CHEMICAL EQUILIBRIUM

❑ INTRODUCTION

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

Ex. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

❑ TYPES OF CHEMICAL REACTION :

On the basis of physical state	
Homogeneous reaction	Heterogeneous reaction
All reactants and products are in same phase $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Reactants and products are in more than one phase $Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)$

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. $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$ $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$ $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$ $2KClO_3 \longrightarrow 2KCl + 3O_2$
(ii) Proceed in forward as well as backward direction.	(ii) Proceed only in one direction (forward).
(iii) To obtain reverisible reactions, if anyone of the reactant or product is in gaseous state, then the reaction should be carried out in closed vessel. $CaCO_3\,(s) \longrightarrow CaO\,(s) + CO_2\,(g) \uparrow$	(iii) Generally possible in open container.
(iv) These attain equilibrium.	(iv) These do not attain equilibrium.
(v) Reactants are never completely converted into products.	(v) Reactants are completely converted into products.
(vi) Generally thermal decomposition in closed vessel. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_2\,(g)$	(vi) Generally thermal decomposition in open vessel. $PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_2\,(g)$

On the basis of speed.	
Fast reactions	Slow reactions
(i) Generally these reactions are ionic reactions. $HCl + NaOH \rightarrow NaCl + H_2O$ Acid Base Salt Water	(i) Generally these reactions are molecular reactions. $H_2 + I_2 \rightarrow 2HI$

On the basis of heat	
Exothermic reaction	**Endothermic reaction**
(i) Heat is evolved in these chemical reaction $R \rightarrow P + x$ kcal	(i) Heat is absorbed in these chemical reaction $R + x$ kcal $\rightarrow P$ or $R \rightarrow P - x$ kcal
(ii) Change in heat energy $\Delta Q = (+)$ ve	(ii) Change in heat energy $\Delta Q = (-)$ ve
(iii) Change in enthalpy $\Delta H = (-)$ ve $\boxed{\Delta H = -\Delta Q}$	(iii) Change in enthalpy $\Delta H = (+)$ ve
Eg. : Formation reaction Exception $N_2 + O_2 \rightarrow 2NO/N_2O/NO_2$ $O_2 + F_2 \rightarrow O_2F_2/OF_2$	Eg. : Dissociation reaction

- **Active mass :** The term active mass means the concentration of the reactants & products expressed in moles per litre (molar concentration). Active mass is usually expressed by enclosing the symbol of the reactant in square bracket [ ]

$$\text{Active mass} = \frac{\text{moles}}{\text{Volume in litres}}$$

$$= \frac{\text{grams(w)}}{\text{mol.wt.}(M_w) \times \text{Volume in litres(V)}} = \frac{w \times 1000}{M_w \times V(\text{mL})}$$

- The active mass of solids and pure liquids is a constant quantity (unity) and solvent (excess) is considered as one. Because there is no change in activity with the change in quantity or volume of vessel.

$$\text{Molar concentration} = \frac{w}{M_w \times V_{\text{lit.}}} = \frac{\rho}{M_w} \quad (\rho = \text{density in g/lit})$$

$$= \frac{\text{density of the substance}}{\text{molecular mass of the substance}}$$

as density of pure solids and liquids is constant and molecular mass is also constant.

But this is not applicable to the substance in aqueous solution or gaseous state because their amount in a given volume can vary.

Following other names of active mass can also be use :

(i) mole/lit.
(ii) gram mole/lit.
(iii) gram molecules/lit.
(iv) molarity
(v) Concentration
(vi) Effective concentration
(vii) active quantity
(viii) n/v
(ix) C
(x) M
(xi) [ ]

◆ **Examples :**

(a) 25.4 g of iodine is present in 2 litres of solution

$$\text{then} \quad [I_2] = \frac{25.4}{254 \times 2} = 0.05 \text{ mole/litre}$$

(b) 8.5 g ammonia is present in a vessel of 0.5 litre capacity then

$$[NH_3] = \frac{8.5}{17 \times 0.5} = 1 \text{ mole / litre}$$

(c) Active mass of C (s) or S(s) or Zn(s) is equal to 1.

❑ RATE OF REACTION :

The change in concentration of reactants or products per mole in unit time is known as rate of the reaction.

$$\text{Rate of reaction} = \frac{\text{(–) change in concentration of rectants}}{\text{time}}$$

$$= -\left(\frac{dc}{dt}\right)\text{reactants.}$$

Here negative sign indicate that concentration of reactants decrease with time.

$$\text{Rate of reaction} = +\frac{\text{change in concentration of products}}{\text{time}} = +\left(\frac{dc}{dt}\right)\text{ products}$$

Here possitive sign indicate that concentration of products increase with time.

Note : The concentration change may be positive or negative but the rate of reaction is always positive.

$$\text{Unit of rate of reaction} = \frac{\text{mole/lit.}}{\text{sec}} = \frac{\text{mole}}{\text{lit.sec}} = \text{mole lit}^{-1}\text{ sec}^{-1}$$

◆ For example $A \longrightarrow B$

For reactant $\longrightarrow -\frac{d[A]}{dt}$ [concentration decreases with time]

For product $\longrightarrow +\frac{d[B]}{dt}$ [concentration increases with time]

Ex. $2A + 3B \rightleftharpoons C + 4D$

Rate of dissappearance of A $= -\frac{d[A]}{dt}$

Rate of dissappearance of B $= -\frac{d[B]}{dt}$

Rate of appearance of C $= +\frac{d[C]}{dt}$

Rate of appearance of D $= +\frac{d[D]}{dt}$

$$\text{Rate of reaction (ROR)} = \frac{-1}{2}\frac{d[A]}{dt} = \frac{-1}{3}\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{1}{4}\frac{d[D]}{dt}$$

Note : Rate of reaction is always for per mole.

◆ $aA + bB \rightleftharpoons cC + dD$

$$\text{Rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{[D]}{dt}$$

Ex. For the reaction

$2SO_2 + O_2 \rightleftharpoons 2SO_3$

rate of reaction is $2.5 \quad 10^{-4}$ moles/lit.sec. then find out the rate of dissappearance of SO_2.

Ans. $\text{ROR} = \frac{-1}{2}\frac{d[SO_2]}{dt} = -\frac{d[O_2]}{dt} = 2.5 \quad 10^{-4}$ mole/lit.sec.

$-\frac{d[SO_2]}{dt} = 5 \quad 10^{-4}$ mole/lit.sec.

FACTORS AFFECTING RATES OF REACTIONS :

(a) **State of matter** : The decreasing order of rate of reaction in gas, liquid and solid state are-

$$g > \ell > s$$

(b) **Temperature** : Rate of reaction α temperature

(c) **Concentration** : Rate of reaction α concentration.

(d) **Catalyst** : Positive catalyst increases the rate of reaction.

CHEMICAL EQUILIBRIUM :

The state of the reversible chemical reaction at which rate of forward reaction becomes equal to rate of backward reaction.

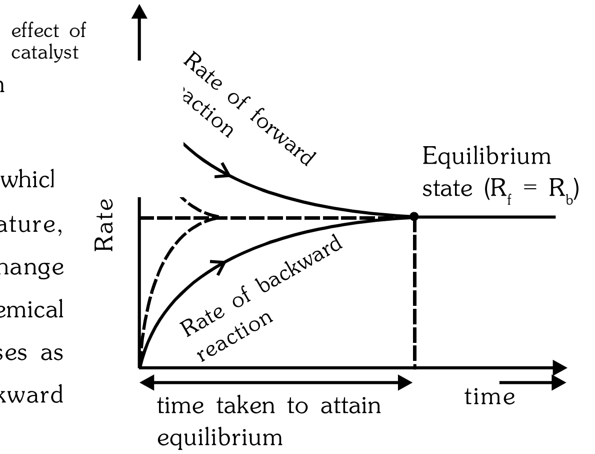
$$A + B \underset{R_b}{\overset{R_f}{\rightleftharpoons}} C + D$$

R_f = forward rate of reaction

R_b = backward rate of reaction

i.e. $R_f = R_b$

or The state of the reversible chemical reaction at which the measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time at the given set of conditions is said to be chemical equilibrium conditions. Rate of forward reaction decreases as the concentration of products increases, rate of backward reaction also starts increasing.



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

AT EQUILIBRIUM STATE :

Rate of forward reaction = Rate of backward reaction

- At this state of equilibrium forward and backward reactions proceeds with same speed.
- The stage of the reversible reaction at which the concentrations of the reactants and products do not change with time is called the equilibrium state.
- The equilibrium state is dynamic in nature.
- The reaction does not stop, but both the opposing reactions are going on continously with same speeds.

CHARACTERISTICS OF EQUILIBRIUM :

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

(b) To obtain equilibrium, if anyone of the reactant or product is in gaseous state then the reaction should be carried out in closed vessel.

(c) At a given temperature and pressure of equilibrium the properties like concentration, colour, density remains constant.

(d) In a reversible chemical reaction the equilibrium state can be attained in lesser time by the use of positive catalyst.

A catalyst doesn't change the equilibrium state becuase it increases the rate of both forward and backward reaction simaltaneously by changing the path of reaction and it helps in attaining equilibrium rapidly.

(e) In order to prevent escape of products, equilibrium is reached in only in closed vessels in reversible reactions.

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

$$CH_3COO\,C_2H_5(\ell)+H_2O(\ell) \rightleftharpoons CH_3COOH(\ell)+C_2H_5OH(\ell)$$

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

$$Zn(s) + CO_2(g) \rightleftharpoons ZnO(s) + CO(g)$$

Note :

(i) Whenever question doesn't ask about direction, then we take forward direction only.

(ii) In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice versa.

❑ TYPES OF EQUILIBRIA :

There is two types of equilibria :

1. Physical equilibria :

If in a system only physical state (phase) is changed and then equilibrium is established, (i.e. there is no chemical change) the equilibrium is called physical equilibrium.

e.g. Fusion of ice, evaporation of water, dissolution of salts and absorption of gases in liquid etc.

Following are the types of common physical equilibria :-

(i) **Liquid-Vapour equilibria** : In a closed vessel, the vapours above the liquid are in equilibrium at given temperature.

Ex. $H_2O\ (\ell) \rightleftharpoons H_2O\ (g)$

(ii) **Solid-Liquid equilibria** : This equilibrium can be established only at melting point of solid. At this stage solid and liquid phases exist simultaneously in equilibrium.

Ex. $H_2O\ (s) \rightleftharpoons H_2O\ (\ell)$ at melting point

(iii) **(Solute-Solvent), Saturated solution equilibria** : If the rate of dissolution of solids in liquid is equal to the rate of crystallization of solid from solution i.e. solution is saturated with respect to solid then saturated solution equilibria established, provided temperature is constant.

Ex. $NaI\ (s) \xrightleftharpoons{H_2O} Na^+\ (aq.) + I^-\ (aq.)$

Note: Above example is of solubility of sparingly soluble salt, which only depends on temperature.

(iv) **(Gas + Solvent), Saturated solution equilibria** : In such equilibriums, solvents is saturated with respect to gas i.e. rate of entering of gas molecules in solvent is equal to rate of escaping of gas molecules from solvents. Above phenomenon can be observed in closed container at definite temperature.

Ex. Dissolved CO_2 in cold drinks. Dissolved O_2 in water etc.

Note :

(i) The solubilities of gases in liquid is a function of pressure of gas over liquid.

(ii) **Henry's law** can be applied on such system, that states, the mass of gas dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent.

$$C_g \propto P_g \quad \text{or} \quad C_g = k\,P_g$$

where k = Henry's constant

C_g = Solubility of gas in the solution (mol L^{-1})

P_g = Pressure of the gas

(iii) One should not compare it with liquid vapour equilibria.

2. Chemical equilibria :

When chemical change occur in a reversible reaction i.e. reactants convert into products and products also convert into reactants under similar conditions of pressure and temperature, the reaction is said to be in chemical equilibria.

(i) $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$ (formation of HI)

(ii) $SO_2\ (g) + Cl_2\ (g) \rightleftharpoons SO_2Cl_2\ (g)$ (formation of SO_2Cl_2)

(iii) $PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)$ (formation of PCl_5)

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

❑ EXAMPLES :

Ex. Chemical equilibrium is a condition :

(A) where all species have same concentration

(B) where all species have constant concentration with respect to time.

(C) where all species have concentration = 1

(D) all of above

Sol. **(B)**

Chemical equilibrium defined as when all species have constant concentration with respect to time.

Ex. Example of physical equilibria, is :

(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (B) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(C) $H_2O(s) \rightleftharpoons H_2O(\ell)$ (D) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Sol. **(C)**

Physical equilibria does not include any chemical change.

Ex. At equilibrium :

(A) the energy of system is minimum (B) the entropy of system is maximum

(C) the energy of system is maximum (D) the entropy of system is minimum

Sol. **(A,B)**

It is the compromising stage of minimum energy and maximum entropy.

❑ LAW OF MASS ACTION OR LAW OF CHEMICAL EQUILIBRIUM :

The law of mass action is given by **Guldberg** and **Waage**.

According to them at a given temperature rate of reaction is proportional to product of active masses of reactants at that instant raised to the powers which are numerically equal to the number of their respective molecule in the stoichiometric equation describing the reaction.

