A Corresponding-States Correlation for Higher Molecular-Weight Liquids

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A corresponding-states correlation for the liquid-state properties of higher molecular-weight substances is presented which contains as reducing parameters the readily measurable (and correlatable) energy vaporization and van der Waals volume instead of the often inaccessible critical constants. One additional parameter characterizing molecular flexibility is introduced.

A single curve of the new reduced density ρ^* vs. the new reduced temperature T^* is shown to represent the atmospheric-pressure-density-temperature relations of paraffinic, naphthenic, and aromatic hydrocarbons with 10 or more carbon atoms per molecule to within $\pm 1\%$ between their melting and their atmospheric boiling points. The reduced surface tension is shown to be a unique function of ρ^* for many compounds, thus permitting prediction of surface tension over wide ranges of temperature. The heat-capacity difference betweeen liquid and vapor proved to be easily correlatable with ρ^*. Finally the compression of numerous hydrocarbons proved to be well correlated in terms of T^*, ρ^*, and P^*. Extensive group data for V_w and E° have been assembled in the appendix in order to enable others to use the proposed method without effort.

GENERAL CORRELATIONS

Purpose and Scope

One of the most powerful methods for the correlation of the physical properties of fluids is that based on the principal of corresponding states. In its original form $V/V_c = f(T/T_c, P/P_c)$ it is valid only for very simple substances, such as the rare gases argon, krypton, xenon and substances composed of simple spherical molecules, such as methane, carbon tetrafluoride, etc. (*13*). In recent years its scope has been extended to many other substances through the introduction of a correction factor based on the deviation of the observed from the generalized vapor-pressure curve of liquids (*14, 19*). A more general equation of state then is $V/V_c = f(T/T_c, P/P_c, Y)$.

This modification has greatly increased the scope of accurate physical-property calculations; however it still requires a knowledge of the critical constants which are experimentally accessible only for hydrocarbons of up to 12 carbon atoms per molecule and not at all for many high-boiling nonhydrocarbons. While there are several fairly reliable methods to predict the critical constants (*6, 18, 19*), it is axiomatic, at least in the authors' view, that one should use only those correlated constants which can be checked experimentally if doubts arise regarding the reliability of a correlation. The increasing technical interest in hydrocarbons with more than 12 carbon atoms per molecule and in high-boiling organic chemicals has motivated the search for a corresponding-states correlation based on reducing parameters which are directly accessible to experimental measurement. Recent developments in liquid-state theory have made such an enterprise more promising, and the following report gives an account of what has been accomplished to date. Progress in the correlation of equilibrium properties will be dealt with now. The more difficult task of correlating transport properties has not yet reached the reporting state.

The reader should be warned at the outset that no attempt has been made to develop a theory because no theory could describe the properties of highly complex molecules with sufficient accuracy for chemical engineering purposes. Instead an empirical correlation of dimensionless property parameters suggested by theory has been developed, which proved basically adequate for the description of the properties of high-boiling paraffin hydrocarbons (*15, 16*). The present report is restricted largely to hydrocarbons. Subsequent reports will show how the new correlations can be applied to nonhydrocarbons.

BASIC PRINCIPLES

The meaning of the critical constants in terms of molecular properties had first been elucidated by Lennard-Jones and Devonshire (*11*), who showed that the critical temperature is related to the potential energy between a pair of molecules (at the minimum of the potential energy-distance curve) by a universal constant, that the critical volume is a universal multiple of the cube of the molecular diameter and that the critical pressure is a universal multiple of the ratio ϵ/σ^3. While no theory has as yet predicted the exact magnitude of the universal constants involved, the empirically determined multipliers proved to be universal for all those simple substances for which quantum mechanical corrections can be neglected (*4*). Furthermore ϵ and σ can be obtained fairly consistently from virial coefficients or the viscosity of the vapor (gas) and from the heat of sublimation and the lattice parameters of the crystal (*9*).

The parameters ϵ and σ are obviously insufficient to describe the properties of substances composed of larger polyatomic molecules. At least one additional molecular-structure parameter, such as the axis ratio, is needed to describe rigid anisometric molecules. They can be found in the theories of Trappeniers (*21*) and of Kihara (*9*). Since many molecules of interest to organic chemists are not rigid but flexible, the additional parameter is only of limited utility. The empirical corrolary is the correction factor mentioned earlier, which has indeed been correlated with

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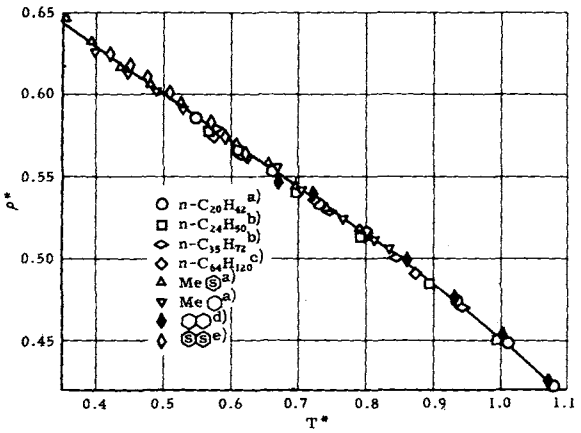


Fig. 1. Generalized density vs. temperature curve for hydrocarbon: (a) 26, (b) 30, (c) 31, (d) 32, (e) 27.

