CHEMICAL EQUILIBRIUM

Chapter 7

Teaching Periods	Assessment	Weightage
9	1	7

Students will be able to:

- **Define** chemical equilibrium in term of a reversible reaction.
- **Write** both forward and reverse reactions an describe the macroscopic characteristics of each.
- **State** the necessary conditions for equilibrium and the ways that equilibrium can be recognized.
- **Write** the equilibrium expression for a given chemical reaction.
- **Relate** the equilibrium expression in terms of concentration, partial pressure, number of moles and mole fraction.
- **Write** expression for reaction quotient.
- **Determine** if the equilibrium constant will increase or decrease when temperature is changed, given the equation for the reaction.
- **Determine** the reactants or products are favored in a chemical reaction, given the equilibrium constant.
- **State** Le Chatelier's Principle and be able to apply it to systems in equilibrium with changes in concentration, pressure, temperature, or the addition of catalyst.
- **Explain** industrial applications of Le Chatelier's Principle using Haber's process as an example.
- **Define** and explain solubility product.
- **Define** and explain common ion effect giving suitable examples.

INTRODUCTION

Chemical reactions are generally treated as the conversion of entire stoichiometric amount of reactants into products. This is true for some reactions which carry out in an open vessel where the product once formed cannot be reversed. These are known as irreversible or unidirectional reactions and are shown by arrow (→) between reactants to products pointing towards products. One of the real life examples of these reactions is the combustion of methane while cooking in kitchen; it gives carbon dioxide and water.

$$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{(l)}$$

However, it is a concerted fact that many reactions do not go to completion under a given set of conditions of temperature, pressure and concentration, especially when carried out in a closed vessel. These are known as reversible reactions. These reactions reached a stage where concentration of reactant and product becomes constant; this is known as chemical equilibrium.

7.1 REVERSIBLE REACTIONS AND DYNAMIC EQUILIBRIUM

Reversible reactions are those which produce only to a certain extent the products formed in these reactions may suddenly recombine and transform back into original reactants. Hence a two way reaction is established which occur simultaneously and continuously until the system reaches the state of equilibrium. We generally denote these type of reactions by a two half-headed arrows (⇌) pointing both directions in the chemical equation.

Some common examples of reversible reactions are mentioned below.

(i) Esterification of acid and alcohol

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \underset{\text{Heat}}{\overset{H_2SO_{4(conc.)}}{\rightleftharpoons}} CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

(ii) Decomposition of N_2O_4 into NO_2

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

(iii) Formation of ammonia by Haber's process

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

(iv) Formation of Nitric oxide by elemental gases

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

7.1.1 Concept and Explanation of Chemical Equilibrium

Chemical equilibrium is a state of a reversible reaction in which all reacting species are present with no net change in their concentrations and this happens only if the two opposing reactions are occurring with the same rate. It means that reactants and products are continuously interconvert to each other with the same rate thus **"Chemical equilibrium is a state in a reversible reaction where no net change in the concentration of reactants and products occur with time"**.

Table 7.1 **Macroscopic characteristics of forward and reverse reaction.**

Forward reaction	Reverse Reaction
Forward reaction in a reversible reaction represents the transformation of reactants into products.	Backward reaction in a reversible reaction specify the conversion of products into reactants.
It takes place from left to right $R \longrightarrow P$	It takes place from right to left. $R \longleftarrow P$
At initial stage the rate of this reaction is found to be very fast.	At initial stage the rate of this reaction is noted to be almost negligible.
As the time going on, this reaction becomes slow down.	As the time passes, this reaction speed up gradually until the equilibrium is reached.

Before going towards mathematical approach of chemical equilibrium, we need to know "when equilibrium is established in a chemical system?" To find the answer let us consider the reaction of Hydrogen and Iodine at an elevated temperature.

$$\underset{\textbf{(Purple)}}{H_{2(g)} + I_{2(g)}} \rightleftharpoons \underset{\textbf{(Colourless)}}{2HI_{(g)}}$$

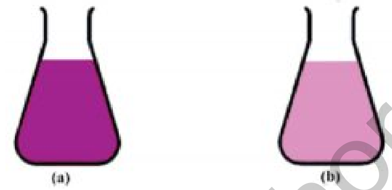

Fig 7.1: (a) When the reaction of H_2 & I_2 starts (b) When equilibrium is reached

When certain amount of hydrogen and iodine are mixed in a sealed container at 500°C they start reacting and form some hydrogen iodide. Initially, only the forward reaction occurs because HI was not present in the vessel but as soon as some HI is formed, it readily decomposes back into H_2 and I_2. Although the rate of reverse reaction is quite slow in the beginning due to the low concentration of HI, but as the time goes on, the rate of forward reaction gradually decreases while the rate of reverse reaction increases in the same manner. Ultimately, the rate at which H_2 and I_2 react to form HI becomes equal to the rate at which HI breaks down back into H_2 and I_2 and thus the "equilibrium" is set up. This can be seen by the intensity of purple colour of Iodine which decreases gradually until a constant light purple colour is settled.

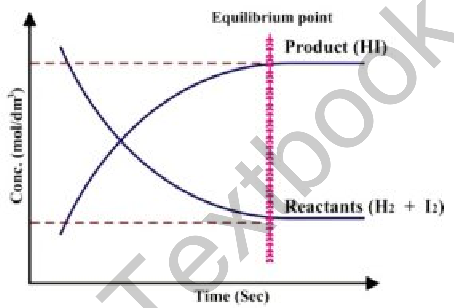

Fig. 7.2:(a) Variation in the molar conc. of H_2 + I_2(reactants) and HI(Products) with time indicating that at equilibrium point conc. of reactant and products become constant

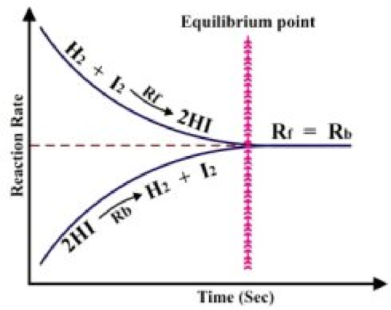

Fig. 7.2:(b) Variation in the rate of forward and backward reaction with time indicating that at equilibrium $R_f = R_b$

Necessary Conditions for equilibrium

For a reaction mixture to exist at equilibrium, it must achieve following conditions.

(i) Chemical equilibrium can only established if it is carried out in a closed vessel because in this system reactant or products particles cannot be escaped out.

