Rate Processes

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Module No. # 01

Lecture No. # 21

Fast Reactions

Hi. Good morning everybody. So, today we are going to talk about fast reactions; techniques for studying fast reactions.

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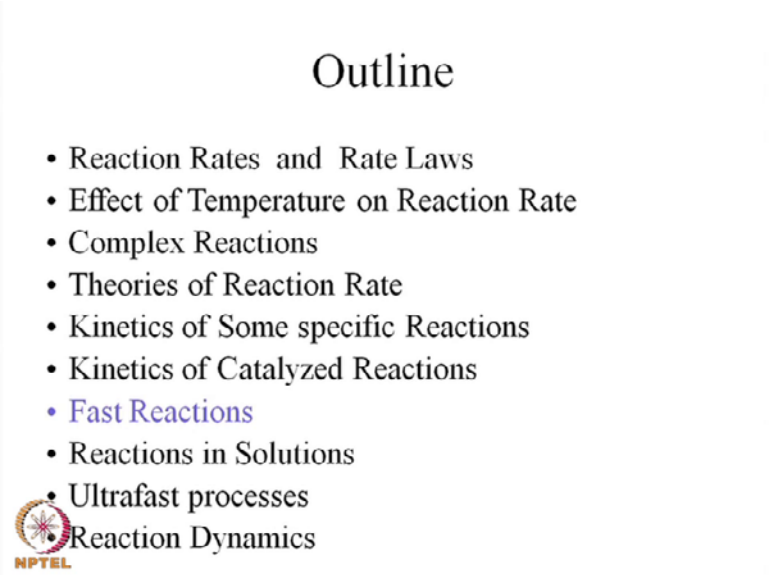

So, let us see again the outline that we have talked about reaction rates, rate laws, effect of temperature on reaction rate, complex reactions, theories of reaction rate, kinetics of some specific reactions, kinetics of catalyzed reactions. So, now, today we will talk about fast reactions.

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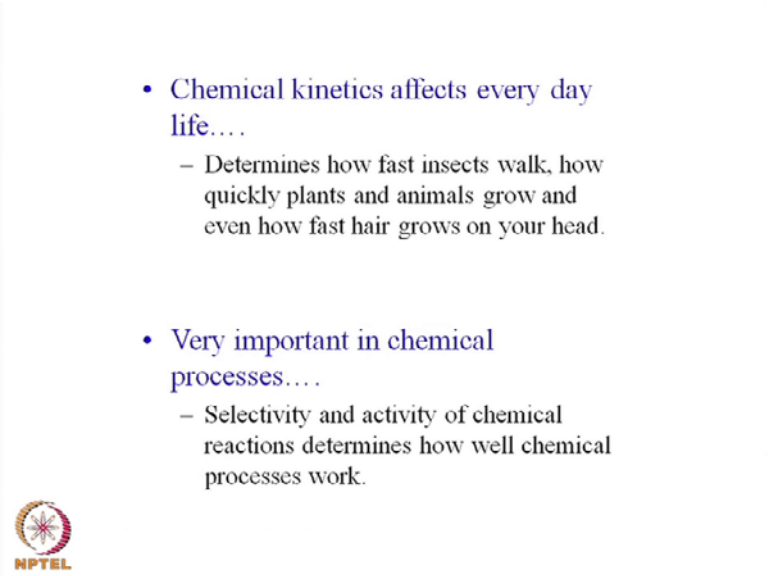

Now, as we all know that chemical kinetics affects everyday life, determines how fast insects walk, how quickly plants and animals grow, even how fast their hair grows; I mean how fast hair grows on your head; that is also a part of your this chemical kinetics. Very important in chemical process; that is, selectivity and activity of chemical reactions determines how well chemical processes work.

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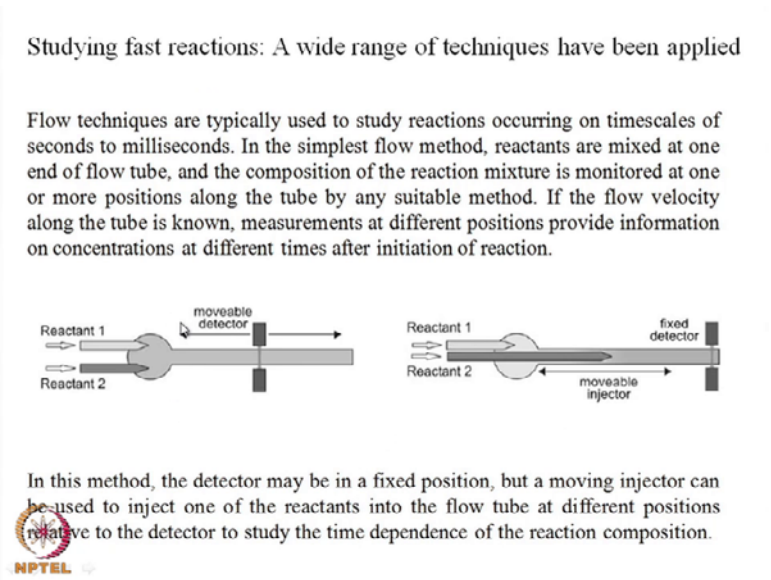

Anyway. So, reactions can be very slow reaction, it can be moderately fast or it may be very fast. So, slow reactions are easy to you know follow; that is, may be with time, you can follow the concentration of you know some reactant or may be some product.

Suppose one reactant is depleted. So, you can find out the concentration if it is depleted slowly. If it is depleted slowly, then suppose taking first reading and whenever you are ready to take the second reading, by the time gap, if it is completely depleted or may be even before the start of your measurement, if all the reactants are depleted, all the reactants are consumed, then it is difficult. You know it is, you know why by conventional method, you cannot you cannot find out that; I mean, you cannot follow the chemical reaction; I mean in terms of kinetics; you cannot follow the kinetics.

