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A. Wilhelm and J.M. Prausnitz

July 1984

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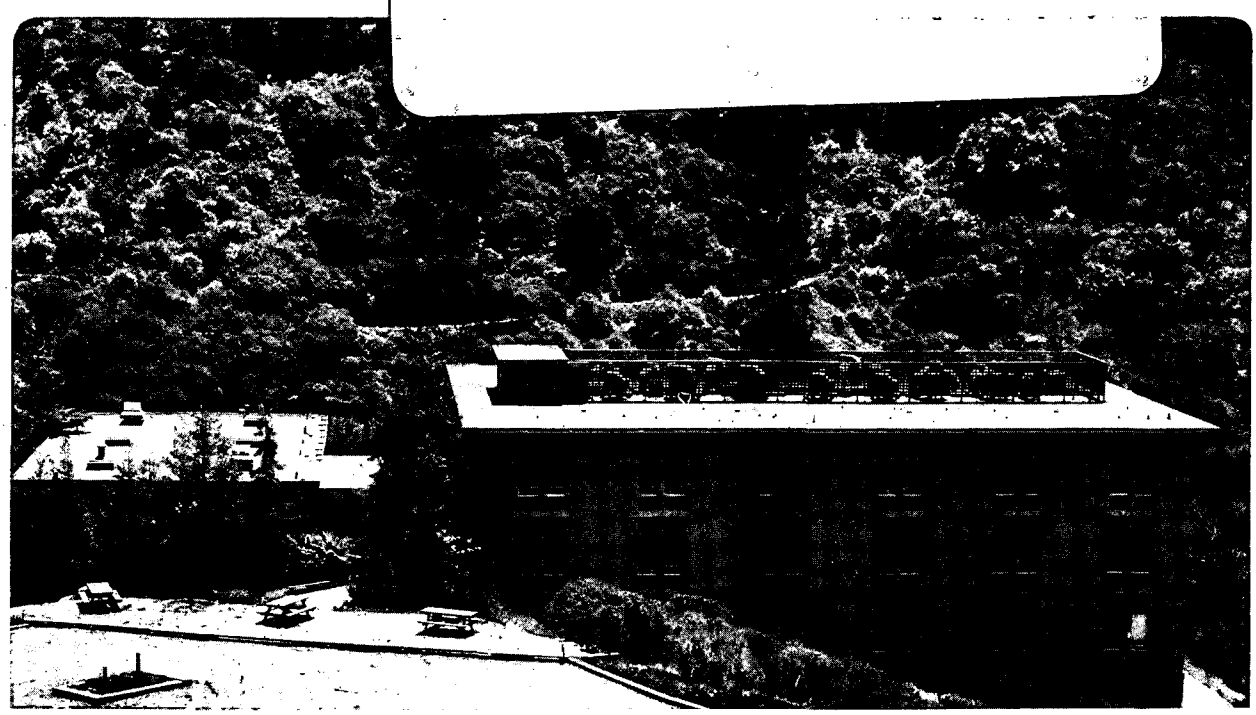

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Vapor Pressures and Saturated-Liquid Volumes for Heavy Fossil-Fuel Fractions from a Perturbed-Hard-Chain Equation of State

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Abstract

A semi-theoretical equation of state is used to correlate residual thermodynamic properties of heavy hydrocarbons; the correlation requires three characteristic molecular parameters as obtained from liquid-density and vapor-pressure data. These parameters are presented for 61 hydrocarbons with molecular weights to 560 g/mole; they are correlated with molecular weight and structural features. The correlation is extended to narrow-boiling fractions; molecular parameters for such fractions are obtained from experimental characerization data (molecular weight, aromaticity, naphthenicity and number of methyl groups per molecule). Calculated vapor pressures and liquid densities are in reasonnable agreement with new experimental results obtained from Belridge crude oil. It is likely that the correlation can be improved through better characterization data as obtained, for example, from ^{13}C-nuclear- magnetic-resonance spectra.

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While much is known about the thermodynamic properties of pure and mixed hydrocarbons in the carbon-number range 1 to 7, such knowledge decreases rapidly as the carbon number rises. However, recent technological interest has become increasingly concerned with heavy hydrocarbons because the economic value of these substances is now much higher than it was say, 10 years ago.

This work is concerned with residual thermodynamic properties of heavy hydrocarbons and their mixtures as commonly encountered in petroleum (or heavy-fossil-fuel) fractions. Here, a residual property is defined as that extensive equilibrium property of a fluid in excess of what it would be if the fluid were an ideal gas at the temperature, density and composition of interest. Residual thermodynamic properties are those that can be calculated from an equation of state. Such properties are essential for rational design of large-scale processes for upgrading heavy-fossil-fuel fractions toward useful products.

For many years, residual thermodynamic properties of low-molecular-weight hydrocarbon mixtures have been conventionally described by well-known equations of state (e.g. Redlich-Kwong-Soave) which are variations on the original equation of van der Waals (1). Several attempts have been made to apply such equations of state to heavy hydrocarbons [see, for example Ref.(2)] but only with marginal success, first, because such equations of state are, in principle, limited to simple (sphere-like) molecules and second, because traditional experimental characterization data (needed to identify molecular size and structure) are often inadequate. Traditional characterization data for petroleum fractions (density and boiling point) provide only very

crude information concerning molecular properties.

In this work , we provide a new correlation of some thermodynamic properties of heavy hydrocarbons and their mixtures. It is based on an equation of state suitable for small or large molecules whose shape is more nearly that of a flexible chain than that of a sphere. Our correlation uses characterization data which provide quantitative measures of molecular size and structure. The correlation is first established using experimental data for many pure hydrocarbons. It is then applied to narrow-boiling petroleum fractions. Since experimental data are rare for properly characterized petroleum fractions, we can provide here only a limited comparison between calculated and measured thermodynamic properties of such fractions. While this comparison indicates the correlation to be promising, it is evident that for high accuracy, it will be necessary to utilize experimental characterization data more refined than those used here.

1. Thermodynamic framework

Vapor pressures and saturated-liquid volumes can be calculated from a suitable equation of state which is applicable to both vapor and liquid phases. Beret and Prausnitz (3) presented a semi-theoretical equation of state which holds for small and large nonpolar molecules. Based on a molecular corresponding-state principle for polymers proposed by Prigogine (4), this equation of state is derived from a partition function for flexible chains. In this perturbed-hard-chain theory (PHC),

each hard segment of the chain is charged with a square-well interaction potential. The perturbed-hard-chain equation of state meets the ideal-gas boundary condition at low densities; for small spherical molecules it reduces to the perturbed-hard-sphere theory of Alder (5). Extended to mixtures by Donohue (6), the PHC equation of state can be used to describe thermodynamic properties of simple and complex hydrocarbons and their mixtures at liquid-like and gas-like densities.

