

- **Irreversible reaction**: The reaction in which reactants are completely consumed & converted into product are called irreversible reaction.  
**example**:  $C + O_2 \longrightarrow CO_2$  is unidirectional

example:  $C + O_2 \rightarrow CO_2$  : unidirectional

- Complete reaction -

- show by single arrow - (single head)

- reaction will stop when limiting reactant is consumed - no sign of equilibrium state.

- **Reversible reaction** in which the products once formed can react together to form original reactant.

ex:  $N_2 + 3H_2 \rightleftharpoons 2NH_3$   $\therefore$  Bidirectional.

- symbolically represented by double headed arrow

Rxn which proceed in both direction i.e. forward & reverse direction.

Rxn never goes to completion (incomplete)

- attain equilibrium state (dynamic)

- **Macroscopic events** refer to the phenomena that can be observed with the naked eye without considering the individual particles involved process. example: change in colour.

- evolution / absorption of heat, formation of ppt, change in volume / pressure, change of physical state, entropy.

Microscopic events, refer to phenomena that cannot be observed with the naked eye but can be observed with microscopic-

example: collision b/w molecule, breaking of formation of bonds, rearrangement molecules, direction of rxn, structure of atom/molecule.

Equilibrium state / Dynamic state: state at which rate of forward rxn become equal to the rate of backward rxn is eq. state - OR state at which concentration of reactant & product become constant.

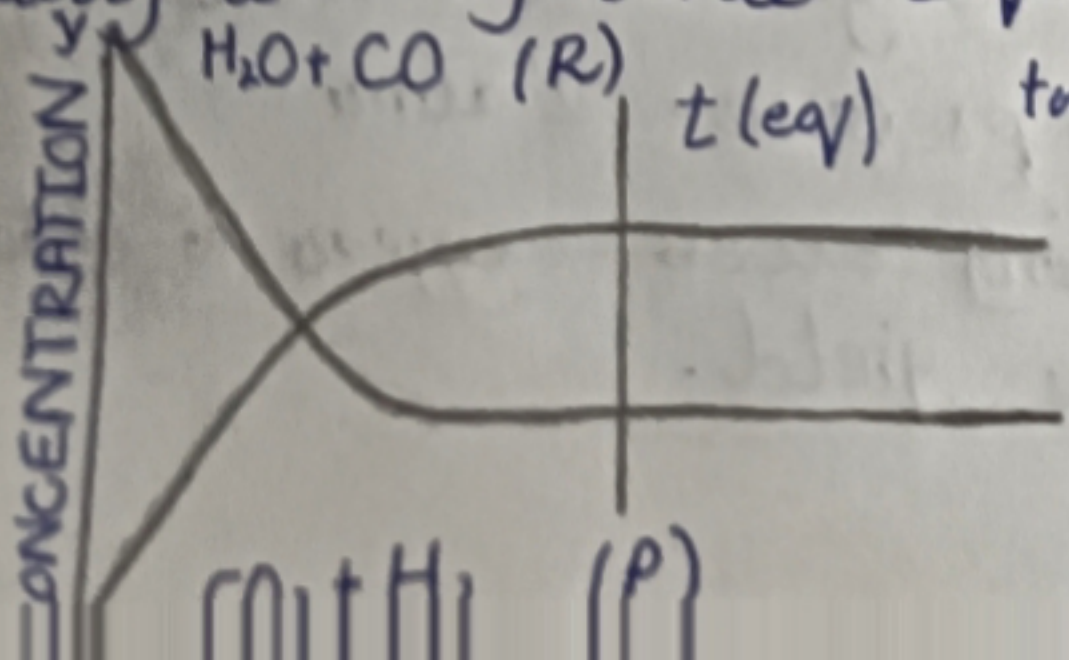
e.g.  $H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$

→ Reactant dec & product inc → Forward rxn rate

reactant inc & product dec  $\rightarrow$  reverse rxn rate

same rate of forward = same rate of reverse

carry at dynamic equilibrium rate.



Concentration =  $\text{mol/dm}^3$   
unit.

Chp: 8. Chemical Equilibrium.

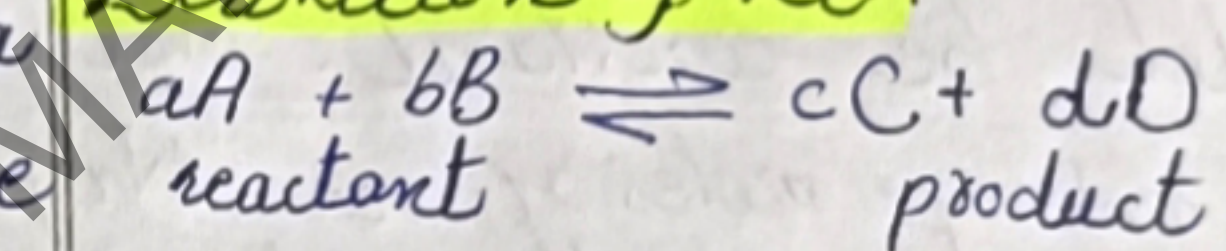
- Law of mass action:

- C.M. Guldberg & P. Waage  
in 1864 proposed.

