

Table 3 Volume properties of hydrocarbons (ml/mole)

Compound	$V_T^{a)}$	V_W	$V_V^{b)}$	$V_E^{b)}$
<i>n</i> -Pentane	116.1	58.0	24.9	33.2
2,2-Dimethylpropane	123.3	58.0	24.5	40.8
<i>n</i> -Hexane	131.6	68.3	28.2	35.1
2,3-Dimethylbutane	131.2	68.2	27.1	35.9
<i>n</i> -Heptane	147.5	78.5	31.5	37.5
<i>n</i> -Octane	163.5	88.7	34.5	40.3
1-Pentene	110.4	54.5	24.5	31.4
1-Hexene	125.9	64.8	28.0	33.1
1-Heptene	141.7	75.0	31.7	35.0

a) At 25°C

b) From V_0 by Eq. (2)

the agreements between the V_0 values derived by different methods are not excellent in higher hydrocarbons. However, they still provide very useful information for our purposes. Table 3 shows V_V and V_E values for several compounds calculated from the values in Tables 1 and 2¹⁸⁾. It can be seen clearly that the van der Waals volume is only about 50–60% of the macroscopic volume at 25°C in those compounds, and about 20–30% is the expansion volume showing the vigorous thermal motions and continuous collisions of molecules¹⁹⁾. It is also important to point out the role of the void volume. It consists of about 20–22% of the macroscopic volume.

The dependence of the void and the expansion volumes on pressure must become important when we deal with the systems under high pressure. It is a difficult task to estimate the compressibility of the hypothetical liquid at 0°K. Probably the most reasonable approach to this problem is the one proposed by Haward²¹⁾. He tried to apply the van der Waals equation to the liquid under high pressure and found the necessity to assign a finite pressure independent isothermal compressibility to the parameter, b_0 , which is equal to our V_0 . From the viscosity measurements at high pressures a

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- 11) G. Thodos, *A. I. Ch. E. J.*, **1**, 168 (1955)
- 12) N. E. Sondak and G. Thodos, *ibid.*, **2**, 347 (1956)
- 13) K. A. Kobe and R. E. Lynn, *Chem. Rev.*, **52**, 117 (1953)
- 14) G. Thodos, *A. I. Ch. E. J.*, **1**, 165 (1955)
- 15) C. H. Smith and G. Thodos, *ibid.*, **6**, 569 (1960)
- 16) G. Thodos, *ibid.*, **2**, 508 (1956)
- 17) G. J. Pasek and G. Thodos, *J. Chem. Eng. Data*, **7**, 21 (1962)
- 18) Although the values of V_V and V_E are given down to the fractions of one millilitre in the following tables, it does not necessarily mean that the authors claim the accuracy of the estimation better than ± 0.5 ml/mole.
- 19) The van der Waals volume change with the temperature²⁰⁾ is neglected in our discussion.
- 20) Ref. 2, p. 38
- 21) R. N. Haward, *Trans. Faraday Soc.*, **62**, 828 (1966)

similar conclusion was reached^{22,23}. The value of $4.5 \times 10^{-6} \text{ atm}^{-1}$ was obtained for *n*-octane by Haward²¹. Later the same author gets $8.1 \times 10^{-6} \text{ atm}^{-1}$ from the internal pressure change with temperature²⁴. In considering the accuracy of our zero-point volumes it may be good enough to assume that the zero-point volumes of *n*-hexane, heptane and octane have the compressibility of $5 \times 10^{-6} \text{ atm}^{-1}$. The volume properties of these hydrocarbons at 25°C under pressure are given in Table 4.

Table 4 Volume properties of hydrocarbons under pressure^{a)} (ml/mole)

<i>P</i> , atm	<i>n</i> -Hexane $V_W=68.3$			<i>n</i> -Heptane $V_W=78.5$			<i>n</i> -Octane $V_W=88.7$		
	$V_T^{b)}$	$V_V^{c)}$	$V_E^{b)}$	$V_T^{b)}$	$V_V^{c)}$	$V_E^{b)}$	$V_T^{b)}$	$V_V^{c)}$	$V_E^{b)}$
1	131.6	28.2	35.1	147.5	31.5	37.5	163.5	34.5	40.3
1,000	119.2	27.7	23.2	134.6	30.9	25.2	150.8	33.9	28.2
2,000	113.1	27.2	17.6	128.0	30.4	19.1	143.9	33.3	21.9
3,000	109.0	26.8	13.9	123.6	29.8	15.3	139.1	32.7	17.7
4,000	105.9	26.3	11.3	120.2	29.3	12.4	135.5	32.0	14.8
5,000	103.5	25.8	9.4	117.5	28.7	10.3	132.6	31.4	12.5

a) Densities from Ref. 25 b) At 25°C c) See text

All of the compression of the zero-point volume is attributed to the void volume. In spite of these rough approximations Table 4 reveals an important and fundamental fact. The expansion volume decreases very rapidly during the initial compression. At 2,000 atm it is already 1/2 of the value at 1 atm and in that pressure range the zero-point volume compression is practically negligible compared with the expansion volume decrease. However, the former contribution will become substantial above 5,000 atm. By extrapolating the plot of $\log V_E$ against pressure it seems that the zero-point volume compression will be as large as the expansion volume compression at about 8,000 atm. Bondi²⁶ has pointed out that about 65,000 atm is required to "squeeze out of all of the empty space in *n*-heptane".

From the examples given so far it is predictable that the void and the expansion volumes play important roles in the determination of reaction and activation volumes under usual conditions.

Reaction volume

In his review, Hamann²⁷ points out the following for the reactions between nearly nonpolar molecules. "(a) The reactions which involve the formation of new carbon-carbon covalent bonds..... are all accompanied by substantial contractions. (c) Reactions in which no new carbon-carbon bonds are formed occur with relatively small volume changes." Several examples for hypothetical reactions are given in Table 5. It is quite obvious from Table 5 that the van der Waals

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25) H. E. Eduljee, D. M. Newitt and K. E. Weale, *J. Chem. Soc.*, 3086 (1951)

26) A. Bondi, *J. Phys. Chem.*, **58**, 929 (1954)

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