

## Catalysis |

**Structure**

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**11.1 INTRODUCTION**

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In the previous unit you have learnt about the meaning and techniques of studying fast reactions. In the present unit we will take up catalysis, i.e., the process of alteration of the rate and/or the outcome of the reaction in presence of a substance called catalyst. You know that a catalyst is a substance, that alters the rate of reaction, but remains chemically unchanged at the end of the reaction. We will start the unit by defining catalysis and the terminology used in the context of catalysis. We would then classify catalysis and outline its characteristics. This will be followed by a discussion on homogeneous catalysis. In this context, you will study the kinetics of homogeneous reactions in terms of a simplified mechanism and analyse the rate expressions under different conditions. Thereafter, before moving on to heterogeneous catalysis we will take up adsorption—a phenomenon critical for heterogeneous catalysis. Herein, we would define adsorption and study the adsorption isotherms for monolayer and multilayer adsorption. This will be followed by the discussion on the kinetics of heterogeneous catalysis. Herein, we will discuss the mechanisms involved in heterogeneous catalysis and derive corresponding rate equations and analyse them.

In the next unit we will take up the kinetics of enzyme reaction i.e., enzyme catalysis.

## Expected Learning Outcomes

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After studying this unit, you should be able to:

- ❖ define a catalyst and discuss the terminology related to catalysis giving suitable examples;
- ❖ differentiate between homogeneous and heterogeneous catalysis;
- ❖ outline the characteristics of catalytic reactions;
- ❖ describe the mechanism of homogeneous catalysis and derive the rate equation corresponding to it;
- ❖ analyse the rate expression for homogeneous catalysis under different conditions;
- ❖ define the term adsorption;
- ❖ define an adsorption isotherm and give the postulates of Langmuir adsorption isotherm;
- ❖ derive the expressions for adsorption isotherms for different types of monolayer adsorption;
- ❖ give the expression for BET adsorption isotherm and outline its significance; and
- ❖ explain different types of mechanisms involved in heterogeneous catalysis and derive the corresponding rate equations.

## 11.2 CATALYSIS AND ITS CHARACTERISTICS

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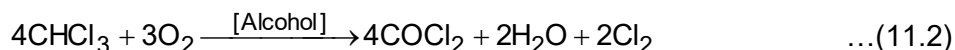
You have learnt in your earlier classes that the conversion of reactant(s) to product(s) in a chemical reaction occurs through a series of steps that constitute the mechanism of the reaction. The slowest of these steps determines the rate of the reaction. Also, you are aware that the rate of reaction depends on temperature—an increase in temperature increases the rate. In industry, and also in the laboratory, it is desirable that we get the largest amount of product in the shortest possible time. To some extent this can be achieved by increasing the temperature, but this approach may not be possible if the reactants and / or the products are thermally unstable. Further, this may also lead to undesirable side reactions giving impurities or may in fact, negatively affect the amount of the product. In such cases, using a catalyst provides a way out.

In 1836, it was observed by Berzelius that there are some substances, which increase the rate of reaction without changing themselves. The substance was called **catalyst** and the process **catalysis**. Now, we know that a catalyst is a substance, that alters the rate of reaction, but remains chemically unchanged at the end of the reaction. It is important to note that the catalyst does not only increase the rate; it can decrease it too. There are a number of important terms that need to be known in the context of catalysts and catalysis. These are briefly given here.

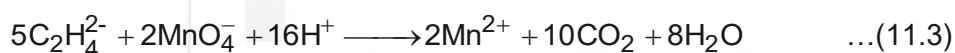
A catalyst that increases the rate of a chemical reaction is called **positive catalyst** and the phenomenon is known as **positive catalysis** for example, in the following reaction,  $\text{MnO}_2$  acts as a positive catalyst.



On the other hand, the catalyst that decreases the rate of a chemical reaction is called **negative catalyst** or an **inhibitor** and the phenomenon is known as **negative catalysis** or **inhibition**. For example, in the following reaction, alcohol acts as a negative catalyst.



In some reactions it is observed that one of the products itself acts as a catalyst for that reaction; the reaction is slow to begin with and becomes faster as some amount of the product is formed. It is called an **autocatalyst** and the phenomena is called **autocatalysis**. For example, in the following reaction manganese ions act as autocatalyst.



Further, it has been observed that in some cases the activity of a given catalyst is increased in presence of small amount of a second substance. Such a substance, that itself is not a catalyst, enhances (or promotes) the activity of a catalyst, is called the **promoter**. For example, in the following reaction



zinc oxide is the catalyst and chromium trioxide is the promoter. Similarly, there are substances which, when present in the reaction mixture, decrease the rate of reaction. These are called **inhibitors** and may act by either destroying the catalyst or may react with reaction intermediates in a chain reaction. A substance that destroys the catalyst, is called a **poison** and the process is called **catalytic poisoning**. For example, in reaction



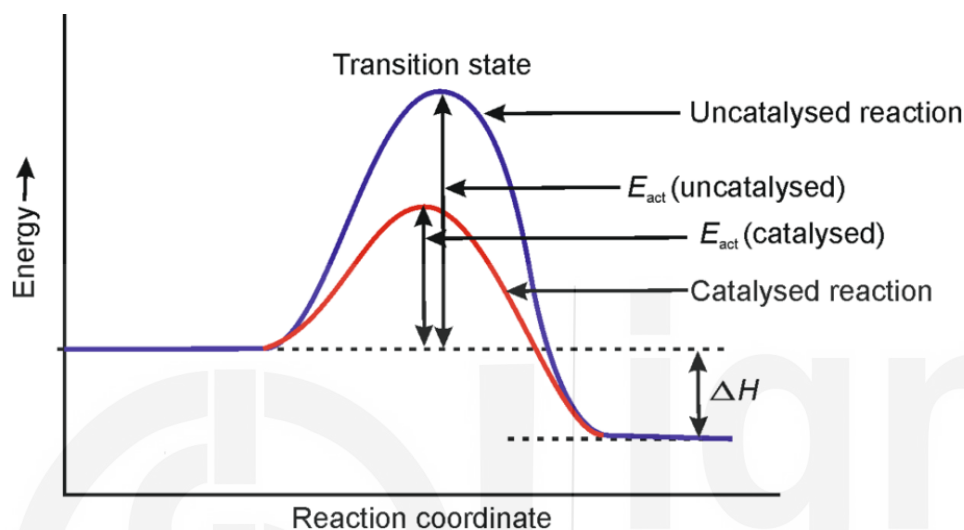
The activity of Fe as catalyst is reduced in the presence of  $\text{H}_2\text{S}$  that is said to poison the catalyst. Having understood the basic terminology of catalytic reactions let us now understand the characteristics of catalytic reactions

### 11.2.1 Characteristics of Catalytic Reactions

The following are the characteristics of catalytic reactions.

- A catalyst does not appear in the overall stoichiometry of the reaction and is not used up in the course of the reaction. It remains unchanged in terms of its mass and composition though its physical properties may change e.g., coarsely grained manganese dioxide used as catalyst in the decomposition of potassium chlorate becomes finely powdered at the end of the reaction. However, in many cases the catalysts lose their effectiveness due to different reasons like, poisoning.

