



# THE IIT - JEE SECRET

JEE MAINS AND JEE ADVANCED

PHYSICAL CHEMISTRY  
VOL - II



## Contents

<b>1. Chemical Equilibrium</b>	<b>1</b>
<b>2. Thermodynamics</b>	<b>63</b>
<b>3. Thermo Chemistry</b>	<b>159</b>
<b>4. Ionic Equilibrium</b>	<b>185</b>

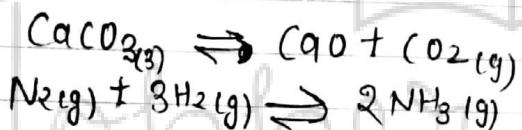
# CHEMICAL EQUILIBRIUM

Reactions are of two types -

1. Irreversible
2. Reversible

Reversible Reactions:-

Reactions which occur in both dir<sup>n</sup> & attain equilibrium after some time in a closed container  
eg-



Irreversible Reactions:-

Reactions which occur in a particular dir<sup>n</sup> if rxn occur in open container  
Some reactions can occur in aqueous medium also without using a closed container but it can give one sided rxn  
eg-  $\text{HCl} + \text{NaOH} \xrightarrow{\text{aq}}, \text{NaCl} + \text{H}_2\text{O}$

As no ions can leave the closed system Do it is not necessary to use closed container here.

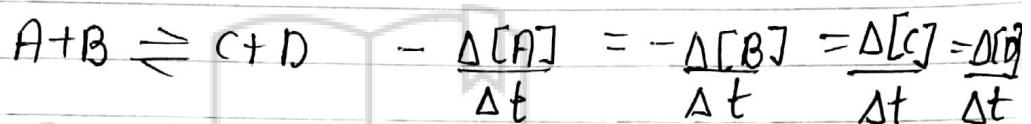
⇒ Closed system:- The actual meaning of closed system is that no ions & no reactant entities & product entities can leave the rxn system during progress of rxn

e.g. Decomposition of any compound in an open container which involves some gases in it is an e.g. of irreversible reactions.

## REVERSIBLE REACTION

(Detail + Equilibrium involved)

Rate of rxn



$$\text{Rate} = - \frac{[A]_f - [A]_i}{t_f - t_i} = \frac{[B]_f - [B]_i}{t_f - t_i} = \frac{[C]_f - [C]_i}{t_f - t_i} = \frac{[D]_f - [D]_i}{t_f - t_i}$$

Rate is defined as concentration change of reactant per unit time or concentration change of product per unit time,

But it is convention that we show rate of reaction with a positive value in a particular direction so we use extra negative sign when we calculate rate of reaction in terms of concentration change of reactant per unit time.

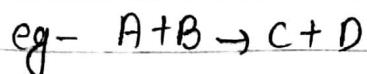
The dependency factor to control the rate of rxn.

Rate of rxn  $\propto [A][B]$

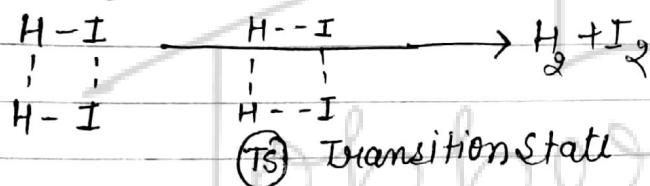
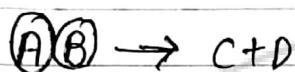
⇒ In general reaction are of two types -

## 1) Elementary Reactions:-

$\text{Rx}^n$ s which complete in one step



In effective collision one molecule of A + One molecule of B involves simultaneously & convert directly into the product following a transition state [entity in which previous bonds break & new bonds form partially & it is highly unstable entity]



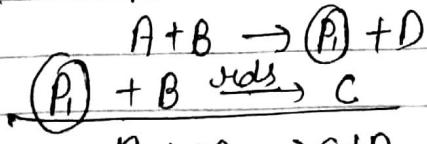
$$\text{Rate of ex}^n \propto [\text{A}][\text{B}]$$

$$\text{Rate of ex}^n = k[\text{A}][\text{B}]$$

Here k is proportionality constant called specific rate or Rate constant.

