

$$\Phi(A) = -nV_E(S) + V_W(A) + V_V(A + nS) - nV_V(S) + V_E(A + nS) \quad (14)$$

$V_V(A + nS)$: total void volume of the solution

$V_E(A + nS)$: total expansion volume of the solution

$$= \delta V_W + \delta V_V + \delta V_E, \quad (15)$$

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 $\Phi(A) = \delta V_E$. Assarsson and Eirick³² 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, King³⁶ 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.

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

- 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. Toppel 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)

$$= \Delta V_W + \Delta V_V + \Delta V_E \quad (17)$$

Likewise,

$$\Delta V^\ddagger = \Delta V_W^\ddagger + \Delta V_V^\ddagger + \Delta V_E^\ddagger \quad (18)$$

As δV_V and δV_E constitute significant parts of Φ , it is reasonable to expect ΔV_V (ΔV_V^\ddagger) and ΔV_E (ΔV_E^\ddagger) to be also important in ΔV (ΔV^\ddagger). 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 cases³⁸⁾ and several accurate experimental results³⁹⁻⁴¹⁾ 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 ΔV_W^\ddagger is not available. However the observed ΔV , ΔV^\ddagger 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 (ml/mole)

Reaction	Solvent	T°C	$\Delta V^\ddagger(a)$	$\Delta V^\ddagger(b)$	ΔV_W	$\Delta V - \Delta V_W$
Maleic anhydride— 1, 3-cyclohexadiene	CH ₂ Cl ₂	35	-39.6	-30.3	-9	-21
Maleic anhydride— isoprene	CH ₃ COCH ₃	35	-39.0	-35.9	-9	-27
Maleic anhydride— isoprene	CH ₃ CO ₂ C ₂ H ₅	35	-37.4	-36.8	-9	-28
Maleic anhydride— isoprene	CH ₃ NO ₂	35	-32.5	-30.7	-9	-22
Dimethyl acetylene- dicarboxylate— cyclopentadiene	CH ₃ CO ₂ C ₂ H ₅	10	-30.2	-33.8	-12	-22

a) Refs. 39, 40 and 41

The difference, $\Delta V^\ddagger - \Delta V_W$, may serve as a fairly good measure for $\Delta V_V^\ddagger + \Delta V_E^\ddagger$ because the transition state is believed to be close to the final product geometrically⁴¹⁾. Furthermore, since the transition state is similar to the initial state electronically⁴²⁾, ΔV_E^\ddagger 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 ΔV^\ddagger in solution.

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. Faraday Soc.*, **66**, 2313 (1970)