- The quantity of catalyst required is often small e.g., various redox reactions can be effectively catalysed by about  $10^{-6}$ - $10^{-8}$  mol dm<sup>-3</sup> of metal ions of platinum group.
- A catalyst works by providing an alternate mechanism having lower Gibbs energy of activation. As the magnitude of energy barrier is reduced, a larger number of molecules of the reactants can cross over it thereby increasing the rate of the reaction. A schematic diagram showing the potential energy profile for uncatalyzed and catalysed reactions is given in Fig. 11.1.

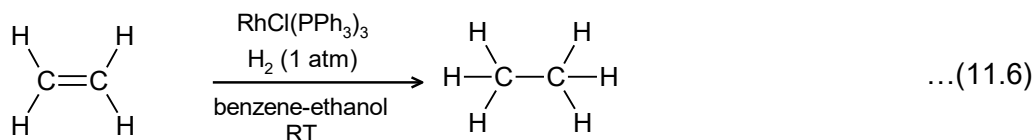


**Fig. 11.1: A schematic diagram showing the potential energy profile for uncatalyzed and catalysed reactions.**

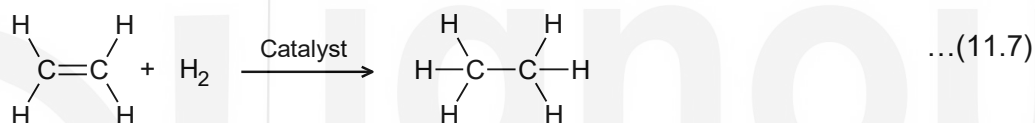
- It is important to note that the mechanism provided by the catalyst enhances the rate of both the forward and the reverse reaction to the same extent and thereby merely reduce the time for equilibrium to be reached. In other words, the catalyst merely increases the rate of approach to equilibrium, and doesn't alter the thermodynamic equilibrium constant. In other words, the addition of a catalyst does not directly affect the enthalpies or Gibbs energies of the reactants and products of the reaction.
- A catalyst cannot start a reaction but can only decrease or increase its rate. In other words, if a reaction is not feasible ( $\Delta G$  is positive), it will not occur by just adding the catalyst.
- As per one of the mechanisms of catalytic action, discussed later, the catalyst combines with the reactant to form an intermediate in the initial step and is released in the product-forming step. Thereby, it does not appear in the chemical equation of the reaction; it is generally placed over the reaction arrow as shown in the examples given above.
- It is important to note that the success of a chemical process often depends on the availability of suitable catalyst. For example, in the manufacture of nitric acid, quick oxidation of  $\text{NH}_3$  (g) in the presence of a Pt–Rh catalyst, gives  $\text{NO}$ (g), instead of usual product  $\text{N}_2$ (g), which can then easily be converted to  $\text{HNO}_3$ .

### Classification of Catalysis

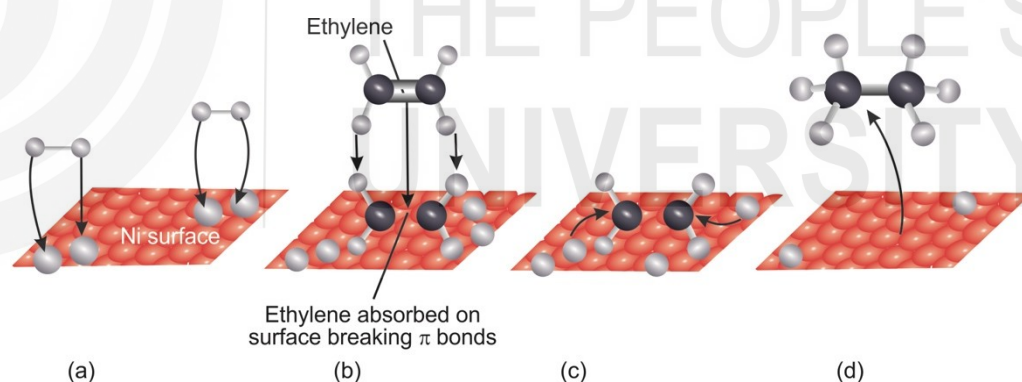
Catalysis can be classified into two types viz., homogeneous catalysis and heterogeneous catalysis. These differ in terms of the phases of the reactants, products and the catalyst. In case of **homogeneous catalysis**, the reactants, products, and the catalyst are all in the same phase, whereas in case of **heterogeneous catalysis**, the catalyst is present in a phase different from that of the reactants and the products. Let us take the example of hydrogenation of alkenes- an important reaction in pharmaceutical and food industries. The hydrogenation can be done via homogeneous catalysis by using Wilkinson's catalyst-a complex of rhodium.



Alternatively, this can as well be done via heterogeneous catalysis by using a metal catalyst.



In the first case, the reactant, product and the catalyst are in the same phase whereas in the second case the gaseous reactants react at the surface of a solid catalyst forming the products as shown schematically in Fig. 11.2.



**Fig. 11.2: A simplified diagram showing heterocatalytic hydrogenation of an alkene.**

In this case, the catalyst is usually a metal such as platinum or nickel. To understand the working of the catalyst, it is necessary to know how do the reactants interact with the metal and with each other. For this we need to understand the phenomenon of adsorption taken up in Section 11.4. Let us first learn about the mechanism of homogeneous catalysis. However, before that answer the following simple question to assess your understanding.

### SAQ 1

What are catalysts and how do they work?

## 11.3 HOMOGENEOUS CATALYSIS

As stated above, in case of homogeneous catalysis, the reactants, products and catalyst are all in the same phase. Further, in homogeneous catalysis the walls of the vessel do not affect the rate of the reaction i.e., if we add glass beads or a chemically inert solid to the reaction mixture to increase the surface-to-volume ratio no change is observed in the rate. As per one of the simplest mechanisms for homogeneous catalysis, initially, the catalyst combines with a reactant and forms an intermediate species which then yields the product, and the catalyst is regenerated as shown below.



Here, the reactant S is called the substrate; C represents the catalyst, P is the product, and SC is an intermediate compound.  $k_{-1}$  and  $k_2$  are the first order rate constants while  $k_1$  is a second order rate constant. The regenerated catalyst can combine with another reactant molecule in a subsequent reaction and the process continues.

### 11.3.1 Kinetics of Reactions Undergoing Homogeneous Catalysis

In terms of the mechanism given above, the rate of the reaction can be expressed as the rate of formation of the product as follows:

$$\text{Rate} = k_2 [\text{SC}] \quad \dots (11.10)$$

Now, the issue is to get the expression for [SC]. There are two possibilities depending on the stability of SC. In the first case, if the intermediate, SC is stable and the rate of its reconversion back into the catalyst and the substrate is far greater than the rate at which it gives the product (i.e.  $k_{-1} \gg k_2$ ), the concentration of the intermediate, can be obtained simply by considering equilibrium constant for the first step as

$$[\text{SC}] = K [\text{S}] [\text{C}] \quad \dots (11.11)$$

where,

$$K = \frac{k_1}{k_{-1}}$$

$$\text{Rate} = k_2 K [\text{S}] [\text{C}] \quad \dots (11.12)$$

This implies that the rate is proportional to the concentrations of the substrate as well as of the catalyst. The stable intermediates in this type of catalysis are known as **Arrhenius intermediates**.

