# Revision Notes

## Chemical & Ionic Equilibrium

**Equilibrium** : Equilibrium is the state of a process in which the properties like temperature, pressure, & concentration etc. of the system do not show any change with passage of time.

In all process which attains equilibrium, two opposing processes are involved:

i) Forward process ii) Backward/reverse process.

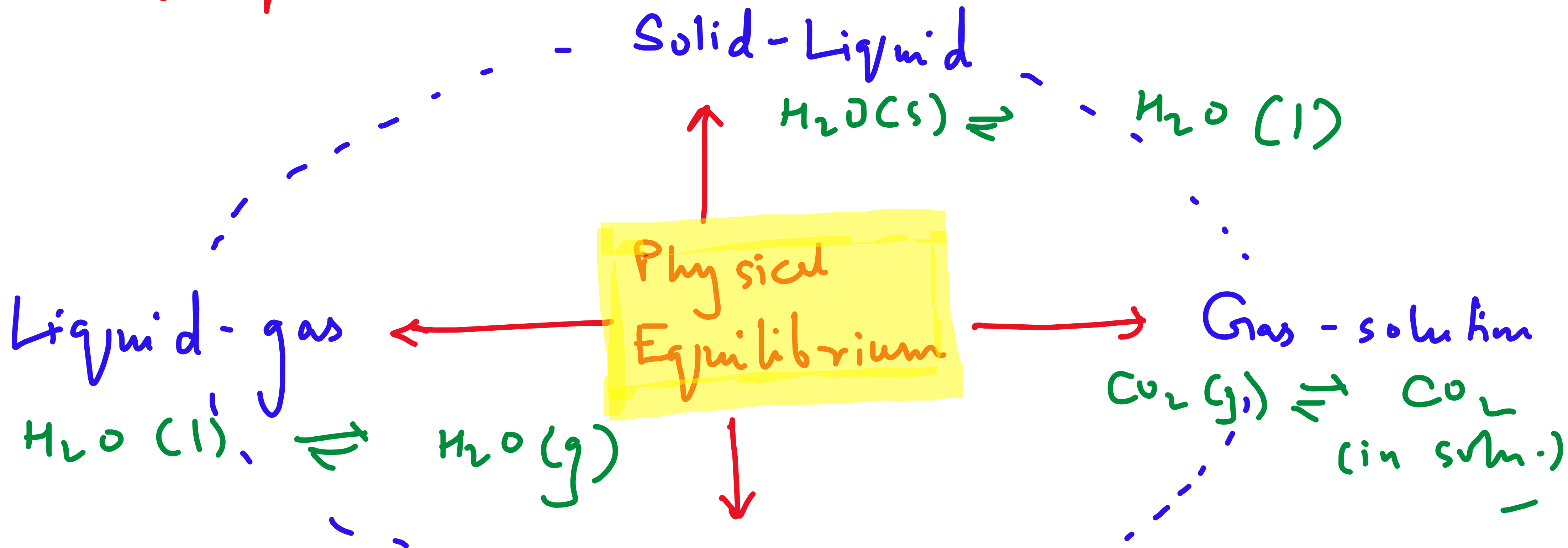
Equilibrium is attained when the rates of the two opposing process i.e. the forward & reverse process are equal.

If the opposing process involve only physical changes, the equilibrium is known as physical equilibrium.

If the opposing processes involve chemical reactions, the equilibrium is known as chemical equilibrium.

Ionic reaction is a special type of chemical equilibrium involving ions in solution.

# Physical Equilibrium



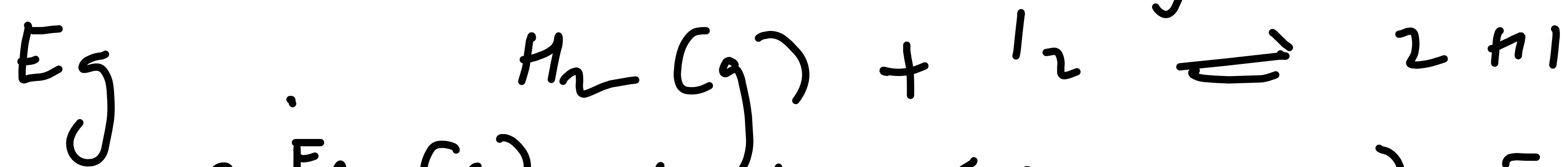

Solid - solution

Salt (solid) $\rightleftharpoons$ Salt (in solution)

Equilibrium in Chemical Process: i) Reversible reaction ii) Irreversible reaction

**Reversible reaction :-** A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form the reactants under the same conditions.

