**23 YEARS** OF LEGACY

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**STUDY CIRCLE**
ACCENTS EDUCATIONAL PROMOTERS
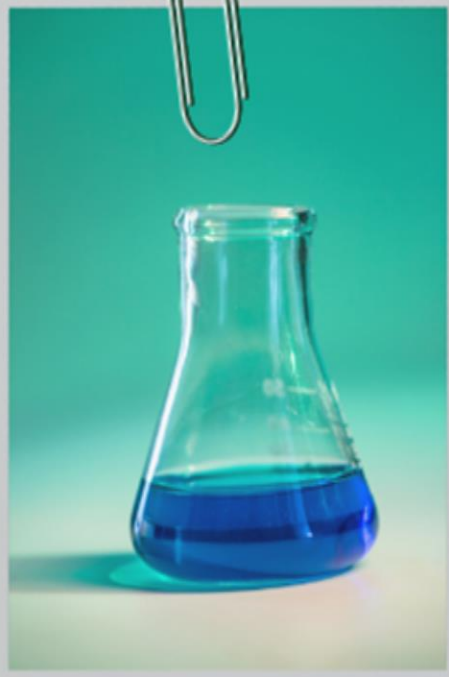
CHEMISTRY

EQUILIBRIUM

REVISION MODULE

CBSE
OFFLINE-ONLINE

IIT-JEE
NEET
LEARNING ACADEMY

$$2Hg + O_2 \qquad H_2$$

$$\text{conc } H_2SO_4 \xrightarrow{\text{heat}}$$

$$O_2 \rightarrow CO_2 + 2H_2O$$

$$C + O_2 \quad \underline{\text{five}}$$
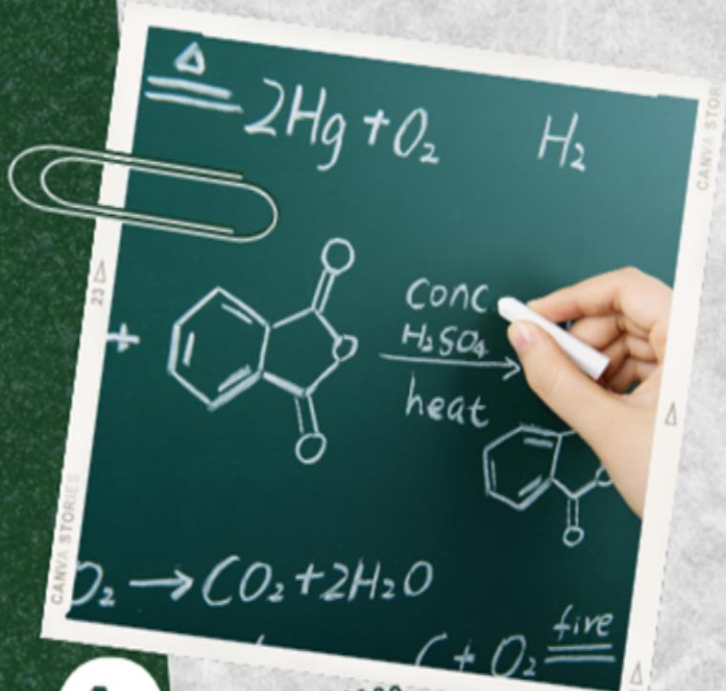
Welcome to the Chemical Equilibrium Revision Module designed specifically for CBSE Class 11 Chemistry students. This module aims to provide a comprehensive review of the concept of chemical equilibrium, a fundamental topic in the study of chemical reactions.

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# EQUILIBRIUM

## REVISION MODULE

- **Comprehensive Coverage:** This module covers all essential aspects of chemical equilibrium, ensuring thorough preparation for exams and assessments.
- **Clear Explanation:** Concepts are explained clearly and concisely, making it easy to understand and apply them in problem-solving.
- **Practice-oriented Approach:** Ample practice problems and quizzes allow for hands-on learning and mastery of the topic.

## Recap Notes

- **Physical equilibrium :** It is the process which involves physical changes only, like equilibrium between different states of substances at a particular temperature.
  - Solid $\rightleftharpoons$ Liquid : ice $\rightleftharpoons$ water at $0\,°C$
    
    rate of melting = rate of freezing
  - Liquid $\rightleftharpoons$ Gas (vapour) :
    
    water (liquid) $\rightleftharpoons$ water (vapours) at $100\,°C$
    
    rate of evaporation = rate of condensation
  - Solid $\rightleftharpoons$ Gas (vapour) :
    
    $CO_2$ (solid) $\rightleftharpoons$ $CO_2$ (vapours)
    
    rate of sublimation = rate of condensation
  - Solid $\rightleftharpoons$ Saturated solution of solid in liquid
    
    rate of dissolution = rate of precipitation
  - Gas $\rightleftharpoons$ Saturated solution of gas in liquid is always exothermic and spontaneous.
  - **Freezing point/melting point :** The temperature at which the solid-liquid equilibrium is reached for a pure substance under one atmospheric pressure is called normal *melting point* or normal *freezing point* of the substance.
  - **Boiling point :** The temperature at which liquid-gas equilibrium is attained for a pure substance under one atmospheric pressure is called normal *boiling point* of the substance.

- **General characteristics of physical equilibria :**
  - Equilibrium can be established only in case of closed system, *i.e.,* the system should neither gain matter from the surroundings nor lose matter to the surroundings.

- ▶ The equilibrium is always dynamic in nature. This means that the process does not stop but the changes take place in the forward and backward directions with the same speed.
- ▶ The measurable properties of the system become constant at equilibrium. This is so because the concentration of the substances become constant.
- ▶ At equilibrium, there exists an expression involving concentration of reacting substances which becomes constant at a given temperature. For example, for the equilibrium,
- ▶ $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ the pressure of water becomes constant.
- ▶ The magnitude of the constant value of the concentration related expression (called *equilibrium constant*) gives an indication of the extent to which the reaction proceeds before acquiring equilibrium.
- ▶ **Some features of physical equilibrium**

| | Process | Conclusion |
|---|---|---|
| 1. | $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ [liquid $\rightleftharpoons$ vapour] | $P_{H_2O}$ is constant at given temperature. |
| 2. | $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$ [solid $\rightleftharpoons$ liquid] | Melting point is constant at a given pressure. |
| 3. | $Sugar_{(s)} \rightleftharpoons Sugar_{(aq)}$ (solution) [Solute$_{(s)}$ $\rightleftharpoons$ Solute$_{(aq)}$] (solution) | Concentration of sugar (solute) in solution is constant at a given temperature. |

| 4. | $CO_{2(g)} \rightleftharpoons CO_{2(aq)}$<br>$[gas_{(g)} \rightleftharpoons gas_{(aq)}]$ | $\dfrac{[CO_{2(aq)}]}{[CO_{2(g)}]}$<br><br>$\left(i.e., \dfrac{[gas_{(aq)}]}{[gas_{(g)}]}\right)$<br><br>is constant at a given temperature. |
|----|---|---|

- **Chemical equilibrium :** If the process involves only chemical change, the equilibrium is called *chemical equilibrium.*
  - ▶ **Reversible reaction :** A reaction in which the reactants are formed back by the reaction of products with each other at the given conditions of the reaction. These reactions if carried out in a closed vessel do not go to completion.

    *e.g.,* $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
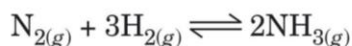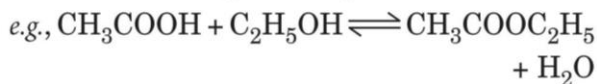
    $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
  - ▶ **Irreversible reaction :** These are the reactions in which products do not react back to give the reactants, *i.e.,* reaction cannot be retraced at any point.
  - ▶ **State of equilibrium :** Chemical equilibrium is that state of a reaction at which the rate of forward reaction becomes equal to rate of backward reaction.
- **Dynamic nature of equilibrium :** In dynamic equilibrium, changes occur but in opposite directions and at constant rate *i.e.,* forward and backward reactions take place even after the equilibrium is attained but at equal speeds.
- **General characteristics of chemical equilibrium :**
  - ▶ It is dynamic in nature.
  - ▶ The observable properties of the system become constant at equilibrium and remain unchanged thereafter.
  - ▶ The equilibrium can be approached from either directions.
  - ▶ The equilibrium can be attained only if the system is a closed one.
  - ▶ The free energy change at constant pressure and temperature is zero.
  - ▶ Addition of a catalyst does not change the equilibrium state, it only helps in attaining the equilibrium faster.

- **Law of chemical equilibrium :**
  - ▶ For the reversible reaction,

    $aA_{(aq)} + bB_{(aq)} \rightleftharpoons xX_{(aq)} + yY_{(aq)}$

    At equilibrium, $\dfrac{[X]^x[Y]^y}{[A]^a[B]^b} = K_c$, $K_c$ is called *equilibrium constant* which is constant for a reaction at constant temperature.
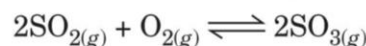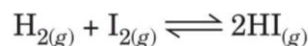  - ▶ Relations between equilibrium constants for a general reaction and its multiples.

| Chemical equation | Equilibrium constant |
|---|---|
| $aA + bB \rightleftharpoons cC + dD$ | $K$ |
| $cC + dD \rightleftharpoons aA + bB$ | $K'_c = (1/K_c)$ |
| $naA + nbB \rightleftharpoons ncC + ndD$ | $K''_c = (K^n_c)$ |

- **Types of equilibrium :**
  - ▶ **Homogeneous equilibrium :**

    Equilibrium is said to be homogeneous if reactants and products are in same phase, *e.g.,*

    $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

    $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

  - ▶ **Relationship between $K_p$ and $K_c$ :**

    For reaction : $aA + bB \rightleftharpoons xX + yY$

    $K_c = \dfrac{[X]^x[Y]^y}{[A]^a[B]^b}$ and $K_p = \dfrac{P_X'^x P_Y'^y}{P_A'^a P_B'^b}$

    (for gaseous reaction)

    For ideal gases $PV = nRT$

    or $\dfrac{P}{RT} = \dfrac{n}{V}$ (concentration in mole L$^{-1}$)

    ∴ Concentration of $A$, $[A] = \dfrac{n_A}{V} = \dfrac{P_A'}{RT}$

    Similarly, $[B] = \dfrac{n_B}{V} = \dfrac{P_B'}{RT}$

    Substituting these values :

    $K_c = \dfrac{\left(\dfrac{P_X'}{RT}\right)^x \left(\dfrac{P_Y'}{RT}\right)^y}{\left(\dfrac{P_A'}{RT}\right)^a \left(\dfrac{P_B'}{RT}\right)^b}$

    $= \dfrac{P_X'^x \cdot P_Y'^y}{P_A'^a \cdot P_B'^b} \times \dfrac{\left(\dfrac{1}{RT}\right)^x \left(\dfrac{1}{RT}\right)^y}{\left(\dfrac{1}{RT}\right)^a \left(\dfrac{1}{RT}\right)^b} = K_p \left(\dfrac{1}{RT}\right)^{(x+y)-(a+b)}$

$(x + y) - (a + b) = \Delta n_g$ (difference in number of moles of gaseous products and reactants)

$$\therefore \quad K_c = K_p \left(\frac{1}{RT}\right)^{\Delta n_g}$$
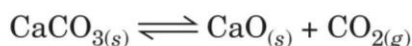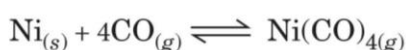
or $\quad K_p = K_c (RT)^{\Delta n g}$

If $\quad \Delta n_g = 0, K_p = K_c$

If $\quad \Delta n_g = +\text{ve}, K_p > K_c$

If $\quad \Delta n_g = -\text{ve}, K_p < K_c$

▶ **Heterogeneous equilibrium :**

Equilibrium is said to be heterogeneous if reactants and products are in different phases, *e.g.,*

$$Ni_{(s)} + 4CO_{(g)} \rightleftharpoons Ni(CO)_{4(g)}$$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

▶ **Units of equilibrium constant :** Concentration of a substance is measured in terms of moles/litre, therefore, unit of $K_c$ is $(\text{mol } L^{-1})^{\Delta n g}$. Similarly, partial pressure is measured in terms of atmosphere, hence, unit of $K_p$ is $(\text{atm})^{\Delta n_g}$
   – If $\Delta n = 0$, both $K_c$ and $K_p$ have no units
   – If $\Delta n > 0$, unit of $K_c = (\text{mol } L^{-1})^{\Delta n_g}$, unit of $K_p = (\text{atm})^{\Delta n_g}$
   – If $\Delta n < 0$, unit of $K_c = (L \text{ mol}^{-1})^{\Delta n_g}$, unit of $K_p = (\text{atm}^{-1})^{\Delta n_g}$

▶ Equilibrium constants can also be expressed as dimensionless quantities if the standard states of reactants and products are specified.

