Step 4: Rate constant (k)

Use any experiment (e.g., Exp 1):

$$\text{Rate} = k[HI]^2$$
$$1.1\times10^{-3} = k(0.015)^2$$
$$K = \frac{1.1\times10^{-3}}{0.000225} \approx 4.89M^{-1}s^{-1}$$

Answer:

- **Rate Law:** Rate = $k[HI]^2$
  $k = 4.89\ M^{-1}s^{-1}$
- **Order:** Second order

ADDITIONAL SLOs BASED MCQs

1. **The rate of a reaction ------------ as the reaction proceeds.**
A. Increases B. Decreases
C. Remains the same D. May increase or decrease

2. **The unit of the rate constant is the same as that of the rate of reaction in ----------- order reaction.**
A. First B. Second C. Third D. Zero

3. **For the reaction:**
$2A + B \xrightarrow{\text{slow}} C$, the rate law for the reaction is
A. rate = $k[A]^2[B]$ B. rate = $k[A][B]$ C. rate = $k[C]$ D. None of these

4. **For the reaction: $2A + B \longrightarrow C + D$**
The expression for the rate law is, rate = $k[A]^2$, the order of reaction in B is
A. First B. Second C. Third D. Zero

5. **The activation energy for a reaction can be:**
A. Increased by increasing temperature
B. Increased by decreasing temperature
C. Decreased by increasing concentration of reactants
D. None of these

6. **Rate law for the reaction**
$R{-}X + H_2O \rightarrow R{-}OH + HX$ is, rate = $k[R{-}X]$. The rate of reaction will be doubled when
A. Concentration of H_2O is doubled B. Concentration of R–X is reduced to half
C. Concentration of both R–X and H_2O is doubled D. None of these

7. **The rate of a catalyzed reaction is independent of the concentration of**
A. Reactants B. Products C. Catalyst D. Zero

8. **If a reaction proceeds in such a way that order of reaction is independent of the reactants concentration, the overall order of reaction would be**
A. First B. Second C. Third D. Zero

9. **Reactions with high activation energy are usually**
A. Fast B. Slow C. Exothermic D. Reversible

10. **In a reversible reaction, catalyst lowers the activation energy of the**
A. Forward reaction B. Reverse reaction
C. Forward as well as reverse reaction D. Forward reaction but increases for the reverse reaction

11. **If rate of reaction doubles for every 10°C rise in temperature what is the increase in rate of reaction if temperature rises from 10°C to 100°C**
A. 112 times B. 100 times C. 400 times D. 512 times

12. **Order of reaction is the number of reacting molecules whose concentration alters as a result of chemical change for which order of reaction the unit of rate constant (k) is the same as that of rate of reaction?**
A. 1st order reaction B. 2nd order reaction C. Zero order reaction D. 3rd order reaction

---

13. **The hydrolysis of $(CH_3)_3CBr$ by OH^- ion proceed in two steps:**
$RBr \rightleftharpoons R^+ + Br^-_{slow}$
$R^+ + OH^- \rightleftharpoons R - OH_{fast}$
Which of the following rate equation is consistent with this scheme?
A. rate = $k[RBr]^2$ B. rate = $k[RBr][OH^{-1}]$ C. rate = $k[R\,Br][OH^-]^2$ D. rate = $k[RBr]$

14. **Which one of the following correctly represents the units of the rate constant k for a first order reaction?**
A. s^{-1} B. $mol\ dm^{-3}s$ C. $mol.dm^{-3}s^{-1}$ D. $mol^{-1}dm^3s$

15. **If the rate of decay of a radioactive isotope decreases from 200 counts per minutes to 25 counts per minute after 24 hours. What is half life?**
A. 3 hours B. 4 hours C. 6 hours D. 8 hours

Answer Key with Explanations

Q.#	Ans.	Explanations
1.	B	The rate of reaction is directly proportional to concentration of reactant. As reaction goes the amount of reactant decrease hence the rate of reaction decreases.
2.	D	$A \longrightarrow \text{Product}$ Rate = $k[A]^0$ So, Rate = k = $mol\ dm^{-3}\ s^{-1}$
3.	A	$2A + B \xrightarrow{\text{Slow}} C$ Since two molecules of 'A' and one molecule of 'B' participate, so rate equation will be Rate = $k[A]^2[B]$ Order of reaction = 2 + 1 = 3
4.	D	Rate equation shows that concentration of reactant 'B' does not affect reaction rate. Therefore the order of reaction in 'B' is zero.
5.	B	k = Ae–Ea/RT Ea ∝ 1 T
6.	D	(i) Rate ∝ [R – X]. It means when concentration of R – X doubles, rate of reaction also doubles. (ii) Concentration of H_2O does not affect the rate of reaction. So to increase rate of reaction, it is not necessary to increase conc. of H_2O.
7.	B	**According to Law of mass action:** The rate of a chemical reaction is directly proportional to the active mass of the reactant or to the product of active masses if more than one reactants are involved in a chemical reaction. As the concentration of a catalyst increases its catalytic activity also increase.
8.	D	**Such a reaction is zero order reaction:** $A + B \longrightarrow \text{Product}$ Rate = $k[A]^0[B]^0$ Order of reaction = zero
9.	B	**According to Arrhenius equation:** $k = Ae^{-Ea/RT}$ k = Rate of reaction (when molar concentration of reactants are in unity) Rate = $Ae^{-Ea/RT}$ Rate ∝ 1/Ea
10.	C	A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.
11.	D	For every 10°C rise rate of reaction become double temp is increase 10°–100°(9 Time) $2^9 = 512$ Time rate of reaction will increase
12.	C	$R = K[conc]^0$ $\frac{mol/dm^3}{sec} = K$

13.	D	Rate expression is always according to slow step
14.	A	$R = K[conc]^1$ $mol/dm^3/sec = k.mole/dm^3$ $K = sec^{-1}$
15.	D	200 → 100 → 50 → 25 Total 3half-life=24 hours 1 Half-life=8 hours

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Differentiate between instantaneous and average rate of reaction.

Ans. Differences between Instantaneous and Average Rate of Reaction:

Average Rate	Instantaneous Rate
"The rate at any one instant during the interval is called the instantaneous rate".	"The rate of reaction between two specific time intervals is called average rage".
Instantaneous rate = $\frac{dx}{dt}$	Average rate = $\frac{\Delta x}{\Delta t}$
At first instantaneous rate is higher than average rate.	At the end, average rate is higher than instantaneous rate.

Q.2 Differentiate between rate and rate constant of a reaction.

Ans. Differences between rate and rate constant of a reaction:

Rate of reaction	Rate constant
(i) It is the speed at which the reactants are converted into the products.	It is a constant of proportionality in the rate law expression.
(ii) Rate = $\frac{\Delta x}{\Delta t}$	Rate = k[Reactants] $\Rightarrow k = \frac{Rate}{[Reactants]}$
(iii) It depends upon the concentration of reactant species at that moment.	It refers to the rate of reaction at specific point when concentration of every reacting species is unity.
(iv) It decreases with the progress of reaction generally.	It is a constant and does not depend on the progress of the reaction.

Q.3 Radioactive decay is always first order reaction. Justify.

Ans. A radioactive substance has a single species at a moment, whose nucleus under goes disintegration. As only one reactant is involved, so it follows 1st order mechanism.

e.g., Half-life of $^{235}_{92}U$ is 710 million years. It means if one kg uranium is present at start, after 710 million years, 0.5 kg of it will disintegrate and after next 710 million years 0.25 kg of it will disintegrate and so on. Therefore we can say that half-life of a radioactive decay is always a 1st order reaction.

Q.4 What is zero order reaction? Give one example.

Ans. Zero Order Reaction: "The reaction which is entirely independent of the concentration of reactant molecules is called zero order reaction"

Mathematical Form:

$$A \longrightarrow Products$$
$$Rate = k[A]^0$$
$$Rate = k$$

Example: All photosynthetic reactions are usually zero order reactions.

Q.5 The order of reaction may be in fraction. Explain.

Ans. Fractional Order Reaction:

The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value.

Example:

Consider the formation of carbon tetrachloride from chloroform.

$$CHCl_{3(l)} + Cl_{2(g)} \longrightarrow CCl_{4(l)} + HCl_{(g)}$$

$$Rate = k[CHCl_3]\ [Cl_2]^{1/2}$$

The sum of exponents will be 1 + 1/2 = 1.5 so,

Order of reaction = 1.5

Q.6 Differentiate between order of reaction and rate of reaction.

Ans. Order of Reaction:

"The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction." **OR**

"The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction."

Rate of Reaction:

(i) It is the speed at which the reactants are converted into the products.

(ii) Rate = $\frac{\Delta x}{\Delta t}$

(iii) It depends upon the concentration of reactant species at that moment.

(iv) It decreases with the progress of reaction generally.

Q.7 Define half-life period of a reaction. Give one example.

Ans. Half-Life Period:

"The time which is required to convert 50% of the reactants into products is called half-life period ($t_{1/2}$)."

Example:

Decomposition of N_2O_5

The half-life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

$$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2 \qquad t_{1/2} = 24 \text{ min at } 45°C$$

[1st order reaction]

Importance:

- We can use the rate of decay of an item to determine the age of item.
- We can predict the amount of radioactive material that will remain after a given amount of time.

Half-Life and Order of Reaction:

"Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction."

$$[t_{1/2}] \propto \frac{1}{a^{n-1}}$$

Half-Life and 2nd Order of Reaction:

For Second Order Reaction: **n = 2**

$$[t_{1/2}]_2 \propto \frac{1}{a^{2-1}} \quad \text{or} \quad [t_{1/2}]_2 \propto \frac{1}{a^1}; \qquad \text{Since} \quad [t_{1/2}]_2 = \frac{1}{ka}$$

Note: In case of second order reaction, the half-life period is inversely proportional to the initial concentration of the reactant.

Half-Life and 3rd Order of Reaction:

For Third Order Reaction: n = 3

$$[t_{1/2}]_3 \propto \frac{1}{a^{3-1}} \quad \text{or} \quad [t_{1/2}]_3 \propto \frac{1}{a^2}; \qquad \text{Since} \quad [t_{1/2}]_3 = \frac{1.5}{ka^2}$$

For a third order reaction, the half-life period is inversely proportional to the square of initial concentration of reactants.

Q.8 What is rate determining step? Give a suitable example.

Ans. Rate Determining Step:

"A slowest step in reaction mechanism which can determine the overall rate of reaction is called rate determining step."

Rate Determining Step:

"Rate-determining step is that step of a chemical reaction which controls the rate of reaction."

- If a reaction occurs in several steps, one of the steps is the slowest.
- The rate of this step determines the overall rate of reaction.
- This slowest step is called the rate determining or rate limiting step.
- The total number of molecules taking part in the rate determining step-appear in the rate equation of the reaction.
- Let us consider the following reaction

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

The rate equation of the reaction is found to be:

$$\text{Rate} = K[NO_2]^2$$

- The reaction is second order with respect to $NO_{2(g)}$. Experiment shows that $CO_{(g)}$ is not taking part in the rate determining step. The proposed mechanism for this reaction is as follows:

Step 1: $NO_{2(g)} + NO_{2(g)} \xrightarrow{\text{Slow}} NO_{3(g)} + NO_{(g)}$ (It is a slow hence rate determining step)

Step 1: $NO_{3(g)} + CO_{(g)} \xrightarrow{\text{fast}} NO_{2(g)} + CO_{2(g)}$

- The first step is the rate determining step and NO_3 which does not appear in the balanced equation, is called the reaction intermediate.
- The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products.

Q.9 Differentiate between fast step and the rate determining step.

Ans.

Fast Step	Rate Determining Step
i. A step in a chemical reaction which proceeds so fastly that we are unable to determine the rate of reaction is called fast step. It has no effect on overall rate of reaction.	A slowest step in reaction mechanism which can determine the overall rate of reaction is called rate determining step.
ii. **For example:** For a reaction $2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$ The steps of reaction mechanisms are a. $2NO_{(g)} + H_2 \xrightarrow{\text{Slow}} H_2O_{2(g)} + N_{2(g)}$ b. $H_{2(g)} + H_2O_{2(g)} \xrightarrow{\text{fast}} 2H_2O_{(g)}$ Step (b) is fast step.	In the example given in left column, step (a) is the rate determining step. $2NO_{(g)} + H_{2(g)} \xrightarrow{\text{slow}} H_2O_{2(g)} + N_{2(g)}$ It is experimentally determined. It involves 2 moles NO and one mole H_2.
iii. Reactants of fast step are eliminated from rate equation. Moreover, in a multistep reaction, number of fast steps can be one or more than one.	Reactants of slow step are present in rate equation i.e., Rate = $k[H_2][NO_2]^2$. Moreover there is only one rate determining step in a multistep reaction.
iv. Fast step is unable to determine order of reaction.	Sum of reactant coefficients of slowest step is the order of reaction. e.g. in the above reaction: Order of reaction = 2 + 1 = 3.

Q.10 The sum of the co-efficient of a balanced chemical equation is no necessarily important to give the order of reaction. Give reasons in support of your answer.

Ans. Order of a chemical reaction is not necessarily the sum of the coefficients of the balanced chemical equation because the order of reaction is determined experimentally and not from the balanced chemical equation.

e.g., $2H_2 + 2NO_2 \longrightarrow 2H_2O_2 + N_2$

For this reaction, the sum of coefficients of balanced equation is 2 + 2 = 4 but the reaction is 3rd order. It is experimentally verified that rate of reaction is directly related to conc. of H_2 and to the square of concentration of NO_2. So the rate equation of this reaction is

$$\text{Rate} \propto [H_2]^1[NO_2]^2$$

$$\text{Rate} = k[H_2]^1[NO_2]^2$$

Order of reaction is sum of exponents of rate equation. So,

Order of reaction = 1 + 2 = 3

Q.11 Define energy of activation. How is it affected by temperature?