**Statement:** The rate at which substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances.

active mass represents the concentration of reactant & product in  $\text{mol} \cdot \text{dm}^{-3}$  & represented by square bracket  $[ ]$  - in dilute solution.

### Derivation of $K_c$



rate of forward,  $R_f \propto [A]^a [B]^b$   
reaction  $= K_f [A]^a [B]^b$  (i)

rate of reverse reaction =  $K_r [C]^c [D]^d$  (ii)

At equilibrium,

$$\text{rate of forward} = \text{rate of reverse}$$

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

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

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{\text{Product}}{\text{reactant}}$$

$$K_f \text{ constant of Forward rxn}$$

$R = K_r$  constant of reverse rxn.

$K_c$  = equilibrium constant

### Conditions for Equilibrium

1-  $K_c$  applies only, at E.S.

subscript "c" indicates the conc. reactants & products in moles per  $\text{dm}^3$  at E.S.

tin Ke-subscript.

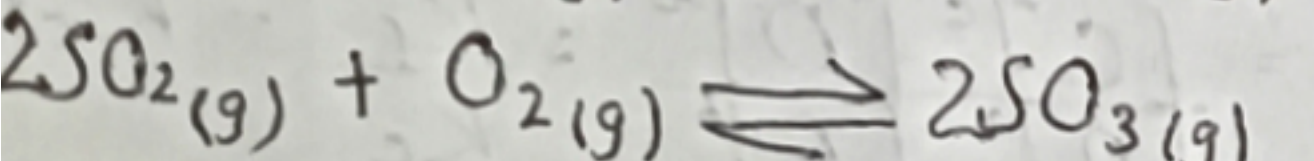
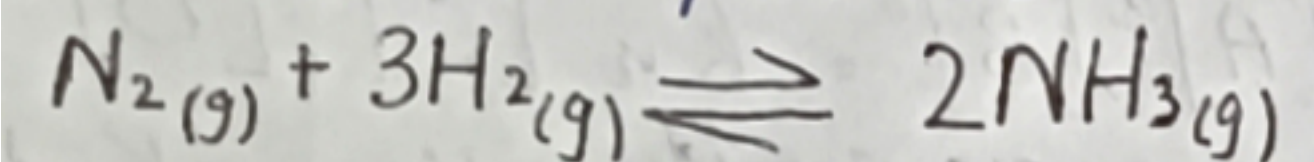
3.  $K_c$  does not depend on initial concentration of reactant & product but depend upon temperature.

3.  $K_c$  is related to coefficient of B.C.E. Product is numerator. reactant is denominator.
1. Magnitude of  $K_c$  indicate position of equilibrium.
- $K_c < 1$  = reactant is greater. direction forward
- $K_c > 1$  = product is greater. direction reverse.
- $K_c = 1 \rightarrow$  at equilibrium. same rate.  $F = r$ .
5. Container should be closed if any reactant or product is in gaseous.
6. Pressure, Volume & catalyst of the system should be constant.
- when moles of reactant = moles of product unit.