● **Applications of equilibrium constant :**
   ▶ **Predicting the extent of a reaction :** The magnitude of equilibrium constant $K$ indicates the extent to which a reaction can go. In other words, it is a measure of the completion of a reversible reaction. Larger the value of $K$, greater will be the equilibrium concentration of the components on the right hand side of reaction relative to those on the left hand side, *i.e.,* the reaction proceeds to a greater extent.

For example, consider the reaction :

$$2NO_{2(g)} \rightleftharpoons N_{2(g)} + 2O_{2(g)} \text{ at } 298 \text{ K}$$
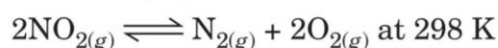
$$K = \frac{[N_2][O_2]^2}{[NO_2]^2} = 6.7 \times 10^{-16}$$

The value of $K$ is very small which means that the forward reaction has proceeded to small extent only. Thus we can say that $NO_2$ is quite stable and decomposes only slightly.

▶ **Predicting the direction of a reaction :** The equilibrium constant helps in predicting the direction in which a reaction can proceed at any stage. By substituting the concentration of substances that exist in a reaction mixture we can calculate the reaction quotient, $Q$ and comparing the value of $Q$ with the equilibrium constant, $K$, we can predict whether the reaction will proceed towards products or towards reactants.

**Case I :** If $Q < K$, the reaction will proceed in the forward direction.

**Case II :** If $Q > K$, the reaction will proceed in the backward direction.

**Case III :** If $Q = K$, the reaction mixture is already at equilibrium.

● **Relation between equilibrium constant ($K$) and $\Delta G°$ :**
   ▶ Free energy change ($\Delta G$) is related to $\Delta G$ as follows, $\Delta G = \Delta G° + 2.303 \, RT \log Q$

But at equilibrium, $Q = K$ and $\Delta G = 0$

$\therefore \quad \Delta G = -2.303 \, RT \log K$

If $K > 1$, then $\Delta G = -$ve, *i.e.,* reaction is spontaneous in forward direction.

If $K < 1$, then $\Delta G = +$ve, *i.e.,* reaction is spontaneous in backward direction.

▶ **Le Chatelier's principle :** The law states that if any kind of change in concentration, temperature or pressure is imposed on the system in equilibrium, then equilibrium shifts in a direction that tends to undo the effect of the change imposed.

▶ **Effect of change in concentration :** In a reaction at equilibrium, if concentration of any reactant or product is increased, the equilibrium shifts in a direction where it will be consumed or if concentration of any reactant or product is decreased, the equilibrium will shift in a direction where it will be produced.

▶ **Effect of change in temperature :** In a reaction at equilibrium if temperature is increased, reaction will proceed in the direction in which some heat can be destroyed *i.e.,* absorbed so that
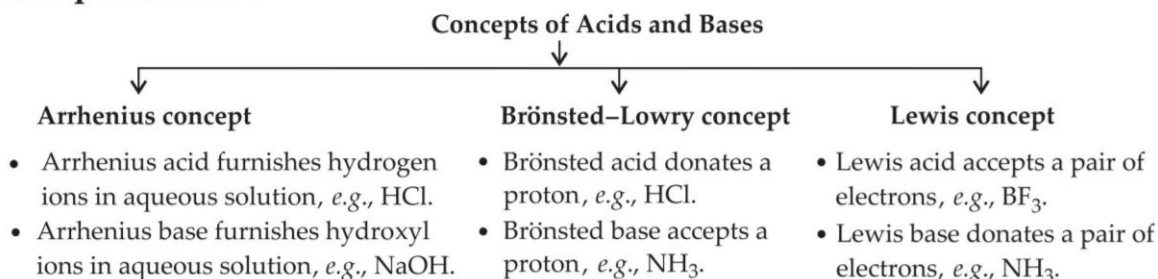
temperature of the system remains constant. It means increase in temperature supports the endothermic reaction, where heat is absorbed. Decrease in temperature favours exothermic reaction in which heat is liberated.

▶ **Effect of change in pressure :** In a reaction at equilibrium if pressure is increased, then according to Le Chatelier's principle, the equilibrium will shift in a direction in which the pressure decreases. This implies that equilibrium will shift in a direction which produces smaller number of moles, since pressure is directly proportional to the number of moles. On the other hand we can say that if the pressure on the system in equilibrium is decreased, the equilibrium will shift in the direction in which it is accompanied by increase in total number of moles.

▶ **Effect of catalyst :** Catalyst increases the speed of forward as well as backward reaction to the same extent. Therefore, it does not affect the equilibrium position. It only helps in attaining the equilibrium state quickly without shifting it in any direction.

▶ **Effect of adding inert gas :**
   - If inert gas is added at constant volume to the reaction at equilibrium, the equilibrium will not be changed/ disturbed, because at constant volume addition of an inert gas will not change the molar concentration of the reactants and products.
   - If inert gas is added at constant pressure to the reaction at equilibrium, the volume of reaction mixture increases and equilibrium will shift in the direction in which there is increase in the number of moles of the gas. If

number of moles on either side of equilibrium are same, there will be no effect of adding an inert gas on the state of equilibrium.

 - **Application of Le Chatelier's principle to chemical equilibria :**
 - For reaction, $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ ; $\Delta H = +ve$
 - **Effect of change in temperature :** The dissociation of $PCl_5$ is endothermic. Hence increase of temperature increases the rate of formation of $PCl_3$ and $Cl_2$.
 - **Effect of change in pressure :** Increase of pressure will favour the backward direction, with decrease in the number of gaseous moles.
 - **Effect of change in concentration :** Addition of $PCl_3$ or $Cl_2$ or removal of $PCl_5$ will shift the equilibrium in backward direction.
 - **Effect of adding an inert gas :** In above reaction, $n_p > n_r$, addition of an inert gas has no effect at constant volume but, at constant pressure, the equilibrium shifts in the forward direction.
 - For reaction, $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ ; $\Delta H = +ve$
 - **Effect of change in temperature :** The dissociation of HI is an endothermic reaction hence increase of temperature favours the formation of $H_2$ and $I_2$.
 - **Effect of change in pressure :** As the number of reactant molecules is equal to the number of product molecules, hence pressure has no effect on the equilibrium.
 - **Effect of change in concentration :** Addition of HI or removal of $H_2$ or $I_2$ favours the forward reaction.
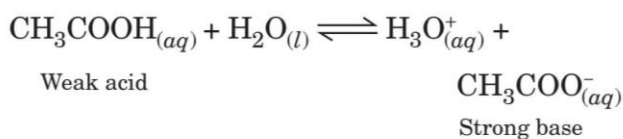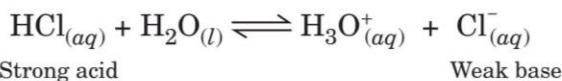
• **Ionic Equilibrium :**

Concepts of Acids and Bases

| Arrhenius concept | Brönsted–Lowry concept | Lewis concept |
|---|---|---|
| • Arrhenius acid furnishes hydrogen ions in aqueous solution, *e.g.*, HCl.<br>• Arrhenius base furnishes hydroxyl ions in aqueous solution, *e.g.*, NaOH. | • Brönsted acid donates a proton, *e.g.*, HCl.<br>• Brönsted base accepts a proton, *e.g.*, NH₃. | • Lewis acid accepts a pair of electrons, *e.g.*, BF₃.<br>• Lewis base donates a pair of electrons, *e.g.*, NH₃. |

▶ **Conjugate acid - base pairs :** These are pairs of acids and bases which differ by a proton, *e.g.*,

$$\text{Acid} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \text{conjugate base}$$
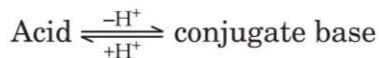
▶ Relative strengths of conjugate acids or bases depend upon their tendency to donate a proton or to accept a proton.

▶ Stronger the acid, weaker is its conjugate base and vice-versa, *e.g.*,

$$\underset{\text{Strong acid}}{HCl_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Weak base}}{Cl^-_{(aq)}}$$

$$\underset{\text{Weak acid}}{CH_3COOH_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Strong base}}{CH_3COO^-_{(aq)}}$$

▶ **Relative strength of acids and bases :** This is the ratio of strengths of acids. *e.g.*, for acids $HA_1$ and $HA_2$:

$$HA_1 \rightleftharpoons H^+ + A_1^-; \ K_{a_1} = C_1\alpha_1^2$$
$$HA_2 \rightleftharpoons H^+ + A_2^-; \ K_{a_2} = C_2\alpha_2^2$$
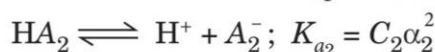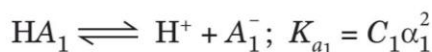
Relative strength

$$= \frac{[H^+] \text{ furnished by } HA_1}{[H^+] \text{ furnished by } HA_2} = \frac{C_1\alpha_1}{C_2\alpha_2}$$
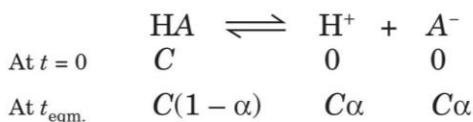
$$(\because \ \alpha = \sqrt{K_a/C})$$

$$= \frac{C_1\sqrt{K_{a_1}/C_1}}{C_2\sqrt{K_{a_2}/C_2}} = \sqrt{(K_{a_1}C_1)/(K_{a_2}C_2)}$$

If concentrations of acids are same, then

$$\text{Relative strength} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

● **Dissociation constant of weak acids and weak bases :** Let us consider the dissociation of a weak acid $HA$ as,

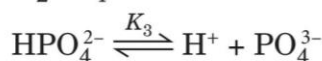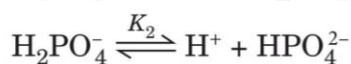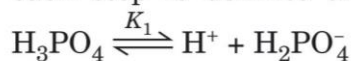| | $HA$ | $\rightleftharpoons$ | $H^+$ | + | $A^-$ |
|---|---|---|---|---|---|
| At $t = 0$ | $C$ | | $0$ | | $0$ |
| At $t_{eqm.}$ | $C(1-\alpha)$ | | $C\alpha$ | | $C\alpha$ |

Dissociation constant of acid,

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

Similarly, for the dissociation of a weak base $BOH$ as $BOH \rightleftharpoons B^+ + OH^-$

Dissociation constant of base,

$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha^2}{(1-\alpha)}$$

▶ **Dissociation constant for polyprotic acids and bases :** These acids involve number of steps to ionise completely, where number of steps is equal to the number of replaceable hydrogen atoms. The value of ionisation constant of each step is definite and constant *e.g.*,

$$H_3PO_4 \overset{K_1}{\rightleftharpoons} H^+ + H_2PO_4^-$$
$$H_2PO_4^- \overset{K_2}{\rightleftharpoons} H^+ + HPO_4^{2-}$$
$$HPO_4^{2-} \overset{K_3}{\rightleftharpoons} H^+ + PO_4^{3-}$$

The overall dissociation constant $(K)$ is given as $K = K_1 \times K_2 \times K_3$ where $K_1 > K_2 > K_3$.

