Rate Processes

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Module No. # 01
Lecture No. # 40
Concluding Remarks

Hello, good morning friends; we are here in the concluding lecture on rate processes. So, in this series of lectures what we have learnt and what is the hope so that we should have an overview on that.

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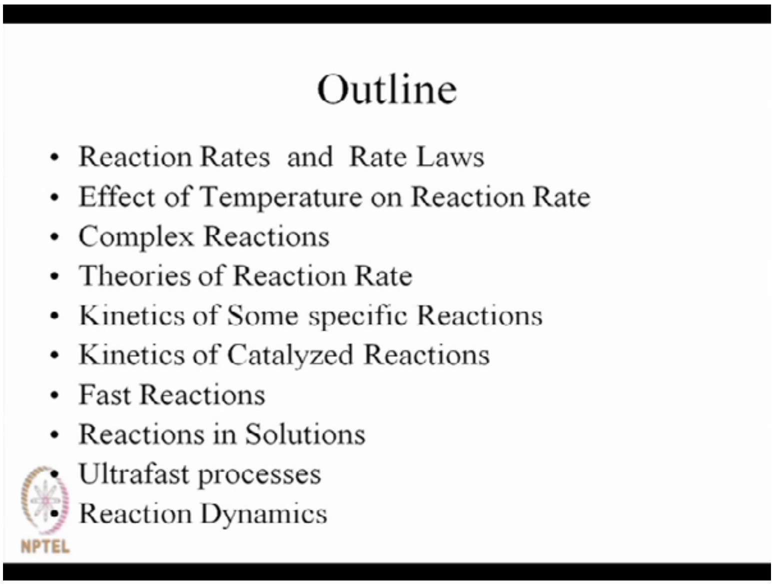

Outline

- Reaction Rates and Rate Laws
- Effect of Temperature on Reaction Rate
- Complex Reactions
- Theories of Reaction Rate
- Kinetics of Some specific Reactions
- Kinetics of Catalyzed Reactions
- Fast Reactions
- Reactions in Solutions
- Ultrafast processes
- Reaction Dynamics

In this series of lecture, this is the outline that we started with; we gave this outline at the very beginning that this series of lecture will have like these topics mainly reaction rates and rate loss. We already discussed on this then, effect of temperature on reaction rate another topic that is how temperature is going to affect the reaction rate. Then, we went to complex reactions that is reactions can be complex; ( ) maybe complex. So, we discussed examples of complex reactions and their corresponding you know kinetic descriptions. Then, theories of reaction rates then, kinetics of some specific reactions we dealt with that. Then, catalysis is a very important thing very important you know, aspect in specially, in chemistry - industrial chemistry, biological chemistry and many places catalysis plays a very very crucial role. So, we discussed on that and catalysis like bio-catalysis we also discussed. Then, we talked about you know, introduction of fast reactions; the reactions which are completed you know in a very short time like in a moment like, maybe within say 1 nanosecond, maybe or maybe 1 millisecond or even less than that, maybe in microsecond; so faster than nanosecond, like picoseconds, or maybe ( ) second. Those are under ultrafast processes but, fast reactions could be like millisecond, microsecond like that. So, those means, those fast reactions are very difficult to probe; so we talked on how to follow those reactions. Then, reactions in solution ultrafast processes we discussed and finally, we dealt with reaction dynamics.

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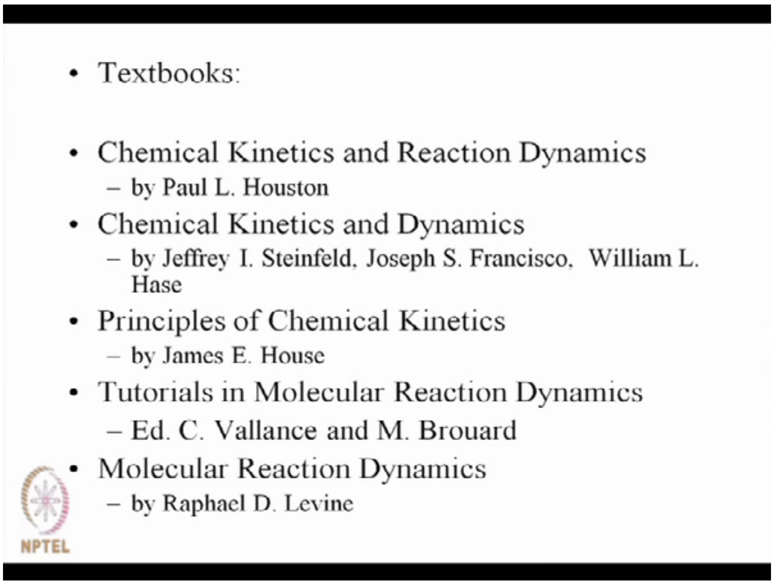

- Textbooks:
- Chemical Kinetics and Reaction Dynamics
  - by Paul L. Houston
- Chemical Kinetics and Dynamics
  - by Jeffrey I. Steinfeld, Joseph S. Francisco, William L. Hase
- Principles of Chemical Kinetics
  - by James E. House
- Tutorials in Molecular Reaction Dynamics
  - Ed. C. Vallance and M. Brouard
- Molecular Reaction Dynamics
  - by Raphael D. Levine

Now, the textbooks which was you know, which I recommended apart from these books; maybe, you can consult other text books as well; or maybe good physical chemistry textbooks you can follow. One is that I recommended is chemical kinetics and reaction dynamics by Houston - Paul Houston. Then, chemical kinetics and dynamics by Steinfeld Francisco and Hase third one was principles of chemical kinetics by House; tutorials in molecular reaction dynamics by Vallance and Brouard; it is a nice book and molecular reaction dynamics by Levine Raphael D Levine. So, these books you can consult apart from other, apart from these books you can consult other textbooks as well.

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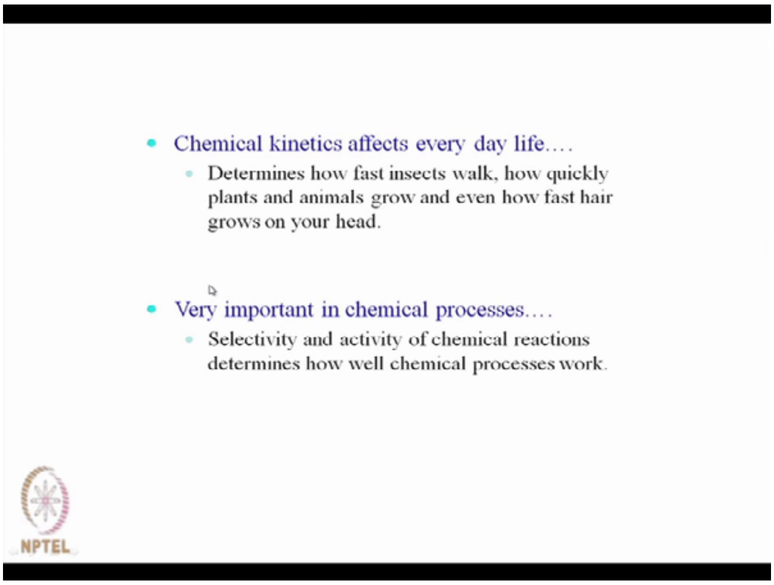

- Chemical kinetics affects every day life....
  - Determines how fast insects walk, how quickly plants and animals grow and even how fast hair grows on your head.
- Very important in chemical processes....
  - Selectivity and activity of chemical reactions determines how well chemical processes work.

Now, why is chemical kinetics because chemical kinetics affects everyday life and it determines how fast insects walk, how quickly plants and animals grow and even how fast hair grows on your head. So, this everything I mean, everything is related to chemical kinetics or maybe bio-chemical kinetics. It is very important in chemical processes selectivity; activity of chemical reactions determines how chemical processes will work; so, very important that is why it is a very important topic.

