# Environmental Chemistry and Microbiology
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## Lecture –19
## Chemical Kinetics-Catalysis (Part-B)

Welcome to our online NPTEL course Environmental Chemistry and Microbiology. This course will be taught by Professor Sudha Goel and myself Professor Anjali Pal. We are both from Civil Engineering Department of IIT Kharagpur. We have divided this course into two parts: environmental chemistry, the first part that will be taught by me and the second part i.e., environmental microbiology will be covered by Professor Sudha Goel.

I already discussed in my first module about the acids, bases and salts. In the second module, I have discussed about the chemical equilibrium. In third module, I have discussed the chemical kinetics. In this module I am extending the chemical kinetics. I will be discussing about the mechanisms of the catalyst which are also under the scope of the chemical kinetics and very important topic today. So, this is my module 4 and 19th lecture. In my last lecture I discussed about the catalysis, but that was Part A and this is the Part B

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Lecture contents

- Mechanism of homogeneous catalysis
- Acid and base catalyzed reaction
- Mechanism of heterogeneous catalysis
- Activation energy and catalysis
- Enzyme as a catalyst

Now all of you know that catalysis is very important for us as I already discussed. We have to develop very new catalyst for different types of reactions and the contents of this lecture is the mechanism of different types of catalysis. I already discussed what is homogeneous catalysis, what is heterogeneous catalysis and what is biocatalysis (i.e., enzyme catalysis) and here I will tell you the mechanisms about those catalysis, how the reaction is going on and what is the activation energy etc.

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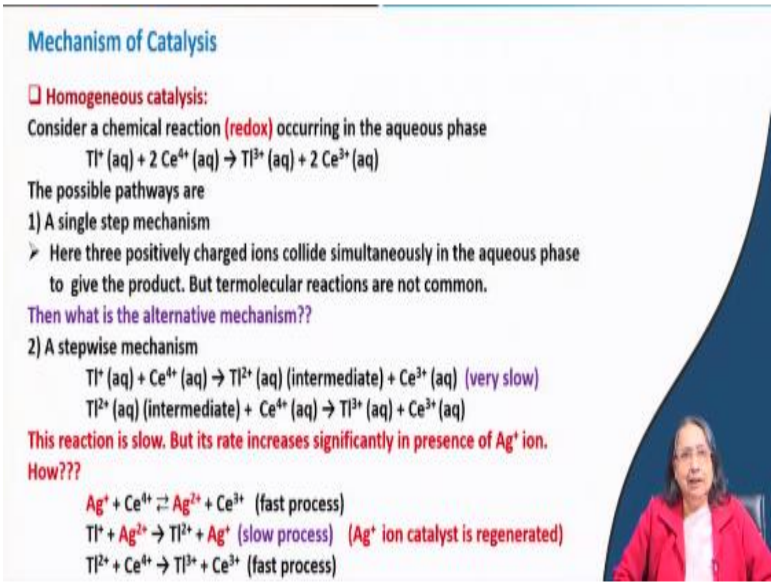

Mechanism of Catalysis

☐ Homogeneous catalysis:

Consider a chemical reaction (redox) occurring in the aqueous phase

$Tl^{+}(aq) + 2\,Ce^{4+}(aq) \rightarrow Tl^{3+}(aq) + 2\,Ce^{3+}(aq)$

The possible pathways are

1) A single step mechanism

- Here three positively charged ions collide simultaneously in the aqueous phase to give the product. But termolecular reactions are not common.

Then what is the alternative mechanism??

2) A stepwise mechanism

$Tl^{+}(aq) + Ce^{4+}(aq) \rightarrow Tl^{2+}(aq)$ (intermediate) $+ Ce^{3+}(aq)$ (very slow)

$Tl^{2+}(aq)$ (intermediate) $+ Ce^{4+}(aq) \rightarrow Tl^{3+}(aq) + Ce^{3+}(aq)$

This reaction is slow. But its rate increases significantly in presence of $Ag^{+}$ ion.

How???