Eg.



$H_2(g) + I_2 \rightleftharpoons 2HI$

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

**Irreversible reaction :-** A reaction that cannot take place / occur in the reverse direction i.e. the products cannot react to form the reactants under same conditions.

Typically, a chemical reaction is represented as

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

where A & B are reactants

C & D " products

a, b, c, d ⇒ molar stoichiometric coefficient i.e. how many moles of A & B reacts to produce C & D.

$\rightleftharpoons$ = double headed arrow represents that changes occur in both forward & reverse/backward direction. (Bidirectional/reverse reaction)

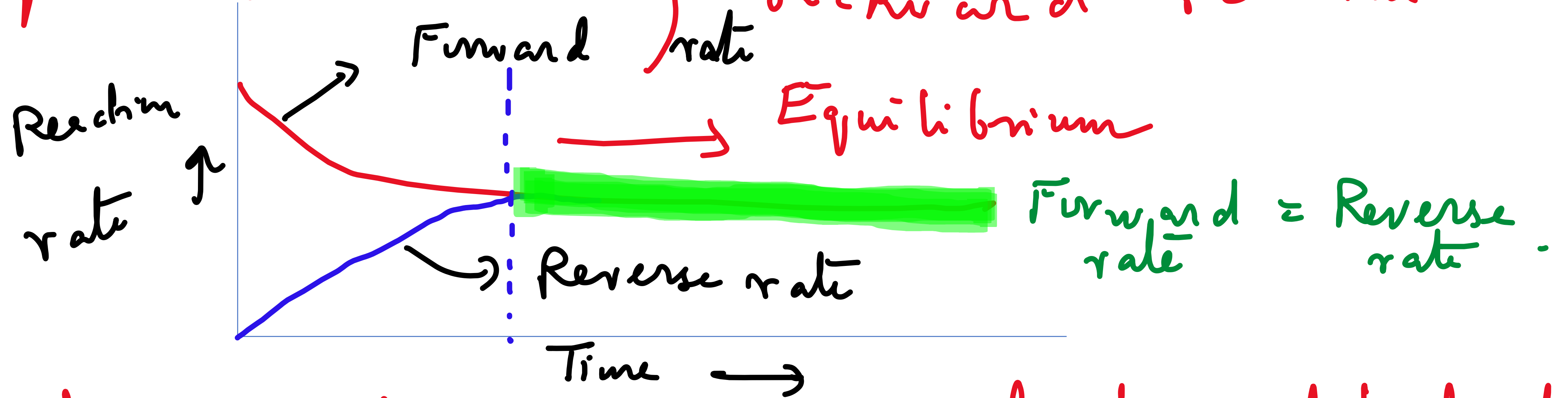
On the basis of extent of reaction, before equilibrium is attained reactions may be classified into 3 different categories :-

1. $\rightleftharpoons$ forward reverse — Those reaction which proceed almost to completion i.e. rate of forward reaction >> rate of backward reaction.

2- Those reaction which proceed only to a little extent. $\rightleftharpoons$

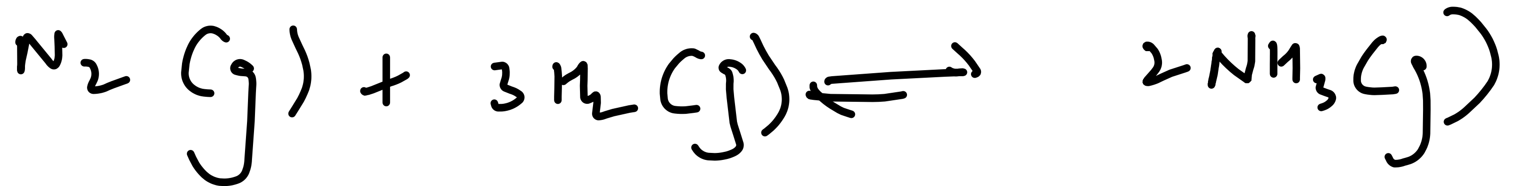
3. Those reactions which proceed to such an extent that concentration of reactants & products at equilibrium are comparable. $\rightleftharpoons$

An equilibrium state is always dynamic & not static in nature. Equilibrium is attained when the rate of forward reaction equals to that of backward reaction.

