02 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 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $3Fe(s) + 4H_2O(\ell) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$ $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(i) Chemical reaction in which products cannot be converted back into reactants. $AgNO_3(aq.) + NaCl(aq.) \longrightarrow AgCl(s) + NaNO_3(aq.)$ $NaCl(aq.) + H_2SO_4(aq.) \longrightarrow NaHSO_4(aq.) + HCl(aq.)$ $Zn(s) + H_2SO_4(aq.) \longrightarrow ZnSO_4(aq.) + H_2\uparrow(g)$ $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$
(ii) Proceed in forward as well as backward direction.	(ii) Proceed only in one direction (forward).
(iii) To obtain reversible 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, but can happen in close container also.
(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. Reactions are reversible in nature. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(vi) Generally thermal decomposition in open vessel. Reactions are irreversible in nature. $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

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

On the basis of heat of reaction	
Exothermic reaction	**Endothermic reaction**
(i) Heat is evolved in these chemical reaction $R \rightarrow P + x$ kcal (ii) Change in enthalpy is negative $\Delta H = (-)$ ve Eg. : Formation reaction Exception $N_2 + O_2 \rightarrow 2NO/N_2O/NO_2$ $O_2 + F_2 \rightarrow O_2F_2/OF_2$; $\Delta H > 0$	(i) Heat is absorbed in these chemical reaction $R + x$ kcal $\rightarrow$ P or R $\rightarrow P - x$ kcal (ii) Change in enthalpy is positive $\Delta H = (+)$ ve Eg. : Dissociation reaction

Active Mass : The mass of a substance which effect the rate of reaction i.e. mass of substance which take a part actively in a reaction. Active mass depends on state of substance.

(i) Solution state : In this state, active mass of a substance is represented by concentration (molarity). Active mass is usually expressed in concentration by enclosing the symbol of the reactant in square bracket [ ].

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

(ii) Gaseous state : In this state, active mass of a substance may be represented as concentration (molarity) or partial pressure.

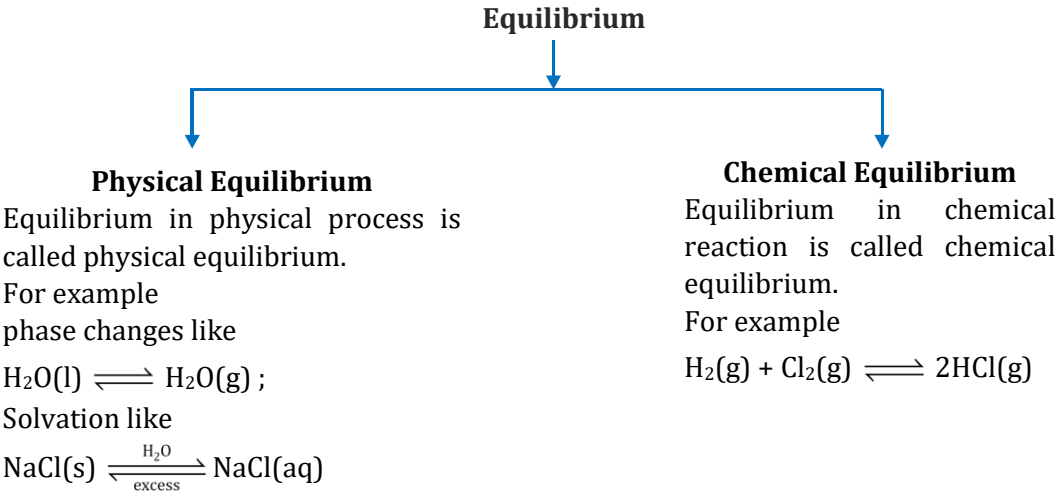
(iii) Pure solid & pure liquid : In this state, active mass of solids , pure liquids and solvents in large excess is a constant quantity because there is no change in activity with the change in quantity or volume of system.

$$\text{Molar concentration (M)} = \frac{w}{M \times V} = \frac{d}{M} = \frac{\text{density of the substance}}{\text{molar mass of the substance}} = \text{constant}$$

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

Equilibrium : In the state of equilibrium, system loses its tendency for a change and all the properties associated with system like pressure, temperature, composition, etc become constant and do not vary without external stimulation. On the basis of nature of process in which state of equilibrium is attained, it may be of two types :

(A) Physical equilibrium (B) Chemical equilibrium



Equilibrium : Physical Equilibrium

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

Example : Fusion of ice, evaporation of water, dissolution of salts , 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 with liquid at a given temperature.

Ex. $H_2O\ (\ell) \rightleftharpoons H_2O\ (g)$ at Boiling Point

(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) Solid-Vapour equilibria : Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine.

Ex. $I_2(solid) \rightleftharpoons I_2\ (vapour)$

Camphor (solid) $\rightleftharpoons$ Camphor (vapour)

NH_4Cl (solid) $\rightleftharpoons$ NH_4Cl (vapour)

(iv) (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 is established, provided temperature is constant.

Ex. $NaI\ (s) \overset{H_2O}{\rightleftharpoons} Na^{\oplus}\ (aq.) + I^{\ominus}\ (aq.)$

(v) (Gas + Solvent) Saturated solution equilibria : In such equilibria, solvent 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.

Equilibrium : Chemical Equilibrium

Analogous to the physical systems, chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products become constant. This is the stage of chemical equilibrium. This equilibrium consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

Characteristics of Chemical Equilibrium :

(i) It is attained in reversible chemical reactions only.

(ii) Equilibrium is possible only in closed system.

(iii) In this state, all the measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any significant change with time, i.e. constant.

(iv) Equilibrium is dynamic in nature i.e., at microscopic level reaction is not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So, there is no net change. Thus, equilibrium is not static in nature.

(v) Chemical equilibrium can be approached from both sides

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

or

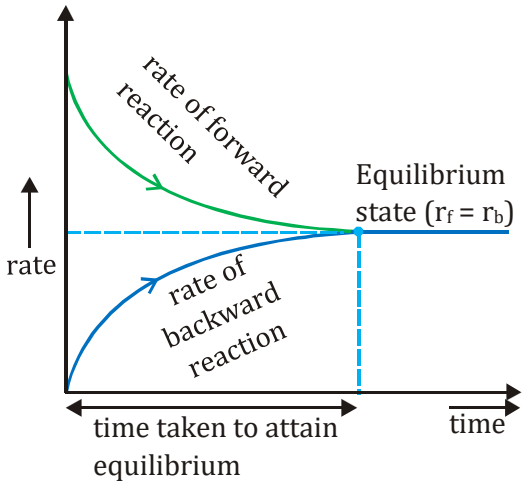
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

At equilibrium, reactants and products have fixed composition and this is independent of the fact whether the reaction start with the reactant or with the product.

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

(vii) At equilibrium, opposing reactions (i.e., forward and backward) proceeds with equal rates.
i.e., rate of forward reaction = rate of backward reaction.

Graph of Rate v/s Time :

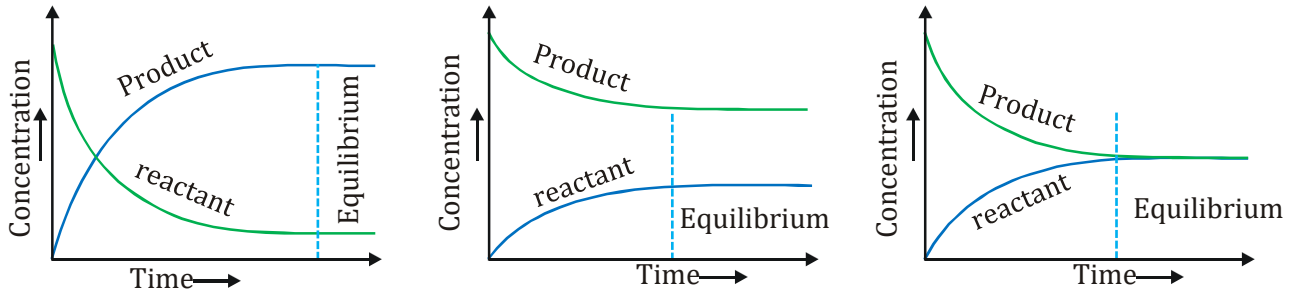


Graph of Concentration v/s Time :

Let us consider a reversible reaction,

$$A + B \underset{\text{backward}}{\overset{\text{forward}}{\rightleftharpoons}} C + D$$

initial concentration.	(t = 0)	1M	1M	0	0
equilibrium concentration.	(t = t)	(1–x)	(1–x)	x	x



Some general curves for equilibrium

Note :

At equilibrium, the concentration of reactant and product will be constant. It means, it may be different as above graph (i) & (ii) or same as above graph (iii) but the rate of forward reaction and the backward reaction will be always same.

Illustration 1:

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

Ans. (C)

Solution:

$H_2O(s) \rightleftharpoons H_2O(\ell)$

Physical equilibria do not include any chemical change.

Types of Chemical Equilibrium
(Basis of physical state)

- Homogeneous equilibrium
- Heterogeneous equilibrium

I. Homogeneous Equilibrium:

It is the equilibrium when all reactants and products are in same phase.

Ex. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

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

II. Heterogeneous Equilibrium:

It is the equilibrium when the reactants and the products are present in different phases. All physical equilibria are heterogeneous.

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

$2Na_2O_2(s) + 2H_2O(\ell) \rightleftharpoons 4NaOH(aq.) + O_2(g)$

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

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

Law of mass action : The law of mass action is given by **Guldberg** and **Waage**. According to it, "the rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers equal to their stoichiometric coefficients".

Consider a reversible reaction : $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

According to law of mass action

rate of forward reaction $(r_f) \propto (a_A)^{m_1}(a_B)^{m_2}$

$$r_f = k_f(a_A)^{m_1}(a_B)^{m_2}$$

rate of backward reaction $(r_b) \propto (a_C)^{n_1}(a_D)^{n_2}$

$$r_b = k_b(a_C)^{n_1}(a_D)^{n_2}$$

At equilibrium $r_f = r_b$

$$k_f(a_A)^{m_1}(a_B)^{m_2} = k_b(a_C)^{n_1}(a_D)^{n_2}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{(a_C)^{n_1}(a_D)^{n_2}}{(a_A)^{m_1}(a_B)^{m_2}}$$

where, K_{eq} = equilibrium constant

k_f = forward rate (velocity) constant

k_b = backward rate (velocity) constant

a_A, a_B = active mass of reactant A & B

a_C, a_D = active mass of product C & D

m_1, m_2 = stoichiometry coefficient of reactant A & B

n_1, n_2 = stoichiometry coefficient of product C & D

At a given temperature, the product of molar concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of molar concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the **Equilibrium Law or Law of Chemical Equilibrium** and the constant is called equilibrium constant (K_{eq}).

Types of Equilibrium Constant ($K_{eq.}$):

(i) Equilibrium constant in terms of concentration (K_C) : K_C is defined for reactions in gas phase & solution phase. Molar concentrations are used to express amounts.