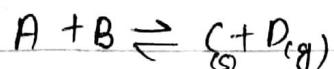
## (e) Complex Reactions:-

$\text{Rx}^n$  which occur in more than one steps & follow some intermediate entity which is product of any step and reactant of other but does not appear in net chemical eqn.



rate determining step (uds)  
uds  $\propto [\text{P}_1][\text{B}]$

$\Rightarrow$  If  $A + B \rightleftharpoons C + D$  can occur in both dir<sup>n</sup> in a closed container



$$t=0 \quad \nu_f = K_f [A][B] = \text{max}$$

$$\nu_b = K_b [C][D] = 0$$

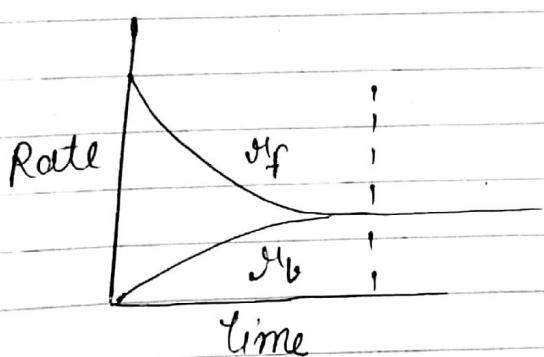
with progress  $\nu_f \downarrow \text{ & } \nu_b \uparrow$

$$t = t_{\text{eq}}: \quad \nu_f = \nu_b$$

$$-\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[C]}{\Delta t}$$

$$\Delta[A] = \Delta[C]$$

Net change in conc. of any entity = 0  
 conc. of all entities involved in equilibrium  
 System becomes equal to constant after equilibrium



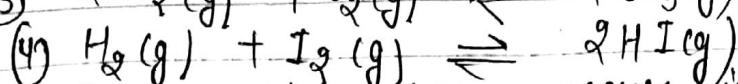
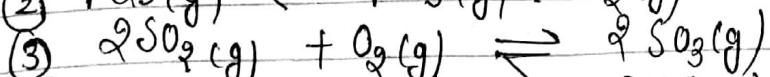
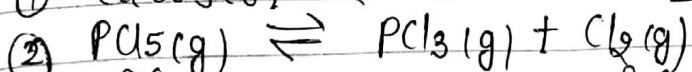
$t < t_{\text{eq}}$ :

$$\nu_{\text{net}} = \nu_f - \nu_b > 0$$

$t = t_{\text{eq}}$ :

$$\nu_{\text{net}} = \nu_f - \nu_b = 0$$

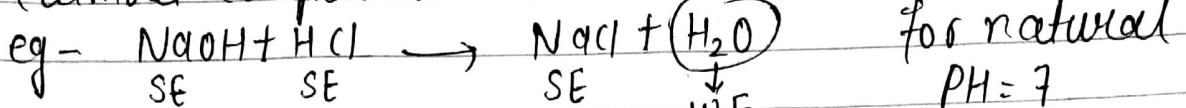
$\Rightarrow$  Some examples of reversible reactions.



All reactions above occur in a closed system.

## CRITERIA USED FOR DECIDING THAT A RXN WOULD BE REVERSIBLE OR IRREVERSIBLE

① when the reactants are all strong electrolytes while at least one of the product is weak electrolyte then the rxn becomes irreversible (almost completed).



