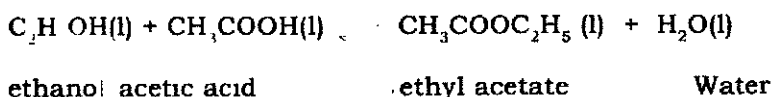


10

CHEMICAL EQUILIBRIUM

10.1 INTRODUCTION

When ethanol and acetic acid are mixed, they react and form ethyl acetate and water.



As soon as ethyl acetate and water are formed, the reverse reaction also starts in which ethanol and acetic acid are formed. After some time, concentrations of all the four substances reach constant values and it is said that a state of equilibrium has been reached.

Whenever two opposing processes, chemical or physical, occur at equal rates in a closed system, a state of equilibrium is reached.

In this unit you will learn about the nature and characteristics of the state of equilibrium.

10.2 OBJECTIVES

After reading this lesson you will be able to :

- identify and differentiate between reversible and irreversible reactions.
 - explain the terms " equilibrium state " and " dynamic equilibrium".
 - list and explain the characteristics of a system at equilibrium.
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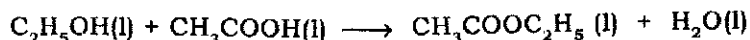
- apply the law of equilibrium and write the expression of equilibrium constant for various types of equilibria, namely, physical, chemical, homogeneous and heterogeneous.
- state and derive the relation between K_c and K_p and Carry out some calculations involving them.
- list the factors which affect the state of equilibrium and state and apply Le chatelliers principle to predict the effects of factors such as concentration, pressure, temperature and _ catalyst on a system at equilibrium.

10.3 REVERSIBLE AND IRREVERSIBLE REACTIONS

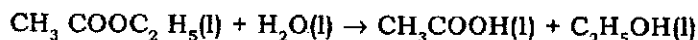
Chemical reactions can be classified as reversible and irreversible reactions.

10.3.1 Reversible Reactions

Consider the reaction between ethanol and acetic acid. When mixed, they react and form ethylacetate and water



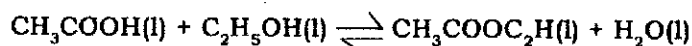
On the other hand, when ethyl acetate and water are mixed, the reverse reaction occurs



Here, both the reactions occur simultaneously and the reaction is called a "reversible reaction "

A reaction is said to be reversible if under certain conditions of temperature and pressure, the forward and reverse reactions occur simultaneously.

Reversible reactions are indicated by placing two half arrows pointing in opposite directions (\rightleftharpoons) between the reactants and products. Thus the above reactions are more appropriately written as :

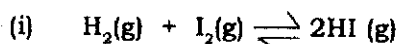


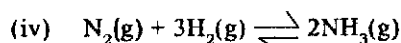
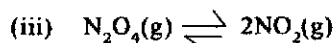
Reversible reactions never reach completion

As we have already seen in section 10.1, after some time the concentrations of all the reactants and products become constant from whichever side the reaction may be started. This happens when the rates of forward and reverse reactions become equal. Now there is no 'net' change in the concentrations of reactants and products and the state of equilibrium is reached. However it may be noted that the state of equilibrium is reached only if the reaction is carried out in a **closed system**, i.e. nothing is permitted to enter or escape from it.

A reversible reaction is said to be in the **equilibrium state** when two opposing reactions occur simultaneously at the same rate in a closed system and the concentrations of the reactants and products do not change with time.

Some Examples of Reversible Reactions

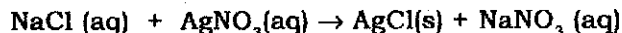




10.3.2 Irreversible Reactions.

Under ordinary conditions of temperature and pressure, most of the reactions occur only in one direction. They are called **irreversible reactions**. However, under a different set of conditions, most of them may proceed in the reverse direction. Under ordinary conditions the reverse reaction is extremely slow and strictly speaking these reactions are also reversible reactions which proceed to almost completion stage leaving only very small amounts of reactants.

For example, when a solution of silver nitrate is added to a solution of sodium chloride, silver chloride is precipitated immediately. The reaction is written as



Which indicates the complete conversion of reactants into the products. However, at the end of the reaction an equilibrium state is reached in which the concentrations of the reactants i.e. sodium chloride and silver nitrate are insignificantly small and taken as zero. All irreversible reactions behave similarly.

10.4 CHARACTERISTICS OF EQUILIBRIUM STATE

The state of chemical equilibrium is reached in a reversible reaction when :

- (i) the temperature of the system attains a constant value.
- (ii) the pressure of the system attains a constant value.
- (iii) the concentrations of all the reactants and products attain constant values.

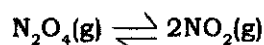
The state of equilibrium has following characteristic properties.

- (i) **Equilibrium is dynamic in nature**

The equilibrium is the result of two equal but opposite processes occurring in the forward and reverse directions and there is no 'net' change occurring in the system.

- (ii) **Equilibrium can be attained from either side**

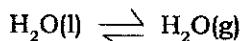
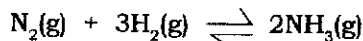
The same state of equilibrium (characterized by its equilibrium constant which is discussed later) is reached whether we start the reaction with reactants or products. For example, the same equilibrium.



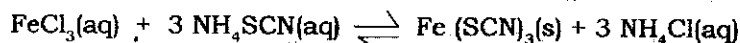
is established whether we start with N_2O_4 or NO_2

(iii) Equilibrium can be attained only in a closed system

Equilibrium can be attained only if no part of system, reactants or products, is allowed to escape i.e. the system is a closed one. Any system consisting of gaseous phase or volatile liquids must be kept in a closed container, e.g.



A system consisting of only non-volatile liquid and solid phases can be kept even in an open container because such substances have no tendency to escape, e.g.

**(iv) A catalyst can not change the equilibrium state**

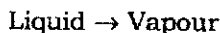
Addition of a catalyst speeds up the forward and reverse reactions by same extent and helps in attaining the equilibrium faster. However, the equilibrium concentrations of reactants and products are not affected in any manner.

10.5 EQUILIBRIUM IN PHYSICAL PROCESSES; PHASE

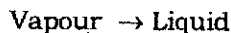
State of equilibrium is the result of two equal but opposite processes and is also reached in physical changes.

10.5.1 Liquid - Vapour Equilibrium

Let us take some quantity of a liquid in an empty container and close it. Initially the pressure above the liquid will be zero. The liquid will evaporate and its vapours will fill the empty space above it.

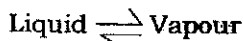


The rate of evaporation is maximum in the beginning. As vapours build up, their pressure increases and the rate of evaporation slows down. Also the reverse process of condensation begins and its rate



gradually increases with the increase in the quantity of vapours.

After some time the two rates (of evaporation and condensation) become equal and the following equilibrium is established



At equilibrium the vapour pressure reaches its maximum value and is known as the **saturated vapour pressure** or simply the vapour pressure. At a fixed temperature, each liquid exerts its own characteristic vapour pressure. The vapour pressure of a liquid increases with rise in temperature.

10.5.2 Solid - Vapour Equilibrium

Volatile solids sublime and form vapours. The situation is just similar to the liquid-vapour system. When kept in a closed container at a constant temperature the following equilibrium is established.

