$\Delta G^0 = -RT \ln(K_{eq})$ 

 $pH = -log[H^+]$ 

 $K_w = K_a \times K_a$ 





 $\Delta G^0 = -RT \ln(K_{eq})$ 

0





properties (pressure, temperature, volume & concentration) remain constant.



In this type of equilibrium, the system is at rest and no actual change is happening either at the macroscopic level or the microscopic level. The dynamic equilibrium can be defined as the state of a system at which the rate of movement in the forward and backward directions (chemical reaction) is equal and no net change takes place.



# Types of Chemical Reactions

#### Irreversible

#### Reversible







### **Irreversible Reaction**





# 



### **Reversible Reaction**





# **Examples of Reversible Reaction**

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$PCl_{5}(g) \rightleftharpoons PCl_{3}(g) + Cl_{2}(g)$$







### Homogeneous Equilibrium

### Heterogeneous Equilibrium



$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

 $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ 

All reactants and products are in the same phase









### Heterogeneous Equilibrium

Reactants and products are in more than one phase

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

$$CaCO_3$$
 (s)  $\rightleftharpoons$  CaO (s) + CO<sub>2</sub> (g)

C (diamond, s)  $\rightleftharpoons$  C (graphite, s)











Physical Equilibrium

#### Equilibrium

**Chemical** Equilibrium





### **Phase Transformation Processes**

B







### **Chemical Equilibrium**

# Equilibrium in chemical processes

State in which the driving forces, i.e., the factors taking the reaction in the forward & the backward direction are balancing each other At t = 0



0





Rate of the backward reaction



### **Chemical Equilibrium**





# **Graphical Representation**







# **Graphical Representation**











No change in the concentration of either the reactants or the products

#### Example:

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







Mixture of reactants & products in the equilibrium state

Example

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







# Conditions for Chemical Equilibrium Involving Gaseous Phase









#### At equilibrium, all macroscopic properties such as



#### of the system appear to be constant





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





### **Extent of the Reaction**



01 **Reactions that proceed nearly** to completion ([R] is very less) 02 Extent of the reaction **Reactions that barely proceed** at equilibrium ([P] is very less) varies with the experimental conditions 03 Reactions in which the [R] & [P] are such as pressure, significant at equilibrium temperature, etc.

# B

## **Characteristics of Chemical Equilibrium**





# B

## **Characteristics of Chemical Equilibrium**



# **Characteristics of Chemical Equilibrium**

In general, the state of equilibrium in a chemical reaction can be achieved from either direction





#### Let after **75** % conversion equilibrium is achieved

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









# Same equilibrium state can be achieved starting from product

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



25% conversion





#### Let after **50 % conversion of N<sub>2</sub>** equilibrium is achieved

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





### Law of Mass Action



Proposed by Guldberg and Waage

#### At a particular temperature,

Rate of a chemical reaction is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients





#### Effective amount of reacting species taking part in the reaction

Active masses are **dimensionless** quantities but for our purposes we generally take them with dimensions of **molarity**, **partial pressure** etc.





### **Active Mass**











# Active Mass









## Mathematical Expression for Law of Mass Action

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

#### According to law of mass action,

	Rate of forward reaction	¢	[ <b>A</b> ]ª [ <b>B</b> ] <sup>b</sup>	=	k <sub>f</sub> [A]ª [B] <sup>b</sup>
--	--------------------------	---	---	---	--------------------------------------

∝	[ <b>C</b> ] <sup>c</sup> [ <b>D</b> ] <sup>d</sup>	=	<b>k<sub>b</sub> [С]<sup>с</sup> [D]<sup>d</sup></b>
	∝	∝ [C] <sup>c</sup> [D] <sup>d</sup>	∝ [C] <sup>c</sup> [D] <sup>d</sup> =




K<sub>c</sub>

#### **Application of Law of Mass Action**





#### Equilibrium Constant



Equilibrium constant in terms of **concentration** 

Equilibrium constant in terms of **partial pressure** 

Equilibrium constant in terms of **mole fractions** 

K<sub>c</sub> and K<sub>P</sub> are temperature dependent only





## Equilibrium Constant (K<sub>c</sub>)

K<sub>c</sub> is the equilibrium constant when the **active masses** are expressed in **concentrations** 

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

 ${\bf k}_{\rm f}$  and  ${\bf k}_{\rm b}$  depends only on temperature.



$$\left(\begin{array}{c} \mathsf{K}_{\mathsf{C}} \end{array}\right) = \left(\begin{array}{c} \frac{\left[\mathsf{CH}_{3}\mathsf{COOH}\right]_{\mathsf{eq}}\left[\mathsf{C}_{2}\mathsf{H}_{5}\mathsf{OH}\right]_{\mathsf{eq}}}{\left[\mathsf{CH}_{3}\mathsf{COOC}_{2}\mathsf{H}_{5}\right]_{\mathsf{eq}}}\right)$$

Example



Activity of pure solids is taken as 1

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

$$K_{C}$$
 =  $[CO_{2}(g)]_{eq}$ 









#### $CH_{3}COOH (I) + C_{2}H_{5}OH (I) \rightleftharpoons CH_{3}COOC_{2}H_{5} (I) + H_{2}O (I)$

#### Here, water is not acting as the solvent









Equilibrium reaction which contains at least one gaseous component

 $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$ 



Equilibrium constant in terms of partial pressure















#### Relation between $K_p$ and $K_c$





#### Relation between $K_p$ and $K_c$



$$K_{c} = K_{P} (RT)^{-\Delta n_{g}}$$

$$\mathbf{K}_{\mathsf{P}} = \mathbf{K}_{\mathsf{c}} (\mathsf{RT})^{\Delta \mathsf{n}_{\mathsf{g}}}$$









Sum of stoichiometric coefficients of gaseous reactants

Example:

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

$$\Delta n_g = 2 - (3 + 1) = -2$$









$$(\mathbf{K}_{\mathbf{P}})^{--\rightarrow} \qquad \frac{(\mathbf{P}_{\mathbf{C}})^{c}{}_{eq}}{(\mathbf{P}_{\mathbf{A}})^{a}{}_{eq}} (\mathbf{P}_{\mathbf{B}})^{b}{}_{eq}}$$

$$K_{\chi} \longrightarrow \left( \begin{array}{c} (\chi_{C})^{c}_{eq} (\chi_{D})^{d}_{eq} \\ \hline (\chi_{A})^{a}_{eq} (\chi_{B})^{b}_{eq} \end{array} \right)$$





#### Relation between $K_P \& K_X$





If reaction is **reversed**, the equilibrium constant is **reciprocated** 

A (aq) + B (aq) 
$$\rightleftharpoons$$
 C (aq)  
 $K_{c} = \frac{[C]}{[A][B]} = K$ 

-- C (aq) 
$$\rightleftharpoons$$
 A (aq) + B (aq)  
 $K_c^{l} = \frac{[A][B]}{[C]} = \frac{1}{K}$ 





$$\begin{array}{c} --A (aq) + B (aq) \rightleftharpoons C (aq) \\ \hline \frac{1}{2}A (aq) + \frac{1}{2}B (aq) \rightleftharpoons \frac{1}{2}C (aq) \\ \hline \frac{1}{2}C (aq)$$

3



 $A + B \rightleftharpoons C$   $C \rightleftharpoons D$   $A + B \rightleftharpoons D$   $A + B \rightleftharpoons D$   $K_{1} = \frac{[C]}{[A] [B]}$   $K_{2} = \frac{[D]}{[C]}$   $K = K_{1} \times K_{2} = \frac{[D]}{[A] [B]}$ 