(ii) Equilibrium constant in terms of partial pressure (K_P) : K_P is defined for reactions in gas phase. Partial pressures are used to express amounts.

Ex. Consider a reversible reaction in gas phase : $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

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

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

here,

[A], [B], [C], [D] = Molar concentration of A, B, C, D respectively at equilibrium.

(P_A), (P_B), (P_C), (P_D) = partial pressure of A, B, C, D respectively at equilibrium.

Units of Equilibrium Constant: The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L or M and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For general reactions,

$aA(g) \rightleftharpoons bB(g)$

(i) $K_C = \frac{[B]^b}{[A]^a}$

unit of $K_C = (\text{bar})^{\Delta n_g} = M^{\Delta n_g}$

here, Δn_g = b – a = (Stoichiometric coefficient of gaseous product – Stoichiometric coefficient of gaseous reactant)

(ii) $K_P = \frac{(P_B)^b}{(P_A)^a}$

unit of $K_p = (\text{atm})^{b-a} = (\text{atm})^{\Delta n_g}$ or $(\text{Pa})^{\Delta n_g}$ or $(\text{bar})^{\Delta n_g}$

here, Δn_g = b – a = (Stoichiometric coefficient of gaseous product – Stoichiometric coefficient of gaseous reactant)

Illustration 2:

Write down the expression and unit for following reaction :

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

$K_C = \frac{[HI]^2}{[H_2][I_2]}$ $\left(\frac{\text{mol}}{\text{L}}\right)^0$

$K_p = \frac{P_{HI}^2}{P_{H_2}P_{I_2}}$ $(\text{atm})^0$

$\therefore$ K_C and K_p have no unit.

(b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$K_C = \frac{[NO_2]^2}{[N_2O_4]}$ $\left(\frac{\text{mol}}{\text{L}}\right)^1$

$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$ $(\text{atm})^1$

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

$K_C = [CO_2]$ $\left(\frac{\text{mol}}{\text{L}}\right)^1$

$K_p = P_{CO_2}$ $(\text{atm})^1$

If equilibrium constant is expressed in standard state that is called standard state equilibrium constant or thermodynamic equilibrium constant, which is dimensionless quantity. It is denoted by K_c^0 and K_p^0. For a pure gas, the standard state is 1 bar. Therefore, a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number and concentration of 3 M solution in standard state can be expressed as $\frac{3M}{1M} = 3$, which is a dimensionless number. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both K_c^0 and K_p^0 are dimensionless quantities but have different numerical values due to different standard states. For example,

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

$K_C = [C]$ (mol/L)

but K_C^0 is a dimensionless quantity so $K_C^0 = \frac{[C]}{1M}$

$K_p = P_C$ $(bar)^1$

but K_p^0 is a dimensionless quantity so $K_p^0 = \frac{P_C}{1\,bar}$

Relation between K_P & K_C :

For the reaction, $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

we can write

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad ...(i)$$

Assuming the gaseous components to behave ideally,

$P_iV_i = n_iRT$

$P_i = (n_i/V_i)\,RT = C_iRT = [i]\,RT$

where [i] is the molar concentration of the species 'i'.

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

$$K_P = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = \frac{([C]RT)^C.([D]RT)^d}{([A]RT)^a.([B]RT)^b} = \frac{[C]^C.[D]^d}{[A]^a.[B]^b} \times (RT)^{(c+d)-(a+b)}$$

from eq. (i)

$K_P = K_C(RT)^{(c+d)\,-\,(a+b)}$

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

Δn_g= (Stoichiometry of gaseous products) - (Stoichiometry of gaseous reactants).

$\Delta n_g = (c + d) - (a + b)$

The units of K_P & K_C are not fixed and depend on stoichiometry of the reaction. In case the number of moles of the reactant & that of the product are same, K_P & K_C will not have any unit.

Different cases for $K_p = K_c(RT)^{\Delta n_g}$:

Case-I : If $\Delta n_g = 0$ then $K_p = K_c$

Ex : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

K_p = unit less ; K_c = unit less ;

Case-II :

$\Delta n_g > 0$

RT>1	RT<1
$K_P > K_C$	$K_P < K_C$

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

$\Delta n_g = 2 - 1 = 1$ then $K_p = K_C(RT)^1$

if RT > 1 then $K_p > K_c$

if RT < 1 then $K_p < K_c$

Unit : $K_p = atm^1$; $K_c = M^1$

Case-III :

$\Delta n_g < 0$

RT>1	RT<1
$K_P < K_C$	$K_P > K_C$

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

$\Delta n_g = 2 - 4 = -2$ then $K_p = K_C(RT)^{-2}$

if RT > 1 then $K_p < K_c$

if RT < 1 then $K_p > K_c$

$K_p = atm^{-2}$; $K_c = M^{-2}$

Case-IV : If $T = \frac{1}{R} = \frac{1}{0.0821} \approx 12.2K$

[$K_P = K_C$; for any value of Δn_g]

Illustration 3:

$C(s) + O_2(g) \rightleftharpoons CO_2(g)$

Mole of O_2 and CO_2 are 5 mole and 10 mole at equilibrium respectively, then find K_P & K_C for above reaction.

Solution:

Partial pressure = Mole fraction × Total pressure

$$P_{CO_2} = X_{CO_2}.P_T = \frac{n_{CO_2}}{n_T} \times P_T = \frac{10}{15} \times P_T$$

$$P_{O_2} = X_{O_2}.P_T = \frac{n_{O_2}}{n_T} \times P_T = \frac{5}{15} \times P_T$$

$$K_P = \frac{P_{CO_2}}{P_{O_2}}$$

$$K_P = \frac{\frac{10}{15} \times P_T}{\frac{5}{15} \times P_T} = 2$$

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

$$K_C = \frac{K_P}{(RT)^{\Delta n_g}} = \frac{2}{(RT)^0} = 2$$

Illustration 4:

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

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

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

Solution:

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

$K_p = 1.8 \times 10^{-2}$ atm and $\Delta n_g = 3 - 2 = 1$

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

$\therefore$ $K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.0821 \times 600} = 3.65 \times 10^{-4}$ M

(b) $K_p = 167$ atm and $\Delta n_g = 1$

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

$\therefore$ $K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1173} = 1.734$ M

Illustration 5:

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

Ans. (B)

Solution:

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

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

Illustration 6:

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}

Ans.(C)

Solution:

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

0.8 0.4 [2.4 – (0.8 + 0.4) = 1.2] (Partial pressures at equilibrium)

Applying law of mass action,

$K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{1.2\times1.2}{0.8\times0.4\times0.4\times0.4} \Rightarrow K_P = 28.125 \text{ atm}^{-2}$

Illustration 7:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; Correct option for reaction is/are :

(A) $K_p = K_c$ (B) $K_p > K_c$

(C) $K_p < K_c$ (D) any of these, depending on temperature.

Ans. (D)

Solution:

If (d) option is not given, then the answer is (b) because $\frac{1}{R} \approx 12.2K$ which is very low relative to room temperature.

Illustration 8:

For which of the following reactions, $K_p > K_c$ at 25°C (298K)

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

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

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_2(g)$

(d) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

Solution:

(b, d, e)

Illustration 9:

For a gaseous reaction $K_p = 0.4\ atm^3$ at 27°C. Calculate K_c.

Solution:

$K_p = K_c (RT)^{(3)}$

$0.4 = K_C(0.0821 \times 300)^3$

$K_C = 2.6 \times 7 \times 10^{-8}\ M^3$

Characteristics of Equilibrium Constant :

(i) The expression for equilibrium constant K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.

(ii) The value of equilibrium constant is independent of initial concentration of the reactants and product.

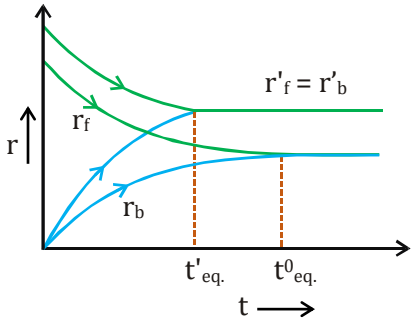
(iii) Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.

(iv) Value of equilibrium constant is not affected by catalyst. Catalyst simply helps in attaining equilibrium earlier.

The relative increase in the rate of forward as well as backward reaction remain same on using the catalyst.

$K_{eq.}$ (un-catalysed) = $\frac{k_f}{k_b}$

$K_{eq.}$ (catalysed) = $\frac{k_f \times x}{k_b \times x} = \frac{k_f}{k_b}$ = $K_{eq.}$ (un-catalysed)



Factor affecting the 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, $K_c' = \frac{[A][B]}{[C][D]}$

The two-equilibrium constant related as; $K_c = \frac{1}{K_c'}$

If the reaction is reversed, the value of the equilibrium constant is inversed.

(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.

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

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

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

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

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

(ii) For reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$K_p = \frac{P_{HI}^2}{P_{H_2}.P_{I_2}}$$

For reaction $2H_2(g) + 2I_2(g) \rightleftharpoons 4HI(g)$

$$K_P' = \frac{P_{HI}^4}{P_{H_2}^2.P_{I_2}^2}$$

The two constants are related as $K_p' = K_p^2$.

In general, $nH_2(g) + nI_2(g) \rightleftharpoons 2nHI(g)$

$K' = K^n$

When the coefficient of a balanced equation is multiplied by a common factor 'n', the equilibrium constant must be raised to the respective factor. The new equilibrium constant becomes K_{eq}^n.

(c) Addition the reaction :

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO$ ...(i)

$2NO + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ ...(ii)

For the 1st step, $K_1 = \frac{[NO]^2}{[N_2][O_2]}$

For the 2nd step, $K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$

from eq. (i) + (ii)

$N_2 + 2O_2 \rightleftharpoons 2NO_2$

For this reaction, $K = \frac{[NO_2]^2}{[N_2][O_2]^2}$

the above reaction is related as

$$\therefore \quad K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K$$

If there is addition of two reaction then the equilibrium constants are multiplied.

(d) Subtract the reaction:

$A(g) \rightleftharpoons B(g)$ ...(i)

$C(g) \rightleftharpoons D(g)$ ...(ii)

For the (i) step, $K_1 = \frac{[B]}{[A]}$

For the (ii) step, $K_2 = \frac{[D]}{[C]}$

from eq. (i) – (ii)

$A_{(g)} + D_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$

For this reaction, $K = \frac{[B][C]}{[A][D]}$

the above reaction is related as, $K = \frac{K_1}{K_2} = \frac{[B]}{[A]} \times \frac{[C]}{[D]} = K$

If we subtract of two reaction, then the equilibrium constants will be divided.

(e) Equilibrium constant depends upon the temperature:

The equilibrium constant of a particularly balanced reaction depends only on temperature. It is independent from all other factor like amount of components, concentration, pressure, volume etc.

Application of Equilibrium Constant:

(a) Predicting the extent of a reaction
(b) Predicting the direction of the reaction and
(c) Calculating equilibrium composition.

(a) Predicting the extent of reaction :

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium does not give any information about the rate at which the equilibrium is reached. The magnitude of K_c or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

(i) If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds almost all the way to completion.

