7

Equilibrium

Facts that Matter

• Chemical Equilibrium

In a chemical reaction chemical equilibrium is defined as the state at which there is no further change in concentration of reactants and products.

For example,

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

At equilibrium the rate of forward reaction is equal to the rate of backward reaction.

Equilibrium mixture: The mixture of reactants and products in the equilibrium state is called an equilibrium mixtures.

Based on the extent to which the reactions proceed to reach the state of equilibrium, these may be classified in three groups:

(*i*) The reactions which proceed almost to completion and the concentrations of the reactants left are negligible.

(*ii*) The reactions in which most of the reactants remains unchanged, *i.e.* only small amounts of products are formed.

(*iii*) The reactions in which the concentrations of both the reactants and products are comparable when the system is in equilibrium.

• Equilibrium in Physical Processes

(*i*) **Solid-Liquid Equilibrium:** The equilibrium is represented as

$$H_2O\ (s) \rightleftharpoons H_2O(l)$$

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

The system here is in dynamic equilibriums and following can be inferred.

(*a*) Both the opposing processes occur simultaneously

(*b*) Both the processes occur at the same rate so that the amount of ice and water remains constant.

(*ii*) **Liquid-Vapour Equilibrium**

The equilibrium can be represented as

$$H_2O\ (l) \rightleftharpoons H_2O\ (\text{vap})$$

Rate of evaporation = Rate of condensation

When there is an equilibrium between liquid and vapours, it is called liquid-vapour equilibrium.

(*iii*) **Solid-Vapour Equilibrium**

This type of equilibrium is attained where solids sublime to vapour phase. For example, when solid iodine is placed in a closed vessel, violet vapours start appearing in the vessel whose intensity increases with time and ultimately, it becomes constant.

The equilibrium may be represented as

$$I_2\text{ (s)} \rightleftharpoons I_2\text{ (vapour)}$$

Rate of sublimation of solid I_2 to form vapour = Rate of condensation of I_2 vapour to give solid I_2

• Equilibrium Involving Dissolution of Solid in Liquid

Solution: When a limited amount of salt or sugar or any solute dissolves in a given amount of water solution is formed.

At a given temperature state is reached when no more solute can be dissolved then the solution is called saturated solution.

The equilibrium between a solid and its solution is indicated by the saturated solution and may be represented as

$$\text{Sugar (in solution)} \rightleftharpoons \text{Sugar (solid).}$$

Here dissolution and precipitation takes place with the same speed.

On adding a small amount of radioactive sugar to the saturated solution it will be found that the sugar present in the solution as well as in the solid state is radioactive.

• Equilibrium between a Gas and its Solution in Liquid

This type of equilibrium can be seen by the following example:

Let us consider a sealed soda water bottle in which CO_2 gas is dissolved under high pressure. A state of equilibrium is attained between CO_2 present in the solution and vapours of the gas.

$$CO_2\text{ (g)} \rightleftharpoons CO_2\text{ (present in solution)}$$

Henry's law: The solubility of a gas in a liquid at a certain temperature is governed by Henry's law. It states that the mass of a gas that dissolves in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the surface of the solvent.

Mathematically, $m \propto p$

$$m = K_H p \text{ (where } K_H = \text{Henry's Constant)}$$

• Characteristics of Equilibria Involving Physical Processes

(*i*) The equilibrium can be attained only in closed systems at a given temperature.
(*ii*) At the equilibrium the measurable properties of the system remain constant.
(*iii*) The equilibrium is dynamic since both the forward and backward processes occur at same rate.
(*iv*) At equilibrium, the concentrations of substances become constant at constant temperature.
(*v*) The value of equilibrium constant represents the extent to which the process proceeds before equilibrium is achieved.

• Equilibrium in Chemical Processes

Like equilibria in physical systems it can also be achieved in chemical process involving reversible chemical reactions carried in closed container.

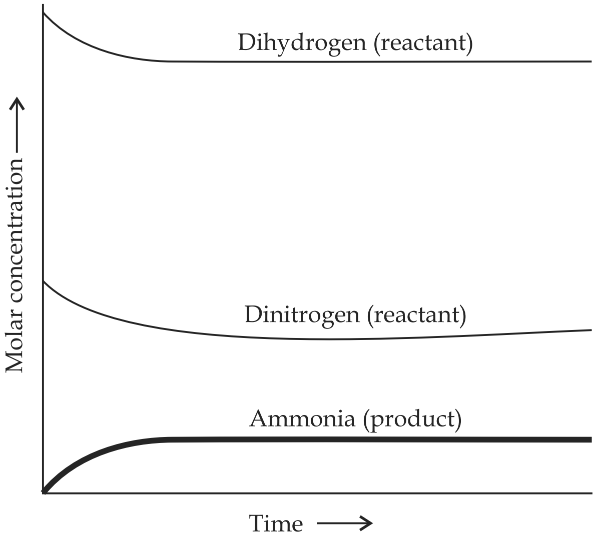
For Example, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. Haber started his experiment with the known amounts of N_2 and H_2 at high temperature and pressure. At regular intervals of time he determined the amount of ammonia present. He also found out concentration of unreacted N_2 and H_2.

After a certain time he found that the composition of mixture remains the same even though some of the reactants are still present. This constancy indicates the attainment of equilibrium. In general, for a reversible reaction the chemical equilibria can be shown by

$$A + B \rightleftharpoons C + D$$

After a certain time the two reactions occur at the same rate and the system reaches a state of equilibrium. This can be shown by the given figure.



Depiction of equilibrium for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

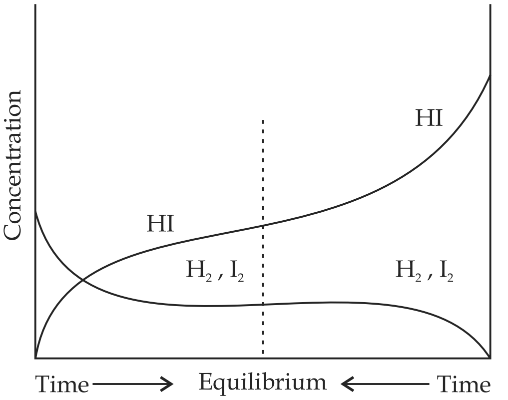
• Equilibrium in Homogeneous System

When in a system involving reversible reaction, reactants and products are in the same phase, then the system is called as homogeneous system.

For Example,

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI\,(g)$$

After some time it can be observed that an equilibrium is formed. The equilibrium can be seen by constancy in the colour of the reaction mixture.



Chemical equilibrium in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ *can be attained from either direction*

• Law of Chemical Equilibrium

At a constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants each raised to a power equal to the corresponding stoichiometric coefficients as represented by the balanced chemical equation. Let us consider the reaction,

$$aA + bB \rightarrow \text{products}$$

By the law, rate of reaction $\alpha[A]^a [B]^b = K[A]^a [B]^b$

Here a and b are stoichiometric coefficients. K is the rate constant.

Let us consider a general reversible reaction

$$A + B \rightleftharpoons C + D$$

Applying Law of Mass Action,

Rate of the forward reaction $\alpha[A]\ [B] = Kf[A]\ [B]$

Where kf is a constant of proportionality and is called velocity constant for the forward reaction.

Rate of backward reaction $\alpha[C]\ [D] = kb[C]\ [D]$.

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$Kf\ [A]\ [B] = kb\ [C]\ [D]$$

or,
$$\frac{[C][D]}{[A][B]} = \frac{Kf}{kb} = K$$

At constant temperatures K is also constant and is called Equilibrium constant.

Now let us consider a more general reversible reaction in a state of equilibrium. By applying law of mass action.

$$aA + bB \rightleftharpoons cC + dD$$

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

Equilibrium constant for the reaction

$$4\ NH_3\ (g) + 5O_2\ (g) \rightleftharpoons 4\ NO\ (g) + 6\ H_2O\ (g)$$

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

• Relationship between Equilibrium constant *K*, reaction Quotient *Q* and Gibbs energy *G*

A mathematical expression of thermodynamic view of equilibrium can be described by the equation.

$$\Delta G = \Delta G^\ominus + RT\ \text{In}\ Q$$

where $G^\ominus$ is standard Gibbs energy.

At equilibrium when $\Delta G = 0$

$$Q = K_c$$

$$\Delta G = \Delta G^\ominus + RT\ \text{In}\ K = 0$$

$$\Delta G^\ominus = -RT\ \text{In}\ K$$

$$\ln K = \frac{-\Delta G^{\ominus}}{RT}$$

Taking antilog on both sides

$$K = e^{-\Delta G^{\ominus}/RT}$$

• Factors Affecting Equilibria

Le Chatelier's principle: If a system under equilibrium is subjected to a change in temperature, pressure or concentration, then the equilibrium shifts in such a manner as to reduce or to counteract the effect of change.

Effect of Change of Concentration: When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium changes so as to minimise the effect.

Effect of Pressure Change

If the number of moles of gaseous reactants and products are equal, there is no effect of pressure.

When the total number of moles of gaseous reactants and total number of moles of gaseous products are different.

On increasing pressure, total number of moles per unit volume increases, thus the equilibrium will shift in direction in which number of moles per unit volume will be less.

If the total number of moles of products are more than the total number of moles of reactants, low pressure will favour forward reaction.

If total number of moles of reactants are more than total number of moles of products, high pressure is favourable to forward reaction.

Effect of Inert Gas Addition

If the volume is kept constant there is no effect on equilibrium after the addition of an inert gas.

Reason: This is because the addition of an inert gas at constant volume does not change the partial pressure or the molar concentration.

The reaction quotient changes only if the added gas is involved in the reaction.

Effect of Temperature Change

When the temperature of the system is changed (increased or decreased), the equilibrium shifts in opposite direction in order to neutralize the effect of change. In exothermic reaction low temperature favours forward reaction *e.g.,*

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$\Delta H = -92.38 \text{ kJ mol}^{-1}$$

but practically very low temperature slows down the reaction and thus a catalyst is used.

In case of endothermic reaction, the increase in temperature will shift the equilibrium in the direction of the endothermic reaction.

Effect of a Catalyst

Catalyst has no effect on the equilibrium composition of a reaction mixture.

Reason: Since catalyst increases the speed of both the forward and backward reactions to the same extent in a reversible reaction.

• Ionic Equilibrium in Solution

Electrolytes: Substances which conduct electricity in their aqueous solution.

Strong Electrolytes: Those electrolytes which on dissolution in water are ionized almost completely are called strong electrolytes.

Weak electrolyte: Those electrolytes which on dissolution in water partially dissociated are called weak electrolyte.

Ionic Equilibrium: The equilibrium formed between ions and unionised substance is called ionic equilibrium. *e.g.,*

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Acids: Acids are the substances which turn blue litmus paper to red and liberate dihydrogen on reacting with some metals.

Bases: Bases are the substances which turn red litmus paper blue. It is bitter in taste.

Common Example: NaOH, Na_2CO_3.

• Arrhenius Concept of Acids and Bases

Acids: According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$.

Bases: Bases are substances that produce $OH^-(aq)$ after dissociation in water.

The ionization of an acid can be represented as

$$\begin{aligned} HX(aq) &\rightarrow H^+(aq) + X^-(aq) \\ HX(aq) + H_2O(l) &\rightarrow H_3O^+(aq) + X^-(aq) \end{aligned}$$

Dissociation of Base molecule in aqueous solution:

$$MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$$

• Limitations of the Arrhenius Concept

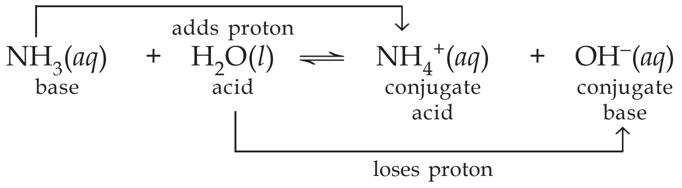
(*i*) According to the Arrhenius concept, an acid gives H^+ ions in water but the H^+ ions does not exist independently because of its very small size (~H^{-18} m radius) and intense electric field.

(*ii*) It does not account for the basicity of substances like, ammonia which does not possess a hydroxyl group.

• The Bronsted-Lowry Acids and Bases

According to Bronsted-Lowry, an acid is a substance which is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion H^+.

In other words, acids are proton donors and bases are proton acceptors. This can be explained by the following example.



$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

• Acid and Base as Conjugate Pairs

The acid-base pair that differs only by one proton is called a conjugate acid-base pair.
Let us consider the example of ionization of HCl in water.

adds proton

$$\underset{\text{acid}}{HCl(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\\text{base}}}{Cl^-(aq)}$$

loses proton

Here water acts as a base because it accepts the proton.
Cl^- is a conjugate base of HCl and HCl is the conjugate acid of base Cl^-. Similarly, H_2O is conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O.

• Lewis Acids and Bases

According to Lewis, acid is a substance which accepts electron pair and base is a substance with donates an electron pair.
Electron deficient species like $AlCl_3$, BH_3, H^+ etc. can act as Lewis acids while species like H_2O, NH_3 etc. can donate a pair of electrons, can act as Lewis bases.

