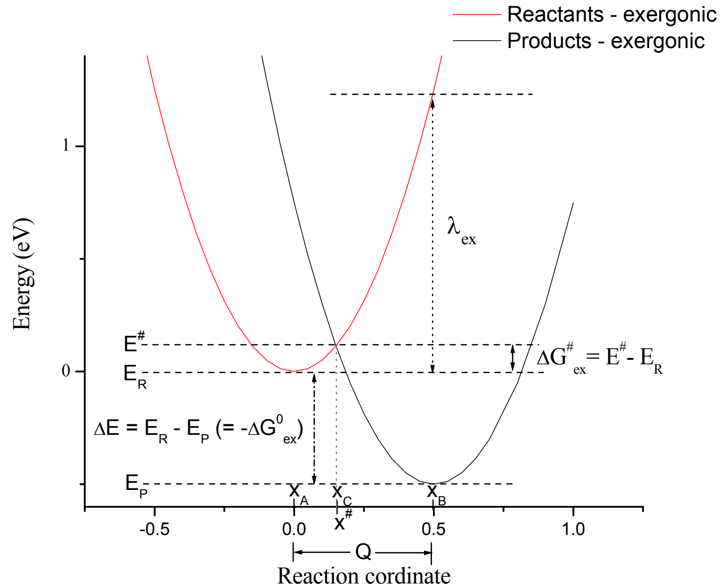
Marcus equation solutions for exergonic reaction



The parabolic equation for the reactants:

$$E = k_R(x - x_A)^2 + E_R \quad (1)$$

The parabolic equation for the products:

$$E = k_P(x - x_B)^2 + E_P \quad (2)$$

Solve for the energy of activation for the exergonic reaction, $\Delta G^{\#}_{ex}$, using equation (1), points $\{x_C, E^{\#}\}$, $\{x_B, \lambda_{ex}+E_R\}$ and equation (2), point $\{x_C, E^{\#}\}$:

i) Substitution of point $\{x_C, E^{\#}\}$ into equation (1):

$$E^{\#} = k_R(x_C - x_A)^2 + E_R$$
$$Substitute: x_C = x^{\#} + x_A$$
$$E^{\#} = k_R((x^{\#} + x_A) - x_A)^2 + E_R$$
$$E^{\#} = k_R(x^{\#})^2 + E_R$$
$$Substitute: \Delta G^{\#}_{ex} = E^{\#} - E_R$$
$$E^{\#} - E_R = \Delta G^{\#}_{ex} = k_R(x^{\#})^2$$
$$x^{\#} = \left(\frac{\Delta G^{\#}_{ex}}{k_R}\right)^{\frac{1}{2}}$$

ii) Substitution of point $\{x_B, \lambda_{ex}+E_R\}$ into equation (1):

$$\lambda_{ex} + E_R = k_R(x_B - x_A)^2 + E_R$$
$$Substitute \quad : Q = x_B - x_A$$
$$\lambda_{ex} = k_R(Q)^2$$
$$Q = \left(\frac{\lambda_{ex}}{k_R}\right)^{\frac{1}{2}}$$

iii) Substitution of point $\{x_C, E^{\#}\}$ into equation (2):

$$E^{\#} = k_P (x_C - x_B)^2 + E_P$$

$$Substitute: x_C = x^{\#} - x_A$$

$$E^{\#} - E_P = k_P ((x^{\#} - x_A) - x_B)^2$$

$$Substitute: Q = x_B - x_A$$

$$E^{\#} - E_P = k_P (x^{\#} - Q)^2$$

$$Substitute: E_P = E_R - \Delta E$$

$$E^{\#} - (E_R - \Delta E) = k_P (x^{\#} - Q)^2$$

$$Substitute: \Delta G_{ex}^{\#} = E^{\#} - E_R$$

$$\Delta G_{ex}^{\#} + \Delta E = k_P (x^{\#} - Q)^2$$

$$From(i) \ \& \ (ii) above$$

$$x^{\#} = (\frac{\Delta G_{ex}^{\#}}{k_R})^{\frac{1}{2}}$$

$$Q = (\frac{\lambda_{ex}}{k_R})^{\frac{1}{2}}$$

$$\Delta G_{ex}^{\#} + \Delta E = k_P ((\frac{\Delta G_{ex}^{\#}}{k_R})^{\frac{1}{2}} - (\frac{\lambda_{ex}}{k_R})^{\frac{1}{2}})^2$$

$$\Delta G_{ex}^{\#} + \Delta E = k_P ((\frac{\Delta G_{ex}^{\#}}{k_R}) - 2(\frac{\lambda_{ex}}{k_R}\frac{\Delta G_{ex}^{\#}}{k_R})^{\frac{1}{2}} + (\frac{\lambda_{ex}}{k_R}))$$

$$Assume: k_P = k_R$$

$$\Delta G_{ex}^{\#} + \Delta E = (\Delta G_{ex}^{\#} - 2(\lambda_{ex}\Delta G_{ex}^{\#})^{\frac{1}{2}} + \lambda_{ex})$$

