Rates and Equilibria

Equilibrium expressions
Rate expressions
Reaction coordinate diagrams

Outline

- Equilibrium constants
- Rate constants
- Reaction coordinate diagrams
  - And equilibrium: Thermodynamics
  - And rates: kinetics

Equlibria and equilibrium constants

$$A + B \rightleftharpoons C + D$$

$$K_{eq} = \frac{[C][D]}{[A][B]}$$

Equlibria and equilibrium constants

$$m\,A + n\,B \rightleftharpoons s\,C + t\,D$$

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[C]^s\,[D]^t}{[A]^m\,[B]^n}$$

Equlibrium constants and reaction free energy

- Endergonic:
  - the overall ΔG° > 1
  - K_{eq} < 1
  - Product G > Reactant G
- Exergonic:
  - the overall ΔG° < 1
  - K_{eq} > 1
  - Product G < Reactant G

$$\Delta G^0 = -RT \ln K_{eq}$$

$$K_{eq} = e^{\frac{-\Delta G^0}{RT}}$$

Example: dissolved CO_2 and H_2CO_3

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$K_{eq} = 0.031$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

$K_{eq} = 10^{-5}$

Reaction rates and concentrations

$$A \longrightarrow B \qquad A + B \longrightarrow C + D$$

rate = k[A] rate = k[A][B]

$$A + A \longrightarrow B$$

rate = k[A]^2

Rates and equilibrium

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

forward rate = reverse rate

$$k_1[A] = k_{-1}[B]$$

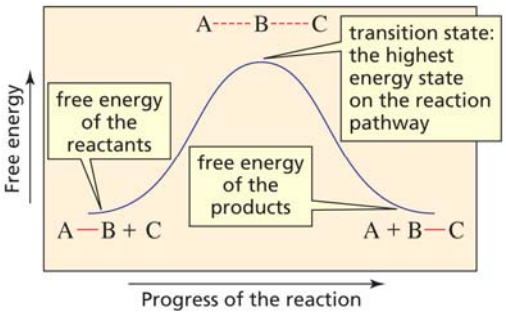
Rates and equilibrium

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

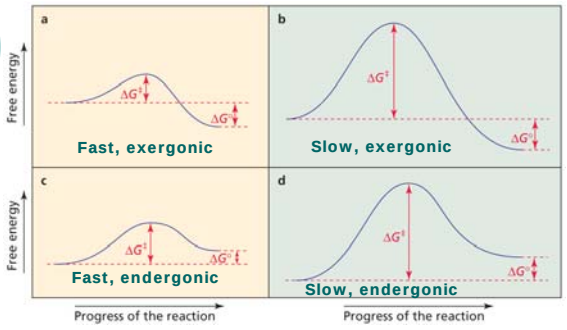
forward rate = reverse rate

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[B]}{[A]}$$

Reaction coordinate diagrams



Rates and Equilibrium are independent



Free Energy: Rate constants vs equilibrium constants

$$k = Ae^{\frac{-E_a}{RT}}$$

$$k = e^{\frac{-\Delta G^{\ddagger}}{RT}} \qquad K_{eq} = e^{\frac{-\Delta G^{0}}{RT}}$$