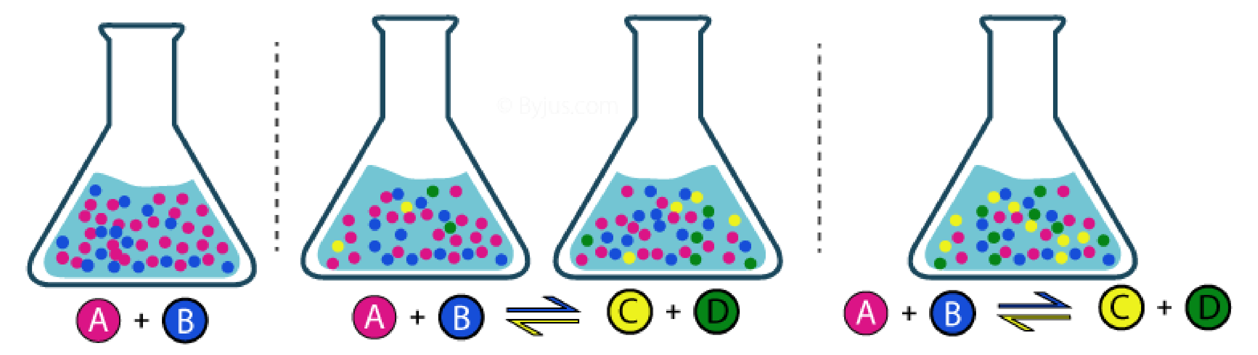
7. EQUILIBRIUM



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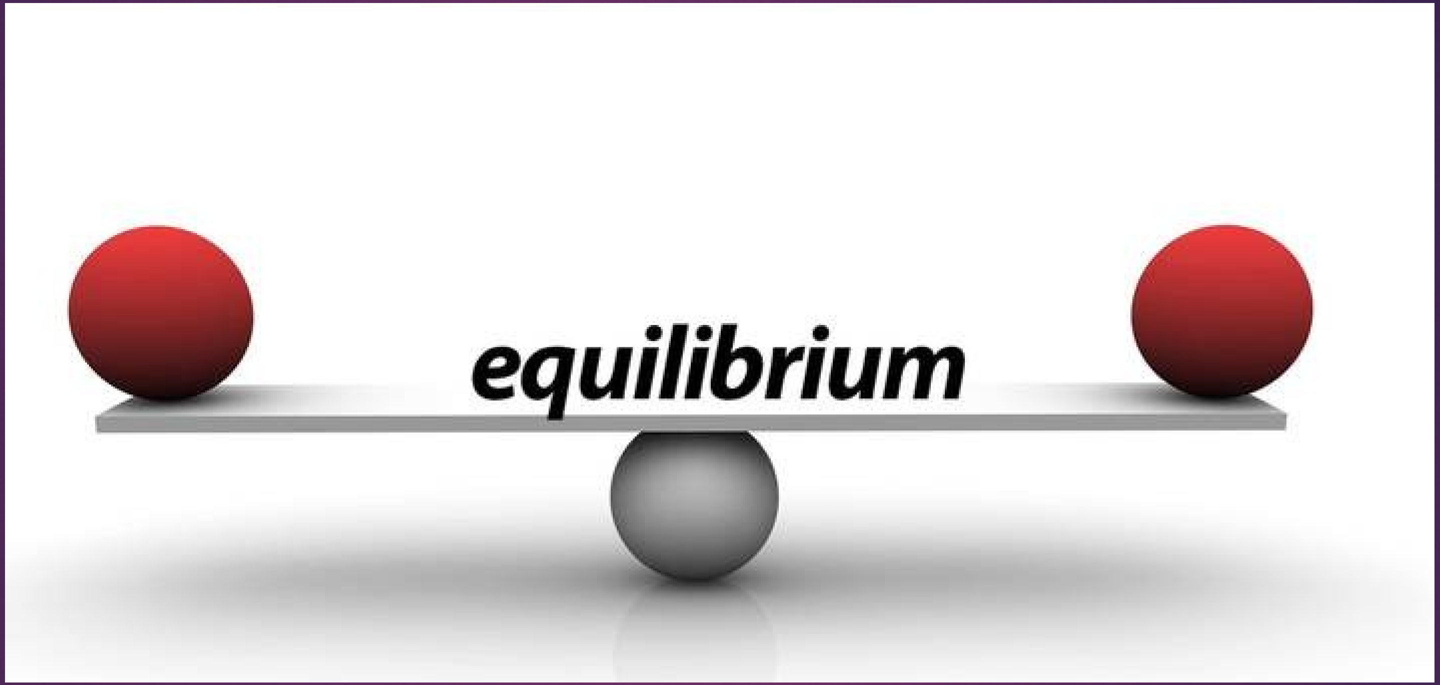
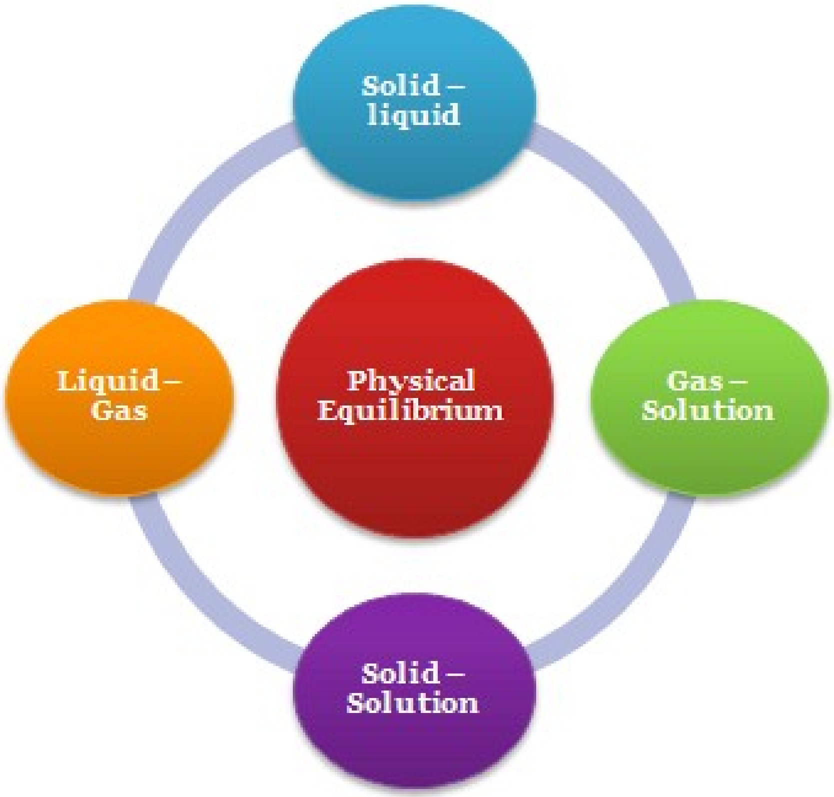

equilibrium

PHYSICAL EQUILIBRIUM

Equilibrium which involves only physical changes is called physical equilibrium.

