Rate Processes

Prof. M. Halder
Department of Chemistry
Indian Institute of Technology, Kharagpur

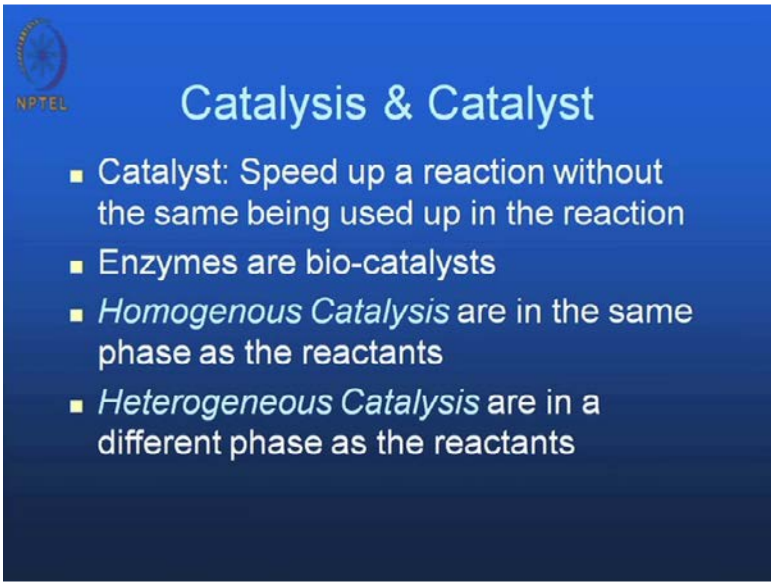
Module No. # 01

Lecture No. # 08

Complex Reaction (contd.)

Hello good morning everybody, so today we will continue with this Rate Process and the topic is Complex Reactions. So, we have talked a lot about complex reactions, so we will conclude this session, so some more aspects are still to be talked about, so let us do that.

(Refer Slide Time: 00:44)



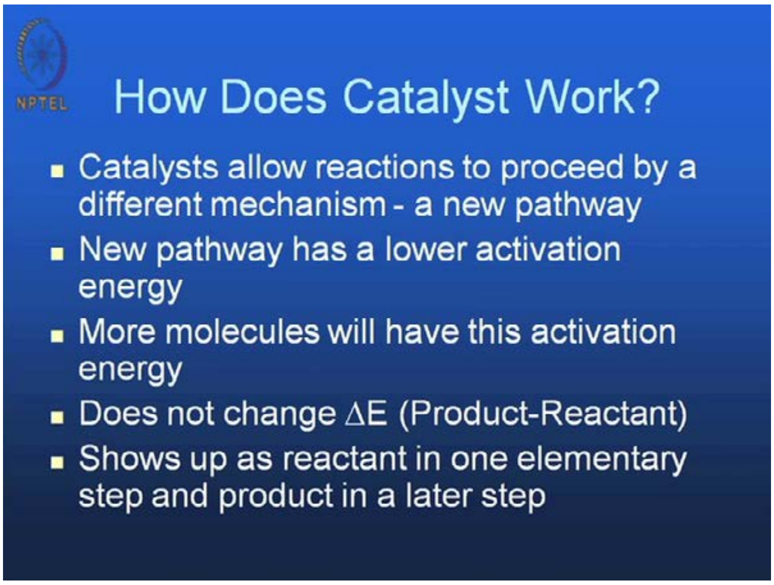
Catalysis & Catalyst

- Catalyst: Speed up a reaction without the same being used up in the reaction
- Enzymes are bio-catalysts
- *Homogenous Catalysis* are in the same phase as the reactants
- *Heterogeneous Catalysis* are in a different phase as the reactants

So, we will talk a little more about catalysis and catalyst, so what is a catalyst I as I already talked about in earlier one of the earlier lectures. Now, basically catalyst is a substance that speeds up the reaction without the same being used up in the reaction that is somehow it speeds up. That is somehow it quickly helps in attaining you know the equilibrium that is the I mean the forward reaction rate as also the backward reaction rate is you know influenced and as a result of which the overall reaction rate is modified.

And enzymes are also biocatalysts you know these are called biocatalysts, because biological molecules are used here. Now, if we think of catalysis it can be of two types, one is homogeneous catalysis, that is the catalyst is in the same phase as the reactant and the other one is the heterogeneous catalysis, where the catalyst and the reactant these two are in different phases. Maybe one is in solid phase, maybe your catalyst and your reactant maybe in gas phase. So, homogeneous gas phase reaction catalyzed by solid surface can be an example of a heterogeneous catalysis.

(Refer Slide Time: 02:27)



How Does Catalyst Work?

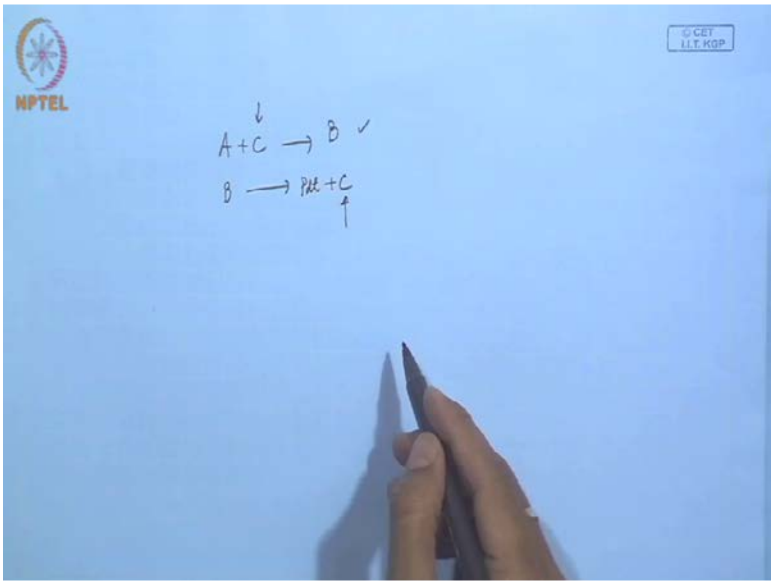
- Catalysts allow reactions to proceed by a different mechanism - a new pathway
- New pathway has a lower activation energy
- More molecules will have this activation energy
- Does not change ΔE (Product-Reactant)
- Shows up as reactant in one elementary step and product in a later step

Let us move onto the you know basic mechanism of of a of catalysis that is how catalysts work. Now, the thing is that I already mentioned that catalysts allow reactants to proceed reaction to proceed by a different mechanism, we having a new pathway. And this new pathway has lower activation energy compared to the original one, recall one of the earlier lectures. Now, the new pathway, since this new pathway demands less activation energy, so as a result of which more molecules will have, means more molecules; since it has got less activation energy.

So, on an average more molecule molecules will remain in the activated state and therefore, therefore, what is happening that, the net reaction rate is influenced, so more molecules will will tend to react to produce your desired product. And but, it does not change the overall energy change associated with the chemical reaction, energy change means maybe enthalpy change or maybe other energy form. Other energy form means maybe internal energy or something I mean maybe, like you know free energy these are not you know changed.

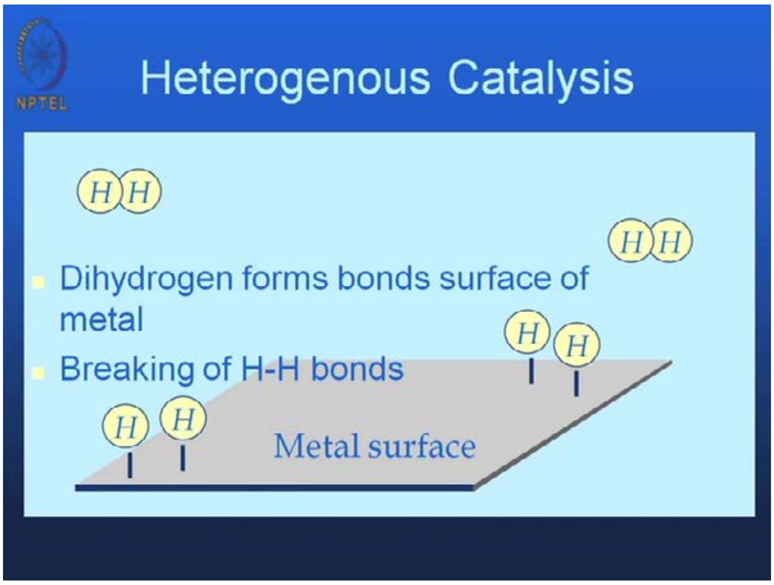
Because the product and the reactant these two states are remaining same, only thing is that the activated state is getting a little modified and as result of which your your this overall reaction rate and the overall activation energy is is reduced. So, and the thing is that, it shows up as a reactant in one of the elementary steps maybe and also it is it is acting as a product in a later step.