The second possibility is that the intermediate complex is not very stable, i.e. rate of its conversion to products is not small as compared with the rate of its reconversion back into catalyst and the substrate. In this case the treatment is

It is interesting to note that if the equilibrium step is sufficiently exothermic, which is possible with associative reactions, the rate of reaction can decrease with an increase in temperature.

a little involved. In such a case, we cannot calculate the concentration of [SC] simply by using equilibrium constant alone because the rate of the second step cannot be neglected. Therefore, we need to use steady-state-treatment. The intermediates in this type of catalysis are known as **Van't Hoff intermediates**.

To determine the concentration of the intermediate, [SC] in this case, we write the expression for its differential rate as

$$\frac{d[\text{SC}]}{dt} = k_1[\text{S}][\text{C}] - k_{-1}[\text{SC}] - k_2[\text{SC}] \quad \dots(11.13)$$

Under steady state condition this rate is zero, therefore we can write,

$$k_1[\text{S}][\text{C}] - k_{-1}[\text{SC}] - k_2[\text{SC}] = 0 \quad \dots(11.14)$$

Rearranging, we get

$$[\text{SC}] = \frac{k_1[\text{S}][\text{C}]}{(k_{-1} + k_2)} \quad \dots(11.15)$$

We define a new constant called **composite constant**, represented as  $k_m$  as

$$k_m = \frac{k_{-1} + k_2}{k_1} \quad \dots(11.16)$$

Substituting in Eq. (11.15), we get

$$[\text{SC}] = \frac{[\text{S}][\text{C}]}{k_m} \quad \dots(11.17)$$

Substituting the expression for [SC] in Eq. (11.10) we get

$$\text{Rate} = \frac{k_2[\text{S}][\text{C}]}{k_m} \quad \dots(11.18)$$

Thus, according to Eq. (11.18) the rate of product formation increases linearly with the concentrations of the substrate as well as the catalyst. However, it is inconvenient to use Eq. (11.18) over the entire course of the reaction because the concentrations here correspond to species that are not involved in the formation of the SC complex and are difficult to measure. To get over this problem, we consider the behaviour of the rate expression only in the initial stage of the reaction. That is, we determine the concentrations of the substrate and the catalyst at the beginning of the reaction.

Using the law of conservation of mass we can write,

$$[\text{S}]_0 = [\text{S}] + [\text{SC}] + [\text{P}] \quad \dots(11.19)$$

$$[\text{C}]_0 = [\text{C}] + [\text{SC}] \quad \dots(11.20)$$

Where,  $[\text{S}]_0$  and  $[\text{C}]_0$  represent the initial concentrations of the substrate and the catalyst. Rearranging Eq. (11.19) we can write the following expression for [S].

$$[\text{S}] = [\text{S}]_0 - [\text{SC}] - [\text{P}] \quad \dots(11.21)$$

Since in the beginning of the reaction  $[P] = 0$ , we can write

$$[S] = [S]_0 - [SC] \quad \dots(11.22)$$

Using Eq. (11.20) we can write the expression for  $[C]$  as

$$[C] = [C]_0 - [SC] \quad \dots(11.23)$$

Using these in Eq. (11.17) and rearranging, we get

$$0 = \{[S]_0 - [SC]\} \{[C]_0 - [SC]\} - k_m [SC] \quad \dots(11.24)$$

Simplifying,

$$[SC]^2 - \{[S]_0 + [C]_0 + k_m\} [SC] + [S]_0 [C]_0 = 0 \quad \dots(11.25)$$

This is a quadratic equation that can be solved to get  $[SC]$ . However, we can simplify it by using conditions that either  $[S]$  or  $[C]$  is present in much lower concentration than the other. In such situations the value of  $[SC]$  is very small and the term  $[SC]^2$  in Eq. (11.25) can be neglected. The expression simplifies to

$$\{[S]_0 + [C]_0 + k_m\} [SC] + [S]_0 [C]_0 = 0 \quad \dots(11.26)$$

Rearranging, we get

$$[SC] = \frac{[S]_0 [C]_0}{[S]_0 + [C]_0 + k_m} \quad \dots(11.27)$$

Substituting in Eq. (11.10), we get

$$(\text{Rate})_0 = \frac{k_2 [S]_0 [C]_0}{[S]_0 + [C]_0 + k_m} \quad \dots(11.28)$$

In this expression for rate, the subscript '0' indicates its applicability to the initial reaction rate.

Let us consider two limiting cases of Eq. (11.28).

### Case 1. $[C]_0 \ll [S]_0$

This is most common case in homogeneous catalysis wherein the concentration of the substrate is far greater than that of the catalyst. In this case, we can ignore  $[C]_0$  in the denominator of Eq. (11.28) and write

$$(\text{Rate})_0 = \frac{k_2 [S]_0 [C]_0}{[S]_0 + k_m} \quad \dots(11.29)$$

We can note that in this case the initial rate is proportional to the catalyst concentration.

Here again, there are two possibilities.

i)  $[S]_0 \ll k_m$

we can write,

$$(\text{Rate})_0 = \frac{k_2 [S]_0 [C]_0}{k_m} = k_{cat} [S]_0 \quad \dots(11.30)$$

$$\text{where, } k_{cat} = \frac{k_2 [C]_0}{k_m} \quad \dots(11.31)$$

The plot of reaction rate versus substrate concentration will be a straight line having a slope equal to  $\frac{k_2 [C]_0}{k_m}$  or  $k_{cat}$

ii)  $[S]_0 \gg k_m$

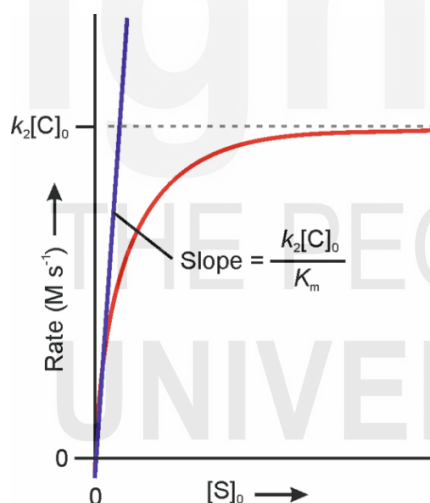
At the elevated concentrations of substrate, the denominator in Eq. (11.29) can be approximated as  $[S]_0$  i.e.,

$$[S]_0 + k_m \approx [S]_0 \quad \dots(11.32)$$

and we get the initial rate expression as

$$(\text{Rate})_0 = k_2 [C]_0 \quad \dots(11.33)$$

i.e., the rate is zero order in substrate concentration. In other words, at higher substrate concentrations, the rate of reaction will reach a limiting value represented as  $R_{max}$ . At this stage, the reaction rate can only be enhanced by increasing the amount of catalyst. A schematic plot of the initial rate of the reaction versus the initial concentration of substrate is given in Fig. 11.3.



