

Law of mass action:

- This law is stated by C.M. Guldberg and P. Waage in 1863.
- This law gives the relation between the rate of a reaction and the concentration of the reactants.
- The rate of a chemical reaction at a temperature at any instant is proportional to the product of the active masses of the reactants.
- This law is applicable to all reactions i.e. reversible and irreversible occurring in the gas phase or in the liquid phase.
- $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant.

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

K_f = forward reaction rate constant.

K_b = backward reaction rate constant.

- The equilibrium constant

$$K_c = \frac{\text{product of the concentration of products}}{\text{product of the concentration of reactants}}$$

- Partial pressure of the gas = mole fraction of gas \times total pressure.

$$K_p = \frac{k_f}{k_b} = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

- $K_p = \frac{\text{product of partial pressures of products}}{\text{product of partial pressures of reactants}}$

K_c = equilibrium constant in terms of molar concentration.

K_p = equilibrium constant in terms of partial pressure.

$$\text{Active mass} = \frac{\text{no. of moles}}{\text{volume in litres}}$$

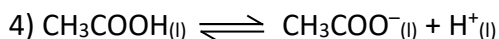
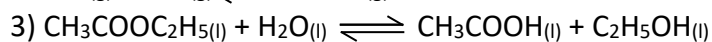
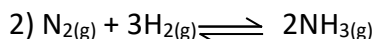
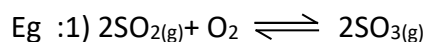
Active mass is considered for gas or liquid.

- The active mass of a solid is unity whatever may be its mass.

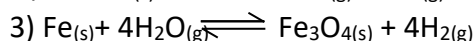
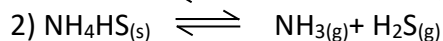
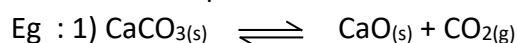
Types of chemical equilibrium:

- Based on the physical states of substances equilibrium is of two types.

1) Homogeneous equilibrium : All the reactants and products are present in same physical state. i.e same phase.



2) Heterogeneous equilibrium : Reactants and products are in different physical states or different phase.



- Relationship between k_p and k_c :**

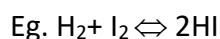
$$k_p = k_c (RT)^{\Delta n}$$

R = gas constant, T = absolute temperature

Δn = change in number of moles

$$= n_p - n_R \text{ (no. of moles of gaseous products – no. of moles of gaseous reactants)}$$

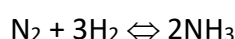
case (i) if $n_p = n_R$, $\Delta n = 0$, $k_p = k_c$



(ii) if $n_p > n_R$, $\Delta n = +ve$, $k_p > k_c$



(iii) If $n_p < n_R$, $\Delta n = -ve$, $k_p < k_c$

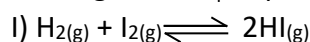


Units of equilibrium constant :

Unit of $k_c = (\text{mol. lit}^{-1})^{\Delta n}$

Unit of $k_p = (\text{atmosphere})^{\Delta n}$

- Writing k_c and k_p expressions and expressing their units

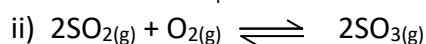


$$k_c = \frac{[HI]^2}{[H_2][I_2]}$$

No unit for K_c

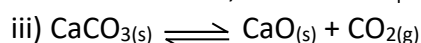
$$k_p = \frac{P_{HI}^2}{p_{H_2} \times p_{I_2}}$$

No unit for K_p



$$k_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}; \quad k_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}$$

$$k_c = \text{lit} \cdot \text{mol}^{-1}; \quad k_p = \text{atm}^{-1}$$



$$k_c = [CO_2]; \quad k_c = \text{mol. lit}^{-1}$$

$$k_p = P_{CO_2}; \quad k_p = \text{atm}$$

Characteristics of equilibrium constant : (k_p or k_c)

- The value of k depends on the nature of the reaction.
- The value of k will be a constant for a given reaction at a given temperature.
- The value of k depends on temperature of reaction.
- The value of k is independent of concentration and pressure.
- The value of k is independent of presence of catalyst and presence of inert gas.
- The value of k depends on stoichiometry of the equation.
- The value of k depends on mode of writing the equilibrium reaction.