(Refer Slide Time: 04:39)



Maybe suppose you have got say an elementary reaction of this form, say A plus catalyst producing some something say B. Then B is giving rise to your product plus catalyst back. So, here in this elementary step, this is acting as a reactant and in this step it is acting as a product. So, they are involved this catalysts are involved in in one of the elementary steps where it is acting as a reactant and maybe in another elementary step later time, where it will it will appear in the right hand side.

(Refer Slide Time: 05:24)



Heterogenous Catalysis

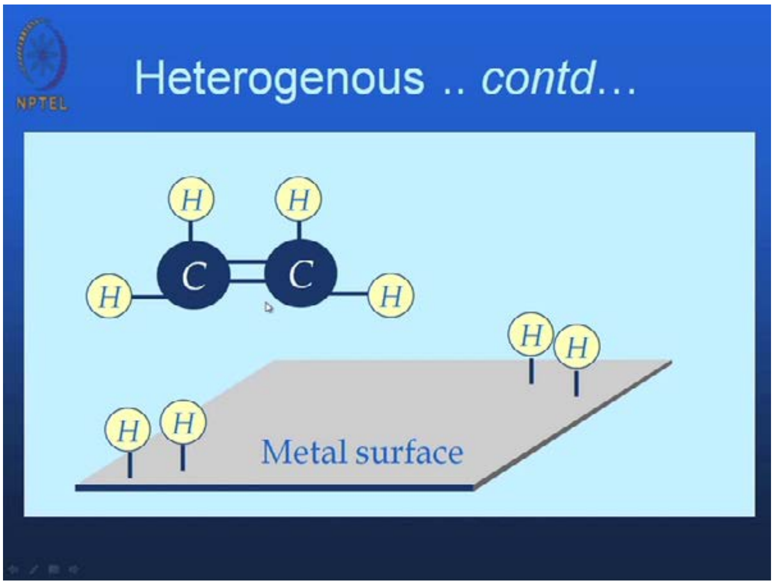
- Dihydrogen forms bonds surface of metal
- Breaking of H-H bonds

Next, let us think of heterogeneous catalysis say, say this is your your surface sorry this is your you know metal surface on which this reaction is taking place. So, this is your surface metal surface and this is hydrogen molecules, I mean dihydrogen molecules. So, these dihydrogen molecules are maybe some of them are close to the surface or some of them are a little apart and this will maybe this will collide with the surface and will form a bond, I mean will form two bonds maybe.

So, the metal it is it is called that the metal I mean this hydrogen is adsorbed on the metal surface, not absorbed that is the concentration of hydrogen concentration of hydrogen on onto the metal surface is high and inside inside the metal I mean the bulk of the metal is not that much. So, they are adsorbed, that is they form a bond with the surface of metal and maybe what will happen that there is a there is there is a breakage of bond breakage of this hydrogen hydrogen original single bond gets broken.

So, now what is happening that after this bond is ruptured, so these there is one isolated I mean bound hydrogen atom, there is another bound hydrogen atom onto the metal surface. And say they are just like nascent hydrogen, having tremendous amount of you know reducing capability. So, if it you know gets second component, I mean second component like some say unsaturated hydrocarbon. Say ethyne that is ethylene c double bond c, then these two hydrogens will quickly attach to that you know double bond producing a saturated carbon-carbon linkage.

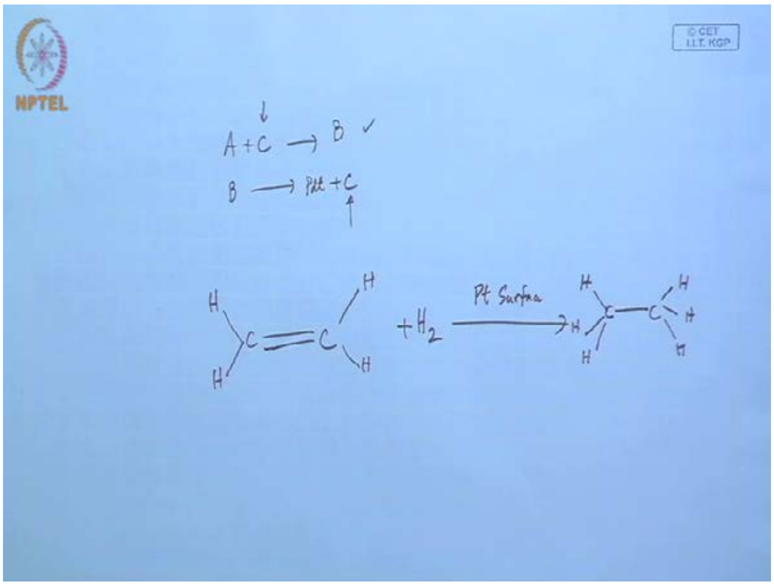
(Refer Slide Time: 07:29)



Heterogenous .. *contd…*

So, think about that that we have got this dihydrogen and then ruptured situation that two hydrogen isolated two hydrogen atoms that is like a just like a nascent hydrogen. And then these ethylene, ethyne molecule one of the reactants. So, what is happening that you have got ethyne.

(Refer Slide Time: 07:56)

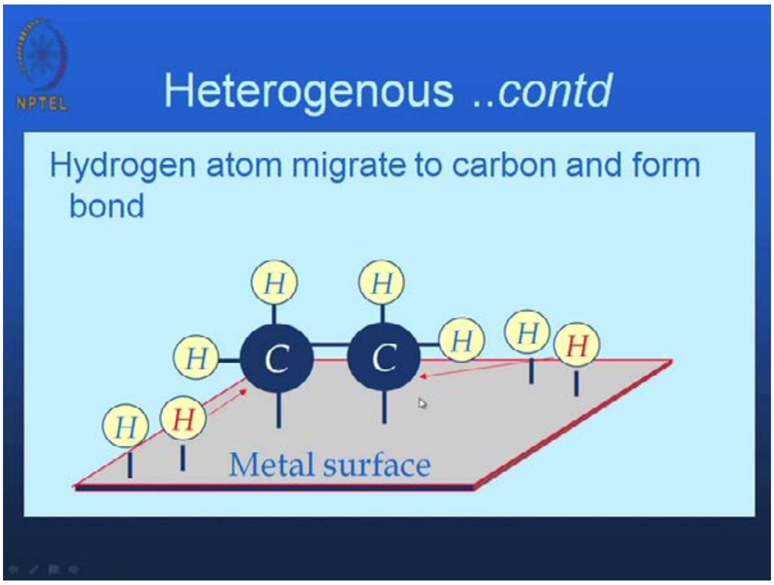


$A + C \rightarrow B$ ✓

$B \rightarrow Pdt + C$

You have got ethyne and you have got hydrogen and say platinum surface your carrying out the reaction. So, what is happened that your end product will be like this, end product will be this, so it is a saturated one. So, what is happening is that this you know this ethyne gets attached to this metal surface, so, two linkages are formed as I will show in the next slide.

(Refer Slide Time: 08:45)



Heterogenous ..*contd*

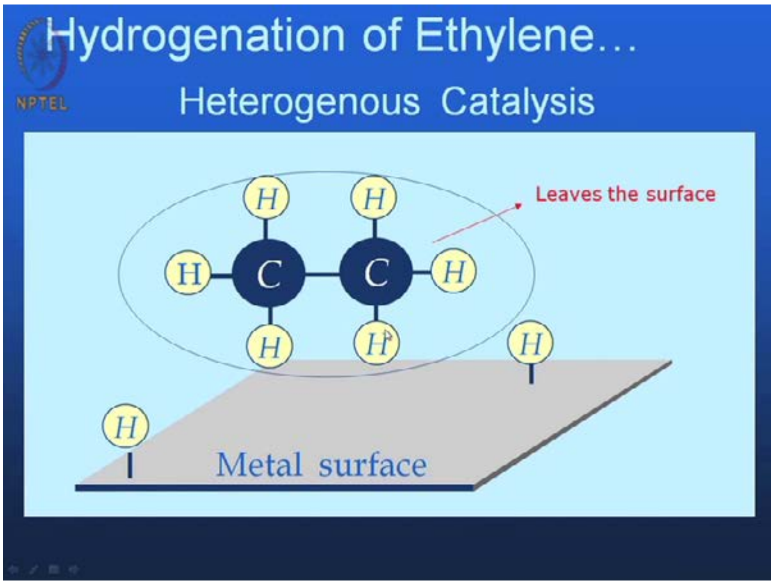
Hydrogen atom migrate to carbon and form bond

That these two there are these two these two carbon atoms and then initially there was a double bond. So, that double bond is now absent and now that as if, this double bond has been used up to create to form a metal surface to carbon bond. So, now, the situation is that, we have got isolated hydrogen I mean not isolated, metal surface bound hydrogen atoms like nascent hydrogen and adsorbed ethylene molecule onto metal surface.