In this work, we use a somewhat simplified (truncated) form of Donohue's PHC equation of state. Details are given in the appendix. The PHC equation of state requires three fundamental molecular parameters:

V^* = the hard-core volume of the molecule
($V^* = r\,\sigma^3/\sqrt{2}$ for a chain molecule consisting of r spherical segments of hard-sphere diameter σ)

$\varepsilon q/k$ = the effective potential energy parameter for the molecule

c = the flexibility of the molecule ($c = 1$ for methane)

The equation of state is of the form:

$$\tilde{P} = \mathcal{F}(\tilde{T}, \tilde{V}, c) \qquad (1)$$

where $\tilde{T} = T / T^*$, $\tilde{V} = V / V^*$ and $\tilde{P} = P / P^*$

and function $\mathcal{F}$ is discussed in the appendix.

Here $T^* = \varepsilon q/(ck)$ and $P^* = R(\varepsilon q/k)/V^*$.

Characteristic temperature T^* is defined in terms of ε, the

segment-segment potential energy well and q , the external surface area per molecule ; k is Boltzmann's constant and 3c is the number of external degrees of freedom per molecule. For small spherical molecules , c=1 , since only three translational degrees of freedom contribute to the molecule's residual thermodynamic properties. However, as molecular size and flexibility increase, external (low frequency and high-amplitude) rotational and vibrational degrees of freedom become increasingly important in the equation of state. The contributions of these external degrees of freedom to the residual properties are taken into account through parameter c which is a measure not only of the molecule's deviation from spherical shape, but also of its overall flexibility. Casting an equation of state in terms of molecular parameters rather than the customary critical parameters, proves especially useful for high-molecular weight hydrocarbons because critical parameters, used in conventional equations of state, cannot be measured for heavy hydrocarbons nor can they be estimated with sufficient accuracy.

The vapor pressure P^s can be calculated from the exact thermodynamic relation:

$$P^s = - \frac{A^{vap} - A^{liq}}{V^{vap} - V^{liq}} \qquad (2)$$

where A is the Helmholtz energy and where V is the molar volume; superscripts vap and liq indicate saturated vapor and saturated liquid, respectively. Helmholtz energy A is obtained from the equation of state using standard thermodynamics. To calculate vapor pressures at tem-

peraure T, given molecular parameters V^* , T^* , c, an iterative procedure is required, because molar volumes V^{vap} and V^{liq} must be found from the pressure-explicit equation of state (Equation (1)).

To facilitate estimates for vapor pressure and saturated-liquid volumes, calculated results obtained from Equations 1 and 2 are presented here in easy-to-use charts. Figures 1 and 2 show reduced vapor pressures and liquid volumes as a function of reduced temperature for different values of c . The lowest value (c = 1) represents the properties of methane, and the highest value (c = 100) corresponds to a n-alkane with molecular weight of about 18,000 g/mole. The reduced vapor pressure is defined by :

$$\tilde{P}^s = P^s / P^* .$$

Figure 1 : Reduced vapor pressure $\tilde{P}$ as a function of reduced temperature $\tilde{T}$

Figure 2 : Reduced saturated-liquid volume $\tilde{V}$ as a function of reduced temperature $\tilde{T}$

According to the molecular corresponding-states principle, reduced properties given in Figures 1 and 2 are valid for all fluids that fall within the assumptions of the PHC theory . Figures 1 and 2 are there-

fore directly useful for esimating vapor pressures and saturated-liquid volumes (at a given temperature) for any PHC fluid, provided that the molecular reducing parameters of this fluid are known. Upon considering narrow-boiling mixtures of molecules of similar size as pseudo-pure components, the chart can also be used for estimating properties of such mixtures. To estimate vapor pressures and liquid volumes for high-boiling crude-oil fractions, the essential problem is to find the molecular parameters which represent the fraction's properties.

2. Correlation of equation-of-state parameters with molecular structure

As shown by Beret and Donohue (3,6), the PHC equation of state yields good representation of vapor pressures and volumetric properties for a variety of large hydrocarbons, especially for large n-alkanes, where experimental data are most plentiful. Therefore, the n-alkane molecule of a given molecular weight is used in the following correlations as a reference. Deviation functions are used to obtain PHC parameters for other hydrocarbon molecules; these are added to the corresponding parameter for the straight-chain (reference) molecule of the same molecular weight, as shown below.

To apply the PHC equation of state to petroleum fractions, it is necessary to account for different hydrocarbon structures present in the fraction.

Figure 3 : Basic structures in hydrocarbon molecules

Fig. 3 shows that the single segments of a long-chain hydrocarbon molecule can be rearranged into two fundamentally different structures: first, isomerization leads to branched molecules with more terminal units (CH_3), and second, ring formation gives aromatic and naphthenic compounds. These forms of molecular structure suggests that, to account for deviation from n-alkane structure, it is useful to define the following structural characterization factors: the number of methyl groups per molecule Z_{CH_3} ;the fractional aromaticity FA; and the fractional naphthenicity FN . As suggested in Figure 3, these structural characterization factors can be used to characterize the deviation in V^* , $\varepsilon q/k$ and c from the corresponding equation-of-state parameters for the reference molecule. Using the molecular weight as a measure of the molecule's size, we calculate the parameter X from:

$$X\,(MW, FA, FN, Z_{CH_3}) = X^{(n\text{-alkane})}(MW) + \Delta X^{(aromatic)}(MW, FA) + \Delta X^{(naphthene)}(MW, FN) + \Delta X^{(CH_3)}(Z_{CH_3})$$

where X stands for V^* , $\varepsilon q/k$ or c.

To establish the reference function $X^{(n\text{-alkane})}(MW)$ and corrections ΔX, we require equation-of-state parameters for a large

number of pure hydrocarbons of known structure. We obtained these parameters by simultaneously fitting the truncated version of the PHC equation of state to experimental vapor pressures and liquid densities. Table 1 gives parameters V^*, $\varepsilon q/k$ and c for 61 hydrocarbons.

Table 1: Molecular Parameters for 61 Hydrocarbon Fluids

Fluid	Formula	Molecular Weight MW	Hard-Core Volume V^*	Energy Parameter $\varepsilon q/k$	Flexibility Parameter c
		g/mole	cm^3/mole	K	
normal-alkanes					
methane	CH4	16.04	20.03	151.1	1.000
ethane	C2H6	30.07	27.98	282.0	1.253
propane	C3H8	44.09	37.49	374.2	1.436
butane	C4H10	58.12	47.06	464.1	1.606
pentane	C5H12	72.15	56.59	556.1	1.802
hexane	C6H14	86.17	65.48	638.7	1.952
heptane	C7H16	100.2	74.56	726.6	2.138
octane	C8H18	114.2	85.42	807.1	2.302
nonane	C9H20	128.2	94.47	899.8	2.519
decane	C10H22	142.2	102.3	985.8	2.697
dodecane	C12H24	170.3	123.7	1119.	2.900
hexadecane	C16H34	226.4	164.1	1447.	3.510
eicosane	C20H42	282.5	199.7	1749.	4.194
triacontane	C30H62	422.8	299.9	2445.	5.577
tetracontane	C40H82	563.0	396.8	3064.	6.752
iso-alkanes					
i-butane	C4H10	58.12	47.15	435.6	1.553
i-pentane	C5H12	72.15	55.97	521.0	1.683
2-methylhexane	C7H16	100.2	75.18	693.2	2.063
3-methylhexane	C7H16	100.2	74.68	694.0	2.044
2-methylheptane	C8H18	114.2	84.83	776.1	2.233
2,2,4-trimethylpentane	C8H18	114.2	85.85	688.9	1.990
2,2,5-trimethylhexane	C9H20	128.2	94.39	783.4	2.242
squalane	C30H62	422.8	299.0	2146.	4.896
naphthenes					
cyclopentane	C5H10	70.13	48.20	561.8	1.632
cyclohexane	C6H12	84.16	57.52	620.9	1.680
bicyclohexyl	C12H20	166.3	103.3	1080.	2.468
alkylnaphthenes					
methylcyclohexane	C7H14	98.18	66.27	661.8	1.735
ethylcyclohexane	C8H16	112.2	76.32	765.2	1.993
n-butylcyclohexane	C10H20	140.1	95.67	921.7	2.308
n-hexylcyclohexane	C12H24	168.1	115.1	1072.	2.593
n-decylcyclohexane	C16H32	224.2	154.1	1382.	3.217
n-hexadecyl-cyclohexane	C22H44	308.3	210.4	1857.	4.230