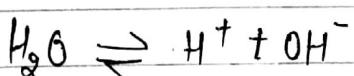
$$\text{PH} = 7$$

$$-\log [\text{H}^+] = 7 \\ [\text{H}^+] = 10^{-7} \text{ M}$$

$$[\text{H}_2\text{O}] = \frac{n \text{ H}_2\text{O}}{V \text{ H}_2\text{O}} = \frac{w \text{ H}_2\text{O}}{\text{mole H}_2\text{O} \times V \text{ H}_2\text{O} (\text{ml})}$$

$$= \frac{d \text{ H}_2\text{O} \times 1000}{\text{mole H}_2\text{O}}$$

$$= \frac{1000}{18} = 55.55 \text{ M}$$



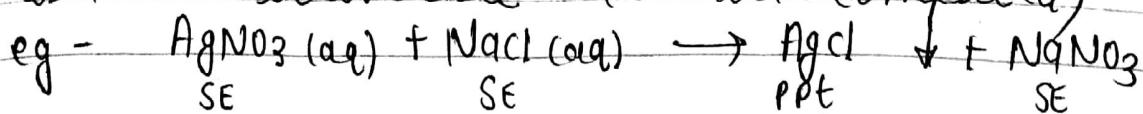
at eq:  $55.55 - x \cdot n \quad n$

$$x = 10^{-7} \text{ M}$$

$$\alpha = \frac{x}{55.55} = \frac{10^{-7}}{55.55}$$

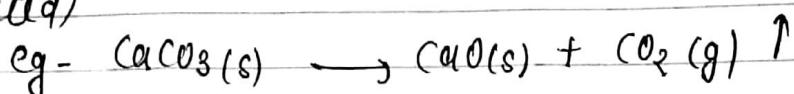
$$\% \text{ dissociation} = 100 \times \alpha = \frac{10^{-7}}{55.55} \times 100$$

② If one of the product formed is insoluble i.e. its precipitate form then the rxn will be irreversible (almost completed)



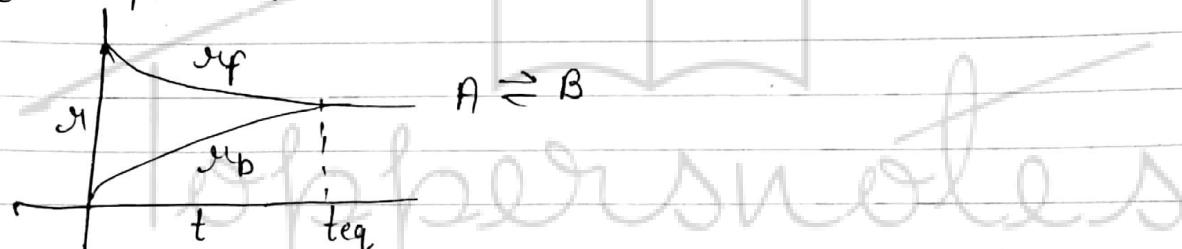
SE SE WE

③ If all the reactants are either solid or liquid and at least one of the product is gas and reaction is carried out in an open vessel then the rxn is irreversible (completed)



### CHARACTERISTIC OF EQUILIBRIUM STATE

(i)  ~~$\Delta H_{\text{forward}}$  &  $\Delta H_{\text{backward}}$~~  = 0



② Concentration of reactants & products remains constant at eq. state & they may be same or may not be.



$$\begin{array}{lll} \text{Conc.} & 1 - 0.3 & 0.3 \\ \boxed{t = t_{\text{eq}}} & = 0.7 & \end{array}$$