So, next what will happen that in order, that these hydrogen atoms should take part in in the formation of C H bond, they should migrate close to this carbon or maybe this carbon and they should come at a at a bonding separation bonding distance and after that they will make a bond. So, that is that is that will be shown in the next slide that you know the hydrogen atom migrate to the carbon and form bonds. So, what is happening that, this atom will migrate close to I mean this carbon and this one will migrate maybe maybe this one will migrate to this.

So, there will be a bond formation, because these these linkages are not like true chemical linkages, so these are these are these are like some physical force or maybe weak chemical force. So, this valency is not fully satisfied, like here this valency is not fully satisfied, that is why it is I i told you that these are like you know like nascent hydrogen. So, then what will happen that this hydrogen will migrate and then they will these two will form bond and thereby making a saturated ethylene system.

(Refer Slide Time: 11:05)



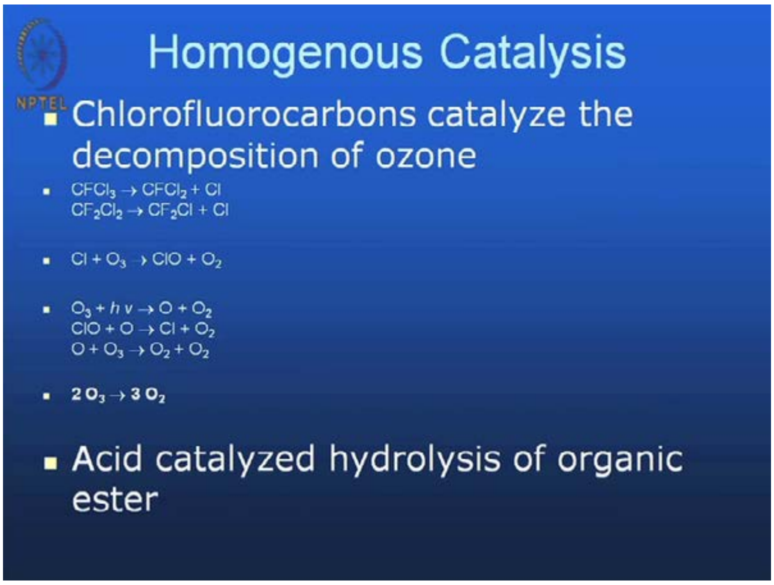
Hydrogenation of Ethylene…

Heterogenous Catalysis

You see that this bond is formed and now since, now this carbon this carbon atom and this carbon atom is you know their their valency; valency is saturated or full satisfied that is four valencies are are occupied. So, this now what is happening after this valency satisfaction, so this initial linkage with that is adsorption linkage will be weaker and they will, so what will happen that this this ethylene molecule ethane molecule will will leave the metal surface the saturated one will leave the metal surface.

So, they will these these molecules will diffuse out to to the gas phase that is what happened that initially they came here, made a linkage they means this ethyne and then this hydrogen got bound to this and then they left, this after this was hydrogenated. So, hydrogenated system leaves leave your metal surface.

(Refer Slide Time: 12:18)



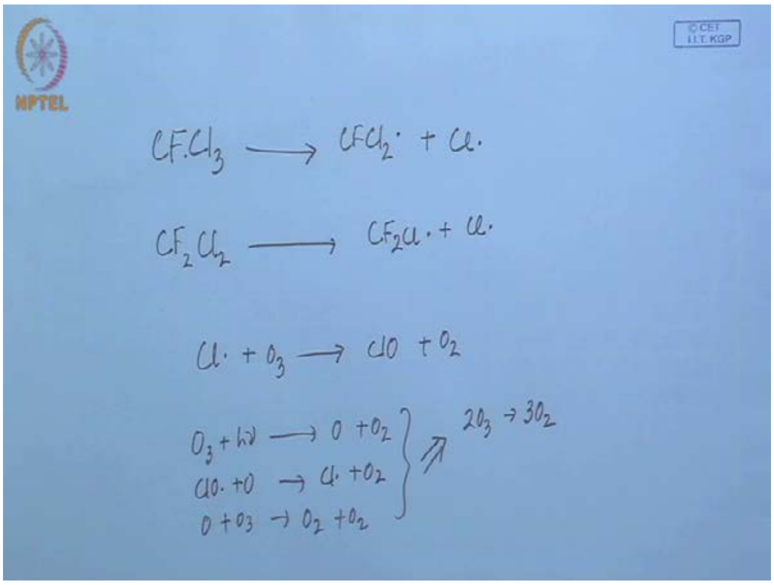
Homogenous Catalysis

- Chlorofluorocarbons catalyze the decomposition of ozone
  - $CFCl_3 \rightarrow CFCl_2 + Cl$
    $CF_2Cl_2 \rightarrow CF_2Cl + Cl$
  - $Cl + O_3 \rightarrow ClO + O_2$
  - $O_3 + h\nu \rightarrow O + O_2$
    $ClO + O \rightarrow Cl + O_2$
    $O + O_3 \rightarrow O_2 + O_2$
  - $2O_3 \rightarrow 3O_2$
- Acid catalyzed hydrolysis of organic ester

Now what is a homogeneous catalysis; homogeneous catalysis is a is a catalysis, where your your catalyst and your reactant, these two are in the same phase but, in case of heterogeneous they are in different phase phases. So, the celebrated example can be chlorofluorocarbons, so this chlorofluorocarbons are the catalyst to decompose this ozone. So, ozone layer (()) the mechanism by which this ozone layer in our atmosphere is ozone sphere is depleted; how this is done that mechanism I am just going to show it to you. So, chlorofluorocarbons are like C F C l 3.

So, chlorofluorocarbons C C C l 3 f or maybe C F 2 C l 2 these are chlorofluorocarbons also called freons. So, what happens that these freons, since this carbon is associated with with fluorine and these two are electronegative elements, fluorine is the highest electronegative. So, electronegative very high, so what happens that, this undergoes this reaction that is C F producing C F C l 2 radical C l radical, in the same way C F 2 C l 2 produces C F 2 C l and C l.

(Refer Slide Time: 14:05)



$$CFCl_3 \longrightarrow CFCl_2^{\cdot} + Cl^{\cdot}$$

$$CF_2Cl_2 \longrightarrow CF_2Cl^{\cdot} + Cl^{\cdot}$$

$$Cl^{\cdot} + O_3 \longrightarrow ClO + O_2$$

$$\left.\begin{array}{l} O_3 + h\nu \longrightarrow O + O_2 \\ ClO^{\cdot} + O \longrightarrow Cl^{\cdot} + O_2 \\ O + O_3 \rightarrow O_2 + O_2 \end{array}\right\} \Rightarrow 2O_3 \rightarrow 3O_2$$

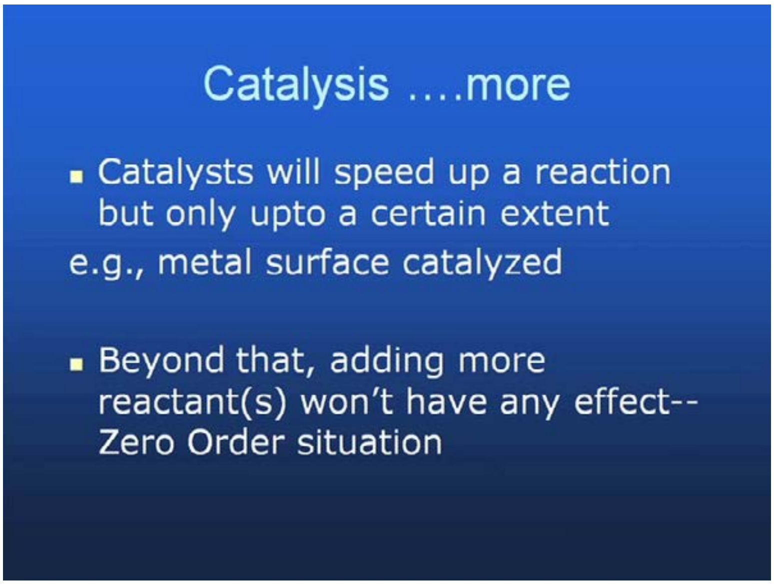
Let me write it over here that C F C l 3 giving rise to C F C l 2 radical plus C l radical, this is one reaction; another reaction could be C F 2 C l 2 giving rise to C F 2 C l dot plus C l dot. Now, these chlorine radicals will will react with this chlorine free radicals will react with ozone with the following you know scheme C l O plus O 2 producing oxygen. And there is another option that that this ozone, they absorb what what is happening that they absorb ultraviolet radiation to give rise to the following reaction that is they undergo reaction in presence of ultraviolet light.