Table 1: continued

naphthenaromatics					
indane	C9H10	118.0	68.67	863.5	1.960
cis-decalin	C10H18	138.2	84.81	887.7	1.982
trans-decalin	C10H18	138.2	87.21	852.9	1.920
tetralin	C10H12	134.2	74.44	940.0	2.045
aromatics					
benzene	C6H6	78.11	47.67	630.1	1.670
naphthalene	C10H8	128.1	71.07	943.0	1.954
diphenyl	C12H10	154.0	83.72	1083.	2.223
phenanthrene	C14H10	178.1	93.95	1207.	2.065
anthracene	C14H10	178.1	93.95	1206.	2.050
alkylbenzenes					
toluene	C7H8	92.14	57.29	716.9	1.869
ethylbenzene	C8H10	106.1	65.75	781.9	1.972
n-butylbenzene	C10H14	134.1	85.16	930.9	2.280
n-hexylbenzene	C12H18	162.1	105.3	1080.	2.580
n-decylbenzene	C16H26	218.2	143.3	1390.	3.214
n-hexadecylbenzene	C22H38	302.3	198.8	1928.	4.447
o-xylene	C8H10	106.1	65.19	799.3	1.969
m-xylene	C8H10	106.1	65.75	791.6	1.989
p-xylene	C8H10	106.1	66.35	784.4	1.965
t-butylbenzene	C10H14	134.2	84.89	879.6	2.192
alkylnaphthalenes					
1-methylnaphthalene	C11H10	142.2	80.28	1031.	2.115
1-ethylnaphthalene	C12H12	156.1	89.00	1108.	2.329
1,2-dimethyl-aphthalene	C12H12	156.1	86.75	1199.	2.588
1-n-propylnaphthalene	C13H14	170.1	98.35	1150.	2.404
1-n-butylnaphthalene	C14H16	184.1	108.7	1182.	2.464
phenylmethanes					
diphenylmethane	C13H12	168.2	95.77	1183.	2.584
isopropyl-diphenyl	C15H16	196.3	107.3	1232.	2.623
ditoluenemethane	C15H16	196.3	114.9	1236.	2.593
dicumenemethane	C19H24	252.0	150.9	1489.	3.219
tetraisopropyl-phenylmethane	C25H36	336.0	204.5	1624.	3.753

The following equations correlate the equation-of-state parameters with molecular structure:

$$V^{*}\ (cm^{3}/mole) = V^{*(n\text{-}alkane)} + \Delta V^{*(aromatic)} + \Delta V^{*(naphthene)}$$

$$V^{*(n\text{-}alkane)} = 6.209 + 0.692\ MW$$

$$\Delta V^{*(aromatic)} = (4.961 - 0.2256\ MW)\ FA$$

$$\Delta V^{*(naphthene)} = (-2.97 - 0.0770\ MW)\ FN$$

$$\varepsilon q/k\ (K) = \varepsilon q/k^{(n\text{-}alkane)} + \Delta\varepsilon q/k^{(aromatic)} + \Delta\varepsilon q/k^{(CH_3)}$$

$$\varepsilon q/k^{(n\text{-}alkane)} = -5.01 + 16.17\ MW^{0.8290}$$

$$\Delta\varepsilon q/k^{(aromatic)} = (51.89 - 0.1427\ MW)\ FA$$

$$\Delta\varepsilon q/k^{(CH_3)} = 45.65\ (2\ (1\text{-}FA\text{-}FN) - Z_{CH_3})$$

$$c = c^{(n\text{-}alkane)} + \Delta c^{(ring)} + \Delta c^{(CH_3)}$$

$$c^{(n\text{-}alkane)} = 0.6520 + 0.0355\ MW^{0.8138}$$

$$\Delta c^{(ring)} = (0.5169 - 0.00847\ MW)\ (FA + FN)$$

$$\Delta c^{(CH_3)} = 0.108\ (2\ (1\text{-}FA\text{-}FN) - Z_{CH_3})$$

The volume correlation reproduces the experimental V^* values with an accuracy usually better than 1 % . For $\varepsilon q/k$ and c the errors are slightly higher.

Figure 4: Close-packed volume V^*, energy $\varepsilon q/k$ and flexibility parameter c per molecule for pure hydrocarbons (■ n-alkanes, ● aromatics, ▲ naphthenes, ○ alkylaromatics, △ alkylnaphthenes)

Figure 4 shows the "experimental" values of V^*, $\varepsilon q/k$ and c and the correlation functions for pure n-alkanes, pure aromatics (FA=1), and pure naphthenes (FN=1) as a function of molecular weight. The close-packed volume V^* is a linear function of the molecular weight for alkanes, aromatics, and naphthenes. No significant difference in V^* is found between normal and iso-alkanes. The effective potential energy parameter $\varepsilon q/k$ is essentially the same for n-alkanes and naphthenes, and is therefore represented using the same correlating equation . The effect of ring formation on flexibility parameter c is similar for aromatics and naphthenes. Because of the large differences between parameter c for the reference n-alkanes and those for ring compounds, it is difficult to extrapolate c values for ring compounds to higher molecular weight with high accuracy. To extrapolate with confidence, we require experimental data for pure ring hydrocarbons with carbon numbers above 20. Figure 5 shows that for alkanes, progressive methyl substitution causes a decrease in c and $\varepsilon q/k$ proportional to the number of

methyl groups per molecule.

Figure 5 : Progressive methyl substitution in alkanes; Effect on energy $\varepsilon q/k$ and on flexibility parameter c per molecule.

