Connection between Kinetics and Equilibrium

For an elementary reaction:

\[ aA + bB \rightleftharpoons cC + dD \]

\[ \text{Rate}_{\text{fwd}} = k_{\text{fwd}}[A]^a[B]^b \quad \text{and} \quad \text{Rate}_{\text{rev}} = k_{\text{rev}}[C]^c[D]^d \]

At equilibrium:

\[ \text{Rate}_{\text{fwd}} = \text{Rate}_{\text{rev}} \]

\[ k_{\text{fwd}}[A]^a[B]^b = k_{\text{rev}}[C]^c[D]^d \]

\[ \Rightarrow \frac{k_{\text{fwd}}}{k_{\text{rev}}} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = Q_c = K_c \quad \Rightarrow \quad K_c = \frac{k_{\text{fwd}}}{k_{\text{rev}}} \]

\[ \Rightarrow K_c \text{ is large when the forward reaction is fast and the reverse is slow (}k_{\text{fwd}} \gg k_{\text{rev}})\]

For an overall reaction (sum of elementary reactions), \( K_c \) is the product of the \( K_c \text{s for the individual elementary steps:} \)

\[ K_c = K'_c \times K''_c \times \ldots = \frac{k'_{\text{fwd}}}{k'_{\text{rev}}} \times \frac{k''_{\text{fwd}}}{k''_{\text{rev}}} \times \ldots \]

\( \Rightarrow \) The magnitude of \( K_c \) is an indication of how far a reaction proceeds toward products at a given \( T \)

\( \rightarrow \) Large \( K_c (K_c >> 1) \) – products dominate

\( \rightarrow \) Small \( K_c (K_c << 1) \) – reactants dominate

\( \rightarrow \) Intermediate \( K_c (K_c \sim 1) \) – significant amounts of both reactants and products are present at equilibrium

Form of \( Q \) and \( K \) for Heterogeneous Equilibria

- **Heterogeneous** equilibria – reactants and products in different phases

**Example:** \( 2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g) \)

\[ Q_c' = \frac{[H_2(g)]^2[O_2(g)]}{[H_2O(l)]^2} \]

\( \Rightarrow \) The concentration of \( H_2O \) in pure liquid water is constant at a given temperature

\[ [H_2O] = \frac{\text{mol}}{V} = \frac{m}{MW} \times V = \frac{d}{MW} \]

\( \Rightarrow \) At 25°C:

\[ [H_2O] = (1.00 \times 10^3 \text{ g/L})/(18.0 \text{ g/mol}) = 55.6 \text{ mol/L} \]

\[ Q_c' \times [H_2O(l)]^2 = [H_2(g)]^2[O_2(g)] = Q_c' \times (55.6)^2 = Q_c \]

\[ \Rightarrow Q_c = [H_2]^2[O_2] \]

\( \Rightarrow \) The molarities of **pure liquids** and **solids** remain constant during the reaction and can be **eliminated** from the expressions for \( Q \) and \( K \)

**Example:** \( \text{AgCl(s)} \leftrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq) \)

\( \Rightarrow \) \( \text{AgCl(s)} \) is a pure solid

\[ \Rightarrow Q_c = [\text{Ag}^+][\text{Cl}^-] \]

**Example:** \( \text{S(s)} + \text{O}_2(g) \rightleftharpoons \text{SO}_2(g) \)

\( \Rightarrow \) \( \text{S(s)} \) is a pure solid

\[ \Rightarrow Q_c = [\text{SO}_2]/[\text{O}_2] \]
17.3 Equilibria Involving Gases

- Gases are quantified easier through partial pressures rather than molarities.

