Molecular Increment of Free Volume in Hydrocarbons, Fluorohydrocarbons, and Perfluorohydrocarbons

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MOLECULAR REFRACTION and molecular volume are intimately related (*11, 13, 20, 31, 34, 35, 56*). The differences and similarities which appear in correlating molecular refraction and molecular volume data for hydrocarbons lead to a reasonable basis for evaluating the volume occupied by hydrogen in hydrocarbons, and a more firm value for the molecular increment of free volume, which has been called the kinetic impact free volume. Molecular volume data for fluorinated and perfluorinated hydrocarbons confirm the value of this molecular increment of volume.

The difference between the molecular refraction and molecular volume of isomeric paraffins from the normal paraffin has been shown by Greenshields and Rossini (*15, 57*) to be related to the Weiner-Platt constants (*41*). There is a systematic relationship between these increments. Figure 1 illustrates graphically the relationship for isomeric hexanes, heptanes, and octanes. If there is a large increment from the normal for molecular volume, there is also a large increment for molecular refraction. Li and others (*36*) presented equations for molecular refraction and molecular volume of normal paraffins which are equivalent to:

$$R = 2.07879 + 4.64187N \qquad (1)$$

and

$$V = 29.33823 + 16.4841N + \frac{14.56329}{N-2} - \frac{4.56336}{(N-2)^2} \qquad (2)$$

where

R = molecular refraction at 25° C.
V = molecular volume at 25° C.
N = number of carbon atoms in the molecule

Molecular refraction is presented here as strictly additive in terms of CH_2 increments, whereas a measurable deviation from linearity is involved in the case of the molecular volume of a series of normal paraffins of increasing molecular weight. These equations differ from those presented by Li in that they are set up in terms of N, the total number of carbon atoms in the molecule, whereas Li used M, the number of carbon atoms attached to the end group. For the molecular volume of normal paraffins, the end group consists of one end CH_2 group plus the volume for two hydrogens and a molecular constant. We prefer to separate this end constant from the last CH_2 increment so that its magnitude can be clearly seen. Over the range from 20 to 40 carbon atoms and adjusting to 20° C., these equations are approximately

$$R = 2.09 + 4.64\,N \qquad (3)$$

and

$$V = 30.2 + 16.40N \qquad (4)$$

Equation 3 for the molecular refraction of normal paraffins can be compared with the equivalent refraction equation for average paraffins using Eisenlohr's constants for 20° C. (*11*).

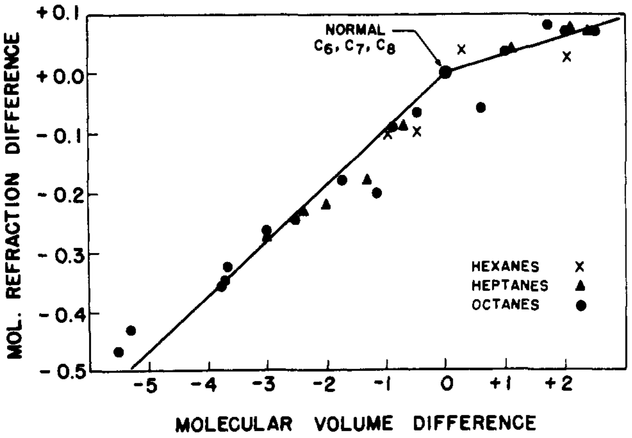

Figure 1. Relation between molecular volume and molecular refraction increments for isomers

$$R_a = 2.2 + 4.618\,N \qquad (5)$$

Equation 4 for the molecular volume of normal paraffins can be compared with the Kurtz and Lipkin's molecular volume equation (*29, 33*) for average paraffins at 20° C.

$$V_a = 31.2 + 16.28\,N \qquad (6)$$

Numerous other equations of similar type, but with slightly different form or constants have been presented by Huggins, Smittenberg, Calingaert, and others. These have been reviewed elsewhere (*15, 20, 31, 36*).

Consideration of the relative magnitudes of the CH_2 increments, the terminal constants, and their significance, is in order, since it brings out a fundamental difference between molecular refraction and molecular volume.