Eg:- solid $\rightleftharpoons$ Liquid, Liquid $\rightleftharpoons$ Gas, Solid $\rightleftharpoons$ Vapour



Solid – liquid

Liquid – Gas

Physical Equilibrium

Gas – Solution

Solid – Solution

GENERAL CHARACTERISTICS OF PHYSICAL EQUILIBRIUM

- **Equilibrium can be established only in case of closed system.**
- **The equilibrium is always dynamic in nature.**
- **The measurable properties of the system become constant at equilibrium.**
- **At equilibrium, there exists an expression involving the concentration of**
- **reacting substances which become constant at a given temperature.**

HENRY’S LAW

- **The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas.**
- **OR**
- **Henry’s law states that, the solubility of a gas is directly proportional to the pressure.**

EXAMPLE

- In soda water bottles, the dissolved and undissolved molecules of CO_2 exist in equilibrium.
- When the bottle is opened, the CO_2 dissolved in it escapes out rapidly with a fizz.
- This fizzing out of soda bottle can be easily understood in terms of Henry's law.

FIZZING OF CARBONATED DRINKS

REVERSIBLE REACTIONS

Reactions in which the products of the reaction can react with one another under suitable conditions to give back the original reactants.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$2SO_2 + O_2 \rightleftharpoons 2SO_3$

$2HI \rightleftharpoons H_2 + I_2$

IRREVERSIBLE REACTIONS

Reactions in which the products of the reaction do not react back to give the reactants.

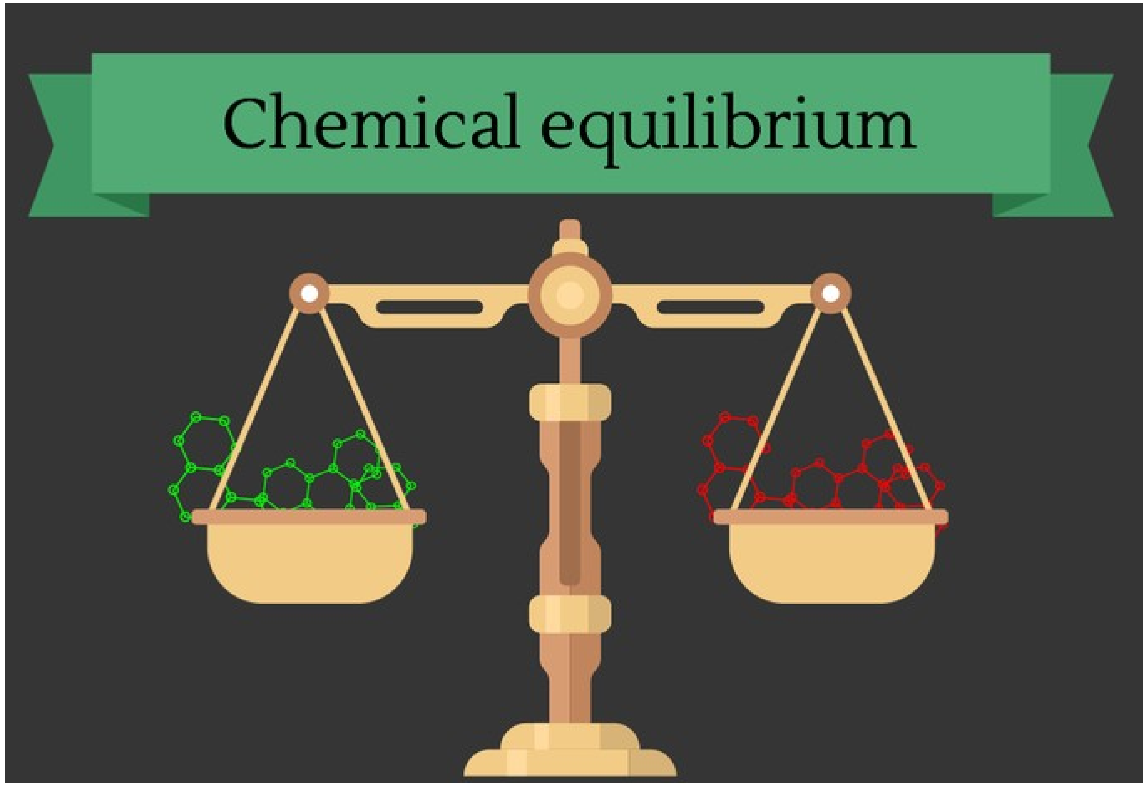
$$\mathrm{HCl} + \mathrm{NaOH} \rightarrow \mathrm{NaCl} + \mathrm{H_2O}$$

$$\mathrm{AgNO_3} + \mathrm{NaCl} \rightarrow \mathrm{AgCl} + \mathrm{NaNO_3}$$

CHEMICAL EQUILIBRIUM

CHEMICAL EQUILIBRIUM

The state of reversible reaction at which the rate of forward reaction is equal to the rate of backward reaction and the composition of the system remains constant.