● **pH and pH-scale :** pH of a solution is defined as the negative logarithm of hydrogen ion concentration.

$$pH = -\log[H^+] \ \text{or} \ pH = -\log[H_3O^+]$$

$$\text{or} \quad pH = \log\frac{1}{[H^+]}$$

Similarly, negative logarithm of hydroxyl ion concentration is called pOH.

$$pOH = -\log[OH^-] \ \text{or} \ pOH = \log\frac{1}{[OH^-]}$$

▶ **pH-scale :** A solution is classified as acidic, basic or neutral based on its pH value.
  – If pH = pOH = 7, then solution will be neutral.
  – If pH < 7 or pOH > 7, then solution will be acidic.
  – If pH > 7 or pOH < 7, then solution will be basic.
  – pH scale varies from 0 to 14.

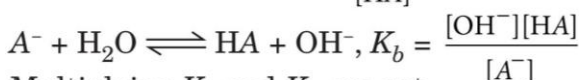● **Relationship between pH and pOH**
pH + pOH = 14 and pH + pOH = $pK_w$

● **Relation between $K_a$ and $K_b$ :** If $K_a$ and $K_b$ are the dissociation constants of weak acid and weak base respectively then,

$$pK_a = -\log K_a \quad \text{and} \quad pK_b = -\log K_b$$

Consider a weak acid, $HA$

$$HA \rightleftharpoons H^+ + A^-, \ K_a = \frac{[H^+][A^-]}{[HA]}$$

$$A^- + H_2O \rightleftharpoons HA + OH^-, \ K_b = \frac{[OH^-][HA]}{[A^-]}$$
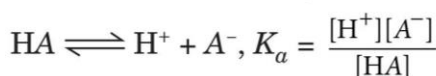
Multiplying $K_a$ and $K_b$, we get

$$K_a \times K_b = [H^+][OH^-]$$

But $[H^+][OH^-] = K_w$

$\therefore \quad K_a \times K_b = K_w$

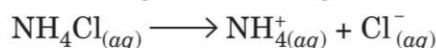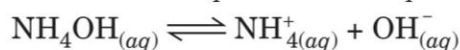Taking log on both sides, we get

$\log K_a + \log K_b = \log K_w$

or $\quad -\log K_a - \log K_b = -\log K_w$

$pK_a + pK_b = pK_w$

- **Common ion effect in the ionisation of acids and bases :** There exists a dynamic equilibrium between unionised molecule and ions of a weak electrolyte : $AB \rightleftharpoons A^+ + B^-$
  - ▶ To this equilibrium if a solution of a strong electrolyte ($AX$ or $YB$) is mixed, due to the presence of a common ion, either $A^+$ or $B^-$, the degree of dissociation is suppressed in both the cases.
  - ▶ The decrease in dissociation is much more in case of weak electrolytes, *e.g.*, if a solution of $NH_4OH$ some $NH_4Cl$ is added,

    $NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

    $NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

    $NH_4Cl$ ionises almost completely leading to a high concentration of $NH_4^+$ (common ion).

    According to Le Chatelier's principle, the dissociation of $NH_4OH$ is suppressed.
  - ▶ Thus, *common ion effect* can be defined as the suppression of the degree of ionisation of a weak electrolyte by the addition of a strong electrolyte having an ion common with the weak electrolyte.

- **Buffer solutions :** *Buffer solution* is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted. Buffer solution has a definite pH value at specific temperature and it does not change on keeping for a long time.

  Buffers are classified into two categories :
  - ▶ **Simple buffers :** These are the solutions of salt of weak acid and weak base. For example, $CH_3COONH_4$ (ammonium acetate).
  - ▶ **Mixed buffers :** These are the mixture of two solutions. These are further of two types :

- **Acidic buffers :** These are the solutions of a mixture of weak acid and salt of this weak acid with strong base.
- For example, $CH_3COOH + CH_3COONa$. They have pH value lesser than 7.
- **Basic buffers :** These are the solutions of mixture of a weak base and salt of this weak base with strong acid. For example, $NH_4OH + NH_4Cl$. They have the pH value more than 7.

- **Solubility product :** *Solubility product* of an electrolyte at a specified temperature may be defined on the product of the molar concentrations of its ions in a saturated solution, each concentration raised to the power equal to the number of ion produced on dissociation of one molecule of electrolyte.

| Salt type | Relation between $K_{sp}$ and $S$ | Examples |
|---|---|---|
| $AB_2$ | $K_{sp} = (S)(2S)^2 = 4S^3$ | $PbCl_2$, $HgCl_2$ |
| $A_2B$ | $K_{sp} = (2S)^2(S) = 4S^3$ | $Ag_2CrO_4$, $Ag_2C_2O_4$, $Ag_2SO_4$ |
| $AB_3$ | $K_{sp} = (S)(3S)^3 = 27S^4$ | $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$ |
| $A_3B_2$ | $K_{sp} = (3S)^3(2S)^2$ $= 108S^5$ | $Ca_3(PO_4)_2$, $Zn_3(PO_4)_2$ |
| $AB$ | $K_{sp} = (S)(S) = S^2$ | $AlPO_4$, $AgCl$, $AgBr$, $PbSO_4$, $BaSO_4$, $ZnS$ |

- **Effect of common ion on solubility :** Addition of a common ion lowers the solubility of a sparingly soluble salt. Let $S$ be the solubility of a salt $AgCl$ in pure water and suppose $x$ g equivalent of $NaCl$ is added to a litre of the saturated solution. Suppose the solubility of $AgCl$ becomes $S'$.

  $K_{sp} = [Ag^+][Cl^-] = S'(S' + x)$

  When the addition of a common ion or an inert salt leads to a considerable increase in the solubility of a salt, then it can be concluded that a complex ion has been formed.

## OBJECTIVE TYPE QUESTIONS

### ➲ Multiple Choice Questions (MCQs)

1. For the following three reactions (i), (ii) and (iii), equilibrium constants are given
   (i) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}; K_1$
   (ii) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}; K_2$
   (iii) $CH_{4(g)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 4H_{2(g)}; K_3$
   Which of the following relations is correct?
   (a) $K_3 K_2^{\ 3} = K_1^{\ 2}$
   (b) $K_1 \sqrt{K_2} = K_3$
   (c) $K_2 K_3 = K_1$
   (d) $K_3 = K_1 K_2$

2. If $K_1$ and $K_2$ are the respective equilibrium constants for the two reactions,
   $XeF_{6(g)} + H_2O_{(g)} \rightleftharpoons XeOF_{4(g)} + 2HF_{(g)}$
   $XeO_{4(g)} + XeF_{6(g)} \rightleftharpoons XeOF_{4(g)} + XeO_3F_{2(g)}$
   The equilibrium constant for the reaction,
   $XeO_{4(g)} + 2HF_{(g)} \rightleftharpoons XeO_3F_{2(g)} + H_2O_{(g)}$ is
   (a) $K_1 K_2$
   (b) $K_1/K_2^2$
   (c) $K_2/K_1$
   (d) $K_1/K_2$

3. For the reversible reaction,
   $A_{(s)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}, \ \Delta G° = -350 \text{ kJ},$
   which one of the following statements is true?
   (a) The reaction is thermodynamically nonfeasible.
   (b) The entropy change is negative.
   (c) Equilibrium constant is greater than one.
   (d) The reaction should be instantaneous.

4. In a chemical equilibrium the rate constant of backward reaction is $3.2 \times 10^{-2}$ and the equilibrium constant is $2^{-5}$. The rate constant of forward reaction is
   (a) $1 \times 10^{-3}$
   (b) $2 \times 10^{-2}$
   (c) $8 \times 10^{-2}$
   (d) $4 \times 10^{-2}$

5. It is not possible to attain equilibrium in
   (a) closed system
   (b) isolated system
   (c) open system
   (d) none of these.

6. Conjugate base for Bronsted acids $H_2O$ and HF are
   (a) $H_3O^+$ and $H_2F^+$, respectively
   (b) $OH^-$ and $H_2F^+$, respectively
   (c) $H_3O^+$ and $F^-$, respectively
   (d) $OH^-$ and $F^-$, respectively.

7. For the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ at 300 K, the value of $\Delta G$ is $-690.9 \ R$. The equilibrium constant value for the reaction at that temperature is ($R$ is gas constant)
   (a) $10 \text{ atm}^{-1}$
   (b) $10 \text{ atm}$
   (c) 10
   (d) 1

8. The solubility product of aluminium sulphate is given by the expression
   (a) $4s^3$
   (b) $6912s^7$
   (c) $s^2$
   (d) $108s^5$

9. In a reversible chemical reaction at equilibrium, if the concentration of any one of the reactants is doubled, then the equilibrium constant will
   (a) also be doubled
   (b) be halved
   (c) remain the same
   (d) become one-fourth.

10. Identify a species which is 'NOT' a Bronsted acid but a Lewis acid.
    (a) $BF_3$
    (b) $H_3O^+$
    (c) $NH_3$
    (d) HCl

11. For the system $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant $K$ is
    (a) $\dfrac{[3A] \times [2B]}{[C]}$
    (b) $\dfrac{[A]^3 \times [B]}{[C]}$
    (c) $\dfrac{C}{[A]^3 \times [B]^2}$
    (d) $\dfrac{[C]}{[3A] \times [2B]}$

12. Among the following, the one which can act as both Bronsted acid as well as Bronsted base is
    (a) $H_3PO_4$
    (b) $AlCl_3$
    (c) $CH_3COO^-$
    (d) $H_2O$

13. The solubility of $Ca_3(PO_4)_2$ in water is $y$ moles/litre. Its solubility product is
    (a) $6y^4$
    (b) $36y^4$
    (c) $64y^5$
    (d) $108y^5$

14. Which of the following is not a characteristic of equilibrium?
    (a) Rate is equal in both directions.
    (b) Measurable quantities are constant at equilibrium.

(c) Equilibrium occurs in reversible condition.

(d) Equilibrium occurs only in an open vessel at constant temperature

**15.** When the rate of formation of reactants is equal to the rate of formation of products, this is known as,

(a) chemical reaction

(b) chemical equilibrium

(c) chemical kinetics

(d) none of these.

**16.** Which of the following options will be correct for the stage of half completion of the reaction $X \rightleftharpoons Y$.

(a) $\Delta G° = 0$    (b) $\Delta G° > 0$

(c) $\Delta G° < 0$    (d) $\Delta G° = -RT \ln 2$

**17.** In Bronsted–Lowry concept of acid-base, $H^+$ donor is a/an

(a) acid

(b) basic

(c) exclusively amphoteric substance

(d) hydroxide acceptor.

**18.** In $HS^-$, $I^-$, $R — NH_2$, $NH_3$ order of proton accepting tendency will be

(a) $I^- > NH_3 > R — NH_2 > HS^-$

(b) $NH_3 > R — NH_2 > HS^- > I^-$

(c) $R — NH_2 > NH_3 > HS^- > I^-$

(d) $HS^- > R — NH_2 > NH_3 > I^-$

**19.** Equilibrium constants are given for the following reactions. Out of the following, which is farthest towards completion?

(a) $K = 100$    (b) $K = 0.1$

(c) $K = 0.01$    (d) $K = 1$

**20.** Of the following the incorrect relation is

(a) $\Delta G = \Delta G° + RT\ln K$    (b) $\Delta G° = -RT\ln K$

(c) $\Delta G° = \Delta G + RT\ln K$    (d) $K = e^{-\Delta G /RT}$

**21.** Calculate $K_c$ for the reversible process given below if $K_p = 167$ and $T = 800°C$.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$
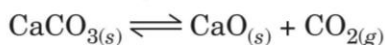
(a) 1.95    (b) 1.85

(c) 1.89    (d) 1.60

**22.** The dissociation constants for acetic acid and HCN at 25°C are $1.5 \times 10^{-5}$ and $4.5 \times 10^{-10}$ respectively. The equilibrium constant for the equilibrium,

$$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$$

would be

(a) $3.0 \times 10^{-5}$    (b) $3.0 \times 10^{-4}$

(c) $3.0 \times 10^4$    (d) $3.0 \times 10^5$

**23.** What will be the solubility product of $AX_3$?

(a) $27S^4$    (b) $4S^3$

(c) $36S^4$    (d) $9S^3$

**24.** Which of the following is a characteristic of reversible reaction?

(a) It never proceeds to completion.