◆ Derivation of equilibrium constant :

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

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

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

◆ According to law of mass action :

rate of forward reaction α [A] [B]

rate of backward reaction α [C] [D]

$R_f = K_f[A][B]$ $\quad$ $R_b = K_b[C][D]$

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

At equilibrium

$$R_f = R_b$$

$$K_f[A][B] = K_b[C][D]$$

$$\frac{K_f}{K_b} = \frac{[C][D]}{[A][B]}$$

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

$$\because \ K_c = \frac{K_f}{K_b}$$

K_c is known as equilibrium constant K_c has a definite value for every chemical reaction at particular tempera ture.

q For a general reaction

$$m_1A + m_2B + m_3C \rightleftharpoons n_1M + n_2N + n_3O$$

$$r_f \propto [A]^{m_1}[B]^{m_2}[C]^{m_3}$$

$r_f = K_f\ [A]^{m_1}[B]^{m_2}[C]^{m_3}$ [K_f = forward rate (velocity) constant]

$$r_b \propto [M]^{n_1}[N]^{n_2}[O]^{n_3}$$

$r_b = K_b\ [M]^{n_1}[N]^{n_2}[O]^{n_3}$ [K_b = backward rate (velocity) constant]

At equilibrium $r_f = r_b$

$$K_f\ [A]^{m_1}[B]^{m_2}[C]^{m_3} = K_b\ [M]^{n_1}[N]^{n_2}[O]^{n_3}$$

$$K_c = \frac{K_f}{K_b} = \frac{[M]^{n_1}[N]^{n_2}[O]^{n_3}}{[A]^{m_1}[B]^{m_2}[C]^{m_3}}$$

u The equilibrium constant, at a given temperature, is the ratio of the rate constants of forward and backward reactions.

Ex. Write down the equilibrium constant for the following reactions.

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

(b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

(c) $3A + 2B \rightleftharpoons C + 4D$

(d) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

(e) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$

(f) $CH_3COOH\ (\ell) + C_2H_5OH\ (\ell) \rightleftharpoons CH_3COOC_2H_5\ (\ell) + H_2O\ (\ell)$

(g) $NH_3\ (aq) + H_2O \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$

(h) $H_2O\ (\ell) \rightleftharpoons H_2O\ (g)$

Ans. (a) $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(b) $K = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

(c) $K = \dfrac{[C][D]^4}{[A]^3\,[B]^2}$

(d) $K = [CO_2]$ (Active mass of solid is 1)

(e) $K = [O_2]^3$

(f) $K = \dfrac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ (here H_2O is not in excess)

(g) $K = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$ (here H_2O is in excess (solvent) so its concentration doesn't change.)

(h) $K = [H_2O]_{(g)}$

q **Possible value of K** $[0 < K < \infty]$

When K = 1 [Product] = [Reactant]

When K > 1 [Product] > [Reactant]

When K < 1 [Product] < [Reactant]

As K ↑ stability of products ↑ stability of reactant ↓ time to attain equilibrium ↓

$t \propto 1/K$

q Stability of reactants and products

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

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

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

For reactants, stability increases when value of K decreases.

For products, stability increases when value of K increases.

(more is the value of equilibrium constant, more is the formation of product means more is the stability of product.)

q Time taken to attain equilibrium increases when value of K decreases.

q **FORMS OF EQUILIBRIUM CONSTANT :**

There are two forms.

(i) Concentration form (K_C) (ii) Partial pressure form (K_p)

◆ **Partial pressure** : The individual pressure exerted by the gases substance of the total pressure is called partial pressure of the gases substance.

Closed vessel

Gaseous moles	A	B	C	D	
	n_1 mol	n_2 mol	n_3 mol	n_4 mol	$\Rightarrow P_{total}$

Partial pressure $= \dfrac{\text{Moles of substance}}{\text{Total moles}} \times P_{total} \Rightarrow \left[\dfrac{\text{Moles of subs tance}}{\text{Total moles}} = \text{Mole fraction}\right]$

= mole fraction P_{total}

let $n_1 + n_2 + n_3 + n_4 = N$

$$P_A = \frac{n_1}{N} P_t, \qquad P_B = \frac{n_2}{N} P_t, \qquad P_C = \frac{n_3}{N} P_t, \qquad P_D = \frac{n_4}{N} P_t$$

$$P_A + P_B + P_C + P_D = P_{total}$$

Q. A vessel contains 5 mole of A & 10 moles of B. If total pressure is 18 atm. Find out partial pressure of gases.

Ans. $P_A = \dfrac{5}{15}$ 18 = 6 atm

$P_B = \dfrac{10}{15}$ 18 = 12 atm

u When the reactants and products are in gaseous state then partial pressure can be used instead of concentration. At a definite temperature, as the partial pressure of a substance is proportional to its concentration in the gas phase.

$$m_1 A + m_2 B \rightleftharpoons n_1 C + n_2 D$$

If partial pressure of A, B, C and D at equilibrium are P_A, P_B, P_C and P_D respectively, then

$$K_P = \frac{(P_c)^{n_1} \times (P_D)^{n_2}}{(P_A)^{m_1} \times (P_B)^{m_2}}$$

RELATION BETWEEN K_P AND K_C :

This relation can be established for reaction not involving liquids because kp is not defined for liquids.

Consider a reversible reaction

$$m_1A + m_2B \rightleftharpoons n_1C + n_2D$$

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

$$K_P = \frac{(P_C)^{n_1}(P_D)^{n_2}}{(P_A)^{m_1}(P_B)^{m_2}}$$

For an ideal gas PV = nRT

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

$\because$ n = number of mole and V = Volume in litre

So $\dfrac{n}{V}$ = molar concentration or active mass

$P = [\ \ ]\,RT$

at constant temperature $P \propto [\ ]$

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

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

$$K_p = \frac{\left[C\right]^{n_1}\left[D\right]^{n_2}}{\left[A\right]^{m_1}\left[B\right]^{m_2}}\times\frac{\left(RT\right)^{n_1+n_2}}{\left(RT\right)^{m_1+m_2}}$$

R = gas constant

= 0.0821 lit. atm. K^{-1} mol^{-1}

= 8.314 J K^{-1} mol^{-1}

= $1.98 \simeq 2$ Cal K^{-1} mol^{-1}

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

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

= total number of gaseous molecules of products − total number of gaseous molecules of reactants.

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

Ex. Find the values of K_c for each of the following equilibria from the value of K_p.

(a) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$ $\quad K_p = 1.8 \quad 10^{-2}$ at 600 K

(b) $CaCO_3\,(g) \rightleftharpoons CaO\,(s) + CO_2\,(g)$ $\quad K_p = 167$ at 1173 K

Sol. (a) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$

$K_p = 1.8 \quad 10^{-2}$

$\Delta n_g = 3 - 2 = 1$

$K_p = K_c\,(RT)^{\Delta n_g}$

$$\therefore\ K_c = \frac{K_p}{RT} = \frac{1.8\times10^{-2}}{0.0821\times600} = 3.65 \quad 10^{-4}$$

(b) $K_p = 167$

$\Delta n_g = 1$

$K_p = K_c\,(RT)^{\Delta n_g} = K_c \quad (RT)$

$$\therefore\ K_c = \frac{K_p}{RT} = \frac{167}{0.0821\times1173} = 1.734$$

Ex. At 540 K, 0.10 moles of PCl_5 are heated in 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.

Sol. $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

PCl_5	PCl_3	Cl_2
0.1	0	0
(0.1–x)	x	x

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x/8 \times x/8}{\left(\frac{0.1-x}{8}\right)} = \frac{x^2}{8(0.1-x)} \qquad \text{........(i)}$$

From gas law

PV = nRT

$\Rightarrow 1 \quad 8 = (0.1 + x) \quad 0.082 \quad 540$

$\therefore\ x = 0.08$ ....(ii)

From eqs. (i) and (ii)

$$K_c = \frac{0.08\times0.08}{8\times(0.1-0.08)} = 4 \quad 10^{-2}\ mol\ L^{-1}$$

$K_p = K_c\,(RT)^{\Delta n_g} \qquad (\Delta n_g = +1)$

$= 4 \quad 10^{-2} \quad (0.082 \quad 540) = 1.77$ atm

Ex. At a given temperature and a total pressure of 1.0 atm for the homogeneous gaseous reaction, $N_2O_4 \rightleftharpoons 2NO_2$, the partial pressure of NO_2 is 0.5 atm.

(a) Calculate the value of K_p.

(b) If the volume of the vessel is decreased to half of its original volume, at constant temperature, what are the partial pressures of the components of the equilibrium mixture ?

Sol. For equilibrium system, $N_2O_4 \rightleftharpoons 2NO_2$, the total pressure is 1.0 atm

$\Rightarrow$ The total pressure = $P_{N_2O_4} + P_{NO_2} = 1$

$\Rightarrow$ $P_{N_2O_4} = 0.5$ atm and $P_{NO_2} = 0.5$ atm

(i) $K_p = \dfrac{\left(P_{NO_2}\right)^2}{P_{N_2O_4}} = \dfrac{(0.5)^2}{0.5} = 0.5$ atm

(ii) As volume is decreased to half its original volume, equilibrium is disturbed and the new initial conditions for the re-establishment of new equilibrium are

$P_{N_2O_4} = 1.0$ atm and $P_{NO_2} = 1.0$ atm

According to Le Chatelier's principal, when volume is decreased, the system moves in that direction where there is decrease in number of moles. Hence, the system (here will moves in reverse direction, as there is a decrease in mole ($\Delta n = 2 - 1 = 1$), i.e. NO_2 will be converted into N_2O_4.

Let, the decrease in pressure of NO_2 be x atm.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial pressure (atm)	1.0		1.0
At equilibrium	$1+x/2$		$1-x$

$\Rightarrow$ $K_p = \dfrac{(1-x)^2}{(1+x/2)} = 0.5 \Rightarrow 4x^2 - 9x + 2 = 0$

$\Rightarrow$ x = 2 or 0.25 ($x \neq 2$ as initial pressure = 1.0) $\Rightarrow x = 0.25$

$P_{N_2O_4} = 1 + \dfrac{x}{2} = 1.125$ atm and $P_{NO_2} = 1 - x = 0.75$ atm

Ex. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction, $2AB_2(g) \rightleftharpoons 2AB\,(g) + B_2(g)$ with degree of dissociation α, which is small compared to unity. Deduce the expression for α in terms of the equilibrium constant K_p and the total pressure P.

Sol.

	$2AB_2\,(g)$	$\rightleftharpoons$	$2AB\,(g)$	$+ Br_2\,(g)$	
Initial (mole)	1		0	0	
At eq. (mole)	$1-\alpha$		α	$\alpha/2$	Total moles at equilibrium = $(1 + \alpha/2)$
At eq. (p.p)	$P\left(\dfrac{1-\alpha}{1+\alpha/2}\right)$		$\dfrac{P.\alpha}{1+\alpha/2}$	$\dfrac{P.\alpha/2}{(1+\alpha/2)}$	

$$K_p = \frac{P_{AB}^2\,P_{Br^2}}{P_{AB_2}^2}$$

$$K_p = \frac{\left(\dfrac{P.\alpha}{1+\alpha/2}\right)^2\left(\dfrac{P.\alpha/2}{1+\alpha/2}\right)}{P^2\left(\dfrac{1-\alpha}{1+\alpha/2}\right)^2} \Rightarrow K_p = \frac{P\alpha^3}{2(1-\alpha)^2(1+\alpha/2)}$$

But $1 >> \alpha \therefore K_p = \dfrac{P\alpha^3}{2}$

$$\alpha = \left(\frac{2K_p}{P}\right)^{1/3}$$

u The K_C is expressed by the units (mole lit^{-1})$^{\Delta n}$ and K_P by (atm)$^{\Delta n}$.

In terms of mole fraction, equilibrium constant is denoted by K_X.

For general reaction $aA + bB \rightleftharpoons mC + nD$

$$K_X = \frac{(X_C)^m (X_D)^n}{(X_A)^a (X_B)^b}$$

$$K_p = K_x (RT)^{\Delta n_g} \qquad \text{...........(i)}$$

$\Delta n_g = (m + n) - (a + b)$

When $\Delta n_g = 0$, $K_p = K_C = K_X$

❑ **Some General Equilibrium Expressions :**

(a)

	H_2 (g)	+	I_2 (g)	$\rightleftharpoons$	2HI (g)
Initially	a		b		0
At equilibrium	(a–x)		(b–x)		2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{\frac{(2x)^2}{(a+b)^2}P^2}{\left(\frac{a-x}{a+b}.P\right)\left(\frac{b-x}{a+b}.P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So $K_c = K_p$ $(\Delta n = 0)$

(b)

	2NO (g)	$\rightleftharpoons$	N_2 (g)	+	O_2 (g)
Initially	a		0		0
At equilibrium	(a–x)		x/2		x/2

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2} = K_P \qquad (\Delta n = 0)$$

(c)

	$CH_3COOH_{(\ell)}$	+	$C_2H_5OH_{(\ell)}$	$\rightleftharpoons$	$CH_3COOC_2H_{5(\ell)}$	+	$H_2O_{(\ell)}$
Initially	a		b		0		0
At equilibrium	(a–x)		(b–x)		x		x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{x^2}{(a-x)(b-x)}$$

K_p should not be given for this reaction

(d)

	PCl_5 (g)	$\rightleftharpoons$	PCl_3 (g)	+	Cl_2 (g)
Initially	a		0		0
At equilibrium	(a–x)		x		x
Active mass	$\frac{(a-x)}{v}$		$\frac{x}{v}$		$\frac{x}{v}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{(a-x)}{v}} = \frac{x^2}{(a-x)v}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{x}{a+x}.P\right) \times \left(\frac{x}{a+x}.P\right)}{\left(\frac{a-x}{a+x}\right)P} = \frac{x^2P}{(a+x)(a-x)} = \frac{x^2P}{a^2-x^2}$$

(e)	N_2 (g) +	$3H_2$ (g) $\rightleftharpoons$	$2NH_3$ (g)
Initially	a	b	0
At equilibrium	(a–x)	(b–3x)	2x
Active mass	$\frac{(a-x)}{v}$	$\left(\frac{b-3x}{v}\right)$	$\left(\frac{2x}{v}\right)$

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

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3} = \frac{\left[\frac{2xP}{a+b-2x}\right]^2}{\left[\frac{(a-x)P}{(a+b-2x)}\right]\left[\frac{(b-3x)P}{(a+b-2x)}\right]^3} = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3P^2}$$

Ex. In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the concentration of H_2, I_2 and HI at equilibrium are 10.0, 6.0 and 28 moles per litre respectively. What will be the equilibrium constant?