Δ

5

Equilibrium constant does not depend upon concentration of reactants, presence of catalyst, direction from which equilibrium is reached

> It depends only on the temperature and the stoichiometric coefficients



# Temperature Dependence of Equilibrium Constant





ΔH° Standard Enthalpy change

R

Universal gas constant







For the reaction:

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$





 $[B_2]_0$  Initial Concentration of  $B_2$ 



$$A_{2}(g) + B_{2}(g) \rightleftharpoons 2AB(g)$$

$$Concentration at t = 0 \qquad 1 \qquad 1 \qquad 0 \qquad (mol L^{-1})$$

$$Concentration at t = t_{eq} \qquad 1 - x \qquad 2x$$

$$Moles of A_{2} and B_{2}$$

x Moles of A<sub>2</sub> and B<sub>2</sub> dissociated





# **Calculating Equilibrium Concentrations**



#### Taking square root on both sides

$$\boxed{\frac{[2x]}{[1-x]}} = 4$$



#### **Calculating Equilibrium Concentrations**





$$x = \frac{2}{3}$$



# Calculating Equilibrium Concentrations



$$[B_2]_{eq} = \left( [B_2]_o - \frac{x}{V} \right) = 1 - \frac{2}{3} = \frac{1}{3} M$$



















If 
$$K_{eq} = 1$$
 [P]<sub>eq</sub> = [R]<sub>eq</sub>









## **Applications of Equilibrium Constant**



#### Predicting the extent of reaction



Predicting the direction of equilibrium







At any point in a reaction, ratio of concentration terms having the same form as the equilibrium constant expression

Reaction quotient in terms of concentration

Q<sub>c</sub>

Reaction quotient in terms of partial pressure

Qp

Reaction Quotient (Q)











# Reaction Quotient (Q)



#### To achieve equilibrium







# Reaction Quotient (Q)



#### To achieve equilibrium


















# Degree of Dissociation $(\alpha)$

At t = 0, only PCI<sub>5</sub> is present











# Degree of Dissociation $(\alpha)$











# Calculating Moles in Terms of $\boldsymbol{\alpha}$



$$\alpha = \frac{x}{a}$$

Total moles  
at equilibrium = 
$$a - a\alpha + na\alpha$$
 =  $a [1 + (n - 1) \alpha]$ 





# Calculating Moles in Terms of $\boldsymbol{\alpha}$

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$





# Equilibrium Molar Mass and Vapour Density

SB





# Molar Mass of Equilibrium Mixture



Let the initial molar mass be **M** and **M**<sub>mix</sub> be the molar mass of the mixture





# Molar Mass of Equilibrium Mixture













# Plot of Vapour Density vs $\alpha$









### Thermodynamics of Equilibrium

Consider a reversible reaction,

 $aA (aq) + bB (aq) \rightleftharpoons cC (aq) + dD (aq)$ 

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$\Delta G = \Delta G^{\circ} + 2.303 RT \log Q$$





# Thermodynamics of Equilibrium

#### At Equilibrium,

$$\Delta G = 0 \& Q = K_{eq}$$

$$\Delta G^{\circ} = - RT \ln K_{eq}$$

$$\Delta G^{\circ} = -2.303 \text{ RT log } K_{eq}$$





# Thermodynamics of Equilibrium



$$-2.303 \text{ RT } \log \text{K}_{eq} = \Delta \text{H}^{\circ} - \text{T} \Delta \text{S}^{\circ}$$

$$\log K_{eq} = -\frac{\Delta H^{\circ}}{2.303 \text{ RT}} + \frac{\Delta S^{\circ}}{2.303 \text{ R}}$$















# Equilibrium Constant & Temperature



 $K_1$  Equilibrium constant at  $T_1$ 

K<sub>2</sub> Equilibrium constant at T<sub>2</sub>





# Equilibrium Constant & Temperature

Assuming  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  remains constant in this temperature range

⇒ Eq. (1) - (2)







#### Remember!!



Reaction at constant T & P is feasible in the direction which leads to a lowering of Gibbs free energy.





Industrially, the aim is to have maximum product yield with minimum energy expenditure

After equilibrium is established, more product formation stops.

**N** 

Equilibrium can be disturbed

And reaction can be carried out in the desired direction





### Le Chatelier's Principle

If a change is applied to the system at equilibrium, then the equilibrium will be shifted in that direction



In which it can minimise the effect of the change applied and the equilibrium is established again under new conditions.





# Factors Affecting Equilibrium

Change in the concentration of reactant or product

Change in pressure

Change in volume

Effect of addition of inert gas

Effect of addition of catalyst

Change in temperature



If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration



A (aq) + B (aq)  $\rightleftharpoons$  C (aq) + D (aq)

$$\left(\begin{array}{c} \mathbf{Q}_{\mathsf{C}} \end{array}\right) = \left(\begin{array}{c} \frac{[\mathsf{C}][\mathsf{D}]}{[\mathsf{A}][\mathsf{B}]} \end{array}\right)$$

Addition of A or B  $Q_c \downarrow \Rightarrow Q_c < K_c$ Equilibrium shifts in the forward direction











Concentration of the added species ([A] or [B]) will be more at new equilibrium than that at the old equilibrium under the same set of conditions.





A (aq) + B (aq)  $\rightleftharpoons$  C (aq) + D (aq) Q<sub>c</sub> =  $\frac{[C][D]}{[A][B]}$ 











Concentration of the added species ([C] or [D]) will be **more at new equilibrium** than that at the old equilibrium under the same set of conditions.



#### Conclusions



Addition of any solid component does not affect the equilibrium

[Reactant]

Equilibrium shifts in the forward direction

Equilibrium shifts in the backward direction









#### **Effect of Temperature**

Reaction shifts in that direction where temperature decreases

Reaction shifts in that direction where temperature increases





## **Exothermic Reaction**

For the reaction,

Reaction shifts in that direction where temperature decreases







## **Endothermic Reaction**

For the reaction,

Reaction shifts in that direction where temperature decreases




ΔH°

R

### Temperature Dependence of Equilibrium Constant

If  $K_1 \& K_2$  are the equilibrium constants at temperature  $T_1 \& T_2$ 



Standard Enthalpy change

Universal gas constant







On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e., number of moles in the reaction decreases and vice versa









#### **Effect of Change in Pressure**

For the reaction,











$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

If 
$$P \uparrow \Rightarrow No Shift as \Delta n_g = 0$$

$$\begin{array}{c|c} \mathsf{P} & \uparrow \\ \end{array} \Rightarrow & \mathsf{V} & \downarrow \\ \end{array} \Rightarrow & [\mathsf{NO}] & \uparrow \\ \end{array}$$





#### **Effect of Change of Pressure**

#### Solids & liquids are incompressible or negligibly compressible.

Change in pressure has no effect on equilibria involving solid & liquid







Hence, the reaction will shift in the direction in which pressure increases i.e., in the direction in which the **number of moles of gases increases** and vice versa.





For the reaction,







For the reaction,

If Volume

Reaction shifts where the moles of gas

Reaction goes forward

$$N_2O_4(g) \implies 2NO_2(g)$$





For the reaction,



If Volume

Reaction shifts where the moles of gas

Reaction goes **backward** 





















 $[NH_3]$  and  $[CO_2]$  remains same





#### **Catalyst and Effect of Catalyst**

Substance which can alter the speed of a chemical reaction without itself getting consumed at the end of the reaction

Due to the catalyst, the state of equilibrium is not affected

Catalyst lowers the activation energy of both the forward and the reverse reactions by the same amount, It alters the forward and the reverse rate equally and hence, the equilibrium will be attained faster



### Effect of Addition of an Inert Gas





#### Effect of Addition of an Inert Gas



#### When $\Delta V = 0$

Partial pressures of the gaseous reactants & products do not change i.e., Q<sub>p</sub> do not change

No disturbance in equilibrium

A (g) 
$$\rightleftharpoons$$
 B (g) A (g)  $\rightleftharpoons$  2 B (g) 2 A (g)  $\rightleftharpoons$  B (g)







Application of Le Chatelier's Principle: Practical Equilibrium Situations









In phase transition processes, the increase in pressure shifts the equilibrium towards the denser phase.





