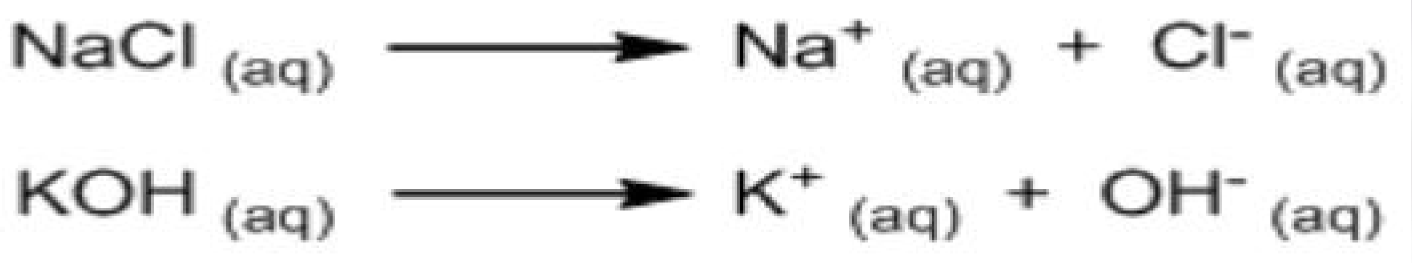
Ionic Equilibrium

Ionic compounds are classifed into 2 groups

- **Electrolyte**: those substance which dissolves in water to make it aqueous solution and can conduct electricity through them, eg: NaCl, HCl conduct electricty in aqueous solution

Faraday futher classifed electrolytes into two types:

Strong Electrolyte: Those ionic compounds which dissolves completely in water: Eg NaCl



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

$$KOH_{(aq)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$$

Weak Electrolytes: Those ionic compounds which partially dissolves or dissolves incompletely in water, Eg; acetic acid

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

Non-electrolyte: Those substance which does not conduct electricity in aqueous or molten state, eg: Glucose in water, HCl in benzene , urea etc

Ionic Equilibrium

- The weak electrolytes are ionized only partially (feebly). The ions produced as a result of ionization of weak electrolytes are present in dynamic equilibrium with the unionized molecules. Such equilibrium is called ionic equilibrium.
- the ionic equilibrium is the equilibrium which is established between the unionized molecules and the ions in solution of weak electrolytes

$$CH_3COOH \underset{\text{equilibrium}}{\overset{\text{water}}{\rightleftharpoons}} CH_3COO^- + H^+$$

Arrhenius Theory of Ionization

- an electrolyte when dissolved in water converts into the charged particles, called ions. This is called ionization. The ions are free to move throughout the bulk of the solution
- The positively charged ions are called cations and the negatively charged ions is called anions
- In an electrolytic solution, the total number of positive charges equals to total number of negative charges so that the solution becomes neutral

The ions have a tendency to reunite to form unionizes molecule, there exist a dynamic quilibrium between the ions and unionized molecules, such equilibrium is characterized by ionization constant.

$$AB \leftrightarrow A^+ + B^-$$

the ionization constant is given by,

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

- The property of an electrolyte in the solution are due to the properties of the ions produced.
- Ionization is an incomplete process. The extent of ionization of electrolyte is expressed in terms of degree of ionization (∝)

$$\propto = \frac{\text{number of moles splitted into ions}}{\text{total number of moles dissolved}}$$

the degree of ionization for strong electrolyte is nearly 1

whereas that for weak electrolyte is very less than 1

- The electrical conductivity is due to migration of ions towards oppositely charged electrodes

Ionization constant and Degree of ionization

- Ionic theory says that a weak electrolyte forms an ionization equilibrium between ionized and unionized species in the solution at a given temperature
- let us consider a weak electrolyte AB in aqueous solution

$$\mathrm{AB} \leftrightarrow \mathrm{A}^{+} + \mathrm{B}^{-}$$

Applying law of mass action,

$$\mathrm{K} = [\mathrm{A}^{+}]\,[\mathrm{B}^{-}]/\,[\mathrm{AB}]$$

Ionization constant(K) is defined as the ratio of product of molar concentration of ionizes species to molar concentration of unionizes species present at the state of equilibrium at a given temperature

K is affected by temperature, higher the temperature, greater the value of K

Degree of Ionization of weak electrolyte

The fraction of the total number of molecules of an electrolyte which ionizes into ions is called degree of ionization or degree of dissociation. It is denoted by α .

$$\alpha = \frac{\text{number of ionized molecules}}{\text{total number of molecules involved}}$$

Factors Affecting Degree of Ionization

- **Nature of solvent**: higher the polarity of a solvent higher will be its ionization power of weak electrolyte, eg: degree of ionization for formic acid in water is much more greater than that in ethanol
- **Effect of temperature**: degree of ionization of a weak electrolyte solution increases with increses in temperature
- **Effect of common ion:** addition of an electrolyte containing one of the common ion to the given weak electrolyte deoresses degree of ionization, which is called common ion effect. eg, degree of ionization of NH_4OH solution decreses at constant temperature with addition of NH_4Cl due to the common ion NH_4^+
- **Effect of dilution of weak electrolyte:** degree of ionization of a weak electrolyte increases with increase in dilution or with drecreas of concentration at constant temperature.

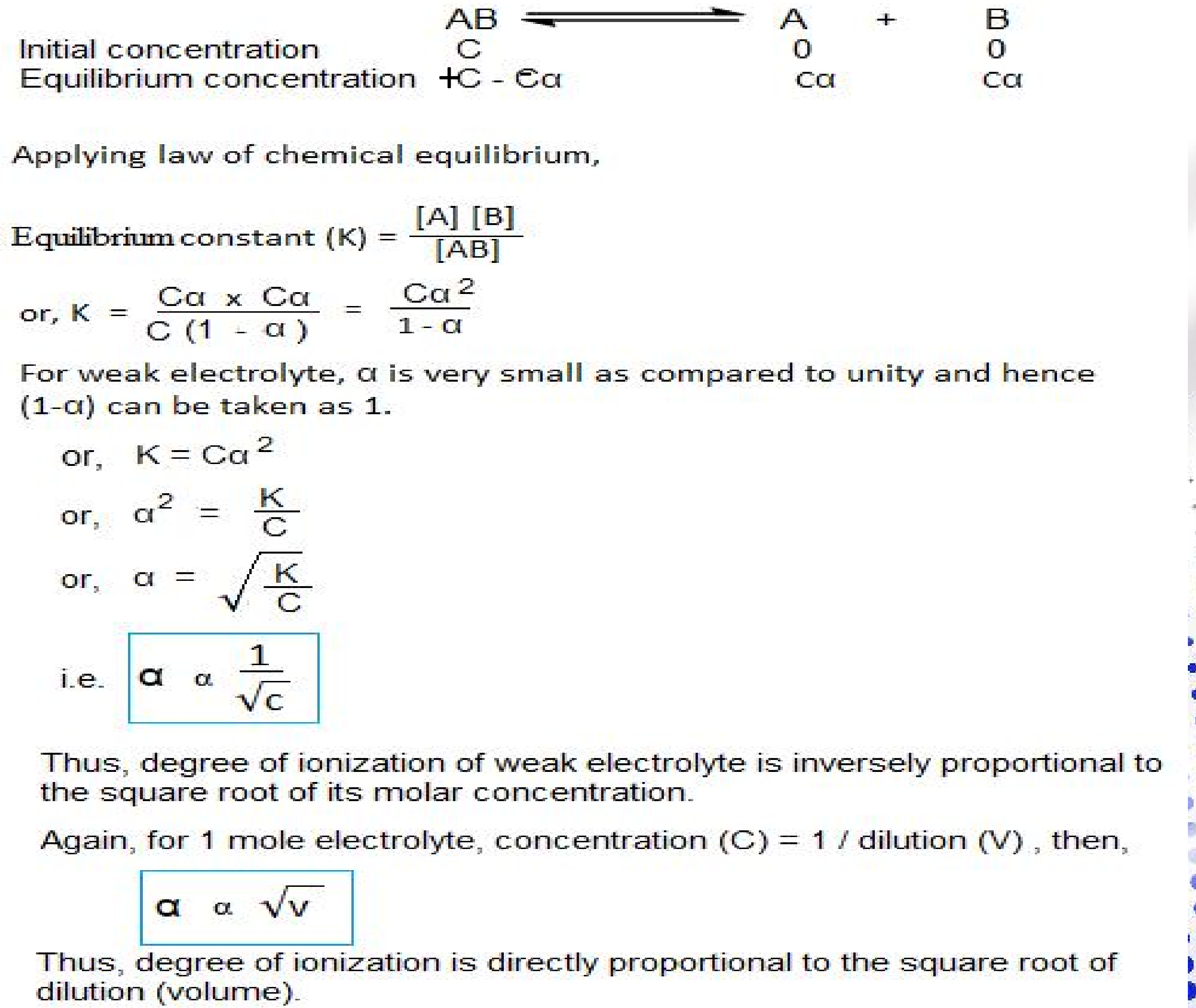
Ostwald’s law of Dilution and degree of Ionization

- **Statement** : At constant temperature, degree of ionization of a weak electrolyte is directly proportional to the square root of dilution(volume) and inversely proportional to the square root of concentration.

Mathematically,

$$\boxed{\alpha \propto \frac{1}{\sqrt{c}}} \quad \text{and} \quad \boxed{\alpha \propto \sqrt{v}}$$

- Let us consider the ionization of weak electrolyte AB in water. Suppose C mole-1 be the concentration of the electrolyte and α be the degree of ionization. Then,



	AB $\rightleftharpoons$	A	+	B
Initial concentration	C	0		0
Equilibrium concentration	C - Cα	Cα		Cα

Applying law of chemical equilibrium,

$$\text{Equilibrium constant (K)} = \frac{[A]\,[B]}{[AB]}$$

$$\text{or, } K = \frac{C\alpha \times C\alpha}{C\,(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

For weak electrolyte, α is very small as compared to unity and hence (1-α) can be taken as 1.

$$\text{or, } K = C\alpha^2$$

$$\text{or, } \alpha^2 = \frac{K}{C}$$

$$\text{or, } \alpha = \sqrt{\frac{K}{C}}$$

$$\text{i.e. } \boxed{\alpha \propto \frac{1}{\sqrt{c}}}$$

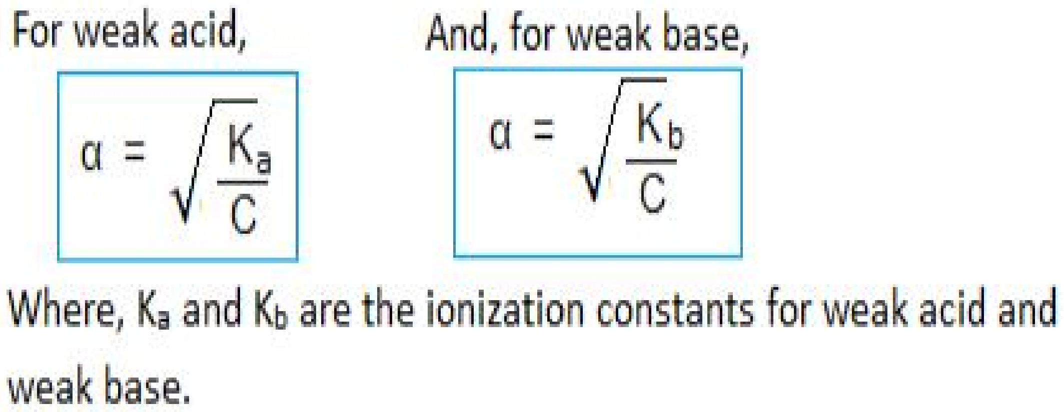
Thus, degree of ionization of weak electrolyte is inversely proportional to the square root of its molar concentration.

