7564	.925[c,d]	1.2287	198.26	14.16	5430	235[n]	104
14	.7628	.89[c,d]	1.2216	212.9	14.19	5560		
15	.7685	.87[c]	1.2172	227.0	14.19	5620		
16	.77344[h]	.855[d]	1.2144	241.1	14.18	5680	248[l]	107
17	.7780[c]	.835[c]	1.2097	255.37	14.19	5760		
18	.7819[d]	.820[c]	1.2063	269.67	14.19	5830		
				Temp. = 50.0°				
6	0.6316	1.51[c,e]	1.3650	99.89	14.27	4480	164[l]	99
7	.6583	1.33[c,e,o,i]	1.3317	114.23	14.28	4720	181(±2),[l,o,q] 169[n]	104(±1), 97
8	.6784	1.225[c,e,i]	1.3162	127.8	14.20	4900	180,[l] 191[o]	101, 107
9	.6944	1.15[c,i]	1.295	142.54	14.25	5050	187(±3)[l-n]	101(±2)
10	.7073	1.095[c]	1.2847	156.49	14.23	5180		
11	.7180	1.045[b,c,i]	1.2745	170.72	14.23	5290	196[n]	103
12	.7271	1.02[b,c]	1.2685	184.58	14.20	5380	204[l]	106
13	.7349	0.98[b,i]	1.2608	198.89	14.21	5490	206[n]	106
14	.7417	.96[b,i]	1.2559	212.86	14.19	5560		
15	.7476	.94[b,c]	1.2513	226.95	14.19	5620		
16	.7528	.92[b,c]	1.2471	241.07	14.18	5680	225[l]	113
17	.7575	.90[b,c,i]	1.2426	255.33	14.19	5750	221[h]	110
18	.7616	.885[b,c]	1.2392	269.51	14.18	5810		
19	.7654	.87[b]	1.2357	283.76	14.19	5850		
20	.7688	.86[b]	1.2336	297.77	14.18	5880	226[n]	111
				Temp. = 100.0°				
7	0.6110	1.58[g]	1.4192	115.48	14.44	4830	116,[n] 130,[l] 154[c]	87, 98, 116
8	.6352	1.42[b,i]	1.3878	129.51	14.39	5030	132,[n] 142[c]	95, 102
9	.6536	1.305[b,i]	1.3645	143.73	14.37	5180	136(±7)[l-n]	95(±5)
10	.6681	1.21[b]	1.344	158.4	14.40	5350		
11	.6800	1.145[b,i]	1.3301	172.72	14.39	5430	142[n]	94
12	.6900	1.10[b]	1.3201	186.90	14.38	5560	158[l]	103
13	.6985	1.06[b,i]	1.311	201.22	14.37	5650	155[n]	99
14	.7059	1.035[b]	1.305	215.24	14.35	5750		
15	.7123	1.01[b]	1.2993	229.4	14.34	5780		
16	.7180	0.985[b]	1.2935	234.69	14.33	5850	167[l]	104
17	.7230	.965[b,i]	1.2888	257.93	14.33	5920	167[n]	104
18	.7276	.95[b]	1.2851	272.1	14.32	5950		
19	.7317	.935[b]	1.2815	286.22	14.31	6020		
20	.7354	.92[b]	1.2776	300.7	14.32	6060	173[n]	105
28	.7555[h]	.84[i]	1.2576	(415.6)	14.33	6370		
30	(.759)[j]	(.825)[j]	1.2542	(441.83)	(14.25)	(6432)	179[n]	105
36	.7667[h]	.795[i]	1.2465		14.34	6580		
				Temp. = 150.0°				
10	0.6260	1.42[b]	1.4243	159.49	14.50	5419		
11	.6396	1.32[b,i]	1.4027	174.13	14.51	5571	102[n]	85
12	.6509	1.25[b]	1.3873	188.6	14.51	5677		
13	.6604	1.185[b,i]	1.3725	202.9	14.49	5798	109[n]	87
14	.6685	1.15[b]	1.3643	217.5	14.50	5867		
15	.6756	1.10[b]	1.3524	232.36	14.52	5980		
16	.6819	1.075[b]	1.3464	246.51	14.50	6035		
17	.6874	1.05[b,i]	1.3402	260.92	14.50	6098	124[n]	94
18	.6924	1.03[b]	1.3352	275.3	14.49	6146		
19	.6968	1.015[b]	1.3315	289.27	14.46	6190		
20	.7009	0.999[b]	1.3274	303.53	14.45	6233	136[n]	97
28	.7235[h]	0.89[i]	1.2992	419.76	14.47	6589		
30	(.727)[j]	(.88)[j]	1.2965	(448.35)	(14.46)	(6615)	142[n]	101
36	.7357[h]	.83[i]	1.2830	536.84	14.51	6897		
40	(.7405)[j]	(.825)[j]	1.2817	(590.88)	(14.41)	(6827)	147[n]	102
64	.7579[h]	.77[i]	1.2664	936.95	14.41	7076		
∞	.779[k]	.685[k]	1.2419		14.50	7539		