**Fig. 11.3:** Plot of initial rate of reaction versus initial concentration of the substrate.

### Case 2. $[S]_0 \ll [C]_0$

In this we can ignore  $[S]_0$  in the denominator of the Eq. (11.28) to get the expression for the initial rate as

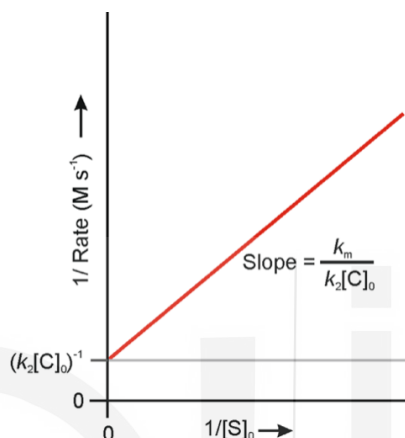
$$(\text{Rate})_0 = \frac{k_2 [S]_0 [C]_0}{[C]_0 + k_m} \quad \dots(11.34)$$

This implies that when the concentration of the catalyst is far greater than the substrate, the reaction rate is first order in  $[S]_0$ . Further, depending on the magnitude of  $[C]_0$  relative to  $k_m$  the rate will be of first or zero order in  $[C]_0$ . However, such a situation is generally avoided in the catalysis studies. More so, since good catalysts are generally expensive; this approach is not cost effective.

An alternative approach to analyse Eq. (11.29) is to invert it as follows

$$\frac{1}{(\text{Rate})_0} = \left( \frac{k_m}{k_2 [C]_0} \right) \frac{1}{[S]_0} + \frac{1}{k_2 [C]_0} \quad \dots(11.35)$$

As per Eq. (11.35) a plot of the inverse of the initial reaction rate versus the inverse of initial substrate concentration should yield a straight line. This is referred to as **double reciprocal plot** and. The reciprocal of the intercept gives  $k_2[C]_0$  which can be used along with the slope to get the values of  $k_2[C]_0$  and  $k_m$ . The variation in reaction rate with substrate concentration in terms of reciprocal plot is illustrated in Fig. 11.4.



**Fig. 11.4: The variation in reaction rate with substrate concentration in terms of double reciprocal plot.**

Having learnt about homogeneous catalysis and the kinetics of the processes involved, let us now take up heterogeneous catalysis. As stated above, the heterogeneous catalysis occurs on the surface of the catalyst. It involves the adsorption of the reactant molecules to be adsorbed on the surface of the catalyst. Therefore, it is desirable to learn about the nature and process of adsorption and the associated characteristics. This is taken up in the next section. However, before moving ahead you may answer the following simple questions to assess your understanding of homogeneous catalysis.

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### SAQ 2

Differentiate between Arrhenius intermediates and van't Hoff's intermediates.

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### SAQ 3

Under what conditions can we apply steady state approximation in homogeneous catalysis?

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## 11.4 ADSORPTION

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You have learnt above that in homogeneous catalysis, the catalyst combines chemically with one of the reactants to form an intermediate that reacts readily to form products. The same mechanism is applicable in case of a surface acting as a catalyst. The chemisorption of the reactants on the surface of the

catalyst is equivalent to the formation of the intermediate in the homogeneous case. In both cases, the catalyst provides an alternative path of lower activation energy thus increasing the rate of reaction. It is important to note that the surface sites on a catalyst differ in their ability to adsorb the reactant molecules. Further, the nature of the surface determines whether or not it can act as a catalyst for a particular type of reaction.

In the example of heterogeneous catalysis given above, Eq. (11.7), the catalyst is a metal such as platinum or nickel, and to understand the working of the catalyst it is necessary to know how hydrogen interacts with metals i.e., what are the interactions between gaseous reactant and surfaces. That is, we need to know about the nature of surface and binding of reactant with it. You have learnt in your earlier classes that the term 'adsorption' refers to the presence of excess concentration of a specific component at the surface of liquid or solid phase as compared to that present in the bulk of the material.

The adsorption arises due to the presence of residual attractive forces at the surface of the body that hold the adsorbed species on the surface. In case of liquids, these forces are due to the nonuniform distribution of molecules at the surface. On the other hand, in case of solids, these forces are due to the presence of unsatisfied valences on the surface. The adsorption is accompanied by a decrease in the Gibbs energy ( $\Delta G$  is  $-ve$ ) and is thus a spontaneous process. As the molecules adsorbed on the surface are more ordered than those in the bulk, the entropy change for the process is negative.

### 11.4.1 Monolayer Adsorption Isotherms

There are different ways in which the reactant molecules can bind to the surface of the catalyst and undergo catalytic reaction. Some of these are

- I. The gaseous reactant (atoms or molecules) occupy single sites on the surface and are not dissociated
- II. The adsorption of the reactant molecule is accompanied by its dissociation on the surface
- III. Two different substances A and B compete for the same sites on the surface for adsorption

Let us learn about adsorption behaviour in these cases.

#### I. The gaseous reactant (atoms or molecules) occupy single sites on the surface and are not dissociated

The process of adsorption of reactant A on the surface S, in this case can be represented as



Langmuir used a kinetic approach to derive the adsorption isotherm-an expression describing the amount or extent of adsorption of molecules onto a surface at a given temperature. The approach is based on the following postulates:

- The surface of the solid is homogenous i.e., each binding site has the same affinity for the gas molecules and is occupied independent of the other sites.
- The adsorbed gas molecules are localised, i.e., they do not move around on the surface.
- The adsorption on a solid surface is reversible i.e., there exists a dynamic equilibrium between the adsorbed and the free molecules.
- The rate of adsorption is proportional to the concentration of the adsorbate in the gas phase and the fraction of unoccupied sites on the surface.
- The adsorbed molecules form a monolayer and are distributed uniformly over the surface implying that once surface sites are covered by gas molecules, no further adsorption of gas molecules would occur.

Let us derive the expression for Langmuir adsorption isotherm.

We begin with the assumption that the gas molecules that are adsorbed directly onto the surface are the ones that are catalysed. This implies that the rate of the catalysed reaction is related to the rate at which the gaseous reactant(s) interact with or are adsorbed on the surface. As stated above, the maximum amount of gas that can be adsorbed and be catalysed would be equal to the amount required to form a complete monolayer of gas molecules. The *coverage* of the surface is defined as the fraction of possible positions on the surface that have an adsorbed gas molecule on them and is symbolized by the Greek letter  $\theta$ . Its value varies from 0 (no coverage) to 1 (complete monolayer). It is further assumed that the molecules adsorbed on top of a monolayer do not experience any catalytic effects.

