DAY NINE

Physical and Chemical Equilibrium

Learning & Revision for the Day

- Equilibrium State
- Equilibria Involving Physical Processes
- Equilibria Involving Chemical Processes
- Factor Affecting Equilibrium
- Equilibrium constant (K_p and K_c) and their Significance

Equilibrium is a general term which applies not only to chemical reactions but applies to physical changes as well, e.g. ice and water are in equilibrium at 0°C and atmospheric pressure.

Equilibrium State

In a reversible reaction, the point at which there is no further change in concentration of reactants and products, is called **equilibrium state**. It gives rise to a constant vapour pressure because of an equilibrium in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour.

Some important features of equilibrium state are

(i) Equilibrium is attained in a closed container.

(ii) Rate of forward reaction = Rate of backward reaction.

(iii) At equilibrium, concentration of reactants and products becomes constant.

Concept of Dynamic Equilibrium

Equilibrium is always dynamic in nature, i.e. the reaction does not stop but goes on forward and backward directions with equal speed. In other words, the equilibrium state is a dynamic balance between the forward and backward reaction.

e.g. $\text{solid} \rightleftharpoons \text{liquid}$ (physical equilibria)

$H_2O(s) \rightleftharpoons H_2O(l)$ (273 K, 1 atm)

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (chemical equilibria)

Catalyst helps in attaining the state of equilibrium quickly without changing the state of equilibrium.

Equilibria Involving Physical Processes

The characteristic of system at equilibrium are better understood by physical processes.

This may be attained by the following ways

1. **Solid-liquid equilibrium**

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

   Rate of melting of ice = rate of freezing of water
2. **Liquid-gas equilibrium**

   $$\text{Water} \rightleftharpoons \text{Water vapours}$$

   Rate of evaporation of water
   = rate of condensation of water vapours
3. **Solid-gas equilibrium**

   Certain solids on heating directly change from solid into vapour state (sublimation).

   $$\underset{\text{(solid)}}{\text{Naphthalene}} \rightleftharpoons \underset{\text{(vapour)}}{\text{Naphthalene}}$$

Henry's Law

The equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure is governed by **Henry's law** which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

General Characteristics of Equilibrium Involving Physical Processes

General characteristics of equilibrium involving a physical process are as follows:

(i) At equilibrium, all the measurable properties of the system remain constant.

(ii) Equilibrium is attained only in a closed system at a given temperature.

(iii) Equilibrium is dynamic in nature, i.e. the opposing processes do not stop but take place simultaneously and with the same rate.

(iv) The physical equilibrium is chracterised by constant value of one of its parameter (such as melting point) at a given temperature.

(v) The magnitude of these parameters at any stage shows the extent of physical process upto which it has proceeded before reaching equilibrium.

Equilibria Involving Chemical Processes

The rate of reversible reactions at which the concentration of the reactants and products do not change with time is known as chemical equilibrium.

Active mass = molar concentration (mol/L)

e.g. $H_2 + I_2 \rightleftharpoons 2HI$

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Types of Chemical Equilibrium

On the basis of physical state of reactants and products, equilibrium may be of the following two types:

1. **Homogeneous equilibria**, in which reactants and products are in same phase, e.g.

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

   $$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$
2. **Heterogeneous equilibria**, in which reactants and products are in different phase, e.g.

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

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

Law of Chemical Equilibrium

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as **"law of chemical equilibrium."**

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

Rate of forward reaction $(R_f) \propto [A]^a\,[B]^b$

$\therefore \qquad R_f = k_f\,[A]^a\,[B]^b$

Rate of backward reaction $(R_b) \propto [C]^c\,[D]^d$

$\therefore \qquad R_b = k_b\,[C]^c\,[D]^d$

At equilibrium, $k_f\,[A]^a[B]^b = k_b\,[C]^c[D]^d$

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

where, k_f = rate constant for forward reaction

k_b = rate constant for backward reaction

The above expression is also known as law of chemical equilibrium.

For a gaseous reaction, $K_p = \dfrac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$

where, K_p = equilibrium constant in terms of partial pressure.

Equilibrium Constants (K_p and K_C) and their Significance

The ratio of the concentrations of the products raised to the power of their stoichiometric coefficients to the concentrations of reactants raised to the power of their stoichiometric coefficients at equilibrium state is called the **equilibrium constant** (K).

The equilibrium constant (K) can be expressed in three ways:

1. **Equilibrium constant in terms of molar concentration (K_C).**

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

2. **Equilibrium constant in terms of partial pressure (K_p).**

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

3. **Equilibrium constant in terms of mole fraction (K_χ).**

$$K_\chi = \frac{\chi_C^c \cdot \chi_D^d}{\chi_A^a \cdot \chi_B^b}$$

Significance of equilibrium constants are as follows :

(i) If $K_C > 10^3$, products predominate over reactants. In other words, if K_C is very large, the reaction proceeds almost in all the way to completion.

(ii) If $K_C < 10^{-3}$, reactants predominate over products. In other words, 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.

Equilibrium constant helps in predicting the direction in which given reaction will proceed at any stage. For this purpose, we find out **reaction quotient**.

It is defined as the ratio of the molar concentration or reaction quotient partial pressure of the product species to that of reactant species at any stage in the reaction.

For a general reaction, $aA + bB \rightleftharpoons cC + dD$

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

and

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

At any stage of the reaction,

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

(ii) if $Q_C < K_C$, the reaction will proceed in the direction of the products.

(iii) if $Q_C = K_C$, reaction mixture is already at equilibrium.

Relation between K_p, K_C and K_χ

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

$$K_p = K_\chi\,(p)^{\Delta n_g}$$

R = gas constant, T = temperature in Kelvin

Δn_g = gaseous moles of products – gaseous moles of reactants

Hence,

(i) If $\Delta n_g = 0$, K_p then $= K_C$ (no units for both K_C and K_p)

(ii) If $\Delta n_g = +$ ve, then $K_p > K_C$ (unit of K_C is $(\text{mol L}^{-1})^{\Delta n_g}$ and that of K_p is $(\text{atm})^{\Delta n_g}$)

(iii) If $\Delta n_g = -$ve then $K_p < K_C$ (unit of K_C is $(\text{L mol}^{-1})^{\Delta n_g}$ and that of K_p is $(\text{atm})^{\Delta n_g}$)

Equilibrium constant in terms of activities, K_a

$$K_a = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

Activity = activity coefficient × molality (or molarity)

i.e. $a = \gamma \times m$

Characteristics of Equilibrium Constant

(i) Equilibrium constant (K_p or K_C) does not depend on pressure, volume, concentration and catalyst but depends only upon temperature.

(ii) Equilibrium constant for a given reaction is independent of the reaction mechanism.

(iii) Equilibrium constant depends on stoichiometric coefficient, e.g.

- $H_2(g) + I_2(g) \overset{K_{C_1}}{\rightleftharpoons} 2HI(g)$; K_{C_1}
- $\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \overset{K_{C_2}}{\rightleftharpoons} HI(g)$; $K_{C_2} = \sqrt{K_{C_1}}$
- $HI\,(g) \overset{K_{C_3}}{\rightleftharpoons} \frac{1}{2} H_2(g) + \frac{1}{2} I_2(g)$; $K_{C_3} = \frac{1}{K_{C_2}} = \frac{1}{\sqrt{K_{C_1}}}$

(iv) If a reaction is multiplied by n, the rate constant, K_C becomes $(K_C)^n$. n can be fractional also (+ve only).

(v) If K_1 be equilibrium constant for $P \rightleftharpoons Q$ and K_2 be equilibrium constant for $R \rightleftharpoons S$, equilibrium constant for $P + R \rightleftharpoons Q + S$ is K_1K_2.

(vi) For exothermic reactions, K_C decreases with increase in temperature. For endothermic reactions, K_C increases with increase in temperature. For reactions having zero heat energy, temperature has no effect.