TABLE I (*Footnotes*)

a Except as otherwise noted, all densities are taken from the American Petroleum Institute compilations, 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.   *b* Computed by graphical-analytical treatment of densities given by F. D. Rossini, *et al.* (see note *a* above) for temperatures in the vicinity of the temperature specified in the table.   *c* From G. Egloff, "Physical Constants of Hydrocarbons," Vol. V, American Chemical Society Monograph Series, No. 78, Reinhold Publishing Corp., New York, N. Y., 1953.   *d* From G. Allen, G. Gee, and G. Wilson, *Polymer*, 1, 456 (1960).   *e* Calculated from results of H. E. Eduljee, D. M. Newitt, and K. E. Weale, *J. Chem. Soc.*, 3086 (1951).   *f* Calculated by interpolation from dv/dT given by J. Gomez-Ibanez, *J. Phys. Chem.*, 65, 2148 (1961).   *g* From data compiled by J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworths, London, 1959, p. 37.   *h* From A. K. Doolittle and R. H. Peterson, *J. Am. Chem. Soc.*, 73, 2145 (1951).   *i* Computed by graphical-analytical treatment of densities given by Doolittle and Peterson (see note *h* above) at temperatures in the vicinity of the temperature specified.   *j* Values of ρ and α given in parentheses were obtained by interpolation with *n*.   *k* From specific volume-temperature relationship determined by M. J. Richardson, P. J. Flory, and J. B. Jackson, *Polymer*, 4, 221 (1963), for linear polyethylene from 140 to 180°.   *l* From pressure-volume data at 0, 30, 60, 90, and 120° by J. W. M. Boelhouwer, *Physica*, 26, 1021 (1960).   *m* From pressure-volume data at 37.8, 54.4, 71.1, 87.8, 104.4, and 121.1° by L. T. Carmichael, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, 45, 2697 (1953).   *n* From Huddleston equation using parameters given at 30, 50, 100, 150, and 200°, by A. K. Doolittle and D. B. Doolittle, *A.I.Ch.E. J.*, 6, 157 (1960).   *o* From Tait equation using parameters given at 0, 25, 40, and 60° by Eduljee, Newitt, and Weale (see note *e* above).   *p* From pressure-volume data at 100 and 125° by W. A. Felsing and G. M. Watson, *J. Am. Chem. Soc.*, 64, 1822 (1942).   *q* From pressure-volume data at 4.4, 37.8, 71.1, and 104.4° by W. B. Nichols, H. H. Reamer, and B. H. Sage, *Ind. Eng. Chem.*, 47, 2219 (1955).   *r* From pressure-volume data at 100 and 150° by L. B. Smith, J. A. Beattie, and W. C. Kay, *J. Am. Chem. Soc.*, 59, 1587 (1937).   *s* Calculated by interpolation of experimentally determined thermal pressure coefficients tabulated between 19 and 36° by W. Westwater, H. W. Frantz, and J. H. Hildebrand, *Phys. Rev.*, 31, 135 (1928).   *t* Calculated by interpolation of experimentally determined thermal pressure coefficients between 8.4 and 50.3° by R. D. Dunlap and R. L. Scott, *J. Phys. Chem.*, 66, 631 (1962).

eq. 12 and 13. It is on this account that the equation of state reduces to parametric form. The first of the parameters is alleged to be the same for all homologs of the series; this follows from the manner of defining a segment and the assumed linearity of xv^* with n. The other parameters are considered to depend asymptotically on n.