$$\hookrightarrow \Delta F = \Delta B$$

$$K_F[A] = K_B[B]$$

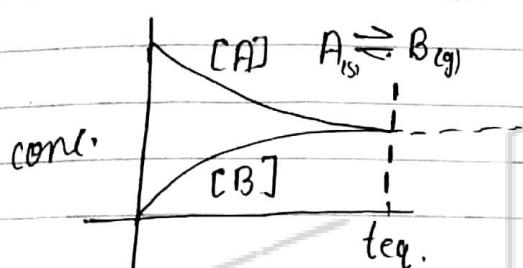
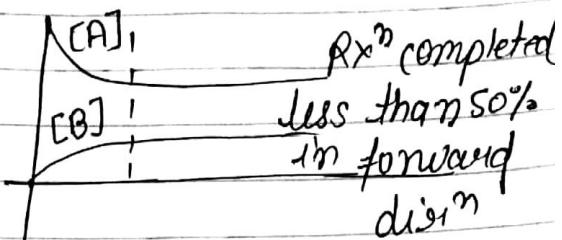
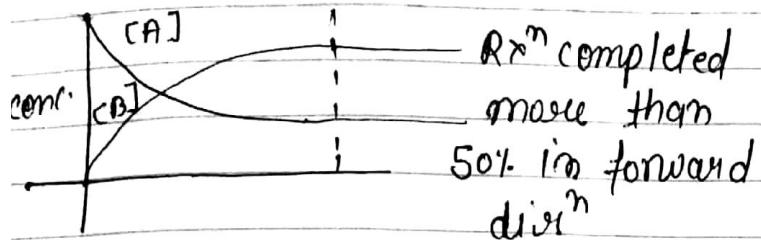
$$K_F \times 0.7 = K_B \times 0.3$$

$$\boxed{t < t_{\text{eq}}} \quad \Delta_{\text{net}} = \Delta F - \Delta B$$

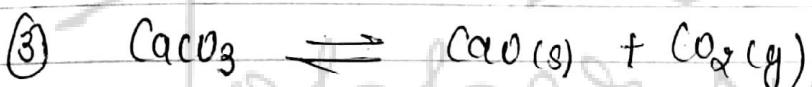
$$= K_F[A] - K_B[B]$$

$$\Delta_{\text{net}} = K_F \times 0.8 - K_B \times 0.2 > 0 \text{ Before eqn}$$

$\Delta_{\text{rxn}}$  moves forward in forward direction

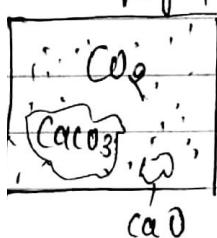


$Rx^n$  just completed 50%



$$[\text{CO}_2] = \frac{n \text{CO}_2}{V_{\text{container}}} = \frac{w_{\text{CO}_2} \times 1}{\text{molar CO}_2 \text{ container}} = \frac{d \text{CO}_2}{\text{molar CO}_2}$$

Rigid



= constant only at eq<sup>n</sup>

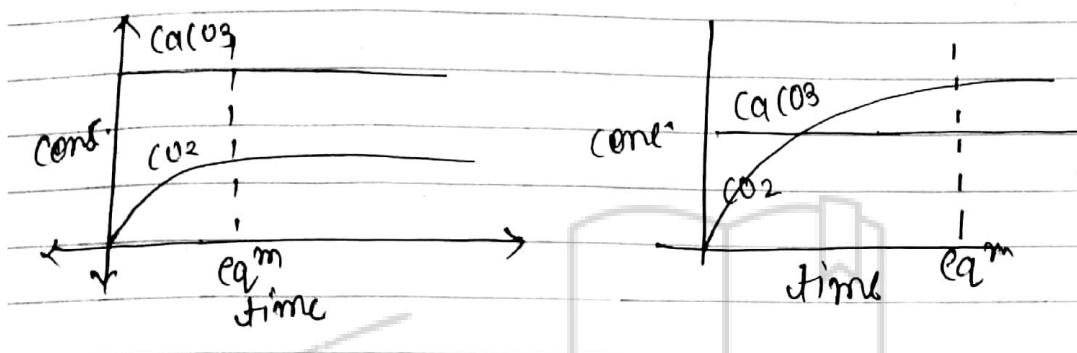
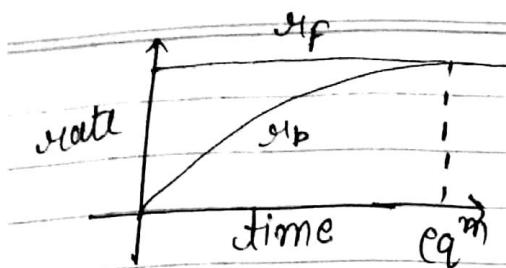
$$[\text{CaO(s)}] = \frac{n \text{CaO}_3}{V_{\text{CaO}_3}} = \frac{w_{\text{CaO}_3} \times 1}{\text{molar CaO}_3 \text{ container}} = \frac{d \text{CaO}_3}{\text{molar CaO}_3}$$

