Reinvestigation of Densimetric Methods of Ring Analysis

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FOR MANY YEARS the chemist has sought a method for determining average structural character of the molecules in a complex mixture. In general, two types of mixtures have received most attention. One has consisted of mixtures of compounds comprising a relatively narrow molecular weight range and where the average molecular weight could be obtained; examples are narrow boiling cuts from petroleum. The second has consisted of very complex systems, such as coals, where molecular weight could not be determined, and, indeed, where the concept of molecular weight might not be applicable.

Present studies in this laboratory have as their objective clarification of the structure of the asphaltic (nonhydrocarbon) constituents of crude oil and of the presumably similar, but higher molecular weight, black, insoluble organic fraction of ancient sedimentary rocks. From the viewpoint of structural type analysis, these substances are thought possibly to represent a situation somewhere between that of a low molecular weight hydrocarbon mixture and the macromolecular structure of coals.

The development of procedures applicable to mixtures of known low molecular weight and to coals has taken place concurrently, many investigators contributing. Vlugter, Waterman, and van Westen (*36, 37*) were among the first to apply a system of ring analysis to complex hydrocarbon mixtures. Van Nes and van Westen (*24*) continued the study, developing the *n-d-M* method primarily for petroleum oils. Using refractive index, density, and elementary analysis, van Krevelen (*13, 14*), van Krevelen and Chermin (*15*), and van Krevelen and Schuyer (*16*) developed a somewhat similar method of statistical analysis, applicable to coals and other substances where molecular weight could not be obtained. Smith (*34*) and Montgomery and Boyd (*21*) elaborated on both methods to obtain further structural parameters, testing the methods using data for a variety of pure hydrocarbon compounds as recorded by the American Petroleum Institute Research Project 42. Good agreement was obtained with respect to paraffins and naphthenes, but discrepancies were observed for fused polycyclic hydrocarbons. Dryden (*8*), working with coals, compared structural information derived from x-ray, nuclear magnetic resonance, and infrared data with comparable information calculated from the densimetric method of van Krevelen and found that agreement usually was poor.

Despite the difficulties encountered in applying the van Krevelen method to highly cyclic systems, re-examination of the problem appeared warranted. It seemed likely that a critical comparison of the results obtained for a variety of cyclic systems, using this equation, with results obtained by other available physical methods, might suggest modification which would render the densimetric method more generally applicable.

For aliphatic-aromatic compounds or mixtures thereof where the molecular weight could be determined, van Krevelen has proposed the following equations (*16*):

$$M/\rho = \sum_i n_i V_i - K_M \tag{1}$$

$$K_M = V_R R \tag{2}$$

where

M = molecular weight of the compound or mixture
ρ = density
n_i = number of the *i*th atomic species
V_i = Traube's atomic volumes
K_M = molar volume contraction
V_R = molar volume contraction per ring
R = number of rings

For aliphatic compounds or mixtures, K_M is approximately zero.

To cope with substances such as coal, where molecular weight is very high or cannot be determined, the equation was converted to the form:

$$\frac{1200}{\%C\,\rho} = \frac{\sum_i n_i V_i}{C} - \frac{V_R R}{C} \tag{3}$$

where $\%C$ is the per cent carbon obtained by elementary analysis and C is the number of carbon atoms in the structural unit.

To calculate the average number of rings per molecule, R, from Equations 1 and 2 or the number of carbons per ring (the reciprocal of the ring condensation index), C/R, from Equation 3, it is necessary to evaluate V_R. Using three reference substances—cellulose, polystyrene, and graphite—van Krevelen and Chermin (*15*) derived the empirical relation:

$$V_R = 9.1 - 3.6H/C \tag{4}$$

where H is the number of hydrogen atoms.

Relations 1 and 3 thus become:

$$R = \frac{9.9C + 3.1H + \ldots - M/\rho}{9.1 - 3.6\,H/C} \tag{5}$$

and

$$C/R = \frac{9.1 - 3.6H/C}{9.9 + 3.1H/C + \ldots - \dfrac{1200}{\%C\,\rho}} \tag{6}$$

Equation 6 was now used to calculate the reciprocal of the ring condensation index, C/R, for a native asphaltene prepared from a Lagunillas (Venezuela) crude oil and for two carbon blacks studied by Kuroda (*17*). For the asphaltene the value is 3.5; for both carbon blacks (Royal Spectra and Statex B) the value is 2.1. For comparison, the C/R value also was estimated independently for the asphaltene as 5.7 (infrared, C—H stretching); 5.5 (NMR, proton type area); 4.8 (x-ray, γ- and 002-bands); and 7.7

(x-ray, 10- and 11-bands). Values for the Royal Spectra and Statex B by the x-ray method (10-band) were, respectively, 2.9 and 2.6. Calculations for the carbon blacks were made on the assumption that all carbons are contained in a condensed aromatic sheet. The results appear to indicate that the van Krevelen method yields low values for both asphaltenes and carbon blacks. Equations 5 and 6, therefore, have been examined more critically.