(b) It can be influenced by a catalyst.

(c) It proceeds only in the forward direction.

(d) Number of moles of reactants and products are equal.

**25.** For the reaction, $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $K_p = K_c(RT)^x$ where the symbols have usual meaning then the value of $x$ is (assuming ideality)

(a) 1    (b) $-1$

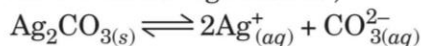(c) $-\frac{1}{2}$    (d) $\frac{1}{2}$

**26.** Which of these is least likely to act as a Lewis base?

(a) $BF_3$    (b) $PF_3$

(c) $CO$    (d) $F^-$

**27.** Which of the following solutions will have pH close to 1.0?

(a) 100 mL of M/10 HCl + 100 mL of M/10 NaOH

(b) 55 mL of M/10 HCl + 45 mL of M/10 NaOH

(c) 10 mL of M/10 HCl + 90 mL of M/10 NaOH

(d) 75 mL of M/10 HCl + 25 mL of M/10 NaOH

**28.** Using the Gibbs' energy change, $\Delta G = +63.3$ kJ, for the following reaction,
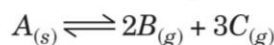
$$Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+_{(aq)} + CO^{2-}_{3(aq)}$$

the $K_{sp}$ of $Ag_2CO_{3(s)}$ in water at 25°C is $(R = 8.314$ J K$^{-1}$ mol$^{-1})$

(a) $3.2 \times 10^{-26}$    (b) $8.0 \times 10^{-12}$

(c) $2.9 \times 10^{-3}$    (d) $7.9 \times 10^{-2}$

**29.** Consider the general hypothetical reaction,

$$A_{(s)} \rightleftharpoons 2B_{(g)} + 3C_{(g)}$$

If the concentration of $C$ at equilibrium is doubled, then after the equilibrium is re-established, the concentration of $B$ will be

(a) two times the original value

(b) one half of its original value

(c) $1/2\sqrt{2}$ times the original value

(d) $2\sqrt{2}$ times the original value.

30. The pH of $10^{-4}$ M KOH solution will be
(a) 4 (b) 11
(c) 10.5 (d) 10

31. If the pH increases from 5 to 7, then acidic strength decreases _____ times.
(a) 2 (b) 20
(c) 10 (d) 100

32. The reaction quotient, $Q_c$ is useful in predicting the direction of the reaction. Which of the following is incorrect?
(a) If $Q_c > K_c$, net reaction goes from right to left.
(b) If $Q_c < K_c$, net reaction goes from left to right.
(c) If $Q_c = K_c$, no net reaction occurs.
(d) If $Q_c > K_c$, net reaction goes from left to right.

33. $\dfrac{K_p}{K_c}$ for following reaction will be

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$
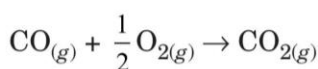
(a) $RT$ (b) $\dfrac{1}{RT}$

(c) $\dfrac{1}{\sqrt{RT}}$ (d) $\dfrac{RT}{2}$

34. Buffer solutions have constant acidity and alkalinity because
(a) these give unionised acid or base on reaction with added acid or alkali
(b) acids and alkalies in these solutions are shielded from attack by other ions
(c) they have large excess of $H^+$ or $OH^-$ ions
(d) they have fixed value of pH.

35. The equilibrium constant, $K_p$ for the reaction,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \text{ is } 1.6 \text{ at } 200°C.$$
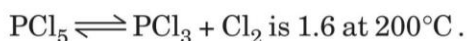
The pressure at which $PCl_5$ will be 50% dissociated at 200°C is
(a) 3.2 atm (b) 4.8 atm
(c) 2.4 atm (d) 6.4 atm
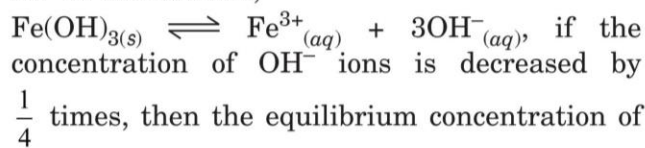
36. In the reaction;
$Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}_{(aq)} + 3OH^-_{(aq)}$, if the concentration of $OH^-$ ions is decreased by $\dfrac{1}{4}$ times, then the equilibrium concentration of $Fe^{3+}$ will increase by
(a) 8 times (b) 16 times
(c) 64 times (d) 4 times.

37. The value of $\Delta H$ for the reaction
$X_{2(g)} + 4Y_{2(g)} \rightleftharpoons 2XY_{4(g)}$ is less than zero.

Formation of $XY_{4(g)}$ will be favoured at
(a) high temperature and high pressure
(b) low pressure and low temperature
(c) high temperature and low pressure
(d) high pressure and low temperature.

38. In which of the following equilibrium $K_c$ and $K_p$ are not equal?
(a) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$
(b) $SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$
(c) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
(d) $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

39. Which will make basic buffer?
(a) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
(b) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M $CH_3COOH$
(c) 100 mL of 0.1 M $CH_3COOH$ + 100 mL of 0.1 M NaOH
(d) 100 mL of 0.1 M HCl + 200 mL of 0.1 M $NH_4OH$

40. 4 moles of $A$ are mixed with 4 moles of $B$, when 2 moles of $C$ and $D$ are formed at equilibrium according to the reaction,
$$A + B \rightleftharpoons C + D$$
the value of equilibrium constant is
(a) 4 (b) 1
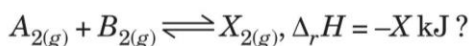(c) 1/2 (d) 1/4

➲ Case Based MCQs

Case I : Read the passage given below and answer the following questions from 41 to 45.

Le Chatelier's principle is also known as the equilibrium law, used to predict the effect of change on a system at chemical equilibrium. This principle states that equilibrium adjust the forward and backward reactions in such a way as to accept the change affecting the equilibrium condition. When factor like concentration, pressure, temperature, inert gas that affect

equilibrium are changed, the equilibrium will shift in that direction where the effects that caused by these changes are nullified. This principle is also used to manipulate reversible reaction in order to obtain suitable outcomes.

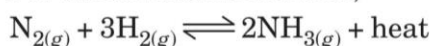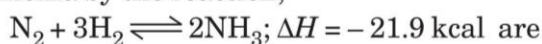41. Which one of the following conditions will favour maximum formation of the product in the reaction
$A_{2(g)} + B_{2(g)} \rightleftharpoons X_{2(g)}, \Delta_r H = -X \, kJ$ ?
(a) Low temperature and high pressure
(b) Low temperature and low pressure
(c) High temperature and high pressure
(d) High temperature and low pressure

42. In which one of the following equilibria will the point of equilibrium shift to left when the pressure of the system is increased?
(a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
(b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$
(c) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$
(d) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$

43. For the reversible reaction,
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + heat$
The equilibrium shifts in forward direction
(a) by increasing the concentration of $NH_{3(g)}$
(b) by decreasing the pressure
(c) by decreasing the concentrations of $N_{2(g)}$ and $H_{2(g)}$
(d) by increasing pressure and decreasing temperature.

44. Favourable conditions for manufacture of ammonia by the reaction,
$N_2 + 3H_2 \rightleftharpoons 2NH_3; \Delta H = -21.9 \, kcal$ are
(a) low temperature, low pressure and catalyst
(b) low temperature, high pressure and catalyst
(c) high temperature, low pressure and catalyst
(d) high temperature, high pressure and catalyst.

45. $X + Y \rightleftharpoons P + Q$
For the above equilibrium, the reactant concentration is doubled, what would happen then to equilibrium constant?
(a) Remains constant
(b) Be doubled
(c) Be halved
(d) Cannot be predicted

Case II : Read the passage given below and answer the following questions from 46 to 50.

Reactants and products coexist at equilibrium, so that the conversion of reactant to products is always less than 100%. Equilibrium reaction may involve the decomposition of a covalent (non-polar) reactant or ionization of ionic compound into their ions in polar solvents. Ostwald dilution law is the application of the law of mass action to the weak electrolytes in solution.
A binary electrolyte $AB$ which dissociates into $A^+$ and $B^-$ ions i.e.
$AB \rightleftharpoons A^+ + B^-$
for every weak electrolyte, Since $\alpha \ll 1$
$$(1 - \alpha) = 1$$
$$K = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{C}} \Rightarrow \alpha = \sqrt{KV}.$$

46. A monobasic weak acid solution has a molarity of 0.005 M and pH of 5. What is its percentage ionization in this solution?
(a) 2.0            (b) 0.2
(c) 0.5            (d) 0.25

47. Calculate ionisation constant for pyridinium hydrogen chloride. (Given that $H^+$ ion concentration is $3.6 \times 10^{-4}$ M and its concentration is 0.02 M.)
(a) $6.48 \times 10^{-2}$      (b) $6 \times 10^{-6}$
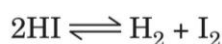(c) $1.5 \times 10^{-9}$      (d) $12 \times 10^{-8}$

48. The hydrogen ion concentration of a $10^{-8}$ M HCl aqueous solution at 298 $K (K_w = 10^{-14})$ is
(a) $9.525 \times 10^{-8}$ M    (b) $1.0 \times 10^{-8}$ M
(c) $1.0 \times 10^{-6}$ M     (d) $1.0525 \times 10^{-7}$ M

49. Ostwald dilution law is applicable to
(a) weak electrolytes
(b) non-electrolyte
(c) strong electrolyte
(d) all type of electrolyte.

50. If $\alpha$ is the fraction of HI dissociated at equilibrium in the reaction :
$$2HI \rightleftharpoons H_2 + I_2$$
then starting with 2 mol of HI, the total number of moles of reactants and products at equilibrium are
(a) 1            (b) 2
(c) $1 + \alpha$       (d) $2 + 2\alpha$

# ⮑ Assertion & Reasoning Based MCQs

For question numbers 51-60, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

**51. Assertion :** At $25°C$ the pH of $10^{-7}$ M HCl is 6.69.
**Reason :** pH of acidic solution is always below 7 at $25°C$.

**52. Assertion :** The value of $K_w$ at $25°C$ is $1.0 \times 10^{-14}$ $mol^2$ $dm^{-6}$.
**Reason :** $K_w$ of water changes with change in temperature.

**53. Assertion :** $K_P$ can be equal to, less than or greater than the value of $K_c$.
**Reason :** $K_p = K_c(RT)^{\Delta n}$ where $\Delta n$ is the change in the number of moles of gaseous reactants and products.

**54. Assertion :** The active mass of pure solid is taken unity.
**Reason :** The active mass of pure solids depends on density and molecular mass. The density and molecular mass of pure solids are constant.

**55. Assertion :** $H_3PO_4$ is a stronger acid than $H_2PO_4^-$
**Reason :** $pK_{a_1}$ is greater than $pK_{a_2}$ for $H_3PO_4$.

**56. Assertion :** For the equilibrium mixture $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$ if the volume is decreased, reaction proceeds in the forward direction.
**Reason :** For the methanation reaction (above), decrease in volume causes $Q_c > K_c$.

**57. Assertion :** At constant temperature, the pressure of the gas is proportional to its concentration.
**Reason :** $K_P = K_c$ for all reactions.

**58. Assertion :** For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.
**Reason :** Equilibrium constant is independent of temperature.

**59. Assertion :** On dilution, the solubility of $BaSO_4$ increases.
**Reason :** On dilution, $K_{sp}$ increases.

**60. Assertion :** The equilibrium constant does not change on addition of catalyst.
**Reason :** A catalyst provides an alternative path of lower activation energy for conversion of reactants to products.