The coefficient of thermal expansion α, the coefficient of compressibility κ, and the thermal pressure coefficient γ (not to be confused with the previous γ) may be expressed in terms of the reduced variables as

$$\alpha = v^{-1}(\partial v/\partial T)_p = (\tilde{T}/T\tilde{v})(\partial \tilde{v}/\partial \tilde{T})_{\tilde{p}}$$

$$\kappa = -v^{-1}(\partial v/\partial p)_T = -(\tilde{p}/p\tilde{v})(\partial \tilde{v}/\partial \tilde{p})_{\tilde{T}}$$

$$\gamma = (\partial p/\partial T)_v = \alpha/\kappa = (\tilde{T}p/T\tilde{p})(\partial \tilde{p}/\partial \tilde{T})_{\tilde{v}}$$

Solving eq. 13 first for $\tilde{T}$ and then for $\tilde{p}$, differentiating the resulting expressions, and finally eliminating $\tilde{T}$ in each case, we obtain

$$(\alpha T)^{-1} = 1/3(\tilde{v}^{1/3} - 1) - 1 + 2\tilde{p}\tilde{v}^2/(\tilde{p}\tilde{v}^2 + 1) \quad (15)$$

$$(\kappa p)^{-1} = [1/3(\tilde{v}^{1/3} - 1) - 1](1 + 1/\tilde{p}\tilde{v}^2) + 2 \quad (16)$$

$$\gamma T/p = 1 + 1/\tilde{p}\tilde{v}^2 \quad (17)$$

At zero pressure[16]

$$(\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} = \tilde{T} \quad (18)$$

$$\alpha T = 3(\tilde{v}^{1/3} - 1)/[1 - 3(\tilde{v}^{1/3} - 1)] \quad (19)$$

$$\kappa = 3(\tilde{v}^{1/3} - 1)\tilde{v}^2/[1 - 3(\tilde{v}^{1/3} - 1)]p^* \quad (20)$$

$$= \alpha T\tilde{v}^2/p^* \quad (20')$$

$$\gamma = p^*/T\tilde{v}^2 \quad (21)$$

These equations furnish a simple basis for evaluating the various parameters. Solving eq. 19 for $\tilde{v}^{1/3} - 1$ we have

$$\tilde{v}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \quad (19')$$

which permits $\tilde{v}$ to be computed from the coefficient of expansion of the liquid at $p = 0$. The net volume v^* follows according to eq. 10 from the measured volume. Substitution of $\tilde{v}$ in eq. 18 yields $\tilde{T}$ and hence T^*

(16) Subscripts denoting that $\tilde{v}$, α, κ, and γ appearing in eq. 18 to 21, inclusive, refer to $p = 0$ have been omitted in the interest of simplicity.

The value of p^* may then be calculated from the limiting compressibility using eq. 20 or 20'. Alternatively, p^* may be obtained from the thermal pressure coefficient using eq. 21. Having evaluated v^*, T^*, and p^*, the primary parameters c and $s\eta$ are available from eq. 11 and 14. Thus

$$s\eta = 2p^*v^{*2} = 2\gamma Tv^2 \quad (22)$$

$$c = p^*v^*/kT^* = (\gamma v/k)(\alpha T)/(3 + 4\alpha T) \quad (23)$$

Application to the Normal Paraffin Hydrocarbons

Experimental values of the density ρ, of the coefficient of thermal expansion α, and of the thermal pressure coefficient γ, all referring to ordinary pressure (*i.e.*, to $p \cong 0$), are presented in the second, third, and eighth columns of Table I for temperatures of 20, 50, 100, and 150°. Sources of these data are indicated in footnotes to the table. Where several sources are indicated, the mean of closely agreeing values is reported. Densities and thermal expansion coefficients have been taken directly from the stated source, or found by interpolation to the specified temperature as indicated in the appropriate footnote. The values of ρ and α, when plotted against $1/n$, are well represented by smooth curves. Deviations for the α-values seldom exceed 1%.