$Ag^{+} + Ce^{4+} \rightleftarrows Ag^{2+} + Ce^{3+}$ (fast process)

$Tl^{+} + Ag^{2+} \rightarrow Tl^{2+} + Ag^{+}$ (slow process) ($Ag^{+}$ ion catalyst is regenerated)

$Tl^{2+} + Ce^{4+} \rightarrow Tl^{3+} + Ce^{3+}$ (fast process)

Now let us come first to the mechanism of homogeneous catalysis. A chemical reaction is represented as follows (1):

$Tl^{+}(aq)+2Ce^{4+}(aq)\rightarrow Tl^{3+}(aq)+2Ce^{3+}(aq)$………………..(1)

It is an aqueous phase redox reaction. $Tl^{+}$ is going to $Tl^{3+}$ and $Ce^{4+}$ is reduced to $Ce^{3+}$. Now let us see the mechanism. If it is a single step mechanism, then the positively charged ions collide simultaneously in the aqueous phase to give the product. So, collision is necessary. If it is a single step process then it will be termolecular reaction and we already know now that termolecular reactions are not very common. Then what is the alternative mechanism that we can think? So instead of single step mechanism, we can think about a stepwise mechanism as follows (2) and (3).

$Tl^{+}(aq)+Ce^{4+}(aq)\rightarrow Tl^{2+}(aq)$ (intermediate) $+Ce^{3+}(aq)$ (very slow)………(2)

$Tl^{2+}(aq)$ (intermediate)$+Ce^{4+}(aq)\rightarrow Tl^{3+}(aq)+Ce^{3+}(aq)$……………………(3)

If we add (2) and (3) we will get (1). But this is a very slow process. Now if we add $Ag^{+}$ ion here then rate increases and it is expressed as:

$Ag^{+}+Ce^{4+}\leftrightharpoons Ag^{2+}+Ce^{3+}$(fast process)………………………………………(4)

$Tl^{+}+Ag^{2+}\rightarrow Tl^{2+}+Ag^{+}$(slow process) ($Ag^{+}$ ion is regenerated)……………..(5)

$Tl^{2+}+Ce^{4+}\rightarrow Tl^{3+}+Ce^{3+}$(fast process)………………………………………..(6)

we will see that the reaction we can think the mechanism in this way.

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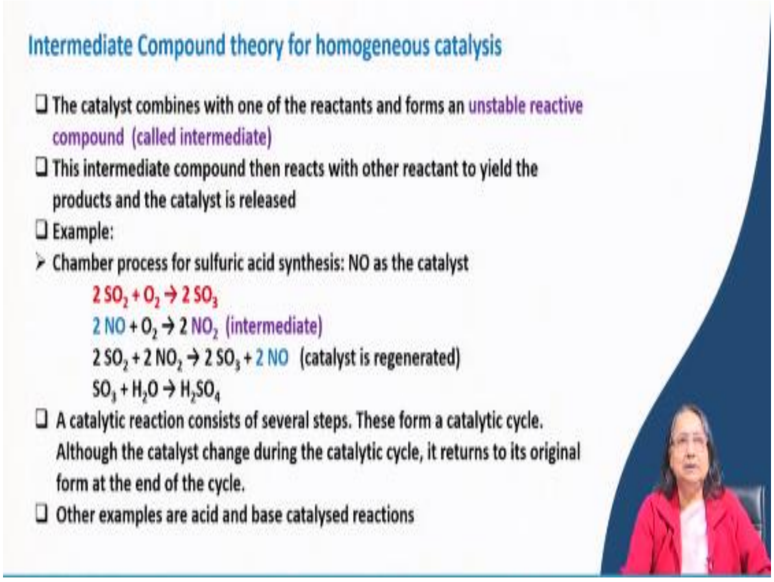

Intermediate Compound theory for homogeneous catalysis

- ❑ The catalyst combines with one of the reactants and forms an unstable reactive compound (called intermediate)
- ❑ This intermediate compound then reacts with other reactant to yield the products and the catalyst is released
- ❑ Example:
  - ➢ Chamber process for sulfuric acid synthesis: NO as the catalyst

$2SO_2 + O_2 \rightarrow 2SO_3$

$2NO + O_2 \rightarrow 2NO_2$ (intermediate)

$2SO_2 + 2NO_2 \rightarrow 2SO_3 + 2NO$ (catalyst is regenerated)

$SO_3 + H_2O \rightarrow H_2SO_4$

- ❑ A catalytic reaction consists of several steps. These form a catalytic cycle. Although the catalyst change during the catalytic cycle, it returns to its original form at the end of the cycle.
- ❑ Other examples are acid and base catalysed reactions

Now we will see intermediate compound theory for homogenous catalysts. The catalyst combines with one of the reactants and forms an unstable reactive compound called the intermediate. This intermediate compounds then reacts with other reactant to yield the products and catalyst is released. We have seen similar thing in the last example.

