Unit 5

CHEMICAL EQUILIBRIUM

Introduction

In the previous unit, you learned about the rate of reactions and how the time taken for half of the reaction to be completed can vary. However, some important questions remain unanswered, such as whether all reactions reach completion, the extent to which a reaction progresses, and why some reactions reach equilibrium instead of completing fully. In this unit, we will explore these concepts by studying **chemical equilibrium**, its attainment, and the factors affecting it.

Irreversible vs. Reversible Reactions

- **Irreversible Reactions:** In some chemical reactions, the reactants are completely converted into products, leaving very little or no reactants behind. These are known as irreversible reactions. For example:

  $C(s) + O_2(g) \rightarrow CO_2(g)$

  A single arrow (→) is used to indicate that the reaction proceeds in only one direction.

- **Reversible Reactions:** In other cases, reactions do not go to completion. Instead, they proceed in both forward (reactants to products) and reverse (products back to reactants) directions. These are known as reversible reactions, denoted by a double arrow (⇌). For example:

  $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3$

  Here, the reaction can move in either direction depending on the conditions.

Attainment of Chemical Equilibrium

In a reversible reaction, the forward reaction (reactants forming products) initially proceeds at a higher rate, while the reverse reaction (products reverting to reactants) starts slowly. Over time, as the concentration of products increases and that of reactants decreases, the rate of the forward reaction decreases while the reverse reaction rate increases. Equilibrium is attained when these two rates become equal:

Rate of forward reaction (r_f)=Rate of reverse reaction (r_r)

At equilibrium, the concentrations of the reactants and products remain constant, although the reactions continue to occur dynamically.

Characteristics of Chemical Equilibrium

- **Reversibility:** The reaction is reversible.
- **Dynamic Nature:** Even though there is no net change in concentrations, the forward and reverse reactions continue to occur.
- **Rate Equality:** The rates of the forward and reverse reactions are equal at equilibrium.
- **No Change in Concentrations:** The concentrations of reactants and products remain constant.
- **Closed System:** Equilibrium can only be reached in a closed system where no substances are added or removed.

Equilibrium Constant (K)

The **equilibrium constant** (K) quantifies the ratio of the concentrations of products to reactants at equilibrium. For a general reversible reaction:

$aA+bB \rightleftharpoons cC+dD$

The equilibrium constant expression is:

$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Where [A],[B],[C], and [D] are the equilibrium concentrations of the reactants and products, and a,b,c, and d are their respective coefficients in the balanced equation.

Types of Equilibrium Constants

- **K_c:** Based on the concentration of reactants and products in a solution.
- **K_p:** Based on the partial pressures of gaseous reactants and products.

Relationship Between K_c and K_p

For reactions involving gases, K_c (concentration-based) and K_p (pressure-based) are related by the equation:

$K_p = K_c(RT)^{\Delta n}$

Where:

- R is the gas constant.
- T is the temperature in Kelvin.
- Δn is the difference in moles of gaseous products and reactants.

Factors Affecting Equilibrium: Le Chatelier's Principle

Le Chatelier's Principle states that if an external change is applied to a system at equilibrium, the system adjusts to counteract that change. Factors that affect equilibrium include:

- **Concentration:** Increasing the concentration of reactants or products shifts the equilibrium towards the other side.
- **Pressure/Volume:** For reactions involving gases, an increase in pressure (or decrease in volume) favors the side with fewer moles of gas.
- **Temperature:** For endothermic reactions, an increase in temperature shifts the equilibrium to the right (towards products), while for exothermic reactions, it shifts to the left (towards reactants).
- **Catalysts:** Catalysts speed up the attainment of equilibrium but do not affect the position of the equilibrium.

Applications of Chemical Equilibrium

- **Haber Process (Ammonia Synthesis):**

  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

  Optimizing conditions (temperature, pressure, catalysts) based on Le Chatelier's principle is crucial for maximizing ammonia production.