(ii) If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.

(iii) If K_c is in the range 10^{-3} to 10^3, appreciable concentration of both reactants and products are present.

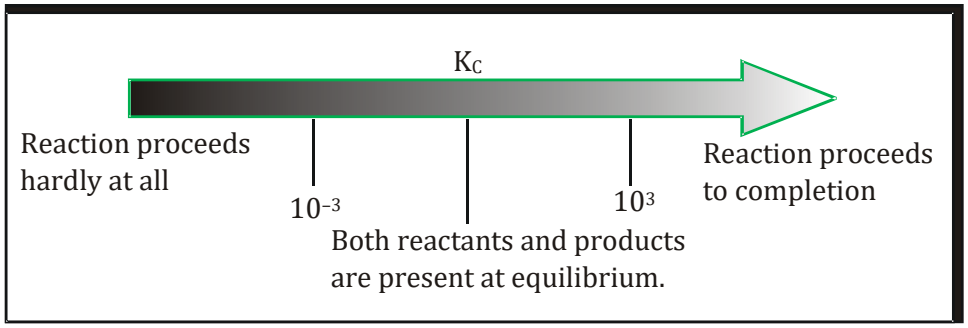


Illustration 10:

In the following cases which is predominant (reactant or product) for the given value of K_c.

(a) $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$, at 300K has $K_c = 4.0 \times 10^{31}$.

(b) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$, at 298 K has $K_c = 4.8 \times 10^{-31}$.

(c) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, at 298 K has $K_c = 4.64 \times 10^{-3}$.

Solution:

(a) If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds almost all the way to completion.

(b) If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.

(c) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2.

(b) Predicting the direction of the reaction:

The equilibrium constant is also used to find in which direction, the reaction mixture of reactants and products will proceed. For this purpose, we calculate the reaction quotient, Q. The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_C, or with partial pressure to give Q_P) at any stage of reaction. For a general reaction:

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

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

Then, if $Q_C > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

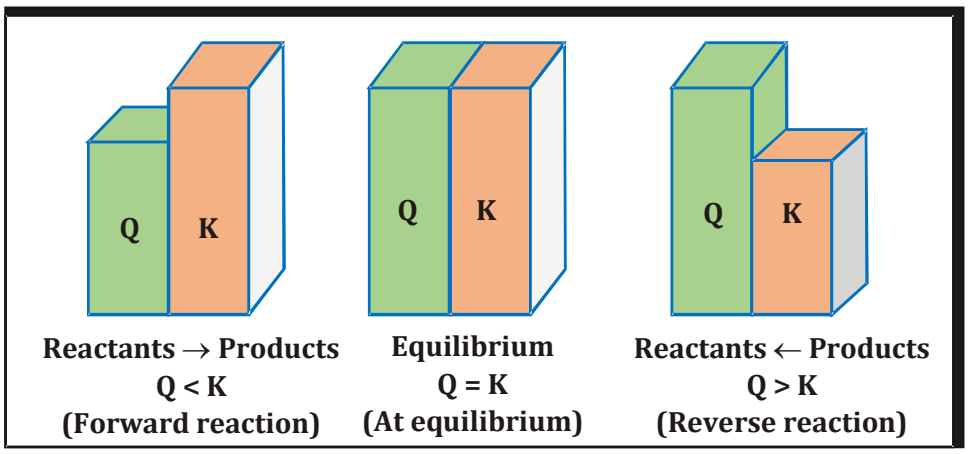
if $Q_C < K_c$, the reaction will move in the direction of the products

if $Q_C = K_c$, the reaction mixture is already at equilibrium.

In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, if the molar concentrations of H_2, I_2 and HI are 0.1 M, 0.2 M and 0.4 M, respectively at 783 K, then reaction quotient at this stage of the reaction is

$$Q_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_C for this reaction at 783 K is 46 and we find that $Q_C < K_C$. The reaction, therefore, will move to right i.e. more $H_2(g)$ and $I_2(g)$ will react to form more HI (g) and their concentration will decrease till $Q_C = K_C$. Thus, a reaction has a tendency to form products if Q < K and to form reactants if Q > K.



Reactants → Products
Q < K
(Forward reaction)

Equilibrium
Q = K
(At equilibrium)

Reactants ← Products
Q > K
(Reverse reaction)

(c) Calculating equilibrium concentrations:

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed :

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction :

(a) the initial concentration,

(b) the change in concentration on going to equilibrium, and

(c) the equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x.

Step 5. Check your results by substituting them into the equilibrium equation.

Some General Equilibrium Expressions:

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

Initially mol	a	b	0
At equilibrium	(a–x)	(b–x)	2x

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

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

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

(b) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

Initially mol	a	0	0
At equilibrium	(a–x)	x/2	x/2

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

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

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

	PCl_5	PCl_3	Cl_2
Initially mol	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) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

	N_2	$3H_2$	$2NH_3$
Initially mol	a	b	0
At equilibrium	(a–x)	(b–3x)	2x
Active mass	$\frac{(a-x)}{V}$	$\left(\frac{b-3x}{V}\right)$	$\left(\frac{2x}{V}\right)$

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

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

Degree of dissociation (α):

It is the fraction of one mole dissociated into products

$$\alpha = \frac{x}{a}\times 100$$

Where α = Degree of dissociation in percentage

x = No. of moles dissociated

a = Given initial no. of moles

M_T = Theoretical molar mass of reactant
M_0 = Observed molar mass of mixture
D_T = Theoretical vapour density
D_0 = Observed vapour density
$D_T = \frac{M_T}{2}$ and $D_0 = \frac{M_0}{2}$

Degree of dissociation in terms of molar mass and vapour density

(i) A(g) $\rightleftharpoons$ nB(g)

$$\alpha = \frac{M_T - M_0}{M_0(n-1)} \quad \text{or} \quad \alpha = \frac{D_T - D_0}{D_0(n-1)}$$

(ii) nA(g) $\rightleftharpoons$ A_n (g)

$$\alpha = \frac{M_T - M_0}{M_0\left(\frac{1}{n} - 1\right)}$$

Illustration 11:

5 moles H_2 gas and 5 moles iodine-vapours are taken in vessel of 10 L capacity. Determine the moles of each at equilibrium. **(Given : $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; K = 49)**

Solution:

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	2HI (g) ;	K = 49
t = 0	5		5		0	
$t = t_{equilibrium}$	5 – x		5 – x		2x	

$$49 = \frac{(2x/V)^2}{\left(\frac{5-x}{V}\right)^2}$$

$$49 = \frac{(2x)^2}{(5-x)^2}$$

$$7 = \frac{2x}{5-x}$$

$35 - 7x = 2x$

$35 = 9x$

$$x = \frac{35}{9}$$

Moles at equilibrium = $\frac{10}{9}, \frac{10}{9}, \frac{70}{9}$

Illustration 12:

How many moles of H_2 (g) should be mixed with each mole I_2 vapours in order to convert 90% of it into HI.

(Given : $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; K = 50)

Solution:

$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	2HI (g);	K = 50
x		1			
x – 0.9		1 – 0.9 = 0.1		1.8	

$$50 = \frac{3.24}{(x-0.9)(0.1)} \Rightarrow x = 1.548$$

Illustration 13:

2 moles of $PCl_5(g)$ is taken in 10 ℓ vessel. Calculate its concentration at equilibrium.

(Given : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; K = 0.2)

Solution:

$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$;	K = 0.2
2 – x		x		x	
$\frac{2-x}{V}$		$\frac{x}{V}$		$\frac{x}{V}$	

$$0.2 = \frac{\left(\frac{x}{V}\right)^2}{\left(\frac{2-x}{V}\right)} \Rightarrow x = 1.24$$

$[PCl_5] = 0.076$ M

$[PCl_3] = 0.124$ M

$[Cl_2] = 0.124$ M

Illustration 14:

1 : 3 molar ratio mixture of N_2 and H_2 yields 20% by mole NH_3 at 30 atm; calculate K_P for the equilibrium.

Solution:

	N_2	+	$3H_2$	$\rightleftharpoons$	$2NH_3$
t = 0	a		3a		0
t = eq.	(a – x)		3(a – x)		2x

Total moles = 4a – 2x

$$X_{NH_3} = 0.2 = \frac{2x}{4a-2x} \Rightarrow 2x = 0.8a - 0.4x \Rightarrow x = a/3$$

$P_{NH_3} = 0.2 \times 30 = 6$ atm

$$P_{NH_3} = X_{N_2} \times P_T = \frac{a-x}{4a-2x} \times 30 = 0.2 \times 30 = 6\,atm$$

$$P_{H_2} = \frac{3(a-x)}{4a-2x} = 0.6 \times 30 = 18\,atm$$

$$\therefore \quad K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{6}{6 \times (18)^2} = 1.03 \times 10^{-3}\ atm^{-2}$$

Illustration 15:

An air sample containing 21:79 (mole ratio) of O_2 & N_2 is heated to 2400°C. If the mole percent of NO at equilibrium is 1.8%, calculate K_P for the reaction $N_2 + O_2 \rightleftharpoons 2NO$.

Solution:

	N_2	+	O_2	$\rightleftharpoons$	2NO
At t = t	0.79 – P		0.21 –P		2P

$X_{NO} = 0.018$

$P_{NO} = 0.018 \times P_T$

$2P = 0.018 \times P_T$ $[\because \Delta n_g = 0 \Rightarrow P_T = 1atm]$

$P = \frac{0.018 \times 1}{2} = 0.009$

$K_P = \frac{[P_{NO}]^2}{P_{N_2} \times P_{O_2}} = \frac{(0.018)^2}{(0.781)(0.201)} = 2.06 \times 10^{-3}$

Illustration 16:

Calculate the degree of dissociation of $PCl_5(g)$ at 20 atm.

(Given : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; K = 0.8 atm)

Solution:

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$;	K = 0.8 atm.
	x		0		0	
	x – a		a		a	

Total mole = x + a

Partial pressure = $\frac{x-a}{x+a}(20)$ $\frac{a}{x+a}(20)$ $\frac{a}{x+a}(20)$

$0.8 = \frac{\left(\frac{a}{x+a}\right)^2 (20)^2}{\left(\frac{x-a}{x+a}\right)20} \Rightarrow 0.04 = \frac{a^2}{x^2 - a^2}$

$\frac{x}{a} = \frac{1}{\sqrt{26}} = 0.2$

$\alpha = 0.2$

Illustration 17:

The vapour density a sample of N_2O_4 (g) is 40 at 10 atm. Calculate K_P for the reaction.