So, there are a wide range of techniques available to study fast kinetics, that is thing is that that reaction happens in a very short period of time. In conventional titrimetric method, you suppose consider that the reaction of ester; that is, hydrolysis of ester by acids or may be by alkali. So, what you do? You take some ester in a conical flask, say if methyl acetate or may be ethyl acetate, you take in a conical flask, then what you do? You add your; that is re-agent; I mean, your acid or base, that may be your catalyst or may be in or other way, you can you can take your acid or base in your conical flask and then half discharge. Take, note down the half discharge of your ester.

And then what you do, after it is mixed thoroughly; that is, with the moment the half discharge time is noted, that is your 0 time. So, then you soil the reaction mixture so that your reactants; that is, acid or alkali and your ester is mixed thoroughly and then maybe you wait say for four to five minutes, take out some definite amount of aliquot; may be 5 ml, and then you discharge that 5 ml aliquot into a ice cold water to arrest the reaction and then you tight fit with I mean; it is it is basically an acid base titration with an appropriate indicator.

But the thing is that between 0 and 5 minutes, if all the reactants are depleted; that is, if most I mean say ninety percent of the reactant concentration is depleted, then what will you do? You will be getting only 1 point. I mean 1 point on your graph paper. So, that is not sufficient to follow the kinetics. So, that is the real problem if your reaction is very

fast. So, in a moment, everything is you know completed, all the reaction is completed. So, it is difficult using the very conventional method to follow the chemical kinetics of the first reaction.

So, in this case you know, a number of techniques are available like flow techniques. These are typically used to study reactions occurring on time scales of seconds to milliseconds; millisecond means 10 to the power minus 3 second. So, that is, 10 to the power minus 3 means 1 by 10 to the power 3 second; that is, 1 by thousand part. 1 part; that is, if you divide your 1 second into thousand parts, and then may be 1 part will be a 1 millisecond. So, in the simplest flow method, reactants are mixed at one end of flow tube here; one end of flow tube and the composition of the reaction mixture is monitored at one or more positions; that is, here you know the reaction mixture is flown this way. So, here, you can monitor the composition of your mixture by a movable detector.

So, that is monitored, that is, composition of the reaction mixture is monitored at one or more positions along the tube by any suitable detection method. So, you mix over here, say you this is your reactant 1, this is your reactant 2, this is an injection method. So, you inject into this reaction vessel, and then you allow you continuously add you continuously inject your reaction; I mean the reactants into this chamber. And it is allowed, I mean the reaction mixture is allowed to flow through this tube and you detect by suitable method the composition of the reaction mixture.

Now if the flow velocity along the tube is known, measurements at a different position provide the information on the concentration at different times after the initiation of the reaction. So, the moment you mix; this is your initiation of the reaction, and then it is flowing through. So, flowing through this tube and then you measure. So; that means, if this flow rate is known, then you should be able to find out the time dependent concentration along this to… That is the time dependent concentration of certain reactant or may be certain product.

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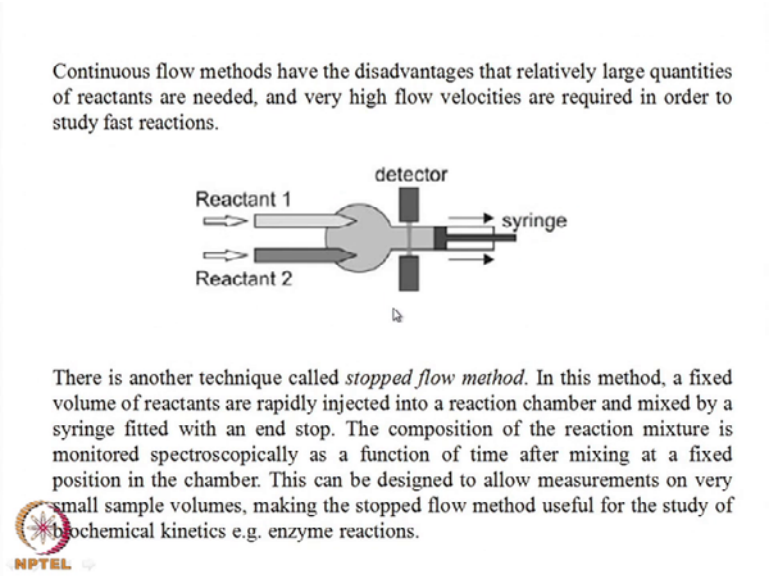

So, this is one way. So, in this case, your detector is movable. In other case, the injector can be movable; that is, your detector is fixed and the injector can be movable. It may be moved from maybe this position to this position. So, in the second method, this detector may be in a fixed position, but moving injector can be used to inject one or more reactants into flow tube at different positions relative to the detector to study the time dependence of the reaction composition.

So, there could be; you can have two ways. In one case, your detector is movable and in the other case, your one of the injectors or may be both can be moved. So, this way you can find out the time dependent concentration. So, that is the goal of you know studying I mean; to know the kinetics, you should know the time dependent concentration of certain reactant or may be product.

So, it is a continuous flow method I just talked about. So, continuous flow methods have the disadvantage that relatively large quantities of reactant are needed. And very high flow velocities are required in order to study fast reactions. For fast reactions, since it is occurring very fast, so to compete with that speed, you should pass your reaction mixture very fast through your flow tube. So, that is a difficulty you know that is a difficulty.

So, that is why I know another modified version of this flow method has been devised. So, it is called another method is just called the stopped flow method. In this method, a fixed volume of reactants are rapidly injected into a reaction chamber and it is mixed by a syringe fitted with at the end stop. So, what is happening that here, it is fitted. This syringe is fitted. It is movable may be so, it is stopped; flow has been stopped at this point.

And now what is happening you are injecting. So, slowly, it is going out; this syringe is going out. So, you are injecting that is injecting this way, and this syringe is going out. So, your injectors here and here; these two are pushed in and it is pushed out. So, the composition of the reaction mixture is monitored here by the help of a detector spectroscopically as a function of time after mixing at a fixed position in the chamber; that is, may be here, at a fixed position. This can be designed to allow measurement on very small sample volumes, making the stopped flow method very useful for studying the biochemical kinetics as for example, enzyme kinetics or enzyme reactions.

