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:

$$k = (k_{\mathrm{B}}T/h)K^{\ddagger}$$

where k_{A} is the Boltzmann constant and h is the Planck constant. The rate constant can also be expressed as:

$$k = (k_{\mathrm{B}}T/h)\ \exp\ (\Delta^{\ddagger}S^{o}/R)\ \exp\ (-\Delta^{\ddagger}H^{o}/RT)$$

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

$$k = (k_{\mathrm{B}}T/h)\ \exp\ (-\Delta^{\ddagger}G^{o}/RT)$$

where $\Delta^{\ddagger}G^{o}$, 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 $\Delta^{\ddagger}S^{o}$, $\Delta^{\ddagger}H^{o}$ and $\Delta^{\ddagger}G^{o}$ 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.

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