CHEMICAL EQUILIBRIUM

Introduction :

Chemical reaction: Symbolic representation of any chemical change in terms of reactants and products is called a chemical reaction.

Types of Chemical Reaction

(a) On the Basis of Heat

(i) Exothermic Reaction

(ii) Endothermic Reaction

(b) On the basis of direction

(i) Reversible Reaction

(ii) Irreversible Reaction

(a) On the basis of heat:

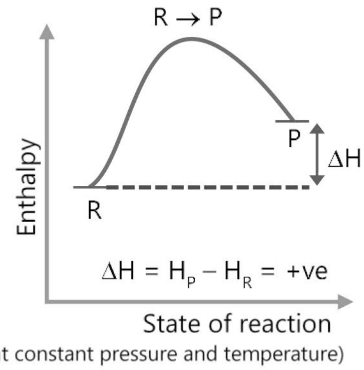
(i) Endothermic reaction:

The reaction in which heat is absorbed is called as an endothermic reaction.

$\boxed{\Delta H = +ve}$

$\Delta H = H_P - H_R = +ve$

i.e. $\boxed{H_P > H_R}$



(i) Stability of reactant > Stability of product (because more heat is required to break the bonds of reactant).

(ii) The product formed in the endothermic reaction is called as an endothermic compound.

(iii) If more heat is absorbed then the product formed in the reaction will be less stable or the reactant is more stable.

Representation of an endothermic reaction :

$A + B + x\,Cal \rightarrow C + D$ (endo)

$A + B \rightarrow C + D - x\,Cal$ (endo)

$A + B \rightarrow C + D, \Delta H = +x\,Cal$ (endo)

Examples:

(I) Dissociation reactions (mostly)
(II) Fusion
(III) Vaporisation
(IV) Sublimation
(V) Photosynthesis

In photosynthesis:

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 ; \Delta H = +ve$

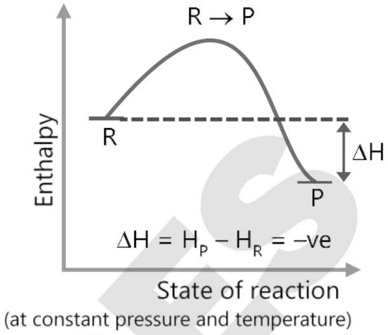
(ii) Exothermic reaction:

The reaction in which heat is evolved is called as an exothermic reaction.

$\boxed{\Delta H = -ve}$

$\Delta H = H_P - H_R = -ve$

i.e. $\boxed{H_P < H_R}$



(i) Stability of reactant < Stability of product.
(Because less heat is required to break the bonds of reactant).

(ii) The product formed in the exothermic reaction is called as an exothermic compound.

(iii) If more heat is released then the product formed in the reaction will be more stable or the reactant is less stable.

Representation of exothermic reaction.

$A + B \rightarrow C + D + x\ Cal$ (exo)

$A + B - x\ Cal \rightarrow C + D$ (exo)

$A + B \rightarrow C + D,\ \Delta H = -x\ Cal$ (exo)

Examples:

(I) Combustion reactions

(II) Neutralisation reactions

(III) Respiration reaction

eg. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

(IV) Formation reactions $\begin{cases} \text{endo} \\ \text{exo (generally)} \end{cases}$

Exceptions of formation reactions :

$$\left[\begin{array}{l} C + 2S \longrightarrow CS_2 \\ \frac{1}{2}N_2 + \frac{3}{2}Cl_2 \longrightarrow NCl_3 \\ N_2 + O_2 \longrightarrow NO/N_2O / NO_2 / N_2O_4 \\ O_2 + F_2 \longrightarrow OF_2 / O_2F_2 \end{array}\right] \Delta H = +ve \text{ (endothermic)}$$

(b) On the basis of direction

	Reversible reaction		Irreversible reaction
(i)	Chemical reaction in which products can be converted back into reactants. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$ $H_2 + I_2 \rightleftharpoons 2HI$	(i)	Chemical reaction in which products cannot be converted back into reactants. $AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$ $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$
(ii)	Proceed in forward as well as in backward direction.	(ii)	Proceed only in one direction (forward direction).
(iii)	Generally possible in closed container	(iii)	Generally possible in open container
(iv)	They can attain equilibrium	(iv)	They do not attain equilibrium
(v)	Reactants are never completely converted into products	(v)	Reactants are nearly completely converted into products.

Equilibrium and Chemical Process

Chemical Equilibrium

The most important characteristic property of a reversible reaction is that it always attains a state of chemical equilibrium.

Consider a general reversible reaction in a closed vessel

$A + B \underset{r_b}{\overset{r_f}{\rightleftharpoons}} C + D$ where r_f = rate of forward reaction

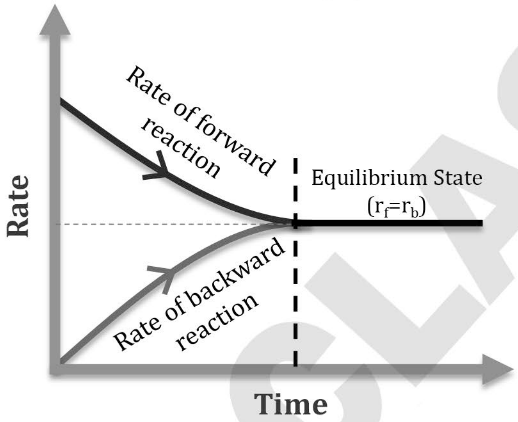
r_b = rate of backward reaction

Initially reaction begins in the forward direction but as the concentration of products increase reaction also begins to occur in the backward direction.

At a certain stage, rate of forward reaction becomes equal to the rate of backward reaction known as the equilibrium state.

At equilibrium state

Rate of forward reaction (r_f) = Rate of backward reaction (r_b)



⇒ The concentration of the reactants and products does not change with time.

⇒ At this stage, number of moles of substances produced per second in the forward reaction is equal to the number of moles of substances which disappear per second in the backward reaction.

Characteristics of equilibrium:

(a) Chemical equilibrium is dynamic in nature i.e. the reaction although appears to be stopped but actually takes place in both the directions with the same speed.

(b) Chemical equilibrium can be approached from both sides

$2HI \rightleftharpoons H_2 + I_2$ or $H_2 + I_2 \rightleftharpoons 2HI$

At equilibrium, each reactant and product have a constant concentration and this is independent of the fact whether the reaction starts from forward direction or backward direction with the reactant or with the product.

(c) Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.

(d) The measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time at the chemical equilibrium conditions.

(e) Homogeneous equilibrium is the equilibrium in which the reactants and products are in the same phase.

$CH_3COOC_2H_{5(\ell)} \overset{H^+}{\rightleftharpoons} CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)}$

(f) Heterogeneous equilibrium is the equilibrium in which the reactants and products are in two or more phases.

$Zn_{(s)} + CO_{2(g)} \rightleftharpoons ZnO_{(s)} + CO_{(g)}$

- **ACTIVE MASS:** The term active mass means the concentration of the reactants expressed in moles per litre (molar concentration) or the pressure of the reacting gas in atmosphere. In case of gases and solutions, the molar concentration means the number of gram molecules present per litre.