So, O plus O 2 then C l O plus O giving rise to C l plus O 2, O plus O 3 giving rise to O 2 plus O 2, so net reaction from this, we can write 2 O 3 giving rise to 3 O 2. So, ozone is now is now broken into oxygen in presence of these, I mean C l O radical. So, these all these happen in in the same phase that is the C F C l 3 or C F 2 C l 2 these are gas. So, in gas phase this catalysis is occurring.

So, this is one celebrated example of you know gas phase homogeneous you know catalysis (Refer Slide Time: 16:14), there can be there can be acid catalyst catalyzed hydrolysis of organic ester as well, where you know this is a that is a case of homogeneous catalysis that that happens in in solution phase. So, this decomposition of ozone to oxygen has got enormous importance to to you know this damage of you know this civilization or maybe civil, I mean human kind or maybe plant, animal. As a result of entry of your ultraviolet radiation.

So, ultraviolet radiation means (Refer Slide Time: 17:08) this ozone molecules what they do is this ozone molecules generally absorb this U V region producing oxygen. And this production of oxygen to ozone and ozone to oxygen there is a there is a dynamic equilibrium. So, this dynamic equilibrium between ozone and oxygen in ozone sphere, so that is a that is a at that height, so there is a dynamic equilibrium. So, that equilibrium is destroyed as a result of which, so ozone is continuously being used up to produce more of oxygen and thereby ozone layer is depleting.

(Refer Slide Time: 17:49)



Catalysis ….more

- Catalysts will speed up a reaction but only upto a certain extent

e.g., metal surface catalyzed

- Beyond that, adding more reactant(s) won't have any effect--Zero Order situation

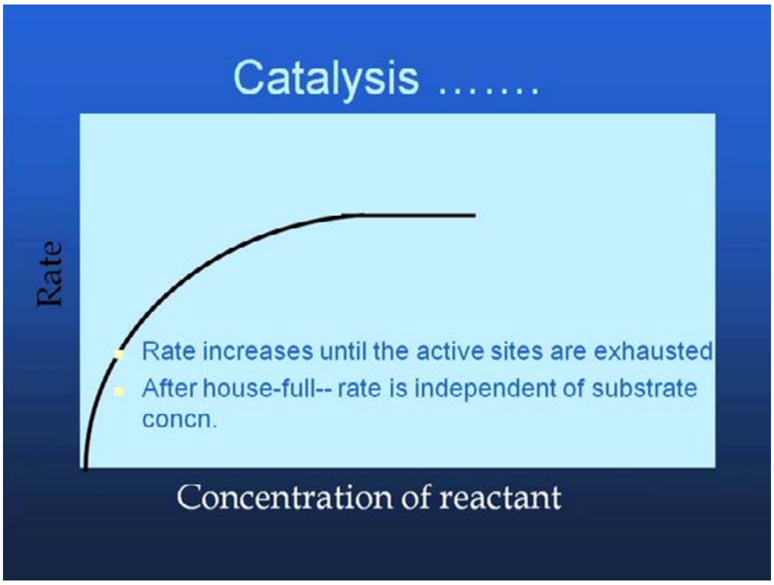
So, so if we talk if we want to talk more catalysis, that catalysts will speed up a reaction but, only up to a certain extent. So, classical example is metal surface catalyzed reaction and why these reactions are of zero order kinetics that that will be clear over here. That you suppose you have got metal surface, where as I explained to you, that adsorption of say ethylene C 2 H 4 and hydrogen takes place onto the metal surface. And then reactions reaction proceeds to a given direction to a to a specific direction.

But, suppose a situation that we have got 100 chairs in a in a in an auditorium and say we have got 90 students to come to to take part in some lecture. So, it is possible it is possible that 90 can be accommodated, because 100 chairs are available. So, you can keep on adding more and more students up to 100. So, beyond 100 it is not possible to accommodate anymore so; that means, these chairs are occupied, the seats are occupied.

So, therefore, further addition does not have any influence, I mean should not do anything extra that is no additional student will be able to attend the lecture. So, same thing happens in case of these metal surface catalyzed reactions, that when you add reactant onto the onto the metal surface, I mean say gaseous reactant. Then these reactants reactant molecules will first get absorbed onto the metal surface and this adsorption will continue until until you know this metal surface is fully occupied by these these molecules these reactant molecules.

So, until and unless there is any any you know any availability availability of vacant position. So, no further molecule can enter into onto the metal surface. So, that is beyond a certain point you know addition of more reactant would not have any effect and the situation is a zero order situation that your keeping on adding more and more reactant but, since your metal surface is covered with reactants. So, further addition will not put any more metal, I mean more reactant onto the metal surface so; that means, the reaction rate will go to a saturation, there is no change even if you add more of reactant.

(Refer Slide Time: 21:07)

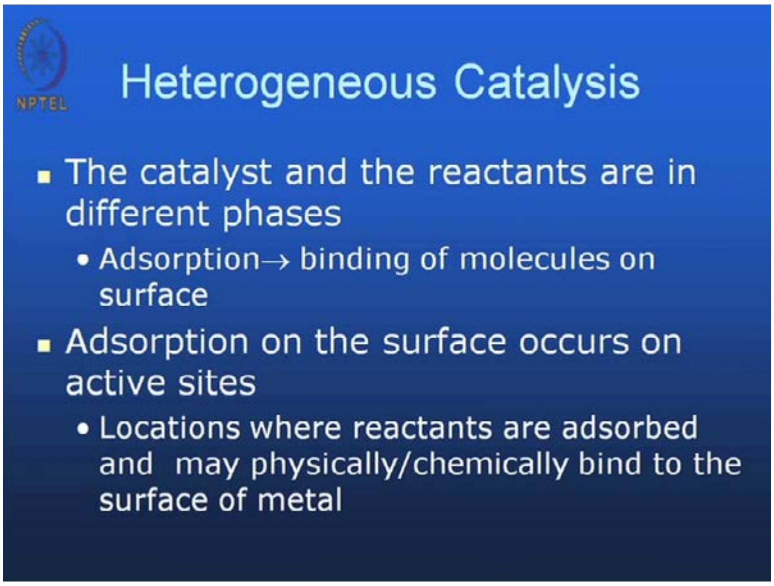

Catalysis …….

- Rate increases until the active sites are exhausted
- After house-full-- rate is independent of substrate concn.

So, that is depicted over here, that you see you see that rate increases until the active sites are exhausted. So, initially when, so this situation this active sites, I mean active sites means the the you know chairs I was referring to in a in a lecture hall in an auditorium. So, this increases means, still the chairs are getting occupied that is why rate is increasing but, you see beyond this point no change; that means, all the chairs are occupied.

So, after a house-full situation rate is independent of substrate concentration and that is why this gas phase metal surface catalyzed say decomposition reactions or zero order in kinetics in general. So, that is the situation for a you know zero order metal, zero order kinetics with metal surface catalysis.

(Refer Slide Time: 22:18)



Heterogeneous Catalysis

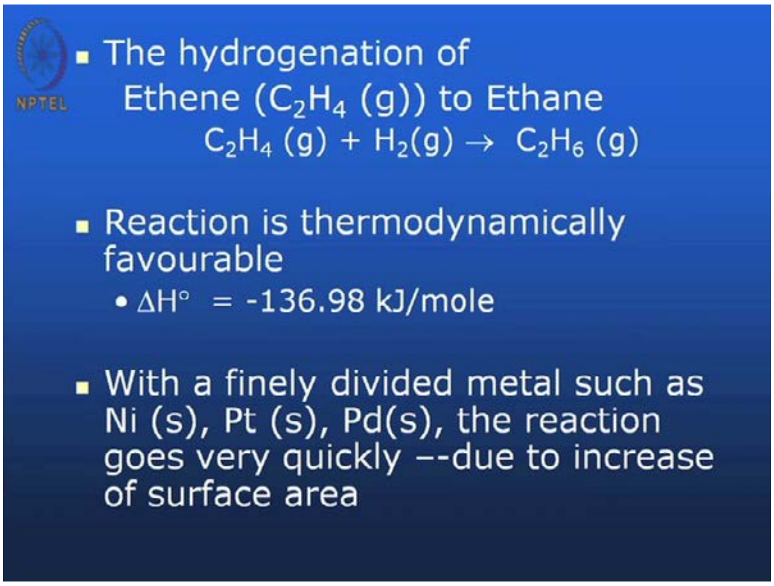
- The catalyst and the reactants are in different phases
  - Adsorption→ binding of molecules on surface
- Adsorption on the surface occurs on active sites
  - Locations where reactants are adsorbed and may physically/chemically bind to the surface of metal

So, so what you can say that in in case of heterogeneous catalysis, the catalyst and the reactant are in different phases, adsorption that is then it this molecule gets adsorbed onto the metal surface. So, adsorption that is the binding of molecule onto metal surface and this adsorption typically occurs onto the active site. So, not all chairs are effective some chairs are dummy.