So, in previous method, I mean flow method, it is continuously flown out the mixture, but here, you see that there is a syringe which is stopping the flow and slowly it is coming out as your reactant syringes are pushed in. So, it is a modified version and it requires lesser volume of your reactant. So, it is now widely used to study biochemical kinetics; the reactions which are occurring very fast. Very fast reactions can be followed. Not only biochemical reactions, may be other reactions as well can be studied using this stopped flow method. So, these two methods are dependent on the, I mean is based on the flow technique.

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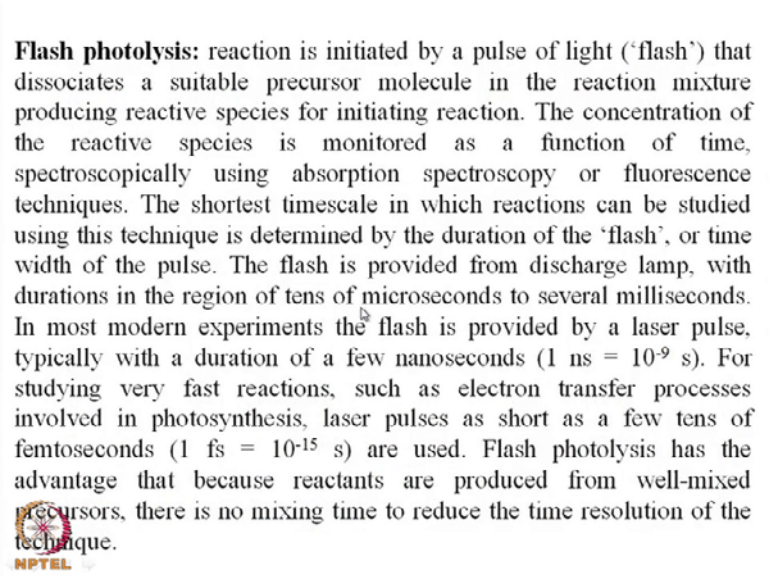

Next is another method which I will discuss may be in a later part of our talk, may be in a next talk in details, but here we are just I am just trying to give you the idea of another technique for studying the fast reactions. It is flash photolysis. I guess all of you have seen flash of light, whenever you use a camera to shoot I mean some photograph.

So, the moment you click, the moment you click, it flashes depending on whether you are using flash or not. May be not in day time, but may be may be when the day light is less or may be in the night time. You have to use a flash. Otherwise your objects are not visible. That is why you have to have you generate you know you generate some light source, I mean you use some lights so that your objects are visible. It is the artificial way of lighting view your objects. So, if you click, it flashes. So, that is called a flash.

Now this flash can initiate a chemical reaction; may be some photo-chemical reaction can be initiated with this; the reactions which are you know very much dependent on the on the amount of photon that is falling on the reaction mixture. So, flash. So, this flash is used and depending on the duration of the flash, if it is very fast; that is, clicks and then it goes, may be or may be some time it remains say for some period of time may be several milliseconds, it can it can it can stay.

So, depending on the stay time of this flash, whether it is long flash or it is a short flash, you can study different reactions, I mean reactions of different fastness or may be different differing in slowness. So, reaction, in this case, the reaction is initiated by a pulse of light. It is called a flash light like your flash of your used in photography. So, that dissociates a suitable precursor molecule in the reaction mixture producing reactive species for initiating the reaction.

The concentration of the reactive species is monitored as a function of time spectroscopically because spectroscopic methods are detection; detector detectors used in spectroscopic methods can be fast. They can detect I mean these detectors can detect your signal very fast; that is, it is time resolution is high compared to other things.

So, optical detectors are very useful in this case. So, that is why spectroscopic detection methods are used here. So, maybe it is using by using absorption spectroscopic; that is, absorbance as a function of time or may be fluorescence spectroscopy; that is, in that case, we monitor the fluorescence intensity as a function of time. So, fluorescence is basically you know getting up some photons out of some process. May be it is a physical process or maybe it is a chemical process. Chemical process may be a chemi-luminescence. Physical process is simply you know phosphorescence or fluorescence.

So, net thing is that you are getting some photons and you adjust measuring the photon intensity, I mean number of photons crossing per unit area. So, you are measuring intensity as a function of time. So, with the help of a photo detector, may be photo multiplier tube, may be photo diode. So, these two uses the simple concept of photo electric effect that when photons are falling on some surface, additional you know I mean secondary electrons are generated. So, those electrons are detected and a current is induced in the circuit. So, that is you know related to I mean that is carbureted with you know related to your amount of fluorescence that you are getting.

So, there is a one to one correspondence between amount of photons generated and the current you are you are getting in this in the electrical circuit. So, I may be spectroscopically or I mean absorption spectroscopy or may be fluorescence technique; the shortest time scale in which the reaction can be studied using this technique is

determined by the duration of the flash or time width of the pulse.

So, the thing is that in earlier days, when manual photography has been used, in that case, what is happening that if your flash is not synchronized is not synchronized with your shutter, then may be your photograph could look like that it is half illuminated and half dark because of the fact that the time for which this shutter was open is much you know it is happening that if this shutter is doing like this, it is moving and then coming back.

So, may be the time for which the shutter was half open, during that time there may be the flash was on and the remaining portion when the shutter was just closing, that time the shutter I mean the light was off. So, what has happened is that that during half shutter, the light was on means half portion of your photograph is illuminated and half is not illuminated.

So, that is why you know your shutter speed and your flash duration is very important and that is synchronization is very important. So that means, it is the width of your flash that determines your ability to follow a particular reaction or not, whether you will be able to follow a fast reaction or you would not be able to follow the fast reaction. So, that is why flash time is important.