Ans. Energy of Activation:

The minimum amount of energy in addition to average kinetic energy which is just sufficient to convert the reactants into products is called energy of activation (E_a).

Effect of Temperature:

According to Arrhenius Equation:

$$k = Ae^{-Ea/RT}$$

k is exponentially related to activation energy E_a and temperature T. The equation shows that the increase in temperature, increase the rate constant and the reaction of high activation energy have low "K" values. It means that if we increase the temperature the activation energy of the reaction decreases.

Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short lived species and decomposes into products immediately. It has a transient existence that is why it is also called a transition state.

Q.12 Describe Half Life Method to determine order of reaction.

Ans. Half-Life Method:

"Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction."

$$[t_{1/2}] \propto \frac{1}{a^{n-1}}$$

Let us perform a reaction twice by taking two different initial concentrations a_1 and a_2 and their half-life periods are found to be t_1 and t_2 respectively.

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the above two equations:

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log on both sides, we have

$$\log\left(\frac{t_1}{t_2}\right) = \log\left[\left(\frac{a_2}{a_1}\right)^{n-1}\right]$$

$$\log\left(\frac{t_1}{t_2}\right) = (n-1)\log\left(\frac{a_2}{a_1}\right)$$

$$n = 1 + \frac{\log\frac{t_1}{t_2}}{\log\frac{a_2}{a_1}}$$

Where, n = order of reaction

Q.13 Define Catalysis. Write two characteristics of a catalyst.

Ans. Catalysis:

"The process, which takes place in the presence of a catalyst, is called catalysis."

Characteristics of a Catalyst:

1. **Unchanged Chemical Composition:**
A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state.
Examples:
(i) MnO_2 is added as a catalyst for the decomposition of $KClO_3$. But MnO_2 is regenerated at the end in the form of a fine powder.
(ii) In some cases, the shining surfaces of the solid catalyst become dull.

2. **Effectiveness of a Catalyst:**
Sometimes, we use a trace of a metal catalyst to effect very large amount of reactants.
Examples:
(i) 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.
(ii) Dry HCl and NH_3 don't combine, but in the presence of trace of moisture, they give dense white fumes of NH_4Cl.
(iii) Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.

Q.14 Define catalysis. Give its different types with one example in each case.

Ans. Catalysis:

"The process, which takes place in the presence of a catalyst, is called catalysis."

Types of Catalysis:

(a) Homogeneous Catalysis **(b)** Heterogeneous Catalysis

(a) Homogeneous Catalysis:

"When the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout, then it is called homogeneous catalysis."

The catalyst is distributed uniformly throughout the system.

Examples:

The formation of SO_3 from SO_2 and O_2 in the lead chamber process for the manufacture of sulphuric acid needs NO as a catalyst. Both the reactants and the catalyst are gases.

(b) Heterogeneous Catalysis:

"When the catalyst and the reactants are in different phases, then it is called heterogeneous catalysis."

Examples:

Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3.

$$4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt_{(s)}} 4NO_{(g)} + 6H_2O_{(g)}$$

Q.15 Differentiate between homogeneous and heterogeneous catalysis. Give example.

Ans.

Homogeneous Catalysis	Heterogeneous Catalysis
(i) It is catalysis in which the catalyst and reacting substances are in same physical state/phase.	(i) It is catalysis in which the catalyst and reacting substances are in different phases.
(ii) Catalyst is uniformly distributed.	(ii) No uniform distribution of catalyst.
(iii) Mostly liquid or gaseous catalysts are used in homogeneous catalysis.	(iii) Catalyst is solid and reacting substances are either liquids or gases.
(iv) e.g., $2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO_{(g)}} 2SO_{3(g)}$	(iv) e.g., $4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt_{(s)}} 4NO_{(g)} + H_2O_{(g)}$

Q.16 Describe the effects of catalyst on reversible reaction.

Ans. Effect of Catalyst on Rate of Reversible Reaction:

In reversible chemical reaction, a catalyst, suitable for forward reaction may be used to carry out back reaction as it increases the rate of both forward and reverse processes by lowering the activation energy of both forward and reverse steps by giving new path to the reaction. This reduces the time to attain the equilibrium state. It does not affect the equilibrium state K_c.

SELF--ASSESSMENT Chapter # 07

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) **The rate of reaction:**
A. Increases as the reaction proceeds
B. Decreases as the reaction proceeds
C. Remains the same as the reaction proceeds
D. May decrease or increase as the reaction proceeds

(ii) **On a Boltzmann distribution curve, the area under the curve represents:**
A. Activation energy of the reaction.
B. Total number of molecules in the sample.
C. Average kinetic energy of the molecules.
D. Rate constant of the reaction.

(iii) **How does the presence of a catalyst affect the rate of a chemical reaction?**
A. It always decreases the rate of the reaction.
B. It always increases the rate of the reaction.
C. It increases the rate of the forward and decreases the rate of the reverse reaction.
D. It increases the rate of both the forward and reverse reactions.

(iv) **A first-order reaction has a half-life (t1/2) of 20 minutes. What is the value of its rate constant (k)?**
A. 0.05 min^{-1} B. 0.693 min^{-1} C. 0.0347 min^{-1} D. 13.86 min^{-1}

(v) **The reaction pathway diagram with a lower peak represents:**
A. A slower reaction B. A reaction with no catalyst
C. A catalyzed reaction D. A reversible reaction

(vi) **The order of a chemical reaction, that is independent of concentration is:**
A. Second order reaction B. First order reaction
C. Zero order reaction D. Pseudo first order reaction

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) Differentiate clearly between order and molecularity of a reaction.
(ii) How does increasing temperature affect the rate of a reaction?
(iii) What is the significance of the rate constant in a rate equation?
(iv) Can a catalyst be consumed in a chemical reaction? Why or why not?
(v) The shape of the Boltzmann distribution curve change with temperature. How?
(vi) What is the order of the reaction? Explain based on the units of the rate constant.
(vii) Calculate the rate of reaction from the following data: 0.5 mol of reactant consumed in 10 s.
(viii) A radioactive isotope decays by a first-order process with a half-life of 12 hours. Calculate the rate constant for the decay in s^{-1}.

Q.3 Extensive Questions. **(2 × 4 = 8)**

(a) How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?
(b) Calculate the reaction rate if the concentration of A is 0.5 M, the concentration of B is 0.2 and the rate constant k is 4.0 $M^{-2}s^{-1}$. Given the rate law for a reaction: Rate = $k[A][B]^2$.

◆

Chapter 08
CHEMICAL EQUILIBRIUM

Student Learning Outcomes

After studying this chapter, students will be able to:

- Describe the microscopic events that occur when a chemical system is in equilibrium. Define with examples. **(Understanding)**
- Differentiate between microscopic and macroscopic events in a chemical reaction. **(Understanding)**
- Propose microscopic that account for observed macroscopic changes that take place during a shift in equilibrium. **(Understanding)**
- Describe what is meant by a reversible reaction and dynamic equilibrium in terms of the rate of forward and reverse reactions being equal and the concentration of reactants and products remaining constant. **(Understanding)**
- Define dynamic equilibrium between two physical states. **(Knowledge)**
- Deduce the equilibrium constant expression [K_c] from an equation for homogeneous reaction. **(Understanding)**
- Determine the relationship between different equilibrium constants (K_c) for the same reaction at the same temperature. **(Understanding)**
- Write the equilibrium expression for a given chemical reaction in terms of concentration, K_c, partial pressure K_p, number of moles K_n and mole fraction K_x. **(Application)**
- State the necessary conditions for equilibrium and the ways that equilibrium can be recognized. **(Knowledge)**
- 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. **(Knowledge)**
- Determine if Kc will increase or decrease when temperature is changed, given the equation for the reaction. **(Understanding)**
- Explain industrial applications of Le Chatelier's Principle using Haber's process and the contact process as an example. **(Understanding)**
- Discuss the industrial applications of chemical equilibria and how it can be used to optimize chemical reactions to maximize yields and minimize waste products. **(Understanding)**
- Use of concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. **(Application)**

➤ **Irreversible Reactions:**

The reactions in which the reactants are completely consumed and converted into products are called irreversible reactions. Such reactions stop when the limiting reactant is used up.

➤ **Reversible Reactions:**

Those reactions which continue in both directions, i.e., forward and reverse, without changing the concentration of reactants and products under the existing conditions. Such reactions never stop and are called reversible reactions. When a reversible chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. These reactions eventually reach a stage called chemical equilibrium.

At Chemical Equilibrium: The concentrations of reactants and products become constant and the rates of the forward and reverse reactions become equal.

Examples of some reversible reactions are given below:

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

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

$$PC\ell_{5(g)} \rightleftharpoons PC\ell_{3(g)} + C\ell_{2(g)}$$

The double arrow tells that the reaction is reversible.

MACROSCOPIC EVENTS AND MICROSCOPIC EVENTS

Macroscopic Events

"Macroscopic events refer to the phenomena that can be observed with the naked eye without considering the individual particles or molecules involved in the process."

Examples:

Change in colour, the evolution or absorption of heat, the formation of precipitate, evolution of a gas, change in volume or pressure, change in the composition of a substance in a chemical reaction are examples of macroscopic properties.

Rack Your Mind!

1. Which of the following is a macroscopic property of a reaction at equilibrium?
A) Molecules continue to collide
B) Forward and reverse rates are equal
C) Concentrations remain constant
D) Bonds are breaking and forming

Microscopic Events

"Microscopic events refer to the phenomena that cannot be observed with the naked eye."

Examples:

The collisions between molecules, breaking and forming bonds, rearrangement of atoms in molecules, loss or gain of electrons are examples of microscopic events.

REVERSIBLE REACTIONS, MICROSCOPIC EVENTS AND DYNAMIC EQUILIBRIUM

Reversible Reaction is at Equilibrium

It would apparently seem to be static. However, at microscopic level, the reaction never stops and molecules are continuously under change. The reactant molecules convert into products, while at the same time, the reverse process happens. To study at micro scale that affect the macroscopic properties of the system.

Example:

Consider the reaction between steam and carbon monoxide under appropriate conditions. On mixing these gases, macroscopic changes are observed (e.g., changes in concentration). Suppose that the reaction is started with same number of moles of both reactants.

Rack Your Mind!

2. What is meant by dynamic equilibrium?

When steam and carbon monoxide are mixed, a maximum number of collisions per second between them will occur is microscopic events. Bonds in CO and H_2O are broken and new bonds are formed to produce H_2 and CO_2. Therefore, the forward reaction has its maximum rate at the beginning. This leads to a decrease in the concentration of the reactants. As H_2O and CO are gradually used up, the forward reaction slows down.

$$H_2O_{(g)} + CO_{(g)} \longrightarrow H_{2(g)} + CO_{2(g)}$$

Reverse Reaction

As the molecules of H_2 and CO_2 accumulate, the reverse reaction also starts. With the increase in the concentration of H_2 and CO_2, more and more collisions per second between these molecules will occur as microscopic events. As bonds in H_2 and CO_2 are broken, the bonds in CO and H_2O are formed.

This means that forward reaction starts with maximum rate and gradually slows down, whereas at the start, the rate of the reverse reaction is low, gradually increases, and finally becomes constant.

$$H_{2(g)} + CO_{2(g)} \longrightarrow H_2O_{(g)} + CO_{(g)}$$

Reaction at Equilibrium

Eventually, a time comes when both reactions proceed at the same rate. The reaction at this stage is said to be in chemical equilibrium and the concentration of reactants and products become constant.

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

Unless the system is somehow disturbed, no further changes in the concentrations will occur.

Chemical Equilibrium

"The state of a reversible reaction at which composition of the reaction mixture does not change and forward and reverse rates are equal is called the state of chemical equilibrium."

Graphical Explanation:

The plots of the concentrations of reactants and products versus time for a general reaction are shown in Figure.

Suppose the reactant A is converted into the product B in a chemical reaction. The graphs in the figure show different possibilities after the equilibrium is established. At the equilibrium position, the concentrations of the reactant and the product may be equal as shown in Figure (a), or the amount of reactant may be lower or greater than that of the product as shown in Figure (b and c). However, for all of these graphs, it is clear that after the equilibrium is established, the concentrations become constant.

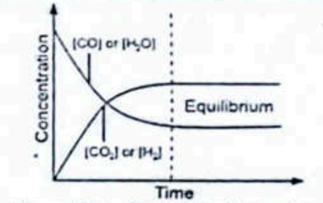


Figure: Plot of concentration vs time

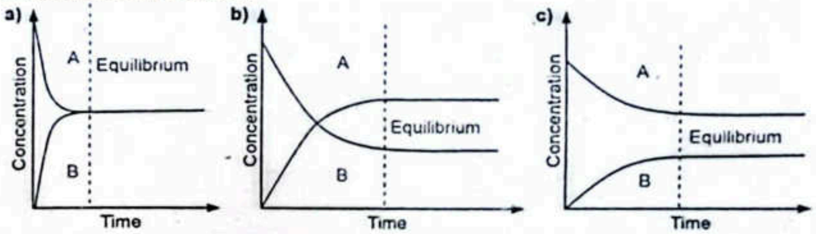


Figure: Plot of concentration vs time (a) Reactant = Product (b) Reactant < Product (c) Reactant > Product

- When the concentrations of reactants and products become constant, the reaction may apparently seem to have stopped. But it is not true.