Again, for 1 mole electrolyte, concentration (C) = 1 / dilution (V) , then,

$$\boxed{\alpha \propto \sqrt{v}}$$

Thus, degree of ionization is directly proportional to the square root of dilution (volume).

From Ostwald’s dilution law



For weak acid,

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

And, for weak base,

$$\boxed{\alpha = \sqrt{\frac{K_b}{C}}}$$

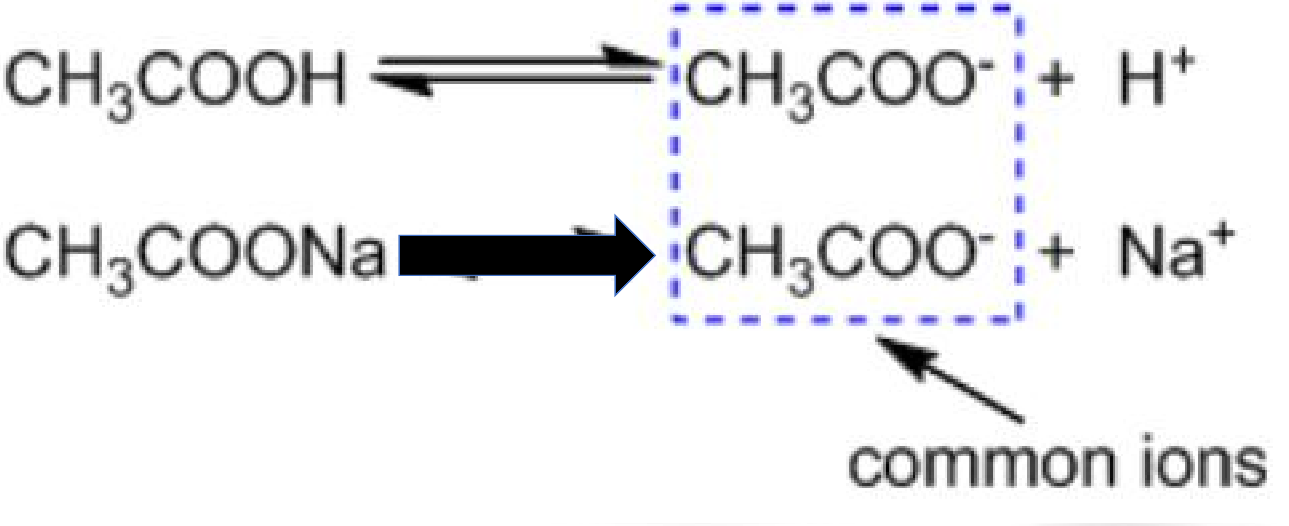
Where, K_a and K_b are the ionization constants for weak acid and weak base.

- **Limitation of Ostwald’s dilution law** : This law is applicable only to weak electrolytes and it fails in case of strong electrolyte.
- **Application**: this law can be applied to find degree of ionization of a weak electrolyte solution at any given temperature, to calculate the value of K

Common Ion Effect and degree of Ionization

- The supression of degree of dissociation of weak electrolyte by adding strong electrolyte having one of the ion common to weak electrolyte is known as common ion effect, eg:

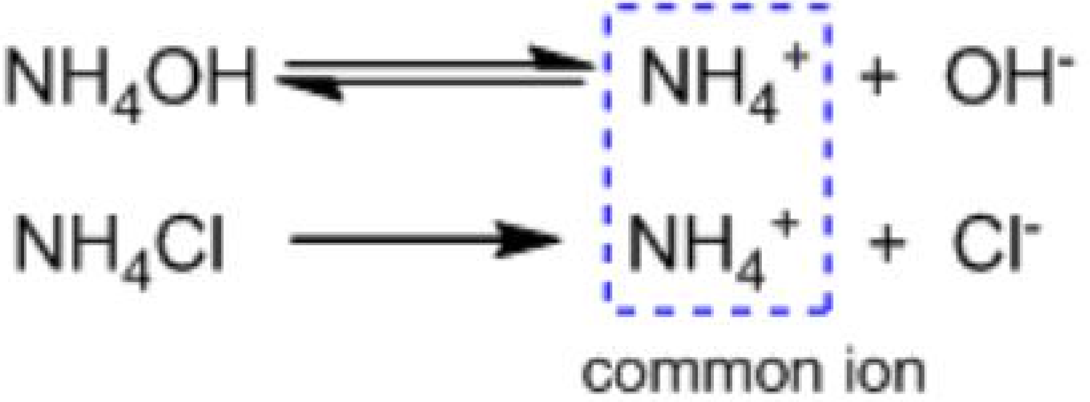
1. degree of dissociation of acetic acid is supressed by adding sodium acetate



$$CH_3COOH \rightleftharpoons \boxed{CH_3COO^-} + H^+$$

$$CH_3COONa \longrightarrow \boxed{CH_3COO^-} + Na^+$$

2. degree of dissociation of ammonium hydroxide is supressed by adding ammonium chloride



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

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

Introduction to Acids and Bases

- chemical substances were classified into groups such as acids, bases and salts
- early views of chemists: for acid - tested sour, changed the colour of blue litmus to red, reacted with certain metals to liberate H_2 gas, produced CO_2 gas from carbonates and bicarbonates
- bases were substance that tested bitter, felt slippery, changed colour of red litmus to blue,
- when an acid and base reacts, neutralization takes place forming salt and water

1. Arrhenius Concept of Acids and Bases

- **An acid is a compound which gives H^+ ions in water. Eg.**

$$HCl \xrightarrow{water} H^+ + Cl^-$$

$$H_2SO_4 \xrightarrow{water} 2H^+ + SO_4^{--}$$

- **A base is a compound which gives OH^- ions in water.**

$$NaOH \xrightarrow{water} Na^+ + OH^-$$

$$Ca(OH)_2 \xrightarrow{water} Ca^{2+} + 2\,OH^-$$

Limitations of Arrhenius concept

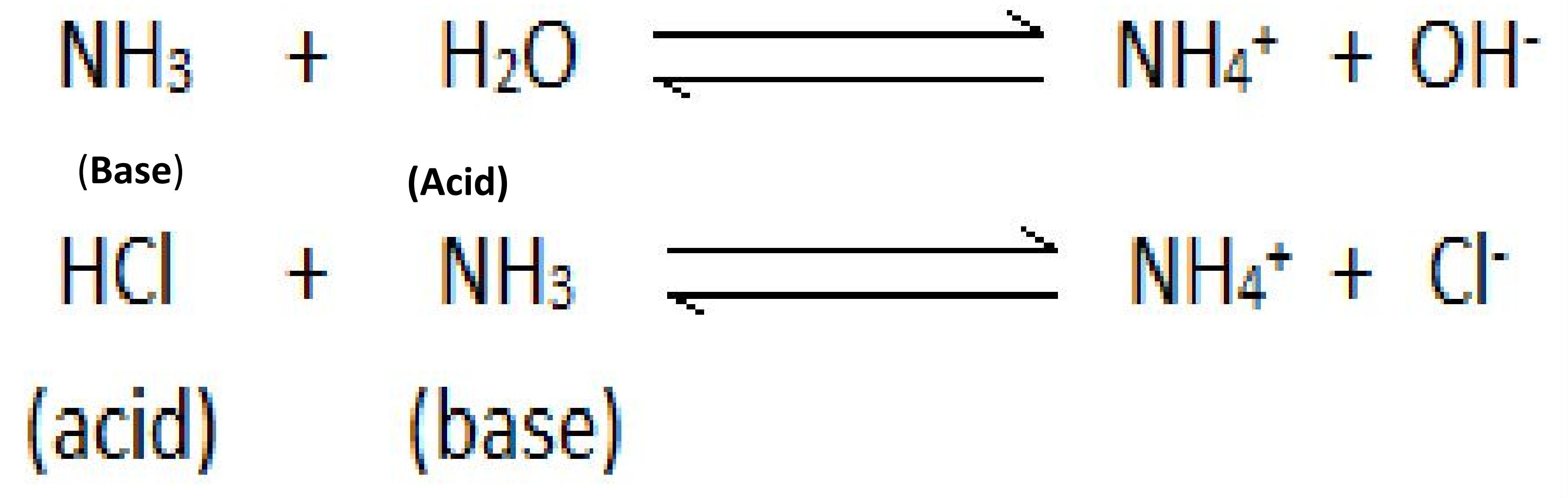
- Arrhenius concept is limited to aqueous medium only. It fails to explain the behavior of acids and bases in non-aqueous medium.
- It fails to explain the acidic nature of CO_2, SO_2, NO_2 etc. which do not contain any hydrogen.
- It fails to explain the basic nature of CaO, NH_3, Na_2CO_3, etc. which do not contain hydroxyl group.
- CH_4 contains hydrogen but is not an acid. Similarly, CH_3OH have OH group but is not a base.

2. Bronsted – Lowry Concept of acids and bases

- It is a protonic concept, I.e Transfer of Proton (H^+)
- An acid is a substance that can donate a proton.
- A base is a substance that accepts a proton. Eg:

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

- HCl donates proton and H_2O accepts proton. Hence HCl is an acid and H_2O is base.