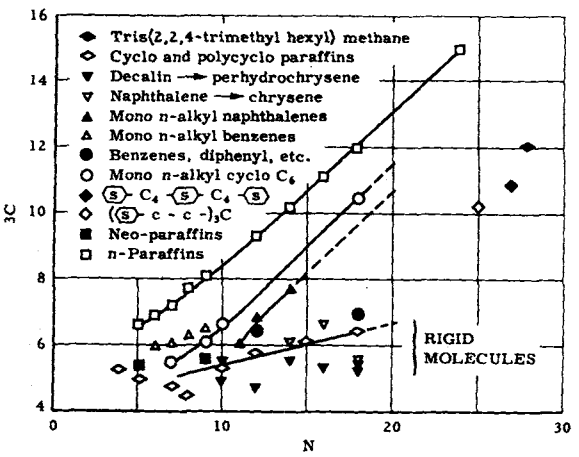


Fig. 2. Number of external degrees of freedom per molecule (3c) as function of molecule size for different hydrocarbon series.

the axis ratio of cigar-shaped molecules and with the core radius of globular molecules.

A significant step forward was made by Prigogine and his collaborators (*15*) when they introduced the subdivision of larger flexible chainlike molecules into the number of chain links r and the total number of external degrees of freedom ($3c$) per molecule which result from the motions of the molecule as a whole and from the independent motions of the chain links. The physical properties of the condensed phase should then be determined by the molecular parameters ϵ and σ, the pair potential and the diameter characterizing a chain link, Z, the number of nearest neighbors around a chain link, r, the number of chain links per molecule, and $3c$, the number of external degrees of freedom per molecule. From statistical mechanics one can show that for rigid molecules $3c = 5$ or 6, depending on the symmetry characteristics of the molecule; for flexible molecules (moderately hindered internal rotation) $3c = r + 3$; and for loose molecules (completely free internal rotation) $3c = 2r + 1$.

Several ways are open to determine ϵ and σ; one way is to calculate them from p-v-t properties with the aid of theory. This has been done by Simha and Hadden (*20*). Their approach did not prove of sufficient generality for the authors' purposes. A second path was followed by Prigogine and Naar-Colin (*16*) who obtained ϵ, σ, and c/r by comparing the properties of many members of the n-paraffin series. Instead the authors decided to express ϵ in terms of the lattice energy taken as the energy of vaporization at a fixed value (1.70) of the reduced volume $V^* = V/V_w$, and to replace σ^3 by V_w/r. V_w is calculated from the bond distances and van der Waals radii as outlined in Appendix I. The standard energy of vaporization ΔE_v° at $V^* = 1.70$, abbreviated as E° in this report, is also easily correlated with molecular structure as outlined in Appendix II. Moreover for many small molecules $E^\circ \approx 10 N_A \epsilon$, when ϵ is estimated from gas properties. This point was also considered in the choice of the standard state $V^* = 1.70$.

The definition of the dimensionless parameters is now straightforward. In accordance with Prigogine the reduced temperature $T^* = ckT/q\epsilon$, where q is defined by $qZ = rZ - 2r + 2$. Now $E^\circ = \frac{1}{2} qZ\epsilon f(V^*)$; hence if one sets $Z = 10$, (*5*), and $f(V^*) \approx 1$,† $T^* = cZRT/2E^\circ = 5cRT/E^\circ$. The reduced density $\rho^* = V_w/V$. The definition of the reduced pressure will be discussed in the p-v-t section of this report. The a priori calculation of c is possible only for the limiting cases mentioned previously. For most substances one has to determine it empirically by means of at least one property measurement, as will be shown in the next section. As c is now essentially an empirical constant, $3c$ can, and does, assume nonintegral values.

Generalized Density-Temperature Relation (at Atmospheric Pressure)

A test of the correct definition of reducing parameters in a corresponding states correlation is the universality of the curve ρ^* vs. T^*. For rigid molecules, such as those of the aromatic and the naphthenic ring series, this proved to be the case. The correlation was constructed by plotting ρ^* vs. T^* for toluene and other cyclic compounds. The value of ϵ/k (toluene)‡ = 460°K. was estimated from the published value ϵ/k (benzene) = 440°K. (*9*).