MOLAR VOLUMES AND DENSITIES OF PARAFFINS AND POLYNUCLEAR HYDROCARBONS

For compounds containing both aromatic and paraffinic groupings, the molar volume can be considered to consist of two portions: one paraffinic, the other aromatic. If the paraffinic portion of the molar volume is the same as that represented by the summation of Traube's atomic volumes (*35*), the aromatic portion can be expressed linearly in terms of Traube's values, less a contraction term which takes account of the strong polarization exerted by ring formation. This statement assumes that the paraffinic molar volume calculated by means of Traube's atomic volume is adequate, and that the extent of the molar volume contraction in aromatic hydrocarbons can be accurately calculated. To investigate these two points, the following two general equations have been derived for the density of paraffins and polynuclear hydrocarbons, respectively:

$$\rho_P^{-1} = \rho_e^{-1} + kC_P^{-1} \tag{7}$$

$$\rho_A^{-1} = \rho_g^{-1} + k'\,C_A^{-1/2} \tag{8}$$

where

ρ_P = density of paraffins
ρ_e = density of polyethylene
C_P = number of atoms of paraffins carbon
ρ_A = density of aromatic hydrocarbons
ρ_g = density of graphite
C_A = number of atoms of aromatic carbon

In Equation 7, $k = 0.80$ for perfect crystalline paraffins, and $k = 0.28$ for mesomorphic substances. For example, the crystalline normal paraffins based on Piper (*25*) and Müller's (*22, 23*) work possess an orthorombic unit cell of $a = 7.45$ A., $b = 4.97$ A., and c is equal to a length varying with the carbon number—e.g., 2.52 A. per CH_2 pair as in a planar zigzag configuration. The length in Angstroms of a paraffinic chain can be expressed as $\frac{1}{2}[2.52(C_P - 1) + 2(1.54)]$ or $1.26\,C_P + 0.28$; hence the molar volume expressed in cubic centimeters is

$$V_M = ab/2(1.26\,C_P + 0.28) \times 100^{-24} N \tag{9}$$

$$= 14.05\,C_P + 3.12$$

Thus, if the molecular weight is expressed as $14\,C_P + 2$, Equation 7 is obtained with a k value of 0.80. In this instance ρ_e is 0.99 gram per cc., which is close to the highest value so far recorded for linear polyethylene, 0.96 to 0.97 gram per cc. (*10*). To justify the molar volume relation, a series of molar volumes calculated from experimental densities (*9*) of C_4 to C_{28} normal paraffins at 0° (Figure 1, *C*) and at 100° (*D*) is plotted *vs.* C_P. *A* represents Equation 9 for perfect crystalline paraffins.