(ii) Temperature, pressure and volume should be constant at equilibrium state. If any one of these variable is changed, the system will not remain in equilibrium.

(iii) The rate in the forward reaction and backword reaction should be the same that is the system attain a dynamic state.

(iv) The concentration of both reactants and products should remain constant. The addition or removal of any one of them causes the equilibrium to be disturbed.

Ways to recognized chemical equilibrium

There are two ways to recognize the formation of a chemical equilibrium.

(i) Physical Method: In this method specific radiations (UV, IR or visible) pass through reaction mixture. Both reactants and products absorb radiations with respect to their equilibrium concentration noted by spectrometer. The % absorbance of these radiations determines the equilibrium concentration of reaction mixture.

Do You Know?

Concentration of a chemical solution is directly proportional to its absorption of light. There is a linear relationship between concentration and absorbance of the solution, which enables the concentration of a solution to be calculated by measuring its absorbance.

(ii) Chemical Method: For determining equilibrium constant by using chemical method let us consider the esterification of ethyl alcohol and acetic acid.

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

Since the equation of esterification tells us that 1 mole of acetic acid and 1 mole of alcohol reacts to form 1 mole of ester and 1 mole of water therefore we conclude that the amount of acid used up in the reaction is equal to the amount of alcohol consumed and thus at equilibrium we have **(a – x)** mole of acetic acid,**(b – x)** moles of alcohol,**x** moles of ester and **x** moles of water. Reaction table now written as:

Conc.(mole/dm³)	CH_3COOH +	C_2H_5OH	$\rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
Initial	a	b		0	0
Change	-x	-x		x	x
Equilibrium	a – x	b – x		x	x

Now applying Law of mass action.

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

$$K_c = \frac{[x][x]}{[a-x][b-x]}$$

$$K_c = \frac{x^2}{[a-x][b-x]}$$

If we repeat the same experiment, by taking different amount of CH_3COOH and C_2H_5OH, we will observe that the value of K_c will be the same with the condition that temperature remains constant.

Self Assessment

(i) Reversible reactions attain the position of equilibrium if they acquire certain necessary conditions. Can you mention these conditions?
(ii) It is said that chemical equilibrium is dynamic. How can you explain it?

7.1.2 Law of Mass Action and Expression for Equilibrium Constant

So far we have learned that whenever an equilibrium point is reached at a certain temperature in a closed chemical system:
(i) The active masses of both reactants and products stay constant.
(ii) The rate of forward and reverse reactions remains same.

Taking the above two necessary conditions of chemical equilibrium into their research two Norwegian scientists C.M Guldberg and Peter Wage (1864) found out that reversible reaction reaches a state where the ratio of its products concentration to that of reactants concentration becomes constant. On behalf of their research conclusions they derived a quantitative relationship between the rate of reaction and active masses of reacting substance known as law of mass action. It states that **"The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of reactants"**. The term active mass refers to molar concentration that is the number of moles of reactants and products per dm^3.

To illustrate this law in a mathematical way let us consider a general reversible reaction in which reacting species A, B, C and D exists in equilibrium state at a certain temperature.

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

According to the law of mass action, the rate of forward reaction (R_f) is directly proportional to the product of active masses of A and B.

$$R_f \propto [A]^a [B]^b \quad \text{or} \quad R_f = K_f [A]^a [B]^b$$

Similarly the rate of backward reaction (R_b) is directly proportional to the active masses of C and D

$$R_b \propto [C]^c [D]^d \quad \text{or} \quad R_b = K_b [C]^c [D]^d$$

Since chemical equilibrium is dynamic in nature representing the equal rate in both direction ($Rf = Rb$), therefore $K_f [A]^a[B]^b = K_b [C]^c [D]^d$
By rearranging this relation we get

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

At any given temperature both K_f and K_b are constant, the ratio K_f/K_b will also be constant and collectively termed as equilibrium constant symbolized by K_c.

$$\mathbf{K_c} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{---------- (i)}$$

This is known as equilibrium expression or equilibrium law. It reveals that 'when at a certain temperature a chemical reaction reaches to equilibrium state the ratio of active masses of products to reactants become constant'.

Effect of change in temperature on the value of Kc

The value of equilibrium constant (K_c) varies with temperature. For example K_c for the synthesis of ammonia by Haber's process is 4.1×10^8 at 25°C but 0.5 at 400°C. Similarly Kc for the decomposition of N_2O_4 at 25°C is 4.64×10^{-3} but at 127°C it is 1.53.

Do You Know?

The unit of Kc depends on the form of equilibrium expression.
(i) If the number of moles of reactants are equal to the number of moles of products, Kc has no unit since conc. units (mol/dm^3) of all species are cancelled by each other.
(ii) If the number of moles of reactants are different from number of moles of product then the unit of Kc is determined by using the formula $(mol/dm^3)^{\Delta n}$.
(iii) In general practice the unit of Kc is not written.

Example 7.1

Write down the expressions of equilibrium constant (Kc) for the following reversible reactions.

$$\text{i) } 4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$$

$$\text{ii) } 2N_2O_{5(g)} \rightleftharpoons 4NO_{(g)} + 3O_{2(g)}$$

Solution:

To write an equilibrium expression, we should have the balanced chemical equation. All products given in the equation should be placed on numerator each separately in square bracket while reactants on denominator. Then finally raise the concentration of each substance to the power of its coefficient in the balance chemical equation.

(i) $K_c = \dfrac{[NO]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^5}$

(ii) $K_c = \dfrac{[NO]^4\,[O_2]^3}{[N_2O_5]^2}$

Example 7.2

An essential step in contact process is the oxidation of SO_2 to SO_3.

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

If in an experiment, there are 5 moles of SO_2, 4 moles O_2 and 2.8 moles of SO_3 present at equilibrium state in a 2dm^3 flask. Calculate Kc.

Solution:

Since equilibrium moles of all components in the reacting mixture are given, we first convert them into molar concentration and then put into equilibrium expression to find out Kc.

$[SO_2]_{eq} = \dfrac{5}{2} = 2.5\ mol/dm^3$

$[O_2]_{eq} = \frac{4}{2} = 2\ mol/dm^3$

$[SO_3]_{eq} = \frac{2.8}{2} = 1.4\ mol/dm^3$

K_c expression for the given reaction may be written as

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\ [O_2]}$$

By substituting the equilibrium concentrations, we get.

$$K_c = \frac{[1.4]^2}{[2.5]^2\ [2.0]} = 0.157\ mol^{-1} \cdot dm^3$$

Example 7.3

Ethyl acetate is an ester of ethanol and acetic acid commonly use as an organic solvent.