  Active mass is usually expressed by enclosing the symbol of the reactant in square bracket [ ].

$$\text{Active mass} = \frac{\text{Number of gram moles of the substance}}{\text{Volume (in L)}}$$

$$= \frac{\text{Weight of substance (in grams)}}{\text{Molecular weight }(M_w)\times\text{Volume (in L)}}$$

$$= \frac{w}{M_w \times V(L)} = \frac{w \times 1000}{M_w \times V(mL)}$$

- The active mass of solids and pure liquids is a constant quantity (unity) because it is an intensive property i.e. number of molecules present per unit volume do not change because density and molecular weight of solids and pure liquids are constant. But it does not apply for gaseous substances because for them number of molecules present per unit volume change with change in volume of vessel.

$$\text{Molar concentration} = \frac{w}{M_w \times V(\text{litre})} = \frac{\rho}{M_w}\ (\text{where } \rho = \text{density in g L}^{-1})$$

$$= \frac{\rho}{M_w} \times 1000\ (\text{where } \rho = \text{density in g/mL})$$

$$\text{Active mass} = \frac{\text{density of the substance (in g L}^{-1})}{\text{molecular mass of the substance}}$$

Other names of active mass can also be used as following:

(i) mole/litre

(ii) gram mole/litre

(iii) gram molecules/litre

(iv) molarity

(v) Concentration

(vi) Effective concentration

(vii) active quantity

(viii) n/v

(ix) C

(x) M

(xi) [ ]

Illustration 1:

In any chemical reaction, equilibrium is supposed to be established when:

(1) Mutually opposite reactions occur.

(2) concentration of reactants and resulting products are equal.

(3) Velocity of mutual opposite reactions become equal.

(4) The temperature of mutual opposite reactions becomes equal.

Solution:

(3)

Illustration 2:

If 8.5 g ammonia is present in a vessel of 0.5 L capacity then find out the active mass of ammonia.

Solution:

$$[NH_3] = \frac{8.5}{17 \times 0.5} = 1\ \text{mol L}^{-1}$$

Illustration 3:

Given below are two statements; one is labelled as **Assertion (A)** and the other is labelled as **Reason(R)** .

Assertion: The active mass of pure solids and pure liquids is taken as unity.

Reason: The active mass of pure solids and pure liquids depends on density and molecular mass. The density and molecular mass of pure solids and pure liquids are constant.

In the light of the above statements, choose the **most appropriate** answer from the options given below :

(1) Both **(A)** and **(R)** are correct but **(R)** is not the correct explanation of **(A).**

(2) **(A)** is correct but **(R)** is not correct.

(3) **(A)** is not correct but **(R)** is correct.

(4) Both **(A)** and **(R)** are correct and **(R)** is the correct explanation of **(A).**

Solution:

(4)

Illustration 4:

What should be the active mass in g mol L^{-1} when 0.585 g NaCl is present in 100 mL aqueous solution

(1) 0.1 (2) 0.5 (3) 1.0 (4) 2.0

Solution:

Molecular weight of NaCl = 23 + 35.5 = 58.5

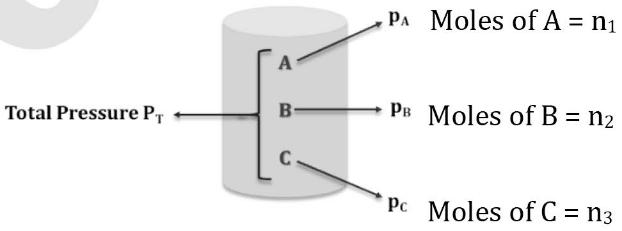
$$[\text{NaCl}] = \frac{\text{Weight in g}}{\text{Molecular weight} \times \text{Volume}} = \frac{0.585 \times 1000}{58.5 \times 100} = 0.1 \text{ g mol L}^{-1}$$

Partial Pressure

It is the pressure of an individual gas in the gaseous mixture.

Dalton's Law

It states that the total pressure of any gas mixture is equal to the sum of the partial pressures of each gas present in the mixture at a constant temperature and volume.



Let us consider a mixture of 3 gases A, B and C

According to Dalton's Law: $P_T = p_A + p_B + p_C$

Derivation

Ideal gas equation can be applied on mixture as a whole.

$P_TV = (n_1 + n_2 + n_3) \times RT$

$P_TV = n_T RT$ ....(1)

Also it can be applied on individual gases.

$p_AV = n_1RT$ ....(2)

$p_BV = n_2RT$ ....(3)

$p_CV = n_3RT$ ....(4)

From Equation (2) / (1)

$$\frac{p_AV}{P_TV} = \frac{n_1RT}{n_TRT}$$

$$p_A = \frac{n_1}{n_T} \times P_T$$

$p_A = \chi_A \times P_T$ ....(5) χ_A = Mole fraction of A

Similarly Equation (3) / (1)

$$p_B = \frac{n_2}{n_T} \times P_T$$

$p_B = \chi_B \times P_T$ ....(6) χ_B = Mole fraction of B

Similarly Equation (4) / (1)

$$p_C = \frac{n_3}{n_T} \times P_T$$

$p_C = \chi_C \times P_T$ ....(7) χ_C = Mole fraction of C

∴ Partial pressure of gas = Mole fraction × Total pressure

From equation (5) + (6) + (7)

$p_A + p_B + p_C = (\chi_A + \chi_B + \chi_C)\, P_T = P_T$ **(Since the sum of mole fractions is always equal to one)**

$p_A + p_B + p_C = P_T$ **(Dalton's Law)**

Illustration 5:

Determine the ratio of partial pressure of O_2 gas and SO_3 gas in the gaseous mixture of equal masses.

Solution:

Wt. of O_2 = Wt. of SO_3 = x g

Moles of O_2 = $\frac{\text{wt.}}{\text{M.wt.}} = \frac{x}{32}$ mole

Moles of SO_3 = $\frac{\text{wt.}}{\text{M.wt.}} = \frac{x}{80}$ mole

$$\Rightarrow P_{O_2} = P_T.X_{O_2}\,;\ P_{SO_3} = P_T.X_{SO_3}$$

$$\Rightarrow \frac{P_{O_2}}{P_{SO_3}} = \frac{X_{O_2}}{X_{SO_3}} = \frac{\frac{n_{O_2}}{n_{O_2}+n_{SO_3}}}{\frac{n_{SO_3}}{n_{O_2}+n_{SO_3}}}$$

$$\Rightarrow \frac{P_{O_2}}{P_{SO_3}} = \frac{n_{O_2}}{n_{SO_3}} = \frac{x}{32} \Big/ \frac{x}{80} = \frac{80}{32} = \frac{5}{2}$$

Illustration 6:

2 moles of H_2 gas and 8 moles of CH_4 gas are present in a closed container at a total pressure of 2 atm. Calculate the partial pressure of H_2 and CH_4

Solution:

$$P_{H_2} = X_{H_2}.P_T$$

$$\Rightarrow P_{H_2} = \frac{n_{H_2}}{n_{H_2}+n_{CH_4}}, P_T = \frac{2}{2+8} \times 2 = 0.4 \text{ atm}$$

$$\Rightarrow P_{CH_4} = x_{CH_4}.P_T$$

$$\Rightarrow P_{CH_4} = \frac{n_{CH_4}}{n_{H_2}+n_{CH_4}}.P_T = \frac{8}{2+8} \times 2 = 1.6 \text{ atm}$$

Law of Mass Action

⇒ The law of mass action was given by Guldberg and Waage (1864).

⇒ It states that the rate of a chemical reaction is directly proportional to the product of active masses of the reacting substances raised to the power equal to the stoichiometric coefficient in the balanced chemical equation.

Derivation of equilibrium constant:

Consider a reversible homogeneous chemical reaction which has attained equilibrium state at a particular temperature:

$m_1A + m_2B \rightleftharpoons n_1C + n_2D$

Let the active masses of A, B, C and D be [A], [B], [C] and [D] respectively at equilibrium.

According to law of mass action:

Rate of forward reaction $(r_f) \propto [A]^{m_1}[B]^{m_2}$

Rate of backward reaction $(r_b) \propto [C]^{n_1}[D]^{n_2}$

$(r_f) \propto [A]^{m_1}[B]^{m_2}$ and $(r_b) \propto [C]^{n_1}[D]^{n_2}$

Where K_f and K_b are forward and backward rate or velocity constants respectively.