(A) 30.61 (B) 13.066 (C) 29.40 (D) 20.90

Sol. **(B)**

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

Applying law of mass action,

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

Given $[H_2] = 10 \text{ mol } L^{-1}$

$[I_2] = 6.0 \text{ mol } L^{-1}$

$[HI] = 28.0 \text{ mol } L^{-1}$

So, $K_c = \frac{(28.0)^2}{(10) \times (6.0)} = 13.066$

Ex. For a gas phase reaction at equilibrium,

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere respectively. The total pressure of the entire system is 2.4 atmosphere. What will be the value of K_p if all the pressures are given in atmosphere ?

(A) 32 atm^{-2} (B) 20 atm^{-2} (C) 28.125 atm^{-2} (D) 80 atm^{-2}

Sol. **(C)**

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

Partial pressures at equilibrium

0.8 0.4 [2.4 – (0.8 + 0.4) = 1.2]

Applying law of mass action,

$$K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{1.2 \times 1.2}{0.8 \times 0.4 \times 0.4 \times 0.4} \Rightarrow K_P = 28.125 \text{ atm}^{-2}$$

Ex. When ethanol and acetic acid were mixed together in equilimolecular proportion 66.6% are converted into ethyl acetate. Calculate K_c. Also calculate quantity of ester produced if one mole of acetic acid is treated with 0.5 mole and 4 mole of alcohol respectively.

(A) 4, 0.93, 0.43 (B) 0.93, 4, 0.43 (C) 0.43, 0.93, 4 (D) 4, 0.43, 0.93

Sol. **(D)**

$$\begin{array}{cccc} CH_3COOH & + \; C_2H_5OH & \rightleftharpoons & CH_3COOC_2H_5 & + \; H_2O \\ 1 & 1 & & 0 & 0 \\ 1-0.666 & 1-0.666 & & 0.666 & 0.666 \end{array}$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{[0.666][0.666]}{[0.333][0.333]} = 4$$

(a) Let x moles of ester is formed from 1 mole of acid and 0.5 mole of alcohol, then

$$K_c = \frac{x^2}{(1-x)(0.5-x)} \Rightarrow \frac{x^2}{(1-x)(0.5-x)} = 4 \quad \Rightarrow \quad x = 0.43$$

(b) $K_c = \dfrac{x^2}{(1-x)(4-x)}$ or $4 = \dfrac{x^2}{(1-x)(4-x)}$ $\Rightarrow$ $x = 0.93$

Ex. Starting with 3 : 1 mixture of H_2 and N_2 at 450 C, the equilibrium mixture is found to be 9.6% NH_3 ; 22.6% N_2 and 67.8 % H_2 by volume. The total pressure is 50 atm. What will be the value of K_P. The reaction is -

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

(A) $3.25 \quad 10^{-5}$ atm^{-2} (B) $5.23 \quad 10^{-5}$ atm^{-2} (C) $6.23 \quad 10^{-5}$ atm^{-2} (D) $8 \quad 10^{-5}$ atm^{-2}

Sol. **(B)**

The ratio of number of moles will be the same as the ratio of volume. According to Dalton's law, the partial pressure of a gas in a mixture is given by the product of its volume fraction and the total pressure. Therefore, the equilibrium pressure of each gas is,

$$P_{NH_3} = \frac{9.6}{100} \times 50 \text{ atm} = 4.8 \text{ atm}$$

$$P_{N_2} = \frac{22.6}{100} \times 50 \text{ atm} = 11.3 \text{ atm}$$

$$P_{H_2} = \frac{67.6}{100} \times 50 \text{ atm} = 33.9 \text{ atm}$$

Total pressure = 50 atm

$$K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3}$$; Substituting the values of partial pressures,

$$K_P = \frac{(4.80 \text{ atm})^2}{(11.3 \text{ atm})(33.9 \text{ atm})^3} = 5.23 \quad 10^{-5} \text{ atm}^{-2}$$

Ex. K_P for the reaction $A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$; is 0.01 atm. What will be its K_c at 1000 K in terms of R ?

(A) $\dfrac{1.0 \times 10^{-5}}{R}$ (B) $\dfrac{R}{5 \times 10^{-5}}$ (C) $5 \quad 10^{-5}$ R (D) none of these

Sol. **(A)**

We know that

$K_P = K_c (RT)^{\Delta n}$ or $K_c = \dfrac{K_P}{(RT)^{\Delta n}}$

Here $\Delta n = 4 - 3 = 1$

$T = 1000$ K, $K_p = 0.01$

$$K_c = \frac{0.01}{(R \times 1000)^1} = \frac{1.0 \times 10^{-5}}{R}$$

Ex. 0.5 mole of H_2 and 0.5 mol of I_2 react in 200 L flask at 448 C. The equilibrium constant K_c is 50 for $H_2 + I_2 \rightleftharpoons 2HI$,

(a) What is the K_p?

(b) Calculate mol of I_2 at equilibrium.

Sol. $H_2 + I_2 \rightleftharpoons 2HI$

H_2	I_2	$2HI$	
0.5	0.5	0	Initial
(0.5–x)	(0.5–x)	2x	at equili.

(a) Since $\Delta n = 0 \Rightarrow K_P = K_c$

(b) $50 = \frac{4x^2}{(0.5 - x)^2}$ or $\frac{2x}{0.5 - x} = \sqrt{50}$

$x = 0.39$

$\therefore$ mol of $I_2 = 0.5 - 0.39 = 0.11$ mol

u Three cases may arise :

(a) When $\Delta n = 0$

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

For example :

$N_2 + O_2 \rightleftharpoons 2NO$ $\qquad$ $H_2 + I_2 \rightleftharpoons 2HI$

u K_C and K_P are unit less in this case.

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

$K_P > K_C$

For example :

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $\qquad \begin{pmatrix} K_C \rightarrow \text{mole lit}^{-1} \\ K_P \rightarrow \text{atm} \end{pmatrix}$

(Δ n = 1)

$2NH_3 \rightleftharpoons N_2 + 3H_2$ $\qquad \begin{pmatrix} K_C \rightarrow \text{mole}^2\,\text{lit}^{-2} \\ K_P \rightarrow \text{atm}^2 \end{pmatrix}$

(Δ n = 2)

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

$K_P < K_C$

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\qquad \begin{pmatrix} K_C \rightarrow \text{mole}^{-2}\,\text{lit}^2 \\ K_P \rightarrow \text{atm}^{-2} \end{pmatrix}$

(Δ n = –2)

u **Factors affecting equilibrium constant :**

(a) Mode of representation of the reaction :

$A + B \rightleftharpoons C + D$

The equilibrium constant for the reaction

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

If the reaction is reversed

$C + D \rightleftharpoons A + B$

then, $K_c^1 = \frac{[A][B]}{[C][D]}$

The two equilibrium constant related as → $K_c = \frac{1}{K_c^1}$

Ex. For $N_2 + 3H_2 \rightleftharpoons 2NH_3$ if $K_C = 5$ then find K_C' for reverse reaction.

Ans. $K_C' = 1/5 = 0.2$

(b) **Stoichiometry of the reaction :**

When a reversible reaction can be written with the help of two or more stoichiometric equation, the value of equilibrium constant will be numerically different.

For reaction $2NO_2 \rightleftharpoons N_2 + 2O_2$

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

For reaction $NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$

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

The two constants are related as $K_c^1 = \sqrt{K_C}$

(c) **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 and ΔH is the heat of reaction at constant volume, then :

$$\frac{d(\ell nk)}{dT} = \frac{\Delta H}{RT^2}$$

$$\log\frac{K_2}{K_1} = \log K_2 - \log K_1 = \frac{-\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$ (According to Vant Hoff equation)

(i) $\Delta H = 0$ (neither heat is absorbed or evolved)

$\log K_2 - \log K_1 = 0$

$\log K_1 = \log K_2$

$K_1 = K_2$

Thus, equilibrium constant remains the same at all temperatures

If temp. T_2 is higher than T_1

$$\frac{1}{T_2} - \frac{1}{T_1} < 0, \ \log K_2 - \log K_1 = \frac{+ve\Delta H}{2.303R}$$

(ii) When ΔH = +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 is higher at higher temperature in case of endothermic reactions.

$K_C \propto T$

(iii) When ΔH = –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 is lower at higher temperature in the case of exothermic reactions.

$K_C \propto 1/T$

u The value of equilibrium constant is independent of the following factors :-

(a) Initial concentrations of reactants.

(b) The presence of a catalyst.

(c) The direction from which the equilibrium has been attained.

(d) Presence of inert materials.

Ex. For the reaction,

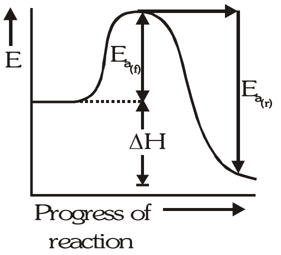
$A \rightleftharpoons B$, ΔH for the reaction is –33.0 kJ/mol.

Calculate :

(i) Equilibrium constant K_c for the reaction at 300 K

(ii) If E_a (f) and E_a (r) in the ratio of 20 : 31, calculate E_a(f) and E_a(r) at 300 K.

Assuming pre-exponential factor same for forward and reverse reaction.



Sol. (i) $\Delta H = E_{a(f)} - E_{a(r)} = -33$ kJ

$$k_f = Ae^{-E_{a(f)}/RT}$$

$$k_b = Ae^{-E_{a(r)}/RT}$$

$$\therefore \quad k_c = \frac{k_f}{k_b} = e^{\left[E_{a(f)}-E_{a(r)}\right]/RT} \Rightarrow e^{\frac{33\times10^3}{8.314\times300}} = 5.572 \quad 10^5 \text{ at } 300 \text{ K}$$

(ii) $\frac{E_{a(f)}}{E_{a(r)}} = \frac{20}{31}$ $\qquad E_{a(f)} - E_{a(r)} = -33\text{kJ}$

$$\therefore E_{a(r)} - \frac{31}{20} \quad E_{a(f)} = -33\text{kJ}$$

$$\therefore E_{a(f)} = \frac{33\times20}{11} = 60\text{kJ}$$

$$E_{a(r)} = +93 \text{ kJ}$$

Ex. The equilibrium constant for the reaction $H_2(g) + S(s) \rightleftharpoons H_2S(g)$; is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be :

(A) – 68000.05 J mol^{-1} (B) –71080.57 J mol^{-1} (C) – 80071.75 J mol^{-1} (D) 57080.75 J mol^{-1}

Sol. **(B)**

Using the relation,

$$\log\frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\frac{9.25}{18.5} = \frac{\Delta H}{2.303\times8.314} \quad \frac{75}{925\times1000}$$

$$-0.301 = \frac{\Delta H\times75}{2.303\times8.314\times925\times1000} \Rightarrow \Delta H = -71080.57 \text{ J mol}^{-1}.$$

Ex. The reaction $CuSO_4.3H_2O(s) \rightleftharpoons CuSO_4.H_2O(s) + 2H_2O\ (g)$; the dissociation pressure is 7 10^{-3} atm at 25 C and ΔH = 2750 cal. What will be the dissociation pressure at 127 C ?

Sol. For given reaction

$$K_p = \left(p_{H_2O}\right)^2$$

so K_p (25 C) = (7 $10^{-3})^2$ atm^2

= 4.9 10^{-5} atm^2

Since ΔH = 2750 cal, so using Vant Hoff eq.

$$\log\left[\frac{K_P(127°C)}{K_P(25°C)}\right]=\frac{\Delta H°}{2.303\times R}\left[\frac{400-298}{400\times298}\right]$$

$$\log\left[\frac{K_P(127°C)}{4.9\times10^{-5}}\right]=\frac{2750}{2.303\times2}\left[\frac{102}{119200}\right]$$

K_p (127 C) = 3.2426 4.9 10^{-5} = 1.58 10^{-4}

so p_{H_2O} at 127 = $\sqrt{K_p(127°C)}$ = $\sqrt{1.58\times10^{-4}}$ = 1.26 10^{-2} atm.