At the Microscopic Level:

- There is intense activity. The individual molecules of the reactants continue to react. Individual product molecules also react to combine to go back to the reactants. The rate of forward process, is exactly equal to the rate of the reverse process.
- Therefore, it is a **dynamic equilibrium**. The system is dynamic because the individual molecules are constantly reacting, but the rates of forward and reverse reactions are the same.

RELATION BETWEEN MACROSCOPIC AND MICROSCOPIC EVENTS

Macroscopic events are the result of multiple simultaneous microscopic events. Understanding the microscopic events helps us to explain and predict the observed macroscopic changes in the equilibrium system.

When a change in equilibrium occurs in a chemical reaction, the microscopic events that explain the observed changes in equilibrium are the collisions and formation of new bonds between particles or molecules. These collisions change the rates of forward and reverse reactions, which are affected by activation energy and external factors. These microscopic events collectively appear as macroscopic changes which are observable by naked eye.

☑ QUICK CHECK 8.1

a) Differentiate between macroscopic and microscopic events.

Ans. Difference Between Macroscopic and Microscopic Events:

Aspect	Macroscopic Events	Microscopic Events
Definition	Observable events visible to the naked eye.	Events at the atomic or molecular level.
Scale	Large scale.	Extremely small scale (atomic or subatomic).
Observation	Can be observed directly.	Cannot be seen directly; studied using instruments or models.
Relevance	Used in everyday applications and measurements.	Important for understanding fundamental chemical behavior.
Example	Melting of ice, boiling of water.	Movement of water molecules, vibration of atoms in ice.

b) The equilibrium is dynamic in nature, explain in terms of microscopic events.

Ans. Equilibrium is described as dynamic because even though the macroscopic properties (like concentrations of reactants and products) appear constant and unchanging, at the microscopic level, the reactions are still occurring.

In terms of microscopic events:

(i) Continuous Forward Reaction:

Individual reactant molecules are constantly colliding, breaking their existing bonds, and forming new bonds to become product molecules.

(ii) Continuous Reverse Reaction:

Simultaneously, individual product molecules are colliding, breaking their bonds, and re-forming the original reactant molecules.

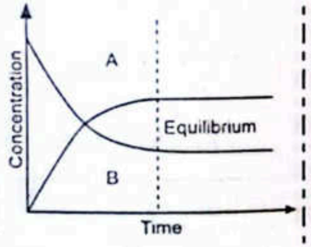
The "dynamic" aspect means these forward and reverse processes **never stop**. The equilibrium is maintained because the rate at which reactant molecules convert to products becomes exactly equal to the rate at which product molecules convert back to reactants. So, there's constant activity at the molecular level, but no net change in overall composition.

c) In the reaction $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$, the concentration of the products is higher at the equilibrium stage.

i. Plot a graph between concentrations of reactants and products vs time.

Ans.

- **Reactants (H_2O and CO):** Start a curve for the concentration of reactants (e.g., labeled "[CO] or [H_2O]") at a high point on the Y-axis at Time = 0. This curve will decrease as time progresses, indicating reactants are being consumed. Eventually, the curve will become horizontal, showing that the concentration of reactants has become constant at equilibrium.
- **Products (H_2 and CO_2):** Start a curve for the concentration of products (e.g., labeled "[CO_2] or [H_2]") at the origin (Y=0, X=0) or a very low point on the Y-axis at Time = 0 (assuming no products initially). This curve will increase as time progresses, indicating products are being formed. Eventually, this curve will also become horizontal, showing that the concentration of products has become constant at equilibrium.
- **Equilibrium Condition:** Crucially, the horizontal line representing the constant concentration of products at equilibrium should be at a **higher level** on the Y-axis than the horizontal line representing the constant concentration of reactants. This fulfills the condition that "the concentration of the products is higher at the equilibrium stage." Both curves become horizontal at the same point in time (when equilibrium is reached).



(This graph would look like Figure (b) as shown below, where the line for 'B' (products) levels off higher than the line for 'A' (reactants)).

ii. Plot a graph between rate of the reaction with respect to time.

Ans. (You would draw a graph with "Rate of Reaction" on the Y-axis and "Time" on the X-axis. The description below explains how it should look).

- **Rate of Forward Reaction:** Start a curve for the rate of the forward reaction ($H_2O + CO \rightarrow H_2 + CO_2$) at a high point on the Y-axis at Time = 0 (since reactant concentrations are initially high). This rate will decrease as time progresses because the concentration of reactants decreases. Eventually, this curve will become horizontal when equilibrium is reached.
- **Rate of Reverse Reaction:** Start a curve for the rate of the reverse reaction ($H_2 + CO_2 \rightarrow H_2O + CO$) at the origin (Y=0, X=0) at Time = 0 (assuming no products initially, so the reverse rate is zero). This rate will increase as time progresses because the concentration of products increases. Eventually, this curve will also become horizontal.
- **Equilibrium Condition:** The point where the curve for the rate of the forward reaction and the curve for the rate of the reverse reaction meet and become a single horizontal line represents the attainment of equilibrium. At this point, the rate of the forward reaction is equal to the rate of the reverse reaction.

DYNAMIC EQUILIBRIUM BETWEEN TWO PHYSICAL STATES

Dynamic Equilibrium

It is a state in a reversible process where the rate of change in one direction is equal to the rate of change in the opposite direction. In other words, although there are continuous changes taking place, no net change in the system as a whole is observed. When a reversible phase change takes place for a substance, there is also a dynamic equilibrium between the two physical states.

Example: At 0°C, ice and water coexist in equilibrium. Water changes into ice whereas ice converts back into water at the same rate.

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

Rock Your Mind!

3. Which of the following represents dynamic equilibrium between two physical states?

A) Ice melting into water

B) Sugar dissolving in water

C) Oxygen reacting with hydrogen

D) Carbon burning in air

Relationship between Dynamic Equilibrium and Vapor Pressure

Studying the behaviour of liquids and their vapour pressures is a significant concept in chemistry. When a liquid is placed in a closed container, some of the liquid molecules near the surface have enough energy to escape into the gaseous phase. This process is called **evaporation**. As more molecules escape into the gaseous phase, the pressure exerted by the gas molecules on the walls of the vessel increases. At the same time, molecules in vapour phase can also collide with the liquid surface and be captured again by the liquid, a process known as **condensation.**

$$\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Gas}$$

As evaporation and condensation continue, the rate of these processes will eventually become equal, and a state of dynamic equilibrium is achieved. In this state, the number of liquid molecules transforming into the gas phase equals the number of gas molecules returning to the liquid phase.

At dynamic equilibrium, the vapor pressure remains constant at a given temperature, as long as the system is undisturbed.

When Temperature Increases

As the temperature increases, the average kinetic energy of the liquid molecules also increases. This leads to a higher rate of evaporation, which in turn increases the vapor pressure. Also, the rate of condensation increases at the higher temperature. Finally, the system will reach a new state of dynamic equilibrium, with a higher equilibrium vapor pressure. In short, dynamic equilibrium in terms of the vapor pressure of a liquid describes the state at which the rates of evaporation and condensation are equal.

QUICK CHECK 8.3

(i) The dynamic equilibrium exists between water and its vapour at 100°C. Justify the statement.

Ans. The dynamic equilibrium exists between liquid water and its vapour (steam) at 100°C in a closed system. Justification:

1. **Constant Temperature (Boiling Point):** 100°C is the normal boiling point of water. At this temperature, [illegible] liquid water [illegible] to steam.
2. **Reversible Process:** In a closed container, as steam forms, steam molecules also collide with the surface of the liquid water and condense back into liquid.

   Liquid Water ⇌ Water Vapor (Steam)
   (Evaporation/Boiling) ⇌ (Condensation)
3. **Equal Rates:** At 100°C, in a closed system at equilibrium, the rate at which liquid water molecules gain enough energy to escape into the vapor phase (boiling/evaporation) becomes equal to the rate at which vapor molecules lose energy and return to the liquid phase (condensation).
4. **Dynamic Nature:** Although the relative amount of liquid water and steam might appear constant, individual water molecules are continuously interchanging between the liquid and vapor phases.
5. **Constant Vapour Pressure:** The pressure exerted by the water vapor at this equilibrium is constant ([illegible] 1 atm, if the external pressure is 1 atm, as 100°C is the normal boiling point). Therefore, the [illegible] interchange of molecules between the liquid and vapor phases at [illegible] together, a dynamic equilibrium at 100°C.

(ii) Do you think that dynamic equilibrium exists between ice and water at 0°C? If yes, explain.

Ans. Yes, dynamic equilibrium exists between ice (solid water) and liquid water at 0°C in a closed system (or an open system where the heat is [illegible] from the surroundings).

Explanation:

1. **Constant Temperature (Melting/Freezing Point):** 0°C is the normal melting point (or freezing point) of water. At this temperature, both solid ice and liquid water can coexist.
2. **Reversible Process:** Ice can melt to form liquid water, and liquid water can freeze to form ice.

   Ice (Solid) ⇌ Liquid Water (Liquid)
   (Melting) ⇌ (Freezing)
3. **Equal Rates:** At 0°C and equilibrium, the rate at which water molecules leave the solid ice structure and enter the liquid phase (melting) is exactly equal to the rate at which water molecules leave the liquid phase and join the ice structure (freezing).
4. **Dynamic Nature:** Even though the macroscopic amounts of ice and liquid water remain constant, at the microscopic level, there is a continuous exchange of molecules between the solid and liquid phases. Some ice molecules are melting, and simultaneously, some liquid water molecules are freezing.
5. **No Net Change:** Because these two opposing processes occur at the same rate, there is no net change in the amount of ice or liquid water.

   This continuous, balanced, and opposing transformation of molecules between the solid and liquid states at the same rate is characteristic of a dynamic equilibrium.

CONDITIONS FOR EQUILIBRIUM

The equilibrium can only be attained when the following conditions are fulfilled:

1. The state of equilibrium only applies to **reversible reactions**.
2. **Closed Vessel:** The equilibrium can be established only if the reaction vessel is closed. No part of the reactants and products is allowed to escape out.

[illegible]

Figure (a): Equilibrium is established when the system is closed
(b) Equilibrium cannot be established in the open system

CHARACTERISTICS OF CHEMICAL EQUILIBRIUM

Important features of equilibrium are as follows:

1. At the stage of chemical equilibrium, the concentrations of reactants and products remain constant.
2. The state of equilibrium in a reversible reaction can be approached from either side whether we start with reactants or products.
3. A catalyst does not change the equilibrium position and the equilibrium constant of the reaction. It helps to attain the equilibrium earlier.
4. The value of equilibrium constant does not depend upon the initial concentrations of reactants, rather it is constant and depends on temperature only.

If pure solids or pure liquids are involved in an equilibrium system, their concentrations are not included in the equilibrium constant expression. This is because the change in concentration of any pure solid or liquid has no effect on the equilibrium constant.

TYPES OF EQUILIBRIUM

With respect to the physical states of reactants and products, there are two types of chemical equilibrium:

Homogeneous Equilibrium

An equilibrium system in which all of the reactants and products are in the same phase.

Example: The following are examples of homogeneous equilibria:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

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

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

Heterogeneous Equilibrium

An equilibrium in which the reactants and products are in more than one phases is called heterogeneous equilibrium.

Example: The following are examples of heterogeneous equilibrium:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$$

QUICK CHECK 8.4

(i) Differentiate between homogeneous and heterogeneous equilibria.

Ans.

- **Homogeneous Equilibrium:** An equilibrium system where all the reactants and products are present in the **same physical phase**. For example, if all substances are gases, or all are dissolved in the same liquid solution.

  Example from Text: $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ (All are gases)
- **Heterogeneous Equilibrium:** An equilibrium system where the reactants and products are present in **more than one physical phase**. For example, a reaction involving solids and gases, or liquids and gases, or immiscible liquids.

  Example from Text: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ (Solids and a gas)

(ii) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Ans. The rates of forward reactions slow down as a reversible reaction approaches the equilibrium stage primarily because the **concentration of the reactants decreases**.

1. **Dependence on Concentration:** According to the Law of Mass Action, the rate of a reaction is directly proportional to the concentration of the reactants (raised to their respective powers).
2. **Consumption of Reactants:** As the forward reaction proceeds, reactants are converted into products. This leads to a gradual decrease in the concentration of the reactants.
3. **Reduced Collision Frequency:** With lower concentrations of reactants, there are fewer reactant molecules per unit volume. This results in fewer effective collisions between reactant molecules per unit of time, which are necessary for the reaction to occur.
   Consequently, the rate of the forward reaction, which depends on these collisions and reactant concentrations, diminishes as the reaction moves towards equilibrium.

c) In capped soda water bottles, gaseous CO_2 is in equilibrium with the aqueous CO_2(HCO_3^- and H^+).

$$CO_{2(s)} + H_2O_{(\ell)} \rightleftharpoons HCO^{3-}{}_{(aq)} + H^+{}_{(aq)}$$

Ans.

- **Closed Cap Required:** Equilibrium requires a closed system to prevent the escape of gaseous CO_2. If CO_2 escapes, the system cannot reach a state where the rates of dissolution and evolution of CO_2 are equal.
- **Cap Removed:** When the cap is removed, the pressure of CO_2 above the liquid decreases. According to Le Chatelier's principle, the equilibrium shifts to the **left** to produce more gaseous CO_2 to counteract the decrease in pressure. This results in the "fizzing" as dissolved CO_2 comes out of solution.