$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

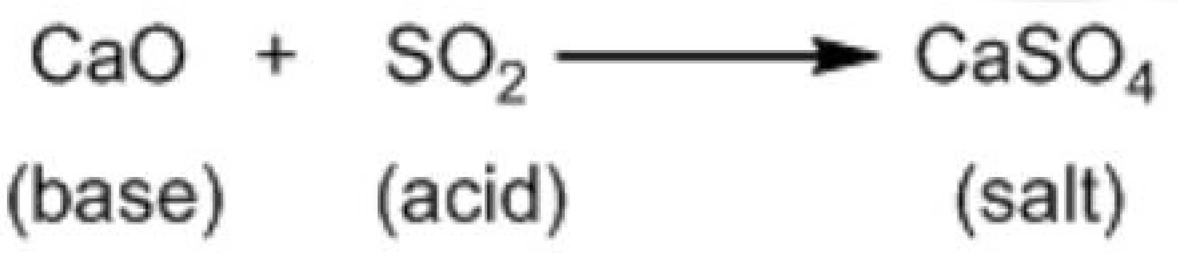
(Base) (Acid)

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

(acid) (base)

Limitations of Bronsted – Lowry Concept :

- Substances like BF_3, $AlCl_3$, etc. do not contain any hydrogen and hence cannot give a proton but behave as acids.
- It can not explain the reaction between acidic oxide like CO_2, SO_2, SO_3, etc and the basic oxides like CaO, MgO, etc. where there is no proton transfer.

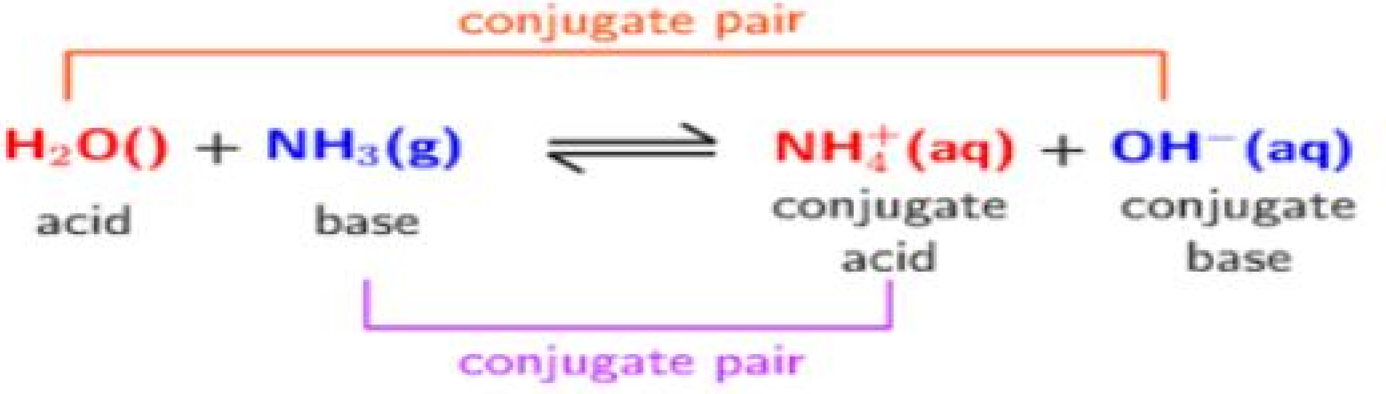


$$\underset{\text{(base)}}{CaO} + \underset{\text{(acid)}}{SO_2} \longrightarrow \underset{\text{(salt)}}{CaSO_4}$$

- it explain the amphoteric nature of NH_3 & H_2O but not the amphoteric nature of **SO_2**

Conjugate Acid- Base pair

- A pair of acid and base that differs from each other by a single proton(H^+) is known as conjugate acid – base pair.



- in this reaction, H_2O and OH^- are conjugate acid-base pair because these two differ from eachother by H^+ , other pair is NH_3 and NH_4^+

Conjugate acid $\rightleftharpoons$ Conjugate base + H^+

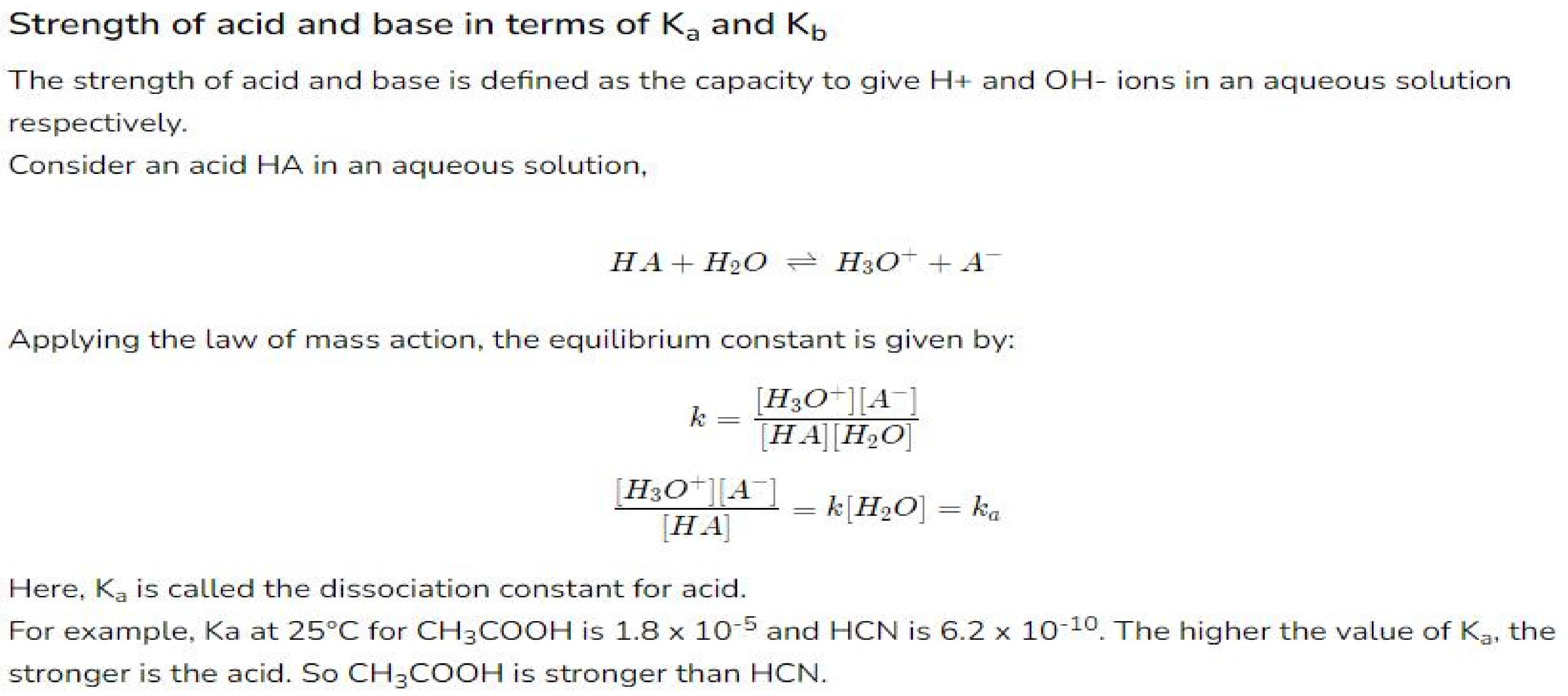
Relative strength of acid and bases

- strength of an acid(or base) is defined as its capacity to give H^+ ion (OH^- ions) in water
- relative strength of two acids or bases can be compared by compairing their H+ ion or OH^- ion concentration reespectively in their equimolar solution in water
- those acids and bases which ionizes completely are called strong acids(HCl, H_2SO_4, HClO) and strong bases(NaOH, KOH, $Ba(OH)_2$) respectively
- those acid and bases which ionizes only to a limited extent in solutions are called weak acids(CH_3COOH, $(COOH)_2$)and weak bases (NH_4OH, $Cu(OH)_2$)

- strength of an acid is expressed in terms of dissociation constant of the acid (Ka)
- higher the value of Ka, higher will be the concentration of H+ ion
- higher the value of Kb, higher will be the concentration of OH- ion,
- relative strength is also expressed in terms of pKa and pKb

  pKa = -logka

  pKb= -logKb



Strength of acid and base in terms of K_a and K_b

The strength of acid and base is defined as the capacity to give H+ and OH- ions in an aqueous solution respectively.

Consider an acid HA in an aqueous solution,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

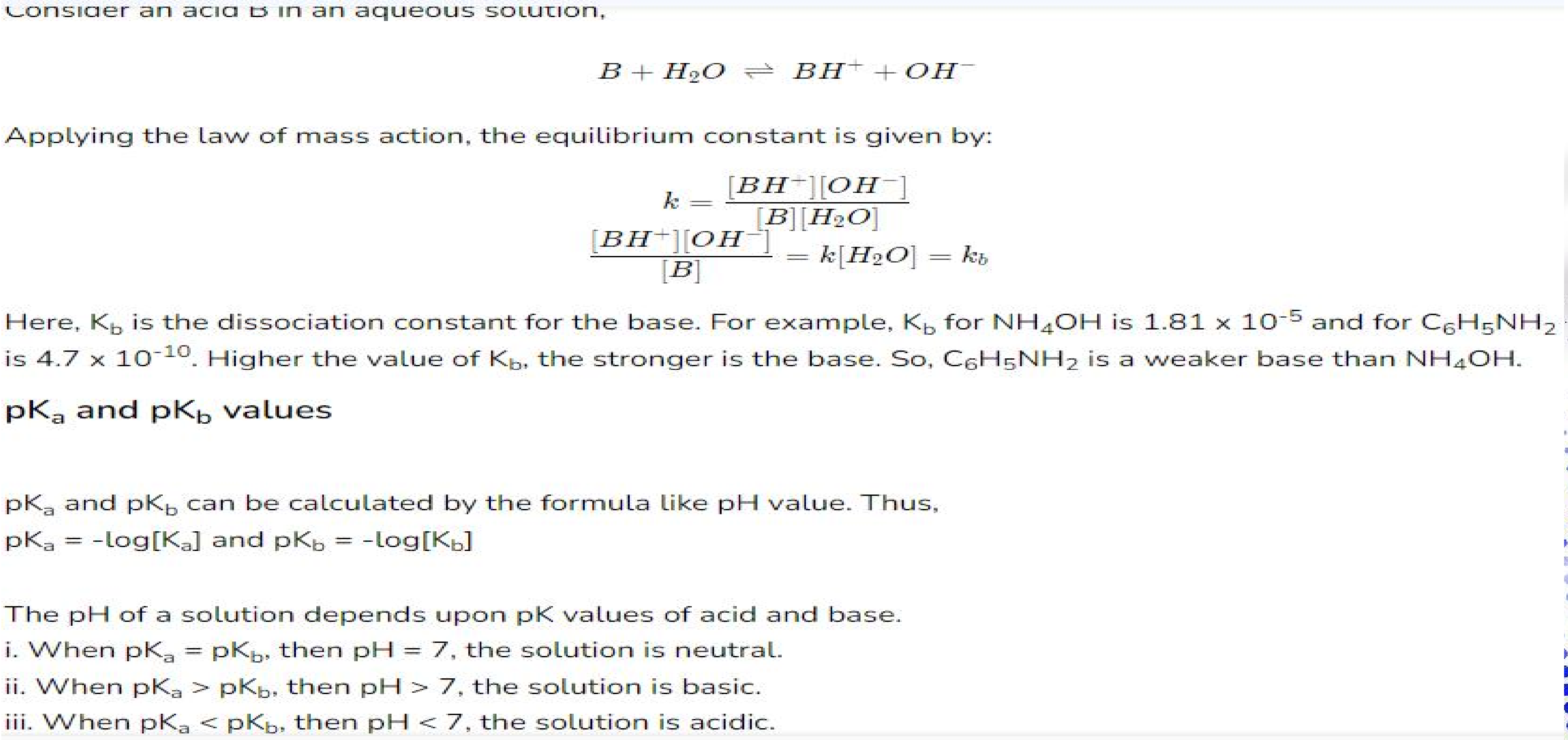
Applying the law of mass action, the equilibrium constant is given by:

$$k = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$\frac{[H_3O^+][A^-]}{[HA]} = k[H_2O] = k_a$$

Here, K_a is called the dissociation constant for acid.

