Table 5   Volume changes for pure liquid reactions at 25°C and 1 atm   (ml/mole)

Reaction	ΔV_T	ΔV_W	ΔV_V[a]	ΔV_E[a]
2 (Propene) $\longrightarrow$ 1-Hexene	−40.7	−3.4	−5.6	−31.7
2(1-Butene) $\longrightarrow$ 1-Octene	−32.7	−3.4	−5.2	−24.1
2 (1-Hexene) $\longrightarrow$ 1-Dodecene	−28.8	−3.4	−8.9	−16.5
1-Pentene $\longrightarrow$ Cyclopentane	−15.7	−4.5	−4.6	− 6.6
1-Hexene $\longrightarrow$ Cyclohexane	−17.2	−4.5	−5.9	− 6.7
1-Heptene $\longrightarrow$ Cycloheptane	−20.5	−4.5	−7.3	− 8.7
n-Pentane $\longrightarrow$ 2,2-Dimethylpropane	+ 7.2	−0.0	−0.4	+ 7.6
n-Hexane $\longrightarrow$ 2,3-Dimethylbutane	− 0.4	−0.0	−1.1	+ 0.8

a) From V_0 by Eq. (2)

volume change constitutes only a small portion ($<15\%$) of the total volume change in the dimerization of olefins.   Even in the cyclization which is accompanied by no molecular weight change, ΔV_W is a minor factor.   These results clearly demonstrate the importance of the void volume and the expansion volume.   Hamann[27] tried to estimate ΔV_T on the molecular basis by means of the cylindrical model and obtained -16 ml/mole for the dimerizations.   He concludes, in the review, "On a molecular scale these effects arise from the large differences between the van der Waals radii and their covalent radii."[28]   However in the light of the present results it seems to be reasonable to conclude that the major part of ΔV_T arises from the void and/or the expansion volume changes at least for the nonpolar reactants in pure state[31].   Considering the uncertainties in the estimation of V_0, it might be unreasonable to elaborate the discussion further on the basis of the data listed in Table 5.   However it may be allowed to point out that ΔV_E must be a function of the external degrees of freedom and, in pure liquid reactions, of the internal pressure of the reactant and the product from the definition of V_E[21].

Before we proceed to the discussion about solution, it seems to be worthwhile to take a look at an interesting model provided by Hamann[29].

"Consider the dimerization of a simple molecule A to A_2.   And suppose that both A and A_2 have the shape of sausages ········· and have the same cross-sectional radii r.   Also suppose that the van der Waals volume of A_2 is exactly twice that of A, so that $\Delta V_W=0$.   Finally, suppose that the molecules are at zero temperature and in a close-packed arrangement in which 'strings' of sausages are aligned parallel and in contact in the x,z plane ········· and are stacked vertically in a hexagonal close-packed array in the y direction" as depicted in Figs. 1 a and b.   The van der Waals volumes and the total volumes are given by Eqs. (7), (8) and (9).

28) He has pointed out later[29] that the value obtained by the cylindrical model includes ΔV_V inherently.   It must be also mentioned here that the late Gonikberg[30] pointed out the importance of "free volume" change in activation volumes. However he has never tried to estimate its magnitude.

29) Private communication

30) M. G. Gonikberg, "Chemical Equilibria and Reaction Rates at High Pressures", Moscow (1969), Japanese translation by Y. Ogo, Nikkan Kogyo Shinbunsha, Tokyo (1972)

31) In the following reactions, ΔV_W seems to be a major contribution to ΔV_T. 1-Hexyne→Cyclohexene, 1-Pentyne→Cyclopentene.
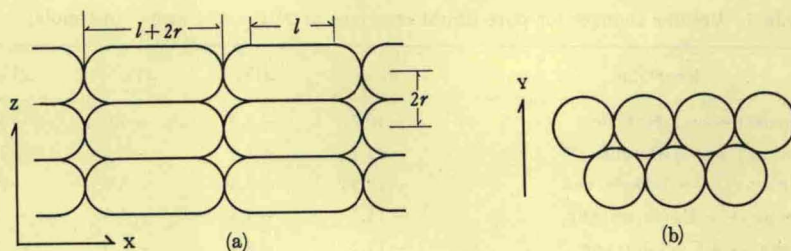
Fig. 1   A hypothetical liquid, A, at 0°K[29]

$$V_W(A) = \frac{1}{2}V_W(A_2) = \pi\left(l + \frac{4r}{3}\right)r^2 N_0, \tag{7}$$

$$V_T(A) = V_0(A) = 2\sqrt{3}\,(l + 2r)r^2 N_0, \tag{8}$$

$$V_T(A_2) = V_0(A_2) = 2\sqrt{3}\left(2l + \frac{10r}{3}\right)r^2 N_0. \tag{9}$$

N_0 : Avogadro's number

Suppose $l=6$Å and $r=2$Å, then we obtain,

$$V_W(A) = \frac{1}{2}V_W(A_2) = 65.59 \text{ m}l/\text{mole}, \tag{10}$$

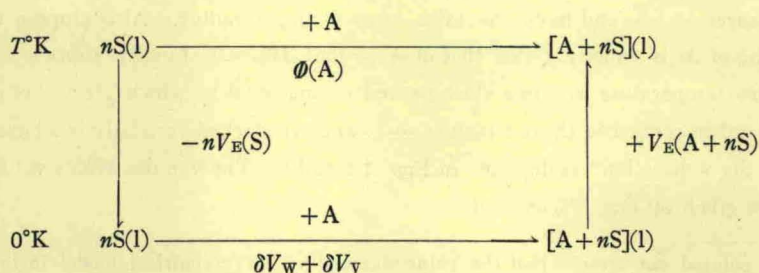$$V_T(A) = 83.45 \text{ m}l/\text{mole}, \tag{11}$$

$$V_T(A_2) = 155.77 \text{ m}l/\text{mole}, \tag{12}$$

$$\Delta V_T = \Delta V_0 = \Delta V_V = -11.13 \text{ m}l/\text{mole (for } 2A \rightarrow A_2). \tag{13}$$

This model demonstrates the importance of the void volume elegantly.

Partial molal volume and solution reactions

So far we have limited our discussion to pure liquid reactions.   In order to proceed to solution reactions it is necessary to understand the physical meaning of partial molal volume.   For this purpose it might be beneficial to use a cycle shown below, where A and S stand for one mole of solute and

$$
\begin{array}{ccc}
T°K & nS(l) \xrightarrow[\varnothing(A)]{+A} & [A+nS](l) \\[2em]
& \Big\downarrow{-nV_E(S)} & \Big\uparrow{+V_E(A+nS)} \\[2em]
0°K & nS(l) \xrightarrow[\delta V_W + \delta V_V]{+A} & [A+nS](l)
\end{array}
$$

solvent respectively and n is a number of mole of the solvent which is large enough to satisfy the condition of infinite dilution.   The molal volume of A, $\varnothing(A)$, is given by Eq. (14) and it is converted to Eq. (15),