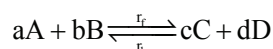


## Chemical Equilibrium

Consider a reversible reaction,



### At Equilibrium State

Rate of forward reaction ( $r_f$ ) = rate of backward reaction ( $r_b$ )

So, at equilibrium,

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{K_f}{K_b} \quad \text{In terms of active mass}$$

$$K_P = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad \text{In terms of partial pressure}$$

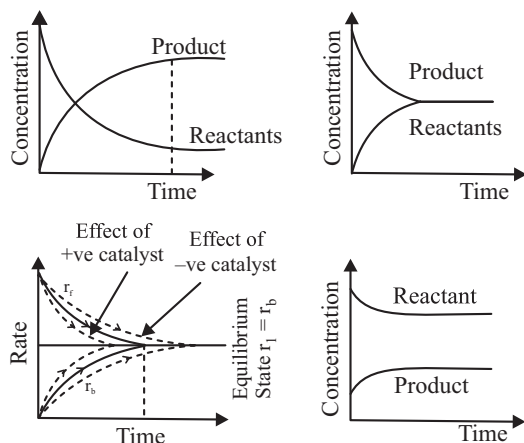
$$K_X = \frac{[X_C]^c [X_D]^d}{[X_A]^a [X_B]^b} \quad \text{In terms of mole fraction}$$

$$K_P = K_C (RT)^{\Delta n_g} = K_X P^{\Delta n_g}$$

While determining  $\Delta n_g$  take only gaseous species.

The active mass of solid & pure liquid is a constant quantity (unity) because it is an intensive property.

### Graphs



### Unit of Equilibrium constant

$$K_C = (\text{mol L}^{-1})^{\Delta n_g}; K_P = (\text{atm})^{\Delta n_g}$$

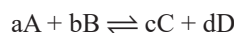
Application of  $K_C$  or  $K_P$

- ❖ More is the value of  $K_P$  or  $K_C$  more is the extent of reaction.
- ❖ Stability of reactant increases when value of  $K$  decreases.
- ❖ Stability of Product increases when value of  $K$  increase.

### Characteristics of Equilibrium Constant

**Predicting the direction of reaction:** Reaction Quotient ( $Q$ ) is expressed in the same way as for equilibrium constant, except that the concentrations may not necessarily be at equilibrium.

In general for the reversible reaction:



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

$$Q = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b} \quad (\text{in terms of pressure})$$

If  $Q = K_{eq}$  then system is in equilibrium

If  $Q > K_{eq}$  then system proceed in backward direction to attain equilibrium.

If  $Q < K_{eq}$  then system proceed in forward direction to attain equilibrium.

### Degree of dissociation ( $\alpha$ )

$$\alpha = \frac{\text{No. of moles of reactant dissociated}}{\text{No. of mole of reactant present initially}}$$

### Le-chatelier's Principle

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature then the equilibrium is shifted in such a way as to nullify the effect of change.

Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

## Chemical Equilibrium

Effect due to change in		$\Delta n_g = 0$ $A \rightleftharpoons B$	$\Delta n_g > 0$ $A \rightleftharpoons 2B$	$\Delta n_g < 0$ $2A \rightleftharpoons B$
Concentration	(i) $\uparrow [A]$	Forward direction	Forward direction	Forward direction
	(ii) $\downarrow [A]$	Backward direction	Backward direction	Backward direction
Pressure	(i) $\uparrow$ in pressure	Unchanged	Backward direction	Forward direction
	(ii) $\downarrow$ in pressure	Unchanged	Forward direction	Backward direction
Temperature	(i) $\uparrow$ in Endothermic	Forward direction	Forward direction	Forward direction
	(ii) $\uparrow$ in Exothermic	Backward direction	Backward direction	Backward direction
Dissociation	(i) $\uparrow$ in pressure	Unchanged	Dissociation Decreases	Dissociation Increases
	(ii) $\uparrow$ in volume	Unchanged	Dissociation Increases	Dissociation Decreases
Mixing of inert gas	(i) at constant P	Unchanged	Dissociation Increases	Dissociation Decreases
	(ii) at constant V	Unchanged	Unchanged	Unchanged

### Relationship between Equilibrium Constant K, Reaction Quotient Q and Gibbs Energy G

$\Delta G = \Delta G^\circ + RT \ln Q$  ... (i) where,  $\Delta G^\circ$  = Standard free energy difference between the products and reactant, T = Absolute temperature in kelvin, R = Universal gas constant.

At equilibrium, when  $\Delta G = 0$  and  $Q = K_c$ , then equation (i) becomes

$$0 = \Delta G^\circ + RT \ln K_c \quad \text{or} \quad \Delta G^\circ = -RT \ln K_c \quad \text{or} \quad \ln K_c = (-\Delta G^\circ / RT)$$

**Case I:** If  $\Delta G^\circ < 0$ , then  $(-\Delta G^\circ / RT)$  is positive, i.e.,  $e^{(-\Delta G^\circ / RT)} > 1$  hence  $K_c > 1$ , which implies a spontaneous reaction, i.e., the reaction proceeds in the forward reaction.