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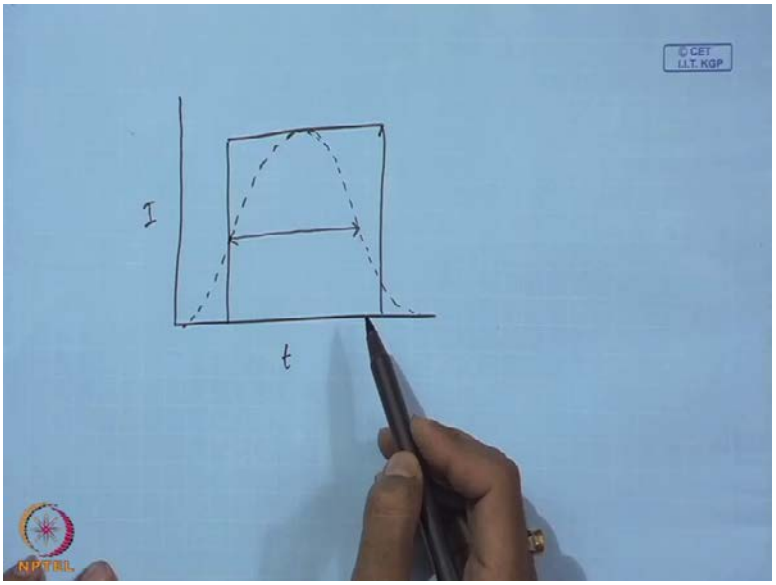

So, the flash it is determined by the duration of the flash or may be full width half maximum; that is, the time duration if you plot the intensity as a function of time like this, see this is your intensity this is time. So, your flash could be like this, it could be like this. There is a ON, then remaining steady for some time and then it is off or may be it can be like this. So, width means this is your full width half maximum. So, this width is a basically determining how fast you will be able to detect a reaction or not. So, that is width of your flash is very important.

Now earlier days, flash is provided from the discharge lamp with duration in the region of tens of microseconds to several milliseconds like discharge lamp, like you see, like in camera; similar to that, but in most modern experiments, the flash is provided by laser pulse.

So, in our next lecture, I will give you brief introduction of laser. So, laser is perhaps may be many of you have seen; that is, it is a laser pointer that is generally used in some demonstration, that is when some somebody is talking. So, laser pointer is used to point, I mean that is a intense dot of light that is coming out of a pin like substance like this and the laser light is coming out. So, you just point out where the portion you want you can highlight or may be in some laser show you can I mean you have seen perhaps; laser

light show.

So, where a you know lots of different types of a patterns can be generated So, this laser lasers can be pulsed or may be it can be continuous wave. I mean it stays with time or may be it goes on and off like that; that is a called that is called a pulsed laser.

So, typically, duration of a pulse laser could be nanosecond; 10 to the power minus 9 second or it may be even less. I mean may be femto second; 10 to the power minus 15 second. So, this laser pulse is very important. So, if you want to study very fast reactions, then in you may need to use femto second pulses or may be if it is moderately fast, you may need to use nanosecond pulses, but depending on the systems that you are using as the lasing substance, your wave length will be generated. It may be in IR region, it may be in visible, it may be in UV region depending on what type of material or what type of lasing system you are using. Anyway.

So, for studying fast reactions such as electron transfer reactions may be in photosynthesis, laser pulses as short as few tens of femto second; 10 to the power minus 15 seconds are used. So, that is why you can choose using different you know duration. Differing in duration of your pulse, you can choose you can choose your system, I mean whether it is a fast reaction.

If it is very fast reaction, you use femto second pulse. If it is moderately fast, then may be accordingly you can choose your light I mean pulse width. So, the flash photolysis has the advantage that because reactants are produced from well mixed precursors. There is no mixing time to reduce I mean there is no mixing time to reduce the time resolution of the technique and also since I mean the beam is generally falling on the sample, the reaction mixture at the at the middle, So, possibility of reactions on the vessel wall is minimized.

So, I will talk on this flash photolysis laser flash photolysis, now a days terms I mean laser flash photolysis now a days term. I mean previously, discharge lamps are used as the source of a flash. Now, a days, lasers are used.

So, I will talk in a more detailed about this flash photolysis and what is laser in a later part of I mean in another class.

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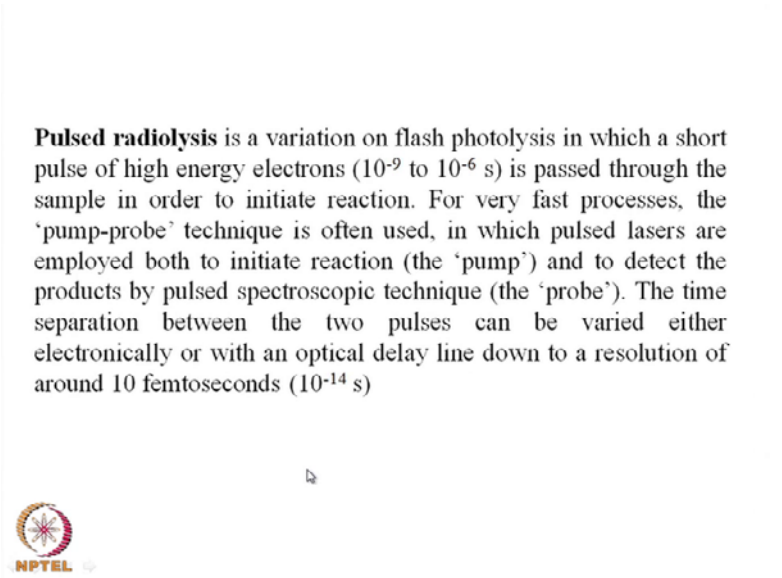

There is another technique like another variation of flash photolysis which is also used for studying the fast reactions. This is called your pulsed radiolysis. It is a variation of a variation of flash photolysis in which a short pulse of high energy electrons; 10 to the power minus 9 to 10 to the power minus 6 second duration is that much is passed through the sample in order to initiate the reaction. For very fast processes, the pump probe technique is often used in which pulsed lasers are employed both to initiate the reaction and also to detect the products by pulsed spectroscopic technique. The time separation between two pulses can be varied may be electronically or may be by using the optical delay line.