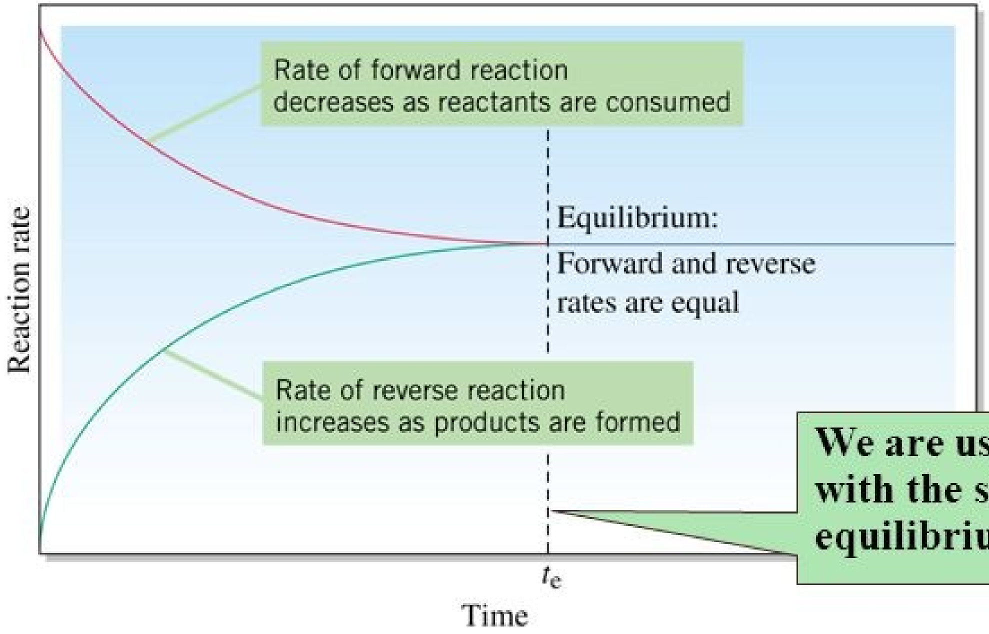


CHEMICAL EQUILIBRIUM IS DYNAMIC IN NATURE

- In a chemical reaction, both forward and backward reactions do not stop but proceed at equal rates.
- The concentration of reactants and products remain constant.
- Therefore, the equilibrium is called dynamic equilibrium.

Dynamic Nature of Equilibrium

When a system reaches ***equilibrium***, the forward and reverse reactions continue to occur … but at equal rates.



We are usually concerned with the situation *after* equilibrium is reached.

After equilibrium the concentrations of reactants and products remain constant.

CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

- **Chemical equilibrium is dynamic in nature.**
- **The observable properties of the system become constant at equilibrium and remain unchanged.**
- **The equilibrium can be approached from either direction.**
- **The equilibrium can be attained only if the system is a closed one.**
- **A catalyst cannot alter the position of equilibrium.**
- **The free energy change at constant temperature and pressure is zero.**

LAW OF MASS ACTION

The law states that, “the rate of a reaction is directly proportional to the product of the molar concentrations of the reacting substances at constant temperature”.

LAW OF MASS ACTION

Consider a reaction $A + B \rightarrow \text{Products}$.

According to law of mass action,

Rate of the reaction, $r \propto [A][B]$

$$r = K[A][B]$$

where [A] and [B] are the molar concentrations of the reactants A and B respectively.

K is a constant known as rate constant.

RATE CONSTANT

According to law of mass action,

$r = K[A][B]$

If the concentration of each of the reactants is unity,

i.e., $[A] = [B] = 1$, then $r = K$.

The rate constant of a reaction at a given temperature may be defined as the rate of the reaction when the concentration of each of the reactants is unity.

EQUILIBRIUM CONSTANT

Consider a general reversible reaction, $aA + bB \rightleftharpoons cC + dD$

According to law of mass action, the rate of the forward reaction is given as

$$r_f \propto [A]^a[B]^b$$

$$r_f = K_f[A]^a[B]^b ....(1)$$

The rate of backward reaction is given as

$$r_b \propto [C]^c[D]^d$$

$$r_b = K_b[C]^c[D]^d ....(2)$$

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

$$\text{i.e., } r_f = r_b ....(3)$$

From (1) and (2)

$$K_f[A]^a[B]^b = K_b[C]^c[D]^d$$

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

But $\frac{K_f}{K_b} = K$

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

EQUILIBRIUM CONSTANT

Equilibrium constant is defined as the ratio of the product of the molar concentrations of the products to that of the reactants with each concentration term raised to the power equal to its stoichiometric coefficient in the balanced chemical equation.

EQUILIBRIUM CONSTANT IN TERMS OF PRESSURE

- **For reactions involving gases, the partial pressure of the reactants and products are proportional to the concentrations.**
- **Therefore, the law of chemical equilibrium can be expressed in terms of partial pressures instead of concentrations.**

For a general gaseous reaction,

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

Equilibrium constant, $K_P = \frac{P_C^c . P_D^d}{P_A^a . P_B^b}$

Where P_A , P_B , P_C , P_D are the partial pressures of A, B, C and D respectively.

K_P is the equilibrium constant in terms of partial pressures.

RELATION BETWEEN K_P AND K_C

Consider the reaction, $aA + bB \rightleftharpoons cC + dD$

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

$$K_P = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} \text{......................}(2)$$

RELATION BETWEEN K_P AND K_C

For an ideal gas, $PV = nRT$

$$P = \frac{nRT}{V}$$

$$P = CRT$$

Thus $P_A = C_A RT$

$$P_B = C_B RT$$

$$P_C = C_C RT$$

$$P_D = C_D RT$$

Substituting these values in equation (2)

$$K_P = \frac{C_C{}^c (RT)^c . C_D{}^d (RT)^d}{C_A{}^a (RT)^a . C_B{}^b (RT)^b}$$

$$K_P = \frac{C_C{}^c . C_D{}^d}{C_A{}^a . C_B{}^b} (RT)^{(c+d)-(a+b)}$$

$$K_P = K_C RT^{\Delta n}$$

Where Δn = [No. of moles of gaseous products ─ No. of moles of gaseous reactants]

$\Delta n = (c + d) - (a + b)$

UNITS OF EQUILIBRIUM CONSTANT

- If the total number of moles of the reactants is exactly equal to the total number of moles of products, ‘K’ has no units.
- If the total number of moles of products and reactants are not equal, ‘K’ will have units.
- Unit of Kc = $(\text{mol L}^{-1})^{\Delta n}$
- Unit of Kp = $(\text{atm})^{\Delta n}$

HOMOGENEOUS EQUILIBRIA

The equilibria in which the substances involved are present in same phases are called homogeneous equilibria.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

HETEROGENEOUS EQUILIBRIA

The equilibria in which the substances involved are present in different phases are called heterogeneous equilibria.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

APPLICATIONS OF EQUILIBRIUM CONSTANT

PREDICTION OF THE EXTENT OF A REACTION

- **Greater the value of equilibrium constant, greater will be the concentration of products.**
- **In general,**
- **If Kc > 10^3 (i.e. Kc is very large), the reaction proceeds nearly to completion.**
- **If Kc < 10^{-3} (i.e. if Kc is very small), the reaction proceeds rarely.**
- **If the value of Kc is in between 10^3 and 10^{-3} appreciable concentrations of both reactants and products are present.**

PREDICTION OF THE DIRECTION OF THE REACTION

- By knowing the values of Kc and Qc, we can predict the direction of a reaction.
- For a general reaction, $aA + bB \rightleftharpoons cC + dD$ the reaction quotient, $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- If Qc > Kc, the reaction will proceed in the direction of reactants.
- i.e., Backward Reaction will proceed.
- If Qc < Kc, the reaction will proceed in the direction of products.

i.e., Forward Reaction will proceed.
If Qc = Kc, the reaction mixture is at equilibrium.