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

In an esterification process 180g of acetic acid and 138g ethanol were mixed at 298K and allowed to start reaction under necessary conditions. After equilibrium is established 60g of unused acetic acid were present in the reaction mixture. Calculate Kc.

Solution:

Moles of $CH_3COOH = \frac{180}{60} = 3$ moles

Moles of $C_2H_5OH = \frac{138}{46} = 3$ moles

	$CH_3COOH_{(l)}$ +	$C_2H_5OH_{(l)}$	$\rightleftharpoons$	$CH_3COOC_2H_{5(l)}$ +	$H_2O_{(l)}$
Initial	3	3		0	0
Equilibrium conc.	3–x	3–x		x	x

But at equilibrium unused acetic acid is 60g which is equal to 1 mole.

Therefore

$3 - x = 1$

And

$x = 2$

Now substituting values of equilibrium mixture in Kc expression.

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

$$K_c = \frac{[2]\ [2]}{[1]\ [1]} \qquad K_c = 4$$

7.1.3 Relationship between Kc, Kp, Kx and Kn

Since equilibrium constant (Kc) has formulated from kinetic aspect of equilibrium law, it represents the molar concentrations of products and reactants. However, there are some other ways to express equilibrium constant for the same reaction. For a homogenous gaseous reaction in which all reacting species appear in gaseous state, the concentration of products and reactants can also be expressed in term of their partial pressure because it is easier for a gas to measure its pressure rather than concentration.

For the reaction $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$

$$K_p = \frac{(P_C)^c \ (P_D)^d}{(P_A)^a \ (P_B)^b} \text{ ---------------------------------- (ii)}$$

P_A, P_B P_C P_D are the partial pressure of gases A, B, C, D and exponents a, b, c, d respectively are the coefficients of balanced equation.

Kp defines as **"the ratio of partial pressure of product gases to that of partial pressure of reactant gases each raised to the power equal to its own coefficient in the balanced chemical equation"**.

Equilibrium constant some time express in terms of K_n and K_x when the number of moles of reactants and products are given at equilibrium.

$$K_n = \frac{(n_C)^c \ (n_D)^d}{(n_A)^a \ (n_B)^b} \text{ ---------------------------------- (iii)}$$

$$K_X = \frac{(X_C)^c \ (X_D)^d}{(X_A)^a \ (X_B)^b} \text{ ---------------------------------- (iv)}$$

Here **n** specify the given number of moles and **X**, represents the mole fractions of A, B, C and D in the equilibrium reaction mixture.

Despite the fact that partial pressure of an ideal gas is directly proportional to its molar concentration at constant temperature, the numerical value of K_c is often not equal to K_p. Accordingly a quantitative relationship has been developed between these two equilibrium constants at a particular constant temperature.

$$\mathbf{Kp=Kc\ (RT)^{\Delta n}} \text{ ---------------------------------- (v)}$$

Here,

R = Gas constant which is taken in 0.082 atm dm^3/mol. K.

T = Absolute temperature

Δn = [Sum of number of moles of products – sum of number of moles of reactants] in the given balance chemical equation.

The relationship between Kp, Kx, and Kn may be written as

$$Kp = Kx\ (P)^{\Delta n} \text{ ---------------------------------- (vi)}$$

$$Kp = Kn \left(\frac{P}{n}\right)^{\Delta n} \text{ ------------------------------ (vii)}$$

Example 7.4

Nitrosyl chloride is a yellow coloured gas prepared by the reaction of NO and Cl_2 gases.

$$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$$

If at certain temperature, the partial pressure of equilibrium mixture is NO = 0.17 atm, Cl_2 = 0.2 atm and NOCl = 1.4 atm, Calculate Kp

Solution:

The equilibrium expression of the given reaction is written as

$$K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2\ (P_{Cl_2})}$$

Substituting the partial pressure in equilibrium expression, we get

$$K_p = \frac{(1.4)^2}{(0.17)^2\ (0.2)} \qquad K_p = \mathbf{339.1}$$

Self Assessment

The reaction of methane with hydrogen sulphide gives carbon disulphide.

$$CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)}$$

If Kc for this reaction at 727°C is 4.2×10^{-3}, Calculate its Kp. (Ans: 28.24)

7.1.4 Importance of K_C and Reaction Quotient

The reaction quotient (Qc) is an expression representing the ratio of molar concentration of products to that of reactants in a reversible reaction; Mathematically it has the same form as that of equilibrium constant expression (Kc), however, the concentration of reactants and products expressed in reaction quotient are not necessarily specify equilibrium state.

Consider a general reversible reaction.

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

The expression of reactant quotient may be written as

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

The subscript 'i' attached with each square bracket represents the concentrations at any particular instant of time not necessarily be at equilibrium.

It is important to note that the numerical value of Qc changes gradually during the course of reaction toward equilibrium state due to continuous change in the concentration of reactants and products. Finally, when reaction reaches the equilibrium, the concentration of reactants and products no longer change and at this moment Qc becomes equal to Kc.

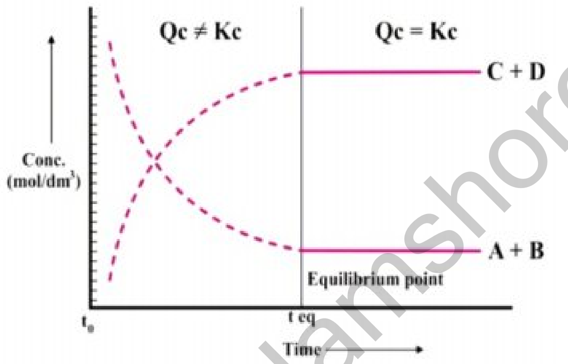

Figure 7.3 It shows that conc. of reactants (A and B) and products (C and D) both gradually change in the course of reaction till the equilibrium is reached where Qc will becomes equal to Kc

The distinction between Qc and Kc is important due to their usefulness in anticipating the direction of reaction. Reaction quotient (Qc) depends on the actual concentration of reactants and products at any time during the course of reaction and is changed with the time. On the other hand equilibrium constant (Kc) is a constant value which specify the equilibrium concentrations of reacting species at particular temperature.

Use of Kc in predicting the direction of reaction

Kc and reaction quotient are a very useful tool in determining whether the reaction has reached to equilibrium, if not, in which direction it proceed at that moment. A comparison of magnitude of Qc with Kc tells us the direction in which the reaction proceed to attain an equilibrium. The three possible cases are as follow.