I. To which direction will the equilibrium shift if the bottle is opened?

Ans. When a bottle containing a gas in equilibrium with its dissolved form is opened, the equilibrium will shift to favor the gaseous phase. This occurs because the partial pressure of the gas in the headspace above the liquid decreases, causing more of the dissolved gas to escape into the gaseous phase to re–establish equilibrium. This principle is known as Le Chatelier's principle, which states that a system at equilibrium will shift to counteract any applied change.

II. Condition for this equilibrium requires the closed cap of the bottle. Why?

Ans. A closed cap is required for this equilibrium because one of the components, $CO_2(g)$, is a gas.

1. **To Maintain Pressure of Gaseous CO_2:** The equilibrium involves gaseous CO_2 above the liquid. A closed cap maintains the pressure of this gaseous CO_2. If the cap is open, the gaseous CO_2 would escape into the atmosphere.
2. **To Prevent Escape of Reactant/Product:** According to Le Chatelier's principle, if gaseous CO_2 (a reactant in the dissolution process, or a "product" of the reverse decomposition of carbonic acid) escapes, the equilibrium will be disturbed. The system needs to be closed to allow the reverse reaction ($HCO_3^- + H^+ \rightarrow H_2O + CO_{2(g)}$) to build up enough CO_2 pressure to balance the forward dissolution rate.
3. **To Achieve Equilibrium:** For equilibrium to be established, the rate of CO_2 dissolving into the water (and reacting to form HCO_3^- and H^+) must become equal to the rate at which HCO_3^- and H^+ react to form H_2O and $CO_{2(g)}$ which then escapes from solution. If $CO_{2(g)}$ can escape, the reverse reaction cannot build up to match the forward rate, ano equilibrium cannot be reached; the reaction would proceed largely to the left as CO_2 leaves.

III. When the cap of the bottle is removed, to which direction the equilibrium shifts?

Ans. When the cap of the bottle is removed:

1. The pressure of gaseous CO_2 above the liquid suddenly decreases because the $CO_2(g)$ can now escape into the atmosphere (where its partial pressure is much lower).
2. According to Le Chatelier's principle, the system will try to counteract this decrease in $CO_2(g)$ pressure.
3. To do this, the equilibrium will shift to the **left** (reverse direction).

$$HCO^-_{3(aq)} + H^+_{(aq)} \longrightarrow CO2_{(g)} + H_2O_{(\ell)}$$

4. This means that dissolved carbonic acid (formed from CO_2 and water, then ionized to HCO_3^- and H^+) will decompose to produce more gaseous CO_2, which then bubbles out of the solution. This is why soda water fizzes when the cap is opened.

EQUILIBRIUM CONSTANT AND POSITION OF EQUILIBRIUM

Position of Equilibrium:

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture.

(Exercise L.Q.1(a))

Q. Define and explain the law of mass action and derive the expression for the equilibrium constant.

Law of Mass Action:

Introduction:

In 1864, the Norwegian chemists C. Guldberg (1836-1902) and P. Waage (1833-1900) carefully measured the compositions of many reaction systems at equilibrium.

Statement:

They discovered that for any reversible reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions.

Rack Your Mind!

4. Write the K_c expression for the reaction:

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

General Reaction:

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

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation.

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

Active Mass:

The rate of the chemical reaction is directly proportional to the active masses of the reactants, raised to the coefficients present in the balanced equation.

- The term active mass is used for the molar concentration.
- It is expressed in moles dm^{-3}.
- This concentration is expressed by square brackets [ ].

Let us consider a general reaction

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

According to the Law of mass action,

Rate of Forward Reaction:

$$\text{Rate of forward reaction} \propto [A][B] = k_f[A][B]$$

'k_f' is the proportionality constant, and is known as forward rate constant.

Rate of Reverse Reaction:

$$\text{Rate of reverse reaction} \propto [C][D] = k_r[C][D]$$

'k_r' is the proportionality constant and is known as reverse rate constant.

At the Equilibrium Stage: The forward and the reverse rates are equal. Hence,

$$k_f[A][B] = k_r[C][D]$$

Equilibrium Constant Expression:

$$\frac{k_f}{k_r^-} = \frac{[C][D]}{[A][B]}$$

The left side of this equation is the ratio of two rate constants, so it gives another constant called the equilibrium constant (K_c).

$$K_c = \frac{k_f}{k_r^-}$$

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

This equation is known as equilibrium constant expression.
Consider the following reversible reaction,

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

where a, b, c and d are the coefficients of balanced equation.

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

Equilibrium Constant Expressions of Some Important Reactions

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

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

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

$$K_c = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

Sample Problem 8.1

Ethanol reacts with ethanoic acid to form ethyl ethanoate and water.

$$\underset{\text{Ethanoic acid}}{CH_3COOH_{(l)}} + \underset{\text{Ethanol}}{C_2H_5OH_{(l)}} \rightleftharpoons \underset{\text{Ethyl Ethanoate}}{CH_3COOC_2H_{5(l)}} + \underset{\text{Water}}{H_2O_{(l)}}$$

500 cm³ of the reaction mixture at equilibrium contained 0.235 mol of ethanoic acid and 0.0350 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water. Use this data to calculate a value of K_c for this reaction.

Solution:

Volume of solution $= 500\ cm^3$
$= 0.5\ dm^3$

Step 1: Write out the balanced chemical equation with the concentrations beneath each substance.

$$\begin{array}{ccccccc} CH_3COOH_{(l)} & + & C_2H_5OH_{(l)} & \rightleftharpoons & CH_3COOC_2H_{5(l)} & + & H_2O_{(l)} \\ \frac{0.235\ mol}{0.5Hm^3} & & \frac{0.0350\ mol}{0.5dm^3} & & \frac{0.182\ mol}{0.5dm^3} & & \frac{0.182\ mol}{0.5dm^3} \\ 0.470\ mol\ dm^{-3} & & 0.070\ mol\ dm^{-3} & & 0.364\ mol\ dm^{-3} & & 0.364\ mol\ dm^{-3} \end{array}$$

Step 2: Write the equilibrium constant for this reaction in terms of concentrations.

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{(0.364\ mol\ dm^{-3})(0.0364\ mol\ dm^{-3})}{(0.470\ mol\ dm^{-3})(0.070\ mol\ dm^{-3})}$$

$$K_c = 4.03$$

No. of moles of reactants = no. of moles of products, so the units of $mol\ dm^{-3}$ cancel out i.e., K_c has no units.

Sample Problem 8.2

Propanone reacts with hydrogen cyanide as follows:

$$\underset{\text{Propanone}}{CH_3COCH_{3(l)}} + \underset{\text{Hydrogen cyanide}}{HCN_{(g)}} \rightleftharpoons \underset{\text{Product}}{CH_3C(OH)(CN)CH_{3(l)}}$$

Propanone Hydrogen cyanide Product

A mixture of $0.0500\ moldm^{-3}$ propanone and $0.0500\ moldm^{-3}$ hydrogen cyanide is left to reach equilibrium at room temperature. At equilibrium the concentration of the product is $0.0233\ moldm^{-3}$. Calculate K_c for this reaction.

Solution:

Step 1: Write out the balanced chemical equation with all the data underneath:

	$CH_3COCH_{3(l)}$ +	$HCN_{(g)}$	$\rightleftharpoons$ $CH_3C(OH)(CN)CH_{3(l)}$
Initial conc.	$0.0500\ moldm^{-3}$	$0.0500\ moldm^{-3}$	$0\ moldm^{-3}$
Equilibrium. conc.	?	?	$0.0233\ moldm^{-3}$

Step 2: Calculate the equilibrium concentrations of the reactants. The chemical equation shows that for every mole of product formed, 1 mole of CH_3COCH_3 and 1 mole of HCN are consumed. So the equilibrium concentrations are as follows:

$CH_3COCH_3;\ 0.0500 - 0.0233 = 0.0267\ moldm^{-3}$
$HCN;\ 0.0500 - 0.0233 = 0.0267\ moldm^{-3}$

Step 3: Write the equilibrium constant for this reaction in terms of concentrations:

$$K_c = \frac{[CH_3C(OH)(CN)CH_3]}{[CH_3COCH_3][HCN]} = \frac{(0.0233\ mol\ dm^{-3})}{(0.05\ mol\ dm^{-3})(0.05\ mol\ dm^{-3})}$$

Step 4: Substitute the equilibrium concentrations into the expression

$$K_c = 32.7\ mol\ dm^{-3}$$

☑ QUICK CHECK 8.4

a) **Write Kc for the following reactions:**

i. $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightleftharpoons Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$

Ans. $K_c = \frac{[Product]}{[Reactants]} = \frac{[Sn^{+4}][Fe^{+2}]^2}{[Sn^{+2}][Fe^{+3}]^2}$

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

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

iii. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Ans. $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

b) **Calculate the value of K_c for the following reaction using the information below:**

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

Initial conc. of $H_{2(g)} = 10.00\ moldm^{-3}$.

Initial conc. of $CO_{2(g)} = 10.00\ moldm^{-3}$.

Equilibrium conc. of $CO_{(g)} = 9.47\ moldm^{-3}$.

Ans.

	$H_{2(g)}$ +	$CO_{2(g)}$	$\rightleftharpoons$ $H_2O_{(g)}$	+ $CO_{(g)}$
When t = 0	10	10	x	x
At t = Equil.	(10–x)	(10 – x)	9.47	9.47

Equil. conc. of CO = x = 9.47 mol dm³
t = Equil.

Equil. conc. of CO = x = 9.47 mol dm³
Equil. conc. of H_2O = x = 9.47 mol dm³
Equil. conc. of H_2 = 10 – x = 10 – 9.47 = 0.53 mol dm³
Equil. conc. of CO_2 = 10 – x = 10 – 9.47 = 0.53 mol dm³

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(9.47)(9.47)}{(0.53)(0.53)} = \frac{89.689}{0.2806}$$

$$K_c = 319.60$$

$$K_c \equiv 320$$

➲ Units of Equilibrium Constants

Case I: $n_r = n_p$

- When the number of moles of reactants and products in balanced chemical equations are equal, then units are canceled out, and equilibrium constant does not have any unit.
- **Example:** The ester formation reaction happens in solution state, and number of moles of reactants and products are equal. The K_c will have no units.

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

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH_{(aq)}][C_2H_5OH_{(aq)}]} = \frac{moldm^{-3} \times moldm^{-3}}{moldm^{-3} \times moldm^{-3}} = nounits$$

Case II: $n_r \neq n_p$

- When the number of moles are unequal, then value of equilibrium constant depend upon the units of reactants and products used. In the synthesis of NH_3 by Haber's process, the units of reactants and products are not cancelled.

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

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}][H_{2(g)}]^3} = \frac{[molsdm^{-3}]^2}{[moldm^{-3}][moldm^{-3}]^3} = \frac{1}{[mol\,dm^{-3}]^2} = mol^{-2}dm^6$$

RELATIONSHIPS BETWEEN VARIOUS EQUILIBRIUM CONSTANTS

There are four different types of quantities which may be used to calculate the equilibrium constants of reversible reaction. Let the general reaction be,

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

(1) K_c: When the concentrations of reactants and products are in mole dm^{-3}, then equilibrium constant is written as:

Rack Your Mind!

5. What happens to the value of K_p if $\Delta n = 0$?

A) $K_p = 0$ B) $K_p = K_c$
C) $K_p > K_c$ D) $K_p < K_c$

$$K_c = \frac{[C]^c[D]^d}{[A]^a\,[B]^b} \quad \text{\_\_\_\_\_\_ (1)}$$

Square brackets [ ] are used for mole dm^{-3}.

(2) K_p: When the concentrations are expressed in terms of partial pressures (p) for gaseous reactants and products, then

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \quad \text{\_\_\_\_\_\_ (2)}$$

(3) K_n: When the concentrations are expressed in terms of number of moles, then

$$K_n = \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b} \quad \text{\_\_\_\_\_\_ (3)}$$

(4) K_x: When the concentrations are expressed in terms of mole fractions, (X) then

$$K_x = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b} \quad \text{\_\_\_\_\_\_ (4)}$$

The relationships between these equilibrium constants are as follows:

$$K_p = K_c(RT)^{\Delta n} \quad \text{\_\_\_\_\_\_ (5)}$$

$$K_p = K_x(P)^{\Delta n} \quad \text{\_\_\_\_\_\_ (6)}$$

$$K_p = K_n(N)^{\Delta n} \quad \text{\_\_\_\_\_\_ (7)}$$

Where:

R = General gas constant

T = Absolute temperature of the system

P = Pressure of the system

N = Total number of moles of reactants and products

Δn = Difference of number of moles of products and reactants in the balanced chemical equation

It depends upon the value of ' Δn ' that which of the equilibrium constants is bigger or smaller than the other. Anyhow, if the number of moles of reactants and products in a balanced chemical equation are equal, and all the constants have equal values.

That is, $\Delta n = 0$

then $K_p = K_c = K_x = K_n$

Hence, whichever concentration units are used, the equilibrium constants are same.

Sample Problem 8.3

$N_{2(g)}$ and $H_{2(g)}$ combine to form $NH_{3(g)}$. The value of K_c at 500°C is 6.0×10^{-2}. Calculate the numerical value of K_p for this reaction.

