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"VOID" AND "EXPANSION" VOLUME CONTRIBUTIONS TO REACTION AND ACTIVATION VOLUMES OF NEARLY NONPOLAR REACTIONS

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The reaction volume, ΔV, (and the activation volume, $\Delta V^{\neq}$) of nearly nonpolar reactions are divided into three terms: i) van der Waals volume change, ΔV_W, ii) void volume change, ΔV_V and iii) expansion volume change, ΔV_E. Each contribution is estimated by means of Bondi's V_W, Miller's V_0 (volume of the hypothetical liquid at 0°K) and the known densities of hydrocarbons for the reactions of pure liquids. Unexpectedly the results clearly indicate that ΔV_W is a rather minor factor.

Introduction

There is one well-known but very often overlooked fact about liquid, *i. e.*, about one half of the volume is empty. It is easily forgotten especially when we use bulk properties, for instance, dielectric constant. Although the continuum model of solvent is quite often successful[1], it fails also quite often to reproduce the observed phenomena probably because of its basically wrong description of liquids. In this communication, we would like to demonstrate that the discontinuity of liquid is one of the essential factors that must be taken into account in the interpretation of reaction volumes and activation volumes for nearly nonpolar reactions on the basis of the known volume properties of liquids.

Discussion

Nomenclature

Because of the current confusion of the terminology, it is necessary to make the definitions of several terms clear before we start discussion[2]. The following definitions and symbols are adopted in this communication.

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[1] For example, see E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms", Academic Press, New York (1966)

[2] J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, "Regular and Related Solutions", p. 42, van Nostrand Reinhold, New York (1970)

(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°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.

$$V_T=V_W+V_V+V_E. \tag{1}$$

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 Bondi[3] 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),

$$V_0=\left(\frac{ab}{\varepsilon_0}\right)^{1/2}, \tag{2}$$

where a and b are the van der Waals constants, *i. e.*, $a=27R^2T_c^2/64P_c$ 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].

$$\log P=A+\frac{B}{T}+C\log T+\cdots\cdots\cdots. \tag{3}$$

$$\varepsilon_0=-2.3RB. \tag{4}$$

For n-alkanes the values of V_0 thus obtained are not only in good agreement with the values by Doolittle[7], Eq. (5), but also consistent with Eq. (6)[8],

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

$$V_0=\left(\frac{P_cV_c}{RT_c}\right)V_c, \tag{6}$$

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

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[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 (m*l*/mole)

Compound	V_T[a]	V_W[b]	V_O 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	—
n-Butane	101.5[g]	47.8	69.0	69.9	69.1	—
n-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	—	—
n-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	—	—
n-Heptane	147.5	78.5	110	111	111	—
2,3-Dimethylpentane	145.0	78.5	—	109	—	—
2,4-Dimethylpentane	150.0	78.5	—	113	—	—
n-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 $d_l - d_v = C''(T_c - T)^{1/3}$ g) At saturation pressure h) *a*, *b* calculated from the critical properties[13]

Table 2 Volume properties of olefinic and naphthenic hydrocarbons (m*l*/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)

Table 3 Volume properties of hydrocarbons (ml/mole)

Compound	V_T a)	V_W	V_V b)	V_E b)
n-Pentane	116.1	58.0	24.9	33.2
2,2-Dimethylpropane	123.3	58.0	24.5	40.8
n-Hexane	131.6	68.3	28.2	35.1
2,3-Dimethylbutane	131.2	68.2	27.1	35.9
n-Heptane	147.5	78.5	31.5	37.5
n-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 2[18]. 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 molecules[19]. 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 Haward[21]. 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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9) J. A. Riddick and W. B. Bunger, "Organic Solvents", Wiley-Interscience, New York (1970)
10) F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburg (1953)
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 temperature[20] 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 4.5×10^{-6} atm^{-1} was obtained for *n*-octane by Haward[21]. Later the same author gets 8.1×10^{-6} atm^{-1} from the internal pressure change with temperature[24]. 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 5×10^{-6} 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)] (m*l*/mole)

P, atm	*n*-Hexane $V_W=68.3$			*n*-Heptane $V_W=78.5$			*n*-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. Bondi[26] 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, Hamann[27] 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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22) A. J. Matheson, *J. Chem. Phys.*, **44**, 695 (1966)

23) D. L. Hogenboom, W. Webb and J. A. Dixon, *ibid.*, **46**, 2586 (1967)

24) R. N. Haward and B. M. Parker, *J. Phys. Chem.*, **72**, 1842 (1968)

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)

27) S. D. Hamann, "High Pressure Physics and Chemistry", Vol. 2, Chapt. 7, ed. by R. S. Bradley, Academic Press, New York (1963)

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

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

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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.