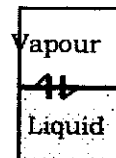


Fig 10.2 Liquid - Vapour equilibrium

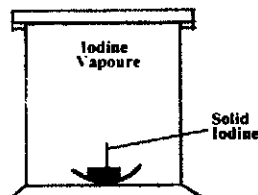
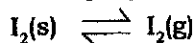


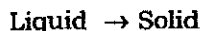
Fig.10.3
Solid vapour equilibrium

Such an equilibrium can be established by keeping some solid iodine in a gas jar and covered with a lid. (Fig. 10.3). Gradually the purple coloured iodine vapour fill the jar and the following equilibrium is established.

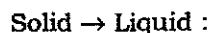


10.5.3 Solid - Liquid Equilibrium

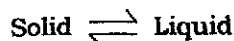
Below its freezing point a liquid freezes spontaneously



When heated above its melting point the solid melts spontaneously :



At the melting point, the two phases are in equilibrium



because the above two processes occur simultaneously and at the same rate. Such an equilibrium is characterized by its temperature i.e. the melting point of the solid.

10.5.4 Solute - Solution Equilibrium

If excess of sugar is added to water at a constant temperature, a part of it dissolves and forms a saturated solution and the rest of it remains undissolved and an equilibrium is established between dissolved and undissolved sugar.

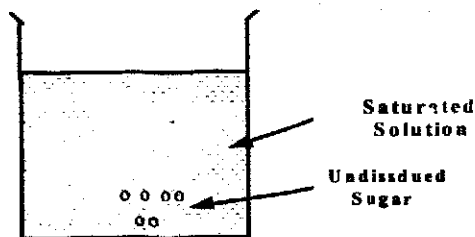
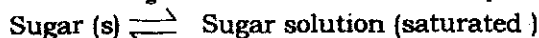
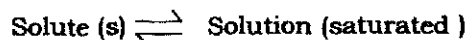


Fig 10.4 Solute - Solution Equilibrium



The equilibrium is established when the rate of dissolution of sugar becomes equal to the rate of crystallization. In general this equilibrium can be represented as



This equilibrium is characterized by the concentration of the saturated solution which is equal to the **solubility of the solute** at the temperature of the solution. That is why this equilibrium is also known as the solubility equilibrium.

10.5.5 Phase and Phase Equilibrium

You must have noticed that in each of the above equilibria (plural of equilibrium) the system consists of two distinct parts out of solid, liquid, solution or vapour. Each of these parts is called a phase.

A phase is defined as a homogeneous part of a system which has uniform composition and properties throughout. A phase is not the same as physical state.

A mixture of two solids, even when powdered finely is a two - phase system. This is because particles of the two solids have different chemical compositions and physical

properties. Completely miscible liquids, solutions and all gaseous mixture constitute only one phase.

All the cases of physical equilibrium are in fact the systems in which different phases are in equilibrium. Such an equilibrium is established between different phases only if they contain at least one common component. It is the dynamic exchange of the components between the phases in two opposite directions but at equal rates that is responsible for the establishment of the equilibrium.

10.6 EQUILIBRIUM IN HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

10.6.1 Homogeneous and Heterogeneous Systems

A system consisting of only one phase is called a homogeneous system.

It has same chemical composition and uniform properties through out. It is formed by particles of molecular size only. Pure solids, liquids and gases and solutions are all examples of homogeneous systems.

On the contrary,

Any system consisting of two or more phases is called heterogeneous system.

A mixture of solids, two immiscible liquids would constitute a heterogeneous system.

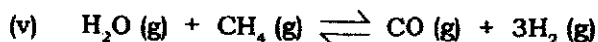
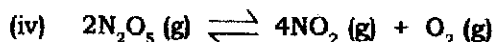
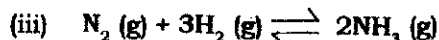
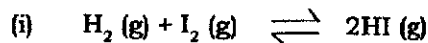
Equilibrium can be established in either type of system. All physical equilibria involve at least two phases and are heterogeneous system. Chemical equilibrium can be homogeneous or heterogeneous. It is homogeneous in nature if all the reactants and products are present in only one phase and heterogeneous in nature if present in more than one phase. In the following sections we shall study systems of both these kinds

10.6.2 Homogeneous Chemical Equilibrium Systems

In such systems all the reactants and products are present in one phase only which may be liquid or gaseous phase.

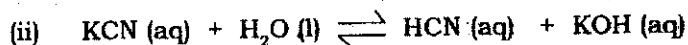
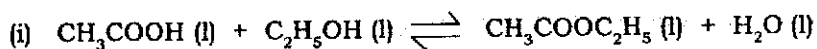
(a) Gas - Phase homogeneous Systems

Such systems contain only gaseous reactants and products. Since all gaseous mixtures are homogeneous in nature they constitute only one phase. Following are some examples of this type.

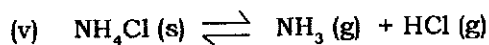
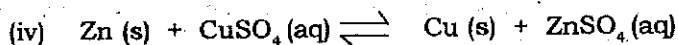
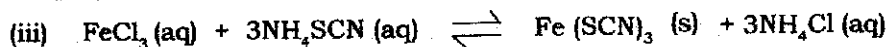
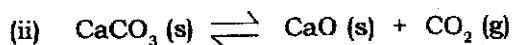
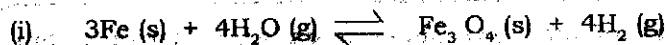


(b) Liquid - phase homogeneous systems

These are the systems in which all the reactants and products are present in one liquid phase (as a solution). For example :

**10.6.3 Heterogeneous Chemical Equilibrium Systems**

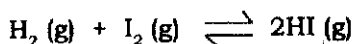
The systems in which reactants and products are present in more than one phase belong to this type. For example :

**INTEXT QUESTIONS 10.1**

1. What is a reversible reaction? Give two examples.
.....
2. When does a reaction reach the equilibrium state?
.....
3. How would you know whether a system has reached the equilibrium state or not?
.....
4. Give two examples of physical equilibrium.
.....
5. What is a phase?
.....
6. Give two example each of chemical, homogeneous and heterogeneous equilibria.
.....

10.7 QUANTITATIVE ASPECTS OF EQUILIBRIUM STATE**10.7.1 Law of Equilibrium And Concentration Equilibrium Constant**

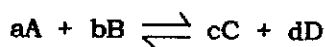
Consider the following equilibrium



At equilibrium the concentrations of H_2 , I_2 and HI become constant. Also it has been found experimentally that irrespective of the starting concentrations of H_2 and I_2 , the following ratio of concentration terms always remains constant (K_c)

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

Here $[H_2]$, $[I_2]$ and $[HI]$ represent the molar concentrations of H_2 , I_2 and HI respectively and K_c is called the concentration equilibrium constant (some times it is written as simply K). In general, for reversible reaction



at equilibrium, the following relation of concentration terms always remains constant at a given temperature.