CALCULATION OF EQUILIBRIUM CONCENTRATIONS

By knowing the value of equilibrium constant, we can calculate the equilibrium concentrations of reactants and products.

RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT (Kc), REACTION QUOTIENT (Qc) AND GIBBS ENERGY (G)

- The Gibb's energy change of a reaction is related to the reaction quotient (Qc) by the equation:

$$\Delta G = \Delta G^0 + RT\ \ln Q$$

- where, ΔG^0 is standard Gibbs energy.
- At equilibrium, $\Delta G = 0$ and $Qc = Kc$

$$0 = \Delta G^0 + RT\ \ln Kc$$

Or, $\Delta G^0 = -\ RT\ \ln Kc$

- On changing the base, we get $\Delta G^0 = -\ 2.303RT\ \log Kc$
- We know that for a spontaneous process ΔG should be negative.
- So the value of Kc should be positive.

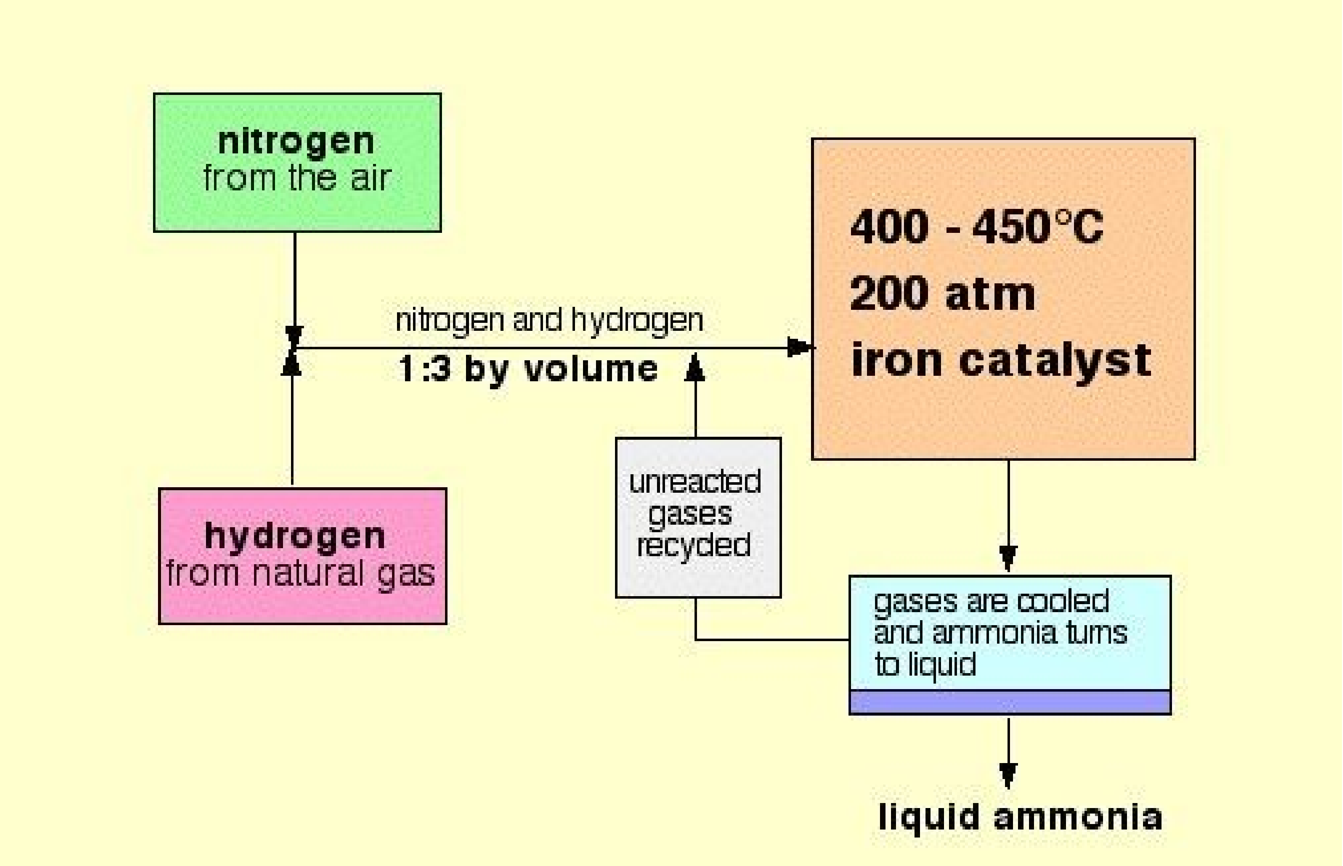
FACTORS INFLUENCING EQUILIBRIUM

LE-CHATLIER’S PRINCIPLE

According to Le-Chatlier Principle, whenever there is a change in pressure, temperature or concentration of a system at equilibrium, the system will try to adjust itself in such a way so as to nullify the effect of that change.

APPLICATIONS OF
LE-CHATLIER’S PRINCIPLE

1. $N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -93.74\ \text{kJ}$



EFFECT OF TEMPERATURE

- Formation of NH_3 is favoured at low temperature as it is an exothermic reaction.
- An increase in temperature will shift the equilibrium in the backward direction as it is endothermic.
- A decrease in temperature favours the forward reaction as it is exothermic.
- So the manufacture of ammonia should be carried out at a lowest possible temperature.
- If the temperature is too low, the kinetic energy of the molecules will be too low and hence the reaction will be extremely slow.
- Therefore, an optimum temperature of about 773K is employed.