- For a gaseous reactant or product, the molarity, \( C_i \), and partial pressure, \( P_i \), are related by the ideal gas law:

\[
P_iV = n_iRT \quad \therefore \quad P_i/RT = n_i/V = C_i
\]

- For a general reaction:

\[
aA(g) + bB(g) \leftrightarrow cC(g)
\]

\[
Q_c = \left( \frac{P_c}{P_A^a P_B^b} \right)^c = \frac{P_c^c}{P_A^a P_B^b} \times \frac{1}{(RT)^\Delta n} = \frac{c}{n_c}
\]

\[
K_p = K_c (RT)^\Delta n
\]

\[
Q_p = Q_c (RT)^\Delta n
\]

- \( Q_p \) and \( K_p \) are the reaction quotient and equilibrium constant in terms of partial pressures. (\( P \) is in atm, \( R = 0.08206 \text{ L.atm/mol.K}, \) \( T \) is in K).

- \( \Delta n \) is the difference between the moles of gaseous products and reactants:

\[
\Delta n = n (\text{g, products}) - n (\text{g, reactants})
\]

Example: For the reaction

\[
\text{CaCO}_3(s) \leftrightarrow \text{CaO}(s) + \text{CO}_2(g)
\]

\[
K_c = 2.6 \times 10^{-6} \text{ at } 1000K. \text{ What is the partial pressure of CO}_2 \text{ in the reaction mixture at this temperature?}
\]

- Calculate \( K_p \)

- \( \Delta n = 1 - 0 = 1 \)

- \( K_p = K_c (RT)^\Delta n = 2.6 \times 10^{-6}(0.0821 \times 1000) = 2.1 \times 10^{-4} \)

- \( K_p = P_{\text{CO}_2} \quad \Rightarrow \quad P_{\text{CO}_2} = 2.1 \times 10^{-4} \text{ atm} \)

Use \( K_c \) (or \( Q_c \)) if molarities are given, \( K_p \) (or \( Q_p \)) if partial pressures are given, or \( K \) (or \( Q \)) for mixed expressions.

Omit the subscript “e” from all expressions for \( K \).

Example: Calculate \( K_c \) and \( K_p \) for the reaction

\[
\text{H}_2\text{S}(g) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_3\text{O}^+(aq) + \text{HS}^-(aq)
\]

\[
K = [\text{H}_3\text{O}^+][\text{HS}^-] / P_{\text{H}_2\text{S}}
\]

Example: Calculate \( K_c \) and \( K_p \) for the reaction

\[
2\text{BrCl}(g) \leftrightarrow \text{Br}_2(g) + \text{Cl}_2(g)
\]

if at 500 K, the equilibrium concentrations of BrCl, Br\(_2\) and Cl\(_2\) are 0.131, 3.51 and 0.156 M, respectively.

\[
K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]} = \frac{0.156 \times 3.51}{0.131^2} = 31.9
\]

- \( \Delta n = 1+1-2 = 0 \quad \Rightarrow \quad K_p = K_c (RT)^{0} = 31.9 \times 1 = 31.9 \)
17.4 The Direction of Reaction

- The direction of a reaction can be predicted by comparing the current value of $Q$ to the value of $K$ at the temperature of the reaction.
- As the reaction approaches equilibrium, $Q$ approaches $K$:
  - If $Q < K$, the concentration of reactants is too high, while that of products is too low ⇒ the reaction proceeds forward.
  - If $Q > K$, the concentration of reactants is too low, while that of products is too high ⇒ the reaction proceeds in reverse.
  - If $Q = K$, the reaction is at equilibrium.

Example: For the reaction

\[ \text{N}_2\text{O}_4(\text{g}) \leftrightarrow 2\text{NO}_2(\text{g}) \]

$K_p = 0.98$ at 298 K. Predict the direction of the reaction at 298 K, if the partial pressures of $\text{N}_2\text{O}_4$ and $\text{NO}_2$ are 2.4 and 1.2 atm, respectively.

\[ Q_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{1.2^2}{2.4} = 0.60 \quad K_p = 0.98 \]

$\rightarrow Q_p < K_p \Rightarrow$ The reaction proceeds forward to produce more $\text{NO}_2$. 