• Ionization of Acids and Bases

Strength of acid or base is determined with the help of extent of ionization in aqueous solution.
pH Scale: Hydrogen-ion concentration are measured as the number of gram ions of hydrogen ions present per litre of solution. Since these concentrations are usually small, the concentration is generally expressed as the pH of the solution. pH being the logarithm of the reciprocal of the hydrogen ion concentration.

$$pH = -\log\{[H^+]/\text{mol } L^{-1}\}$$

pH of pure water at 25°C is given as

$$\begin{aligned} pH &= -\log(10^{-7}) = 7 \\ \text{Acidic solution has } pH &< 7 \\ \text{Basic solution has } pH &> 7 \\ \text{Neutral solution has } pH &= 7 \\ K_w &= [H_3O^+]\,[OH^-] = 10^{-14} \\ pK_w &= pH + pOH = 14 \end{aligned}$$

• Di and Polybasic Acids

Acids which contain more than one ionizable proton per molecule are called Dibasic acids or polybasic acids or polyprotic acids.
Common examples are oxalic acid, sulphuric acid, phosphoric acid etc.
The ionization reactions for a dibasic acid can be represented as.

$$\begin{aligned} H_2X(aq) &\rightleftharpoons H^+(aq) + HX^-(aq) \\ HX^-(aq) &\rightleftharpoons H^+(aq) + X^{2-}(aq) \end{aligned}$$

Their equilibrium constants can be written as

$$K_{a_1} = \frac{[H^+][HX^-]}{[H_2X]};\ K_{a_2} = \frac{[H^+][X^{2-}]}{[HX^-]}$$

K_{a_1} and K_{a_2} are called first and second ionization constants respectively.

$$K_{a_1} > K_{a_2} \text{ for dibasic acid.}$$

Factors Affecting Acid Strength

When the strength of H-A bond decreases

$$\underset{\xrightarrow[\text{Acid strength increases}]{}}{\overset{\xrightarrow{\text{Size increases}}}{\mathrm{HF << HCl << HBr << HI}}}$$

The energy required to break the bond decreases, H-A becomes a stronger acid.

As the size of A increases down the group, H – A bond strength decreases and so the acid strength increases.

In a period, as the electronegativity of A increases, the strength of the acid increases.

$$\underset{\xrightarrow[\text{Acid strength increases}]{}}{\overset{\xrightarrow{\text{Electronegativity of A increases}}}{CH_4 < NH_3 < H_2O < HF}}$$

• Common Ion Effect

If in a aqueous solution of a weak electrolyte, a strong electrolyte is added having an ion common with the weak electrolyte, then the dissociation of the weak electrolyte is decreased or suppressed. The effect by which the dissociation of weak electrolyte is suppresed is known as common ion effect.

For example: In an aqueous solution of CH_3COOH, a small amount of CH_3COONa (strong electrolyte) has been added.

Due to the presence of common $CH_3\ COO^-$ (*aq*) ions, the equilibrium will be shifted to the left.

$$CH_3\ COOH\ (aq) \rightleftharpoons CH_3COO^-\ (aq) + H^-\ (aq)$$
$$CH_3COONa\ (aq) \underset{\text{Common ion}}{\rightleftharpoons} CH_3COO^-(aq) + Na^+\ (aq)$$

Thus, the dissociation of CH_3COOH will get decreased or suppressed.

• Hydrolysis of Salts and the pH of their Solutions

Salt Hydrolysis: Salt + water $\rightleftharpoons$ Acid + Base

Hydrolysis is a process which is reverse of neutralization reaction.

Hydrolysis of Salts of Strong Acids and Weak Base

e.g., NH_4Cl, NH_4NO_3 etc.

$$NH_4\,NO_3 + H_2O \rightleftharpoons NH_4\,OH + HNO_3$$
$$NH_4^+ + NO_3^- + H_2O \rightleftharpoons NH_4\,OH + H^+\,NO_3^-$$

or
$$NH_4^+ + H_2O \rightleftharpoons NH_4\,OH + H^+$$

After hydrolysis solution will be acidic pH < 7.

Since only cations of the salt participate in the hydrolysis, it is known as cationic hydrolysis.

Hydrolysis of salts of strong base and weak acids

Salts in this category are CH_3COONa, Na_2CO_3, Na_3PO_4 etc.

$$CH_3\ COONa + H_2O \rightleftharpoons CH_3\ COOH + NaOH$$

$$CH_3\,COO^- + Na^+\ H_2O \rightleftharpoons CH_3\,COOH + Na^+ + OH^-$$

or $$CH_3\,COO^- + H_2O \rightleftharpoons CH_3\,COOH + OH^-$$

After hydrolysis, solution will be basic pH > 7

In this type of hydrolysis, only anions of salt take part in the hydrolysis, it is known as anionic hydrolysis.

Hydrolysis of Weak Acid and Weak Base

Salts belong to this type are: CH_3COONH_4, $(NH_4)_2CO_3$ etc.

$$CH_3\,COONH_4 + H_2O \rightleftharpoons CH_3\,COOH + NH_4OH$$

or $$CH_3\,COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3\,COOH + NH_4OH$$

pH of solution depends upon the relative strengths of acid and base.

- **Buffer Solutions**

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali, are called Buffer solutions.

e.g., $CH_3\,COOH + CH_3COONa$,

$H_2CO_3 + HCl$

Acidic Buffer: Weak acid and its salt with strong base are known as acidic buffer. PH < 7.

e.g., CH_3COOH and CH_3COONa, H_2CO_3 and HCl

Basic Buffer: Weak base and its salt with strong acid are known as basic buffer.

pH > 7 *e.g.*, NH_4Cl and NH_4OH

- **Solubility Products**

It is applicable to sparingly soluble salt. There is equilibrium between ions and unionised solid substance.

Consider an equation

$$BaSO_4\,(s) \xrightleftharpoons[\text{in water}]{\text{Saturated solution}} Ba^{2+}(aq) + SO_4^{2-}\,(aq)$$

$$K = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$$

$$K_{sp} = K[BaSO_4] = [Ba^{2+}]\,[SO_4^{2-}]$$

K_{sp} is called the solubility product constant or simply solubility product.

Under equilibrium conditions

$$K_{sp} = Q_{sp}$$

The solubility of salts of weak acids like, phosphates, increases at lower pH.

Words that Matter

- **Equilibrium:** It can be established for both physical and chemical processes. At the state of equilibrium rate of forward and backward reactions are equal.
- **Equilibrium constant:** K_c is expressed as the concentration of products divided by reactants each term raised to the stoichiometric coefficients.

  For reactions,

$$aA + bB \rightleftharpoons cC + dD$$

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

- **Le Chatelier's principle:** It states that the change in any factor such as temperature, pressure, concentration etc., will cause the equilibrium to shift in such a direction so as to reduce the effect of the change.
- **Electrolytes:** Substances that conduct electricity in aqueous solutions are called electrolytes.
- **Arrhenius Concept:** According to Arrhenius, acids give hydrogeneous while bases produce hydroxyl ions in their aqueous solution.
- **Bronsted-Lowry concept:** Bronsted-Lowry defined acid as proton donor and a base as a proton acceptor.
- **Conjugate base and Conjugate acid:** When a Bronsted-Lowry acid reacts with a base it produces its conjugate base and conjugate acid.
- **Conjugate pair of acid and base:** Conjugate pair of acid and base differs only by one proton.
- **Lewis acids:** Define acid as an electron pair acceptor and a base as an electron pair donor.
- **pH Scale:** Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the pH scale. The pH of pure water is 7.
- **Buffer solution:** It is the solution whose pH does not change by addition of small amount of strong acid or base.

  For example: $CH_3COOH + CH_3COONa$.
- **Solubility product (K_{sp}):** For a sparingly soluble salt, it is defined as the product of molar concentration of the ions raised to the power equal to the number of times each ion occurs in the equation for solubilities.

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+]\,[Cl^-].$$

NCERT TEXTBOOK QUESTIONS SOLVED

Q1. *A liquid is in equilibrium with its vapours in a sealed container at a fixed temperature. The volume of the container is suddenly increased. (i) What is the initial effect of the change on the vapour pressure? (ii) How do the rates of evaporation and condensation change initially? (iii) What happens when equilibrium is restored finally and what will be the final vapour pressure?*

Ans. (*i*) On increasing the volume of the container, the vapour pressure will initially decrease because the same amount of vapours are now distributed over a larger space.

(*ii*) On increasing the volume of the container, the rate of evaporation will increase initially because now more space is available. Since the amount of the vapours per unit volume decrease on increasing the volume, therefore, the rate of condensation will decrease initially.

(*iii*) Finally, equilibrium will be restored when the rates of the forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

Q2. *What is K_c for the following reaction in state of equilibrium?*

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

Given: $[SO_2] = 0.6$ M; $[O_2] = 0.82$ M; and $[SO_3] = 1.90$ M

Ans.

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

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.9\ M)\times(1.9\ M)}{(0.6\ M)\times(0.6\ M)\times(0.82\ M)}$$

$$= 12.229\ M^{-1} = \mathbf{12.229\ L\ mol^{-1}}$$

Q3. *At a certain temperature and total pressure of 10^5 Pa, iodine vapours contain 40% by volume of iodine atoms in the equilibrium $I_2(g) \rightleftharpoons 2I\,(g)$. Calculate K_p for the equilibrium.*

Ans. According to available data:

Total pressure of equilibrium mixture $= 10^5$ Pa

Partial pressure of iodine atoms (I) $= \frac{40}{100} \times (10^5\ Pa) = 0.4 \times 10^5$ Pa

Partial pressure of iodine molecules (I_2) $= \frac{60}{100} \times (10^5\ Pa) = 0.6 \times 10^5$ Pa

$$\underset{(0.6 \times 10^5\ Pa)}{I_2\,(g)} \rightleftharpoons \underset{(0.4 \times 10^5\ Pa)}{2I\,(g)}$$

$$K_p = \frac{p_{I^2}}{p_I} = \frac{(0.4\times10^5 Pa)^2}{(0.6\times10^5 Pa)} = \mathbf{2.67 \times 10^4\ Pa}$$

Q4. *Write the expression for the equilibrium constant for each of the following reactions*

(*i*) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(*ii*) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(*iii*) $CH_3COOC_2H_5(aq) + H_2\,O(l) \rightleftharpoons CH_3\,COOH(aq) + C_2H_5OH\,(aq)$

(*iv*) $Fe^{3+}\,(aq) + 3OH^-(aq) \rightleftharpoons Fe\,(OH)_3\,(s)$

(*v*) $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5\,(l)$

Ans. (*i*)
$$K_c = \frac{[NO(g)]^2[Cl_2(g)]}{[NOCl(g)]^2}$$

(*ii*)
$$K_c = \frac{[CuO(g)]^2[NO_2(g)]^4[O_2(g)]}{[Cu\,(NO_3)_2(s)]^2} = [NO_2(g)]^4\,[O_2(g)]$$

(*iii*)
$$K_c = \frac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)][H_2O(l)]}$$

$$= \frac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)]}$$

(*iv*)
$$K_c = \frac{[Fe(OH)_3(s)]}{[Fe^{3+}(aq)][OH^-(aq)]^3} = \frac{1}{[Fe^{3+}(aq)][OH^-(aq)]^3}$$

(*v*)
$$K_c = \frac{[IF_5(l)]^2}{[I_2(s)][F_2(g)]^5} = \frac{[IF_5(l)]^2}{[F_2(g)]^5}$$

Q5. *Find the value of K_c for each of the following equilibria from the value of K_p*

(a) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$; $K_p = 1.8 \times 10^{-2}$ atm at 500 K

(b) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$; $K_p = 167$ atm at 1073 K.

Ans. K_p and K_c are related to each other as $K_p = K_c\,(RT)^{\Delta ng}$

The value of K_c can be calculated as follows:

(*a*) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2$

$$K_p = 1.8 \times 10^{-2}\ \text{atm},$$

$$\Delta^{ng} = 3 - 2 = 1\ ;\ R = 0.0821\ \text{litre atm}\ K^{-1}\ \text{mol}^{-1}\ ;\ T = 500\ \text{K}$$

$$\therefore \quad K_c = \frac{K_p}{(RT)^{\Delta ng}} = \frac{(1.8 \times 10^{-2}\ \text{atm})}{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 500\ \text{K})^1}$$

$$= \mathbf{4.4 \times 10^{-4}\ mol\ L^{-1}}$$

(*b*) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

$$K_p = 167\ \text{atm}, \quad \Delta^{ng} = 1$$

$$R = 0.0821\ \text{liter atm}\ K^{-1}\ \text{mol}^{-1}\ ;\ T = 1073\ K$$

$$K_c = \frac{K_p}{(RT)^{\Delta ng}} = \frac{(167\ \text{atm})}{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 1073\ \text{K})^1}$$

$$= \mathbf{1.9\ mol\ L^{-1}}$$

Q6. *For the following equilibrium, $K_c = 6.3 \times 10^{14}$ at 1000 K*

$NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2\,(g)$

Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is K_c for the reverse reaction?

Ans. For the reverse reaction $K_c = \dfrac{1}{K_c} = \dfrac{1}{6.3 \times 10^{14}} = \mathbf{1.59 \times 10^{-15}}$.

Q7. *Explain why pure liquids and solids can be ignored while writing the value of equilibrium constants.*

Ans. This is because molar concentration of a pure solid or liquid is independent of the amount present.

$$\text{Molar concentration} = \frac{\text{No. of moles}}{\text{volume}} \times \frac{\text{Mass}}{\text{volume}} \times \text{Density}$$

Since density of pure liquid or solid is fixed and molar mass is also fixed. Therefore molar concentration are constant.

Q8. *Reaction between nitrogen and oxygen 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 reaction vessel of volume 10 L and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of the equilibrium mixture.

Ans. Let x moles of $N_2(g)$ take part in the reaction. According to the equation, $x/2$ moles of $O_2\,(g)$ will react to form x moles of $N_2O(g)$. The molar concentration per litre of different species before the reaction and at the equilibrium point is:

	$2N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2N_2O(g)$
Initial mole/litre:	$\frac{0.482}{10}$		$\frac{0.933}{10}$		Zero

Mole/litre at eqm. point: $\frac{0.482-x}{10}$ $\frac{0.933-\frac{x}{2}}{10}$ $\frac{x}{10}$

The value of equilibrium constant (2.0×10^{-37}) is extremely small. This means that only small amounts of reactants have reacted. Therefore, x is extremely small and can be omitted as far as the reactants are concerned.