❑ **Law of Mass Action as Applied to Heterogeneous Equilibrium :**

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

For example : The dissociation of $CaCO_3$ in closed vessel.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_C = [CO_2]$, $K_P = p_{CO_2}$

u $PCl_5(s) \rightleftharpoons PCl_3(\ell) + Cl_2(g)$

$K_C = [Cl_2]$, $K_P = p_{Cl_2}$

u $2H_2O(\ell) \rightleftharpoons 2H_2(g) + O_2(g)$

$K_C = [H_2]^2[O_2]$, $K_P = (p_{H_2})^2\,(p_{O_2})$

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

$$K_C = \frac{[H_2]^4}{[H_2O]^4},\ K_P = \frac{(p_{H_2})^4}{(p_{H_2O})^4}$$

Ex. One mole of ammonium carbamate dissociate as shown below at 500 K.

$NH_2COONH_4\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2\ (g)$

If the pressure exerted by the released gases is 6.0 atm, the value of K_P is -

(A) 7 atm (B) 3 atm (C) 32 atm (D) 8 atm

Sol. (C)

Applying the law of chemical equilibrium, we get

$K_p = (P_{NH_3})^2\,(P_{CO_2})$

Since total pressure is 6 atm, the partial pressures of NH_3 (g) and CO_2 (g) are

$(P_{NH_3}) = 6 \quad \frac{2}{3} = 4$ atm

$(P_{CO_2}) = 6 \quad \frac{1}{3} = 2$ atm

$K_p = [4.0]^2\,[2.0] = 32.0$ atm

Ex. For the reaction.

$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$; K_p = 1.16 atm. at 800 C. If 40 g of $CaCO_3$ was put into a 20 L container and heated to 800 C, what percent of $CaCO_3$ would remain unreacted at equilibrium.

Sol. $K_p = P_{CO_2}$ = 1.16 atm

$n(CO_2) = PV/RT = \dfrac{1.16\times20}{0.0821\times1073} = 0.26335$ mol

moles of $CaCO_3$ initially present

= 40/100 = 0.4 mol

So % decomposition of $CaCO_3 = \dfrac{0.26335}{0.4} \times 100$ = 65.83 % decomposed

Hence 34.17 % remain unreacted.

Ex. For the reaction :

$$SnO_2\,(s) + 2H_2\,(g) \rightleftharpoons 2H_2O\,(g) + Sn\,(s)$$

Calculate K_p at 900 K where the equilibrium steam hydrogen mixture was 35 % H_2 by volume.

Sol. $K_p = \dfrac{(P_{H_2O})^2}{(P_{H_2})^2}$

given H_2 is 35% by volume at constant temperature in closed vessel ($P \propto V$)

so $P_{H_2O} = 0.65$ atm and $P_{H_2} = 0.35$ atm

$$K_p = \left(\frac{0.65}{0.35}\right)^2 = 3.448$$

❑ LE-CHATELIER'S PRINCIPLE :

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

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

(b) **Change of pressure** : When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume increases. According to Le-Chatelier's principle, the equilibrium shift in the direction in which there is decrease in number of moles.

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

(c) **Change in temperature** :- If the temperature at equilibrium is increased reaction will proceed in the 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 in exothermic reactions.

❑ APPLICATION OF LE-CHATELIER'S PRINCIPLE :

(A) **Chemical equilibria** :

(a) **Formation of HI**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + 3000 \text{ Cals}$$

(i) **Effect of concentration** : When concentration of H_2 or I_2 is increased at equilibrium, the system moves in a direction in which decreases the concentration. Thus the rate of forward reaction increases thereby increasing the concentration of HI.

(ii) **Effect of pressure** :- In formation of HI, there is no change in the number of moles of reactants and products ($\Delta n = 0$). Thus it is not affected by the change in pressure or volume.

(iii) **Effect of temperature** :- The formation of HI is exothermic reaction. Thus the backward reaction moves faster when temperature is increased. i.e. formation of HI is less.

In short favourable conditions for greater yield of HI :

- High concentration of H_2 and I_2.
- Low temperature.
- No effect of pressure

(b) **Formation of NO** :

$$N_2 + O_2 \rightleftharpoons 2NO - 43200 \text{ cals.}$$

(i) **Effect of concentration** : When concentration of N_2 or O_2 is increased, the system moves in a direction in which N_2 or O_2 is used up or rate of forward increases.

(ii) **Effect of pressure** : The formation of NO is not affected by change in pressure.

$(\Delta n = 0)$.

(iii) **Temperature** : The formation of NO is endothermic. Thus increase in temperature favours to forward reaction.

Favourable conditions for greater yield of NO :

- High concentration of N_2 and O_2.
- High temperature.
- No effect of pressure

(c) Dissociation of PCl_5 :

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - 15000 \text{ cals.}$$

(i) **Effect of concentration** : When concentration of PCl_5 is increased at equilibrium, the rate of forward reaction increases as to decrease the added concentration. Thus dissociation of PCl_5 increases.

(ii) **Effect of pressure** : The volume increases in the dissociation of PCl_5 when pressure is increased, the system moves in the direction in which there is decrease in volume. Thus high pressure does not favour dissociation of PCl_5.

(iii) **Effect of temperature** :- The dissociation of PCl_5 is an endothermic reaction. Thus increase of temperature favours the dissociation.

Favourable conditions for dissociation of PCl_5 are :-

- High concentration of PCl_5.
- Low pressure.
- High temperature.

(d) Synthesis of ammonia :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22400 \text{ Cals.}$$

The favourable conditions for greater yield of NH_3 are :-

- High concentration of N_2 and H_2.
- High pressure.
- Low temperature.

(e) Formation of SO_3 :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3 + 45200 \text{ Cals.}$$

The favourable conditions for greater yield of SO_3 are :-

- High concentration of SO_2 and O_2.
- High pressure.
- Low temperature.

Ex. In reaction,

$$CO(g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g) \qquad \Delta H = -92 \text{ kJ/mol}^{-1}$$

concentrations of hydrogen, carbon monoxide and methanol become constant at equilibrium. What will happen if :

(A) volume of the reaction vessel in which reactants and products are contained is suddenly reduced to half ?

(B) partial pressure of hydrogen is suddenly doubled?

(C) an inert gas is added to the system at constant pressure?

(D) the temperature is increased ?

Sol. For the equilibrium,

$$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$$

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} \Rightarrow K_p = \frac{P_{CH_3OH}}{P_{CO} \times P_{H_2}^2}$$

(A) When the volume of the vessel is suddenly reduced to half, the partial pressures of various species gets doubled. Therefore, $Q_p = \frac{2P_{CH_3OH}}{2P_{CO} \times \left(2P_{H_2}\right)^2} = \frac{1}{4}K_p$

Since Q_p is less than K_p, the equilibrium shift in the forward direction producing more CH_3OH.

(B) When partial pressure of hydrogen is suddenly doubled, Q_p changes and is no longer equal to K_p.

$$Q_p = \frac{P_{CH_3OH}}{P_{CO} \times \left(2P_{H_2}\right)^2} = \frac{1}{4}K_p$$

Equilibrium will shift from left to right.

(C) When an inert gas is added to the system at constant pressure, equilibrium shifts from lower number of moles to higher number of moles (in backward direction).

(D) By increasing the temperature, K_p will decrease and equilibrium will shift from right to left.

❑ SPECIAL POINTS :

(1) Irreversible reaction proceeds in one direction and completed with time while reversible reaction proceeds in both direction and are never completed.

(2) Equilibrium is defined as the point at which the rate of forward reaction is equal to the rate of backward reaction.

(3) Chemical equilibrium is dynamic in nature and equilibrium state can be approached from both sides.

(4) Active mass is molar concentration of the substance. Active mass of solid and pure liquid is taken as unity.

(5) Equilibrium constant has definite value for every chemical reaction at a given temperature. It is independent of concentration and catalyst.

(6) 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 equilibrium constant of individual reaction.

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 $K = K_1 \times K_2$

(7) Change in temperature, pressure or concentration favours one of the reactions and thus shift the equilibrium point in one direction.

(8) A catalyst ables the system to reach a state of equilibrium more quickly.

(9) Pressure and volume has no effect on the reaction in which there is no change in the number of moles.

(10) If the concentration of reactants is increased and product is removed, the reaction will take place in forward direction.

(11) Free energy change

$\Delta G = \Delta G + 2.303\ RT \log Q$ At equilibrium $\Delta G = 0$, (T is in Kelvin), $Q = K$ so

$\Delta G = -\ 2.303\ RT \log K$, where K is equilibrium constant.

Ex. ΔG for ½ $N_2 + 3/2\ H_2 \rightleftharpoons NH_3$ is -16.5 kJ mol^{-1}. Find out K_p for the reaction at 25 C. Also report K_p and ΔG for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 25 C.

Sol. $\log K_P = -\dfrac{\Delta G^\circ}{2.303RT} = \dfrac{+16.5 \times 10^3}{2.303 \times 8.314 \times 298} = 2.8917$

K_P = antilog (2.8917) = 779.41

Now given reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ can be obtained by multiplying eq. $1/2\ N_2 + 3/2\ H_2 \rightleftharpoons NH_3$ by 2.

so $K_p' = (779.41)^2 = 6.07\ \ 10^5$

and $\Delta G = -2.303\ RT \log K_p' = -\ 2.303\ \ 8.314\ \ 298 \log (6.07\ \ 10^5)$ J

$\Delta G = -32.998$ kJ mol^{-1}.

Ex. For the gaseous reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ the following thermodynamics data are given.

$\Delta H_{300\ K} = -\ 41.16$ kJ mol^{-1} ; $\Delta S_{300\ K} = -0.0424$ kJ mol^{-1}.

$\Delta H_{1200\ K} = -\ 32.93$ kJ mol^{-1} ; $\Delta S_{1200\ K} = -0.0296$ kJ mol^{-1}.

Assuming partial pressure of each component at 1 atm. determine the direction of spontaneous reaction at
(i) 300 K
(ii) 1200 K. Also calculate K_p for the reaction at each temperature.

Sol. Using $\Delta G = \Delta H - T\Delta S$

$\Delta G_{300\ K} = -41.16 - 300\ (-0.0424)$

$= -28.44$ kJ mol^{-1}

so reaction is spontaneous in given direction since ΔG is negative

$CO + H_2O \rightleftharpoons CO_2 + H_2$

at 1200 K

$\Delta G_{1200\ K} = -32.93 - 1200\ (-0.0296)$

$= 2.56$ kJ mol^{-1}

so reaction will not be spontaneous in given direction, but reverse reaction spontaneous i.e.

$CO + H_2 \rightleftharpoons CO + H_2O$

We know $\Delta G = -\ 2.303\ RT \log K_P$

so K_P (300 K)

$= \text{antilog}\left(\dfrac{-28.44 \times 10^3}{-2.303 \times 8.314 \times 300}\right) = 8.8\ \ 10^4$

K_P = (1200 K)

$$= \text{antilog}\left(\frac{+2.59\times10^{3}}{-2.303\times8.314\times1200}\right) = 0.77$$

☐ REACTION QUOTIENT AND EQUILIBRIUM CONSTANT :

Consider the follwong reversible reaction

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

The reaction quotient (Q_C) is ratio of the product of active masses of the products and product of active masses of the reactants, at any given time.

$$\therefore\ Q_C = \frac{[C][D]}{[A][B]}$$

The concentration are not necessarily equilibrium concentration.

[At equilibrium $Q_C = K_C$]

Case I :

If $Q_C < K_C$ then : [Reactants] > [Products]

then the system is not at equilibrium

The value of $\frac{[\text{Product}]}{[\text{Reactant}]}$ is small

$\therefore$ For establishment of equilibrium the reaction will go in forward direction. [Reactants → Products]

Case II :

If $Q_C = K_C$ then : The system is at equilibrium and the concentration of the species C,D,B,A are at equilibrium.

Case III :

If $Q_C > K_C$ then : [Product] > [Reactants]

The system is not at equilibrium.

The value of $\frac{[\text{Product}]}{[\text{Reactant}]}$ is large

$\therefore$ For establishment of equilibrium the reaction will go in backward direction. [Products → Reactants]

Ex. A mixture of 4.2 moles of N_2, 2.0 moles of H_2 and 10.0 moles of NH_3 is introduced into a 10.0 L reaction vessel at 500 K. At this temperature, equilibrium constant K_c is 1.7 10^2, for the reaction $N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3\,(g)$

(i) is the reaction mixture at equilibrium ?

(ii) if not, what is the direction of the reaction?

Sol. $[N_2] = \frac{4.2}{10} = 0.42$ M

$[H_2] = \frac{2.0}{10} = 0.2$ M

$[NH_3] = \frac{10}{10} = 0.1$ M

For these concentration, reaction quotient (Q) for the reaction

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

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.1)^2}{(0.42)\times(0.2)^3} = 2.976$$

But $K_c = 1.7 \quad 10^2$

(i) Since $Q \neq K_c$, hence reaction is not at equilibrium.

(ii) Also $Q < K_c$, the reaction will proceed from left to right.

CALCULATION OF DEGREE OF DISSOCIATION FROM VAPOUR DENSITY MEASUREMENT :

Degree of dissociation :

Degree of dissociation of a substance at a particular temperature is defined as the fraction of total number of moles dissociated into simpler molecules at that particular temperature.

$$\text{Degree of dissociation } (\alpha) = \frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}}$$

Degree of dissociation can be calculated from vapour density measurements for those substance which are accompanied by change in the number of moles.e.g.