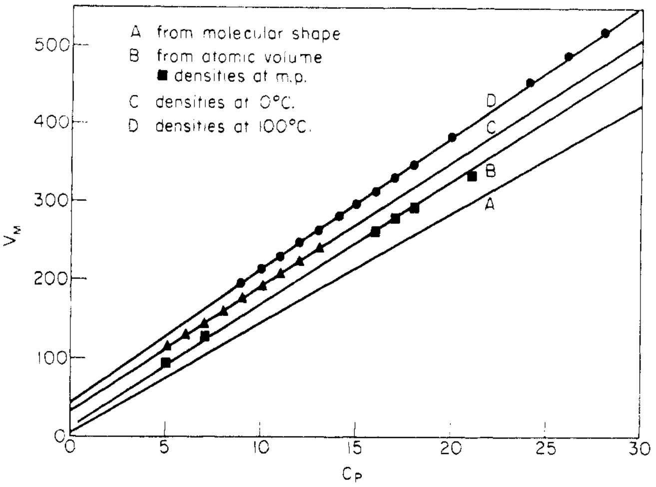

Figure 1. Dependence of molar volume on carbon number for normal paraffins

In Figure 1, the points based on the densities at the melting temperature almost coincide with *B*, which is based on Traube's atomic volumes. The earlier work of Kopp and Le Bas (*12*) and of Traube (*35*) has indicated that densities at either the boiling point or melting point of an organic substance can be used for the additive correlation of structural work. Most polymers and resins at room temperature are considered as mesomorphic substances. Validity of the application of Traube's atomic volumes to polymers is illustrated by the 45° straight line when the V_M derived from Traube's atomic volume is plotted *vs.* the actual M/ρ (*30*) values at room temperature, as in Figure 2. Usually Traube's values are adopted for systems of low crystalline content—i.e., mesomorphic substances. The crystallinity-density relationships of some poly-α-olefins, as derived from both x-ray and nuclear magnetic resonance (*33*), are shown in Figure 3. If Traube's values of 9.9 cc. for carbon and 3.1 cc. for hydrogen are adopted for calculation of Equation 7, in this instance ρ_e is 0.87 and k is 0.28. The 0.87 value of polyethylene would correspond to a crystallinity equivalent in the range 20 to 30%. In general, k varies with the crystallinity and physical state of normal paraffins, but Traube's value holds true only for mesomorphic substances. The indication is that Equation 7 for paraffinic hydrocarbons is valid. More generally, this equation may be written:

$$\rho_e/\rho_P - 1 = gC_P^S \tag{10}$$

where $g = k/\rho_e$ and $S = 1$.

Molecular interaction is favored by close proximity of orderly packed rod- or plate-shaped molecules. Experimental facts such as x-ray diffraction, electron diffraction, and Kerr effect provide evidence that nonpolar chain

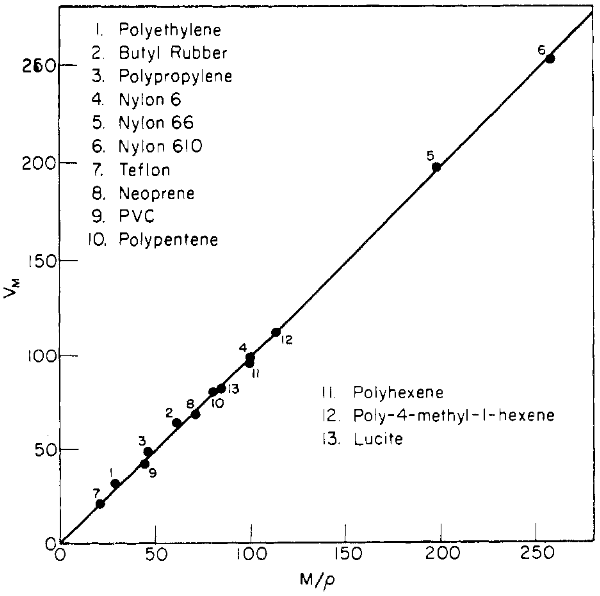

Figure 2. Validity of Traube's atomic volumes as demonstrated by a series of polymers

molecules orient themselves parallel to their long axes, whereas flat ring systems arrange themselves parallel to the plane of the ring. De Boer (*2*) has shown that the interaction between two benzene molecules is optimum when they are in stacked positions and the easily polarizable components of the charge clouds can be arranged directly opposite each other. At ordinary temperature the benzene rings in polystyrene are stacked in close spatial proximity and through such mutual attraction that the flexibility of the polymethylene chain is inhibited. In the case of a two-dimensional hexagonal net, the area of the equilateral triangle formed by joining the centers of three adjacent rings can be expressed as:

$$\Delta = 3^{3/2} r^2/4 \qquad (11)$$

If the net is comprised of aromatic carbon atoms, r is the bond distance and Δ the area occupied by one carbon atom. For a system consisting of uniformly stacked sheets, the minimum interlayer distance is 3.34 A. and hence the maximum density, 2.28 grams per cc., can be calculated. In the case of graphite, the helium displacement density is 2.26 grams per cc. (*31*).

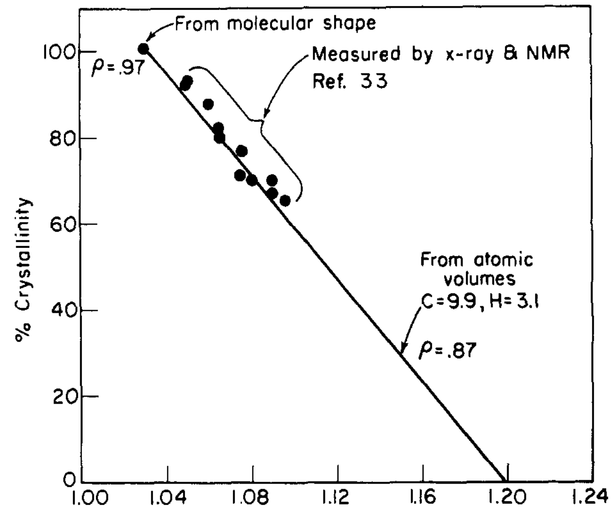

Figure 3. Relation of crystallinity and density in polyolefins

For aromatic hydrocarbons, it is logical to assume that a relation similar to Equation 10 will apply where the reference density of graphite is used to replace the reference density of polyethylene. Thus,