The adsorption of gas molecules on the surface is taken as an elementary process so that the rate of adsorption can be determined directly from the stoichiometry of the reaction. This rate of adsorption is directly proportional to the concentration of the gaseous reactant,  $[gas]$  as well as to the amount of surface positions available for the gas to be adsorbed. Now, if at an instant the coverage is  $\theta$ , then the number of sites available (i.e., not covered) will be  $(1-\theta)$ . The rate of adsorption can be written as

$$Rate_{ads} = k_{ads} [A](1-\theta) \quad \dots(11.36)$$

Once the reaction on the surface is over, the gas molecules leave the surface, or get *desorbed*. The process is called **desorption** and depends on the extent of the coverage of the surface. In other words, it is assumed to be a zeroth-order reaction, the rate of desorption can be given as

$$Rate_{des} = k_{des} \cdot \theta \quad \dots(11.37)$$

At a certain stage, the process achieves a steady rate i.e., the rates of adsorption and desorption is equal to each other i.e.,

$$Rate_{ads} = Rate_{des} \quad \dots(11.38)$$

$$k_{ads} [A](1-\theta) = k_{des} \cdot \theta \quad \dots(11.39)$$

On solving the above equation we get the following expression for the coverage  $\theta$ :

$$\theta = \frac{k_{ads} [A]}{k_{ads} [A] + k_{des}} \quad \dots(11.40)$$

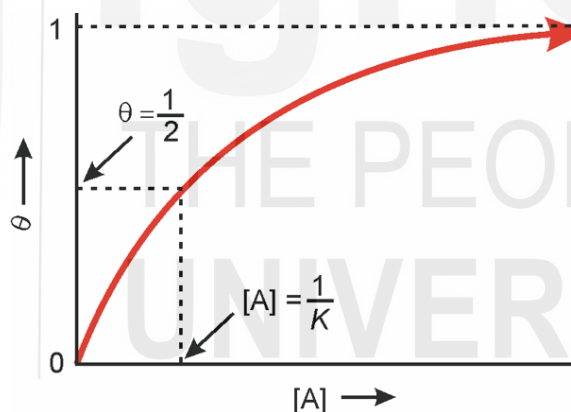
We can write the equilibrium constant for the adsorption-desorption process as

$$K = \frac{k_{ads}}{k_{des}} \quad \dots(11.41)$$

Dividing the numerator and the denominator on the right side of Eq. (11.40) by  $k_{des}$  and simplifying, we can write the expression in terms of  $K$  as

$$\theta = \frac{K[A]}{K[A] + 1} \quad \dots(11.42)$$

Since the numerator will always be less than the denominator it implies that  $\theta$  will always be less than 1. The Eq. (11.40) and (11.42) give the variation of  $\theta$  with the concentration of the gas,  $[A]$  and are called **Langmuir adsorption isotherms**. The word "isotherm" here signifies that the process is considered at constant-temperature conditions. It is difficult to measure the value of  $\theta$  directly. We can do so indirectly by measuring mass of the gas adsorbed. A schematic Langmuir adsorption isotherm is shown in Figure 11.5.



**Fig. 11.5: A schematic plot of Langmuir adsorption isotherm for adsorption without dissociation. At  $\theta = \frac{1}{2}$ ,  $[A]$  is equal  $1/K$ .**

At sufficiently low concentrations (or pressures),  $K[A]$  is small in comparison with unity, and  $\theta$  is proportional to  $[A]$ .

$$\theta \sim K[A] \quad \dots(11.43)$$

The bare fraction of surface i.e., the surface available for adsorption (*or the surface not occupied*) is given by

$$(1-\theta) = \frac{1}{1+K[A]} \quad \dots(11.44)$$

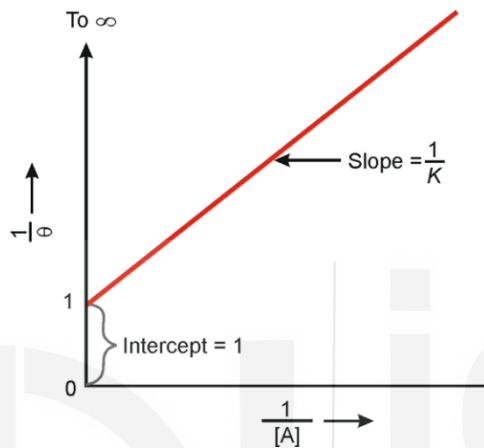
When  $\theta$  to equal  $\frac{1}{2}$ ,  $[A] = \frac{1}{K}$ ; i.e., we can determine the value of  $K$  from the plot by determining the concentration of the gas corresponding to  $\theta = \frac{1}{2}$ .

Alternatively, we can write the Eq. (11.42) in terms of the reciprocal of the coverage  $\theta$ , as follows

$$\frac{1}{\theta} = \frac{K[A] + 1}{K[A]} \quad \dots(11.45)$$

or 
$$\frac{1}{\theta} = \frac{1}{K[A]} + 1 \quad \dots(11.46)$$

The Eq. (11.46) represents a straight line i.e., a plot of  $1/\theta$ , versus  $1/[A]$ , will be a straight line with a slope  $=1/K$ . A schematic plot of the same is given in Fig. 11.6.



**Fig. 11.6: Alternative presentation of Langmuir adsorption isotherm for adsorption without dissociation. The intercept equals 1 and the slope is equal to  $1/K$ .**

## II. The adsorption of the reactant molecule is accompanied by its dissociation on the surface

In cases where the process of adsorption of the molecule,  $A_2$  on the surface is accompanied by its dissociation, the mechanism can be represented as:



The process of adsorption in this case can be seen as a reaction between  $A_2$  and two reaction sites. If  $\theta$  is the fraction of surface occupied, the surface available for adsorption would be  $(1 - \theta)$ . We can write the expression for the rate of adsorption as

$$\text{Rate}_{ads} = k_{ads} [A_2] (1 - \theta)^2 \quad \dots(11.47)$$

The desorption process involves a bimolecular reaction between two adsorbed atoms, and the rate of desorption will be proportional to the square of the fraction of surface occupied i.e.,

$$\text{Rate}_{des} = k_{des} \theta^2 \quad \dots(11.48)$$

At equilibrium the rates of adsorption and desorption are equal, and we can write

$$k_{ads} [A_2] (1 - \theta)^2 = k_{des} \theta^2 \quad \dots(11.49)$$

Rearranging and simplifying, we get

$$\frac{\theta}{1-\theta} = \left( \frac{k_{ads} [A_2]}{k_{des}} \right)^{1/2} \quad \dots(11.50)$$

$$\frac{\theta}{1-\theta} = \sqrt{K[A_2]} \quad K = \frac{k_{ads}}{k_{des}} \quad \dots(11.51)$$

Rearranging, we get

$$\theta = (1-\theta)\sqrt{K[A_2]} \quad \Rightarrow \theta = \sqrt{K[A_2]} - \theta\sqrt{K[A_2]} \quad \dots(11.52)$$

Which gives,

$$\theta(1 + \sqrt{K[A_2]}) = \sqrt{K[A_2]} \quad \Rightarrow \theta = \frac{\sqrt{K[A_2]}}{1 + \sqrt{K[A_2]}} \quad \dots(11.53)$$

At low concentration of the reactant,  $1 \gg \sqrt{K[A_2]}$ , i.e., we can ignore  $\sqrt{K[A_2]}$  in the denominator,  $\theta \approx \sqrt{K[A_2]}$  i.e.,  $\theta$  is proportional to  $\sqrt{[A_2]}$ .