At equilibrium state –

$r_f = r_b$

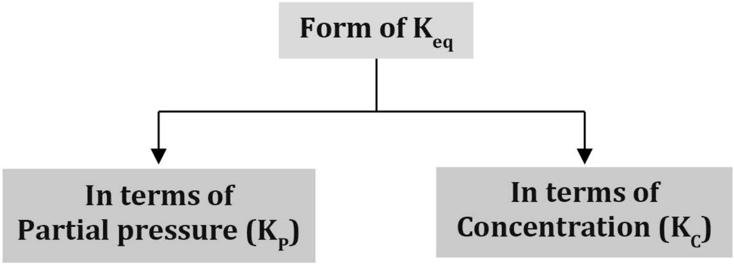
$$k_f[A]^{m_1}[B]^{m_2} = k_b[C]^{n_1}[D]^{n_2}$$

$$\frac{k_f}{k_b} = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$$

$$K = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}} \quad \because \quad K = \frac{k_f}{k_b}$$

K is known as equilibrium constant and has a definite value for every chemical reaction at a given temperature.

⇒ The equilibrium constant at a given temperature is the ratio of the rate constants of forward and backward reactions $K = \frac{k_f}{k_b}$



For the reaction $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$K_C = \frac{[C]^{n_1}\,[D]^{n_2}}{[A]^{m_1}\,[B]^{m_2}} \qquad K_P = \frac{(P_C)^{n_1}(P_D)^{n_2}}{(P_A)^{m_1}(P_B)^{m_2}}$$

Unit of **[ ]** = mol L^{-1} Unit of P = atm.

Relation between K_P and K_C:

Consider a reversible homogeneous chemical equilibrium reaction

$m_1A + m_2B \rightleftharpoons n_1C + n_2D$

According to law of mass action (LOMA)

$$K_C = \frac{[C]^{n_1}\,[D]^{n_2}}{[A]^{m_1}\,[B]^{m_2}}, \qquad K_P = \frac{(P_C)^{n_1}(P_D)^{n_2}}{(P_A)^{m_1}(P_B)^{m_2}}$$

For an ideal gas **PV = nRT**

Where – P = Pressure in atm

V = Volume in Litres

n = Number of gaseous moles

R = Gas constant = 0.0821 L atm $mol^{-1}K^{-1}$

T = Temperature in Kelvin

$$P = \frac{n}{V}RT = \text{active mass} \times RT$$

$$\frac{n}{V} = \text{molar concentration or active mass}$$

$P_A = [A]\,RT$, $P_B = [B]\,RT$, $P_C = [C]\,RT$ and $P_D = [D]\,RT$

Put all these values in K_P expression.

$$\text{So } K_P = \frac{[C]^{n_1}(RT)^{n_1} \times [D]^{n_2}(RT)^{n_2}}{[A]^{m_1}(RT)^{m_1} \times [B]^{m_2}(RT)^{m_2}} = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}} \times \frac{(RT)^{n_1+n_2}}{(RT)^{m_1+m_2}}$$

$$K_P = K_C\left(RT\right)^{(n_1+n_2)-(m_1+m_2)}$$

$\Delta n_g = (n_1 + n_2) - (m_1 + m_2)$

Δn_g = Sum of stoichiometric coefficient of gaseous products – sum of stoichiometric coefficient of gaseous reactants

$$\boxed{K_P = K_C\left(RT\right)^{\Delta n_g}}$$

⇒ The K_C is expressed by the units $(\text{mol L}^{-1})^{\Delta n_g}$ and K_P by $(\text{atm})^{\Delta n_g}$.

Three cases of Δn_g

(a)	(b)	(c)
When $\Delta n_g = 0$	**When $\Delta n_g = +ve$**	**When $\Delta n_g = -ve$**

(a) When $\Delta n_g = 0$

$K_P = K_C (RT)^0 = K_C$

For example:

(i) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

(ii) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

K_C and K_P are unit less in this case.

(b) When $\Delta n_g = +ve$

$K_P > K_C$

For example :

(i) $PCl_5 \rightleftharpoons PCl_3 + Cl_2 \left(\begin{matrix} K_C \rightarrow \text{mol L}^{-1} \\ K_P \rightarrow \text{atm} \end{matrix}\right)$

(ii) $2NH_3 \rightleftharpoons N_2 + 3H_2 \left(\begin{matrix} K_C \rightarrow \text{mol}^2\,\text{L}^{-2} \\ K_P \rightarrow \text{atm}^2 \end{matrix}\right)$

(c) When $\Delta n_g = -ve$

$K_P < K_C$

For example:

(i) $N_2 + 3H_2 \rightleftharpoons 2NH_3 \left(\begin{matrix} K_C \rightarrow \text{mol}^{-2}\,\text{L}^2 \\ K_P \rightarrow \text{atm}^{-2} \end{matrix}\right)$

(ii) $PCl_3 + Cl_2 \rightleftharpoons PCl_5 \left(\begin{matrix} K_C \rightarrow \text{mol}^{-1}\,\text{L}^1 \\ K_P \rightarrow \text{atm}^{-1} \end{matrix}\right)$

Special point:

If $T = \frac{1}{R}$ then

$$K_P = K_C\left(R \times \frac{1}{R}\right)^{\Delta n_g}$$

$K_P = K_C\,(1)^{\Delta n_g}$

$K_P = K_C$ (irrespective of the value of Δn_g)

Illustration 7:

For a gaseous reaction $2A + B \rightleftharpoons 4C$ at 27°C, $K_C = 3 \times 10^{-5}$ Find out K_P in terms of R.

Solution:

$K_P = K_C (RT)^{\Delta n_g}$

$K_P = 3 \times 10^{-5} (R \times 300)^1$

$K_P = 9 \times 10^{-3}\,R$

Illustration 8:

Compare K_P & K_C for each of the following equilibria:

(1) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

(2) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

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

(4) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$

Solution:

(1) $K_P = K_C$ (2) $K_P < K_C$

(3) $K_P > K_C$

(4) $K_P = K_C$

Illustration 9:

For a gaseous reaction, $2A + 3B \rightleftharpoons 2C$, which option is correct?

(1) $\log \frac{K_P}{K_C} - \log \frac{1}{RT} = 0$

(2) $\log \frac{K_P}{K_C} - 3 \log \frac{1}{RT} = 0$

(3) $\log \frac{K_P}{K_C} + 3 \log \frac{1}{RT} = 0$

(4) $\log \frac{K_P}{K_C} + 2 \log \frac{1}{RT} = 0$

Solution:

$K_P = K_C \, (RT)^{\Delta n_g}$

$\frac{K_P}{K_C} = (RT)^{\Delta n_g}$

$\log \frac{K_P}{K_C} = \log (RT)^{\Delta n_g}$

$\log \frac{K_P}{K_C} - \Delta n_g \log RT = 0$

Given $\Delta n_g = -3$

$\log \frac{K_P}{K_C} + 3 \log RT = 0$

$\log \frac{K_P}{K_C} - 3 \log \frac{1}{RT} = 0$

Illustration 10:

For $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$, $2K_P = K_C$ is possible, When:

(1) T = 6.09 K (2) T = 12.18 K (3) T = 24.36 K (4) T = 25. 2 K

Solution:

$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)} : \Delta n_g = -1$

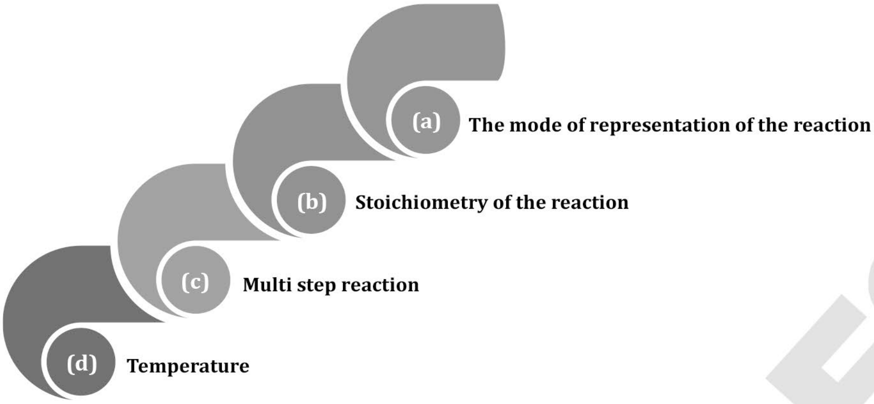
$\frac{K_P}{K_C} = (RT)^{\Delta n_g}$: given $\frac{K_P}{K_C} = \frac{1}{2}$

$(0.0821 \times T)^{-1} = \frac{1}{2}$

$\Rightarrow \frac{1}{0.0821 \times T} = \frac{1}{2}$

$T = \frac{2}{0.0821} = 24.36 \text{ K}$

Factors affecting the equilibrium constant:



(a) The mode of representation of the reaction:

Consider the reversible chemical equilibrium reaction $A + B \rightleftharpoons C + D$

The equilibrium constant for the reaction is $K_C = \frac{[C][D]}{[A][B]}$

If the reaction is reversed $C + D \rightleftharpoons A + B$

The equilibrium constant for the reaction is $K_C^{'} = \frac{[A][B]}{[C][D]}$

The equilibrium constant K_C' is actually the reciprocal of K_C

Thus, the two equilibrium constants are related as → $\boxed{K_C^{'} = \frac{1}{K_C}}$

(b) Stoichiometry of the reaction:

When a reversible reaction can be written with the help of two or more stoichiometric equations then the value of equilibrium constants will be numerically different in these cases.

For example the dissociation of NO_2 can be represented as:

$2NO_2 \rightleftharpoons N_2 + 2O_2$ ....(1)

$$K_C = \frac{[N_2][O_2]^2}{[NO_2]^2}$$

(i) If reaction (1) is divided by 2

Then the reaction becomes $NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$

$$K_C^{'} = \frac{[N_2]^{\frac{1}{2}}[O_2]}{[NO_2]}$$

Thus, the two equilibrium constants are related as $K_C^{'} = \sqrt{K_C}$

So if reaction is divided by n then $\boxed{K_C' = (K_C)^{\frac{1}{n}}}$

(ii) If reaction (1) is multiplied by 2

Then the reaction becomes $4NO_2 \rightleftharpoons 2N_2 + 4O_2$

$$K_C^{'} = \frac{[N_2]^2[O_2]^4}{[NO_2]^4}$$

Thus, the two equilibrium constants are related as $K'_C = (K_C)^2$

So if reaction is multiplied by n then $\boxed{K_C^{'} = (K_C)^n}$

(c) Multi step reaction: If a reaction can be expressed as the sum of two or more reactions then overall K_C will be equal to the product of the individual equilibrium constants of the reactions.

Example: $SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g) \rightarrow K_1$

$NO_2(g) \rightleftharpoons NO(g) + \frac{1}{2} O_2(g) \rightarrow K_2$

then $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g) \rightarrow K$

So $\boxed{K = K_1 \times K_2}$

(d) Temperature: The value of equilibrium constant changes with the change of temperature. If K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2 Kelvin and ΔH is the change in enthalpy then

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^o}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{or} \quad \log K_2 - \log K_1 = \frac{\Delta H^o}{2.303R}\left[\frac{T_2 - T_1}{T_1.T_2}\right]$$

(According to van't hoff equation)

If the temperature T_2 is higher than T_1

then $\left(\frac{T_2 - T_1}{T_1.T_2}\right) > 0$.

(i) When $\Delta H = +ve$ (endothermic reaction)
$\log K_2 - \log K_1 > 0$ or $\log K_2 > \log K_1$
$K_2 > K_1$
The value of equilibrium constant increases when temperature increases in case of endothermic reactions.

(ii) When $\Delta H = -ve$ (exothermic reaction)
$\log K_2 - \log K_1 < 0$
$\log K_2 < \log K_1$
$K_2 < K_1$
The value of equilibrium constant decreases when temperature increases in case of exothermic reactions.

Note: Factors not affecting the equilibrium constant:

The value of equilibrium constant is independent of the following factors–

(a) Concentration of reactants and products.
(b) Pressure
(c) Volume
(d) The presence of catalyst.
(e) Presence of inert gas.

Note: The value of equilibrium constant depends only on temperature for a given reaction.

Illustration 11:

$XeF_6 + H_2O \rightleftharpoons XeOF_4 + 2HF$ equilibrium constant = K_1, $XeO_4 + XeF_6 \rightleftharpoons XeOF_4 + XeO_3F_2$ equilibrium constant = K_2. The equilibrium constant for the reaction $XeO_4 + 2HF \rightleftharpoons XeO_3F_2 + H_2O$ will be–

(1) $\frac{K_1}{K_2}$ (2) $K_1 + K_2$ (3) $\frac{K_2}{K_1}$ (4) $\frac{K_1}{(K_2)^2}$

Solution:

(3)

Illustration 12:

Assertion: In the presence a catalyst, the value of equilibrium constant K increases.

Reason: Catalyst increases the rate of forward and backward reaction to the same extent.

(1) 1 (2) 2 (3) 3 (4) 4

Solution:

(3)

Application of K

<u>Stability of reactants and products:</u>

Stability of reactants increases when value of K decreases

Stability of products increases when value of K increases

Ex: In the following reactions which oxide is more stable.

$2XO\,(g) \rightleftharpoons X_2(g) + O_2(g)$; $K_1 = 1 \times 10^{24}$

$2XO_2\,(g) \rightleftharpoons X_2(g) + 2O_2(g)$; $K_2 = 2.5 \times 10^{10}$

$\because$ $K_1 > K_2$ So the stability of $XO_2 > XO$

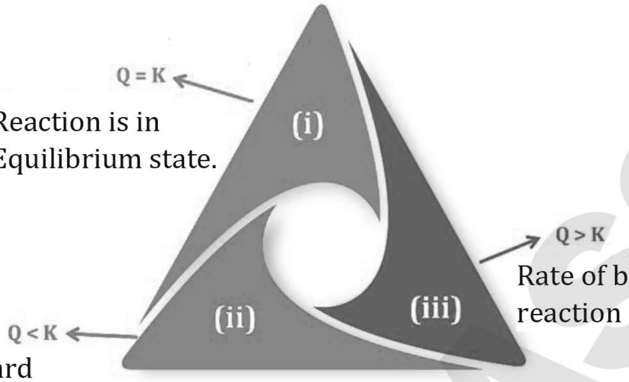
Reaction Quotient (Q)

Consider a general homogeneous reversible reaction:

$m_1A + m_2B \rightleftharpoons n_1C + n_2D$

Reaction Quotient (Q) = $\dfrac{[C]^{n_1}\,[D]^{n_2}}{[A]^{m_1}\,[B]^{m_2}}$, (Can be applied at any stage of reaction)

Equilibrium constant K = $\dfrac{[C]^{n_1}\,[D]^{n_2}}{[A]^{m_1}\,[B]^{m_2}}$, (Can be applied only at equilibrium state)



Reaction is in Equilibrium state.

Rate of backward reaction increases.