The terminal constant in refraction Equations 1, 3, and 5 can be interpreted as the molecular refraction of two hydrogens. Calculation of the molecular refraction of gaseous H_2 using Koch's data (*18, 19*) leads to a value of 2.232, which is reasonably close in magnitude to the constant in refraction Equations 3 and 5. Therefore, there can be little doubt that the constant in the refraction equations for normal or average paraffins is due to the two terminal hydrogens. Eisenlohr (*11*) subtracted the value 2.2 for two hydrogens from the value for the CH_2 increment to get his value for the refraction of carbon in organic compounds, which is 2.418.

Comparing the molecular volume equation with the molecular refraction equation, it is significant that the ratio of the CH_2 increments is roughly 3.5 to 1, whereas the ratio of the constants is about 14 to 1. In the molecular volume equation, the constant cannot be interpreted as the volume of two hydrogens, since it is nearly twice as large as the CH_2 increment.

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MOLECULAR INCREMENT OF VOLUME

For compounds at a temperature reasonably well below their boiling points—for example, at a reduced temperature of 0.5 or less up to seven carbon atoms, and 0.6 or less above seven carbon atoms—this constant is essentially independent of the number of carbon atoms or structures. It has, therefore, been possible (*29, 33*) to write a general molecular volume equation, which ignores isomer effects, as follows:

$$MV\ 20^\circ \text{ C. and 1 atm.} = 16.28n_1 + 13.15n_2 + 9.7n_3 - 6.2n_4 + 31.2 \quad (7)$$

where

n_1 = number of chain carbon atoms
n_2 = number of carbon atoms in rings
n_3 = number of carbon atoms at ring junctions
n_4 = number of double bonds
31.2 = terminal constant, or molecular increment of volume

This equation is set up in terms of the type of carbon atoms and the number of double bonds but does not specifically provide terms for carbon atoms and hydrogen atoms as such. This general equation has been found very useful (*9, 10, 28, 43, 44, 50*).

Since the end term, 31.2, in the molecular volume equation was found to be essentially independent of molecular weight and structure, but very sensitive to changes in temperature or pressure, it has been interpreted (*33*) as kinetic impact free volume, and given the symbol, K_5. This interpretation is entirely consistent with corresponding state theory (*26*).

The terminology to use for the term K_5 deserves comment. When dealing with normal paraffins it at first seems logical to interpret K_5 as end effect. However, the effect is large. Hence one would expect branched paraffins, with an additional end for each branch, to show progressive increase in volume with each additional end. However, we find that branched hydrocarbons may have either larger or smaller volumes than the normal compound, depending on the relative location of the branches (*20, 31*) The sum of the end effects for branched paraffins is almost constant, but it is easier to refer to a molecular increment of volume, especially since cyclic compounds, which have no ends in the ordinary sense, require about the same molecular volume increment.

The major difference between molecular refraction and molecular volume is that molecular refraction can be accounted for as the sum of atomic constants only, whereas in the case of molecular volume, there is a volume increment which is molar rather than atomic in its origin. This is the basic reason why the earlier attempts (*2, 8, 14*) to treat molecular volume at constant temperature and pressure on an atomic basis were relatively unsuccessful. This constant term in the molecular volume equation might include the volume of two hydrogens, but this volume increment for hydrogen has been difficult to evaluate, and therefore was not separately treated.

Simha and Hadden in studying hydrocarbons from the point of view of cell theory found a molecular volume increment of 26.8 ml. per gram mole for paraffins at 20° C. (*46*). Additional work by these authors (*47*) shows that for hydrocarbons containing rings, they obtain K_5 volumes nearer 30.

Many years ago (*52, 53*) Traube made a careful study of molecular volume of organic compounds in solution. He obtained the following constants for molecular volume of CH_2, C, hydrogen, and the molecular solution covolume at 15° C.: CH_2, 16.1 cc., C, 9.9 cc., H, 3.1 cc, and molecular solution covolume, 25.9 cc.

Traube's molecular solution covolume is very close in magnitude to Simha and Hadden's molecular volume increment K_5 for paraffins. Traube (*53*) gives data from which one can derive a coefficient of 0.12 ml. per ° C. for this covolume over the range 0° to 100° C. The corresponding coefficient based on our molecular volume data is 0.11 ml. per ° C. for the same temperature interval (*25*).

Considering the information so far presented, it seemed probable that the differences between our molecular increment of volume, that derived by Simha and Hadden for paraffins, and also Traube's molecular solution covolume might result from our not having evaluated the volume occupied by two hydrogens.