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3. Calculation of V^*, $\varepsilon q/k$, c for petroleum fractions

The correlations presented here are based on experimental data for a wide range of pure hydrocarbons. Our purpose is to use the correlations to estimate PHC parameters for ill-defined mixtures with many components, such as narrow-boiling petroleum fractions. These fractions are considered to be pseudo components; their properties are calculated using average values for V^*, $\varepsilon q/k$ and c. These average parameters are obtained from the pure-hydrocarbon correlations and from measured average characterization data that reflect molecular size and structure. We use these characterization data to obtain V^* and $\varepsilon q/k$ for the fraction. However, since an accurate extrapolation of the flexibility parameter c to higher molecular weights is difficult, we suggest that c be obained from Figure 6 using one measured vapor pressure P^o of the fraction at a temperature T^o. One measured vapor pressure is usually available from the fractionation procedure (e.g. mid- boiling point of the fraction). Using the correlated values of V^* and $\varepsilon q/k$, c is found from Figure 6 at the reduced values $\tilde{P}^o = P^oV^*/(R(\varepsilon q/k))$ and $\varepsilon q/(kT^o)$. Since vapor pressures of extremely heavy fractions are essentially zero, Figure 6 ex-

tends only over the range $1 < c < 20$.

Figure 6: Reduced vapor pressure chart to estimate c

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4. Experimental

To test the correlation, vapor pressures and saturated-liquid volumes were measured for five characterized petroleum fractions. Crude oil (from Belridge, California) was fractionated in an annular-still, spinning-band column into narrow-boiling fractions, or cuts. Each cut was then characterized by the following average properties:

- Number-average molecular weight, from freezing-point depression measurements (solvent: nitrobenzene)

- Fractional aromaticity, from standard proton NMR and elemental analysis (solvent: deuterated pyridine, internal standard: hexamethyldisiloxane)

- Fractional naphthenicity, from standard PNA analysis

- Number of methyl groups per molecule, from IR-spectroscopy (the absorption is measured at 1380 wavenumbers using dichloromethane as solvent)

In addition to these characterization parameters, we also obtain one vapor-pressure datum from the fractionation procedure (mid-boiling point). Details of the fractionation and characterization procedure are given elsewhere (7).

Table 2 shows fractionation and characterization data for five Belridge fractions. These data are used to estimate equation-of-state parameters as required for our correlation.

Table 2 : Fractionation and characterization data for Belridge crude-oil fractions

FRACTION No.	API-GRAVITY (°API)	BOILING RANGE (K) #	MW (g/mole)	FA	FN	Z_{CH_3}
1	44.6	422 - 478	148	0.230	0.53	2.4
2	35.2	478 - 535	189	0.283	0.56	3.2
3	26.9	533 - 617	245	0.298	0.51	4.2
4	17.5	617 - 705	340	0.312	0.49	5.9
5	16.3	705 - 811	464	0.302	0.52	8.2

at P = 0.1013 MPa

Vapor pressures are measured in a static equilibrium apparatus (sample volume 5 cm^3) in the subatmospheric pressure range to 300 °C. Saturated-liquid volumes were determined in calibrated fused-glass cells (sample volume 1.5 cm^3). Figure 7 compares experimental vapor pressures and saturated-liquid volumes with results calculated from our correlation and from the characterization data in Table 2.

Figure 7: Calculated and observed vapor pressures and saturated-liquid volumes for Belridge crude-oil fractions

5. Discussion and conclusion

A comparison of experimental and calculated results shows that the correlation gives reasonable estimates for the vapor pressures and saturated-liquid volumes of the five crude-oil fractions. However, the results are not of very high accuracy. The accuracy of the presented method can be improved in many ways; the most important is to improve characterization of the fuel fractions. The largest uncertainty results from naphthenicity, determined from PNA analysis. For fractions of higher molecular weight, PNA analysis provides poor estimates of molecular structure. Further, the correlation can be improved by introducing more characerization variables, e.g., number of aromatic and naphthenic rings per molecule, degree of methylsubstitution of rings, degree of condensed aromatic rings,etc.. These variables, determined from fraction-average measurable properties, could account in a more sophisticated way for the different hydrocarbon structures in complex molecules of high molecular weight. Thus it should be possible to calculate the flexibility parameter c without using a vapor-pressure datum. This may be particularly useful for very heavy hydrocarbon residues since their vapor pressures are not easily measured.

A suitable analytical method to obtain the desired structural information is provided by ^{13}C-NMR spectroscopy. A new ^{13}C-NMR technique , recently proposed by Snape (8), also determines the number of CH_3-groups per molecule more accurately than does IR spectroscopy. A further improvement of accuracy can be obtained by expanding the data base of pure components. For improved parameter correlation, the data

base should include experimental results for hydrocarbons with heteroatoms S, N, O, present in all fossil fuels, as well as results for polymers. However, even at this present state of development, the correlation presented here may be useful for estimating thermodynamic properties of heavy fossil-fuel fractions as required in engineering calculations.

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Appendix

Details concerning the equation of state

The equation of state used in this paper is a truncated version of Donohue's equation. The molar Helmholtz energy is given by the perturbation expansion:

$$A(T,V) - A^{IG}(T,V) = A^{(0)} + \frac{A^{(1)}}{T} + \frac{A^{(2)}}{T^2} \qquad (A\text{-}1)$$

where $A^{IG}(T,V)$ is the Helmholtz energy of the ideal gas at given T and V:

$$A^{IG}(T,V) = -RT \ln\left(\frac{V}{V^{\ddagger}}\right) + \text{a function of T only,} \qquad (A\text{-}2)$$

where $V^{\ddagger}$ is an arbitrarily chosen reference volume.
$A^{(0)}$ accounts for the repulsive forces; it is based on the expression of Carnahan and Starling (9), here applied to hard-sphere segments in a chain with 3c external degrees of freedom:

$$A^{(0)} = RTc\left[\frac{4\left(\frac{\tau}{\tilde{V}}\right) - 3\left(\frac{\tau}{\tilde{V}}\right)^2}{\left(1 - \frac{\tau}{\tilde{V}}\right)^2}\right] \qquad (A\text{-}3)$$

$$(\text{ with } \tau = \pi\sqrt{2}/6 = 0.7405 \text{ })$$

The remaining terms $A^{(n)}$ correct for molecular attractions arising from the square well potential:

$$A^{(n)} = RTc \sum_{m=1}^{5} \frac{\mathcal{A}_{nm} T^{*n}}{\tilde{V}^{m}} , \qquad (A-4)$$

$$(n = 1,2) .$$

Constants $\mathcal{A}_{nm}$ in the attraction term are universal constants based on molecular-dynamic studies of Alder . These constants have been re-fitted to the truncated PHC equation of state by Gmehling (10). Values of $\mathcal{A}_{nm}$ are given in Table 3.

Using the fundamental relation:

$$P = - \left(\frac{\partial A}{\partial V} \right)_T , \qquad (A-5)$$

we obtain the PHC equation of state in a form similar to that of Equation (A-1):

$$P - P^{IG} = P^{(0)} + \frac{P^{(1)}}{T} + \frac{P^{(2)}}{T^2} \qquad (A-6)$$

where P^{IG} is the ideal-gas reference pressure at given T and V

($P^{IG} = RT/V$).