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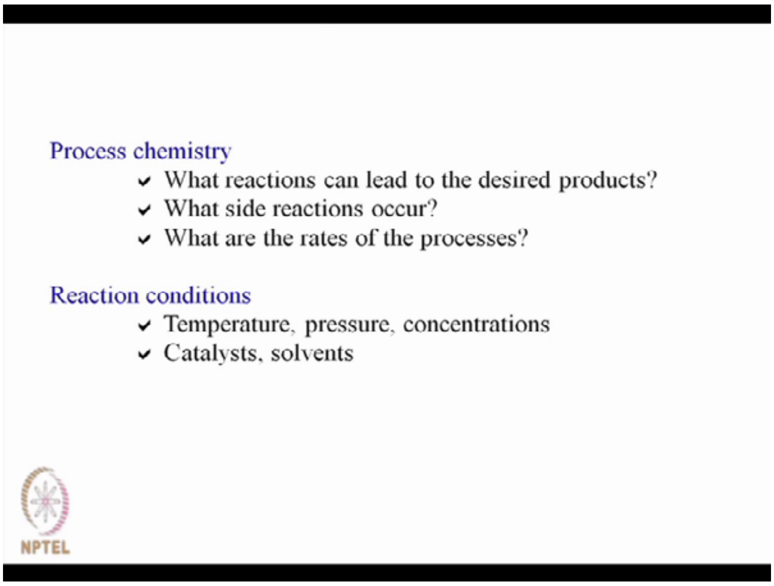

Process chemistry
- ✓ What reactions can lead to the desired products?
- ✓ What side reactions occur?
- ✓ What are the rates of the processes?

Reaction conditions
- ✓ Temperature, pressure, concentrations
- ✓ Catalysts, solvents

In process chemistry like what reactions can lead to desired products, what side reactions are possible is it going to affect the main reaction of our interest, yes or no? Or, if it is there how do you know get rid of that problem and also of course, what are the rates of such processes? Next is conditions which is very important whether the reaction is possible in gas phase whether the reaction is possible in aqueous phase, non aqueous phase and so on. And, if the reaction is possible then, what are the factors that are responsible for you know, controlling the rate of the process that is factors on which rates are dependant like temperature, pressure concentrations. How this is going to affect? These are going to affect you know the reaction; that is, reaction condition also ( ) very important. Next is a catalyst if this reaction is catalyzed then, whether it is a normal catalytic reaction? Then it is an autocatalytic reaction or maybe if there is a poison for the catalyst that we should also know that suppose a… because of some secondary agent these catalysts are poison. So, reaction you know rate is decreased; so these are the things that we should look into and these are the parts and pieces of chemical kinetics and rate processes specially rate processes because, we are dealing with rate processes in chemistry rate processes could be somewhere some other places. Also, at some other you know subject also like you know physical rate; that we are not going to discuss out here that is rate of flow of something that we are not going to discuss over here like flow of material. So, maybe we are not here what we are interested in is everything means everything related to rate processes in chemistry and chemical systems.

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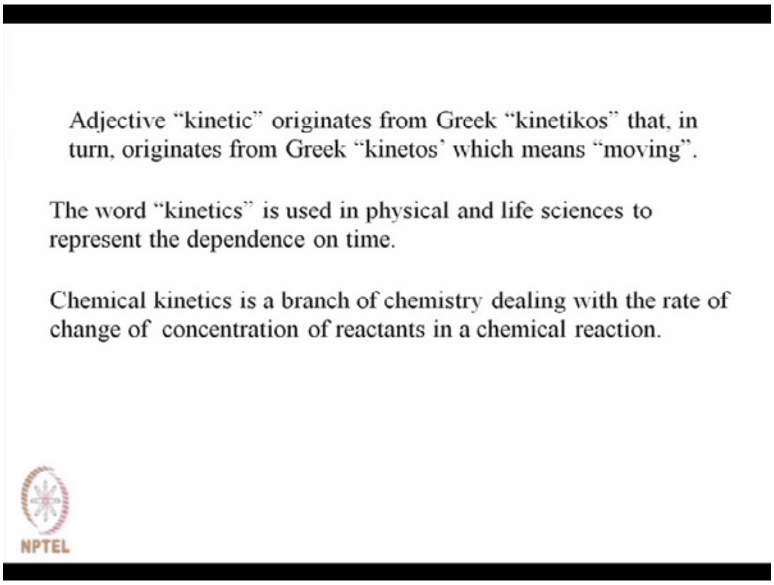

Adjective “kinetic” originates from Greek “kinetikos” that, in turn, originates from Greek “kinetos’ which means “moving”.

The word “kinetics” is used in physical and life sciences to represent the dependence on time.

Chemical kinetics is a branch of chemistry dealing with the rate of change of concentration of reactants in a chemical reaction.

The adjective kinetic originates from Greek ‘kinetikos’ that, in turn, originates from Greek ‘kinetos’ which means ‘moving’. So, it is something moving though what kinetics is used in physical and life sciences to represent dependence on time dependence of some of something on time dependence of in physical science you know or may be chemical sciences. So, dependence on something on time in physical science, in chemistry, dependence of concentration chemical kinetics are rate process is in chemistry, is a branch of chemistry that is dealing with rate of change of concentration of reactants in chemical reaction. So, that is what we are going to going to you know, learn I mean, what we already learnt in this in this series of lectures.

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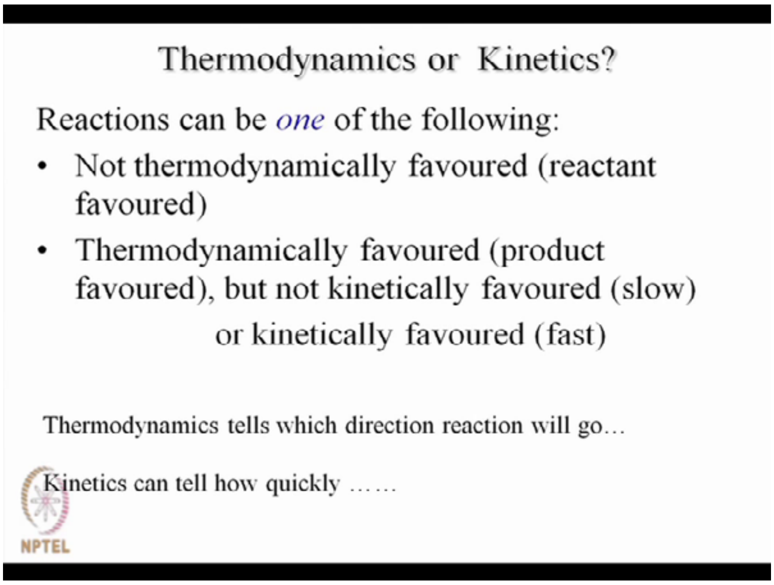

Thermodynamics or Kinetics?

Reactions can be *one* of the following:

- Not thermodynamically favoured (reactant favoured)
- Thermodynamically favoured (product favoured), but not kinetically favoured (slow) or kinetically favoured (fast)

Thermodynamics tells which direction reaction will go…

Kinetics can tell how quickly ……

Then we also discussed this point; I mean, thermodynamics and kinetics is there any tussle between them whether thermodynamics is more important or kinetics is more important. Apparently, it looks like thermodynamics you know controls everything but, at the same time we should remember that even if a process is thermodynamically feasible because of its very low speed I mean, very low rate maybe may be the substance is not degraded so that is why kinetics and thermodynamics for a chemical reaction these are you know somehow interlinked together like 2 parallel threads running you know parallel to each other. Reactions can be one of the following like I told that which is not thermodynamically favored, reactant favored, thermodynamically favored which is product favored but, not kinetically favored which is basically a slow process or kinetically favored it is a fast process that is kinetically very fast. So, that is why you know, as I told you that thermodynamics and kinetics they should you know should be considered. You know parallel you know in dealing with rate processes in chemistry in chemical system and thermodynamics tells us which that means, thermodynamics tells us which direction reaction will go and kinetics tells how quickly it will go; whether it is slow or it is fast that is what pretty much related to you know thermodynamics and kinetics.