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

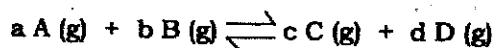
The above relation is known as the **law of equilibrium** and K_c is called the concentration equilibrium constant. It may be noted here that all the concentration values in the law of equilibrium are the equilibrium concentrations of reactants and products. The numerator of the law of equilibrium is the product of equilibrium molar concentrations of products, each term being raised to the power equal to its stoichiometric coefficient in the chemical equation and the denominator contains products of similar concentration terms of reactants.

10.7.2 Pressure Equilibrium Constant K_p .

In case of gases, their partial pressures are used in place of molar concentrations (since the two are directly proportional to each other) in the law of equilibrium. The new equilibrium constant, K_p , is called the pressure equilibrium constant. For the reaction between H_2 and I_2 , K_p is given by

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

Here P_{H_2} , P_{I_2} and P_{HI} are the **equilibrium partial pressures** of H_2 , I_2 and HI respectively. For the general gas phase reaction :

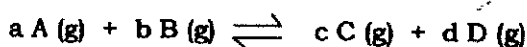


it is given by :

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

10.7.3 Relation between K_p and K_c

For a general gas phase reaction at equilibrium



The pressure and concentration equilibrium constants K_p and K_c are

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \quad \text{and} \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For a gaseous substance 'i', the ideal gas equation is

$$p_i V = n_i RT$$

Where p_i and n_i are its partial pressure and amount in a gaseous mixture and V and T are its volume and temperature and R is the gas constant. The relation may be written as

$$p_i = \frac{n_i}{V} RT$$

$$= c_i RT$$

Where c_i is the molar concentration of 'i' expressed in moles per litre. This relation can be used for replacing the partial pressure terms in the expression for K_p

$$K_p = \frac{(c_C RT)^c (c_D RT)^d}{(c_A RT)^a (c_B RT)^b}$$

$$= \frac{c_C^c \times c_D^d}{c_A^a \times c_B^b} (RT)^{(c+d) - (a+b)}$$

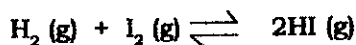
Using the usual square bracket notation for molar concentration the relation can be written as

$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(n_p - n_r)}$$

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

Where Δn_g is the change in the amount of gaseous substances in the reaction and is equal to the difference in the amount of gaseous products, n_p , and the amount of gaseous reactants, n_r . Δn_g may be zero, positive or negative.

(i) In the reaction



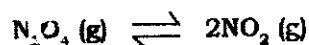
Here n_p = amount of the product = 2

n_r = amount of the reactants, H_2 and $\text{I}_2 = 1 + 1 = 2$

$$\Delta n_g = n_p - n_r = 2 - 2 = 0$$

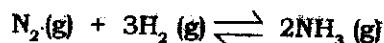
$$\Delta n_g = 0$$

(ii) In the reaction



$n_p = 2$ and $n_r = 1$. Therefore $\Delta n_g = 2 - 1 = 1$

(iii) In the reaction

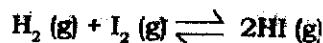


$$n_{\text{p}} = 2; n_{\text{r}} = 1 + 3 = 4 \text{ and } \Delta n_{\text{g}} = 2 - 4 = -2$$

10.8 CHARACTERISTICS OF EQUILIBRIUM CONSTANT

10.8.1 Equilibrium Constant and Chemical Equation

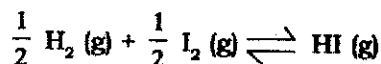
The expression of equilibrium constant depends upon the manner in which the chemical equation representing it is written. For the reaction



The equilibrium constant K is given by

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

When the same reaction is written as



the corresponding equilibrium constant K' is given by

$$K' = \frac{[\text{HI}]^2}{[\text{H}_2]^{1/2} [\text{I}_2]^{1/2}}$$

The two equilibrium constant K and K' are related as

$$K' = \sqrt{K}$$

Similar relationship is also observed in the pressure equilibrium constant K_p . Thus the expression of equilibrium constant depends upon how the reaction is expressed in the form of a chemical equation.

10.8.2 Units of Equilibrium Constant

Units of equilibrium constant (K_c or K_p) depend upon the fact whether during the reactions there is any change in the amount of substance or not. This can be seen in the following examples.

(a) **The reactions in which there is no change in amount of substances i.e. $\Delta n = 0$**

The equilibrium constant K for such reaction has no units. Consider the reaction between H_2 and I_2 , which is of this type



As seen earlier, $\Delta n = \Delta n_p - \Delta n_r = 2 - 2 = 0$. Here

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2] [\text{I}_2]} \quad ; \quad K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} \times P_{\text{I}_2}}$$

$$K_c = \frac{(\text{concentration})^2}{\text{concentration} \times \text{concentration}} \quad \text{and} \quad K_p = \frac{(\text{pressure})^2}{\text{pressure} \times \text{pressure}}$$

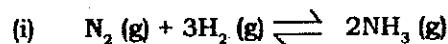
$$K_c = \frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1}) \times (\text{mol L}^{-1})} \quad ; \quad K_p = \frac{(\text{Pa})^2}{\text{Pa} \times \text{Pa}}$$

$$\therefore K_p = K_c$$

The unit in the numerator and denominator cancel out each other and K_p have no units :

(b) The reaction in which there is change in amounts of substances i.e. $\Delta n \neq 0$

The equilibrium constant for such reactions has units which depend upon the change in amounts of substances.



$$\Delta n = 2 - 4 = -2$$

The equilibrium constant of the reaction are :

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3} \quad \text{and} \quad K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3}$$

$$K_c = \frac{(\text{concentration})^2}{\text{concentration} \times (\text{concentration})^3} \quad ; \quad K_p = \frac{(\text{pressure})^2}{\text{pressure} \times (\text{pressure})^3}$$

$$\text{or } K_c = \frac{1}{(\text{concentration})^2} \quad ; \quad K_p = \frac{1}{(\text{pressure})^2}$$

$$\text{or } K_c = (\text{concentration})^{-2} \quad ; \quad K_p = (\text{pressure})^{-2}$$

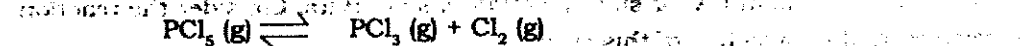
$$\text{or } K_c = (\text{concentration})^{\Delta n} \quad ; \quad K_p = (\text{pressure})^{\Delta n}$$

$$\text{or } K_c = (\text{mol L}^{-1})^{\Delta n} \quad ; \quad K_p = (\text{Pa})^{\Delta n}$$

$$\text{or } K_c = \text{L}^2 \text{mol}^{-2} \quad ; \quad K_p = \text{Pa}^{-2}$$

If the pressure is expressed in its common unit of atmosphere, the unit of K_p is atm

In the reaction



$$n_r = 1; n_p = 1 + 1 = 2 \quad \text{and} \quad \Delta n = 2 - 1 = +1$$

The units of K_c and K_p are

$$K_c = \frac{(\text{concentration})^{\Delta n}}{\dots} \text{ and } K_p = \frac{(\text{Pressure})^{\Delta n}}{\dots}$$

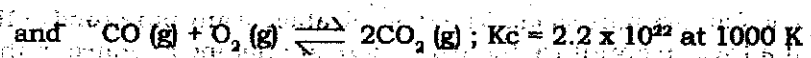
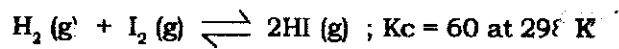
$$= \frac{\text{concentration}}{\dots} \text{ Pressure}$$

$$= \text{mol L}^{-1} \dots \text{ Pa or atm}$$

10.8.3 Significance of the magnitude of K

Equilibrium constant of a reaction has a constant and characteristic value. The changes in starting concentrations, pressure and the presence of a catalyst do not change the value of the equilibrium constant. However, if the temperature is changed, the value of equilibrium constant also changes.