Significance of ΔG and $\Delta G°$ in Chemical Equilibria

- ΔG for a reactions under any set of conditions is related to its value under standard conditions, i.e. $\Delta G°$ by the equation,

$$\Delta G = \Delta G° + 2.303\,RT \log Q$$

- Under equilibrium condition, for same number of moles of reactants and products.

$$Q = K_p = K_C = K \text{ and } \Delta G = 0$$

$$\therefore \quad \Delta G° = -2.303\,RT \log K$$

Significance of $\Delta G°$ are given below:

(i) If $\Delta G° < 0$, $\log K > 1 \Rightarrow K > 1$
Therefore, forward reaction is spontaneous.

(ii) If $\Delta G° > 0$, $\log K < 1 \Rightarrow K < 1$
Therefore, backward reaction is spontaneous.

(iii) If $\Delta G° = 0$, $\log K = 0$, $\Rightarrow K = 1$
Therefore, reaction is at equilibrium.

NOTE **Relation between Degree of Dissociation and Density**

Degree of dissociation (α) of a gaseous compound is related to its vapour density by

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

Here, D = molar density before dissociation / initial density

d = density after dissociation/density of the gaseous mixture

y = number of moles of products

$$\text{Density of gas} = \frac{\text{molecular weight}}{2}$$

Molecular weight = Density of gas × 2

$$M_O = D \times 2 \quad \text{or} \quad M_C = d \times 2$$

Here,

M_O = Observed molecular weight [Abnormal]

M_C = Calculated molecular weight [Theoretical]

Factors Affecting Equilibrium

(Le-Chatelier's Principle)

The principle states that change in any of the factors that determine the equilibrium conditions of a system, will cause the system to change in such a manner, so as to reduce or to counteract the effect of the change.

Different factors affecting equilibrium are discussed below:

1. Effect of Concentration Change

The concentration stress of an added reactant or product is relieved by net reaction in the direction that consumes the added substance. e.g.

$$A + B \rightleftharpoons C$$

(i) If we increase the concentration of either A or B (reactants), the equilibrium goes in the direction that consumes A or B, i.e. forward direction.

(ii) If we increase the concentration of C (product), the equilibrium goes in the direction that consumes C, i.e. backward direction.

(iii) If we remove C (product), the equilibrium goes in the direction in which its concentration increases, i.e. forward direction.

(iv) If any of the species is in solid or liquid state, its addition does not alter the original equilibrium.

Sweet substances cause tooth decay because on fermentation these produce H^+ ions which combine with OH^- ions and shift the equilibrium in forward direction.

$$Ca_5(PO_4)_3OH(s) \underset{\text{Remineralisation}}{\overset{\text{Demineralisation}}{\rightleftharpoons}} 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

2. Effect of Pressure

At high pressure, reaction goes from higher number of moles to lower number of moles or from higher volume to lower volume and *vice-versa*.

(i) If $\Delta n_g = 0$, no effect on equilibrium due to pressure change.

(ii) If $\Delta n_g > 0$, the increase in pressure favours backward reaction.

(iii) If $\Delta n_g < 0$, the increase in pressure favours forward reaction. (Δn_g = number of moles of gaseous products − number of moles of gaseous reactants).

3. Effect of Temperature

At high temperature, reaction goes to **endothermic direction** while at low temperature reaction goes to **exothermic direction.** The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

$$K \propto T;\ \text{if } \Delta H^\circ = +\text{ve} \qquad \text{(endothermic)}$$

$$K \propto \frac{1}{T};\ \text{if } \Delta H^\circ = -\text{ve} \qquad \text{(exothermic)}$$

4. Effect of Catalyst

A catalyst increases the rate of forward reaction as well as the rate of backward reaction, so it does not affect the equilibrium and equilibrium constant.

5. Effect of Inert Gas

At constant volume, there is no effect of addition of inert gas. At constant pressure, when inert gas is added, reaction goes from lower number of moles to higher number of moles.

Application of Le-Chatelier Principle

The Le-Chatelier's principle is applicable to physical as well as chemical equilibria. Some of its applications are mentioned below:

1. To Chemical Equilibria

Haber's processes of synthesis of ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H = -\text{ve}$$

To get better yield of ammonia, required conditions are:

- High pressure as $\Delta n_g = -\text{ve}$
- Low temperature as reaction is exothermic
- High concentration of reactants
- Removal of NH_3

2. To Physical Equilibria

Some of the application for physical equilibria is as follows:

(i) Effect of pressure on melting point

(ii) Ice-water equilibrium,

$$\text{Ice }(s) \rightleftharpoons \text{water }(l)$$

An increase in pressure favours the melting of ice into water because $V_{\text{ice}} > V_{\text{water}}$. Therefore, on increasing pressure, more and more ice will melt.

(ii) **Effect of pressure on solubility of gases**

$$\text{Gas} + \text{solvent} \rightleftharpoons \text{solution}$$

An increase in pressure always favours the dissolution of gas in the solvent. Therefore, solubility of gas increases with increase in pressure.

The amount of gas dissolved per unit volume of solvent is directly proportional to its pressure (Henry's law), i.e. $m \propto p$.

(iii) **Effect of temperature on solubility of solids**

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

An increase in temperature always favours endothermic reaction, therefore solutes having endothermic dissolution show an increase in their solubility with temperature and solutes having exothermic dissolution (dissolution of lime in water) show a decrease in their solubility with temperature.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 In a chemical reaction, the rate constant for the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5. The rate constant for the forward reaction is

(a) 5×10^{-4}
(b) 2×10^{-3}
(c) 1.125×10^{-3}
(d) 9.0×10^{-4}

2 56 g of N_2 and 6 g of H_2 were kept at 400°C in 1 L vessel. The equilibrium mixture contained 27.54 g of NH_3. The approximate value of K_C for the above reaction in $\text{mol}^{-2}\,\text{L}^2$ is

(a) 0.128 (b) 0.118
(c) 0.148 (d) 0.008

3 The concentration of CO_2 which will be in equilibrium with 2.5×10^{-2} mol L^{-1} of CO at 100°C. For the reaction $FeO(s) + CO(g) \rightleftharpoons Fe\,(s) + CO_2\,(g); K_C = 5.0$ will be

(a) 0.5×10^{-1} mol L^{-1} (b) 1.25×10^{-1} mol L^{-1}
(c) 2×10^{-2} mol L^{-1} (d) None of these

4 1.1 moles of A are mixed with 2.2 moles of B and the mixture is kept in a 1 L flask till the equilibrium, $A + 2B \rightleftharpoons 2C + D$ is reached. At equilibrium, 0.2 mole of C is formed. The equilibrium constant of the above reaction is

(a) 0.0002 (b) 0.004
(c) 0.001 (d) 0.003

5 In aqueous solution, the ionisation constants for carbonic acid are $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid. → AIEEE 2010

(a) The concentration of CO_3^{2-} is 0.034 M
(b) The concentration of CO_3^{2-} is greater than that of HCO_3^-
(c) The concentration of H^+ and HCO_3^- are approximately equal
(d) The concentration of H^+ is double that of CO_3^{2-}

6 The standard Gibbs energy change at 300 K for the reaction, $2A \rightleftharpoons B + C$ is 2494. 2 J.

At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}, [B] = 2$ and $[C] = \frac{1}{2}$. The reaction proceeds in the

$[R = 8.314 \text{ JK/mol}, e = 2.718]$ → JEE Main 2015

(a) forward direction because $Q > K_C$
(b) reverse direction because $Q > K_C$
(c) forward direction because $Q < K_C$
(d) reverse direction because $Q < K_C$