= constant with progress of rx<sup>n</sup>

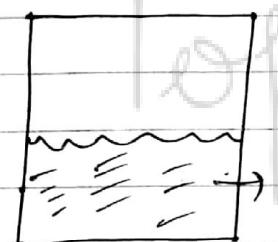
$$[\text{CaO(s)}] = \frac{d \text{CaO}_3}{\text{molar CaO}_3} = \text{constant}$$

$$J_{\text{f}} = K_f [\text{CaO}_3] = K_f'$$

$$J_{\text{b}} = K_b [\text{CaO}] [\text{CO}_2] = K_b' [\text{CO}_2]$$

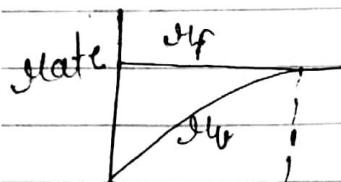


next example



$$\begin{aligned} J_f &= J_{\text{evaporation}} = K_f [H_2O(l)] = K_f' \\ J_b &= J_{\text{condensation}} = K_b [H_2O(g)] \end{aligned}$$

$$[H_2O(l)] = \frac{n H_2O(l)}{V H_2O(l)} = \frac{w H_2O(l)}{m H_2O(l) V(l)} = \frac{d H_2O(l)}{m H_2O(l) V(l)} = \text{const.}$$

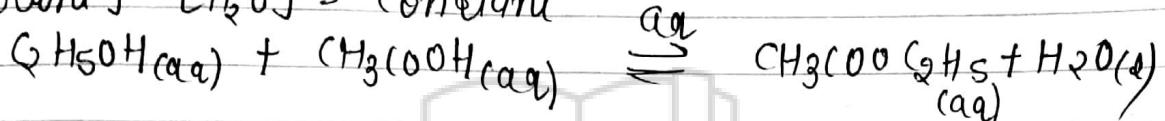


⇒ for a pure solid or a pure liquid substance which gain their own volume, the conc. remains constant with progress of  $J_b^m$ , because density  $m$  is fixed for such substances with progress of reaction.

→ for gases & species that exist in solution phase the conc. changes with time as their density changes.

$$[\text{ions}] = \frac{\text{no. of ions}}{\text{Vol}^n} = \text{Variable}$$

$$[\text{Solvent}] = [\text{H}_2\text{O}] = \text{constant}$$

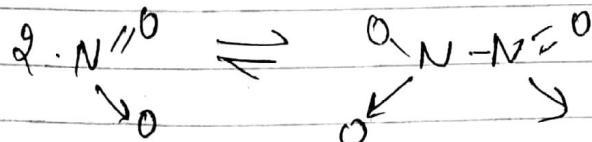
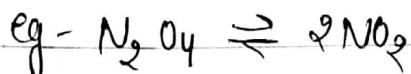