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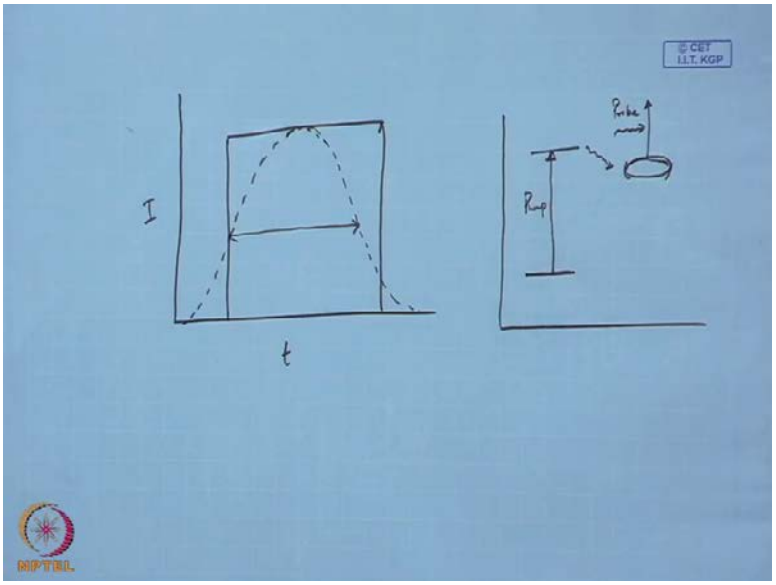

So, in one case, you pump with a laser generating your exited stretch species or may be reactive species like you know you have got your energy level diagram over here. Say this is your substance which is which is the reactant may be in not in the grounds it brought in the steady state.

So, here say you pump like you pump water from you know from the lower level to the upper level, may be may be in a in a housing complex and then it is stored in to your water tank. This is your pump. Then suppose this excited stretch species undergo some chemical reaction producing another species and say this species has got some absorption in another regions. So, another you know say this is your species. So, another probe laser is used to probe this one. So, this higher state absorption.

So, when you shine with another probe another probe light, so, what it is doing is that this probe light is absorbed by this species. So, reduction in probe light intensity has been used to monitor the extent of reaction on how much this reactive species is generated or may be time development of this species; that is, with time, how this the concentration of this species; this reactive species or may be the product is changing with time.

So, that is our goal. I mean to study kinetics, you need to find or you need to know the concentration of certain substance; certain may be it is reactant or maybe it is product in a way. How it is changing with time. So, if you know this time (( )), I mean time if you know the concentration as the function of time of that particular species, you will be able to know the kinetics, the rate of reaction rate constants.

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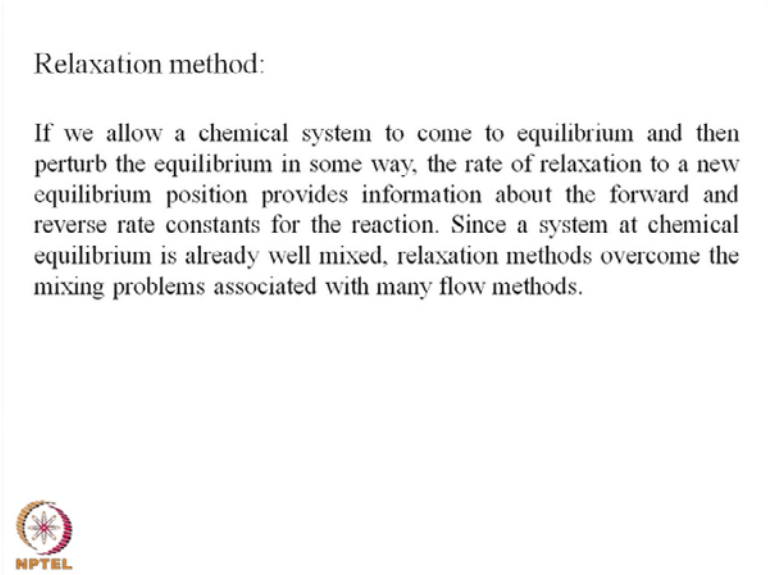

There is another method which is called the relaxation method. So, for studying fast reactions, if we allow a chemical system to come to equilibrium and then perturb that equilibrium in some way, may be suddenly which you do something may be you do rapid temperature change, may be rapidly you push the system external; that is, you put pressure or maybe you change the volume very fast. So, in some way in some way, you change the equilibrium. The rate of relaxation to new equilibrium position provides information about the forward and reverse rate constants for the reaction and since a system at chemical equilibrium is already well mixed, the relaxation methods overcome the mixing problem associated with any flow methods.

So, the system is in equilibrium initially. Say this is your equilibrium system and then what you do, you perturb. So, system is now is now perturbed. So, it will try to find out another equilibrium state in this perturbed condition.

So, it will tend to relax to a new equilibrium system. So, you want to want to want to follow that. You would like to follow that. So, it does not suffer from the problems of mixing associated with the relaxation methods; I mean associated with the flow methods. So, mixing problem is overcome in this relaxation method because flow methods have real problem of mixing.

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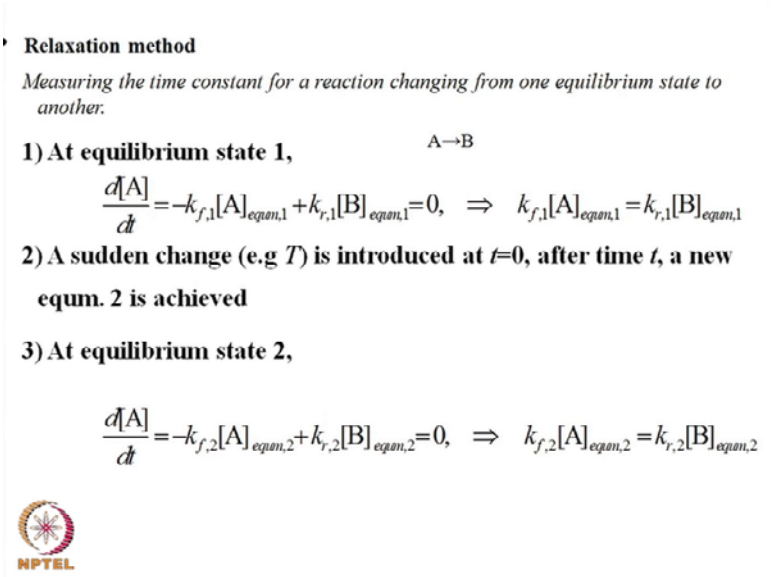

So, mathematically, we can have this one that we want to find out the time constant of reaction changing from one equilibrium state to another. So, a to b equilibrium. At equilibrium state 1, you can write this; rate of change of concentration with time, you can write this one and this is correspondingly you can write this.

