

transition state theory

A theory of the rates of elementary reactions which assumes a special type of equilibrium, having an equilibrium constant K^\ddagger , to exist between reactants and activated complexes. According to this theory the rate constant is given by:

$$k = \frac{k_B T}{h} K^\ddagger$$

where k_B is the Boltzmann constant and h is the Planck constant. The rate constant can also be expressed as:

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta^\ddagger S^\circ}{R}\right) \exp\left(-\frac{\Delta^\ddagger H^\circ}{R T}\right)$$

where $\Delta^\ddagger S^\circ$, the entropy of activation, is the standard molar change of entropy when the activated complex is formed from reactants and $\Delta^\ddagger H^\circ$, the enthalpy of activation, is the corresponding standard molar change of enthalpy. The quantities E_a (the energy of activation) and $\Delta^\ddagger H^\circ$ are not quite the same, the relationship between them depending on the type of reaction. Also:

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta^\ddagger G^\circ}{R T}\right)$$

where $\Delta^\ddagger G^\circ$, known as the Gibbs energy of activation, is the standard molar Gibbs energy change for the conversion of reactants into activated complex. A plot of standard molar Gibbs energy against a reaction coordinate is known as a Gibbs-energy profile; such plots, unlike potential-energy profiles, are temperature-dependent. In principle the equations above must be multiplied by a transmission coefficient, κ , which is the probability that an activated complex forms a particular set of products rather than reverting to reactants or forming alternative products. It is to be emphasized that $\Delta^\ddagger S^\circ$, $\Delta^\ddagger H^\circ$ and $\Delta^\ddagger G^\circ$ occurring in the former three equations are not ordinary thermodynamic quantities, since one degree of freedom in the activated complex is ignored. Transition-state theory has also been known as absolute rate theory, and as activated-complex theory, but these terms are no longer recommended.

Source:

PAC, 1996, 68, 149 (*A glossary of terms used in chemical kinetics, including reaction dynamics (IUPAC Recommendations 1996)*) on page 190