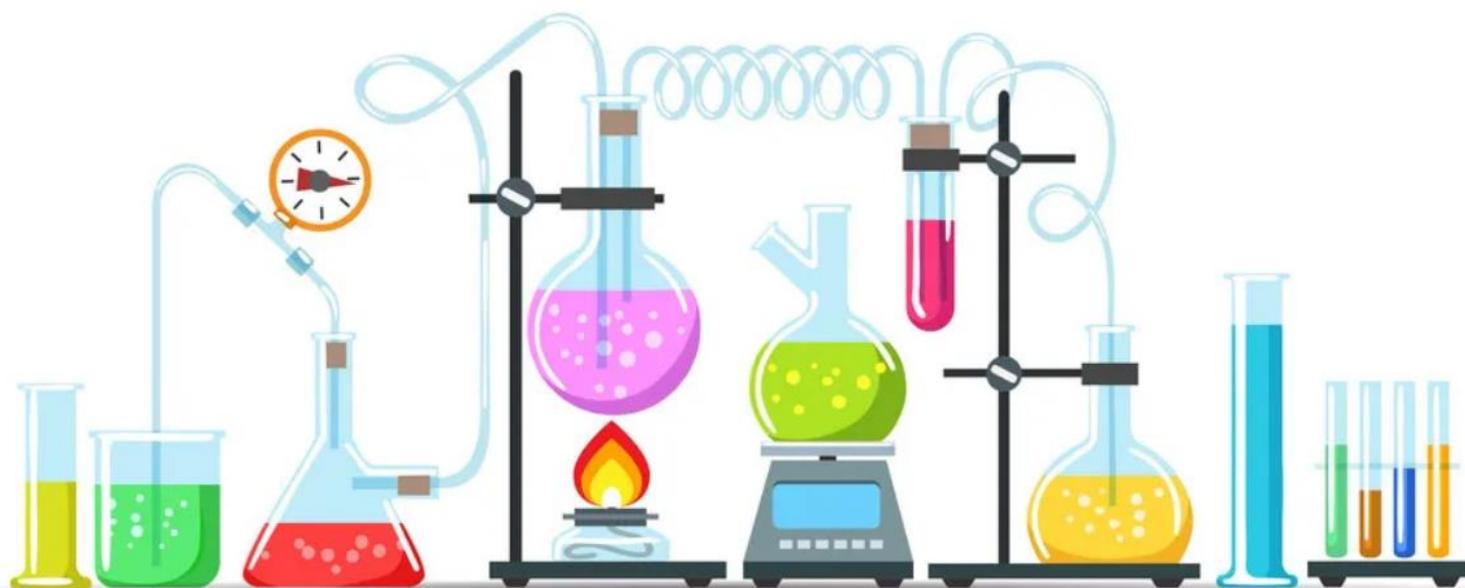


# CHEMISTRY

## CHAPTER 7: EQUILIBRIUM



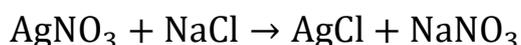
# EQUILIBRIUM

## Introduction

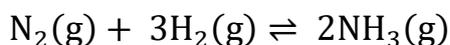
Equilibrium is the most important characteristic property of reversible reactions. These reactions for which the forward reaction occurs to a much greater extent are considered to be unidirectional in nature and whenever the rate of forward reaction is equal to rate of backward reaction, equilibrium is attained, not to forget that equilibrium exists only in closed system.

It is the state of system at which temperature, pressure, volume and composition have fixed value and does not vary with time. Chemical Reactions can be divided into two categories:

**Irreversible Reactions:** The reactions which proceed to completion and the products fail to recombine to give back reactants. For example:

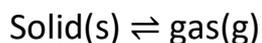
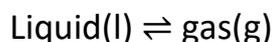
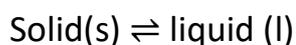


**Reversible Reactions:** The reactions which never go to completion and products recombine to give back reactants. For example:



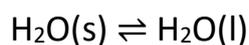
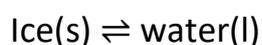
## Physical EquilibriumA

We know that solid, liquid and gas are the three states of substance. Therefore, three types of physical equilibrium are possible. These are



Here the sign double half arrows ( $\rightleftharpoons$ ) pointing in the opposite directions is both for the reversible change as well as for the equilibrium state.

1. **Solid(s) – liquid(l) equilibrium:** At equilibrium two processes takes place at the same rate i.e.,



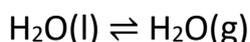
At equilibrium,

Rate of melting of ice = Rate of freezing of water

The temperature at which the solid and liquid states of a pure substance are in equilibrium at the atmospheric.

pressure is called the normal freezing point or melting point of that substance.

2. Liquid(l) – gas(g) equilibrium:



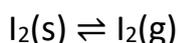
In such type of equilibrium,

Rate of vaporisation of water = Rate of condensation of water vapour

3. **Solid(s) – gas(g) equilibrium:** Such type of equilibrium is attained in case of volatile solids.

Example: If solid iodine is placed in a closed vessel, violet vapours starts appearing in the vessel.

The intensity of violet vapour increases with time and ultimately it becomes constant.

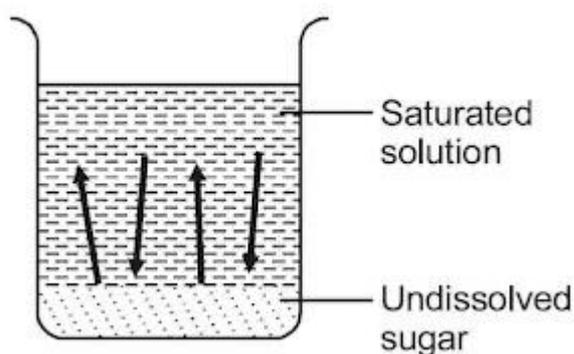


In this equilibrium,

Rate of sublimation = Rate of condensation

4. **Solids in liquids:** Suppose sugar is added continuously into a fixed volume of water at room temperature and stirred thoroughly with a glass rod. First the sugar will keep on dissolving but then a stage will come when no more sugar dissolves. Instead it settles down at the bottom. The solution is now said to be saturated and in a state of equilibrium. In this state

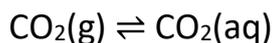
Rate of dissolution = Rate of precipitation



The amount of the solid in grams that dissolves in 100 g of the solvent to form a saturated solution at a particular temperature is called the solubility of that solid in the given solvent at that temperature.

## Gases in liquids

Such type of equilibrium is present in soda water bottle in which  $\text{CO}_2$  gas is dissolved in water under high pressure. There is a state of dynamic equilibrium between the  $\text{CO}_2$  present in the solution and the vapours of the gas above the liquid surface at a given temperature.



## Law Of Mass Action

### Law Of Mass Action

The rate at which a substance reacts is proportional to its active mass and hence the rate of a chemical reaction is proportional to the product of the active masses of the reactants.

The active mass means molar concentration i.e. number of moles dissolved per litre of the solution.

Suppose  $x$  g of NaOH are dissolved in  $V$  litres of solution. Then we can say:

Concentration of NaOH solution =  $x$  g in  $V$  litre =  $x/40$  moles in  $V$  litres =  $x / 40 \times V$  moles/Litre

Consider the reaction



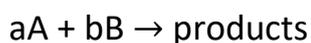
According to Law of mass action,

Rate at which A reacts  $\propto [\text{A}]$

Rate at which B reacts  $\propto [\text{B}]$

Rate at which A and B react together  $\propto [\text{A}]^{[A]} [\text{B}]^{[B]} = K^{[A][B]}$

where  $K$  is a constant of proportionality and is called velocity constant.



rate  $\propto [\text{A}]^m [\text{B}]^n$

The rate of a reaction is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation.

## Henry's law

Periodic table may be defined as the tabular arrangement of elements in such a way that the elements having same properties are kept together.

$$m \propto p$$

$$m = kp$$

where  $k$  is Henry's constant and its value depends upon the nature of the gas, nature of liquid and temperature.

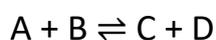
### General Characteristics of Physical Equilibrium:

1. Equilibrium is possible only in a closed system at a given temperature.
2. Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
3. All measurable properties of the system remain constant.
4. When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature.
5. The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

## Chemical Equilibrium

Every reversible reaction consists of one pair of reaction, one is forward and other is backward reaction. At one stage during reversible reactions, forward and backward reaction proceed at the same time with the same rate, the reaction is then said to be in equilibrium. If the opposing processes involve chemical reactions, the equilibrium is called Chemical equilibrium.

1. **Law of Chemical Equilibrium:** This law states that the rate of an elementary reaction is proportional to the product of the concentration of the reactants. 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,



$$r_f = K_f[A][B]$$

$$r_b = K_b[C][D]$$

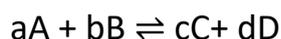
At equilibrium  $r_f = r_b$ .

$$K_f[A][B] = K_b[C][D]$$

$$K_c = \frac{K_c}{K_c} = \frac{[C][D]}{[A][B]}$$

$K_c$  is called the equilibrium constant, [ ]  $\rightarrow$  denotes active masses.

For a general reversible reaction,



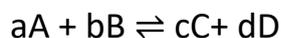
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

2. **Equilibrium constant of reverse reaction:** Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

$$K'^c = \frac{1}{K_c}$$

Relation between  $K_p$  and  $K_c$

For a general reversible reaction



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \dots (1)$$

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

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

$$K_p = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}}$$

From Eq. (1),

$$K_p = K_c (RT)^{(c+d)-(a+b)}$$

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

Where,  $\Delta n$  = difference of stoichiometric coefficients of gaseous products and reactants.