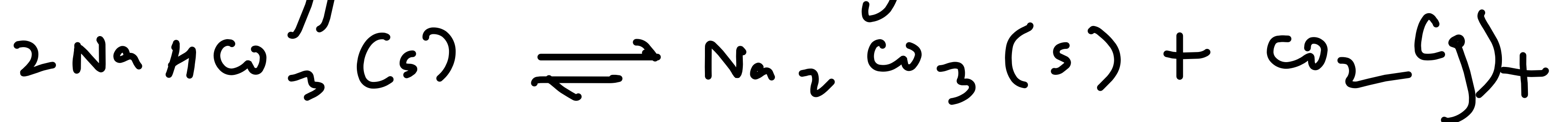


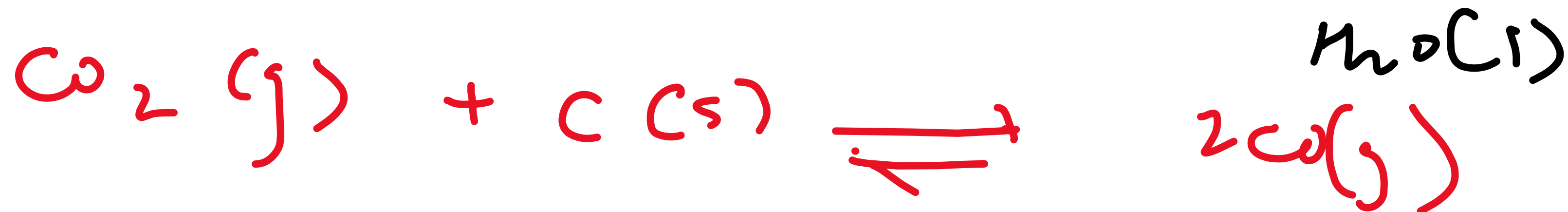

Based on the physical state of reactants and products chemical equilibrium can be divided into –
1) Homogeneous & 2) Heterogeneous equilibrium.

**Homogeneous equilibrium:** All the reactants & products in equilibrium are under the same physical state.




**Heterogeneous equilibrium:** Physical states of one or more of the reacting species may be different. Eg.:



# Salient features of chemical equilibrium.

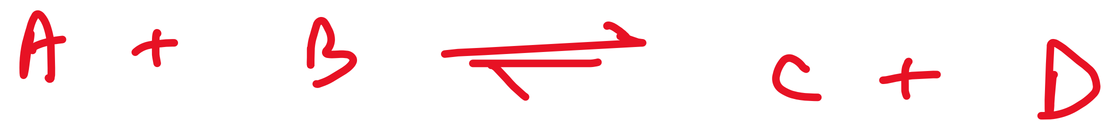
1. Chemical equilibrium can be attained only if the reversible reaction is carried out in closed vessel.
2. Equilibrium can be attained from either side.
3. Catalysts can hasten the approach of equilibrium but cannot alter the state of equilibrium.
4. Dynamic in nature.
5. Change of pressure, concentration, temperature can shift the equilibrium point in a particular direction.

# The Law of Mass Action.

The rate at which a substance reacts is proportional to its active mass, & the rate of a chemical reaction is proportional to the product of the active mass of the reacting substance.

Active mass implies activity. For the sake of simplicity, active mass can be taken as equivalent to molar concentration.

Let us consider the following reversible reaction taking place at constant temperature.



$$A + B \rightleftharpoons C + D$$

According to law of mass action,

$r_1 \propto [A][B] \Rightarrow r_1 = k_1 [A][B]$

$r_2 \propto [C][D] \Rightarrow r_2 = k_2 [C][D]$

where $r_1$ = rate of forward reaction

$r_2$ = " " reverse "

$k_1$ = rate constant for forward reaction

$k_2$ = " " " backward "

[ ] → molar concentration of the reactants / products.

