Law of mass action:

- This laws stated by C.M. Guldberg and P. Wage 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 ⇔ 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

$$k_c = \frac{productoftheconcentrationofproducts}{productoftheconcentrationofreac\tan t\,s}$$

- Partial pressure of the gas = mole fraction of gas × total pressure.

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

- $K_p = \frac{prodctofpatialpressuresofproducts}{productofpartialpressuresofreac\tan ts}$

  k_c= equilibrium constant in terms of molar concentration.

  k_p=equilibrium constant in terms of partial pressure.

  Active mass = $\frac{no.ofmoles}{volumeinlitres}$

  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.

  Eg :1) $2SO_{2(g)} + O_2 \rightleftharpoons 2SO_{3(g)}$

  2) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

  3) $CH_3COOC_2H_{5(l)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(l)} + C_2H_5OH_{(l)}$

  4) $CH_3COOH_{(l)} \rightleftharpoons CH_3COO^-_{(l)} + H^+_{(l)}$

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

  Eg : 1) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

  2) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

  3) $Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

- **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
  $= n_P - n_R$ (no.of moles of gaseous products – no.of moles of gaseous reactants)

  case (i) if $n_P = n_R$, $\Delta n = 0$, $k_p = k_c$
  Eg. $H_2 + I_2 \Leftrightarrow 2HI$
  (ii) if $n_P > n_R$, Δn = +ve, $k_p > k_c$
  $PCl_5 \Leftrightarrow PCl_3 + Cl_2$
  iii) If $n_P < n_R$, Δn = -ve, $k_p < k_c$
  $N_2 + 3H_2 \Leftrightarrow 2NH_3$

Units of equilibrium constant :

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

- Writing k_c and k_p expressions and expressing their units
  I) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
  $k_c = \frac{[HI]^2}{[H_2][I_2]}$
  No unit for K_c
  $$k_p = \frac{P_{HI}^2}{p_{H_2} \times p_{I_2}}$$
  No unit for K_p
  ii) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
  $k_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; $k_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}$
  $k_c = lit\ .\ mol^{-1}$; $k_p = atm^{-1}$
  iii) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
  $k_c = [CO_2]$; $k_c = mol.\ lit^{-1}$
  $k_p = P_{CO_2}$; k_p = 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.