Solution:

	N_2O_4	$\rightleftharpoons$	$2NO_2(g)$
Initial	a		0
	a – x		2x

Total mole = (a – x) + 2x = a + x

$P_{N_2O_4} = \frac{a-x}{a+x}P$ $P_{NO_2} = \frac{2x}{a+x}P$

$V.D. = \frac{M_{avg}}{2}$

$M_{avg} = 2 \times 40 = 80$

$M_{avg} = \frac{\text{Total mass}}{\text{Total moles}} = \frac{92a}{a+x} = 80$

$x = \frac{12}{80}a = 0.15a$

$K_P = \frac{4x^2}{a^2 - x^2} = 9.2 \times 10^{-2}$

Illustration 18:

At what pressure an equimolar mixture of PCl_3 (g) and Cl_2(g) should be taken in order to convert 75% of PCl_3 into PCl_5.

(Given : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; $K_P = 0.4$ atm)

Solution:

	$PCl_3(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$;	$K_P = 0.4$ atm
Initial moles	a		a		0	
Final moles	a – 0.75 a = 0.25a		a – 0.75a = 0.25a		0.75a	

Total mole = 1.25a

Equilibrium partial pressure	$\frac{0.25a \times P}{1.25a}$	$\frac{0.25a \times P}{1.25a}$	$\frac{0.75a \times P}{1.25a}$
	$\frac{P}{5}$	$\frac{P}{5}$	$\frac{3P}{5}$

$$K_P = \frac{P_{PCl_5}}{P_{PCl_3} P_{Cl_2}} \Rightarrow 0.4 = \frac{\frac{3P}{5}}{\frac{P}{5} \times \frac{P}{5}} \Rightarrow P = 37.5$$

But this is pressure at equilibrium but we have to find initial pressure

Now, from PV = nRT

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} \Rightarrow \frac{P_1}{37.5} = \frac{2}{1.25} \Rightarrow P = 60 \text{ atm}$$

Illustration 19:

100 gm $CaCO_3$ is taken in 30 ℓ empty vessel and the vessel is sealed and the sample is heated to 627°C. Calculate the mass % of $CaCO_3$ decomposed.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_P = 0.821$ atm

Solution:

	$CaCO_3(s)$	$\rightleftharpoons$	$CaO(s)$	+	$CO_2(g)$
Initial	1 mole		1		0
Final	1 – x		x		x

Total mole = 1 + x

$$K_P = \frac{P_{CO_2}}{1} = P_{CO_2} \Rightarrow P_{CO_2} = \frac{n.RT}{V}$$

$$0.821 = \frac{x \times 0.0821 \times 900}{30} \Rightarrow x = \frac{1}{3}$$

$$\% \text{ of } CaCO_3 \text{ decomposed} = \frac{1}{3} \times 100 = \frac{100}{3}\%$$

Illustration 20:

Some solid ammonium carbonate NH_4COONH_4 is take in an evacuated vessel and the vessel is sealed. After a very long time a constant pressure of 0.6 atm is observed due to dissociation of the solid into NH_3 and CO_2 gas. Calculate the dissociation constant of solid.

Solution:

	$NH_2COONH_4(s)$	$\rightleftharpoons$	$2NH_3(g)$	+	$CO_2(g)$
Equilibrium partial pressure			$2P$		P
			$= 0.4$ atm		$= 0.2$ atm

$$K_P = \frac{[0.4]^2[0.2]}{1} = 0.032 \text{ atm}^3$$

Illustration 21:

Some solid ammonium hydrogen sulphide NH_4HS is a vessel containing ammonium gas at 0.5 atm. Calculate the equilibrium partial pressure of gas.

(Given : $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$; $K_P = 0.24$ atm^2)

Solution:

	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g); K_P = 0.24$ atm^2
Initial			0.5 atm		0
Equilibrium partial pressure			$0.5 + x$		x

$$K_P = \frac{P_{NH_3}}{1} \cdot P_{H_2S} \Rightarrow 0.24 = (0.5 + x)x \Rightarrow x = 0.3 \text{ atm.}$$

Illustration 22:

0.6 moles of $H_2(g)$ and 0.4 moles of Br_2 vapour are allowed to reactant. Calculate the moles of each gas at equilibrium.

(Given : $H_2(g) + Br_2(g) \rightleftharpoons 2HBr\ (g)$; $K_P = 5 \times 10^8$)

Solution:

	$H_2(g)$	+	$Br_2(g)$	$\rightleftharpoons$	$2HBr\ (g);\ K_P = 5 \times 10^8$
Initial	0.6 moles		0.4 moles		0
Final	$0.6 - x$		$0.4 - x$		$2x$

Total = 1 mole

$$K = \frac{(2x)^2}{(0.6-x)(0.4-x)} = \frac{4x^2}{x^2 - x + 0.24}$$

$(5 \times 10^8 - 4)x^2 - 5 \times 10^8 x + 1.2 \times 10^8 = 0$

$5 \times 10^8 x^2 - 5 \times 10^8 x + 1.2 \times 10^8 = 0$

$8x^2 - x + 0.24 = 0$

$x = 0.4, 0.6$(Not acceptable)

As K_P is much larger than 1000 the reaction almost completes.

Final moles of HBr = 0.8

Final moles of H_2 = 0.2

But Final moles of $Br_2 \neq 0$

Illustration 23:

Calculate concentration of A at equilibrium for a reaction, $A(g) \rightleftharpoons B(g)$; $K_C = 10^{50}$, if the initial concentration of A is 2 M.

Solution:

	$A_{(g)}$ $\rightleftharpoons$	$B_{(g)}$
Initial conc.	2	0
Equilibrium conc.	$2 - x \simeq y$	$0 + x$

K_C is very-very high so maximum reactant converted into product.

$\because \quad \frac{K_C}{\text{initial conc.}} \geq 10^3$ then $\frac{10^{50}}{2} \geq 10^3$.

So $2-x \simeq 0 \Rightarrow x \simeq 2$ but reactant never zero.

eq. conc. $2-x \simeq y, x \simeq 2$

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

$$10^{50} = \frac{x}{2-x}$$

$$10^{50} = \frac{2}{y} \Rightarrow y = 2 \times 10^{-50}\ M$$

$[A] = 2 \times 10^{-50}$ M

Illustration 24:

For the reaction $NOBr\ (g) \rightleftharpoons NO(g) + \frac{1}{2} Br_2\ (g)$

$K_P = 0.15$ atm at 90°C. If NOBr, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 2.0 atm respectively. Will Br_2 be consumed or formed?

Solution:

$$Q_P = \frac{[P_{Br_2}]^{1/2}[P_{NO}]}{[P_{NOBr}]} = \frac{[0.20]^{1/2}[0.4]}{[0.50]} = 0.36$$

$\therefore \quad K_P = 0.15$

Hence, reaction will shift in backward direction

$\therefore$ Br_2 will be consumed

Illustration 25:

Predict weather 1% CO_2 in air be sufficient to prevent any loss in weight of $MgCO_3$ or not.

Solution:

$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$; $\quad K_P = 0.095$ atm

$$Q = \frac{P_{CO_2}}{1} = P_{CO_2} = \chi_{CO_2}.1(atm)$$ (Total pressure = 1 atm)

$\frac{1}{100} \times 1$ atm = 0.01 atm < K_P

It will go in forward direction therefore, 0.1% CO_2 is not sufficient.

Illustration 26:

Predict weather $CuSO_4.5H_2O(s)$ be efflorescent or $CuSO_4.3H_2O(s)$ be hygroscopic, if vapour pressure of H_2O at 25°C is 0.04 atm.

Solution:

$CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$ $\quad K_P = 4 \times 10^{-4}$ atm

Partial pressure of H_2O at equilibrium = P_{H_2O}

$K_p = P_{H_2O}^2$

$P_{H_2O} = \sqrt{4\times10^{-4}} = 2 \times 10^{-2}$ atm

$Q = 4 \times 10^{-2}$ atm

So, $CuSO_4.3H_2O$ will be hygroscopic in this condition.

Le Chatelier's Principle : Le Chatelier's principle is applicable for any system in equilibrium which states as : When a system in equilibrium is disturbed by external agency, the system tends to attain equilibrium once again by adjusting itself. These are some factors by which a system in equilibrium can be disturbed.

(a) Changing the concentration of reactant and product.

(b) Changing the pressure (or volume) of the system.

(c) Changing the temperature.

For a chemical reaction in equilibrium, Le Chatelier's principle can be stated as,

If we change concentration, pressure or temperature of a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimise the change.

Le Chatelier's Principle: Effect of a change in concentration

(a) If more reactant is added or some product is removed from an equilibrium mixture having equilibrium constant K then the reaction moves in the forward direction (as $Q_c < K_C$) to give a new equilibrium and more products are produced.

(b) If more product are added to or some reactant are removed from an equilibrium mixture, the reaction moves in the reverse direction (as $Q_C > K_C$) to give a new equilibrium and more reactant are produced.

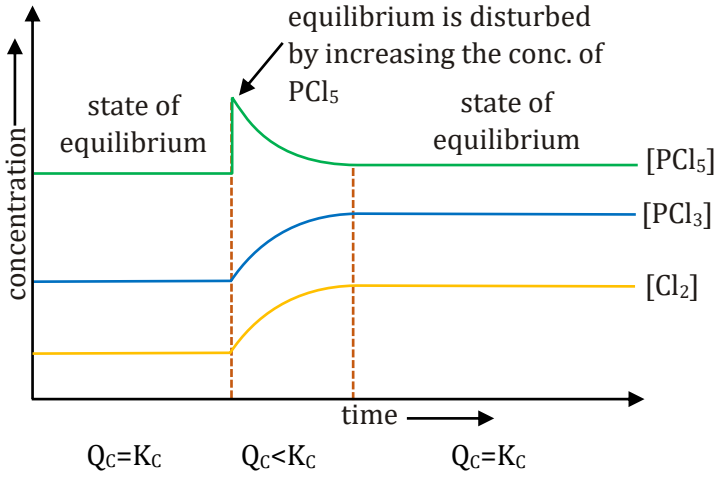
Ex. The decomposition of gaseous PCl_5 is a reversible reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Let the equilibrium concentrations of PCl_5, PCl_3 and Cl_2 are respectively $[PCl_5]$, $[PCl_3]$ and $[Cl_2]$. The K_C for this reaction can be written as :

$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$ Also, we know that at equilibrium $K_C = Q_C$.

Case-I : Let us assume, the equilibrium is disturbed by doubling the concentration of PCl_5. This will change the reaction quotient, Q_C to :

$$Q_C = \frac{[PCl_3][Cl_2]}{[2PCl_5]} = \frac{1}{2}\frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{K_C}{2}$$

After disturbing the equilibrium, the value of Q_C becomes less than K_C. In order to restore the Q_C value to K_C, the concentration of PCl_5 must be decreased while the concentrations of PCl_3 and Cl_2 are to be increased. This is achieved by favouring the forward reaction.