Using Eq. (11.53), we can write for bare fraction

$$1-\theta = 1 - \frac{\sqrt{K[A_2]}}{1 + \sqrt{K[A_2]}} = \frac{1}{1 + \sqrt{K[A_2]}} \quad \dots(11.54)$$

At high concentrations,  $\sqrt{K[A_2]} \gg 1$ , we can write the bare fraction as:

$$1-\theta = \frac{1}{\sqrt{K[A_2]}} \quad \dots(11.55)$$

That is, the fraction of the bare surface is inversely proportional to the square root of the reactant concentration (or pressure of the gas). The Langmuir isotherm associated with dissociation is given in Fig. 11.7.

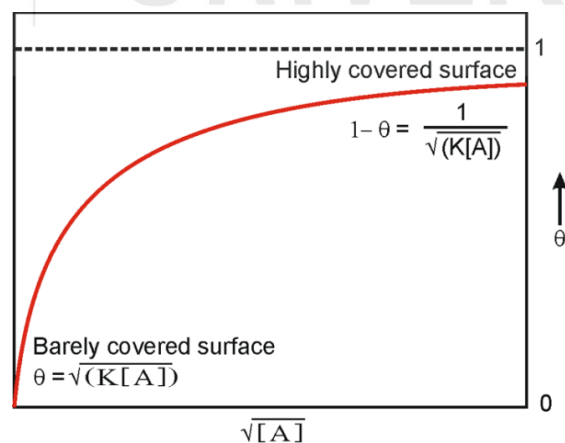


Fig. 11.7: Langmuir adsorption isotherm representing dissociation of the adsorbate on the surface.

### III. Two different substances A and B compete for the same sites on the surface for adsorption

In case there are two substances A and B that can adsorb on the same surface and compete for the same sites, the adsorption is called **competitive**

**adsorption.** This can cause the inhibition of the catalysis. Let us derive an expression for the adsorption isotherm for such a case.

Let us take the fraction of surface covered by substance A as  $\theta_A$  and that for B as  $\theta_B$ .

→ The uncovered fraction of the surface will be  $(1-\theta_A-\theta_B)$ .

We further assume that both the species are adsorbed without dissociation.

The rate of adsorption of gas A will be given as

$$(\text{Rate})_{ads}^A = k_{ads}^A [A](1-\theta_A - \theta_B) \quad \dots(11.56)$$

The corresponding rate of desorption will be

$$(\text{Rate})_{des}^A = k_{des}^A \theta_A \quad \dots(11.57)$$

We can write similar expressions for the gas B as

$$(\text{Rate})_{ads}^B = k_{ads}^B [B](1-\theta_A - \theta_B) \quad \dots(11.58)$$

$$(\text{Rate})_{des}^B = k_{des}^B \theta_B \quad \dots(11.59)$$

At equilibrium, since the rates of adsorption and desorption for each gas will be equal. Therefore, for gases A and B we can write

$$\frac{\theta_A}{1-\theta_A - \theta_B} = K_A [A] \quad \dots(11.60)$$

and  $\frac{\theta_B}{1-\theta_A - \theta_B} = K_B [B] \quad \dots(11.61)$

Here,  $K_A = k_{ads}^A / k_{des}^A$  and  $K_B = k_{ads}^B / k_{des}^B$

Solving Eq. (11.60) and Eq. (11.61) for the surface coverages we get

$$\theta_A = \frac{K_A [A]}{1 + K_A [A] + K_B [B]} \quad \dots(11.62)$$

$$\theta_B = \frac{K_B [B]}{1 + K_A [A] + K_B [B]} \quad \dots(11.63)$$

The Eq. (11.62) suggests that the coverage of A decreases with an increase in the concentration of B. Similarly, from Eq. (11.63) the coverage of B decreases with an increase in the concentration of A. This is so because the two gases compete for a limited number of active sites, hence the term **competitive adsorption**.

### 11.4.2 Multilayer Adsorption Isotherm

In addition to the expressions for the extent of adsorption and the concentration (or pressure) of the gas discussed above, some other types of behaviours are also observed. These are associated with the formation of multilayers of adsorbate on the surface. To explain these behaviours

Brunauer-Emmett-Teller extended Langmuir's approach by invoking multilayer adsorption and assuming non-uniform distribution of adsorbate molecules on the surface. The BET approach is based on the following postulates:

- The adsorption occurs reversibly on a solid surface and is a fast equilibrium process.
- The rate of adsorption is proportional to the concentration of the adsorbate in the gas phase and the fraction of unoccupied sites on the surface.
- The adsorbed molecules form multilayers and are distributed non-uniformly over the surface.
- The energy of adsorption is not constant and varies with the coverage of the surface by adsorbate molecules.
- The enthalpy of adsorption is proportional to the surface area of the adsorbent and is the same for all molecules.

The mechanism of multilayer adsorption of the gas, A on the substrate, S can be represented as



Here  $K$ 's are the equilibrium constants for the corresponding equilibria related to the formation of different layers. Using the postulates and the mechanism given above, Brunauer Emmett and Teller derived the following expression for the adsorption isotherm.

$$\text{Rate} = \frac{V_m c p}{(p^0 - p) \left[ 1 + (c - 1) \left( \frac{p}{p^0} \right) \right]} \quad \dots (11.68)$$

where  $V$  is the volume of adsorbed gas at standard conditions,

$p$  and  $T$  are the pressure and temperature of the gas,

$p^0$  is the saturated vapor pressure of the adsorbate (gas),

$V_m$  is the volume of adsorbate (gas) required to form a monolayer under standard conditions, and  $c$  is a constant related to the enthalpy of adsorption of a monolayer and the enthalpy of liquefaction of the gas.

This is called B.E.T. adsorption isotherm and describes the relationship between the amount of adsorbate adsorbed per unit area of solid and the pressure of the adsorbate in the gas phase at a constant temperature. It is widely used to determine the specific surface area of porous solids. We will not take up the derivation of the expression here. Let us now move on to heterogeneous catalysis. However, before that answer the following simple question to assess your understanding.

## SAQ 4

Write the expressions for the rate of adsorption and desorption when the adsorption of the reactant molecule is accompanied by its dissociation on the surface.

## 11.5 HETEROGENOUS CATLYSIS

In heterogeneous catalysis, the surface of a solid serves as a catalyst while the reactants are in gaseous or liquid phase i.e., the catalyst is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. One or more reactants get adsorbed on the surface of the solid. This is somewhat like the formation of an intermediate in homogeneous catalysis.

The process can be considered to consists of the following consecutive steps.

- i. Diffusion of reactants to the surface.
- ii. Adsorption of reactants on the surface.
- iii. Reaction on the surface i.e., chemical transformation.
- iv. Desorption of the products and
- v. Diffusion of the products away from the surface.

Anyone of these or a combination of these steps may be slow and determine the rate. The concentration of reactant molecules which are adsorbed on the surface is important as these will undergo the catalytic reaction. The concentration of these adsorbed molecules at any instant is proportional to the fraction of the surface (say  $\theta$ ) covered. Accordingly, the rate of reaction is also proportional to this fraction.