The magnitude of the equilibrium constant is a measure of the extent up to which a reaction proceeds before the equilibrium is reached. A large magnitude of K is obtained when the products are present in larger amounts than the reactants in the equilibrium mixture.



A very large value of K_c for the second reaction indicates that at equilibrium only negligible amount of reactants is left unreacted and products are present in very large excess. i.e. the reaction proceeds to almost completion.

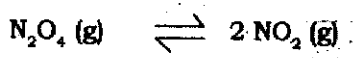
A comparatively low values of K_c for the first reaction indicates that quite significant amounts of reactants are still present at equilibrium. Thus, the magnitude of equilibrium constant tells us about the position of the equilibrium.

10.9 EXPRESSIONS OF EQUILIBRIUM CONSTANTS FOR SOME REACTIONS

The law of equilibrium can be applied to write down expressions of K_c and K_p for any reaction.

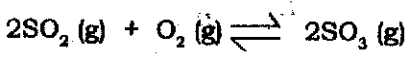
10.9.1 Homogeneous Equilibria

(i) Decomposition of N_2O_4

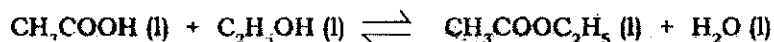


$$K_c = \frac{[NO_2]^2}{[N_2O_4]} ; K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

(ii) Oxidation of sulphur dioxide



$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} ; K_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}$$

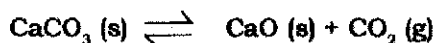
(iii) Esterification of acetic acid with ethanol

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}] [\text{C}_2\text{H}_5\text{OH}]}$$

In this reaction no gas is involved, therefore expression for K_p cannot be written.

10.9.2 Heterogeneous Equilibria

Consider the following equilibrium



According to the law of equilibrium

$$K_c = \frac{[\text{CaO}] [\text{CO}_2]}{[\text{CaCO}_3]}$$

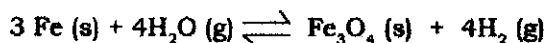
Here CaCO_3 and CaO are pure solids. The concentration of any pure solid or liquid is constant at a fixed temperature therefore these are not incorporated in the expression for equilibrium constant for heterogeneous reactions. Thus the equilibrium constant for the reaction can be written as

$$K_c = [\text{CO}_2] \text{ and } K_p = P_{\text{CO}_2}$$

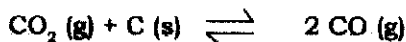
Following are some more examples of heterogeneous equilibrium systems :

(i) Decomposition of ammonium chloride

$$K_c = [\text{NH}_3] [\text{HCl}] \quad ; \quad K_p = P_{\text{NH}_3} \times P_{\text{HCl}}$$

(ii) Reaction between iron and steam

$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} \quad ; \quad K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$$

(iii) Reaction between carbon and carbon dioxide

$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} \quad ; \quad K_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}$$

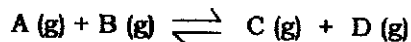
(iv) Liquid - Vapour Equilibrium

$$K_c = [\text{H}_2\text{O, g}] \quad ; \quad K_p = P_{\text{H}_2\text{O}}$$

10.10 CALCULATION OF EQUILIBRIUM CONSTANTS

Equilibrium constants K_c and K_p can be calculated if the equilibrium concentrations or partial pressures are known or can be obtained from the given data. The following examples illustrate the calculations.

Example 10.1 : Calculate the equilibrium constant for the reaction



If at equilibrium 1 mol of A, 0.5 mol of B, 3.0 mol of C and 10 mol of D are present in a one litre vessel.

Solution : From the law of equilibrium

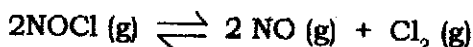
$$K_c = \frac{[C][D]}{[A][B]}$$

Since the volume of the vessel is one litre, the number of moles of A, B, C and D are eq 1a to their concentrations. Thus

$[A] = 1 \text{ mol L}^{-1}$, $[B] = 0.5 \text{ mol L}^{-1}$, $[C] = 3.0 \text{ mol L}^{-1}$ and $[D] = 10 \text{ mol L}^{-1}$ and

$$\begin{aligned} K_c &= \frac{(3.0 \text{ mol L}^{-1})(10 \text{ mol L}^{-1})}{(1 \text{ mol L}^{-1})(0.5 \text{ mol L}^{-1})} \\ &= \frac{3.0 \times 10}{1 \times 0.5} = 60 \end{aligned}$$

Example 10.2 In an experiment carried out at 298 K, 4.0 mol of NOCl were placed in a 2 litre flask and after the equilibrium was reached 1.32 mol of NO were formed. Calculate K_c at 298 K for the reaction



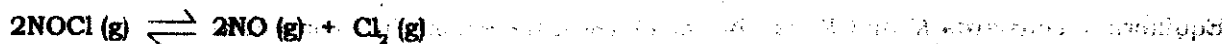
Solution Calculation of equilibrium concentrations

$$(i) \quad [\text{NO}] = \frac{\text{No. of moles of NO}}{\text{Volume}} = \frac{1.32 \text{ mol}}{2\text{L}} = 0.66 \text{ mol L}^{-1}$$

$$(ii) \quad [\text{Cl}_2] = \frac{\text{No. of moles of Cl}_2}{\text{Volume}} = \frac{\frac{1}{2} (\text{No. of moles of NO})}{\text{Volume}} = \frac{1.32 \text{ mol}}{2 \times 2\text{L}} = 0.33 \text{ mol L}^{-1}$$

$$\begin{aligned} (iii) \quad [\text{NOCl}] &= \frac{\text{No. of moles of NOCl}}{\text{Volume}} = \frac{(\text{Initial moles} - \text{moles decomposed})}{\text{Volume}} \\ &= \frac{(4.0 - 1.32) \text{ mol}}{2\text{L}} = \frac{2.68 \text{ mol}}{2\text{L}} = 1.34 \text{ mol L}^{-1} \end{aligned}$$

For the reaction



$$K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.66 \text{ mol L}^{-1})^2 (0.33 \text{ mol L}^{-1})}{(1.34 \text{ mol L}^{-1})^2} = \frac{(0.66)^2 \times 0.33}{(1.34)^2}$$

$$= 0.080 \text{ mol L}^{-1}$$

$$K_c = 0.080 \text{ mol L}^{-1}$$

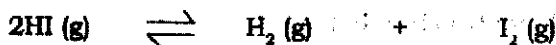
Example 10.3 : 2 moles of HI were heated in a vessel of one litre capacity at 713 K till the equilibrium was reached. At equilibrium HI was found to be 25% dissociated. Calculate K_c and K_p for the reaction.