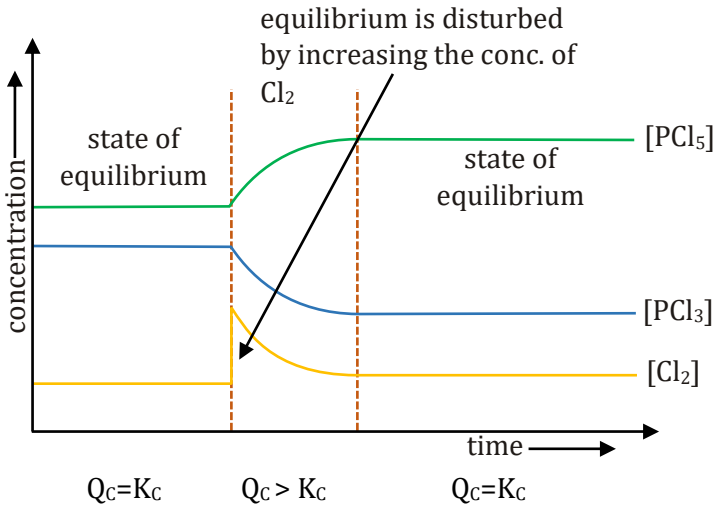


The forward reaction is also favoured by removing the products from the reaction mixture (decrease in the concentration of products). Upon removal of products, the rate of forward reaction becomes greater than that of backward reaction momentarily. This will also decrease the reaction quotient. Hence the system tries to re-establish the equilibrium by converting more reactants to products so as to make the rates of both forward and backward reactions become equal again.

Case-II : For example, in case of the decomposition of PCl_5, if the concentration of Cl_2 is increased by two times at equilibrium, the Q_C value becomes greater than the K_C value.

$$Q_C = \frac{[PCl_3][2Cl_2]}{[PCl_5]} = 2x\frac{[PCl_3][Cl_2]}{[PCl_5]} = 2K_C$$

Hence the system tries to restore the value of Q_C to K_C again. The backward reaction is favoured to decrease the concentration of Cl_2. However, the concentration of PCl_3 also decreases automatically while the concentration of PCl_5 increases while doing so.



Le Chatelier's Principle: Effect of a change in pressure

We know that, if we increase the volume of container then the pressure inside the container decreases and if we decrease the volume of container then the pressure inside the container increases.

i.e., Pressure (P) $\propto \frac{1}{\text{Volume(V)}}$

Hence, if the pressure is decreased by increasing the volume of a reaction mixture, the reaction shifts in the direction of more moles of gas while if the pressure is increased by decreasing the volume of a reaction mixture, the reaction shifts in the direction of fewer moles of gas.

Here moles of reactant or product means co-efficient of reactant or product.

(a) Suppose a general equation

$$A_3(g) + B_3(g) \rightleftharpoons 3AB(g)$$

at eq. a M b M c M

For this reaction, moles of product > moles of reactant i.e., [$\Delta n = (3 - 2) > 0$]

$$K_C = \frac{(c)^3}{a \times b}$$

If we increase the pressure of the system from 0.5 atm pressure to 1 atm pressure by decreasing the volume of container from 5 litre to 2.5 litre. Hence, concentration of all the reactant and product will change and it will be greater than the initial value. Hence, we can say that,

If pressure becomes double then volume becomes half and hence concentration becomes double as

$$\left(\text{Concentration} \propto \frac{\text{Moles}}{\text{Volume}}\right)$$

$\therefore$ Concentration $\propto$ Pressure

$$Q_C = 2 \times \frac{c^3}{a \times b} > K_C$$

Hence reaction will move from right to left i.e. in the backward direction.

Hence,	$A_3(g)$	+	$B_3(g)$	$\rightleftharpoons$	$3AB(g)$
Moles at eq.	2a+x		2b+x		2c–3x

It can be simply said that, reaction will move from right to left by increasing the pressure of the system as moles of product > moles of reactant i.e., move in the direction of fewer moles.

(b) If pressure decreases from 1 atm to 0.5 atm. Volume will increase by a factor of 2, concentration will decrease by a factor of 1/2

Hence,	$A_3(g)$	+	$B_3(g)$	$\rightleftharpoons$	$3AB(g)$
changed conc.	a/2		b/2		c/2
at eq. conc.	a/2–x		b/2 – x		c/2 + 3x

$$Q_C = \frac{(c/2)^3}{a/2 \times b/2} = \frac{1}{2}\left(\frac{c^3}{a \times b}\right) < K_C$$

i.e., $Q_C < K_C$

Therefore, reaction will move from left to right and as moles of product > moles of reactants, therefore reaction will move from left to right by decreasing the pressure of the system i.e. move in the direction of greater moles.

(c) If moles of reactant = moles of product i.e., $\Delta n_g = 0$ then change in pressure of equilibrium mixture has no effect i.e. at this position $Q_C = K_C$ will always exist.

Le Chatelier's Principle: Effect of a change in temperature

Effect of temperature can be Explained by Von't Hoff Relation :

Von't Hoff Relation : $\boxed{\ln\left(\frac{K_2}{K_1}\right)=\frac{\Delta H^\circ}{R}\left(\frac{1}{T_1}=\frac{1}{T_2}\right)}$

Case-I Endothermic Reaction [ΔH=positive] High temperature : $T_2 > T_1$ $K_2 > K_1$

Case-II Exothermic Reaction [ΔH=positive] High temperature : $T_2 > T_1$ $K_2 < K_1$

(i) In case of endothermic reaction:

$T\uparrow$ $K_{eq}\uparrow$ $\Rightarrow$ Reaction shifts in Forword direction to attain equilibrium state.

$T\downarrow$ $K_{eq}\downarrow$ $\Rightarrow$ Reaction shifts in backward direction attain equilibrium state.

(ii) In case of exothermic reaction:

$T\uparrow$ $K_{eq}\downarrow$ $\Rightarrow$ Reaction shifts in backward direction to attain equilibrium state

$T\downarrow$ $K_{eq}\uparrow$ $\Rightarrow$ Reaction shifts in forward direction to attain equilibrium state

Equilibrium constant depends upon the temperature.

$K_{eq.}=\frac{k_f}{k_b}$

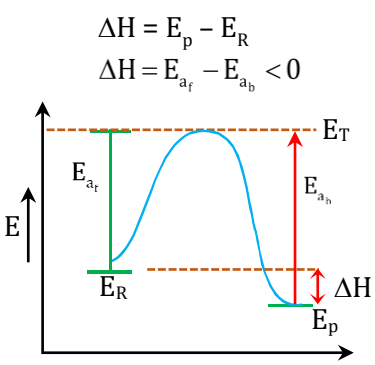
And rate constant, $k=A\cdot e^{-E_a/RT}$

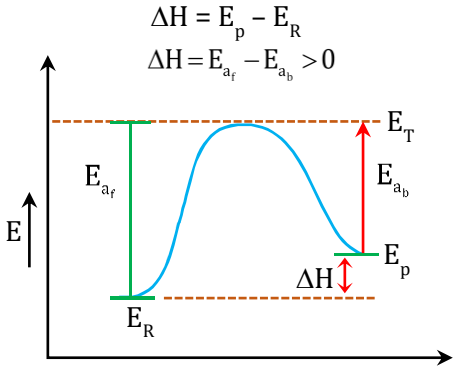
Now, $K_{eq.}=\frac{k_f}{k_b}=\frac{A_f.e^{-E_{a_f}/RT}}{A_b.e^{-E_{a_b}/RT}}=\frac{A_f}{A_b}\cdot e^{-(Ea_f-Ea_b)/RT}$

$K_{eq.}=A\cdot e^{-\Delta H/RT}$ (Van't Hoff's equation)

where $A=\frac{A_f}{A_b}=$ constant

and $\Delta H = E_{a_f} - E_{a_b}$





If K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2, then

$$\ell n\frac{K_2}{K_1}=\frac{\Delta H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

On increasing the temperature, the rate constant of reaction increases. But the reaction with higher activation energy is more sensitive towards temperature change. For the reaction of higher activation energy, the value of rate constant increases largely on increasing temperature as well as the rate constant decreases largely as decrease in temperature.

Illustration 27:

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}

Ans. (B)

Solution:

Using the relation,

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

$$\log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.301 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000} \Rightarrow \Delta H = -71080.57 \text{ J mol}^{-1}.$$

Illustration 28:

From the following data :

(i) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\quad K_{2000K} = 4.4$

(ii) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $\quad K_{2000K} = 5.31 \times 10^{-10}$

(iii) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $\quad K_{1000K} = 2.24 \times 10^{22}$

State whether the reaction (iii) is exothermic or endothermic?

Solution:

Adding (ii) with 2 × (i) and then reversing the net reaction will give (iii) reaction.

$$\therefore \quad K_{2000(iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$\therefore$ $T \uparrow K \downarrow \Rightarrow$ reaction is exothermic.

Le Chatelier's Principle: Effect of addition of inert gas at the equilibrium

(i) Effect of addition of inert gas at constant volume:

When the addition of inert gas (non-reacting gas) is carried out at constant volume (V), the equilibrium remains unaffected for reactions whether they have $\Delta n = 0$ or $\Delta n \neq 0$.

Let us consider a general equation at temperature T K, and a, b, c and d are the moles of A, B, C and D respectively,

	A	+	B	$\rightleftharpoons$	C	+	D
conc.	$\frac{a}{V}$		$\frac{b}{V}$		$\frac{c}{V}$		$\frac{d}{V}$

Since, V = constant, so addition of inert gas has no effect on equilibrium

$\therefore$ $\frac{a}{V}$, $\frac{b}{V}$, $\frac{c}{V}$ and $\frac{d}{V}$ will not change

$Q_C = K_C$ or $Q_P = K_p$

(ii) Effect of addition of inert gas at constant pressure :

(a) The addition of an inert gas at constant pressure to an equilibrium, the equilibrium shifts in the direction of greater number of moles.

At constant pressure, addition of inert gas or non-reacting gas means increase in volume of the system.

Suppose a reaction having $\Delta n > 0$ and a, b, c and d are the moles of A, B, C and D respectively and V be the volume before addition of inert gas.

$A_3(g) + B_3(g) \rightleftharpoons 3AB(g)$

$\frac{a}{V} \quad \frac{b}{V} \quad \frac{c}{V}$ [equilibrium conc. before addition of inert gas]

Let us consider V' be the total volume of the system after addition of inert gas So, V' > V

$A_3(g) + B_3(g) \rightleftharpoons 3AB(g)$

conc. after addition of inert gas $\frac{a}{V'} \quad \frac{b}{V'} \quad \frac{c}{V'}$

$\therefore \frac{a}{V'} < \frac{a}{V}$, $\frac{b}{V'} < \frac{b}{V}$ and $\frac{c}{V'} < \frac{c}{V}$

Now, $K_c = \frac{\left(\frac{c}{V}\right)^3}{\left(\frac{a}{V}\right)\left(\frac{b}{V}\right)} = \frac{1}{V} \times \frac{c^3}{a \times b}$ and $Q_c = \frac{\left(\frac{c}{V'}\right)^3}{\left(\frac{a}{V'}\right)\left(\frac{b}{V'}\right)} = \frac{1}{V'} \times \frac{c^3}{a \times b}$

$K_c > Q_c$, hence reaction will move from left to right (forward direction) as $\Delta n > 0$ and similarly we can prove that for a reaction having $\Delta n < 0$

i.e., $3AB(g) \rightleftharpoons A_3(g) + B_3(g)$

For this reaction $K_c < Q_c$, after addition of inert gas. Hence, reaction will move from right to left (reverse direction) as $\Delta n < 0$.