EFFECT OF PRESSURE

- **Increase in pressure will favour the formation of ammonia because its formation is accompanied by a decrease in the number of moles.**
- **On the other hand, a decrease in pressure will favour its dissociation.**

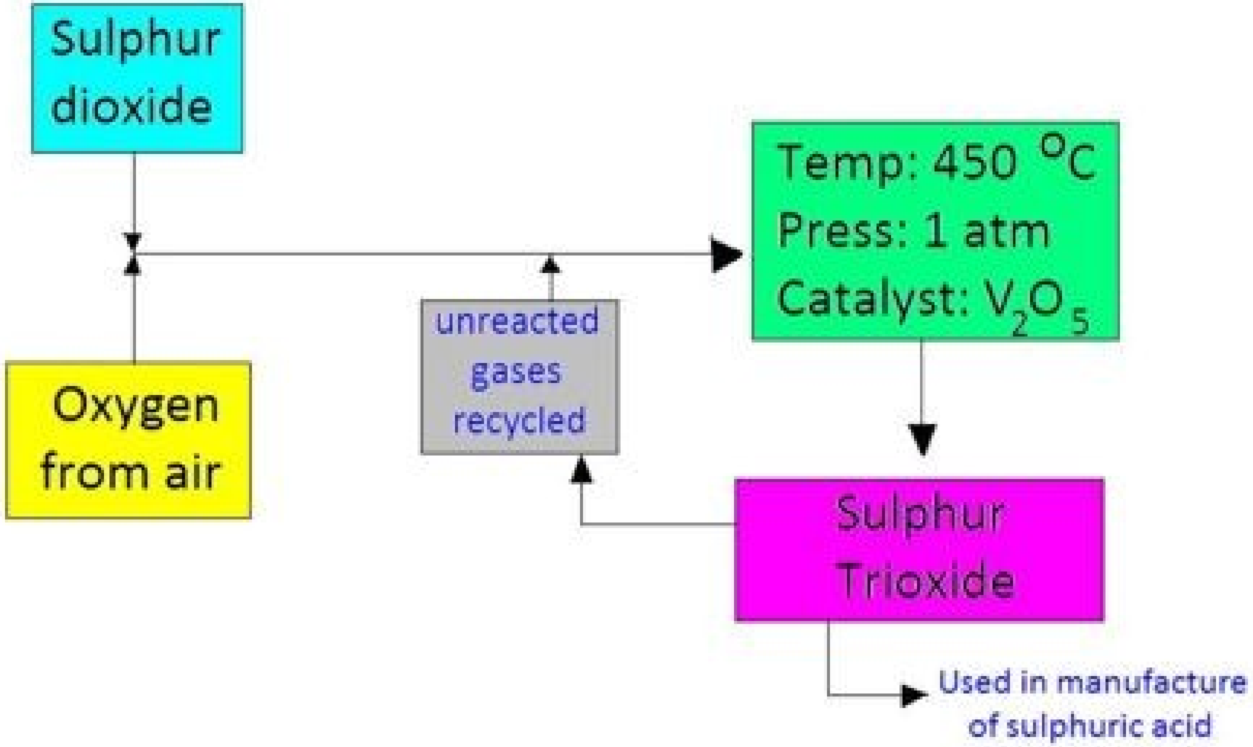
EFFECT OF CONCENTRATION

- **Addition of N_2 or H_2 or removal of NH_3 will favour the formation of ammonia.**
- **Addition of NH_3 or removal of H_2 or N_2 will favour the decomposition of NH_3 .**

TO SUM UP

Low temperature, high pressure and high concentration of N_2 and H_2 will favour the formation of NH_3 .

2. $2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H = -192.50\ kJ$



Sulphur dioxide

Oxygen from air

unreacted gases recycled

Temp: 450 °C
Press: 1 atm
Catalyst: V_2O_5

Sulphur Trioxide

Used in manufacture of sulphuric acid

EFFECT OF TEMPERATURE

- **The formation of SO_3 is exothermic.**
- **Therefore, a decrease in temperature will favour the formation of SO_3 .**
- **An increase in temperature will favour the backward direction.**

EFFECT OF PRESSURE

- Increase in pressure will favour the formation of SO_3 as it is accompanied by a decrease in the number of moles.
- A decrease in pressure will favour its decomposition.

EFFECT OF CONCENTRATION

Addition of SO_2 or O_2 or removal of SO_3 will shift the equilibrium in the forward direction.

TO SUM UP

Low temperature, high pressure and high concentration of SO_2 and O_2 will favour the formation of SO_3 .

3. $PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad \Delta H = +92.05\ kJ$

EFFECT OF TEMPERATURE

- **The dissociation of PCl_5 is endothermic.**
- **Therefore, an increase in temperature will favour its decomposition.**
- **On the other hand, a decrease in temperature will shift the equilibrium in the backward direction.**

EFFECT OF PRESSURE

- Decrease in pressure will favour the decomposition of PCl_5 as it is accompanied by an increase in the number of moles.
- On the other hand, an increase in pressure will shift the equilibrium in the backward direction.

EFFECT OF CONCENTRATION

Addition of PCl_5 increases the rate of decomposition of PCl_5.

TO SUM UP

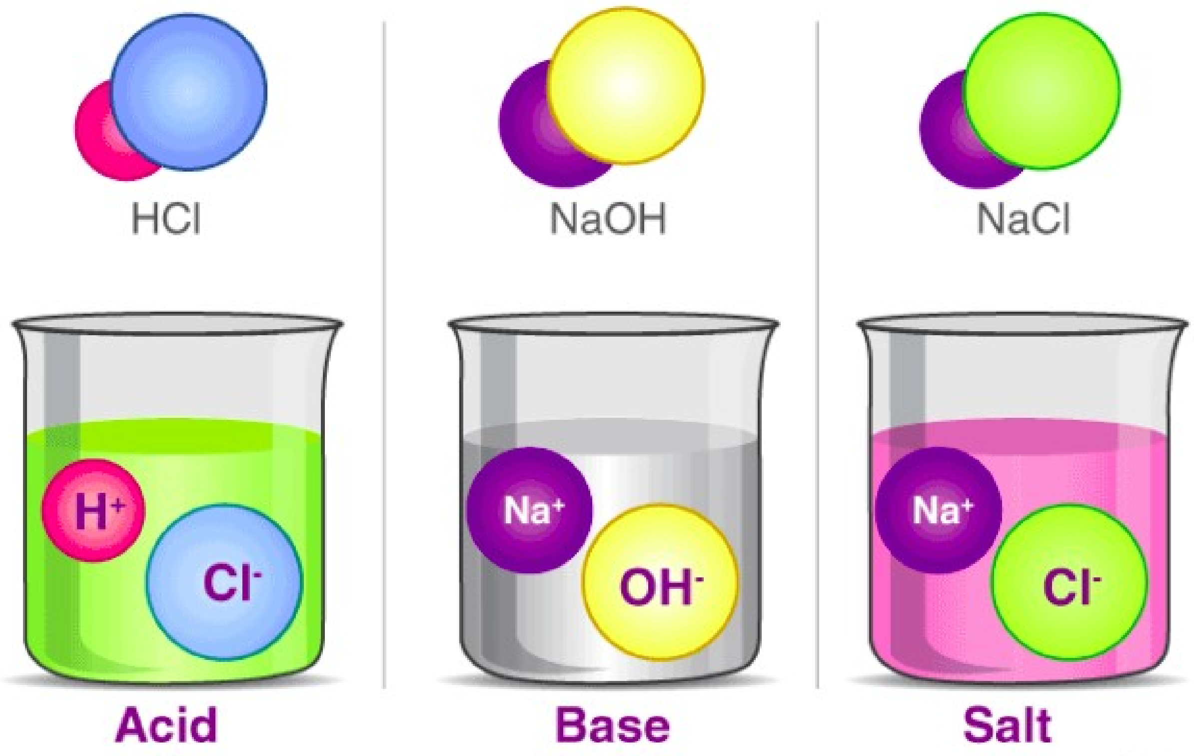
High temperature, low pressure and high concentration of PCl_5 will favour the dissociation of PCl_5.