**Case II:** If  $\Delta G^\circ > 0$ , then  $(-\Delta G^\circ / RT)$  is negative, i.e.,  $e^{(-\Delta G^\circ / RT)} < 1$ , hence  $K_c < 1$ , which implies a non-spontaneous reaction or the reaction proceeds in the forward direction to a very small extent i.e., only a very small quantity of product is formed.

## Ionic Equilibrium

ACID			BASE	
Strong	Weak		Strong	Weak
HClO <sub>4</sub> HI HBr H <sub>2</sub> SO <sub>4</sub> HCl HNO <sub>3</sub>	HClO <sub>3</sub> HClO <sub>2</sub> HClO H <sub>3</sub> PO <sub>4</sub> H <sub>3</sub> PO <sub>3</sub> H <sub>3</sub> PO <sub>2</sub> H <sub>2</sub> S	H <sub>2</sub> CO <sub>3</sub> HNO <sub>2</sub> H <sub>2</sub> SO <sub>3</sub> HCN H <sub>3</sub> BO <sub>3</sub> HF Almost all organic acid Like: [acetic acid oxalic acid]	Group-1 hydroxide except-LiOH NaOH KOH RbOH Group-2 hydroxide except Be(OH) <sub>2</sub> and Mg(OH) <sub>2</sub> **Ca(OH) <sub>2</sub> Sr(OH) <sub>2</sub> Ba(OH) <sub>2</sub>	All other bases like NH <sub>4</sub> OH Zn(OH) <sub>2</sub> Al(OH) <sub>3</sub> Fe(OH) <sub>3</sub> Cu(OH) <sub>2</sub> etc.

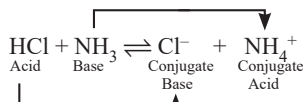
### Acid Base Theories (Arrhenius Concept)

Acid	Base
Which produce H <sup>+</sup> ion in aqueous solution. e.g. HCl, H <sub>2</sub> SO <sub>4</sub> , HClO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , CH <sub>3</sub> COOH but <b>H<sub>3</sub>BO<sub>3</sub> is not an Arrhenius acid.</b> <b>Major Limitation:</b> Defined only in water solvent.	Which produce OH <sup>-</sup> ion in aqueous solution. e.g. NaOH, Mg(OH) <sub>2</sub> , Ba(OH) <sub>2</sub>

### Bronsted – Lowry Concept

**Acid:** Which gives  $H^+$  in any solvent.

**Base:** Which accepts  $H^+$  in any solvent



**Major Limitation:** Does not explain acidic behaviour of aprotic acids e.g.  $SO_2$ ,  $CO_2$ ,  $AlCl_3$ ,  $SiCl_4$

- ❖ To find conjugate base of any Acid  $\rightarrow$  Remove one  $H^+$
- ❖ To find conjugate acid of any Base  $\rightarrow$  add one  $H^+$
- ❖ Water is Amphoteric solvent (can accept as well as lose  $H^+$ )  
 $H_2O \rightleftharpoons H^+ + OH^-$   
 $H_2O + H^+ \rightleftharpoons H_3O^+$

### Lewis Theory

Acid		Base	
Types of Lewis Acid		Types of Lewis Base	
Lewis acid is an electron pair acceptor.		Lewis base is an electron pair donor.	
1.	<b>Having Incomplete octet:</b> $BF_3$ , $BCl_3$ , $B(OH)_3$ , $AlCl_3$ etc.	1.	<b>Neutral molecule having lone pair</b> $\ddot{N}H_3$ , $R-\ddot{N}H_2$ , $R_2-\ddot{N}H$ , $H-\ddot{O}-H$ , $R-\ddot{O}-R$ etc.
2.	<b>Having vacant d-orbitals:</b> $SF_4$ , $SF_6$ , $SnCl_2$ , $SnCl_4$ etc.	2.	<b>Anions:</b> $O^{2-}$ , $SO_4^{2-}$ , $CO_3^{2-}$ , $Cl^-$ , $Br^-$ , $I^-$ , $CH_3COO^-$ etc. ❖ All the Lewis bases are Bronsted bases but all the Lewis acids are not Bronsted acids. ❖ All Arrhenius acids are Bronsted acid but it is not so for bases.
3.	<b>Having multiple bonds between atoms of different EN:</b> $CO$ , $SO_2$ , $SO_3$ etc.		
4.	<b>Cations</b> $Ag^+$ , $Li^+$ , $Al^{3+}$ , $Mg^{2+}$ <b>False cations (which cannot act as Lewis acid):</b> $NH_4^+$ , $H_3O^+$ , $PH_4^+$ etc.		