During the synthesis of sulphuric acid by Chamber process nitric oxide (NO) is used as catalyst.

$2SO_2+O_2\rightarrow2SO_3$……………………………………………………..(7)

$2NO+O_2\rightarrow2NO_2$ (intermediate)………………………………………(8)

$2SO_2+2NO_2\rightarrow2SO_3+2NO$ (catalyst is regenerated)……………………..(9)

$SO_3+H_2O\rightarrow H_2SO_4$…………………………………………………….(10)

sulfur dioxide ($SO_2$) reacts with oxygen to give sulfur trioxide ($SO_3$) (7). NO is used as the catalyst. NO first reacts with the oxygen to form $NO_2$. This is an intermediate and then $NO_2$ is reacting with $SO_2$ to give $SO_3$ and NO. So, catalyst is regenerated and then finally $SO_3$ is reacting with $H_2O$ to give the $H_2SO_4$. So, it is the synthesis of $H_2SO_4$ at industrial level. So, in this case $NO_2$ is an intermediate compound and in the last case it was ion. So, some intermediate should be formed in the homogenous catalysis and this is the common mechanism. A catalytic reaction consists of several steps. These form a catalytic cycle. Although the catalyst changes during the catalytic cycle, it returns to its original form at the end of the cycle.

Other examples are acid and base catalyzed reactions. So, I will show you some acid and base catalyzed reactions.

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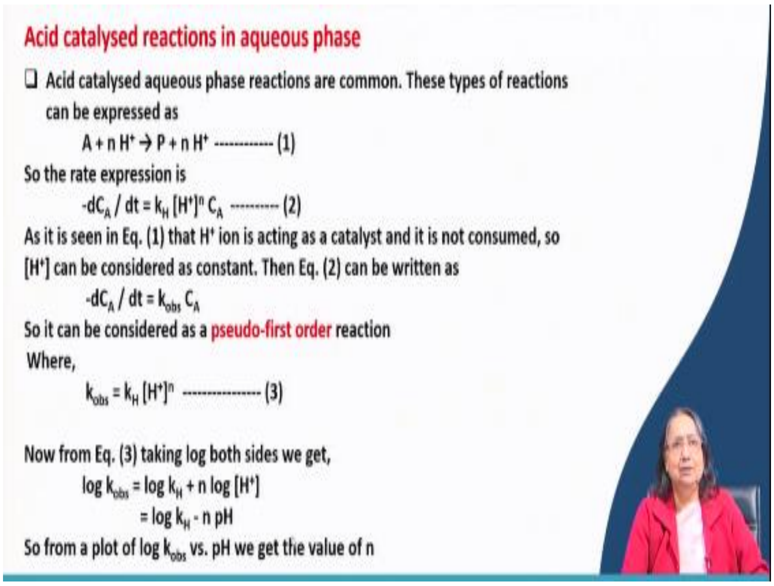

## Acid catalysed reactions in aqueous phase

❑ Acid catalysed aqueous phase reactions are common. These types of reactions can be expressed as

$A + n\,H^+ \rightarrow P + n\,H^+$ ----------- (1)

So the rate expression is

$-dC_A / dt = k_H\,[H^+]^n\,C_A$ --------- (2)

As it is seen in Eq. (1) that $H^+$ ion is acting as a catalyst and it is not consumed, so $[H^+]$ can be considered as constant. Then Eq. (2) can be written as

$-dC_A / dt = k_{obs}\,C_A$

So it can be considered as a pseudo-first order reaction

Where,

$k_{obs} = k_H\,[H^+]^n$ --------------- (3)

Now from Eq. (3) taking log both sides we get,

$\log k_{obs} = \log k_H + n \log [H^+]$

$= \log k_H - n\,pH$

So from a plot of $\log k_{obs}$ vs. pH we get the value of n

Acid catalyzed aqueous phase reactions are very common as I have already given you some examples like hydrolysis of cane sugar to form glucose and fructose. An acid catalyzed reaction in general way can be shown as:

$A + nH^+ \rightarrow P + nH^+$ ……………………………..(11)

The kinetic rate expression can be written as:

$-dC_A/dt = k_H[H^+]^n C_A$……………………………...(12)

So here you can see that when A is giving P it is catalyzed by $H^+$ (i.e., acid) and acid is staying back as $nH^+$. As seen from (11) that $[H^+]$ is acting as catalyst and it is not consumed and hence $[H^+]$ is constant. So (12) can be written as:

$-dC_A/dt = k_{obs}C_A$…………………………………(13)

So, it can be considered as pseudo first-order reaction. By comparing (12) and (13),

$k_{obs} = k_H[H^+]^n$

Taking log on both sides,

$\log k_{obs} = \log k_H + n \log[H^+]$

$= \log k_H - npH$

By plotting $\log k_{obs}$ vs. pH, value of n can be obtained from the slope of the straight line.

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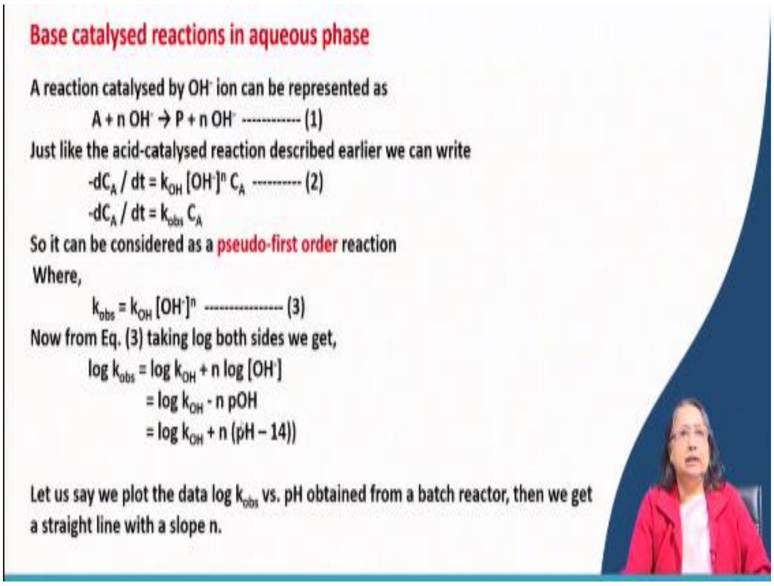

## Base catalysed reactions in aqueous phase

A reaction catalysed by $OH^-$ ion can be represented as

$A + n\,OH^- \rightarrow P + n\,OH^-$ ----------- (1)

Just like the acid-catalysed reaction described earlier we can write

$-dC_A / dt = k_{OH} [OH^-]^n C_A$ --------- (2)

$-dC_A / dt = k_{obs} C_A$

So it can be considered as a pseudo-first order reaction

Where,

$k_{obs} = k_{OH} [OH^-]^n$ --------------- (3)

Now from Eq. (3) taking log both sides we get,

$\log k_{obs} = \log k_{OH} + n \log [OH^-]$

$= \log k_{OH} - n\,pOH$

$= \log k_{OH} + n\,(pH - 14))$

Let us say we plot the data $\log k_{obs}$ vs. pH obtained from a batch reactor, then we get a straight line with a slope n.

Now base catalyzed reactions also similar and can be expressed as

$A + nOH^- \rightarrow P + nOH^-$……………..(14)

The kinetic rate expression can be written as:

$-dC_A/dt=k_{OH}[OH^-]^nC_A$

or, $-dC_A/dt=k_{obs}C_A$………………(15)

Similarly, it is also a pseudo first order reaction and therefore from (14) and (15),

$k_{obs}=k_{OH}[OH^-]^n$

Taking log on both sides,

$\log k_{obs} = \log k_{OH} + n\log[OH^-]$

$=\log k_{OH} - npOH$

$=\log k_{OH} + n(pH-14)$

By plotting of $\log k_{obs}$ vs pH, a straight line is obtained and from the slope n is obtained.