Le Chatelier's Principle: Application of Le-Chatelier's Principle on physical equilibrium:

The principle is applicable not only to chemical equilibria but also to physical equilibria in similar way.

(a) Dissolution of ammonium chloride in water

$Heat + NH_4Cl(s) + H_2O(\ell) \rightleftharpoons NH_4^{\oplus}(aq) + Cl^{\ominus}(aq)$; ΔH = +ve

With rise in temperature, equilibrium will shift in direction which will lower the temperature i.e. counteract the effect. So, equilibrium shifts in forward direction which is endothermic reaction. Hence, solubility of NH_4Cl increases with rise in temperature.

(b) Dissolution of sodium hydroxide in water

$NaOH(s) + H_2O(\ell) \rightleftharpoons Na^{\oplus}(aq) + OH^{\ominus}(aq) + Heat$; ΔH = –ve

Sodium hydroxide dissolve in water with evolution of heat. Therefore, a rise in temperature will decrease its solubility. On the other hand, a decrease in temperature will increase the solubility of sodium hydroxide and reaction will shift in forward direction.

(c) Effect of pressure on boiling point :

$$\text{Water} \rightleftharpoons \text{Vapour}$$

An increase in pressure will favour backward reaction i.e., the reaction in which volume decreases ($V_{vap.} > V_w$). Thus, more water will exist at equilibrium (Boiling point of solvent increases with increase in pressure). So, decrease in pressure will shift the reaction forward.

(d) Effect of pressure on melting point :

$$\text{Ice} \rightleftharpoons \text{Water}$$

increase in pressure will favour forward reaction because $V_{ice} > V_{water}$. Thus, more ice melt or the melting point of ice is lowered with pressure.

For, $\text{Solid} \rightleftharpoons \text{Liquid}$

An increase in pressure will favour backward reaction because volume of liquid is more than solid thus more solid will exist at equilibrium (melting point of solid increases with pressure).

(e) Effect of pressure on solubility of gases :

$$\text{gas} + H_2O \rightleftharpoons \text{solution}$$

increase in pressure favour forward reaction. [Henry's law]

(f) In solid reactants equilibrium will not shift to the right side even if the more reactants are added.

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

$$K_P = P_{CO_2}$$

Equilibrium will not be affected by adding CaO or $CaCO_3$ at that temperature. But if volume is increased the equilibrium will shift to the right side to keep the pressure of CO_2 constant.

(g) Effect of temperature on solubility

$$\text{Solute} + \text{solvent} \rightleftharpoons \text{solution} + \text{Heat}; \quad \Delta H = +ve$$

An increase in temperature favour endothermic or forward reaction i.e., solubility increases (urea, glucose).

$$\text{Solute} + \text{solvent} \rightleftharpoons \text{solution}; \quad \Delta H = -ve$$

In exothermic dissolution solubility decreases with temperature i.e., reaction will be in backward direction.

Illustration 29:

Manufacture of ammonia from the elements is represented by

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22.4 \text{ kcal}$$

The maximum yield of ammonia will be obtained when the process is made to take place

(A) At low pressure and high temperature (B) At low pressure and low temperature

(C) At high pressure and high temperature (D) At high pressure and low temperature

Ans. (D)

Solution:

Δn_g = negative, ΔH = negative

For maximum yield of ammonia high pressure and low temperature is favourable.

Illustration 30:

In the dissociation of $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociation will be affected by

(A) Increase of temperature (B) Addition of an inert gas

(C) Addition of H_2 and I_2 (D) Increase of pressure

Ans. (A)

Solution:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta n_g = 0$$

At equilibrium $1-\alpha$ $\frac{\alpha}{2}$ $\frac{\alpha}{2}$

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

$\alpha = \frac{2\sqrt{K_C}}{1+2\sqrt{K_C}}$, on increasing the temperature K_C value changes hence α value gets affected.

Illustration 31:

For the chemical reaction

$$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$$

The amount of X_3Y at equilibrium is affected by

(A) Temperature and pressure (B) Temperature only

(C) Pressure only (D) Temperature, pressure and catalyst

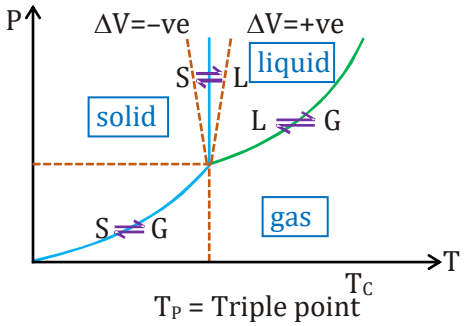
Ans. (A)

Solution:

Δn_g = negative

The amount of X_3Y at equilibrium is affected by temperature and pressure

General observations of Phase diagram:



T_P = Triple point

(i) The combination of temperature and pressure at which all the three-physical state of matter co-exist is called triple point of that matter.

(ii) The vapour pressure of solid is minimum (0) at absolute zero and maximum at triple point.

(iii) The vapour pressure of liquid is minimum at triple point and maximum at critical temperature.

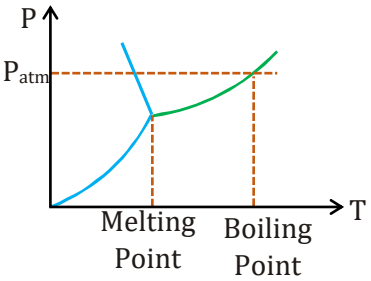
(iv) On each line in the graph, the matter exist in two physical states is equilibrium.

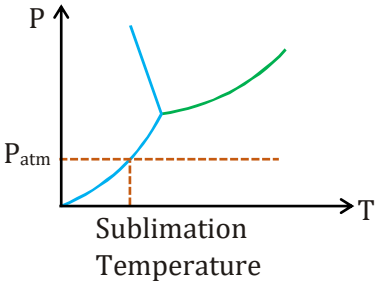
(v) In between two lines, the matter exists in only one physical state.

(vi) The melting point of solid and the triple point of matter differs slightly.

(vii) Any solid may be directly converted into gaseous state or through liquid state by adjusting the external pressure relative to triple point pressure.

(viii)





Simultaneous Equilibrium: If in any container there are two or more equilibria existing simultaneously involving one or more than one common species, then in both/all the equilibria, the concentration of common species is the total concentration of that species due to all the equilibria under consideration.

e.g.	A(s)	$\rightleftharpoons$	X(g)	+	Y(g)
t = 0	a		0		0
$t = t_{eq.}$	a – t		t		t + u
	B(s)	$\rightleftharpoons$	Z(g)	+	Y(g)
	b		0		0
	b – u		u		u + t

$K_{C_1} = t\,(u + t)$

$K_{C_2} = (u + t)\,u$

Illustration 32:

Two solid compounds A and B dissociate into gaseous products at 20°C as

(i) $A(s) \rightleftharpoons A'(g) + H_2S(g)$ (ii) $B(s) \rightleftharpoons B'(g) + H_2S(g)$

At 20°C, pressure over excess solid A is 50 mm and that over excess solid B is 68 mm find

(a) The dissociation constant of A and B

(b) Relative no. of moles of A and B in the vapour phase over a mixture of solid A and B.

(c) Show that the total pressure of the gas over the solid mixture would be 84.4 mm

Solution:

$A(s) \rightleftharpoons A'(g) + H_2S(g)$ $\quad P = 50$ mm $\quad \Rightarrow P_{H_2S} = P_{A'} = \frac{P}{2} = 25$ mm

$B(s) \rightleftharpoons B'(g) + H_2S(g)$ $\quad P = 68$ mm $\quad \Rightarrow P_{H_2S} = P_{B'} = \frac{P}{2} = 34$ mm

(i) $K_{P_1} = (25)^2 = 625\ mm^2$

$K_{P_2} = (24)^2 = 1156\ mm^2$

(ii) Ratio of moles is same as that of partial pressure so,

$A(s) \rightleftharpoons A'(g) + H_2S(g)$

$P_1 \qquad P_1 + P_2$

$B(s) \rightleftharpoons B'(g) + H_2S(g)$

$P_2 \qquad P_2 + P_1$

$K_{P_1} = P_{A'} \times P_{H_2S} = P_1(P_1 + P_2)$ ...(i)

$K_{P_2} = P_{B'} \times P_{H_2S} = P_2(P_1 + P_2)$ ...(ii)

$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_1}{P_2} = \frac{625}{1156}$$

(iii) total pressure = $P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2)$

(i) + (ii) = $(P_1 + P_2)^2$

$\sqrt{K_{P_1} + K_{P_2}} = P_1 + P_2 \quad \Rightarrow \quad P_T = 2\sqrt{K_{P_1} + K_{P_2}} = 84.4\ mm$

Sequential Equilibrium

$A(s) \longrightarrow B(g) + C(g); \qquad K_{C_1} = (x)(x - y)$

$a - x \qquad x \qquad x - y$

$C(g) \longrightarrow D(g); \qquad K_{C_2} = \frac{y}{x - y}$

$x - y \qquad y$

Illustration 33:

102 g of solid NH_4HS is taken in the 2L evacuated flask at 57°C. Following two equilibria exist simultaneously

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

$$NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$$

one mole of the solid decomposes to maintain both the equilibrium and 0.75 mole of H_2 was found at the equilibrium then find the equilibrium concentration of all the species and K_C for both the reaction.

Solution:

Moles of $NH_4HS = \frac{102}{51} = 2$

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g); \qquad K_{C_1}$

$2 \qquad 0 \qquad 0$

$1 \qquad 1 - x \qquad 1$

$NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g); \qquad K_{C_2}$

$1 - x \qquad \frac{x}{2} \qquad \frac{3x}{3}$

Given that moles of $H_2 = \frac{3x}{3} = 0.75 \quad \Rightarrow \quad x = \frac{1}{2}$

$K_{C_1} = \frac{1}{2}\frac{(1-x)}{2} = \frac{1}{8}$ [Since V = 2L]

$K_{C_3} = \frac{\left(\frac{3x}{4}\right)^{3/2}\left(\frac{x}{4}\right)^{1/2}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2}\left(\frac{1}{8}\right)^{1/2}}{\left(\frac{1}{4}\right)} = (3)^{3/2}\frac{1}{64}\times\frac{4}{1} = \frac{(3)^{3/2}}{16}$

Illustration 34:

When $N_2O_5(g)$ is heated it dissociates to give N_2O_3 and O_2. K_c for $N_2O_5 \longrightarrow N_2O_3 + O_2$ is 7.75 and Kc for $N_2O_3 \longrightarrow N_2O + O_2$ is 4.0 mol L^{-1} (both K_c are at same temperature). 4 mol of N_2O_5 in 1.0 L vessel is kept at a certain temperature. The concentration of O_2 was 4.5 mol L^{-1}. Find the concentration of N_2O_5, N_2O_3 and N_2O at equilibrium.