7 For the reaction,

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

$[K_C = 1.8 \times 10^{-6}$ at 184°C, $R = 0.00831$ kJ/(mol K)]

when K_p and K_C are compared at 184°C it is found that

(a) whether K_p is greater than, less than or equal to K_C depends upon the total gas pressure
(b) $K_p = K_C$
(c) K_p is less than K_C
(d) K_p is greater than K_C

8 For the reaction, $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, the K_p/K_C is equal to

(a) $1/RT$ (b) RT
(c) $\sqrt{RT}$ (d) 1.0

9 For the following reaction in gaseous phase

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2 . K_C/K_p \text{ is}$$

(a) $(RT)^{1/2}$ (b) $(RT)^{-1/2}$
(c) (RT) (d) $(RT)^{-1}$

10 For the reaction,

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

if $K_p = K_C(RT)^x$ where, the symbols have their usual meaning then the value of x is (assuming ideality) → JEE Main 2014

(a) -1 (b) $-\frac{1}{2}$ (c) $\frac{1}{2}$ (d) 1

11 The ratio $\frac{K_p}{K_C}$ for the reaction,

$$CO(g)+\frac{1}{2}O_2(g)\rightleftharpoons CO_2(g) \text{ is}$$

➞ JEE Main (Online) 2013

(a) $\frac{1}{\sqrt{RT}}$ (b) $(RT)^{1/2}$ (c) RT (d) 1

12 A reversible chemical reaction is having two reactants in equilibrium. If the concentration of the reactants are doubled then the equilibrium constant will

(a) be doubled (b) become one fourth
(c) be halved (d) remain the same

13 Consider the equilibrium reactions,

$$H_3PO_4 \overset{K_1}{\rightleftharpoons} H^+ + H_2PO_4^-$$

$$H_2PO_4^- \overset{K_2}{\rightleftharpoons} H^+ + HPO_4^{2-}$$

$$HPO_4^{2-} \overset{K_3}{\rightleftharpoons} H^+ + PO_4^{3-}$$

The equilibrium constant, K for the following dissociation

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}, \text{ is}$$

(a) $K_1/K_2\cdot K_3$ (b) $K_1\cdot K_2\cdot K_3$
(c) $K_2/K_1\cdot K_3$ (d) $K_1+K_2+K_3$

14 If K_1 and K_2 are the equilibrium constants of the equilibria (I) and (II) respectively, what is the relationship between the two constants ?

I. $SO_2(g)+\frac{1}{2}O_2(g) \overset{K_1}{\rightleftharpoons} SO_3(g)$

II. $2SO_3(g) \overset{K_2}{\rightleftharpoons} 2SO_2(g)+O_2(g)$

(a) $(K_1)^2=\frac{1}{K_2}$ (b) $K_2=(K_1)^2$
(c) $K_1=\frac{1}{K_2}$ (d) $K_1=K_2$

15 For the following three reactions (I), (II) and (III), equilibrium constants are given

I. $CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g); K_1$

II. $CH_4(g)+H_2O(g) \rightleftharpoons CO(g)+3H_2(g); K_2$

III. $CH_4(g)+2H_2O(g) \rightleftharpoons CO_2(g)+4H_2(g); K_3$

Which of the following relation is correct?

(a) $K_3=K_1K_2$ (b) $K_3K_2^3=K_1^2$
(c) $K_1\sqrt{K_2}=K_3$ (d) $K_2K_3=K_1$

16 The equilibrium constant, K_C for the reaction,

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

is 4.9×10^{-2}. The value of K_C for the reaction,

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

will be approximately equal to

(a) 416 (b) 2.40×10^{-3}
(c) 9.8×10^{-2} (d) 4.9×10^{-2}

17 An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is ➞ JEE Main 2018

(a) 5×10^{-8} (b) 3×10^{-20}
(c) 6×10^{-21} (d) 5×10^{-19}

18 $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g); K_1$ ...(i)

$N_2(g)+O_2(g)\rightleftharpoons 2NO(g); K_2$ ...(ii)

$H_2(g)+\frac{1}{2}O_2(g)\rightleftharpoons H_2O(g); K_3$ ...(iii)

The equation for the equilibrium constant of the reaction $2NH_3(g)+\frac{5}{2}O_2(g)\rightleftharpoons 2NO(g)+3H_2O(g), (K_4)$ in terms of K_1, K_2 and K_3 is ➞ JEE Main (Online) 2013

(a) $\frac{K_1K_2}{K_3}$ (b) $\frac{K_1K_3^2}{K_2}$ (c) $K_1K_2K_3$ (d) $\frac{K_2K_3^3}{K_1}$

19 The equilibrium constant (K_C) for the reaction $N_2(g)+O_2(g)\rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_C for the reaction.

$NO(g)\rightleftharpoons\frac{1}{2}N_2(g)+\frac{1}{2}O_2(g)$ at the same temperature is

➞ AIEEE 2012

(a) 0.02 (b) 2.5×10^2 (c) 4×10^{-4} (d) 50.0

20 For the following equilibrium, $N_2O_4\rightleftharpoons 2NO_2$ in gaseous phase, NO_2 is 50% of the total volume when equilibrium is set up. Hence, per cent of dissociation of N_2O_4 is

(a) 50% (b) 25%
(c) 66.66% (d) 33.33%

21 At certain temperature and a total pressure of 10^5 Pa, iodine vapours contains 40% by volume of iodine atoms. K_p for the equilibrium $I_2(g)\rightleftharpoons 2I(g)$ will be

(a) 0.67 (b) 1.5
(c) 2.67×10^4 (d) 9.0×10^4

22 For the reaction, $N_2O_4(g)\rightleftharpoons 2NO_2(g)$ the degree of dissociation at equilibrium is 0.2 at 1 atm pressure. The equilibrium constant, K_p will be

(a) 1/2 (b) 1/4 (c) 1/6 (d) 1/8

23 At 30°C, K_p for the dissociation reaction

$$SO_2Cl_2(g)\rightleftharpoons SO_2(g)+Cl_2$$

is 2.9×10^{-2} atm. If the total pressure is 1 atm, the degree of dissociation of SO_2Cl_2 is (assume, $1-\alpha^2=1$)

(a) 87% (b) 13%
(c) 17% (d) 29%

24 The equilibrium constant K_p for the reaction,

$$PCl_5\rightleftharpoons PCl_3+Cl_2 \text{ is 1.6 at 200°C.}$$

The pressure at which PCl_5 will be 50% dissociated at 200°C is

(a) 3.2 atm (b) 4.8 atm
(c) 2.4 atm (d) 6.4 atm

25 XY_2 dissociates as $XY_2(g) \rightleftharpoons XY(g) + Y(g)$.
When the initial pressure of XY_2 is 600 mm Hg, the total equilibrium pressure is 800 mm Hg. Calculate K for the reaction assuming that the volume of the system remains unchanged.

(a) 50 (b) 100 (c) 166.6 (d) 400.0

26 A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_p is → AIEEE 2011

(a) 1.8 atm (b) 3 atm (c) 0.3 atm (d) 0.18 atm

27 Ammonium carbamate decomposes as

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

For this reaction, $K_p = 2.9 \times 10^{-5} \text{atm}^3$. If we start with 1 mole of the compound, the total pressure at equilibrium would be

(a) 0.0766 atm (b) 0.0581 atm
(c) 0.0388 atm (d) 0.0194 atm

28 In reaction $A + 2B \rightleftharpoons 2C + D$, initial concentration of B was 1.5 times of $[A]$, but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is → JEE Main (Online) 2013

(a) 8 (b) 4 (c) 12 (d) 6

29 The equilibrium constant at 298K for a reaction, $A + B \rightleftharpoons C + D$ is 100. If the initial concentrations of all the four species were 1M each, then equilibrium concentration of D (in mol L^{-1}) will be → JEE Main 2016

(a) 0.818 (b) 1.818
(c) 1.182 (d) 0.182

30 Match standard free energy of the reaction with the corresponding equilibrium constant.

Column I	Column II
A. $\Delta G^\ominus > 0$	1. $K > 0$
B. $\Delta G^\ominus < 0$	2. $K = 1$
C. $\Delta G^\ominus = 0$	3. $K = 0$
	4. $K < 1$

Codes

	A	B	C		A	B	C
(a)	2	1	3	(b)	3	4	1
(c)	4	1	2	(d)	3	1	4

31 On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le-Chatelier's principle. Consider the reaction,

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

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(a) K will remain same
(b) K will decrease
(c) K will increase
(d) K will increase initially and decrease when pressure is very high

32 In the given reaction,

$$2X(g) + Y(g) \rightleftharpoons Z(g) + 80 \text{ kcal}$$

which combination of pressure and temperature gives the highest yield of Z at equilibrium?