Consistent with Equations (A-3) and (A-4), we obtain $P^{(0)}$ and $P^{(n)}$:

$$P^{(0)} = c \left[\frac{4 \left(\frac{\tau}{\tilde{V}}\right) - 2 \left(\frac{\tau}{\tilde{V}}\right)^2}{\left(1 - \frac{\tau}{\tilde{V}} \right)^3} \right] \qquad \text{(A-7)}$$

$$P^{(n)} = c \sum_{m=1}^{5} \frac{{}_m\mathcal{A}_{nm} \, T^{*n}}{\tilde{V}^{m}} \qquad \text{(A-8)}$$

(with n = 1,2)

Table 3 : Universal Constants $\mathcal{A}_{nm}$

m =	1	2	3	4	5
n = 1	-7.04677	-7.22626	-3.16539	14.34352	-1.26227
n = 2	-3.56999	11.35209	10.85375	-3.6131	7.34334

Nomenclature

A = molar Helmholtz energy

$\mathcal{A}_{nm}$ = Alder's universal constants (modified by Gmehling)

c = one third of the number of exernal degrees of freedom

k = Boltzmann's constant

m,n = index of Alder's constants

P = pressure

q = external surface area per molecule

R = gas constant

T = absolute temperature

V = molar volume

Greek letters

ε = segment-segment potential energy

σ = hard-core diameter

τ = a constant equal to 0.7405

Superscripts

liq = liquid phase

vap = vapor phase

s = saturated

IG = ideal gas

* = molecular reducing parameter

~ = reduced property

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List of captions to figures:

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Figure 1: Reduced vapor pressure $\tilde{P}$ as a function of reduced temperature $\tilde{T}$

Figure 2: Reduced saturated-liquid volume $\tilde{V}$ as a function of reduced temperature $\tilde{T}$

Figure 3: Basic structures in hydrocarbon molecules

Figure 4: Close-packed volume V^*, energy $\varepsilon q/k$ and flexibility parameter c per molecule for pure hydrocarbons
(■ n-alkanes, ● aromatics, ▲ naphthenes, ○ alkylaromatics, △ alkylnaphthenes)

Figure 5: Progressive methyl substitution in alkanes; Effect on energy $\varepsilon q/k$ and on flexibility parameter c per molecule.

Figure 6: Reduced vapor pressure chart to estimate c

Figure 7: Calculated and observed vapor pressures and saturated-liquid volumes for Belridge crude-oil fractions

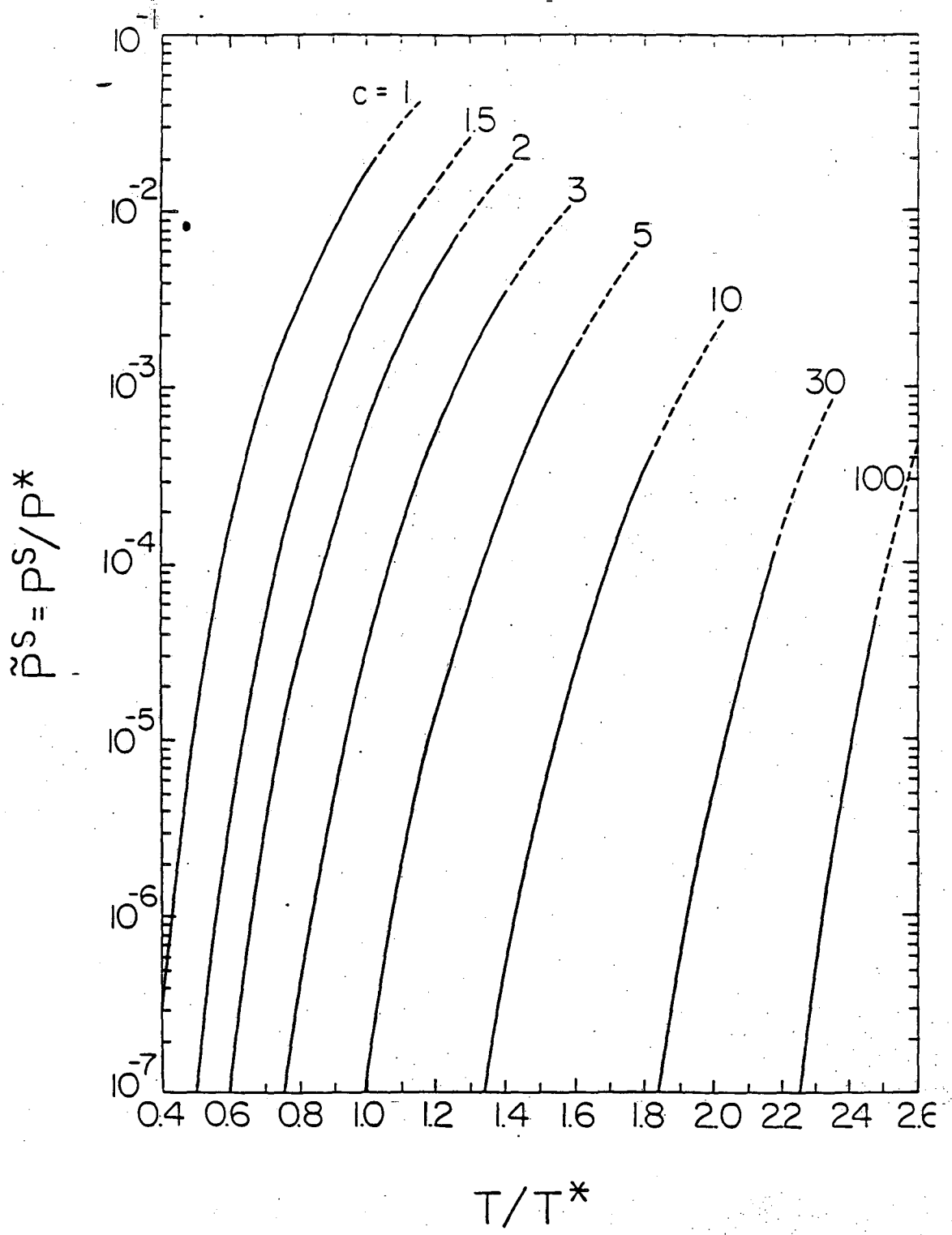

c = 1
1.5
2
3
5
10
30
100
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
$\tilde{P}^S = P^S/P^*$
T/T^*