## Types of Equilibrium

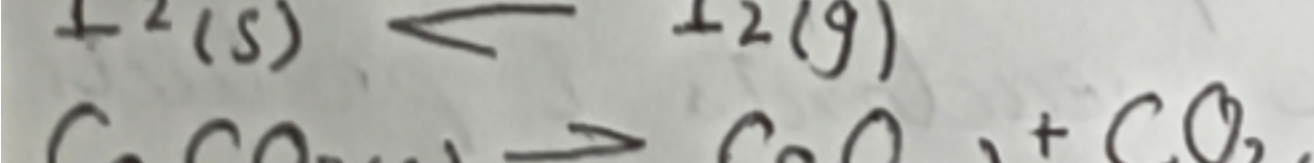
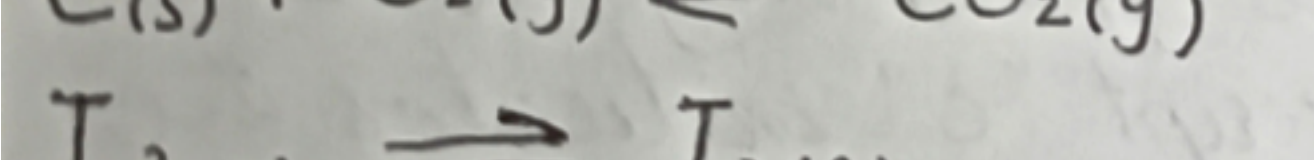
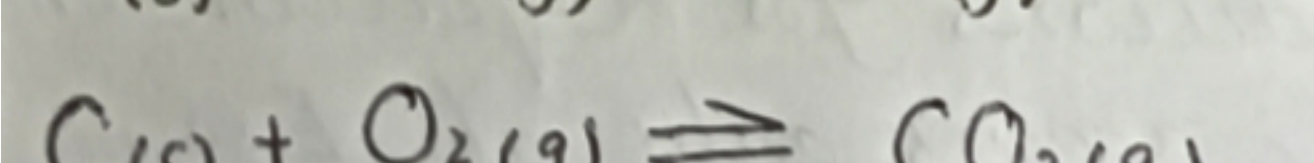
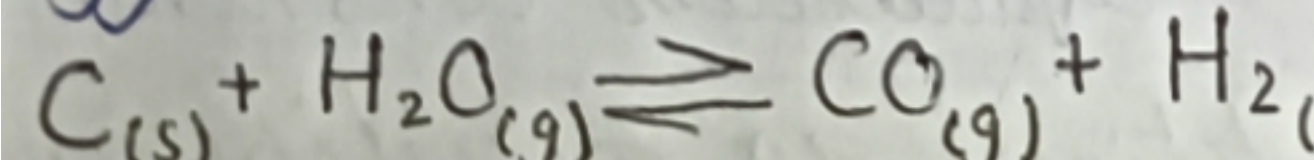
### Homogenous equilibrium

The type of equilibrium in which physical state of reactant & product are in same phase.

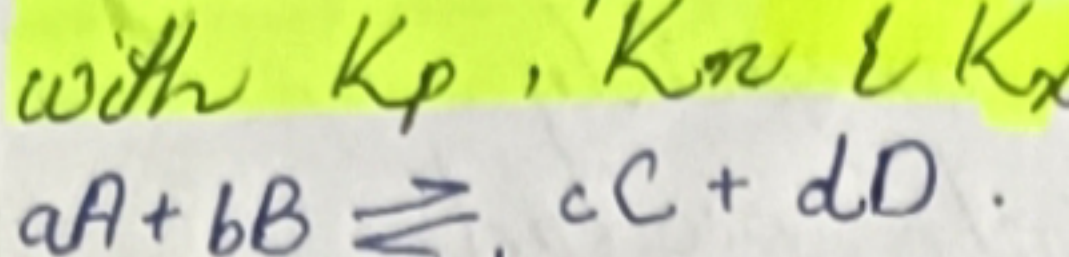


### Heterogenous equilibrium

The type of equilibrium in which physical state of reactant & product is different. more than 1 phase.



## Relationship of $K_c$ with $K_p$ , $K_n$ & $K_x$



$$K_c = \frac{\text{product}}{\text{reactant}} \quad \text{molar, C}$$

### Henry law

$P_{\text{gas}} \propto [G_{\text{gas}}]$   
At constant temp partial pressure of gas is directly proportional to its molar concentration.

$K_p$  E.C  $K_p$  of partial pressure

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} \Rightarrow K_p = K_c (RT)^{\Delta n}$$

$K_n$  in terms of moles.

$$K_n = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b} \Rightarrow K_p = K_n \left(\frac{P}{n}\right)^{\Delta n}$$

$K_x$  mole fraction.

$$K_x = \frac{x_C^c \times x_D^d}{x_A^a \times x_B^b} \Rightarrow K_p = K_x (P)^{\Delta n}$$

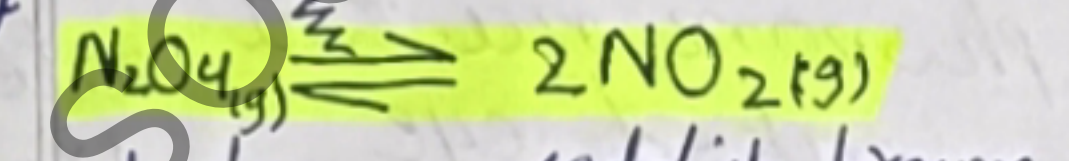
$$K_p = K_c (RT)^{\Delta n} = K_n \left(\frac{P}{n}\right)^{\Delta n} = K_x (P)^{\Delta n} \quad (4)$$

## Ways to reconize equilibrium

### Physical method

#### Spectrometric method

Property is measured during the rxn without removing sample from the reaction mixture.



colourless reddish brown.

This method can be applied when the reactant or product absorbs ultraviolet, visible, infrared radiation.