(a) 1000 atm and 500°C (b) 500 atm and 500°C
(c) 1000 atm and 100°C (d) 500 atm and 100°C

33 The following reactions are known to occur in the body

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

If CO_2 escapes from the system

(a) pH will decreases
(b) hydrogen ion concentration will diminish
(c) H_2CO_3 concentration will be altered
(d) the forward reaction will be promoted

34 Consider the following equilibrium in a closed container

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

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant K_p and degree of dissociation (α)?

(a) Neither K_p nor α changes
(b) Both K_p and α changes
(c) K_p changes but α does not
(d) K_p does not change but α changes

35 The equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 64. If the volume of the container is reduced to half of the original volume, the value of the equilibrium constant will be

(a) 16 (b) 32 (c) 64 (d) 128

36 The exothermic formation of $ClF_3(g)$ is represented by the equation,

$$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g); \ \Delta H_r = -329 \text{ kJ}$$

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3?

(a) Adding F_2
(b) Increasing the volume of the container
(c) Removing Cl_2
(d) Increasing the temperature

37 Consider the reaction equilibrium,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \quad \Delta H^\circ = -198 \text{ kJ}$$

On the basis of Le-Chatelier's principle, the condition favourable for the forward reaction is

(a) lowering of temperature as well as pressure
(b) increasing of temperature as well as pressure
(c) lowering the temperature and increasing the pressure
(d) any value of temperature and pressure

Direction (Q. Nos. 38-41) *In the following questions Assertion (A) followed by Reason (R) is given. Choose the correct optoin out of the choices given below.*

(a) Both A and R are true and R is the true explanation of A
(b) Both A and R are true but R is not the true explanation of A
(c) A is true but R is true
(d) Both A and R are false

38 **Assertion** (A) In the dissociation of PCl_5 at constant pressure and temperature, addition of helium at equilibrium increases the dissociation of PCl_5.

Reason (R) Helium removes Cl_2 from the field of action.

39 **Assertion** (A) The reaction,

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2(g)$$

is favoured in the forward direction with increase of pressure.

Reason (R) The reaction is exothermic.

40 **Assertion** (A) The equilibrium constant for a reaction having positive $\Delta H°$ increases with increase of temperature.

Reason (R) The temperature dependence of the equilibrium constant is related to $\Delta S°$ and $\Delta H°$ for the reaction.

41 **Assertion** (A) Haber's synthesis of NH_3 is carried out in the presence of a catalyst.

Reason (R) The catalyst shifts the position of the equilibrium of reaction,

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

to the product side.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Formaldehyde polymerises to form glucose according to the reaction, $6HCHO \rightleftharpoons C_6H_{12}O_6$

The theoretically computed equilibrium constant for this reaction is found to be 6×10^{22}. If 1M solution of glucose dissociates according to the above equilibrium, the concentration of formaldehyde in the solution will be

(a) 1.6×10^{-2} M
(b) 1.6×10^{-4} M
(c) 1.6×10^{-6} M
(d) 1.6×10^{-8} M

2 1% CO_2 in air is sufficient to prevent any loss in weight when M_2CO_3 is heated at 120°C.

$$M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(g),$$

$K_p = 0.0095$ atm at 120°C. How much would the partial pressure of CO_2 have to be to promote this reaction at 120°C ?

(a) $p'_{CO_2} < 0.0095$
(b) $p'_{CO_2} = 0.0095$
(c) $p'_{CO_2} > 0.0095$
(d) Cannot be predicted

3 Starting with one mole of O_2 and two moles of SO_2, the equilibrium for the formation of SO_3 was established at a certain temperature. If V is the volume of the vessel and $2x$ is the number of moles of SO_3 present, the equilibrium constant will be

(a) $\dfrac{x^2V}{(1-x)^3}$
(b) $\dfrac{4x^2}{(2-x)(1-x)}$
(c) $\dfrac{(1-x)^3}{2V}$
(d) $\dfrac{x^2}{(2-x)(1-x)}$

4 For $N_2 + 3H_2 \rightleftharpoons 2NH_3$, 1 mole of N_2 and 3 moles of H_2 are at 4 atm. Equilibrium pressure is found to be 3 atm. Hence, K_p is

(a) $\dfrac{1}{(0.5)\,(0.15)^3}$
(b) $\dfrac{1}{(0.5)\,(1.5)^3}$
(c) $\dfrac{3 \times 3}{(0.5)\,(0.5)^3}$
(d) None of these

5 Reaction between nitrogen and oxygen takes place as following

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O\,(g)$$

If a mixture of 0.482 mole of N_2 and 0.933 mole of O_2 is placed in a reaction vessel of volume 10 L and allowed to form N_2O at a temperature for which $K_C = 2.0 \times 10^{-37}$, the equilibrium concentration of $[N_2O]$ will be

(a) 7.06×10^{-20} mol L^{-1}
(b) 6.58×10^{-21} mol L^{-1}
(c) 4.82×10^{-4} mol L^{-1}
(d) 9.36×10^{-7} mol L^{-1}

6 The values of K_{p1} and K_{p2} for the reactions,

$$X \rightleftharpoons Y + Z \quad \ldots(i)$$
$$A \rightleftharpoons 2B \quad \ldots(ii)$$

are in the ratio of 9 : 1. If degree of dissociation of X and A be equal, then total pressure at equilibrium of reactions (I) and (II) are in the ratio.

(a) 3 : 1
(b) 1 : 9
(c) 36 : 1
(d) 1 : 1

7 The following equilibrium constants are given,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3;\ K_1$$
$$N_2 + O_2 \rightleftharpoons 2NO;\ K_2$$
$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O;\ K_3$$

The equilibrium constant for the oxidation of NH_3 by oxygen to given NO is

(a) $\dfrac{K_2K_3^3}{K_1}$
(b) $\dfrac{K_2K_3^2}{K_1}$
(c) $\dfrac{K_2^2K_3^6}{K_1^2}$
(d) $\dfrac{K_1K_2}{K_3}$

8 At 600°C, K_p for the following reaction is 1atm,

$$X(g) \rightleftharpoons Y(g) + Z(g)$$

at equilibrium, 50%, of $X(g)$ is dissociated. The total pressure of the equilibrium system is p atm. What is the partial pressure (in atm) of $X(g)$ at equilibrium?

(a) 1 (b) 4 (c) 2 (d) 0.5

9 N_2 and H_2 in 1 : 3 molar ratio are heated in a closed container having a catalyst. When the following equilibrium, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is attained, the total pressure is 10 atm and mole fraction of NH_3 is 0.60. The equilibrium constant K_p for dissociation of NH_3 is

(a) 1.333 atm^{-2} (b) 0.75 atm^{2}
(c) 0.75 atm^{-2} (d) 1.333 atm^{2}

10 At 77°C and one atmospheric pressure, N_2O_4 is 70% dissociated into NO_2. What will be the volume occupied by the mixture under these conditions if we start with 10g of N_2O_4?

