

CHEMICAL EQUILIBRIUM

- **Equilibrium:** It is a state in a process when two opposing processes (forward and reverse) occur simultaneously at the same rate.
- The free energy change at equilibrium state is zero i.e., $\Delta G = 0$

STATIC AND DYNAMIC EQUILIBRIUM

- **Dynamic equilibrium** is the steady state of a reversible reaction where the rate of the forward reaction is the same as the reaction rate in the backward direction.
- **Static equilibrium**, also known as mechanical equilibrium, means the reaction has stopped.

REVERSIBLE AND IRREVERSIBLE REACTIONS

- **Reversible reaction:** A reaction is said to be reversible if under certain conditions of temperature and pressure, the forward and reverse reactions occur simultaneously.
- Reversible reactions are indicated by placing two half arrows pointing in opposite directions (\rightleftharpoons) between the reactants and products.

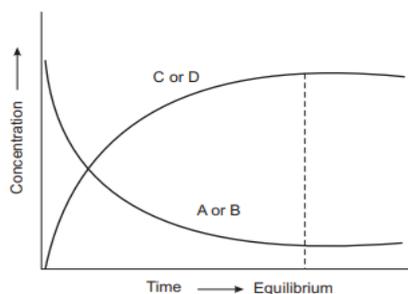
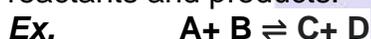


Fig. 11.1: Equilibrium in reversible reaction

- **Irreversible Reaction:** Most of the reactions occur only in one direction. They are called irreversible reactions.
Ex. $C(s) + O_2(g) \longrightarrow CO_2(g)$

CHARACTERISTICS OF EQUILIBRIUM STATE

- Chemical Equilibrium is dynamic in nature
- Equilibrium can be attained from either side
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- A catalyst cannot change the equilibrium state

EQUILIBRIUM IN PHYSICAL PROCESSES; PHASE EQUILIBRIUM

- Solid-Liquid Equilibrium:** The equilibrium is represented as:



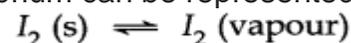
- Rate of melting of ice = Rate of freezing of water.

- Liquid-Vapour Equilibrium:** The equilibrium can be represented as



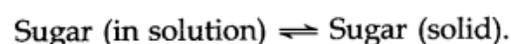
- Rate of evaporation = Rate of condensation

- Solid-Vapour Equilibrium:** The equilibrium can be represented as



- Rate of sublimation of liquid I_2 = Rate of condensation of I_2 vapour to give solid I_2

- Solute - Solution Equilibrium:** The equilibrium can be represented as:

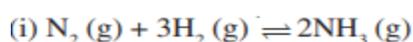


- Here dissolution and precipitation takes place with the same speed.
- **(v) Phase and Phase Equilibrium:** A phase is defined as a homogenous part of a system which has uniform

composition and properties throughout.

EQUILIBRIUM IN HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

- A system consisting of only one phase is called a **homogeneous system**
- Any system consisting of two or more phases is called **heterogeneous system**
- Homogeneous Equilibrium Systems:** Are of two types:
 - (a) **Gas – Phase homogeneous systems:** Such systems contain only gaseous reactants and products. **Ex.**



- (b) **Liquid – Phase homogeneous systems:** These are the systems in which both the reactants and products are present in only one liquid phase (as a solution). **Ex**



- Heterogeneous Chemical Equilibrium Systems:** The systems in which reactants and products are present in more than one phase belong to this type. For example :



LAW OF MASS ACTION

- The law of mass action states that the rate of a reaction is proportional to the product of the concentrations of each reactant.

$$K_{\text{eqm}} = \frac{k_f}{k_b} = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

QUANTITATIVE ASPECT OF EQUILIBRIUM STATE

- (i) **Equilibrium constant :** For a general reaction : $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \text{ and } K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

- Relationship between K_p and K_c :**

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

$$\Delta n_g = n_p(\text{g}) - n_r(\text{g})$$

- Units of Equilibrium Constant:** Units of equilibrium constant K_c or K_p depend upon the fact whether during the reactions there is any change in the moles of substance or not.
- (a) The reactions in which there is no change in moles of substance i.e. $\Delta n = 0$.
 K_p and K_c have no units in such cases.
- (b) The reaction where there is change in the moles of substance i.e. $\Delta n \neq 0$. The equilibrium constant for such reactions has units which depend upon the change in moles of substances.
- Significance of the Magnitude of K:** Magnitude of equilibrium constant depends upon the way in which a reaction is written:

FACTORS AFFECTING EQUILIBRIUM STATE

- Le-Chatelier's Principle:** When a system of equilibrium is subjected to a change in temperature, pressure or concentration, the equilibrium shifts itself in such a way so as to undo or counter out the effect of change.