Applying Law of Chemical Equilibrium $K_c = \frac{[N_2O(g)]^2}{[N_2(g)]^2[O_2(g)]}$

$$2.0 \times 10^{-37} = \frac{\left(\frac{x}{10}\right)^2}{\left(\frac{0.482}{10}\right)^2 \times \left(\frac{0.933}{10}\right)} = \frac{0.01\,x^2}{2.1676 \times 10^{-4}}$$

$$x^2 = 43.352 \times 10^{-40} \quad \text{or} \quad x = 6.6 \times 10^{-20}$$

As x is extremely small, it can be neglected.
Thus, in the equilibrium mixture

Molar conc. of N_2 = **0.0482 mol L^{-1}**
Molar conc. of O_2 = **0.0933 mol L^{-1}**
Molar conc. of N_2O = $0.1 \times x = 0.1 \times 6.6 \times 10^{-20}$ mol L^{-1}
= **6.6×10^{-21} mol L^{-1}**

Q9. *Nitric oxide reacts with bromine and gives nitrosyl bromide as per reaction given below:*

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

When 0.087 mole of NO and 0.0437 mole of Br_2 are mixed in a closed container at constant temperature, 0.0518 mole of NOBr is obtained at equilibrium. Determine the compositions of the equilibrium mixture.

Ans. The balanced chemical equation for the reaction is:

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

According to the equation, 2 moles of NO (*g*) react with 1 mole of Br_2 (*g*) to form 2 moles of NOBr (*g*). The composition of the equilibrium mixture can be calculated as follows:

No. of moles of NOBr (*g*) formed at equilibrium = 0.0518 mol (given)
No. of moles of NO (*g*) taking part in reaction = 0.0518 mol
No. of moles of NO (*g*) left at equilibrium = 0.087 – 0.0518 = 0.0352 mol
No. of moles of Br_2 (*g*) taking part in reaction = 1/2 × 0.0518 = 0.0259 mol
No. of moles of Br_2 (*g*) left at equilibrium = 0.0437 – 0.0259
= 0.0178 mol

The initial molar concentration and equilibrium molar concentration of different species may be represented as:

	$2NO(g)$ +	$Br_2(g)$ $\rightleftharpoons$	$2NOBr(g)$
Initial moles	0.087	0.0437	0
Moles at eqm. point:	0.0352	0.0178	0.0518

Q10. *At 450 K, $K_p = 2.0 \times 10^{10}$ bar^{-1} for the equilibrium reaction:*

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

What is K_c at this temperature?

Ans. $K_p = K_c (RT)^{\Delta ng}$ or $K_c = \dfrac{K_p}{(RT)^{\Delta ng}} = K_p (RT)^{-\Delta ng}$

$K_p = 2.0 \times 10^{10}$ bar^{-1} ; R = 0.083 L bar K^{-1} mol^{-1} ; T = 450 K; $\Delta^{ng} = 2 - 3 = -1$

$K_c = (2.0 \times 10^{10}\ \text{bar}^{-1}) \times [(0.083\ \text{L bar K}^{-1}\ \text{mol}^{-1}) \times (450\ \text{K})]^{-(-1)}$

$= 7.47 \times 10^{11}$ mol^{-1} **L = 7.47×10^{11} M^{-1}**

Q11. *A sample of HI (g) is placed in a flask at a pressure of 0.2 atm. At equilibrium partial pressure of HI (g) is 0.04 atm. What is K_p for the given equilibrium?*

$$2HI\ (g) \rightleftharpoons H_2(g) + I_2\ (g)$$

Ans. $pHI = 0.04$ atm, $pH_2 = 0.08$ atm; $pI_2 = 0.08$ atm

$$K_p = \frac{pH_2 \times pI_2}{p^2_{HI}} = \frac{(0.08\ \text{atm}) \times (0.08\ \text{atm})}{(0.04\ \text{atm}) \times (0.04\ \text{atm})} = \mathbf{4.0}$$

Q12. *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 1.7×10^{-2}.

Is this reaction at equilibrium? If not, what is the direction of net reaction?

Ans. The reaction is: $N_2(g) + 3\ H_2(g) \rightleftharpoons 2NH_3(g)$

$$\text{Concentration quotient } (Q_c) = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(8.13/20\ \text{mol L}^{-1})^2}{(1.57\ /\ 20\ \text{mol L}^{-1}) \times (1.92\ /\ 20\ \text{mol L}^{-1})^3}$$

$$= \mathbf{2.38 \times 10^3}$$

The equilibrium constant (K_c) for the reaction = 1.7×10^{-2}

As $Q_c \neq K_c$; this means that the reaction is not in a state of equilibrium.

Q13. *The equilibrium constant expression for a gas reaction is,*

$$K_c = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

Ans. Balanced chemical equation for the reaction is

$4\ NO\ (g) + 6H_2O(g) \rightleftharpoons 4\ NH_3\ (g) + 5\ O_2(g)$

Q14. *If 1 mole of H_2O and 1 mole of CO are taken in a 10 litre vessel and heated to 725 K, at equilibrium point 40 percent of water (by mass) reacts with carbon monoxide according to equation.*

$$H_2O + CO(g) \rightleftharpoons H_2\ (g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

Ans. Number of moles of water originally present = 1 mol

Percentage of water reacted = 40%

Number of moles of water reacted = $\dfrac{1 \times 40}{100}$ = 0.4 mol

Number of moles of water left = (1 – 0.4) = 0.6 mol

According to the equation, 0.4 mole of water will react with 0.4 mole of carbon monoxide to form 0.4 mole of hydrogen and 0.4 mole of carbon dioxide.

Thus, the molar conc. per litre of the reactants and products before the reaction and at the equilibrium point are as follows:

	$H_2O\ (g)$	+	$CO(g)$	$\rightleftharpoons$	$H_2\ (g)$	+	$CO_2(g)$
Initial moles/litre	$\frac{1}{10}$		$\frac{1}{10}$		0		0
Mole/litre at the equilibrium point	$\frac{1-0.4}{10}=\frac{0.6}{10}$		$\frac{1-0.4}{10}=\frac{0.6}{10}$		$\frac{0.4}{10}$		$\frac{0.4}{10}$

Applying law of chemical equilibrium,

$$\text{Equilibrium constant } (K_c) = \frac{[H_2(g)][CO_2(g)]}{[H_2O(g)][CO(g)]} = \frac{\left(\frac{0.4}{10}\text{ mol L}^{-1}\right)\times\left(\frac{0.4}{10}\text{ mol L}^{-1}\right)}{\left(\frac{0.6}{10}\text{ mol L}^{-1}\right)\times\left(\frac{0.6}{10}\text{ mol L}^{-1}\right)}$$

$$= \frac{0.16}{0.36} = \mathbf{0.44}$$

Q15. *At 700K, equilibrium constant for the reaction:*

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$$

is 54.8. If 0.5 mol L $^{-1}$ of HI(g) is present at equilibrium at 700K, what are the concetration of H_2 (g) and I_2(g) assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700K?

Ans. Do yourself.

Q16. *What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?*

$$2ICl(g) \rightleftharpoons I_2\ (g) + Cl_2(g)\ ;\ K_c = 0.14$$

Ans. Suppose at equilibrium, the molar concentration of both I_2 (g) and Cl_2 (g) is x mol L^{-1}.

	$2ICl(g)$	$\rightleftharpoons$	$I_2(g)$	+	$Cl_2(g)$
Initial molar conc.	0.78 M		0		0
Eqn. molar conc.	$(0.78 - 2x)$M		x		x

$$K_c = \frac{[I_2(g)][Cl_2(g)]}{[ICl\ (g)^2]} = \frac{(x)\times(x)}{(0.78-2x)^2}$$

$$\frac{x}{(0.78-2x)} = (0.14)^{1/2} = 0.374 \quad \text{or} \quad x = 0.374\ (0.78 - 2x)$$

$$x = 0.292 - 0.748x \quad \text{or} \quad 1.748x = 0.292\ ;\ x = \frac{0.292}{1.748} = 0.167$$

$$[ICl] = (0.78 - 2 \times 0.167) = (0.78 - 0.334) = \mathbf{0.446\ M}$$

$$[I_2] = 0.167\ M\ ;\ [Cl_2] = \mathbf{0.167\ M}$$

Q17. *K_p = 0.04 atm at 898 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4 atm pressure and allowed to come to equilibrium.*

$$C_2H_6(g) \rightleftharpoons C_2\,H_4(g) + H_2(g)$$

Ans. The equilibrium in the reaction is:

	$C_2H_6(g)$	$\rightleftharpoons$	$C_2H_4(g)$	$+ H_2(g)$
Initial pressure:	4 atm		0	0
Eqn. pressure:	$(4 - p)$ atm		p atm	p atm

$$K_p = \frac{p_{C_2H_4} \times p_{H_2}}{p_{C_2H_6}} \quad \text{or} \quad 0.04 = \frac{p^2}{(4-p)}$$

$$p^2 = 0.04\,(4 - p) \quad \text{or} \quad p^2 + 0.04\,p - 0.16 = 0$$

$$p = \frac{(-0.04) \pm \sqrt{0.0016 - 4\,(-0.16)}}{2}$$

$$= \frac{(-0.04) \pm 0.8}{2} = \frac{0.76}{2} = 0.38$$

Equilibrium pressure or concentration of C_2H_6 = (4 – 0.38) **= 3.62 atm.**

Q18. *The ester, ethyl acetate is formed by the reaction of ethanol and acetic acid and the equilibrium is represented as:*

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2\,O(l)$$

(*i*) *Write the concentration ratio (concentration quotient) Q for this reaction. Note that water is not in excess and is not a solvent in this reaction.*

(*ii*) *At 293 K, if one starts with 1.000 mol of acetic acid and 0.180 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.*

(*iii*) *Starting with 0.50 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after some time. Has equilibrium been reached?*

Ans. (*i*) The concentration ratio (Concentration quotient) Q_c for the reaction is:

$$Q_c = \frac{[CH_3COOC_2H_5(l)]\,[H_2O(l)]}{[CH_3COOH(l)]\,[C_2H_5OH(l)]}$$

(*ii*)

	$CH_3COOH(l)$	$+ C_2H_5OH(l)$	$\rightleftharpoons CH_3COOC_2H_5(l)$	$+ H_2O(l)$
Initial molar conc.	1.0 mol	0.18 mol	0	0
Molar conc. at equilibrium point	(1 – 0.171) = 0.829 mol	(0.18 – 0.171) = 0.009 mol	0.171 mol	0.171 mol

Applying Law of Chemical equilibrium,

$$K_c = \frac{[CH_3COOC_2H_5](l)[H_2O(l)]}{[CH_3COOH(l)][C_2H_5OH(l)]}$$

$$= \frac{(0.171\text{ mol}) \times (0.171\text{ mol})}{(0.829\text{ mol})\,(0.009\text{ mol})} = \mathbf{3.92}$$

(*iii*)

	$CH_3COOH(l)$	$+ C_2H_5OH(l)$	$\rightleftharpoons CH_3COOC_2H_5(l)$	$+ H_2O(l)$
Initial molar conc.	1.0 mol	0.5 mol	0.214 mol	0.214 mol
Molar conc. at equilibrium	1.0 – 0.214 = 0.786 mol	0.5 – 0.214 = 0.286 mol		

$$Q_c = \frac{[CH_3COOC_2H_5(l)]\,[H_2O(l)]}{[CH_3COOH(l)]\,[C_2H_5OH(l)]}$$

$$= \frac{(0.214\ \text{mol}) \times (0.214\ \text{mol})}{(0.786\ \text{mol})\,(0.286\ \text{mol})} = \mathbf{0.204}$$

Since Q_c is less than K_c, this means that the equilibrium has not been reached. The reactants are still taking part in the reaction to form the products.

Q19. *A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was reached, the concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?*

Ans. Let the initial molar concentration of PCl_5 per litre = x mol

Molar concentration of PCl_5 at equilibrium = 0.05 mol

∴ Moles of PCl_5 decomposed = $(x - 0.05)$ mol

Moles of PCl_3 formed = $(x - 0.05)$ mol

Moles of Cl_2 formed = $(x - 0.05)$ mol

The molar conc./litre of reactants and products before the reaction and at the equilibrium point are:

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial moles/litre	x		0		0
Moles/litre at eqm. point	0.05		$(x - 0.05)$		$(x - 0.05)$

Equilibrium constant (K_c) = 8.3×10^{-3} = 0.0083

Applying Law of chemical equilibrium,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}; \quad 0.0083 = \frac{(x - 0.05) \times (x - 0.05)}{0.05}$$

$$(x - 0.05)^2 = 0.0083 \times 0.05 = 4.15 \times 10^{-4}$$

$$(x - 0.05) = (4.15 \times 10^{-4})^{1/2} = 2.037 \times 10^{-2} = 0.02 \text{ moles}$$

$$x = 0.05 + 0.02 = 0.07 \text{ mol}$$

The molar concentration per litre of PCl_3 at eqm. = 0.07 – 0.05 = **0.02 mol**

The molar concentration per litre of Cl_2 at eqm. = 0.07 – 0.05 = **0.02 mol.**

Q20. *One of the reactions that takes place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2*

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)\ ;\ K_p = 0.265 \text{ atm at } 1050 \text{ K}$$

What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial pressures are:

$$p_{CO} = 1.4 \text{ atm and } p_{CO_2} = 0.80 \text{ atm?}$$

Ans.