IONIC EQUILIBRIUM

IONIC EQUILIBRIUM

- **When an electrolyte is dissolved in water, it splits up into the ions.**
- **The process of ionisation is reversible in nature.**
- **Thus there is a state of dynamic equilibrium between the ions and the unionized molecules.**
- **Ionic equilibrium is the equilibrium which is established between the unionized molecules and the ions in solution of weak electrolytes.**

CONCEPTS OF ACIDS, BASES AND SALTS



1. ARRHENIUS CONCEPT

ACID

An acid is a substance which gives H^+ ions in aqueous solutions.

Eg:- HCl, HNO_3 , CH_3COOH etc.

$$HCl \rightleftharpoons H^+ + Cl^-$$

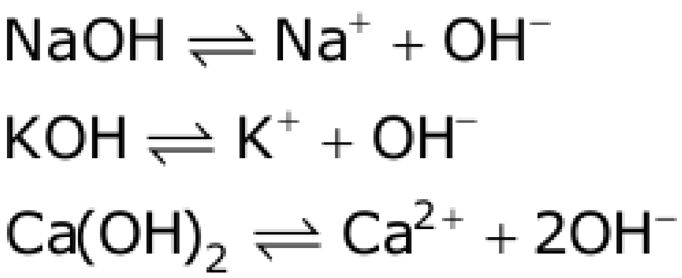
$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

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

BASE

Base is a substance which gives OH^- ions in aqueous solutions.

Eg:- NaOH, KOH, $Ca(OH)_2$ etc.



$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$KOH \rightleftharpoons K^+ + OH^-$$

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

STRONG AND WEAK ACIDS

- Acids which are almost completely ionized in aqueous solutions are called strong acids.
- Eg:- HCl, HNO_3 etc.
- Acids which are only slightly ionized in aqueous solutions are called weak acids. Eg:- CH_3COOH, HCOOH etc.

STRONG AND WEAK BASES

- **Bases which are almost completely ionized in aqueous solutions are called strong base. Eg:- NaOH, KOH etc.**
- **Bases which are only weakly ionized in aqueous solutions are called weak bases. Eg:- NH_4OH, $Ca(OH)_2$ etc.**

2. BROSTED AND LOWRY CONCEPT

- This concept was put forward by Bronsted and Lowry in 1923.
- An acid is a substance which can donate a proton.
- Base is a substance which can accept a proton.
- In other words, an acid is a proton donor and base is a proton acceptor.

- Eg:-$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$
- Here HCl loses a proton and is an acid, whereas NH_3 accepts a proton and is a base.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

$$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$$

AMPHOTERIC SUBSTANCES

- **Substances which are capable of donating as well as accepting protons are called amphoteric substances.**
- **Eg:- H_2O behaves as an acid as well as a base.**

As a base: $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

As an acid: $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$

CONJUGATE ACID BASE PAIRS

- **Consider an acid base reaction,** $HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$
- **Here acid donates a proton and becomes a base.**
- **The base accepts a proton and becomes an acid.**
- **The base formed from an acid is called conjugate base of the acid**
- **The acid formed from a base is called the conjugate acid of the base.**

- In the above example, Cl^- is the conjugate base of HCl and NH_4^+ is the conjugate acid of NH_3 .
- The pairs of acids and bases which are formed from each other by the gain or loss of a proton are called conjugate acid base pairs.

RELATIVE STRENGTH OF CONJUGATE ACIDS AND BASES

- According to Bronsted Lowry Concept, the strength of an acid depends upon its tendency to donote a proton.
- The strength of a base depends up on its tendency to accept a proton.

Eg:- $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

- **HCl has a strong tendency to donate proton, therefore it is a strong acid.**
- **But Cl ─ ion has very little tendency to accept a proton.**
- **Therefore, Cl^- ion is a weak base.**
- **The conjugate base of a strong acid is a weak base.**
- **The conjugate base of a weak acid is a strong base.**

3. LEWIS CONCEPT

- An acid is a substance which can accept a pair of electrons.
- A base is a substance which can donate a pair of electrons.
- In other words, an acid is an electron pair acceptor and base is an electron pair donor.
- Eg:- BF_3 , $AlCl_3$, H^+ etc are Lewis acids.
- Eg:-—NH_3 , R—O—H, CN^- , I^- , OH^- etc are Lewis bases.

IONIC PRODUCT OF WATER

- Water is a weak electrolyte and undergoes ionisation as $H_2O \rightleftharpoons H^+ + OH^-$
- According to the law of chemical equilibrium,

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

- Since water dissociates only very slightly, the concentration of undissociated water may be taken as a constant.