#### C (Graphite, s) $\rightleftharpoons$ C (Diamond, s)

$$\Delta_{\rm r}$$
H = + 1.9 kJ mol<sup>-1</sup>









### **Phase Transition**

**Increase in pressure** favours the formation of the **denser state**, **i.e. diamond** 







#### **Phase Transition**

As  $\Delta H$  is +ve, the increase in temperature favours the formation of diamond













$$\Delta_{\rm r} {\rm H}^{\rm o} = + 6 \, {\rm kJ} \, {\rm mol}^{-1}$$

Increase in pressure favours the formation of the denser state, i.e. water

As  $\Delta H$  is +ve, the increase in temperature favours the formation of water







#### **Phase Transition**



Pressure

Equilibrium shifts where the volume is decreasing i.e., **backward** 







#### Formation of Ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \longrightarrow \Delta H = -22.4 \text{ kcal/mol}$$

The reaction will shift in the forward direction at low temperature

1

At high pressure, the reaction will shift in the forward direction

2





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0



Container with two or more equilibria existing simultaneously involving one or more common species

Then in all equilibrium, the concentration of the common species is the total concentration of that species due to all the equilibria







A (s) 
$$\rightleftharpoons$$
 X (g) + Y (g)





At

At <sup>·</sup>

$$A(s) \rightleftharpoons M(g) + N(g) = B(s) \rightleftharpoons W(g) + N(g)$$

$$t = 0 \qquad a \qquad 0 \qquad 0 \qquad b \qquad 0 \qquad 0$$

$$t = t_{eq} \qquad -w \qquad p_1 \qquad p_1 + p_2 \qquad -q \qquad p_2 \qquad p_2 + p_1$$

$$Kp_1 = (p_1)(p_1 + p_2) \qquad Kp_2 = (p_2)(p_2 + p_1)$$



# Ionic Equilibrium

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Equilibrium between the ionized and the non-ionized form of a species

AB (aq)  $\rightleftharpoons$  A<sup>+</sup> (aq) + B<sup>-</sup> (aq)

Non-electrolytic substance

Substance which dissolves in water

Electrolytic substance

## **Quick Contrast**

	R
	V

Non - electrolytic substances	Electrolytic substances
Do not produce ions in H <sub>2</sub> O	Have tendency to produce ions in H <sub>2</sub> O
Their solutions do not conduct electricity	Their solutions conduct electricity
E.g: Urea, Glucose	E.g: Acids, Bases, Salts



















#### Equilibrium is observed in

#### Weak electrolytes

Weak electrolytes undergo partial ionization in aqueous solutions












**Arrhenius Acid** 

Substances that dissociates in water to give hydrogen ion or H<sup>+</sup> (aq)

HA (aq) 
$$\longrightarrow$$
 H<sup>+</sup> (aq) + A<sup>-</sup> (aq)





# Types of Acids











HCI (aq) 
$$\longrightarrow$$
 H<sup>+</sup> (aq) + Cl<sup>-</sup> (aq)

$$H_2SO_4$$
 (aq)  $\longrightarrow 2H^+$  (aq) +  $SO_4^{2-}$  (aq)

 $H_3PO_4$  (aq)  $\rightleftharpoons$   $3H^+$  (aq) +  $PO_4^{3-}$  (aq)







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

H<sup>+</sup> ions in water are extremely hydrated (in form of  $H_3O^+$ ,  $H_5O_2^+$ ,  $H_7O_3^+$ ) due to its high charge density

H<sup>+</sup> ions form bonds with the oxygen atoms of the solvent water molecules to form trigonal pyramidal hydronium ions.

 $H_{3}O^{+} \text{ or } [H (H_{2}O)]^{+}$ 





## Existence of H<sup>+</sup> in Water

Generalised formula of hydronium ion:

[H (H<sub>2</sub>O)<sub>x</sub>]<sup>+</sup> where 'x' is the number of water molecules attached

> $H_5O_2^+, H_7O_3^+, H_9O_4^+$ etc.





# Existence of H<sup>+</sup> Ion in Water

 $H_9O_4^+$ 

╋



 $H_5O_2^+$ 







**Arrhenius Base** 

Substances that dissociates in water to produce hydroxyl ions or OH<sup>-</sup> (aq)

BOH (aq) 
$$\longrightarrow$$
 B<sup>+</sup> (aq) + OH<sup>-</sup> (aq)







Arrhenius Bases		
Monoacidic	Diacidic	Triacidic
Gives single OH <sup>-</sup> per molecule	Gives a maximum of <mark>two OH<sup>-</sup></mark> per molecule	Gives a maximum of three OH <sup>-</sup> per molecule
кон	Ca(OH) <sub>2</sub>	AI(OH) <sub>3</sub>
Examples:	NaOH (aq) $\longrightarrow$ Na <sup>+</sup> (aq) + OH <sup>-</sup> (aq)	
	NH₄OH (aq) ≓ ۱	$NH_4^+$ (aq) + OH <sup>-</sup> (aq)





# Limited to aqueous solutions only

Does not account for the basic nature of substances that do not contain hydroxide ion (E.g. NH<sub>3</sub>)















#### **Conjugate Acid-Base Pair**









# **Conjugate Acid-Base Pair**



#### $CH_3COOH (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq) + CH_3COO^- (aq)$







# **Conjugate Acid**

Species formed by the gain of a proton by a base is called the conjugate acid of that base.





# **Conjugate Base**







# **Conjugate Acid-Base Pairs**





# Relative Strength of Acid - Base Pair



Reaction will always favour in a direction from a stronger acid to a weaker acid or from a stronger base to a weaker base













H<sup>+</sup>, Fe<sup>3+</sup>

species





















#### **Properties of Water**

Water acts as an acid as well as base according to Arrhenius & Bronsted-Lowry theory, but according to Lewis concept it is a base, not an acid

#### Self ionization of water or Autoprotolysis

 $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ 

Or  $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ 



#### **Properties of Water**



So, pure water is neither acidic nor basic





#### Molarity of water

=

#### Number of moles

Volume of the solution

For water

- Density = 1 g/cc
- Molar mass = 18 g/mol
- Volume = 1 L







# **Molar Concentration**











# Ionization Constant of Water (K<sub>w</sub>)

$$H_{2}O(I) \rightleftharpoons H^{+}(aq) + OH^{-}(aq)$$

$$K_{w} = K_{eq}[H_{2}O] \xrightarrow{} constant$$

$$K_{eq} = \frac{[H^{+}][OH^{-}]}{[H_{2}O]}$$

$$K_{w} = K_{eq}[H_{2}O] \xrightarrow{} constant$$

$$K_{eq}[H_2O] = [H^+][OH^-]$$

$$\mathbf{K}_{\mathsf{w}} = [\mathbf{H}^+] [\mathbf{O}\mathbf{H}^-]$$

B







# **Degree of Ionization of Water**

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$





# Degree of Ionization of Water











ions is written in a

simplified form

known as pH scale



#### Sorenson

#### pH is defined as **negative** logarithm of activity of H<sup>+</sup> ions





Activity of H<sup>+</sup> ions





#### In a dilute solution,

=

Activity of H<sup>+</sup> ions **Concentration** of free  $H^+$  ions or  $H_3O^+$  ions

pH scale was marked from 0 to 14 with the central point at 7 at 25 °C taking water as the solvent