VOLUME OCCUPIED BY HYDROGEN IN HYDROCARBONS

One value for the volume of two hydrogens can be obtained assuming that all the volume change which occurs when a double bond is hydrogenated equals the volume of two hydrogens. This has been shown to average 6.2 ml. per gram mole (*24, 32*). However, the carbon-carbon double bond is 0.2 A. shorter than the carbon-carbon single bond (*23*).

This shortening corresponds to 2.5 ml. per gram mole. If allowance is made for the angle of the double bond with the long axis, the shortening of the molecule is 0.165 A., and the volume increment is 2.09 ml. per gram mole. Subtracting 2.09 from 6.2 (for the whole effect of removing two hydrogens and forming a double bond) leaves 4.1 as the volume of two hydrogens.

Another approach provides information in regard to this molecular increment of volume. A graph of molecular volume of the ring portion of naphthene molecules plotted against the number of carbon atoms in the ring has been shown to give a straight line (*22, 30*). The equation of this line is that molecular volume equals $13.15n_2 + 31.2$, where n_2 is the number of carbons in unfused rings. This equation is based on data for single-ring naphthenes and naphthenes containing two unfused rings per molecule. The former are of the C_nH_{2n} series and the latter C_nH_{2n-2}. Therefore, the slope of this line has built into it the increment for the loss of two hydrogens. At 5 or 6 carbon atoms, the correct value is obtained for one ring. Extrapolating back to 0 carbon atoms will lead to an increment (K_5) equal to the volume of two hydrogens plus the true molecular increment of free volume (kinetic impact free volume). This conclusion can be substantiated by comparing it with the corresponding graph for molecular refraction or molecular weight.

If the increment per CH_2 in rings (ΔC_R) can be accurately evaluated by substracting the volume of five-membered rings from the volume of six-membered rings, then one can extrapolate back to 0 carbon atoms using this slope. This should give the corrected kinetic impact free volume (corrected K_5) without the H_2 increment.

Values for the basic C_5 ring volume and basic C_6 ring volume, using the data of Li and others, are shown in Table I, along with the CH_2 increment and the corresponding corrected K_5—namely, 22.1 ml.

The volume occupied by two hydrogens calculated in this way is 9.1 ml. This is 2.9 ml. more than the value obtained from the paraffin-olefin increment (*32*).

A value can also be arrived at for the volume occupied by two hydrogens by using the data shown in Table II, part of which have already been published (*21, 30*). In this case the CH_2 increment (ΔC_R) comes out to be 14.1 and the value for two hydrogens, 4.4. Calculations of this sort (Table VI, *20*) lead to lower values for the CH_2 increment and for the volume of two hydrogens. The latter data include more compounds, but larger side chain corrections, so that the C_5 and C_6 ring values are not considered as good as those in Tables I and II.

Table I. Calculation of Volume Occupied by Hydrogen in Hydrocarbons Using Basic Ring Volumes (*36*)

No. Carbons in Basic Ring	Basic Ring Volume (*36*)	Corrected K_5[a]	2H[b]
6	110.53675	22.127	9.1
5	95.80176	22.127	9.1
	$14.73499 = \Delta C_R$		

[a] Basic ring volume − (n_2 × 14.735) = kinetic impact free volume. [b] Increment for 2 hydrogens = 31.2 − corrected K_5.

The value for two hydrogens obtained from the data of Li and others (*36, 57*) corresponds to the higher values obtained from the paraffin-olefin increment data; the data from Table II correpond to the lower increments obtained from the paraffin-olefin increment (*24*). The average, 6.75, is of the same order of magnitude as the average increment, 6.2, used for double bonds of all types based on comparison of the molecular volume of olefins and the corresponding saturated hydrocarbons (*32*). This increment varies appreciably with the structure of the molecule near the double bond (*24*). If the bond shortening correction (allowing for angle with the chain axis) is applied to the average olefin increment, then the value obtained, 4.1 ml., is nearer the low value, 4.4 (*23*).