### 3. Characteristics of Equilibrium

- i. At the state of equilibrium, certain available properties like pressure, concentration and density becomes constant.
- ii. Chemical equilibrium can be established from either side.
- iii. A catalyst can cause the state of equilibrium to be reached faster, but does not alter the state of equilibrium.
- iv. Chemical equilibrium is dynamic in nature.
- v. Any change in external stress (Pressure, temperature or concentration) causes disturbance in equilibrium state. The state of equilibrium being stable, is again reached by some adjustment.
- vi. If temperature is changed, a new equilibrium is achieved with a new value for relative concentration of products and reactants.
- vii. If temperature is kept constant, pressure and concentration of reactants / products is altered, system shifts in forward or backward direction in order to nullify the alteration (stress).

#### Factors Affecting Equilibria

- i. **Change in Concentration:** When the concentration of any of the reactants or products in an equilibrium reaction is altered, the equilibrium mixture's composition changes in order to minimize the effect of the concentration change.
- ii. **Change in Temperature:** According to Le-Chatelier's principle if the temperature of an equilibrium system is increased, the equilibrium will move in the direction of the added heat.
- iii. **Change in Pressure:** The pressure has no effect on the equilibrium if the number of moles of gaseous reactants and products does not change. The change in pressure in both liquids and solids can be neglected in heterogeneous chemical equilibrium.
- iv. **Change in Volume:** When the volume of a gaseous mixture at equilibrium is increased, the equilibrium moves in the direction of a larger number of gaseous molecules.
- v. **Effect of a Catalyst:** The equilibrium is unaffected by the catalyst. This is due to the fact that the catalyst favours both forward and backward reactions equally.

#### Factors Affecting Acid Strength:

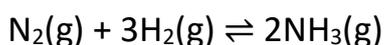
The weaker the bond, the lesser the energy required to break it. Hence, the acid is strong. The polarity of the H-A bond affects its acid strength. If the bond is highly polar, the proton tends to leave the molecule more easily, making it a strong acid.

## 5.4: Factors That Determine Acid Strength

- Periodic trends.
- The resonance effect.
- The inductive effect.

## Homogeneous Equilibria

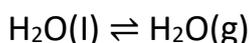
When in an equilibrium reaction, all the reactants and the products are present in the same phase (i.e., gaseous or liquid) it is called a homogeneous equilibrium. For example,



## Heterogeneous Equilibria

When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.

The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.



## Le Chatelier's Principle

It states that if a stress is applied to a system in equilibrium, the equilibrium for the time being gets disturbed. As a result system moves in a direction which tends to relieve the external stress and finally a new equilibrium is attained.

## Ionic Equilibrium

**Electrolyte:** Electrolytes are the substances which conduct electricity in molten state or in solution. Example HCl, NaCl, KCl, CH<sub>3</sub>COOH etc.

**Arrhenius theory of Electrolytic dissociation:** When an electrolyte is dissolved in a solvent it spontaneously dissociates into oppositely charged particles called ions, to a considerable extent. Electrolytic ionization or dissociation gives ions and unionized molecules in solution. For neutrality, the total charge on cations is equal to the total charge on the anions.

**Degree of Dissociation ( $\alpha$ ):** It is the fraction of one mole of the electrolyte that has dissociated under the given conditions. The value of  $\alpha$  depends on temperature, dilution of electrolyte, nature of electrolyte and solvent.

$$\alpha = \text{No. of ionized moles} / \text{Total mo. Moles}$$

**Ostwald's Law of Dilution:**

According to this law, "The degree of ionization (or dissociation) of any weak electrolyte is inversely proportional to the square root of concentration."

$$\alpha = \sqrt{\frac{K}{C}}$$

Where, K = proportionality constant

## Equilibrium Constant

The equilibrium constant for a chemical reaction can be described as the ratio between the amount of reactant and the amount of product that is used to determine chemical behaviour. The rate constants are constant at a given temperature. The ratio of the forward reaction rate constant to the backward reaction rate constants should be constant, and this is referred to as the equilibrium constant ( $K_{\text{equ}}$ ).

## Characteristics of Equilibrium Constant

1. It is reaction-specific and fixed at a steady temperature.
2. A catalyst modifies the rate of forwarding and backward reactions in such a way that the value of the equilibrium constant is unaffected.
3. Changes in concentration, pressure, temperature and inert gases can all have an effect on the equilibrium, favouring either forward or backward reaction but not the equilibrium constant.
4.  $G^0 = -RT \ln K_{\text{equ}}$  is related to the standard free energy.
5.  $K_{\text{equ}}$  has varying values at different temperatures for the same reversible reaction.
6. The reverse equilibrium's equilibrium constant is the reciprocal of the original equilibrium, i.e.  $K_{\text{rev}} = 1/K_{\text{equ}}$ .
7. When the stoichiometry of the equilibrium reaction changes, the power of the equilibrium constant changes by the same amount.
8. In the scenario of stepwise multiple equilibria leading to the final products, the net equilibrium constant = product of each stepwise equilibrium constant. As a result, the net equilibrium constant  $K = K_1 * K_2 * K_3$ .

9. Equilibrium reactions occur at the same time and produce the same product. The equilibrium constant of the reactions remains constant. Product concentrations will be reduced due to the larger concentration of the common product.

## Relationship between K and G

$\Delta G^\circ$  is related to K by the equation  $\Delta G^\circ = -RT \ln K$ . If  $\Delta G^\circ < 0$ , then  $K > 1$ , and products are favored over reactants at equilibrium. If  $\Delta G^\circ > 0$ , then  $K < 1$ , and reactants are favored over products at equilibrium.

### Relationship

$$\Delta G^\circ = -RT \ln K$$

$\Delta G^\circ$  = Gibbs Free Energy (must be in J, not kJ)

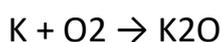
R = gas constant (must use the one with units of J)

T = temperature (in Kelvin)

ln = natural log (find this button on your calculator!)

K = equilibrium constant

## Relationship between K and O<sub>2</sub>



**Word equation:** Potassium + Oxygen gas  $\rightarrow$  Potassium oxide

**Type of Chemical Reaction:** For this reaction we have a combination reaction.

**Balancing Strategies:** In this equation we have potassium and oxygen gas combining to form potassium oxide. This is a combination reaction.

To balance the equation, the first thing to do is to change the coefficient in front of K<sub>2</sub>O if and to balance the oxygen atoms.

## Application of Equilibrium

It is used to predict the extent of a reaction on the basis of its magnitude. It is used to predict the direction of the reaction. It is used in calculations of the equilibrium concentrations.

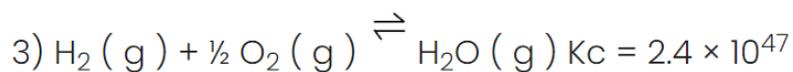
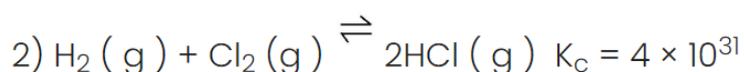
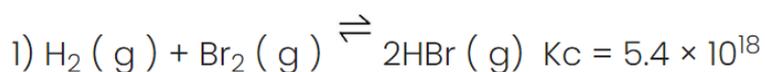
- The balanced reaction and value of  $K_c$ .
- The initial concentration of the reactants, or the initial moles.
- Volume of the container.

## Application of Equilibrium constant

**1) Predicting the extent of reaction:** The magnitude of the equilibrium constant gives an idea of the relative amount of the reactants and the products.

a) larger value of the equilibrium constant ( $> 10^3$ ) shows that forward reaction is favoured i.e. concentration of products is much larger than that of the reactants at equilibrium.

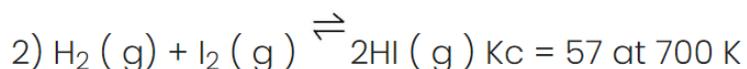
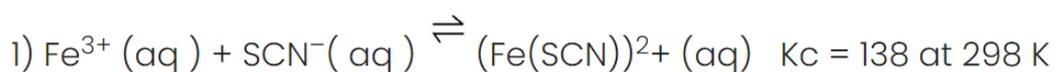
**For Ex:**



This shows that at equilibrium, concentration of the products is very high, i.e. reaction goes almost to completion.

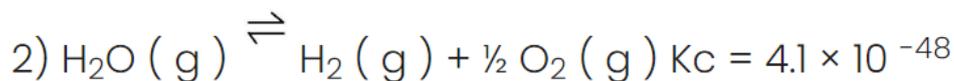
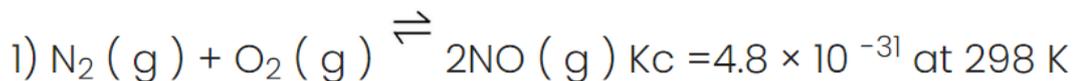
b) Intermediate value of  $K$  ( $10^{-3}$  to  $10^3$ ) shows that the concentration of the reactants and products are comparable.

**For Ex:**



c) low value of  $K$  ( $< 10^{-3}$ ) shows that backward reaction is favoured i.e. concentration of reactants is much larger than that of products i.e. the reaction proceeds to a very small extent in the forward direction.