Rate of forward reaction increases

Illustration 13:

For the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $K_C = 6\ mol^{-2}L^2$. At a certain time, the concentration of N_2, H_2 and NH_3 is found to be 0.1, 0.2 and 0.3 mol L^{-1} respectively, then, determine the direction of reaction at this instant.

Solution:

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[0.3]^2}{(0.1)(0.2)^3} = 112.5$$

$Q > K_C \Rightarrow$ reaction is moving in backward direction.

Illustration 14:

In which reaction, reactant is least stable?

(1) $A \rightleftharpoons B + C$, $K_1 = 2 \times 10^{-4}$

(2) $A \rightleftharpoons 2B + C$, $K_2 = 10^{-8}$

(3) $2A \rightleftharpoons B + C$, $K_3 = 10^{-10}$

(4) $A \rightleftharpoons B + 2C$, $K_4 = 10^{-15}$

Solution:

Stability of reactant $\propto \dfrac{1}{K_C}$

$K_1 > K_2 > K_3 > K_4$

Reactant in (1) is least stable Ans. (1)

Illustration 15:

Assertion: For a reaction, reaction quotient (Q) is equal to K when the reaction is in equilibrium.

Reason: If a catalyst is added to the reaction at equilibrium, the value of Q remains no longer equal to K.

(1) 1 (2) 2 (3) 3 (4) 4

Solution:

(2)

Degree of Dissociation (α)

It is the fraction of moles of reactant dissociated

$$\alpha = \frac{x}{a_0}$$

$$\% \alpha = \frac{x}{a_0} \times 100$$

Where, α = Degree of dissociation

x = Number of dissociated moles

a_0 = Initial number of moles (given)

Let us consider a general reversible reaction:

	n_1A	$\rightleftharpoons$	n_2B	+	n_3C
t = 0	a_0		0		0

Suppose y mole of A reacted and equilibrium is achieved

$t = t_{eq}$	$a_0 - y$	$\frac{n_2}{n_1}y$	$\frac{n_3}{n_1}y$

$$\alpha = \frac{\text{moles reacted}}{\text{moles taken}} = \frac{y}{a_0}$$

$\therefore y = a_0\,\alpha$

Substituting:

$t = t_{eq}$	$a_0 - a_0\alpha$	$\frac{n_2}{n_1}a_0\alpha$	$\frac{n_3}{n_1}a_0\alpha$

Example:

	$2NH_3 \rightleftharpoons$	N_2 +	$3H_2$
t = 0	a_0		
$t = t_{eq}$	$a_0 - a_0\alpha$	$\frac{a_0\alpha}{2}$	$\frac{3a_0\alpha}{2}$

	$2HI \rightleftharpoons$	H_2 +	I_2
t = 0	a_0		
$t = t_{eq}$	$a_0 - a_0\alpha$	$\frac{a_0\alpha}{2}$	$\frac{a_0\alpha}{2}$

Extent of Reaction (x)

$$\text{Extent of reaction (x)} = \frac{\text{Moles reacted or formed}}{\text{Stoichiometric Coefficient}}$$

	n_1A +	n_2B $\rightleftharpoons$	n_3C +	n_4D
t = 0	a_0	b_0	0	0
$t = t_{eq}$	$a_0 - y$	$b_0 - \frac{n_2}{n_1}y$	$\frac{n_3}{n_1}y$	$\frac{n_4}{n_1}y$

$$x = \frac{y}{n_1}$$

$$\therefore \quad y = n_1x$$

$a_0 - n_1x$	$b_0 - n_2x$	n_3x	n_4x

Example:

	N_2 +	$3H_2$ $\rightleftharpoons$	$2NH_3$
	a_0	b_0	
At eq.	$a_0 - x$	$b_0 - 3x$	$2x$

	$2NO_2 \rightleftharpoons$	N_2O_4
	a_0	
At eq.	$a_0 - 2x$	x

Illustration 16:

In the beginning of the reaction, A $\rightleftharpoons$ B + C, 2 moles of A are taken, out of which 0.5 moles gets dissociated. What is the amount of dissociation of A ?

(1) 0.5 (2) 1 (3) 0.25 (4) 4.2

Solution:

	A	$\rightleftharpoons$	B	+	C
Initially	2		0		0
Given x = 0.5					
Moles at eq.	2 – x		x		x
	2 – 0.5		0.5		0.5

Since, two moles dissociated into 0.5

Therefore, one mole will dissociated into 0.25

Law of Mass Action as Applied to Heterogeneous Equilibrium:

In such cases, the active mass of pure solids and pure liquids is taken as unity and the value of equilibrium constant is determined by the gaseous substances only.

(i) The dissociation of $CaCO_3$ in closed vessel.

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ $K_P = P_{CO_2}$

(ii) $2H_2O_{(\ell)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$ $K_P = \left(p_{H_2}\right)^2\left(p_{O_2}\right)$

(iii) $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$ $K_P = \dfrac{\left(p_{H_2}\right)^4}{\left(p_{H_2O}\right)^4}$

Illustration 17:

$N_2O_4 \rightleftharpoons 2NO_{2(g)}$

The given reaction is started with 5 moles of N_2O_4. At equilibrium moles of NO_2 are found to be double that of N_2O_4. Determine K_C if the volume of the container is 500 mL.

Solution:

	N_2O_4	$\rightleftharpoons$	2NO(g)
t = 0	5 mole		0
$t = t_{eq}$	5 – x		2x

At equilibrium: $n_{NO_2} = 2 \times n_{n_2O_4}$

$\Rightarrow 2x = 2\,(5 - x)$

$\Rightarrow 2x = 10 - 2x$

$\Rightarrow x = 2.5$

$\therefore \left(n_{NO_2}\right)_{eq} = 2x = 2 \times 2.5 = 5$ mole

$\therefore \left(n_{N_2O_4}\right)_{eq} = 5 - x = 5 - 2.5 = 2.5$ mole

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(5/V)^2}{(2.5/V)} = \frac{25}{2.5 \times V}$$

$$\Rightarrow K_C = \frac{10}{V} = \frac{10}{500} \times 1000 = 20$$

Illustration 18:

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

The given reaction started with certain quantity of PCl_5. The mole fraction formed of Cl_2 at equilibrium is 0.25 and the pressure of the equilibrium mixture is 4 atm. Determine partial pressure of PCl_3 at equilibrium.

Solution:

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
$t = 0$	a mole		0		0
$t = t_{eq}$	$a - x$		x		x

$$\left(X_{Cl_2}\right)_{eq} = \frac{n_{Cl_2}}{n_{total}} = \frac{x}{a - x + x + x} \Rightarrow 0.25 = \frac{x}{a + x} \qquad ....(i)$$

Mole fraction of both the products i.e. PCl_3 & Cl_2 will be same.

$$P_{PCl_3} = X_{PCl_3}.P_T = \frac{x}{a + x}.P_T$$

= 0.25 × 4 = 1 atm

Illustration 19:

$2A_{(g)} \rightleftharpoons B_{(g)}$

The given reaction is started with 8 moles of A in a closed container of 10 L capacity. At equilibrium, the concentration of B is found to be 0.2 M. Determine:

(a) DOD of A

(b) Total moles of equilibrium mixture

(c) K_C

Solution:

	2A(g)	$\rightleftharpoons$	B(g)
$t = 0$	8 moles		0 moles
$t = 0$	conc. $\frac{8}{10} = 0.8$		0
$t = t_{eq}$	$0.8 - 2x$		x

conc. of B at eq. = 0.2, x = 0.2 M

conc. of A at eq. = 0.8 – 2 × 0.2 = 0.4 M

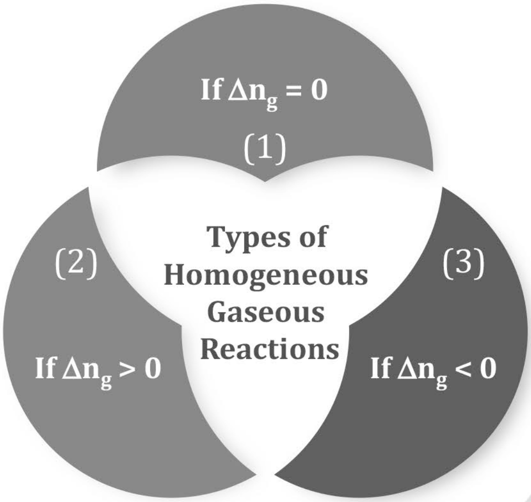
∴ Moles of A at eq. = conc. × V = 0.4 × 10 = 4 moles

Moles of B at eq. = 0.2 × 10 = 2 moles

Degree of dissociation of A = $\frac{2x}{0.8} = \frac{2 \times 0.2}{0.8} = \frac{1}{2}$

Applications of Law of Mass Action

[Relation of dissociation (x) with volume (V) and pressure (P)]



Homogeneous Gaseous Reactions of Type-I ($\Delta n_g = 0$)

Synthesis of HI:

(i) The formation of HI from H_2 and I_2 is represented by following reaction

	1	1	2
	$H_2\,(g)$ +	$I_2\,(g) \rightleftharpoons$	$2HI\,(g)$
Initial moles	a	b	0
Moles at equilibrium	(a – x)	(b – x)	2x

Let us start with 'a' moles of H_2 and 'b' moles of I_2 in a closed bulb of V volume. If at equilibrium x moles of each of H_2 and I_2 have reacted, then 2x moles of HI will be formed so active masses:

$$[H_2] = \frac{(a-x)}{V}\ ;\ [I_2] = \frac{(b-x)}{V}\ ;[HI] = \frac{2x}{V}$$

Applying law of mass action

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

$$K_C = \frac{4x^2}{(a-x)(b-x)}$$

⇒ When a = b = 1, x becomes degree of dissociation of H_2(or I_2).

$$K_C = \frac{4x^2}{(1-x)^2}$$

Let if $x <<< 1$ then $1 - x \simeq 1$ So $K_C = 4x^2$

$$x = \sqrt{\frac{K_C}{4}} \qquad \text{i.e.} \quad \boxed{x \propto V^\circ}$$

At equilibrium, the degree of dissociation is independent of the volume.

(ii) The equilibrium constant K_P can also be calculated considering partial pressures of reactants and products at equilibrium.

Total number of moles at equilibrium = (a – x) + (b – x) + 2x = (a + b)

If total pressure of the system at equilibrium be P, then,

Partial pressure of H_2 = $\frac{(a-x)}{(a+b)}P$,

Partial pressure of I_2 = $\frac{(b-x)}{(a+b)}P$

Partial pressure of HI= $\frac{2x}{(a+b)}P$

$$K_P = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} \qquad = \frac{\left(\frac{2x}{a+b}\right)^2 P^2}{\left(\frac{a-x}{a+b}\right)\left(\frac{b-x}{a+b}\right)P^2}$$

$$K_P = \frac{4x^2}{(a-x)(b-x)} \qquad \text{Thus,} \qquad K_P = K_C$$

Let if $x <<< 1$ then $1 - x \simeq 1$ So $K_P = 4x^2$

$$x = \sqrt{\frac{K_P}{4}} \quad \text{i.e.} \quad \boxed{x \propto P^{\circ}}$$

At equilibrium, the degree of dissociation is independent of the pressure also as well.

Homogeneous Gaseous reactions of Type-II ($\Delta n_g > 0$)

Dissociation of PCl_5:

(i) The dissociation of PCl_5 takes place according to the equation

	1		1	1
	PCl_5	$\rightleftharpoons$	PCl_3 +	Cl_2
Initial moles	a		0	0
Moles at equilibrium	(a – x)		x	x

Let 'a' moles of PCl_5 be taken in a closed vessel of volume V. At equilibrium x moles of PCl_5 are dissociated into x moles of each PCl_3 and Cl_2.

$$[PCl_5] = \frac{(a-x)}{V} \quad ; \quad [PCl_3] = \frac{x}{V}\,; \quad [Cl_2] = \frac{x}{V}$$

On applying law of mass action,

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

⇒ When a =1, x becomes degree of dissociation (α)

$$K_C = \frac{\alpha^2}{(1-\alpha)V}$$

If $\alpha <<< 1$ then $1 - \alpha \simeq 1$

$$K_C \approx \frac{\alpha^2}{V} \qquad \text{or} \qquad \boxed{\alpha \propto \sqrt{V}}$$

The degree of dissociation of PCl_5 at equilibrium is directly proportional to the square root of the volume.

(ii) **Expression for K_P :**

Let the total pressure at equilibrium be P.

Total number of moles at equilibrium = (a – x) + x + x = a + x

$$p_{PCl_5} = \left(\frac{a-x}{a+x}\right)P, \qquad p_{PCl_3} = \left(\frac{x}{a+x}\right)P, \qquad p_{Cl_2} = \left(\frac{x}{a+x}\right)P$$

On applying law of mass action, $K_P = \frac{p_{PCl_3} \cdot p_{Cl_2}}{p_{PCl_5}} = \frac{x^2 p}{(a+x)(a-x)}$

When a = 1, x becomes degree of dissociation (α) $K_P = \frac{\alpha^2 P}{(1+\alpha)(1-\alpha)} = \frac{\alpha^2 P}{1-\alpha^2}$

If $\alpha <<< 1$ then $1-\alpha^2 \simeq 1$, $K_P \simeq \alpha^2 P$

$\alpha^2 \propto \frac{1}{P}$ $\Rightarrow$ $\boxed{\alpha \propto \frac{1}{\sqrt{P}}}$

⇒ The degree of dissociation of PCl_5 is inversely proportional to the square root of the total pressure at equilibrium.

Homogeneous Gaseous reactions of Type-III ($\Delta n_g < 0$)

Synthesis of Ammonia:

(i) The formation of ammonia from nitrogen and hydrogen is represented by the equation:

	1		3		2
	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
Initial moles	a		b		0
Moles at equilibrium	(a – x)		(b – 3x)		2x

Let us start with 'a' moles of N_2 and 'b' moles of H_2 in a closed vessel of Volume V. At equilibrium, x moles of N_2 combines with 3x moles of H_2 and produces 2x moles of NH_3.

At equilibrium,

$$[N_2] = \frac{(a-x)}{V}; \qquad [H_2] = \frac{(b-3x)}{V}; \; [NH_3] = \frac{2x}{V}$$

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

If a = 1, b = 3 then, $K_C = \frac{4x^2V^2}{27(1-x)^4}$

If x <<< 1 then $1 - x \approx 1$

$K_C = \frac{4x^2V^2}{27}$ i.e. $\boxed{x \propto \frac{1}{V}}$

At equilibrium, the degree of dissociation is inversely proportional to the volume of vessel.