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

Initial pressure: 1.4 atm 0.8 atm

$$Q_p = \frac{p_{CO_2}}{p_{CO}} = \frac{(0.8\ \text{atm})}{(1.4\ \text{atm})} = 0.571$$

Since $Q_p > K_p$ (0.265), this means that the reaction will move in the backward direction to attain the equilibrium. Therefore, partial pressure of CO_2 will decrease while that of CO will increase so that the equilibrium may be attained again. Let p atm be the decrease in the partial pressure of CO_2. Therefore, the partial pressure of CO will increase by the same magnitude *i.e.,* p atm.

$$p_{CO_2} = (0.8 - p) \text{ atm}; \ p_{CO}(g) = (1.4 + p) \text{ atm}$$

At equilibrium,
$$K_p = \frac{p_{CO_2}}{p_{CO}} = \frac{(0.8 - p)\ \text{atm}}{(1.4 + p)\ \text{atm}} = \frac{(0.8 - p)}{(1.4 + p)}$$

or $$0.265 = \frac{(0.8-p)}{(1.4+p)}$$

$$0.371 + 0.265\,p = 0.8 - p \quad \text{or} \quad 1.265\,p = 0.8 - 0.371 = 0.429$$

$$p = 0.429/1.265 = 0.339 \text{ atm}$$

$$(p_{\text{CO}})_{\text{eq}} = (1.4 + 0.339) = \mathbf{1.739\ atm}$$

$$(p_{\text{CO}_2})_{\text{eq}} = (0.8 - 0.339) = \mathbf{1.461\ atm}$$

Q21. *Equilibrium constant K_c for the reaction, $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ at 500 K is 0.061. At particular time, the anaylsis shows that the composition of the reaction mixture is: 3.0 mol L^{-1} of N_2 ; 2.0 mol L^{-1} of H_2; 0.50 mol L^{-1} of NH_3. Is the reaction at equilibrium? If not, in which direction does the reaction tend to proceed to reach the equilibrium?*

Ans. The given reaction is:

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

According to available data.

$$N_2 = [3.0]\,;\, H_2 = [2.0]\,;\, NH_3 = [0.50]$$

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{[0.50]^2}{[3.0][2.0]^3} = \frac{0.25}{24} = \mathbf{0.0104.}$$

Since the value of Q_c is less than that of K_c (0.061), the reaction is not in a state of equilibrium. It will proceed in the **forward direction** till Q_c becomes the same as K_c.

Q22. *Bromine monochloride (BrCl) decomposes into bromine and chlorine and reaches the equilibrium:*

$$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$$

The value of K_c is 32 at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration in the mixture at equilibrium?

Ans. Let x moles of BrCl decompose in order to attain the equilibrium. The initial molar concentration and the molar concentration at equilibrium point of different species may be represented as follows:

	$2BrCl\,(g)$	$\rightleftharpoons$ $Br_2(g)$	+ $Cl_2(g)$
Initial moles/litre	0.0033	0	0
Moles/litre at eqm. point	$0.0033 - x$	$x/2$	$x/2$

Applying Law of chemical equilibrium, $K_c = \dfrac{[Br_2][Cl_2]}{[BrCl]^2}$ or $32 = \dfrac{(x/2) \times (x/2)}{(0.0033 - x)^2}$

On taking the square root, $5.656 = \dfrac{x/2}{(0.0033 - x)}$

$$\frac{x}{(0.0033-x)} = 11.31 \quad \text{or} \quad 12.31x = 0.037 \quad ; \quad x = \frac{0.037}{12.31} = 0.003$$

$\therefore$ Molar concentration of BrCl at equilibrium point = 0.0033 − 0.003

= 0.0003 mol L^{-1} = $\mathbf{3 \times 10^{-4}\ mol\ L^{-1}}$.

Q23. *At 1127 K and 1 atmosphere pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass.*

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Calculate K_c for the reaction at the above temperature.

Ans. **Step I:** Calculation of K_p for the reaction

Let the total mass of the gaseous mixture = 100 g

$$\text{Mass of CO in the mixture} = 90.55 \text{ g}$$

$$\text{Mass of } CO_2 \text{ in the mixture} = (100 - 90.55) = 9.45 \text{ g}$$

$$\text{No. of moles of CO} = \frac{90.55\text{g}}{(28g \text{ mol}^{-1})} = 3.234 \text{ mol}$$

$$\text{No. of moles of } CO_2 = \frac{9.45}{(44g \text{ mol}^{-1})} = 0.215 \text{ mol}$$

$$p_{CO} \text{ in the mixture} = \frac{(3.234 \text{ mol})}{(3.234 + 0.215)} \times 1 \text{ atm} = \frac{(3.234 \text{ mol})}{(3.449 \text{ mol})} \times 1 \text{ atm} = 0.938 \text{ atm}$$

$$p_{CO_2} \text{ in the mixture} = \frac{(0.215 \text{ mol})}{(3.449 \text{ mol})} \times 1 \text{ atm} = 0.062 \text{ atm}$$

$$\begin{array}{lccc} & C(s) + CO_2(g) & \rightleftharpoons & 2CO(g) \\ \text{Eqm. pressure} & 0.062 \text{ atm} & & 0.938 \text{ atm} \end{array}$$

$$K_p = \frac{p^2CO}{pCO_2} = \frac{(0.938 \text{ atm})^2}{(0.062 \text{ atm})} = 14.19 \text{ atm}$$

Step II. Calculation of K_c for the reaction.

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

$K_p = 14.19$ atm, $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$, $T = 1127$ K ; $\Delta^{ng} = 2 - 1 = 1$

$$K_c = \frac{(14.19 \text{ atm})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (1127 \text{ K})^1} = \mathbf{6.46}$$

Q24. *Calculate (a) $\Delta G^\ominus$ and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K*

$NO(g) + 1/2\ O_2(g) \rightleftharpoons NO_2(g)$ where

$\Delta_f G^\ominus (NO_2) = 52.0$ kJ/mol, $\Delta_f G^\ominus (NO) = 87.0$ kJ/mol, $\Delta_f G^\ominus (O_2) = 0$ kJ/mol,

Ans. **Step I.** Calculation of $\Delta G^\ominus$

$$\begin{aligned} \Delta G^\ominus &= \Delta_f G^\ominus (NO_2) - [\Delta_f G^\ominus (1/2O_2)] \\ &= 52.0 - (87 + 0) = -35 \text{ kJ mol}^{-1} \end{aligned}$$

Step II. Calculation of K_c

$$\Delta G^\ominus = -2.303\ RT \log K_c$$

$$\log K_c = -\frac{\Delta G^\ominus}{2.303\ RT} = -\frac{(-35 \times 10^3 \text{ J mol}^{-1})^3}{2.303 \times (8.314 \text{ kJ mol}^{-1}) \times (298 \text{ K})} = 6.134$$

$$K_c = \text{Antilog } 6.314 = \mathbf{1.36 \times 10^6.}$$

Q25. *Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?*

(i) $PCl_5\ (g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(ii) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(iii) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Ans. (*i*) Pressure will increase in the forward reaction and **number of moles of products will increase.**

(*ii*) Pressure will increase in backward reaction and **number of moles of products will decrease.**

(*iii*) The change in pressure will have **no effect** on the equilibrium constant and there will be **no change in the number of moles.**

Q26. *Which of the following reactions will get affected by increase in pressure? Also mention whether the change will cause the reaction to go to the right or left direction.*

(*i*) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$

(*ii*) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(*iii*) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(*iv*) $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$

(*v*) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

(*vi*) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Ans. Only those reactions will be affected by increasing the pressure in which the number of moles of the gaseous reactants and products are different ($n_p \neq n_r$) (gaseous). With the exception of the reaction (1); all the reamaining five reactions will get affected by increasing the pressure. In general,

- The reaction will go to the left if $n_p > n_r$.
- The reaction will go to the right if $n_r > n_p$.

Keeping this in mind,

(*i*) Increase in pressure will **not affect equilibrium** because $n_p = n_r = 3$.

(*ii*) Increase in pressure will **favour backward reaction** because n_p (2) > n_r (1)

(*iii*) Increase in pressure will **favour backward reaction** because n_p (10) > n_r (9)

(*iv*) Increase in pressure will **favour forward reaction** because n_p (1) < n_r (2)

(*v*) Increase in pressure will **favour backward reaction** because n_p (2) > n_r (1)

(*vi*) Increase in pressure will **favour backward reaction** because n_p (1) > n_r (0).

Q27. *The equilibrium constant for the following reaction is 1.6 × 10⁵ at 1024 K.*

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

Ans. Step I. *Calculation of* K_p.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^0 \qquad (\because \Delta_n = 2 - 2 = \text{zero})$$

$$K_p = K_c = 1.6 \times 10^5.$$

Step II. *Calculation of partial pressure of gases*

	$2HBr(g)$	$\rightleftharpoons$	$H_2(g)$	+	$Br_2(g)$
Initial pressure	10 bar		zero		zero
Eqm. pressure	(10 – P) bar		P/2 bar		P/2 bar

$$K_p' = \frac{pH_2 \times pBr_2}{p^2HBr} \text{ or } \frac{1}{1.6 \times 10^5} = \frac{P/2 \times P/2}{(10 - P)^2} = \frac{P^2}{4(10 - P)^2}$$

On taking square root; $\dfrac{P^2}{4(10-P)^2} = \left(\dfrac{1}{1.6\times10^5}\right)^{1/2}$ or $\dfrac{2(10-P)}{P} = (1.6\times10^5)^{1/2}$

$$= 4 \times 10^2$$

$$20 - 2P = 4 \times 10^2\,P \quad \text{or} \quad P(4 \times 10^2 + 2) = 20$$

or $$P = \frac{20}{(400+2)} = \frac{20}{402} = 0.050 \text{ bar}$$

pH_2 = 0.025 bar; pBr_2 = **0.025 bar:** $pHBr$ = 10 – 0.05 = 9.95 bar ≈ 10.0 bar.

Q28. *Hydrogen gas is obtained from the natural gas by partial oxidation with steam as per following endothermic reaction:*

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Write the expression for K_p for the above reaction

How will the value of K_p and composition of equilibrium mixture be affected by:

(i) increasing the pressure. (ii) increasing the temperature, (iii) using a catalyst?

Ans. The expression for K_p for the reaction is:

$$K_p = \frac{(pCO)\times(pH_2)^3}{(pCH_4)\times(pH_2O)}$$

(*i*) By increasing the pressure, the number of moles per unit volume will increase. In order to decrease the same, the equilibrium gets shifted to the left or in the backward direction. As a result, more of reactants will be formed and the value of K_p **will decrease.**

(*ii*) If the temperature is increased, according to Le Chatelier's principle, the forward reaction will be favoured as it is endothermic. Therefore, the equilibrium gets shifted to the right and the value of K_p **will increase**.

(*iii*) The addition of catalyst will not change the equilibrium since it influences both the forward and the backward reactions to the same extent. But it will be attained more quickly.

Q29. *What is the effect of:*

(i) addition of H_2 *(ii) addition of CH_3OH*

(iii) removal of CO *(iv) removal of CH_3OH*

On the equilibrium $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

Ans. (*i*) Equilibrium will be shifted in the **forward direction.**

(*ii*) Equilibrium will be shifted in the **backward direction.**

(*iii*) Equilibrium will be shifted in the **backward direction.**

(*iv*) Equilibrium will be shifted in the **forward direction.**

Q30. *At 473 K, the equilibrium constant K_c for the decomposition of phosphorus pentachloride (PCl_5) is 8.3×10^{-3}. If decomposition proceeds as:*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)\ ;\ \Delta H = +\,124.0 \text{ kJ mol}^{-1},$$

(a) Write an expression for K_c for the reaction

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

(c) What would be the effect on K_c if

(i) More of PCl_5 is added *(ii) Temperature is increased.*

Ans. (*a*) The expression for $K_c = \dfrac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$

(*b*) For reverse reaction $(K_c') = \dfrac{PCl_5(g)}{[PCl_3(g)][Cl_2(g)]} = \dfrac{1}{8.3 \times 10^{-3}} = 120.48$

(*c*) (*i*) By adding more of PCl_5, value of K_c will remain constant because there is no change in temperature.

(*ii*) By increasing the temperature, the forward reaction will be favoured since it is endothermic in nature. Therefore, the value of equilibrium constant will increase.

Q31. *Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H_2. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction.*

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam so that $p_{CO} = p_{H_2O} = 4.0$ bar, what will be the partial pressure of H_2 at equilibrium? $K_p = 0.1$ at 400°C.

Ans. Let the partial pressure of hydrogen (H_2) at equilibrium point = p bar

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

	$CO(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
Initial pressure:	4.0 bar	4.0 bar	0	0
Eqm. pressure:	$(4-p)$bar	$(4-p)$ bar	p bar	p bar

$$K_p = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}} \quad \text{or} \quad 0.1 = \frac{(p \text{ bar}) \times (p \text{ bar})}{(4-p) \text{ bar} \times (4-p) \text{ bar}}$$

$$\frac{p^2}{(4-p)^2} = 0.1 \quad \text{or} \quad \frac{p}{(4-p)} = (0.1)^{1/2} = 0.316$$

$$p = 0.316\,(4-p) \quad \text{or} \quad p = 1.264 - 0.316\,p$$

$$1.316\,p = 1.264 \quad \text{or} \quad p = \frac{1.264}{1.316} = \mathbf{0.96 \text{ bar}}$$

Q32. *Predict which of the following will have appreciable concentration of reactants and products:*

(*a*) $Cl_2(g) \rightleftharpoons 2Cl(g)\ ;\ K_c = 5 \times 10^{-39}$

(*b*) $Cl_2(g) + 2NO\,(g) \rightleftharpoons 2NOCl\,(g)\ ;\ K_c = 3.7 \times 10^{8}$

(*c*) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl\,(g)\ ;\ K_c = 1.8.$

Ans. Following conclusions can be drawn from the values of K_c.

(*a*) Since the value of K_c is very small, this means that the molar concentration of the products is very small as compared to that of the reactants.

(*b*) Since the value of K_c is quite large, this means that the molar concentration of the products is very large as compared to that of the reactants.