A sudden change as for example, temperature is introduced at time t equal to 0. So, the success of this method is that you have to change or you have to perturb very fast. If your perturbation takes time, then it is it is not very useful. So, it relies on the fact that how fast you can perturb. The moment it is perturbed, then it will try to relax. The system will try to relax from the one equilibrium state to another equilibrium state with time and that will give you that will guide you to find out the kinetics of the process.

So, after sudden change, you get new equilibrium. This is equilibrium 1. This is

equilibrium 2. So, this is equilibrium 1 corresponding expression, this is equilibrium 2 expression.

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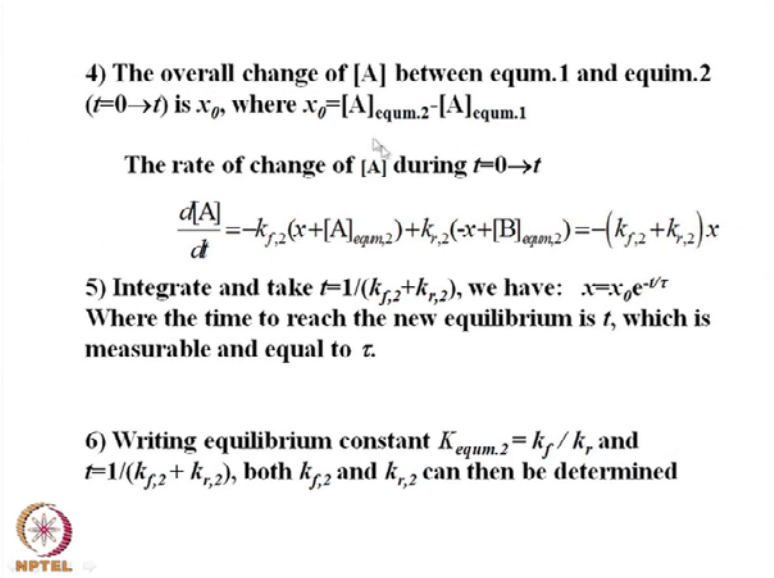

Though what I will change of concentration of a between equilibrium 1 and equilibrium 2 due to… It takes time; this much of time, time t. If it is x 0, so, x 0 is equal to this much. The rate of change of a during t equal to… So, you can write this one; t equal to 0 to t and integration and then taking this, taking this that t is equal to 1 by this, we have this 1 by tau is the time for relaxation; this is your relaxation time.

So, from this, they from this calculations and these mathematical manipulation and writing your equilibrium constants, new equilibrium constant like this, you can find out k f forward and k r; I mean forward rate for the second equilibrium case and the backward rate for I mean backward rate for your second equilibrium can be determined.

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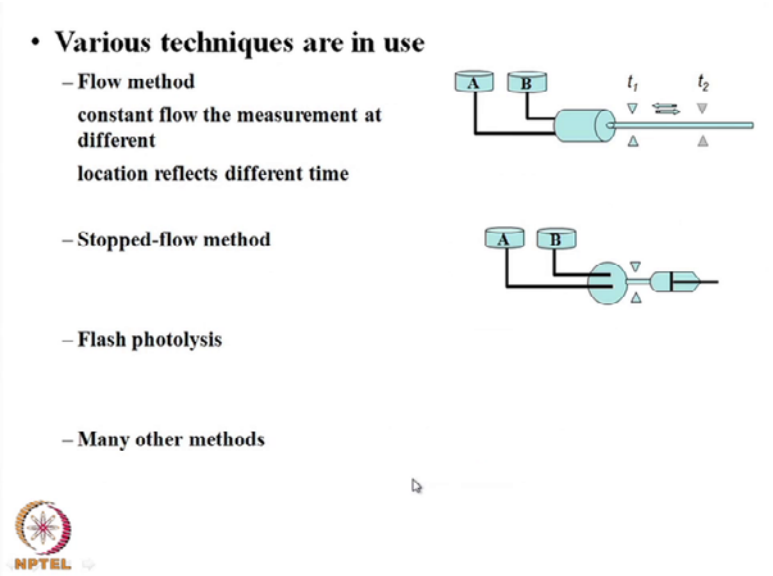

So, this method relies on, this method relies on how fast you can perturb. So, this is another useful method; that is, your relaxation method like other methods I talked about. This is also a very useful method, but it relies on the fact that that how fast you can you can perturb your system. If you perturb your system very slowly, then the system will also try to relax slowly and so, may be in that case, it will not be very useful you know to follow your fast kinetics. So, fastness I mean to follow fastness, I mean fast process you have to perturb very fast.

So, we talked about flow methods. So, a-b mixing chamber, then it is flowing out. So, your measure I mean you are moving your detector from here to here, since you know the flow rate. So, time difference I mean how much time should the reactant, I mean mixed reactant take while moving from this position to this position will give you the time difference. So, from that, you can find out the rate; that is, different location of a detector reflects different time. Stopped flow; you know these two are mixed very fast and then this one, this one I mean stops the flow and the moment it is stopped flow or flow is stopped, you keep on injecting. So, it is coming out. This cylinder is coming out.

So; that means, what is happening that you can find out you know you can find out the concentration I mean in terms of absorbance or may be fluorescence of I mean

concentration of your reactant or may be your product. You can find out and I also talked about this flash photolysis and there are still many methods.