# SUBJECTIVE TYPE QUESTIONS

# ⮑ Very Short Answer Type Questions (VSA)

1. A mixture of 1.57 mol of $N_2$, 1.92 mol of $H_2$ and 8.13 mol of $NH_3$ is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, $K_c$ for the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is $1.7 \times 10^2$. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

2. Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression.

3. Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?

$OH^-$, $RO^-$, $CH_3COO^-$, $Cl^-$

4. Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base : (a) $OH^-$ (b) $F^-$ (c) $H^+$ (d) $BCl_3$.

5. Calculate the pH of a solution formed by mixing equal volumes of two solutions $A$ and $B$ of a strong acid having pH = 6 and pH = 4 respectively.

6. Give two important characteristics of chemical equilibrium.

7. What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?
$$2ICl_{(g)} \rightleftharpoons I_{2(g)} + Cl_{2(g)}; K_c = 0.14$$
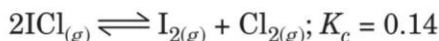
8. Give relation between $[A]$ and $[B]$ for the stage of half completion of the reaction $A \rightleftharpoons B$.

9. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ions in it.

## ➲ Short Answer Type Questions (SA-I)

10. Equilibrium constant for a reaction is 10. What will be the equilibrium constant for the reverse reaction?

11. Write the expression for the equilibrium constant $K_c$ for the following equilibrium :
$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$$

12. For the system $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant $K$ is?

13. Differentiate between homogeneous and heterogeneous equilibrium giving examples.

14. $K_{a_1}, K_{a_2}$ and $K_{a_3}$ are the respective ionisation constants for the following reactions.
$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{2-}$$
$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
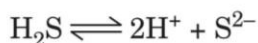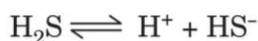
The correct relationship between $K_{a_1}, K_{a_2}$ and $K_{a_3}$ is

15. Write expressions for $K_p$ and $K_c$ for the decomposition reaction of calcium carbonate.

16. The ionization constant of HF, HCOOH and HCN at 298 K are $6.8 \times 10^{-4}$, $1.8 \times 10^{-4}$ and $4.8 \times 10^{-9}$ respectively. Calculate the ionization constants of the corresponding conjugate base.

17. Write the relation between $Q_c$ and $K_c$ for reverse reaction.

18. We know that the relationship between $K_c$ and $K_p$ is
$$K_p = K_c(RT)^{\Delta n}$$
What would be the value of $\Delta n$ for the reaction
$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$$
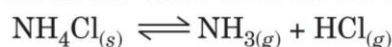
19. What will be the conjugate bases for the Bronsted acids: HF, $H_2SO_4$ and $HCO_3^-$?

## ➲ Short Answer Type Questions (SA-II)

20. Calculate (a) $\Delta G$ and (b) the equilibrium constant for the formation of $NO_2$ from NO and $O_2$ at 298 K.
$$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{2(g)}$$
where $\Delta_f G^\circ (NO_2) = 52.0 \text{ kJ mol}^{-1}$,
$\Delta_f G^\circ (NO) = 87.0 \text{ kJ mol}^{-1}$,
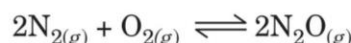$\Delta_f G^\circ (O_2) = 0 \text{ kJ mol}^{-1}$
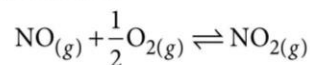
21. What will be the correct order of vapour pressure of water, acetone and ether at 30 C? Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?

22. In 1 L saturated solution of AgCl $[K_{sp} = 1.6 \times 10^{10}]$, 0.1 mol of CuCl $[K_{sp} = 1.0 \times 10^{-6}]$ is added. Find out the resultant concentration of $Ag^+$ in the solution.

23. Reaction between $N_2$ and $O_2$ takes place as follows :
$$2N_{2(g)} + O_{2(g)} \rightleftharpoons 2N_2O_{(g)}$$
If a mixture of 0.482 mol of $N_2$ and 0.933 mol of $O_2$ is placed in a 10 L reaction vessel and allowed to form $N_2O$ at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.
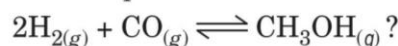
24. Equal volumes of 0.002 M solutions of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate? (For copper iodate, $K_{sp} = 7.4 \times 10^{-8}$)

25. Define Le-Chatelier's Principle. What is the effect of :
(i) addition of $H_2$
(ii) removal of CO
on the equilibrium :
$$2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}?$$

26. The value of $\Delta G^\circ$ for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of $K_c$ at 298 K.

27. For the reaction,

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}; \Delta H_r = -92 \text{ kJ/mol}$$

predict the direction of the reaction when

(i) pressure is doubled

(ii) temperature is doubled.

28. What is the effect of increase of temperature on the pH of a buffer solution?

29. Equilibrium constant, $K_c$ for the reaction,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \text{ at 500 K is 0.061.}$$

At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L$^{-1}$ N$_2$, 2.0 mol L$^{-1}$ H$_2$ and 0.5 mol L$^{-1}$ NH$_3$. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

30. (i) Define Lewis acids and bases with example.

(ii) The value of $K_{sp}$ of two sparingly soluble salts Ni(OH)$_2$ and AgCN are $2 \times 10^{-15}$ and $6 \times 10^{-17}$. Which salt is more soluble and why?

31. Which of the following combinations would result in the formation of a buffer solution?

(i) NH$_4$Cl + NH$_3$

(ii) CH$_3$COOH + HCl

(iii) CH$_3$COONa + CH$_3$COOH

(iv) NH$_3$ + HCl in the molar ratio of 2 : 1

(v) HCl + NaOH

32. A sparingly soluble salt having general formula $A_x^{p+}B_y^{q-}$ and molar solubility $S$ is in equilibrium with its saturated solution. Derive a relationship between the solubility and solubility product for such salt.

33. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
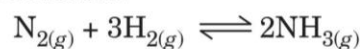
What will be the effect on $K$. if the total pressure at which the equilibrium is established, is increased without changing the temperature?

34. The solubility product of AgCl is $1.5 \times 10^{-10}$. Predict whether there will be any precipitation by mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M AgNO$_3$ solution.

35. What is the pH of 0.001 M aniline solution? The ionisation constant of aniline is $4.27 \times 10^{-10}$. Calculate the degree of ionisation of aniline in the solution. Also calculate the ionisation constant of the conjugate acid of aniline.

## ⮕ Long Answer Type Questions (LA)

36. (i) Point out the differences between ionic product and solubility product.

(ii) The solubility of AgCl in water at 298 K is $1.06 \times 10^{-5}$ mole per litre. Calculate its solubility product at this temperature .

37. (i) Derive the relationship between p$K_w$, pH and pOH starting from ionisation constant of water, $K_w$. What is the numerical value of p$K_w$ at 298 K?

(ii) If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of K$^+$ and OH$^-$. What is its pH? (Give atomic masses K = 39, O = 16, H = 1)

38. (i) What is common ion effect?

(ii) Write the $K_{sp}$ expressions for Ag$_2$CrO$_4$ and zirconium phosphate.

(iii) Calculate the pH of 0.005 M HCl solution.

39. At 473 K, equilibrium constant, $K_c$ for decomposition of PCl$_5$ is $8.3 \times 10^{-3}$. If decomposition is depicted as :

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}; \Delta_r H = 124.0 \text{ kJ mol}^{-1}$$
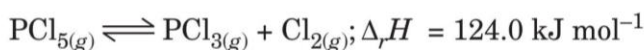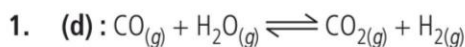
(a) Write an expression for $K_c$ for the reaction.

(b) What is the value of $K_c$ for the reverse reaction at same temperature?

(c) What would be the effect on $K_c$ if

(i) the pressure is increased

(ii) the temperature is increased?

40. One mole of N$_2$ and 3 moles of PCl$_5$ are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl$_5$ and $K_p$ for the reaction
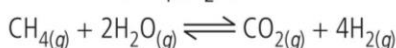
$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

## ANSWERS

### OBJECTIVE TYPE QUESTIONS

1. **(d)** : $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

$$K_1 = \frac{[CO_2][H_2]}{[CO][H_2O]} \qquad ...(i)$$

$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$

$$K_2 = \frac{[CO][H_2]^3}{[CH_4][H_2O]} \qquad ...(ii)$$

$CH_{4(g)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 4H_{2(g)}$

$$K_3 = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2} \qquad ...(iii)$$

From equations (i), (ii) and (iii) ; $K_3 = K_1 \times K_2$

2. **(c)** : $K_1 = \frac{[XeOF_4][HF]^2}{[XeF_6][H_2O]} \qquad ...(i)$
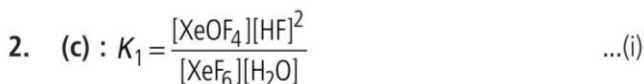
$$K_2 = \frac{[XeOF_4][XeO_3F_2]}{[XeO_4][XeF_6]} \qquad ...(ii)$$

Dividing Eq. (ii) by (i) we have,

$$\frac{K_2}{K_1} = \frac{[XeO_3F_2][H_2O]}{[XeO_4][HF]^2} = K'$$

3. **(c)** : For a reversible reaction,
$A_{(s)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$, $\Delta G° = -350$ kJ
Standard free energy change can be thermodynamically calculated as,
when $\Delta G° < 0$, i.e., negative, then $K_c > 1$. In this case forward reaction is feasible. The reaction is spontaneous reaction.
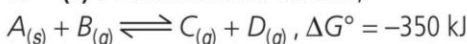
4. **(a)** : In a chemical equilibrium
Equilibrium constant,

$$K = \frac{\text{Rate constant of forward reaction, } k_f}{\text{Rate constant of backward reaction, } k_b}$$

$$\therefore \quad k_f = k_b \times K = 3.2 \times 10^{-2} \times 2^{-5} = \frac{3.2 \times 10^{-2}}{32} = 1 \times 10^{-3}$$

5. **(c)** : In open system equilibrium cannot be attained.

6. **(d)** :

| Bronsted acid | Conjugate base |
|---|---|
| $H_2O$ | $OH^-$ |
| $HF$ | $F^-$ |

7. **(a)** : $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
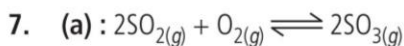
$\Delta G = -RT \ln K \Rightarrow -690.9\ R = -RT \ln K$ or $\dfrac{690.9}{300} = \ln K$

$2.303 = \ln K \Rightarrow 2.303 = 2.303 \log K$, $K = 10^1$

$$K_p = \frac{p_{SO_3}^2}{p_{SO_2}^2 \times p_{O_2}} \times \frac{atm^2}{atm^3} = atm^{-1}$$

$\therefore K_p = 10$ atm$^{-1}$

8. **(d)** : $Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$
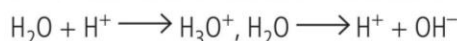$\qquad\qquad\qquad\quad 2s \qquad\quad 3s$
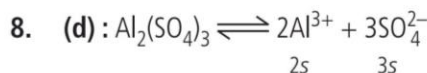
$K_{sp} = (2s)^2 (3s)^3 = 4 \times 27s^5 = 108s^5$

9. **(c)** : Equilibrium constant depends only on temperature.

10. **(a)** : Molecules having a central atom with incomplete octet, act as a Lewis acid not Brönsted acid (proton donor). In $BF_3$, B is having six electrons.

11. **(c)** : $K = \dfrac{[C]}{[A]^3[B]^2}$

12. **(d)** : $H_2O$ can accept or give a proton hence, it acts both as Bronsted acid as well as Bronsted base.
$H_2O + H^+ \longrightarrow H_3O^+$, $H_2O \longrightarrow H^+ + OH^-$

13. **(d)** : $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$
Concentrations of various species at equilibrium
$\qquad Ca^{2+} = 3y$, $PO_4^{3-} = 2y$
Solubility product $= (3y)^3 (2y)^2 = 27y^3 \times 4y^2 = 108y^5$

14. **(d)** : Equilibrium state can only be achieved if a reversible reaction is carried out in a closed vessel.