For the n-paraffin series one has a somewhat more complicated situation because of the different flexibility of the methyl-methylene group as compared with the methylene-methylene linkage. Fortunately there is very little change beyond n-C_{10}, and the general correlation was constructed as follows. First p* vs. T^* was plotted for propane for which ϵ/k is known (254°K.) (*9*) and for which a very long liquid range yields extensive density data. This curve crosses that of toluene at $V^* = 1.80$. Hence ρ^* vs. T^* was plotted on the assumption that all have the same value of T^* at $V^* = 1.80$ ($\rho^* = 0.5556$). The result, Figure 1, shows that all curves for n-paraffins with C_{18} to C_{64}, the naphthenes beginning with methyl cyclohexane and including tricyclohexyl methane, etc., and the aromatics from toluene through all the polyaromatic hydrocarbons for which data are available fit on a single curve, with no significant loss in accuracy.† (Needless to say, better than 0.5% accuracy cannot be expected from any corresponding states correlation.) Since for the hydrocarbons of interest (C_{12}^+) $\rho^* < 0.45$ is generally above the atmospheric boiling point and therefore not accessible experimentally without decomposition, the curves have not been carried beyond that point. The upper limit of the graph has been set up by the fact that practically all substances are solids when $\rho^* > 0.65$. All n-paraffins above C_6 are solid at $\rho^* > 0.59$.

The equation of the general correlation curve is

$$\rho^* = 0.726 - 0.249T^* - 0.019T^{*2}$$

(at atmospheric pressure)

The constant 0.726 has the physical meaning of a universal reduced density for all liquid hydrocarbons at $T = 0$.

† As turns out to be the case for $V^* = 1.70$ and the chosen lattice geometry.

‡ Owing to accidental cancellation of numerical data, in this case $5cRT/E = kT/\epsilon$.

† The n-paraffins below C_{10} do not fit the curve of Figure 2 but exhibit a smaller slope. Cyclohexane and benzene are not included in the correlations because their short liquid range does not permit a test of the fit.

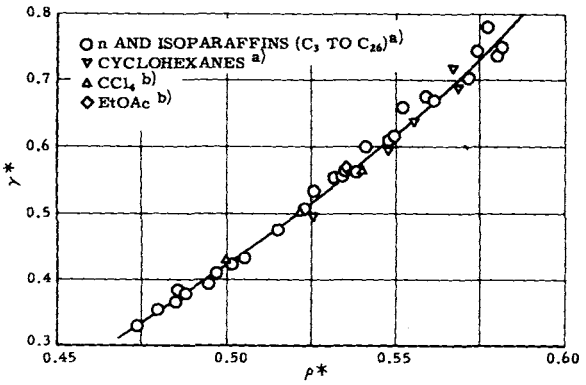


Fig. 3. Reduced surface tension as function of reduced density: (*a*) up to C_{20} (*26*), higher hydrocarbons (*33*); (*b*), *34*.

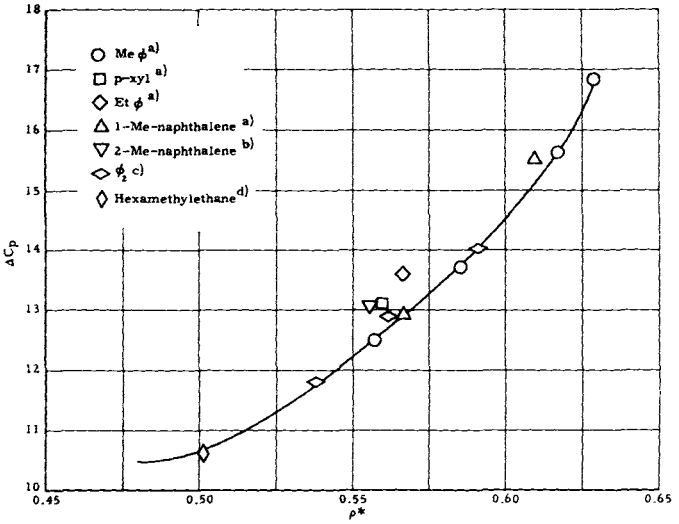


Fig. 4. Correlation of ΔC_p vs. reduced density for aromatic hydrocarbons, from heat-capacity data: (*a*) ΔC_p calculated from (*35*), (*b*) C_p (liq.) (*36*) and C_p (g.) (*37*), (*c*) C_p (liq.) (*38*) and $C_p°$ (g.) (*39*), (*d*) C_p (liq.) and $C_p°$ (g.) (*40*).

The data of Table 1 show that the observed values of ρ^* = near 0°K. are of the order of 0.72.

The linearity of the curve at $T^* < 0.8$ is in agreement with the well-known linearity of the density vs. temperature curve of most liquids, much below their atmospheric boiling point (*12*). It is of practical interest that the existence of a single density measurement at a known temperature now permits the extrapolation of the entire density vs. temperature curve of a compound.

Reduced Density and Molecular Structure

As the reduced density is a unique function of the ratio of kinetic to potential energy per molecule it is relatively easy to locate the specific effects. of molecular structure. The potential energy, given by the lattice energy $E°$, is a relatively nonspecific property, as is evident from the narrow range of variations in the magnitude of $E°$ per carbon atom demonstrated in Appendix II. The kinetic energy by contrast is proportional to the number of external degrees of freedom per molecule and thus directly related to the flexibility of the molecular structure. This effect is more striking when one compares for a given series of molecules the temperature at which $V^* = 1.70$ than the comparison of the degrees of freedom $3c$, also shown in Table 2. To state the case more directly, ρ^* is a direct measure of molecular flexibility; it is high for rigid molecules and is lower the more flexible a molecule.