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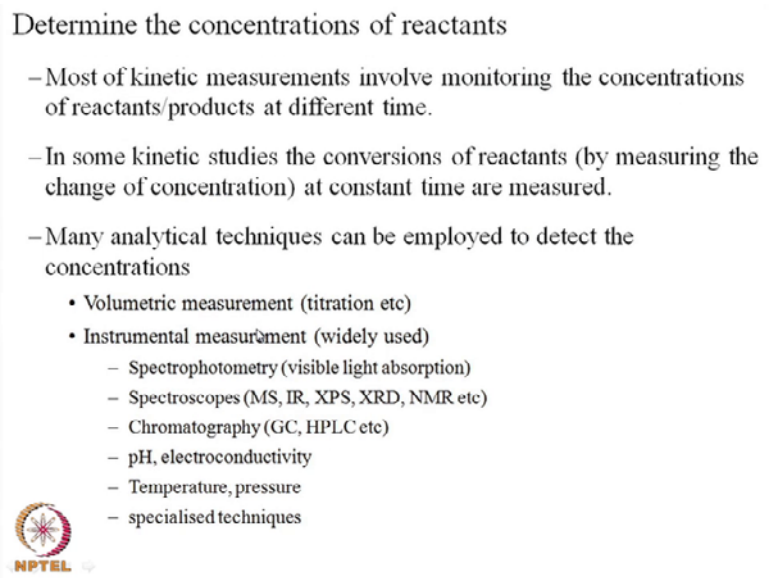

Now, next thing is determination of concentration of reactants. Most kinetic measurement involves monitoring the concentration of reactants at different times. As I told you that for slow reactions, it is maybe you monitor concentration at say I mean 2 minutes interval or may be 5 minutes interval, may 10 minutes interval, and by simple titration in some kinetic studies, the conversions of reactants at constant time is measured. Say after 2 minutes, how much reactants are converted, you measure. That is that can also be a technique.

Many analytical techniques can be employed to detect concentration. One is volumetric measurement as I told you that simple titrations are used to find out the concentration, may be may be acid base titration, may be precipitation titration, may be conductometric titration. There are several ways and with pH metry, with time you find out the pH. How pH is changing with time. That can also be a good way of looking into the concentration.

So, this is the volumetric measurement. Another thing I mean other things are instrumental measurements like spectrophotometry, using Lambert Beer's law, you can

find out the concentration. I told you that using a suitable method, you find out you know in the in the during our first part of the lecture today, I talked about, by any suitable method, I told you that the composition of reaction mixture is monitored at one or more positions along the tube by any suitable method.

So, that I mean suitable method means, your may be spectrophotometry, may be spectroscopic method, mass spectroscopy, IR spectroscopy, x-ray photo electron spectroscopy, XRD; it is diffractometry, NMR, etcetera; nuclear magnetic resonance. It may be chromatography, gas chromatography, liquid high performance liquid chromatography, high (( )) then HPLC fast proton liquid chromatography and so on. pH conductivity as I told you may be temperature, may be pressure, may be volume and specialized techniques as I just talked about can be useful in finding out in determining the concentration of reactants.

So, these are and you know instrumental methods. These are all instrumental methods. By means of by using instrumental techniques, you will be able to find out the concentration. In case of spectrometry, it relies on the fact that out of your many reactants or maybe I mean suppose there are two reactants and say there are two products, may be out of out of this four species may be one out of this four is absorbing at a fixed wave length; maybe say at 500 nanometer. So, what you do?

You monitor absorbance at 500 nanometer as a function of time. That will give you that will give you the concentration and even if your detector is very fast detector, then you can follow their concentration using absorbance spectroscopy also. Maybe also by fluorescence; with time you monitor the fluorescence. If it is a very short period of time may be say 1 nanosecond, may be 1 pico second, even in that case, you can you can find out the (( )) I mean the signal.

So, from the intensity of your signal or from the height of your signal as a function of your of time, you can find out find out the rate constant of the decay or may be rate constant of the rise of the signal; either way.

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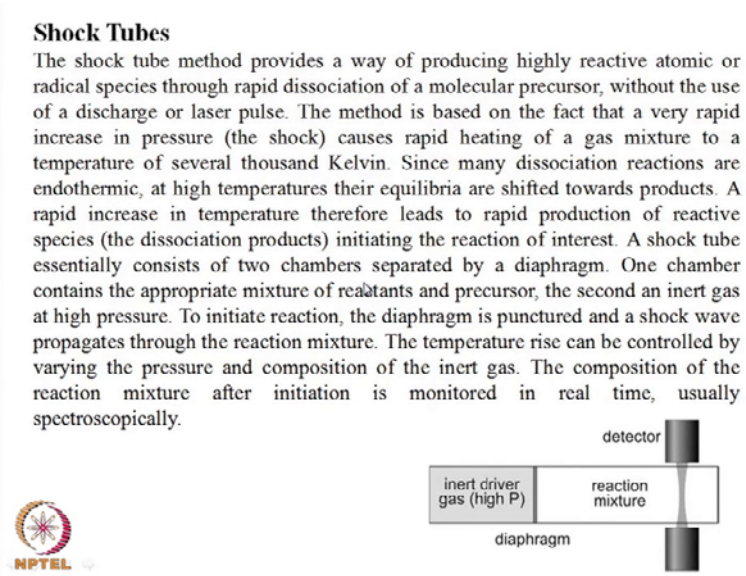

There is another method which is called the shock tubes. The shock tube method provides a very I mean way of producing highly reactive atomic or radicals species through rapid dissociation of molecular precursor without the use of a discharge or laser pulse. In that case, you do not use you do not use any laser pulse, may be discharge or may be discharge. You do not use anything.

So, what you do? You just put some shock. The method is based on the fact that a very rapid increase in pressure; that is, the shock causes a rapid heating of a gas mixture. Generally, gases reactions are followed I mean followed through soft tube method, and a rapid heating of a gas mixture to a temperature of several thousand Kelvin. So, huge increase in temperature.

And in many dissociation reactions, it has been found that this is these reactions are endothermic. So, at high temperature, their equilibrium is shifted towards the products. Rapid increase in temperature therefore, leads to a rapid production of reactive species; that is, dissociation of products initiating the reaction of your interest.

A shock tube essentially consists of two chambers separated by a diaphragm. One chamber contains the appropriate mixture of reactant and precursor and the shock wave propagates through the reaction mixture. The temperature rise can be controlled by varying the pressure and composition of the inert gas and composition of the reaction mixture after initiation is monitored in real time using spectroscopically.

So, this is a spectroscopic detector. So, you know inert driver gas at high pressure; it is your reaction mixture and there is a diaphragm. So, to initiate the reaction, the diaphragm is punctured and a shock wave is propagating through the reaction mixture. So, you have to puncture it. It is a very high pressure. So, if you puncture, then it rapidly flows I mean this high pressure under high pressure, this gas was there. So, rapidly it flows from here to here causing a huge increase in temperature. That is a shock.