These values are all of the same order of magnitude. The space occupied by two hydrogens is probably not absolutely constant, as indicated by the data for the difference between the molecular volume of olefins and the corresponding paraffins (*32, 24*). If the olefin increment is taken as the increment for two hydrogens, then the molecular increment of free volume should be corrected by this amount—that is, 31.2 − 6.2 = 25.0. If bond shortening correction is applied, two hydrogens occupy on the average approximately 4.1 ml. per gram mole. On this basis, the corrected molecular increment of free volume is 31.2 − 4.1 or 27.1. Based on normal paraffin data the corresponding value would be 1 ml. less, or 26.1. These values are close to the values shown on Table II. They are also close to the values for K_5 calculated by Simha and Hadden (*46*) for alkanes—namely, 26.8—and to Traube's value for molecular solution covolume, which at 20° C. is 26.5.

Simha and Hadden's more recent calculations (*47*) for cyclic compounds give values for K_5 which are near 30. They attribute the differences in K_5 to the fact that no allowance for end effect is made in their treatment. Simha and Hadden now regard the K_5 term as a complex function defined by their equation, rather than kinetic impact volume, but they are aware that some allowance needs to be made for end effect.

Based on the data now available, each hydrogen atom is assigned a value in hydrocarbons of 2.1 ml. per gram mole and the symbol K_6. The corrected molecular increment of free volume is assigned the symbol K_7 and is defined by the relation:

$$K_7 = K_5 - 2K_6 \text{ or } 31.2 - 4.2 = 27.0$$

The lower value of the corrected molecular increment of free volume (about 22), which would be obtained if the H_2 increment derived from the equation of Li (Table I) were used, can be regarded as a lower limit. The degree of agreement between the various methods of deriving the volume of two hydrogens in hydrocarbons is probably as good as should be expected.

The value of 27 ml. per gram mole for the corrected molecular increment of free volume K_7 (corrected kinetic impact free volume) at 20° C. confirms the order of magnetic of Simha's calculation of 26.8 for K_5 for paraffins.

Future experience will show whether or not the correction of the olefin-paraffin increment of 6.2 for the difference in length between C—C and C=C is worthwhile in deriving the volume of two hydrogens. It now seems probable that it is, and that 4.2 ml. is a good value for the volume of two hydrogens in hydrocarbons. Using this value for the volume of two hydrogens, the following equation can be derived:

$$\text{Mol. vol., } 20^\circ \text{ C., 1 atm.} = 12.08\,N_1 + 9.65\,N_2 + 6.9\,N_3 - 2.0\,N_4 + 2.1\,N_6 + Y + 27 \tag{8}$$

N_1 = number of chain carbons
N_2 = number of carbons in rings, but not at ring junctions
N_3 = number of carbon atoms at ring junctions
N_4 = number of double bonds
N_6 = number of hydrogen atoms
Ring Size Correction
Y = +1.4 for rings with 4 carbons
= +0.7 for rings with 5 carbons
= 0.0 for rings with 6 carbons
= −0.7 for rings with 7 carbons
= −1.4 for rings with 8 carbons
27 = corrected molecular increment of free volume (or corrected kinetic impact free volume), K_7.

This equation will give results numerically identical with Equation 7. The only advantage of Equation 8 over Equation 7 is that the volume of hydrogen is defined and the constant can be interpreted more precisely.

The variation in the volume assigned to carbon in different structural locations probably reflects the freedom of motion of carbon atoms in these various locations. The ring size correction is necessary to relate the hydrogen deficiency to the number of carbon atoms in each ring. The coefficient of N_2 in Equation 8 was obtained by adding ⅙ of 4.2 to 13.15 and substracting 4.2, the volume of two hydrogens. The addition of ⅙ of 4.2 is necessary so that the slope of the CH_2 increment over a range of six carbon atoms does not allow for the loss of two hydrogens, as is the case in Equation 7. Similar adjustment of Equation 4 for normal

Table II. Calculation of Volume Occupied by Two Hydrogens Using Data for Cyclopentanes and Cyclohexanes Containing 7 and 8 Carbon Atoms

No. C Atoms in Mol.	Av. Total Mol. Vol.				Ring Vol. A[a]		Increment for CH_2 in Rings[b]	M.I.F.V.[c]		Increment for 2 Hydrogens, 31.2 − M.I.F.V.	
	C_5 ring	No. Compd.	C_6 ring	No. Compd.	C_5	C_6	ΔC_R	C_5	C_6	Based on C_5 ring	Based on C_6 ring
7	129.82	6	127.51	1	97.26	111.33	14.07	26.76	26.73		
8	146.10	15	143.94	8	97.26	111.38	14.12	26.76	26.78		
						Av.	14.1	26.76	26.75	4.4	4.4