Case-1:

If Qc < Kc, indicates that the system proceeds from left to right to a greater extent and the rate of formation of product is higher. The reason is that the conc. of reactants (denominator) is large relative to the conc. of products (numerator) in the reaction quotient expression.

Case-2:

If Qc > Kc, indicates that the system proceeds from right to left to a greater extent and the rate of formation of reactant is higher because the conc. of reactant (denominator) is smaller than conc. of product (numerator) in the reaction quotient expression.

Case-3:

If Qc = Kc, indicates that the system is in dynamic equilibrium and the rate of reaction in both the directions remains same.

Example 7.5

Kc for the given reaction at certain temperature is 2.72.

$$A + 3B \rightleftharpoons 2C$$

If in a 5dm^3 reaction vessel the reaction mixture contains 8 moles A, 6 moles B, and 5 moles C. Predict whether the reaction is in equilibrium, if not what is the direction of net reaction?

Solution:

To find the answer, we first need to know what is the numerical value of Qc. It will be determined by substituting the values of conc. of A, B and C in reaction quotient expression then compare it with Kc. The relative values of Qc and Kc tells us whether the reaction is at equilibrium or proceed in a particular direction for getting equilibrium.

The molar concentrations of A, B and C can be calculated as

$$[A]= \frac{8}{5}=1.6 \text{ mol/dm}^3$$

$$[B]= \frac{6}{5}=1.2 \text{ mol/dm}^3$$

$$[C]= \frac{5}{5}=1 \text{ mol/dm}^3$$

Qc expression of the reaction is written as

$$Qc= \frac{[C]^2}{[A]\,[B]^3}$$

Substituting these values in reaction quotient

$$Qc= \frac{(1)^2}{(1.6)\,(1.2)^3}=0.36$$

Since Qc < Kc, the reaction mixture is not at equilibrium but proceed from left to right to increase the concentration of product.

Use of Kc in the prediction of extent of reaction

The value of K_c enables us to tell roughly, at a glance how far the reaction precedes before the equilibrium state is reached.

Since reactions have a long range of K_c values, the extent to which a chemical reaction proceeds is substantially discussed into three destinations in the reaction pathway.

Very large value of K_c Shows that ratio of products to reactants at equilibrium is very large and it infers that reaction is nearly to completion.

Very small value of K_c Shows that the ratio of products to reactants at equilibrium is very small and it infers that reaction proceeds hardly at all before reaching the equilibrium.

Intermediate value of K_c Shows that appreciable amount of both reactants and products are present in the equilibrium mixture.

Table 7.2	Prediction of extent of reaction at particular temperature.	
Reactions	**Value of Kc at 25°C**	**Extent to which reaction proceed before equilibrium is reached**
$CH_{4(g)} + Cl_{2(g)} \rightleftharpoons CH_3Cl_{(g)} + HCl_{(g)}$	1.2×10^{18}	Almost go to completion
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	4.5×10^{-31}	Proceed negligibly
$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$	43.44	Proceed moderately

7.2 FACTORS AFFACTING EQUILBRIUM (Le-chatelier's principle)

Our area of study in this section is how an equilibrium system becomes temporarily unbalance by the change in experimental conditions such as temperature, pressure and concentration of reacting species and how the system restore its balance by speeding up either in forward or backward direction. These equilibrium constraints or reaction parameters may affect the position of equilibrium.

In 1884, Le-Chatelier, a French chemist introduced a general rule after a long research on how and why the balance of a chemical equilibrium is disturbed by some change of conditions, this is known as Le-Chatelier's principle. It states that **'If an external stress such as concentration pressure or temperature is applied to a system at equilibrium, the equilibrium is disturbed and tends to shift in a direction to offset the effect of stress imposed'**.

There are two parts in the statement of Le-Chatelier's Principle which need further explanation.

First part which refers to 'disturbance on equilibrium' means an altering in the experimental conditions push the system temporary out of equilibrium so that 'Qc' will no more equal to Kc. The second part which specifies the shifting of equilibrium position to left or right means system tends to repair its equilibrium by reducing the stress and tends to attain a new equilibrium where Qc = Kc.

We now study the effect of above mentioned factors on quantitative and descriptive view point.

7.2.1 Effect of Change in Concentration

When a system at equilibrium is disturbed by increasing or decreasing the concentrations of one or more species involved in the reaction, the equilibrium tends to shift towards left or right in order to reduce the effect of this stress and re adjust itself until Qc = Kc, thus

(i) The equilibrium position shifts towards the right if the amount of reactant is added or product is removed.

(ii) The equilibrium position shift to the left if reactant is removed or product is added.

In general whenever we add or remove some of the reacting species from a system at equilibrium, the system reacts in a particular direction to reduce the amount of added substance or to produce certain amount of removed substance so that the stress imposed on the system will be offset. To understand the guideline provided by Le-Chatelier's principle for the stress caused by change in the concentration considers the following system at equilibrium.

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$$

When certain amount of $CO_{(g)}$ or $H_{2(g)}$ is added to the system, the value of reaction Quotient (Q) is lowered than its K_c and the reaction is no longer at equilibrium. The stress caused by added $CO_{(g)}$ or $H_{2(g)}$ is alleviated by shifting the equilibrium to the right side. In doing so some amount of $CO_{(g)}$ and $H_{2(g)}$ has consumed and turning the value of Qc back to K_c. In kinetic aspect, it is simply said that the addition of $CO_{(g)}$ or $H_{2(g)}$ increases the rate in the forward direction by consuming more CO and H_2 and producing more CH_4 and H_2O until at a certain point a new equilibrium will be established. The effect of change in concentration on equilibrium position may be illustrated table 7.3.

Table 7.3 **Effect of change in conc. of reacting mixture on equilibrium position**

Stress type	Effect on equilibrium position $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$Q_c = \frac{[CH_{4(g)}]\,[H_2O_{(g)}]}{[CO_{(g)}]\,[H_{2(g)}]^3}$
Adding more $CO_{(g)}$ or $H_{2(g)}$	Shift to the right	Qc < Kc
Removing some $CO_{(g)}$ or $H_{2(g)}$	Shift to the left	Qc > Kc
Adding more $CH_{4(g)}$ or $H_2O_{(g)}$	Shift to the left	Qc > Kc
Removing some $CH_{4(g)}$ or $H_2O_{(g)}$	Shift to the right	Qc < Kc

7.2.2 Effect of Change in Pressure or Volume

The effect of pressure change in altering the position of equilibrium is noticeably observed if all reacting species are in gaseous state where the numbers of moles of reactant gases are differ from number of moles of product gases ($\Delta n \neq 0$). The reason is that gases are highly compressible therefore referring to ideal gas laws (PV = nRT) the pressure applied to the system is directly proportional to the concentration of reacting species but inversely proportional to the volume at given constant temperature.