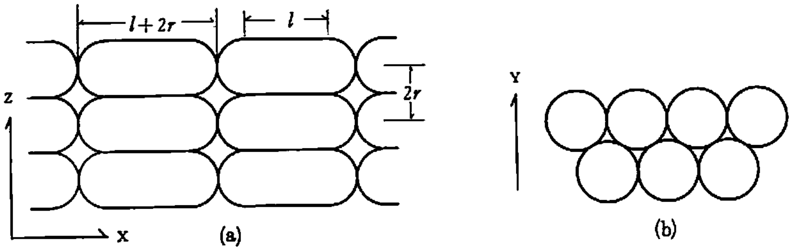

Fig. 1 A hypothetical liquid, A, at 0°K[29)]

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

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

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

N_0 : Avogadro's number

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

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

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

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

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

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

$$\begin{tikzcd}
T^\circ\text{K} & nS(l) \arrow[r, "+A", "\Phi(A)"'] \arrow[d, "-nV_E(S)"'] & {[A+nS](l)} \\
0^\circ\text{K} & nS(l) \arrow[r, "+A", "\delta V_W+\delta V_V"'] & {[A+nS](l)} \arrow[u, "+V_E(A+nS)"']
\end{tikzcd}$$

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, $\Phi(A)$, is given by Eq. (14) and it is converted to Eq. (15),

$$\Phi(\mathrm{A})=-nV_E(\mathrm{S})+V_W(\mathrm{A})+V_V(\mathrm{A}+n\mathrm{S})-nV_V(\mathrm{S})+V_E(\mathrm{A}+n\mathrm{S}) \tag{14}$$

$V_V(\mathrm{A}+n\mathrm{S})$: total void volume of the solution

$V_E(\mathrm{A}+n\mathrm{S})$: total expansion volume of the solution

$$=\delta V_W+\delta V_V+\delta V_E, \tag{15}$$

where the operator, δ, means to take the difference before and after the operation to add one mole of A. The role of δV_V is easily realized if we think a small spherical solute with a radius which is no greater than 0.414 times that of the solvent sphere. Such a solute can occupy the octahedral hole without disturbing the closest-packed lattice of the solvent at 0°K. Therefore, $\delta V_V=-\delta V_W$ and $\Phi(\mathrm{A})=\delta V_E$. Assarsson and Eirick[32] have shown the possibility to explain the volume of transfer of dimethylacetamide into water as the void volume change during the mixing. However, it is impossible to calculate δV_V in actual solutions at this stage. The role of δV_E is demonstrated by the examples given in Table 6.

Table 6 Partial molal volume of methane and ethane in several solvents at 25°C[a] (ml/mole)

Solvent	Methane $V_W=17.1$		Ethane $V_W=27.3$	
	Φ	$\Phi-V_W$	Φ	$\Phi-V_W$
Perfluoroheptane	68.4	51.3	82.9	55.6
n-Hexane	60.0	42.9	69.3	42.0
Carbontetrachloride	52.4	35.3	65.9	38.6
Benzene	52.0	34.9	66.0	38.7
Water	37.3[b]	20.2	51.2[b]	23.9

a) Partial molal volumes from Ref. 33 for organic solvents and from Ref. 34 for water
b) 37.4 (methane), 53.3 (ethane), Ref. 35

The large positive molal volumes of these rather small solutes clearly indicate large positive δV_E in both solutes. It is this δV_E term that is responsible for the temperature and pressure effects on partial molal volumes. The ratio, $V_W/\Phi=\delta V_W/\Phi$, is the so-called packing density. Recently, King[36] has demonstrated that the ratio becomes nearly constant in alkylammonium salts with increasing molecular weight and successfully applied the fact to estimate the ionic molal volume of H^+[37].

From Eq. (14) the following relations are derived.

$$\begin{aligned}
\Delta V&=\Sigma\Phi\,(\text{products})-\Sigma\Phi\,(\text{reactants})\\
&=V_W(\mathrm{P})+V_V(\mathrm{P}+n\mathrm{S})-nV_V(\mathrm{S})+V_E(\mathrm{P}+n\mathrm{S})-nV_E(\mathrm{S})-V_W(\mathrm{R})\\
&\quad-V_V(\mathrm{R}+n\mathrm{S})+nV_V(\mathrm{S})-V_E(\mathrm{R}+n\mathrm{S})+nV_E(\mathrm{S})\\
&=\{V_W(\mathrm{P})-V_W(\mathrm{R})\}+\{V_V(\mathrm{P}+n\mathrm{S})-V_V(\mathrm{R}+n\mathrm{S})\}+\{V_E(\mathrm{P}+n\mathrm{S})\\
&\quad-V_E(\mathrm{R}+n\mathrm{S})\}
\end{aligned} \tag{16}$$