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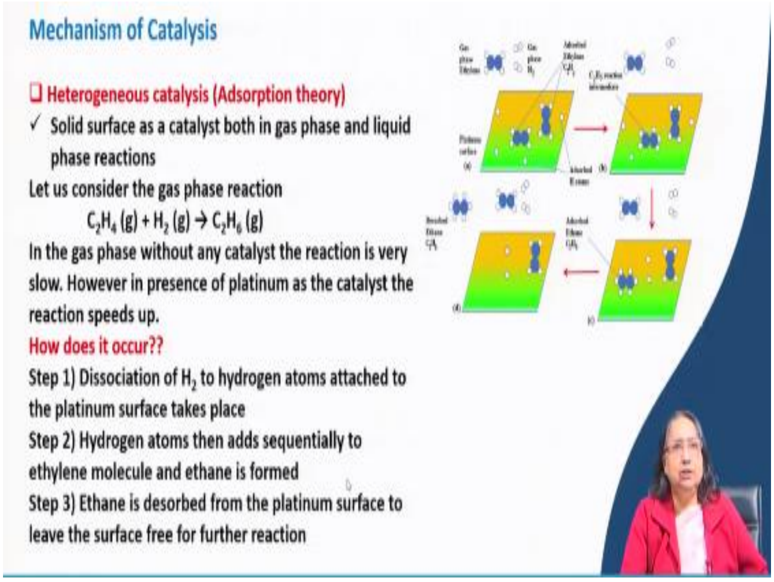

## Mechanism of Catalysis

❑ **Heterogeneous catalysis (Adsorption theory)**

✓ Solid surface as a catalyst both in gas phase and liquid phase reactions

Let us consider the gas phase reaction

$$C_2H_4 (g) + H_2 (g) \rightarrow C_2H_6 (g)$$

In the gas phase without any catalyst the reaction is very slow. However in presence of platinum as the catalyst the reaction speeds up.

How does it occur??

Step 1) Dissociation of $H_2$ to hydrogen atoms attached to the platinum surface takes place

Step 2) Hydrogen atoms then adds sequentially to ethylene molecule and ethane is formed

Step 3) Ethane is desorbed from the platinum surface to leave the surface free for further reaction

Now what is the mechanism for heterogeneous catalysis? Heterogeneous catalysis is mainly explained by adsorption theory. So, adsorption is a one step that should occur. Now in most heterogeneous catalysis, solid surface act as a catalyst both in gas phase and liquid phase reactions. I have given already some examples for this type of reactions.

In the last slide, an example is given. In ethylene molecule some double bond is there and some hydrogen is added on to this double bond to form the ethane. This is a gas phase reaction. In the gas phase without any catalyst the reaction is very slow. However, in presence of platinum as the catalyst the reaction speeds up. How it is happening? It is happening in several steps. In the first step, hydrogen and ethylene both are adsorbed on the platinum surface. Then hydrogen atoms are produced and they are added up in the stepwise manner and then the finally the ethane molecule is going out. Finally, ethane is desorbed from the surface of the catalyst. Then again new molecules are getting the chance to get adsorbed and then again reaction is going on. It is a catalytic cycle. So, hydrogen atoms add sequentially to ethylene molecule and ethane is formed. Then ethane is desorbed from the platinum surface to leave the surface free for further reaction. So, in this way the heterogeneous catalysis based on the adsorption theory it is explained.

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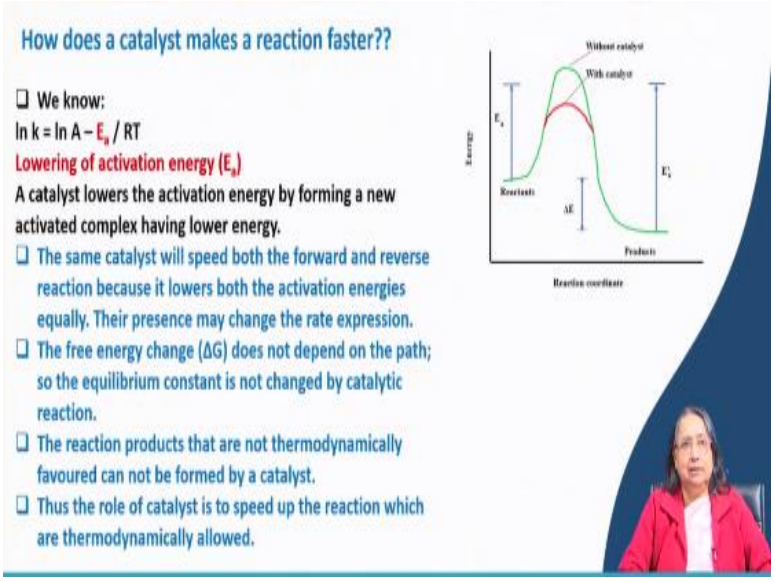