Solution Initial moles of HI = 2

$$\text{Moles of HI dissociated} = 25/100 \times 2 = 0.5 \text{ mol}$$

$$\text{Moles of HI at equilibrium} = 2.0 - 0.5 = 1.5 \text{ mol}$$

The dissociation of HI occurs as



Initial moles	2	0	0
Equilibrium moles	(2 - 0.5)	0.25	0.25
Equilibrium concn.	1.5 mol	0.25 mol	0.25 mol
	1L	1L	1L
	1.5 mol L ⁻¹	0.25 mol L ⁻¹	0.25 mol L ⁻¹

For the reaction

$$K_c = \frac{[\text{H}_2] [\text{I}_2]}{[\text{HI}]^2} = \frac{(0.25 \text{ mol L}^{-1}) (0.25 \text{ mol L}^{-1})}{(1.5 \text{ mol L}^{-1})^2}$$

$$= \frac{(0.25)^2}{(1.5)^2} = 0.028$$

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

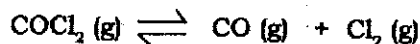
$$\text{For this reaction } \Delta n_g = n_p - n_r = 2 - 2 = 0$$

$$\therefore K_p = K_c = 0.028$$

Example 10.4 : Calculate K_p for the reaction $\text{COCl}_2 \rightleftharpoons \text{CO} + \text{Cl}_2$ in atm and Nm^2 . The equilibrium partial pressures of COCl_2 , CO and Cl_2 are 0.20, 0.16 and 0.26 atm respectively.

$$(1 \text{ atm} = 101300 \text{ Nm}^{-2})$$

Solution : (i) K_p in atmospheres



$$K_p = \frac{P_{\text{CO}} \times P_{\text{Cl}_2}}{P_{\text{COCl}_2}} = \frac{(0.16 \text{ atm})(0.26 \text{ atm})}{(0.20 \text{ atm})} = \frac{0.16 \times 0.26}{0.20} \text{ atm}$$

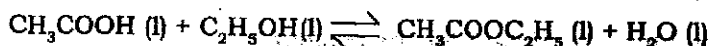
$$= 0.21 \text{ atm.}$$

(ii) K_p in Nm^{-2}

$$K_p = 0.21 \text{ atm and } 1 \text{ atm} = 101300 \text{ Nm}^{-2}$$

$$\therefore K_p = (0.21 \text{ atm}) (101300 \text{ Nm}^{-2} \text{ atm}^{-1}) = 21273 \text{ Nm}^{-2}$$

Example 10.5 : When equal number of moles of ethanol and acetic acid were mixed at 300 K, two-thirds of each had reacted when the equilibrium was reached. What is the equilibrium constant for the reaction



Solution : Let n moles each of acetic acid and ethanol be mixed initially. Then the number of moles of each reacted = $\frac{2}{3}n$.

Let V be the volume of the reaction mixture in litres.



Initial mole	n	n	0	0
Equilibrium moles	$(n - \frac{2}{3}n)$	$(n - \frac{2}{3}n)$	$\frac{2}{3}n$	$\frac{2}{3}n$

	$\frac{1}{3}n$	$\frac{1}{3}n$	$\frac{2}{3}n$	$\frac{2}{3}n$
Equilibrium concentrations	$\frac{n}{3V}$	$\frac{n}{3V}$	$\frac{2n}{3V}$	$\frac{2n}{3V}$

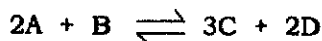
$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

$$= \frac{\left(\frac{2n}{3V}\right)\left(\frac{2n}{3V}\right)}{\left(\frac{n}{3V}\right)\left(\frac{n}{3V}\right)} = 2 \times 2 = 4$$

$$K_c = 4$$

INTEXT QUESTIONS 10.2

1. For a reversible reaction



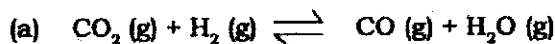
Write the expression for the equilibrium constant

.....

2. What is the relation between K_p and K_c .

.....

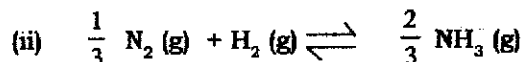
3. (i) Apply the law of equilibrium to the following and write the expression for K_p and K_c



(ii) In which of the above cases $K_c < K_p$

.....

4. The equilibrium constant for the reactions



are K_1 and K_2 respectively. What is the relation between them.

.....

5. What is the significance of the magnitude of equilibrium constant ?

.....

10.11 INFLUENCE OF VARIOUS FACTORS ON EQUILIBRIUM

10.11.1 The Factors Affecting the Equilibrium

The state of equilibrium is in a dynamic balance. It can be disturbed by changing concentration, temperature or pressure. If done so, a certain amount of 'net' change occurs in the system. The direction of change can be predicted with the help of Le chatelier's principle.

10.11.2 Le Chatelier's Principle

It states that when a system at equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occur in it in a direction that tends to decrease the disturbing factor.

This principle can be applied to various situations.

(i) **Increase in the concentration of any reactant** : Addition of a reactant would result in a 'net' forward reaction which consumes some of the added reactant (the disturbing factor)

- (ii) **Increase in the concentration of any product** : Addition of a product would result in some 'net' backward reaction which would consume some of it.
- (iii) **Increase in Pressure** : Increase in pressure results in 'net' direction which tends to decrease the pressure of the system. It would happen if the 'net' reaction occurs in that direction in which the number of moles of gaseous substances decreases ($\Delta n_g = -ve$) or which results in a decrease in volume of the system. Pressure has no effect on such systems in which $\Delta n_g = 0$ or there is no change in total volume.
- (iv) **Increase in temperature** : It would result in the endothermic direction of the reaction which would absorb some of the supplied heat. In case of endothermic reactions, the 'net' change would occur in forward direction and in case of exothermic reaction in the reverse direction.
- (v) **Addition of a Catalyst** : It does not affect the equilibrium. If added after equilibrium has been reached, no 'net' reaction would occur and it has no effect at all. However, if added in the beginning of the reaction, the catalyst would make it fast and help in reaching the equilibrium state faster.

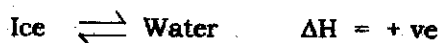
10.11.3 Applications of Le Chatelier's Principle

It can be applied to physical as well as chemical equilibria

(A) Physical Equilibria

(1) Melting of Ice

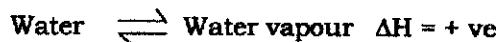
This process occurs with decrease in volume and absorption of heat.



Here, the increase of both the pressure and the temperature will result in 'net' forward change i.e. some ice will melt. We may say that the equilibrium has shifted in forward direction.

(2) Vaporization of Water

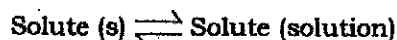
This process occurs with a large increase in volume since $\Delta n_g = 1 - 0 = +1$, and it occurs with absorption of heat.



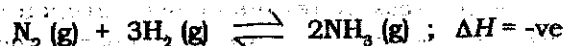
Increasing the temperature results in more vapour formation (endothermic process). Since $\Delta n_g = +1$, increase in pressure results in some condensation.