Solution:

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

$$K_c = 6.0 \times 10^{-2}$$

$$T = 500^\circ C + 273 = 773\ K$$

$$R = 0.0821 dm^3\ atm\ K^{-1}\ mol^{-1}$$

$$K_p = ?$$

The formula for conversion of K_c to K_p is,

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

$$\Delta n = \text{Number of moles of product} - \text{Number of moles of reactants}$$

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

Substituting these values in the expression

$$K_p = 6.0 \times 10^{-2}\left(0.0821 dm^3\ atm\ K{-}1\ mol^{-1} \times 773\ K\right)^{-2}$$

$$K_p = 6.0 \times 10^{-2}\left(63.5 dm^3\ atm\ mol^{-1}\right)^{-2}$$

$$K_p = \frac{6.0 \times 10^{-2}}{(63.5)^2} = \frac{0.06}{4032.25}$$

$$K_p = 1.4 \times 10^{-5}$$

So, the value of K_p is less than K_c.

Sample Problem 8.4

In the reaction

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

the equilibrium partial pressures at constant temperature are $SO_2 = 1.0 \times 10^6$ Pa, $O_2 = 7.0 \times 10^6$ Pa, $SO_3 = 8.0 \times 10^6$ Pa. Calculate the value of K_p for this reaction.

Solution

Step 1: Write the equilibrium expression for the reaction in terms of partial pressures.

$$K_p = \frac{P^2_{SO_3}}{P^2_{SO_2} \times P_{O_2}}$$

Step 2: Substitute the equilibrium concentrations into the expression.

$$K_p = \frac{(8.0\times10^6)^2}{(1.0\times10^6)^2\times7.0\times10^6} = 9.1\times10^{-6}\ Pa^{-1}$$

☑ QUICK CHECK 8.5

a) Compare the magnitudes of K_c and K_p, for the following reversible reactions.
i) Ammonia synthesis **ii) Dissociation of $PC\ell_5$**

Ans. Compare magnitudes of K_c and K_p

Use the formula:

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

Where:

Δn = moles of gaseous products – moles of gaseous reactants

$R = 0.0821\ dm^3 \cdot atm \cdot mol^{-1} \cdot k^{-1}$

i) Ammonia Synthesis

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

$\Delta n = 2-(1+3) = -2,\quad K_p = K_c(RT)^{-2}\quad$ i.e., $(RT)^{\Delta n} < 1$ So $K_p < K_c$

ii) Dissociation of $PC\ell_5$

$$PC\ell_{5(g)} \rightleftharpoons PC\ell_{3(g)} + C\ell_{2(g)}$$

$\Delta n = 2-1 = +1\quad$ As $K_p = K_c(RT)^{\Delta n}\quad$ i.e., $(RT)^{\Delta n} > 1$ So $K_p > K_c$

(b) Nitrogen reacts with hydrogen to form ammonia.

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

The pressure exerted by this mixture of hydrogen, nitrogen and ammonia at constant temperature is 2.0×10^7 Pa. Under these conditions, the partial pressure of nitrogen is 1.5×10^7 Pa and the partial pressure of hydrogen is 0.4×10^7 Pa. Calculate the value of K_p for this reaction.

Ans. Calculate K_p for ammonia formation

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

Given Data:

- Total pressure = $P_t = 2.0\times10^7$ Pa
- Partial pressure of $N_2 = P_{N2} = 1.5\times10^7$ Pa
- Partial pressure of $H_2 = P_{H2} = 0.4\times10^7$ Pa

Let the partial pressure of NH_3 be x

Use the balanced equation:

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

So, $K_p = \dfrac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$

But the total pressure is the sum of partial pressure:

$$P_{total} = P_{N_2} + P_{NH_3}\ ;\ 2.0\times10^7 = 1.5\times10^7 + 0.4\times10^7 + X;\qquad X = 0.1\times10^7 = 1.0\times10^6\ Pa$$

Now plug into the Kp formula:

$$K_p = \frac{(1.0\times10^6)^2}{(1.5\times10^7)(0.4\times10^7)^3}$$

First, simplify:

Numerator: $(1.0\times10^6)^2 = 1.0\times10^{12}$

Denominator:

$$(1.5\times10^7)(0.4\times10^7)^3 = (1.5\times10^7)(6.4\times10^{20}) = 9.6\times10^{27}$$

$$K_p = \frac{1.0\times10^{12}}{9.6\times10^{27}} = 1.04\times10^{-16}$$

POSITION OF EQUILIBRIUM AND REACTION CONDITIONS

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture.

If a system in equilibrium is disturbed.

- If the concentration of products is increased relative to the reactants, we say that the position of equilibrium has shifted to the left.
- If the concentration of products is decreased relative to the reactants, we say that the position of equilibrium has shifted to the right.

LE-CHATELIER'S PRINCIPLE

Le-Chatelier's principle can be stated as follows:

"If a system in equilibrium is disturbed, it behaves in such a way as to nullify the effect of that disturbance".

Le-Chatelier's principle describes what happens to a system when something momentarily takes it away from equilibrium.

Applications of Le-Chatelier's Principle

Some of the most common applications of this principle with reference to certain physical and chemical equilibria are discussed below:

i) Effect of change in concentration
ii) Effect of change in pressure
iii) Effect of change in temperature.
iv) Effect of catalyst on equilibrium.

Henry-Louis Le Chatelier

(1850-1936)

A French chemist of the late 19th and early 20th centuries. He proposed the Le-Chatlier Principle, a significant achievement in chemistry

THE EFFECT OF CHANGE OF CONCENTRATIONS

If the system is at the equilibrium position and a certain amount of one of the reactants or products is added or removed, the equilibrium position is disturbed.

There are four possibilities for the change in concentrations of reactants and products.

(i) Hydrolysis of $BiC\ell_3$

Consider the following reversible reaction in which $BiC\ell_3$ reacts with water to give a white insoluble compound, $BiOC\ell$.

$$BiC\ell_3 + H_2O \rightleftharpoons BiOC\ell + 2HC\ell$$

The expression for this reaction can be written as

$$K_c = \frac{[BiOC\ell][HC\ell]^2}{[BiC\ell_3][H_2O]}$$

When water is added in $BiC\ell_3$ solution, it becomes cloudy due to the formation of white precipitate of $BiOC\ell$. At equilibrium, a certain amount of $BiOC\ell$ and $HC\ell$ has been produced and certain number of moles of $BiC\ell_3$ are left behind.

Rack Your Mind!

6. In the reaction:

$$BiC\ell_4 + H_2O \rightleftharpoons BiOC\ell + 2HC\ell$$

what will happen if more $BiC\ell_4$ is added at equilibrium?

A) The reaction will stop
B) The equilibrium will shift to the left
C) The equilibrium will shift to the right
D) K_c will increase

Adding of the Reaction:

If a few moles of $BiC\ell_3$ are added at equilibrium, the reaction is pushed to the forward direction.

The addition of $BiC\ell_3$ or H_2O disturbs the equilibrium position. To re-establish the equilibrium, more $BiOC\ell$ and $HC\ell$ are produced. In other words, the reaction is pushed to the forward direction. K_c remains constant, but equilibrium position has changed.

The addition of BiOCl or HCl, or both disturbs the equilibrium position. To re-establish the equilibrium, more $BiCl_3$ is produced and the reaction moves in the reverse direction. The K_c remains the constant, but position of equilibrium changes.

If a certain amount of $BiCl_3$ is removed at equilibrium stage, the reaction will move in the reverse direction to compensate that change. A new equilibrium position is established, K_c being constant.

If a certain amount of BiOCl or HCl or both is removed at equilibrium stage, the reaction will move in the forward direction to compensate that change. A new equilibrium position is established; however, K_c remains constant.

THE EFFECT OF CHANGE IN PRESSURE OR VOLUME

Rack Your Mind!

7. How does increasing pressure affect the equilibrium of ammonia synthesis?

The effect of change of volume or pressure is not applicable when

(a) The system does not involve gaseous components.

(b) The number of moles of reactants and products are equal in gaseous phase (homogeneous equilibrium).

$$n_{reactants} = n_{products}$$

This effect can only be discussed if **the gaseous moles of reactants and products are unequal i.e.,**

$$n_{reactants} \neq n_{products}$$

In order to explain this effect, let us consider the synthesis of ammonia by Haber's process.

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

a) Increase in Pressure or Decrease in Volume

For the forward reaction, the number of moles and hence volume decreases. At equilibrium stage the volume occupied by the mixture is less than the volume at the initial stage under the given conditions. So, if pressure is increased at equilibrium, more ammonia is produced. It means, that reaction is shifted to the forward direction.

b) Decrease in Pressure or Increase in Volume

If the pressure is decreased or volume is increased, the reaction will move to that side, where the reaction occupies greater volume. Ammonia synthesis is shifted to the reverse direction.

☑ QUICK CHECK 8.6

The change of volume or pressure for the following reactions only changes the equilibrium position but not the equilibrium constant. How the direction of reaction changes for each of the following reactions.

(a) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$ **(Increasing P)**

(b) $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$ **(Increasing V)**

(c) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ **(Increasing P)**

(d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ **(Increasing V)**

Ans.

(a) $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$

- **Increasing pressure (P)**: The equilibrium will shift to the **right** (toward the side with fewer moles of gas) to reduce the pressure.
    - **Left side:** 3 moles of gas ($2H_2 + 1O_2$)
    - **Right side:** 2 moles of gas ($2H_2O$)
    - Thus, the reaction favors the formation of **$H_2O_{(g)}$** when pressure is increased.

(b) $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$

- Increasing volume (decreasing pressure) shifts the equilibrium toward the side with more moles of gas to counteract the change.
- Here, the left side has 3 moles of gas ($2CO + 1O_2$), while the right side has 2 moles ($2CO_2$).
- Thus, the equilibrium shifts left (toward reactants) when volume increases.

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

In this reaction, there is 1 mole of gaseous reactant (N_2O_4) and 2 moles of gaseous product (NO_2). Increasing the pressure will shift the equilibrium to the side with fewer moles of gas to reduce the pressure. Therefore, increasing pressure will shift the equilibrium to the **left**, favoring the formation of N_2O_4.

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

- This gas phase reaction proceeds with the decrease in number of moles and hence decreases in volume at equilibrium stage.
- As the reaction approaches the equilibrium stage, the volume of the equilibrium mixture is less than the volume of reactants taken initially.
- When we decrease the volume further at equilibrium stage, the reaction is disturbed. It will move to the forward direction to minimize the effect of disturbance. It establishes a new equilibrium position while K_c remains constant.
- The reverse happens when the volume is increased or pressure is decreased at equilibrium stage.
- It is noted that the pressure is increased in a reaction having unequal number of moles of reactants and products then the reaction will move in that direction where the number of moles are less.

THE EFFECT OF CHANGE IN TEMPERATURE

Rack Your Mind!

8. In the equilibrium:

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H^\circ = -198$ kJ

What happens if the temperature is increased?

A) Concentration of SO_3 increases

B) Concentration of SO_2 decreases

C) Equilibrium shifts to the left

D) Value of Kc increases

Le-Chatelier's Principle can be used to predict the direction of a reaction with a change in temperature. **Temperature is the only factor that also affects the value of equilibrium constant (K_c).**

➤ **For an Exothermic Reaction:**

For an exothermic reaction, an increase in temperature (adding heat) favours the reverse reaction. A decrease in temperature (removing heat) favours the forward reaction.

The equation for the conversion of SO_2 to SO_3 is given below:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H^\circ = -198\text{ kJ}$$

According to the Le-Chatelier's principle, an increase in temperature will shift the reaction from right to left.

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

As a result of this change, the concentration of SO_3 will decrease and concentrations of SO_2 and O_2 will increase. Therefore, the value of the equilibrium constant will decrease. The equilibrium will shift towards left. The decrease in temperature will favour the forward reaction and the formation of the product. The production of SO_3 is favoured at a lower temperature. On the other hand, an increase in temperature will shift the reaction from left to right.

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

Due to this change, the concentration of SO_3 will increase and concentrations of SO_2 and O_2 will decrease. Therefore, the value of the equilibrium constant will increase.

The equilibrium will shift towards right. The increase in temperature will favour the reverse reaction and the formation of the reactants. The production of SO_3 is not favoured at a higher temperature. K_c for this reaction is 2.8×10^2 at 1000 K ; whereas, at 298 K the value of K_c is 1×10^{26}.

➤ **For an Endothermic Reaction:**

For an endothermic reaction, an increase in temperature (adding heat) favours the forward reaction. A decrease in temperature (removing heat) favours the reverse reaction.

The equation for the conversion of N_2O_4 to NO_2 is given below:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H^\circ = +57.2\text{ kJ}$$

According to the Le-Chatelier's Principle, an increase in temperature will shift the reaction from left to right.

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

As a result of this change, the concentration of N_2O_4 will decrease and concentration of NO_2 will increase. Therefore, the value of the equilibrium constant (K_c) will increase. The equilibrium will shift towards right. The increase in temperature will favour the forward reaction and the formation of the product.

On the other hand, a decrease in temperature will shift the reaction from right to left. The decrease in temperature will favour the reverse reaction and the formation of the reactant.

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

K_c for this reaction is 7.7×10^{-5} at 273 K, whereas 0.4 at 373 K.

EFFECT OF CATALYST ON EQUILIBRIUM

A catalyst is that substance which increases the rate of a chemical reaction without itself being consumed in the reaction.