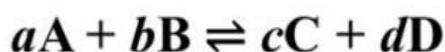
**For Ex:**



## 2) Predicting the direction of a reaction

At any stage of the reaction, other than the stage of chemical equilibrium, concentration ratio, as given by the expression for the law of chemical equilibrium, is called concentration quotient or reaction quotient.

It is usually represented by  $Q_c$  or  $Q$ . Thus,



$$Q_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} = K_c \quad (\text{at equilibrium})$$

1. If  $Q = K_c$ , the reaction is in equilibrium
2. If  $Q > K_c$ ,  $Q$  will tend to decrease so as to become equal to  $K$ . As a result, the reaction will proceed in the backward direction.
3. If  $Q < K_c$ ,  $Q$  will tend to increase so as to become equal to  $K$ . As a result, the reaction will proceed in the forward direction.

## 3) Calculating equilibrium concentration

Knowing the initial concentration of reactants, equilibrium concentration of all the reactants and products can be calculated as:

1. Write the balanced equation for the reaction.
2. Assume  $x$  as the amount of the reactants reacted or a product formed.
3. Calculate the equilibrium concentration of each reactant and product from its stoichiometry of the equation.
4. Write expression for  $K_c$  or  $K_p$ .
5. Substitute equilibrium concentration and calculate  $x$ .
6. Check the result by substituting calculated values of equilibrium concentration to get the value of  $K_c$  or  $K_p$

## Concepts of Acids and Bases

### 1. Arrhenius Concept:

- **Acid:** Any substance when dissolved in water, increases the concentration of  $H^+$ . e.g.,  $HCl$ ,  $H_2SO_4$ ,  $HNO_3$  etc.
- **Base:** Any substance when dissolved in water, increases the concentration of  $OH^-$ . e.g.,  $NaOH$ ,  $KOH$  etc.

## 2. Bronsted - Lowry Concept:

- **Acid:** Species (Molecule or ion) that donates a proton to another species.
- **Base:** Species (Molecule or ion) that accepts a proton from another species.  
 $HCl(\text{Acid}) + NH_3(\text{Base}) \rightarrow NH_4^+ + Cl^-$

## 3. Lewis acids and bases:

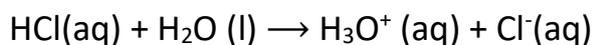
According to Lewis concept of acids and bases, a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor.

**Lewis acids:**  $H^+$ ,  $Ag^+$ ,  $Fe^{2+}$ ,  $AlCl_3$ ,  $BF_3$ ,  $BCl_3$ ,  $BeCl_2$  etc.

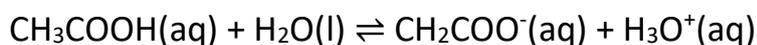
**Lewis Bases:**  $Cl^-$ ,  $CN^-$ ,  $OH^-$ ,  $X^-$ ,  $NH_2^-$ ,  $SH^-$  etc.

An acid base reaction is the sharing of an electron pair with an acid by a base. This process is simply defined as coordination or neutralisation.

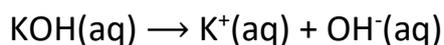
- a. A strong acid is an acid that ionizes completely in water.



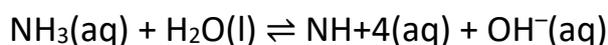
- b. A weak acid is an acid that is only partially ionized in water



- c. A strong base is a base that ionizes completely in water.



- d. A weak base is a base which is partially ionized in water



## The pH Scale

pH of solution may be defined as negative logarithm of hydronium ion concentration.

$$pH = -\log [H_3O^+]$$

$$pH = \log \frac{1}{[H_3O^+]}$$

The pH range at  $25^\circ C$  is taken as 0 to 14.

pH = 7 Neutral

pH > 7 Basic

pH < 7 Acidic

## Common Ion Effect

The suppression in the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion is called common ion effect.

For example: Ionisation of acetic acid ( $\text{CH}_3\text{COOH}$ ) and effect of addition of a small amount of acetate ion.



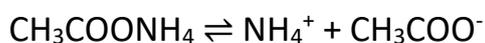
## Buffer Solution

A buffer solution is that solution which resists any change in its pH value on addition of small amount of acid or base. Although the pH of buffer changes on doing so, but the change in pH value will be less than the expected change. There are three types of buffer solution.

**Acidic Buffer:** This consists of solution of a weak acid and its salt with strong base. Example;  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ .

**Basic Buffer:** This consists of solution of weak base and its salt with strong acid. e.g.,  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$

**Salt Buffer:** It is a solution of salt which itself can act as a buffer. Such a salt is the salt of weak acid and weak base. For example,



When an acid is added, it reacts with  $\text{CH}_3\text{COO}^-$  to produce  $\text{CH}_3\text{COOH}$  and when a base is added, it react with  $\text{NH}_4^+$  to produce  $\text{NH}_4\text{OH}$ .

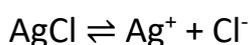
## Buffer Capacity

It is the number of moles of acid or base required by one litre of a buffer solution for changing its pH by one unit.

Buffer Capacity = No. of moles of acid or base added per litre / Change in pH

## Solubility and Solubility Product

The number of moles of solute in one litre of a saturated solution (mole / L) is defined as solubility. Let us calculate solubility of salt  $\text{AgCl}$ .



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

$K_{sp}$  is called solubility product.

In pure water,

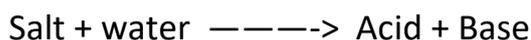
$$K_{sp} = [Ag^+][Cl^-]$$

$$K_{sp} = S^2 \quad \{\because S = [Ag^+] = [Cl^-]\}$$

$$S = \sqrt{K_{sp}}$$

## Salt Hydrolysis

Salt hydrolysis is defined as the process in which a salt reacts with water to give back the acid and the base.

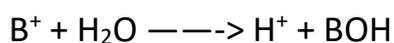


All salts are strong electrolytes and thus ionize completely in the aqueous solution.

(1) If the acid produced is strong and the base produced is weak.

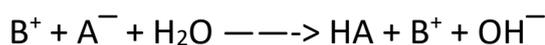


or



In this case the cation reacts with water to give an acidic solution. This is called cationic hydrolysis.

(2) If the acid produced is weak and the base produced is strong.



or

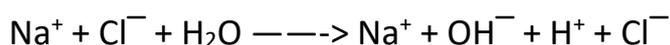
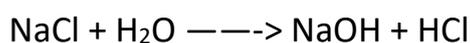


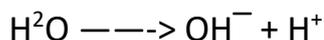
In this case the anion reacts with water to give basic solution. This is called anionic hydrolysis.

Salt hydrolysis may be defined as the reaction of the cation or the anion of the salt with water to produce acidic or basic solution.

Depending upon the relative strength of the acid and the base produced, the resulting solution is acidic, basic or neutral.

### (1) Salts of strong acid and strong base

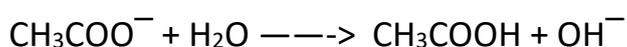
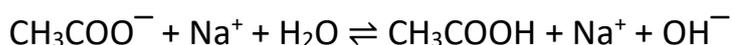
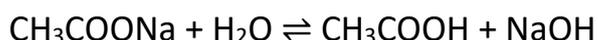




It involves only ionization of water and no hydrolysis. So the solution is neutral.

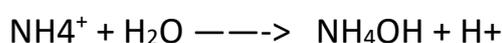
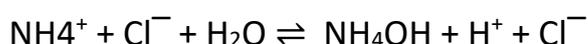
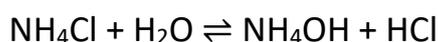
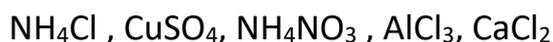
The salts of strong acids and strong bases do not undergo hydrolysis and the resulting solution is neutral.

### (2) Salts of weak acid and strong bases



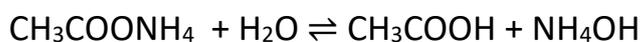
As it produces  $\text{OH}^-$  ions, the solution of such a salt is alkaline in nature.

### (3) Salts of strong acid and weak base



As it produces  $\text{H}^+$  ions, the solution of such a salt is acidic in nature.

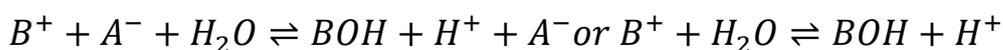
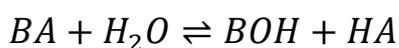
### (4) Salts of weak acid and weak base



**It involves both anionic and cationic hydrolysis**

#### Hydrolysis constant

Equation for the hydrolysis of a salt (BA) may be written as:



$$\text{Hydrolysis constant, } K_h = \frac{[\text{BOH}][\text{H}^+]}{[\text{B}^+]}$$

Degree of Hydrolysis

The degree of hydrolysis of a salt is defined as the fraction of the total salt which is hydrolysed i.e.

$$h = \frac{\text{No. of moles of the salt hydrolysed}}{\text{Total no. of moles the salt taken}}$$

## Strengths of Acids And Bases

According to Arrhenius concept, an acid is defined as a substance which when dissolved in water gives  $H^+$  and a base is defined as a substance which when dissolved in water give  $OH^-$  ions.

Greater the number of  $H^+$  ions produced in the aqueous solution, the stronger is the acid.

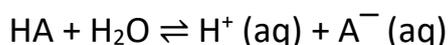
Greater the number of  $OH^-$  ions produced in the aqueous solution, the stronger is the base.

As greater is the dissociation constant of the weak acid ( $K_a$ ), greater is the amount of  $H^+$  (aq) produced, therefore stronger is the acid.