The thermal pressure coefficients γ have been deduced from the relationship of volume to pressure at different temperatures. Where available, experimental results have been used directly for this purpose; in other instances, empirical equations (Tait's or Huddleston's) for the isotherm, with parameters given by the quoted source, have afforded the required relationship. In either case, the pressure required at temperature T' $> T$ to restore the volume $V_{0,T}$ for $p = 0$ at the specified temperature T has been determined; T' exceeds T by 15 to 50°, depending on the data available. The approximate linearity of pressure with temperature at constant volume[17,18] justifies evaluation of γ in this manner. Results obtained are, of course, subject to whatever errors are inherent in empirical equations used to refine the experimental data. Values of γ from different sources are so disparate in some instances

(17) J. W. M. Boelhouwer, *Physica*, 26, 1021 (1960).
(18) H. E. Eduljee, D. M. Newitt, and K. E. Weale, *J. Chem. Soc.*, 3086 (1951).
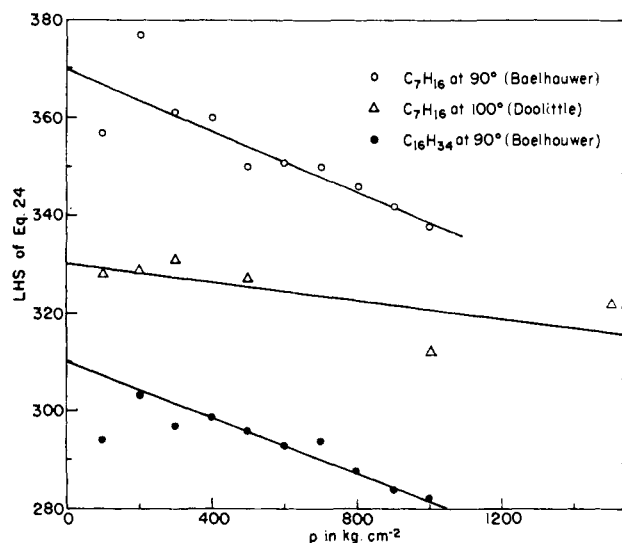
Fig. 1.—The left-hand member of eq. 24 expressed in cal. cc.$^{-1}$ plotted against the pressure p in kg. cm.$^{-2}$. Experimental data of Boelhouwer,[17] and of Doolittle and Doolittle.[19]

as to have rendered averaging inadvisable. Separate values have then been included in Table I.

Several sets of data representing p, V isotherms have been compared directly with the reduced equation of state as follows. Let $\tilde{\rho}_0$ denote the reduced density at $\tilde{p} = 0$ and reduced temperature $\tilde{T}$. Subtraction of $0 = \tilde{T}/\tilde{\rho}_0(1 - \tilde{\rho}_0^{'/3}) - 1$ from eq. 13' leads to

$$p/[\tilde{\rho}(1 - \tilde{\rho}^{'/3})^{-1} - (\tilde{\rho}^2/\tilde{\rho}_0)(1 - \tilde{\rho}_0^{'/3})^{-1}] = p^*\tilde{T} \quad (24)$$

The left-hand side of this equation is plotted against p in Fig. 1 using data of Boelhouwer[17] and of Doolittle and Doolittle.[19] Because this quantity depends on the small difference between two terms, it is subject to a large error at low pressures. By extrapolation, the value of $p^*\tilde{T}$ applicable at $p = 0$ can be obtained, and in this way results of measurements at higher pressures where errors have a lesser effect can be brought to bear on the evaluation of p^*, and of γ. Results thus determined usually exceed those given in Table I; in a few instances the difference is as great as 10%. These differences are believed to reflect irregularities in the experimental data. In the interest of achieving consistency with values of γ and κ reported in the literature, we have chosen to rely on values of p^* deduced by the procedure described in the preceding paragraph, which gives greater weight to measurements at comparatively low pressures.