- The catalyst does not change the equilibrium position and the equilibrium constant of a chemical reaction.
- A catalyst speeds up the rate at which equilibrium is attained. It means that the yield of the chemical reaction remains the same.
- A catalyst provides new path of lower activation energy for a reaction.
- If we plot a graph between reaction coordinate on x-axis and potential energy of the chemical reaction on y-axis, then the maxima of the curve become lower in the presence of a catalyst as shown in Figure 8.3.

Rack Your Mind!

9. How does a catalyst affect the rate of a reaction and its equilibrium?

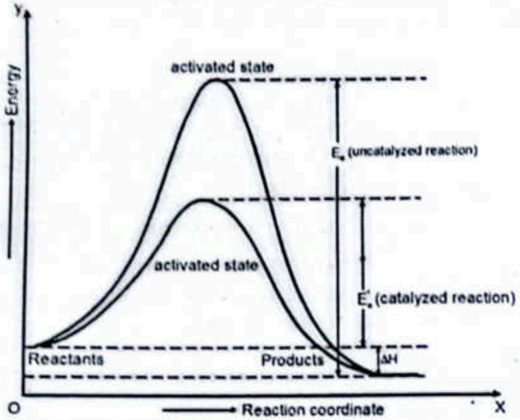


Figure: Effect of a catalyst on Reversible Reactions

INDUSTRIAL APPLICATIONS OF CHEMICAL EQUILIBRIUM

Synthesis of Ammonia by Haber's Process

It is one of the basic needs of industry to have maximum yield of the product. We can apply the concept of equilibrium in order to have the maximum yield from the industrial synthesis of ammonia. Ammonia synthesis from nitrogen and hydrogen is a reversible process.

Rack Your Mind!

10. How can the yield of ammonia be increased in the Haber process using Le Chatelier's Principle?

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -46.11 \text{ kJ mol}^{-1}$$

The maximum yield of ammonia can be achieved by the following ways:

1. Decrease the concentration of ammonia by removing it from the reaction vessel from time to time. Equilibrium will shift to the forward direction in accordance with Le-Chatelier's principle.
2. Since, four moles of reactants combine to give two moles of products, reaction happens with the decreasing volume. High pressure will shift the equilibrium position to the right to give more and more ammonia.
3. This is an exothermic reaction. By decreasing temperature, it will shift to the forward direction according to Le-Chatelier's principle.

When we look at the Table given below and the Figure, then it becomes clear that the effect of pressure and temperature on the yield of ammonia is very prominent. The most complete conversion is 98.3% at 473 K(200°C) and 1000 atmospheric pressure.

Table: Effect of Temperature on K_c for Ammonia Synthesis.

T(K)	K_c
200	7.15×10^{15}
300	2.69×10^{8}
400	3.94×10^{4}
500	1.72×10^{2}
600	4.53×10^{0}
700	2.96×10^{-1}
800	3.96×10^{-2}

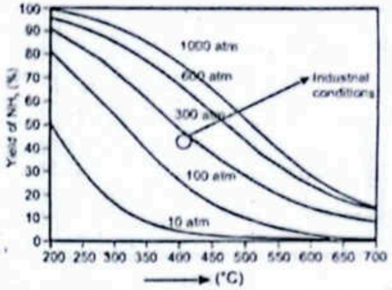


Fig: Percent yield of ammonia vs. Temperature (°C) at five different operating pressures. At very high pressure and low temperature (top left), the yield is high, but the rate of formation is low. Industrial conditions (circle) are between 200 and 300 atm at about 400°C.

At 200°C, the yield is being favoured but the rate of reaction becomes very slow and the process becomes uneconomical. So, the temperature is raised to a moderate level i.e. 400°C and a catalyst is used to increase the rate. If we want to achieve the same rate without a catalyst then we require much higher temperature, which lowers the yield.

Optimum Conditions to get Best Yield of Ammonia

The most suitable conditions to get maximum yield of ammonia are:

a) **Pressure** = 200-300 atmospheres

b) **Temperature** = Around 673 K(400°C)

c) **Catalyst:** Pieces of iron crystals present in a fused mixture of MgO, Al_2O_3 and SiO_2, as catalyst

Preparation of Sulphur Trioxide

To manufacture H_2SO_4, sulphur trioxide gas is produced from SO_2 and O_2, in a reversible process.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -97.9 \text{ kJ mol}^{-1}$$

According to Le-Chatelier's principle, a high pressure and low temperature are the essential conditions to have better yield of SO_3. At low temperature, the equilibrium constant for the formation of SO_3 is large, but equilibrium is achieved very slowly. As the temperature is raised, the rate increases but the yield of SO_3 drops off.

The following Table helps us to understand the parameters, when pressure is maintained at 1 atmosphere.

Table: Effect of temperature on equilibrium position of SO_3 formation

1. Temperature (°C)	200	300	400	500	600	700
2. K_c	5500	690	160	55	25	13
3. Mole % of SO_3	98	91	75	61	46	31

➢ Optimum Conditions

In order to have a best yield of SO_3, within a reasonable time, a mixture of $SO_{2(g)}$ and $O_{2(g)}$ (air) at one atmospheric pressure is passed over a solid catalyst, such as V_2O_5. But due to the exothermic reaction, the temperature of the gas increases to 60°C. The equilibrium mixture is recycled at low temperature of 400 – 500°C to increase the yield of $SO_{3(g)}$.

☑ QUICK CHECK 8.7

Look at the information given in the table below:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H^\circ = -92\ kJ\ mol^{-1}$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^\circ = +57\ kJ\ mol^{-1}$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H^\circ = -197\ kJ\ mol^{-1}$

	$K_p = \dfrac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3}$		$K_p = \dfrac{(P_{NO_2})^2}{P_{N_2O_4}}$		$K_p = \dfrac{(P_{SO_3})^2}{(P_{SO_2})^2 P_{O_2}}$
T/K	K_p / atm^{-2}	T/K	K_p / atm^{-2}	T/K	K_p / atm^{-1}
400	1.0×10^{2}	200	1.9×10^{-6}	600	3.2×10^{3}
500	1.6×10^{-1}	300	1.7×10^{-1}	700	2.0×10^{2}
600	3.1×10^{-3}	400	5.1×10	800	3.2×10
700	6.3×10^{-5}	500	1.5×10^{3}	900	6.3
800	7.9×10^{-6}	600	1.4×10^{4}	1000	2.0

i) How does the proportion of products in the above system change as the temperature increases?

Ans. In ammonia synthesis, increasing the temperature shifts the equilibrium towards the reactants, decreasing the proportion of products. This is because the reaction is exothermic, meaning it releases heat. According to Le Chatelier's principle, when the temperature of an exothermic reaction is increased, the equilibrium shifts to favor the endothermic direction, which in this case, is the reverse reaction that consumes heat and produces reactants. Therefore, a higher temperature results in a lower yield of ammonia.

In decomposition reaction of N_2O_4 to NO_2 i.e.:

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

This reaction is endothermic in the forward direction (i.e., it absorbs heat). $\Delta H > 0$

According to Le Chatelier's Principle, increasing the temperature will favor the endothermic direction (the forward reaction). Therefore:

As temperature increases, the equilibrium shifts to the right. More NO_2 (product) is formed and less N_2O_4 reactant remains.

Contact process is used for the manufacturing of H_2SO_4 on industrial scale in which the conversion of SO_2 to SO_3 is achieved in a reversible reaction.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -194\ kJ\ mol^{-1}$$

At low temperature, the equilibrium constant for formation of SO_3 is large but equilibrium is reached very slowly.

- As the temperature is raised the rate increases but the yield of SO_3 drops off according to Le-Chatelier's principle.
- High pressure tends to increase yield of SO_3. However, instead of using high pressure, the concentration of O_2 (air) is increased to increase the yield of SO_3.

Effect of Temperature on the Yield of SO_3

The table helps to understand the effect of different conditions on the yield of SO_3. During the process pressure is kept at one atmosphere.

Temperature (°C)	K_c	Mole% of SO_3
200	5500	98
300	690	91
400	160	75
500	55	61
600	25	46
700	13	31

ii) Calculate the values of K_c for the reactions at 600 K?

Ans. To calculate the value of K_c at 600 K, the equilibrium concentrations of the reactants and products must be known. Since these concentrations are not provided, the exact value of Kc cannot be determined.

- In an endothermic reactions, rise in temperature (600 K) at equilibrium favours the reaction to shift to the forwards direction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H^\circ = +57\ kJ\ mol^{-1}$$

- For an exothermic reaction, an increase in temperature shifts the equilibrium to the left, favoring the reactants. As a result, the proportion of products decreases e.g.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^\circ = -92\ kJ\ mol^{-1}$$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^\circ = -197\ kJ\ mol^{-1}$$

(a) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H^\circ = -92\ kJ\ mol^{-1}$

(i) Above reaction is Endothermic, as obvious from ΔH value. Exothermic reactions are not favoured at high temp. Therefore, product decrease with increase in temp. This is justified from data.

(ii) K_c at 600 K = ?

$$\begin{aligned}
K_p &= 3.1\times10^{-3} \text{ at } 600\ K\\
\Delta n &= n_P - n_R = 2 - 4 = -2\\
I &= 600\ K\\
R &= 0.0821\ atm\ dm^3\ mol^{-1}\ k^{-1}\\
K_p &= K_c(RT)^{\Delta n}\\
3.1\times10^{-3} &= K_c(RT)^{-2}\\
3.1\times10^{-3} &= \frac{K_c}{(RT)^2} = \frac{K_c}{(0.0821\times600)^2}\\
K_C &= (3.1\times10^{-3})\times(0.0821\times600)^2 = 7.5\ mol^{-2}dm^{+6}
\end{aligned}$$

(b) $N_2O_4 \rightleftharpoons 2NO_2\,\Delta H^\circ = +57\ kJ\ mol^{-1}$

(i) Endothermic reactions are favoured at high (Temperature). Product increases with increase in Temp.

(ii) K_c at 600 K = ?

$$\begin{aligned}
K_p &= 3.4\times10^{4}\ atm\\
\Delta n &= n_P - n_R = 2 - 1 = 1\\
I &= 600\ K\\
R &= 0.0821\ atm\ dm^3\ mol^{-1}\ k^{-1}\\
K_p &= K_c(RT)^{\Delta n}\\
K_p &= K_c(RT)^1\\
K_c &= \frac{K_c}{(RT)^1} = \frac{1.4\times10^4}{(0.0821\times600)^2} = \frac{1.4\times10^4}{49.26}\\
K_C &= 0.0284\times10^4\\
K_c &= 2.84\times10^2\ mol/dm^3
\end{aligned}$$

(c) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H^\circ = -197\ kJ\ mol^{-1}$

(i) Endothermic reactions are not favoured at high temperature. Amount of product decreases with increase in temperature, as it is evident from data given in the table.

(ii)

$$
\begin{aligned}
K_p &= 3.2 \times 10^{3}\ \text{atm} \\
\Delta n &= n_P - n_R = 2 - 3 = -1 \\
T &= 600\ \text{K} \\
R &= 0.0821\ \text{atm dm}^3\ \text{mol}^{-1}\ \text{k}^{-1} \\
K_p &= K_c\,(RT)^{\Delta n} \\
K_p &= K_c\,(RT)^{-1} \\
K_p &= \frac{K_c}{(RT)^1} \\
K_p &= K_p \times (RT)^1 \\
K_c &= 3.2 \times 10^{-3} \times 0.0821 \times 600 \\
K_c &= 157.632 \times 10^{-3} \\
K_c &= 1.6 \times 10^{5}\ \text{mol}^{-2}\ \text{dm}^{+6}
\end{aligned}
$$

Solution File Rack Your Brain!

Sr. #	Option	Explanation
1.	C	At equilibrium, the concentration of reactants and products remains constant. This constancy is a key macroscopic property of equilibrium systems.
2.	S.Q	The state of equilibrium where forward and reverse reactions occur at the same rate, keeping the concentrations of all substances constant is called dynamic equilibrium.
3.	A	$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$ This represents the dynamic equilibrium between ice (solid) and water (liquid) at the melting point.
4.	S.Q	K_c expression for the reaction is given below; $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
5.	B	When $\Delta n = 0$, the number of moles of gaseous products equals the number of moles of gaseous reactants, so $K_p = K_c(RT)^0 = K_c$.
6.	C	Adding more $BiCl_3$ increases the concentration of reactants, causing the equilibrium to shift to the right to consume some of the added $BiCl_3$ and form more products.
7.	S.Q	In the reaction: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ Increasing pressure shifts the equilibrium **to the forward direction** (towards ammonia) because it reduces the number of gaseous moles from 4 moles to 2 moles.
8.	C	The reaction is exothermic, so increasing temperature favours the reverse reaction, shifting the equilibrium to the left. $2SO_2 + O_2 \rightleftharpoons 2SO_3$
9.	S.Q	A catalyst increases the rate of a chemical reaction by providing an alternative pathway with **lower activation energy.** It does not affect the position of equilibrium or the value of the **equilibrium constant,** but helps the system reach equilibrium faster.
10.	S.Q	The yield of ammonia can be increased by: 1. **Removing ammonia** regularly to shift equilibrium forward. 2. **Applying high pressure** because fewer gas molecules are formed. 3. **Lowering temperature** since the reaction is exothermic, favoring ammonia formation.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. For which system, does the equilibrium constant, K_c has units of (concentration)$^{-1}$?

a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ b) $H_2 + I_2 \rightleftharpoons 2HI$ c) $2NO_2 \rightleftharpoons N_2O_4$ d) $2HF \rightleftharpoons H_2 + F_2$

II. Which statement about the following equilibrium is correct?

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -197.9\,\text{kJmol}^{-1}$$

a) The value of K_p falls with a rise in temperature.
b) The value of K_p falls with increasing pressure.
c) Adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide.
d) The value of K_p is equal to K_c.