(*c*) Since the value of K_c is 1.8, this means that both the products and reactants have **appreciable concentration.**

Q33. *The value of K_c for the reaction $3O_2(g) \rightleftharpoons 2O_3(g)$ is 2.0×10^{-50} at 25°C. If equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}, what is the concentration of O_3?*

Ans. $3O_2(g) \rightleftharpoons 2O_3(g)$

$$K_c = \frac{[O_3]^2}{[O_2]^3} \quad \text{or} \quad (2.0 \times 10^{-50}) = \frac{[O_3]^2}{(1.6 \times 10^{-2})^3}$$

or $[O_3]^2 = (2.0 \times 10^{-50}) \times (1.6 \times 10^{-2})^3$

$[O_3]^2 = 8.192 \times 10^{-56}$ or $[O_3] = (8.192 \times 10^{-56})^{1/2} = \mathbf{2.86 \times 10^{-28}\ M.}$

Q34. *The reaction $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of H_2 and 0.02 mol of H_2O and an unknown amount of CH_4 in the flask. Determine the concentration of CH_4 in the mixture. The equilibrium constant, K_c for the reaction at the given temperature is 3.90.*

Ans. $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

According to available data

$$K_c = \frac{[CH_4]\times[H_2O]}{[CO]\times[H_2]^3} \quad \text{or} \quad 3.90 = \frac{[CH_4]\times[0.02]}{[0.30]\times[0.1]^3}$$

$$[CH_4] = \frac{(3.9)\times(0.30)\times(0.001)}{(0.02)} = \mathbf{5.85 \times 10^{-2}\ M}$$

Q35. *What is meant by conjugate acid-base pair? Find the conjugate acid/base for the following species:*

HNO_2, CH^-, $HClO_4$, OH^-, CO_3^{2-}, S^{2-}.

Ans. An acid-base pair which differs by a proton only ($HA \rightleftharpoons A^- + H^+$) is known as conjugate acid-base pair.

Conjugate acid: HCN, H_2O, HCO_3^-, HS^-.

Conjugate base: NO_2^-, ClO_4^-, O_2^-.

Q36. *Which of the following are Lewis Acids?*

H_2O, BF_3, H^+ and NH_4^+,

Ans. BF_3, H^+, ions are Lewis acids.

Q37. *What will be the conjugate bases for the Bronsted acids? HF, H_2SO_4 and H_2CO_3?*

Ans. Conjugate bases: F^-, HSO_4^-, HCO_3^-.

Q38. *Write the conjugate acids for the following Bronsted bases:*

NH_2^-, NH_3 and $HCOO^-$

Ans. NH_3, NH_4^+ and HCOOH

Q39. *The species H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acid and base. For each case, give the corresponding conjugate acid and base.*

Ans.

Conjugate acid		**Species**		**Conjugate base**
H_2O^+		H_2O		OH^-
H_2CO_3	$\xleftarrow{+H^+}$	HCO_3^-	$\xrightarrow{-H^+}$	CO_3^{2-}
H_2SO_4		HSO_4^-		SO_4^{2-}
NH_4^+		NH_3		NH_2^-

Q40. *Classify the following species into Lewis acids and Lewis bases and show how these can act as Lewis acid/Lewis base?*

(a) OH^- ions (b) F^- (c) H^+ (d) BCl_3

Ans. (*a*) **OH^-** ions can donate an electron pair and act as **Lewis base.**

(*b*) **F^-** ions can donate an electron pair and act as **Lewis base.**

(*c*) **H^+** ions can accept an electron pair and act as **Lewis acid.**

(*d*) **BCl_3** can accept an electron pair since Boron atom is electron deficient. It is a Lewis acid.

Q41. *The concentration of hydrogen ions in a sample of soft drink is 3.8×10^{-3} M. What is the pH value?*

Ans. pH = – log [H^+] = – log (3.8×10^{-3}) = – log 3.8 + 3 = 3 – 0.5798 = 2.4202 **= 2.42**

Q42. *The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.*

Ans. pH = – log [H^+] or log [H^+] = – pH = – 3.76 = $\bar{4}.24$

$$\therefore \qquad [H^+] = \text{Antilog } \bar{4}.24 = 1.738 \times 10^{-4}\text{ M} = \mathbf{1.74 \times 10^{-4}\ M}$$

Q43. *The ionization constant of HF, HCOOH and HCN at 298 K are is 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively, Calculate the ionization constant of the corresponding conjugate base.*

Ans. For F^-, $K_b = K_w/K_a = 10^{-14}/(6.8 \times 10^{-4}) = 1.47 \times 10^{-11} \simeq \mathbf{1.5 \times 10^{-11}}$.

For $HCOO^-$, $K_b = 10^{-14}/(1.8 \times 10^{-4}) = \mathbf{5.6 \times 10^{-11}}$

For CN^-, $K_b = 10^{-14}/(4.8 \times 10^{-9}) = \mathbf{2.08 \times 10^{-6}}$

Q44. *The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?*

Ans.

$$\begin{array}{llll} & C_6H_5OH & \rightleftharpoons C_6H_5O^- & + H^+ \\ \text{Initial} & 0.05\text{ M} & & \\ \text{After disso.} & 0.05 - x & x & x \end{array}$$

$$\therefore \quad K_a = \frac{x \times x}{0.05 - x} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad \frac{x^2}{0.05} = 1.0 \times 10^{-10}$$

or $x^2 = 5 \times 10^{-12}$ or $x = \mathbf{2.2 \times 10^{-6}\ M}$

In presence of 0.01 C_6H_5ONa, suppose y is the amount of phenol dissociated, then at equilibrium

$$[C_6H_5OH] = 0.05 - y \simeq 0.05,$$
$$[C_6H_5O^-] = 0.01 + y \simeq 0.01\text{ M}, [H^+] = y\text{ M}$$

$$\therefore \qquad K_a = \frac{(0.01)(y)}{0.05} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad y = 5 \times 10^{-10}$$

$$\therefore \qquad \alpha = \frac{y}{c} = \frac{5 \times 10^{-10}}{5 \times 10^{-2}} = \mathbf{10^{-8}}.$$

Q45. *The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ions in its 0.1 M solution and how will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.*

Ans. To calculate [HS^-]

$$\begin{array}{llll} & H_2S & \rightleftharpoons H^+ & + \ HS^- \\ \text{Initial} & 0.1\text{ M} & & \\ \text{After disso.} & 0.1 - x & x & x \\ & \simeq 0.1 & & \end{array}$$

$$K_a = \frac{x \times x}{0.1} = 9.1 \times 10^{-8} \quad \text{or} \quad x^2 = 9.1 \times 10^{-9} \quad \text{or} \quad x = \mathbf{9.54 \times 10^{-5}}.$$

In presence of 0.1 M HCl, suppose H_2S dissociated is y. Then at equilibrium,
$[H_2S] = 0.1 - y \simeq 0.1$, $[H^+] = 0.1 + y \simeq 0.1$, $[HS^-] = y$ M

$K_a = \dfrac{0.1 \times y}{0.1} = 9.1 \times 10^{-8}$ (*Given*) or $y = \mathbf{9.1 \times 10^{-8}}$ **M**

To calculate $[S^{2-}]$

$$H_2S \overset{K_{a_1}}{\rightleftharpoons} H^+ + HS^- \quad ; \qquad HS^- \overset{K_{a_2}}{\rightleftharpoons} H^+ + S^{2-}$$

For the overall reaction,

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$K_a = K_{a_1} \times K_{a_2} = 9.1 \times 10^{-8} \times 1.2 \times 10^{-13} = 1.092 \times 10^{-20}$$

$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

In the absence of 0.1 MHCl, $[H^+] = 2\,[S^{2-}]$
Hence, if $[S^{2-}] = x$, $[H^+] = 2x$

$$\therefore \quad \frac{(2x)^2 x}{0.1} = 1.092 \times 10^{-20} \quad \text{or} \quad 4x^3 = 1.092 \times 10^{-21} = 273 \times 10^{-24}$$

$$3 \log x = \log 273 - 24 = 2.4362 - 24$$

$$\log x = 0.8127 - 8 = \bar{8}.8127,$$

$$\text{or} \quad x = \text{Antilog } \bar{8}.8127 = 273 \times 10^{-24} = 6.497 \times 10 = \mathbf{6.5 \times 10^{-8}\ M.}$$

In presence of 0.1 M HCl, suppose $[S^{2-}] = y$, then

$$[H_2S] = 0.1 - y \simeq 0.1 \text{ M}, \quad [H^+] = 0.1 + y \simeq 0.1 \text{ M}$$

$$K_a = \frac{(0.1)^2 \times y}{0.1} = 1.09 \times 10^{-20} \quad \text{or} \quad y = \mathbf{1.09 \times 10^{-19}\ M.}$$

Q46. *The ionization constant of acetic acid is 1.74 × 10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ions in the solution and its pH.*

Ans.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

$$\text{or} \quad [H^+] = \sqrt{K_a\,[CH_3COOH]} = \sqrt{(1.74 \times 10^{-5})\,(5 \times 10^{-2})} = 9.33 \times 10^{-4} \text{ M}$$

$$[CH_3COO^-] = [H^+] = \mathbf{9.33 \times 10^{-4}\ M}$$

$$\text{pH} = -\log (9.33 \times 10^{-4}) = 4 - 0.9699 = 4 - 0.97 = \mathbf{3.03}$$

Q47. *It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a.*

Ans.

$$HA \rightleftharpoons H^+$$

$$pH = -\log [H^+] \quad \text{or} \quad \log [H^+] = -4.15 = \bar{5}.85$$

$$\therefore \quad [H^+] = 7.08 \times 10^{-5} \text{ M} = 7.08 \times 10^{-5} \text{ M}$$

$$[A^-] = [H^+] = 7.08 \times 10^{-5} \text{ M}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(7.08 \times 10^{-5})\,(7.08 \times 10^{-5})}{10^{-2}} = \mathbf{5.0 \times 10^{-7}}$$

$$pK_a = -\log K_a = -\log (5.0 \times 10^{-7}) = 7 - 0.699 = \mathbf{6.301}$$

Q48. *Assuming complete dissociation, calculate the pH of the following solutions:*
(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

Ans. (*a*) $HCl + aq \rightarrow H^+ + Cl^-$, ∴ $[H^+] = [HCl] = 3 \times 10^{-3}$ M, pH = $-\log(3 \times 10^{-3}) = 2.52$

(*b*) $NaOH + aq \rightarrow Na^+ + OH^-$

$$\therefore \quad [OH^-] = 5 \times 10^{-3}\text{ M}, [H^+] = 10^{-14}/(5 \times 10^{-3}) = 2 \times 10^{-12}\text{ M}$$

$$\text{pH} = -\log(2 \times 10^{-12}) = \mathbf{11.70}$$

(*c*) $HBr + aq \rightarrow H^+ + Br^-$, ∴ $[H^+] = 2 \times 10^{-3}$ M, pH = $-\log(2 \times 10^{-3}) = 2.70$

(*d*) $KOH + aq \rightarrow K^+ + OH^-$,

$$\therefore \quad [OH^+] = 2 \times 10^{-3}\text{ M}, [H^+] = 10^{-14}/(2 \times 10^{-3}) = 5 \times 10^{-12}$$

$$\text{pH} = -\log(5 \times 10^{-12}) = \mathbf{11.30}$$

Q49. *Calculate the pH of the following solutions:*

(a) 2g of TlOH dissolved in water to give 2 litre of the solution

(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of the solution

(c) 0.3 g of NaOH dissolved in water to give 200 mL of the solution

(d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of the solution.

Ans. (*a*) Molar conc. of TlOH $= \dfrac{2g}{(204+16+1)\,g\text{ mol}^{-1}} \times \dfrac{1}{2\text{ L}} = 4.52 \times 10^{-3}$ M

$$[OH^-] = [TlOH] = 4.52 \times 10^{-3}\text{ M}$$

$$[H^+] = 10^{-14}/(4.52 \times 10^{-3}) = 2.21 \times 10^{-12}\text{ M}$$

$$\therefore \quad \text{pH} = -\log(2.21 \times 10^{-12}) = 12 - (0.3424) = 11.66$$

(*b*) Molar conc. of $Ca(OH)_2 = \dfrac{0.3\,g}{(40+34)g\text{ mol}^{-1}} \times \dfrac{1}{0.5\text{ L}} = 8.11 \times 10^{-3}$ M

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

$$[OH^-] = 2[Ca(OH)_2] = 2 \times (8.11 \times 10^{-3})\text{ M} = 16.22 \times 10^{-3}\text{ M}$$

$$\text{pOH} = -\log(16.22 \times 10^{-3}) = 3 - 1.2101 = 1.79$$

$$\text{pH} = 14 - 1.79 = \mathbf{12.21}$$

(*c*) Molar conc. of NaOH $= \dfrac{0.3\,g}{40\,g\text{ mol}^{-1}} \times \dfrac{1}{0.2\text{ L}} = 3.75 \times 10^{-2}$ M

$$[OH^-] = 3.75 \times 10^{-2}\text{ M}$$

$$\text{pOH} = -\log(3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$$

$$\text{pH} = 14 - 1.43 = \mathbf{12.57}$$

(*d*) $M_1V_1 = M_2V_2$ ∴ 13.6 M × 1m L = M_2 × 1000 mL ∴ $M_2 = 1.36 \times 10^{-2}$ M

$$[H^+] = [HCl] = 1.36 \times 10^{-2}\text{ M}, \text{pH} = -\log(1.36 \times 10^{-2}) = 2 - 0.1335 \simeq \mathbf{1.87}$$

Q50. *The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.*

Ans.