(ii) **Expression for K_P:**

Total number of moles at equilibrium = (a – x) + (b –3x) + 2x = a + b – 2x

If total pressure is P at equilibrium then

Partial pressure

$$p_{N_2} = \frac{(a-x)}{(a+b-2x)}P; \quad p_{H_2} = \frac{(b-3x)}{(a+b-2x)}P; \qquad p_{NH_3} = \frac{2x}{(a+b-2x)}P$$

According to Law of mass action

$$K_P = \frac{P_{NH_3}^2}{\left(P_{N_2}\right)\left(P_{H_2}^3\right)} = \frac{\left(\frac{2x}{a+b-2x}P\right)^2}{\left(\frac{a-x}{a+b-2x}\right)\left(\frac{b-3x}{a+b-2x}\right)^3} = \frac{4x^2\left(a+b-2x\right)^2}{(a-x)(b-3x)^3 P^2}$$

If a = 1, b = 3 then $K_P = \frac{16x^2(2-x)^2}{27(1-x)^4 P^2}$

If x < < < 1 then 2 – x ≈ 2 and 1 – x ≈ 1

$K_P = \frac{64x^2}{27P^2}$ i.e. $x^2 \propto P^2 \Rightarrow \boxed{x \propto P}$

At equilibrium, the degree of dissociation is directly proportional to the pressure.

$$\alpha \propto (V)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficient of gaseous products}}}$$

or

$$\alpha \propto \left(\frac{1}{P}\right)^{\frac{\Delta n_g}{\text{sum of stoichiometric coefficient of gaseous products}}}$$

S.No.		**$\Delta n_g = 0$** **$H_2 + I_2 \rightleftharpoons 2HI$**	**$\Delta n_g > 0$ or +ve** **$PCl_5 \rightleftharpoons PCl_3 + Cl_2$**	**$\Delta n_g < 0$ or –ve** **$N_2 + 3H_2 \rightleftharpoons 2NH_3$**
	Effect	$x \propto (v)^o \propto (P)^o$	$x \propto (v)^{1/2} \propto \left(\frac{1}{P}\right)^{1/2}$	$x \propto \left(\frac{1}{V}\right) \propto (P)$
(i)	Pressure (↑)	x unchanged	x decreases	x increases
(ii)	Volume (↑)	x unchanged	x increases	x decreases
(iii)	Mixing of inert gas at (a) constant pressure (b) constant volume	x unchanged x unchanged	x increases x unchanged	x decreases x unchanged

Illustration 20:

Two sample of HI each of 5 grams were taken separately into vessels of volume 5 and 10 litres respectively at 27°C. The extent of dissociation of HI will be:

(1) More in 5 litre vessel

(2) More in 10 litre vessel

(3) Equal in both vessel

(4) None of these

Solution:

(3)

Illustration 21:

What will be the amount of dissociation, if the volume is increased 16 times of initial volume in the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$?

(1) 4 times (2) ½ times (3) 2 times (4) 8 times

Solution:

$x \propto \sqrt{V}$ or $x \propto \sqrt{16}$

Thus. 4 times.

Illustration 22:

Assertion: For the reaction, $N_2 + O_2 \rightleftharpoons 2NO$, increase in pressure at equilibrium has no effect on the reaction.

Reason: The reaction is not accompanied by any change in number of moles of gaseous species.

(1) A (2) B (3) C (4) D

Solution:

(1)

BEGINNER'S BOX-4

1. $A + B \rightleftharpoons C + D$ If initially A and B both are taken in equal amount but at equilibrium concentration of D will be twice of that of A then what will be the equilibrium constant of reaction :-

(1) $\frac{4}{9}$ (2) $\frac{9}{4}$ (3) $\frac{1}{9}$ (4) 4

2. At a certain temperature, only 50% HI is dissociated at equilibrium in the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ The equilibrium constant for the reaction is :-

(1) 0.25 (2) 1.0 (3) 3.0 (4) 0.5

3. The equilibrium constant K_P for the reaction $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ is 4.0 at 1660°C. Initially, 0.80 mole H_2 and 0.80 mole CO_2 are injected into a 5.0 liter flask. What is the equilibrium concentration of $CO_2(g)$?

(1) 0.533 M (2) 0.0534 M (3) 5.34 M (4) None of these

4. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ for the reaction initially the mole ratio was 1 : 3 of $N_2 : H_2$. At equilibrium 50% of each has reacted. If the equilibrium pressure is p, the partial pressure of NH_3 at equilibrium is :-

(1) $\frac{p}{3}$ (2) $\frac{p}{4}$ (3) $\frac{p}{6}$ (4) $\frac{p}{8}$

5. For the reaction $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$, if the initial concentration of $[H_2] = [CO_2]$ and if x moles/litre of hydrogen is consumed at equilibrium, the correct expression of K_P is :-

(1) $\frac{x^2}{(1-x)^2}$ (2) $\frac{(1+x)^2}{(1-x)^2}$ (3) $\frac{x^2}{(2+x)^2}$ (4) $\frac{x^2}{1-x^2}$

6. For the equilibrium $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ $K_p = 63$ atm at 1000 K. If at equilibrium $P_{CO} = 10\ P_{CO_2}$ then total pressure at equilibrium is :-

(1) 6.30 atm (2) 0.693 atm (3) 6.93 atm (4) 69.3 atm

Calculation of α from Vapour Density:

	$n_1A \rightleftharpoons$	n_2B	$+ \quad n_3C$
$t = 0$	a_0		
$t = t_{eq}$	$a_0 - a_0\alpha$	$\frac{n_2}{n_1}a_0\alpha$	$\frac{n_3}{n_1}a_0\alpha$

$$\text{Total moles at equilibrium} = a_0 + a_0\alpha\left(\frac{n_2}{n_1} + \frac{n_3}{n_1} - 1\right) = a_0 + a_0\alpha\left(\frac{n_2 + n_3 - n_1}{n_1}\right)$$

$= a_0 + a_0\alpha\left(\frac{\Delta ng}{n_1}\right)$ $\Delta n_g = (n_2 + n_3) - (n_1)$

Initial mass $= a_0 \times MW_A$

$= a_0 \times MW_{th}$

Note: The molecular weight of reactant is also called as Theoretical Molecular Weight (MW_{th})

Total moles at equilibrium $= a_0 + a_0\alpha\left(\frac{\Delta n_g}{n_1}\right)$

Final mass $= \left(a_0 + a_0\alpha\frac{\Delta n_g}{n_1}\right)\times MW_{mix}$

By mass conservation; Initial mass = Final Mass

$$a_0 \times MW_{th} = \left(a_0 + a_0\alpha\frac{\Delta n_g}{n_1}\right)\times MW_{mix}$$

$$\frac{MW_{th}}{MW_{mix}} = 1 + \frac{\Delta n_g}{n_1}\alpha$$

$$\frac{\Delta n_g}{n_1}\alpha = \frac{MW_{th}}{MW_{mix}} - 1 = \frac{MW_{th} - MW_{mix}}{MW_{mix}}$$

$$\alpha = \left(\frac{MW_{th} - MW_{mix}}{MW_{mix}}\right)\frac{n_1}{\Delta n_g}$$

Note: The molecular weight of equilibrium mixture (MW_{mix}) is also called as Observed Molecular Weight (MW_{obs})

$MW_{mix} = MW_{obs}$

$$\boxed{\alpha = \left(\frac{MW_{th} - MW_{obs}}{MW_{obs}}\right)\frac{n_1}{\Delta ng}}$$

∵ Vapour density = MW/2

$$\boxed{\alpha = \left(\frac{D - d}{d}\right)\frac{n_1}{\Delta ng}}$$

D = Theoretical Vapour Density

d = Observed Vapour Density

Example:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$\alpha = \left(\frac{D-d}{d}\right)\frac{n_1}{\Delta n_g}$$

$$\alpha = \left(\frac{D-d}{d}\right)\frac{1}{2-1} = \frac{D-d}{d}$$

$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

$$\alpha = \left(\frac{D-d}{d}\right)\frac{n_1}{\Delta n_g} = \left(\frac{D-d}{d}\right)\frac{2}{3+1-2} = \frac{D-d}{d}$$

Illustration 23:

The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2. The percentage dissociation of N_2O_4 at the final temperature is -