	$PCl_5 \longrightarrow$	PCl_3 +	Cl_2
Initial moles	1	0	0
No. of moles after dissociation	$(1-\alpha)$	α	α

Total number of moles = $1 - \alpha + \alpha + \alpha = (1 + \alpha)$

Let, volume occupied by the vapour per mole = V litres.

Initial vapour density = D

Vapour density after dissociation = d

As, vapour density $\propto \frac{1}{V}$

$$\therefore D \propto \frac{1}{V}$$

$$d \propto \frac{1}{(1+\alpha)V}$$

$$\therefore \frac{D}{d} = \frac{1/V}{1/(1+\alpha)V} = (1+\alpha)$$

$$\Rightarrow \alpha = \frac{D}{d} - 1 = \frac{(D-d)}{d}$$

As, mol. wt. = 2   vapour density

$$\text{Also, } \alpha = \frac{M_t - M_o}{M_o}$$

M_t = theoretical molecular mass

M_o = observed (experimental) molecular mass

M_o can be calculated from the mass of definite volume of the vapour at particular temperature.

$$\text{Also, } PV = nRT = \frac{W}{M_o}RT$$

$$M_o = \frac{W}{v} \times \frac{RT}{P} = \frac{\rho RT}{P}$$

where ρ = density of the vapour.

In general, if one mole dissociates to give n moles of products, then

A	$\longrightarrow$	nB
1		0
$(1-\alpha)$		$n\alpha$

Total no. of moles = $1 - \alpha + n\alpha = 1 + (n - 1)\alpha$

$$\therefore\ \frac{D}{d} = 1 + (n-1)\times\alpha \quad \Rightarrow \quad \alpha = \frac{(D-d)}{(n-1)\times d}$$

Also, $\alpha = \dfrac{M_t - M_o}{(n-1)\times M_o}$

Let us, consider the reaction, $2NH_3\,(g) \rightleftharpoons N_2(g) + 3H_2(g)$

If the initial moles of NH_3 (g) be 'a' and x moles of NH_3 dissociated at equilibrium.

	$2NH_3\,(g) \rightleftharpoons$	$N_2\,(g)$ +	$3H_2\,(g)$
Initial moles	a	0	0
At equilibrium	$a - x$	$\dfrac{x}{2}$	$\dfrac{3x}{2}$

Degree of dissociation (α) of NH_3 is defined as the number of moles of NH_3 dissociated per mole of NH_3.

$\therefore$ If x moles dissociate from 'a' moles of NH_3 then, the degree of dissociation of NH_3 would be $\dfrac{x}{a}$.

We can also look at the reaction in the following manner.

	$2NH_3\,(g) \rightleftharpoons$	$N_2\,(g)$ +	$3H_2\,(g)$
Initial moles	a	0	0
At equilibrium	$a(1-\alpha)$	$\dfrac{a\alpha}{2}$	$\dfrac{3a\alpha}{2}$
or	$a - 2x'$	x'	$3x'$

where $\alpha = \dfrac{2x'}{a}$

Here, total number of moles at equilibrium is $a - 2x' + x' + 3x' = a + 2x'$

Mole fraction of $NH_3 = \dfrac{a-2x'}{a+2x'}$

Mole fraction of $N_2 = \dfrac{x'}{a+2x'}$

Mole fraction of $H_2 = \dfrac{3x'}{a+2x'}$

The expression of K_p is

$$K_p = \frac{\left(\dfrac{x'}{a+2x'}\right)P_T \times \left(\dfrac{3x'}{a+2x'}\right)^3 \times P_T^3}{\left(\dfrac{a-2x'}{a+2x'}\right)^2 \times P_T^2} = \frac{27x'^4}{(a-2x')^2} \times \frac{P_T^2}{(a+2x')^2}$$

In this way, you should find the basic equation. So, it is advisable to follow the below mentioned steps while solving the problems.

- Write the balanced chemical reaction (mostly it will be given).
- Under each component write the initial number of moles.
- Do the same for equilibrium condition.
- Then derive the expression for K_p and K_c accordingly.

Ex. Vapour density of the equilibrium mixture NO_2 and N_2O_4 is found to be 42 for the reaction, $N_2O_4 \rightleftharpoons 2NO_2$. Find

(a) Abnormal molecular weight

(b) Degree of dissociation

(c) Percentage of NO_2 in the mixture

Sol. (a) For the reaction, $N_2O_4 \rightleftharpoons 2NO_2$

Observed value of vapour density = 42

Abnormal molecular weight = 42   2   (d = 42)

(b) Theoretical molecular weight = 92

2   D = 92

$$\therefore \ D = \frac{92}{2} = 46$$

$$\therefore \ \alpha = \frac{D-d}{d} = \frac{46-42}{42} = 0.095$$

(c)
$$\begin{array}{cc} N_2O_4 & \rightleftharpoons \ 2NO_2 \\ 1 & 0 \\ (1-\alpha) & 2\alpha \\ 0.905 & 0.19 \end{array}$$

Total moles at equilibrium = 1 + α = 1 + 0.095

$$\therefore \ \% \text{ of } NO_2 = \frac{2\alpha}{(1+\alpha)} \times 100 = \frac{0.19}{1.095} \times 100 = 17.35\ \%$$

Ex. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB\ (g)$ at 50 C is 50. If one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2, how many moles of AB will be formed at 323 K.

Sol.

$$A_2\ (g) \ + \ B_2\ (g) \rightleftharpoons 2AB\ (g)\ ;\ K_c = 50$$

Initial mole	1	2	0
At eq. mole	1 − x	2 − x	2x
At eq. conc.	$\frac{1-x}{3}$	$\frac{2-x}{3}$	$\frac{2x}{3}$

$$K_c = \frac{\left(\frac{2x}{3}\right)^2}{\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)} = 50 \Rightarrow 23x^2 - 75x + 50 = 0$$

x = 0.934 or 2.326

Only 0.934 values is permissible

So, moles of AB = 1.868

Ex. Calculate the % age dissociation of H_2S (g) if 0.1 mole of H_2S is kept in a 0.4 L vessel at 900 K. The value of K_c for the reaction, $2H_2S\ (g) \rightleftharpoons 2H_2(g) + S_2(g)$, is 1.0 10^4.

Sol. $2H_2S \rightleftharpoons 2H_2 + S_2$

Volume of vessel = V = 0.4 L

Let, x be the degree of dissociation

Moles	$2H_2S$	$\rightleftharpoons$	$2H_2$	+	S_2
Initially	0.1		0		0
At equilibrium	0.1 – 0.1x		0.1x		0.1x/2

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{0.01x}{v}\right)^2\left(\frac{0.01}{2v}\right)}{\left(\frac{0.01-0.01x}{v}\right)^2} = 10^4 \Rightarrow x = 0.02 \quad \text{or} \quad 2\% \text{ dissociation of } H_2S$$

Ex. The degree of dissociation of HI at a particular temperature is 0.8. Find the volume of 1.5 M sodium thiosulphate solution required to react completely with the iodine present at equilibrium in acidic condition, when 0.135 mol each of H_2 and I_2 are heated at 440 K in a closed vessel of capacity 2.0 L.

Sol. First find the value of K_c for dissociation of HI from its degree of dissociation

$2HI \rightleftharpoons H_2 + I_2$ (degree of dissociation is 0.8)

Concentrations	$2HI$	$\rightleftharpoons$	H_2	+	I_2
Initially	1.0		0		0
At new equilibrium	1.0–0.8		0.4		0.4

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.4)(0.4)}{(0.2)^2} = 4$$

Now, we have to start with 0.135 mol each of H_2 and I_2 and the following equilibrium will be established.

$H_2 + I_2 \rightleftharpoons 2HI$ with K_c =

Concentrations	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initially	0.135		0.135		0
At new equilibrium	0.135–x		0.135–x		2x

$$\Rightarrow \quad K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(0.135-x)(0.135-x)} = \frac{1}{4}$$

$\Rightarrow$ x = 0. 135/5 = 0.027 moles

Now, find the moles of I_2 left unreacted at equilibrium.

n_{I_2} = 0.135 – 0.027 = 0.108 moles

I_2 reacts with sodium thiosulphate ($Na_2S_2O_3$) as follows :

$2Na_2S_2O_3 + I_2 \rightleftharpoons Na_2S_4O_6 + 2NaI$

Applying mole concept, we have 2 moles of $Na_2S_2O_3 \equiv$ 1 mole of I_2

$\Rightarrow$ 0.108 moles of $I_2 \equiv$ 2   0.108 = 0.216 moles of $Na_2S_3O_3$ are used up

$\Rightarrow$ Moles = MV_n (M = Molarity, V_n = volume in litres)

$\Rightarrow$ 0.216 = 1.5 V

$\Rightarrow$ V = 0.144 lt = 144 mL.

S. No.	Reaction	Δn		Relation between K_P & K_C	values of K_C	values of K_P	Unit of K_C	Unit of K_P	Relation between amount of dissociation (volume and pressure)	ΔH	Conditions for obtaining more product
1.	$H_2 + I_2$ $2HI$	0	$K_P=K_C(RT)^0$	$K_P=K_C$			None	None	None	–ve(exo-thermic)	Low temperature No pressure High concentration
2.	$2HI$ $H_2 + I_2$	0	$K_P=K_C(RT)^0$	$K_P=K_C$			None	None	None	+ve(endo-thermic)	High temperature No pressure High concentration
3.	PCl_5 PCl_3+Cl_2	+ 1	$K_P=K_C(RT)^1$	$K_P>K_C$			gram mol^1 lit^{-1}	(Atm. press.$)^1$	or	+ve(endo-thermic)	High temperature Low pressure High concentration
4.	N_2O_4 $2NO_2$	+ 1	$K_P=K_C(RT)^1$	$K_P>K_C$			gram mol^1 lit^{-1}	(Atm. press.$)^{-1}$	or	+ve(endo-thermic)	High temperature Low pressure High concentration
5.	$2NH_3$ N_2+3H_2	+ 2	$K_P=K_C(RT)^2$	$K_P>K_C$			gram mol^2 lit^{-2}	(Atm. press.$)^2$	or	+ve(endo-thermic)	High temperature Low pressure High concentration
6.	N_2+3H_2 $2NH_3$	-2	$K_P=K_C(RT)^{-2}$	$K_P<K_C$			gram mol^{-2} lit^2	(Atm. press.$)^{-2}$	or	–ve (exo-thermic)	Low temperature High pressure High concentration
7.	PCl_3+Cl_2 PCl_5	-1	$K_P=K_C(RT)^{-1}$	$K_P<K_C$			gram mol^{-1} lit^{+1}	(Atm. press.$)^{-1}$	or	–ve (exo-thermic)	Low temperature High pressure High concentration
8.	$2SO_2+O_2$ $2SO_3$	-1	$K_P=K_C(RT)^{-1}$	$K_P<K_C$			gram mol^{-1} lit^{+1}	(Atm. press.$)^{-1}$	or	–ve (exo-thermic)	Low temperature High pressure High concentration

MEMORY TIPS

1. **Law of mass action.** It was put forward by Guldberg and Waage. It states that the rate at which a substance reacts is directly proportional to its active mass and hence the rate at which substances react together is directly proportional to the product of their active masses. Active mass means molar concentration.

2. **Law of chemical equilibrium.** For the reaction aA + bB $\rightleftharpoons$ xX + yY, $\frac{[X]^x[Y]^y}{[A]^a[B]^b} = K$, called equilibrium constant which is constant for a reaction at constant temperature.

3. **Equilibrium constant in terms of concentrations (K_c)** is $K_c = \frac{[X]^x[Y]^y}{[A]^a[B]^b}$.

   It has units = $(\text{mol L}^{-1})^{(x + y) - (a + b)}$

   Equilibrium constant in terms of pressures is $K_p = \frac{P_X^x P_Y^y}{P_A^a P_B^b}$

   It has units = $(\text{atm})^{(x + y) - (a + b)}$

   Expressed in terms of activities (in place of molar concentration), equilibrium constant is dimensionless.

4. **Relation between K_p and K_c.** K_p and K_c are related to each other as $K_p = K_c (RT)^{\Delta n_g}$

   Where $\Delta n_g = (n_p - n_r)$ gaseous

5. **Concentration Quotient condition or Reaction Quotient (Q).** For the reaction aA + bB $\rightleftharpoons$ xX + yY, at any other than the stage of equilibrium, the expression $\frac{[X]^x[Y]^y}{[A]^a[B]^b} = Q$ is called concentration quotient or reaction quotient.

   (i) If Q = K, the reaction is in equilibrium.

   (ii) If Q < K, Q will tend to increase till it becomes equal to K. Hence, reaction proceeds in the forward direction.

   (iii) If Q > K, Q will tend to decrease. As a result, the reaction will proceed in the backward direction.

6. **Effect of temperature on K.** For aA + bB $\underset{k_b}{\overset{k_f}{\rightleftharpoons}}$ C + D, $K = \frac{k_f}{k_b}$.

   For exothermic reaction, k_f decreases with increase of temperature, so K decreases.

   For endothermic reaction, k_f increases with increase of temperature, so K increases.

7. **Effect of adding inert gas at equilibrium.**

   (i) For reactions in which $n_p = n_r$, there is no effect of adding an inert gas at constant volume or at constant pressure on the equilibrium.

   (ii) For reaction in which $n_p > n_r$ (e.g. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$), there is no effect of adding inert gas on the equilibrium at constant volume but at constant pressure, equilibrium shifts in the forward direction.