$K_a$  value gives a measure of the relative strength of the weak acid.

$K_b$  value gives a measure of the relative strength of the weak base.

Suppose the weak acid is represented by HA. Suppose the initial concentration of HA is C mol/L and  $\alpha$  is the degree of dissociation.



C 0 0 Initial conc

C (1- $\alpha$ )C $\alpha$  C $\alpha$  Conc at equilibrium

$$K_a = \frac{[H^+][A_{weak}^-]}{[HA_{weak}]}$$

where  $K_a$  is called dissociation constant of the acid.

$$K = \frac{Ca^2}{1-a}$$

If a is very small  $1-a \approx 1 \Rightarrow K_a = Ca^2$

$$\text{or } a = \sqrt{\frac{K_a}{C}}$$

If two acids of equimolar concentration are taken

$$\frac{\text{strength of the acid } HA_1}{\text{strength of the acid } HA_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

The relative strength of two acids of equimolar concentration can be compared by taking

square root of the ratios of their dissociation constants.

$$\begin{aligned} K_a, \text{ for } \text{CH}_3\text{COOH} &= 1.8 \times 10^{-5} \\ K_a \text{ for HCN} &= 4.0 \times 10^{-10} \\ \therefore \frac{\text{Strength of } \text{CH}_3\text{COOH}}{\text{Strength of HCN}} &= \sqrt{\frac{1.8 \times 10^{-5}}{4.0 \times 10^{-10}}} \\ &= \sqrt{4.5 \times 10^4} = 2.1 \times 10^2 = 210 \end{aligned}$$

$\text{CH}_3\text{COOH}$  is nearly 192 times stronger than HCN.

The relative strength of two weak bases of equimolar concentration can be compared by taking square root of the ratios of their dissociation constants.

$$\frac{\text{Strength of base } (\text{BOH})_1}{\text{Strength of base } (\text{BOH})_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

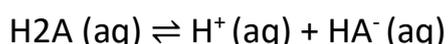
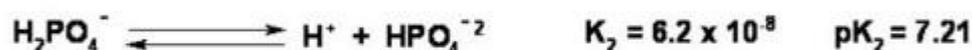
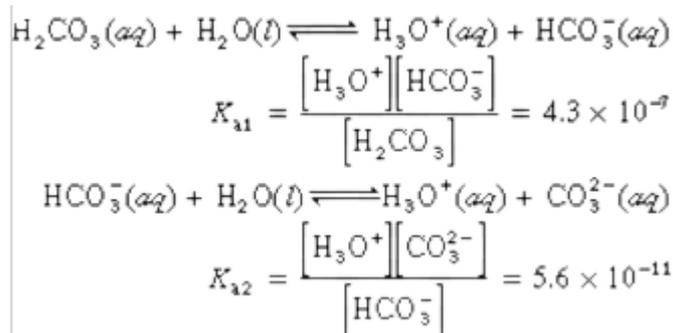
where  $K_{b_1}$  and  $K_{b_2}$  are the dissociation constants of the two bases.

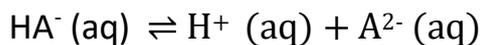
Since the ionization of an acid or a base increases with dilution, the strength of the acid or base increases with dilution.

$K_a$  and  $K_b$  are taken as dimensionless quantities because the standard state concentration of all species involved is taken as  $\text{mol L}^{-1}$

### Polyprotic acid and polyacidic bases

Some acids like  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{CO}_3$ ,  $(\text{COOH})_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{AsO}_4$  contain more than one ionizable proton. Such acids are called polybasic or polyprotic acids. They ionize in steps.





$$K_{a1} = \frac{[\text{HA}^-][\text{H}^+]}{[\text{H}_2\text{A}]}$$

$$K_{a2} = \frac{[\text{A}^{2-}][\text{H}^+]}{[\text{HA}^-]}$$

$$K_a = K_{a1} \times K_{a2}$$

For a tribasic acid, the overall ionization constant will be product of the ionization constant of the three steps i.e.

$$K_a = K_{a1} \times K_{a2} \times K_{a3}$$

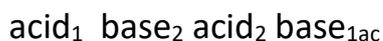
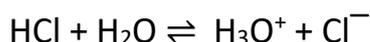
$$K_{a1} > K_{a2} > K_{a3}$$

It is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces.

Greater the charge on the negative ion, more difficult it becomes to remove a proton.

According to Bronsted -Lowry concept, the relative strength of two acids are compared by comparing their tendencies to donate protons. The relative strength of two bases are compared by comparing their tendencies to accept proton.

The relative strength of the two acids or the two bases involved in the two acid-base conjugate pairs can be found out if we know whether forward reaction is favoured or backward reaction is favoured.



## Di and polybasic acids and Di and Polyacidic bases

Ionization of di- and polybasic acids and di- and polyacidic bases. Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.

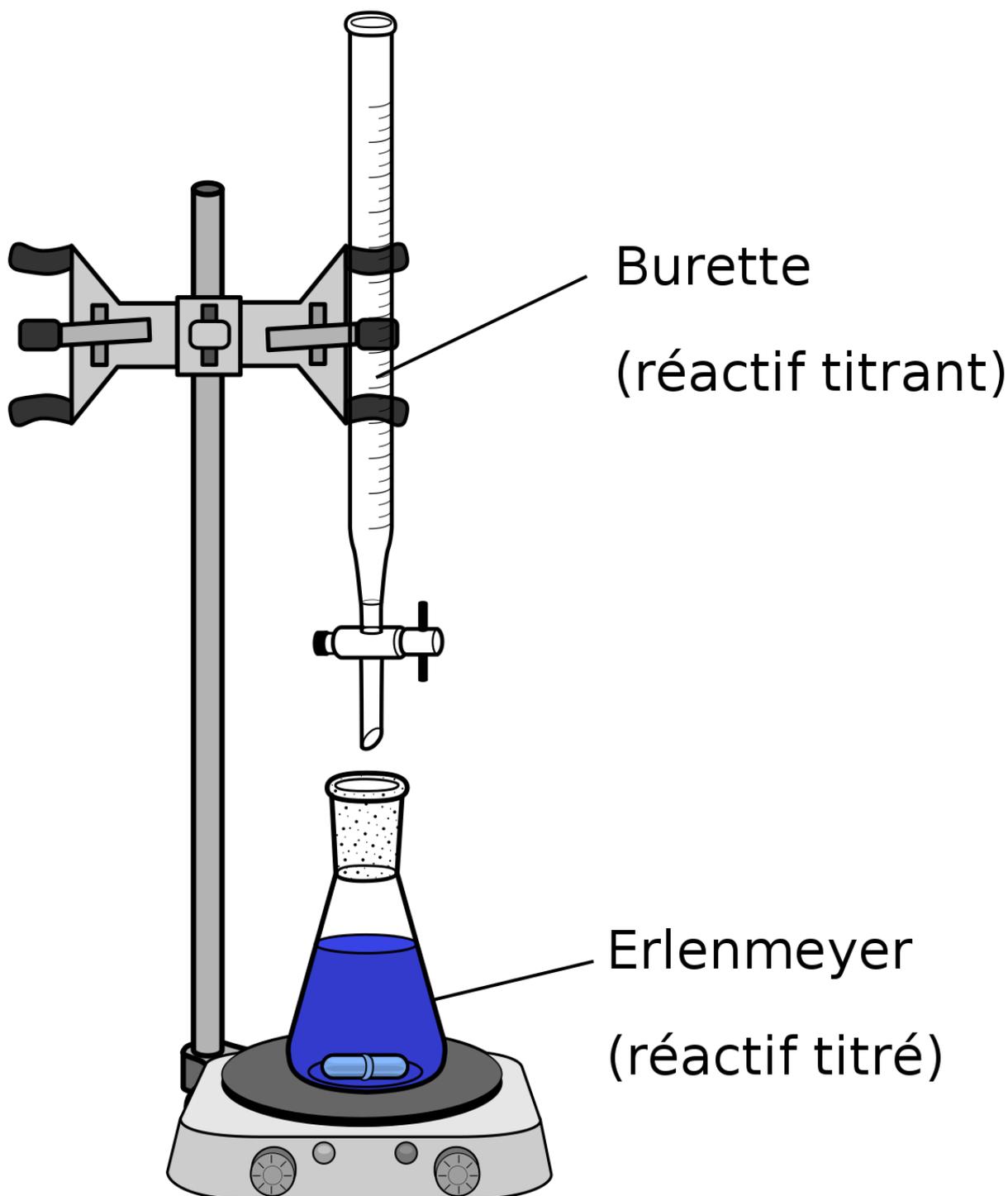
## Acid- Base Titration using Indicator

Titration is the measurement of the volume of a solution of one reactant that is required to react completely with a measured amount of another reactant.

As both the reactants are taken in the form of solution and the titration is the measurement of volume of one solution that must be added to another solution till the reaction is complete, this method of quantitative analysis is called volumetric analysis.

The concentration of the solution called as standard solution is known and it is desired to find the concentration of other by titration.

### Apparatus of Titration



### Procedure

- 1) A known volume of the solution is taken in the titration flask with the help of a pipette.
- 2) The other solution is taken in the burette which is graduated in cc's and has a stop cock at bottom to control the amount of flow into the flask.

3) The solution to be titrated is taken in the flask and is called titrate and the solution with which the titration is to be done that is taken in the burette is called the titrant.

The point at which the required volume of one solution has been added to the other to exactly complete the reaction between the two is called end point or equivalence point.