Fig. 1

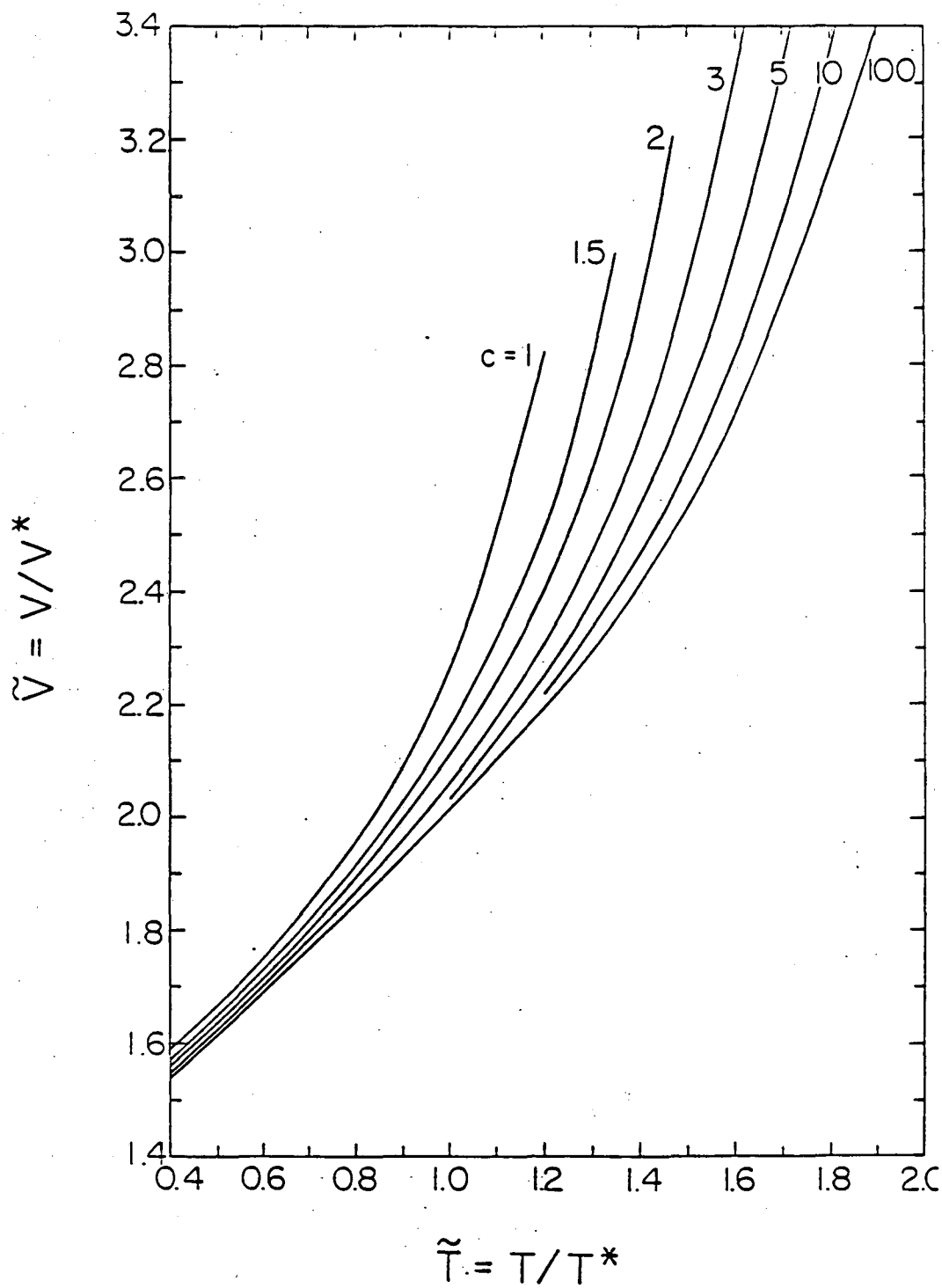
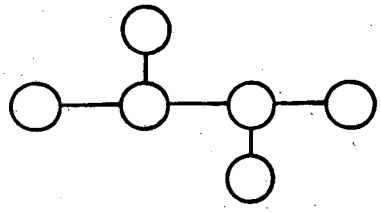

3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
c = 1
1.5
2
3
5
10
100
$\tilde{V} = V/V^*$
$\tilde{T} = T/T^*$

Fig. 2

Reference molecule

Long chain *n*-alkane

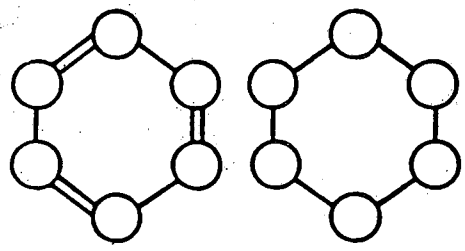
Isomerisation



Characterization parameter:

Number of methyl groups Z_{CH_3}

Ring formation



Characterization parameters:

Fractional aromaticity $FA = \frac{n_c^{aromatic}}{n_c^{total}}$

Fractional naphthenicity $FN = \frac{n_c^{naphthenic}}{n_c^{total}}$

(n_c = number of carbon atoms)

Fig. 3

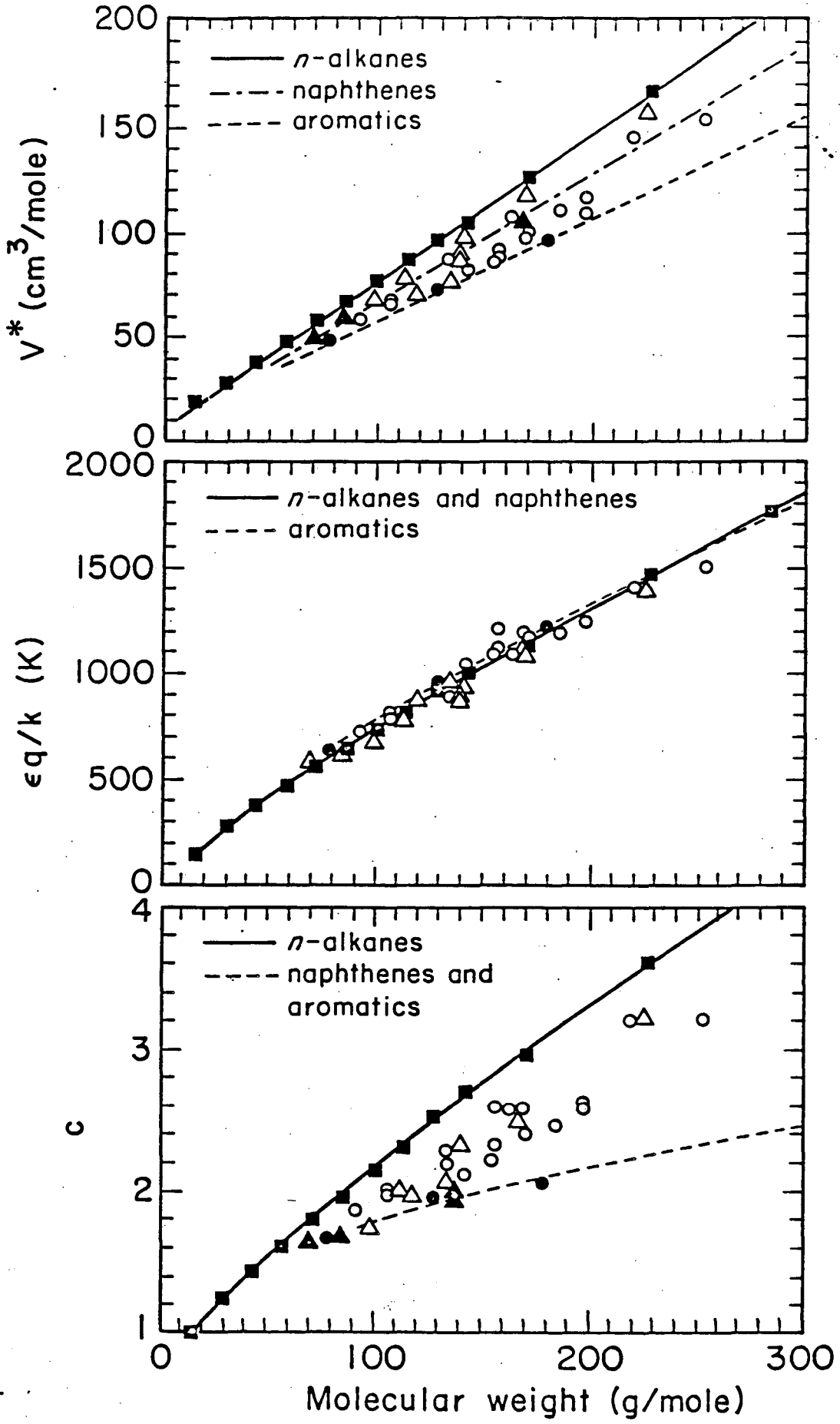

200
150
100
50
0
v^* (cm^3/mole)
n-alkanes
naphthenes
aromatics
2000
1500
1000
500
0
$\epsilon q/k$ (K)
n-alkanes and naphthenes
aromatics
4
3
2
1
c
n-alkanes
naphthenes and aromatics
0
100
200
300
Molecular weight (g/mole)