$$\rho_g/\rho_A - 1 = g'\, C_A^{S'} \qquad (12)$$

To test the applicability of this equation and to evaluate the constants, the experimental values of the densities for a series of aromatic hydrocarbons, listed in Table I, are plotted *vs.* the carbon number on a logarithmic scale as shown in Figure 4. The points fall close to a straight line, in conformity with Equation 12. From the slope and intercept, one can obtain $S' = -0.56 \cong \frac{1}{2}$ and $g' = 3.15$. Since $g' = k'/\rho_g$, the k' of Equation 8 assumes the value, 1.38. In Figure 5, this relationship is linearly plotted to include the six amorphous carbon blacks described in Table II. It can be seen that, if $k' = 1.38$, Equation 8 holds true for crystalline as well as amorphous substances. This fact is in contrast to the case of paraffins, where the k values differ with degree of crystallinity. Equation 8 will be used in the subsequent section to derive an expression for K_M for mesomorphic substances.

RING NUMBER AND MOLAR VOLUME CONTRACTION OF AROMATIC COMPOUNDS

To treat the problem of a condensed ring aromatic system—i.e., of a hexagonal network in two dimensions,—it is necessary to assume some sort of model. Several models are possible,—e.g., a circle, exemplified by coronene; a square, by anthrodianthrene; a triangle, by perinaphthindene; a pentagon, by 1,12-benzperylene; and a rectangle, by perylene. For any of these models the number of rings can be expressed as a function of the number of aromatic carbon atoms and the number of aromatic hydrogen atoms by the equation:

$$R = 1 + \frac{C_A - H_A}{2} \qquad (13)$$

where

$$H_A = rC_A + pC_A^{1/2} + q \qquad (14)$$

Here, r, p, and q are shape factors; in the case of fused aromatic hydrocarbons, $r = 0$. p usually ranges from 2.44 to 3, and q, from 0 to −2. The specific values for the different models are listed in Table III.

Table I. Density, Ring Number, and Molar Volume Contraction for Compounds Consisting of Condensed Ring Systems

No.	Compound	Formula	M	ρ	K_M	$R_{theo.}$	$R_{calcd.}$
1	Benzene	C_6H_6	78	1.0126 (*9*)	1	1	0.1
2	Naphthalene	$C_{10}H_8$	128	1.152 (*27*)	12.7	2	1.4
3	Anthracene	$C_{14}H_{10}$	178	1.25 (*20*)	27.2	3	3.0
4	Pyrene	$C_{18}H_{10}$	202	1.27 (*26*)	30.3	4	3.3
5	Triphenylene	$C_{18}H_{12}$	228	1.302 (*20*)	40.3	4	4.4
6	Chrysene	$C_{18}H_{12}$	228	1.274 (*20*)	36.4	4	4.0
7	Perylene	$C_{20}H_{12}$	252	1.35 (*7*)	48.5	5	5.3
8	1,2,5,6-Dibenzanthracene	$C_{22}H_{14}$	278	1.282 (*28*)	44.4	5	4.9
9	Anthanthrene	$C_{22}H_{12}$	276	1.39	56.4	6	6.2
10	Coronene	$C_{24}H_{12}$	300	1.377 (*29*)	57.0	7	6.3
11	Ovalene	$C_{32}H_{14}$	398	1.477 (*8, 6*)	90.7	10	10.0
12	Circumanthracene	$C_{40}H_{16}$	496	1.52 (*4*)	119.0	13	13.1
13	Phenanthrene	$C_{14}H_{10}$	178	1.179 (*20*)	18.6	3	2.1
14	Fluorene[a]	$C_{13}H_{10}$	166	1.203 (*18*)	21.7	3	2.4
15	3,4,5,6-Dibenzphenanthrene	$C_{22}H_{14}$	278	1.264 (*19*)	41.3	5	4.6
16	1,12-Benzperylene	$C_{22}H_{12}$	276	1.35 (*38*)	50.6	6	5.6
17	Fluoranthene[a]	$C_{15}H_{10}$	190	1.252 (*18*)	27.8	4	3.1

[a] Containing one 5-membered ring.