$$K[H_2O] = [H^+][OH^-]$$

$$K \text{ x a constant} = [H^+][OH^-]$$

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

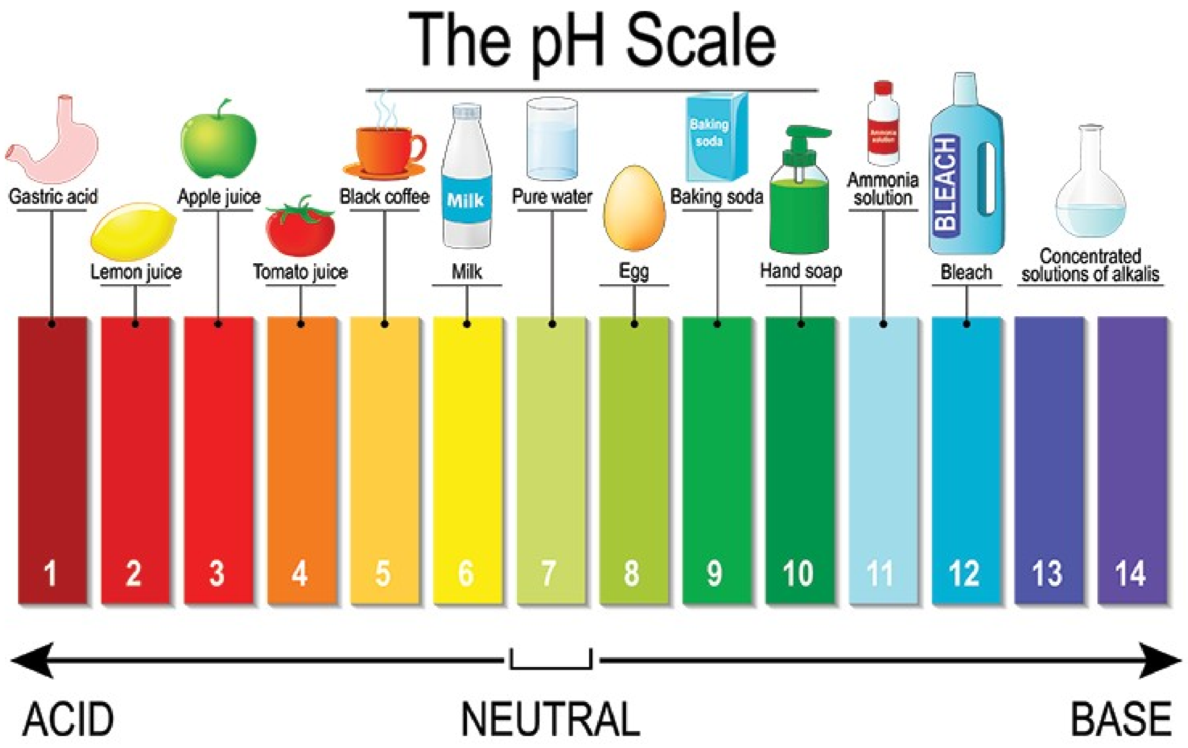
- Ionic product of water is the product of the concentrations of hydrogen ions and hydroxyl ions in water or any aqueous solution at a given temperature.

pH SCALE

- **The term pH was introduced by Sorenson.**
- **It is the short form of the Danish words Potenz Hydrogen, meaning power of hydrogen.**
- **It measures the concentrations of H^+ ions.**
- **pH is defined as the negative logarithm of hydrogen ion concentration in moles per litre.**

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

- For acidic solution, $pH < 7$
- For basic solution, $pH > 7$
- For neutral solution $pH = 7$


The pH Scale
Gastric acid
Lemon juice
Apple juice
Tomato juice
Black coffee
Milk
Milk
Pure water
Egg
Baking soda
Baking soda
Hand soap
Ammonia solution
Bleach
BLEACH
Concentrated solutions of alkalis
1
2
3
4
5
6
7
8
9
10
11
12
13
14
ACID
NEUTRAL
BASE

pOH

pOH is defined as the negative logarithm of the hydroxyl ion concentration in moles per litre.

$P^{OH} = -\log[OH^-]$

Pkb

It is the negative logarithm of K_b .

P^{kb} = -logk_b

Lower the value of $P^{k}b$, stronger will be the base.

Pkw

It is the negative logarithm of K_w .

P^{Kw} =- log Kw

RELATION BETWEEN pH AND pOH

$$pH + pOH = 14$$

IONISATION CONSTANTS OF WEAK ACIDS AND WEAK BASES

- Consider a solution of acetic acid as an example.
- Suppose the concentration of acetic acid before dissociation is ‘C’ moles per litre, while the degree of ionisation is ‘α’.

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

- **Initial Conc.** $C \qquad 0 \qquad 0$
- **Conc. at equilibrium** $C(1-\alpha) \qquad C\alpha \qquad C\alpha$
- Substituting the values in equilibrium constant, we get

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$K_a = \frac{C\alpha . C\alpha}{C(1-\alpha)}$$

$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)}$$

$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$

- ❖ Since the degree of ionisation of acetic acid is very small as compared to 1, therefore $1-\alpha$ may be taken as approximately equal to 1.

- ❖ Then $K_a = C\alpha^2$

$$\alpha^2 = \frac{K_a}{C}$$

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

INDICATORS

- A substance which indicates the completion of a chemical reaction by a sharp colour change.
- An acid base indicator is a substance which changes colour according to the hydrogen ion concentration or pH of the solution to which it is added.
- An acid base indicator is either a weak organic acid or a weak base.
- They possess different colours in ionized and unionized state.

- Consider the dissociation of the acid base indicator, HIn.

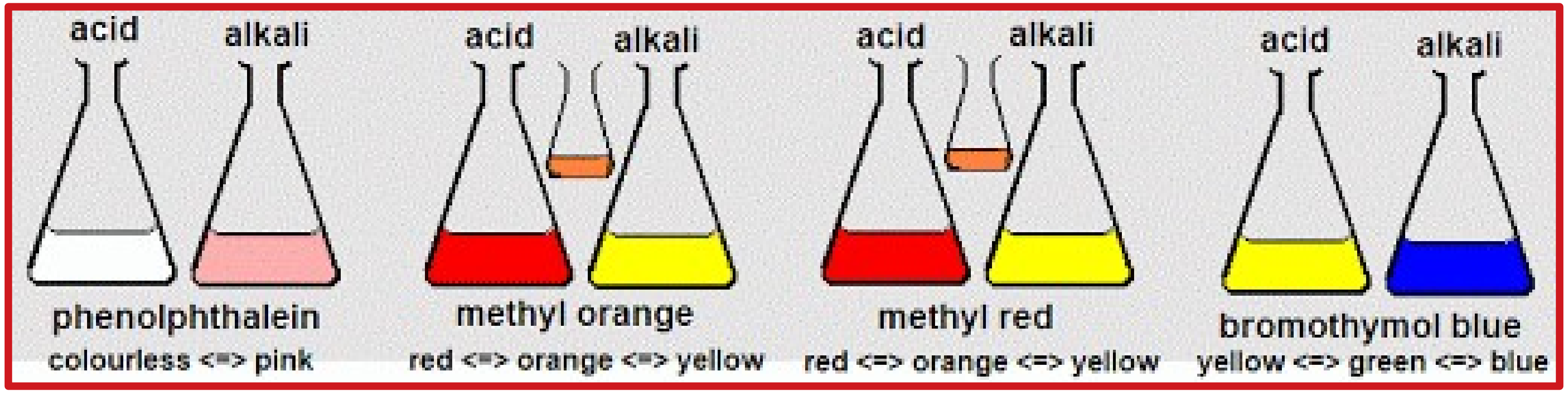
$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

Colour 1 **Colour 2**

- The equilibrium constant can be represented as

$$KIn = \frac{[H_3O^+][In^-]}{[HIn][H_2O]}$$

- But $[H_2O]$ is a constant.
- Therefore, $KIn = \frac{[H_3O^+][In^-]}{[HIn]}$
- Where Kin is the indicator constant.


acid
alkali
phenolphthalein
colourless <=> pink
acid
alkali
methyl orange
red <=> orange <=> yellow
acid
alkali
methyl red
red <=> orange <=> yellow
acid
alkali
bromothymol blue
yellow <=> green <=> blue

SOLUBILITY PRODUCT

- Consider a saturated solution of a sparingly soluble salt.
- In the saturated solution of a sparingly soluble salt, a dynamic equilibrium is established between undissolved molecules and the dissociated ions.