For example, Ka at 25°C for CH_3COOH is 1.8×10^{-5} and HCN is 6.2×10^{-10}. The higher the value of K_a, the stronger is the acid. So CH_3COOH is stronger than HCN.



Consider an acid B in an aqueous solution,

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Applying the law of mass action, the equilibrium constant is given by:

$$k = \frac{[BH^+][OH^-]}{[B][H_2O]}$$
$$\frac{[BH^+][OH^-]}{[B]} = k[H_2O] = k_b$$

Here, K_b is the dissociation constant for the base. For example, K_b for NH_4OH is 1.81×10^{-5} and for $C_6H_5NH_2$ is 4.7×10^{-10}. Higher the value of K_b, the stronger is the base. So, $C_6H_5NH_2$ is a weaker base than NH_4OH.

pK_a and pK_b values

pK_a and pK_b can be calculated by the formula like pH value. Thus,
$pK_a = -\log[K_a]$ and $pK_b = -\log[K_b]$

The pH of a solution depends upon pK values of acid and base.
i. When $pK_a = pK_b$, then pH = 7, the solution is neutral.
ii. When $pK_a > pK_b$, then pH > 7, the solution is basic.
iii. When $pK_a < pK_b$, then pH < 7, the solution is acidic.

Auto Ionization, Equilibrium and Ionic product(Kw) of water

water is very weak electrolyte, ionizes by itself at constant temp

$H_2O + H_2O \leftrightarrow H_3O+ + OH-$

The eq. constant is

$Keq= [H_3O^+]\ [OH^-]/[H_2O][H_2O]$

or, $K= [H_3O][OH^-]/[H_2O]$

where, $K=Keq[H_2O]$ is ionization constant for water which is a constant term denoted by Kw i.e;

$Kw= [H_3O+][OH-]$

for simplicity,

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

where,**Kw is called ionic product of water and it is constant at a given temp**

Hence, ionic product of water is defined as the product of molar concentration of H+ and OH- ion present at state of auto ionization at constant temp. its value is **$1x10^{-14}$ at 25^0C**

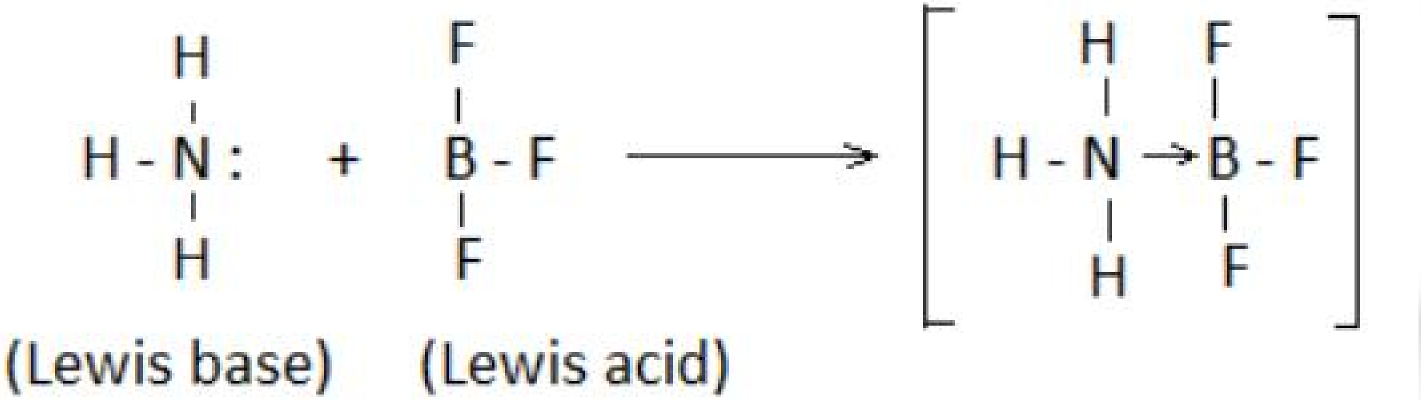
Significance of Kw

1. for pure water, [H+]=[OH-].= 10^{-7}M at 25^{0}C
2. for acid solution,[H+]>[OH-], i.e; [H+]> 10^{-7}M , [H+][OH-]=10^{-14} at 25^{0}C
3. for basic solution,[H+] < [OH-], i.e; [H+]< 10^{-7}M, [H+][OH-]=10^{-14} at 25^{0}C

- value of Kw increases with increase in temperature, at 65^{0}C, Kw= 1×10^{-13}

Lewis concept of acids and bases:

- An acid is a substance which can accept a pair of electrons.
- A base is a substance which can donate a pair of electrons.



$$H_3N: + BF_3 \longrightarrow [H_3N \rightarrow BF_3]$$

Limitations of Lewis concept:

- It does not explain the acidic behavior of well known protic acids such as HCl, H_2SO_4, etc. which do not form coordinate bond with bases.
- It does not explain the relative strength of acids and bases , as it is not based on ionization.
- it cannot explain how NH4Cl is strong acid in liquid ammonia
- it cannot explain the acidic nature of NH3 and H2S in following reaction;

$NH_3 + Cl^- \rightarrow NH_2^- + HCl$

(acid)

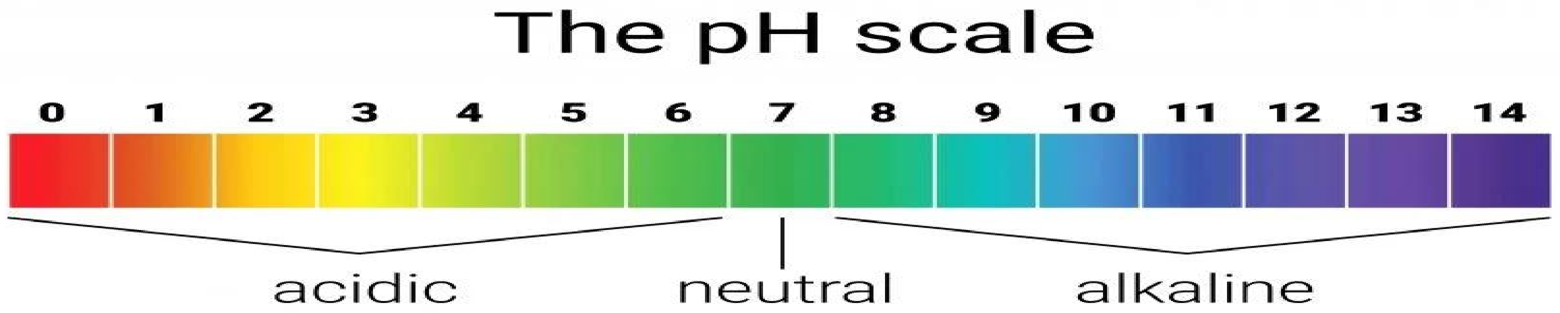
$H_2S + 2OH^- \rightarrow S^{--} + 2H_2O$

(acid)

pH and pH-Scale of Aqueous Solution

- nature of aq. solution can be described quantitatively in terms of H+ ion concentration as ($[H^+]\,[OH^-] = kw = 10^{-14}$ at 25^0C) , which shows that H+ concentration of aq. solution is generally in the range of 10^0 M to 10^{-14}M
- Sorensen introduced a convienent working scale to express H+ concentration called as pH scale, pH is defined as negative logarithm of H+ ion concentration in molarity:

  i.e**. pH = - log[H⁺]**



Relation between pH and pOH

in place of pH , pOH scale can also be used and is defined as

$pOH=-\log[OH^-]$

we know,

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

or, $-\log k_w= -\log[H^+][OH^-]$

or, $pk_w= -\log[H^+] + -\log[OH^-]$

or, $pk_w= pH + pOH$

or **$14= pH + pOH$ at 25^0C**

pH Scale and Temperature

- ionic product kw increases with increase in temp because auto ionization of water is endothermic and is decreases the value of pkw,
- eg; kw= 10^{-14} at 25^{0}C and pH range is 0-14
- kw = 10^{-13} at 65^{0}C and pH range is 0-13

Limitation of pH Scale

- limited to aqueous solution only
- temperature sensitive
- scale doesnot work for very concentrated acid or base

Numericals related to pH

- Calculate the pH of 1.0M solution of acetic acid. To what volume one litre of this solution be diluted so that the pH of the solution that is formed will be twice of original value [ka = 1.8 x 10^{-5}]

solution,

Given that, molarity of CH3COOH = 1.0 M

ionization constant of acetic acid = 1.8 x 10^{-5}

pH of acetic acid = ?

volume solution (V1) = 1 L = 1000ml

volume of solution (V2) at which pH doubles =?