$$K_f = k_f [\text{CH}_3\text{COOH}] [\text{H}_3\text{O}^{+}]$$

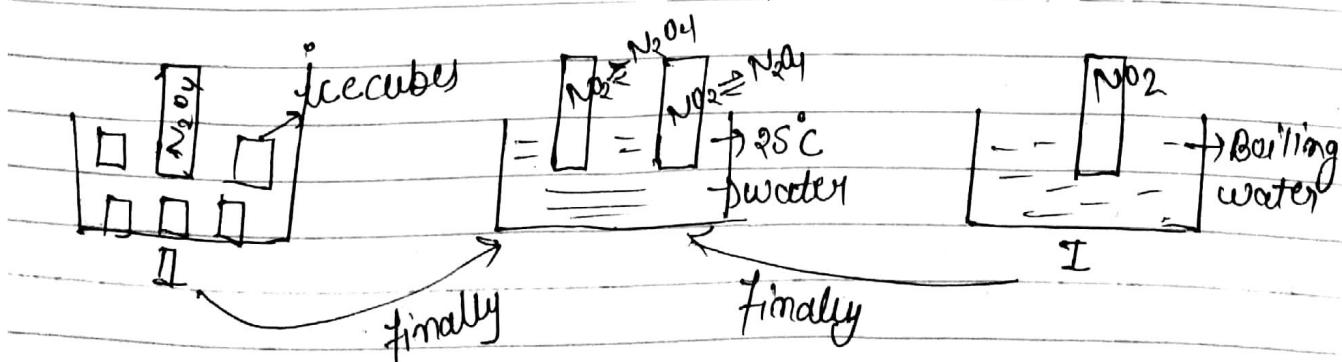
$$K_b = k_b [\text{Ester}] [\text{H}_2\text{O}] = K_b' [\text{Ester}]$$

(4) → All measurable quantities like conc, pressure, colour (if involved) of soln steps changing

(5) All equilibriums are dynamic in nature. That means the espn in forward & backward dirn does not stops but occurs in both directions in same rate



esp can be achieved from either directions



## EQUILIBRIUM CONSTANT



$$\begin{aligned} \alpha_f &= k_f [A]^a [B]^b \\ \alpha_b &= k_b [C]^c [D]^d \end{aligned} \quad \text{assume elementary reactions.}$$

at eq<sup>n</sup>: -

$$\begin{aligned} k_f [A]^a [B]^b &= k_b [C]^c [D]^d \\ K_{eq}^m &= \frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \end{aligned}$$

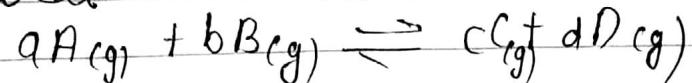
$$\frac{\alpha_f \times \alpha_b}{k_f [A]^a [B]^b} > k_b [C]^c [D]^d$$

$$\frac{k_f}{k_b} > \frac{[C]^c [D]^d}{[A]^a [B]^b} \Rightarrow \alpha$$

## LAW OF CHEMICAL EQUILIBRIUM

or law of mass action

A general reaction is



According to this law rate of any chemical reaction is directly proportional to the product of active masses of the reacting species raised to the power of their stoichiometric co-efficients (with the above statement is given only for elementary reactions).

$$y_f \propto (\text{active mass of A})^a \times (\text{active mass of B})^b$$

$$\text{activity of A} = a_A = \sqrt{A} \frac{[A]}{1\text{m}}$$

$$\text{activity of A} = a_A = \sqrt{A} \frac{P_A}{1\text{bar}} \quad (1\text{atm} = 1.01325 \text{ bar})$$

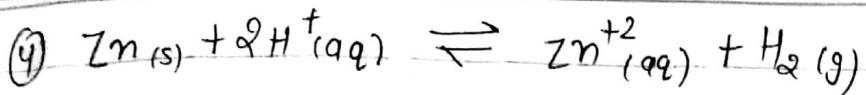
### ACTIVE Mass

Active masses of the ~~surface~~ substance are those parameters (not necessarily mass) which are responsible for variation of state of system. Depending upon the substance active mass can be defined as following -

- ① If a substance is a gas then active mass can be taken as partial pressure of gas or its molar concentration (molarity).
- ② If the substance is solid or liquid since their conc. does not change during system so state of system will be unaffected by change in parameter of these solids & liquid.