To understand the effect of pressure change on an equilibrium let us consider the following gaseous system in a cylinder fitted with a moveable piston.

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

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

When the external pressure increases at constant temperature, the piston move downward causing a decrease in the volume which in general increases the concentration of all components of reacting mixture but since the number of moles of products are lesser than reactant, the denominator value exceed the numerator. Thus the system is no longer in equilibrium and to reduce this stress the reaction tends to shift on right side.

In general, the effect of pressure on a homogenous gaseous equilibrium system may be summarizing in the guidance of Le-Chatelier's Principle as **"An increase of pressure shift the equilibrium in the direction of decrease volume where as a decrease pressure shift the equilibrium in the direction of increase volume"**.

Table 7.4 **Effect of change in pressure on some gaseous equilibria**

Equilibria	Effect of Increase pressure	Effect of decrease pressure
$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$	Equilibrium shift to the left	Equilibrium shift to the right
$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$	Equilibrium shift to the right	Equilibrium shift to left
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$	Equilibrium remains unchanged	Equilibrium remains unchanged

7.2.3 Effect of Change in Temperature

Reactions in term of enthalpy change are classified into exothermic and endothermic (Sec-11.2) and if we are talking about reversible reactions, these are exothermic in one direction and endothermic in other direction. However, when the equilibrium is shown in an equation form, the sign of enthalpy term (ΔH°) refer to the forward direction.

Consider the reaction

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)} \quad (\Delta H^{\circ} = -ve) \quad K_C = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

Sign of ΔH° shows that the reaction exothermic in the forward direction. If we increase the temperature of this equilibrium system by providing some heat, then according to Le-Chatelier's principle the system tends to speed up in the left side so that the added heat is absorbed and the stress of increased temperature is reduced. In doing so the rate of decomposition of PCl_5 becomes faster than its formation thus numerator value in the equilibrium constant expression becomes smaller than denominator. Finally, the system reaches to a new equilibrium state with lower value of Kc.

On the other hand, if we lower the temperature by removing heat from the system at constant pressure, it shifts to the right to produce more PCl_5. In this way the value of Kc to attain new equilibrium will be enhanced.

The effect of temperature may be summarized in Le-Chatelier's perspective as **"a decrease in temperature of a chemical system at equilibrium favours the reaction to proceed in the exothermic direction where as an increase in temperature favours the reaction to turn in the endothermic direction"**.

Table 7.5 **Effect of change in temperature on equilibria**

Chemical Systems	Change of Temperature	Effect on equilibrium
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ (ΔH = -ve)	Temperature Increases	Shift to the left
	Temperature Decreases	Shift to the right
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ (ΔH = +ve)	Temperature Increases	Shift to the right
	Temperature Decreases	Shift to the left

Self Assessment

For the reaction
$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ (ΔH = +ve)
Predict the direction when following stresses are applied.
(a) Pressure increases (b) Temperature decreases (c) More PCl_5 is added

Effect of Catalyst

A catalyst minimizes the time to reach equilibrium but does not effect on change in equilibrium position of the system.

7.3 INDUSTRIAL APPLICATION OF LE CHATELIER'S PRINCIPLE (Haber's process)

The synthesis of ammonia by Haber's process is an industrial application of Le Chatelier's principle.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \ (\Delta H = -ve)$$

The equation tells us that the reaction is exothermic and proceeds with decrease in number of moles of product. To get the maximum promising yield of ammonia following conditions of Le Chatelier's principle should be maintained.

(i) Effect of Pressure

In the given equation four moles of gases on the left side and two mole on the right side, an increase in the pressure shifts the reaction on the right side and favours the formation of ammonia gas. Since a very high pressure may be dangerous for the process, an optimum pressure should be settled. The optimum compromising pressure to a good yield of ammonia is 200 to 300 atm.

(ii) Effect of Temperature

As the reaction is exothermic ($\Delta H° = -ve$), a decrease in temperature shift the reaction to the right side and favours the formation of NH_3 gas. The lowering in temperature do favours the high yield of ammonia but on the other hand it slows down the rate of reaction. The optimum choice of temperature on operational level is 400-500°C.

(iii) Effect of Concentration Change

Increase in concentration of nitrogen (N_2) or hydrogen (H_2) or decrease in the concentration of Ammonia (NH_3) shift the reaction in the forward direction and yield the maximum amount of ammonia.

(iv) Addition of Catalyst

Catalyst speed up the reaction without effecting on equilibrium position. Finely divided Iron is used as a catalyst in the synthesis of ammonia.

Example 7.6

In the synthesis of nitric acid by Ostwald process, one of the important reactions is the oxidation of nitric oxide to nitrogen dioxide.

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad (\Delta H° = -114\ KJ/mol)$$

Use Le Chatelier's principle to predict the direction of reaction when the equilibrium is disturbed by

(a) Increasing the pressure **(b) Increasing the temperature**

(c) Adding O_2 **(d) Removing NO**

Solution:

To predict the effect of each factor asking in the question we should apply Le Chatelier's principle individually.

(a) Since 3 moles of reactant gases reacts to form 2 moles of gaseous product, an increasing pressure shift the equilibrium to the right thus more NO_2 will form.

(b) The negative sign of $\Delta H°$ indicates that forward reaction is exothermic so increasing temperature shift the equilibrium to the left thus more NO and O_2 will form.

(c) Adding more O_2 gas in the reaction mixture shift the reaction to the right. Thus more NO_2 will produce.

(d) Removing NO gas from the reaction mixture shift the system to the left.

7.4 SOLUBILITY PRODUCT

Various ionic compounds such as $Ca_3(PO_4)_2$, AgCl, $BaSO_4$ etc are practically very slightly soluble in water and commonly known as sparingly soluble salts.