CH_3COOH dissociates as, $CH_3COOH \leftrightarrow CH_3COO^- + H^+$

initially	c	0	0
at equilibruim	(c-ca)	ac	ac

we know that, from ostwald's dilution law,

$a = \sqrt{Ka/c} = \sqrt{1.8x\ 10^{-5}/1.0} = \sqrt{1.8x10^{-5}} = 4.24x10^{-3}$

Now, $[H+] = ac = 4.24x10^{-3} x\ 1.0 = 4.24x10^{-3}$ M we know that, pH = -log[H+]

= -log[4.24x10-3]

= 2.37

now, according to this question, pH of solution becomes double , pH= 2x 2.37 = 4.47

to calculate [H+] ion concn.

pH = -log[H+]

or, [H+] = antilog[-pH] ,

[H+] = antilog[-4.47]

= 1.819×10^{-5} M

Molarity of acetic acid = 1.819×10^{-5} M

now,

S1= 4.24 x10-3 S2= 1.819x 10-5

V1= 1000ml V2= ?

from normality equation,

V1S1= V2S2

$$V2 = \frac{V1 \times S1}{S2}$$

$$V2 = \frac{1000 \times 4.24\times10^{-3}}{1.819\times10^{-5}}$$

= 233095ml

= 233.095 l

Hence, required volume of solution is 233.095 litre.

Q. Explain why ph of 10^{-8} M HCl solution cannot be more than 7 at 25^0 C?

Here, one mole of HCl gives one mole of hygrogen ion.

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

1M   1M

10^{-8}M 10^{-8}M

we have, $pH = -\log[H^+]$

$= -\log[10^{-8}]$

$= 8$

This is not correct because pH of HCl must be less than 7. For acidic solution, ionization of water should not be neglected.

$H_2O \rightarrow H^+ + OH^-$

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

$10^{-14} = [H^+]^2$

now total $[H^+]$ ions in solutions = $10^{-7} + 10^{-8}$

$= 1.1 \times 10^{-7}$ mol/L

therefore, $pH = -\log[H^+] = -\log(1.1 \times 10^{-7})$

$pH = 6.95$

Solubility and Solubility product

- solubility of a solute is a property that describes the extent of its dissolution in a given solvent at a given temperature,
- defined as the amount if solute required to saturate a given amount of solvent or solution

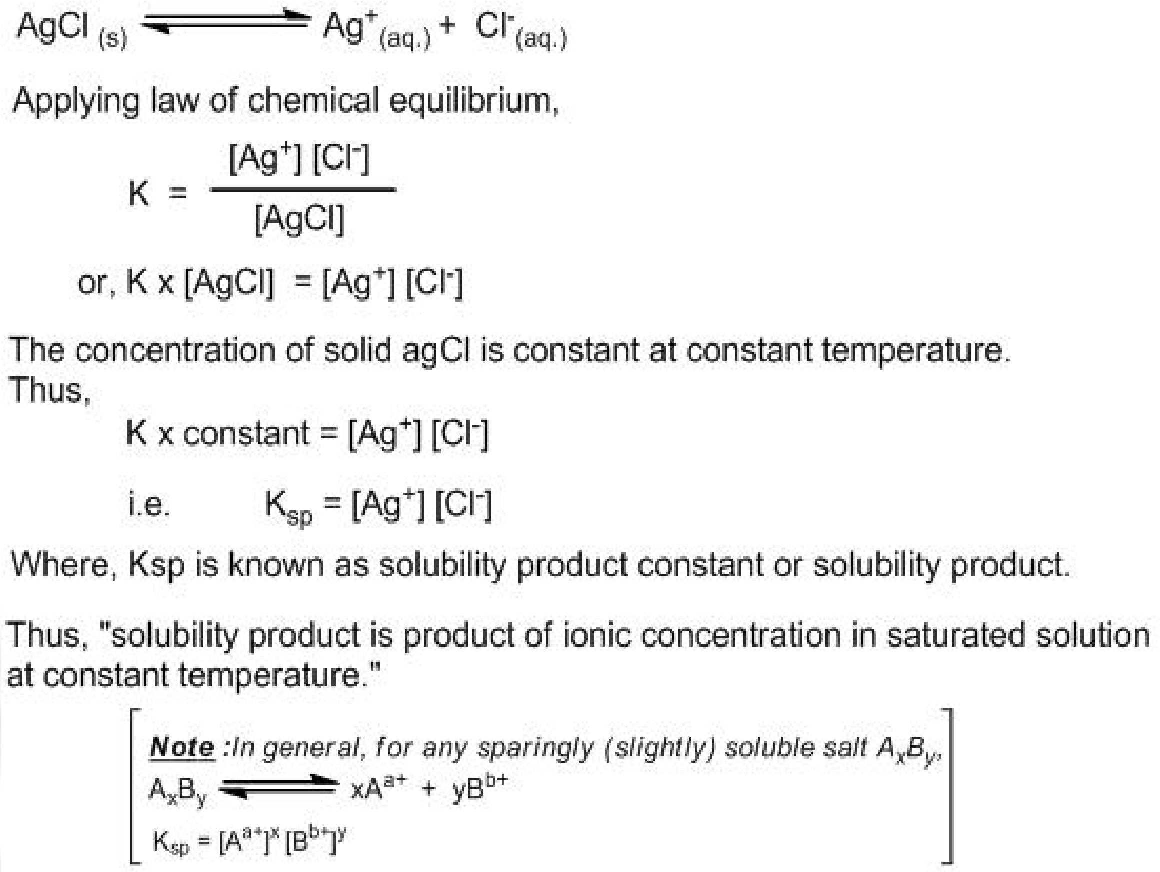
$$\text{solubility} = \frac{mass\ of\ solute\ x100}{mass\ of\ solvent}$$

- it can be expressed in g/L or mol/L or mol/Kg etc
- based upon solubilty, electrolytes are classified as **highly soluble, and sparingly soluble**
- eg. NaCl, Na_2CO_3, $AgNO_3$ etc are highlt soluble where as AgCl, $CaCO_3$ etc are sparingly soluble in water(solvent)

Solubility product

- Solubility product is defined as the product of ionic concentration in saturated solution at constant temperature.
- If a pinch of sparingly soluble salts like AgCl, $BaSO_4$, $PbCl_2$, etc. is dissolved in water, a saturated solution will be formed in which there exists an equilibrium between solid salt and its ions.

for eg; AgCl dissociates as;



$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq.)} + Cl^-_{(aq.)}$$

Applying law of chemical equilibrium,

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

$$\text{or, } K \times [AgCl] = [Ag^+][Cl^-]$$

The concentration of solid agCl is constant at constant temperature. Thus,

$$K \times \text{constant} = [Ag^+][Cl^-]$$

$$\text{i.e.} \quad K_{sp} = [Ag^+][Cl^-]$$

Where, Ksp is known as solubility product constant or solubility product.

Thus, "solubility product is product of ionic concentration in saturated solution at constant temperature."

Note *:In general, for any sparingly (slightly) soluble salt A_xB_y,*

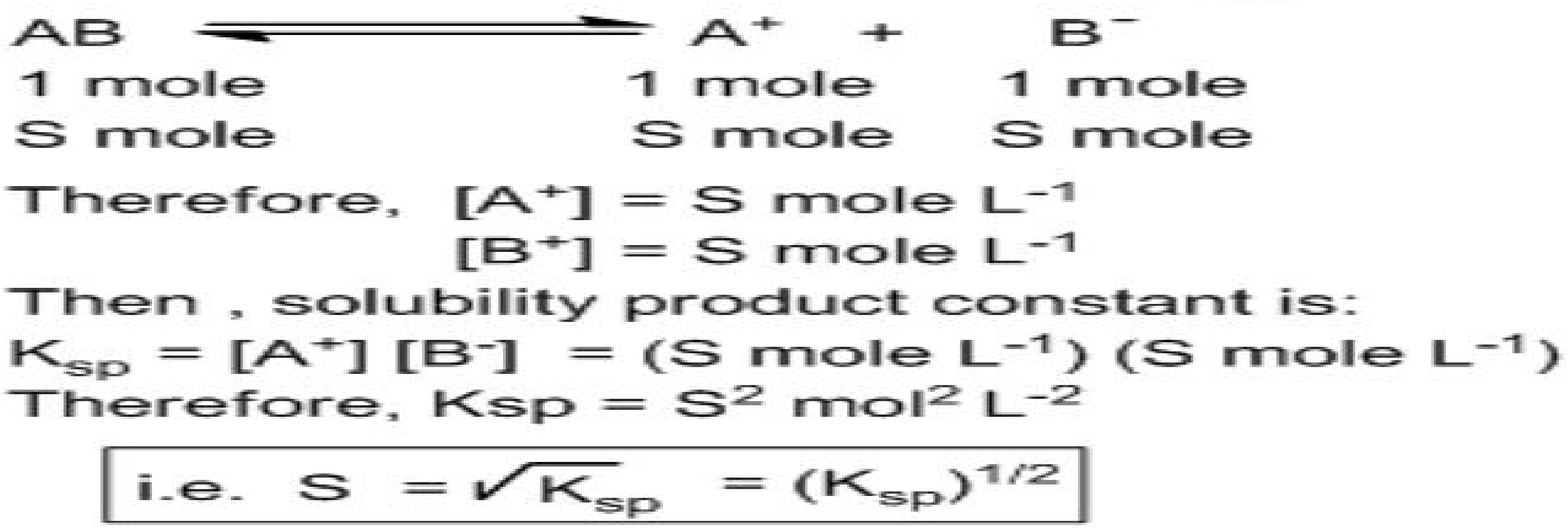
$$A_xB_y \rightleftharpoons xA^{a+} + yB^{b+}$$

$$K_{sp} = [A^{a+}]^x [B^{b+}]^y$$

Relation between solubility and solubility product:

- Let, solubility of sparingly (weakly) soluble salt is S mole L^{-1} ,

For AB type salts :