[a] Ring volume A (total mol. vol. − mol. vol. side chains) is total mol. vol., 16.28 N_1. [b] Ring vol. A for C_6 − ring vol. A for C_5. [c] Corrected molecular increment of free volume calculated by substracting 14.1 × number of carbon atoms from ring volume A.

paraffins in the range from C_{20} to C_{40} gives the following equation:

$$V = 12.2\,N_1 + 2.1\,N_6 + 26.0 \qquad (9)$$

For single saturated rings having four to eight carbon atoms in the ring and no side chain, 2.5 may be substracted from the molecular volume calculated with Equation 8. The slightly smaller molecular volume for the normal compounds and rings without chains may reflect better packing in the liquid with such molecules.

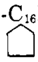
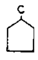
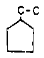
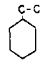
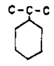
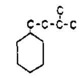
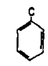
Equation 8 has been derived in such a way that it must give identical results with Equation 7. Therefore, it is not necessary to present an elaborate evaluation of Equation 8, since this has already been done for Equation 7 (*28, 29, 33, 50*).

MOLECULAR VOLUME OF FLUORINATED COMPOUNDS

As a further check on the reliability of the molecular increment of free volume (kinetic impact free volume) data (*4, 5, 7, 16, 38-40, 45, 48, 51, 58*) for fluorinated and perfluorinated compounds were studied. Table III shows that for 14 perfluorinated compounds the average increase in molecular volume of the perfluorinated compound over the corresponding hydrocarbon is 4.9 ml. per fluorine atom, which corresponds to 7.0 ml. actually occupied for fluorine atoms.

Starting with this increment per fluorine, an equation for the molecular volume of perfluorinated compounds was developed. This equation is:

Table III. Effect of Perfluorination on Molecular Volume of Hydrocarbons[a]

			Mol. Vol., Ml./G. Mol.				
Formula	Structure	Temp.,[b] ° C.	Corr. Hydrocarbon	Fluorocarbon[c]	ΔV	$\Delta V/F$	Ref. Fluorocarbon
C_5F_{12}	n-C_5F_{12}	20	115.2	173.1	57.9	4.83	(*38*)
		25	116.1	183	66.9	5.58	(*45*)
$(CF_3)_2CFC_2F_5$		20	116.4	177.8	61.4	5.12	(*38*)
C_6F_{14}	n-C_6F_{14}	25	131.6	204.8	73.2	5.23	(*38*)
		25	131.6	205	73.4	5.24	(*45*)
C_7F_{16}	n-C_7F_{16}	25	147.5	226.4	78.9	4.93	(*38*)
		25	147.5	227	79.5	4.97	(*45*)
		20	146.5	233.2	86.6	5.42	(*38*)
		20	146.5	227.4	80.8	5.05	(*38*)
C_8F_{18}	n-C_8F_{18}	20	162.6	253.2	90.6	5.04	(*38*)
		25	163.5	253	89.5	4.97	(*45*)
C_9F_{20}	n-C_9F_{20}	25	179.7	274.2	94.5	4.73	(*38*)
		25	179.7	271.3	91.6	4.58	(*38*)
		25	179.7	279	99.3	4.96	(*45*)
		20	178.7	271.2	92.5	4.62	(*38*)
$C_{16}F_{34}$	n-$C_{16}F_{34}$	20	262.7	453.0	190.3	5.60	(*4*)
C_5F_{10}		25	94.7	152	57.3	5.73	(*45*)
C_6F_{12}		20	108.1	178.2	70.1	5.84	(*38*)
		25	108.7	170	61.3	5.11	(*45*)
		20	112.4	166.7	54.3	4.53	(*38*)
C_7F_{14}		20	127.6	197.1	69.5	4.96	(*38*)
		25	128.3	196.2	67.9	4.85	(*38*)
		25	128.3	195	66.7	4.76	(*45*)
		20	128.1	197.7	69.6	4.97	(*38*)
		20	128.1	199.4	71.3	5.09	(*38*)
		25	128.8	198	69.2	4.94	(*45*)
		20	130.1	198.2	68.1	4.86	(*38*)
C_8F_{16}		25	143.1	219.1	76.0	4.75	(*38*)
		25	137.9	218.7	83.8	5.24	(*38*)
C_9F_{18}		20	159.8	238.4	78.6	4.36	(*38*)
$C_{11}F_{22}$		20	192.8	289.7	96.9	4.40	(*38*)
C_6F_6		25	89.4	115	25.6	4.27	(*45*)
C_7F_8		25	106.8	142	35.2	4.40	(*45*)
					Av. =	4.9	