Solution:

(I)	N_2O_5	$\rightleftharpoons$	N_2O_3	+	O_2;	$K_c = 7.75$
	$4 - x$		$x - y$		$x + y$	

(II)	N_2O_3	$\rightleftharpoons$	N_2O	+	O_2;	$K_c = 4$
	x		0		x	
	$x - y$		y		$x + y$	

$\therefore \quad x + y = [O_2] = 4.5$

From I, $K_c = \frac{[N_2O_3][O_2]}{[N_2O_5]}$

$7.75 = \frac{[N_2O_3][O_2]}{[N_2O_5]} = \frac{(x-y)(4.5)}{4-x}$

From II, $K_c = \frac{[N_2O][O_2]}{[N_2O_3]}$, $4 = \frac{y\times(4.5)}{x-y}$

Solve to find x and y [x = 3.06, y = 1.44].

Illustration 35:

1 mol of A in 1 litre vessel maintained at constant T shows the equilibrium

$A(g) \rightleftharpoons B(g) + 2C(g), \quad K_{C_1}$

$C(g) \rightleftharpoons 2D(g) + 3B(g), \quad K_{C_2}$

If the equilibrium pressure is $\frac{13}{6}$ times of initial pressure and $[C]_{eq.} = \frac{4}{9}[A]_{eq.}$, Calculate K_{C_1} and K_{C_2}.

Solution:

$A(g) \rightleftharpoons B(g) + 2C(g)$ and $C(g) \rightleftharpoons 2D(g) + 3B(g)$

1	0	0			
1 – a	(a + 3b)	2a – b	2a – b	2b	(a + 3b)

$\therefore$ Σ mole at equilibrium = 1 – a + a + 3b + 2a – b + 2b

= 2a + 4b + 1

Now, $P_{initial} \propto 1$

$P_{equilibrium} \propto 2a + 4b + 1$

$\therefore \quad 2a + 4b + 1 = \frac{13}{6}$ ...(i)

Or $2a + 4b = \frac{7}{6}$

Also $[C]_{eq.} = \frac{4}{9}[A]_{eq.}$

$2a - b = \frac{4}{9} \times (1-a)$ ...(ii)

By equations (i) and (ii) a = 0.25, b = 0.167

$\therefore \quad K_{C_1} = \frac{[B][C]^2}{[A]} = \frac{(a+3b)(2a-b)^2}{(1-a)}$

$= \frac{[0.25+(3\times0.167)][0.5-0.167]^2}{(1-0.25)} = 0.11$

$\therefore \quad K_{C_2} = \frac{[D]^2[B]^2}{[C]} = \frac{(2b)^2(a+3b)^3}{(2a-b)}$

$= \frac{[2\times0.167]^2[0.25+(3\times0.167)]^3}{[0.5-0.167]} = 0.142$

Thermodynamics involved in reaction at Equilibrium

Let us consider the following reversible reaction

$aA + bB \rightleftharpoons cC + dD$

Gibbs free energy relation : $\Delta G = \Delta G^\circ + RT\ell n\, Q$ ...(i)

Q : Reaction Quotient

ΔG° : Gibbs free energy at the standard state

R : universal gas constant

T : absolute temperature

Standard state : P = 1 bar, Concentration : 1 M Temperature :

any specified temperature default : 25°C (298 K)

At equilibrium state : $\Delta G = 0$, $Q = K_{eq}$ from equation $0 = \Delta G^\circ + RT\ell n\ K_{eq}$ ...(i)

$\Rightarrow\ \Delta G^\circ = -RT \ln K_{eq}$

$\Rightarrow\ \Delta H^\circ - T\Delta S^\circ = -RT\ell n\ K_{eq}$

$\begin{cases}\Delta H^\circ : \text{Entropy of Reaction} \\ \Delta S^\circ : \text{Entropy of Reaction}\end{cases}$

$$\boxed{\ell n\ K_{eq} = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}} \qquad \text{...(ii)}$$

Temp. dependence equation of equation constant

Let at $T = T$, $K_{eq} = K_1$

and $T = T_2$, $K_{eq} = K_2$

from equation : $$\ell n\ K_2 = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2}\right) + \frac{\Delta S^\circ}{R}$$

$$\ell n\ K_1 = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_1}\right) + \frac{\Delta S^\circ}{R}$$

From the above equation:

$$\ell n\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Or $$\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Note : ΔH and ΔS both are temperature terms but in the given temperature range it is considered as constant.

SOLVED EXAMPLE

1. When two reactants, A and B are mixed to give products C and D, the reaction quotient Q at the initial stages of the reaction
(A) is zero.
(B) decreases with time.
(C) is independent of time.
(D) increases with time.

Ans. **(D)**

Sol. At the initial stage means time after start of reaction, not at t = 0.

2. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = \frac{4x^2P}{1-x^2}$, where P = total pressure at equilibrium, x = extent of decomposition.
Which one of the following statements is true?
(A) K_p increases with increase of P.
(B) K_p increases with increase of x.
(C) K_p increases with decrease of x.
(D) K_p remains constant with change in P and x.

Ans. **(D)**

Sol. Equilibrium constant is a function of temperature only.

3. For the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, the value of K_P is

(A) P_{CO_2}

(B) $\frac{P_{CO_2}}{P_{CaCO_3}}$

(C) $\frac{[CaO][CO_2]}{[CaCO_3]}$

(D) $\frac{P_{CaCO_3}}{P_{CaO}P_{CO_2}}$

Ans. **(A)**

Sol. $K_p = \frac{1.P_{CO_2}}{1} = P_{CO_2}$

4. The following reaction has an equilibrium constant K_C equal to 3.07×10^{-4} at 24°C.

$$2NOB(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

The correct set of concentrations at which the rate of forward reaction is greater than that of backward reaction is
(A) [NOBr] = 0.06 M, [NO] = 0.015 M, [Br_2] = 0.01 M
(B) [NOBr] = 0.15 M, [NO] = 0.025 M, [Br_2] = 0.014 M
(C) [NOBr] = 0.18 M, [NO] = 0.012 M, [Br_2] = 0.02 M
(D) [NOBr] = 0.045 M, [NO] = 0.0105 M, [Br_2] = 0.01 M

Ans. **(C)**

Sol. For $r_f > r_b$ means the net reaction in forward direction, the reaction quotient Q should be less than K_{eq}.

5. The equilibrium constant for the reaction $3C_2H_2 \rightleftharpoons C_6H_6$ is 4.0 at T K. If the equilibrium concentration of C_2H_2 is 0.5M, then the concentration of C_6H_6 at equilibrium is

(A) 0.5 M
(B) 1.5 M
(C) 5×10^{-2} M
(D) 0.25 M

Ans. **(A)**

Sol. $K = \frac{[C_6H_6]}{[C_2H_2]^3} \Rightarrow 4 = \frac{[C_6H_6]}{[0.5]^3} \Rightarrow [C_6H_6] = 0.5 \text{ M}$

6. A gaseous mixture contains 0.30 moles of CO, 0.10 moles of H_2, and 0.03 moles of H_2O vapour and an unknown amount of CH_4 per litre. This mixture is in equilibrium at 1200 K.

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$; $K_C = 3.9$

What is the concentration of CH_4 in this mixture?

(A) 0.39 M
(B) 0.039 M
(C) 0.78 M
(D) 0.078 M

Ans. **(B)**

Sol. $K_C = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \Rightarrow 3.9 = \frac{[CH_4] \times 0.03}{0.3 \times (0.1)^3}$

$\Rightarrow [CH_4] = 0.039 \text{ M}$

7. For the reaction $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, $\Delta H^\circ = 18$ kcal and $\Delta S^\circ = 30$ cal/K at 300 K. The equilibrium constant K_P° for the reaction at 300 K is

(A) e^{15} (B) e^{-15}
(C) e^{-18} (D) e^{-12}

Ans. **(B)**

Sol. $\Delta G^\circ = \Delta H^\circ - T.\Delta S^\circ = -RT. \ln K_p^\circ$

or, $18 - 300 \times \frac{30}{1000} = -\frac{2}{1000} \times 300 \times \ln K_p^\circ$

or, $\ln K_p^\circ = -15 \Rightarrow K_p^\circ = e^{-15}$

8. For the gas phase reaction $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $\Delta H = -43.5$ kcal. Which one of the following is true for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$?

(A) K is independent of T.
(B) K decreases as T decreases.
(C) K increases as T decreases.
(D) K varies with addition of NO.

Ans. **(B)**

Sol. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; OH = +43.5 Kcal

For endothermic reactions, K_{eq} increases with the increase in temperature.

9. If K_1 and K_2 are the equilibrium constants for a reversible reaction at T_1 K and T_2 K temperature, respectively ($T_1 < T_2$) and the reaction takes place with neither heat evolution nor absorption, then
(A) $K_1 > K_2$ at high temperature.
(B) $K_1 < K_2$ at high temperature.
(C) $K_1 = K_2$ only at high temperature.
(D) $K_1 = K_2$ at any temperature.

Ans. **(D)**

Sol. $H° = O \Rightarrow K_{eq}$ is independent from T

10. The equilibrium constants for the reaction $A_2 \rightleftharpoons 2A$ at 500 K and 1000 K are 1×10^{-10} and 1×10^{-5}, respectively. The reaction is
(A) exothermic
(B) very slow
(C) very fast
(D) endothermic

Ans. **(D)**

Sol. On increasing temperature, K_{eq} is increasing and hence, the reaction is endothermic.

11. For a gaseous equilibrium $2A(g) \rightleftharpoons 2B(g) + C(g)$, K_P has a value 1.8 at 700K. The value of K_C for the equilibrium $2B(g) + C(g) \rightleftharpoons 2A(g)$ at that temperature is about

(A) 0.031 (B) 32
(C) 57.4 (D) 103.3

Ans. **(B)**

Sol. $K_P = K_C . (RT)^{\Delta Hg}$
or $1.8 = K_C \times (0.0821 \times 700)' \Rightarrow K_C = 0.031$
Hence, for reverse reaction, $K_c' = \frac{1}{K_C} = 31.93$

12. The amounts of 0.8 mol of PCl_5 and 0.2 mole of PCl_3 are mixed in a 1 L flask. At equilibrium, 0.4 mole of PCl_3 is present. The equilibrium constant for the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ will be
(A) 0.05 mol L^{-1} (B) 0.13 mol L^{-1}
(C) 0.013 mol L^{-1} (D) 0.60 mol L^{-1}

Ans. **(B)**

Sol.

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
	0.8 mole	0.2 mole	0
Equilibrium	0.8 – x	0.2 + x	x
	= 0.6	= 0.4	= 0.2
		$\therefore$ x = 0.2	

Now, $K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{0.4}{1}\right) \times \left(\frac{0.2}{1}\right)}{\left(\frac{0.6}{1}\right)} = 0.133$ M

13. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$,

if initial moles of PCl_5 is 'x', α is the degree of dissociation and P is the total pressure at equilibrium, then $P_{PCl_3} \cdot P^{-1}$ is equal to

(A) $\frac{x}{1+x}$ (B) $\frac{\alpha x}{\alpha + x}$

(C) $\frac{\alpha}{1+\alpha}$ (D) $\frac{\alpha}{x+\alpha x}$

Ans. **(C)**

Sol.