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

1 mole 1 mole 1 mole

S mole S mole S mole

Therefore, $[A^+]$ = S mole L^{-1}

$[B^+]$ = S mole L^{-1}

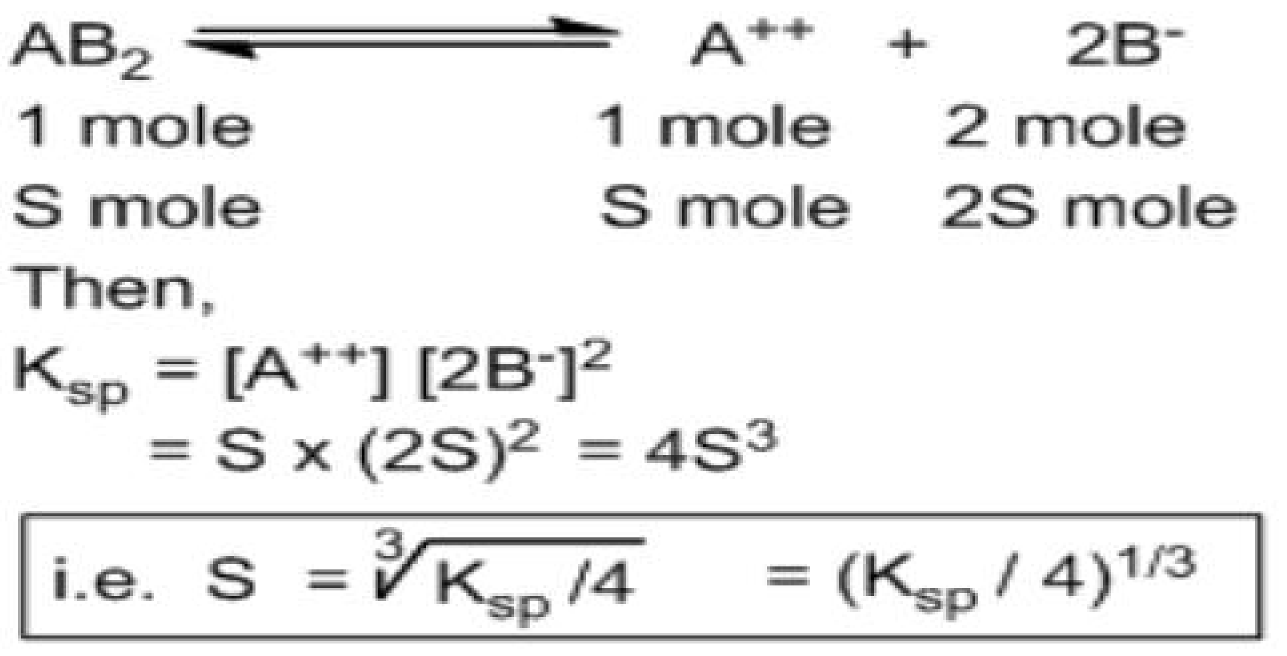
Then , solubility product constant is:

$K_{sp} = [A^+]\,[B^-]$ = (S mole L^{-1}) (S mole L^{-1})

Therefore, Ksp = S^2 $mol^2\,L^{-2}$

$$\boxed{\text{i.e. } S = \sqrt{K_{sp}} = (K_{sp})^{1/2}}$$

- For AB2 type salt :



$$AB_2 \rightleftharpoons A^{++} + 2B^-$$

AB_2	A^{++}	$2B^-$
1 mole	1 mole	2 mole
S mole	S mole	2S mole

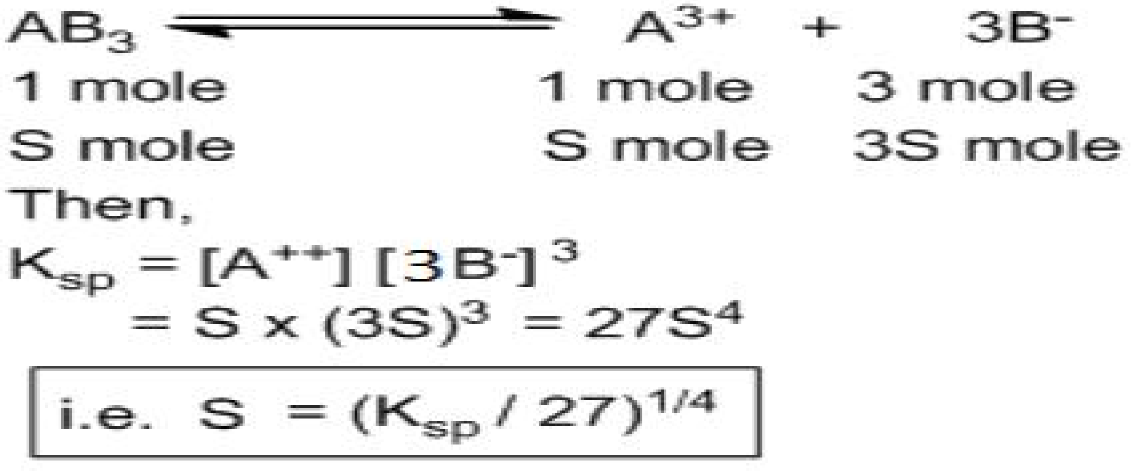
Then,

$$K_{sp} = [A^{++}]\,[2B^-]^2$$

$$= S \times (2S)^2 = 4S^3$$

$$\boxed{\text{i.e. } S = \sqrt[3]{K_{sp}/4} = (K_{sp}/4)^{1/3}}$$

- For AB3 type salt :



$$\begin{array}{lll} AB_3 \rightleftharpoons & A^{3+} & + \quad 3B^- \\ 1 \text{ mole} & 1 \text{ mole} & 3 \text{ mole} \\ S \text{ mole} & S \text{ mole} & 3S \text{ mole} \end{array}$$

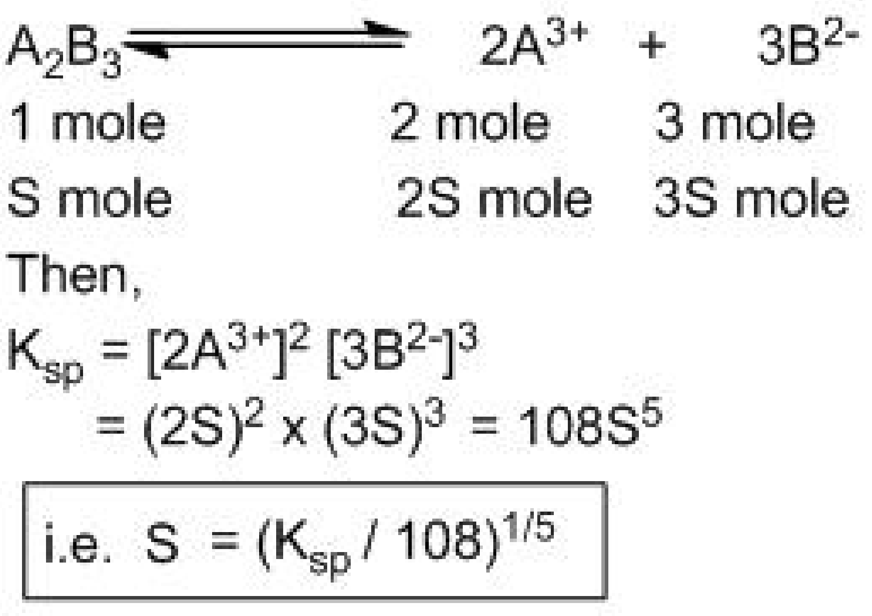
Then,

$$K_{sp} = [A^{++}]\,[3B^-]^3$$

$$= S \text{ x } (3S)^3 = 27S^4$$

$$\boxed{\text{i.e. } S = (K_{sp} / 27)^{1/4}}$$

- For A2B3 type salt:



$$A_2B_3 \rightleftharpoons 2A^{3+} + 3B^{2-}$$

A_2B_3	$2A^{3+}$	$3B^{2-}$
1 mole	2 mole	3 mole
S mole	2S mole	3S mole

Then,

$$K_{sp} = [2A^{3+}]^2 [3B^{2-}]^3$$
$$= (2S)^2 \times (3S)^3 = 108S^5$$

$$\boxed{\text{i.e. } S = (K_{sp} / 108)^{1/5}}$$

Relation between ionic product and solubility product and precipitation:

- A sparingly soluble salt precipitates from a solution only when its ionic product exceeds solubility product value. Thus when
- Ionic product > Ksp, solution is supersaturated and hence precipitation takes place.
- Ionic product < Ksp, solution is unsaturated and hence precipitation does not take place.
- Ionic product = Ksp, solution is saturated.

Common ion effect

- When a strong electrolyte having one ion common to weak electrolyte is added to the solution of weak electrolyte then the ionization of weak electrolyte is decreased. This effect is called common ion effect
- For example:
- a. Ionization of ammonium hydroxide is decreased by the addition of ammonium chloride.

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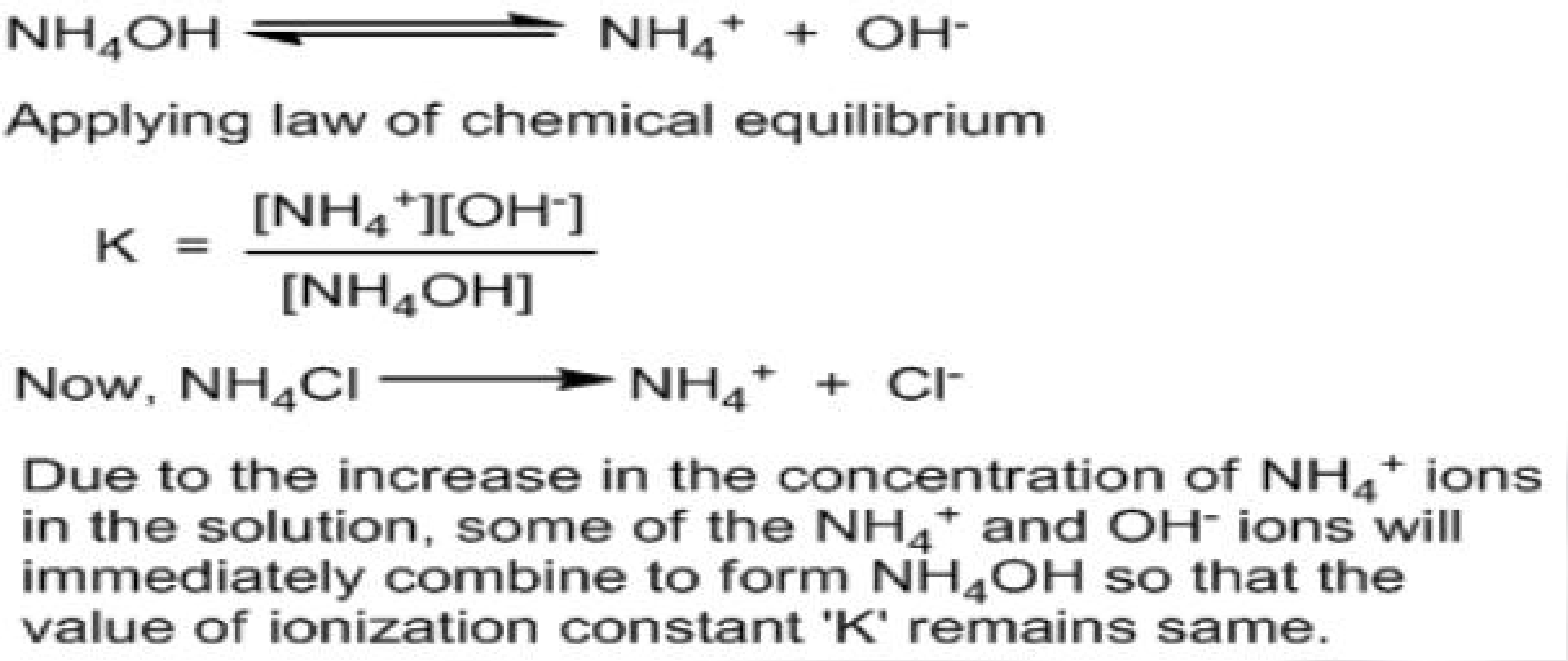


$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Applying law of chemical equilibrium

$$K = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$\text{Now, } NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

Due to the increase in the concentration of NH_4^+ ions in the solution, some of the NH_4^+ and OH^- ions will immediately combine to form NH_4OH so that the value of ionization constant 'K' remains same.