(a) 6.32 L (b) 5.32 L
(c) 6.38 L (d) 5.38 L

11 Volume of the flask in which species are transferred is double of the earlier flask. In which of the following cases, equilibrium constant is affected?

I. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
II. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
III. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
IV. $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

(a) Both I and II (b) Both II and III
(c) Both I and III (d) Both III and IV

12 The rate of the elementary reaction,
$H_2(g) + I_2(g) \longrightarrow 2HI(g)$ at 25°C is given by

$$\text{rate} = 1.7 \times 10^{-18}\ [H_2]\ [I_2]$$

The rate of decomposition of gaseous HI to $H_2(g)$ and $I_2(g)$ at 25°C is rate $= 2.4 \times 10^{-21}\ [HI]^2$. Equilibrium constant for the formation of one mole of gaseous HI from the $H_2(g)$ and $I_2(g)$ is

(a) 708 (b) 354 (c) 0.0014 (d) 26.6

13 In the reaction, $AB(g) \rightleftharpoons A(g) + B(g)$ at 30°C, K_p for the dissociation pressure at equilibrium is 2.56×10^{-2} atm. If the total equilibrium is 1 atm, then the percentage dissociation of AB is

(a) 43.5% (b) 13% (c) 87% (d) 16%

14 The rate of the elementary gaseous phase reaction,

$2NO + O_2 \rightleftharpoons 2NO_2$ at 380°C is given by

$$\text{rate} = 2.6 \times 10^3\ [NO_2]^2[O_2]$$

The rate of the reverse reaction at 380°C is given by

$$\text{rate} = 4.1\ [NO_2]^2$$

Hence, equilibrium constant for the formation of NO_2 by chemical equation, $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ is

(a) 6.34×10^2 (b) 1.577×10^{-3}
(c) 25.18 (d) 3.97×10^{-2}

15 When NH_3 is heated in a 0.50 L flask at 700 K and 100 atm pressure, it decomposes into N_2 and H_2 and their equilibrium moles are given below:

$$\underset{0.30}{2NH_3(g)} \rightleftharpoons \underset{0.30}{N_2(g)} + \underset{0.90}{3H_2(g)}$$

Which of the pairs given represents correct value?

	Initial moles of NH_3	**K_C for NH_3 formation**
(a)	0.80	9.72
(b)	0.90	9.72
(c)	0.80	0.103
(d)	0.90	0.103

ANSWERS

SESSION 1

1 (c)	**2** (c)	**3** (b)	**4** (c)	**5** (c)	**6** (b)	**7** (d)	**8** (a)	**9** (a)	**10** (b)
11 (a)	**12** (d)	**13** (b)	**14** (a)	**15** (a)	**16** (a)	**17** (b)	**18** (d)	**19** (d)	**20** (d)
21 (c)	**22** (c)	**23** (c)	**24** (b)	**25** (b)	**26** (a)	**27** (b)	**28** (b)	**29** (b)	**30** (c)
31 (a)	**32** (c)	**33** (b)	**34** (d)	**35** (c)	**36** (a)	**37** (c)	**38** (c)	**39** (b)	**40** (b)
41 (c)									

SESSION 2

1 (b)	**2** (c)	**3** (a)	**4** (b)	**5** (b)	**6** (c)	**7** (c)	**8** (a)	**9** (b)	**10** (b)
11 (c)	**12** (d)	**13** (d)	**14** (c)	**15** (d)					

Hints and Explanations

SESSION 1

1 $K = k_f / k_b,\ 1.5 = k_f \big/ (7.5 \times 10^{-4})$

or $k_f = 1.125 \times 10^{-3}$

2 $56\text{ g N}_2 = \dfrac{56}{28} = 2\text{ mol}$

$6\text{ g H}_2 = \dfrac{6}{2} = 3\text{ mol}$

$27.54\text{g NH}_3 = \dfrac{27.54}{17} = 1.62\text{ mol}$

At equilibrium $N_2 = \dfrac{1.62}{2} = 0.81$

At equilibrium $H_2 = \dfrac{1.62}{3} = 0.54$

$$\begin{array}{lccc} & N_2 & +\ 3H_2 \rightleftharpoons & 2NH_3 \\ \text{Initial moles} & 2 & 3 & 0 \\ \text{At equil.} & 2 - 0.81 & 3 - 0.54 & 1.62 \\ & = 1.19 & = 2.46 & \end{array}$$

$$K_C = \frac{(1.62)^2}{(1.19)(2.46)^3} = 0.148$$

3 $K_C = \dfrac{[CO_2]}{[CO]}$ or $5 = \dfrac{[CO_2]}{2.5 \times 10^{-2}}$

or $[CO_2] = 1.25 \times 10^{-1}\text{ mol L}^{-1}$

4

$$\begin{array}{lccccc} & A & + & 2B \rightleftharpoons & 2\,C & +\,D \\ \text{Initial moles} & 1.1 & & 2.2 & 0 & 0 \\ \text{Moles at eq.} & 1.0 & & 2.0 & 0.2 & 0.1 \end{array}$$

$$\therefore \quad K = \frac{(0.2/V)^2 (0.1/V)}{(1/V)\ (2/V)^2} = 0.001$$

5 $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-;$

$K_1 = 4.2 \times 10^{-7}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-};$

$K_2 = 4.8 \times 10^{-11}$; Thus, $K_1 >> K_2$

$\therefore \quad [H^+] = [HCO_3^-]$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

So, $[CO_3^{2-}] = K_2 \Rightarrow 4.8 \times 10^{-11}$

6 Given, $\Delta G° = 2494.2\text{ J}$

For the reaction,

$$2A = B + C$$

$$Q = \frac{[B][C]}{[A]^2} = \frac{2 \times (1/2)}{(1/2)^2} = 4$$

$\therefore$ We know, $\Delta G = \Delta G° + RT\ln Q$

$= 2494.2 + 8.314 \times 300 \ln 4$

$= 5951.90 =$ positive value

Also, we have $\Delta G = RT\ln \dfrac{Q}{K_C}$

If ΔG is positive, $Q > K_C$.

Therefore, reaction is spontaneous in reverse direction.

7 $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$K_C = 1.8 \times 10^{-6}$ at 184°C (= 457 K)

$R = 0.00831\text{ kJ mol}^{-1}\text{ K}^{-1}$

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

$\Delta n_g = 3 - 2 = 1$

$\therefore \quad K_p = 1.8 \times 10^{-6} \times 0.00831 \times 457$

$= 7.0637 \times 10^{-6} > 1.8 \times 10^{-6}$

Thus, $K_p > K_C$

8 $K_p = K_C\,(RT)^{\Delta n_g}$

$CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$

$\therefore \quad \Delta n_g = 1 - 2 = -1$

$\therefore \quad K_p = K_C \times (RT)^{-1}$

$$\frac{K_p}{K_C} = (RT)^{-1} = \frac{1}{RT}$$

9 $K_p = K_C\,(RT)^{\Delta n_g} \Rightarrow \Delta n_g = 1 - 1.5 = -0.5$

$K_p = K_C\,(RT)^{-1/2}$

$$\therefore \quad \frac{K_C}{K_p} = (RT)^{1/2}$$

10 For the given reaction, $\Delta n_g = n_p - n_R$

where, $n_p =$ number of moles of products

$n_R =$ number of moles of reactants

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

$$\Delta n_g = 1 - 1.5 = -\frac{1}{2}$$

11 We know that, $K_p = K_C\,(RT)^{\Delta n_g}$

For the given reaction,

$$\Delta n_g = 1 - \left(1 + \frac{1}{2}\right) = -0.5$$

On putting the value of Δn_g,

$$K_p = K_C\,(RT)^{-0.5} \Rightarrow K_p = \frac{K_C}{\sqrt{RT}}$$

$$\frac{K_p}{K_C} = \frac{1}{\sqrt{RT}}$$

12 Equilibrium constant depends only upon the temperature, not upon the concentration of reactant. Thus, on doubling concentration, equilibrium constant remains the same.