A more general comparison is presented in Figure 2, where $3c$ is plotted for several groups of compounds as a function of molecular size. One sees rather clearly the difference between the flexible *n*-paraffins on the one hand and the stiff aromatic and naphthenic ring system on the other. The naphthenic ring systems of nearly spherical symmetry approach the rigid spheres in their small number of external degrees of freedom.

The prediction of $3c$ for hydrocarbons not covered by the data of Figure 2 may best be performed by interpolation between the existing data. Estimation of $3c$ for alkyl derivatives of specific ring systems may be carried out, for example by laying a curve paralleling the *n*-paraffin line through the particular ring compound.

Reduced Surface Tension

Molecular theory of surface energy shows that the reduced total surface energy $U^* = U.A_w/E°$ and the reduced surface free energy (surface tension) $\gamma^* = \gamma A_w/E°$ of simple liquids are unique functions of the reduced density (*7, 9*). The plot of γ^* vs. ρ^* in Figure 3 shows that this prediction is valid for all the normal and isoparaffins,

TABLE 1. REDUCED DENSITY AT 0°K.

Substance	ρ_0^* Crystal (exp.) (*22*)	ρ_0^* Liq. (exp.) (*22*)	ρ_0^* Liq. (calc.) (*23*)
n-Pentane	0.710		0.702(*24*); 0.700(*23*)
iso-Pentane	0.701	0.683*	0.701(*24*)
n-Nonane	0.726		0.705(*24*); 0.714(*23*)
$(CH_2)\infty$	0.757		0.716(*24*); 0.732(*23*)
Toluene	0.712		0.713(*24*)
CCl_4	0.690		0.711(*23*)

* This is probably not the equilibrium density, but, as is usual with glasses, the frozen-in density of a higher temperature.

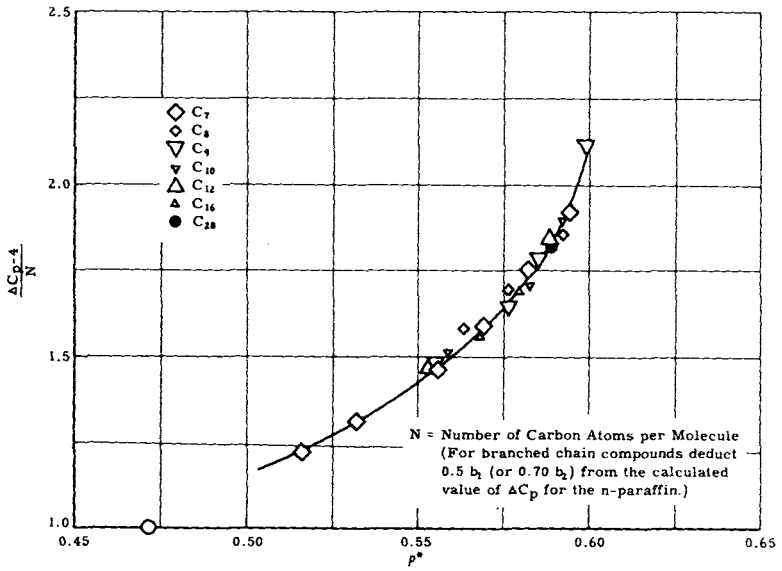


Fig. 5. Correlation of ΔC_p vs. reduced density for *n*-paraffins ($N \geqq 7$) from heat-capacity data: C_p (liq.) (*41*), $C_p°$ (g.) (*42*).

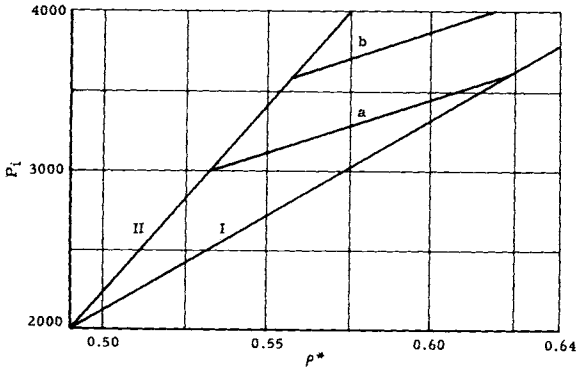


Fig. 6. Correlation of internal pressure with reduced density at atmospheric pressure: I *n*-paraffins (also for *iso*-paraffin and napthenes), II aromatic nuclei (for alkyl aromatics use also the cross-over lines), *a* for 40 ± 10% aromatic C atoms per molecule, *b* for 80 ± 10% aromatic C atoms per molecule; *n*-paraffins (*31, 43*), aromatics (*44*), all classes (*45, 46*).

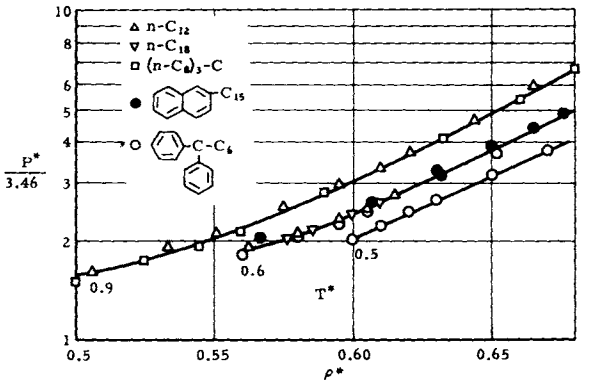


Fig. 7. Generalized P^*-V^*-T^* correlation for different hydrocarbons (*45*).

for monocyclic naphthenes, and for several nonpolar or slightly polar nonhydrocarbons.