How does a catalyst makes a reaction faster??

❑ We know:

$\ln k = \ln A - E_a / RT$

Lowering of activation energy ($E_a$)

A catalyst lowers the activation energy by forming a new activated complex having lower energy.

- ❑ The same catalyst will speed both the forward and reverse reaction because it lowers both the activation energies equally. Their presence may change the rate expression.
- ❑ The free energy change (ΔG) does not depend on the path; so the equilibrium constant is not changed by catalytic reaction.
- ❑ The reaction products that are not thermodynamically favoured can not be formed by a catalyst.
- ❑ Thus the role of catalyst is to speed up the reaction which are thermodynamically allowed.

Now how does a catalyst makes a reaction faster. I told you already that by it goes through another route. You can recall Arrhenius equation (16) which I discussed in chemical kinetics.

$\ln k = \ln A - E_a/RT$………………..(16)

So, this $E_a$ is the activation energy. Using catalyst, $E_a$ is lowered. However, the position of the reactants and products remain the same, as shown in the last slide, but with and without catalyst the reaction proceeds in different way. Catalyst will speed both the forward and reverse reaction. It lowers both the activation energies equally. The free energy change does not depend on the path and so it is not changing. So, reactions which are not thermodynamically favored cannot be formed by a catalyst. This is very important that if some reaction is not possible then whatever catalyst be provided, it will not be possible. So once the reaction is possible then by using the catalyst you can make the reaction faster or slower. Thus, the role of catalyst is to speed up the reaction which are thermodynamically allowed This is very important concept.

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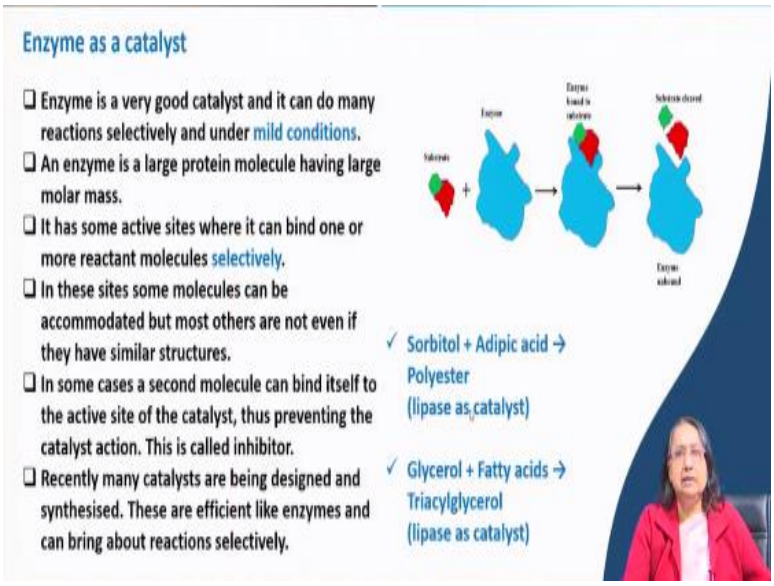

### Enzyme as a catalyst

- ☐ Enzyme is a very good catalyst and it can do many reactions selectively and under mild conditions.
- ☐ An enzyme is a large protein molecule having large molar mass.
- ☐ It has some active sites where it can bind one or more reactant molecules selectively.
- ☐ In these sites some molecules can be accommodated but most others are not even if they have similar structures.
- ☐ In some cases a second molecule can bind itself to the active site of the catalyst, thus preventing the catalyst action. This is called inhibitor.
- ☐ Recently many catalysts are being designed and synthesised. These are efficient like enzymes and can bring about reactions selectively.