The left-hand member of eq. 24 would remain unchanged with pressure at constant temperature if the equation of state, eq. 13, afforded an accurate representation of experimental data. The decreases shown in Fig. 1, and in other sets of data treated in like manner, are generally somewhat less than 10% at 1000 kg. cm.$^{-2}$. At $90°$, n-heptane and n-hexadecane sustain compressions of about 12 and 8%, respectively, at this pressure. The departures from constancy in the quantity plotted in Fig. 1 correspond to errors of 5 to 10% in the coefficient $(\partial\kappa/\partial p)_T$ at zero pressure as calculated from the equation of state. The coefficient itself is negative; the calculated values are greater in magnitude than the available experimental data indicate. In other words,

(19) A. K. Doolittle and D. B. Doolittle, J. Appl. Phys., 6, 157 (1960).

the calculated compressions err in being slightly too large at high pressures.

The reduced volumes $\tilde{v}$ given in the fourth column of Table I have been computed from the coefficients of expansion using eq. 19'. Net volumes per mole, $v^* = M \tilde{v}\rho$, M being the molecular weight of the n-mer, are given in the next column. These are quite accurately linear when plotted against n. The results at each temperature are well represented by an equation of the form

$$v^* = v^*(n + n_e) \quad (25)$$

Values of the constants are given in Table II. Identification of x with $n + n_e$ is implicit in eq. 25. The end group contribution n_e is close to unity, and in Table I, v^* is tabulated on the basis $x = n + 1$, the small departures of n_e from unity being ignored.

The linear dependence of the "hard core" volume v^* per molecule on the chain length n accords with the deductions of Prigogine and co-workers,[2] corroborated subsequently by others,[5-7] from the principle of corresponding states. Thus, volumes of n-paraffins when compared at the same *reduced* temperature are linear with n and approximately proportional to $(n + 1)$ throughout the series. Prigogine chose a segment twice as large as ours, namely, the unit consisting of two CH_2 groups.

The value of v^*, although remarkably constant with n, displays a perceptible dependence on temperature. This is most readily apparent in Table II. Although the change is only 2% for a temperature change of $130°$, it corresponds to about 15% of the coefficient of thermal expansion for $n = 10$ to 20.

TABLE II

REFERENCE VOLUMES PER SEGMENT AT VARIOUS TEMPERATURES

T, °C.	v^*, cc. mole^{-1}	n_e
20	14.15 ± 0.02	1.04 ± 0.02
50	$14.14 \pm .03$	$1.08 \pm .02$
100	$14.25 \pm .05$	$1.11 \pm .03$
150	$14.42 \pm .07$	$1.08 \pm .05$

The departure of v^* from constancy marks a limit on the accuracy of the present treatment which is best judged by comparing observed and calculated isobars for $p = 0$. Inasmuch as parameters are chosen to match the first derivatives of v, the divergence must appear in the second derivatives. According to eq. 18 and 19

$$d\alpha/dT = (7 + 4\alpha T)\alpha^2/3 \quad (26)$$

This equation correctly predicts an increase in the thermal expansion coefficient with temperature. The change is so small, however, as to require better data than are available for reliable determination of this higher coefficient. Existing data indicate values of $d\alpha/dT$ about 25% less than predicted by eq. 26. The effect of this rather large percentage error is mitigated by the smallness of $d\alpha/dT$. Thus, the isobar actually is fairly well approximated by the equation of state, eq. 13.