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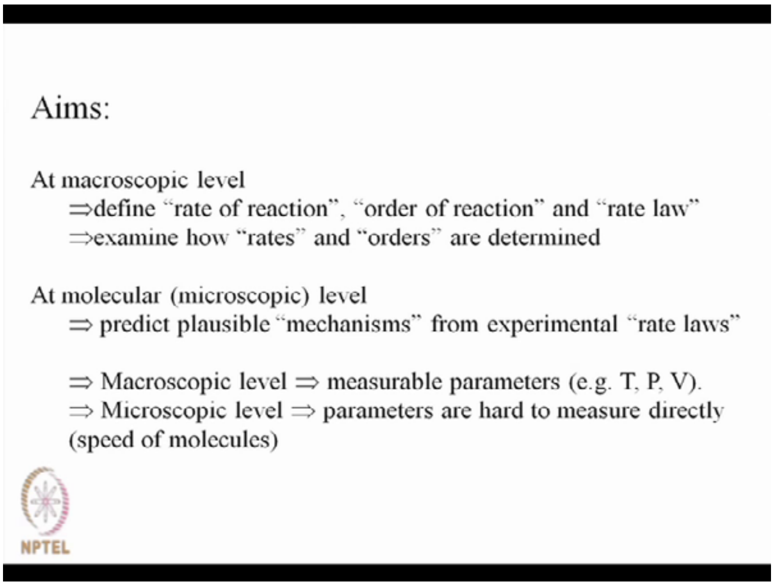

Aims:

At macroscopic level
- ⇒define "rate of reaction", "order of reaction" and "rate law"
- ⇒examine how "rates" and "orders" are determined

At molecular (microscopic) level
- ⇒ predict plausible "mechanisms" from experimental "rate laws"

- ⇒ Macroscopic level ⇒ measurable parameters (e.g. T, P, V).
- ⇒ Microscopic level ⇒ parameters are hard to measure directly (speed of molecules)

Aims for studying rate processes at macroscopic level, you have to define rate of reaction, order of reaction and rate law and you have to examine how rates and orders are determined. So, we determine rates and orders for chemical reactions; so we define rate of reaction then order of reaction and also rate law for any chemical process and microscopic molecular level. What we want to learn here I mean, what we learnt here is the is the you know predict a plausible mechanism from experimental observations maybe rate laws rate equations we would like to you know formulate a plausible mechanism so that is pretty much what is related to the aims of this and specially at the at the molecular level of understanding. So, macroscopic in macroscopic level measurable parameters are T P V and microscopic levels you know parameters are hard to you know, measure directly it is very difficult because microscopically you have to pick up you know, certain molecules and then you have to find out what is the speed it is difficult so macroscopically. It is somehow you know it is it is easy but, microscopically the parameters which are which are important like speed of molecules what we what we talked in collision. So, collisions are responsible for chemical reaction to occur; so like these parameters like speed of molecule is hard to find out. So, anyway these are the these are pretty much what is rated you know I mean what I know pretty much the aims and objectives.

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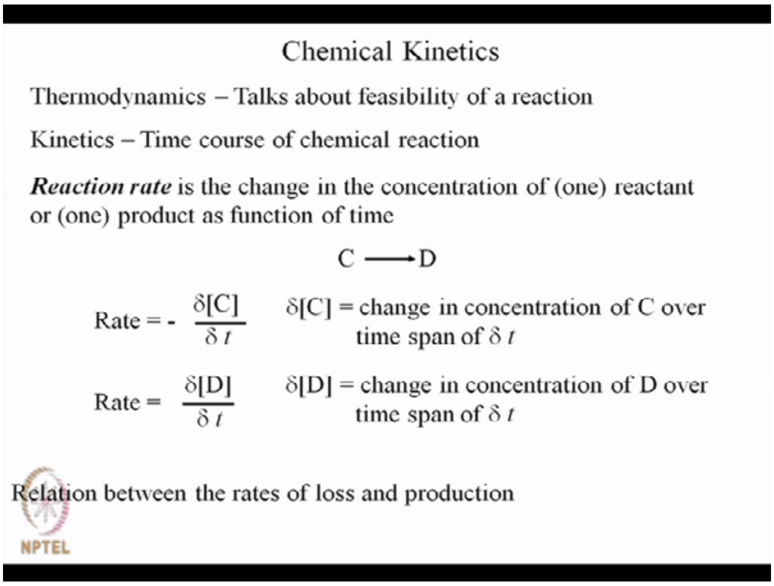

Chemical Kinetics

Thermodynamics – Talks about feasibility of a reaction

Kinetics – Time course of chemical reaction

Reaction rate is the change in the concentration of (one) reactant or (one) product as function of time

$$C \longrightarrow D$$

$$\text{Rate} = -\frac{\delta[C]}{\delta t}$$

$\delta[C]$ = change in concentration of C over time span of δt

$$\text{Rate} = \frac{\delta[D]}{\delta t}$$

$\delta[D]$ = change in concentration of D over time span of δt

Relation between the rates of loss and production

Chemical kinetics means as I told you like these things already I have talked about that feasibility and codes of reaction like reaction rate I you know discussed like this way you can you can like write the reaction rate that is rate of disappearance and rate of appearance and it is basically you know this rate equation is nothing but, the relation between rates of loss or production of certain you know chemical certain substances maybe substrate or maybe a product.

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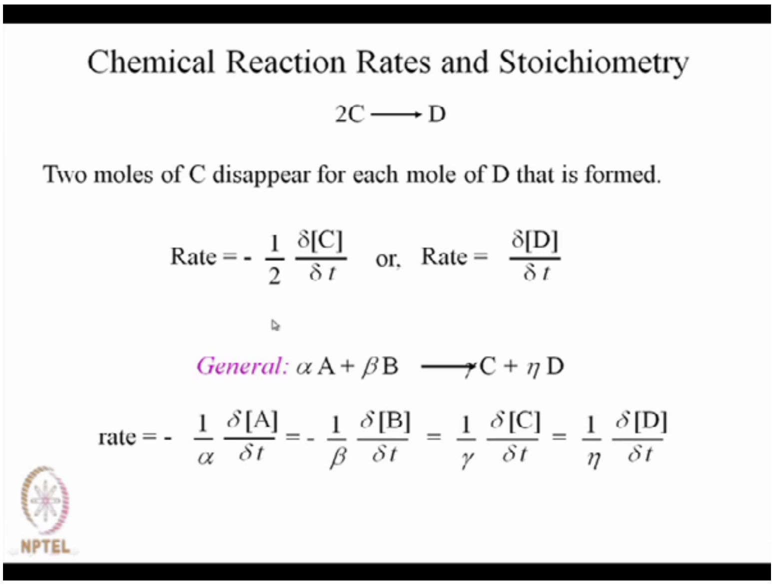

Chemical Reaction Rates and Stoichiometry

$$2C \longrightarrow D$$

Two moles of C disappear for each mole of D that is formed.

$$\text{Rate} = -\frac{1}{2}\frac{\delta[C]}{\delta t} \quad \text{or,} \quad \text{Rate} = \frac{\delta[D]}{\delta t}$$

General: $\alpha A + \beta B \longrightarrow C + \eta D$

$$\text{rate} = -\frac{1}{\alpha}\frac{\delta[A]}{\delta t} = -\frac{1}{\beta}\frac{\delta[B]}{\delta t} = \frac{1}{\gamma}\frac{\delta[C]}{\delta t} = \frac{1}{\eta}\frac{\delta[D]}{\delta t}$$

So and we discussed reaction rates and stoichiometry relation between stoichiometry and reaction rate and the relation was like pretty much like this for a general reaction. You can write like this stoichiometry alpha, beta, gamma and eta. These are the stoichiometry so you can write; it can relate this for a balanced chemical reaction.

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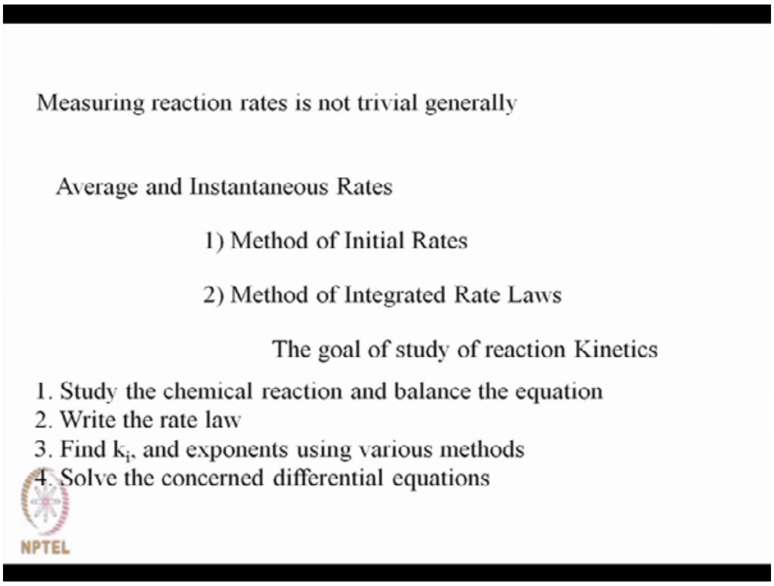