[a] References for hydrocarbons (*57*), except $C_{16}F_{34}$ (*4*). [b] Data for 20° and 25° do not indicate clear effect of temperature on increment; average increment used. [c] Two sets of data for compound at same temperature indicate work of two investigators.

Mol. vol., 20° C., perfluorinated hydrocarbon

$$= 12.08\,N_1 + 9.65\,N_2 + 4.2\,N_3 - 3.34\,N_4 - 3.0\,N_B + 7.0\,N_F + Y + 27) \qquad (10)$$

N_1, N_2, N_3, and N_4 have the same meaning as in Equation 8
N_B = number of alkyl branches on rings or chains
N_F = number of fluorine atoms
Ring size correction
Y = +2.33 for ring with 5 carbons
= 0.0 for ring with 6 carbons
= −2.33 for ring with 7 carbons
= −4.66 for ring with 8 carbons
27 = corrected molecular increment of free volume, K_7

The numerical value for carbon at ring junctions in perfluorinated compounds was adjusted to obtain reasonably good agreement with the data as shown in Table IV. The fluorine atoms being larger than the hydrogen atoms probably results in crowding at the ring junction, and hence a decrease in volume of about 2.7 ml. for ring junction carbon. This crowding also requires a correction of −3.0 ml. for each alkyl branch on a chain or ring. The double bond value was adjusted using a shortening of the bond of 0.2A. (linear shortening of the chain of 0.165A.) and using the cross section of the normal perfluorinated chain.

Equation 10 was tested with data for 66 perfluorinated compounds with results as shown in Table V. The deviation of the average, which measures systematic deviations, shows little systematic deviation for paraffins, naphthenes, or fused naphthenes. The standard deviation for all 66 compounds is a little less than 5 ml. Considering the difficulties of preparing and purifying perfluorinated compounds, we believe this degree of agreement is good.

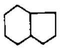
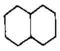
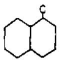
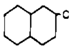
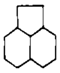
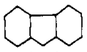
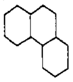
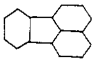
The corrected molecular increment of volume corresponding to the deviation of the average is shown in the last column. In other words, if the value shown in the last column had been used instead of 27.0, the deviation of the average would have been zero in each case.

The data in Table V show that the corrected molecular increment of volume (K_7) for perfluorinated hydrocarbons averages out very well in the vicinity of 27 ml., but that the value, as calculated by substraction, may vary between 22 and 32 ml.

Molecular volumes for partly fluorinated hydrocarbons were calculated using the increment +4.9 ml. per fluorine atom over the volume of the corresponding hydrocarbon, or using the appropriate terms from the equation for hydrocarbons (Equation 8) or perfluorinated hydrocarbons (Equation 10). For 225 partly fluorinated compounds having a wide variety of structures, the deviation of the average is +2.2 and the standard deviation 3.2. Supporting data are filed with the American Documentation Institute (*27*).

These data indicate that the corrected molecular increment of volume of 27 ml. applies with reasonable accuracy to hydrocarbons, fluorinated hydrocarbons, and perfluorinated hydrocarbons. This is strong evidence of the kinetic origin of this corrected molecular volume increment, K_7.

Table IV. Coefficient for Ring Junction Carbon Atoms

Formula	Structure	Exptl. Mol. Vol., 20° C.	Mol. Vol.[b] Calcd.	Diff.	Corresponding K_7
C_9F_{16}		218.7	217.3	−1.4	28.4
$C_{10}F_{18}$		240.7[c]	238.6	−2.1	29.1
		237.5	238.6	+1.1	25.9
$C_{11}F_{20}$		261.3	264.7	+3.4	26.6
		260.9	264.7	+3.8	26.2
$C_{12}F_{20}$		263.6	263.3	−0.3	27.3
$C_{13}F_{22}$		289.7	287.0	−2.7	29.7
$C_{14}F_{24}$		309.0	308.3	−0.7	27.7
$C_{16}F_{26}$		331.1	333.0	−0.1	27.1
			Av.	−0.56	27.6

[a] Data (*38*). [b] Using Equation 10. [c] Two sets of data for compound at same temperature indicate work of two investigators.