Characteristic temperatures T^* given in Table I have been calculated from $\tilde{v}$ using eq. 18 to obtain $\tilde{T} = T/T^*$. According to the defining eq. 11, T^* depends on both

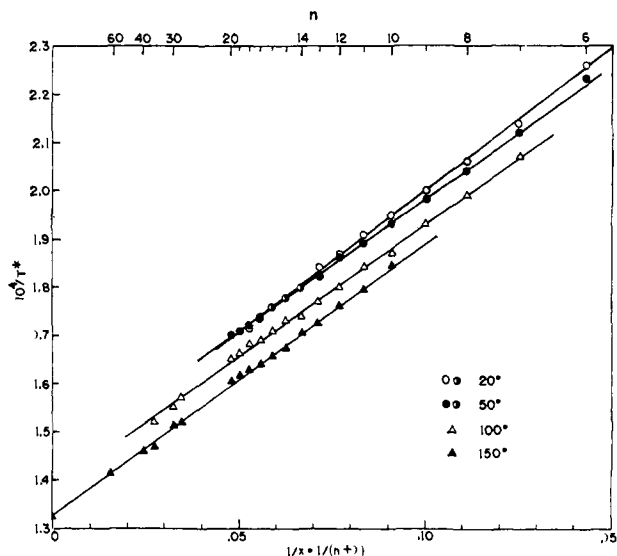Fig. 2.—Reciprocal reference temperatures T^* from Table I plotted against $1/x$ in accordance with eq. 30.

c and $s\eta$, and each of these quantities is acknowledged to depend on x. The dependence of c on x is prescribed by eq. 2; the dependence of $s\eta$ on x is implicit in eq. 7 or 9 but requires elucidation.

According to eq. 7

$$s\eta = s_m\eta_m(s/s_m)^{-1}[1 + (2s_e\eta_{em}/s_m\eta_m)x^{-1} + (s_e^2\eta_e/s_m^2/\eta_m)x^{-2}] \quad (7')$$

Substitution of $1 + (s_e/s_m)x^{-1}$ for s/s_m (see eq. 1) and expansion of the reciprocal of this binomial to the second power in $1/x$ yields

$$s\eta \cong s_m\eta_m(1 + a/x + b/x^2) \quad (27)$$

where

$$a = (2\eta_{em}/\eta_m - 1)(s_e/s_m) \quad (28)$$

$$b = (\eta_e/\eta_m - 2\eta_{em}/\eta_m + 1)(s_e/s_m)^2 \quad (29)$$

Or, by substitution of eq. 28 in 29

$$b = (\eta_e/\eta_m)(s_e/s_m)^2 - a(s_e/s_m) \quad (29')$$

Substituting eq. 2 for c and eq. 27 for $s\eta$ in eq. 11, we obtain

$$1/T^* \cong (1/T_\infty^*)[1 + (c_e/c_m - a)x^{-1} + (a^2 - b - ac_e/c_m)x^{-2}] \quad (30)$$

where

$$T_\infty^* = s_m\eta_m/2kv^*c_m \quad (31)$$

Plots of $1/T^*$ vs. $1/x$ shown in Fig. 2 appear to be approximately linear, with only intimations of small positive curvature. The coefficient of x^{-2} in eq. 30 is thus indicated to be small. A downward displacement with temperature is evident. Equations of the lines drawn through the several sets of points are

$$20°: \ 10^4/T^* = 1.413(1 + 4.17/x)$$

$$50°: \ 10^4/T^* = 1.436(1 + 3.81/x)$$

$$100°: \ 10^4/T^* = 1.384(1 + 3.95 \ x) \quad (32)$$
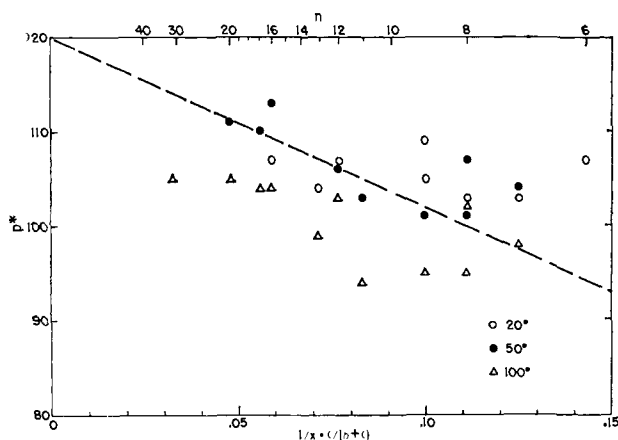
$$150°: \ 10^4/T^* = 1.326(1 + 4.25/x)$$

Fig. 3.—Reference pressures from Table I for 20, 50, and 100° plotted against $1/x$. Dashed line drawn according to eq. 35.