In general, for any quantity **'X'**, we can define a term **pX** as











#### Taking logarithm and multiplying by (-1) on both sides,








### At any temperature,

$$pK_w = pH + pOH = 14$$







B









$$H_2O(I) \rightleftharpoons H^+(aq) + OH^-(aq)$$

### Dissociation of water is endothermic



























K<sub>w</sub> decreases from 10<sup>-14</sup> at 25 °C to (0.293 x 10<sup>-14</sup>) at 10 °C



Now 7.27 is the midpoint of the new pH scale









K<sub>w</sub> increases from 10<sup>-14</sup> at 25 °C to 38.02 x 10<sup>-14</sup> at 90 °C

$$[H^{+}] = \sqrt{K_{w}} = \sqrt{38.02 \times 10^{-14}} = 10^{-6.21}$$

$$pH = -\log [H^{+}] = 6.21$$

Now 6.21 is the midpoint of the new pH scale





### **Strong Acid Solution**



### H<sup>+</sup> ions coming from water can be neglected







### **Strong Acid Solution**



#### H<sup>+</sup> ions coming from water cannot be neglected







## Mixture of Two Strong Acids







## Mixture of Two Strong Acids



 $[H^{+}]_{1}V_{1}$ 

 $[H^{+}]_{2}V_{2}$ 

Moles of H<sup>+</sup> ions from I - solution

Moles of H⁺ions from II - solution =





# Mixture of Two Strong Acids



$$[H^{+}]_{f}V_{f} = [H^{+}]_{1}V_{1} + [H^{+}]_{2}V_{2}$$

$$[H^{+}]_{f} = \frac{[H^{+}]_{1}V_{1} + [H^{+}]_{2}V_{2}}{V_{1} + V_{2}}$$





## Mixture of Two Strong Bases







## Mixture of a Strong Acid and a Strong Base

### Acid - base neutralization reaction will take place

Solution will be acidic or basic depending upon which is taken in excess





# Mixture of a Strong Acid and a Strong Base





# Mixture of a Strong Acid and a Strong Base

If 
$$[H^+]V_1 > [OH^-]V_2$$

If 
$$[H^+]V_1$$
 <  $[OH^-]V_2$ 

$$[H^{+}]_{f} = \underbrace{ \begin{bmatrix} [H^{+}] V_{1} - [OH^{-}] V_{2} \\ V_{1} + V_{2} \end{bmatrix} }_{V_{1} + V_{2}}$$

$$\begin{bmatrix} OH^{-}]_{f} \end{bmatrix} = \begin{bmatrix} OH^{-}]V_{2} - [H^{+}]V_{1} \\ V_{1} + V_{2} \end{bmatrix}$$

#### Final solution will be acidic in nature

Final solution will be **basic** in nature





















### **Ionization of Weak Acids**

Consider a weak acid 'HA'

HA (aq) + 
$$H_2O$$
 (/)  $\rightleftharpoons$  A<sup>-</sup> (aq) +  $H_3O^+$  (aq)















## pH of a Weak Acid





At infinite dilution,  $\alpha$  reaches its maximum value, i.e. unity. Weak electrolyte starts behaving like a strong electrolyte!



### pH of a Weak Acid











### pH of a Weak Acid





Now pH calculation can be done



















# Ionization Constant of Weak Bases (K<sub>b</sub>)











# Remember!!





Now pOH calculation can be done





# Relation between pK<sub>a</sub> and pK<sub>b</sub>

### Consider a weak acid HA,

### Conjugate base of HA is A-

HA (aq) 
$$\rightleftharpoons$$
 H<sup>+</sup> (aq) + A<sup>-</sup> (aq)

 $A^{-}(aq) + H_2O(l) \rightleftharpoons OH^{-}(aq) + HA(aq)$ 





# Relation between pK<sub>a</sub> and pK<sub>b</sub>

### Multiply equation (i) and (ii)







pK<sub>a</sub> + pK<sub>b</sub>

At 25°C

# Relation between pK<sub>a</sub> and pK<sub>b</sub>

Taking logarithm and multiplying by -1 on both sides

$$-\log (K_a \times K_b) = -\log (K_w)$$

$$-\log (K_a) - \log (K_b) = -\log (K_w)$$

рК<sub>w</sub>

=

14






# B

#### **Dissociation of Electrolytes in Water**





















 $CH_3COOH (aq) \rightleftharpoons CH_3COO^- (aq) + H^+ (aq)$ 

On adding HCl,

HCl (aq) 
$$\longrightarrow$$
 Cl<sup>-</sup> (aq) + H<sup>+</sup> (aq)

Concentration of the common ion (H<sup>+</sup>)









#### **Based on Le Chatelier's Principle**

 $CH_3COOH$  (aq)  $\rightleftharpoons$   $CH_3COO^-$  (aq) + H<sup>+</sup> (aq)

Equilibrium will be shifted backwards

When a substance is present in a solution, it **may affect** the dissociation of **another substance**.



#### **Common Ion Effect**

Eq

ba

#### If H<sup>+</sup> is the common ion,

Suppression in the dissociation of a weak electrolyte by the addition of a strong electrolyte having a common ion

uilibrium shifts ackward	>	Dissociation of CH <sub>3</sub> COOH is suppressed	>	But [H⁺] in ↑ solution
		<b>pH</b> of the solutio	n	



### Mixture of Weak Acid & Strong Acid



$$K_{a} = \frac{(c_{1} + c_{2}\alpha) (c_{2}\alpha)}{(c_{2} (1 - \alpha))} \cdots \cdots (i)$$





### Mixture of Weak Acid & Strong Acid

Weak acid's dissociation will be further suppressed because of presence of strong acid therefore  $\alpha \ll 1$ 

$$\begin{bmatrix} c_1 + c_2 \alpha \end{bmatrix} \rightleftharpoons \begin{bmatrix} c_1 \\ c_1 \end{bmatrix} \& \begin{bmatrix} 1 - \alpha \end{bmatrix} \rightleftharpoons \begin{bmatrix} 1 \\ c_1 \end{bmatrix}$$

$$K_a \simeq c_1 \alpha \cdots \cdots (ii)$$





### B

#### Mixture of Weak Acid & Strong Acid





# Isohydric solutions

If the concentration of the common ions in the solution of two electrolytes is the same, then on mixing them, there is **no change in the degree of dissociation** of either of the electrolytes.







