

### Marcus–Hush relationship

Relationship between the barrier ( $\Delta G^\ddagger$ ) to thermal *electron transfer*, the energy of a corresponding optical *charge-transfer transition* ( $\Delta E_{\text{op}}$ ), and the overall change in standard Gibbs energy accompanying thermal electron transfer ( $\Delta G^0$ ). Assuming a quadratic relation between the energy of the system and its distortions from equilibrium (harmonic oscillator model) the expression obtained is:

$$\Delta G^\ddagger = \Delta E_{\text{op}}^2 / 4(\Delta E_{\text{op}} - \Delta G^0)$$

The simplest form of this expression obtains for degenerate electron transfer ( $\Delta G^0$ ) in e.g. symmetrical mixed valence systems:

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

Note that for this situation the *Marcus equation* reads:

$$\Delta G^\ddagger = \lambda / 4$$

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