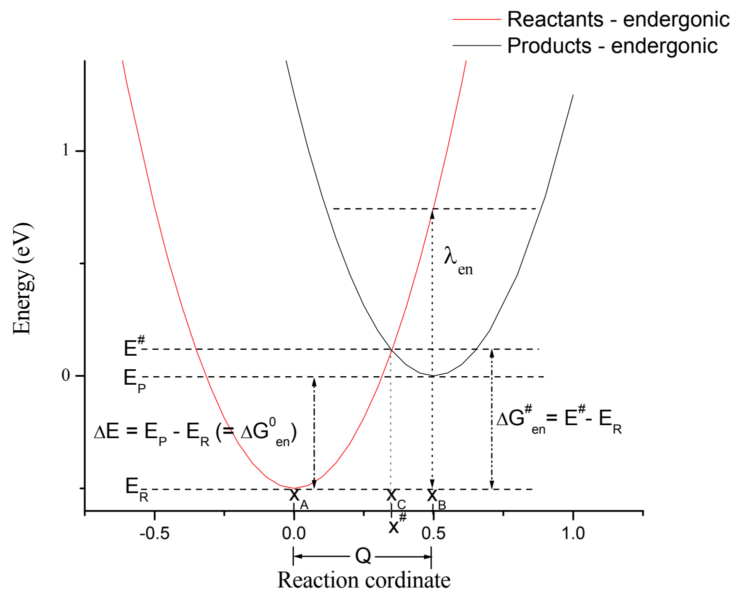
$$\Delta E = -2(\lambda_{ex}\Delta G_{ex}^{\#})^{\frac{1}{2}} + \lambda_{ex}$$

$$\Delta G_{ex}^{\#} = \frac{(\lambda_{ex} - \Delta E)^2}{4\lambda_{ex}}$$

$$Substitute: \Delta E = -\Delta G_{ex}^{0}$$

$$\Delta G_{ex}^{\#} = \frac{(\lambda_{ex} + \Delta G_{ex}^{0})^2}{4\lambda_{ex}}$$

Marcus equation solutions for endergonic reaction



The parabolic equation for the reactants:

$$E = k_R(x - x_A)^2 + E_R \quad (1)$$

The parabolic equation for the products:

$$E = k_P(x - x_B)^2 + E_P \quad (2)$$

Solve for the energy of activation for the endergonic reaction, $\Delta G^{\#}_{en}$, using equation (1), points {x_C, $E^{\#}$}, {x_B, $\lambda_{en}+E_R$} and equation (2), point {x_C, $E^{\#}$}:

iv) Substitution of point {x_C, $E^{\#}$} into equation (1):

$$E^{\#} = k_R(x_C - x_A)^2 + E_R$$
$$Substitute: x_C = x^{\#} + x_A$$
$$E^{\#} = k_R((x^{\#} + x_A) - x_A)^2 + E_R$$
$$E^{\#} = k_R(x^{\#})^2 + E_R$$
$$Substitute: \Delta G^{\#}_{en} = E^{\#} - E_R$$
$$E^{\#} - E_R = \Delta G^{\#}_{en} = k_R(x^{\#})^2$$
$$x^{\#} = \left(\frac{\Delta G^{\#}_{en}}{k_R}\right)^{\frac{1}{2}}$$

v) Substitution of point {x_B, $\lambda_{en}+E_R$} into equation (1):

$$\lambda_{en} + E_R = k_R(x_B - x_A)^2 + E_R$$
$$Substitute: Q = x_B - x_A$$
$$\lambda_{en} = k_R(Q)^2$$
$$Q = \left(\frac{\lambda_{en}}{k_R}\right)^{\frac{1}{2}}$$

vi) Substitution of point $\{x_C, E^{\#}\}$ into equation (2):

$$E^{\#} = k_P(x_C - x_B)^2 + E_P$$

$$Substitute: x_C = x^{\#} + x_A$$

$$E^{\#} - E_P = k_P((x^{\#} + x_A) - x_B)^2$$

$$Substitute: Q = x_B - x_A$$

$$E^{\#} - E_P = k_P(x^{\#} - Q)^2$$

$$Substitute: E_P = E_R + \Delta E$$

$$E^{\#} - (E_R + \Delta E) = k_P(x^{\#} - Q)^2$$

$$Substitute: \Delta G_{en}^{\#} = E^{\#} - E_R$$

$$\Delta G_{en}^{\#} - \Delta E = k_P(x^{\#} - Q)^2$$

$$From (i) \ \& \ (ii) above$$

$$x^{\#} = (\frac{\Delta G_{en}^{\#}}{k_R})^{\frac{1}{2}}$$

$$Q = (\frac{\lambda_{en}}{k_R})^{\frac{1}{2}}$$

$$\Delta G_{en}^{\#} - \Delta E = k_P((\frac{\Delta G_{en}^{\#}}{k_R})^{\frac{1}{2}} - (\frac{\lambda_{en}}{k_R})^{\frac{1}{2}})^2$$

$$\Delta G_{en}^{\#} - \Delta E = k_P((\frac{\Delta G_{en}^{\#}}{k_R}) - 2(\frac{\lambda_{en}}{k_R}\frac{\Delta G_{en}^{\#}}{k_R})^{\frac{1}{2}} + (\frac{\lambda_{en}}{k_R}))$$

$$Assume: k_P = k_R$$

$$\Delta G_{en}^{\#} - \Delta E = (\Delta G_{en}^{\#} - 2(\lambda_{en}\Delta G_{en}^{\#})^{\frac{1}{2}} + \lambda_{en})$$

$$-\Delta E = -2(\lambda_{en}\Delta G_{en}^{\#})^{\frac{1}{2}} + \lambda_{en}$$

$$\Delta G_{en}^{\#} = \frac{(\lambda_{en} + \Delta E)^2}{4\lambda_{en}}$$

$$Substitute: \Delta E = \Delta G_{en}^{0}$$

$$\Delta G_{en}^{\#} = \frac{(\lambda_{en} + \Delta G_{en}^{0})^2}{4\lambda_{en}}$$

$$\Delta G_{en}^{\#} = \frac{(\Delta G_{en}^{0} + \lambda_{en})^2}{4\lambda_{en}}$$