Fig. 4

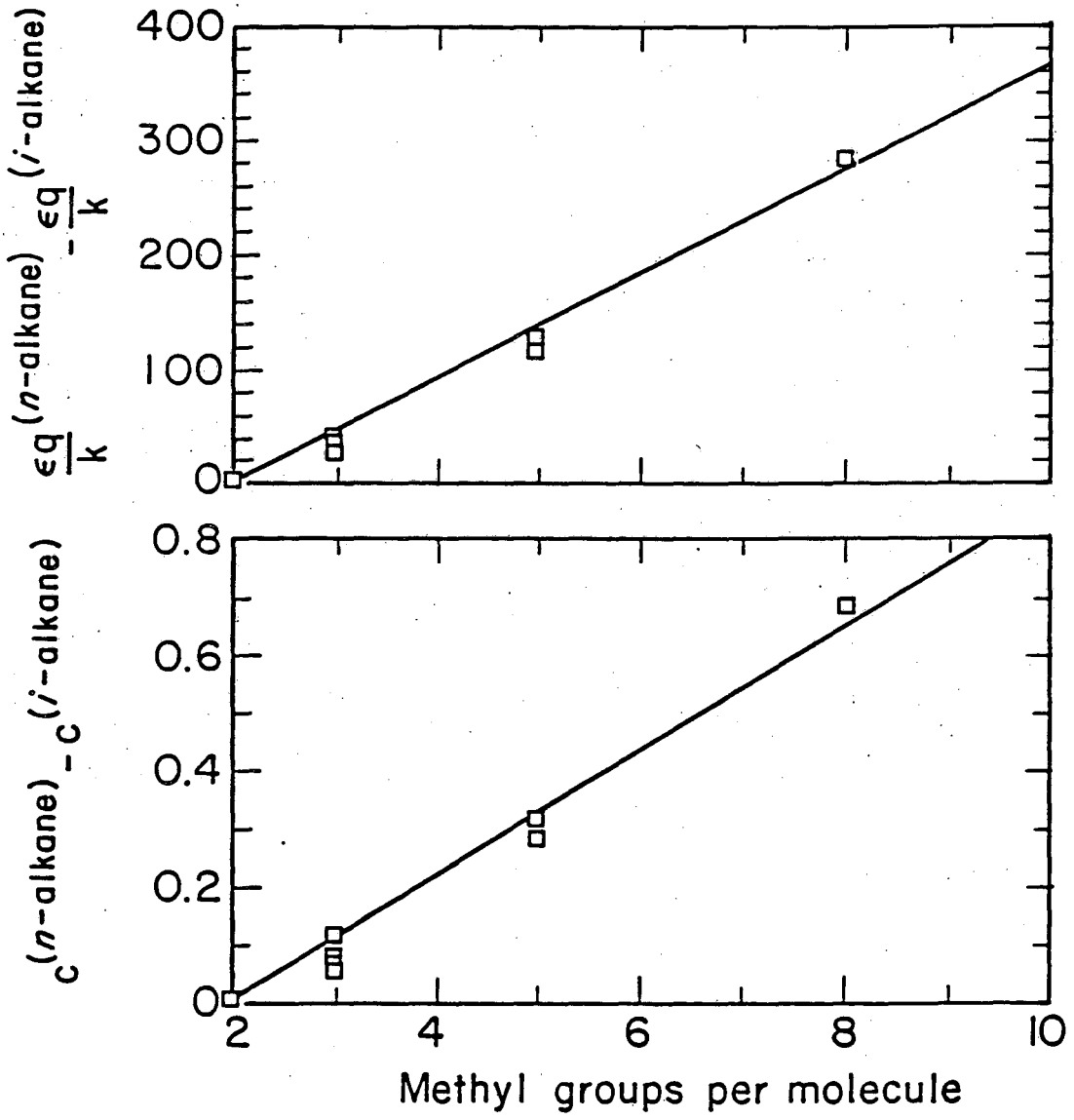

400
300
200
100
0
$\frac{\epsilon q}{k}^{(n\text{-alkane})} - \frac{\epsilon q}{k}^{(i\text{-alkane})}$
0.8
0.6
0.4
0.2
0
$c^{(n\text{-alkane})} - c^{(i\text{-alkane})}$
2
4
6
8
10
Methyl groups per molecule