Active masses of solids or liquids are assigned as unity

- ③ If the substance is in solution phase (ion in water medium) then active mass is taken as molar concentration



$$\alpha_f = K_f [\text{H}^+]^2$$

$$\alpha_b = K_b [\text{Zn}^{+2}] [\text{H}_2]$$

$$\alpha_b = K_b [\text{Zn}^{+2}] p_{\text{H}_2}$$

$$\text{at eqn} \Rightarrow \alpha_f = \alpha_b$$

$$K_f [\text{H}^+]^2 = K_b [\text{Zn}^{+2}] p_{\text{H}_2}$$

$$\frac{K_f}{K_b} = K_{eq^n}$$

$$K_{eq^n} = \frac{[\text{Zn}^{+2}]}{[\text{H}^+]^2} p_{\text{H}_2}$$

In a heterogeneous reaction system if gas phase as well as  $\text{SOL}^n$  phase is involved simultaneously in a reaction then active masses of gases are preferred to be expressed in terms of their partial pressure while active masses of entity in  $\text{SOL}^n$  phase are expressed in terms of their molarity.

Activity represents the part of active mass which is actually influenced the rate of rxn

$$\alpha_A = \frac{\gamma_A [A]}{1m}$$

$\gamma_A$  = activity constant & it is the fraction by which active mass influence the rate.

Here active mass is (conc. [molarity])

of A. To make activity unitless we divide standard conc 1 molar with conc. term

$$\alpha_A = \frac{\gamma_A [P_A]}{1bar}$$

If active mass equal to pressure than divide by standard pressure 1 bar with pressure to make activity unitless term.

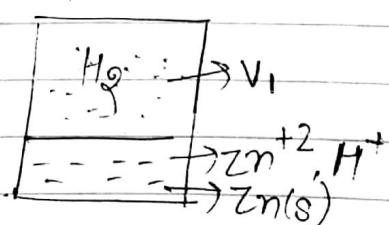
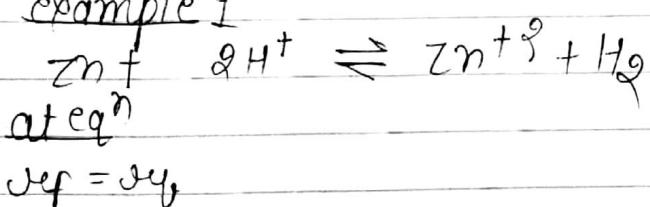
for ideal gas + dilute soln, we assume activity co-eff equal to 1 Activity is a unitless term while active mass has its unit according to property.

### Types of Equilibrium constant

$K_{eq}$	$K_C/K_C^0$	$K_P/K_P^0$	$K_x$	$K_P C$
General equilibrium constant	In terms of conc. Unitless	In terms of partial pressure of gases involved	In terms of mole fraction of involved entities	In terms of Partial P of gas + conc. of entity in soln phase

Ques In which System we define  $K_p$ ,  $K_c$  or  $K_p C$ ?

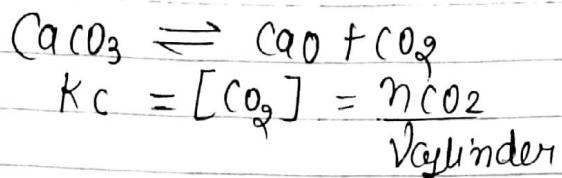
Ans Example 1



$$\frac{k_f}{k_b} = K_p C = \frac{[Zn^{+2}]P_{H_2}}{[H^+]^2}$$

$$K_c = \frac{[Zn^{+2}][H_2]}{[H^+]^2} \text{ not defined}$$

Example - 2



$$K_p = P_{\text{CO}_2} = [\text{CO}_2]RT$$

$$K_p = K_c (RT)$$

NOTE : If  $K_p$  is not defined for a system, as in Example (1) then we can use  $K_p$  in place of that along with  $K_c$  value.

Example - 3



$$\text{Or } \alpha_b = K_b P_{\text{H}_2\text{O}(g)} - (3)$$

$K_x$

Equilibrium constant in terms mole fraction of involved reactant + product in the reaction.  
In general, we use  $K_c$  in completely homogeneous gas system.

Relation between equilibrium constants