- Outcomes of Le-Chatelier's Principle:**

Change at equilibrium	Shift in equilibrium
Increase in temperature	Endothermic direction
Decrease in temperature	Exothermic direction
Increase in pressure	Towards lesser gaseous moles
Decrease in pressure	Towards greater gaseous moles
Increase in Conc. of reactants	Forward direction
Increase in Conc. of products	Reverse direction

Applications of Le Chatelier's Principle:

- Le Chatelier's principle** can be used to predict the behavior of a system due to changes in pressure, temperature,

or concentration. **Le Chatelier's principle** implies that the addition of heat to a reaction will favor the endothermic direction of a reaction as this reduces the amount of heat produced in the system.

- The classic **example** of the practical use of the **Le Chatelier principle** is the Haber-Bosch process for the synthesis of ammonia, in which a balance between low temperature and high pressure must be found.

Calculation of Equilibrium Constants:

Equilibrium constants K_c and K_p can be calculated if the equilibrium concentrations or partial pressures are known or can be obtained from the given data.

- Reversible reactions do not reach completion stage and result in a state of equilibrium which is reached when two opposite processes occur at the same rate.
- The macroscopic properties of the system do not change once the equilibrium has been established.
- Irreversible reactions are in fact the reversible reactions in which the equilibrium is reached only when a negligible amount of the reactants is left unreacted.
- Chemical equilibrium is **dynamic** in nature. It can be attained by starting the reaction from any side and only in a closed system.
- When equilibrium is reached as a result of two opposite physical changes, it is called physical equilibrium and when as a result of two opposite chemical changes it is called **chemical equilibrium**.

- **Chemical equilibrium** can be homogeneous or heterogeneous while **physical equilibrium** is always heterogeneous.

- For a general reaction

$$aA + bB \rightleftharpoons cC + dD$$
- According to the law of equilibrium, the equilibrium constant K is given by the expression:

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

- Concentration equilibrium constant K_c is obtained when molar concentration are used for calculating K . Concentrations of pure solids and liquids are constant and are not included in the expression of K_c .
- In case of gaseous systems, the concentrations of gases are expressed in terms of their partial pressures. The equilibrium constant thus obtained is called the **pressure equilibrium constant, K_p** .
- A catalyst does not change the equilibrium constant. It only helps in reaching the equilibrium state quicker.

Predicting the Direction of the Reaction:

- If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).
- If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).
- If $Q_c = K_c$, the reaction mixture is already at equilibrium.
- Le Chatelier's Principle It can be applied to physical as well as chemical equilibrium

Check Yourself

- The solubility of $\text{Ca}_3(\text{PO}_4)_2$ in water is y mol/L. Its solubility product is:
 (A) $6y^2$ (B) $36y^4$
 (C) $64y^5$ (D) $108y^5$
- Which of the following aqueous solutions will have highest pH?
 (A) NaCl (B) CH_3COONa
 (C) Na_2CO_3 (D) NH_4Cl
- What is the pH of a 0.10 M solution of barium hydroxide, $\text{Ba}(\text{OH})_2$?
 (A) 11.31 (B) 11.7
 (C) 13.30 (D) None of these
- Which of the following oxides is not expected to react with sodium hydroxide?
 (A) CaO (B) SiO_2
 (C) BeO (D) B_2O_3
- The pH of a 10^{-10} M NaOH solution is nearest to
 (A) 10 (B) 7
 (C) 4 (D) -10

Test Yourself

Question: Can a catalyst change the position of equilibrium in a reaction?

Answer: No, a catalyst cannot change the position of equilibrium in a chemical reaction. A catalyst, however, affects the rate of reaction.

Stretch Yourself

- How does dilution with water affect the pH of a buffer solution?
- What conclusion is drawn from the following –
 Solid \rightleftharpoons Liquid
 $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$
- Write the expression for equilibrium constant K_p for the reaction
 $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$
- The equilibrium constant for the reaction $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$ is 0.44 at 1260K. What will be the value of the equilibrium constant for the reaction :
 $2\text{H}_2(\text{g}) + 2\text{CO}(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ at 1260 K
- If $Q_c > K_c$, what would be the type of reaction?



Answers

Check Yourself

Answer: 1(D); 2(C); 3(C); 4(A); 5(C)

Stretch Yourself

1. Dilution with water has no effect on the pH of any buffer. This is because pH of a buffer depends on the ratio of the salt, acid or salt base and dilution does not affect this ratio.
2. Melting point is fixed at constant pressure.
- 3.

$$K_p = \frac{(PH_2)^4}{(PH_2O)^4} = \frac{PH_2}{PH_2O}$$

4. The reaction is reversed and also doubled,

$$\therefore K_c = \left(\frac{1}{0.44}\right)^2 = \underline{\underline{5.16}}$$

5. If $Q_c > K_c$, the reaction will proceed in the direction of the reactants (reverse reactions)