$CaSO_4$ is a slightly soluble salt, when it is put into water, a very small part becomes ionized and certainly an equilibrium exists between its solid phase and ions in a saturated solution.

$$CaSO_{4(s)} \xrightleftharpoons{H_2O} Ca^{+2}_{(aq)} + SO^{-2}_{4(aq)}$$

The equilibrium expression of this ionic equilibrium may be written as

$$K_C = \frac{[Ca^{+2}_{(aq)}]\,[SO^{-2}_{4(aq)}]}{CaSO_4}$$

Since concentration of solid $CaSO_4$ in solution is fixed therefore it is not included in the equilibrium expression and thus Kc is replaced by Ksp which is known as solubility product constant or if shortens the term called as solubility product.

Do You Know?

In tropical regions NaCl is obtained by solar evaporation of sea water. The impurities of $CaCl_2$ and $MgCl_2$ are removed by treating the brine with sodium carbonate which gives insoluble precipitates of $CaCO_3$ and $MgCO_3$.

$$Ksp = [Ca^{+2}]\,[SO_4^{-2}]$$

Solubility product (Ksp) of a sparingly soluble salt may define as **"the product of molar concentration of its positive and negative ions each raised to the power of its coefficient in ionized equilibrium equation"**.

Solubility product (Ksp) of a substance in saturated solution remains constant. Like other equilibrium constants it also changes with temperature.

Table 7.6 **Solubility product (Ksp) of some slightly soluble ionic compounds in aqueous medium at 25°C.**

Group of Compounds	Formula	Ksp	Group of Compounds	Formula	Ksp
Hydroxides	$Mg(OH)_2$	1.8×10^{-11}	Chlorides	AgCl	1.6×10^{-10}
	$Zn(OH)_2$	2.1×10^{-16}		$PbCl_2$	1.8×10^{-5}
Carbonates	$CaCO_3$	3.8×10^{-9}	Fluorides	CaF_2	3.9×10^{-11}
	$BaCO_3$	8.1×10^{-9}		MgF_2	6.6×10^{-9}
Sulphate	$CaSO_4$	2.4×10^{-5}	Sulphide	Pbs	8.5×10^{-28}
	$PbSO_4$	1.7×10^{-8}		CuS	8.7×10^{-36}

Example 7.7

Write the solubility product expression for the following slightly soluble salts $CaSO_4$, $PbCl_2$, $Fe(OH)_3$.

Solution:

First we illustrate the balance equation of ionic equilibrium to find out coefficient of each ion and then write the Ksp expression.

$CaSO_{4(s)} \rightleftharpoons Ca^{+2}_{(aq)} + SO^{-2}_{4(aq)}$ $\quad$ $Ksp = [Ca^{+2}]\,[SO_4^{-2}]$

$PbCl_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Cl^{-}_{(aq)}$ $\quad$ $Ksp = [Pb^{+2}]\,[Cl^{-}]^2$

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{+3}_{(aq)} + 3OH^{-}_{(aq)}$ $\quad$ $Ksp = [Fe^{+3}]\,[OH^{-}]^3$

Example 7.8

Silver sulphate (Ag_2SO_4) is used for medicinal purpose to fill wounds. Its solubility in water at 25°C is 1.43×10^{-2} mol/dm^3. What will be its Ksp.

Solution:

First write a net ionic equation of Ag_2SO_4 to note the number of coefficient of each ion. Then put the values of ionic concentration in ksp expression.

$$Ag_2SO_{4(s)} \rightleftharpoons 2Ag^{+}_{(aq)} + SO^{-2}_{4(aq)}$$

The ionic concentrations of 2 moles Ag^+ and 1 mol SO_4^{-2} are illustrated as

$[Ag^+] = 2 \times 1.43 \times 10^{-2} = 2.86 \times 10^{-2}$ mol/dm^3

$[SO_4^{-2}] = 1.43 \times 10^{-2}$ mol/dm^3

Now inserting these values in ksp expression

$Ksp = [Ag^+]^2\,[SO_4^{-2}]$

$Ksp = [2.86 \times 10^{-2}]^2\,[1.43 \times 10^{-2}]$

$Ksp = 1.17 \times 10^{-5}$ mol^3/dm^9

Example 7.9

The Ksp of $Zn(OH)_2$ is 2.1×10^{-16} mol^3/dm^9 at 25°C. Calculate its solubility in g/dm^3. (The atomic mass of Zn = 65.4)

Solution:

This problem is exactly reverse from previous one. Here we are given with the value of Ksp and the task is to find out solubility in g/dm^3. Making the strategy, first write the Ksp expression in which ionic concentration will be written in term of 'S' then calculate molar solubility from known Ksp value. Finally convert it into g/dm^3 by multiplying it with molecular mass of $Zn(OH)_2$.

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2OH^{-}_{(aq)}$$

$Ksp = [Zn^{+2}]\,[O\bar{H}]^2$

Since there are two hydroxide ions for every zinc ion, we may rewrite the expression as

$Ksp = [X]\,[2X]^2$

$Ksp = 4x^3$

$2.1 \times 10^{-16} = 4x^3$

$\dfrac{2.1 \times 10^{-16}}{4} = X^3$

$X = 3.74 \times 10^{-6}\ mol/dm^3$

To get the solubility in gram/dm^3, find the molecular mass of $Zn(OH)_2$ which is

$65.4 + 32 + 2 = 99.4$

$$\text{Solubility} = \frac{3.74 \times 10^{-6} mol}{dm^3} \times \frac{99.4g}{mol} = 3.717 \times 10^{-4} g/dm^3$$

Application of Ksp

Precipitation is a kind of double displacement reaction in which two solutions of different salts mixed together to form two products, one of these product is insoluble in solution and called as precipitate. For example when an aqueous solution of silver nitrate and potassium chloride mix together, the Ag^+ ions of $AgNO_3$ combine with $C\bar{l}$ ions of KCl and form an insoluble silver chloride (AgCl) which can be precipitated out.

Do You Know?

Sparingly soluble salts play significant role in many aspects of our life including medicine, industry and even in several natural processes. For example $BaSO_4$ is opaque to X-rays and use to diagnose ulcer in food canal.

$$AgNO_{3(aq)} + KCl_{(aq)} \rightleftharpoons AgCl_{(s)} + KNO_{3(aq)}$$

The net ionic equation of the above precipitation reaction is shown as

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightleftharpoons AgCl_{(s)}$$

The Ksp of AgCl (Table-7.6) tells us about its limit of solubility in solution but the question is that whether or not a precipitate of AgCl forms when aqueous solutions of $AgNO_3$ and KCl of specific concentrations mixed together. To reach the answer we should know another term known as ionic product.