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
	X mole		0		0
Equilibrium	$x(1-\alpha)$		$x \cdot \alpha$		$x \cdot \alpha$

E $P_{PCl_3} = \frac{x \cdot a}{x(1+a)} \times P \Rightarrow P_{PCl_3} \cdot P^{-1} = \frac{\alpha}{1+\alpha}$

14. In a 5.76 L vessel, 0.5 moles of H_2 gas and 0.5 moles of I_2 vapours are allowed to react to form HI (g) at 447°C, then the total pressure of gases at equilibrium would be (R = 0.08 L-atm/K-mol)

(A) 20 atm (B) 10 atm

(C) 5 atm (D) 1 atm

Ans. **(B)**

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

As $\Delta n_g = 0$, moles of system is not changing.

$P = \frac{nRT}{V} = \frac{(0.5+0.5)\times 0.08 \times 720}{5.76} = 10$ atm

15. In a closed tube, HI(g) is heated at 440°C up to establishment of equilibrium. If it dissociates into $H_2(g)$ and $I_2(g)$ up to 22%, then the dissociation constant is

(A) 0.282 (B) 0.0796

(C) 0.0199 (D) 1.99

Ans. **(C)**

Sol.

	2HI(g)	$\rightleftharpoons$	H2(g)	+	I2(g)
Equilibrium	$1-\alpha$		$\frac{\alpha}{2}$		$\frac{\alpha}{2}$
	= 0.78		= 0.11		= 0.11

$K = \frac{0.11 \times 0.11}{(0.78)^2} = 0.0199$

16. At 444°C, HI is 30% dissociated. If initially 3 moles of HI are taken, then the number of moles of HI at equilibrium is

(A) 0.9 (B) 2.1

(C) 0.45 (D) 1.8

Ans. **(B)**

Sol. $n_{HI} = 3 - 3 \times \frac{30}{100} = 2.1$

17. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atm. It is heated to 600 K when 20% by mass of N_2O_4(g) decomposes to NO_2(g). The resultant pressure is
(A) 1.2 atm
(B) 2.4 atm
(C) 2.0 atm
(D) 1.0 atm

Ans. **(B)**

Sol.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
	1 mole		0
Final 1	– 0.2		2 × 0.2
	= 0.8 mole		= 0.4 mole

Now, $\frac{P_1}{n_1T_1}=\frac{P_2}{n_2T_2} \Rightarrow \frac{1}{1\times300}=\frac{P_2}{1.2\times600}$

$\Rightarrow$ P_2 = 2.4 atm

18. At total pressure P_1 atm and P_2 atm, N_2O_4 is dissociated to an extent of 33.33% and 50.00%, respectively. The ratio of pressures P_1 and P_2 is
(A) 3 : 8 (B) 2 : 1
(C) 8 : 3 (D) 1 : 2

Ans. **(C)**

Sol. $K_p = \frac{4\alpha^2.P}{1-\alpha^2}$ = Constant

$\therefore \quad \frac{4\times\left(\frac{1}{3}\right)^2\times P_1}{1-\left(\frac{1}{3}\right)^2}=\frac{4\times\left(\frac{1}{2}\right)^2\times P_2}{1-\left(\frac{1}{2}\right)^2} \Rightarrow \frac{P_1}{P_2}=\frac{8}{3}$

19. At 0°C and 1 atm pressure, 1 L of N_2O_4 decomposes to NO_2 according to the equation $N_2O_4(g) \rightleftharpoons 2NO_2$ (g). To what extent has the decomposition proceeded when the original volume is 25% less than that of existing volume?
(A) 0.67 (B) 0.33
(C) 0.25 (D) 0.75

Ans. **(B)**

Sol.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial mole	a		0
Mole at Equilibrium	$a - x$		$2x$

From question, $(a + x) \times \frac{75}{100} = a \Rightarrow = \frac{x}{a} = \frac{1}{3}$

20. In a closed container maintained at 1 atm pressure and 25°C, 2 moles of SO_2(g) and 1 mole of O_2(g) were allowed to react to form SO_3(g) under the influence of a catalyst.

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

At equilibrium, it was found that 50% of SO_2(g) was converted to SO_3(g). The partial pressure of O_2(g) at equilibrium will be
(A) 0.17 atm (B) 0.5 atm
(C) 0.33 atm (D) 0.20 atm

Ans. **(D)**

Sol.

	$2SO_2$	+	O_2	$\rightleftharpoons$	$2SO_3$
	2 mole		1 mole		0
Equilibrium	$2-2\times\frac{50}{100}$		$1-\frac{1}{2}$		1
	= 1		= 0.5		

$\therefore \quad P_{O_2}=\frac{\frac{1}{2}0.5}{2.5}\times 1=0.2 \text{ atm}$

21. For the reaction $XY_2(g) \rightleftharpoons XY(g) + Y(g)$, the reaction is started with initial pressure of XY_2, 600 mm Hg. The total pressure for gases at equilibrium is 800mm Hg. Assuming that volume and temperature of the system remains constant, the value of K_P is

(A) 100 atm (B) 100 mm Hg

(C) 0.01 atm (D) 400 mm Hg

Ans. **(B)**

Sol.

	XY_2	$\rightleftharpoons$	XY	+	Y
	600 mm		0		0
Equilibrium	(600 – x) mm		x mm		x mm

From Question: $(600 - x) + x + x = 800 \Rightarrow x = 200$

$\therefore \quad Kp = \frac{x.x}{(600-x)} = 100 \text{ mm Hg}$

22. For the reaction $A + B \rightleftharpoons C + D$, the initial concentration of A and B is equal, but the equilibrium concentration of C is twice that of equilibrium concentration of A. The equilibrium constant is

(A) 4 (B) 9

(C) ¼ (D) 1/9

Ans. **(A)**

Sol.

	A	+	B	$\rightleftharpoons$	C	+	D
Initial	cM		cM		0		0
Equilibrium	(c – x)M		(c - x)M		x M		x M

From Question: $x = 2 \times (c - x) \Rightarrow x = \frac{2}{3}c$

$\therefore \quad K=\frac{x.x}{(c-x)(c-x)} = 4$

23. $I_2 + I^- \rightleftharpoons I_3^-$. This reaction is set up in aqueous medium. We start with 1 mol of I_2 and 0.5 mol of I^- in 1 L flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mol of yellow precipitate. The equilibrium constant is

(A) 1.33 (B) 2.66

(C) 0.375 (D) 0.75

Ans. **(A)**

Sol. At equilibrium, mole of I^- = mole of AgI (yellow) precipitate

= 0.25

	I_2	+	I–	$\rightleftharpoons$	I_3^-
	1 mole		0.5 mole		0

Equilibrium	$1-x$	$0.5-x$	x
	$=0.75$	$=0.25$	$=0.25$

$\therefore x = 0.25$

$$\therefore K = \frac{\left(\frac{0.25}{1}\right)}{\left(\frac{0.75}{1}\right)\times\left(\frac{0.25}{1}\right)} = 1.33$$

24. The equilibrium constant for the mutarotation, α-D–glucose $\rightleftharpoons$ β–D–glucose is1.8. What percent of the -form remains under equilibrium?

(A) 35.7 (B) 64.3

(C) 55.6 (D) 44.4

Ans. **(A)**

Sol. α – D – Glucose $\rightleftharpoons$ b – D – Glucose

	a	0
Equilibrium	a – x	x

$$K = \frac{x}{a-x} = 1.8 \Rightarrow x = \frac{9}{14}a$$

$$\therefore \%\text{ of – D – Glucose remained} = \frac{a-x}{a}\times 100 = 35.7\ \%$$

25. The value of K_P for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2$ is 640 mm at 775 K. The percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm is

(A) $\frac{100}{\sqrt{2}}$ (B) 50

(C) $\frac{50}{\sqrt{2}}$ (D) $10\sqrt{2}$

Ans. **(A)**

Sol. $$K_p = \frac{4\alpha^2.P}{1-\alpha^2} \Rightarrow 640 = \frac{4\alpha^2\times 160}{1-\alpha^2} \Rightarrow \alpha = \frac{1}{\sqrt{2}}$$

26. At a certain temperature, K_P for the dissociation of solid $CaCO_3$ is 4.5×10^{-2} atm and for the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the K_P value is 2.0 atm. The pressure of carbon monoxide at this temperature, when solid carbon CaO and $CaCO_3$ are mixed together and allowed to attain equilibrium is

(A) 0.09 atm (B) 0.30 atm

(C) 2.1 atm (D) 0.47 atm

Ans. **(B)**

Sol. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$;

$K_p = 4.5 \times 10^{-2}$ atm

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$; $K_p = 2.0$ atm

On adding, $CaCO_3(s) + C(s) \rightleftharpoons CaO(s) + 2CO(g)$;

$Kp = 9 \times 10^{-2}$ atm^2

or $P_{CO}^{\ 2} = 9 \times 10^{-2} \Rightarrow P_{CO} = 0.3$ atm

27. Iron fillings and water were placed in a 5L vessel and sealed. The tank was heated to 1000°C. Upon analysis, the tank was found to contain 1.2 g of $H_2(g)$ and 54.0 g of $H_2O(g)$. If the reaction is represented as $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$, then the value of equilibrium constant is

(A) 0.2
(B) 0.04
(C) 0.008
(D) 0.0016

Ans. **(D)**

Sol.

	$CO_2(g)$	+	$C(s)$	$\rightleftharpoons$	$2CO(g)$
Given:	a mole				9a mole
Required:	b mole				4b mole

28. For a reversible reaction : $X + 2Y \longrightarrow 2Z$, the equilibrium concentrations of X, Y and Z are 0.32, 0.40 and 0.35 moles L^{-1} respectively at 25°C.

a. If initially the system contained only X and Y and then reached the state of equilibrium, what were the initial concentrations of X and Y.
b. If at the start only X and Z were present, what were the initial concentrations?

Sol.

X	+	2Y	$\rightleftharpoons$	2Z
0.32		0.4		0.35 M

$\Rightarrow K = \frac{[Z]^2}{[X][Y]^2} = 2.392$

a.

X	+	2Y	$\rightleftharpoons$	2Z
a		b		–
a – x		b – 2x		2x

$\Rightarrow 2x = 0.35 \Rightarrow x = 0.175$

$\Rightarrow a = [X]_0 = x + 0.32 = 0.495$ M

$b = [Y]_0 = 2x + 0.4 = 0.75$ M

b. Since we start with X and Z

$\Rightarrow$ 'Z' will decompose to produce X and Y.

2Z	$\rightleftharpoons$	X	+	2Y		
p		q				
P – y		q + y/2		y	$\Rightarrow$	y = 0.4 M

$p = [Z] = 0.35 + y = 0.75$ M

$q = [X] = 0.33 - y/2 = 0.12$ M