### Ostwald's Dilution Law

OSTWALD'S DILUTION LAW	FOR PURE WATER
(Only for weak electrolytes) $\alpha \propto \sqrt{\text{dilution}}$ dilution $\uparrow \Rightarrow \alpha \uparrow$ <b>Explanation of water</b> $H_2O \rightleftharpoons H^+ + OH^-$ $K_w$ = Ionic product of water $pK_w = pH + pOH$ $K_w$ = dissociation constant of water $K = \frac{K_w}{[H_2O]} [\because [H_2O] = 55.5]$	1. $[H^+] = [OH^-]$ 2. $pH = pOH$ 3. $(pH)_{\text{pure water}} = \frac{pK_w}{2}$ + pH of an acidic solution is always less than pH of pure water. + pH of a basic solution is always greater than pH of pure water.

### Hydrolysis of Salts

Salt	Hydrolysis	Resulting solution	Hydrolysis constant ( $K_h$ )	Degree of hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline $pH > 7$	$k_w / k_a$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$
Strong acid and Weak base	Cationic	Acidic $pH < 7$	$k_w / k_b$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w - pK_b - \log C]$
Weak acid and Weak base	Anionic and Cationic both	Neutral, $pH = 7$ (If $K_a = K_b$ )	$k_w / (k_a \cdot k_b)$	$h = \sqrt{K_h}$	$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

## Buffer Solutions

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

Buffers are classified into two categories:

- ❖ **Simple buffers:** These are the solutions of salts of weak acid and weak base. For example,  $\text{CH}_3\text{COONH}_4$  (ammonium acetate).
- ❖ **Mixed buffers:** These are the mixtures of two solutions. These are further of two types:
  - + **Acidic buffers:** These are the solutions of mixtures of weak acid and salt of this weak acid with strong base. For example,  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ . They have pH value lesser than 7.
  - + **Basic buffers:** These are the solutions of mixtures of weak base and salt of this weak base with strong acid. For example,  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ . They have the pH value more than 7.

- ❖ pH of an acidic buffer:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{pK}_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

- ❖ pH of a basic buffer:

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]} = \text{pK}_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

$$\text{Buffer capacity} = \frac{\text{No. of moles of acid or base added per litre of buffer}}{\text{Change in pH}}$$

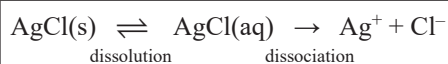
The range of pH over which the buffer solutions remain effective is called **buffer range**.

Buffer	Buffer range in pH
Acidic	$\text{pK}_a \pm 1$
Basic	$(\text{pK}_w - \text{pK}_b) \pm 1$

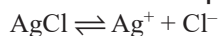
## Solubility (s) & Solubility Product ( $K_{sp}$ )

### Solubility

The maximum amount of solute that can be dissolved in a particular amount of solvent at a given temperature is called solubility(s). It is generally expressed in molarity.



### Solubility Product ( $K_{sp}$ )



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

$K_{sp}$  depends only on temperature.

**Expressions of  $K_{sp}$  :**  $\text{A}_x\text{B}_y \rightleftharpoons x\text{A}^{y+} + y\text{B}^{x-}$

$$\text{General form } K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

In terms of 'S':  $K_{sp} = (xS)^x (yS)^y = x^x \cdot y^y \cdot S^{(x+y)}$

### Ionic Product ( $Q_{sp}$ )

$$\text{A}_x\text{B}_y \rightleftharpoons x\text{A}^{y+} + y\text{B}^{x-}; Q_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

In  $Q_{sp}$  the concentration taken are at any time but in  $K_{sp}$  the concentration are at equilibrium time/saturation time.

### Application

1. If  $Q_{sp} < K_{sp}$  [unsaturated]
2. If  $Q_{sp} = K_{sp}$  [saturated]
3. If  $Q_{sp} > K_{sp}$  [super saturated/ppt. will form]

### Effect of Common Ion

Presence of common ion decreases the solubility but has no effect on  $K_{sp}$  as it depends only on temperature.

### Effect of Odd Ion

Presence of odd ion increases the solubility but has no effect on  $K_{sp}$ .

Acid-base Titration		
Type of titration	pH range of titration	Suitable indicators
SA/SB	3-11	All indicators (MeOH, HPh etc.)
SA/WB	3-7	Methyl orange (MeOH) and methyl red
WA/SB	7-11	Phenolphthalein (HPh)
WA/WB	6.5-7.5	Phenol red

### Key Tips

- ❖ Buffer capacity =  $\frac{\text{No. of moles of acid/base added per litre}}{\text{change in pH of buffer solution}}$
- ❖ Maximum buffer action when  $[\text{salt}] = [\text{acid}]$
- ❖ pH of Amphiprotic species: ( $\text{NaHPO}_4$ ,  $\text{NaHCO}_3$ ) which can donate as well as accept  $\text{H}^+$ ;  $\text{pH} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2}$