(3) Solubility Equilibrium

The equilibrium is



The process of dissolution can be endothermic or exothermic. In case of solutes like KCl, KNO_3 and NH_4Cl , ΔH is positive (endothermic) and more solute will dissolve on heating. Thus, the solubility increases with rise in temperature. In case of solutes like KOH and NaOH the ΔH is negative (exothermic) and their solubility decreases on heating.

(B) Chemical Equilibria**(i) Synthesis of Ammonia**

The reaction is exothermic and $\Delta n_g = 2 - 4 = -2$, hence it occurs with a decrease in volume. Various factors affect this equilibrium in the following manner.

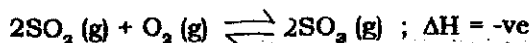
- (a) **Addition of N_2 or H_2** : This would increase the concentration of the reactants and result in 'net' forward reaction and some more ammonia would be formed.
- (b) **Addition of NH_3** : This would result in a 'net' reverse change and some of it would decompose in to nitrogen and hydrogen. However, if ammonia is removed from the equilibrium mixture, a 'net' forward reaction would occur and more ammonia is formed.
- (c) **Change of Temperature** : The reaction is exothermic in nature therefore increase in temperature favours reverse change which is endothermic and decrease favours forward change.
- (d) **Addition of Catalyst** : It helps in reaching the equilibrium state quicker.

Favourable Conditions for Synthesis of Ammonia : This reaction is of great industrial importance. During the synthesis of ammonia such conditions are maintained which favour the 'net' forward reaction namely low temperature and high pressure. Addition of catalyst makes the reaction occur fast. Besides, nitrogen and hydrogen gases are continuously fed into the reaction chamber and ammonia is continuously removed. All this keeps the system under stress and equilibrium is never permitted to be attained, so that the synthesis of ammonia continues to occur.

In industry the reaction is carried out at 450°C and 200 atm pressure in the presence of finely divided iron (catalyst) and molybdenum (promotor)

(ii) Formation of SO_3

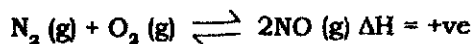
The reaction



is exothermic and $\Delta n_g = 2 - 3 = -1$ Formation of SO_3 will be favoured by high pressure and low temperature in the presence of a catalyst.

(iii) Formation of NO

The reaction



is endothermic and $\Delta n_g = 2 - 2 = 0$. The reaction is not affected by pressure changes and is favoured at high temperature. Presence of a suitable catalyst would be helpful.

INTEXT QUESTIONS 10.3

1. What is Le Chatelier's principle ?
.....
2. What are the factors that can affect a system at equilibrium ?
.....
3. What will happen to solid-vapour equilibrium when the temperature and pressure are decreased.
.....
4. (a) Which of the following will result in 'net' forward reaction in case of

$$A(g) + 2B(s) \rightleftharpoons C(s) + D(g) ; \Delta H = +ve$$
 - (i) addition of C
 - (ii) addition of A
 - (iii) decrease in pressure
 - (iv) increase in temperature
- (b) What are the most favourable conditions for the formation of C and D ?
.....

10.12 WHAT YOU HAVE LEARNT

- A chemical reaction is said to be reversible under certain conditions, if along with the reactants forming the products, the products also react and form back the reactants simultaneously.
- Reversible reactions do not reach completion and result in a state of equilibrium which is reached when two opposite processes occur at the same rate.
- The macroscopic properties of the system do not change once the equilibrium has been established.
- Irreversible reactions are in fact the reversible reactions in which the equilibrium is reached only when a negligible amount of the reactants is left unreacted.
- Chemical equilibrium is dynamic in nature. It can be attained by starting the reaction from any side and only in a closed system.
- When equilibrium is reached as a result of two opposite physical changes, it is called physical equilibrium and when as a result of two opposite chemical changes it is called chemical equilibrium.
- A phase is a homogeneous system or a part of a system which has same composition and uniform properties throughout. It is not same as physical state.

- A system with only one phase is called a homogeneous system and the one with more than one phases is called a heterogeneous system
- Chemical equilibrium can be homogeneous or heterogeneous while physical equilibrium is always heterogeneous.
- For a general reaction $aA + bB \rightleftharpoons cC + dD$ according to the law of equilibrium, the equilibrium constant K is given by the expression

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

- Concentration equilibrium constant K_c is obtained when molar concentration are used for calculating K . Concentration of pure solids and liquids are constant and are not included in the expression of K_c .
- In case of gaseous systems, the concentration of gases are expressed in terms of their partial pressures. The equilibrium constant thus obtained is called the pressure equilibrium constant, K_p .
- The relation between K_p and K_c is $K_p = K_c (RT)^{\Delta n_g}$ Where Δn_g is the change in the number of moles of gaseous substances during the reaction.
- Expression of equilibrium constant depends upon how the chemical equation is written for the reaction.
- Magnitude of the equilibrium constant is a measure of how close the reaction is to the completion stage.
- Units of K depend upon the change in the number of moles of the substances during the reaction.
- Concentration, pressure and temperature can affect the equilibrium systems and the effect can be qualitatively predicted by Le Chatelier's principle which states that when a system at equilibrium is disturbed by changing concentration, pressure or temperature, a 'net' change occurs in the direction that tends to neutralize the effect of the disturbing factor.
- Changes in concentration and pressure do result in some chemical reaction, but the value of the equilibrium constant is not changed.
- A catalyst does not change the equilibrium constant. It only helps in reaching the equilibrium state quicker.
- A change in temperature change the value of the equilibrium constant.

10.13 TERMINAL EXERCISE

1. What do you understand by reversible and irreversible reactions ? Give one example of each.

.....

2. What is physical equilibrium ? Give one example ?
.....
3. Give characteristics of equilibrium state.
.....
4. Is the phase same as physical state ? Illustrate your answer with one example of each.
.....
5. How do homogeneous and heterogeneous systems differ from each other ? Which of the following are homogeneous systems ?
- (a) Liquid \rightleftharpoons Vapour
- (b) $\text{N}_2\text{O}_4 (\text{g}) \rightleftharpoons 2\text{NO}_2 (\text{g})$
- (c) $\text{NH}_4\text{Cl} (\text{s}) \rightleftharpoons \text{NH}_3 (\text{g}) + \text{Cl}_2 (\text{g})$
- (d) $\text{CH}_3\text{COOH} (\text{l}) + \text{C}_2\text{H}_5\text{OH} (\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 (\text{l}) + \text{H}_2\text{O} (\text{l})$
.....
6. What are K_p and K_c ? Derive a relation between them.
.....
7. Write down the expression of K_c for the following. Also give units in each case.
- (a) $\text{N}_2\text{O}_5 (\text{g}) \rightleftharpoons 2\text{NO}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g})$
- (b) $\text{CH}_4 (\text{g}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{CO} (\text{g}) + 3\text{H}_2 (\text{g})$
- (c) $\text{FeCl}_3 (\text{aq}) + 3\text{NH}_4\text{SCN} (\text{aq}) \rightleftharpoons \text{Fe} (\text{SCN})_{3(\text{aq})} + 3\text{NH}_4\text{Cl} (\text{aq})$
.....
8. Write down the expression of K_p for the following and give its units (in terms of atmosphere) in each case
- (a) $\text{CO}_2 (\text{g}) + \text{H}_2 (\text{g}) \rightleftharpoons \text{CO} (\text{g}) + \text{H}_2\text{O} (\text{l})$
- (b) $3\text{Fe} (\text{s}) + 4\text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{Fe}_3\text{O}_4 (\text{s}) + 4\text{H}_2 (\text{g})$
- (c) $\text{SO}_3 (\text{g}) \rightleftharpoons \text{SO}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g})$
.....
9. Give the relation between K_c and K_p for the reaction
- $\text{CaCO}_3 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$
.....