Measuring reaction rates is not trivial generally

Average and Instantaneous Rates

1) Method of Initial Rates

2) Method of Integrated Rate Laws

The goal of study of reaction Kinetics

1. Study the chemical reaction and balance the equation
2. Write the rate law
3. Find k_i, and exponents using various methods
4. Solve the concerned differential equations

Next measuring of reaction rate next question which we discussed was, how to measure the reaction rate. And, it is not very trivial you know sometime it is difficult to find it if it is a very slow reaction. Then, maybe it is easy to find out but, it is a if it is a moderately fast reaction then maybe various methods can be employed like one is method of initial rates. That is, at the very you know you can plot concentration versus time and you take slope at different times; so you can this is concentration versus time. So, that will give you give you the you know that will give you the rate maybe at different instants maybe there are there are methods that that I already discussed method of integrated rate loss you device the rate law and then you integrate I mean if you device your differential equation and then you integrate to find a relation between the concentration of your reactant and time and then you know you put your put in your necessary inputs and then find out the rate constants that maybe another way. So, the goal of study of reactions kinetic is the study of the chemical reaction balance the chemical equation write the rate law find respective the ith rate constant exponents. I mean, exponents using various methods like methods of initial rate method of integrated rate laws and so on I discussed so many methods of finding out and then solved the concerned differential equations like that will you know, that will end up in getting you the information related to the kinetics of a particular reaction rate constants rate law half ( ) and then also of course, the plots concentration versus time maybe (( )) concentration versus time.

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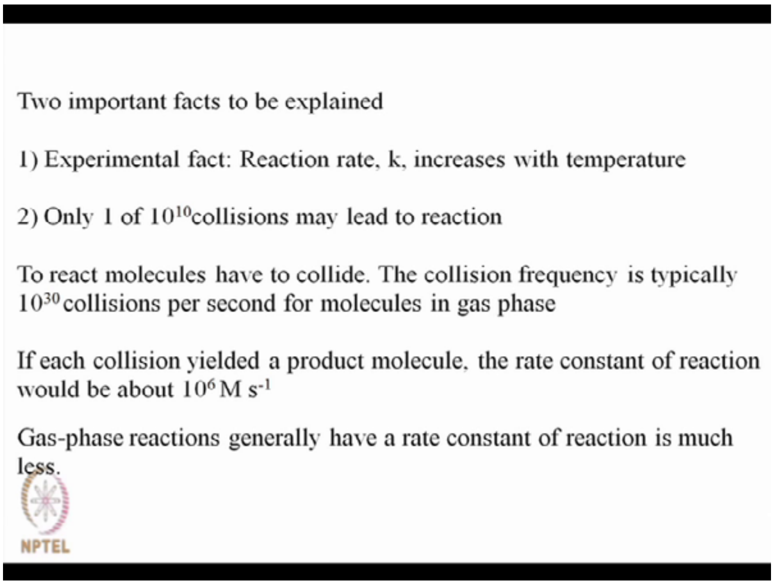

Two important facts to be explained

1) Experimental fact: Reaction rate, k, increases with temperature

2) Only 1 of 10^{10}collisions may lead to reaction

To react molecules have to collide. The collision frequency is typically 10^{30}collisions per second for molecules in gas phase

If each collision yielded a product molecule, the rate constant of reaction would be about 10^6 M s^{-1}

Gas-phase reactions generally have a rate constant of reaction is much less.

Now 2 important facts that has to be explained whenever we deal with any chemical reaction: the experimental fact is reaction rate that I mean, rate constant increases with temperature, why it is increasing? So, we should have a have a justification of that and another important point that 1 out of 10 to the power 10 collisions may lead to reaction so there are so many collisions but, not all of them are effective.

So, to react molecules have to collide and the collision frequency is typically 10 to the power 30 collisions per second for molecules and gas phase and if each collision yielded a product molecule then, the reaction rate could have been 10 to the power 6 mole per second or even more. But, in you know in reality gas phase reactions have much less value like maybe 10 to the power of 1 maybe one mole per second like that so, these are much less.

So, in order to explain this fact so we have to we have to have justification why it is like if it is based on collision theory then why it is so less what are the factors why to when temperature is increased rate constants are increased and if you if you rise the temperature if you increase the temperature by 10 degrees then rate constants are generally increased by 2 to 3 times, a factor of 2 to 3. So, this we wanted to explain this we wanted to justify based on you know certain available physical models; so these are the 2 important things; that we should have in our minds.

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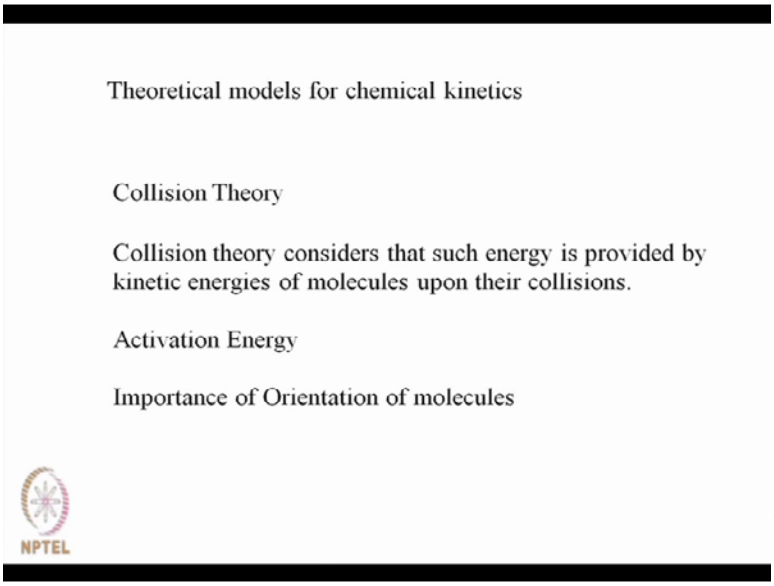

Theoretical models for chemical kinetics

Collision Theory

Collision theory considers that such energy is provided by kinetic energies of molecules upon their collisions.

Activation Energy

Importance of Orientation of molecules

Theoretical models as I told you, that we used different available theoretical models to justify. One is very you know, popular that is collision theory based on kinetic molecular theories of gas that whenever you have a container full of gas molecules then, there will be collision between them and it is thought that collision is responsible for the reaction to occur. That is the postulate that collision is responsible for reaction and next question comes that that whether all collisions are effective because, as I told you that there are you know there are only out of 1 to the power 10, one collision maybe you know fruitful so why it is so.

So, that means there must be something inherent so that we discussed that not all collisions are effective. Collision theory considers that such energy I mean, the energy which is required for reaction to occur is provided by kinetic energies of molecules upon their collision. So, that means for a reaction to occur, a definitive amount of energy must be must be supplied and then, we introduced the concept of activation energy. What is activation energy? Activation energy is the minimum amount of energy that is required for the reaction; I mean, that must be acquired by the molecules or the atomic species to undergo chemical reaction and importance. Here, one more important point is that the orientation is very important; I mean suppose, if you have a collision of this sort that may lead to chemical reaction but, if the collision is like this maybe reaction will not take place. So, that means orientation factor is another important thing that we you know we should include I mean, that has been included over there and so that means not all collisions are effective in bringing out bringing chemical reaction.

