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 \(\rightarrow\) 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 \(\rightarrow\) an equilibrium state

\[\Rightarrow \text{At equilibrium } \rightarrow Rate_{\text{fwd}} = Rate_{\text{rev}}\]

**Example:** \(\text{N}_2\text{O}_4(\text{g; colorless}) \leftrightarrow 2\text{NO}_2(\text{g; brown})\)

- The reaction can be started from pure \(\text{N}_2\text{O}_4(\text{g; colorless})\) or from pure \(\text{NO}_2(\text{g; brown})\).
- In both cases at equilibrium, the same light-brown color is reached (the same proportion of \(\text{N}_2\text{O}_4\) and \(\text{NO}_2\) is produced)
- The reaction has a single step mechanism (the forward and reverse reactions are elementary), so at equilibrium:

\[Rate_1 = Rate_{-1} \rightarrow k_1[\text{N}_2\text{O}_4] = k_{-1}[\text{NO}_2]^2\]

\[\Rightarrow \frac{k_1}{k_{-1}} = K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}\]

\(K\) is a constant which depends on \(T\) (\(K = 0.211\) at 100°C)

\(K\) determines the proportion of \(\text{N}_2\text{O}_4\) and \(\text{NO}_2\) 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:
  
  \[ aA + bB \leftrightarrow cC + dD \]
  
  \[ K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]
  
  \( K_c \) 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:
  
  \[ aA + bB \leftrightarrow cC + dD \]
  
  \[ Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]
  
  \( Q_c \) 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, \( Q_c = K_c \)
  
  \( Q = K \)
  
Example: Write the mass action expression for the reaction: \( 2H_2(g) + O_2(g) \leftrightarrow 2H_2O(g) \)

\[ Q_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} \]

At equilibrium \( Q_c = K_c \)

• The mass-action expressions for \( Q \) and \( K \) depend on the form of the chemical equation

\[ \Rightarrow Q \text{ (or } K) \text{ of the reverse reaction is the reciprocal of } Q \text{ (or } K) \text{ of the forward reaction} \]

Multiplying a reaction by a factor, \( n \), raises \( Q \) (or \( K \)) to \( n^{th} \) power

1. \( A \leftrightarrow B \) \quad or \quad \( nA \leftrightarrow nB \)
  
  \[ Q_c = \frac{[B]}{[A]} \quad Q'_c = \frac{[B]^n}{[A]^n} = (Q_c)^n \]

\( \Rightarrow \) Multiplying a reaction by a factor, \( n \), raises \( Q \) (or \( K \)) to \( n^{th} \) power

1. \( A + B \leftrightarrow C \)
  
  \[ Q_1 = \frac{[C]}{[A][B]} \]

2. \( A + B \leftrightarrow D \)
  
  \[ Q_2 = \frac{[D]}{[C]} \]

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

\( \Rightarrow Q \) (or \( K \)) of the sum of two or more reactions is the product of their \( Qs \) (or \( Ks \))
**Example:** For the gas phase reaction

$$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \leftrightarrow \text{HCl}(\text{g})$$

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

$$2\text{HCl}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})?$$

$\Rightarrow$ The given reaction has been reversed $\Rightarrow$ take the reciprocal of $K_c$

$\Rightarrow$ The given reaction has been multiplied by 2 $\Rightarrow$ take the square of $K_c$

$\Rightarrow K_c' = (1/K_c)^2 = (1/3.6 \times 10^{-5})^2 = 7.7 \times 10^8$

**Example:** Given the following two reactions and their $K_c$s at a certain temperature:

$\text{N}_2\text{O}_4(\text{g}) \leftrightarrow 2\text{NO}_2(\text{g}) \quad K_{c1} = 2.2 \times 10^6$

$2\text{NO}_2(\text{g}) \leftrightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \quad K_{c2} = 1.6 \times 10^{-10}$

Calculate $K_c$ at this temperature for the reaction

$$\text{N}_2\text{O}_4(\text{g}) \leftrightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$$

$\Rightarrow$ The sum of the given reactions yields the desired reaction $\Rightarrow$ multiply the $K_c$

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

$\Rightarrow K_c = 3.5 \times 10^{-4}$