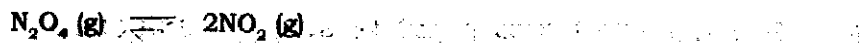
10. Using the relation between K_p and K_c . Write the expression of
- K_p for the reactions given in Q.No.7
 - K_c for the reactions given in Q. No.8
-
11. List the factors that can affect
- a system at equilibrium and
 - equilibrium constant of a system
-
12. State the Le Chatelier's Principle
-
13. What will be the effect of the following factors on the following systems at equilibrium ?



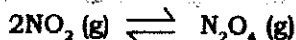
- Addition of X,
 - removal of Z
 - addition of a catalyst
 - increasing the pressure and
 - increasing the temperature.
-
14. 5 moles of HI were produced by the reaction between 7.5 moles of H_2 and 2.6 moles of I_2 vapours at $444^\circ C$. What is the equilibrium constant of the reaction



15. The equilibrium constant K_p for the reaction



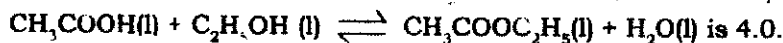
at 333 k is found to be 1.33 atm under a total pressure of 1 atm. Calculate K_p for the reaction



at 333k and under 1atm pressure.

16. At $444^\circ C$ 0.30 mole of H_2 and 0.30 mole of I_2 were taken in a one litre flask. After some time the equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ was established and it was found that the concentration of I_2 decreased to 0.06 mol L^{-1} . Calculate the value of K_c for the reaction at this temperature.
-

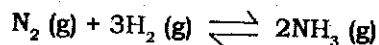
17. The equilibrium constant for the reaction.



What will be the composition of the equilibrium mixture if 1 mole of acetic acid is taken with 8 moles of ethanol ?

.....

18. K_c for the reaction



at 400°C was found to be $0.5 \text{ L}^2 \text{ mol}^{-2}$. Calculate K_p of this reaction in atm.

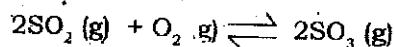
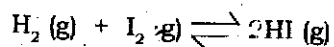
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CHECK YOUR ANSWERS

INTEXT QUESTIONS 10.1

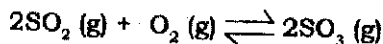
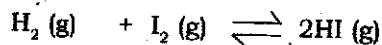
1. A chemical reaction is said to be reversible, if under certain conditions its products also react and form back the reactants.

Examples :

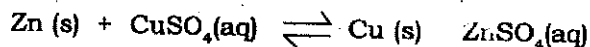
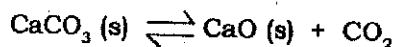


- A reaction reaches an equilibrium state when two opposing reactions occur at the same rate and balance each other at a particular temperature.
- When a system reaches the equilibrium state, its temperature, pressure and concentrations of all the reactants and products do not change any further.
- (i) Water-vapour system in a closed container at a constant temperature.
(ii) A saturated solution containing some undissolved solute at a constant temperature.
- A phase is a homogeneous system or a part of a system which has uniform composition and same physical properties through out.

6. (i) Homogeneous systems :



(ii) Heterogeneous systems :



INTEXT QUESTIONS 10.2

$$1. \quad K = \frac{[\text{C}]^3 [\text{D}]^2}{[\text{A}]^2 [\text{B}]}$$

$$2. \quad K_p = K_c (\text{RT})^{\Delta n}$$

$$3. (i) (a) K_c = \frac{[\text{CO}] [\text{H}_2\text{O}]}{[\text{CO}_2] [\text{H}_2]} ; \quad K_p = \frac{p_{\text{CO}} \times p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} \times p_{\text{H}_2}} ;$$

$$(b) K_c = [I_2] ; \quad K_p = p_{I_2} .$$

(ii) For the first reaction $\Delta n_g = (1 + 1) - (1 - 1) = 0$, hence $K_c = K_p$ while for the second reaction $\Delta n_g = 1 - 0 = +1$

$$\therefore K_p = K_c (RT) \quad \text{or} \quad K_c = \frac{K_p}{RT} \quad \text{or} \quad K_c < K_p .$$

$$4. \quad K_1 = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3} \quad \text{and} \quad K_2 = \frac{[\text{NH}_3]^{2/3}}{[\text{N}_2]^{1/3} [\text{H}_2]}$$

$$\therefore K_1 = [K_2]^3 .$$

5. It is a measure of the extent up to which a reaction proceeds before the equilibrium is reached.

INTEXT QUESTIONS 10.3

- Le Chatelier's principle states that when a system at equilibrium is disturbed by changing concentration, pressure or temperature, a 'net' change occurs in a direction that tends to neutralize the effect of the disturbing factor.
- Changes in pressure, temperature and concentrations of reactants or products.

When the temperature is decreased some vapour will condense and when the pressure is decreased some solid will sublime.

- (a) (ii) and (iv)
(b) High temperature, presence of a catalyst and continuous removal of D.

TERMINAL EXERCISE

- See section 10.3

Examples (i) Reversible, $\text{CH}_3\text{COOC}_2\text{H}_5 (\text{l}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{CH}_3\text{COOH} (\text{l}) + \text{C}_2\text{H}_5\text{OH} (\text{l})$

(ii) Irreversible, $\text{BaCl}_2 (\text{aq}) + \text{Na}_2\text{SO}_4 (\text{aq}) \rightleftharpoons \text{BaSO}_4 (\text{s}) + 2\text{NaCl} (\text{aq})$

- See section 10.5; water \rightleftharpoons vapour in a closed vessel
- See section 10.4
- See section 10.5.5
- A homogeneous system has only one phase in it while a heterogeneous system has more than one phase.
(b) and (d) are homogeneous systems
- See section 10.7

$$7. \quad (a) \quad K_c = \frac{[\text{NO}_2]^2 [\text{O}_2]^{1/2}}{[\text{N}_2\text{O}_5]} ; \text{Units : (concentration)}^{2+1/2} = \text{Concn}^{3/2} \\ = (\text{mol L}^{-1})^{3/2}, \text{ mol}^{3/2} \text{ L}^{-3/2}.$$

$$(b) \quad K_c = \frac{[\text{CO}] [\text{H}_2]^3}{[\text{CH}_4]} ; \text{Units : (concn)}^{1+3-1} = \text{Concn}^3 \\ = (\text{mol L}^{-1})^3 = \text{mol}^3 \text{ L}^{-3}$$

$$(c) \quad K_c = \frac{[\text{Fe}(\text{SCN})_2] [\text{NH}_4\text{Cl}]^3}{[\text{FeCl}_3] [\text{NH}_4\text{SCN}]^3} ; \text{Units : (concn)}^{(1+3-3)-3} = (\text{Concn})^0$$