## B

#### Mixture of Two Weak Monoprotic Acids





# Mixture of Two Weak Monoprotic Acids $\frac{(c_1\alpha_1 + c_2\alpha_2) (c_1\alpha_1)}{(c_1)(1 - \alpha_1)}$ **(i)** K<sub>a₁</sub> $\frac{(c_1\alpha_1 + c_2\alpha_2) (c_2\alpha_2)}{(c_2)(1 - \alpha_2)}$ (ii

Both acids will dissociate less than in their individual aqueous solutions of the same concentration because of

 $K_{a_2}$ 

Common ion effect exerted by H<sup>+</sup> ions of one on other





 $\therefore$  From (i) and (ii) we get

$$K_{a_1}c_1$$
 = (c<sub>1</sub>α<sub>1</sub> + c<sub>2</sub>α<sub>2</sub>) (c<sub>1</sub>α<sub>1</sub>) ..... (iii)

$$K_{a_2}c_2 = (c_1\alpha_1 + c_2\alpha_2) (c_2\alpha_2)$$
 ..... (iv





#### Adding (iii) and (iv)









#### Contribution of HB in [H<sup>+</sup>] can be neglected

$$[H^+] = \left[ c_1 \alpha_1 + c_2 \alpha_2 \right] \approx \left[ c_1 \alpha_1 \right]$$





#### Acidity of a Base









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

$$AI(OH)_3$$
 (aq)  $\rightleftharpoons$   $AI^{3+}$  (aq) +  $3OH^-$  (aq)



#### **Basicity of an Acid**









$$H_3PO_4$$
 (aq)  $\rightleftharpoons$   $3H^+$  (aq) +  $PO_4^{3-}$  (aq)

Number of ionizable protons in  $H_3PO_4 = 3$ 



### B

#### K<sub>a</sub> for the Dissociation of a Dibasic Acid





$$K_{a_1}$$
  
 $H_2X (aq) \longrightarrow H^+ (aq) + HX^- (aq)$ 

$$\begin{array}{c} \mathsf{K}_{\mathsf{a}_2}\\ \mathsf{HX}^- (\mathsf{aq}) & \longleftarrow & \mathsf{H}^+ (\mathsf{aq}) + \mathsf{X}^{2-} (\mathsf{aq}) \end{array}$$





#### **Overall K a for the Reaction**

$$H_2X$$
 (aq)  $\rightleftharpoons$   $2H^+$  (aq) +  $X^{2-}$  (aq)



$$K_{a} = K_{a_1} \times K_{a_2}$$

Where  $K_a$  is the ionization constant of  $H_2X$ 





2

### K<sup>a</sup> for the Dissociation a Tribasic Acid

$$K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$$





#### **Polyprotic Acids**

Let's consider a weak polyprotic acid  $H_2CO_3$  of concentration  $c_1$ 

$$\begin{array}{ccc} H_2CO_3(aq) &\rightleftharpoons & H^+(aq) &+ & HCO_3^-(aq) \end{array}$$

$$\begin{array}{ccc} Att = t_{eq} & c_1(1 - \alpha_1) & c_1\alpha_1(1 + \alpha_2) & c_1\alpha_1(1 - \alpha_2) \end{array}$$

$$\begin{array}{ccc} HCO_3^-(aq) &\rightleftharpoons & H^+(aq) &+ & CO_3^{2-}(aq) \end{array}$$

$$\begin{array}{ccc} Att = t_{eq} & c_1\alpha_1(1 - \alpha_2) & c_1\alpha_1(1 + \alpha_2) & c_1\alpha_1\alpha_2 \end{array}$$





# **Polyprotic Acids**

$$\begin{array}{c} & [H^{+}] [HCO_{3}^{-}] \\ & [H_{2}CO_{3}] \end{array} \end{array} = \begin{array}{c} & c_{1} \alpha_{1}(1 + \alpha_{2}) c_{1} \alpha_{1}(1 - \alpha_{2}) \\ & c_{1}(1 - \alpha_{1}) \end{array} \end{array}$$

$$\begin{array}{c} & [H^{+}] [CO_{3}^{2^{-}}] \\ \hline & [HCO_{3}^{-}] \end{array} \end{array} = \begin{array}{c} c_{1} \alpha_{1} (1 + \alpha_{2}) c_{1} \alpha_{1} \alpha_{2} \\ \hline & c_{1} \alpha_{1} (1 - \alpha_{2}) \end{array}$$



#### **Polyprotic Acids**



B



#### Total [H<sup>+</sup>] released after ionization,





#### Mixture of a Polyprotic Weak Acid & a Strong Acid

рН

Generally, pH can be calculated by taking the concentration of strong acid only

Other calculations can be done by considering the **dissociation equilibria** of the weak polyprotic acid



# pH of a Mixture of a Weak Monoprotic & a Weak Polyprotic Acid



[H<sup>+</sup>] calculation can be done similar to the case of a mixture of two weak monoprotic acids



# Hydrolysis of Salts and pH of their Solutions

۲

0

0

0

SB



#### Salts and Salt Hydrolysis

Salts formed by the reaction between an acid & a base in definite proportions undergo ionization in water

lons formed either exist as hydrated ions or interact with water Process of interaction of water with cations/anions or both of the salts is called hydrolysis



Salts of strong acids & bases only get hydrated and not hydrolysed, whereas salts of other types do get hydrolysed.

**Cation** of weak base on reaction with water will produce H<sup>+</sup> ions and the **anion** of weak acid on reaction with water produce OH<sup>-</sup> ions

> pH of the solution is affected by this interaction.









#### **Cationic Hydrolysis**

 $B^+$  (aq) + 2H<sub>2</sub>O (/) BOH (aq) + H<sub>3</sub>O<sup>+</sup> (aq)

#### **Anionic Hydrolysis**

 $A^-$  (aq) +  $H_2O$  (/)  $\rightleftharpoons$  HA (aq) +  $OH^-$  (aq)




Weak Base

WB

WA

Weak Acid











#### Salt of Strong Acid - Strong Base





#### Salt of WA + SB









 $CH_3COO^-$  (aq) +  $H_2O$  (/)  $\rightleftharpoons$   $CH_3COOH$  (aq) +  $OH^-$  (aq)

 $\Box COO^{-}(aa) \pm \Box O(b) \rightarrow C\Box COOU(aa) \pm OU^{-}(aa)$ 

 $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$ 

## $CH_3COONa (aq)$ $CH_3COO^-(aq) + Na^+$ (aq)

Acetate ion formed undergoes hydrolysis in water

$$CH_3COOH$$
 (aq)  $\rightleftharpoons$   $CH_3COO^-$  (aq) + H<sup>+</sup> (aq)



$$H_2O(I) \rightleftharpoons H^+(aq) + OH^-(aq)$$

$$K_{w} = [H^+][OH^-]$$















$$CH_{2}COO^{-}$$
 (ag) +  $H_{2}O$  (/)  $\longrightarrow$   $CH_{2}COOH$  (ag) +  $OH^{-}$  (ag)







If h << 1







$$h = \sqrt{\frac{K_{h}}{c}} = \sqrt{\frac{K_{w}}{K_{a}c}}$$

$$[OH^{-}] = c \times \sqrt{\frac{K_{w}}{K_{a}c}} \longrightarrow [OH^{-}] = \sqrt{\frac{K_{w}c}{K_{a}}}$$





$$[H^+] = \frac{K_w}{[OH^-]} = \sqrt{\frac{K_w K_a}{c}}$$

#### Taking logarithm on both sides and multiplying by (-1)

$$-\log [H^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_a + \frac{1}{2} \log c$$





pH = 
$$\frac{1}{2}$$
 [pK<sub>w</sub> + pK<sub>a</sub> + log c] Valid if,  
h < 0.1 or 10%

pH = 
$$7 + \frac{1}{2} [pK_a + \log c]$$

If h obtained from 
$$\sqrt{\frac{K_h}{c}} > 0.1$$
, then solve  
the quadratic equation and get h











#### Hydrolysis of Salt of Strong Acid & Weak Base



B

Hydrolysis of Salt of Strong Acid & Weak Base

$$NH_4Cl$$
 (aq)  $\longrightarrow NH_4^+$  (aq) +  $Cl^-$  (aq)

Ammonium ion formed undergoes hydrolysis in water

$$NH_4^+$$
 (aq) +  $H_2O$  (/)  $\rightleftharpoons$   $NH_4OH$  (aq) +  $H^+$  (aq)





