

**volume of activation,  $\Delta^\ddagger V$**

A quantity derived from the pressure dependence of the *rate constant* of a reaction (mainly used for reactions in solution), defined by the equation:

$$\Delta^\ddagger V = -RT(\partial \ln k / \partial p)_T$$

providing that the rate constants of all reactions (except first-order reactions) are expressed in pressure-independent concentration units, such as mol dm<sup>-3</sup> at a fixed temperature and pressure.

The volume of activation is interpreted, according to *transition state theory*, as the difference between the partial molar volumes of the transition state ( $V$ ) and the sums of the partial volumes of the reactants at the same temperature and pressure, i.e.

$$\Delta^\ddagger V = {}^\ddagger V - \sum (rV_R)$$

where  $r$  is the order in the reactant R and  $V_R$  its partial molar volume.

1994, 66, 1175; see also 1996, 68, 191; G.B. 56