

Marcus equation (for electron transfer)

Relation between the rate of outer-sphere electron transfer and the thermodynamics of this process. Essentially, the rate constant within the encounter complex (or the rate constant of intramolecular transfer) is given by the Eyring equation:

$$k_{\text{ET}} = (\kappa_{\text{ET}} k T / h) \exp(-\Delta G^\ddagger / RT)$$

where k is the Boltzmann constant, h the Planck constant, R the gas constant and κ_{ET} the so-called electronic transmission factor ($\kappa_{\text{ET}} \sim 1$ for adiabatic and $\ll 1$ for diabatic electron transfer). For outer-sphere electron transfer the barrier height can be expressed as:

$$\Delta G^\ddagger = (\lambda + \Delta_{\text{ET}}G^\circ)^2 / 4\lambda$$

where $\Delta_{\text{ET}}G^\circ$ is the standard Gibbs energy change accompanying the electron-transfer reaction and λ the total reorganization energy.

Note: Whereas the classical Marcus equation has been found to be quite adequate in the normal region, it is now generally accepted that in the inverted region a more elaborate formulation, taking into account explicitly the Franck-Condon factor due to quantum mechanical vibration modes, should be employed.

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