8. **Le Chatelier's principle** states that "if a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed."

9. **Van't Hoff reaction isotherm.** It is an equation which gives the relationship between standard free energy change (ΔG) of a reaction and its equilibrium constant (K_p),

   i.e. $\Delta G = - RT \ln K_p$

   This equation helps to calculate ΔG of a reaction at temperature T if its equilibrium constant at this temperature is known or vice-versa.

10. **Van't Hoff equation.** This equation gives the variation of equilibrium constant of a reaction with temperature. The equation is

$$\frac{d\ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$

The integrated form of this equation is

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

where ΔH = enthalpy change of the reaction (assumed to the constant in the temperature range T_1 to T_2).

11. Units of equilibrium const. = $(\text{mol L}^{-1})^{(x+y)-(a+b)}$ or $(\text{atm})^{(x+y)-(a+b)}$

12. Degree of dissociation of PCl_5 or N_2O_4 is given by $\propto = \frac{D-d}{d} = \frac{M_t - M_o}{M_o}$

where D = theoretical vapour density and d = vapour density after dissociation (observed V.D.), M_t = theoretical (calculated) molecular mass and M_o = observed molecular mass.

13. From integrated form of van't Hoff equation, viz.

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

We may conclude that

(i) If ΔH = 0, i.e. no heat is evolved or absorbed in the reaction.

log (K_2/K_1) = 0, i.e. $K_2/K_1 = 1$ or $K_2 = K_1$.

So, equilibrium constant does not change with temperature.

(ii) If ΔH = +ve, i.e. heat is absorbed in the reaction, then

log (K_2/K_1) = +ve or log $K_2 >$ log K_1 or $K_2 > K_1$.

So, equilibrium constant increases with increase in temperature.

(iii) If ΔH = –ve, i.e. heat is evolved in the reaction, then

log (K_2/K_1) = –ve, i.e. log $K_2 <$ log K_1 or $K_2 < K_1$.

So, equilibrium constant decreases with increase in temperature.

SOLVED PROBLEMS (SUBJECTIVE)

Ex.1 (i) Consider the heterogeneous equilibrium

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (s) \qquad K_p = 4 \quad 10^{-2}\ \text{atm} \qquad \text{..........(i)}$$

$$C\ (s) + CO_2\ (g) \rightleftharpoons 2CO\ (g) \qquad K_p' = 4.0\ \text{atm} \qquad \text{.........(ii)}$$

Calculate the partial pressure of CO (g) when $CaCO_3$ and C are mixed and allowed to attain equilibrium at the temperature for which the above two equilibria have been studied.

(ii) Calculate the pressure of CO_2 gas at 700 K in the heterogeneous equilibrium reaction.

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

If ΔG for this reaction is 120.2 kJ/mol.

Sol. (i) For Eq. (i), $K_p = P_{CO_2}$

From Eq. (ii), $K_p' = P^2_{CO} / P_{Co_2}$

$\therefore\ K_p \quad K_p' = (P_{CO})^2 = 4 \quad 10^{-2} \quad 4 = 16 \quad 10^{-2}\ \text{atm}^2$

$\therefore\ P_{CO} = \sqrt{16 \times 10^{-2} \text{atm}^2} = 0.4$ atm

(ii) $\Delta G = -2.303\ RT \log K_p$

$$\therefore\ \log K_p = -\frac{\Delta G^\circ}{2.303 \times R \times T} = -\frac{120.2 \times 10^3 \text{Jmol}^{-1}}{2.303 \times (8.314 \text{JK}^{-1}\text{mol}^{-1}) \times (700\,\text{K})}$$

$\therefore\ K_p = 1.00 \quad 10^{-9}\ \text{atm} = P_{CO_2}$

Ex.2 For the dissociation reaction $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

derive the expression for the degree of dissociation in terms of K_p and total pressure P.

Sol.

	$N_2O_4\ (g) \rightleftharpoons$	$2NO_2\ (g)$
Let initial no. of moles	1	0
Moles at equilibrium	$(1-\alpha)$	2α

$$K_p = \frac{(n_{NO_2})^2}{n_{N_2O_4}}\left[\frac{P}{\sum n}\right]^{\Delta n_g}$$

$$= \frac{(2\alpha)^2}{(1-\alpha)}\left[\frac{P}{(1-\alpha+2\alpha)}\right]^{(2-1)}$$

$$= \frac{4\alpha^2}{(1-\alpha)}\left[\frac{P}{(1+\alpha)}\right]^1 = \frac{4\alpha^2}{(1-\alpha^2)} \times P$$

$$\Rightarrow \frac{4P}{K_P} = \frac{(1-\alpha^2)}{\alpha^2} = \frac{1}{\alpha^2} - 1$$

$$\frac{1}{\alpha^2} = \left(1 + \frac{4P}{K_p}\right) = \frac{4P + K_p}{K_p} \Rightarrow \alpha^2 = \frac{K_p}{4P + K_p} \Rightarrow \alpha = \sqrt{\frac{K_p}{4P + K_p}}$$

Ex.3 The value of K_p is $1\quad 10^{-3}$ atm^{-1} at 25 C for the reaction, $2NO + Cl_2 \rightleftharpoons 2NOCl$. A flask contains NO at 0.02 atm and 25 C. Calculate the moles of Cl_2 that must be added if 1% of NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 moles of the gas produce 1 atm pressure at 25 C (Ignore the probable association of NO to N_2O_2).

Sol. Let, initial pressure of added Cl_2 is p atm.

	$2NO$	+	Cl_2	$\rightleftharpoons$	$2NOCl$
Initial	0.02atm		p atm		0
At equilibrium	$\left(0.02-\frac{0.02}{100}\right)$ $= 2\quad 10^{-4}(100-1)$ $= 198\quad 10^{-4}$ atm		$\left(p-\frac{0.01}{100}\right)$ $= p-10^{-4}$ atm		$\frac{0.02}{100}$ $= 2\quad 10^{-4}$atm

$$K_p = \frac{P^2_{NOCl}}{P^2_{NO}\times P_{Cl_2}}$$

$$\Rightarrow 10^{-3} = \frac{(2\times10^{-4})^2}{(198\times10^{-4})^2\times(p-10^{-4})}$$

$$\Rightarrow p - 10^{-4} = \frac{4}{(198)^2\times10^{-3}} = 0.102$$

$\therefore$ p = 0.102 + 0.0001 = 0.1021 atm

Volume of the vessel can be calculated as follows,

PV = nRT

$$\text{or } V = \frac{nRT}{P} = \frac{0.2\times0.082\times298}{1}L = 4.887\ L$$

Again applying, (PV = nRT) we can calculate the number of moles of Cl_2

$$n_{Cl_2} = \frac{PV}{RT} = \frac{0.1021\times4.887}{0.082\times298} = 0.0204\ \text{mol.}$$

Ex.4 When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175 C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at 175 C. Calculate ΔG for the following equilibria.

$B \rightleftharpoons A \qquad \Delta G_1^\circ = ?$

$B \rightleftharpoons C \qquad \Delta G_2^\circ = ?$

From the calculated value of ΔG_1° and ΔG_2° indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

Sol.

	Pentyne	$\overset{KOH}{\rightleftharpoons}$	2-Pentyne	+	1,2-Pentadiene
	(A)		(B)		(C)
At eqm.%	1.3		95.5		3.5

$$K_c = \frac{[B][C]}{[A]} = \frac{95.2\times3.5}{1.3} = 256.31 \qquad \text{..........(i)}$$

From eqm. $B \rightleftharpoons A$

$$K_1 = \frac{[A]}{[B]}$$

$$\text{From Eqs. (i) and (ii), } K_1 = \frac{[C]}{K_c} = \frac{3.5}{256.31} = 0.013 \qquad \text{..........(ii)}$$

$\Delta G = -2.303\ RT\ \log_{10} K_1$

$= -\ 2.303\quad 8.314\quad 448\ \log_{10}0.013$

$= 16178.4$

$= 16.1784$ kJ

Stability order for A and B is B > A

Similarly, $B \rightleftharpoons C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_c \times [A]}{[B]^2} = \frac{256.31 \times 3.1}{95.2 \times 95.2} = 0.0876$$

$\therefore \Delta G_2 = -2.303 \text{ RT} \log_{10} K_2$

$= -2.303 \quad 8.314 \quad 448 \log_{10} 0.0876$

$= 9068.06 \text{ J} = 9.068 \text{ kJ}$

Thus, stability order for B and C is B > C

Total order of stability is B > C > A.

Ex.5 The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g/L at 288 K and 1.84 g/L at 348 K. Calculate the entropy change during the reaction at 348 K.

Sol. $N_2O_4 \rightleftharpoons 2NO_2$

Case (i)

$$PV = nRT = \frac{w}{m_{mix}} RT$$

$$\Rightarrow m_{mix} = \frac{w}{V} \times \frac{RT}{P} = \frac{dRT}{P} = 3.62 \quad 0.082 \quad 288 = 85.6$$

Let, a mole of N_2O_4 and (1–a) mole of NO_2 exist at equilibrium

$\therefore a \quad 92 + (1 - a) \quad 46 = 85.6$

$\therefore a = 0.86$

$\therefore n_{N_2O_4} = 0.86 \text{ mol}, \; n_{NO_2} = 0.14 \text{ mol}$

$$K_p = \frac{0.14 \times 0.14}{0.86} \times \left[\frac{1}{1}\right]^1 = 0.0228 \text{ atm at } 288 \text{ K.}$$

Case (ii)

$$m_{mix} = \frac{dRT}{P} = 1.84 \quad 0.0821 \quad 348 = 52.57$$

Let, a' mol of N_2O_4 and (1 – a') mol of NO_2 exist at equilibrium

$\therefore a' \quad 92 + (1 - a') \quad 46 = 52.57$

$\therefore a' = 0.14$

$\therefore n_{N_2O_4} = 0.14 \text{ mol}, \; n_{NO_2} = 0.86 \text{ mol}$

$$\therefore K_p = \frac{0.86 \times 0.86}{0.14} \left[\frac{1}{1}\right]^1 = 5.283 \text{ atm at } 348 \text{ K}$$

$$\log_{10}\left(\frac{K_{p_2}}{K_{p_1}}\right) = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Rightarrow \log_{10} \frac{5.283}{0.0228} = \frac{\Delta H}{2 \times 2.303} \left[\frac{348 - 288}{348 \times 288}\right]$$

$\therefore \Delta H = 18195.6 \text{ cal} = 18.196 \text{ Kcal}$

$\Delta G = -2.303 \text{ RT} \log K_p$

$= - 2.303 \quad 2 \quad 348 \quad \log 5.283$

$= -1158.7$ cal.

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{18195.6 + 1158.7}{348} = 55.62 \text{ cal}$$

Ex.6 For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant, K_c at 27 C is $4.0 \quad 10^{-19}$. To find the silver ion concentration in a solution which is originally 0.10 M in KCN and 0.03 M in $AgNO_3$.

Sol. $Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$

$$K_c' = \frac{[Ag(CN)_2]^-}{[Ag^+][CN^-]^2} = \frac{1}{K_c} = 2.5 \quad 10^{20} \qquad \text{........(i)}$$

Very high value of K_c' show that complex forming equilibrium is spontaneous and almost all the Ag^+ ion would have reacted leaving xM in solution :

	Ag^+	+	$2CN^-$	$\rightleftharpoons$	$[Ag(CN)_2]^-$
initial	0.03M		0.1M		0
At eqm.	xM		(0.1 – 0.03 2x)M		0.03 M

$$K_c' = 2.5 \quad 10^{20} = \frac{0.03}{x(0.1 - 0.03 \times 2x)^2}$$

$\therefore$ $x = [Ag^+] = 7.5 \quad 10^{-18}$ M

Ex.7 In an experiment, 5 moles of HI were enclosed in a 10 litre container. At 817 K equilibrium constant for the gaseous reaction, $2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$, is 0.025. Calculate the equilibrium concentrations of HI, H_2 and I_2. What is the fraction of HI that decomposes?

Sol. Let, 2n be the number of moles of HI which is decomposed, the number of moles of H_2 and I_2 produced will be n mole each. Then molar concentrations of various species at equilibrium are

$$[HI] = \frac{(5-2n)}{10} \text{ mol/L}, \qquad [H_2] = \frac{n}{10} \text{ mol/L, and} \quad [I_2] = \frac{n}{10} \text{ mol/L}$$

Also, $$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\frac{n}{10} \times \frac{n}{10}}{\left(\frac{5-2n}{10}\right)^2}$$

$$0.025 = \frac{n^2}{(5-2n)^2}$$

Solving for n, we get n = 0.6

$$\therefore\ [HI] = \frac{5 - 2 \times 0.6}{10} = \frac{3.8}{10} = 0.38 \text{ mol/L}$$

$$[H_2] = \frac{0.6}{10} = 0.06 \text{ mol/L}$$

$$[I_2] = \frac{0.6}{10} = 0.06 \text{ mol/L}$$

Fraction of HI decomposed $= \dfrac{2 \times 0.6}{5}$

$= 0.24$ or 24%

Ex.8 0.5 moles of N_2 and 3 moles of PCl_5 are placed in a 100 litre container heated to 227 C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation of PCl_5 and value of K_p for its dissociation.

