Diffusion Controlled Rxn

$$A + B \xrightarrow{k_d} AB$$

$$AB \xrightarrow{k_r} A + B$$

$$AB \xrightarrow{k_p} P$$

a) $k_r >> k_p$

$$K = \frac{[AB]}{[A][B]} = \frac{k_d}{k_r}$$

$$[AB] = \frac{k_d}{k_r}[A][B]$$

$$\text{rate} = k_p[AB] = \frac{k_p k_d}{k_r}[A][B]$$

b) $k_r \approx k_p$

$$\frac{d[AB]}{dt} = k_d[A][B] - k_r[AB] - k_p[AB] = 0$$

$$[AB] = \frac{k_d}{k_r + k_p}[A][B]$$

$$\text{rate} = \frac{k_p k_d}{k_r + k_p}[A][B]$$

$k_p >> k_r$

$$\text{rate} = k_d[A][B]$$

Solutions

$$k_\phi = k^{qm} + k^{phy}$$

$k^{mq} >> k^{pks}$

SLOWEST STEP IS DIFFUSION

$$k_d \triangleq k^{pks} = 4\pi (D_{AB}) N_A (r_A + r_B)$$

$D \sim 10^{-5}\ cm^2\ s^{-1}$

$r_A + r_B \sim 5\ Å$

$$k_d \sim 10^{10}\ M s^{-1}$$

$$D = \frac{kT}{6\pi \eta r}$$

Activated Complex

$$A + B \longrightarrow P$$

$$A + B \rightleftharpoons AB^{\ddagger} \xrightarrow{k_2} P$$

$$K_c^{\ddagger} = \frac{[AB^{\ddagger}]/c^\circ}{\frac{[A]}{c^\circ}\frac{[B]}{c^\circ}} = \frac{[AB^{\ddagger}]\,c^\circ}{[A][B]}$$

$$\text{rate} = k_2 [AB^{\ddagger}] = \left(\frac{k_2 K_c^{\ddagger}}{c^\circ}\right)[A][B]$$

QM → Activated complex ⟶ Vib → ν

$$k_2 = \kappa \nu$$

κ = transmission coeff.

$K_c^{\ddagger}$ → Stat Mech → $q_{RC}\ \bar{K}_c^{\ddagger}$ — Reactive coordinate

$$\downarrow$$

$$\frac{k_B T}{h\nu}$$

$$k^{obs} = \kappa \frac{k_B T}{h c^\circ} \bar{K}_c^{\ddagger} = \kappa \frac{k_B T}{h c^\circ} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

$$k^{obs} = \frac{\kappa k_B T}{h c^\circ} e^{\frac{\Delta S^{\ddagger}}{R}} e^{-\frac{\Delta H^{\ddagger}}{RT}}$$

In general we define

$$\boxed{E_a \equiv RT^2 \frac{d}{dT} \ln k}$$