Ionic product or reaction quotient is **"the product of molar concentration of the ions each raised to the power by its coefficient mentioned in net ionic equation"**. Ionic product is relevant to both saturated and unsaturated solution while ksp is only applicable to saturated solution which involves a dynamic equilibrium between an insoluble salt and its aqueous ions.

Now by using the following three relationships between ionic product (Qsp) and solubility product (Ksp), one can predict even if the salt form precipitate by mixing two different salt solution.

Ksp > Qsp	Solution is unsaturated in which no ppt is formed
Ksp = Qsp	Solution is saturated
Ksp < Qsp	Solution is supersated in which ppt is formed

Example 7.10

A solution is prepared by mixing 600cm^3 of 7.5×10^{-4}M $BaCl_2$ into 300cm^3 of 2.4×10^{-3}M Na_2SO_4. Will a precipitate of $BaSO_4$ form when equilibrium is reached?
(Ksp of $BaSO_4 = 1.1 \times 10^{-10}$ mol^2/dm^6)

Solution:

To solve this problem, first we determine the concentration of Ba^{+2} ions and SO_4^{-2} ion in the total volume of the mixture i.e. in 900cm^3. Then determine ionic product (Q_{sp}) and finally compare it with ksp value of $BaSO_4$ to decide whether precipitate will form or not

$$[Ba^{+2}] = 7.5 \times 10^{-4}M\left(\frac{600}{900}\right) = 5 \times 10^{-4}M$$

$$[SO_4^{-2}] = 2.4 \times 10^{-3}M\left(\frac{300}{900}\right) = 8 \times 10^{-4}M$$

Now substitute these ionic concentrations into ionic product expression

$Q_{sp} = [Ba^{+2}]\,[SO_4^{-2}]$

$Q_{sp} = [5 \times 10^{-4}]\,[8 \times 10^{-4}] = 4 \times 10^{-7}$

But ksp of $BaSO_4$ is 1.1×10^{-10}.

Because Q_{sp} > ksp, precipitates of $BaSO_4$ will be formed in the solution.

7.5 COMMON ION EFFECT

In previous section we studied about precipitation of a sparingly soluble salt (AgCl) by the mixing of two highly soluble electrolytes such as $AgNO_3$ and KCl. We turn now to a different kind of process which involves the effect on solubility of a sparingly soluble salt when another salt having the same cation or an ion is added.

Do You Know?

Sink or wash basin pipes in our homes get chocked due to Mg^{+2} and Ca^{+2} ions of hard water which are precipitated as their oxides.

Consider the equilibrium settled when a saturated solution of silver chloride is prepared in water.

$$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

If now we add some amount of a soluble salt like sodium chloride (NaCl) which has Cl^- ion common to silver chloride. What will happen in Le Chatelier perspective? The increased Cl^- ions concentration in the solution produce a stress on AgCl equilibrium and to reduce this effect satisfactorily the excess Cl^- ions reacts with some Ag^+ ions and shift the equilibrium to the left and form precipitates of AgCl. Conclusively, solubility of silver chloride in the solution decreases if sodium chloride is added, thus **"to decrease the solubility of a sparingly soluble salt in solution by the addition of a highly soluble salt with one common ion refers as common ion effect"**.

Since common ion effect is related to the lowering in the solubility of slightly soluble salt in the precipitation formation, it plays versatile roles in many areas of analytical chemistry such as buffering of solutions, purification of salts, soap precipitation and other qualitative and quantitative analysis.

Society, Technology and Science

Application of chemical equilibrium in industrial process

Obtaining the maximum amount of product in a concerned chemical reaction is the main task in many industrial processes and it depends on proper selection of reaction conditions as described by Lechatlier principle. It is a skill of a chemist to choose conditions that fovours the maximum yield of a commercially significant compound. For example in the manufacturing of H_2SO_4 by contact process, oxidation of SO_2 is a reversible and exothermic reaction.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \ (\Delta H = -45 \text{ KJ/mol})$$

Since according to Lechatlier principle a low temperature and high pressure favour the maximum yield, but low temperature slow down the rate of reaction and high pressure dangerous for the equipment so an optimum temperature (450°C) and pressure (1 – 2 atmosphere) is opted for the process with a suitable catalyst (V_2O_5).

Activity

In this activity you will observe how the disturbance in the chemical equilibrium between gaseous CO_2 and carbonic acid of beverage bottle causes you to lose the appealing taste of a soft drink.

Take a bottle of a fizzy drink. The soft drink bottle, when sealed, contain the dissolved carbon dioxide (in the form of carbonic acid) and gaseous CO_2 (in the space between the liquid and the lid) which are in equilibrium with each other. Just open the lid and you get to hear the hissing sound of CO_2 escaping out and hence the equilibrium gets disturbed thereby causing carbonic acid to produce CO_2 that comes out and takes the place of escaped gas. Now keep the bottle opened for an hour and then taste it. You'll find it less fizzy or mild since it would have lost much of its dissolved CO_2.

SUMMARY with Key Terms

- **Chemical Equilibrium** is a state in a reversible reaction where rate in both directions are equal and no net change in the conc. of reactants and products occur with time.
- **Equilibrium Constant (Kc)** is a quantity that represents the ratio of molar concentration of product to that of reactant at equilibrium state. It is independent upon concentration of reaction mixture, however change with the temperature.
- **Equilibrium Expression** reveals that when at certain temperature a chemical reaction reaches to equilibrium state the ratio of active mass of products to reactants become constant.
- **Reaction Quotient (Qc)** represents the ratio of molar conc. of products to reactants in a reversible reaction, its value however not necessarily equal to Kc.
- **Equilibrium Constant (Kp)** represents the ratio of partial pressure of products gases to that of reacting gases at equilibrium state of a homogenous gaseous reaction.
- **$K_p = K_c (RT)^{\Delta n}$** is a relationship between Kp and Kc of a gas phase reaction at specific temperature. If one is known, other can be determined at given temperature.
- **Law of mass action** tells that the rate in the forward and backward directions of a reversible reaction is proportional to the active masses of reacting species at constant temperature.
- **Direction of reversible Reaction** can be predicted at particular instant of time by comparing the value of Qc and Kc. If Qc = Kc then it is said to be at equilibrium.
- **Extent of reversible reaction** can be predicted by knowing the value of Kc. Hence if Kc is very large, the reaction is expected to proceed to maximum extent. Likewise a very small value of Kc tells us that the reaction proceed hardly at all.