So, you cannot occupy those chairs, maybe something like a broken chair although it looks like a chair but, it is not safe to use. So, adsorption on the surface occurs on only on the active site and locations for reactants are adsorbed, locations are where the reactants are adsorbed and may physically and chemically bind to the surface of the metal. So, maybe a physical binding physis option maybe a chemis option. So, these active site locations are the locations where this molecules are adsorbed.

So, and this adsorption can be physis option or maybe chemis option. So, chemis option is associated with a higher amount of energy change and physis option is associated with a lesser amount of energy change. So, not that much stronger bondage onto the metal surface.

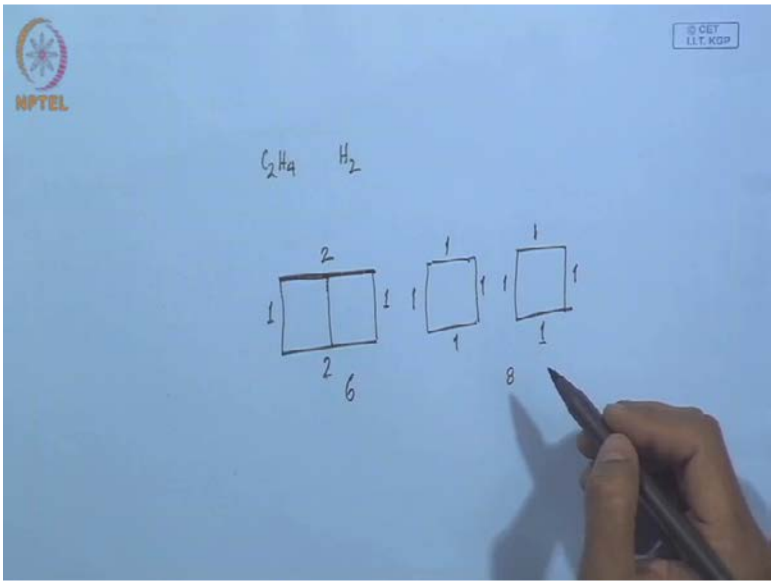
(Refer Slide Time: 24:04)



- The hydrogenation of Ethene (C_2H_4 (g)) to Ethane
  C_2H_4 (g) + H_2(g) → C_2H_6 (g)
- Reaction is thermodynamically favourable
  - ΔH° = -136.98 kJ/mole
- With a finely divided metal such as Ni (s), Pt (s), Pd(s), the reaction goes very quickly --due to increase of surface area

So, the hydrogenation of ethyne to ethane, so the reaction is thermodynamically favorable that is delta h is with a negative value. And of course, with finely divided metals such as nickel, platinum, palladium the reaction rate is found to increase very quickly, because that increases the surface area. That is you have got if you have got a bulk metal say say A 1 C C, 1 cubic centimeter of a metal and then if you crush it into into into small powder, I mean small particles in a in a powder and if you power it then the effective surface area is increased like.

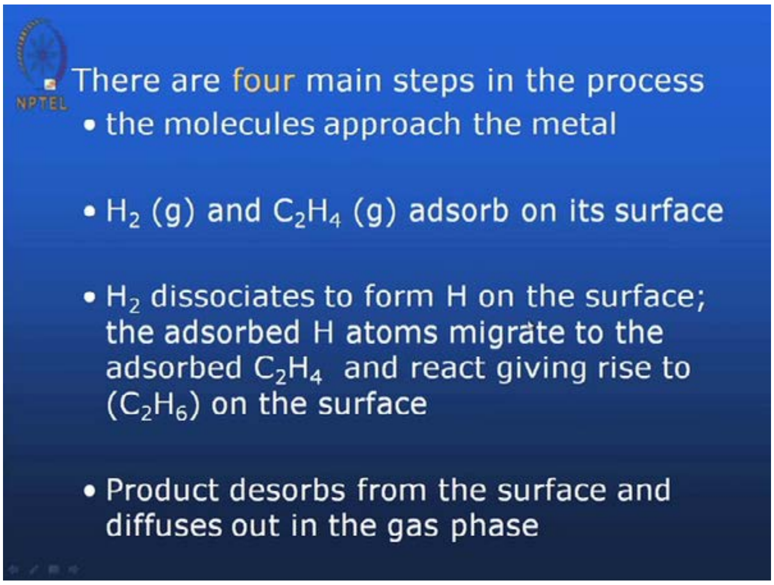
(Refer Slide Time: 24:58)



If if we have a you know 2 2 dimensional description that you have got a material of this sort. So, so you have got four sides say it is it is 2 centimeter, say it is 2 in in some units. So, this is 2 say this is 1, say this is 1, this is 2 (Refer Slide Time: 25:14), so, what is the you know total length of the you know outside length is 2 plus 2 2 plus 2, 4, 5, 6. Now if you divide it into this, like this that is you have got two such small from rectangle you you generated 2 squares. So, now, it is 1, 1, 1, 1, 1, 1, 1, 1. So, what is the length outside length perimeter, so 1, 2, 3, 4, 5, 6, 7, 8, so now, it is 8 initially it was 2, 4, 6.

So, there is there is a increase in this way if you keep on dividing and it is of course, it is a 2 dimensional case in the in case of 3 dimension another another dimension is added then the similar situation will happen. So, that is why if you divide that is, if the particle is finally, divided then then its surface area is increased enormously. And you know surface area increase means you are increasing the number of active sites, I mean the number of chairs on which these ethylene molecules will occupy and will react with hydrogen nascent hydrogen type situation. So, react with nascent hydrogen or like nascent hydrogen to produce your ethane.

(Refer Slide Time: 26:55)



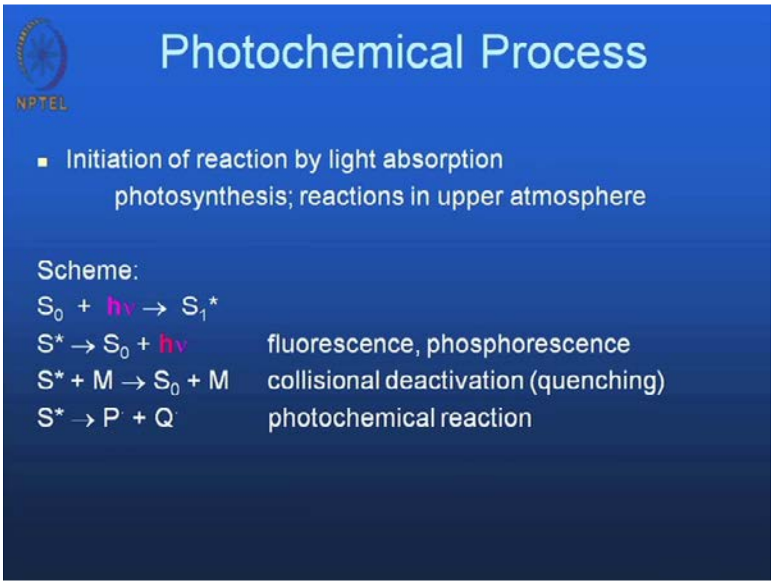
- There are four main steps in the process
  - the molecules approach the metal
  - H_2 (g) and C_2H_4 (g) adsorb on its surface
  - H_2 dissociates to form H on the surface; the adsorbed H atoms migrate to the adsorbed C_2H_4 and react giving rise to (C_2H_6) on the surface
  - Product desorbs from the surface and diffuses out in the gas phase

So, there are four main steps that is the molecules must approach the metal the molecules will come close to you know metal like say this is your metal surface, say this is your molecule. So, I mean this is coming like this, say this is your molecule say this is your surface like this, say this is your surface and say this is your molecule. So, this is coming; that means, they have to approach these molecules will have to approach to the metal surface.

So, this is one requirement that they must approach the metal, then this hydrogen and ethene will get adsorbed onto the metal surface otherwise no effect. So, in normal case if you do not put any metal or metal surface no reaction happens. Next is hydrogen dissociates to form I mean H 2 dihydrogen dissociates to form hydrogen atom onto the on the metal surface. They adsorb hydrogen atoms then migrate to the adsorbed C 2 H 4 in an appropriate fashion that that there is a formation of linkage.

So, react and then react giving rise to C 2 H 6 onto the metal surface and then the product desorbs from the surface and diffuses out in the gas phase. So, this way the reaction occurs. So, these are the four main or key steps in the process of heterogeneous catalysis that is typically this metal surface catalyzed reaction it is a typical hydrogenation process.