✓ Sorbitol + Adipic acid → Polyester (lipase as catalyst)

✓ Glycerol + Fatty acids → Triacylglycerol (lipase as catalyst)

Enzyme acts as a catalyst. In our body system I told you that many enzymatic reactions are going on. Many free radicals are generated and then free radicals are destroyed. Enzymes are protein molecules having large molar mass. They possess very complex structure. Many active sites are there. An example by means of an image is shown in the last slide. So, in the active site in a particular substrate can come here and fit itself. So, there are two things (last slide): red one and green one. It can fit and the reaction goes on here. After the reaction they are separated. They are cleaved. They are very good catalyst and under very mild conditions they can do the reaction. They are very selective also. There may be many compounds in the system. But only particular substance will come in the active site and do the reaction. That is very important for enzyme. In these sites some molecules can be accommodated, but most others are not even if they have similar structure, but still they cannot be accommodated. There are many factors such as size factor and functionality factor etc. So, they cannot be accommodated. So if they are not accommodated then catalytic affect will not be there for that other substance. in some cases, a second molecule can bind itself to the active site of the catalyst and thus prevents the catalyst action. This is called inhibitor. Recently many catalysts are being designed and synthesized which are not enzyme, but are efficient like enzyme. They have the similar properties of enzymes and can bring about reaction selectively.

Now I will give some examples. You know that adipic acid and sorbitol can react to form a polyester. Lipase is an enzyme that can act as a catalyst in that particular reaction and it is very important in textiles and many other purposes. Another example is that glycerol combines with fatty acid to form triacylglycerol. Here also lipase as the catalyst.

Sometimes these enzymes are also immobilized on some solid surface to show that it can be recovered easily. It is supported enzyme and also a very good catalyst. So, there are many awards if you can develop some novel catalysts maintaining green chemistry principles for environmental purpose.

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References

1) "Process Chemistry for Water and Wastewater Treatment" by L. D. Benefield, J. F. Judkins, Jr., B. L. Weand, Prentice Hall, Inc., Englewood Cliffs, N.J. (1982)
2) "Chemistry Science of Change" by D. W. Oxtoby, N. H. Nachtrieb, W. A. Freeman, Saunders College Publishing, USA (1990)
3) Dutt PK, Dutt PK (2000) General & Inorganic Chemistry, Calcutta

Now the references are given in the last slide.

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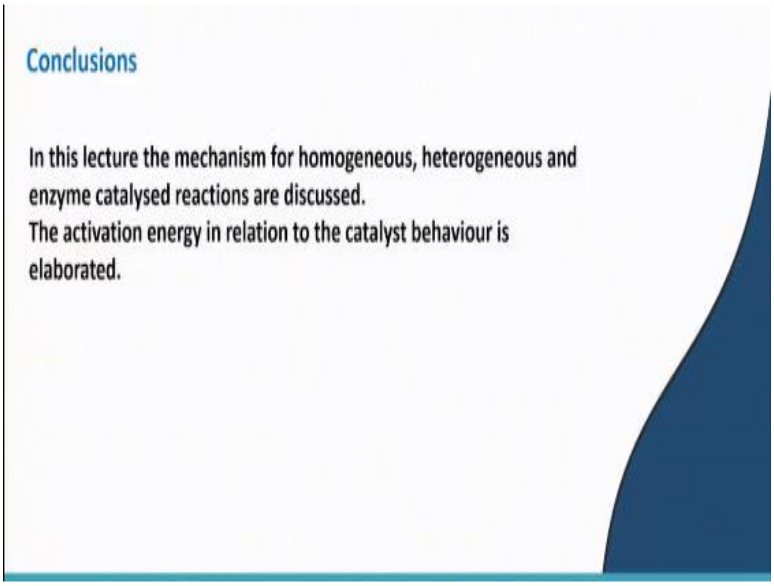

Conclusions

In this lecture the mechanism for homogeneous, heterogeneous and enzyme catalysed reactions are discussed.
The activation energy in relation to the catalyst behaviour is elaborated.

So, in this lecture you have seen that how we can explain the homogenous and heterogeneous catalysis and enzyme catalysis, what are the mechanisms that is happening there, what is activation energy and how the catalyst behaves. Thank you.