15. **(b)** : At equilibrium, rate of forward reaction is equal to rate of backward reaction.
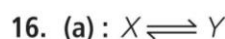
16. **(a)** : $X \rightleftharpoons Y$
$\Delta G° = -RT \ln K$
At the stage of half completion of reaction $[X] = [Y]$.
Therefore, $K = 1$. Thus, $\Delta G° = 0$.

17. **(a)**

18. **(c)** : Proton accepting tendency is known as the strength of basicity.
In $R-\ddot{N}H_2$, N has lone pair of electrons which intensify due to electron releasing $R$ group and increase the tendency to donate lone pair of electrons to $H^+$.
Secondly, as the size of the ion increases there is less attraction for $H^+$ to form weaker bonds with H – atom and are less basic. The order of the given series is: $RNH_2 > NH_3 > HS^- > I^-$.

19. **(a)** : Higher the value of equilibrium constant, the reaction is farther towards completion.

20. **(c)** : $\Delta G = \Delta G° + RT \ln K$
at equilibrium $\Delta G = 0$
$\qquad \Delta G° = -RT \ln K$ and $K = e^{-\Delta G°/RT}$

21. **(c)** : $K_p = K_c(RT)^{\Delta n}$; $\Delta n = n_p - n_r = 1$
$K_p = K_c(0.0821 \times 1073) \Rightarrow K_c = \dfrac{167}{0.0821 \times 1073} = 1.891$

**22. (c) :** Given, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.5 \times 10^{-5}$$

$HCN \rightleftharpoons H^+ + CN^-$

$$K_2 = \frac{[CN^-][H^+]}{[HCN]} = 4.5 \times 10^{-10}$$

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$

$$K = \frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$$

$$K = \frac{K_1}{K_2} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} \approx 0.3 \times 10^5 \text{ or } K = 3 \times 10^4$$

**23. (a) :** $AX_3 \rightleftharpoons \underset{S}{A^{3+}} + \underset{3S}{3X^-}$

$K_{sp} = [A^{3+}][X^-]^3 = (S) \cdot (3S)^3 = 27S^4$

**24. (a) :** Reversible reaction never goes to completion, rather attains an equilibrium point.

**25. (c) :** For the reaction, $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$

Using formula, $K_p = K_c(RT)^{\Delta n_g}$
where, $\Delta n_g$ = no. of products$_{(g)}$ – no. of reactants$_{(g)}$

$$= 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2} = x$$

**26. (a) :** $BF_3$ is Lewis acid (electron pair acceptor).

**27. (d) :** (a) is exact neutralisation. Hence pH = 7
(b) After neutralisation, M/10 HCl left = 10 mL
Total volume = 100 mL
Dilution = 10 times. ∴ $[H^+] = 10^{-2}$ or pH = 2
(c) After neutralisation, M/10 NaOH left = 80 mL
Total volume = 100 mL, pH > 7
(d) After neutralisation, M/10 HCl left = 50 mL
Total volume = 100 mL
Dilution = 2 times

$$\therefore [H^+] = \frac{1}{2 \times 10} = \frac{10^{-1}}{2} \text{ M or pH} = 1.3$$

**28. (b) :** $\Delta G^\circ = -2.303RT \log K_{sp}$
$63.3 \times 10^3 \text{ J} = -2.303 \times 8.314 \times 298 \log K_{sp}$
$63.3 \times 10^3 \text{ J} = -5705.84 \log K_{sp}$

$$\log K_{sp} = -\frac{63.3 \times 10^3}{5705.84} = -11.09$$

$K_{sp}$ = antilog (–11.09) = $8.128 \times 10^{-12}$

**29. (c) :** $K = [B_{(g)}]^2[C_{(g)}]^3 = x^2 y^3$.
If $[C_{(g)}]$ is doubled i.e. = 2y, suppose $[B_{(g)}]$ is z, then

$$K = z^2(2y)^3 = x^2y^3 \text{ or } z^2 = \frac{1}{8}x^2 \text{or } z = \frac{1}{\sqrt{8}}x = \frac{1}{2\sqrt{2}}x$$

**30. (d) :** $\underset{10^{-4} \text{ M}}{KOH} \longrightarrow \underset{}{K^+} + \underset{10^{-4} \text{ M}}{OH^-}$

∴ $[OH^-] = 10^{-4}$ M
∴ $pOH = -\log_{10}[OH^-] = -\log_{10}(10^{-4}) = 4$
∴ pH = 14 – 4 = 10

**31. (d) :** pH = 5 $\Rightarrow [H^+] = 10^{-5}$
pH = 7 $\Rightarrow [H^+] = 10^{-7}$
∴ Acidic strength decreases $10^2$ or 100 times.

**32. (d)**

**33. (c) :** $\Delta n_g = n_p - n_r = 1 - \frac{3}{2}$

$\Delta n_g = \frac{-1}{2}$. Hence $K_p = K_c(RT)^{-1/2}$

$$\frac{K_p}{K_c} = \frac{1}{(RT)^{1/2}} = \frac{1}{\sqrt{RT}}$$

**34. (a)**

**35. (b) :**

| | $PCl_5$ | $\rightleftharpoons$ | $PCl_3$ | + | $Cl_2$ |
|---|---|---|---|---|---|
| Initial moles | 1 | | 0 | | 0 |
| Moles at eqm. | 0.5 | | 0.5 | | 0.5 |

Total moles at equilibrium = 1.5

Partial pressures $\frac{0.5}{1.5}P \quad \frac{0.5}{1.5}P \quad \frac{0.5}{1.5}P$

(where P is the total pressure.)

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} \text{ or } 1.6 = \frac{\left(\frac{0.5}{1.5}P\right)\left(\frac{0.5}{1.5}P\right)}{\left(\frac{0.5}{1.5}P\right)}$$

or $\frac{1}{3}P = 1.6$ (Given) or $P = 4.8$ atm

**36. (c) :** $K_c = [x][3x]^3$ ...(i)

When concentration of $OH^-$ ions is decreased by $\frac{1}{4}$ times,

$$K_c = [x']\left[\frac{3x}{4}\right]^3 \quad ...(ii)$$

Equating eq. (i) and (ii), $x \times (3x)^3 = x'\left(\frac{3x}{4}\right)^3 \Rightarrow 64x = x'$

**37. (d) :** $X_{2(g)} + 4Y_{2(g)} \rightleftharpoons 2XY_{4(g)}$
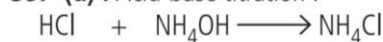$\Delta n_g = -ve$ and $\Delta H = -ve$
The reaction is favoured in forward direction at low temperature and high pressure

**38. (d) :** $K_p$ and $K_c$ are related by the equation,
$K_p = K_c(RT)^{\Delta n_g}$ where, $\Delta n_g$ = difference in the number of moles of products and reactants in the gaseous state.
For $2C_{(s)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$, $\Delta n_g = 2 - (1) = 1 \neq 0$

**39. (d) :** Acid-base titration :
$\underset{10 \text{ mmol}}{HCl} + \underset{20 \text{ mmol}}{NH_4OH} \longrightarrow NH_4Cl$
∴ HCl is the limiting reagent.

Solution contains $NH_4OH$ (weak base) and $NH_4Cl$ (salt of strong acid and weak base). Therefore, a basic buffer will be formed.

**40. (b)**

**41. (a) :** On increasing the pressure and decreasing the temperature, equilibrium will shift in forward direction.

**42. (b) :** An increase in pressure applied to a system at equilibrium, favours the reaction in the direction that produces smaller no. of gaseous moles. Thus, only in the reaction, $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$ there are smaller no. of gaseous moles on left hand side.

**43. (d) :** As the forward reaction is exothermic and leads to lowering of pressure (produces lesser number of gaseous moles) hence, according to Le Chatelier's principle, at high pressure and low temperature, the given reversible reaction will shift in forward direction to form more product.

**44. (b) :** The formation of ammonia is favoured by high pressure which would shift the reaction in the forward direction. The reaction shifts in forward direction at low temperature and more product formation occurs.

Fe acts as a positive catalyst and also shifts the reaction in forward reaction.

**45. (a) :** Value of equilibrium constant is independent of initial concentration of reactants.

**46. (b) :** $HA \rightleftharpoons H^+ + A^-$

$K_a = \dfrac{[H^+][A^-]}{[HA]}$, $pH = -\log[H^+]$

$[H^+] = 10^{-5}$ ; $[H^+] = [A^-]$

$K_a = \dfrac{10^{-5} \times 10^{-5}}{0.005} = 2 \times 10^{-8}$ ; $\alpha = \sqrt{\dfrac{K_a}{C}} = 2 \times 10^{-3}$

Percentage ionization = 0.2

**47. (c) :** Pyridinium hydrochloride is a salt of weak base and strong acid.

$pH = -\log[H^+] = -\log(3.6 \times 10^{-4}) = 3.44$

Now, $pH = -\dfrac{1}{2}[\log K_w - \log K_a + \log C]$

$\Rightarrow \quad 3.44 = -\dfrac{1}{2}[-14 - \log K_a + \log(2 \times 10^{-2})]$

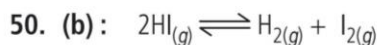$\Rightarrow \quad 6.88 = 14 + \log K_a + 1.70 \Rightarrow \log K_a = -8.82$

$\Rightarrow \quad K_a = $ antilog $(-8.82) = 1.5 \times 10^{-9}$

**48. (d) :** $10^{-8}$ M HCl = $10^{-8}$ M $H^+$
Also from water, $[H^+] = 10^{-7}$ M

$\therefore \quad$ Total $[H^+] = 10^{-7} + 0.10 \times 10^{-7} = 1.1 \times 10^{-7}$ M

**49. (a)**

**50. (b) :**

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

| | | | |
|---|---|---|---|
| Initial moles | 2 | 0 | 0 |
| At eqm. | $2(1-\alpha)$ | $\alpha$ | $\alpha$ |

Total number of moles $= 2(1-\alpha) + \alpha + \alpha = 2$

**51. (a) :** Since HCl is a strong acid therefore, its pH should be less than 7. In this case we should also consider the $[H^+]$ which comes from water i.e.

$[H^+] = 10^{-7}$ M from $H_2O$ + [Acid]
$= 10^{-7} + 10^{-7} = 2 \times 10^{-7}$
$pH = -\log[H^+] = -\log(2 \times 10^{-7}) = 6.69$
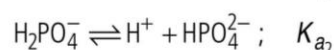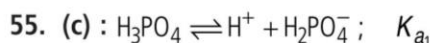
**52. (b) :** The value of $K_w$ at 25°C is about $1.0 \times 10^{-14}$ $mol^2$ $dm^{-6}$. Since in pure water, the concentration of $H^+$ and $OH^-$ ions must be equal to one another i.e., $1.0 \times 10^{-7}$ $mol\, dm^{-3}$.

**53. (a) :** If $\Delta n = +ve$, $K_p > K_c$
$\Delta n = -ve$, $K_p < K_c$
$\Delta n = 0$, $K_p = K_c$

**54. (a)**

**55. (c) :** $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ ; $\quad K_{a_1}$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$ ; $\quad K_{a_2}$

$H^+$ and $H_2PO_4^-$ are having stronger ion-pair attraction.

Hence, $K_{a_2} < K_{a_1}$ and $pK_{a_2} > pK_{a_1}$.

**56. (c) :** Volume is decreased, reaction proceeds in the forward direction because decrease in volume increases the number of moles per unit volume. In order to undo the effect the reaction shifts towards the direction which produces lesser number of moles. Concentration increases, $Q_c$ must be lesser than $K_c$. Suppose volume is decreased to half, concentration becomes 2 times.

$K_c = \dfrac{[CH_4][H_2O]}{[CO][H_2]^3}$

after decreasing $Q_c = \dfrac{[2CH_4] \cdot [2H_2O]}{[2CO][2H_2]^3}$

$Q_c = \dfrac{K_c}{4}$

**57. (c) :** $K_p \neq K_c$ for all reactions.
$K_p = K_c (RT)^{\Delta n}$

$\Delta n$ = number of moles of gaseous products − number of moles of gaseous reactants in the balanced chemical equation.