MOLECULAR REFRACTION OF HYDROCARBONS

With regard to molecular refraction, the Eisenlohr constants (*11, 20*) have been widely used and generally accepted for many years. Occasional efforts have been made to improve on these general constants (*54, 55*), but the

Table V. Agreement for Molecular Volume of Perfluorinated Hydrocarbons at 20° C.[a]

Type of Compd.	Range of Carbon Atoms	No. of Compd.	Deviation of Av. Ml.[b]	Standard Dev., Ml.	Cor. Mol. Increment of Vol. K_7
Perfluorinated paraffins[c]	C_5-C_{16}	25	−0.58	5.7	27.6
Perfluorinated naphthenes[d] nonfused (5 and 6 numbered monocyclics only)	C_5-C_{11}	28	+0.19	4.1	26.8
Perfluorinated naphthenes, fused[e]	C_9-C_{16}	8	−0.56	2.1	27.6
Perfluorinated aromatics, benzene	...	1	+1.9[f]	...	25.1
toluene	...	1	−2.3[f]	...	30.3
Perfluorinated olefins					
	...	1	−4.6[f]	...	31.6
C=C—C=C—C=C	...	1	+0.9[f]	...	26.1
All		66	−0.36	4.53	27.4

[a] Data from (*5, 38, 39, 40, 45, 48, 51*). [b] Deviation of average = sum of differences taking sign into account, divided by number of data. [c] Includes 4 branched paraffins and 21 normal compounds. Complete data filed (*27*). [d] Includes perfluorocyclopentane and cyclohexane and derivatives having up to three alkyl groups on ring. Complete data filed (*27*). [e] See Table IV. [f] Deviation for one compound only.

revised values proposed for the atomic constants have not had sufficient advantage over Eisenlohr's values to gain general acceptance. In view of the good data now available (*9, 10, 42, 4, 57*), it appeared worthwhile to develop equations for molecular refraction similar in form to Equations 7 and 8 for molecular volume, to see if there might be any advantage. Chances of any significant improvement were small, but direct comparison of the equations in corresponding form might yield some additional information. Equations 11 and 12 for molecular refraction correspond to Equations 7 and 8 for molecular volume.

$$\text{Mole refraction, } 20^\circ\text{ C., 1 atm.} = R_1N_1 + 4.25\,N_2 + 3.80\,N_3 - 0.40\,N_4 + 1.40\,N_5 + 2.1 \qquad (11)$$

$R_1 = 4.64$ if any alkyl side chain in the molecule contains a single unbranched alkyl chain of 6 or more carbon atoms.
$= 4.618$ if there is no straight alkyl chain at 6 or more carbon atoms
N_1 = chain carbons
N_2 = ring carbons not at ring junctions
N_3 = ring junction carbons
N_4 = double bonds
N_5 = pairs of double bonds requiring conjugation correction. Examples:
Benzene, zero correction
Butadiene, +1.4 correction
Styrene, +1.4 correction
Naphthalene, +2.8 correction
2.1 = terminal refraction constant, refraction of 2 H

$$\text{Mol. refraction } 20^\circ\text{ C., 1 atm.} = R_1N_1 + 2.5\,N_2 + 2.4\,N_3 + 1.70\,N_4 + 1.40\,N_5 + 1.05\,N_6 + Y \qquad (12)$$

$R_1 = 2.54$ if any alkyl side chain in the molecule contains a single unbranched alkyl chain of 6 or more carbon atoms.
$R_1 = 2.518$ if there is no straight alkyl chain of 6 or more carbon atoms.

