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Marcus–Hush relationship

Relationship between the barrier ($\Delta G^{\ddagger}$) to thermal electron transfer, the energy of a corresponding optical charge-transfer transition (ΔE_{op}), and the overall change in standard Gibbs energy accompanying thermal electron transfer (ΔG^{o}). Assuming a quadratic relation between the energy of the system and its distortions from equilibrium (harmonic oscillator model) the expression obtained is:

$$\Delta G^{\ddagger} = \frac{{\Delta E_{op}}^2}{4\,(\Delta E_{op} - \Delta G^{o})}$$

The simplest form of this expression obtains for degenerate electron transfer (ΔG^{o}) in e.g. symmetrical mixed valence systems:

$$\Delta G^{\ddagger} = \frac{\Delta E_{op}}{4}$$

Note that for this situation the Marcus equation reads:

$$\Delta G^{\ddagger} = \frac{\lambda}{4}$$

Source:
PAC, 1996, *68*, 2223 *(Glossary of terms used in photochemistry (IUPAC Recommendations 1996))* on page 2253