The small change of T^* with the temperature at which the data used for its evaluation were determined is significant. It is directly related to the increase in v^* with T noted above. In fact, eq. 18 and 19 require that

$$d \ln T^*/dT = (\alpha T)^{-1} d \ln v^*/dT$$

The slope of the line described by the 50° data stands at variance with data for other temperatures. The source of this anomaly is not apparent. Its effect on the excess quantities for mixtures, calculation of which involves use of the empirical eq. 32, will be shown in the following paper.[20]

The characteristic volume v^* and the characteristic temperature T^* depend only on the density and the thermal expansion coefficient, both of which are known to high accuracy. Characteristic pressures p^* given in the last column of Table I have been calculated from the thermal pressure coefficients γ and reduced volumes $\tilde{v}$, using eq. 21. Where two values are quoted for γ in the next-to-last column, the corresponding values of p^* are given separately in the last column of the table. The large experimental uncertainties previously noted are reflected in the p^* values.

By substitution of eq. 27 in 22

$$p^* \cong p_\infty^*(1 + a/x + b/x^2) \quad (33)$$

where

$$p_\infty^* = s_m\eta_m/2v^{*2} = c_mkT_\infty^*/v^* \quad (34)$$

According to the analysis of properties of mixtures presented in the following paper,[20] b is quite small compared to a. Hence, it may sometimes suffice to write

$$p^* \cong p_\infty^*(1 + a/x) \quad (33')$$

Characteristic pressures from the last column of Table I are plotted in Fig. 3 in accordance with eq. 33'. Data for 150° have been omitted in consideration of the paucity of experimental results. Several widely discrepant values for other temperatures have been omitted as well. Although the scatter of the points precludes quantitative deductions, it is evident that p^* decreases appreciably with x; a moderate downward displacement with temperature is indicated also.

(20) P. J. Flory, R. A. Orwoll, and A. Vrij, J. Am. Chem. Soc., 86, 3515 (1964).

It is unfortunately impossible to arrive at reliable values of the parameters $p_\infty*$ and a from these data. The approximate linearity of $1/T^*$ with $1/x$ in Fig. 2 argues according to eq. 30 for a small (negative) value of a. On the other hand, enthalpies of mixing of n-paraffin hydrocarbons treated in the following paper[20] require a somewhat larger value of $-a$ than the linearity of the plate in Fig. 2 seems to suggest. The broken line in Fig. 3 has been drawn with the slope required to approximate[20] the experimental enthalpies of mixing. Its equation is

$$p^* = 120(1 - 1.5/x), \text{ cal. cc.}^{-1} \qquad (35)$$

which, by comparison with eq. 33', fixes the values of $p_\infty* = 120$ cal. cc.$^{-1}$ and $a = -1.5$.

Parameters for n-Paraffin Hydrocarbons

The net volume per mole, $v^* = xv^* \cong (n + 1)v^*$, very nearly equals the molar volume of higher n-paraffin crystals, $v^c = 14.16n + 7.15$ cc. mole^{-1} at 20°, as calculated from their crystallographic dimensions.[21] Although this virtual coincidence must be partly fortuitous, it enhances confidence in $v^* = 14.15$ cc. mole^{-1} as a hard core volume.

From results at 20° we have therefore (see especially eq. 30, 32, 33', and 35).

$$T_\infty* = 7080°K.$$

$$p_\infty* = 120 \pm 5 \text{ cal. cc.}^{-1}$$

$$a = -1.5$$

$$c_e/c_m - a = 4.17$$

Although the constant a has been chosen (see eq. 35 above) to fit enthalpies of mixing treated in the paper which follows,[20] its value could, in principle, be determined from compression data of greater accuracy than that now available. All parameters could then be evaluated from equation of state data. Owing to the evident limitations of existing results, it has been necessary to draw upon thermochemical measurements to complete the set of parameters.