13 For the reaction,

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$$

$$K = K_1 \cdot K_2 \cdot K_3$$

14 Reaction (ii) is double and reverse of (i).

Hence, $K_2 = \dfrac{1}{K_1^2}$ or $K_1^2 = \dfrac{1}{K_2}$

15 $K_1 = \dfrac{[CO_2][H_2]}{[CO][H_2O]} \Rightarrow K_2 = \dfrac{[CO][H_2]^3}{[CH_4][H_2O]}$

$$K_3 = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}$$

Thus, $K_1 \times K_2 = K_3$

16 Equilibrium constant for the reaction,

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

$$K_C = \frac{1}{4.9 \times 10^{-2}}$$

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

$$K_C = \left(\frac{1}{4.9 \times 10^{-2}}\right)^2 = \frac{10^4}{(4.9)^2} = 416.493$$

$$\approx 416$$

17 Given, $[H_2S] = 0.10\text{ M}$

$[HCl] = 0.20\text{ M}$ So, $[H^+] = 0.20\text{ M}$

$H_2S \rightleftharpoons H^+ + HS^-;\ K_1 = 1.0 \times 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-};\ K_2 = 1.2 \times 10^{-13}$

It means for,

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$K = K_1 \times K_2 = 1.0 \times 10^{-7} \times 1.2 \times 10^{-13}$

$= 1.2 \times 10^{-20}$

Now, $[S^{2-}] = \dfrac{K \times [H_2S]}{[H^+]^2}$

[according to the final equation]

$$= \frac{1.2 \times 10^{-20} \times 0.1}{(0.2)^2}$$

$$= \frac{1.2 \times 10^{-20} \times 1 \times 10^{-1}\text{ M}}{4 \times 10^{-2}\text{M}}$$

$= 3 \times 10^{-20}\text{M}$

18 In the required equation, NH_3 is on LHS, so invert the equation (i)

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

$$K_5 = \frac{1}{K_1} \qquad \ldots\text{(iv)}$$

Moreover, there are three moles of H_2O, so multiply Eq. (iii) by 3.

$3H_2(g) + \dfrac{3}{2}O_2(g) \rightleftharpoons 3H_2O(g);$

$$K_6 = K_3^3 \qquad \ldots\text{(v)}$$

(because when a reaction is multiplied by n, K becomes K^n).

$$N_2(g)+O_2(g) \rightleftharpoons 2NO(g),\ K_2$$

On adding Eqs. (iv), (ii) and (v) we get

$$2NH_3(g)+\frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g);$$

$$K_4 = K_2 \times K_5 \times K_6$$

On putting the values of K_5 and K_6, we get

$$K_4 = K_2 \cdot \frac{1}{K_1} \cdot K_3^3 = \frac{K_2K_3^3}{K_1}$$

19 $N_2(g)+O_2(g) \rightleftharpoons 2\,NO\,(g)$

$$K_C = \frac{[NO]^2}{[N_2]\,[O_2]} = 4\times 10^{-4}$$

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

$$K_C' = \frac{1}{K_C} = \frac{[N_2]\,[O_2]}{[NO]^2}$$

$$= \frac{1}{4\times 10^{-4}} = \frac{10^4}{4}$$

$$NO(g) \rightleftharpoons \frac{1}{2}N_2(g)+\frac{1}{2}O_2(g)$$

$$K_C'' = \frac{[N_2]^{1/2}\,[O_2]^{1/2}}{[NO]}$$

$$= \sqrt{K_C'} = \sqrt{\frac{10^4}{4}} = \frac{100}{2} = 50$$

20 $$N_2O_4 \rightleftharpoons 2NO_2$$

	N_2O_4	$2NO_2$
Initial at moles	1	0
Moles at equili.	$(1-x)$	$2x$

Total moles $= 1-x+2x = 1+x$

$\therefore$ % of NO_2 by volume $= \dfrac{2x}{1+x}\times 100 = 50$

or $x = \dfrac{1}{3} = 0.33$

Hence, per cent of dissociation of N_2O_4 33.33%.

21 $I_2(g) \rightleftharpoons 2I\,(g)$

Partial pressure of iodine atoms (p_I)

$$= \frac{40}{100}\times 10^5 = 0.40\times 10^5 \text{ Pa}$$

Partial pressure of $I_2(p_{I_2})$

$$= \frac{60}{100}\times 10^5 \text{ Pa} = 0.60\times 10^5 \text{ Pa}$$

$$\therefore \quad K_p = \frac{{p_I}^2}{p_{I_2}} = \frac{(0.40\times 10^5)^2}{0.60\times 10^5}$$

$$= 2.67\times 10^4$$

22 $$N_2O_4 \rightleftharpoons 2\,NO_2$$

	N_2O_4	$2\,NO_2$
Initial moles	a	0
Moles at equili.	$a-0.2a$ $=0.8a$	$0.4a$

Total moles $= 1.2a$

$$p_{N_2O_4} = \frac{0.8a}{1.2a}\times 1 \text{ atm} = 2/3 \text{ atm},$$

$$p_{NO_2} = \frac{0.4a}{1.2a}\times 1 \text{ atm} = 1/3 \text{ atm}$$

$$K_p = \frac{(1/3)^2}{(2/3)} = 1/6$$

23 $$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$$

	SO_2Cl_2	SO_2	Cl_2
Initial	1	0	0
At equil.	$1-\alpha$	α	α

Total moles $= 1+\alpha$

$$p_{SO_2Cl_2} = \frac{1-\alpha}{1+\alpha},\ p_{SO_2} = \frac{\alpha}{1+\alpha},$$

$$p_{Cl_2} = \frac{\alpha}{1+\alpha}$$

$$K_p = \left(\frac{\alpha}{1+\alpha}\right)^2 \Big/ \left(\frac{1-\alpha}{1+\alpha}\right) = \frac{\alpha^2}{1-\alpha^2}$$

$$= \alpha^2;\ (1-\alpha^2 = 1)$$

$$\alpha = \sqrt{K_p} = \sqrt{2.9\times 10^{-2}} = 0.17$$

$\therefore$ Degree of dissociation $= 17\%$

24 $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
Initial moles	1	0	0
Moles at equil.	0.5	0.5	0.5

Total moles $= 1.5$

Partial pressure

$$p_{PCl_5} = \frac{0.5}{1.5}p;\ \ p_{PCl_3} = \frac{0.5}{1.5}p;\ \ p_{Cl_2} = \frac{0.5}{1.5}p$$

(where, p is the total pressure)

$$K_p = \left(\frac{0.5}{1.5}p\right)^2 \Big/ \left(\frac{0.5}{1.5}p\right) = \frac{1}{3}p$$

$$k_p = 1.6 \text{ (Given)}$$

$$\therefore \quad p = 4.8 \text{ atm}$$

25 $$XY_2 \rightleftharpoons XY + Y$$

	XY_2	XY	Y
Initial	600 mm	0	0
At equili.	$600-p$	p	p

Total pressure

$$= 600 - p + p + p = 600 + p$$

or $\quad 600 + p = 800$ mm

$\Rightarrow \quad p = 200$ mm

$$XY_2 = 400 \text{ mm}$$

$$K = \frac{200\times 200}{400} = 100$$

26 $$CO_2(g) + C\,(s) \rightleftharpoons 2CO(g)$$

	$CO_2(g)$	$2CO(g)$
Initial	0.5 atm	0
At equil .	$(0.5-p)$	$2p$ atm

This is a case of heterogeneous equilibrium.