Table II. Density and X-Ray Layer Diameters of Carbon Blacks

No.,	Name	ρ^a	L_a^a	C_A^b
a	Royal Spectra (HCC)	1.68	13.1	65.6
b	Philblack E (SAF)	1.76	12.0	55.0
c	Peerless Mark II A	1.82	14.2	77.0
d	Tokyo gas carbon	1.68	13.4	68.8
e	Statex B (FF)	1.81	16.9	109.0
f	Philblack O (HAF)	1.81	13.3	67.5

[a] Data from (*17*).

[b] Calculated for $C_A = 4/3^{3/2} L_a^2/r^2$, Equation 11.

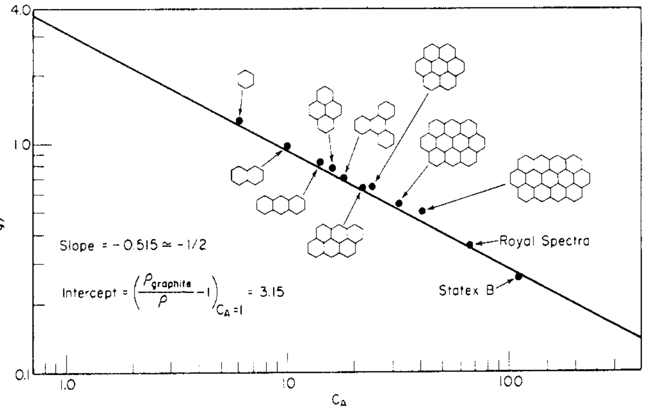

Figure 4. Relation of density to aromatic carbon number

For illustration, the rectangular model shown will be used for development of the shape factors and ring number. If an aromatic cluster is defined by $[m, n]$, where m denotes the number or relative length of biphenyl-type rings along the x-axis, and n the naphthalene-type rings along the y-axis (*5*), the following relations can be deduced by inspection:

$$H_A = 2(2m + n) \tag{15}$$

$$C_A = 2m(2n + 1) \tag{16}$$

$$R = mn + (m - 1)(n - 1) \tag{17}$$

$$= 2mn - m - n + 1$$

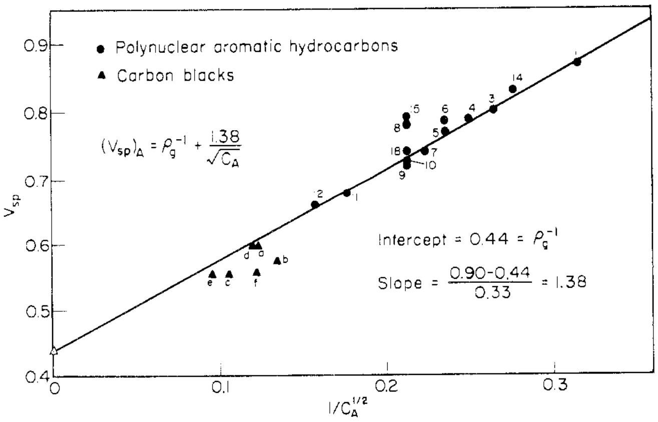

Figure 5. Dependence of specific volume on carbon number for polynuclear aromatic hydrocarbons

Key to identification of numbers and letters in Tables I and II

By solving for m and n in Equations 15 and 16 and finally substituting into Equation17, the ring number relations of Equation 13 can be obtained. For fused rings with equal chance of growing in both x and y directions ($m \cong n$) H_A can be expressed in terms of C_A in Equations 15 and 16 with shape factors p = 3 and q = −1.5. In general, for any aromatic hydrocarbon,

$$R = \frac{1-r}{2} C_A - p/2\, C_A^{1/2} + \frac{2-q}{2} \tag{18}$$

The next step is to evaluate K_M for aromatic hydrocarbons based on the definition

$$K_M = \sum_i n_i V_i - M/\rho_A \tag{19}$$

The numerical values of Traube's atomic volumes of hydrogen and carbon—i.e., 3.1 and 9.9—the molecular weight defined as 12 C_A + H_A, and the density relation from Equation 8 are substituted into Equation 19. After replacing H_A by its value from Equation 15 and neglecting the $C_A^{-1/2}$ term, since C_A is large, the equation

$$K_M = (4.6 + 2.7r)C_A + (2.7p - 16.6 - 1.4r)C_A^{1/2} + (2.7q - 1.4p) \tag{20}$$

is obtained.