	$CH_2(Br)\ COOH$	$\rightleftharpoons$	$CH_2(Br)COO^-$	+	H^+
Initial conc.	C		0		0
Conc. at eqm.	C – Cα		C α		C α

$$K_a = \frac{C\alpha\,.\,C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$

$$pK_a = -\log(1.74 \times 10^{-3}) = 3 - 0.2405 = \mathbf{2.76}$$

$$[H^+] = C\,\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2}\text{ M}$$

$$\text{pH} = -\log(1.32 \times 10^{-2}) = 2 - 0.1206 = \mathbf{1.88}$$

Q51. *The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate the ionization constant and pK_b.*

Ans. $$\text{Cod} + H_2O \rightleftharpoons \text{Cod H}^+ + OH^-$$

$$\text{pH} = 9.95 \quad \therefore \text{pOH} = 14 - 9.95 = 4.05, \quad \textit{i.e.,}\ -\log[OH^-] = 4.05$$

or $$\log[OH^-] = -4.05 = \bar{5}.95 \quad \text{or} \quad [OH^-] = 8.913 \times 10^{-5}\ \text{M}$$

$$K_b = \frac{[\text{CodH}^+][OH^-]}{[\text{Cod}]} = \frac{[OH^-]^2}{[\text{Cod}]} = \frac{(8.91 \times 10^{-5})^2}{5 \times 10^{-3}} = \mathbf{1.588 \times 10^{-6}}$$

$$pK_b = -\log(1.588 \times 10^{-6}) = 6 - 0.1987 = \mathbf{5.8}$$

Q52. *What is the pH of 0.001 M aniline solution? The ionization constant of aniline is 4.27×10^{-10}. Calculate degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.*

Ans. (*i*) $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

$$K_a = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{[OH^-]^2}{[C_6H_5NH_2]}$$

$$[OH^-] = \sqrt{K_a[C_6H_5NH_2]} = \sqrt{(4.27 \times 10^{-10})(10^{-3})} = 6.534 \times 10^{-7}\ \text{M}$$

$$\text{pOH} = -\log(6.534 \times 10^{-7}) = 7 - 0.8152 = 6.18$$

$$\therefore \quad \text{pH} = 14 - 6.18 = \mathbf{7.82}$$

(*ii*) Also $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5\ NH_3^+ + OH^-$

Initial: C

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

$$K_b = \frac{C\alpha \,.\, C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2$$

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

(*iii*) $pK_a + pK_b = 14$ (for a pair of conjugate acid and base)

$$pK_b = -\log(4.27 \times 10^{-10}) = 10 - 0.62 = 9.38$$

$$\therefore \quad pK_a = 14 - 9.38 = 4.62$$

i.e., $$-\log K_a = 4.62 \quad \text{or} \quad \log K_a = -4.62 = \bar{5}.38$$

$$K_a = \text{Antilog}\ \bar{5}.38 = 2.399 \times 10^{-5} \simeq \mathbf{2.4 \times 10^{-5}}$$

Q53. *Calculate the degree of ionization of 0.05 M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01 M (b) 0.1 M HCl?*

Ans. $$pK_a = \textit{i.e.,}\ -\log K_a = 4.74$$

or $$\log K_a = -4.74 = \bar{5}.26 \quad \therefore K_a = 1.82 \times 10^{-5}$$

$$\alpha = \sqrt{K_a / C} = \sqrt{(1.82 \times 10^{-5}) / (5 \times 10^{-2})} = \mathbf{1.908 \times 10^{-2}}$$

In presence of HCl, due to high concentration of H^+ ion, dissociation equilibrium will shift backward, *i.e.,* dissociation of acetic acid will decrease.

(*a*) In presence of 0.01 MHCl, if x is the amount dissociated, then

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
Initial	0.05 M		
After disso.	$0.05 - x$ $\simeq 0.05$	x	$0.01 + x$ $\simeq 0.01$ M

(0.01 MH^+ ions are obtained from 0.01 MHCl)

$$\therefore \quad K_a = \frac{x(0.01)}{0.05} \quad \text{or} \quad \frac{x}{0.05} = \frac{K_a}{0.01} = \frac{1.82\times10^{-5}}{10^{-2}} = 1.82 \times 10^{-3}$$

$$\text{or} \quad \alpha = 1.82 \times 10^{-3} \quad \left(\because \alpha = \frac{\text{Amount dissociated}}{\text{Amount taken}}\right)$$

(*b*) In the presence of 0.1 M HCl, if y is the amount of acetic acid dissociated, then at equilibrium

$$[CH_3COOH] = 0.05 - y \simeq 0.05 \text{ M}$$
$$[CH_3COO^-] = y, [H^+] = 0.1 \text{ M} + y \simeq 0.1 \text{ M}$$

$$K_a = \frac{y\,(0.1)}{0.05} \quad \text{or} \quad \frac{y}{0.05} = \frac{K_a}{0.1} = \frac{1.82\times10^{-5}}{10^{-1}} = 1.82 \times 10^{-4}, \textit{ i.e.,}$$

$$\alpha = \mathbf{1.82 \times 10^{-4}}$$

Q54. *The ionization constant of dimethylamine is 5.4 × 10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M in NaOH?*

Ans. $(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2\, NH^+\, OH + OH^-$

	$(CH_3)_2NH$		
Initial	0.02 M		
After disso.	$0.02 - x$ $\simeq 0.02$	x	$0.1 + x$ $\simeq 0.1$

$$\therefore \quad K_a = \frac{x(0.1)}{0.02} \quad \text{or} \quad \frac{x}{0.02} = \frac{K_a}{0.1} = \frac{5.4\times10^{-4}}{10^{-1}} = 5.4 \times 10^{-3}$$

i.e., $\alpha = 5.4 \times 10^{-3}$ ∴ % ionized = **0.54.**

Q55. *Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:*

(a) Human muscle-fluid, 6.83 *(b) Human stomach fluid, 1.2*

(c) Human blood, 7.38 *(b) Human saliva, 6.4*

Ans. (*a*) $\log [H^+] = -pH = -6.83 = \bar{7}.17$ ∴ $[H^+] = \text{Antilog } \bar{7}.17 = 1.479 \times 10^{-7}$ M

(*b*) $\log [H^+] = -pH = -1.2 = \bar{2}.8$ ∴ $[H^+] = \text{Antilog } \bar{2}.8 = 6.31 \times 10^{-2}$ M

(*c*) $\log [H^+] = -pH = -7.38 = \bar{8}.62$ ∴ $[H^+] = \text{Antilog } \bar{8}.62 = 4.169 \times 10^{-8}$ M

(*d*) $\log [H^+] = -pH = -6.4 = \bar{7}.60$ ∴ $[H^+] = \text{Antilog } \bar{7}.60 = 3.981 \times 10^{-7}$ M

Q56. *The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.*

Ans. Similar to Q7.55 [**Ans.** 1.5 × 10^{-7} M, 10^{-5} M, 6.31 × 10^{-5} M, 6.31 × 10^{-3} M, 1.58 × 10^{-8}M]

Q57. *If 0.561 g KOH is dissolved in water to give 200 mL of solution at 298 K, calculate the concentration of potassium, hydrogen and hydroxyl ions. What is its pH?*

Ans.
$$[KOH] = \frac{0.561}{56} \times \frac{1000}{200} \text{ M} = 0.050 \text{ M}$$

As $KOH \rightarrow K^+ + OH^-$, ∴ $[K^+] = [OH^-]$ **= 0.05 M**

$$[H^+] = K_w/[OH^-] = 10^{-14}/0.05 = 10^{-14}/(5 \times 10^{-2}) = \mathbf{2.0 \times 10^{-13}\ M.}$$
$$pH = -\log [H^+] = -\log (2.0 \times 10^{-13}) = 13 - 0.3010 = \mathbf{12.699}$$

Q58. *The solubility of Sr $(OH)_2$ at 298 K is 19.23g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution. (Atomic mass of Sr = 87.6)*

Ans. Molar mass of $Sr(OH)_2 = 87.6 + 34 = 121.6 \text{ g mol}^{-1}$

Solubility of $Sr(OH)_2$ in moles $L^{-1} = \dfrac{19.23 g\ L^{-1}}{121.6\ g\ mol^{-1}} = 0.1581$ M

Assuming complete dissociation, $Sr(OH)_2 \rightarrow Sr^{2+} + 2OH^-$

$$\therefore \quad [Sr^{2+}] = \mathbf{0.1581\ M},\ [OH^-] = 2 \times 0.1581 = \mathbf{0.3162\ M}$$

$$pOH = -\log 0.3162 = 0.5, \quad \therefore\ pH = 14 - 0.5 = \mathbf{13.5}$$

Q59. *The ionization constant of propanoic acid is 1.32 × 10^{-5}. Calculate the degree of ionization of the acid in its 0.05 M solution and also its pH. What will be its degree of ionization if the solution is 0.01 M HCl also?*

Ans. Assuming α to be very small, applying the formula

$$\alpha = \sqrt{K_a / C}$$

$$= \sqrt{1.32 \times 10^{-5} / 0.05} = 1.62 \times 10^{-2}$$

$$CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$$

In pressure of HCl, equilibrium will shift in the backward direction, *i.e.,* the amount of dissociation will be less.

If C is the initial concentration, x is the amount now dissociated, then at equilibrium,

$$[CH_3CH_2COOH] = C - x$$

$$[CH_3CH_2COO^-] = x[H^+] = 0.01 + x$$

$$K_a = \frac{x(0.01 + x)}{C - x} = \frac{x(0.01)}{C}$$

or
$$\frac{x}{C} = \frac{K_a}{0.01} = \frac{1.32 \times 10^{-5}}{10^{-2}}$$

$$= 1.32 \times 10^{-3}$$

$$\alpha = 1.32 \times 10^{-3}$$

Q60. *The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.*

Ans.
$$HCNO \rightleftharpoons H^+ + CNO^-$$

$$pH = 2.34 \text{ means } -\log [H^+] = 2.34 \text{ or } \log [H^+] = -2.34 = 3.86$$

or
$$[H^+] = \text{Antilog } \bar{3}.86 = 4.57 \times 10^{-3}\ M$$

$$[CNO^-] = [H^+] = 4.57 \times 10^{-3}\ M$$

$$K_a = \frac{(4.57 \times 10^{-3})(4.57 \times 10^{-3})}{0.1} = \mathbf{2.09 \times 10^{-4}}$$

$$\alpha = \sqrt{K_a / C} = \sqrt{2.09 \times 10^{-4} / 0.1} = \mathbf{0.0457.}$$

Q61. *The ionization constant of nitrous acid is 4.5 × 10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.*

Ans. Sodium nitrite is a salt of weak acid, strong base. Hence,

$$K_h = 2.22 \times 10^{-11}\ K_w/K_a = 10^{-14}/(4.5 \times 10^{-4})$$

$$h = \sqrt{K_h / c} = \sqrt{2.22 \times 10^{-11} / 0.04} = \sqrt{5.5 \times 10^{-11}} = 2.36 \times 10^{-5}$$

	NO_2^-	+	H_2O	$\rightleftharpoons$	HNO_2	+	OH^-
Initial	c						
After hydrolysis	$c - ch$				ch		ch

$$[OH^-] = ch = 0.04 \times 2.36 \times 10^{-5} = 9.44 \times 10^{-7}$$

$$pOH = -\log(9.44\times10^{-7}) = 7 - 0.9750 = 6.03$$
$$pH = 14 - pOH = 14 - 6.03 = \mathbf{7.97.}$$

Q62. *A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.*

Ans. pH = 3.44, *i.e.,* $\log[H^+] = -3.44 = \bar{4}.56$ $\therefore$ $[H^+] = 3.63\times10^{-4}$ M

$$C_5H_5\overset{+}{N}HCl^- + aq \rightleftharpoons C_5H_5\overset{+}{N}Cl^- + H^+$$

$$K_a = \frac{[C_5H_5\overset{+}{N}Cl^-][H^+]}{[C_5H_5\overset{+}{N}HCl^-]} = \frac{(3.63\times10^{-4})(3.63\times10^{-4})}{2\times10^{-2}}$$
$$= 6.588\times10^{-6}$$
$$pK_a = -\log(6.588\times10^{-6}) = 6 - 0.8187 = 5.18$$
$$pK_a + pK_b = 14 \quad \therefore \quad pK_b = 14 - 5.18 = 8.82$$
$$-\log K_b = 8.82 \quad \text{or} \quad \log K_b = -8.82 = \bar{9}.18 \quad \therefore \quad \mathbf{K_b = 1.514\times10^{-9}}$$

Alternatively, Pyridine hydrochloride is a salt to weak base and strong acid. Hence,

$$pH = -\frac{1}{2}[\log K_w - \log K_b + \log c], \textit{ i.e., } 3.44 = -\frac{1}{2}[-14 - \log K_b + \log(2\times10^{-2})]$$

or $6.88 = 14 + \log K_b + 1.70$ or $\log K_b = -8.83 = \bar{9}.18$ or $\mathbf{K_b = 1.5\times10^{-9}.}$

Q63. *Predict the acidic, basic or neutral nature of the solutions of the following salts:*
NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$, KF.

Ans. NaCN, $NaNO_2$, KF solutions are basic, as they are salts of strong base, weak acid.
NaCl, KBr solutions are neutral, as they are salts of strong acid, strong base.
NH_4NO_3 solution is acidic, as it is a salt of strong acid, weak base.