(Refer Slide Time: 28:59)



Photochemical Process

- Initiation of reaction by light absorption
  photosynthesis; reactions in upper atmosphere

Scheme:

$S_0 + h\nu \rightarrow S_1^*$

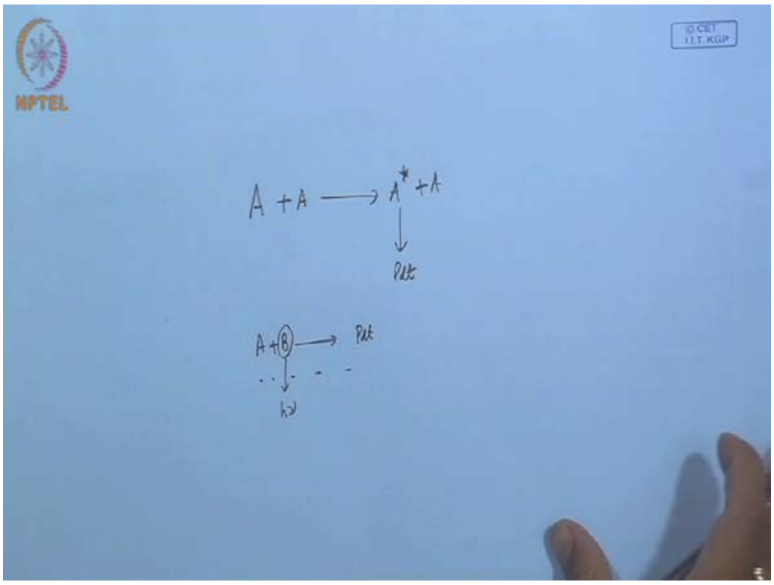
$S^* \rightarrow S_0 + h\nu$ fluorescence, phosphorescence

$S^* + M \rightarrow S_0 + M$ collisional deactivation (quenching)

$S^* \rightarrow P + Q$ photochemical reaction

Next is we move on to another a very important aspect is photochemical process. Now, so far we have talked about here that you have got you have got reactant, say one reactant maybe in case of unimolecular reaction.

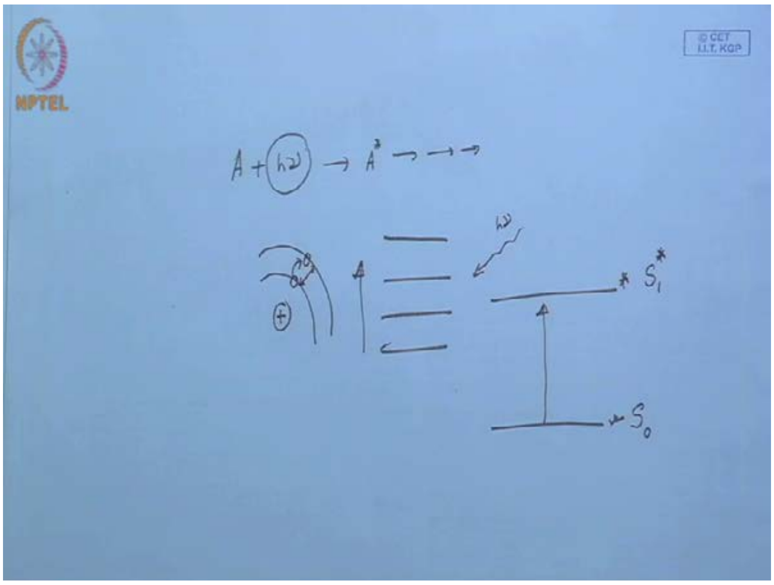
(Refer Slide Time: 29:19)



The same reactant A plus A giving rise to A star plus A, then A star is giving rise to product. So, this A star is basically the energetic, I mean energetic version or energy-rich version of A, energetically excited. Or maybe in this case you see the same molecule I mean same molecule or same atom, same species, better to say same species, two of the same species. Another situation can be A plus B giving rise to your product or maybe several of this sort.

So, where you see that your reactants are this is one chemical substance, this is another chemical substance, A is a chemical substance B is another chemical substance. So, there is a reaction between two chemical substances. But, in case of photochemical process if I replace this by a photon h nu it is generally denoted by h nu Planck's constant into frequency it is the energy packet associated with the photon. So, energy is you know coming in discrete packet of packet called the quantum. And so, photochemical reaction occurs where these photon is is a is a reactant.

(Refer Slide Time: 30:55)



So, say A plus h nu giving rise to A star. So, it is called the photochemically excited one and then this A star will will proceed for further reactions and so on. So, here this is a reactant, this photon is a reactant. Now, why does it happen, because atoms or molecules these are associated with a number of quantized energy levels, if you recall any quantum mechanics course, you will be finding that say hydrogen.

If you if you recall Bohr theory you will be seeing that postulates are like you know you have got nucleus over here, it is just like a solar system; that plus edge is over here and outside there are orbits, although orbit concept is an is a classical concept. So, now it is replaced by orbital concept that is the you know probability density plot of electron. So, atoms or molecules they are associated with a number of energy levels like this which are those are denoted by these lines. So, energy is increasing this way.

So, maybe this is the lowest energy, then gradually it increases. So, maybe these are all electronic energy levels. Now if you shine, so this is this is a system, so this system is a is having a bunch of energy levels. So, if you shine this this system with radiation h nu, then if you recall Bohr theory, that there will be an electronic transition from here to here which is which is possible only if this energy gap matches. So, if you supply a photon of this energy gap, then and only then the transition from here to here will take place.

So, transition from a lower energy state to an upper energy state and these are all quantized discreet states. So, you need to supply a packet of energy called the quantum and this quantum will take this system onto the next higher level or maybe next to next higher level depending on how much of how much of energy you are providing. So, in general that happens there there are you know different situations also but, I am not going to talk into going to talk on that.

So, it is basically this reaction is initiated by a photon, so photon is just like an initiator or or it is a reactant as well, because you know this is destroyed after it hits your molecule the energies are absorbed and it is destroyed. So, it you may call this as as a reactant as well. So, that means, you were means your system was at at this energy level initially you shine with h nu, you reach here with a starred starred means energetically excited.

And then in this excited state this reaction may, I mean this species will undergo several processes. That maybe a physical process, that does not lead to any change in you know chemical composition of of your starting material or maybe a chemical process, where a new chemical species is generated. So, this photochemical process it is the initiation of a reaction by light absorbed and typical examples are photosynthesis. So, it has got a complicated kinetics.

So, photosynthesis and of course, reactions in upper atmosphere like I told you this reaction, ozone layer depletion or you know absorption of ozone, I mean ultraviolet light by ozone, so that that is typically a photochemical process. So, schematically we can write a a scheme like this that the lowest state I mean most of the molecules are having are having ground singlet state; ground triplet state is possible for oxygen. So, oxygen is a triplet in origin. Triplet state means two electrons spins are you know up maybe and singlet means one is up another is down.

So, it is a singlet situation and triplet situation is this or maybe this. So, so let us start from singlet state, so say this say this is S, since it is the lowest one that is why it is given S 0. So, transition occurs say to S 1, S 1 means it is the first singlet state of course, it is excited. So, therefore, it is S 1 star, so schematically it is written like S 0 plus h nu producing S 1 star.

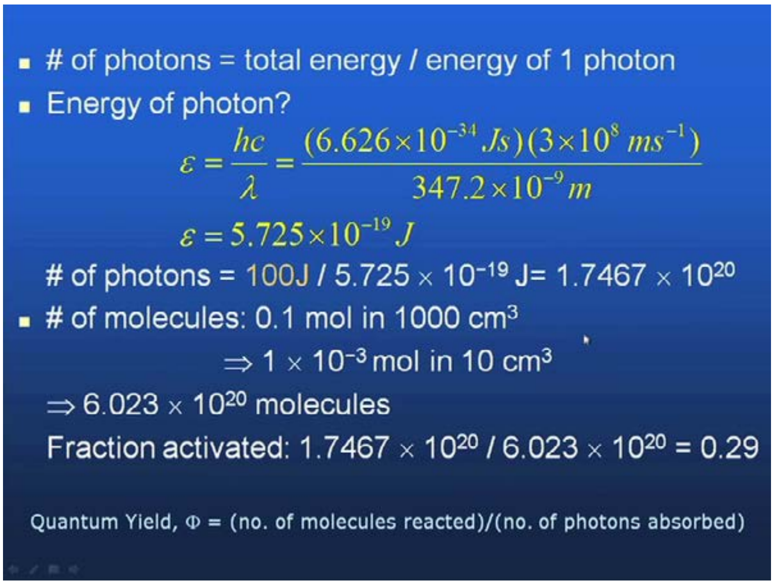
Then this this S 1 star may undergo several several processes, maybe physical process that, this excess energy is given back in the form of fluorescence or maybe in the form of form of phosphorescence. I am not going into the details of that, because that will be taken up in in a separate course, that is the fluorescence or phosphorescence. Next it is it is the possibility that this excited molecule, this excited species will undergo collision with another molecule.