### Types of titrations

- Redox titrations involving oxidation and reduction.
- Acid -base titrations involving neutralization
- Precipitation titration
- Complexometric titration involving formation of complexes.

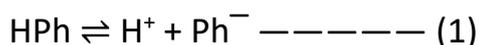
The substance usually added into the solution taken in the titration flask to detect the equivalence point is called an indicator

### Theory of acid base indicators

Acid base indicators are mostly complex organic molecules which are either weak acid or weak bases

For ex: Phenolphthalein is a weak organic acid (HPh) and methyl orange is a weak organic base ( MeOH) .

Phenolphthalein and methyl orange dissociates in aqueous solution as :



colourless    pink



Yellow    red    colourless

The unionized form has one colour and the ions have different colour.

For Ex: HPh is colourless while Ph ions have pink colour. Similarly , MeOH has yellow colour while Me<sup>+</sup> have red colour.

As the medium changes from acidic to basic or vice versa , the equilibrium shifts either towards the right or towards the left and so the colour changes.

In acidic medium the equilibrium 1 is towards left and the solution is colourless while in the basic medium, OH<sup>-</sup> ions will combine with the H<sup>+</sup> to form unionized water molecules, the equilibrium shifts towards the right and the solution has a pink colour.

In methyl orange in basic medium the equilibrium 2 is towards left and the colour is yellow while in the acidic medium  $H^+$  ions combine with the  $OH^-$  ions and the equilibrium 2 shifts towards the right and the colour is red.

Phenolphthalein cannot be used as an indicator if the base is weak because the  $OH^-$  ions produced from the weak base are insufficient to shift the equilibrium 1 towards the right.

Methyl orange is not a suitable indicator if the acid is weak because the  $H^+$  ions produced are insufficient to combine with  $OH^-$  ions and shift the equilibrium 2 towards the right.

### **pH at the end point of acid – base Titration**

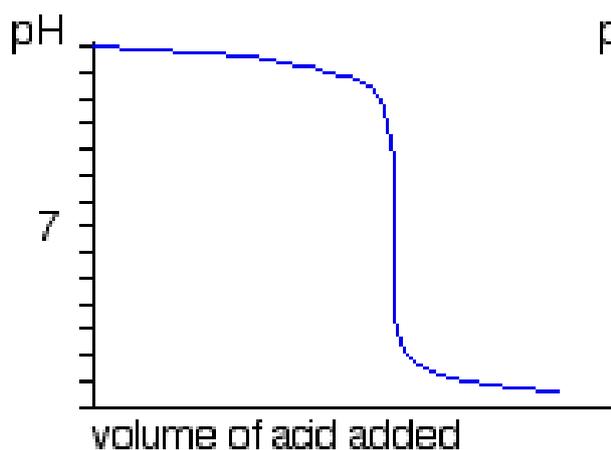
(1) If strong acid has been titrated with strong base, the pH at the end point is 7.

(2) If a weak acid or a weak base is involved in the titration, pH at the end point depends upon the hydrolysis of salt formed. In any type of acid-base titration, it is found that there is a sudden change in the pH value at the end.

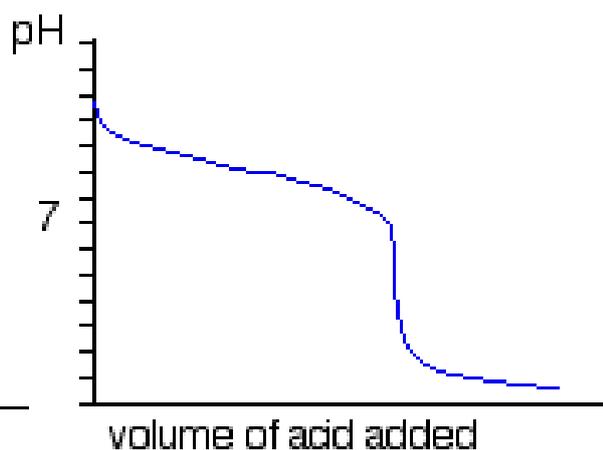
As the titration proceeds, if the pH values of the solution are measured or calculated theoretically and then plotted against the volume of the solution added, the curve obtained is called titration curve.

Titration Curve

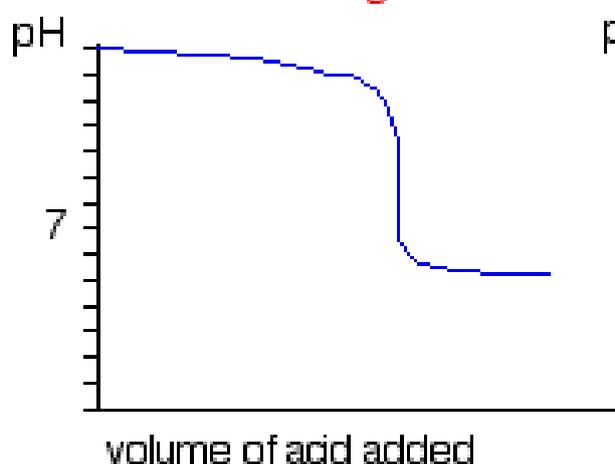
strong acid - strong base



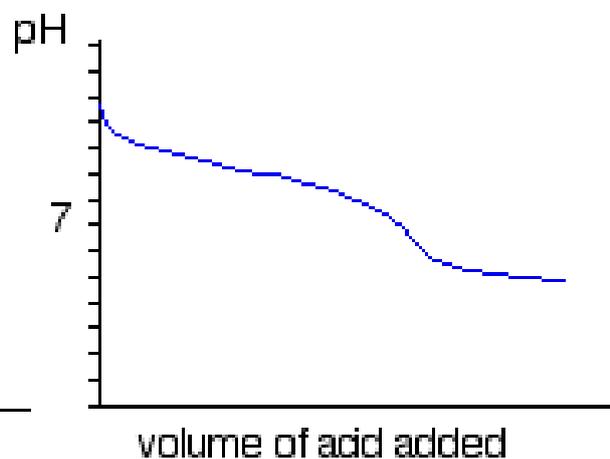
strong acid - weak base



weak acid - strong base



weak acid - weak base



The point at which there is sudden change in pH when a very small amount of titrant is added to the titrate is called point of inflection.

The steepness of the slope around the equivalence point is quite large in case of titration of strong acid against strong base whereas it is less steep if the acid or base is weak.

Large steepness means large change in pH on adding a very small volume of the solution. It may be pointed out that if a weak acid is titrated against a weak base, the change in pH at the end is so small that it is difficult to determine the end.

### Selection of a Suitable Indicator

The indicator used should be such that it shows change in colour in the same pH range as required around the equivalence point.

Indicator	pH Range	Acid	Base
Thymol Blue	1.2-2.8	red	yellow
2,4-Dinitrophenol	2.4-4.0	colorless	yellow
Methyl yellow	2.9-4.0	red	yellow
Methyl orange	3.1-4.4	red	orange
Bromphenol blue	3.0-4.6	yellow	blue-violet
Methyl red	4.4-6.2	red	yellow
<i>p</i> -Nitrophenol	5.0-7.0	colorless	yellow
Phenol red	6.4-8.0	yellow	red
Thymol blue	8.0-9.6	yellow	blue
Phenolphthalein	8.0-10.0	colorless	red
Alizarin yellow	10.0-12.0	yellow	lilac
Salicyl yellow	10.0-12.0	yellow	orange-brown
Trinitrobenzoic acid	12.0-13.4	colorless	orange-red

(1) For titration of a strong acid against a strong base, any indicator out of methyl orange, methyl red, phenolphthalein or bromothymol blue can be used to determine the endpoint.

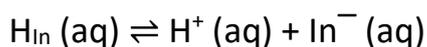
(2) For titration of weak acid like acetic Acid against a strong base, only phenolphthalein is a suitable indicator.

(3) For titration of weak base against strong acid, methyl orange or methyl red or bromothymol blue can be used as an indicator.

(4) For titration of weak acid with weak base, no indicator is found to function satisfactorily.

### Colour change $pK_{\text{indicator}} = \text{pH}$ at the equivalence point

Consider an indicator which is a weak organic acid. Let it be represented by  $\text{HIn}$ . In aqueous solution, it dissociates as:



$\text{HIn}$  and  $\text{In}^-$  have different colours. The equilibrium constant for the above reaction is :

$$K_{\text{in}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

The exact point of colour change will be at the pH when  $[\text{HIn}] = [\text{In}^-]$

$$K_{\text{in}} = -\log k_{\text{in}} = -\log [\text{H}^+]$$

For a particular titration, the indicator selected should be such for which  $pK_{in} = pH$

## Summary

1. **Equilibrium:** It represents the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with the passage of time.
2. **Physical equilibrium:** It is a state of equilibrium in which the two opposing processes involve changes in physical state only.
3. **Chemical equilibrium:** It is a state of equilibrium in which the two opposing processes involve change of chemical species.
4. **Reversible reaction:** A reversible reaction is one which proceeds in both the forward and backward directions.
5. **Law of mass action:** This law states that at constant temperature, the rate of chemical reaction is directly proportional to the product of molar concentrations of the reacting substances.
6. **Equilibrium constant (K):** It is the ratio of the product of the molar concentrations of the substances formed to that of the reacting substances raised to the powers equal to their stoichiometric coefficients in the chemical equation at a particular temperature.
7. **Henry's law:** The mass of a gas dissolved in a given mass of a solvent at any temperature is directly proportional to the pressure of the gas above the solvent.
8. **Le Chatelier's Principle:** When a system in dynamic equilibrium is subjected to a stress such as a change in concentration, pressure or temperature, the equilibrium shifts in a direction that opposes or reduces the stress.
9. **Strong electrolytes:** Electrolytes which are ionized almost completely in aqueous solution under similar conditions of concentration and temperature are called strong electrolytes.
10. **Weak electrolytes:** Electrolytes which are poorly ionized in aqueous solution under similar conditions of concentration and temperature are called weak electrolytes.
11. **Solubility product:** It is the product of concentration of ions in a saturated solution of a sparingly soluble salt at a given temperature.
12. **Arrhenius acid-base concept:** According to Arrhenius, an acid is a substance which gives hydrogen ions and base is a substance which gives hydroxyl ions in aqueous solutions.
13. **Bronsted-Lowry acid-base concept:** According to this concept, an acid is a proton donor and base is a proton acceptor.
14. **Lewis acid-bases concept:** According to this concept, an acid is an electron pair acceptor and base is an electron pair donor.