N_1, N_2, N_3, N_4, and N_5 have same significance as in Equation 11
N_6 = number of hydrogen atoms in the molecule
Ring size correction
$Y = +0.7$, for rings with 4 carbons
$= +0.35$, for rings with 5 carbons
$= +0.00$, for rings with 6 carbons
$= -0.35$ for rings with 7 carbons
$= -0.70$, for rings with 8 carbons

Equations 11 and 12 give numerically identical results. The tabular data developed in deriving Equations 11 and 12, and comparing them with the Eisenlohr constants, are documented (*27*). Equations 11 and 12 showed better agreement with API 44 data than the Eisenlohr constants because of the large number of data for long-chain normal alkyl compounds in the API 44 tables. On the other hand, the agreement with API 42 data, especially for fused ring structures, indicated that original Eisenlohr constants (1.10 for hydrogen, 2.418 for carbon, and +1.73 for a double bond) were a little better, except where conjugated double bonds were involved (*27*). Equations 11 and 12 also agreed better with the data of Stabley (*49*) and Jaffrey (*17*) for derivatives of cyclopropane. For general use, the Eisenlohr constants are still the best, if one general and relatively simple set of constants is used for figuring molecular refraction of a wide variety of hydrocarbons. In considering the constants in Equation 12, Bruhl in 1891 (*6*) proposed the value 2.50 for carbon and 1.05 for hydrogen.

More precise specialized equations for molecular refraction can be developed, as been done by Rossini and others, for particular types of structures (*15, 36, 42, 57*). This reappraisal of the Eisenlohr constants relative to Equations such as 11 and 12 is pertinent because it confirms the belief that molecular refraction can properly be considered additive on an atomic and structural basis, without any molecular constant.

The conjugation constant is a useful addition to the constants for the calculation of molecular refraction. A summary of supporting data is given in Table VI. Detailed data are on file (*27*). The fact that both double bonds in the second ring of naphthalene require the conjugation correction is significant in considering the fundamental difference between the first and second rings in naphthalene.

Table VI. Plus Deviations of Molecular Refraction for Compounds Containing Conjugated Double Bonds

Type	No. of Compd.	Av. Diff. of Exptl. MR from Formula Without Conjugation Factor[a]	Diff. per Conjugated Double Bond	Ref.
Diolefins (noncyclic)	9	1.38	1.38	(*57*)
Styrenes	6	1.28	1.28	(*57*)
Dihydronaphthalene	1	1.51	1.51	(*1*)
Alkylnaphthalenes C_{11} and C_{12}	8	2.75	1.38	(*57*)
Normal α-alkyl naphthalenes	12	2.71	1.36	(*57*)
Normal β-alkyl naphthalenes	11	3.08	1.54	(*57*)
α- and β-alkyl naphthalenes	15	3.18	1.59	(*12*)
	62			
		Av. by compounds	1.44	
		Av. by group	1.43	

[a] Using $\left.\begin{matrix}4.618\\4.64\end{matrix}\right\}N_1 + 4.25\,N_2 + 3.80\,N_3 - 0.40\,N_4 + 2.1$.
(4.64 used for normal alkyl chains of 6 or more carbon atoms).

CALCULATED PROPERTIES OF SEGMENTS

Since we now have available increments for molecular volume and molecular refraction for structural segments of hydrocarbon molecules, it is possible to calculate the apparent local properties of these segments, such as local density and local refractive index. For example, to get the local density of the CH_2 group in chains, we divide the weight of CH_2 by the volume increment for CH_2. Similarly to get the local refractive index we divide the refraction increment for CH_2 by the volume for CH_2, obtaining the Lorentz (*37*) function $(n^2 - 1)/(n^2 + 2)$ which is then solved for n by using interpolation tables.

These calculations have been made (*27*) and are helpful in giving an understanding of the relation between the molecular volume and molecular refraction equations. They are not included in the present publication, since a detailed discussion of all of them at this time does not seem necessary.

The corrected molecular increment of free volume K_7, however, deserves special attention, since it has the same numerical value, at any one specified temperature and pressure, for hydrocarbons, fluorinated hydrocarbons, and perfluorinated hydrocarbons having a wide range of molecular weight and structure. It is part of what Bondi (*3*) calls empty volume. In 1954 we pointed out (*33*) that molecular kinetic energy is constant at a specified temperature and pressure. It is therefore reasonable to interpret the molecular increment of volume as being of kinetic origin. At that time, we did not know how to correct for the value of the terminal hydrogen or fluorine atoms. The data now available make it clear that the corrected molecular increment of free volume K_7, which by our hypothesis is of kinetic origin, has a value of 27.0 ml. per gram mole for hydrocarbons, fluorohydrocarbons, and perfluorohydrocarbons. This conclusion is entirely consistent with corresponding states relationships (*26*).

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