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

The conventional equilibrium constant expression (K_c) for the system as described by the above equation is:

a) $[SO_2]^2/[SO_3]$ b) $[SO_2]^2[O_2]/[SO_3]^2$ c) $[SO_3]^2/[SO_3]^2[O_2]$ d) $[SO_2][O_2]$

IV. A saturated solution represents a dynamic equilibrium. Macroscopically, the concentration of dissolved solute is constant. Microscopically, this occurs because:

a) No more solute particles are dissolving.
b) The rate of dissolution of solute is zero.
c) Solute particles are dissolving and precipitating at the same rate.
d) All solute particles have dissolved.

V. Which of the following statements correctly describes the effect of temperature on the equilibrium constant?

a) K_c is directly proportional to temperature.
b) K_c is inversely proportional to temperature.
c) K_c depends on the enthalpy change of the reaction.
d) Temperature has no effect on the value of K_c.

VI. Consider the gas-phase equilibrium system represented by the equation:

$$2H_2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$$

Given that the forward reaction is endothermic, which of the following changes will decrease the equilibrium amount of H_2O ?

a) Adding more oxygen
b) Adding a solid phase catalyst
c) Decreasing the volume of the container (the total pressure increases)
d) Increasing the temperature at constant pressure

VII. $K_c = 0.040$ at 450°C for the given reaction, evaluate K_p for the reaction:

$$PC\ell_{5(g)} \rightleftharpoons PC\ell_{3(g)} + C\ell_{2(g)}$$

a) 0.40 b) 0.64 c) 2.4 d) 0.052

VIII. In which of the following gaseous equilibria, pressure has no effect on the equilibrium position?

a) $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ b) $PC\ell_{5(g)} \rightleftharpoons PC\ell_{3(g)} + C\ell_{2(g)}$
c) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

IX. **Consider the equilibrium $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. If the concentration of $H_2O_{(g)}$ is increased, the concentrations of $H_{2(g)}$ and $O_{2(g)}$ will:**

a) Increase b) Decrease c) Remain the same d) Change irregularly

X. **For a specific reaction, the value of the equilibrium constant, K_c:**

a) Always remains the same at different reaction conditions.
b) Increases if the concentration of one of the products is increased.
c) Changes with changes in the temperature.
d) Increases if the concentration of one of the reactants is increased.

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	c	$2NO_2 \rightleftharpoons N_2O_4$	The units of Kc depend on the change in moles of gas (Δn) in the reaction: $K_c = \frac{[N_2O_4]}{[NO_2]_2} \Rightarrow \text{Units} = \frac{M}{M_2} = M^{-1} = (\text{concentration})^{-1}$ For option c, $\Delta n = 1-2 = -1$, leading to Kc units of M^{-1}.
II.	a	The value of K_p falls with a rise in temperature.	The reaction is exothermic ($\Delta H = -197.9$ kJ/mol). Le-Chatelier's Principle: Increasing temperature shifts equilibrium left (toward reactants), reducing K_p. **Why other options are wrong:** b) K_p is independent of pressure (only composition changes). c) Catalyst speeds up equilibrium but does not affect yield. d) $K_p \neq K_c$ because $\Delta n = 2-3 = -1$
III.	b	$[SO_2]^2[O_2]/[SO_3]^2$	K_c is products over reactants, raised to their stoichiometric coefficients.
IV.	c	Solute particles are dissolving and precipitating at the same rate.	Macroscopic constancy results from equal dissolution and precipitation rates at equilibrium.
V.	c	K_c depends on the enthalpy change of the reaction.	K_c changes with temperature only if $\Delta H \neq 0_{(exo/endothermic)}$
VI.	d	Increasing the temperature at constant pressure	Endothermic forward reaction favours products (more $H_2 + O_2$) when heated.
VII.	c	2.4	$K_p = K_c(RT)^{\Delta n}$, $\Delta n = 1$ $K_p = 0.040 \times (0.0821 \times 723)1 = 2.4 (T = 450°C = 723K)$
VIII.	c	$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$	$\Delta n = 0$ (2 gas moles $\rightleftharpoons$ 2 gas moles), so pressure changes do not shift equilibrium.
IX.	a	Increase	Adding product (H_2O) shifts equilibrium left (Le-Chatelier's Principle), increasing $[H_2]$ and $[O_2]$.
X.	c	changes with changes in the temperature.	K_c is constant for a given temperature but varies with temperature (depends on ΔH).

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. What is meant by the state of chemical equilibrium?

Ans. Chemical equilibrium is the state in a reversible reaction when the rate of the forward reaction equals the rate of the reverse reaction, and the concentrations of reactants and products remain constant.

b. Define reversible reaction. Give an example.

Ans. A reversible reaction is a chemical reaction that proceeds in both forward and reverse directions under the same conditions.

Example:

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

c. The change of volume disturbs the equilibrium position for some of the gas phase reactions but not the equilibrium constant.

Ans. Volume changes affect the pressure, thus shifting the equilibrium position (Le-Chatelier's principle), but the equilibrium constant K_c or K_p remains unchanged as long as temperature is constant.

d. Mention the characteristics of chemical equilibrium.

Ans. **Characteristics of Chemical Equilibrium:**

(i) Rate of forward reaction equals rate of reverse reaction.
(ii) Concentrations of reactants and products remain constant.
(iii) Dynamic in nature.
(iv) Can be established from either side.
(v) Only affected by temperature, not by pressure or concentration (for K_c).

e. Reversible reaction attains the position of equilibrium which is dynamic in nature and not static. Explain it.

Ans. At equilibrium, the forward and reverse reactions continue to occur, but at the same rate. This means particles are still reacting, but no net change occurs. Hence, it is **dynamic**, not static.

f. Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Ans. As the concentration of reactants decreases and products increase, the forward reaction slows due to fewer collisions of reactant particles, while the reverse reaction rate increases.

g. Why ice at 0°C can be melted by applying pressure without supply of heat from outside?

Ans. Applying pressure favors the liquid phase (as it is denser than ice), shifting equilibrium towards melting even without external heat (Le-Chatelier's principle).

h. Write two conditions of equilibrium constant.

Ans.

(i) Temperature must remain constant.
(ii) The reaction must be in a closed system and reach equilibrium.

i. The reversible reaction:

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

has come to equilibrium in a vessel of specific volume at a given temperature. Before the reaction began, the concentrations of the reactants were $0.060\,mol/dm^3$ of SO_2 and $0.050\,mol/dm^3$ of O_2. After equilibrium is reached, the concentration of SO_3 is $0.040\,mol/dm^3$. What is the equilibrium concentration of O_2?

Ans.

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

Given Data:

- Initial $[SO_2] = 0.060\ mol/dm^3$
- Initial $[O_2] = 0.050\ mol/dm^3$
- At equilibrium: $[SO_3] = 0.040\ mol/dm^3$

From Stoichiometry:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$\Rightarrow$ If 0.040 mol of SO_3 formed, then 0.020 mol of O_2 used Equilibrium $[O_2] = 0.050 - 0.020 = 0.030\ mol/dm^3$

DESCRIPTIVE QUESTIONS

Q.3 (a) Define and explain the law of mass action and derive the expression for the equilibrium constant.

Ans. See Page No. (267)

(b) Write the expression for K_c for the following reactions:

i) $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightleftharpoons Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$

ii) $Ag^{1+}_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ag_{(s)}$

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

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

v) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Ans.

(i) $Sn^{+2}_{(aq)} + 2Fe^{+3}_{(aq)} \rightleftharpoons Sn^{+4}_{(aq)} + 2Fe^{+2}_{(aq)}$

$$K_c = \frac{[Product]}{[Reactants]} = \frac{[Sn^{+4}][Fe^{+2}]^2}{[Sn^{+2}][Fe^{+3}]^2}$$

(ii) $Ag^{+}_{(aq)} + Fe^{+2}_{(aq)} \rightleftharpoons Fe^{+3}_{(aq)} + Ag^{\circ}$

$$K_c = \frac{[Fe^{+3}][Ag^{\circ}]}{[Ag^{+}][Fe^{+2}]}$$

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

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

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

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

(v) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Q.4 Write down the K_c for the following reactions. Suppose that the reaction mixture in all the case is 'V' dm^{-3}.

i) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

ii) $2HI \rightleftharpoons H_2 + I_2$ **iii)** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Ans.

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

moles at t = 0 "a" mol "b" mol $\rightleftharpoons$ "0" mol "0" mol

moles at t = equilibrium $(a - x) + (b - x) \rightleftharpoons (x) + (x)$

conc. in mol/v (dm^3) so $\left(\frac{a-x}{v}\right) + \left(\frac{b-x}{v}\right) \rightleftharpoons \left(\frac{x}{v}\right) + \left(\frac{x}{v}\right)$

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

$$\text{So } K_c = \frac{x^2}{(a-x)(b-x)}$$

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

t = 0 a mole $\rightleftharpoons 0 + 0$

t = equilibrium $(a - 2x) \rightleftharpoons x + x$

$$\left(\frac{a-2x}{v}\right) \rightleftharpoons \left(\frac{x}{v}\right) + \left(\frac{x}{v}\right)$$

$$K_c = \frac{[Products]}{[Reactant]} \Rightarrow K_c = \frac{[H_2][I_2]}{[HI]^2} \Rightarrow K_c = \frac{\left(\frac{x}{v}\right)\times\left(\frac{x}{v}\right)}{\left(\frac{a-2x}{v}\right)^2} \Rightarrow K_c = \frac{x^2}{(a-2x)^2}$$

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

moles at t = 0 $a + b \rightleftharpoons 0$

moles at t = equilibrium $(a - x) + (b - 3x) \rightleftharpoons 2x$

concentration in moles/'V' dm^3 $\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right) \rightleftharpoons \frac{2x}{v}$

$$K_c = \frac{[Product}{[Reactant]} \Rightarrow K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$$

$$\text{So } K_c = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3} \Rightarrow K_c = \frac{4x^2v^2}{(a-x)(b-3x)^3}$$

Q.5 In the equilibrium

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = 90\ kJ\ mol^{-1}$$

What is the effect on the following changes? Explain your answer.

i) If temperature is increased **ii) volume of the container is decreased**

iii) catalyst is added **iv) chlorine is added**

Ans. Equilibrium

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = 90\ kJ\ mol^{-1}$$

a. Position of equilibrium **b.** Equilibrium constant

If:

i. Temperature is Increased: Temperature change will affect both equilibrium position and equilibrium constant. This is endothermic reaction, the increase of temperature shifts equilibrium positon in forward direction to re-establish equilibrium. Hence, the value of K_c increase.

ii. Volume is Decreased: The volume change affects equilibrium position only. When volume is decreased, reaction moves in backward direction to establish equilibrium again.

Since equilibrium constant has a constant value at a particular temperature, it is not affected by change in volume.

iii. Catalyst is Added: Catalyst has no effect on the equilibrium position and equilibrium constant. When catalyst is added at equilibrium, it enhances both the rates equally. Hence, equilibrium is not affected.

iv. Chlorine is Added: The addition of a substance at equilibrium affects the equilibrium position only. Equilibrium constant remains the same.

When Cl_2 is added at equilibrium, the conc. of products increases and equilibrium position is shifted in backward direction.

Q.6 Synthesis of ammonia by Haber's process is an exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92.46\ kJ$$

What should be the possible effect of change of temperature at equilibrium stage?

Ans. Since reaction is endothermic in backward direction, rise of temperature will shift equilibrium to left. Low temperature shifts the equilibrium to right and yield of NH3 will increase.

Q.7 K_c for the following reaction is 0.016 at 520°C

$$2HI_{(g)} \rightleftharpoons H_2 + I_{2(g)}$$

The equilibrium mixture contains HI = 0.08 M; H_2 = 0.01 M and I_2 = 0.01 M. To this mixture, more HI is added. So that its new concentration is 0.096 M. What will be the concentrations of HI, H_2 and I_2 when equilibrium is re-established?

Ans. Given Data:
Initial concentration of HI = 0.08 M
Initial concentration of H_2 = 0.01 M
Initial concentration of I_2 = 0.01 M
New concentration of HI = 0.096 M

Required: [HI], $[H_2]$ and $[I_2]$ = ?

Solution: $2HI \rightleftharpoons H_2 + I_2$

Initial concentration

$$0.08\ M \rightleftharpoons 0.01\ M + 0.01\ M$$

At equilibrium, the new concentrations

$$(0.096 - 2x) \rightleftharpoons (0.01 + x) + (0.01 + x)$$

$$K_c = \frac{\text{concentration of product}}{\text{concentration of reactants}} = \frac{[H_2][I_2]}{[HI]^2}$$

$$0.016 = \frac{[0.01 + x][0.01 + x]}{[0.096 - 2x]^2}$$

$$0.016 = \frac{(0.01 + x)^2}{(0.096 - 2x)^2}$$

Taking square root on both sides

$$\sqrt{0.016} = \sqrt{\frac{(0.01 + x)^2}{(0.096 - 2x)^2}}$$

$$0.126 = \frac{0.01 + x}{0.096 - 2x}$$

$$0.126(0.096 - 2x) = 0.01 + x$$

$$0.012096 - 0.252x = 0.01 + x$$

$$0.012096 - 0.01 = x + 0.252x$$

$$0.002096 = 1.252x$$

$$x = \frac{0.002096}{1.252}$$

$$x = 1.68 \times 10^{-3}\ M \quad \text{or} \quad 0.00168\ M$$

Concentrations at equilibrium can be calculated as follows

(i) $[HI] = (0.096 - 2x)$
$= 0.096 - 2 \times 0.00168 = 0.096 - 0.00336$
$= 0.09264\ M$

(ii) $[H_2] = 0.01 + x = 0.01 + 0.00168$
$= 0.01168\ M$

(iii) $[I_2] = 0.01 + x = 0.01 + 0.00168$
$= 0.01168\ M$

$[HI]$ = 0.0926 M
$[H_2]$ = 001168 M
$[I_2]$ = 0.01168

Q.8 The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4. A mixture of 3 moles of acetic acid and 1 mole of ethyl alcohol is allowed to come to equilibrium. Calculate the amount of ethyl acetate present at equilibrium.