15. **pH value:** pH value of a solution is the negative logarithm of the hydrogen ion concentration (in moles per litre) present in it. Thus  $\text{pH} = -\log[\text{H}^+]$
16. **Irreversible reaction:** If a reaction cannot take place in the reverse direction i.e., the products formed do not react to give back the reactants under the same conditions is called an irreversible reaction.
17. **Homogeneous equilibria:** When in an equilibrium reaction, all the reactants and the products are present in the same phase (i.e., gaseous or liquid), it is called a homogeneous equilibrium.
18. **Heterogeneous equilibrium:** When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.
19. **Buffer solution:** It is defined as a solution which resists in its pH value even when small amounts of the acid or the base are added to it.
20. **Conjugate base:** A base formed by the loss of proton by an acid is called conjugate base of the acid.

- Le Chatelier's principle: A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to counteract the effect of the change.
- Effect of Concentration Change: If concentration of reactants is increased, equilibrium will shift in forward direction and vice-versa.
- Effect of Pressure Change: No effect if moles of reactants and products are same. If there is change in number of moles, equilibrium will shift in the direction having smaller number of moles when the pressure is increased and vice-versa.
- Effect of Inert Gas Addition: If volume is constant, i.e., addition does not change partial pressure or molar concentrations, equilibrium is not affected.
- Effect of Temperature change: For exothermic, low temperature favours formation of reactants; for endothermic, high temperature favours formation of products.

- Step 1: Write the balanced equation for the reaction.  
Step 2: Make a table that lists for each substance involved in reaction; Initial concentration, change in concentration, equilibrium concentration.  
Step 3: Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve.  
Step 4: Calculate equilibrium concentrations from the calculated value of concentration of substances.  
Step 5: Check results by substituting them into the equilibrium equation.
- Buffer Solutions are the solutions which resist change in pH on dilution or addition of acid or alkali.  
Solubility Product ( $K_{sp}$ ): For a sparingly soluble salt, it is the product of molar concentration of ions raised to power equal to numbers of times each ion.

Factors Affecting Equilibrium

Calculating Equilibrium Concentrations

Predicting the direction of a Reaction

Predicting the Extent of a Reaction

Equilibrium

- If  $Q_c < K_c$ , net reaction goes from left to right.
- If  $Q_c > K_c$ , net reaction goes from right to left.
- If  $Q_c = K_c$ , no net reaction occurs

- $K_c < 10^{-3}$  reaction proceeds rarely.
- $K_c > 10^3$  reaction proceeds nearly to completion
- $K_c \rightarrow 10^{-3}$  to  $10^3$ , reaction is at equilibrium

Reactants and products are in same phase.

Types

Reactants and products are present in two or more phases.

Equilibrium set up in physical processes like evaporation of water, etc.

- Solid  $\rightleftharpoons$  Liquid
- Liquid  $\rightleftharpoons$  Gas
- Solid  $\rightleftharpoons$  Gas

**Characteristics:**

- Possible only in a closed system at a given temperature.
- Both the reactions occur at same rate.
- All measurable property remains constant.
- When equilibrium is attained one of its parameter remains constant at given temperature.
- Magnitude of such quantities at any stage indicates the extent to which process has proceeded before reaching equilibrium.

pH of a solution is negative logarithm to base 10 of the activity of hydrogen ion

$$\begin{array}{c} \text{Size increases} \\ \text{HR} < \text{HCl} < \text{HB} < \text{HI} \\ \text{Size increases} \\ \text{Acidic strength increases} \end{array}$$

Speed of forward reaction equals that of backward reaction.

**Characteristics:**

- Can be achieved from either side.
- Dynamic in nature.
- There is no change in concentration of various species.
- Observable physical properties become constant.
- Equilibrium is attained rapidly by the presence of catalyst.

G is negative, reaction is spontaneous and proceeds in forward reaction.

G is positive, reaction is non-spontaneous and proceeds in reverse reaction.

G is 0, reaction has achieved equilibrium.

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

Arrhenius Concept of Acids and Bases:

Arrhenius theory states that acids are substances that dissociate in water give hydrogen ions and bases are substances that produce hydroxyl ions.

Bronsted Lowry Theory states that acid is a substance that is capable of donating hydrogen ion and bases are substances capable of accepting a hydrogen ion.

• Weak acids have very strong conjugate bases.

Acids turn blue litmus into red and liberate dihydrogen on reacting with some metals.

Bases turn red litmus into blue, taste bitter and feel soapy. Salts are formed when acids and bases are mixed in right proportion. Lewis Acid accepts an electron pair. Lewis Base donates an electron pair.

Acidic:  $[H_3O^+] > [OH^-]$

Neutral  $[H_3O^+] = [OH^-]$

Basic  $[H_3O^+] < [OH^-]$

Equilibrium Law or Law of Chemical Equilibrium

Acid and bases

Relationship Between Equilibrium Constant K, Reaction Quotient Q And Gibbs Energy G

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentration of the reactions raised to their individual stoichiometric coefficients has a constant value:  $aA + bB \rightleftharpoons cC + dD$

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

Under given set of conditions

Equilibrium

Equilibrium In Chemical Processes

if a chemical reaction is carried out in a closed container, a constancy in some observable properties like colour, pressure is observed. Such a state is referred to as equilibrium.

Equilibrium constant

Dynamic Equilibrium: Chemical reactions reach a state of dynamic equilibrium in which the rate of forward and reverse reactions are equal and there is no net change in composition.

for the reverse reaction is the inverse of the equilibrium constant for reaction in the forward direction.

**Applications of Equilibrium Constants:**

- Applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.
- Value of  $K_c$  is independent of initial concentrations of the reactants and products.
- Equilibrium constant is temperature dependent.

$$K_c \text{ reverse} = \frac{1}{K_c}$$

- Equilibrium constant for a reacting is related to equilibrium constant of corresponding reaction.

## Important Questions

### Multiple Choice questions-

Question 1. Which of the following fluoro-compounds is most likely to behave as a Lewis base?

- (a)  $\text{BF}_3$
- (b)  $\text{PF}_3$
- (c)  $\text{CF}_4$
- (d)  $\text{SiF}_4$

Question 2. Calculate the pOH of a solution at  $25^\circ\text{C}$  that contains  $1 \times 10^{-10}$  M of hydronium ions, i.e.  $\text{H}_3\text{O}^+$ .

- (a) 4.000
- (b) 9.000
- (c) 1.000
- (d) 7.000

Question 3. When two reactants, A and B are mixed to give products C and D, the reaction quotient, Q, at the initial stages of the reaction

- (a) is zero
- (b) Decreases With Time
- (c) Is Independent of Time
- (d) Increases With Time

Question 4. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is

- (a) Not a buffer solution with  $\text{pH} < 7$
- (b) Not a buffer solution with  $\text{pH} > 7$
- (c) A buffer solution with  $\text{pH} < 7$
- (d) A buffer solution with  $\text{pH} > 7$

Question 5. If, in the reaction  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ , x is that part of  $\text{N}_2\text{O}_4$  which dissociates, then the number of molecules at equilibrium will be

- (a) 1
- (b) 3
- (c)  $(1 + x)$
- (d)  $(1 + xy)^2$

Question 6. The solubility product of a salt having general formula  $\text{MX}_2$ . In water is:  $4 \times 10^{-12}$ .

The concentration of  $M^{2+}$  ions in the aqueous solution of the salt is

- (a)  $4.0 \times 10^{-10} \text{ M}$
- (b)  $1.6 \times 10^{-4} \text{ M}$
- (c)  $1.0 \times 10^{-4} \text{ M}$
- (d)  $2.0 \times 10^{-6} \text{ M}$

Question 7. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH?

- (a)  $\text{CaCl}_2$
- (b)  $\text{SrCl}_2$
- (c)  $\text{BaCl}_2$
- (d)  $\text{MgCl}_2$

Question 8. Oxidation number of Iodine varies from

- (a) -1 to +1
- (b) -1 to +7
- (c) +3 to +5
- (d) -1 to +5

Question 9. Which of the following molecular species has unpaired electrons?