#### Hydrolysis of Salt of Strong Acid & Weak Base

**K**<sub>h</sub>





K<sub>w</sub>

K<sub>b</sub>







#### Hydrolysis of Salt of Strong Acid & Weak Base

Κ<sub>h</sub>

$$NH_4^+$$
 (aq) +  $H_2O$  (/)  $\rightleftharpoons$   $NH_4OH$  (aq) +  $H^+$  (aq)





=

 $[\mathsf{NH}_4\mathsf{OH}] [\mathsf{H}^+]$ 

[NH<sub>4</sub><sup>+</sup>]



# B

#### Hydrolysis of Salt of Strong Acid & Weak Base



### Hydrolysis of Salt of Strong Acid & Weak Base



Taking logarithm on both sides and multiplying by -1

$$-\log [H^+] = -1 \quad \log K_w - 1 \quad \log c + 1 \quad \log c +$$

pH = 
$$\frac{1}{2} [pK_w - pK_b - \log c]$$
 Valid if  
h < 0.1 or 10%

pH = 
$$7 - \frac{1}{2} [pK_b + \log c]$$
 At 25 °C







 $NH_4^+$  (aq) +  $CH_3COO^-$  (aq) +  $H_2O$  (/)  $\rightleftharpoons$   $CH_3COOH$  (aq) +  $NH_4OH$  (aq)

 $CH_3COO^-(aq) + NH_4^+(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NH_4OH(aq)$ 



lons formed undergo hydrolysis as

Hydrolysis of Salt of Weak Acid & Weak Base







$$K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]}$$

$$CH_3COOH (aq) \rightleftharpoons CH_3COO^- (aq) + H^+ (aq)$$

H













$$NH_4^+$$
 (aq) +  $CH_3COO^-$  (aq) +  $H_2O$  (/)  $CH_3COOH$  (aq)

Hydrolysis of Salt of Weak Acid & Weak Base



 $(aq) + NH_4OH$ 



#### Remember!!



For numerical analysis, even if  $K_a$  of weak acid &  $K_b$  of weak base are different.

Degree of hydrolysis of cations & anions are taken equal as they are very close to each other.







#### Hydrolysis of Salt of Weak Acid & Weak Base

pH = 
$$\frac{1}{2} [pK_w + pK_a - pK_b]$$
  
pH =  $7 + \frac{1}{2} [pK_a - pK_b]$  At 25 °C

This formula is **always valid for any K<sub>a</sub> and K<sub>b</sub>** at any temperature and for any value of h.

2

1

pH is **independent** of the concentration of the salt solution



### Hydrolysis of Salt of Weak Acid & Weak Base

If K <sub>a</sub> = K <sub>b</sub>	pH = 7	Neutral solution
If K <sub>a</sub> > K <sub>b</sub>	pH < 7	Acidic solution
If K <sub>a</sub> < K <sub>b</sub>	pH > 7	Basic solution



B

Type of Salt	Expressio n for K <sub>h</sub>	Expression for h	Expression for pH
Salt of WA & SB	$K_{h} = \frac{K_{w}}{K_{a}}$	$h = \sqrt{\frac{K}{h}}$	pH = $\frac{1}{2}$ [pK <sub>w</sub> + pK <sub>a</sub> + log c] (if h < 0.1)
Salt of SA & WB	$K_{h} = \frac{K_{w}}{K_{b}}$	$h = \sqrt{\frac{K}{h}}$	pH = <mark>1</mark> [pK <sub>w</sub> - pK <sub>b</sub> - log c] (if h < 0.1)
Salt of WA & WB	$K_{h} = \frac{K_{w}}{K_{a}K_{b}}$	$\frac{h}{1-} = \sqrt{K_h}$	$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$



#### Remember!!



If h is not less than 0.1, then solve quadratic equation in order to obtain h and then determine  $[H^+]$  or  $[OH^-]$ .





#### Consider H<sub>3</sub>PO<sub>4</sub>





$$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$$

$$K_{h_2} = \frac{K_w}{K_{a_2}}$$

w

 $a_3$ 

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^{-}(aq) + OH^{-}(aq)$$

Η

$$_{2}PO_{4} (aq) + H_{2}O (l) + H_{3}PO_{4} (aq) + OH^{-}$$
(aq)

$$K_{h_3} = \frac{K_w}{K_{a_1}}$$







# Thus, pH is calculated only using the first step of hydrolysis

#### Consider a salt $Na_3PO_4$ of concentration = c







If h << 1






### Salt of Weak Polyprotic Acids







С





[OH<sup>-</sup>]

=

ch

## Salt of Weak Polyprotic Acids

Taking logarithm on both sides and multiplying by (-1)

$$-\log [H^{+}] = -\frac{1}{2} \log K_{w} - \frac{1}{2} \log K_{a_{3}} + \frac{1}{2} \log c$$

$$pH = -\frac{1}{2} [pK_{w} + pK_{a_{3}} + \log c]$$

$$If h > 0.1$$
Then its exact value should be obtained by solving quadratic equation.









But in Na<sub>2</sub>HPO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub>, the ions 2. hydrolyzed are HPO<sub>4</sub> and  $H_2PO_4$ . Both are amphiprotic ions.













## Amphiprotic lons

Assuming



or  $[HPO_4^{2-}] = [H_3PO_4]$ 

pH = 
$$\frac{1}{2} \left( pK_{a_1} + pK_{a_2} \right)$$







$$+ H^{+} (aq)$$
  
 $+ H^{+} (aq)$   
 $+ H^{+} (aq)$   
 $+ H^{2}PO_{4}^{-} (aq)$   
 $+ H^{2}PO_{4}^{-} (aq)$   
 $+ PO_{4}^{3-} (aq)$   
 $- H^{+} (aq)$ 

pH = 
$$\frac{1}{2} \left( pK_{a_2} + pK_{a_3} \right)$$



B





Solutions which resist a change in pH upon addition of small amount of acid or base

pH of a buffer solution changes on the addition of an acid or a base, but it would be less than the change that would have occurred had it not been a buffer





## **Types of Buffer Solutions**







#### **Acidic Buffer Solutions**

Solution of a weak acid and its salt with a strong base

CH<sub>3</sub>COOH + CH<sub>3</sub>COONa

 $H_3PO_4 + NaH_2PO_4$ 

























#### Taking logarithm on both the sides and multiplying by (-1),







Mixing a weak acid solution and a solution of its salt with a strong base

For e.g.: Mixture of 1 mol  $CH_3COOH$  and 1 mol  $CH_3COONa$ 



## **Dissociation of a Weak Electrolyte in Water**

$$CH_3COOH (aq) \rightleftharpoons CH_3COO^- (aq) + H^+$$
  
(aq)

# Adding CH<sub>3</sub>COONa to CH<sub>3</sub>COOH solution

#### $CH_3COOH$ (aq) + $CH_3COONa$ (aq) + $H_2O$ (/)







#### **Preparation of Acidic Buffer**

Mixing a weak acid solution and lesser amount of a strong base solution than that required for neutralization

For e.g. Mixture of 1 mol  $CH_3COOH$  and 0.5 mol NaOH

Mixing a salt solution of a weak acid and a strong base with lesser amount of a strong acid solution than that required for complete reaction