Hence, No units

$$8. \quad (a) \quad K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} \times P_{\text{H}_2}} ; \text{Units : (Pressure)}^{(1+1)-(1+1)} = (\text{Pressure})^0$$

Hence no units

$$(b) \quad K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4} ; \text{Units} = (\text{Pressure})^{4-4} = (\text{Pressure})^0 \\ \therefore \text{No units}$$

$$(c) \quad K_p = \frac{P_{\text{SO}_2} \times P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} ; \text{Units : (Pressure)}^{(1+\frac{1}{2})-1} = \text{Pressure}^{\frac{1}{2}} \\ = \text{atm}^{\frac{1}{2}}$$

9. In the reaction $\Delta n_g = 1+0-0 = +1$

$$K_p = K_c \cdot RT$$

10. (i) K_p for the reaction of Q.No. 7.

$$(a) \quad \Delta n_g = (2 + \frac{1}{2}) - 1 = \frac{3}{2} ; K_p = K_c (RT)^{\frac{3}{2}} = \frac{[\text{NO}]^2 [\text{O}_2]^{1/2}}{[\text{N}_2\text{O}_5]} (RT)^{\frac{3}{2}}$$

$$(b) \quad \Delta n_g = (3+1) - 1 = +3 ; K_p = K_c (RT)^3 = \frac{[\text{CO}] [\text{H}_2]^3}{[\text{CH}_4]} (RT)^3$$

$$(c) \quad \Delta n_g = (0 - 0) = 0 ; K_p = K_c = \frac{[\text{Fe}(\text{SCN})_2] [\text{NH}_4\text{Cl}]^3}{[\text{FeCl}_3] [\text{NH}_4\text{SCN}]^3}$$

(ii) K_c for the reactions given in Q. No. 8

$$(a) \quad \Delta n_g = (1+1) - (1+1) = 0 ; K_c = K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} \times P_{\text{H}_2}}$$

$$(b) \Delta n_g = 4 - 4 = 0 ; K_c = K_p = \frac{P_{H_2}^4}{P_{H_2O}^4}$$

$$(c) \Delta n_g = (1 + \frac{1}{2}) - 1 = + \frac{1}{2} ; K_c = K_p (RT)^{-\frac{1}{2}} = \frac{P_{SO_2} \times P_{O_2}^{\frac{1}{2}}}{P_{SO_3}} (RT)^{-\frac{1}{2}}$$

11. (i) Temperature, pressure and concentrations of reactants or products
 (ii) Only temperature
12. It states that when a system at equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occurs in it in a direction that tends to decrease the disturbing factor.
13. (i) Addition of X : Some forward reaction would occur
 (ii) Removal of Z : Some forward reaction would occur
 (iii) Addition of catalyst : Equilibrium will be attained fast.
 (iv) Increasing the pressure: Since number of moles of gases is decreasing in the forward direction, the equilibrium will shift in the forward direction.
 (v) Increasing the temperature : Since the reaction is endothermic, some forward reaction would occur.
14. Let us first calculate the equilibrium concentration assuming that the volume of the reaction vessel is V litres.

	$H_2(g)$	+	$I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial Moles	7.5		2.6		0
Equilibrium moles	(7.5-2.5) = 5.0		(2.6-2.5) = 0.1		5.0 = 5.0
Equilibrium Concentration	$\frac{5}{V}$		$\frac{0.1}{V}$		$\frac{5}{V}$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{5}{V}\right)^2}{\left(\frac{5}{V}\right)\left(\frac{0.1}{V}\right)} = \frac{(5)^2}{5 \times 0.1} = \frac{5}{0.1} = 50$$

$$\therefore K_c = 50$$

15. Since the two reactions are just reverse of each other

$$K_2 = \frac{1}{K_1} = \frac{1}{1.33} = 0.752 \text{ atm}^{-1}$$

16. Since the volume of the reaction vessel is one litre, the number of moles of a substance would be numerically equal to its molar concentration. The initial and equilibrium moles of I_2 are 0.3 and 0.06 respectively. Therefore the number of moles of I_2 reacted = 0.3 - 0.06 = 0.24. We can now calculate the equilibrium

concentration as follows.

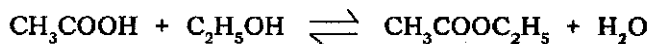
	H_2 (g)	+	I_2 (g)	\rightleftharpoons	2HI (g)
Initial concentrations/ (mol L ⁻¹)	0.30		0.30		0
Equilibrium concentrations/ (mol L ⁻¹)	0.30 - 0.24 0.06		0.30 - 0.24 0.06		2 × 0.24 0.48

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.48 \text{ mol L}^{-1})^2}{(0.06 \text{ mol L}^{-1})(0.06 \text{ mol L}^{-1})}$$

$$= \frac{(0.48)^2}{(0.06)^2} = (8)^2 = 64$$

$$K_c = 64$$

17. Let 'x' moles each of the acetic acid and ethanol react. Then the equilibrium concentration would be (assuming that volume of the reaction mixture is V litre)



Initial Moles	1	8	0	0
Equilibrium moles	1 - x	8 - x	x	x
Equilibrium Concentrations	$\frac{1-x}{V}$	$\frac{8-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{1-x}{V} \times \frac{8-x}{V}} = \frac{x^2}{(1-x)(8-x)} = 4.0$$

$$\frac{x^2}{8-x-8x+x^2} = \frac{x^2}{8-9x+x^2} = 4.0$$

$$x^2 = 4(8-9x+x^2) = 32-72x+4x^2$$

$$\text{or } 3x^2 - 72x + 32 = 0$$

on solving $x = 0.45$

Amounts of :

$$[\text{CH}_3\text{COOH}] = 1 - 0.45 = 0.55 \text{ mol}$$

$$\text{C}_2\text{H}_5\text{OH} = 8 - 0.45 = 7.55 \text{ mol}$$

$$\text{CH}_3\text{COOC}_2\text{H}_5 = \text{H}_2\text{O} = 0.45 \text{ mol each}$$

18. For the reaction



$$\Delta n_g = 2 - 1 - 3 = -2$$

$$K_c = 0.5 \text{ L}^2 \text{ mol}^{-2}$$

$$T = 400 + 273 = 673 \text{ K}, R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$K_p = K_c (RT)^{-2}$$

$$= (0.5 \text{ L}^2 \text{ mol}^{-2}) (0.0821 \times 673 \text{ L atm mol}^{-1})^{-2}$$

$$= 0.5 \text{ L}^2 \text{ mol}^{-2} \times (55.25 \text{ L mol}^{-1} \text{ atm})^{-2}$$

$$= 0.5 \text{ L}^2 \text{ mol}^{-2} \times 0.00033 \text{ L}^{-2} \text{ mol}^{-2} \text{ atm}^{-2}$$

$$= 0.000165 \text{ atm}^{-2} = 1.65 \times 10^{-4} \text{ atm}^{-2}$$

$$\therefore K_p = 1.65 \times 10^{-4} \text{ atm}^{-2}$$