# Connection between Kinetics and Equilibrium

➢ For an **elementary** reaction:

$$aA + bB \leftrightarrow cC + dD$$

$Rate_{fwd} = k_{fwd}[A]^a[B]^b$ and $Rate_{rev} = k_{rev}[C]^c[D]^d$

➢ At equilibrium:

$$Rate_{fwd} = Rate_{rev} \quad \rightarrow \quad k_{fwd}[A]^a[B]^b = k_{rev}[C]^c[D]^d$$

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

→ $K_c$ is large when the forward reaction is fast and the reverse is slow ($k_{fwd} >> k_{rev}$)

➢ For an **overall** reaction (sum of elementary reactions), $K_c$ is the product of the $K_c$s for the individual elementary steps:

$$\boxed{K_c = K_c' \times K_c'' \times \ldots = \frac{k'_{fwd}}{k'_{rev}} \times \frac{k''_{fwd}}{k''_{rev}} \times \ldots}$$

→ The magnitude of $K_c$ is an indication of how far a reaction proceeds toward products at a given $T$

→ Large $K_c$ ($K_c >> 1$) – products dominate

→ Small $K_c$ ($K_c << 1$) – reactants dominate

→ 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:** $2H_2O(l) \leftrightarrow 2H_2(g) + O_2(g)$

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

➢ The concentration of $H_2O$ in pure liquid water is constant at a given temperature

$[H_2O] = mol/V = (m/MW)/V = d/MW$

➢ At 25°C:

$[H_2O] = (1.00\times10^3 \text{ g/L})/(18.0 \text{ g/mol}) = 55.6 \text{ mol/L}$

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

$$\boxed{\Rightarrow \quad Q_c = [H_2]^2[O_2]}$$

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

**Example:** $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$

→ $AgCl(s)$ is a pure solid

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

**Example:** $S(s) + O_2(g) \leftrightarrow SO_2(g)$

→ $S(s)$ is a pure solid

$$\boxed{\Rightarrow Q_c = [SO_2]/[O_2]}$$

# 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

$$P_iV = n_iRT \qquad P_i/RT = n_i/V = C_i$$

➢ For a general reaction

$$a\mathrm{A(g)} + b\mathrm{B(g)} \leftrightarrow c\mathrm{C(g)}$$

$$\boxed{Q_c = \frac{[\mathrm{C}]^c}{[\mathrm{A}]^a[\mathrm{B}]^b}}$$

$$\boxed{Q_c = \frac{(P_C/RT)^c}{(P_A/RT)^a(P_B/RT)^b} = \frac{P_C{}^c}{P_A{}^a P_B{}^b} \times \frac{1}{(RT)^{c-(a+b)}}}$$

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$$Q_c = \frac{P_C{}^c}{P_A{}^a P_B{}^b} \times \frac{1}{(RT)^{\Delta n}} \qquad \Delta n = c - (a+b)$$

$$Q_c = Q_p \times \frac{1}{(RT)^{\Delta n}} \qquad Q_p = \frac{P_C{}^c}{P_A{}^a P_B{}^b}$$

$$\boxed{Q_p = Q_c(RT)^{\Delta n} \qquad K_p = K_c(RT)^{\Delta n}}$$

→ $Q_p$ and $K_p$ are the reaction quotient and equilibrium constant in terms of partial pressures (***P*** is in atm, ***R*** = 0.08206 L.atm/mol.K, ***T*** is in K)

→ $\Delta n$ is the difference between the moles of gaseous products and reactants

$\Delta n$ = ***n*** (g, products) – ***n*** (g, reactants)

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**Example:** For the reaction

$$\mathbf{CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)}$$

$K_c = 2.6\times10^{-6}$ at 1000K. What is the partial pressure of $CO_2$ in the reaction mixture at this temperature?

→ Calculate $K_p$

→ $\Delta n = 1 - 0 = 1$

→ $K_p = K_c(RT)^{\Delta n} = 2.6\times10^{-6}(0.0821\times1000) = 2.1\times10^{-4}$

→ $K_p = P_{CO_2} \quad \Rightarrow \quad P_{CO_2} = \mathbf{2.1\times10^{-4}}$ **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***

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**Example:**

$$\mathbf{H_2S(g) + H_2O(l) \leftrightarrow H_3O^+(aq) + HS^-(aq)}$$

$$\boxed{K = [\mathrm{H_3O^+}][\mathrm{HS^-}]/P_{H_2S}}$$

**Example:** Calculate $K_c$ and $K_p$ for the reaction

$$\mathbf{2BrCl(g) \leftrightarrow Br_2(g) + Cl_2(g)}$$

if at 500 K, the equilibrium concentrations of BrCl, $Br_2$ and $Cl_2$ are 0.131, 3.51 and 0.156 M, respectively.

$$K_c = \frac{[\mathrm{Br_2}][\mathrm{Cl_2}]}{[\mathrm{BrCl}]^2} = \frac{3.51\times0.156}{0.131^2} = 31.9$$

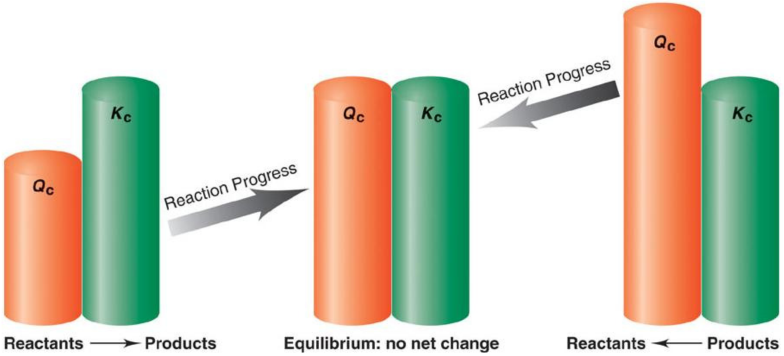
→ $\Delta n = 1+1-2 = 0 \Rightarrow K_p = K_c(RT)^0 = 31.9\times1 = 31.9$

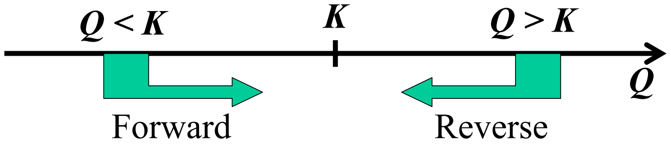
# 17.4 The Direction of Reaction

- 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

$$N_2O_4(g) \leftrightarrow 2NO_2(g)$$

$K_p = 0.98$ at 298 K. Predict the direction of the reaction at 298 K, if the partial pressures of $N_2O_4$ and $NO_2$ are 2.4 and 1.2 atm, respectively.

$$Q_p = \frac{P_{NO_2}{}^2}{P_{N_2O_4}} = \frac{1.2^2}{2.4} = 0.60 \qquad K_p = 0.98$$

$\rightarrow Q_p < K_p \Rightarrow$ The reaction proceeds forward to produce more $NO_2$