Equilibrium: The Extent of Reactions

- Chemical equilibrium – studies the extent of reactions and the ways it can be altered
- Kinetics and equilibrium are two *different* aspects of chemical reactions (fast reactions may proceed to a great, lesser or a limited extent; same is true for slow reactions)

16.1 The Dynamic Nature of the Equilibrium State

- **Chemical equilibrium** – a state in which the concentrations of reactants and products no longer change

➢ Equilibrium **is not** a stationary state or a unidirectional process

Example: $(A \rightarrow B \rightarrow C)$

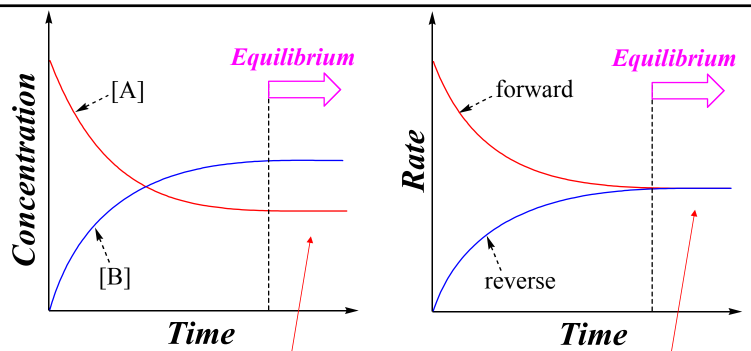
If the rates of step 1 and step 2 are equal, [B] remains constant → not an equilibrium state

➢ **Equilibrium is a dynamic state** achieved by the equalization of the forward and reverse rates of a **reversible** (bidirectional) **process**

Example: $(A \leftrightarrow B)$

If the rates of the forward and reverse reactions are equal, [A] and [B] remain constant → an equilibrium state

⇒ At equilibrium → $\boxed{\boldsymbol{Rate_{fwd} = Rate_{rev}}}$



$\boxed{[A] = \text{constant} \quad [B] = \text{constant}}$

$\boxed{\boldsymbol{Rate_{fwd} = Rate_{rev}}}$

– At a given $\boldsymbol{T}$, the same equilibrium state is reached even if the process is started from different starting points

Example: $\mathbf{N_2O_4}$**(g; colorless)** $\leftrightarrow$ $\mathbf{2NO_2}$**(g; brown)**

➢ The reaction can be started from pure N_2O_4(g; colorless) or from pure NO_2(g; brown).

➢ In both cases at equilibrium, the same light-brown color is reached (the same proportion of N_2O_4 and NO_2 is produced)

➢ The reaction has a single step mechanism (the forward and reverse reactions are elementary), so at equilibrium:

$$Rate_1 = Rate_{-1} \quad \rightarrow \quad k_1[N_2O_4] = k_{-1}[NO_2]^2$$

$$\boxed{\Rightarrow \frac{k_1}{k_{-1}} = K = \frac{[NO_2]^2}{[N_2O_4]}}$$

→ $\boldsymbol{K}$ is a constant which depends on $\boldsymbol{T}$ (K = 0.211 at 100°C)

→ $\boldsymbol{K}$ determines the proportion of N_2O_4 and NO_2 at equilibrium

17.2 The Equilibrium Constant and the Reaction Quotient

The Law of Mass-Action

- **Equilibrium constant (*K*)**
  - For a general reaction at equilibrium:

$$aA + bB \leftrightarrow cC + dD \qquad \boxed{K_c = \frac{[C]_e^c [D]_e^d}{[A]_e^a [B]_e^b}}$$

→ K_c is the **equilibrium constant** in terms of concentration (depends on T and the specific reaction)

→ $[A]_e$, $[B]_e$, $[C]_e$, and $[D]_e$ are the **equilibrium concentrations** of the reactants and products

→ ***a***, ***b***, ***c***, and ***d*** are the **stoichiometric coefficients** of the reactants and products

- **Reaction quotient (*Q*)** – has the same mass-action expression as ***K***
  - For a general reaction at any given time:

$$aA + bB \leftrightarrow cC + dD \qquad \boxed{Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}}$$

→ Q_c is the **reaction quotient** in terms of concentration (Q_c varies during the reaction)

→ [A], [B], [C], and [D] are the **current concentrations** of the reactants and products at any given time during the reaction

→ When the current concentrations become equal to the equilibrium concentrations, $Q_c = K_c$

$$\boxed{\Rightarrow \textbf{At equilibrium} \rightarrow Q = K}$$

Example: Write the mass action expression for the reaction: $2H_{2(g)} + O_{2(g)} \leftrightarrow 2H_2O_{(g)}$

$$Q_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} \qquad \textit{At equilibrium} \rightarrow Q_c = K_c$$

- The mass-action expressions for ***Q*** and ***K*** depend on the form of the chemical equation

$$\boxed{A \leftrightarrow B \quad Q_c^{\rightarrow} = \frac{[B]}{[A]}} \quad \text{or} \quad \boxed{B \leftrightarrow A \quad Q_c^{\leftarrow} = \frac{[A]}{[B]} = \frac{1}{Q_c^{\rightarrow}}}$$

⇒ ***Q*** **(or** ***K*****) of the reverse reaction is the *reciprocal* of** ***Q*** **(or** ***K*****) of the forward reaction**

$$\boxed{A \leftrightarrow B \quad Q_c = \frac{[B]}{[A]}} \quad \text{or} \quad \boxed{nA \leftrightarrow nB \quad Q_c' = \frac{[B]^n}{[A]^n} = (Q_c)^n}$$

⇒ **Multiplying a reaction by a factor, *n*, raises *Q* (or *K*) to *n*th *power***

$$\boxed{\begin{array}{lll} \textbf{1.} & A + B \leftrightarrow C & Q_1 = [C]/[A][B] \\ \textbf{2.} & C \leftrightarrow D & Q_2 = [D]/[C] \\ \hline & A + B \leftrightarrow D & Q_c = [D]/[A][B] \end{array}}$$

$$Q_1 \times Q_2 = \frac{\cancel{[C]}}{[A][B]} \times \frac{[D]}{\cancel{[C]}} = \frac{[D]}{[A][B]} = Q_c$$

⇒ ***Q*** **(or** ***K*****) of the sum of two or more reactions is the *product* of their** ***Q*****s (or** ***K*****s)**

Example: For the gas phase reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \leftrightarrow HCl(g)$$

K_c is 3.6×10^{-5} at 1200 K. What is K_c' for the reaction

$$2HCl(g) \leftrightarrow H_2(g) + Cl_2(g) \ ?$$

→ The given reaction has been reversed ⇒ take the reciprocal of K_c

→ The given reaction has been multiplied by 2 ⇒ take the square of K_c

$$\Rightarrow K_c' = (1/K_c)^2 = (1/3.6\times10^{-5})^2 = 7.7\times10^8$$

Example: Given the following two reactions and their K_cs at a certain temperature:

$N_2O_4(g) \leftrightarrow 2NO_2(g)$ $\quad K_{c1} = 2.2\times10^6$

$2NO_2(g) \leftrightarrow 2NO(g) + O_2(g)$ $\quad K_{c2} = 1.6\times10^{-10}$

Calculate K_c at this temperature for the reaction

$$N_2O_4(g) \leftrightarrow 2NO(g) + O_2(g)$$

→ The sum of the given reactions yields the desired reaction ⇒ multiply the K_c

$$\Rightarrow K_c = K_{c1}\times K_{c2} = (2.2\times10^6)\times(1.6\times10^{-10})$$

$$\Rightarrow K_c = 3.5\times10^{-4}$$