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32) P. Assarsson and F. R. Eirick, *J. Phys. Chem.*, **72**, 2710 (1968)
33) J. C. Gjaldbaek and J. H. Hildebrand, *J. Am. Chem. Soc.*, **72**, 1077 (1950)
34) W. L. Masterton, *J. Chem. Phys.*, **22**, 1830 (1954)
35) E. W. Tiepel and K .E. Gubbins, *J. Phys. Chem.*, **76**, 3044 (1972)
36) E. J. King, *ibid.*, **73**, 1220 (1969)
37) E. J. King, *ibid.*, **74**, 4590 (1970)

$$=\Delta V_{\mathrm{W}}+\Delta V_{\mathrm{V}}+\Delta V_{\mathrm{E}}. \tag{17}$$

Likewise,

$$\Delta V^{\neq}=\Delta V_{\mathrm{W}}^{\neq}+\Delta V_{\mathrm{V}}^{\neq}+\Delta V_{\mathrm{E}}^{\neq}. \tag{18}$$

As δV_{V} and δV_{E} constitute significant parts of Φ, it is reasonable to expect ΔV_{V} ($\Delta V_{\mathrm{V}}^{\neq}$) and ΔV_{E} ($\Delta V_{\mathrm{E}}^{\neq}$) to be also important in ΔV ($\Delta V^{\neq}$). Probably the Diels-Alder reactions will provide the best examples to have an insight into the real situation, because they are believed to be nonionic in many cases[38] and several accurate experimental results[39-41] are available. Unfortunately we are not able to get ΔV_{V} and ΔV_{E} separately. In addition because of the lack of the information about the structure of the activated complex, even $\Delta V_{\mathrm{W}}^{\neq}$ is not available. However the observed ΔV, $\Delta V^{\neq}$ and the estimated ΔV_{W} show that ΔV_{W} is less than one half of ΔV. Several examples are given in Table 7.

Table 7 Changes in the volume properties for several Diels-Alder reactions (m*l*/mole)

Reaction	Solvent	T°C	$\Delta V^{\neq}$ a)	ΔV a)	ΔV_{W}	$\Delta V-\Delta V_{\mathrm{W}}$
Maleic anhydride— 1, 3-cyclohexadiene	CH_2Cl_2	35	−39.6	−30.3	− 9	−21
Maleic anhydride— isoprene	CH_3COCH_3	35	−39.0	−35.9	− 9	−27
Maleic anhydride— isoprene	$CH_3CO_2C_2H_5$	35	−37.4	−36.8	− 9	−28
Maleic anhydride— isoprene	CH_3NO_2	35	−32.5	−30.7	− 9	−22
Dimethyl acetylene-dicarboxylate— cyclopentadiene	$CH_3CO_2C_2H_5$	10	−30.2	−33.8	−12	−22

a) Refs. 39, 40 and 41

The difference, $\Delta V^{\neq}-\Delta V_{\mathrm{W}}$, may serve as a fairly good measure for $\Delta V_{\mathrm{V}}^{\neq}+\Delta V_{\mathrm{E}}^{\neq}$ because the transition state is believed to be close to the final product geometrically[41]. Furthermore, since the transition state is similar to the initial state electronically[42], $\Delta V_{\mathrm{E}}^{\neq}$ may be determined mainly by the loss of the degrees of freedom of the reactants during the activation step.

Although the examples given here are rather limited, there seems to be little cause to doubt that the void and the expansion volume changes constitute a major part of ΔV and $\Delta V^{\neq}$ in solution.

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38) For example, see J. Hine, "Physical Organic Chemistry", Chapt. 25, 2nd ed., McGraw-Hill, New York (1962).

39) R. A. Grieger and C. A. Eckert, *Trans. Faraday Soc.*, **66**, 2579 (1970)

40) R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, **92**, 2918 (1970)

41) R. A. Grieger and C. A. Eckert, *ibid.*, **92**, 7149 (1970)

42) K. F. Wong and C. A. Eckert, *Trans. Fraday Soc.*, **66**, 2313 (1970)

Conclusion

The volume change and the activation volume for nonplolar reactions are used to be attributed to the difference between the van der Waals and covalent radii with possible minor geometrical contributions from the solvent packing. However as demonstrated here, the van der Waals volume change is not a dominant factor in many cases. Quite often the change in the void and/or the expansion volume is much larger than the van der Waals volume change. The hypothetical division of volumes proposed here seems to be beneficial when we deal with the effects of pressure, temperature and steric hindrance on $\varDelta V$ and $\varDelta V^{\ddagger}$. The last case will be discussed in near future.

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