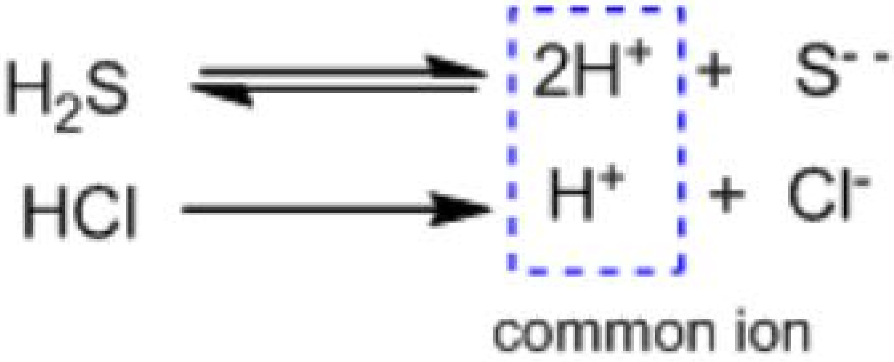
Application of common ion effect and solubility product principle in precipitation reaction

- In qualitative analysis, metal ions are precipitated as their insoluble salts.

a. Precipitation of sulphides of group-II metal ions:

- In group II of qualitative analysis, when H_2S gas is passed into the original solution containing HCl then metal ions such as Pb++, Cu++, Hg++, Cd++,etc. are precipitated in the form of their sulphides. The ionization of H2S is suppressed due to the presence of common hydrogen ion(H+) produced by HCl
- Here, the concentration of S^{--} ions is decreased due to common ion effect. The solubility product of sulphides of group II metal ions is relatively low. Therefore, the ionic product of sulphide ions and metal ions exceeds the solubility product and hence the the metal ions of group II are precipitated as sulphide (PbS, CuS, HgS, CdS, etc.)

- But, the reduced concentration of S^{--} ions is not sufficient to precipitate metal ions of other groups (III, IV and V) because their solubility products are comparatively high.

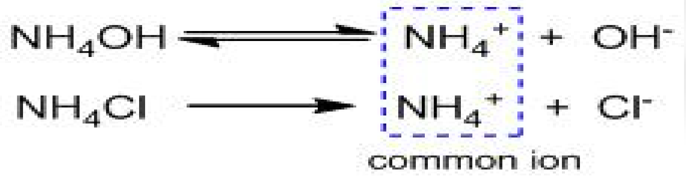


$$H_2S \rightleftharpoons 2H^+ + S^{--}$$

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

b. Precipitation of hydroxides of group-IIIA metal ions:

- In group IIIA of qualitative analysis, when NH4OH is passed into the original solution containing NH4Cl then metal ions such as Fe^{+++}, Al^{+++}, Cr^{+++},etc. are precipitated in the form of their hydroxides. The ionization of NH4OH is suppressed due to the presence of common $NH4^+$ ion produced by NH4Cl.
- Here, the ionic product of hydroxide ions and metal ions exceeds the solubility product of metal hydroxides of group IIIA only and hence the metal ions of group IIIA are precipitated as their hydroxides {Al(OH)3, Fe(OH)3, Cr(OH)3, etc.
- But, the reduced concentration of OH^- ions is not sufficient to precipitate metal ions of other groups (IV and V) because their solubility products are comparatively high.



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

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

Buffer solution

- A solution which can resist change in pH even on addition of small amount of acid or base is called buffer solution
- a buffer solution is one which maintains its pH, even upon addition of small amount of acid or base
- a buffer solution resist the change in its pH
- a buffer solution is very important to maintain a fixed pH of a solution in biological and analytical process.
- the resistance in change in pH of the solution is called buffer action
- buffer solutions are of two types; Acidic buffer and Basic buffer

i. **Acidic buffer:** a buffer solution is said to be acidic if its pH is less than 7

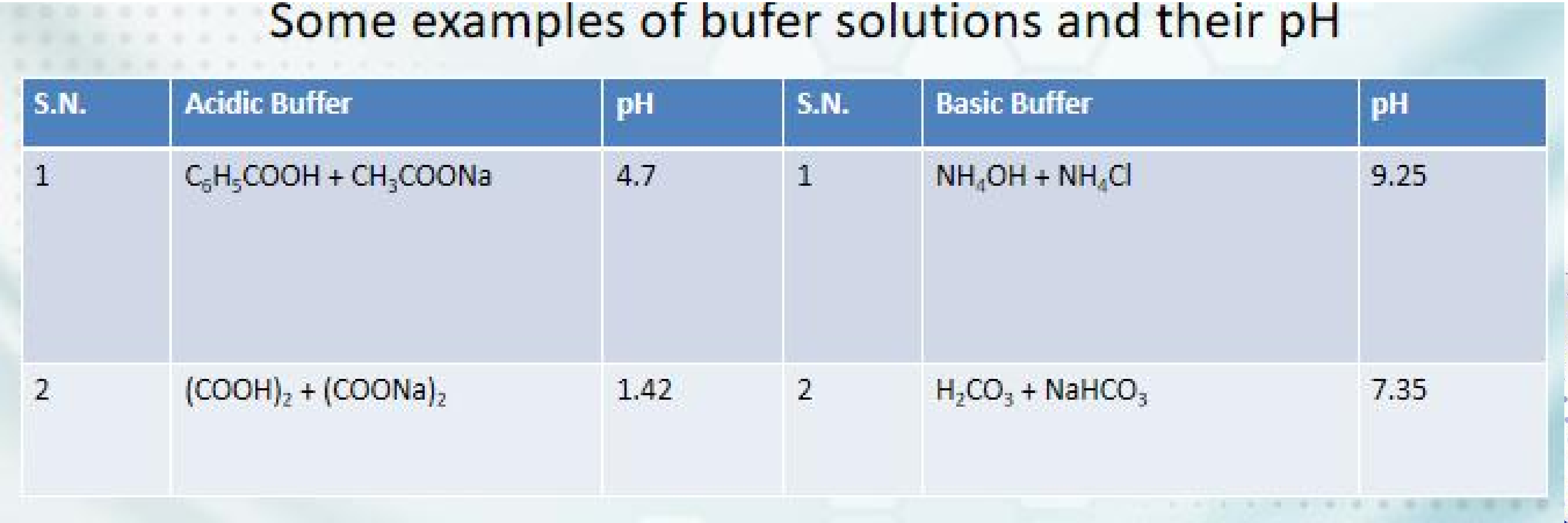
it is prepared by mixing a weak acid and its conjugate salt (strong)

Example: A solution containing equimolar quantities of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) is acidic buffer.

ii. Basic buffer: a buffer solution is said to be basic if its pH is greater than 7

it is prepared by mixing a weak base and its conjugate salt (strong salt)

Example: A solution containing equimolar quantities of ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl) is acidic buffer.



Some examples of bufer solutions and their pH

S.N.	Acidic Buffer	pH	S.N.	Basic Buffer	pH
1	$C_6H_5COOH + CH_3COONa$	4.7	1	$NH_4OH + NH_4Cl$	9.25
2	$(COOH)_2 + (COONa)_2$	1.42	2	$H_2CO_3 + NaHCO_3$	7.35

Calculation of pH of buffer solution

calculated by **Henderson’s equation**:

$pH= pK_a + \log [salt]\backslash [Acid]$ for acidic buffer

$pOH= pK_b + \log[salt]\backslash [base]$ for basic buffer

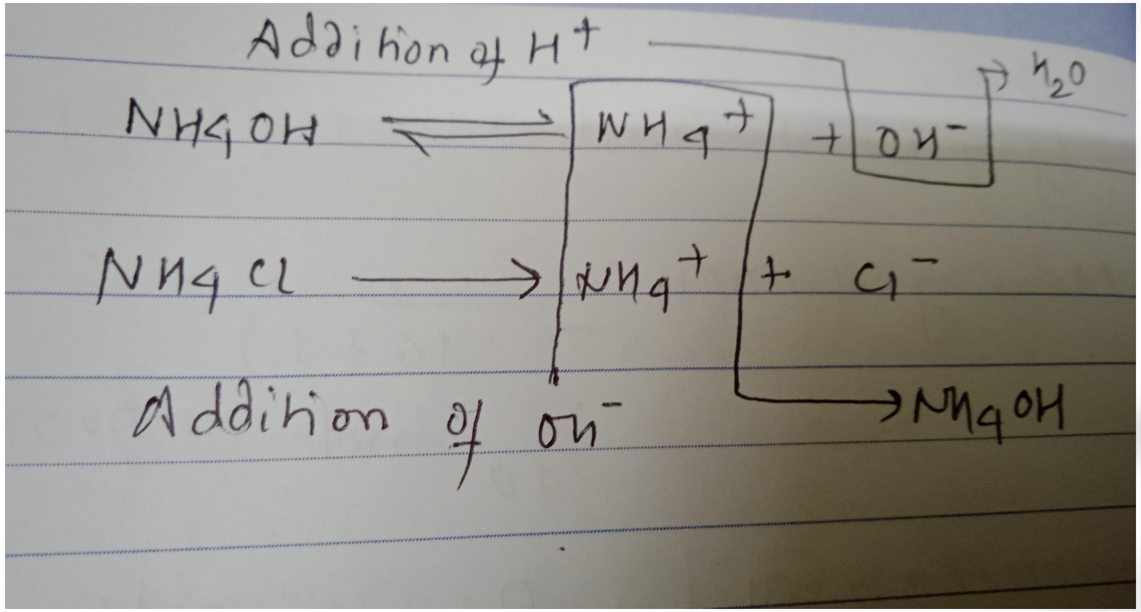
where $pk_a= -\log k_a$ and $pk_b= -\log k_b$

k_a = dissociation constant of acid

k_b= dissociation constant of base

Buffer action of basic buffer

- consider a basic buffer NH_4OH +NH_4CL , the buffer action on addition of small amount of acid or base can be shown as:



- **on addition of H^+ (acid from HCl):** H^+ from acid combines with OH^- ion from base to give undissociated H2O molecule and hence there is no change in pH of solution due to addition of H^+ ions
- **on additon of OH^- (base from NaOH):** OH^- ions from base combines with excess of NH_4^+ ion in the solution forming unionized weak base NH_4OH and hence there is no change in pH of the solution due to the addition of small amount of base

Application of buffer solution

- **Maintainance of life:** Most biochemical processes work within a realtively small pH range. The body uses buffer solution to maintain a constant pH . For example, blood contains carbonate/ bicarbonate buffer that keeps the pH closwe to 7.35.
- **Biochemical assays:** Enzyme activity depends on pH, so the pH during an enzyme assay must stay constant.
- **In shampoos:** Many shampoos uses a citric acid/sodium citratre to maintain a slightly acidic ‘pH balance ‘. This counteracts the basicity of detergents present in shampoo.