Fig. 5

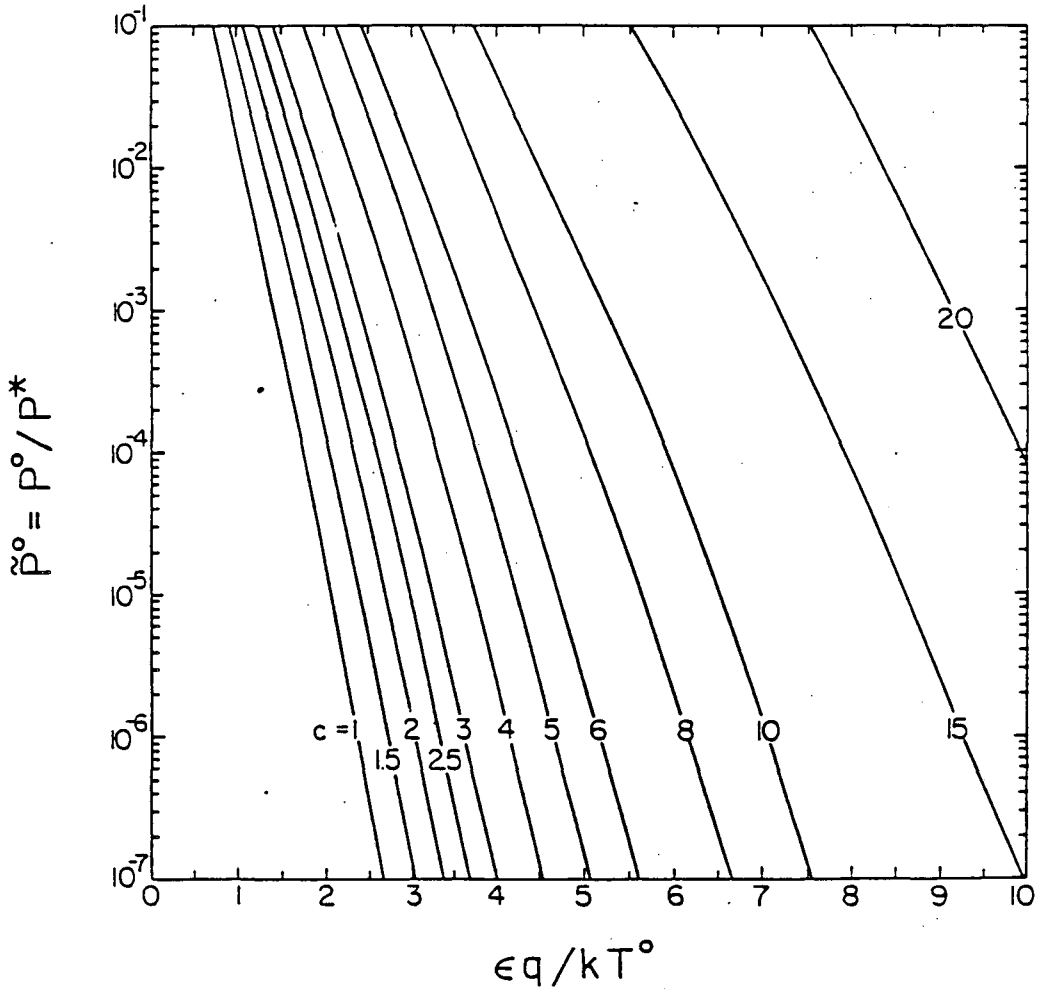
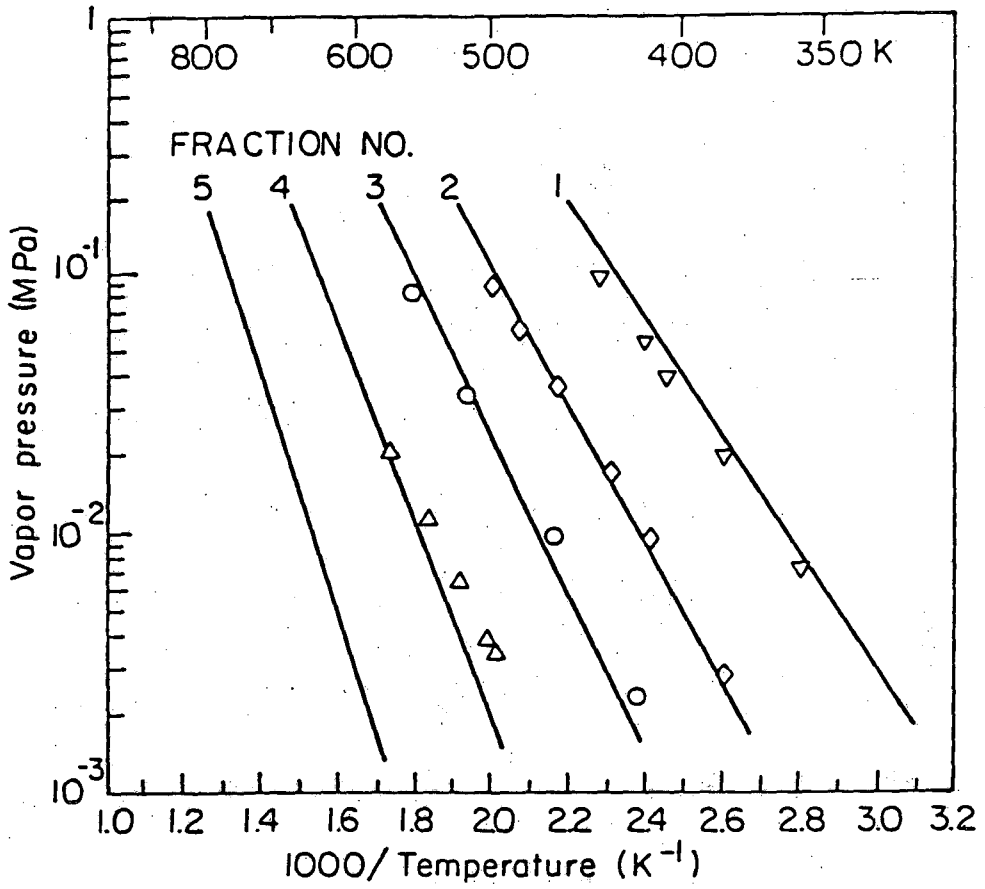

10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
$\tilde{P}^{o} = P^{o}/P^{*}$
0
1
2
3
4
5
6
7
8
9
10
$\epsilon q/kT^{o}$
c = 1
1.5
2
2.5
3
4
5
6
8
10
15
20

Fig. 6


800
600
500
400
350 K
FRACTION NO.
5
4
3
2
1
Vapor pressure (MPa)
1
10^{-1}
10^{-2}
10^{-3}
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
1000/ Temperature (K^{-1})

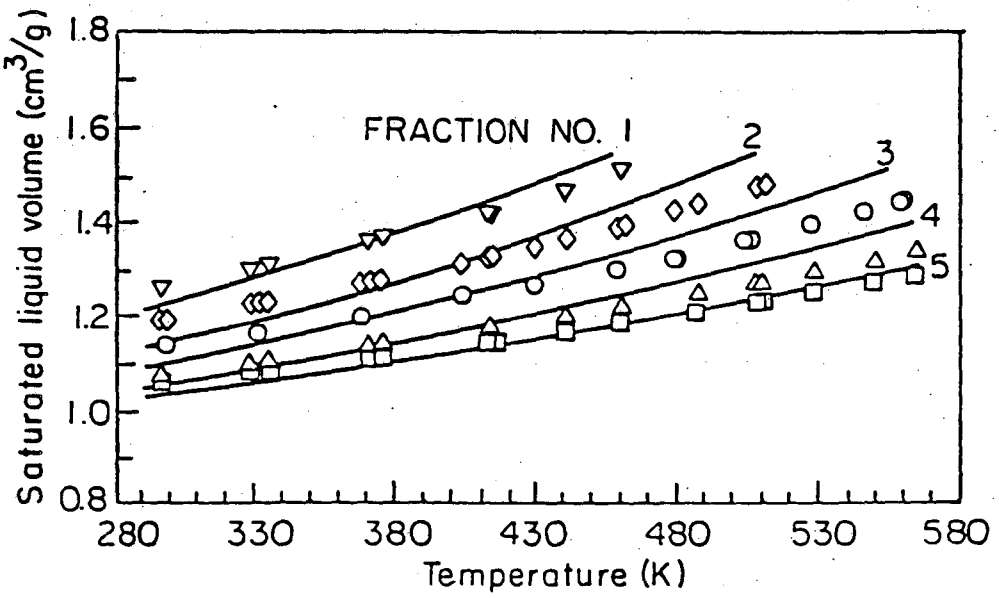

Saturated liquid volume (cm^3/g)
1.8
1.6
1.4
1.2
1.0
0.8
FRACTION NO. 1
2
3
4
5
280
330
380
430
480
530
580
Temperature (K)

Fig. 7

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