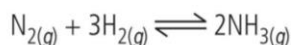So, if for a reaction $\Delta n = 0$, then $K_p = K_c$.

**58. (c) :** Equilibrium constant is temperature dependent.

**59. (c) :** $K_{sp}$ remains constant at a particular temperature.

**60. (b) :** A catalyst increases the rate of forward and backward reactions by same factor hence, does not change the equilibrium constant.

## SUBJECTIVE TYPE QUESTIONS

1. The reaction is :

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\frac{8.13}{20} \text{ mol L}^{-1}\right)^2}{\left(\frac{1.57}{20} \text{ mol L}^{-1}\right)\left(\frac{1.92}{20} \text{ mol L}^{-1}\right)^3} = 2.38 \times 10^3$$

As $Q_c \neq K_c$, the reaction mixture is not in equilibrium.

As $Q_c > K_c$, the net reaction will be in the backward direction.

2. For the concentration of pure solid or pure liquid,

$$\text{Molar conc.} = \frac{\text{Moles of the substance}}{\text{Volume of the substance}}$$

$$= \frac{\text{Mass/Molar mass}}{\text{Volume}} = \frac{\text{Mass}}{\text{Volume}} \times \frac{1}{\text{Molar mass}}$$

$$= \frac{\text{Density}}{\text{Molar mass}}$$

Since density of pure solid or liquid is constant at constant temperature and molar mass is also constant therefore, their molar concentrations are constant and are included in the equilibrium constant.

3. Conjugate acids of given bases are $H_2O$, $ROH$, $CH_3COOH$, $HCl$.

Their acidic strength is in the order

$$HCl > CH_3COOH > H_2O > ROH$$

Hence, basic strength is in the order

$$RO^- > OH^- > CH_3COO^- > Cl^-$$
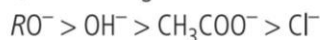
4. **(a) :** $OH^-$ : $OH^-$ is a Lewis base because it can donate lone pair of electrons.

(b) $F^-$ : $F^-$ is a Lewis base because it can donate lone pair of electrons.

(c) $H^+$ : $H^+$ is a Lewis acid because it can accept lone pair of electrons.

(d) $BCl_3$ : $BCl_3$ is a Lewis acid because it is electron deficient and can accept a lone pair of electrons.

5. pH of solution $A = 6$

$[H^+] = 10^{-6}$ mol L$^{-1}$

pH of solution $B = 4$

$[H^+] = 10^{-4}$ mol L$^{-1}$

On mixing one litre of each solution

Total volume = 1 L + 1 L = 2 L

Total amount of $H^+$ in 2 L solution formed by mixing solutions $A$ and $B$ = $10^{-6} + 10^{-4}$ mol

$$\text{Total } [H^+] = \frac{10^{-4}(1+0.01)}{2} = \frac{1.01 \times 10^{-4}}{2}$$

$$= 5 \times 10^{-5} \text{ mol L}^{-1}$$

$$\begin{aligned}
\text{pH} &= -\log[H^+] = -\log(5 \times 10^{-5}) \\
&= -\log 5 - (-5\log 10) = -\log 5 + 5 \\
&= 5 - \log 5 = 5 - 0.6990 = 4.3010 = 4.3
\end{aligned}$$

6. Characteristics of chemical equilibrium are as follows :

(i) Chemical equilibrium is dynamic in nature.

(ii) A catalyst does not alter the state of equilibrium.

7.

$$2ICl_{(g)} \rightleftharpoons I_{2(g)} + Cl_{2(g)}; \quad K_c = 0.14$$

| | | | |
|---|---|---|---|
| Initial molar conc. | 0.78 | 0 | 0 |
| Eqm. molar conc. | 0.78 − 2x | x | x |

Applying law of chemical equilibrium,

$$K_c = \frac{[I_2][Cl_2]}{[ICl]^2} \Rightarrow 0.14 = \frac{x \cdot x}{(0.78 - 2x)^2}$$

$$x^2 = 0.14(0.78 - 2x)^2$$

or $\quad \dfrac{x}{0.78 - 2x} = \sqrt{0.14} = 0.374$

or $\quad x = 0.292 - 0.748x$

or $\quad 1.748x = 0.292$ or $x = 0.167$

Hence at equilibrium, $[I_2] = [Cl_2] = 0.167$ M

$[ICl] = 0.78 - 2 \times 0.167 = 0.446$ M

8. $A \rightleftharpoons B$

At the stage of half completion of reaction $[A] = [B]$.

9. We know that pH = $-\log[H^+]$

$$\therefore \quad [H^+] = \text{antilog}[-\text{pH}] = \text{antilog}(-3.76)$$

$$= 1.738 \times 10^{-4} \text{ M}$$

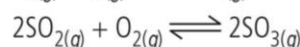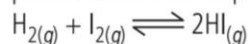10. $K'_c = \dfrac{1}{K_c} = \dfrac{1}{10} = 0.1$

11. $K_c = \dfrac{[H_{2(g)}]^4[Fe_3O_{4(s)}]}{[Fe_{(s)}]^3[H_2O_{(g)}]^4} = \dfrac{[H_{2(g)}]^4}{[H_2O_{(g)}]^4}$
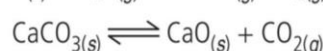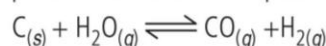
($\because$ concentration of solids is taken as unity)
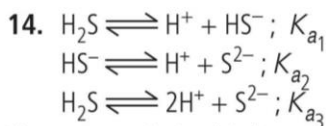
12. $K = \dfrac{[C]}{[A]^3[B]^2}$

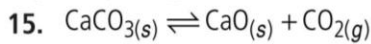13. Equilibrium is said to be homogeneous if reactants and products are in same phase, *e.g.*,

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Equilibrium is said to be heterogeneous if reactants and products are in different phases, *e.g.*,

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

**14.** $H_2S \rightleftharpoons H^+ + HS^-$ ; $K_{a_1}$
$HS^- \rightleftharpoons H^+ + S^{2-}$ ; $K_{a_2}$
$H_2S \rightleftharpoons 2H^+ + S^{2-}$ ; $K_{a_3}$
The correct relationship between $K_{a_1}$, $K_{a_2}$ and $K_{a_3}$ is
$K_{a_3} = K_{a_1} \times K_{a_2}$.

**15.** $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
$$K_c = \frac{[CaO_{(s)}][CO_{2(g)}]}{[CaCO_{3(s)}]}$$
Taking active masses of solids to be unity,
$K_c = [CO_{2(g)}]$, $K_p = p_{CO_2}$

**16.** $K_b = \dfrac{K_w}{K_a}$
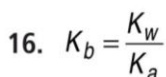
For $F^-$, $K_b = \dfrac{10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$

For $HCOO^-$, $K_b = \dfrac{10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$

For $CN^-$, $K_b = \dfrac{10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}$

**17.** $Q_c > K_c$, for reverse reaction.

**18.** $\Delta n = n_p - n_r = 2 - 0 = 2$

**19.**

| Bronsted acid | Conjugate base |
|---|---|
| HF | $F^-$ |
| $H_2SO_4$ | $HSO_4^-$ |
| $HCO_3^-$ | $CO_3^{2-}$ |

**20.** $NO_{(g)} + \dfrac{1}{2} O_{2(g)} \rightleftharpoons NO_{2(g)}$
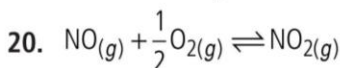
$\Delta G^\circ = \Delta_f G^\circ(NO_2) - [\Delta_f G^\circ(NO) + \dfrac{1}{2}\Delta_f G^\circ(O_2)]$

$= 52.0 - 87.0 - \dfrac{1}{2} \times 0 = -35 \text{ kJ mol}^{-1}$

Now, $\log K = -\dfrac{\Delta G^\circ}{2.303 \, RT}$
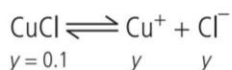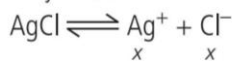
$= -\dfrac{-35 \times 10^3 \, \text{J mol}^{-1}}{2.303 \times 8.314 \, \text{JK}^{-1}\text{mol}^{-1} \times 298 \, K} = 6.314$

or $K = 2.06 \times 10^6$

**21.** Higher the boiling point, lesser the vapour pressure hence the order of V.P. is
water < acetone < ether

**22.** Let the concentration of AgCl be x mol/litre and that of CuCl be y mol/litre
$\underset{\substack{x \quad x}}{AgCl \rightleftharpoons Ag^+ + Cl^-}$
$\underset{\substack{y = 0.1 \quad y \quad y}}{CuCl \rightleftharpoons Cu^+ + Cl^-}$

$K_{sp}$ of AgCl = $[Ag^+][Cl^-] = x(x+y)$ ...(i)
$K_{sp}$ of CuCl = $[Cu^+][Cl^-] = y(x+y)$ ...(ii)
On solving (i) and (ii), we get
$$\frac{K_{sp} \text{ of AgCl}}{K_{sp} \text{of CuCl}} = \frac{x}{y} \Rightarrow \frac{1.6 \times 10^{-10}}{1.0 \times 10^{-6}} = \frac{x}{0.1}$$
$\Rightarrow x = 1.6 \times 10^{-5}$ mol/litre

**23.**

| | $2N_{2(g)}$ | + | $O_{2(g)}$ | $\rightleftharpoons$ | $2N_2O_{(g)}$ |
|---|---|---|---|---|---|
| Initial moles : | 0.482 | | 0.933 | | 0 |
| Moles at eqm. : | (0.482 – x) | | (0.933 – x/2) | | x |
| Molar conc : | $\dfrac{0.482-x}{10}$ | | $\dfrac{0.933-(x/2)}{10}$ | | $\dfrac{x}{10}$ |

As $K_c = 2.0 \times 10^{-37}$ is very small, this means that the amount of $N_2$ and $O_2$ reacted (x) is very small. Hence, at equilibrium, we have
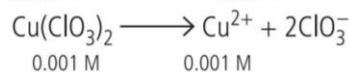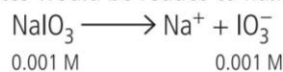$[N_2] = 0.0482 \text{ mol L}^{-1}, [O_2] = 0.0933 \text{ mol L}^{-1}, [N_2O] = 0.1x \text{ mol L}^{-1}$
$\therefore K_c = \dfrac{(0.1x)^2}{(0.0482)^2(0.0933)} = 2.0 \times 10^{-37}$ (given)
On solving this we get, $x \approx 6.6 \times 10^{-20}$
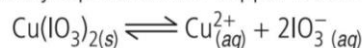$\therefore [N_2O] = 0.1x = 6.6 \times 10^{-21} \text{ mol L}^{-1}$

**24.** When equal volumes of sodium iodate and copper chlorate are mixed, the molar concentrations of both the solutes would be reduce to half *i.e.*, 0.001 M.
$\underset{\substack{0.001 \text{ M} \qquad 0.001 \text{ M}}}{NaIO_3 \longrightarrow Na^+ + IO_3^-}$
$\underset{\substack{0.001 \text{ M} \qquad 0.001 \text{ M}}}{Cu(ClO_3)_2 \longrightarrow Cu^{2+} + 2ClO_3^-}$
$\therefore$ After mixing, $[IO_3^-] = [NaIO_3] = 0.001$ M
$[Cu^{2+}] = [Cu(IO_3)_2] = 0.001$ M
Solubility equilibrium for copper iodate may be written as,
$Cu(IO_3)_{2(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2IO_3^-{}_{(aq)}$
Ionic product of copper iodate
$= [Cu^{2+}][IO_3^-]^2 = (0.001)(0.001)^2 = 1 \times 10^{-9}$
Since ionic product ($1 \times 10^{-9}$) is less than $K_{sp}$($7.4 \times 10^{-8}$), therefore, no precipitation will take place.