- Consider the sparingly soluble salt AB

$$\underset{\text{Undissolved molecules}}{AB} \rightleftharpoons \underset{\text{Dissociated ions}}{A^+ + B^-}$$

$$K = \frac{[A^+][B^-]}{[AB]}$$

$$K[AB] = [A^+][B^-]$$

- At a given temperature, for a saturated solution, [AB] is a constant. i.e., K’

$$KK' = [A^+][B^-]$$

$$K_{sp} = [A^+][B^-]$$

- **Where Ksp is known as solubility product.**
- **Solubility product of an electrolyte at a fixed temperature is the product of the concentrations of the ions in a saturated solution of an electrolyte.**

COMMON ION EFFECT

In a solution of a weak electrolyte, a dynamic equilibrium is established between the un dissociated molecules and the dissociated ions.

- Consider a weak electrolyte AB,

$$AB \rightleftharpoons A^{+} + B^{-}$$

- Applying law of mass action

$$K = \frac{[A^{+}][B^{-}]}{[AB]}$$

- **To this solution, another electrolyte which can supply the common ion A^+ or B^- is added.**
- **In order to keep the K value constant, AB must suppress its ionisation.**
- **Therefore, the ionisation of a weak electrolyte can be suppressed by the addition of another electrolyte containing a common ion.**
- **This effect is known as common Ion effect.**
- **The suppression of the dissociation of the weak acid or a weak base by the addition of a strong electrolyte containing a common ion is called common ion effect.**

- **Eg:-Consider the dissociation of the weak base NH_4OH.**

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

- **The dissociation of NH_4OH will be suppressed by the addition of an electrolyte like NH_4Cl which can supply the common ion, NH_4^+.**

BUFFER SOLUTION

- A solution which maintains its pH fairly constant even on the addition of a small amount of an acid or a base. **OR**
- A buffer solution is a solution which resists the change in pH value on the addition of small amount of acid or base.
- Buffers are of two types.

ACIDIC AND BASIC BUFFER

A mixture of a weak acid and its salt with a strong base is called an **acid buffer.**

Eg:- A mixture of CH_3COOH and CH_3COONa

A mixture of weak base and its salt with a strong acid are called **basic buffer.**

Eg:- A mixture of NH_4OH and NH_4Cl

BUFFER ACTION

The ability of the buffer solution to resist the change in pH value on the addition of small amount of an acid or a base is called buffer action.

pH OF A BUFFER SOLUTION
HENDERSON - HASSELBALCH EQUATION

- Consider an acidic buffer prepared by mixing a weak acid HA and its conjugate base A^-.
- The weak acid HA ionises in water as $HA + H_2O \rightleftharpoons H_3O^+ + A^-$
- The dissociation constant of weak acid, $Ka = \frac{[H_3O^+][A^-]}{[HA]}$
- On rearranging the expression, we get $[H_3O^+] = Ka \frac{[HA]}{[A^-]}$
- Taking –ve logarithm on both sides:
- $-\log[H_3O^+] = -\log Ka - \log \frac{[HA]}{[A^-]}$
- $pH = pK^a + \log \frac{[A^-]}{[HA]}$
- This equation is known as **Henderson-Hasselbalch equation**.

HENDERSON - HASSELBALCH EQUATION

- The equation can be written in general form as
- For a acidic buffer, $pH = pK^{a} + \frac{\log[Salt]}{[Acid]}$
- For a basic buffer, $pOH = pK^{b} + \frac{\log[Salt]}{[Base]}$
- $pH = 14 - pOH$
- $pH = 14 - \left[pk^{b} + \frac{\log[Salt]}{[Base]}\right]$

HYDROLYSIS OF SALTS

- **The phenomenon of interaction of anions and cations of the salt with H^+ or OH^- ions furnished by water to give alkaline or acidic solutions is known as salt hydrolysis.**
- **The cations of strong bases and anions of strong acids do not get hydrolyse.**
- **So the solutions of salts formed from strong acids and bases are neutral.**
- **i.e., their pH is 7.**
- **Eg. $NaCl$, KCl, $NaNO_3$, KNO_3 , Na_2SO_4 , K_2SO_4 etc.**

HYDROLYSIS OF SALT OF STRONG BASE AND WEAK ACID

- **Sodium acetate (CH_3COONa), sodium carbonate (Na_2CO_3), potassium cyanide (KCN) etc.are examples for such type of salts.**
- **Here only the anion of the weak base undergoes hydrolysis (since cation of the strong base does not hydrolyse).**
- **So the solution of such salts will be basic. i.e. $pH > 7$.**
- **pH of such salt solution is given by $pH = 7 + ½ (pKa + \log C)$**
- **Where C is the concentration of salt.**

HYDROLYSIS OF SALT OF WEAK BASE AND STRONG ACID

- **NH_4Cl, NH_4NO_3 , $CuSO_4$ etc are examples for such type of solutions.**
- **Here only cation of weak base undergoes hydrolysis.**
- **So the solution is acidic.**
- **pH of such a solution is given by $pH = 7 + \frac{1}{2}(pKb + \log C)$.**

HYDROLYSIS OF SALT OF WEAK BASE AND WEAK ACID

- Ammonium acetate (CH_3COONH_4), ammonium carbonate [$(NH_4)_2CO_3$] etc. are examples for such type of salts.
- Here both cation and anion undergo hydrolysis.
- Hence weak acid and weak base are produced in solution.
- So the solution may be neutral, acidic or basic depending upon the relative strength of acid and base formed.
- pH of such a solution is given by $pH = 7 + ½ (pKa + pKb)$.


Thank You!