At equilibrium, $r_1 = r_2$

$\Rightarrow k_1 [A][B] = k_2 [C][D]$

$\Rightarrow \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$

$\Rightarrow K = \frac{[C][D]}{[A][B]}$

equilibrium constant expressed in terms of concentration

$K_c$ = equilibrium constant

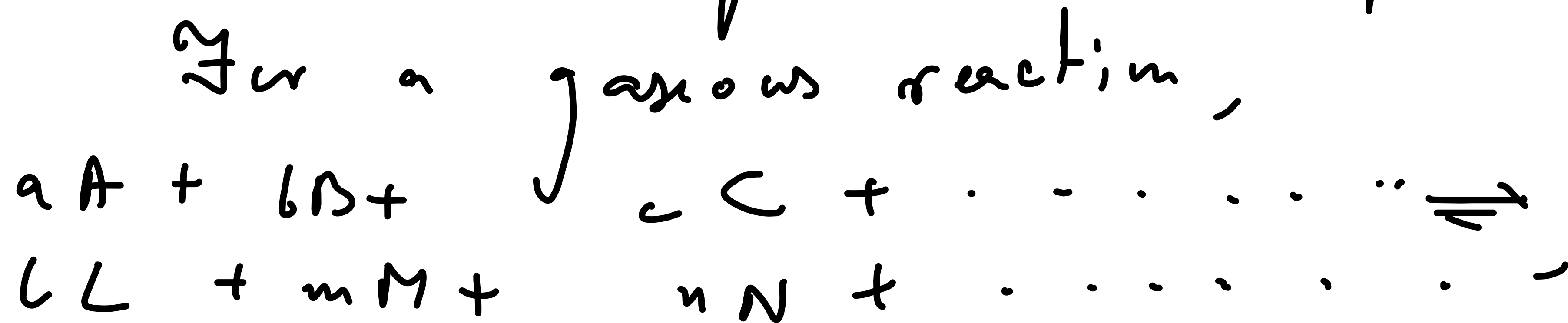
= ratio of the rate constants of two opposing reaction.

For a general reaction of the type,

$aA + bB + cC + \ldots \rightleftharpoons lL + mM + nN + \ldots$

$$K = K_c = \frac{[L]^l [M]^m [N]^n \cdots}{[A]^a [B]^b [C]^c \cdots}$$

For a gaseous reaction, it is more convenient to use partial pressure instead of concentrations. The equilibrium constant is expressed as $K_p$ in that case.



For a gaseous reaction,

$$aA + bB + cC + \cdots \rightleftharpoons lL + mM + nN + \cdots$$

$$K_p = \frac{(p_L)^l \times (p_M)^m \cdots\cdots}{(p_A)^a \times (p_B)^B \cdots\cdots}$$

$K_p$ has the same unit as pressure.

N.B: Equilibrium constant $K_c$ being the ratio of concentrations raise to the stoichiometric coefficient, the unit of $K_c$

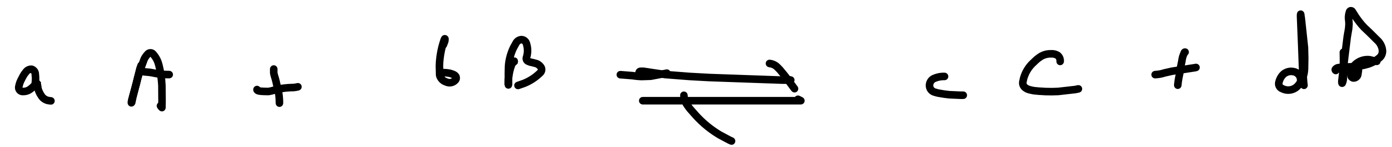
$$= (\text{mole } L^{-1})^{\Delta n}$$

From gas law, $PV = nRT$

$$\Rightarrow P = \left(\frac{n}{V}\right) RT$$

$$\Rightarrow P = (C) RT$$

concentration




$$K_p = \frac{(p_C)^c \times (p_D)^d}{(p_A)^a \times (p_B)^b}$$

$$= \frac{[C]^c \times (RT)^c \times [D]^d \times (RT)^d}{[A]^a \times (RT)^a \times [B]^b \times (RT)^b}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{\{c+d\} - \{a+b\}}$$