- **Lechatlier Principle** tells that if a stress is imposed on a system at equilibrium, the equilibrium is unbalanced and it tends to turn in forward or backward direction to reduce the effect of this applied stress.
- **Change in Concentration** of any reacting substance make the system unbalance and for reducing the effect of this stress, system turns toward the direction of decreased concentration.
- **Change of Pressure** Increase pressure shift the equilibrium point in the direction of less volume where as decrease pressure shifts it in the direction of greater volume.
- **Change of Temperature** In endothermic reactions, an increase in temperature shift the equilibrium to the right where as in exothermic reactions an increase in temperature shift the reaction to the left.
- **Solubility Product (Ksp)** is the product of molar concentration of ions of a sparingly soluble salt and related to saturated solution which involves dynamic equilibrium between insoluble salt and its aqueous ions.
- **Ionic Product (Qsp)** is also the product of molar conc. of ions of a salt. It is relevant to both saturated and unsaturated solution.
- **Common Ion Effect** tells that the solubility of a sparingly soluble salt in a solution can be decreased by a adding a highly soluble salt with one ion common to it.

EXERCISE

Multiple Choice Questions

1. Choose the correct answer

(i) In the equilibrium system of $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$, the correct relationship between Kc and Kp is:
(a) Kp> Kc (b) Kp< Kc (c) Kp = Kc (d) $\frac{K_p}{K_c} = 1$

(ii) The equilibrium of which of the following reaction would not be affected by an increase in pressure:
(a) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
(b) $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$
(c) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$
(d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

(iii) What happens to the value of Kc when a catalyst is added to a chemical system at equilibrium?
(a) It decreases
(b) It increases
(c) It becomes zero
(d) It remains unchanged

(iv) The correct Ksp expression of a sparingly soluble salt $Li_2C_2O_4$ among the following is:
(a) $Ksp=[Li^+][C_2O_4^{-2}]$
(b) $Ksp=[Li^+]^2[C_2O_4^{-2}]$
(c) $Ksp=[2Li^+][C_2O_4^{-2}]$
(d) $Ksp=[2Li^+]^2[C_2O_4^{-2}]^2$

(v) If the equilibrium expression of a reversible reaction is

$$Kc= \frac{[C]^2}{[A][B]}$$

The balanced equilibrium equation should be:
(a) $C \rightleftharpoons A+B$
(b) $A+B \rightleftharpoons C$
(c) $2C \rightleftharpoons A+B$
(d) $A+B \rightleftharpoons 2C$

(vi) The equilibrium of $N_{2(g)}+O_{2(g)} \rightleftharpoons 2NO_{(g)}$ (ΔH = +ve) is affected by change in:
(a) Temperature only
(b) Pressure only
(c) Both temperature and pressure
(d) Neither temperature nor pressure

(vii) In the reaction $A_{(g)} + B_{(g)} \rightleftharpoons 2C_{(g)}$, the equilibrium constants Kp = Kc because:
(a) $\Delta n > 1$ (b) $\Delta n < 1$ (c) $\Delta n = 1$ (d) $\Delta n = 0$

(viii) The term active mass use in law of mass action means:
(a) No. of mole
(b) No. of molecules
(c) mole per dm^3
(d) gram per dm^3

(ix) NaCl when added to an aqueous silver chloride solution:
(a) Decreases the solubility of AgCl
(b) Increases the solubility of AgCl
(c) Forms a clear solution
(d) Does not effect

(x) Some reactions are nearly to completion in the forward direction and identified by their:
(a) Very high value of Kc
(b) Very low value of Kc
(c) Very high value of ΔH
(d) Very low value of ΔH

Short Questions

1. Define the following:
   (i) Reversible reaction (ii) Chemical equilibrium
2. Write expression of Kc and Kp for the following reversible reactions.
   (i) $2NO_{2(g)} + 7H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 4H_2O_{(g)}$
   (ii) $2H_2S_{(g)} + 3O_{2(g)} \rightleftharpoons 2H_2O_{(g)} + 2SO_{2(g)}$
3. (a) Define solubility product.
   (b) Write the solubility product expression of the following salts.
   BaF_2, $Li_2C_2O_4$, $MgCO_3$, Ag_3PO_4
4. Using Le-Chatelier's principle, explain three ways in which yield of SO_3 can be increase in Contact process.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad (\Delta H^\circ = \text{-ve})$$

Descriptive Questions

1. State Law of mass action and derive Kc expression of a general reversible reaction.
2. State Le-Chatelier's principle. Explain the industrial application of Le-Chatelier's principle using Haber's process.
3. Give brief account on Common ion effect.
4. Define equilibrium constant (Kc). How it helps in predicting the
   (i) Direction of reaction (ii) Extent of reaction.

Numerical Questions

1. At 444°C reaction of hydrogen and iodine is performed in a sealed $1dm^3$ steel vessel.
   $$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$
   If equilibrium mixture contains 1 mole of H_2, 1 mole of I_2 and 7 moles of HI. Calculate
   (a) Equilibrium constant (Kc) (b) Initial concentration of H_2 and I_2
   [Ans: Kc = 49, initial conc. of $H_2 = I_2 = 4.5$ moles]
2. Lead fluoride (PbF_2) is a high melting white solid used in glass coating to reflect IR rays. Its solubility in water at 25°C is $0.58g/dm^3$. Calculate its Ksp.
   (At. mass of Pb = 207 and F = 19) [Ans: 5.3×10^{-8} mol^3/dm^9]
3. 3. A solution of $CaCO_3$ is prepared by mixing $200cm^3$ of $2.4 \times 10^{-4}M$ $Ca(NO_3)_2$ and $300cm^3$ of $4.5 \times 10^{-2}M$ K_2CO_3. Will $CaCO_3$ precipitate upon cooling to 25°C if Ksp of $CaCO_3$ at 25°C is 3.8×10^{-9}. [Ans: $CaCO_3$ precipitate]
4. Hydrogen iodide is a colourless gas prepared by reacting H_2 and I_2.
   $$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$
   In an equilibrium study of above reaction, 1.2 mole of H_2 and 1.2 moles of I_2 were injected in an evacuated $1000cm^3$ sealed flask and start the reaction to occur at 440°C until the equilibrium is formed. If Kc for this reaction is 49, calculate the equilibrium concentration of H_2, I_2 and HI.
   [Ans: $[H_2] = 0.267$ mol/dm³, $[I_2] = 0.267$ mol/dm³, $[HI] = 1.866$ mol/dm³]