- (a)  $\text{N}_2$
- (b)  $\text{F}_2$
- (c)  $\text{O}_2^-$
- (d)  $\text{O}_2^{-2}$

Question 10. A certain buffer solution contains equal concentration of  $X^-$  and  $\text{HX}$ . The  $K_a$  for  $\text{HX}$  is  $10^{-8}$ . The pH of the buffer is

- (a) 3
- (b) 8
- (c) 11
- (d) 14

Question 11. Among the following the weakest Bronsted base is

- (a)  $\text{F}^-$
- (b)  $\text{Cl}^-$
- (c)  $\text{Br}^-$
- (d)  $\text{I}^-$

Question 12. Which of the following statements is correct about the equilibrium constant?

- (a) Its value increases by increase in temperature
- (b) Its value decreases by decrease in temperature
- (c) Its value may increase or decrease with increase in temperature
- (d) Its value is constant at all temperatures

Question 13. pH value of which one of the following is NOT equal to one.

- (a) 0.1 M  $\text{CH}_3\text{COOH}$
- (b) 0.1 M  $\text{HNO}_3$
- (c) 0.05 M  $\text{H}_2\text{SO}_4$
- (d)  $50\text{cm}^3$  0.4 M  $\text{HCl}$  +  $50\text{cm}^3$  0.2 M  $\text{NaOH}$

Question 14.  $[\text{OH}^-]$  in a solution is  $1 \text{ mol L}^{-1}$ . The pH the solution is

- (a) 1
- (b) 0
- (c) 14
- (d)  $10^{-14}$

Question 15. What is the pH of a 0.10 M solution of barium hydroxide,  $\text{Ba}(\text{OH})_2$ ?

- (a) 11.31
- (b) 11.7
- (c) 13.30
- (d) None of these

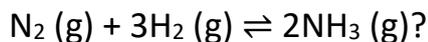
### Very Short:

1. Write the expression for the equilibrium constant  $K_p$  for the reaction  $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$
2. How are  $K_c$  and  $K_p$  related to each other in the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
3. What is the equilibrium constant expression for the reaction  $\text{Al}(\text{s}) + 3\text{H}^+(\text{aq}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + \frac{3}{2}\text{H}_2(\text{g})$
4. What happens to the equilibrium  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$  if nitrogen is added to it
  - (i) at constant volume
  - (ii) at constant pressure?
5. What does the equilibrium  $K < 1$  indicate?
6. For an exothermic reaction, what happens to the equilibrium constant if the

temperature is increased?

7. Under what conditions, a reversible process becomes irreversible?

8. What is the effect of increasing pressure on the equilibrium?



9. For which of the following cases does the reaction go farthest to completion:  $K = 1$ ,  $K = 1010$ ,  $K = 10^{-10}$ .

10. Under what conditions ice water system is in equilibrium?

(a) at 273 K

(b) below 273 K

(c) above 273 K.

### Short Questions:

1. Justify the statement that water behaves like acid as well as a base on the basis of the protonic concept.
2. What is  $p^{\text{OH}}$ ? What is its value for pure water at 298 K?
3. Calculate the  $p^{\text{H}}$  of a buffer solution containing 0.1 moles of acetic acid and 0.15 mole of sodium acetate. The ionization constant for acetic acid is  $1.75 \times 10^{-5}$ .
4. An aqueous solution of  $\text{CuSO}_4$  is acidic while that of  $\text{Na}_2\text{SO}_4$  is neutral. Explain.
5. The dissociation constants of  $\text{HCN}$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{HF}$  are  $7.2 \times 10^{-10}$ ,  $1.8 \times 10^{-5}$ , and  $6.7 \times 10^{-4}$  respectively. Arrange them in increasing order of acid strength.
6. The dissociation of  $\text{PCl}_5$  decreases in presence of  $\text{Cl}_2$ . Why?

### Long Questions:

1. Explain chemical equilibrium with the help of an example of formation and decomposition of hydrogen iodide.
2. Name and explain the factors which influence the equilibrium state.
3. What is salt hydrolysis? Explain hydrolysis of salts of
  - (i) strong acids and strong bases
  - (ii) strong acids and weak bases
  - (iii) strong bases and weak acids
  - (iv) strong acids and weak bases.
4. Calculate the pH of  $\frac{\text{N}}{1000}$  Sodium hydroxide solution assuming complete ionisation ( $K_w = 1.0 \times 10^{-14}$ ).
5. Calculate the  $p^{\text{H}}$  of a 0.01 N solution of acetic acid.  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$  at  $25^\circ\text{C}$

## Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

**Assertion (A) :** Increasing order of acidity of hydrogen halides is  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

**Reason (R) :** While comparing acids formed by the elements belonging to the same group of periodic table, H–A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

- (i) Both A and R are true and R is the correct explanation of A.  
(ii) Both A and R are true but R is not the correct explanation of A.  
(iii) A is true but R is false.  
(iv) Both A and R are false.
2. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

**Assertion (A) :** A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amounts of acid or alkali.

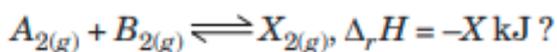
**Reason (R) :** A solution containing a mixture of acetic acid and sodium acetate acts as a buffer solution around pH 4.75.

- (i) Both A and R are true and R is correct explanation of A.  
(ii) Both A and R are true but R is not the correct explanation of A.  
(iii) A is true but R is false.  
(iv) Both A and R are false.

## Case Study Based Question:

1. Le Chatelier's principle is also known as the equilibrium law, used to predict the effect of change on a system at chemical equilibrium. This principle states that equilibrium adjusts the forward and backward reactions in such a way as to accept the change affecting the equilibrium condition. When factor-like concentration, pressure, temperature, inert gas that affect equilibrium are changed, the equilibrium will shift in that direction where the effects caused by these changes are nullified. This principle is also used to manipulate reversible reactions in order to obtain suitable outcomes.

(1) Which one of the following conditions will favour the maximum formation of the product in the reaction?



- (a) Low temperature and high pressure
- (b) Low temperature and low pressure
- (c) High temperature and high pressure
- (d) High temperature and low pressure

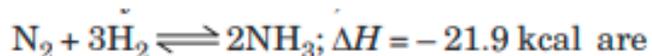
(2) For the reversible reaction,



The equilibrium shifts in forwarding direction

- (a) By increasing the concentration of  $NH_3(g)$
- (b) By decreasing the pressure
- (c) By decreasing the concentrations of  $N_2(g)$  and  $H_2(g)$
- (d) By increasing pressure and decreasing temperature

(3) Favourable conditions for manufacture of ammonia by the reaction,



- (a) Low temperature, low pressure and catalyst
- (b) Low temperature, high pressure and catalyst
- (c) High temperature, low pressure and catalyst
- (d) High temperature, high pressure and catalyst

(4) For the above equilibrium, the reactant concentration is doubled, what would happen then to equilibrium constant?



- (a) Remains constant
- (b) Be doubled
- (c) Be halved
- (d) Cannot be predicted

(5) In which one of the following equilibria will the point of equilibrium shift to left when the pressure of the system is increased?

- (a)  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$   
 (b)  $2\text{NH}_{3(g)} \rightleftharpoons \text{N}_{2(g)} + 3\text{H}_{2(g)}$   
 (c)  $\text{C}_{(s)} + \text{O}_{2(g)} \rightleftharpoons \text{CO}_{2(g)}$   
 (d)  $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{H}_2\text{O}_{(g)}$

### Answer Key:

#### MCQ

- (b)  $\text{PF}_3$
- (a) 4000
- (d) Increases With Time
- (a) Not a buffer solution with  $\text{pH} < 7$
- (a) 1
- (c)  $1.0 \times 10^{-4} \text{ M}$
- (c)  $\text{BaCl}_2$
- (b) -1 to +7
- (c)  $\text{O}_2^-$
- (b) 8
- (d)  $\text{I}^-$
- (c) Its value may increase or decrease with increase in temperature
- (a) 0.1 M  $\text{CH}_3\text{COOH}$
- (c) 14
- (c) 13.30

#### Very Short Answer:

1.

$$K_p = \frac{p_{\text{H}_2}^4}{p_{\text{H}_2\text{O}}^4} = \frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}$$

2.  $K_p = K_c$ .

3.  $K_c = [\text{Al}^{3+}(\text{aq})][\text{H}_2(\text{g})]^{3/2}/[\text{H}^+(\text{aq})]^3$ .

4. The state of equilibrium remains unaffected.

(ii) Dissociation increases, i.e., the equilibrium shifts forward.

5. The reaction does not proceed much in the forward direction.

6.  $K = K/K_b$ .

$K_b$  increases much more than when the temperature is increased in an exothermic reaction. Hence  $K$  decreases.

7. If one of the products (gaseous) is allowed to escape out (i.e., in the open vessel).

8. Equilibrium will shift in the forward direction forming more ammonia

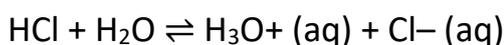
9. The reaction having  $K = 10^{10}$  will go farthest to completion because the ratio (product)/(reactants) is maximum in this case.

10. (a) At 273 K.

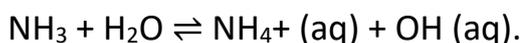
### Short Answer:

**Ans: 1.** Water ionizes as  $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

With strong acids, water behaves as a base by accepting a proton from an acid.



