

This is explained completely by the transition state theory. The rate constant k is proportional to the equilibrium constant K^\ddagger of the reaction in which the activated complex is formed from the initial reactants

$$K = \kappa \frac{KT}{h} K^\ddagger, \quad (1)$$

where K and h are the Boltzmann and Plank constants, respectively, and κ is the transmission coefficient which indicates the probability that the activated complex, upon reaching the reaction barrier peak, will pass toward the reaction products. Taking the logarithm of equation (1) and differentiating with regard to the pressure at constant temperature (assuming that κ is independent of pressure), we obtain

$$\frac{\partial \ln k}{\partial P} = \frac{\Delta v^\ddagger}{RT}, \quad (2)$$

where Δv^\ddagger is the volume change during the formation of the activated complex from the reactants, R is the gas constant, T is the absolute temperature.

From equation (2) it is possible to determine the volume change during the formation of the activated complex by experimental measurement of the rate constant dependence on pressure, and, consequently, also the volume of the activated complex itself (provided the volume of the reactants is known). On the other hand, Δv^\ddagger can be estimated in some cases by means of reasonable models for the transition state. Comparison of the measured and calculated value of Δv^\ddagger enables one to verify the model and the implied structure of the activated complex.

From equation (2) the following deductions are made. The rate of unimolecular reactions (in which the volume of the activated complex is larger than the reactant because of the stretching bond) decreases with increasing pressure. The rate of a bi- or multi-molecular reaction,