(1) 87 (2) 60 (3) 40 (4) 70

Solution:

(1)

$$\alpha = \frac{D_T - D_0}{D_0} = \frac{46-24.5}{24.5} = 0.87 = 87\%$$

Illustration 24:

If PCl_5 is 80% dissociated at 250° C then its vapour density at room temperature will be

(1) 56.5 (2) 104.25 (3) 101.2 (4) 52.7

Solution:

(2)

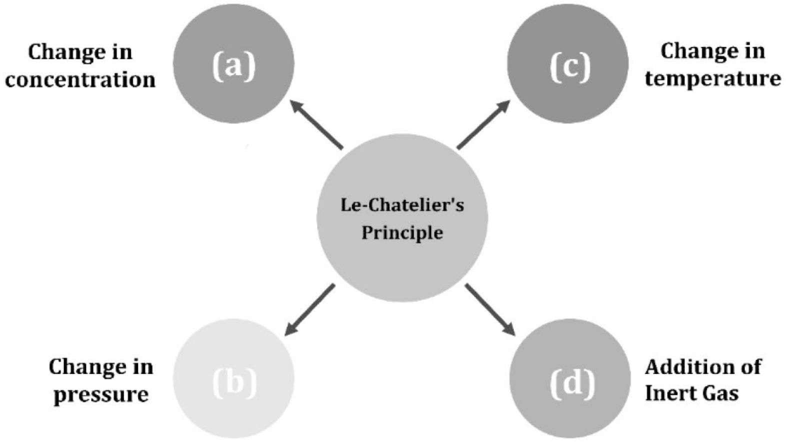
$$\alpha = \frac{D_T - D_o}{D_o}\ ;\ D_T = \frac{\text{Molecular weight}}{2}$$

Vapour density at room temperature (D_T) is 104.25, which is fixed.

Le-Chatelier's Principle

Principle:

According to this principle, if a system at equilibrium is subjected to a change of concentration, pressure or temperature then the equilibrium is shifted in such a way so as to nullify the effect of that change.



(a) Change in concentration: In an equilibrium increasing the concentration of reactants results in shifting the equilibrium in favour of products while increasing concentration of products results in shifting the equilibrium in favour of the reactants.

(b) Change in pressure: When the pressure on the system is increased, the volume decreases proportionately i.e. the total number of moles present per unit volume increase. According to Le-Chatelier's principle, the equilibrium shifts in that direction in which there is decrease in number of moles.

⇒ If there is no change in number of moles of gases in a reaction then the pressure change does not affect the equilibrium.

(c) Change in temperature: If the temperature of the system at equilibrium is increased then reaction will proceed in that direction in which heat can be used. Thus, increase in temperature will favour the forward reaction for endothermic reaction.

Similarly, increase in temperature will favour the backward reaction for exothermic reactions.

Special point: Le-Chatelier's principle is applicable for both chemical and physical equilibrium.

(d) Adding of Inert Gas

(i) At Constant Pressure

- To maintain constant pressure after addition of inert gas, volume must be increased.
- So, partial pressure of each gas decreases and equilibrium shifts in the direction in which more moles are formed.
  - If $\Delta n_g = 0 \Rightarrow$ No Effect on Equilibrium State.
  - If $\Delta n_g \neq 0 \Rightarrow$ Equilibrium Shifts in direction of more number of moles of gases.

(ii) At Constant Volume

Inserting inert gas at constant volume will have no effect on equilibrium.

There is no change in pressure of reaction system.

This is because the partial pressure of gases remains unchanged.

Catalyst

- No effect on equilibrium state.
- Catalyst increases the rate of forward reaction and rate of backward reaction equally and hence helps in attaining the equilibrium state in lesser time.

Illustration 25:

For a reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H = -ve$, then, determine the effect at equilibrium due to following changes:

(1) Decreasing concentration of H_2
(2) Increasing the pressure
(3) Decreasing the temperature
(4) Catalyst
(5) Increasing the volume

Solution:

(1) Backward (2) Forward (3) Forward (4) No effect
(5) Backward

Illustration 26:

Determine effect on equilibrium system due to following changes:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $\Delta H = +ve$

(1) Decreasing concentration of CO_2
(2) Increasing the volume
(3) Increasing the temperature
(4) Adding Ne at constant volume
(5) Increasing the moles of $CaCO_3$
(6) Adding Ne at constant pressure

Solution:

(1) Forward (2) Forward (3) Forward (4) No effect
(5) No effect (6) Forward

Illustration 27:

For $A(s) + B(g) \rightleftharpoons C(g)$,

if reaction shifts in forward direction, then, incorrect option is:

(1) [C] Increases
(2) dissociation of B increases
(3) [A] decreases
(4) [B] decreases

Solution:

On forward shifting $\Rightarrow [C] \uparrow$
$\Rightarrow [B] \downarrow$
$\Rightarrow x$ (dissociation) $\uparrow$
$\Rightarrow [A]$ = unchanged ($\because$ A is solid)

Physical Equilibrium

Example:

(a) Ice-water system (melting of ice):

Melting of ice is accompanied by absorption of heat (endothermic) and decrease in volume

$Ice_{(s)}$	$\rightleftharpoons$	$water_{(\ell)}$
(H_2O)		(H_2O)
1g (1.09 mL)		1g (1.01 mL)

Hence, increase of temperature and also increases of pressure will favour the melting of ice into water.

(b) Water-water vapour system (Vapourisation of water):

Vapourisation of water is an endothermic process and condensation of vapour into water is an exothermic reaction:

$$\underset{(H_2O)}{\text{Water}(\ell)} \rightleftharpoons \underset{(H_2O)}{\text{Vapour(g)}}$$

⇒ The equilibrium shifts towards right side when the temperature is increased so rise in temperature will increase the vapour.

⇒ The equilibrium shifts towards left side when the pressure is increased (i.e. volume is decreased) so increase in pressure will favour the rate of condensation of vapour into water.

⇒ Thus favourable conditions for conversion of water into vapour are high temperature and low pressure.

(c) Solubility of gases:

$$\underset{\text{(Solute)}}{\text{Gas}_{(g)}} + \underset{\text{(Solvent)}}{\text{Water}_{(\ell)}} \rightleftharpoons \underset{\text{(Solution)}}{\text{Aqueous solution }(\ell)}$$

⇒ Effect of pressure → Solubility of such gases increases with increasing pressure which dissolves in a solvent with a decrease in volume.

Illustration 28:

On applying pressure to the equilibrium, ice $\rightleftharpoons$ water, which phenomenon will happen?

(1) More ice will be formed
(2) More water will be formed
(3) Equilibrium will not be disturbed
(4) Water will evaporate

Solution:

(2)

Illustration 29:

Which of the following conditions should be more favourable for increasing the rate of forward reaction in the equilibrium $H_2 \rightleftharpoons H + H$ ($\Delta H = +ve$) ?

(1) 2000° C temperature and 760 mm of Hg pressure.
(2) 3500° C temperature and 100 cm of Hg pressure.
(3) 3500° C temperature and 1 mm of Hg pressure.
(4) All are wrong.

Solution:

(3)

In $H_2 \rightleftharpoons H + H$, heat has to be provided to dissociate H_2 into H. Therefore, the reaction is endothermic (ΔH will be positive). So, temperature should be high. Since, one mole of H_2 forms two atoms of H, so volume is increasing (Δn is positive) so pressure should be low for increasing the rate of forward reaction.

Illustration 30:

Assertion:

$SO_{2(g)} + ½\ O_{2(g)} \rightleftharpoons SO_{3(g)}$

Forward reaction is favoured at low temperature and high pressure.

Reason: Reaction is endothermic.

(1) A (2) B (3) C (4) D

Solution:

(3)