Both the ring number and the molar volume contraction can be expressed as polynomials of C_A. Since a direct solution for R and K_M by elimination of C_A is complicated, the operation is accomplished graphically as shown in Figure 6, by substituting in the equations arbitrary values of C_A and the shape factors. The points represent data for typical, fully aromatic hydrocarbons, as listed in Table I.

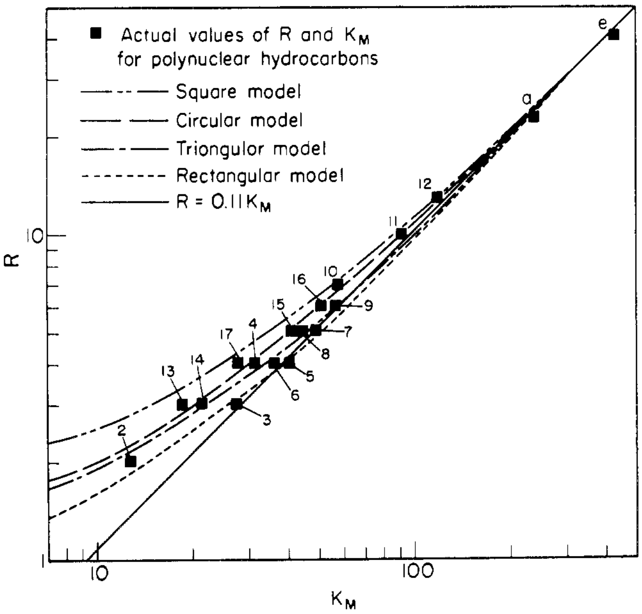

Figure 6. Graphical solutions on relation of molar volume contraction and ring number

Key to identification of numbers and letters in Tables I and II

Table III. Shape Factors of Condensed Aromatic Hydrocarbons[a]

Model	p	q
Square (including parallelograms and one-end indented tier strip)	2.82	−2
Rectangular (two-end indented tier strip)	3	−1.5
Triangular	3	−1
Chevron (pentagon)	2.68	−0.6
Circular (round, hexagon)	2.44	0

[a] Unpublished results of authors.

Mathematically, if the coefficient ratios of the first and second terms of two half-order equations approach each other, the curve will tend to approach a straight line. If this is the case, the average slope of the curve becomes a constant, and consequently K_M is a linear function of R. Actually, since $r = 0$, the coefficient ratios of Equations 18 and 20 are 0.5/4.6 and $-0.5\ p/(2.7p - 16.6)$, respectively, and, since p varies from 2.42 to 3, they approach each other. Figure 6 demonstrates that the curves for the various models of fused aromatic hydrocarbons approach the limiting slope after R becomes large.

$$\frac{dK_M}{dR} \cong \frac{4.6}{0.5} = 9.2 \tag{21}$$

or, after integration

$$K_M = 9.2\ R + \text{const.} \tag{22}$$

Furthermore, the nearly straight-line relationship of these curves can be seen by a linear plot in Figure 7. For simplicity, a boundary condition is imposed so that when $R = 0$, $K_M = 0$, and the integration constant in Equation 22 is zero. Therefore, for fused ring compounds of more than three rings, the following relation can be applied to yield apparently reliable results:

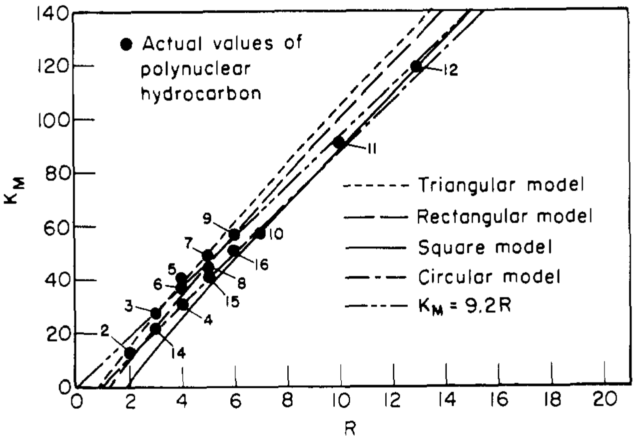

Figure 7. Relation of molar volume contraction and ring number

Key to identification of numbers in Table I

$$V_R = K_M/R = 9.2 \tag{23}$$

MODIFIED RING ANALYSIS OF AROMATIC AND MIXED AROMATIC-ALIPHATIC COMPOUNDS

On the basis of the above results, it is proposed that the following equations be used for substances containing condensed ring systems:

$$R = 0.11\ (9.9C + 3.1H + \ldots - M/\rho) \tag{24}$$

where molecular weight can be determined, and by

$$C/R = \frac{9.2}{9.9 + 3.1\ H/C + \ldots - \dfrac{1200}{\%C\rho}} \tag{25}$$

for substances where molecular weight cannot be determined.