Sol. Dissociation of PCl_5 is written as

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

Let, x be the no. of moles of PCl_5 decomposed at equilibrium

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g)$	$+\ Cl_2(g)$
Initial moles	3	0	0
Moles at eqm.	3–x	x	x

Now, total gaseous moles in the container = n_T

n_T = moles of $(PCl_5 + PCl_3 + Cl_2)$ + moles of N_2

$n_T = 3 - x + x + x + 0.5 = 3.5 + x$

The mixture behaves ideally, hence $PV = n_TRT$

Let us, calculate no. of moles by using gas equation

$$\Rightarrow n_T = \frac{PV}{RT} = \frac{2.05 \times 100}{0.0821 \times 400} \Rightarrow n_T = 5$$

Now, equating the two values of n_T, we have

$3.5 + x = 5 \Rightarrow x = 1.5 \Rightarrow$ degree of dissociation = 1.5/3 = 1/2 = 0.5

$$\text{Now, } K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

$$P_{PCl_5} = \frac{3-x}{3.5+x}P = \frac{1.5}{5} \times 2.05 = 0.615 \text{ atm}$$

$$P_{PCl_3} = \frac{1.5}{5} \quad 2.05 = 0.615 \text{ atm}$$

$$P_{Cl_2} = \frac{1.5}{5} \quad 2.05 = 0.615 \text{ atm}$$

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} \text{ atm} \Rightarrow K_p = \frac{0.615 \times 0.615}{0.615} = 0.615 \text{ atm}$$

$K_p = 0.615$ atm

Note : The inert gases like N_2 or noble gases (He, Ne etc.) though do not take part in the reaction, but still they affect the degree of dissociation and equilibrium concentrations for the reactions in which $\Delta n \neq 0$. They add to the total pressure of the equilibrium mixture ($p \propto n$).

Ex.9 For the reaction, $CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2\,(g)$; K = 0.059 atm at 1000 K. 1 g of $CaCO_3$ is placed in a 10 litre container at 1000 K to reach the equilibrium. Calculate the mass of $CaCO_3$ left at equilibrium.

Sol.

	$CaCO_3\,(s) \rightleftharpoons$	$CaO(s)$	$+\ CO_2\,(g)$
At equilibrium	a – x	x	x

Here, a = initial moles of $CaCO_3$

$K_p = P_{CO_2} = 0.059$

$$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{0.059 \times 10}{0.082 \times 1000} = 7.2 \quad 10^{-3} \text{ moles}$$

Moles of $CaCO_3$ left = 0.01 – 0.0072 = 0.0028

Mass of $CaCO_3$ left = 0.28 g

Ex.10 The value of K_p for the reaction, $2H_2O\ (g) + 2Cl_2\ (g) \rightleftharpoons 4HCl\ (g) + O_2\ (g)$ is 0.035 atm at 500 C, when the partial pressures are expressed in atmosphere. Calculate K_c for the reaction,

$$\frac{1}{2}O_2\ (g) + 2HCl\ (g) \rightleftharpoons Cl_2\ (g) + H_2O\ (g)$$

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

Δn = moles of products – moles of reactants = 5 – 4 = 1

R = 0.0821 L atm/mol/K, T = 500 + 273 = 773 K

$\therefore\ 0.035 = K_c\ (0.0821\quad 773)$

$K_c = 5.515\quad 10^{-4}\ \text{mol L}^{-1}$

$\therefore\ K_c'$ for the reverse reaction would be $\dfrac{1}{K_c}$

$$\therefore\ K_c' = \frac{1}{5.515 \times 10^{-4}} = 1813.24\ (\text{mol L}^{-1})^{-1}$$

When a reaction is multiplied by any number n (integer or a fraction) then K_c' or K_p' becomes $(K_c)^n$ or $(K_p)^n$ of the original reaction.

$\therefore\ K_c$ for $\dfrac{1}{2}O_2\ (g) + 2HCl\ (g) \rightleftharpoons Cl_2\ (g) + H_2O\ (g)$

is $\sqrt{1813.24} = 42.58\ (\text{mol.L}^{-1})^{-½}$

Ex.11 K_p for the reaction $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$ is 0.66 at 46 C. Calculate the percent dissociation of N_2O_4 at 46 C and a total pressure of 0.5 atm. Also calculate the partial pressure of N_2O_4 and NO_2 at equilibrium.

Sol. This problem can be solved by two methods.

Method 1 : Let, the number of moles of N_2O_4 initially be 1 and α is the degree of dissociation of N_2O_4.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial moles	1		0
Moles at equilibrium	$1-\alpha$		2α

Total moles at equilibrium = $1 - \alpha + 2\alpha = 1 + \alpha$

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha}\quad P_T$$

$$p_{NO_2} = \frac{2\alpha}{1+\alpha} \times P_T$$

$$\therefore\ K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{4\alpha^2 P_T}{(1-\alpha)(1+\alpha)} = \frac{4\alpha^2 \times 0.5}{1-\alpha^2}$$

α = 0.5, i.e. 50% dissociation

Hence, partial pressure of N_2O_4 = 0.167 atm.

and partial pressure of NO_2 = 0.333 atm.

Method 2 : Let, the partial pressure of NO_2 at equilibrium be p atm, then the partial pressure of N_2O_4 at equilibrium will be (0.5 – p) atm.

$$\therefore\ K_p = \frac{p^2}{(0.5-p)} = 0.66$$

$p^2 + 0.66\ p - 0.33 = 0$

On solving, p = 0.333 atm.

$\therefore\ p_{NO_2}$ = 0.333 atm and $p_{N_2O_4}$ = 0.167 atm.

Ex.12 Ammonium hydrogen sulphide dissociated according to the equation,

$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$. If the observed pressure of the mixture is 2.24 atm at 106 C, what is the equilibrium constant K_p of the reaction ?

Sol. The reaction is $NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$.

If α is the degree of dissociation of equilibrium,

Total moles of NH_3 and H_2S at equilibrium = 2α.

$$\text{Partial pressure} = \frac{\text{Moles of substance}}{\text{Total no. of moles}} \times \text{Total pressure}$$

$$\therefore p_{NH_3} = \frac{\alpha}{2\alpha}\ P = 0.5\ P\ ;\ p_{H_2S} = \frac{\alpha}{2\alpha}\ P = 0.5\ P$$

$K_p = p_{NH_3} \times p_{H_2S} = 0.5\ P \quad 0.5\ P = 0.25P^2$

Substituting the value of P = 2.24 atm.

$K_p = 0.25 \quad 2.24 \quad 2.24 = 1.2544\ atm^2$

Alternatively :

At equilibrium $p_{NH_3} + p_{H_2S} = 2.24$ atm

As $p_{NH_3} = p_{H_2S}$

$$\therefore\ p_{NH_3} = \frac{2.24}{2} = 1.12 \text{ atm}$$

$\therefore\ K_p = 1.12 \quad 1.12 = 1.2544\ atm^2$

Ex.13 In a mixture of N_2 and H_2, initially they are in a mole ratio of 1 : 3 at 30 atm and 300 C, the percentage of ammonia by volume under the equilibrium is 17.8%. Calculate the equilibrium constant (K_p) of the mixture, for the reaction, $N_2\ (g) + 3H_2(g) \rightleftharpoons 2NH_3\ (g)$.

Sol. Let, the initial moles N_2 and H_2 be 1 and 3 respectively (this assumption is valid as K_p will not depend on the exact number of moles of N_2 and H_2. One can even start with x and 3x)

	$N_2(g)$	$+\ 3H_2(g)$	$\rightleftharpoons$	$2NH_3\ (g)$
Initially	1	3		0
At equilibrium	1–x	3–3x		2x

Since % by volume of a gas is same as % by mole,

$$\therefore\ \frac{2x}{4-2x} = 0.178$$

$$\therefore\ x = \frac{4 \times 0.178}{(2 + 2 \times 0.178)} = 0.302$$

$$\therefore\ \text{Mole fraction of } H_2 \text{ at equilibrium} = \frac{3-3x}{4-2x} = 0.6165$$

Mole fraction of N_2 at equilibrium = 1 – 0.6165 – 0.178 = 0.2055

$$\therefore\ K_p = \frac{(X_{NH_3} \times P_T)^2}{(X_{N_2} \times P_T)(X_{H_2} \times P_T)^3} = \frac{(0.178 \times 30)^2}{(0.2055 \times 30)(0.6165 \times 30)^3}$$

$K_p = 7.31 \quad 10^{-4}\ atm^{-2}$.

Ex.14 Given below are the values of ΔH and ΔS for the reaction at 27 C,

$SO_2\ (g) + \frac{1}{2} O_2\ (g) \longrightarrow SO_3\ (g)$

$\Delta H = 98.32$ kJ/mol $\quad\quad \Delta S = -95$ J/mol. Calculate the value of K_p for the reaction.

Sol.

$$\log_{10} K_p = \frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303 \times R}$$

$$\therefore\ \log_{10} K_p = \frac{98320}{2.303 \times 8.314 \times 300} - \frac{95}{2.303 \times 8.314} \Rightarrow K_p = 1.44 \quad 10^{12}\ atm^{-1/2}$$

SOLVED EXAMPLES

Ex.1 The volume of a closed reaction vessel in which the equilibrium :

$2SO_2\,(g) + O_2(g) \rightleftharpoons 2SO_3\,(g)$ sets is halved, Now -

(A) the rates of forward and backward reactions will remain the same.

(B) the equilibrium will not shift.

(C) the equilibrium will shift to the left.

(D) the rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

Sol. **(D)**

In the reaction

$2SO_2\,(g) + O_2(g) \rightleftharpoons 2SO_3\,(g)$

In this reaction three moles (or volumes) of reactants are converted into two moles (or volumes) of products i.e. there is a decrease in volume and so if the volume of the reaction vessel is halved the equilibrium will be shifted to the right i.e. more product will be formed and the rate of forward reaction will increase i.e. double that of reverse reaction.

Ex.2 The equilibrium constant of the reaction $A_2\,(g) + B_2(g) \rightleftharpoons 2AB\,(g)$ at 100 C is 50. If one litre flask containing one mole of A_2 is connected to a 3 litre flask containing two moles of B_2 the number of moles of AB formed at 373 K will be -

(A) 1.886 (B) 2.317 (C) 0.943 (D) 18.86

Sol. **(A)**

The equilibrium is represented as :

	$A_2\,(g)$ +	$B_2(g)$ $\rightleftharpoons$	$2AB\,(g)$
Initial concentration	1	2	0
Moles at equilibrium	1–x	2–x	2x

Total volume = 1 + 3 = 4 litres

$$[A_2] = \frac{1-x}{4},\ [B_2] = \frac{2-x}{4} \text{ and } [AB] = \frac{2x}{4}$$

$$K = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2x}{4}\right)^2}{\left(\frac{1-x}{4}\right)\left(\frac{2-x}{4}\right)} = 50$$

On solving we get $23x^2 - 75\,x + 50 = 0$

$\therefore$ x = 2.31 or 0.943, since x can't be more than 1

so, x = 0.943

$\therefore$ moles of AB formed = 2 0.943 = 1.886

Ex.3 $H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$

When 92 g of I_2 and 1g of H_2 are heated at equilibrium at 450 C, the equilibrium mixture contained 1.9 g of I_2. How many moles of I_2 and HI are present at equilibrium.

(A) 0.0075 & 0.147 moles (B) 0.0050 & 0.147 moles

(C) 0.0075 & 0.7094 moles (D) 0.0052 & 0.347 moles

Sol. **(C)**

moles of I_2 taken $= \frac{92}{254} = 0.3622$

moles of H_2 taken $= \frac{1}{2} = 0.5$

moles of I_2 remaining $= \frac{1.9}{254} = 0.0075$

moles of I_2 used = 0.3622 – 0.0075 = 0.3547

moles of H_2 used = 0.3547

moles of H_2 remaining = 0.5 – 0.3547 = 0.1453

moles of HI formed = 0.3547 2 = 0.7094

At equilibrium

moles of I_2 = 0.0075 moles

moles of HI = 0.7094 moles

Ex.4 When 1.0 mole of N_2 and 3.0 moles of H_2 was heated in a vessel at 873 K and a pressure of 3.55 atm. 30% of N_2 is converted into NH_3 at equilibrium. Find the value of K_P for the reaction.

(A) $3.1\ \ 10^{-2}\ atm^{-2}$ (B) $4.1\ \ 10^{-2}\ atm^{-2}$ (C) $5.1\ \ 10^{-2}\ atm^{-2}$ (D) $6.1\ \ 10^{-2}\ atm^{-2}$

Sol. **(C)**

$N_2(g)$ +	$3H_2(g)$ $\rightleftharpoons$	$2NH_3(g)$	
1 mole	3 moles	0	Initial moles
1–0.3 = 0.7 moles	3.0 –0.9 =2.1 moles	0.6 moles	at equilibrium

Total no. of moles at equilibrium = 3.4

$$K_P = \frac{\left(\frac{0.6}{3.4}\times 3.55\right)^2}{\left(\frac{0.7}{3.4}\times 3.55\right)\left(\frac{2.1}{3.4}\times 3.55\right)^3} = 5.1\ \ 10^{-2}\ atm^{-2}$$

Ex.5 $2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$

If the partial pressure of SO_2, O_2 and SO_3 are 0.559, 0.101 and 0.331 atm respectively. What would be the partial pressure of O_2 gas, to get equal moles of SO_2 and SO_3.