$K_c \propto$  amount of radiation

### Importance

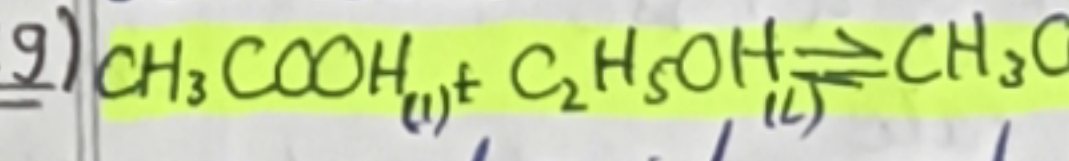
reactant can be used & reused.

reactant or product have ability to absorb radiation.

helps to find value of  $K_c$  through radiation absorbed.

### Chemical method

amount of reactant & product is determined by a suitable chemical reaction.



mineral acid used to catalyze the rxn.

### estripication

## Lechatelier's principle

if a change is imposed on a system at equilibrium the position of equilibrium will shift in a direction that tends to reduce the change.

### Effect of concentration

Reactant inc  $\rightarrow$  Forward direction

Reactant dec  $\leftarrow$  backward.

Product inc  $\leftarrow$  backward

Product dec  $\rightarrow$  Forward.

### Effect of pressure change

$P \propto \frac{1}{V}$  Boyles law.

Pressure inc  $\rightarrow$  volume dec

Pressure dec  $\rightarrow$  volume inc.

EQ shift in direction 2) shift in to inc total no of molecule.

### Effect of change in temp

Endothermic = temp = shift to  $K_c$  inc. reaction. inc. forward

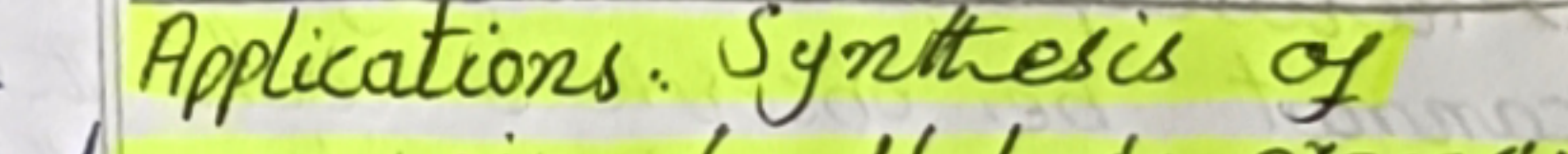
Endothermic " temp = forward.  $K_c$  dec

Exothermic " temp = forward.  $K_c$  dec

Exothermic " temp = forward.  $K_c$  inc.

No effect of catalyst bcz it proceed both forward & reverse rxn.

### Applications. Synthesis of ammonia by Haber's process



Low temp  $400^\circ\text{C}$  (673K)

High pressure = 200-300 atm.

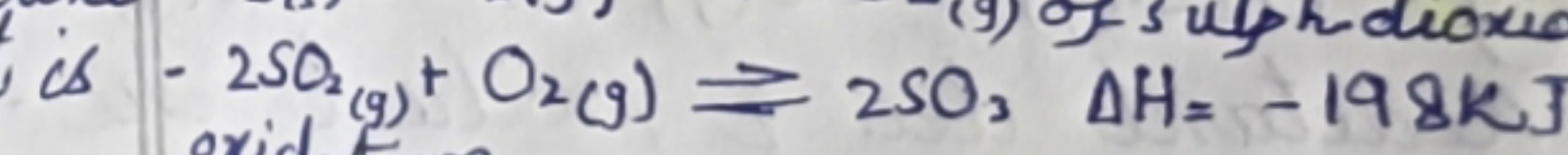
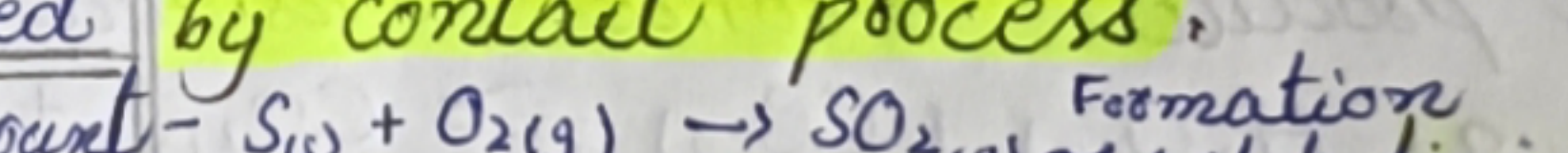
Catalyst = pieces of iron crystals.

in fused mixture of  $MgO$ ,  $Al_2O_3$  &  $SiO_2$ .

Continual removal of ammonia.

at  $-33.4^\circ\text{C}$ .

### Synthesis of sulphuric acid by contact process



oxidation.

both are exothermic reaction.

Conversion  $S_d$  into sulphuric acid.

low temp =  $450 - 500^\circ\text{C}$

high pressure = 2 atm.

Adding excess oxygen to obtain high yield.