C(s) being solid is not considered.

$$p_{CO_2} + p_{CO} = p_{total}$$

$$0.5 - p + 2p = 0.8$$

$$p = 0.3 \text{ atm}$$

$$\therefore \quad p_{CO_2} = 0.5 - 0.3 = 0.2 \text{ atm}$$

$$p_{CO} = 2p = 0.6 \text{ atm}$$

$$K_p = \frac{p^2_{CO}}{p_{CO_2}} = \frac{0.6\times 0.6}{0.2} = 1.8 \text{ atm}$$

27 At equilibrium, if partial pressure of $CO_2 = p$, and that of $NH_3 = 2p$

$$K_p = p^2_{NH_3} \times p_{CO_2} = (2p)^2 \times p = 4p^3$$

$$K_p = 2.9\times 10^{-5} = 4p^3$$

$$p^3 = 7.25\times 10^{-6}$$

$$p = 1.935\times 10^{-2}$$

Hence, total pressure

$$= 3p \Rightarrow 3\times 1.935\times 10^{-2}$$

$$= 5.81\times 10^{-2} = 0.0581 \text{ atm}$$

28 Let the degree of dissociation $= x$

$$A + 2B \rightleftharpoons 2C + D$$

	A	$2B$	$2C$	D
Initial conc.	1	1.5	0	0
At equili.	$(1-x)$	$(1.5-2x)$	$2x$	x

Given, $\quad (1-x) = (1.5-2x)$

$$1 = 1.5 - 2x + x$$

$$1 = 1.5 - x$$

$$x = 1.5 - 1 = 0.5$$

Equilibrium constant for the reaction

$$K_C = \frac{[C]^2\,[D]}{[A]\,[B]^2} = \frac{(2x)^2\,(x)}{(1-x)\,(1.5-2x)^2} = 4$$

$(\because x = 0.5)$

29 $$A + B \rightleftharpoons C + D$$

	A	B	C	D
Initially at $t=0$	1	1	1	1
At equili.	$1-x$	$1-x$	$1+x$	$1+x$

$$K_{eq} = \frac{[C][D]}{[A][B]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = \frac{(1+x)^2}{(1-x)^2}$$

or $\quad 100 = \left(\dfrac{1+x}{1-x}\right)^2$ or $10 = \dfrac{1+x}{1-x}$

or $\quad 10 - 10x = 1 + x$

$$10 - 1 = x + 10x$$

$$9 = 11x$$

$$x = \frac{9}{11} = 0.818$$

$\therefore$ $[D] = 1 + x = 1 + 0.818 = 1.818$

30 A → 4; B → 1; C → 2

31 In the reaction,

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

If the total pressure at which the equilibrium is established, is increased without changing the temperature, K will remain same. K changes only with change in temperature.

32 Since, $n_p < n_R$ and the reaction is exothermic. So, high pressure and low temperature favour forward reaction. To favour forward reaction, pressure of 1000 atm and temperature of 100°C is required.

33 If CO_2 escapes, equilibrium will shift in the backward direction, so that $[H^+]$ will diminish.

34 K_p is constant at constant temperature. As volume is halved, pressure will be doubled. Hence, equilibrium will shift in the backward direction, i.e. degree of dissociation (α) decreases.

35 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

For this reaction, $\Delta n_g = 0$

$\therefore$ The reaction and its equilibrium constant is not affected by change in volume. Moreover, equilibrium constant depends only on temperature.

36 Reaction is exothermic.By Le-Chatelier's principle, a reaction is spontaneous in forward direction (in the direction of formation of more ClF_3, if F_2 is added, temperature is lowered and ClF_3 is removed.

37 $\Delta n_g = -$ ve ; Reaction takes place with decrease in number of moles or pressure; hence increase in pressure shifts the equilibrium in forward side.

$\Delta H° = -$ ve ; Reaction takes place with evolution of heat or increase in temperature, hence decrease in temperature shifts the equilibrium in forward side.

38 In dissociation of $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the addition of inert gast (He) at constant pressure and temperature results increase in the dissociation of PCl_5 in accordance with Le-Chatelier's principle.

39 With increase of pressure, equilibrium shifts in that direction in which lesser number of gaseous moles are produced.

40 Increased temperature always shifts the equilibrium towards endothermic reaction.

41 Catalyst does not affect equilibrium. It increases the rate of chemical reactions by providing a new low energy pathway for the forward and reverse reactions by exactly the same amount.

SESSION 2

1 A very high value of K for the given equilibrium shows that dissociation of glucose to form HCHO is very small. Hence, at equilibrium, we can take $C_6H_{12}O_6 = 1M$

$$K = \frac{C_6H_{12}O_6}{[HCHO]^6}$$

i.e. $$6 \times 10^{22} = \frac{1}{[HCHO]^6}$$

or $$[HCHO] = \left(\frac{1}{6 \times 10^{22}}\right)^{\frac{1}{6}} = 1.6 \times 10^{-4} M$$

2 $M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(g)$

$\therefore$ $K_p = p'_{CO_2} = 0.0095$ atm

$\because$ CO_2 is 1% in air,

$$\therefore p'_{CO_2} = \frac{1}{100} \times p_{air} = \frac{1}{100} \times 1 = 0.01$$

3 $2SO_2 + O_2 \rightleftharpoons 2SO_3$

Initial	2 mol	1 mol	0 mol
At equil.	$(2-2x)$ $= 2(1-x)$	$(1-x)$	$(2x)$
Molar conc.	$2(1-x)/V$	$(1-x)/V$	$2x/V$

$$K_C = \frac{(2x/V)^2}{[2(1-x)/V]^2 (1-x)/V} = \frac{x^2 V}{(1-x)^3}$$

4 $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Initial	1	3	0
Equili.	$(1-x)$	$(3-3x)$	$2x$

Initial moles, $n_1 = 4$

Pressure, $p_1 = 4$ atm

At equilibrium moles, $n_2 = 4 - 2x$

At equilibrium pressure, $p_2 = 3$ atm

$$\frac{n_2}{n_1} = \frac{p_2}{p_1} \Rightarrow \frac{4-2x}{4} = \frac{3}{4}$$

$$4 - 2x = 3 \quad \text{or} \quad x = 0.5$$

$$\chi_{N_2} = \frac{1-x}{4-2x} = \left(\frac{0.5}{3}\right)$$

$$\chi_{H_2} = \frac{3-3x}{4-2x} = \frac{1.5}{3}$$

$$\chi_{NH_3} = \frac{2x}{4-2x} = \frac{1}{3}$$

$$p_{N_2} = 3 \times \frac{0.5}{3} = 0.5 \text{ atm}$$

$$p_{H_2} = 0.5 \times 3 = 1.5 \text{ atm}$$

and $$p_{NH_3} = \frac{1}{3} \times 3 = 1 \text{ atm}$$

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2}(p_{H_2})^3} = \frac{1}{(0.5)(1.5)^3}$$