Let us take up the kinetics of some common types of reactions undergoing heterogeneous catalysis.

### 11.5.1 Kinetics of Reactions Undergoing Heterogeneous Catalysis

As discussed in the previous section, there are different ways in which a heterogeneous catalytic reaction can take place. Each of these will follow a different kinetic pathway and would have a corresponding expression for the rate law. Let us take up some common cases.

- I. A unimolecular reaction involving a single species adsorbing on the surface of the catalyst
- II. A bimolecular reaction between two reactants both of which are adsorbed on the catalyst's surface
- III. A bimolecular reaction between two reactants when one of the reactants is adsorbed on the catalyst's surface and the other is in gas phase

Let us derive rate expressions for these three cases

### I. A unimolecular reaction involving a single species adsorbing on the surface of the catalyst

The surface reactions of the type that involve a single molecule adsorbing on the surface are classified as **unimolecular reactions**. If the adsorption follows a Langmuir isotherm, the rate of catalysed reaction will be proportional to  $\theta$ , the fraction of the surface covered. Using Eq. (11.42) the rate expression can be written as

$$\text{Rate} = k\theta = \frac{kK[A]}{1 + K[A]} \quad \dots(11.69)$$

where  $k$  is the rate constant.

At high concentrations of the reactant,  $K[A] \gg 1$ , the expression for the rate of reaction becomes,

$$\text{Rate} = k \quad \dots(11.70)$$

i.e., the rate of the reaction is constant i.e., it follows zero order kinetics. However, at low concentrations, the rate law corresponds to a first-order kinetic process:

$$\text{Rate} = kK[A] \quad \dots(11.71)$$

The decomposition of  $\text{NH}_3$  on a surface of platinum is a typical example of this kind of unimolecular reaction.

### II. A bimolecular reaction between two reactants both of which are adsorbed on the catalyst's surface

For a bimolecular reaction to occur on the catalyst's surface, the reactants or intermediates must have enough energy, to cross over an activation barrier. Further, the reactants or intermediates must be in close proximity to react. It is proposed that the reaction takes place by encounters between molecules adsorbed on the surface. The mechanism of such a surface reaction between two reactants A and B when both are adsorbed on the surface, is called **Langmuir-Hinshelwood mechanism**.

The rate of reaction following Langmuir-Hinshelwood mechanism is proportional to the fractions of the molecules of A and B that are adsorbed on the surface of the catalyst. For a reaction between species A and B, the rate law is expected to be first order each in the fractional coverage of A ( $\theta_A$ ), and B ( $\theta_B$ ), and second order overall., i.e.,

$$\text{Rate} = k\theta_A\theta_B \quad \dots(11.72)$$

Substituting the expressions for these fractions ( $\theta_A$  and  $\theta_B$ ) from Eq. (11.62) and Eq. (11.63) respectively, we can write the rate as

$$\text{Rate} = \frac{kK_A K_B [A][B]}{(1 + K_A [A] + K_B [B])^2} \quad \dots(11.73)$$

We can follow the rate of reaction as a function of concentration of A, while keeping the concentration of B as constant. It is observed that the rate initially increases with an increase in the concentration of A, and reaches a maximum before decreasing again. This decrease in the rate at high concentration of A can be understood in terms of the displacement of the reactant, B, with an increase in the concentration of A. The variation of the rate of reaction as a function of the concentration of A, while keeping that of B constant is illustrated in Fig. 11.7.

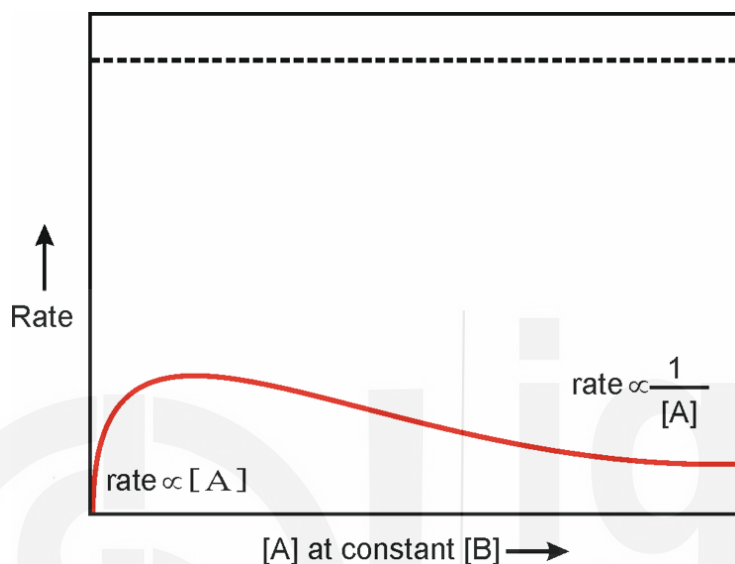


Fig. 11.8: A plot corresponding to the Langmuir-Hinshelwood mechanism of surface bimolecular reaction rate as a function of one of the reactants.

### III. Bimolecular reaction between two reactants when one of the reactants is adsorbed on the catalyst's surface and the other is in gas phase

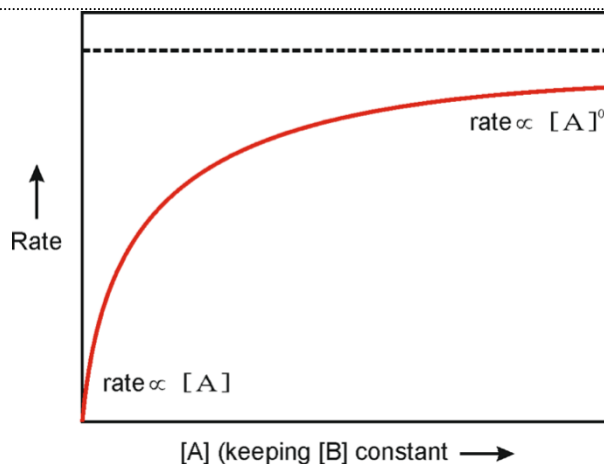
Such reactions are said to follow the **Eley-Rideal mechanism**. The characteristic feature of these reactions is that the reactant that is not chemisorbed on the catalyst is not in equilibrium with the surface. If the reactant A is in the gas phase and B is adsorbed, the rate is given as:

$$\text{Rate} = k\theta_B [A] \quad \dots(11.74)$$

Substituting the expression for  $\theta_B$  we get

$$\text{Rate} = \frac{kK_B [A][B]}{1 + K_A [A] + K_B [B]} \quad \dots(11.75)$$

At a given concentration of B, an increase in the concentration of A decreases the rate of reaction because the reactant A occupies sites that are no longer available for B. A schematic plot of the variation in the rate of reaction with increase in  $[A]$ , at constant concentration of B is given in Fig. (11.8). You may note here that in this case the rate does not reach a maxima like the one observed in Langmuir-Hinshelwood mechanism. This fact can be used to distinguish this mechanism from the Langmuir-Hinshelwood mechanism.