This correlation can be valid only for molecules with isotropic force fields. Since a molecule with anisotropic force fields would orient in the surface such as to minimize the surface free energy, the term $E°/A_w$ would cease to describe the potential-energy contribution to the surface properties. The deviation of the behavior of a given compound from the curve of Figure 4 is by the same token a sensitive measure of orientation effects. Aromatic hydrocarbons exhibit a sufficiently anisotropic force field for their reduced surface tension to fall on curves below that of Figure 3. The reason for the deviations of the condensed cyclic naphthenes from the basic correlation curve of Figure 3 is obscure at present. Since the extent of molecular orientation depends on the ratio of orientation energy to kT, the reduced surface tension of anisotropic systems is likely to depend on temperature explicitly and not only on density. Concurrently the extent of deviation from the general correlation should decrease with increasing temperature.

Heat-Capacity Difference

One of the most peculiar features of the liquid state is its high heat capacity as compared with both the solid and the vapor state. The heat capacity of the vapor in the ideal gas state is very well understood; the differences between the liquid and the vapor (as ideal gas) are therefore of particular interest.

Molecular theory tells us that ΔC_v of simple liquids is a unique function of T^* and therefore also of V^* (*1, 17*). The experimental heat capacity of liquid argon and mercury have been shown to conform rather closely to the predictions of theory. The maximum value of ΔC_v predicted by theory is identical with that for the ideal crystal, namely $(3/2)R$. Almost all organic substances exhibit ΔC_v's significantly in excess of the value predicted by simple molecular theory, especially if $\rho^* > 0.5$. Assuming ΔC_v for argon at a given ρ^* as that for the perfect liquid one may consider $[\Delta C_v - \Delta C_v(A)]_{\rho}^* = \Delta C'_v$ as the specific characteristic of the liquid under consideration.

A plot of $\Delta C'_v$ vs. ρ^* for several liquids shows the same upward trend. But no other correlating feature of this highly specific property has as yet become apparent.

The physically less meaningful ΔC_p

Table 2. Effect of Molecular Flexibility on the Temperature at which $V^* = 1.70$

Substance	T, °K.	$3c$
1, 3, 5-Hexatriene (cis) (25)	199*	6.8
2, 3, 4-Hexatriene (25)	241	5.6
n-Nonane (26)	236	8.0
Tetraethyl methane (26)	286	5.6
1, 1-Dicyclohexyl heptane (27)	373	7.9
Tricyclohexyl methane (27)	425	6.4
o-Terphenyl (28)	397	6.8
Triphenylene (28)	565	5.4

* Extrapolated below *Fp*.

The references pertain mostly to the density data. The vapor-pressure data required to calculate *c* come from many additional sources.

Table 3. Recommended van der Waals Radii for Carbon and Hydrogen, Å.

Bond type	$r_w(C)$	$r_w(H)$
Single (aliphatic)	1.70	1.20
Olefinic double bond	1.70	1.20
Aromatic ring	1.77	1.00

Table 4. Group Contributions to V_w for Hydrocarbons

Group	$-\overset{\vert}{C}-$	$-\overset{\vert}{C}H$†	$>CH_2$†	$-CH_3$†	CH_4	n-paraffins‡
V_w (cc/mole)	3.33	6.78	10.23	13.67	17.12	6.88 + 10.23N
$A(10^9$ sq. cm./mole)	0	0.57	1.35	2.12	2.90	1.54 + 1.35N

Group (aromatic)	$\diagup\!\!\diagdown CH$	$\diagup\!\!\diagdown C-$ (Alkyl)	$\diagup\!\!\diagdown C-$ (Condensation)	Benzene	Phenyl*	Naphthalene	Naphthyl*
V_w) cc./mole)	8.06	5.54	4.74	48.36	45.84	73.97	71.45
$A(10^9$ cc./mole)	1.00	0.30	0.21	6.01	5.33	8.44	7.76

Group (olefinic)	$=\overset{\vert}{C}H$	$=CH_2$	$\equiv C-$	$\equiv CH$	$\equiv C-$ (in diacetylene)
V_w (cc./mole)	8.47	11.94	6.87	10.42	6.65
$A(10^9$ sq. cm./mole)	1.08	1.86	0.85	1.64	

Group (olefinic)	$H_2C=CH_2$	$-HC=CH_2$	$>C=CH_2$	$>C=\overset{\vert}{C}H$	$\overset{\vert}{C}=\overset{\vert}{C}$	$=C=$
V_w (cc./mole)	23.87	20.41	16.95	13.49	10.02	6.96
$A(10^9$ sq. cm./mole)	3.72	2.94	2.17	1.39	0.61	

Group (olefinic)	$HC\equiv CH$	$-C\equiv CH$	$-C\equiv C-$
V_w (cc./mole)	20.83	17.30	13.75
$A(10^9$ sq. cm./mole)	3.28	2.50	1.71

† Correction for vicinal effects: Methyl or methylene group next to carboxyl or amide group: subtract 0.22 cc., methylene ring condensed to an aromatic system as in tetralin; subtract 0.52 cc./ring.