The modified Equations 24 and 25 have been used to calculate the reciprocal of the ring condensation index for several asphaltenes prepared from crude oils of widely different geographic origin and for the two carbon blacks. The data in Table IV show that the values calculated by the modified Equation 25 are higher than those calculated by the van Krevelen Equation 6 and that they are in better agreement with the values determined by infrared, nuclear magnetic resonance, and x-ray, as described earlier in this article.

Many natural, macromolecular compounds of either mixed aromatic-aliphatic or naphthenic-aliphatic nature possess mesomorphic properties. Petroleum asphaltenes are mesomorphic, if the x-ray classification according to Herman's type of designation is followed (*3*). Since the densities of polynuclear hydrocarbons do not vary as much as those of the paraffins in the amorphous to crystalline region, it is safe to say that the derived relation is valid for mesomorphic substances.

The assumptions made in the development of the treatment in this article limit the application of the method to mesomorphic substances of high molecular weight where:

1. Heteroatoms—i.e., atoms other than carbon and hydrogen—are not major components.
2. Olefinic unsaturation is absent.
3. The number of rings is greater than one.
4. The rings are peri-condensed or fused.

The method does not provide for differentiation between naphthenic and aromatic ring systems in the condensed clusters.

Calculation of ring number by means of the modified equation is well supported by data in Tables I and V. The calculation requires only the density and the number of carbon, hydrogen, and heteroatoms as provided by the formula. The compounds in Table I are unsubstituted aromatic hydrocarbons containing condensed ring systems.

Table IV. Values for Reciprocal of Ring Condensation Index for Three Petroleum Asphaltenes and Two Carbon Blacks

Sample	ρ	H/C	O/C[a]	N/C	S/C	% C	C/R van Krevelen Eq. 6	C/R Modified Eq. 25[b]
Petroleum asphaltenes								
Langunillas (Western Venezuela)	1.158[c]	1.125	0.01425	0.0204	0.0214	84.2	3.46	6.24
Wafra (Kuwait-Saudi Arabia Neutral Territory; Middle East)	1.164[c]	1.184	0.01381	0.0107	0.0356	81.8	3.14	5.90
Baxterville (Mississippi)	1.172[c]	1.051	0.0150	0.0081	0.0249	84.5	3.62	6.19
Carbon blacks								
Royal Spectra	1.68[d]	0.348[e]	...	...	...	97.3[e]	2.13	2.54
Statex B	1.81[d]	0.270[e]	...	...	...	97.8[e]	2.06	2.32

[a] Oxygen by Unterzaucher method. [b] Graphical densimetric method (*16*) yields f_a values in substantial agreement with modified C/R values reported here. [c] Measured by helium displacement. [d] (*17*). [e] Approximated from Table II, assuming a condensed aromatic sheet.

Table V. Calculation of Ring Number for Compounds of Varying Structure and Elementary Composition

				Rings per Molecule	
Compound	Formula	M	ρ	Theoret. from formula	Modified Eq. 25
d-Tartaric acid	$C_4H_8O_6$	150	1.759 (*1*)	0	0
Hexachloroethane	C_2Cl_6	237	2.09 (*20*)	0	0
o-Chlorobenzoic acid	$C_7H_5ClO_2$	157	1.544 (*20*)	1	0.5
p-Hydroxybenzoic acid	$C_7H_6O_3$	138	1.46 (*20*)	1	0.5
Anthraquinone	$C_{14}H_8O_2$	208	1.43 (*20*)	3	2.8
1-Naphthylphenylmethane	$C_{17}H_{14}$	218	1.165 (*9*)	3	2.7
Papaverine	$C_{20}H_{21}NO_4$	339	1.337 (*11*)	3	2.8
Rosin	$C_{20}H_{29}O_2$	302	1.095 (*32*)	3	2.5
Laudanine	$C_{20}H_{25}NO_4$	243	1.26 (*20*)	3	2.1
α-Progesterone	$C_{21}H_{30}O_2$	314	1.166 (*20*)	4	4.2
20-Methylcholanthrene	$C_{21}H_{16}$	268	1.28 (*20*)	5	4.2
Strychnine	$C_{21}H_{22}N_2O_2$	334	1.359 (*11*)	5	4.5

The compounds in Table V in many instances contain heteroatoms and range from aliphatic to cyclic where aliphatic chains sometimes are attached to the rings. The good agreement between the calculated ring number and that indicated by the structural formula is evident. Finally, it is believed that this new relation is applicable to asphaltic fractions of crude oil and to the black, insoluble, organic fraction of ancient sedimentary rocks.