And thereby this excited species comes back to the ground state and making you the the other species maybe either excited or maybe maybe the excess energy is given out in the form of heat. So, that is called the deactivation maybe collisional deactivation is is a is a classic you know situation or maybe photochemical reaction that this S star giving rise to to I mean two radicals P dot and Q dot. So, it is called the photochemical reaction.

So, first excitation it is the energy absorption, then it is called your emissive de-excitation which is called phosphorescence or it maybe phosphorescence it maybe fluorescence. Phosphorescence is you know emission without change in overall spin and phosphorescence is the you know an emission with a change in electron spin. So, details is a we do not have scope scope to detail this.

Now next is next step could be collisional deactivation, that is just mere collision like a like collision of gas molecules of which one is excited another is unexcited and the last one is photochemical reaction. So, photochemical reaction is a true reaction others are like phosphorescence, fluorescence and collisional deactivation these are generally you know physical processes, that is not attended by any change in you know chemical composition of that system.

(Refer Slide Time: 38:54)



- # of photons = total energy / energy of 1 photon
- Energy of photon?

$$\varepsilon = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,Js)(3\times10^{8}\,ms^{-1})}{347.2\times10^{-9}\,m}$$

$$\varepsilon = 5.725\times10^{-19}\,J$$

# of photons = 100J / 5.725 × 10^{-19} J= 1.7467 × 10^{20}

- # of molecules: 0.1 mol in 1000 cm^3

$\Rightarrow$ 1 × 10^{-3} mol in 10 cm^3

$\Rightarrow$ 6.023 × 10^{20} molecules

Fraction activated: 1.7467 × 10^{20} / 6.023 × 10^{20} = 0.29

Quantum Yield, Φ = (no. of molecules reacted)/(no. of photons absorbed)

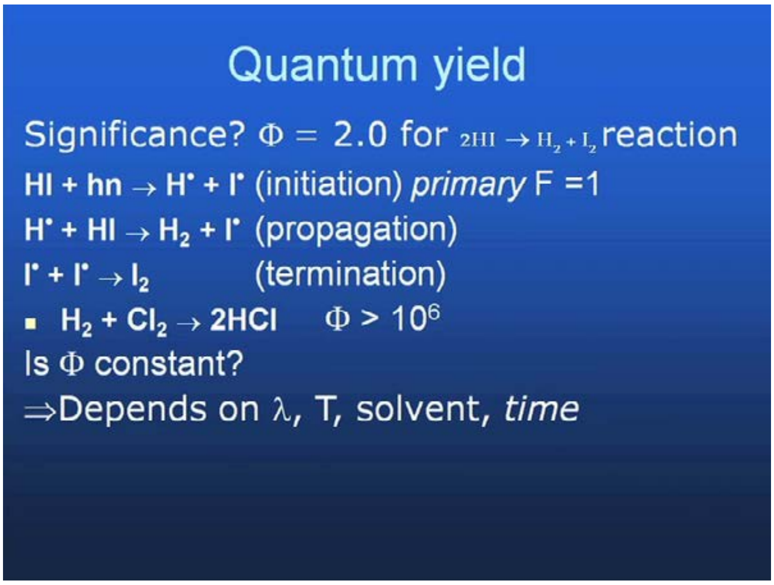
So, number of photons you can calculate is the total energy, which you are supplying to the system total energy which you are supplying to the system divided by the energy of a photon. Suppose, you are looking into 347.2 nanometer photon, so energy will be like this and energy ultimately comes out to be this much of joule. So, if you supply with 100 joule, then this this will be of this much of number of photons that you are supplying inside your your chemical system, chemical solution.

And if you have a 0.1 molar 1 litre solution, then you have got how many number of molecules it is of the order of 10 to the power 10 to the power 20, it is of 10 to the power 20 means 6.023 into 10 to the power 20 and the other 1 is 1.7 into 10 to the power 20. So, if you divide this one, then you will be getting that only 0.29 is the fraction that is activated, if all the photons are used up in true activation. Suppose if it is a one to one correspondence that one photon absorbed means that is used up to activate the molecule. So, that is the limiting value is 0.29.

So, it is just simple activation that is A plus h nu giving rise to A star. Now what is quantum yield, quantum yield is the number I mean reaction quantum yield, if we since we are discussing here the chemical reaction. So, reaction quantum yield is the point, which we should you know focus onto. So, it is it is the quantum yield, which is equal to number of molecules reacted divided by the number of photons absorbed; that means, number of photons in and number of molecules out. So, number of molecules out will be on the numerator and in the denominator number of photons in.

So, so that means, it is the it is the percentage or or maybe the fraction of effective you know like absorption means, not all absorption lead to chemical reaction like that, if it is a true one to one correspondence. Then quantum yield should be like should be 1 or in some cases quantum yield has been found to be more than one as well that I am I will be giving you an example at least to show that quantum yield is is more than one, it maybe huge. So, quantum yield is a measure of the extent of reaction in terms of means with respect to number of photons, which you have added into this into into your system.

(Refer Slide Time: 42:05)



Quantum yield

Significance? $\Phi = 2.0$ for $2HI \rightarrow H_2 + I_2$ reaction

$HI + hn \rightarrow H^{\bullet} + I^{\bullet}$ (initiation) *primary* F =1

$H^{\bullet} + HI \rightarrow H_2 + I^{\bullet}$ (propagation)

$I^{\bullet} + I^{\bullet} \rightarrow I_2$ (termination)

- $H_2 + Cl_2 \rightarrow 2HCl$ $\Phi > 10^6$

Is Φ constant?

$\Rightarrow$Depends on λ, T, solvent, *time*

So, quantum yield significance what is the significance, if you think of a 2 H I to H 2 I 2 decomposition. So, H I then this will be h nu, n means nu. So, H I will will generate H dot I dot is an initiation step, F is phi basically maybe, because of some profound problem this F phi is coming as F. So, anyway this is phi is equal to 1; that means, 1 photon in 1 molecule you know broken. So, that is why phi is 1 then it is a propagation step, it is a termination step.

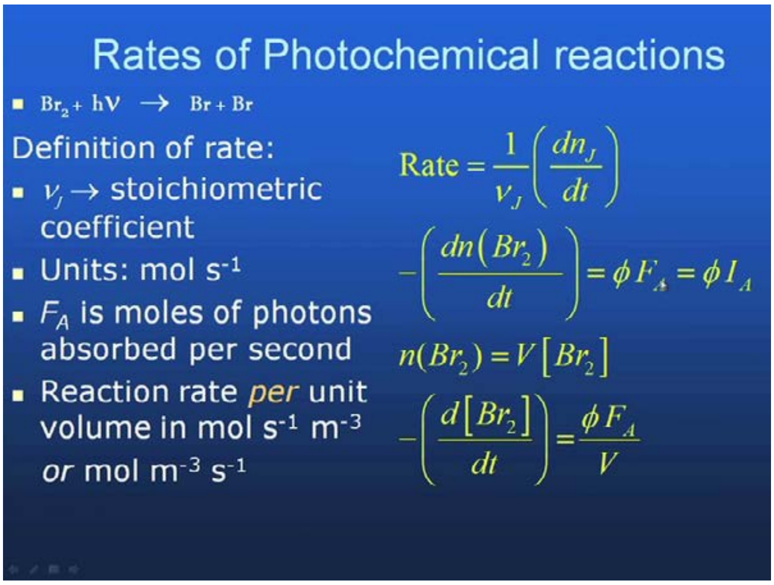
So, this primary primary phi is 1, but significance is that you know if you put 1 photon in, then you will in principle generate you will in principle generate say 2 hydrogen iodides to get decomposed; that means, you see 2 H I is actually taking part in reaction although you have put only 1 photon. So, that is why overall phi is 2 2 molecules reacted because of one photon.

So, therefore, phi is 2 for H 2 plus C l 2 to H 2 I mean 2 H C l reaction phi has been found to be 10 to the power 6 it is a very high value. So, you know it is a it is a kind of chain reaction, it is a chain reaction that is why it is very high so; that means, you you just put 1 photon and n number of you know molecules will be decomposed. So, is phi constant. So, means what is the what are the factors on which phi should depend phi depends on lambda means why lambda?

Because suppose, you if you are supplying supplying this much of energy nor this much this say less amount of energy, then these molecules will not get activated to I mean excited to S 1. So, this reaction will not take place. So, that is why lambda means you know frequency it is ultimately frequency related to the energy. So, it depends on energy temperature is also an important factor, because if you increase the temperature.