Q64. *The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1 M acid and its 0.1 M sodium salt solution?*

Ans. $$ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+$$

$$K_a = \frac{[ClCH_2COO^-][H^+]}{[ClCH_2COOH]} = \frac{[H^+]^2}{C}$$

$$[H^+] = \sqrt{K_a\times c} = \sqrt{1.35\times10^{-3}\times0.1} = 1.16\times10^{-2}\text{ M}$$
$$pH = -\log(1.16\times10^{-2}) = 2 - 0.06 = \mathbf{1.94}$$

Sodium salt of chloroacetic acid is a salt of strong base and weak acid. Hence,

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log c]$$
$$\therefore \quad pH = -\frac{1}{2}[\log 10^{-14} + \log 1.35\times10^{-3} - \log 0.1]$$
$$= -\frac{1}{2}[-14 + (-3 + 0.1303) - (-1)] = 7 + 1.44 - 0.5 = \mathbf{7.94}$$

Q65. *Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?*

Ans. $$[H^+] = \sqrt{K_w} = \sqrt{2.7\times10^{-14}} = 1.643\times10^{-7}\text{ M}$$
$$pH = -\log[H^+] = -\log(1.643\times10^{-7}) = 7 - 0.2156 = \mathbf{6.78}$$

Q66. *Calculate the pH of the resultant mixtures*

(a) 10 mL of 0.2 M Ca $(OH)_2$ *+ 25 mL of 0.1 M HCl*

(b) 10 mL of 0.01 M H_2SO_4 *+ 10 mL of 0.01 M Ca* $(OH)_2$

(c) 10 mL of 0.1 M H_2SO_4 *+ 10 mL of 0.1 M KOH*

Ans. (*a*) 10 mL of 0.2 M Ca (OH_2) = 10 × 0.2 millimoles = 2 millimoles of Ca $(OH)_2$

25 mL of 0.1 M HCl = 25 × 0.1 millimoles = 2.5 millimoles of HCl

$$Ca(OH)_2 + 2\,HCl \rightarrow CaCl_2 + 2H_2O$$

0.1 millimole of Ca $(OH)_2$ reacts with 2 millimoles of HCl

∴ 2.5 millimole of HCl will react with 1.25 millimoles of Ca $(OH)_2$

∴ $Ca(OH)_2$ left = 2 – 1.25 = 0.75 millimoles (HCl is the limiting reactant)

Total volume of the solution = 10 + 25 mL = 35 mL

∴ Molarity of $Ca(OH)_2$ in the mixture solution = $\dfrac{0.75}{35}$ M = 0.0214 M

∴ $[OH^-] = 2 \times 0.0214 \text{ M} = 0.0428 \text{ M} = 4.28 \times 10^{-2}$

$pOH = -\log(4.28 \times 10^{-2}) = 2 - 0.6314 = 1.3686 \simeq 1.37$

∴ $pH = 14 - 1.37 =$ **12.63**

(*b*) 10 mL of 0.01 M H_2SO_4 = 10 × 0.01 millimole = 0.1 millimole

10 mL of 0.01 M $Ca(OH)_2$ = 10 × 0.01 millimole = 0.1 millimole

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

1 mole of $Ca(OH)_2$ reacts with 1 mole of H_2SO_4

∴ 0.1 millimole of $Ca(OH)_2$ will react completely with 0.1 millimole of H_2SO_4.

Hence, solution will be neutral with pH = **7.0**

(*c*) 10 mL of 0.1 M H_2SO_4 = 1 millimole

10 mL of 0.1 M KOH = 1 millimole

$$2\,KOH + H_2SO_4 \rightarrow K_2SO_4 + 2\,H_2O$$

1 millimole of KOH will react with 0.5 millimole of H_2SO_4

∴ H_2SO_4 left = 1 – 0.5 = 0.5 millimole

Volume of reaction mixture = 10 + 10 = 20 mL

∴ Molarity of H_2SO_4 in the mixture solution = $\dfrac{0.5}{20} = 2.5 \times 10^{-2}$ M

$[H^+] = 2 \times 2.5 \times 10^{-2} = 5 \times 10^{-2}$

$pH = -\log(5 \times 10^{-2}) = 2 - 0.699 = 1.3$

Q67. *Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide 298 K. Given* K_{sp} *values:*

$Ag_2CrO_4 = 1.1 \times 10^{-12}$, $BaCrO_4 = 1.2 \times 10^{-10}$, $Fe(OH)_3 = 1.0 \times 10^{-38}$, $PbCl_2 = 1.6 \times 10^{-5}$, $Hg_2I_2 = 4.5 \times 10^{-29}$

Determine also the molarities of individual ions.

Ans. $\underset{s}{Ag_2CrO_4} \rightleftharpoons 2\,\underset{2s}{Ag^+} + \underset{s}{CrO_4^{2-}}$; $K_{sp} = (2\,s)^2\,(s) = 4\,s^3$, ∴ $s^3 = K_{sp}/4$

$= (1.1 \times 10^{-12})/\,4 = 0.275 \times 10^{-12} = 2.75 \times 10^{-13}$

∴ $3 \log s = \log(2.75 \times 10^{-13}) = -13 + 0.4393 = -12.5607$

or $\log s = -4.1869 = \bar{5}.8131$ ∴ $s = 6.5 \times 10^{-5}$ mol L^{-1}

$[Ag^+] = 2 \times 6.5 \times 10^{-5} = 13.0 \times 10^{-5} \text{ M} = 1.30 \times 10^{-4}$ M

$[CrO_4^{2-}] = 6.5 \times 10^{-5}$ M

For other salts, proceed exactly in similar manner.

[**Ans.** S[$BaCrO_4$] = 1.1×10^{-5} M = [Ba^{2+}] = [CrO_4^{2-}]
S ($Fe(OH)_3$)= 1.39×10^{-10} M = [Fe^{3+}], [OH^-] = 3 × 1.39 × 10^{-10} M = 4.17 × 10^{-10} M
S ($PbCl_2$) = 1.59×10^{-2} M = [Pb^{2+}], [Cl^-] = 2 × 1.59 × 10^{-2} M = 3.18 × 10^{-2} M
S (Hg_2I_2) = 2.24×10^{-10} M = [Mg_2^{2+}], [I^-] = 2 × 2.24 × 10^{-10} M = 4.48 × 10^{-10} M]

Q68. *The solubility product constants of Ag_2CrO_4 and AgBr are 1.1 × 10^{-12} and 5.0 × 10^{-13} respectively. Calculate the ratio of molarities of their saturated solutions.*

Ans. Calculate their solubilities separately and then calculate the ratio.

$$\left[\textbf{Ans.}\ \frac{S(Ag_2CrO_4)}{S\,(AgBr)} = \frac{6.5\times10^{-5}\,M}{7.07\times10^{-7}} = 91.9\right]$$

Q69. *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, $K_{sp} = 7.4 \times 10^{-8}$.*

Ans. $2\,NaIO_3 + CuCrO_4 \rightarrow Na_2\,CrO_4 + Cu\,(IO_3)_2$

After mixing, $$[NaIO_3] = [IO_3^-] = \frac{2\times10^{-3}}{2} = 10^{-3}\,M$$

$$[CuCrO_4] = [Cu^{2+}] = \frac{2\times10^{-3}}{2} = 10^{-3}\,M$$

Ionic product of $Cu(IO_3)_2 = [Cu^{2+}]\,[IO_3^-]^2 = (10^{-3})\,(10^{-3})^2 = 10^{-9}$
As ionic product is less than K_{sp}, no precipitation will occur.

Q70. *The ionization constant of benzoic acid is 6.46 × 10^{-5} and K_{sp} for silver benzoate is 2.5 × 10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?*

Ans. $C_6H_5COOAg \rightarrow C_6H_5COO^- + Ag^+$

Solubility in water. Suppose solubility in water = x mol; L^{-1}. Then

$$[C_6H_5COO^-] = [Ag^+] = x \text{ mol } L^{-1}.$$

$$\therefore \quad x^2 = K_{sp} \quad \text{or} \quad x = \sqrt{K_{sp}} = \sqrt{2.5\times10^{-13}}$$
$$= 5 \times 10^{-7} \text{ mol } L^{-7}$$

Solubility in buffer of pH = 3.19

$$\text{pH} = 3.19 \text{ means } \quad -\log\,[H^+] = 3.19$$
$$\text{or} \quad \log\,[H^+] = -3.19 = \bar{4}.81 \quad \text{or} \quad [H^+] = 6.457 \times 10^{-4}\,M$$

$C_6H_5COO^-$ ions now combine with the H^+ ions to form benzoic acid but [H^+] remains almost constant because we have buffer solution. Now

$$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$$

$$\therefore K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]} \text{ or } \frac{[C_6H_5COOH]}{[C_6H_5COO^-]} = \frac{[H^+]}{K_a} = \frac{6.457\times10^{-4}}{6.46\times10^{-5}} = 10 \qquad ...(i)$$

Suppose solubility in the buffer solution is y mol L^{-1}. Then as most of the benzoate ions are converted into benzoic acid molecules (which remain almost ionized), we have

$$y = [Ag^+] = [C_6H_5COO^-] + [C_6H_5COOH] = [C_6H_5COO^-] + 10\,[C_6H_5COO^-]$$
$$= 11[C_6H_5COO^-] \qquad \text{(using eqn.}(i)\text{)}$$

$$\therefore [C_6H_5COO^-] = \frac{y}{11} \qquad \therefore K_{sp} = [C_6H_5COO^-]\,[Ag^+]$$

i.e., $2.5 \times 10^{-13} = \frac{y}{11} \times y$ or $y^2 = 2.75 \times 10^{-12}$ or $y = 1.66 \times 10^{-6}$

$$\therefore \qquad \frac{y}{x} = \frac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = \mathbf{3.32.}$$

Note that in case of salts of weak acids, the solubility is more in the acidic solution than in water. The reason, in general, may be explained as follows:
Taking example of C_6H_5COOAg, we have

$$C_6H_5COOAg \rightleftharpoons C_6H_5COO^- + Ag^+$$

In acidic solution, the anions ($C_6H_5COO^-$ in the present case) undergo protonation in presence of acid. Thus, $C_6H_5COO^-$ ions are removed. Hence, equilibrium shifts forward producing more Ag^+ ions. Alternatively, as $C_6H_5COO^-$ ions are removed, Q_{sp} decreases. In order to maintain solubility product equilibrium ($Q_{sp} = K_{sp}$), Ag^+ ion concentration must increase. Hence, solubility is more.

Q71. *What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide,* $K_{sp} = 6.3 \times 10^{-18}$*.)*

Ans. Suppose the concentration of each of $FeSO_4$ and Na_2S is x mol L^{-1}. Then after mixing equal volumes,

$$[FeSO_4] = [Na_2S] = \frac{x}{2}\text{M}, \quad \textit{i.e.,} \quad [Fe^{2+}] = [S^{2-}] = \frac{x}{2}\text{M},$$

$$K_{sp} \text{ for } \quad FeS = [Fe^{2+}]\,[S^{2-}], \quad \textit{i.e.,} \quad 6.3 \times 10^{-18} = \frac{x}{2} \times \frac{x}{2}$$

$$\text{or} \quad x^2 = 25.2 \times 10^{-18}, \quad \text{or} \quad x = \mathbf{5.02 \times 10^{-9}\ M.}$$

Q72. *What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K. For calcium sulphate,* $K_{sp} = 9.1 \times 10^{-6}$*.*

Ans. $CaSO_4(s) \rightleftharpoons Ca^2\,(aq) + SO_4^{2-}\,(aq)$

If s is the solubility of $CaSO_4$ in moles L^{-1}, then $K_{sp} = [Ca^{2+}] \times [SO_4^{2-}] = s^2$

$$\text{or} \quad s = \sqrt{K_{sp}} = \sqrt{9.1 \times 10^{-6}} = 3.02 \times 10^{-3} \text{ mol L}^{-1}$$

$$= 3.02 \times 10^{-3} \times 136 \text{ g L}^{-1} = 0.411 \text{ gL}^{-1}$$

(Molar mass of $CaSO_4$ = 136 g mol^{-1})

Thus, for dissolving 0.411 g, water required = 1L

$$\therefore \text{ For dissolving 1g, water required} = \frac{1}{0.411}\text{ L} = \mathbf{2.43\ L}$$

Q73. *The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is* 1.0×10^{-19} *M. If 10 mL of this solution is added to 5 mL of 0.04 M solution of* $FeSO_4$*,* $MnCl_2$*,* $ZnCl_2$ *and* $CdCl_2$*, in which of these solutions precipitation will take place? Given* K_{sp} *for FeS =* 6.3×10^{-18}*, MnS =* 2.5×10^{-13}*, ZnS =* 1.6×10^{-24} *and CdS =* 8.0×10^{-27}*.*

Ans. Precipitation will take place in the solution for which ionic product is greater than solubility product. As 10 mL of solution containing S^{2-} ion is mixed with 5 mL of metal salt solution, after mixing.

$$[S^{2-}] = 1.0 \times 10^{-19} \times \frac{10}{15} = 6.67 \times 10^{-20},$$

$$[Fe^{2+}] = [Mn^{2+}] = [Zn^{2+}] = [Cd^{2+}] = \frac{5}{15} \times 0.04 = 1.33 \times 10^{-2}\text{ M}$$

MORE QUESTIONS SOLVED

I. VERY SHORT ANSWER TYPE QUESTIONS

Q1. *What is meant by equilibrium?*

Ans. Equilibrium is a state at which rate of forward reaction is equal to the rate of backward reaction.

Q2. *State the law of mass action?*

Ans. It states that the rate at which a substance reacts is directly proportional to its molar concentration.

Q3. *What is meant by reaction quotient?*

Ans. It is defined as the ratio of product of molar concentration of products to the product of molar concentration of reactants at any stage of reaction.

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

For the reaction

$$aA + bB \rightleftharpoons cC + dD$$

Q4. *Define ionic equilibrium.*

Ans. The equilibrium between ions and unionised molecules is called ionic equilibrium.

Q5. *What is meant by ionic product of water (k_w)?*

Ans. It is the product of concentration of $[H_3O^+]$ and $[OH^-]$ at a specific temperature.

$$\begin{aligned} K_w &= [H_3O^+]\,[OH^-] \\ &= 1.0 \times 10^{-14} \text{ at } 298 \text{ K} \end{aligned}$$

Q6. *Define solubility product.*

Ans. It is product of molar concentration of ion raised to the power of number of ions produced per compound in saturated solution.

Q7. *How does common ion affect the solubility of electrolyte?*

Ans. Solubility of electrolyte decreases due to common ion effect.