LITERATURE CITED

(1) Bailey, T., "Bailey's Chemists' Pocket Book," 20th ed., E. and F.N. Spon., London, 1948.

(2) Boer, J.H. de, *Trans. Faraday Soc.* **32**, 10 (1936).

(3) Brown, G.H., Shaw, W.G., *Chem. Revs.* **57**, 1049 (1957).

(4) Clar, E., Kelley, W., Robertson, J.M., Rossmann, M.G., *J. Chem. Soc.* **1956**, p. 3876.

(5) Coulson, C.A., Schaad, L.J., Burnelle, L., *in* "Proceedings of the Conference on Carbon," p. 27, University of Buffalo, Symposium Publication Division, Pergamon Press, New York, 1959.

(6) Donaldson, D.M., Robertson, J.M., *Proc. Roy. Soc. (London)* **A220**, 157 (1953).

(7) Donaldson, D.M., Robertson, J.M., White, J.G., *Ibid.*, **A220**, 311 (1953).

(8) Dryden, I.G.C., *Fuel* **37**, 444 (1958).

(9) Egloff, Gustav. "Physical Constants of Hydrocarbons," Vols. 4 and 5, Reinhold., New York, 1947.

(10) Gaylord, N.G., Mark, M.F., "Linear and Stereoregular Addition Polymers," Interscience., New York, 1959.

(11) Hodgman, C.D., Weast, R.C., Selby, S.M., "Handbook of Chemistry and Physics," 41st ed., Chemical Rubber Publishing Co., Cleveland, 1959.

(12) Kopp, H., Le Bas, G., in "Physical Chemistry," S. Glasstone, ed., 2nd ed., p. 524, Van Nostrand, New York, 1956.

(13) Krevelen, P.W., van, *Brennstoff. Chem.* **33**, 260 (1952).

(14) *Ibid.*, **34**, 167 (1953).

(15) Krevelen, P.W., van, Chermin, H.A.G., *Fuel* **33**, 79 (1954).

(16) Krevelen, P.W., van, Schuyer, J., "Coal Science," Elsevier., New York, 1957.

(17) Kuroda, H., *J. Colloid Sci.* **12**, 496 (1957).

(18) Lange, N.L., "Handbook of Chemistry," 9th ed., Handbook Publishers, Sandusky, Ohio, 1956.

(19) McIntoch, A.O., Robertson, J.M., Vand, V., *J. Chem. Soc.* **1959**, p. 1661.

(20) Merck & Co. Inc., Rahway, N. J., "Merck Index of Chemicals and Drugs," 6th ed., 1952.

(21) Montgomery, D.S., Boyd, M.L., *Anal. Chem.* **31**, 1290 (1959).

(22) Müller, A., *Proc. Roy. Soc. (London)* **A114**, 542 (1927).

(23) *Ibid.*, **A127**, 417 (1930).

(24) Nes, L. van, Westen, H.A. van, "Aspects of the Constitution of Mineral Oils," Elsevier., New York, 1951.

(25) Piper, S.H., Brown, D., Dyment, S., *J. Chem. Soc.* **127**, 2194 (1925).

(26) Robertson, J.M., *Ibid.*, **1947**, 358.

(27) Robertson, J.M., White, J.G., *Acta Cryst.* **2**, 233 (1949).

(28) Robertson, J.M., White, J.G., *J. Chem. Soc.* **1947**, 1001.

(29) Robertson, J.M., White, J.G., *Nature* **154**, 605 (1944).

(30) Roff. W.J., "Fibres, Plastics and Rubbers," Butterworths, London, 1956.

(31) Rossman, R.P., Smith, W.R., *Ind. Eng. Chem.* **35**, 972 (1943).

(32) Simonds, H.R., Weith, A.J., Bigelow, M.H., "Handbook of Plastics," 2nd ed., Van Nostrand, New York, 1949.

(33) Smith, D.C., *Ind. Eng. Chem.* **48**, 1161 (1956).

(34) Smith, E.E., Ohio State University, Bulle. **152**, 1 (1953).

(35) Traube, J., *Ber.* **28**, 2722 (1895).

(36) Vlugter, J.C., Waterman, H.I., Westen, H.A. van, *J. Inst. Petrol Technol.* **18**, 735 (1932).

(37) *Ibid.*, **21**, 661 (1935).

(38) White, J.G., *J. Chem. Soc.* **1948**, 1398.

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