‡ N = number of carbon atoms per molecule.

* Subtract 2.52 cc./mole for each additional branch point on the ring.

proved far more readily correlated. The correlation for rigid molecules is shown in Figure 4. It appears here that ΔC_p can be described to a fair degree of approximation as a function of ρ° (or of $T^\bullet$). The flexible n-paraffins above C_7 are also well correlated as function of $\rho^\bullet$ by the scheme shown in Figure 5. The meaning of that correlation is most likely that the surrounding molecules increase the hindrance to the rotation of each chain link relative to that occurring in the gas. The origin of that increase, namely the strong tendency to parallel alignment due to polarization anistropy of the C-H bond, has been discussed previously (*1*).

P-V-T Relations

One of the incentives to prepare the correlation at hand has been the availability of extensive compression data on higher molecular-weight hydrocarbons (*2, 3*), covering a pressure range up to 10,000 atm. and a temperature range from 0° to 200°C. The authors have yet to define a reduced pressure $P^\bullet$. Simple molecular theory suggests

$$P^\bullet = P.\sigma^3/\epsilon$$

and Prigogine's theory for polymers yields

$$P^\bullet = Pr\sigma^{\bullet 3}/q\epsilon^\circ$$

which in the language of the current work would be

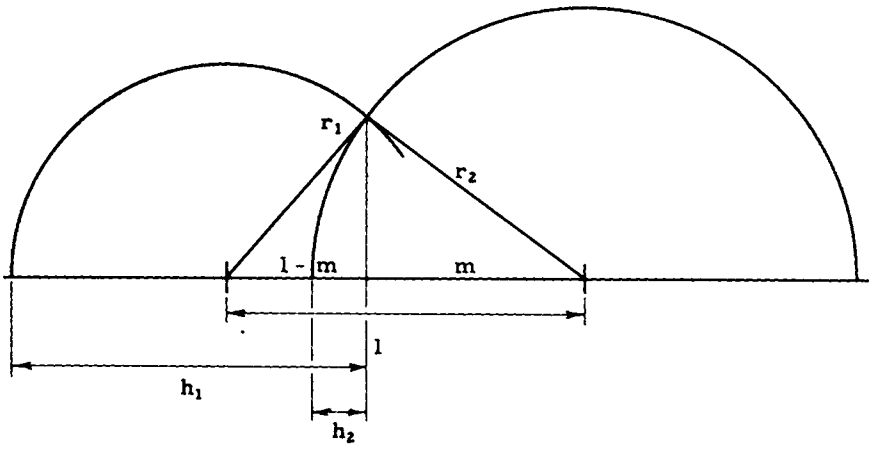
$$P^\bullet = PZV_w/2E^\circ$$

However both of these definitions exhibit a serious inherent deficiency. They do not take into consideration that the external pressure is in reality additive to the intermolecular attractive forces. Specifically an external pressure of 1,000 atm. should not increase $P^\bullet$ by a factor of 1,000, as compared with atmospheric pressure, but only by a factor $(P_i + 1{,}000)/(P_i + 1)$. The experimental definition of P_i is $(\partial E/\partial V)_T$. The theoretical significance is not entirely clear. The attractive potential per unit volume is probably a reasonable interpretation (*8*). Hence the authors choose as the definition of reduced pressure $P^\bullet = (P + P_i)ZV_w/2E^\circ$, which equals $(P + P_i)\ 5V_w/E^\circ$ if $Z = 10$.

The internal pressure used here is that determined at atmospheric pressure and is hence experimentally accessible without direct compressibility measurement, for example via the sound velocity. But even that information is usually not available over the entire temperature range of interest. The ability to predict P_i in some other way is therefore important. An approximate empirical correlation of P_i with ρ° is shown in Figure 6.

A few typical correlations of $P^\bullet$ vs. ρ° and $T^\bullet$ are shown in Figure 7. The wide range of compounds covered by a single graph is rather gratifying; however the generality is not complete. Very rigid and nearly spherical molecules, such as perhydrochrysene, decalin, etc., do not fit into this scheme without extra effort. This peculiarity might have been predicted from the anomalously low value of 3c mentioned earlier and tentatively ascribed to a smaller number of nearest neighbors than that obtained with flexible-chain substances. Such adjustment of Z moves the p-v-t curves of condensed cyclic polymethylenes in the right direction and yields plausible values for 3c.