equilibrium constant in terms of concentration

$$= K_c \times (RT)^{\Delta n}$$

where $\Delta n = \{(c+d) - (a+b)\}$

$$K_p = K_c \cdot (RT)^{\Delta n}$$

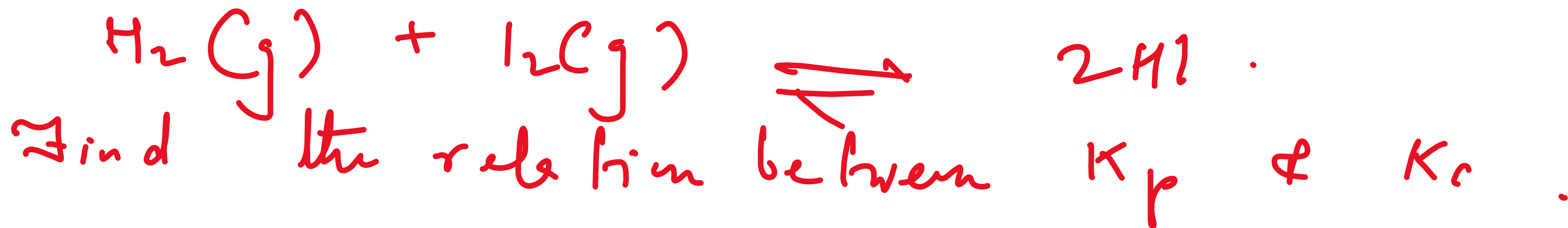
If $\Delta n = 0$ for a particular reaction then —

i) $K_p = K_c$.

If $\Delta n > 0$, $K_p > K_c$

" $\Delta n < 0$, $K_p < K_c$

$\Delta n$ = no. of moles of product − no. of moles of reactant.




$\Delta n = 2 - (1+1) = 0$ $\therefore K_p = K_c$.

# Le Chatelier's Principle

When a chemical reaction at equilibrium is subjected to any stress, then the equilibrium will shift in that direction in which the effect of the stress is reduced.

1. Effect of addition of inert gas:

At constant volume : No effect on equilibrium

" " pressure : Equilibrium will shift in a direction where there is increase in no. of moles.

2. Effect of change in temperature

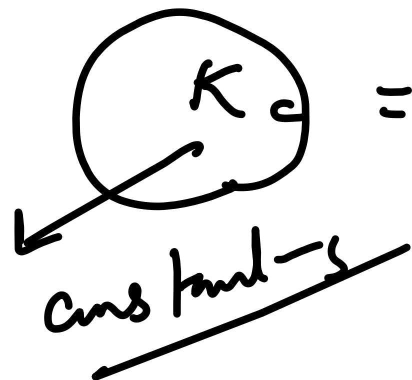
In a system at equilibrium, both exothermic & endothermic reaction takes place simultaneously.

Increase in temperature ⟶ Shift the equilibrium in the direction of endothermic reaction.

Decrease in temperature ⟶ Shift the equilibrium in direction of exothermic reaction

3 - Effect of change in concentration.

Concentration of reactants increased → Equilibrium shifts to forward direction.




$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$ → reactant increased ↓ product has to increase proportionally so that Kc is constant.

Concentration of products increased:
Equilibrium shifts to backward direction.

4. **Effect of change in pressure**

Increase in pressure → shifts the equilibrium in the direction of lesser no. of gaseous molecules.

Decrease in pressure shifts the equilibrium in the direction of larger no. of gaseous molecules.

5. **Effect of Catalyst**: Catalyst does not change the equilibrium.

# Thermodynamics of Chemical Equilibrium

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

$\downarrow$ $RT \ln Q$

the difference in chemical energy between non-standard state starting conditions & the standard state

At equilibrium,

$$\Delta G = \Delta G^\circ + 2.303\, RT \log K$$

($\Delta G$) $= 0$

or,

$$\Delta G^\circ = -2.303\, RT \log K$$

$$\log K = -\frac{\Delta H^\circ}{2.303\, RT} + \frac{\Delta S^\circ}{2.303\, RT}$$

assuming $\Delta H^\circ$ to be constant in temperature rang $T_1$ & $T_2$ .

$$\frac{d \log K}{dT} = \frac{\Delta H^{\circ}}{2.303\, RT^2}$$