So, so this elementary reactions are modified and that will indeed affect your your overall phi solvent is very important important parameter, if you take a polar solvent the answer is different than compared to a non polar solvent. If you give more time, if you shine I mean after after shining if you allow the reaction to to go for long time, then then what is happening that you know you know you will be getting you will be getting more of phi.

(Refer Slide Time: 45:03)



Rates of Photochemical reactions

- $Br_2 + h\nu \rightarrow Br + Br$

Definition of rate:

- $\nu_J \rightarrow$ stoichiometric coefficient
- Units: mol s^{-1}
- F_A is moles of photons absorbed per second
- Reaction rate *per* unit volume in mol s^{-1} m^{-3} *or* mol m^{-3} s^{-1}

$$\text{Rate} = \frac{1}{\nu_J}\left(\frac{dn_J}{dt}\right)$$

$$-\left(\frac{dn(Br_2)}{dt}\right) = \phi F_A = \phi I_A$$

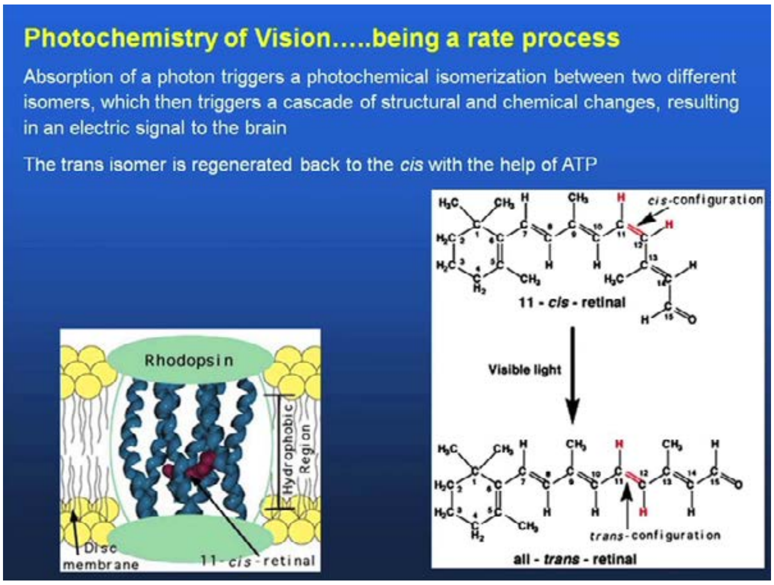
$$n(Br_2) = V[Br_2]$$

$$-\left(\frac{d[Br_2]}{dt}\right) = \frac{\phi F_A}{V}$$

So, next is rates of photochemical reaction, so your B r 2 plus h nu giving rise to B r B r. So, it is a it is a just a homolytic cleavage. So, as per definition rate is 1 by nu j d n j d t as I told you in in in first lecture. So, so d n d t d n d t means number of molecules of B r 2 that is broken, so which is nothing but, equal to you know phi is the quantum yield times F A, so so that is basically I A.

So, ultimately n B r 2 is V into because it is the number of moles of B r 2 which is nothing but, your concentration into total volume and that gives you overall rate of reaction is phi times F A F A by V; where F A is the moles of photon absorbed per second. So, F A is basically your intensity, number of photons absorbed per second actually intensity per unit area should be there but, we are ignoring per unit area. That is why ultimately you know F A is means you can write F A is similar to I A I A means intensity of absorbed radiation, you can write in this way.

(Refer Slide Time: 46:29)



Photochemistry of Vision…..being a rate process

Absorption of a photon triggers a photochemical isomerization between two different isomers, which then triggers a cascade of structural and chemical changes, resulting in an electric signal to the brain

The trans isomer is regenerated back to the *cis* with the help of ATP

Finally, it is a very interesting aspect of you know photochemical reaction, that photochemistry of vision that you know we we can see we can visualize thing. So, there is there is a there is a photochemistry involved here. So, the the molecule the the effective molecule is you know this 11 cis-retinal and this is in cis configuration and this is all-trans-retinal. So, if you have the visible light then this 11 cis-retinal is converted to all-trans-retinal, so just you know this this cis 1 becomes a trans 1, so this cis trans isomerization happens. So, through a visible light through, means through absorption of visible light.

So, absorption of a photon triggers a photochemical isomerization, so this is an absorption of by means of absorption of photon. So, isomerization happens between 11 cis to 11 all-trans-retinal and this then triggers a cascade of structural and chemical changes, resulting an electrical signal to a brain. So, that electrical signal is the signal tha, translates the information that we are you know viewing through our eyes.

So, basically the image information is transferred to the brain in the form of electrical you know a bunch of electrical signals and we see this that is we see whatever is in front of us. And this happens in in this occurs in visible light, it does not happen in ultraviolet or maybe not in ultraviolet have may happen but, that will damage other components I mean inside eye inside eyes but, not by I R light infrared light that is why we we do not see in nighttime but, you know dog or you know cat they can see they might have some different you know option.

So, the transisomer is regenerated back to the cis with the help of A T P. So, then it is coming back it is coming back to this, with the help of A T P that is some energy is needed to put this back to here. So, so it is a very very interesting situation that you know and this this is a this you know cyclic process a forward reaction, backward reaction forward reaction, backward reaction. So, if it is not taken back to here then you know with time our vision should have been diminished but, it never happens.

So, that means, there is a there is an opposing process, opposing I mean not opposing there is there is a back reaction; opposing reaction does not mean that it opposes your vision. So, this back reaction, there is a back channel, so that is why complicated reaction like you know sequential reaction or maybe parallel reaction or maybe opposed reaction are sometimes beneficial to us like we see here that you know this forward process is good for vision.

And backward process is also needed to have a you know sufficient amount of 11 cis-retinal. So, that next times next time we can see like like it suppose we are we are seeing something for long time; that means, there must be a continuous you know flow of, I mean the flow of the process from this direction to this direction that helps in seeing. And also this direction that is back reaction ensures, that after certain time this will not be depleted that is if it happened, that it is with time eventually say it is, if it is exhausted then we should have seen something you know black in in front of us.

So, that is why this forward reaction and back back reaction maybe in a different path is very important. So, back reaction is another you know, it is it is a consecutive reaction so but, this that consecutive reaction regenerates your reactant and that helps the viewing process, that is vision process. So, that is all about you know various type of types of you know complex reaction it is also a complex reaction this photochemistry of vision is a complex reaction.

So, that completes our you know initial part of complex reaction, I mean complex reaction is completed. So, we will then, in our lecture you know next lecture we will talk about these theories of chemical reaction rate (Refer Slide Time: 51:43) So, that is theories of reaction rate but, before that what we have learnt in this lecture, that what is catalysis and what is catalyst? Then we talked about homogeneous and heterogeneous catalysis.

(Refer Slide Time: 52:00) Then a classic example of heterogeneous catalysis, metal catalyzed, metal surface catalyzed reaction that is hydrogenation of ethyne and homogeneous catalysis one celebrated example, is the depletion of ozone by chlorofluorocarbon C F C. Then we talked about you know talked about this characteristic of this metal catalyzed reaction, why it is zero order reaction and also this importance of this.

And also we talked about this photochemical reaction we gave a brief introduction of photochemical reaction, we have not talked more on this, because photochemistry is a is a separate topic that will be taken up in in in a different course. Now, and and the and one important thing is that we have we have just given an idea of this photochemistry of vision, that is the importance of studying chemical reaction, why do we study, what is the importance of your consecutive reaction, what is the importance of back reaction, how does it help in some cases.

Although in some other cases this you know side reactions may may lead to some you know undesired product, may lead to you know reduction of your overall yield. So, that is not good for us but, but there are examples like like the photochemistry, the example which I gave to you in connection with photochemistry of vision, here you see that this back reaction is very important to maintain the equilibrium or equilibrium concentration of both components involved in that is involved in this process that is 11 cis-retinal and 11 all-trans-retinal.

So, in our in our next lecture, we will will talk on these theories of reaction rate and we will start from collision theory. So, homogeneous gas phase reaction that that say two molecules are colliding. So, we will start from kinetic theory of gas that, the basic postulates of kinetic theory says, that there is continuous you know collision between one molecule with another molecule or maybe there is a collision between this molecule with the wall of the container.

So, unless these two components come close to each other, there is no possibility of say exchange of atom or reaction, because you know rearrangement of atoms is basically you know chemical reaction. So, if they do not come close to each other, then the possibility is less. So, that is why it is necessary to have some collision maybe at least for gas phase reaction and this collision mechanism can explain many of the features of gas phase reaction. So, we will take up that we will take up those issues in the in the next next lecture. So, till then have nice time, thank you.