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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:

$$\Delta^{\ddagger}V = -RT\left(\frac{\partial(\ln k)}{\partial p}\right)_T$$

providing that the rate constants of all reactions (except first-order reactions) are expressed in pressure-independent concentration units, such as $\mathrm{mol\,dm^{-3}}$ 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.

$$\Delta^{\ddagger}V = {}^{\ddagger}V - \sum(r\,V_{\mathrm{R}})$$

where r is the order in the reactant R and V_{R} its partial molar volume.

Source:
PAC, 1994, *66*, 1077 *(Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994))* on page 1175

See also:
PAC, 1996, *68*, 149 *(A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996))* on page 191
Green Book, 2nd ed., p. 56