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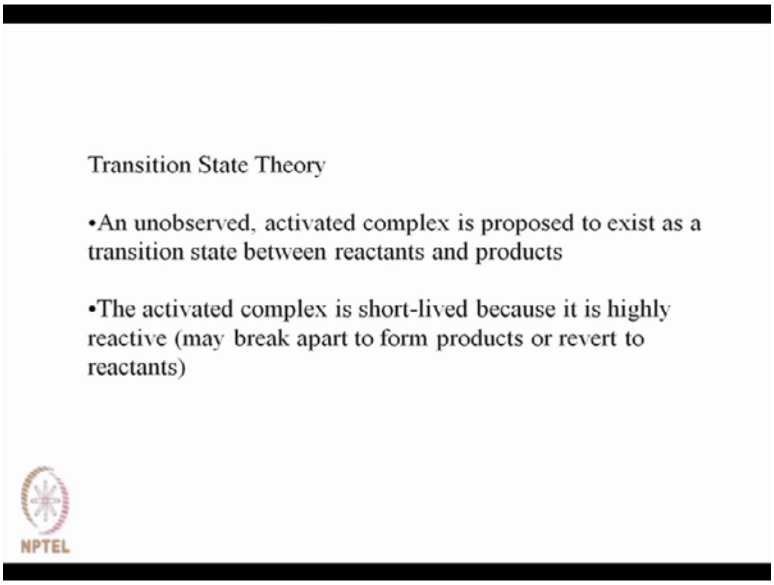

Transition State Theory

- An unobserved, activated complex is proposed to exist as a transition state between reactants and products
- The activated complex is short-lived because it is highly reactive (may break apart to form products or revert to reactants)

Then we introduced transition state theory and an unobserved activated complex is proposed here an activated complex is formed that is the that is the transition state and this transition state is there in between your reactant and product. And, it is thought that this activated complex is short-lived means it was it was thought in that way and it is slightly reactive and maybe out of many vibrational modes. One mode is converted to you know converted to translational mode maybe low frequency high amplitude mode. So, it is short-lived and it is in equilibrium with reactant and then, slowly it is converted to product that is out of its many vibrational modes maybe one is converted to translation which is responsible for the passage from reactant side to the product side. So, this way we tried to justify I mean, theoretically we tried to justify reaction I mean reaction rate and effect of temperature; I mean, implication of these theory I mean we tried to apply this theory to justify.

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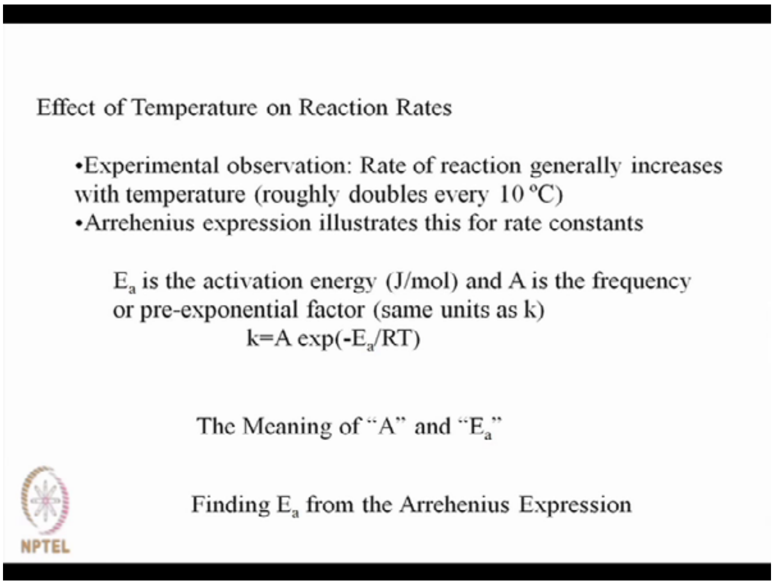

Effect of Temperature on Reaction Rates

- Experimental observation: Rate of reaction generally increases with temperature (roughly doubles every 10 °C)
- Arrehenius expression illustrates this for rate constants

E_a is the activation energy (J/mol) and A is the frequency or pre-exponential factor (same units as k)

$$k=A \exp(-E_a/RT)$$

The Meaning of "A" and "E_a"

Finding E_a from the Arrehenius Expression

And effect of temperature of course, we talked in terms of this Arrhenius expression k is equal to a into exponential minus E a by R T where E a is the activation energy and we discussed what is E a in terms of a in terms of the potential energy diagram like this.

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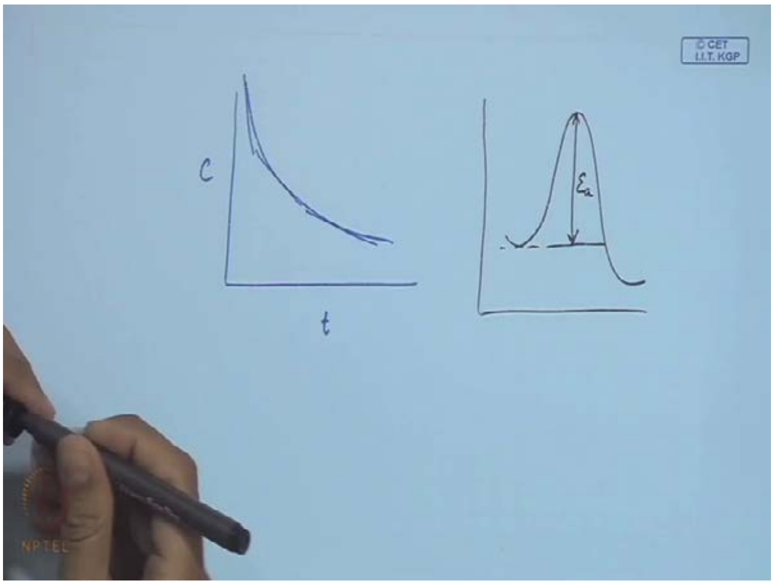

So this is your forward activation energy E a. This is E a and it is clear from this expression that if you increase temperature, since it is minus e a by r t so k is going to be increased so using this expression using this and e a is called the activation energy it is in kilojoule per mole or maybe in joule per mole and a is the pre-exponential or maybe the frequency factor now this using this expression you know we can find out I mean the activation energy by doing the experiment by carrying out the experiment maybe at 2 or 3 different temperatures. I mean, we find out the rate constant at 2 to 3 different temperature and then we plot l n k versus one upon temperature which will you know from the from your like from the plot you can find out this activation energy that is from the slope you can get the activation energy and from the intercept you will be able to find out the pre-exponential term so it is indeed interesting that we are able to find out you know, the activation energy that is the barrier height which is a very important thing very important parameter in chemical reaction.

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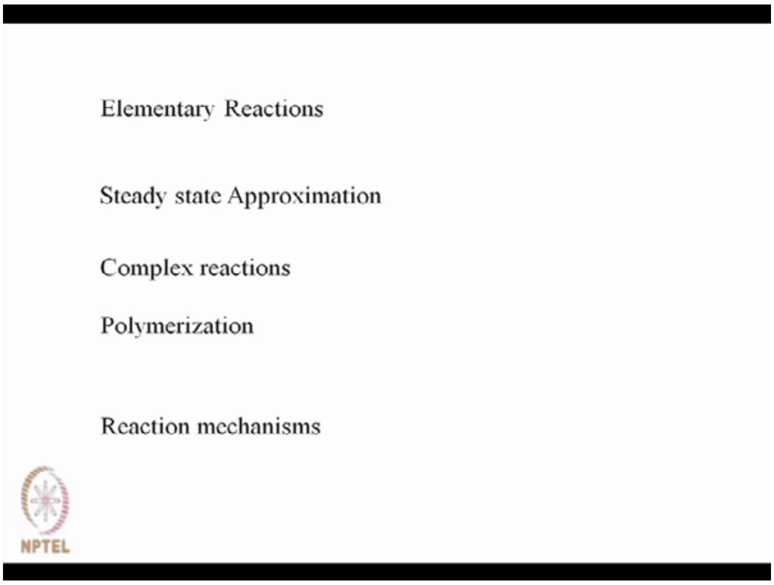

Elementary Reactions

Steady state Approximation

Complex reactions

Polymerization

Reaction mechanisms

We discussed then, we discussed elementary reaction and whenever there is a question of elementary reaction then comes the question of order and molecularity. So, order and molecularity is basically order is an experimentally determined quantity it is the sum of the power terms that is involved in the rate expression and it can be fractional but, molecularity is the is the number of species that is involved in an elementary state so it has to be it has to be a whole number it cannot be fractional so bimolecular, unimolecular you know reactions could be there and we in that heading we discuss this unimolecular Lindeman mechanism and its pressure dependence of reaction.

That we also discussed then whenever there is elementary set of elementary reaction then comes the question of steady state that is a reactive species which is responsible for further reaction to proceed that is in that is in equilibrium I mean, that is that is that will have steady state that is whose concentration should not change with time. So, we apply steady state approximation to find out the rate expression and we using that we can find out the rate equation for some complicated reaction that is having many steps that is for complex reaction then we discussed polymerization reaction so maybe radical polymerization reaction we discussed this thing in in detail and with all these with all these ideas like we came to came to reaction mechanism that is mechanism for chemical reaction like if you think of ah think of say hydrolysis of ester so whether protonation of your if it is an acid catalyzed reaction whether protonation onto the carbonyl oxygen is the rate limiting step or the attack of your nucleophile is the rate limiting state so there are various ways you can you can you can find out whether I mean which one is the rate determining part I mean rate determining state. So, from that you can you can tell I mean whether the you protonation or maybe the nucleophilic attack is the slowest step or not. So, that gives you the idea of I mean that gives you pretty much what is the what is the mechanism of a of a reaction and also we talked about photochemical reactions where photon is you know, involved photon is one of the ingredients. I mean, maybe you can think that photon maybe your basically reactant so when you know when you shine your substance with photon maybe it is it is photo excited. Then, photo excited substance I mean, chemical maybe it undergoes some reaction maybe pericyclic reaction maybe photochemical you know transformation where photon is involved.

