

(1) The van der Waals volume : V_W = the volume of the space occupied by the "van der Waals spheres" of one mole of molecules.

(2) The zero-point volume : V_0 = the volume of the space occupied by one mole of hypothetical liquid at 0°K.

(3) The void volume : $V_V = V_0 - V_W$.

(4) The expansion volume : $V_E = V_T - V_0$. V_T ; molal volume of liquid at $T^\circ\text{K}$.

From the above definitions we have Eq. (1) for molal volume and our first aim is to find out the relative importance of the three contributions to V_T .

$$V_T = V_W + V_V + V_E. \quad (1)$$

Estimation of V_W and V_0

There have been a few attempts to estimate the van der Waals volumes of organic and inorganic compounds. Recently Bondi³⁾ published tables of group contributions to the van der Waals volume of organic compounds calculated from "the most reliable X-ray diffraction data". His work includes a number of elements and functional groups and enables us to calculate the van der Waals volumes of various kinds of organic molecules.

It is proposed by Miller^{4,5)} that the zero-point volume can be obtained by Eq. (2),

$$V_0 = \left(\frac{ab}{\epsilon_0} \right)^{1/2}, \quad (2)$$

where a and b are the van der Waals constants, *i. e.*, $a = 27R^2T_c^3/64P_c$ and $b = RT_c/8P_c$ in terms of the critical constants, and ϵ_0 is the vaporization energy for the hypothetical liquid at 0°K which, in turn, can be obtained from the B constant of the Frost-Kalkwarf vapor pressure equation, (3), by Eq. (4)⁶⁾.

$$\log P = A + \frac{B}{T} + C \log T + \dots \quad (3)$$

$$\epsilon_0 = -2.3RB. \quad (4)$$

For n -alkanes the values of V_0 thus obtained are not only in good agreement with the values by Doolittle⁷⁾, Eq. (5), but also consistent with Eq. (6)⁸⁾,

$$V_0 = Me^{10/M}, \quad M: \text{molecular weight} \quad (5)$$

$$V_0 = \left(\frac{P_c V_c}{RT_c} \right) V_c, \quad (6)$$

and Miller claims that the Eqs. (2), (4) and (6) are applicable "to a wide variety of polar and non-polar, organic and inorganic liquids, where hydrogen bonding is absent". Table 1 lists the zero-point volumes of saturated hydrocarbons obtained by several methods along with the molal and the van der Waals volumes. The values for olefinic and naphthenic hydrocarbons are given in Table 2. Obviously

3) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964)

4) A. A. Miller, *ibid.*, **69**, 3190 (1965)

5) A. A. Miller, *J. Polymer Sci. A-2*, **4**, 415 (1966)

6) A. A. Miller, *J. Phys. Chem.*, **68**, 3900 (1964)

7) A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951)

8) A. P. Mathews, *J. Phys. Chem.*, **20**, 554 (1916)

Table 1 Volume properties of saturated hydrocarbons (ml/mole)

Compound	$V_T^a)$	$V_W^b)$	V_0			
			c)	d)	e)	f)
Methane	—	17.1	30.1	28.6	—	—
Ethane	—	27.3	42.0	42.1	42.0	—
Propane	89.5 ^{g)}	37.6	55.7	55.3	55.4	—
<i>n</i> -Butane	101.5 ^{g)}	47.8	69.0	69.9	69.1	—
<i>n</i> -Pentane	116.1	58.0	82.9	83.6	83.0	82.4
2-Methylbutane	117.4	58.0	—	82.5	—	83.1
2,2-Dimethylpropane	123.3	58.0	82.5	81.5	—	—
<i>n</i> -Hexane	131.6	68.3	96.5	97.2	96.8	95.0
2,2-Dimethylbutane	133.7	68.3	—	98.5	—	—
2,3-Dimethylbutane	131.2	68.2	95.3 ^{h)}	96.5	—	—
<i>n</i> -Heptane	147.5	78.5	110	111	111	—
2,3-Dimethylpentane	145.0	78.5	—	109	—	—
2,4-Dimethylpentane	150.0	78.5	—	113	—	—
<i>n</i> -Octane	163.5	88.7	123	126	125	125

a) Densities (25°C) from Refs. 9 and 10 b) Ref. 3 c) Eq. (2), *a*, *b* from Ref. 11 and *B* from Ref. 12 d) Eq. (6), critical properties from Ref. 13 e) Eq. (5) f) Ref. 8, by $d_1 - d_v = C''(T_c - T)^{1/3}$ g) At saturation pressure h) *a*, *b* calculated from the critical properties¹³⁾

Table 2 Volume properties of olefinic and naphthenic hydrocarbons (ml/mole)

Compound	$V_T^a)$	$V_W^b)$	V_0	
			c)	d)
Propene	83.3 ^{e)}	34.1	50.9 ^{f)}	49.9 ^{g)}
1-Butene	95.3 ^{e)}	44.3	64.4 ^{f)}	66.4 ^{g)}
2-Methylpropene	95.5 ^{e)}	44.3	64.5 ^{f)}	65.8 ^{g)}
1-Pentene	110.4	54.5	79.0 ^{f)}	78.0 ^{h)}
1-Hexene	125.9	64.8	92.8 ^{f)}	91.2 ^{h)}
1-Heptene	141.7	75.0	107 ^{f)}	104 ^{h)}
1-Octene	157.9	85.2	120 ^{f)}	116 ^{h)}
1-Dodecene	223.0	126.2	173 ^{f)}	158 ^{g)}
Cyclopentane	94.7	50.0	69.9 ⁱ⁾	71.6 ^{j)}
Cyclohexane	108.7	60.2	82.3 ⁱ⁾	83.8 ^{j)}
Cycloheptane	121.2	70.5	94.9 ⁱ⁾	94.8 ^{k)}

a) Densities (25°C) from Ref. 10 b) Ref. 3 c) Eq. (2) d) Eq. (6) e) At saturation pressure f) *a*, *b* from Ref. 14 or calculated by the method in Ref. 14, *B* from Ref. 15 g) Critical properties from Ref. 13 h) Critical properties calculated as described in Ref. 14 i) *a*, *b* from Ref. 16, *B* from Ref. 17 j) Critical properties from Ref. 16 (observed value) k) Critical properties from Ref. 16 (calculated value)