Ans. Given Data:
K_c = 4
Moles of acetic acid = 3
Moles of ethyl alcohol = 1

Required:
Moles of ethyl acetate = ? , Amount of ethyl acetate = ?
Moles of acid = ? , Amount of acid in gram = ?
Moles of alcohol = ? , Amount of alcohol in gram = ?

Solution: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
at t = 0 3 mol + 1 mol $\rightleftharpoons$ 0 mol + 0 mol
at t = equilibrium(3 – x) mol + (1 – x)mol $\rightleftharpoons$ (x) mol + (x) mol

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

$$4 = \frac{(x)(x)}{(3 - x)(1 - x)} = \frac{x^2}{x^2 - 4x + 3}$$

$$x^2 = 4(x^2 - 4x + 3)$$

$$x^2 = 4x^2 - 16x + 12$$

$$4x^2 - x^2 - 16x + 12 = 0$$

$$3x^2 - 16x + 12 = 0$$

It is a quadratic equation. To evaluate the value of x, the formula used is:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Let us consider that [a = 3, b = –16, c = 12] for above reaction

Thus,
$$x = \frac{-(16) \pm \sqrt{(16)^2 - 4 \times 3 \times 12}}{2 \times 3}$$

$$= \frac{16 \pm \sqrt{256 - 144}}{6} = \frac{16 \pm \sqrt{112}}{6} = \frac{16 \pm 10.58}{6}$$

So,
$$x = \frac{16 + 10.58}{6} = 4.43 \text{ moles or}$$

$$x = \frac{16 - 10.58}{6} = 0.903 \text{ moles}$$

From the above two values of x

x ≠ 4 as initial concentration of CH_3COOH is less i.e., 3 moles. So value of x = 0.903 moles.

(i) Concentration of (CH_3COOH) at equilibrium
= 3 – x = 3 – 0.903 = 2097 moles

(ii) Concentration of (C_2H_5OH) at equilibrium
= 1 – x = 1 – 0.903 = 0.097 moles

(iii) Concentration of ethyl acetate = x = 0.903 moles

(iv) Mass = Moles × Mol. mass

(a) Amount of CH_3COOH = 2.097 × 60 = 125.82 g

(b) Amount of C_2H_5OH = 0.1 × 46 = 4.6 g

(c) Amount of ethyl acetate = 0.9 × 88 = 79.46 g

Moles of ethyl acetate = 0.9 moles
Mass of ethyl acetate = 79.46 g
Mass of acid left behind = 126 g
Mass of alcohol left = 4.6 g

Q.9 Study the equilibrium

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

i) Write the expression of K_p.

ii) When 1.00 mole of steam and 1.00 mole of CO are allowed to reach equilibrium, 33.3% of equilibrium mixture is hydrogen. Calculate the value of K_p. State the units of K_p.

Ans. Given Data: Moles of steam = 1.00

Moles of CO = 1.00

% of H_2 at equilibrium = 33.3%

Required: (i) Value of K_p = ?

(ii) Unit of K_p = ?

Solution:

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

Concentration at t = 0 (1.00) mole + (1.00) mole ⇌ 0 + 0

Concentration at t = eq (1 − x) mole + (1 − x) mole ⇌ x + x

Total moles of reaction mixture = 1 + 1 = 2 mol.

Moles of H_2 at equilibrium = 33.3%

It means that $\frac{x}{2} = \frac{\text{conc. of } H_2}{100}$

$$\frac{x}{2} = \frac{33.3}{100}$$

$$x = \frac{2 \times 33.3}{100} = 0.666 \text{ moles}$$

So $[H_2O] = 1 - x$

$= 1 - 0.666 = 0.333$ moles

$[CO] = 1 - x$

$= 1 - 0.666 = 0.333$ moles

$[H_2] = [CO_2] = x = 0.666$ moles

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

as $\Delta n = 0$ so,

$K_p = K_c$

$$K_p = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{0.666 \times 0.666}{0.333 \times 0.333} = 4$$

$$\text{Units of } K_p = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{\text{mol dm}^{-3}.\text{ mol dm}^{-3}}{\text{mol dm}^{-3}.\text{ mol dm}^{-3}} = \text{no unit}$$

$K_p = 4$

K_p has no unit.

ADDITIONAL SLOs BASED MCQs

1. **Reactions that proceed in both forward and reverse directions without changing the concentration of reactants and products under existing conditions are called:**
A. Irreversible reactions B. Reversible reactions C. Complete reactions D. Spontaneous reactions

2. **The observation of a color change in a reaction is an example of a:**
A. Microscopic event B. Macroscopic event C. Quantum event D. Nuclear event

3. **In the reaction $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$, the forward reaction rate is maximum:**
A. At equilibrium B. At the beginning
C. When product concentration is high D. When the reverse reaction rate is maximum

4. **Which of the following is an example of dynamic equilibrium between two physical states?**
A. Burning of wood B. Rusting of iron
C. Evaporation of water in an open container D. Ice and water coexisting at 0°C in a closed container

5. **At dynamic equilibrium between a liquid and its vapor, the rate of evaporation is:**
A. Greater than the rate of condensation B. Less than the rate of condensation
C. Equal to the rate of condensation D. Zero

6. **Which of the following is NOT a necessary condition for establishing chemical equilibrium?**
A. The reaction must be reversible B. The system must be closed
C. A catalyst must be present D. Temperature should be constant

7. **The concentration of pure solids and pure liquids are not included in the Kc expression because:**
A. They do not react
B. Their concentrations are variable
C. Their concentrations (active masses) are considered constant
D. They are not part of the equilibrium

8. **Which of the following is an example of heterogeneous equilibrium?**
A. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3(g)$
B. $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$
C. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
D. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

9. **The term "active mass" in the Law of Mass Action refers to:**
A. Total mass of the reactant B. Molar concentration
C. Number of moles D. Density

10. **For the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, the correct Kc expression is:**
A. $\frac{[NH_3]}{([N_2][H_2])}$ B. $\frac{[NH_3]^2}{([N_2][H_2]^3)}$ C. $\frac{([N_2][H_2]^3)}{[NH_3]^2}$ D. $\frac{[N_2][H_2]}{[NH_3]}$

11. **For which reaction will K_c have units of mol^{-2} dm^{+6}?**
A. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ B. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
C. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ D. $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

12. **For the Haber process $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, the value of Δn is:**
A. −1 B. −2 C. +1 D. +2

13. **Le Chatelier's principle is used to predict the effect of a disturbance on:**
A. The rate of reaction only B. The equilibrium position
C. The activation energy D. The mechanism of reaction

14. **For the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, increasing the pressure will shift the equilibrium:**
A. To the left, favoring reactants B. To the right, favoring products
C. No effect D. To increase Δn

15. **For an exothermic reaction (ΔH = −ve), increasing the temperature will:**
A. Shift equilibrium to the right and increase K_c B. Shift equilibrium to the left and decrease K_c
C. Shift equilibrium to the right and decrease K_c D. Shift equilibrium to the left and increase K_c

16. **A catalyst increases the rate of a chemical reaction by:**
A. Increasing the activation energy B. Decreasing the activation energy
C. Shifting the equilibrium to the right D. Increasing the yield of products

17. **To maximize the yield of ammonia in the Haber process ($N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$; ΔH = −ve), conditions should be:**
A. High temperature, low pressure B. Low temperature, high pressure
C. High temperature, high pressure D. Low temperature, low pressure

18. **In the Contact process for SO_3 production ($2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$; ΔH = −ve), a decrease in temperature favors:**
A. Formation of SO_2 and O_2 B. Formation of SO_3
C. No change in equilibrium D. An increase in K_c value

Answers Key

1. B	2. B	3. B	4. D	5. C	6. C	7. C	8. C	9. B	10. B	11. B
12. B	13. B	14. C	15. B	16. B	17. C	18. B				

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Differentiate between Reversible and Irreversible reaction.

Ans.

Reversible Reaction	Irreversible Reaction
1. "The chemical reaction in which products of a reaction can react to form the original reactants under the same set of conditions is called a reversible reaction."	1. "A chemical reaction in which products of the reaction do not react to form the original reactants under same conditions is called irreversible reaction."
2. "The chemical reaction which takes place in both directions i.e. forward and reverse under same conditions is called reversible reaction." $\underset{\text{Reactants}}{A + B} \rightleftharpoons \underset{\text{Products}}{C + D}$	2. "A chemical reaction which takes place in one direction only under same conditions is called irreversible reaction." $\underset{\text{Reactants}}{A + B} \longrightarrow \underset{\text{Products}}{C + D}$
3. It is represented by writing a double headed arrow ($\rightleftharpoons$) between reactants and products.	3. It can be represented by an arrow ($\longrightarrow$) from reactants to products.
4. It can be carried out in a closed system.	4. It may or may not be carried out in a closed or an open system.
5. Chemical equilibrium is not established in it.	5. Chemical equilibrium is established in it.
Examples: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(s)}$	**Examples:** $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ $2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$

Q.2 Define Law of Mass Action and Equilibrium Constant (K_c).

Ans. Law of Mass Action:

"The rate at which the reaction proceeds is directly proportional to the product of active masses of the reactants".

Equilibrium Constant (K_c):

The ratio of product of concentration of products and product of concentration of reactants is called equilibrium Constant (K_c).

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Chemical Equilibrium:

"The state achieved by reversible chemical reaction in which the forward and reverse processes are occurring at the same rate is called state of chemical equilibrium or equilibrium state."

Q.3 Justify that Chemical Equilibrium is dynamic in nature.

Ans. A chemical equilibrium state in a reversible reaction is a state where the rate of forward reaction becomes equal to rate of reverse reaction. It shows that at this state both reaction are taking place simultaneously and not stop thus equilibrium is dynamic not static. If it would be static reaction would stop.

Q.4 What is effect of change in pressure on a system in equilibrium for gases?

Ans. (i) If reaction mixture is in gaseous state then at equilibrium if volume is changed it will effect the equilibrium.

(ii) If number of moles of reactants are not equal to number of moles of product then those gaseous reactions are effected by volume change at equilibrium.

For Example:

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

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

Q.5 What will be the effect of increase of pressure and temperature on the following reaction?

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.46\ kJ$$

Ans. (a) Since reaction is endothermic in backward direction, rise of temperature will shift equilibrium to left. Low temperature shifts the equilibrium to right and yield of NH_3 will increase

(b) Increase of pressure decreases the volume and equilibrium position is shifted in forward direction. As a result yield of ammonia increases and vice versa.

Q.6 Briefly explain the effect of pressure on the equilibrium position for the dissociation of PCl_5.

Ans. Dissociation of PCl_5:

In the same way, effect of change of pressure on the equilibrium position can be explained for the dissociation of PCl_5. This is homogeneous gaseous phase reaction.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_2$$

K_c for this reaction is,

$$K_c = \frac{x^2}{(a - x)V}$$

Conclusion: In the dissociation of PCl_5 the factor of volume is present in the denominator. The reason is that number of moles of products are greater than those of reactants. So, increase in pressure will decrease the 'x' to keep the value of K_c constant and the reaction will be pushed to the backward direction. The equilibrium position is disturbed but not the K_c value.

Q.7 How does a catalyst affect on equilibrium constant?

Ans. Effect of Catalyst on Equilibrium Constant:

In most of the reversible reactions, the equilibrium is not always reached within a suitable short time. So an appropriate catalyst is used.

- A catalyst does not affect the equilibrium position of the reactions. It increases the rates of both forward and backward reactions and this reduces the time to attain the equilibrium state.
- A catalyst lowers the energy of activation of both forward and reverse steps by giving new path to the reaction.

Q.8 Write down equilibrium constant expression for the reactions:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Ans. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Equllibrium Constant Expression:

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Q.9 Write down K_c units for the reaction $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Ans. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Equilibrium constant for this reaction:

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]}{[\text{mol dm}^{-3}]} = \text{mol dm}^{-3}$$

Q.10 State Le Chatelier's Principle.

Ans. Le-Chatelier's Principle:

"If a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the affect of that stress is called Le-Chatelier's Principle".

Q.11 What are the optimum conditions of temperature and pressure to get maximum yield of ammonia?

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.46\ kJ$$

Ans. $N_2 + 3H_2 \rightleftharpoons 2NH_3 - 92.46\ kJ \qquad \Delta H = -92.46\ kJ$

Optimum Conditions:

The optimum conditions for synthesis of Ammonia gas by Haber's processes are:

- **Temperature:** 400°C (673 K)
- **Pressure:** 200-300 atm
- **Catalyst:** pieces of iron crystals embedded in a fused mixture of MgO, Al_2O_3 and SiO_2.