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:

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

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

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

where $\Delta_{\mathrm{ET}}G^{\mathrm{o}}$ 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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