5 $2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$

Initial	0.482	0.933	0
At equil.	$(0.482 - 2x)$	$0.933 - x$	$2x$
Active mass	$\left(\frac{0.482-2x}{10}\right)$	$\left(\frac{0.933x}{10}\right)$	$\left(\frac{2x}{10}\right)$

$$K_C = 2.0 \times 10^{-37}$$

Magnitude of K_C is very very small such that at equilibrium

$$\frac{0.482 - 2x}{10} \approx \frac{0.482}{10} = 0.0482$$

$$\therefore \quad [N_2]_{eq} = 0.0482 \text{ mol L}^{-1}$$

$$[O_2]_{eq} = 0.0933 \text{ mol L}^{-1},$$

$$K_C = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

$$2.0 \times 10^{-37} = \frac{\frac{4x^2}{100}}{(0.0482)^2 \; (0.0933)}$$

$$x = 3.29 \times 10^{-20}$$

$$\therefore \quad [N_2O] = \frac{2x}{10}$$

$$\therefore \quad [N_2O] = \frac{2 \times 3.292 \times 10^{-20}}{10}$$

$$= 6.58 \times 10^{-21} \text{ mol L}^{-1}$$

6 Suppose total pressure at equilibrium for reactions (i) and (ii) are p_1 and p_2 respectively, then

$X \rightleftharpoons Y + Z$

Initial moles	1 mol	0	0
Moles at equil.	$1-\alpha$	α	α

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

$$p_X = \frac{1-\alpha}{1+\alpha} \times p_1$$

$$p_Y = \frac{\alpha}{1+\alpha} \times p_1$$

$$p_Z = \frac{\alpha}{1+\alpha} \times p_1$$

$$K_{p_1} = \frac{\left(\frac{\alpha}{1+\alpha} p_1\right)^2}{\frac{1-\alpha}{1+\alpha} \times p_1}$$

$$= \frac{\alpha^2 p_1}{1-\alpha^2} \approx \alpha^2 p_1$$

$A \rightleftharpoons 2B$

Initially	1 mol	0
At equil.	$1-\alpha$	2α

Total moles $= 1 + \alpha$

$$p_A = \frac{1-\alpha}{1+\alpha} \times p_2,$$

$$p_B = \frac{2\alpha}{1+\alpha}p_2$$

$$K_{p\,2} = \frac{\left(\frac{2\alpha}{1+\alpha}p_2\right)^2}{\frac{1-\alpha}{1+\alpha}p_2} = \frac{4\alpha^2}{1-\alpha^2}p_2 = 4\alpha^2 p_2$$

$$\frac{K_{p\,1}}{K_{p\,2}} = \frac{\alpha^2 p_1}{4\alpha^2 p_2} = \frac{p_1}{4p_2} = \frac{9}{1} \text{ (given)}$$

or $$\frac{p_1}{p_2} = \frac{36}{1} = 36:1$$

7 The required equation for the oxidation of NH_3 by oxygen to given NO is

$$4NH_3 + 5O_2 \xrightarrow[800^\circ C]{\text{Pt (gauze)}} 4NO + 6H_2O$$

For this, $$K = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

For the Eq. (i), $$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

For the Eq. (ii), $$K_2 = \frac{[NO]^2}{[N_2][O_2]^{1/2}}$$

For the eq. (iii) $$K_3 = \frac{[H_2O]}{[H_2]\,[O_2]^{1/2}}$$

For getting the K, we must do

$$K_1^2 = \frac{[NH_3]^4}{[N_2]^2[H_2]^6},$$

$$K_2^2 = \frac{[NO]^4}{[N_2]^2[O_2]^2},$$

$$K_3^6 = \frac{[H_2O]^6}{[H_2]^6[O_2]^{\frac{6}{2}=3}},$$

$$K = \frac{K_2^2 \times K_3^6}{K_1^2}$$

On substituting the values, we get

$$K = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

8 $$X(g) \rightleftharpoons Y(g) + Z(g)$$

	$X(g)$	$Y(g)$	$Z(g)$
Initial	1	0	0
At equil.	0.5	0.5	0.5

Total pressure = 1.5

∴ Partial pressure	$\frac{0.5p}{1.5}$	$\frac{0.5p}{1.5}$	$\frac{0.5p}{1.5}$

$$K_p = \frac{p_Y \cdot p_Z}{p_X}$$

$$1 = -\frac{\frac{p}{3}\times\frac{p}{3}}{\frac{p}{3}} \Rightarrow p = 3\,\text{atm}$$

Partial pressure of $X = \frac{p}{3} = 1\,\text{atm}$

9 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Mole fraction of NH_3 $(\chi_{NH_3}) = 0.6$

Mole fraction of N_2 and $H_2 = 1 - 0.6 = 0.4$

Total number of moles of N_2 and $H_2 = 1 + 3 = 4$

Then, $\chi_{N_2} = \frac{1}{4}\times 0.4 = 0.1,$

$\chi_{H_2} = \frac{3}{4}\times 0.4 = 0.3$

Partial pressure of

$N_2(p_{N_2}) = 0.1\times 10 = 1\,\text{atm}$

Partial pressure of

$H_2(p_{H_2}) = 0.3\times 10 = 3\,\text{atm}$

Partial pressure of

$NH_3(p_{NH_3}) = 0.6\times 10 = 6\,\text{atm}$

Dissociation of ammonia

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

$$K_p = \frac{p_{N_2}\times p_{H_2}^3}{p_{NH_3}^2} = \frac{1\,\text{atm}\times(3\,\text{atm})^3}{(6\,\text{atm})^2}$$

$$= \frac{27}{36} = 0.75\,\text{atm}^2$$

10 Molar mass of

$N_2O_4 = 28 + 64 \Rightarrow 92\text{ g mol}^{-1}$

	N_2O_4 $\rightleftharpoons$	$2NO_2$
Initial moles	$\frac{10}{92}$	0
After dissociation	$\frac{10}{92} - \frac{70}{100}\times\frac{10}{92}$	2×0.076
	$= 0.109 - 0.076$	$= 0.152$
	$= 0.033$	

∴ Total moles after dissociation

$= 0.033 + 0.152 = 0.185$

$T = 77^\circ C = 77 + 273\,K = 350\,K$

$pV = nRT$ or $V = \frac{nRT}{p}$

$$= \frac{0.185\,\text{mol}\times 0.0821\text{ L atm K}^{-1}\text{ mol}^{-1}\times 350\,K}{1\text{ atm}}$$

$V = 5.32$ L

11 In case I and III $\Delta n_g \neq 0$, thus, equilibrium constant is affected.

12 $$H_2 + I_2 \longrightarrow 2HI$$

$$\left(\frac{dx}{dt}\right)_f = K_f[H_2][I_2]$$

$$= 1.7\times 10^{-18}\,[H_2][I_2]$$

$$2HI \longrightarrow H_2 + I_2$$

$$\left(\frac{dx}{dt}\right)_b = K_b[HI]^2$$

$$= 2.4\times 10^{-21}\,[HI]^2$$

∴ $H_2 + I_2 \rightleftharpoons 2HI$

$$K_C = \frac{K_f}{K_b} = \frac{1.7\times 10^{-18}}{2.4\times 10^{-21}}$$

∴ $\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$

$K_C = \sqrt{K_C} = 26.6$

13 $$AB(g) \rightleftharpoons A(g) + B(g)$$

∴ $$K_p = p\frac{\alpha^2}{(1-\alpha^2)} = 2.56\times 10^{-2}\text{ atm}$$

$$\alpha^2\times\frac{1\,\text{atm}}{(1-\alpha^2)} = 2.56\times 10^{-2}\text{ atm}$$

Assuming $1 - \alpha \approx 1$

$\Rightarrow$ $\alpha = 0.16\%$ or 16%

14 $(\text{Rate})_f = K_f[NO]^2\,[O_2]$;

$(\text{Rate})_b = K_b[NO_2]^2$

∴ At equilibrium

$$\frac{K_f}{K_b} = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$= \frac{2.6\times 10^3}{4.1} = K_C$$

∴ For $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$

$$K_C{}' = \sqrt{K_C} = 25.18$$

15 $$2NH_3 \rightleftharpoons N_2(g) + 3H_2(g)$$

	$2NH_3$	$N_2(g)$	$3H_2(g)$
Initial	a	0	0
Equil.	$(a-2x)$	x	$3x$

$x = 0.30$

∴ $a - 2x = 0.30$

∴ $a = 0.90$

Thus, initial moles of $NH_3 = 0.90$ mol

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

$$= \frac{\left(\frac{0.30}{0.50}\right)\left(\frac{0.90}{0.50}\right)^3}{\left(\frac{0.30}{0.50}\right)^2} = 9.72$$

Thus, K_C for NH_3 formation

$$= \frac{1}{9.72} = 0.103$$