For e.g.: Mixture of 1 mol CH<sub>3</sub>COONa and 0.5 mol HCl





#### **Basic Buffer Solutions**

Solution of a weak base and its salt with a strong acid

 $NH_4OH + NH_4CI$ 

 $NH_4OH + (NH_4)_2SO_4$ 





#### Buffer solution consisting of a weak base ( $[NH_4OH] = c_1$ ) & its salt ( $[NH_4CI] = c_2$ )























#### Taking logarithm on both the sides and multiplying by (-1),

















#### **Preparation of Basic Buffer**



Mixing a weak base solution and a solution of its salt with a strong acid

For e.g.: Mixture of 1 mol NH<sub>4</sub>OH and 1 mol NH<sub>4</sub>Cl



## **Dissociation of a Weak Electrolyte in Water**

 $NH_4OH$  (aq)  $\rightleftharpoons$   $NH_4^+$  (aq) +  $OH^-$  (aq)

## Adding NH<sub>4</sub>Cl to NH<sub>4</sub>OH Solution

 $NH_4OH$  (aq) +  $NH_4CI$  (aq) +  $H_2O$  (/)







#### **Preparation of Basic Buffer**

Mixing a weak base solution and lesser amount of a strong acid solution than that required for neutralization

For e.g.: Mixture of 1 mole NH<sub>4</sub>OH and 0.5 mole HCl

Mixing a salt solution of a weak base and a strong acid with lesser amount of a strong base solution than that required for complete reaction

For e.g.: Mixture of 1 mole  $NH_4Cl$  and 0.5 mole NaOH









Solution of CH<sub>3</sub>COONH<sub>4</sub>







Solution of a weak acid (HA) and its highly ionized salt

Addition of acid

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

Thus, the solution does not contain excess of  $H_3O^+$ 

pH value remains almost the same





Solution of a weak acid (HA) and its highly ionized salt

Addition of base

$$OH^- + HA \longrightarrow H_2O + A^-$$

Thus, the solution does not contain excess of OH<sup>-</sup>

pH value remains almost the same





#### pH Range of Buffer



Particular weak acid (or base) that can be employed for making useful buffer solution of pH (or pOH) lies within the range of  $(pK_a \pm 1)$  or  $(pK_b \pm 1)$ .







It is defined as the moles of a strong acid or a strong base required to change the pH of 1 L of a buffer by one unit.







The ratio of the small amount of acid or base added to the change in pH caused in the buffer.

Let there be a buffer solution of volume **1** L with **'b' mol** of anion (coming from salt) and **'a' mol of weak acid.** If **'x' mol** of a strong acid (monobasic) is added to it,







Buffer shows maximum buffer capacity when the amounts of acid (or base) and the anion (or cation) from the salt are the same.









## Maximum Buffer Capacity











# For preparing a buffer solution of the required pH

Acid whose pK<sub>a</sub> value is close to the required pH is taken



#### **Applications of Buffer**

In industrial processes e.g. Electroplating, leather industry

In biological processes, e.g., pH of our blood remains constant at about 7.4. Buffer action in blood is due to  $H_2CO_3 + HCO_3^-$  ions







Out of an acid & a base solution, taking a known volume of one of them in a flask & taking the other in a burette & finding the volume required for complete **neutralization**.

> Equivalence point is achieved when stoichiometrically equivalent amount of acid & base have combined



#### Acid - Base Titration

pH calculation at equivalence point can be done according to the nature of the species formed at the equivalence point

If the salt of a weak acid & a strong base is formed

pH = 
$$7 + \frac{1}{2} (pK_a + \log c)$$

If the salt of a strong acid & a weak base is formed

pH = 
$$7 - \frac{1}{2} (pK_b + \log c)$$







#### Indicator

Substances which indicate the end point of a titration generally by changing their colour.

#### Phenolphthalein

#### Methyl orange

Common acid-base indicators


Indicators are either weak organic acids or weak organic bases having characteristically different colours in their ionised & unionised forms.











#### Indicators



**Example:** 

#### Phenolphthalein (HPh) is a weak acid;









#### Methyl orange (MOH) is a weak base;





# Did You Know?





Human eye **can't identify** color change of indicators accurately!!

Solution acquires a distinct colour characteristic of Inif [In-] ≥ 10 [HIn]





## Indicators

. . .









#### Indicators















pH range between which the indicator changes its colour.





**Methyl Orange** 

Phenolphthalein

14 -7.6 -6.0 \_ لـ0.0

Phenol Red

14-

8.2

6.4

لـ0.0

**Bromothymol Blue** 







# pH Range of Indicator

Indicator	pH Range of Indicator	Colour changed
Phenolphthalein	(8.3 - 10)	Colourless to pink
Methyl Orange	(3.1 - 4.4)	Red to yellow
Phenol Red	(6.4 - 8.2)	Yellow to red
Bromothymol blue	(6 - 7.6)	Yellow to blue



	C	Consider	r 40 mL, 0.1 M HCl v	s 0.1 M NaOH
	itration of Strong Acid v Strong Base	/s	Volume of NaOH added	pH of solution
			0 mL	1
Eg. HCl vs NaOH		10 mL	1.22	
		20 mL	1.48	
			30 mL	1.84
			39 mL	2.90



Volume of NaOH added	pH of solution
39.9 mL	3.9
40 mL	7
40.1 mL	10.1
41 mL	11.1
50 mL	12.05





#### Strong Acid & Strong Base







#### **Selection of Indicator**

Selected indicator should be such that It offers a **colour change** near the vicinity of the pH of the solution at the **equivalence point**.

The steep section of the titration curve at the equivalence point must encompass an interval of pH values at least as large as the pH transition range of an indicator.

pH transition range of the indicator **must coincide** with the steep portion of the titration curve.



## In a Nutshell...

An indicator can be considered suitable for detecting the end-point of a particular titration if

Some part of pH range of the indicator lies within the pH range of the titration



pH range of titration: 4 – 10

Almost all common indicators (E.g.: Phenolphthalein, Methyl orange, Phenol red) can be used for endpoint detection.

**Bromothymol blue** indicator has its pH range containing the equivalence point pH. So it will serve as the **best indicator** for the given titration.



# Titration of Weak Acid vs Strong Base

#### 20 mL, 0.5 M $CH_3COOH$ (pK<sub>a</sub> = 4.7) vs 0.5 M NaOH

Titration of Weak Acid vs Strong Base

Eg: CH<sub>3</sub>COOH vs NaOH

Volume of NaOH added	pH of solution
0	2.5
5 mL	4.23
10 mL	4.7 [pH = pK <sub>a</sub> ]
15 mL	5.17

Half Equivalence Point (both components of buffer in equal amounts)



# Titration of Weak Acid vs Strong Base

Volume of NaOH added	pH of solution	
19 mL	6	
20 mL	9.05	
21 mL	12.09	
30 mL	13	

Equivalence point: Complete Neutralization Salt of WA & SB (CH<sub>3</sub>COONa = 0.25 M)





# Titration of Weak Acid vs Strong Base

Weak Acid & Strong Base



Volume Of NaOH (mL) —

pH range of titration: 7 – 10

Common indicators that can be used are Phenolphthalein & Phenol red.





## Titration of Strong Acid vs Weak Base

100 mL, 0.05 M  $NH_4OH$  (pK<sub>b</sub> = 4.74) vs 0.1 M HCL

Titration of Strong Acid	Volume of HCL added	рН
vs Weak Base	0 mL	10.98
	10 mL	9.86
Eg: HCl vs NH <sub>4</sub> OH	20 mL	9.43
	25 mL	9.26

Half Equivalence Point (Maximum buffer capacity)



# Titration of Strong Acid vs Weak Base

#### 100 mL, 0.05 M $NH_4OH$ (pK<sub>b</sub> = 4.74) vs 0.1 M HCL

Volume of HCL added	рН	
40 mL	8.65	
50 mL	5.37	
60 mL	2.2	
70 mL	1.93	

Equivalence point





# Titration of Strong Acid vs Weak Base

Strong Acid & Weak Base



#### pH range of titration: 4 – 7

Common indicators that can be used are Methyl orange, Methyl red & Phenol red.