**Fig. 11.8: A plot corresponding to the Eley-Rideal mechanism of surface bimolecular reaction rate as a function of the concentration of the reactants not chemisorbed.**

Almost all surface-catalysed reactions are thought to take place by the Langmuir-Hinshelwood mechanism, however, a few reactions do follow the Eley-Rideal mechanism. For example, Surface combinations of atoms and free radicals generally occur by Eley-Rideal mechanisms. Let us sum up what have we discussed in this unit.

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### SAQ 5

What type of reactions follow Eley-Rideal mechanism in heterogeneous catalysis?

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## 11.6 SUMMARY

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We started the unit by defining catalysis as the process of alteration of the rate and/or the outcome of the reaction in presence of a catalyst and discussed the terminology used in the context of catalysis. Herein, we talked about the terms like positive / negative catalysts, autocatalyst, inhibitor, promotor and catalytic poisoning. Thereafter, we outlined the characteristics of catalysis. This was followed by a discussion on homogeneous catalysis wherein, we studied the kinetics of homogeneous reactions in terms of a simplified mechanism and derived and analysed the rate expressions for the same under different conditions.

The discussion on kinetics of homogeneous catalysis was followed by a discussion on adsorption—a surface phenomenon critical for heterogeneous catalysis. In this context we defined adsorption and discussed different ways in which the reactant could adsorb on the surface and derived expressions for the corresponding adsorption isotherms. We took different cases of adsorption involving the formation of monolayer or multilayers on the surface. The notable isotherms discussed and explained are Langmuir adsorption isotherms and Brunauer-Emmett-Teller isotherms. This was followed by the discussion on the kinetics of reactions undergoing heterogeneous catalysis. Herein, we talked about the Langmuir-Hinshelwood and Rideal-Eley mechanisms and stated the corresponding rate equations and their analysis.

## 11.7 TERMINAL QUESTIONS

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1. Can a catalyst change the equilibrium constant for a reaction? Justify.
2. What is the difference between homogeneous and heterogeneous catalysis.
3. Give different ways in which the reactant molecules can bind to the surface of the catalyst during a catalytic reaction.
4. Write the expression for adsorption isotherm in terms of equilibrium constant and discuss the variation of fraction of surface uncovered as a function of the concentration (or pressure) of the gaseous adsorbate.
5. Give Langmuir's postulates of monolayer adsorption on a surface.
6. Derive rate equation for the kinetics of a unimolecular catalytic reaction involving a single species adsorbing on the surface of the catalyst. Comment on the order of the reaction at i) low and ii) high concentrations of the reactant.

## 11.8 ANSWERS

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### Self-Assessment Questions

1. A catalyst is a substance, that alters the rate of reaction, but remains chemically unchanged at the end of the reaction. It works by providing an alternate mechanism of lower Gibbs energy of activation.
2. In the context of homogeneous catalysis if the intermediate, SC is stable and the rate of its reconversion into catalyst and the substrate is far greater than the rate at which it gives the product then it is referred to as Arrhenius intermediate. On the other hand, if the intermediate complex is not very stable, i.e., rate of its conversion to products is not small compared with the rate of its reconversion into catalyst and the substrate, then it is referred to as van't Hoff's intermediate.
3. We can apply steady state approximation in homogeneous catalysis when the rate of conversion of the intermediate to products is not small as compared to the rate of its reconversion back into catalyst and the substrate.
4. The process of adsorption in this case can be seen as a reaction between  $A_2$  and two reaction sites. If  $q$  is the fraction of surface occupied, the surface available for adsorption would be  $(1 - \theta)$ . Since two sites are to be occupied, the expression for the rate of adsorption will be.

$$\text{Rate}_{ads} = k_{ads} [A_2] (1 - \theta)^2$$

Since the desorption process involves a bimolecular reaction between two adsorbed atoms, the rate of desorption will be proportional to the square of the fraction of surface occupied i.e.,

$$\text{Rate}_{des} = k_{des} \theta^2$$

The bimolecular reaction between two reactants when one of the reactants is adsorbed on the catalyst's surface and the other is in gas phase follow Rideal-Eley mechanism

### Terminal Questions

1. No, a catalyst cannot change the equilibrium constant for a reaction. In a catalytic reaction, the catalyst enhances the rate of both the forward and the reverse reaction to the same extent and thereby reduce the time for equilibrium to be reached but the equilibrium does not change.
2. In case of homogeneous catalysis, the reactants, products and catalyst are all in the same phase, whereas in case of heterogeneous catalysis, the catalyst is present in a phase different from that of the reactants and the products.
3. Different ways in which the reactant molecules can bind to the surface of the catalyst during a catalytic reaction are as under.
  - i. The gaseous reactant (atoms or molecules) occupy single sites on the surface and are not dissociated
  - ii. The adsorption of the reactant molecule is accompanied by its dissociation on the surface
  - iii. Two different substances A and B compete for the same sites on the surface for adsorption

4. The expression for adsorption isotherm in terms of equilibrium constant,  $K$  is as follows

$$\theta = \frac{K[A]}{K[A] + 1}$$

Where,  $\theta$  is the fraction of surface coverage and  $[A]$  is the concentration of the gaseous adsorbate

At sufficiently low concentrations (or pressures),  $K[A]$  is small in comparison with unity, and we can write

$$\theta \sim K[A]$$

This implies that  $\theta$  is proportional to  $[A]$ .

At high concentrations (or pressures),  $K[A]$  is much larger than 1, and  $\theta \sim 1$  implying almost coverage of surface or formation of monolayer.

5. Langmuir's postulates of monolayer adsorption on a surface are as under:
  - The surface of the solid is homogenous i.e., each binding site has the same affinity for the gas molecules and is occupied independent of the other sites.
  - The adsorbed gas molecules are localised, i.e., they do not move around on the surface
  - The adsorption on a solid surface is reversible i.e., there exists a dynamic equilibrium between the adsorbed and the free molecules.

- The rate of adsorption is proportional to the concentration of the adsorbate in the gas phase and the fraction of unoccupied sites on the surface.
  - The adsorbed molecules form a monolayer and are distributed uniformly over the surface implying that once surface sites are covered by gas molecules, no further adherence of gas molecules would occur.
6. For a unimolecular catalytic reaction involving a single species adsorbing on the surface of the catalyst. The rate of catalysed reaction will be proportional to  $\theta$ , the fraction of the surface covered i.e.,

$$\text{Rate} = k\theta$$

For an adsorption process following Langmuir isotherm the fraction of the surface covered is given as

$$\theta = \frac{K[A]}{K[A] + 1}$$

Where  $k$  is the rate constant,  $K$  is equilibrium constant and  $\theta$  is the fraction of the surface covered.

Substituting, we get

$$\text{Rate} = k\theta = \frac{kK[A]}{1 + K[A]}$$

**i) At high concentrations:**

$$K[A] \gg 1,$$

Ignoring 1 in comparison to  $K[A]$ , the expression for the rate becomes,

$$\text{Rate} = k$$

The rate is constant i.e., it follows zero order kinetics.

**ii) At low concentrations**

$$K[A] \ll 1,$$

Ignoring  $K[A]$  in comparison to 1, the expression for the rate becomes,

$$\text{Rate} = kK[A]$$

i.e., the reaction follows first-order kinetics.