Primary parameters obtained from eq. 34, 31, and 30 and the values of v^*, $T_\infty*$, and $p_\infty*$ together with numerical data given above are[22]

$$s_m\eta_m = 2v^{*2}p_\infty* = 4.8 \times 10^4 \text{ cc. cal. mole}^{-2}$$

$$c_m = v^*p_\infty*/RT_\infty* = 0.121$$

$$c_e/c_m = 4.17 + a \cong 2.7$$

$$c_e \cong 0.32$$

Geometrical considerations of the exposed molecular surface about the end groups of a polymethylene chain molecule suggest that the ratio s_e/s_m should be in the range of 1 to 2. A negative value of a indicates according to eq. 28 therefore that η_e/η_m is near zero, or possibly negative. Although interactions of methyl groups probably are somewhat less than those for mid-

(21) J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, N. Y., 1953, p. 169; A. E. Smith. *J. Chem. Phys.*, **21**, 2229 (1953).

(22) By a corresponding states analysis of p, v, T data for n-paraffin hydrocarbons up to $n = 16$, Hijmans arrived at $c_m = 0.195 \pm 0.035$. His method is a generalization of that of Prigogine, Bellemans, and Naar-Colin. By similar analysis of compressibilities, he found $c_m = 0.131 \pm 0.025$. The significance of any comparison of these values, deduced from the principle of corresponding states, with our results is obscure.

chain methylene, the difference should not be great. The significance in this connection of the numerical comparison cited is obscured by the arbitrary designation of those sites in excess of xs_m as the terminal ones, and the attribution of the entire interaction deficit to these sites only. To the extent that interactions of additional sites around terminal segments are depressed, the indicated disparity between η_e and η_m would be markedly diminished by a realistic reckoning of terminal sites.

Conclusions

The scheme here proposed succeeds remarkably in correlating equation of state data for the n-paraffin hydrocarbons from $n = 6$ to $n \cong 40$, and probably to $n = \infty$. The representation of the equation of state for any given member of the series over wide ranges of temperature and pressure is somewhat less satisfactory. The observed isobar displays less curvature than is predicted, *i.e.*, $d\alpha/dT$ is over-estimated. Additionally, the compression along the observed isotherm exceeds that calculated from the theoretical equation of state, as is evident from Fig. 1. These discrepancies are minor: although they may restrict application of the expression for the equation of state, they by no means invalidate its use.

Several measures for improving the theory suggest themselves. Alteration of the dependence of the intermolecular energy E_0 on the volume by expressing eq. 5 as

$$E_0 = -xNs\eta/2v^m$$

where $m \neq 1$ is a possibility. However, correction of the departure of the isotherm from theory (Fig. 1) requires $m > 1$, and the error in the isobar calls for $m < 1$. The treatment of the number c of external degrees of freedom as a constant presents itself as a further likely source of error. This number must depend to some extent on the volume, as remarked earlier; it may conceivably depend also on the temperature. Treatment of c as variable with v would severely complicate the manipulation of the partition function.

Any elaboration of the present scheme along lines suggested above will demand additional parameters beyond the three already acknowledged for a given substance, and to evaluate these from equation of state data would place greater demands on available experimental information. Existing data for the n-paraffin hydrocarbons are scarcely sufficient for application of the comparatively simple formulation here proposed; a much more elaborate scheme would require better data for justification of its use. Moreover, any of the several revisions considered for achieving a better fit to equation of state data would greatly complicate application to mixtures. The latter has been our main objective. Exploration of the representation of the equation of state has been undertaken with this in view. The fact that nearly the full span of liquid n-paraffin hydrocarbons is well represented by the present formulation encourages its application to nonpolar liquid mixtures generally and especially to mixtures of chain molecules.