# Titration of Weak Acid vs Weak Base



#### Eg: CH<sub>3</sub>COOH vs NH<sub>4</sub>OH

Titration of weak acid & weak base is generally **not carried out in laboratory** because of the **very small pH range** of this titration (6.5 - 7.5).



## Titration of Weak Acid vs Weak Base

In this particular case, neither the steep rise of pH near the equivalence point occurs Nor the rise of pH encompasses an interval equal to the pH transition range of any of the indicators.

**No common indicators** can perform appropriately in this **small pH range**.

However, if this titration is carried out, then Phenol Red would be the best indicator.





Maximum amount of solute that can be dissolved in a specified amount of solvent at a specified temperature to form a saturated solution.







# **Classification of Salts**

Category I	Soluble	Solubility > 0.1 M
Category II	Slightly soluble	0.01 M < Solubility < 0.1 M
Category III	Sparingly soluble	Solubility < 0.01 M

Solubility > 0.1 M	0.01 M < Solubility < 0.1 M	Solubility < 0.01 M	
Soluble	Slightly soluble	Sparingly soluble	





An equilibrium is established between the undissolved salt and its ions in the solution.

Considering **BaSO**<sub>4</sub>, a sparingly soluble salt, being added in water:





Precipitation













Κ<sub>sp</sub>

Product of molar concentrations of ions in the saturated solution raised to a power equal to the coefficient of the ion







#### For a solid salt of the general formula $M_x X_y$ with molar solubility S,

$$M_x X_y$$
 (s)  $\rightleftharpoons x M^{p+}$  (aq) +  $y X^{q-}$  (aq)

XS

ys

Equilibrium concentration

Where,  $x \times p = y \times q$ 







#### **Relation between K**<sub>sp</sub> & Solubility











**K**<sub>ip</sub>



For a solution of a salt at a **specific concentration**, the product of the concentrations of the ions, each raised to the power equal to the coefficient of the ions





# Solubility Product vs Ionic Product

Solubility product (K<sub>sp</sub>)

Ionic product (K<sub>ip</sub>)

Applicable to only saturated solutions

Applicable to saturated as well as unsaturated solutions

Measures the maximum amount of ions that the solution can dissolve Measures the actual amount of ions in the solution





## **Solubility Product vs Ionic Product**

$$M_x X_y$$
 (s)  $\rightleftharpoons$   $x M^{p+}$  (aq) +  $y X^{q-}$  (aq)



Solution is More salt can No precipitate dissolve formation




#### **Solubility Product vs Ionic Product**

$$M_x X_y$$
 (s)  $\rightleftharpoons$   $xM^{p+}$  (aq) +  $yX^{q-}$  (aq)



Solution will become No precipitate saturated formation





#### **Solubility Product vs Ionic Product**

$$M_x X_y$$
 (s)  $\rightleftharpoons$   $x M^{p+}$  (aq) +  $y X^{q-}$  (aq)



Solution is holding more salt that it can dissolve

Precipitate formation takes place





#### **Conditions for Precipitation**





# Solubility in the Presence of a Common Ion

0

0

0

•

0

B



## Effect of Common Ion on the Solubility of Sparingly Soluble Salts

Presence of a common ion in the solution decreases the solubility of a given sparingly soluble salt.



## Solubility in the Presence of a Common Ion









At lower pH

Solubility of salts of weak acids like phosphates increases

At low pH, [Anion]

Due to its protonation

Solubility of salt



When two sparingly soluble salts are added in water simultaneously, there will be simultaneous equilibrium in the solution.

Simultaneous solubility of each salt will be **less** than its individual solubility because of

**Common ion effect** exerted by ion coming from other salt



. . .

AgCl (s) + H<sub>2</sub>O (/) 
$$\rightleftharpoons$$
 Ag<sup>+</sup> (aq) + Cl<sup>-</sup> (aq)  $K_{sp_1}$ 

$$s_1 + s_2$$
  $s_1$ 

AgBr (s) + 
$$H_2O(l) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

$$s_1 + s_2 \qquad s_2$$
  

$$s_1 \qquad Solubility of AgCl \qquad S_2 \qquad Solubility of AgB$$





Therefore,

$$K_{sp_{1}} = (s_{1} + s_{2}) (s_{1}) - \dots (i)$$

$$K_{sp_{2}} = (s_{1} + s_{2}) (s_{2}) - \dots (ii)$$

Adding equation (i) & (ii)

$$K_{sp_1} + K_{sp_2} = (s_1 + s_2)^2$$





Therefore,





$$s_{2} = \frac{K_{sp_{2}}}{\sqrt{K_{sp_{1}} + K_{sp_{2}}}}$$







One precipitate is mixed with a solution of an ion to get another precipitate and another ion in solution.

AgCl (s) + NaBr (aq) 🛁 AgBr (s) + NaCl (aq)

$$K_{sp} (AgCl) = [Ag^+] [Cl^-]$$
$$K_{sp} (AgBr) = [Ag^+] [Br^-]$$







#### **Selective Precipitation**

If a single solution has **two or more ions** both having the tendency to precipitate with an ion of a reagent

The ion which requires less concentration of ions of the reagent for precipitation will precipitate out first.





Consider a sparingly soluble salt 'MA' where  $A^{-}$  is the anion of weak acid 'HA'

$$K_{sp} = s [A^-]$$

$$A^{-}(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^{-}(aq)$$
  $K_h = \frac{K_h}{K_h}$ 









$$HA (aq) \rightleftharpoons H^{+} (aq) + A^{-} (aq)$$

$$[HA] = \left( \frac{[H^{+}] [A^{-}]}{K_{a}} \right)$$

$$[HA]$$



#### Putting equation (ii) in equation (i)













Solubility of Salts Involving Anion from Weak Acid in a Buffer Solution

•

0

0

Let AgCN (s) be added to a buffer solution having  $H^+$  ([ $H^+$ ] = c)

S - X

S

$$K_{eq} = K_{sp}$$

$$CN^{-}(aq) + H^{+}(aq) \rightleftharpoons HCN(aq)$$
  
s-x c x



Adding both equations, we get







`sp



















## Effect of Complex Formation on Solubility

Consider the solubility of AgCl in a solution of  $NH_3$  (where  $[NH_3] = a$ )

$$\begin{array}{ccc} Ag^{+}(aq) &+& 2NH_{3}(aq) \rightleftharpoons [Ag(NH_{3})_{2}]^{+}(aq) \\ \hline & & & & \\ x - y & & & a - 2y & y \end{array}$$



# B

# Effect of Complex Formation on Solubility

$$K_{sp} (AgCl) = (x - y) x$$









## Effect of Complex Formation on Solubility

Adding equations (i) & (ii), we get

AgCl (s) + 2NH<sub>3</sub> (aq) 
$$\rightleftharpoons$$
 [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (aq) + Cl<sup>-</sup> (aq)

$$K = K_{sp} \times K_{f}$$

$$\left(\begin{array}{c} K_{sp} \times K_{f} \\ \end{array}\right) = \left(\begin{array}{c} xy \\ (a - 2y)^{2} \end{array}\right)$$





## Effect of Complex Formation on Solubility

If the complex is stable, then  $\mathrm{K}_{\mathrm{f}}$  will be high



$$\left(\begin{array}{c} K_{sp} \times K_{f} \end{array}\right) = \left(\begin{array}{c} \frac{x^{2}}{(a - 2x)^{2}} \end{array}\right)$$

Due to the formation of complex, solubility increases.