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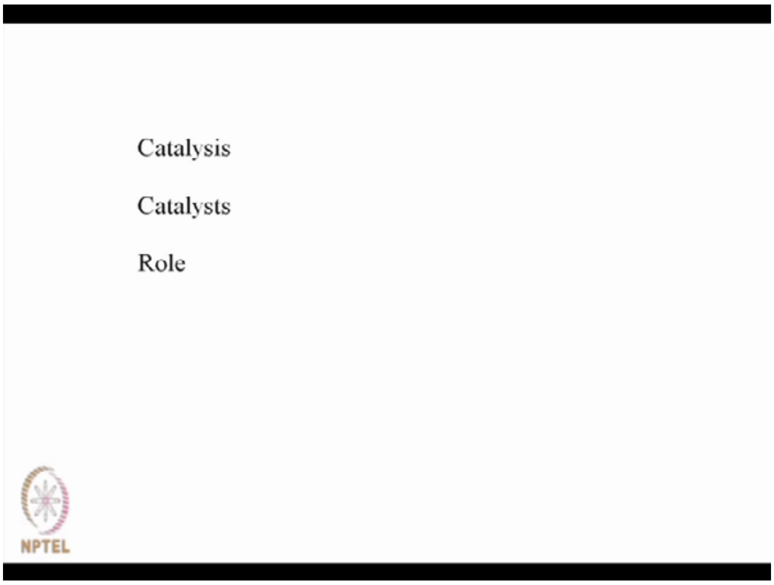

Catalysis

Catalysts

Role

Then we discussed you know catalyst and catalysis and its role in various like various places so catalysis is you know that catalyst basically provides an alternate path having I mean, requiring lesser activation energy and thereby rate is increased. I mean, if activation energy is less naturally you know rate constant I mean, if you recall Arrhenius expression. So, if activation energy somehow in you know, reduced then rate is expected to be more so catalyst is important. So, it provides alternative path so catalysis and catalysts so many types of catalysts are there maybe homogeneous catalysts or maybe heterogeneous catalysts that they those are used in industrial synthesis maybe like I discussed ammonia and other synthesis. So, that they are means heterogeneous catalysts are used in homogeneous catalysts there are plenty of examples and this is where your role of catalyst is very important; so we also discussed biocatalysis.

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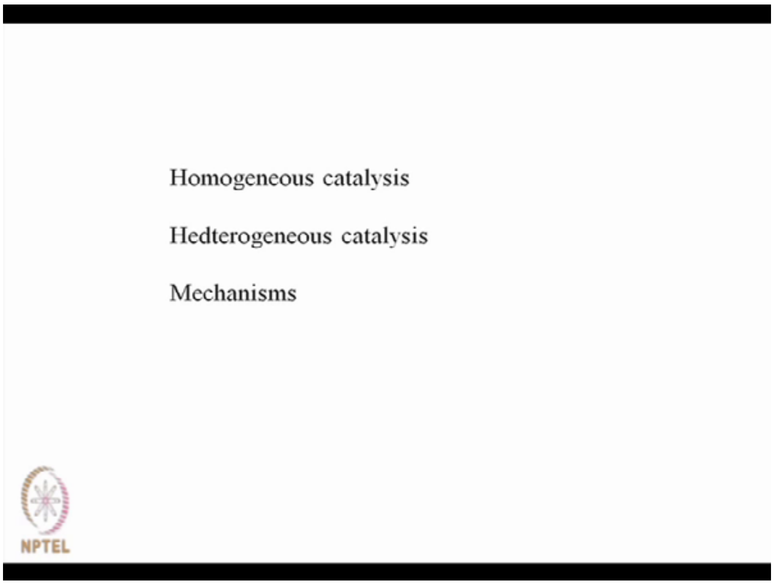

Homogeneous catalysis

Hedterogeneous catalysis

Mechanisms

There is a typo anyway heterogeneous catalysis homogeneous catalysis and mechanism mechanism of catalysis that we also discussed.

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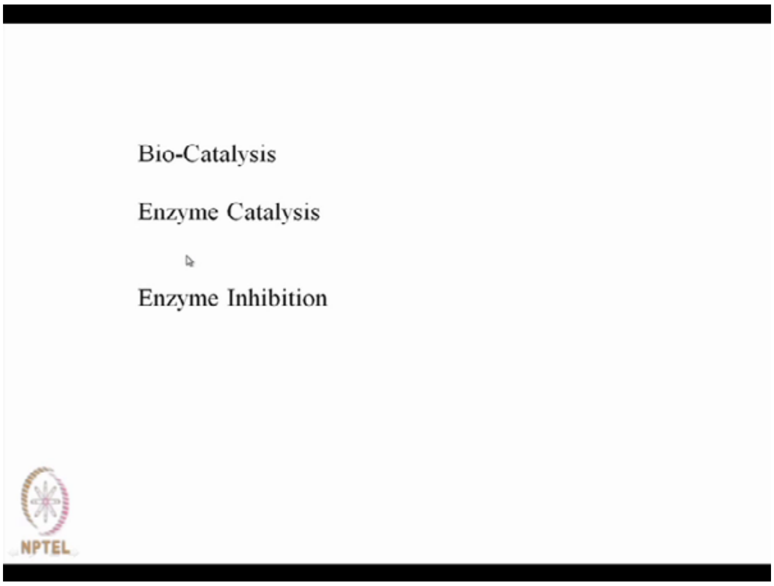

Bio-Catalysis

Enzyme Catalysis

Enzyme Inhibition

So, when it is the question of catalysis mechanism catalysis we discussed bio-catalysis. Bio-catalysis means, in that case, catalyst is a biomolecule large biomolecule it is a protein called enzyme so it has got a specific you know structure which binds or maybe it has got a specific pocket which binds your you know, this substrate into its pocket and then it does the reaction. And then, when the reaction is completed then it is released so this way it is used up so catalyst is used up it is regenerated and then it is used up. So, it is a cyclic way and we also discussed you know, enzyme inhibition like you know means these inhibitors are basically you know they tend to impair enzyme action. That is catalyst catalyst's action so we discussed this in detail so it is this part is also you know discussed.

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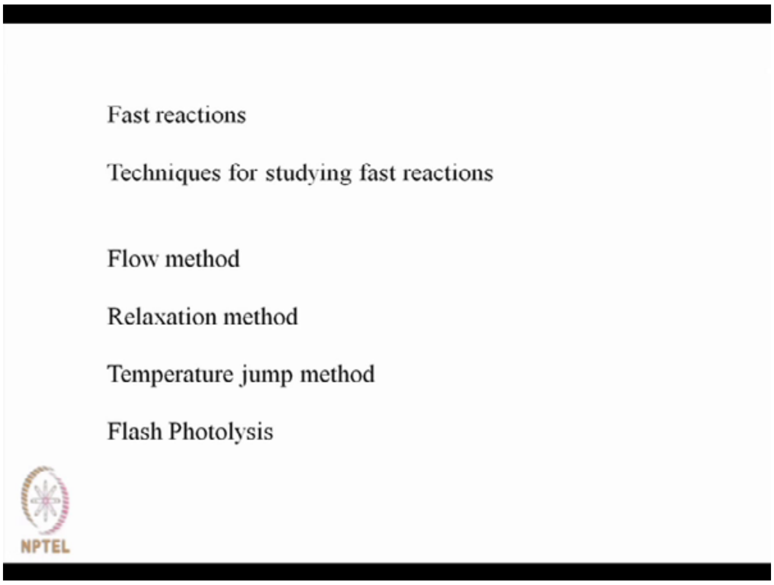