- **Contact Process (Sulfuric Acid Production):**

  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Again, optimal conditions must be chosen to favor the production of sulfur trioxide, the precursor to sulfuric acid.

Understanding chemical equilibrium is essential in predicting the extent of a reaction and manipulating conditions to favor desired outcomes. The concept is widely applied in industrial processes, such as the Haber and Contact processes, to maximize efficiency and yield.

Applications of Equilibrium Constant

The equilibrium constant (Kc or Kp) of a reaction provides valuable insights into the behavior of a chemical system at equilibrium. It can be used to predict the composition of the equilibrium mixture, the direction in which a reaction will proceed, and the equilibrium concentrations of reactants and products.

A. Predicting the Composition of an Equilibrium Mixture

The magnitude of the equilibrium constant helps in determining the extent of a reaction.

- **Large K_c or K_p Values**: If K_c or K_p is very large (e.g., greater than 10^{10}), it indicates that the reaction strongly favors the formation of products, and the equilibrium lies far to the right. This means that the equilibrium mixture will predominantly consist of products, implying the reaction goes nearly to completion.
- **Small K_c or K_p Values**: If K_c or K_p is very small (e.g., less than 10^{-10}), it suggests that the reaction favors the reactants, and the equilibrium lies far to the left. In this case, the equilibrium mixture will consist mostly of reactants, indicating that the reaction proceeds very little towards the products.

B. Predicting the Direction of the Reaction

The direction in which a reaction will proceed to reach equilibrium can be predicted by comparing the reaction quotient (Q_c) with the equilibrium constant (K_c).

- **Reaction Quotient (Q_c)**: Q_c is calculated using the same expression as K_c but with the concentrations at any point during the reaction, not necessarily at equilibrium.

For a general reaction:
$aA+bB \rightleftharpoons cC+dD$

$Q_C = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$

Comparing Qc with Kc:

1. **If $Q_c = K_c$**: The reaction is already at equilibrium.
2. **If $Q_c < K_c$**: The reaction will proceed in the forward direction (to the right) to produce more products until equilibrium is reached.
3. **If $Q_c > K_c$**: The reaction will proceed in the reverse direction (to the left) to produce more reactants until equilibrium is reached.

Example: For the reaction CO (g) + Cl_2 (g) ⇌ $COCl_2$ (g), if Kc = 13.8 and the initial concentrations are [CO] = 2.5 M, [Cl_2] = 1.2 M, and [$COCl_2$] = 5.0 M, we calculate Qc as follows:

$Q_C = [\frac{COCl2]}{[CO] \times [Cl2]} = \frac{5.0}{2.5 \times 1.2} = 1.67$

Since $Q_C < K_C$, the reaction will proceed to the right, forming more products.

C. Calculating Equilibrium Concentrations

To find the equilibrium concentrations of reactants and products, follow these steps:

1. **Write the balanced equation** and the expression for K_c or K_p.
2. **List the initial concentrations** of reactants and products.
3. **Calculate Q_c** to determine the direction of the reaction.
4. **Define the change in concentrations** needed to reach equilibrium and express the equilibrium concentrations in terms of this change.
5. **Substitute these equilibrium concentrations into the K_c or K_p expression** and solve for the unknown concentration.
6. **Check** the calculated concentrations to ensure they give the correct value of K_c or K_p.

Example: For the reaction H_2 (g) + I_2 (g) ⇌ 2HI (g) with Kc = 69 and initial concentrations of [H_2] = 2.0 M, [I_2] = 4.0 M, and [HI] = 0 M, we find the equilibrium concentrations as follows:

Let the change in concentration of H_2 and I_2 be -x and that of HI be +2x:

[H2]=2.0−x

[I2]=4.0−x

$[HI] = 2x$

Substituting into the K_c expression:

$$69 = \frac{(2x)^2}{(2.0 - x)(4.0 - x)}$$

Solving the quadratic equation gives the value of x, which can be used to find the equilibrium concentrations of H_2, I_2, and HI.