Q8. *Write conjugate acid and conjugate base of H_2O?*

Ans. Conjugate acid is H_3O^+ and conjugate base is OH^-.

Q9. *Give two characteristics of a buffer solution.*

Ans. (*i*) Its pH does not change on the addition of small amount of acid or base.

(*ii*) Its pH does not change on dilution or standing.

Q10. *How does a catalyst affect the equilibrium constant?*

Ans. The equilibrium constant is not affected by a catalyst.

Q11. *State Ostwald's dilution law.*

Ans. Ostwald's dilution law states that the degree of dissociation of weak electrolyte is inversely proportional to square root of its concentration.

$$\alpha = \sqrt{\frac{K_a}{C}}, \alpha = \sqrt{\frac{K_b}{C}}$$

Where, K_a and K_b are acid dissociation and base dissociation constants.

Q12. *What is basic buffer?*

Ans. Basic buffer is the buffer whose pH is more than 7. It is a mixture containing weak base and its salt with a strong acid. *e.g.*, $NH_4Cl + NH_4OH$

Q13. *SO_3^{2-} is Bronsted base or acid and why?*

Ans. SO_3^{2-} is Bronsted base because it can accept H^+.

Q14. $H_2\ (g) + I_2(g) \rightleftharpoons 2HI\ (g)$

What is the relationship between K_p and K_c?

Ans. $K_p = K_c$

because $\Delta n = 0$.

Q15. *Define common ion effect.*

Ans. The supervision in concentration of one of the ions by adding other ion as common ion is called common ion effect.

II. SHORT ANSWER TYPE QUESTIONS

Q1. *The following concentration were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500 K.*

$$[N_2\ (g)] = 1.5 \times 10^{-2}\ M$$
$$[H_2\ (g)] = 3.0 \times 10^{-2}\ M$$
$$[NH_3] = 1.2 \times 10^{-2}\ M.$$

Calculate equilibrium constant.

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

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

$$= \frac{[1.2 \times 10^{-2} M]^2}{[1.5 \times 10^{-2} M][3.0 \times 10^{-2} M]^3}$$

$$= \mathbf{3.55 \times 10^{-2}\ M}$$

Q2. *Write the equilibrium constant (K_c) expression for the following reactions.*

(i) $Cu^{2+}(aq) + 2\ Ag\ (s) \rightleftharpoons Cu(s) + 2Ag^{+}\ (aq)$

(ii) $4HCl\ (g) + O_2(g) \rightleftharpoons 2Cl_2\ (g) + 2H_2O(g)$

Ans. (i) $$K_c = \frac{\left[Ag^{+}(aq)\right]^2}{\left[Cu^{2+}(aq)\right]}$$

(ii) $$K_c = \frac{[Cl_2(g)]^2\,[H_2O(g)]^2}{[HCl(g)]^4\,[O_2(g)]}$$

Q3. *Given the equilibrium*

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \text{ with}$$
$$K_p = 0.15 \text{ atm at } 298\ K$$

(a) *What is K_p using pressure in torr?*

(b) *What is K_c using units of moles per litre.*

Ans. (a) $$K_p = \frac{(760 \text{ torr}) \times (0.15 \text{ atm})}{(1 \text{ atm})}$$

$$= \mathbf{1.14 \times 10^{2}\ torr}$$

(*b*)

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

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

$$= \frac{(0.15\text{ atm})}{\left(0.0821\text{ L atm K}^{-1}\text{ mol}^{-1} \times 298\text{ K}\right)^{2-1}}$$

$$= \mathbf{6.13 \times 10^{-3}\ mol\ L^{-1}}$$

Q4. *(a) In the reaction* $A + B \rightleftharpoons C + D$, *what will happen to the equilibrium if concentration of A is increased?*

(b) The equilibrium constant for a reaction is 2×10^{-23} *at 25°C and* 2×10^{-2} *at 50°C. Is the reaction endothermic or exothermic?*

(c) Mention at least three ways by which the concentration of SO_3 *can be increased in the following reaction in a state of equilibrium.*

Ans. (*a*) The reaction will shift in the forward direction.

(*b*) Endothermic

(*c*) (*i*) lowering the temperature

(*ii*) increasing pressure.

(*iii*) increasing concentration of oxygen.

Q5. *(i) Define Le Chatelier's principle.*

(ii) Following reactions occur in a Blast furnace.

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g)$$

use Le chatelier's principle to predict the direction of reaction when equilibrium mixture is disturbed by

(a) adding Fe_2O_3 *(b) removing* CO_2.

(c) removing CO.

Ans. (*i*) When a system under equilibrium is subjected to a change in temperature, pressure or concentration, then the equilibrium shifts in such a direction so as to undo the effect of the change.

(*ii*) (*a*) On adding $Fe_2O_3(s)$, the equilibrium will remain unaffected.

(*b*) By removing $CO_2(g)$, the equilibrium will be shifted in the forward direction.

(*c*) By removing CO(g), the equilibrium will be shifted in the backward direction.

III. LONG ANSWER TYPE QUESTIONS

Q1. *(i) Point out the differences between ionic product and solubility product.*

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

Ans. (*i*)

Ionic Product	*Solubility Product*
(*a*) It is applicable to all types of solutions. (*b*) Its value changes with the change in concentration of the ions.	(*a*) It is applicable to the saturated solutions. (*b*) It has a definite value for an electrolyte at a constant temperature.

(*ii*) The solubility equilibrium in the saturated solution is

$$\text{AgCl}\,(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

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

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

Q2. *At certain temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated at temperature remaining constant.*

Ans. Calculation of K_p

$$\begin{array}{ccccc}
\mathrm{PCl_5(g)} & \rightleftharpoons & \mathrm{PCl_3(g)} & + & \mathrm{Cl_2\ (g)} \\
1 & & 0 & & 0 \\
(1-\alpha) & & \alpha & & \alpha
\end{array}$$

Total no. of moles in the equilibrium mixture $= 1 - \alpha + \alpha + \alpha$

$= (1 + \alpha)$ mol.

Let the total pressure of equilibrium mixture = p atm

Partial pressure of PCl_5

$$p_{\mathrm{PCl_5}} = \frac{1-\alpha}{1+\alpha} \times p \text{ atm}$$

Partial pressure of $PCl_3 = \dfrac{\alpha}{1+\alpha} \times p$ atm

Partial pressure of Cl_2

$$p_{\mathrm{Cl_2}} = \frac{\alpha}{(1+\alpha)} \times p \text{ atm}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_s}}$$

$$= \frac{\left(\dfrac{\alpha}{1+\alpha} p \text{ atm}\right) \times \left(\dfrac{\alpha}{1+\alpha} p \text{ atm}\right)}{\dfrac{1-\alpha}{1+\alpha} p \text{ atm}} = \frac{\alpha^2 p}{1-\alpha^2} \text{ atm}$$

$$P = 4 \text{ atm and } \alpha = 10\% = \frac{10}{100} = 0.1$$

$$K_p = \frac{(0.1) \times (0.1) \times (4 \text{ atm})}{1 - (0.1)^2}$$

$$= \frac{0.04}{0.99} = 0.04 \text{ atm.}$$

Calculation of P under new condition

$$\alpha = 0.2,\ K_p = 0.04 \text{ atm}$$

$$K_p = \frac{\alpha^2 p}{1-\alpha^2} \text{ or } p = \frac{K_p(1-\alpha^2)}{\alpha^2}$$

$$= \frac{(0.04 \text{ atm})[(1-(0.2)^2]}{(0.2)^2} = \frac{0.04 \text{ atm} \times 0.96}{0.04}$$

$$= \mathbf{0.96 \text{ atm.}}$$

IV. MULTIPLE CHOICE QUESTIONS

1. The equilibrium expression, $K_c = [CO_2]$ represents the reaction.

(*a*) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$
(*b*) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(*c*) $CO(g) + \frac{1}{2} O_2(g) \rightleftharpoons CO_2(g)$
(*d*) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

2. Hydrogen molecule (H_2) can be dissociated into hydrogen atoms (H). Which one of the following changes will not increase the number of atoms present at equilibrium?

(*a*) adding H atoms
(*b*) increasing the temperature
(*c*) increasing the total pressure
(*d*) increasing the volume of the container

3. What is the expression for K_{eq} for the reaction

$$2N_2O\ (g) + O_2\ (g) \rightleftharpoons 4NO\ (g)?$$

(*a*) $\frac{[N_2][O_2]}{[NO]}$
(*b*) $\frac{[NO]^4}{[N_2O]^2}$
(*c*) $\frac{[NO]^4}{[N_2O]^2\ [O_2]}$
(*d*) $\frac{[N_2O]^2\ [O_2]}{[NO]^4}$

4. A catalyst will increase the rate of a chemical reaction by

(*a*) shifting the equilibrium to the right
(*b*) shifting the equilibrium to the left
(*c*) lowering the activation energy
(*d*) increasing the activation energy

5. What is the correct expression for the representation of the solubility product constant of $Ag_2\ CrO_4$?

(*a*) $[Ag^+]^2\ [CrO_4^{2-}]$
(*b*) $[2Ag^+]\ [CrO_4^{2-}]$
(*c*) $[Ag^+]\ [CrO_4^{2-}]$
(*d*) $[2Ag^+]^2\ [CrO_4^{2-}]$

6. In a closed system

$$A(S) \rightleftharpoons 4\ B(g) + 3\ C(g)$$

If partial pressure of *C* is doubled, then partial pressure of *B* will be

(*a*) $2\sqrt{2}$ times the original value
(*b*) $\frac{1}{2}$ times the original value
(*c*) 2 times of the original value
(*d*) $\frac{1}{2\sqrt{2}}$ times of the original value

7. $H_2 + S \rightleftharpoons H_2S$ + energy.

In this reversible reaction, select the factor which will shift the equilibrium to the right.

(*a*) adding heat
(*b*) adding H_2S
(*c*) blocking hydrogen gas reaction
(*d*) removing hydrogen sulphide gas

8. What effect does a catalyst have on the equilibrium position of a reaction?

(*a*) a catalyst favours the formation of products
(*b*) a catalyst favours the formation of reactants

(*c*) a catalyst does not change the equilibrium position of a reaction
(*d*) a catalyst may favour reactants or product formation, depending upon the direction in which the reaction is written.

9. A chemist dissolves an excess of $BaSO_4$ in pure water at 25°C if its $K_{sp} = 1 \times 10^{-10}$ what is the concentration of barium in the water?

(*a*) 10^{-4} M (*b*) 10^{-5} M (*c*) 10^{-15} M (*d*) 10^{-6} M

10. If in a mixture where $Q = k$ is combined, then what happens?

(*a*) the reaction shift towards products
(*b*) the reaction shift towards reactants
(*c*) nothing appears to happen, but forward and reverse are continuing at the same rate
(*d*) nothing happens

Ans. 1. (*b*) 2. (*c*) 3. (*c*) 4. (*c*) 5. (*a*)
6. (*d*) 7. (*a*) 8. (*c*) 9. (*c*) 10. (*c*)

V. HOTS QUESTIONS

Q1. *For the equilibrium* $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ *the value of the equilibrium constant Kc is* 3.75×10^{-6} *at 1069 K. Calculate the Kp for the reaction at this temperature?*

Ans. We know that $Kp = Kc\,(RT)^{\Delta n}$

For the above reaction, $\Delta n = (2 + 1) - 2 = 1$

$Kp = 3.75 \times 10^{-6}\,(0.0831 \times 1069)$

$Kp = 0.033$.

Q2. *The values of Ksp of two sparingly soluble salts* $Ni(OH)_2$ *and AgCN are* 2.0×10^{-15} *and* 6×10^{-17} *respectively. Which salt is more soluble? Explain.*

Ans. $AgCN \rightleftharpoons Ag^+ + CN^-$

$Ksp = [Ag^+][CN^-] = 6 \times 10^{-17}$

$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

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

Let $[Ag^+] = S_1$, then $[CN^-] = S_1$

Let $[Ni^{2+}] = S_2$, then $[OH^-] = 2S_2$

$S_1^2 = 6 \times 10^{-17}$, $S_1 = 7.8 \times 10^{-9}$

$(S_2)(2S_2)^2 = 2 \times 10^{-15}$, $S_2 = 0.58 \times 10^{-4}$

$Ni(OH)_2$ is more soluble than AgCN.

Q3. *The value of Kc for the reaction* $2A \rightleftharpoons B + C$ *is* 2×10^{-3}*. At a given time, the composition of reaction mixture is* $[A] = [B] = [C] = 3 \times 10^{-4}$ *M. In which direction the reaction will proceed?*

Ans. For the reaction the reaction quotient Qc is given by $Qc = [B]\,[C]/[A]^2$

as $[A] = [B] = [C] = 3 \times 10^{-4}$ M

$Qc = (3 \times 10^{-4})\,(3 \times 10^{-4})/(3 \times 10^{-4})^2 = 1$

as $Qc > Kc$, so, the reaction will proceed in the reverse direction.

Q4. PCl_5*,* PCl_3 *and* Cl_2 *are at equilibrium at 500 K and having concentration 1.59M* PCl_3*, 1.59M* Cl_2 *and 1.41M* PCl_5*. Calculate Kc for the reaction* $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Ans. The equilibrium constant *Kc* for the above reaction can be written as:

$$Kc = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{(1.59)^2}{1.41} = 1.79$$

Q5. *Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:*

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

(a) Write an expression for Kp for the above reaction.

(b) How will the values of Kp and composition of equilibrium mixture be affected by (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?

Ans. (*a*) $K_p = \frac{[p_{CO}][p_{H_2}]^3}{[p_{CH_4}][p_{H_2O}]}$

(*b*) (*i*) value of Kp will not change, equilibrium will shift in backward direction.

(*ii*) value of Kp will increase and reaction will proceed in forward direction.

(*iii*) no effect.

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