Fast reactions

Techniques for studying fast reactions

Flow method

Relaxation method

Temperature jump method

Flash Photolysis

We discussed fast reactions fast reactions means like as I told you, that when the reaction is very fast then you know ordinary methods like ordinary methods like you know what we do in laboratory burette, pipette, then collar reactions maybe titration, these are not you know very useful because, the moment you start doing your titrations by taking out some amount of ( ) by that time your reaction is over. So, titrimetric or you know classical you know classical methods are not very useful. That is why you have to we had to means device alternative way alternative ways means like techniques; alternative techniques like flow methods like stopped flow, plugged flow, these are the methods that I already have discussed and it may you know, use absorption technology. I mean, technique or maybe emission spectroscopy relaxation methods are also used. Temperature jump methods are used and last one which I discussed in detail, that is a flash photolysis and the modern version of it is laser flash photolysis I discussed and typical time resolution is much improved. But, only point is that you know your substance; you know that should absorb at a given wavelength. Otherwise, you cannot detect it; your product has to absorb so that it relies on the applicability of spectroscopic determination of the chemical, I mean, of the substance which is generated due to chemical reaction. So, flash photolysis is a very you know efficient, method by which you can you know you can look into the fast processes fast means moderately fast and its time resolution it is you know determined by electronics used maybe the detector and typical time resolution and also of course, the laser pulse width and like it is typical of the order of several nanoseconds like about 5 to 10 nanoseconds. Generally, India glazers - pulsed India glazers are used for laser flash photolysis and it’s time resolution is several nanosecond that is not below nanosecond.

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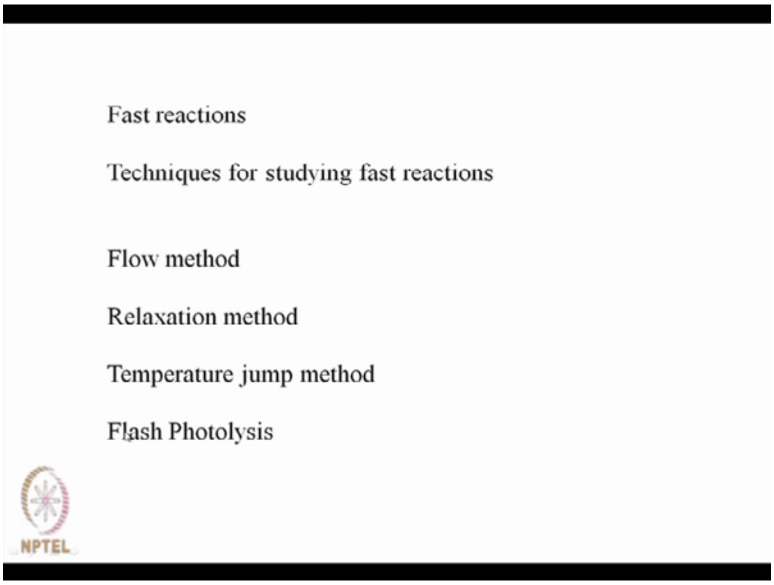

Fast reactions

Techniques for studying fast reactions

Flow method

Relaxation method

Temperature jump method

Flash Photolysis

Then we you know talked about this ultrafast processes because when it is the question of time resolution in flash photolysis then we are limited by the detection system and also by the laser pulse so flash photolysis you know it is flash photolysis you know it is it is a bottle neck I mean general flash photolysis so we had to use we have to have some modern version of it which is called a pump probe technique where you use even faster lasers even faster lasers like you know picosecond lasers or maybe femtosecond lasers and using that I mean, due to the advent of fast lasers and of course, when laser came into science I mean into the use of you know research, I mean mankind.

Then you know the overview of you know detection limit I mean, overall detection limit is much increased I mean limit is increased means we can go down to faster times so, that you know flash photolysis is the first step. Laser flash photolysis is a little bit further ahead and then ultrafast lasers advent of ultrafast lasers you know and their application in spectroscopy is very useful and in this under this heading we discussed this you know this pump probe spectroscopy where a pump laser is used. And, so it is a 2 color experiment; so using ultrafast laser we can do pump probe it maybe 2; color it maybe or it maybe one color and because of the faster timescale its bandwidth is more wavelength bandwidth is more. So, you can probe for more wavelengths and using this using this ultrafast spectroscopic techniques maybe using fluorescence of conversion and related techniques you can follow faster processes like solvation dynamics or maybe some rearrangement dynamics maybe excited state you know isomerization dynamics that you can follow very efficiently using ultrafast spectroscopic techniques. So, use of this ultrafast lasers you know you can probe transition state for which Ahmed Zivel is awarded Nobel prize in 1999. So, that is you know that is also using ultrafast spectroscopic I mean he used ultrafast spectroscopic techniques to probe this transition state. I know use of this ultrafast techniques we can really probe transition state I mean long time back when people started to think about the mechanism I mean mechanism and also the theory of reaction chemical reaction. Then, this transition state theory was implemented and after a long time after waiting for a long time after the advent of ultrafast lasers, we are now able to look into this transition states by means of ultrafast by using ultrafast spectroscopy. So, it is a you know ultrafast spectroscopy is a nice gift to mankind for probing such process fast processes which is completed within the persistence of vision much faster; you know much short in shorter time maybe several you know million times faster than the persistence of vision. So, long time back people even could not think of think of you know a technique which can probe maybe millisecond process but, now you think it is, it was like 10 to the power minus 3 second. Now, it is 10 to the power minus 15; maybe soft femtosecond, maybe attosecond. Techniques, I mean attosecond spectroscopy is emerging. So, attosecond techniques are you know slowly emerging means, it is faster than your femtosecond. So, we discussed you know probing means probing of transitions we gave some example.

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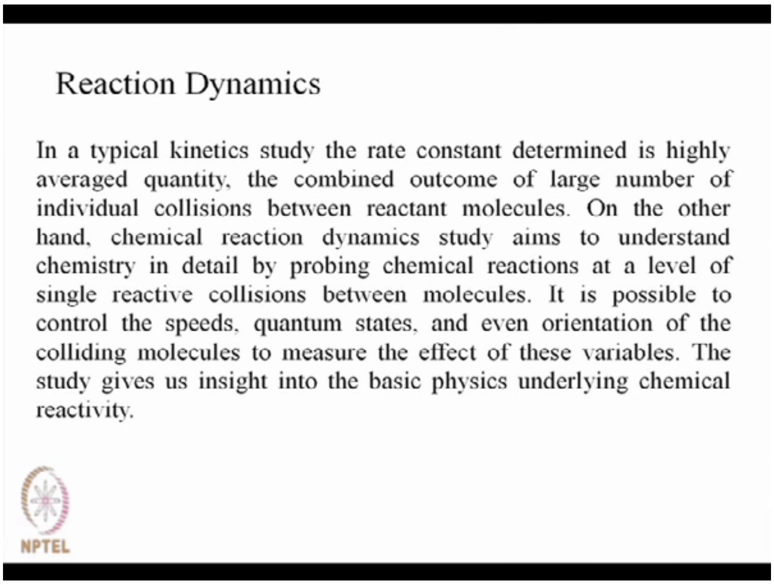

Reaction Dynamics

In a typical kinetics study the rate constant determined is highly averaged quantity, the combined outcome of large number of individual collisions between reactant molecules. On the other hand, chemical reaction dynamics study aims to understand chemistry in detail by probing chemical reactions at a level of single reactive collisions between molecules. It is possible to control the speeds, quantum states, and even orientation of the colliding molecules to measure the effect of these variables. The study gives us insight into the basic physics underlying chemical reactivity.

Next, we discussed this reaction dynamics. Now, why do we need means we discussed many things it appeared to you that maybe it is complete. I mean, you should not think of anything else; maybe measuring rate constant then, probing ultrafast processes, fast processes maybe you know probing your transition state, that is all we can think of. But, one important point that we must look into is in a typical kinetic study rate constant which is determined I mean, what we determine you know in laboratory like using burette pipette maybe doing some you know titrimetric method the rate constants which are determined is highly and average quantity, it is an average quantity. It is an you know in symbol average quantity. The combined outcome of large number of individual collisions between reactant molecule; so there are there are number of collisions. So, it is the overall thing whether you know some collision is very rigorous or maybe some collisions are very less effective so everything it is the combined you know combined effect so everything it is in average form it is basically an average quantity. So, we have no idea it is there is no microscopic description as I as I started with that there are 2 aspects one is microscopic aspect another is macroscopic aspect. So, determination of rate constant it is an average quantity. It is a macroscopic aspect; we do not have any idea of your microscopic you know things like speed. Actually, understanding at the molecular level we have no you know understanding on the other hand, this chemical reaction dynamics study has the aim to understand chemistry in detail. So, we want to know chemistry at the molecular level, not in the you know average level not in the gross level but, in the you know molecular level at the molecular level so we it aims to understand chemistry in detail by probing chemical reactions.