Expression of these results in the form of an equation of state will only be attempted once a broader range of



r_1, r_2 = van der Waals radii
l = covalent bond distance
m = auxiliary parameter
h_1, h_2 = height of sphere segments

$$m = \frac{r_2^2 - r_1^2 + l^2}{2l}\ ;\ h_1 = r_1 + l - m;\ h_2 = r_2 - m$$

$$V_1^1 = \pi h_1^2 \left(r_1 - \frac{h_1}{3}\right);\quad \Delta V_{2-1} = \pi h_2^2 \left(r_2 - \frac{h_2}{3}\right);\quad V_2 = \frac{4\pi}{3} r_2^3$$

Example:
van der Waals volume of diatomic molecule:

$V_W = N_A [V_1^1 + V_2 - \Delta V_{2-1}]$ cm³/mole
where $N_A = 6.02 \times 10^{23}$ molecules/mole
and r's are given in Angstrom units

Volume of center atom = Total volume of atom
Surface area = $2\pi rh$

Fig. 8. Method of calculation.

TABLE 5. STANDARD ENERGY OF VAPORIZATION E° FOR n-PARAFFINS†

N°	2	3	4	5	6	7	8	9	10	12	
E°	3.94	5.29	6.26	7.25	8.40	9.54	10.69	11.80	12.92	14.98	kcal./mole

° N = number of carbon atoms per molecule.
† Density and ΔH_{vap} from A.P.I. Project 44 Tables, ΔC_p from the references of Figure 6.

TABLE 6. STANDARD ENERGY OF VAPORIZATION FOR ISO-PARAFFINS† (KCAL./MOLE)

Substance	i-C_4	i-C_5	3-methylpentane	2, 2-dimethylbutane
E°	6.02	7.00	8.15	7.78
Substance	3-ethylpentane		2, 4-dimethylpentane	2, 2-dimethylpentane
E°	8.94		8.87	8.79
Substance	3-methyl, 3-ethylpentane		2, 5-dimethylhexane	2, 4-trimethylpentane
E°	9.30		9.97	9.38
Substance		tetraethylmethane	2, 6-dimethylheptane	
E°		9.98	11.25	

† Density and ΔH_{vap} from A.P.I. Project 44 Tables; ΔC_p from the references of Figure 6.

TABLE 7. CORRELATIONS FOR CALCULATING E° (ALL IN KCAL./MOLE)

1. Paraffins	
a) *n*-Paraffins ($N > 12$)	$E^\circ = 14.98 + 1.07(N - 12)$
b) Isoparaffins*	$E^\circ = E^\circ(n\text{-paraffin}) - 0.30b_1 - 0.40b_2$
2. Olefins and diolefins	
a) Straight chain	$E^\circ = E^\circ(n\text{-paraffin})$
b) Branched chain	$E^\circ = E^\circ(\text{iso-paraffin}) + 0.90$
3. Cycloparaffins (one ring system per molecule)	
a) Rings without chains	$E^\circ = 3.27 + 0.76N$
b) Monoalkylcyclopentanes	$E^\circ = 5.90 - 0.20 \sum_{2}^{N_B} \frac{1}{N_B - 1} + \frac{1}{2}E^\circ(P_2)$†
c) Dialkylcyclopentanes	$E^\circ = 4.60 + \sum_{b} \frac{1}{2}E^\circ(P_2)$
d) Monoalkylcyclohexanes	$E^\circ = 6.60 - 0.20 \sum_{2}^{N_B} \frac{1}{N_B - 1} + \frac{1}{2}E^\circ(P_2)$
e) Dialkylcyclohexanes	$E^\circ = 5.25 + \sum_{b} \frac{1}{2}E^\circ(P_2)$
f) Monoalkyldecalins	$E^\circ = 9.12 + \frac{1}{2}E^\circ(P_2)$
4. Aromatics (one ring system per molecule)	
a) Monoalkylbenzenes	$E^\circ = 7.27 - 0.30 \sum_{2}^{N_B} \frac{1}{N_B - 1} + \frac{1}{2}E^\circ(P_2)$
b) Polyalkylbenzenes	$E^\circ = 7.27\text{-}1.2(b-1) - 0.30 \sum_{2}^{N_B} \frac{1}{N_B - 1} + \sum_{1}^{b} \frac{1}{2}E^\circ(P_2) - 0.30b_{i2} - 0.20b_{i3}$
c) 2-Monoalkylnaphthalenes	$E^\circ = 10.65 + \frac{1}{2}E^\circ(P_2)$
d) 9-Monoalkylanthracenes	$E^\circ = 14.10 + \frac{1}{2}E^\circ(P_2)$
5. Polycyclic naphthenes	
a) Cyclopentanes**	$E^\circ = 5.22R_1 + 4.20R_2 + 1.1M - 2.25X + \frac{1}{2}E^\circ(P_2)$
b) Cyclohexanes**	$E^\circ = 6.22R_1 + 5.20R_2 + 1.05M - 2.25X - 1.0P_o - 0.30P_m + \frac{1}{2}E^\circ(P_2)$
c) Condensed cyclic polymethylenes: (except those containing endo methylene groups)	$E^\circ = 1.30M_c - 0.20T - 2.0$
6. Polycyclic aromatic	
a) Polyphenyls	$E^\circ = 6.85R_1 + 5.32R_2 - 1.0P_m - 2.3P$
b) Kata and peri condensed rings††	$E^\circ = 1.41S + 0.45T$