**25.** When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.
(i) When $H_2$ is added, the rate of forward reaction will increase.
(ii) Addition of $CH_3OH$ will lead to increase in rate of backward reaction

**26.** $\Delta G^\circ = -RT \ln K_c$
$-13.8 \times 10^3 = 8.314 \times 298 \times \ln K_c$
$\therefore \ln K_c = -5.569$
$K_c = e^{-5.569} \Rightarrow K_c = 3.81 \times 10^{-3}$

**27.** $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}; \Delta H_r^° = -92$ kJ/mol

(i) When pressure is doubled, equilibrium will shift in the direction where pressure decreases *i.e.*, forward direction.

(ii) As this is an exothermic reaction, so the equilibrium will shift in backward direction when the temperature is doubled.

**28.** pH of a buffer changes with temperature because concentration of $H^+$ ions increases, thus pH decreases with increase of temperature.

**29.** $Q_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = \dfrac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$

Given, $K_c = 0.061$

As $Q_c \neq K_c$, reaction is not in equilibrium.

As $Q_c < K_c$, reaction will proceed in the forward direction.

**30.** (i) Lewis acids are those which can accept a pair of electrons or negatively charged ions *e.g.*, $BCl_3$. Lewis bases can donate a pair of electrons or negatively charged ions *e.g.*, $NH_3$.

(ii) Given, $K_{sp}$ of $Ni(OH)_2 = 2 \times 10^{-15}$

$K_{sp}$ of $AgCN = 6 \times 10^{-17}$

*i.e.*, $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

$K_{sp} = [Ni^{2+}][OH^-]^2 = 2 \times 10^{-15}$

$AgCN \rightleftharpoons Ag^+ + CN^-$
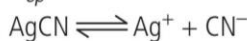
$K_{sp} = [Ag^+][CN^-] = 6 \times 10^{-17}$

Suppose $[Ag^+] = [CN^-] = s_1$ and $[Ni^{2+}] = s_2$

Hence, $[OH^-] = 2s_2$

Since, $s_1^2 = 6 \times 10^{-17} \Rightarrow s_1 = \sqrt{60 \times 10^{-18}}$

$\Rightarrow s_1 = 7.7 \times 10^{-9}$ M

Since, $s_2 \times (2s_2)^2 = 2 \times 10^{-15} \Rightarrow 4s_2^3 = 2 \times 10^{-15}$

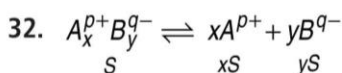$\Rightarrow s_2^3 = 0.5 \times 10^{-15} \Rightarrow s_2^3 = 5 \times 10^{-16}$

$\Rightarrow s_2^3 = 500 \times 10^{-18}$

$\Rightarrow s_2 = \sqrt[3]{500 \times 10^{-18}} = 7.9 \times 10^{-6}$ M
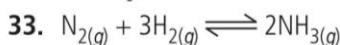
$s_2 = 7.9 \times 10^{-6}$ M

Since $s_2 > s_1$, therefore $Ni(OH)_2$ is more soluble than $AgCN$.

**31.** (i), (iii), (iv) would result in the formation of a buffer solution.

**32.** $A_x^{p+}B_y^{q-} \rightleftharpoons xA^{p+} + yB^{q-}$

$\qquad S \qquad\qquad xS \qquad yS$

$K_{sp} = [A^{p+}]^x [B^{q-}]^y = (xS)^x (yS)^y = x^x \cdot y^y \cdot S^{(x+y)}$

$S^{(x+y)} = K_{sp}/x^x \cdot y^y$

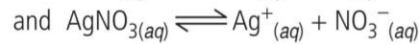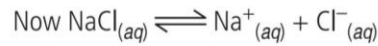**33.** $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

According to Le Chatelier's principle, at constant temperature, the equilibrium composition will change but $K$ will remain same.

**34.** On mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M $AgNO_3$ the total volume becomes 100 mL.

Therefore,

Conc. of NaCl in 100 mL $= \dfrac{0.01 \times 50}{100} = 0.005$ M

Conc. of $AgNO_3$ in 100 mL $= \dfrac{0.01 \times 50}{100} = 0.005$ M

Now $NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$

and $AgNO_{3(aq)} \rightleftharpoons Ag^+_{(aq)} + NO_3^-{}_{(aq)}$

$[Cl^-] = [NaCl] = 0.005$ M

$[Ag^+] = [AgNO_3] = 0.005$ M

$\therefore$ Ionic product of $[Ag^+][Cl^-] = 0.005 \times 0.005$

$\qquad\qquad\qquad\qquad\qquad\qquad = 2.5 \times 10^{-5}$

Since, ionic product is greater than its solubility product, precipitation will occur.

**35.** $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$
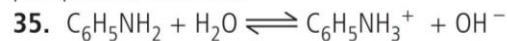
$K_b = \dfrac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \dfrac{[OH^-]^2}{[C_6H_5NH_2]}$

$[OH^-] = \sqrt{K_b[C_6H_5NH_2]}$

$= \sqrt{(4.27 \times 10^{-10})(10^{-3})}$

$= 6.534 \times 10^{-7}$ M

$pOH = -\log(6.534 \times 10^{-7}) = 6.18$

$\therefore pH = 14 - 6.18 = 7.82$

$\qquad\qquad C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

Initial : $\qquad\quad C \qquad\qquad\qquad\qquad 0 \qquad\quad 0$

At. eqm. : $\quad C - C\alpha \qquad\qquad\qquad C\alpha \qquad C\alpha$

$K_b = \dfrac{C\alpha.C\alpha}{C(1-\alpha)} = \dfrac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad (\because 1 \ggg \alpha)$

$\therefore \alpha = \sqrt{\dfrac{K_b}{C}} = \sqrt{\dfrac{4.27 \times 10^{-10}}{10^{-3}}} = 6.53 \times 10^{-4}$

$pK_b = -\log(4.27 \times 10^{-10}) = 9.37$

$pK_a + pK_b = 14$

(for a pair of conjugate acid and base)

$\therefore pK_a = 14 - 9.37 = 4.63$

*i.e.*, $-\log K_a = 4.63$ or, $\log K_a = -4.63$

or, $K_a = $ antilog $(-4.63) = 2.34 \times 10^{-5}$

**36.** (i) The term ionic product has a broad meaning since it is applicable to all types of solution, may be unsaturated or saturated. On the other hand, the solubility product has restricted meaning since it applies only to a saturated solution in which there exists a dynamic equilibrium between the undissolved salt and the ions present in solution. Thus, the solubility product is, in fact the ionic product for a saturated solution.

The solubility product of a salt is constant at constant temperature whereas ionic product depends upon the concentrations of ions in the solution.

(ii) The solubility equilibrium in the saturated solution is
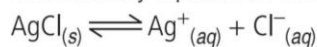
$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

The solubility of AgCl is $1.06 \times 10^{-5}$ mole per litre.

$$[Ag^+_{(aq)}] = 1.06 \times 10^{-5} \text{ mol L}^{-1}$$

$$[Cl^-_{(aq)}] = 1.06 \times 10^{-5} \text{ mol L}^{-1}$$

$$\begin{aligned} K_{sp} &= [Ag^+_{(aq)}] [Cl^-_{(aq)}] \\ &= (1.06 \times 10^{-5} \text{ mol L}^{-1}) \times (1.06 \times 10^{-5} \text{ mol L}^{-1}) \\ &= 1.12 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2} \end{aligned}$$

**37.** (i) Sorensen (1909) defined pH of a solution as negative logarithm of the hydrogen ion concentration of the solution.

Thus, $pH = -\log[H^+] = \log\dfrac{1}{[H^+]}$ or $[H^+] = 10^{-pH}$

Likewise, pOH of a solution

$pOH = -\log[OH^-] = \log\dfrac{1}{[OH^-]}$ or $[OH^-] = 10^{-pOH}$

$K_w = [H^+][OH^-]$ = Ionic product of water $= 10^{-14}$ (mol/L)$^2$

$pK_w = -\log K_w$

$pK_w = pH + pOH = 14$

(ii) $KOH = \dfrac{0.561}{56} \times \dfrac{1000}{200} = 0.05$ M

As, $KOH \longrightarrow K^+ + OH^-$
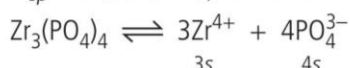
$[K^+] = [OH^-] = 0.05$ M

$[H^+] = K_w/OH^- = 10^{-14}/0.05$

$\quad = 10^{-14}/(5 \times 10^{-2}) = 2.0 \times 10^{-13}$ m

$pH = -\log 2 \times 10^{-13} = 13 - \log 2 = 12.69$

**38.** (i) Common ion effect can be defined as the suppression of the degree of ionisation of a weak electrolyte by the addition of a strong electrolyte having an ion common with the weak electrolyte.

(ii) $\underset{2s \quad\quad s}{Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}}$
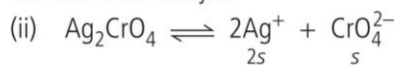
$K_{sp} = [Ag^+]^2 [CrO_4^{2-}] = (2s)^2 \times s = 4s^3$

$\underset{3s \quad\quad 4s}{Zr_3(PO_4)_4 \rightleftharpoons 3Zr^{4+} + 4PO_4^{3-}}$

$K_{sp} = [Zr^{4+}]^3 [PO_4^{3-}]^4 = (3s)^3 \times (4s)^4 = 6912 s^7$

(iii) $pH = -\log[H_3O^+] = -\log(0.005) = 2.30$

**39.** $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$; $\Delta_f H° = 124.0$ kJ mol$^{-1}$

(a) $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = 8.3 \times 10^{-3}$

(b) $K_c$ for the reverse reaction

$$= \dfrac{1}{K_c \text{ for the forward reaction}}$$

$$= \dfrac{1}{8.3 \times 10^{-3}} = 120.48$$

(c) (i) When pressure increases, $K_c$ remains unchanged.

(ii) $K_c$ increases with increase in temperature because the reaction is endothermic.

**40.**

| | $PCl_{5(g)}$ | $\rightleftharpoons$ | $PCl_{3(g)}$ + | $Cl_{2(g)}$ |
|---|---|---|---|---|
| $t = 0$ | 3 | | 0 | 0 |
| $t_{eqm}$ | $3(1-x)$ | | $3x$ | $3x$ |
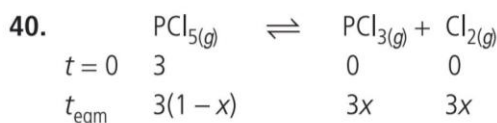
where $x$ = degree of dissociation of $PCl_{5(g)}$ at 227°C

Total no. of moles at equilibrium $= [(3 - 3x) + 3x + 3x + 1$ (molar concentration of $N_2$)] $= 4 + 3x$.

From gas equation : $PV = nRT$

Total pressure $(P) = \dfrac{(4+3x)}{100} \times 0.082 \times 500$ atm

$\quad\quad\quad = 2.05$ atm (given)

Thus, $4 + 3x = 5.0$

or $\quad 3x = 1.0$

Hence, $x = \dfrac{1.0}{3} = 0.33$

Percentage dissociation = 33%

$pPCl_5 = \dfrac{3-3x}{4+3x} \times P = \dfrac{(3-0.99) \times 2.05}{4+0.33 \times 3} = \dfrac{2.01 \times 2.05}{4.99} = 0.825$

$pPCl_3 = \dfrac{3x}{4+3x} \times P = \dfrac{3 \times 0.33 \times 2.05}{4.99} = \dfrac{2.03}{4.99} = 0.4067$

$pCl_2 = \dfrac{3x}{4+3x} \times P = \dfrac{3 \times 0.33 \times 2.05}{4.99} = \dfrac{2.03}{4.99} = 0.4067$

Hence, $K_p = \dfrac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \dfrac{0.4067 \times 0.4067}{0.825} = 0.200$ atm.

☺☺☺