Now, we have to probe chemical reaction at a level of single reactive collision between molecules at a level of single reactive collision between molecules. We want to approach to understanding at the molecular level and it is possible to control you know, the speed the quantum states like as I discussed like quantum state selection even orientation of the colliding molecules to find out the effect of these variables. So, these are the variables I mean, speed is one variable, quantum say selected quantum state then, orientation these are very important variables that can control the chemical reaction, so that we want to want to have a clear-cut understanding at the molecular level. It means, how this is going to affect the overall thing and preferably in the gas phase? It is easy to you know control so this study gives us insight into basic physics underlying chemical reactivity. So, this way we want to probe the you know, probe the basic physics underlying chemical reactivity. I mean, from the purely physical aspect we want to study what is the orientation. I mean, what is the orientation factor or maybe what is the speed factor or whether the reaction occurs in the ground state or maybe occurs in the vibrationally excited state. If it occurs in the vibrationally excited state then, what happens like I discussed one thing like early transition state and late transition state. What is happening when it is you know vibrationally excited or it is translationally excited? These are the things that that gives you a important idea about the nature of the potential energy surface which is involved in the chemical reaction. So, potential energy surface is important so, earlier when we talked about the energy of activation, it is basically giving you the barrier height but, it does not give you any insight of the you know nature of the potential energy surface involved.

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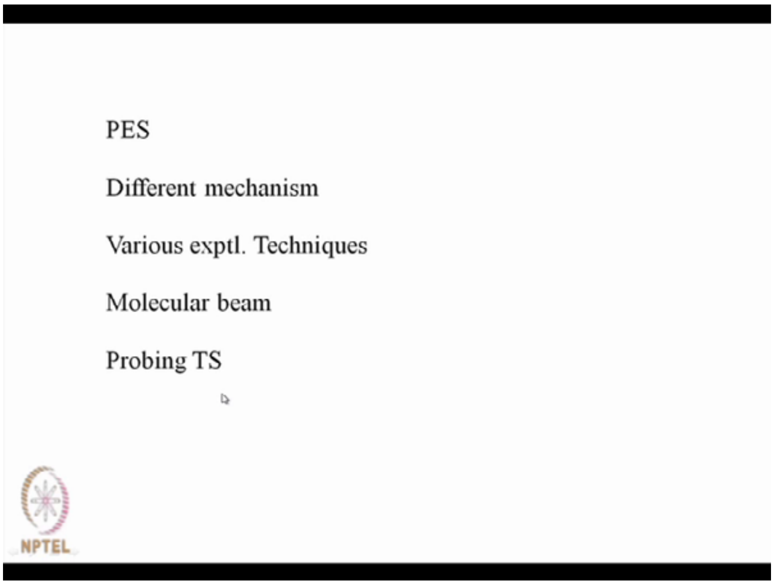

PES

Different mechanism

Various exptl. Techniques

Molecular beam

Probing TS

These studies I mean, this reaction dynamic studies will give you the potential energy surface I mean, the nature of the potential energy surface involved whether it is it has got single minima or it has got a double minima or something else; whether there is a level crossing I mean whether there is a crossing with you know with an unbound state then, what is going to happen? Like I gave you the example of sodium iodide decomposition, there is there is a crossing between you know this ionic potential energy diagram and also your covalent one at certain distance. They are crossing; so, if weight packet is moving back and forth and if it is appropriately excited I mean in the vibrationally excited so that it can cross you know it can reach this crossing point so that, your ionic surface I mean ionic from it means the your weight packet can be transferred from your ionic surface to the covalent one and thereby, it may undergo dissociation.

These aspects you know, are very important. This gives you the idea of the potential energy surface. So, looking at the potential energy surface is very important I mean very important aspect in molecular dynamics I mean, molecular reaction dynamics. This is very important; so that is why we intend to study ah reaction dynamics so it gives you the idea of the I mean nature of the potential energy surface involved and what is the minimum energy path. So, means these are the things that you can, we can know different mechanisms we discussed like harpoon mechanism. As for example, harpoon mechanism we discussed then you know rebound dynamics then and so on. And, various experimental techniques like molecular beam we dealt with then also like ultrafast techniques these are very important with respect to you know studies of reaction dynamics so we all dealt with these things and molecular. Whenever it is the question of molecular beam then it is a crossed molecular beam experiment so crossed molecular beam like 2 beams are you know cutting like this and your detector is somewhere over here, so that, you can detect the scattered product and whenever the question of potential energy surface, we can we can have a you know quantum mechanical way of calculating it although we have not discussed that in detail.

So, molecular beam experiment and other experimental techniques and special detection techniques that you all you know, we discussed all these things and also, how this beam angle you know changing the beam angle what is the outcome that we also have discussed. So and also probing the transition state these are these are the important you know things that we discussed under the heading of your molecular reaction dynamics and lastly, we also talked about this corrosion kinetics I mean, not in detail but, we gave you the idea of corrosion kinetics I mean, how to measure corrosion etcetera.

So, these are these are the things that we have talked about here. At the end, it appears that we go back to that slide I mean, early slide again that that chemical kinetics it is it is the aspect which aspect in important aspect in chemistry that affects everyday life. As I told you, this movement of an insect it is also a chemical reaction because, it requires energy. We move from one place to another it requires energy; so that energy is given by that energy, given by some reaction that is some reaction happens within our body I mean within cell that generates the energy and that is used up to do some work. So, again it is thermodynamics because of chemical reaction energy is released and that is used up for doing some work. So, it is you know conversion of chemical energy into you know mechanical energy. Here also means, like when we require to walk fast then fast generation of your energy is required. That means, there must be some machinery which controls, which you know measures that need which you know which monitors the need that we now we need more energy. I mean, energy output I mean rate of output energy I mean rate of giving out energy is more when you need to walk fast. Again, that means again it is kinetics; we need faster kinetics. So, that is why kinetics is a very important thing like something is growing here, like we grow up it is also it has got kinetics. So, these are very important things; these are very important aspects I mean, kinetics and specially and it is a broad heading. It is you know rate process so how these rate process influence our life. How these rate process influences you know other processes and how this rate processes can be influenced by external agents? How can we monitor? How can we monitor such rate processes? Can we see the transition state I mean, can we see the transition state which we have postulated longtime back? We answer is yes, we have been able to probe; that is the ultimate answer that we, yes we have been able to probe catalysis is another important thing and that changes our life. Anyway, that is all about this course. I hope you enjoyed and if you have any question you can you can write to me about this topic.

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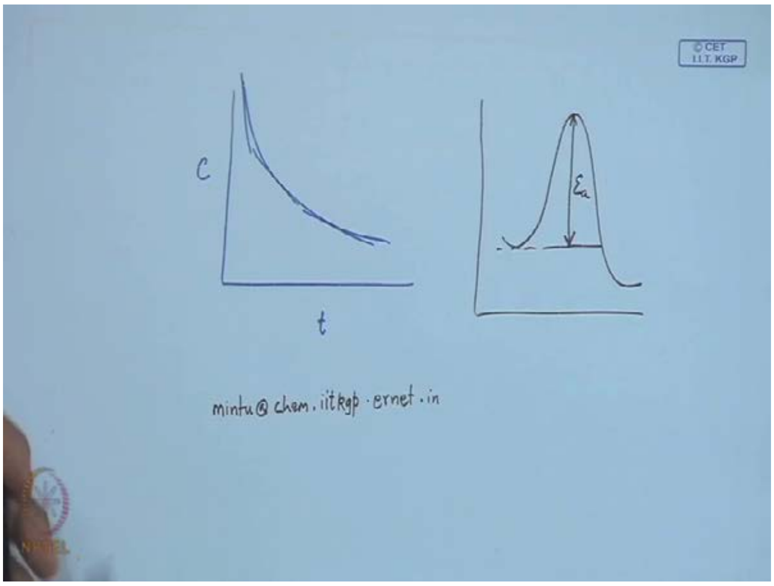

So, you can write, my e-mail address is mintu @chem dot I I T k g p dot e r net dot in; questions are welcome. I hope you enjoyed this series of lecture; thanks for your patience, I wish you all the best; thank you.