* b = total number of branches; b_1 = branches in isolated position; b_2 = branches in neo position.
† P_2 = appropriate paraffin hydrocarbon for which $N = 2N_B$, N_B = number of carbon atoms in alkyl chain.
** For systems where the rings are connected by chains of 6 carbon atoms or less.
R_1 = number of rings with single attachment point.
R_2 = number of rings with two attachment points.
M = number of methylene groups between rings.
M_c = number of methylene groups in a condensed ring system.
T = number of tertiary carbon atoms in a condensed ring system.
X = 1, 1 di-ring attachment to a chain or to a chain or ring system larger than 4 carbon atoms; P_o, P_m = ortho and meta attachments respectively.
†† S = CH group; T = carbon atom without hydrogen for phenanthrene and chrysene $E^\circ = 1.41S + 0.10T$.

compounds has been covered. In the meantime only qualitative considerations apply. Theory predicts an equation of the form

$$\frac{(P + P_i)V}{cRT} = \frac{1}{1 - A\rho^{*1/3}} + \frac{24}{T^*}[B\rho^{*4} - D\rho^{*2}]$$

when the constants A, B, D are given by the assumed packing geometry. The predicted linear relation between P^*V^*/T^* and $1/T^*$ is quite well fulfilled. The location of the curves as function of ρ^* is also in qualitative agreement with theory.

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NOTATION

A_w	= surface area of a mole of molecules, sq. cm.
A,B,D	= constants in equation of state
c	= one-third of the number of external degrees of freedom per molecule
ΔC_p	= $= C_p(\text{liq}) - C_p(g)$ = heat-capacity difference between liquid and gas, cal. mole^{-1} °K.$^{-1}$
E°	= standard energy of vaporization = $(\Delta H_{vap} - RT)$ at $V^* = 1.70$, kcal./mole
l	= covalent bond distances
N	= number of carbon atoms per molecule
N_A	= Avogadro's number
P	= external pressure, atm.
P_i	= internal pressure, atm.
P_c	= critical pressure, atm.
P^*	= reduced pressure $= 5V_w(P + P_i)/E^\circ$
q	= magnitude defined by $qZ = Zr - 2r + 2$
R	= gas constant
r	= number of chain links in a chainlike molecule $(= (N + 1)/2$
r_w	= Van der Waals radius, Å.
T	= temperature, °K.
T_c	= critical temperature, °K.
T^*	= reduced temperature $= 5cRT/E^\circ$
U	= total surface energy, erg. cm.$^{-2}$
U^*	= reduced total surface energy $= UA_w/E^\circ$
V	= molal volume, cc. mole^{-1}
V_c	= critical molal volume, cc. mole^{-1}
V_w	= Van der Waals volume, reducing parameter, cc. mole^{-1}
V^*	= reduced volume $= V/V_w$
Y	= correction constant
Z	= number of nearest neighbors

Greek Letters

γ	= surface free energy, erg. cm.$^{-2}$
γ^*	= reduced surface free energy $= \gamma A_w/E^\circ$
ϵ	= pair potential at distance of potential minimum
ρ	= density, g. cm.$^{-3}$
ρ^*	= reduced density $= V_w/V$
σ	= molecular diameter at steepest ascent of repulsion curve

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APPENDIX I

Recommended Van der Waals Radii and Volumes

The calculation of V_w requires knowledge of the van der Waals radii and of the appropriate covalent bond distances between two bonded atoms in a molecule. A recent reevaluation of r_w data from X-ray diffraction patterns of crystals together with crystal density data at O°K, gas kinetic collision radii of small molecules, and critical densities,* has yielded the radii shown in Table 3.

The van der Waals volume and the molecular surface area are calculated by combination of r_w with the covalent bond distance (data for which can be found in most chemistry text books) according to the model shown in Figure 8. The results are presented in the form of V_w and A_w group increments in Table 4. Special effects due to bond contraction or expansion in cases of double-bond conjugation or hyperconjugation can be found in the footnotes to the table.

APPENDIX II

Energy of Vaporization Data

The reducing parameter for temperature proposed in this paper is $E°/R$, where $E°$ is defined as $\Delta E_v = \Delta H_v - RT$ at the temperature where $V^* = 1.70$. This temperature and the appropriate heat of vaporization have been calculated from density and low-temperature vapor-pressure data for a large number of hydrocarbons. Tables 5, 6, and 7 contain the information necessary to estimate the energy of vaporization of a number of different hydrocarbons. The same scheme is being developed for nonhydrocarbon substances.

* It is noteworthy that for 100 out of 124 substances tried, $V_c = 5.3 \pm 0.3\ V_w$. Details of this correlation will be published elsewhere.

Concurrent Gas Absorption Mass Transfer

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Concurrent flow in gas absorption may be used to practical advantage when liquid partial pressure is minor. The higher transfer coefficients of this operation are reported and analyzed in reference to pertinent variables.

Gas absorption in packed towers with countercurrent flow of gas and liquid has been studied extensively. Several investigators (*1*, *2*, *4* to *9*, *11* to *15*) have reported on the materials of this study; however mass transfer in concurrent flow systems has received little attention.

The general preference for counter-