(A) 0.188 atm (B) 0.288 atm (C) 0.388 atm (D) 0.488 atm

Sol. **(B)**

$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$

$$K_P = \frac{[P_{SO_3}]^2}{[P_{SO_2}]^2[P_{O_2}]} = \frac{(0.331)^2}{(0.559)^2(0.101)} = 3.47$$

If SO_2 and SO_3 have same number of moles, their partial pressure will be equal and

$$P_{SO_3} = P_{SO_2}\ \therefore\ P_{O_2} = \frac{1}{3.47} = 0.288\text{atm}$$

Ex.6 $A_2(g)$ and $B_2(g)$ at initial partial pressure of 98.4 and 41.3 torr, respectively were allowed to react at 400 K. At equilibrium the total pressure was 110.5 torr. Calculate the value of K_P for the following reaction at 400 K.

$2A_2(g) + B_2(g) \rightleftharpoons 2\ A_2B\ (g)$

(A) 124 (B) 134 (C) 154 (D) 174

Sol. **(B)**

The given reaction is,

$2A_2(g)$ +	$B_2(g)$	$\rightleftharpoons$ $2A_2B$ (g)	
Initial pressure (torr)	98.4	41.3	0
At equilibrium	98.4–x	$41.3-\frac{x}{2}$	x

Total pressure at equilibrium = 110.5 torr.

$$(98.4 - x) + (41.3 - \frac{x}{2}) + x = 110.5$$

$\therefore$ x = 58.4 torr (760 torr = 1 atm)

$P_{(A_2B)} = 58.4 \text{ torr} = 7.68 \quad 10^{-2}$ atm

$P_{(A_2)} = 98.4 - 58.4 = 40 \text{ torr} = 5.26 \quad 10^{-2}$ atm

$P_{(B_2)} = 41.3 - \dfrac{58.4}{2} = 12.1 \text{ torr} = 1.59 \quad 10^{-2}$ atm

$$K_P = \frac{P^2_{A_2B}}{P^2_{A_2} \times P_{B_2}} = \frac{(7.68 \times 10^{-2})^2}{(5.26 \times 10^{-2})(1.59 \times 10^{-2})} = 134$$

Ex.7 K_P for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 400 C is $3.28 \quad 10^{-4}$. Calculate K_c.

(A) 0.3 mole^{-2} litre^2 (B) 0.4 mole^{-2} litre^2 (C) 1.0 mole^{-2} litre^2 (D) 0.6 mole^{-2} litre^2

Sol. **(C)**

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\Delta n = -2$ and $K_P = K_C\,(RT)^{\Delta n}$

$3.28 \quad 10^{-4} = K_c\,(0.0821 \quad 673)^{-2}$

and K_c = 1.0 mole^{-2} litre^2.

Ex.8 0.96 g of HI were heated to attain equilibrium $2\,HI \rightleftharpoons H_2 + I_2$. The reaction mixture on titration requires 15.7 mL of N/20 hypo. Calculate % dissociation of HI.

(A) 18.9% (B) 19.9% (C) 10.46% (D) 21.9%

Sol. **(C)**

	$2HI$	$\rightleftharpoons$	H_2 +	I_2
Initial moles	$\frac{0.96}{128}$ $= 7.5 \quad 10^{-3}$		0	0
Moles at equilibrium	$(7.5 \quad 10^{-3} - x)$		x/2	x/2

Now Meq. of I_2 formed at equilibrium = Meq. of hypo used

$$\frac{W}{E} \times 1000 = 15.7 \quad \frac{1}{20} \qquad \text{or} \qquad \frac{W}{E} \text{ of } I_2 = 0.785 \quad 10^{-3}$$

$\therefore$ Moles of I_2 formed at equilibrium $= \dfrac{0.785 \times 10^{-3}}{2} = 0.3925 \quad 10^{-3}$

or $\dfrac{x}{2} = 0.3925 \quad 10^{-3}$ or $x = 0.785 \quad 10^{-3}$

$\therefore$ degree of dissociation of HI $= \dfrac{\text{moles dissociated}}{\text{initial moles}} = \dfrac{x}{7.5 \times 10^{-3}}$

$$\alpha = \frac{0.785 \times 10^{-3}}{7.5 \times 10^{-3}} = 0.1046 = 10.46\%$$

Ex.9 A mixture of H_2 and I_2 in molecular proportion of 2 : 3 was heated at 444 C till the reaction $H_2 + I_2 \rightleftharpoons 2HI$ reached equilibrium state. Calculate the percentage of iodine converted into HI. (K_C at 444 C is 0.02)

(A) 3.38 % (B) 4.38% (C) 5.38% (D) 6.38%

Sol. **(C)**

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial moles	2		3		0
Equi.conc.	$\frac{2-x}{v}$		$\frac{3-x}{v}$		$\frac{2x}{v}$

$$K_C = \frac{4x^2}{(2-x)(3-x)} = 0.02$$

$199\,x^2 + 5x - 6 = 0$

$x = 0.1615$

Out of 3 moles, 0.1615 moles I_2 is converted into HI.

$\therefore$ Percentage of I_2 converted to HI $= \dfrac{0.1615 \times 100}{3} = 5.38\%$

Ex.10 The equilibrium composition for the reaction is :

PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
0.20		0.05		0.40 moles/litre

If 0.25 moles of Cl_2 is added at same temperature. Find equilibrium concentration of PCl_5 ($K_C = 20$)

(A) 0.48 moles/litre (B) 0.38 moles/litre (C) 0.56 moles/litre (D) 1.20 moles/litre

Sol. **(A)**

PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
0.20		0.05		0.40 moles/litre

If 0.25 moles of Cl_2 is added then at equilibrium [Let V = 1L]

$0.20 - x$ $\quad 0.30 - x$ $\quad 0.40 + x$

$$20 = \frac{0.40 + x}{(0.20 - x)(0.30 - x)} \quad \text{or} \quad x = 0.08$$

$[PCl_5] = 0.4 + 0.08 = 0.48$ moles/litre

Ex.11 The equilibrium constant K, for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64 10^{-4} atm^{-2} at 300 C. What will be the equilibrium constant at 400 C, if heat of reaction in this temperature range is – 105185.8 Joules.

(A) 0.64 10^{-5} atm^{-2} (B) 6.4 10^{-3} atm^{-2} (C) 0.64 10^{-3} atm^{-2} (D) 0.64 10^{-1} atm^{-2}

Sol. **(A)**

$K_{p_1} = 1.64 \quad 10^{-4}\ atm^{-2}$, $K_{p_2} = ?$

$T_1 = 300 + 273 = 573$ K

$T_2 = 400 + 273 = 673$ K

$\Delta H = -105185.8$ Joules

R = 8.314 J/K/mole

Applying equation

$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log K_{p_2} - \log 1.64 \quad 10^{-4} = -\frac{105185.8}{2.303 \times 8.314}\left(\frac{673-573}{673 \times 573}\right)$$

or $K_{p_2} = 0.64 \quad 10^{-5}\ atm^{-2}$

Ex.12 In an experiment at 500 K, the concentration of different species are $[NH_3] = 0.105\ mol\ dm^{-3}$, $[N_2] = 1.10\ mol\ dm^{-3}$ and $[H_2] = 1.50\ mol\ dm^{-3}$ then find the followings :-

(a) values of K_C and K_P for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(b) value of K_c for the reaction -

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Sol. (a) For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$[NH_3] = 0.105\ mol\ dm^{-3}$, $[N_2] = 1.10\ mol\ dm^{-3}$ and

$[H_2] = 1.50\ mol\ dm^{-3}$

$$K_C = \frac{(0.105\,mol\,dm^{-3})^2}{(1.10\,mol\,dm^{-3})\times(1.50\,mol\,dm^{-3})^3} = 2.97 \quad 10^{-3}\ mol^{-2}dm^6$$

Now $K_P = K_C \quad (RT)^{\Delta n}$ $\qquad \Delta n = -2,$

$R = 0.082\ atm\ dm^3\ K^{-1}\ mol^{-1}$, $T = 500\ K$

$\therefore$ $K_P = (2.97 \quad 10^{-3}\ mol^{-3}\ dm^6) \quad [(0.082\ atm\ dm^3\ K^{-1}\ mol^{-1}) \quad (500\ K)]^{-2}$

$= 1.76 \quad 10^{-6}\ atm^{-2}$

(b) The equilibrium constant K_C for the reverse reaction is related to the equilibrium constant K_C for the forward reaction as :

$$K'_C = \frac{1}{K_c} = \frac{1}{2.97\times10^{-3}mol^{-2}dm^6} = 3.37 \quad 10^{-2}\ mol^2\ dm^{-6}$$

Ex.13 The equlibrium pressure of $NH_4CN\ (s) \rightleftharpoons NH_3(g) + HCN\ (g)$ is 0.298 atm. Calculate K_P. If NH_4CN (s) is allowed to decompose in presence of NH_3 at 0.50 atm then calculate partial pressure of HCN at equilibrium.

Sol.

	$NH_4CN\ (s)$	$\rightleftharpoons NH_3(g)$	$+ HCN\ (g)$
Pressure at equilibrium	–	P	P

$\therefore$ Total pressure at equilibrium = 2P = 0.298 atm

$\therefore$ P = 0.149 atm

$\therefore$ $K_P = P_{NH_3} \times P_{HCN} = 0.149 \quad 0.149 = 0.0222\ atm^2$

If dissociation is made in presence of NH_3 at 0.5 atm

	$NH_4CN\ (s)$	$\rightleftharpoons NH_3(g)$	$+ HCN\ (g)$
Initial pressure	–	0.50	0
Pressure at equli.	–	(0.50+P')	P'

Also K_P = P' (0.50 + P')

or 0.0222 = P' (0.50 + P')

$\therefore$ P' = 0.1656 atm

Ex.14 The value of K_C for the reaction,

$N_2 + 2O_2 \rightleftharpoons 2NO_2$ at a certain temperature is 900. Calculate the value of equilibrium constant for

(i) $2NO_2 \rightleftharpoons N_2 + 2O_2$

(ii) $\frac{1}{2} N_2 + O_2 \rightleftharpoons NO_2$

Sol. Equilibrium constant (K_C) for the reaction

$N_2 + 2O_2 \rightleftharpoons 2NO_2$ is

$$K_C = \frac{[NO_2]^2}{[N_2][O_2]^2} = 900$$

(i) For the reaction $2NO_2 \rightleftharpoons N_2 + 2O_2$, $K'_C = \frac{[N_2][O_2]^2}{[NO_2]^2} = \frac{1}{K_c}$

$$K'_C = \frac{1}{900} = 0.0011 \text{ mole litre}^{-1}$$

(ii) For the reaction $\frac{1}{2} N_2 + O_2 \rightleftharpoons NO_2$

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

$$K''_C = \sqrt{900} = 30 \text{ lit}^{1/2} \text{ mol}^{-1/2}$$

Ex.15 Ice melts slowly at higher altitude, why ?

Sol. According to Le Chatelier principle, the melting of ice is favoured at high pressure because the forward reaction ice $\longrightarrow$ water shows a decrease in volume. At higher altitude atmospheric pressure being low and thus ice melts slowly.

Ex.16 Both metals Mg and Fe can reduce copper from a solution having Cu^{+2} ion according to equilibria.

$Mg(s) + Cu^{+2} \rightleftharpoons Mg^{+2} + Cu(s)$; $K_1 = 5 \quad 10^{90}$

$Fe(s) + Cu^{+2} \rightleftharpoons Fe^{+2} + Cu(s)$; $K_2 = 2 \quad 10^{26}$

Which metal will remove cupric ion from the solution to a greater extent.

Sol. Since $K_1 > K_2$, the product in the first reaction is much more favoured than in the second one. Mg thus removes more Cu^{+2} from solution than Fe does.

Ex.17 The equilibrium constant K_C for $Y(g) \rightleftharpoons Z(g)$ is 1.1. Which gas has molar concentration greater than 1.

Sol. For $Y(g) \rightleftharpoons Z(g)$

$$K_C = \frac{[Z]}{[Y]} = 1.1$$

if Z = 1 ;	[Y] = 0.91
Case I	0.9 < [Y] < 1 only Z = 1
Case II	[Y] > 1 both [Y] and [Z] > 1

Ex.18 When S in the form of S_8 is heated 800 K, the initial pressure of 1 atmosphere falls by 30 % at equilibrium. This is because of conversion of some S_8 to S_2. Calculate the K_P for reaction.

Sol.

	$S_8\,(g) \rightleftharpoons$	$4\,S_2\,(g)$
Initial pressure	1 atm	0
Equilibrium pressure	(1–0.30) = 0.70 atm	4 0.30 = 1.2 atm

$$\text{Now, } K_P = \frac{P_{S_2}^4}{P_{S_8}} = \frac{(1.2)^4}{0.70} = 2.9622 \text{ atm}^3$$

Ex.19 A vessel at 1000 K contains CO_2 with a pressure of 0.6 atm. some of the CO_2 is converted into CO on addition of graphite. Calculate the value of K, if total pressure at equilibrium is 0.9 atm.

Sol.

	$CO_2\,(g)$	+ $C\,(s) \rightleftharpoons$	$2\,CO\,(g)$
Initial pressure	0.6 atm	–	0
Equilibrium pressure	(0.6–x)atm		2x atm

From question, (0.6 – x) + 2x = 0.9 hence, x = 0.3 atm.

$$\text{Now, } K_P = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(2x)^2}{(0.6 - x)} = 1.2 \text{ atm.}$$