While with bases, water behaves as an acid by liberating a proton



**Ans: 2.**  $p^{\text{OH}} = -\log [\text{OH}^-]$

$$p\text{H} + p^{\text{OH}} = 14 \text{ for pure water at } 298 \text{ K}$$

$$p\text{H} = 7$$

or

$$p^{\text{OH}} \text{ of water at } 298 = 7.$$

**Ans: 3.**

$$\begin{aligned}
 p^{\text{H}} &= p^{\text{K}_a} + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\
 &= -\log 1.75 \times 10^{-5} + \log \frac{0.15}{0.10} \quad [p^{\text{K}_a} = -\log K_a] \\
 &= -\log 1.75 \times 10^{-5} + \log 1.5 = 4.9.
 \end{aligned}$$

**Ans: 4.**  $\text{CuSO}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})_2 + \text{H}_2\text{SO}_4$  (weak base strong acid)

$\text{CuSO}_4$  is the salt of weak base  $\text{Cu}(\text{OH})_2$  and a strong acid  $\text{H}_2\text{SO}_4$ .

Thus, the solution will have free  $\text{H}^+$  ions and will, therefore, be acidic.

$\text{Na}_2\text{SO}_4$ , being the salt of a strong acid  $\text{H}_2\text{SO}_4$  and a strong base.

$\text{NaOH}$  does not undergo hydrolysis. The solution is, therefore, neutral.

**Ans: 5.** More the value of  $K_a$ , the stronger the acid

Their  $K_{a1}$ s are  $6.7 \times 10^{-4} > 1.8 \times 10^{-5} > 7.2 \times 10^{-10}$

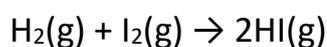
$\therefore \text{HCN} < \text{CH}_3\text{COOH} < \text{HF}$ .

**Ans: 6.** For  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ .

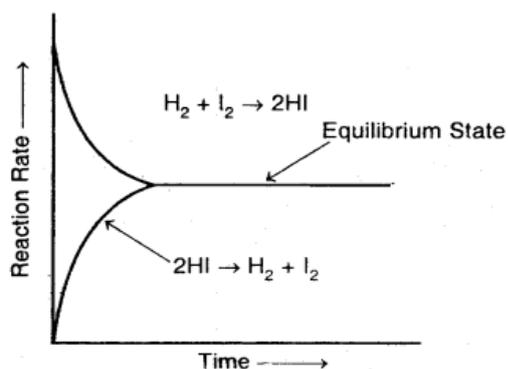
According to Le Chatelier's principle, an increase in the concentration of  $\text{Cl}_2$  (one of the products) at equilibrium will favor the backward reaction, and thus the dissociation of  $\text{PCl}_5$  into  $\text{PCl}_3$  and  $\text{Cl}_2$  decreases

## Long Answer:

**Ans: 1.** Consider the reaction between hydrogen and iodide at a constant temperature of 720 K in a closed vessel. The reaction involved is:



Accordingly, the effective collision amongst the reactant molecules will result in the production of  $\text{HI}$ . Since the product molecules are not permitted to leave the vessel (i.e., the reaction is carried out in a closed vessel), they will also collide amongst themselves leading to the formation of reactant molecules. Under these conditions, the reaction takes place in both directions. Hence, it is called a reversible reaction.



Graphical representation of the change of reaction rates with time for the formation and decomposition of hydrogen iodide

Forward reaction:  $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \rightarrow 2\text{HI} (\text{g})$

Backward reaction:  $2\text{HI} (\text{g}) \rightarrow \text{H}_2 (\text{g}) + \text{I}_2 (\text{g})$

Reversible reaction:  $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \rightleftharpoons 2\text{HI} (\text{g})$ .

To begin with, with the concentration of the reactants being higher in comparison to the product molecules, the rate of the forward reaction will be high as compared to the backward reaction. As the reaction proceeds further, the molar concentration of the reactants will gradually decrease while that of the product will gradually increase.

Apparently, the rate of forwarding reaction goes on decreasing while that of the backward reaction. This state is the reversible chemical reaction is called a chemical equilibrium state.

**Ans: 2.** The various factors which influence the equilibrium state are:

1. Concentration: Concentration change influences the equilibrium state. If the concentration of the reactants is increased, the equilibrium will shift in such a direction in which more to the products are formed and vice-versa. On the other hand, if the concentration of the products is increased, the equilibrium will shift in such a direction in which more of the reactants are formed.
2. Temperature: Like concentration, the temperature change also affects the equilibrium state. An increase in temperature of the system will shift the equilibrium in such a direction in which heat is absorbed (i.e. rate of endothermic reaction will increase).

On the other hand, a decrease in temperature of the system will shift the equilibrium in such a direction in which heat is evolved (i.e., rate of exothermic reaction will increase).

3. Pressure: Like concentration and temperature, the pressure also influences the

equilibrium state only when the reaction proceeds with a change in volume. An increase in pressure of the system will shift the equilibrium in such a direction in which the volume of the system decreases.

On the other hand, a decrease in pressure of the system will shift the equilibrium in such a direction in which the volume of the system increases.

To explain the effect of temperature, pressure, and concentration on the equilibrium state, consider the combination of  $N_2$  and  $H_2$  to form  $NH_3$



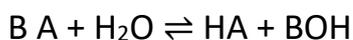
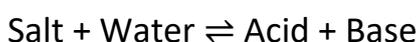
The reaction is reversible, exothermic, and accompanied by a decrease in volume.

Effect of temperature: According to Le-Chatelier's principle, an increase in temperature shifts the equilibrium in the direction in which heat is absorbed, and a decrease in temperature shifts the equilibrium in the direction in which heat is evolved. Since the formation of ammonia is accompanied by the evolution of heat, it is favored by a decrease in temperature.

Effect of pressure: According to Le-Chatelier's principle, an increase of pressure on a system in equilibrium, favors the direction which is accompanied by a decrease in volume and vice-versa. While going from, left to right in the above reaction, there is a decrease in the number of moles or say volume, the formation of ammonia is favored by an increase in pressure.

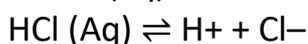
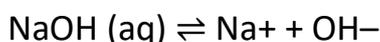
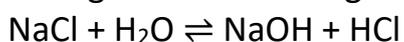
Effect of concentration: According to Le-Chatelier's principle, an increase of concentration of any of the substances in the system shifts the equilibrium in the direction in which the concentration of that substance is reduced. Thus, the addition of  $N_2$  or  $H_2$  favors the formation of ammonia.

**Ans: 3.** Salt hydrolysis: Hydrolysis is a process in which a salt reacts with water to form acid and base.



That is the interaction of the cations of the salt with  $OH^-$  ions furnished by water and anions of the salt with  $H^+$  ions furnished by water to form an acidic or basic solution is called salt hydrolysis.

(i) Salts of strong acids and strong bases like  $NaCl$ ,  $KCl$ ,  $KNO_3$ ,  $NaNO_3$ ,  $Na_2SO_4$ ,  $K_2SO_4$  do not undergo hydrolysis because the acids and bases furnished by them in aqueous solutions are strong acids and strong bases which are completely dissociated.

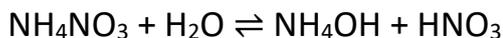


Since  $[H^+] = [OH^-]$  the resulting solution is neutral and its  $pH = 7$ .

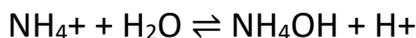
(iii) Hydrolysis of salts of strong acids and weak bases:

The salts belonging to this type are  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CuSO}_4$ ,  $\text{AlCl}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ , etc.

Let us take the case of  $\text{NH}_4\text{NO}_3$



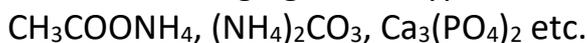
or



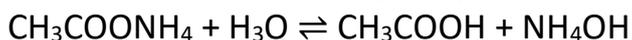
The resulting solution after hydrolysis is basic ( $\text{pH} > 7$ ). Since only the anions of the salt have taken place in the hydrolysis, it is called anionic hydrolysis.

(iv) Hydrolysis of salts of weak acids and weak bases:

The salts belonging to this type are:



Let us take the case of hydrolysis of  $\text{CH}_3\text{COONH}_4$



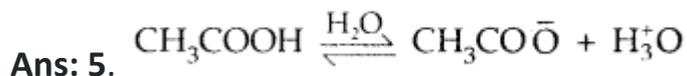
or



Since both the cations and anions of the salt have participated in the hydrolysis, it is known as cationic as well as anionic hydrolysis. The nature of the solution or pH depends upon the relative strengths of the acid and base that are formed on hydrolysis.

**Ans: 4.** Since NaOH is completely ionized

$$\therefore [\text{NaOH}] = [\text{OH}^-] = 10^{-3} \text{ N} = 10^{-3} \text{ M}$$



Applying the law of chemical equilibrium

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\therefore [\text{H}_3\text{O}^+] = \sqrt{K_a[\text{CH}_3\text{COOH}]}$$

$$\text{as } [\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+]$$

Putting the value of  $K_a = 1.8 \times 10^{-5}$  and

$$[\text{CH}_3\text{COOH}] = 0.01 \text{ N} = 0.01 \text{ M} = 10^{-2} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \sqrt{1.8 \times 10^{-5} \times 10^{-2}}$$

$$= \sqrt{18} \times 10^{-4} \text{ g ion L}^{-1}$$

$$\therefore p^{\text{H}} = -\log [\text{H}_3\text{O}^+] = -\log (4.242 \times 10^{-4})$$

$$= -(0.6276 - 4) = 3.37$$

### Assertion Reason Answer:

- (i) Both A and R are true and R is the correct explanation of A.
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### Case Study Answer:

#### 1. Answer:

- (a) Low temperature and high pressure
- (d) By increasing pressure and decreasing temperature
- (b) Low temperature, high pressure and catalyst
- (a) Remains constant