- **In baby lotions:** Baby lotions are buffered to the pH of about 6. This hinders the growth of bacteria within the diaper and help prevent diaper rash.
- **In the brewing industry:** Buffer solutions are added before fermentation begins. This prevents the solution becoming too acidic and spoiling the product.
- **In textile industries:** Many dyeing processes use buffers to maintain the correct pH for various dyes.

Types of saltss

- salt is described as a chemical compound that consists of an ionic assembly of cations and anions
- salts are composed of related numbers of cations (which are positively charged ions) and anions (which are negatively charged ions) so that the product is defined as electrically neutral (without any net charge)

Generally five types:

1. **Normal salt:** a salt produced by complete neutralization of an acid by a base is , example: NaCl, KCl, Na_2SO_4, $MgSO_4$, K_2SO_4, $Ca(NO_3)_2$ etc.

   $HCl + NaOH \rightarrow NaCl + H_2O$

2. **Acidic salt:** The salt that is formed by the partial neutralization of a polyprotic or diprotic acid is called acidic salt. These salts contain ionizable H+ ions along with another cation , example; KH_2PO_4, NaH_2PO_4

   $H_2SO_4 + NaOH \rightarrow NaHSO_4 + H2O$

3. **Basic Salt -** The salt that is formed by the partial neutralization of a strong base by the weak acid is called a basic salt. These salts hydrolyze to produce a basic solution, example: $Ca(OH)Cl$, $Al(OH)_2Cl$, $Mg(OH)Cl$, white lead ($2PbCO3 \cdot Pb(OH)2$), etc.

$$Mg(OH)_2 + HCl \rightarrow Mg(OH)Cl + H_2O$$

4. **Mixed salt or double salt**: formed by the combination of two normal salts

- they are stable in solid state but they lose their identity when dissolved in polar solvents like water
- the solution of the soluble salts have the same properties as the mixture of the individual compounds
- example: Mohr's salt ($FeSO_4.(NH_4)_2SO_4.6H_2O$), Potash alum: $K_2SO_4.Al_2(SO_4)_3.24H_2O$

  Carnalite: $KCL.MgCl_2.6H_2O$

5. complex salt: such salt are formed by the combination of central metal atom or ion with the number of neutral molecules or anions and retain their identity i.e. there properties remains same either in the solid state or in the solution

example; when ammonia solution is added to the solution of nickel chloride and the resulting solution is evaporated, the purple crystal of a new compound is formed, which is a complex compound

$$NiCl_2 + 6NH_3 \rightarrow [\,Ni(NH_3)_4]Cl_2$$

(tetramine nickel(II) chloride)

here, Ni = central metal atom, Cl_2 = ion

Hydrolysis of salts

- the term hydrolysis derived from Greek word: hydro- means water and lysis - means to break apart
- hydrolysis is a decomposition reaction in which water is one of the reacting substances
- salt hydrolysis is defined as a reaction in which the cation or anion of a salt reacts with H^+ and OH^- ions of the water to produce acidic or basic or neutral solution.

Mechanism of salt hydrolysis:

- H_2O gets feebly ionized and produces equal number of H+ and OH- ions

$$H_2O \leftrightarrow H^+ + OH^-$$

- the salt MA is obtained from base (MOH) and acid(HA)

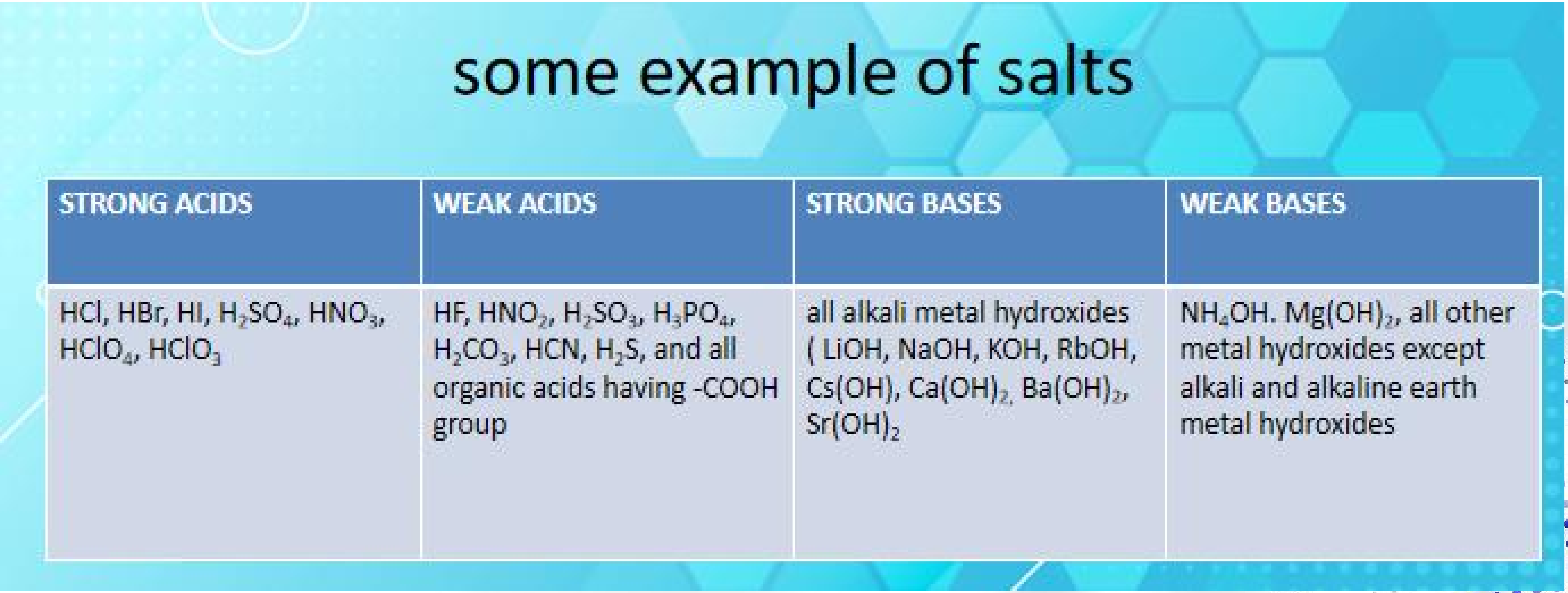
$$MA \leftrightarrow M^+ + A^-$$

- during hydrolysis process, M+ combines with OH- and gives MOH (base) while A- combines with H+ to give HA (acid)

$$M^+ + OH^- \leftrightarrow MOH(alkali)$$

$$A^- + H^+ \leftrightarrow HA(acid)$$

- the nature of acid and base so formed during hydrolysis determines the nature of salt solution wheather it is acidic or basic or neutral
- strong acids and strong bases are completely ionized in water but weak acid and weak bases are partially ionizes in water



some example of salts

STRONG ACIDS	WEAK ACIDS	STRONG BASES	WEAK BASES
HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_4$, $HClO_3$	HF, HNO_2, H_2SO_3, H_3PO_4, H_2CO_3, HCN, H_2S, and all organic acids having -COOH group	all alkali metal hydroxides (LiOH, NaOH, KOH, RbOH, Cs(OH), $Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$	NH_4OH. $Mg(OH)_2$, all other metal hydroxides except alkali and alkaline earth metal hydroxides

There are four types of salts based on phenomenon of hydrolysis

1. **salt of strong acids and strong bases**: when strong acid reacts with strong base, the salts obtained are: NaCl, KBr, $BaCl_2$, KNO_3, Na_2SO_4, $Mg(NO_3)_2$, etc.

- When these salts are dissolved in water, they produce strong acid and strong base
- there is no any H^+ and OH^- remain in the solution, it means the solution becomes **neutral** or it can be said that the salts of strong acid and strong base **donot under go hydrolysis**
- consider the dissociation of NaCl in water:

$NaCl \rightarrow Na^+ + Cl^-$

H2O → $H^+ + OH^-$

$Na^+ + OH^- \rightarrow$ NaOH(highly ionized)

$H^+ + Cl^- \rightarrow$ HCl(highly ionized)

2. salt of strong acid and weak bases: the salt obtained from strong acids and weak bases like NH_4Cl, $(NH_4)_2SO_4$, $CuCl_2$, $FeCl_3$, $AlCl_3$ undergo hydrolysis to give acidic solutions.

- consider the dissociation of NH_4Cl in water,

$NH_4CL \rightarrow NH_4^+ + Cl^-$

$H_2O \leftrightarrow H^+ + OH^-$

$NH_4^+ + OH^- \leftrightarrow$ NH_4OH(weak base, feebly ionized)

$H^+ + Cl^- \rightarrow$ HCl(strong acid, highly ionized)

3. **salt of weak acid and strong bases:** the salt obtained from weak acids and strong bases like Na_2CO_3, CH_3COONa, HCOOK, NaCN, undergo hydrolysis to give basic solutions.

consider the dissociation of CH_3COONa in water,

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

$$H_2O \leftrightarrow H^+ + OH^-$$

$Na^+ + OH^- \rightarrow$ NaOH(strong base, highly ionized)

$H^+ + CH3COO^- \leftrightarrow$ CH3COOH (weak acid, feebly ionized)

4. **salt of weak acid and weak bases:** the salt obtained from weak acids and weak bases like $(NH_4)_2CO_3$, CH_3COONH_4, $(CH_3COO)_2Ca$, undergo hydrolysis to give acidic or basic solutions depending upon the nature of acid or base produced,

consider the dissociation of CH_3COONH_4 in water,

$CH_3COONH_4 \rightarrow CH_3COO^- + NH4^+$

$H_2O \leftrightarrow H^+ + OH^-$

$NH_4^+ + OH^- \rightarrow NH_4OH$(weak base, highly ionized)

$H^+ + CH_3COO^- \leftrightarrow CH_3COOH$ (weak acid, feebly ionized)

Thank you!