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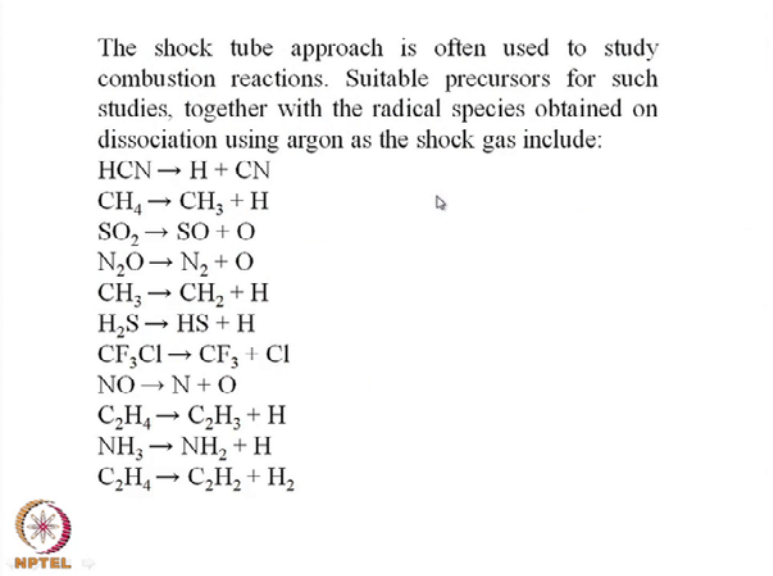

So, the shock tube approach is often used to study combustion reaction. And suitable precursors for such studies together with radical species obtained on dissociation using argon as shock gas include. So, these are the typical example of shock I mean example of reaction studied by shock method; shock tube method.

So, you have got your high pressure inert gas. So, it is not going to hamper your reaction I mean hamper in the sense; that it is not going to react with your reaction mixture. So, it is the means to provide your shock. So, it is a huge pressure. So, the moment it this is released through I mean by making a puncture, so, it will pass through and it is I mean a temperature is increased several thousand Kelvin; rapid heating. So, rapid heating causes the reaction to get to be initiated and then reaction is followed I mean by the help of a detector. These are the examples.

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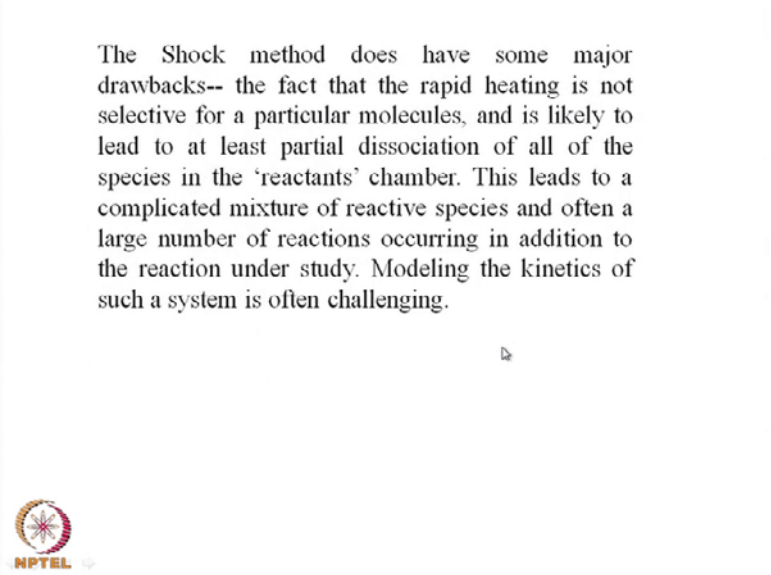

Now, the shock method does have some major difficulties. The fact that the rapid heating is not selective for a particular molecule and is likely I mean suppose you have got more than one molecules in the mixture and you want to selectively heat one molecule. It is not possible. That is why rapid heating is not selective for a particular molecule and is likely to lead to at least partial dissociation of all the species in the reactant chamber. This leads to a complicated mixture of reactive species and often large number of reactions occurring in addition to reaction under study in addition to the reaction which is of our interest.

So, modeling the kinetics of such reaction is very challenging and the problem is that, sometime it is difficult I mean I mean difficult to reproduce, reproduce the reaction. Suppose you do some reaction in this shock tube by puncturing your high pressure argon or helium gas, the second time you want to do may be you know since it is a mechanical way of puncturing, you may not be able to reproduce the first one.

So, that is why it is a very challenging one and modeling sometime very difficult because you cannot selectively heat. You cannot selectively heat, out of many a particular molecule.

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Conventional	1) Mix reactants together in a batch reactor 2) Measure concentration versus time	10 sec or more
Stopped flow	1) Set of continuous-flow systems where reactants are fed into the reactor, and flow out again so quickly that there is negligible reaction 2) Stop the flow so that the reactants can react 3) Measure conversion vs time	10^{-1} sec or more
Temperature jump	1) Mix reactants at such a low temperature that the reaction rate is negligible 2) Use CO_2 laser to suddenly heat reactants 3) Measure concentration vs time	10^{-6} sec or more

So, let us look into various techniques. All though we are we are interested, now we are we are focusing on to the fast reactions, but anyway.

So, let us have a look into various methods. Conventional method mix reactants together in a batch reactor measure concentration versus time. So, it is you know it is a I mean time required is 10 seconds or it may take more time 10 second or more. For stopped flow; set of continuous flow systems where reactants are fed into the reactor and flown out again click quickly that there is negligible reaction stop the flow so that the reaction can react I mean reactants can react and measure the conversion versus time. So, in that

case, it is 10 to the pressure minus 1 second or more.

Temperature jump method. Temperature jump method is the mix reactant at such a low temperature that the reaction rate is negligible. Use carbon dioxide laser to suddenly heat the reactants and measure concentration versus time. So, in that case, you get a 10 to the power minus 6 second I mean in that case, your time required is 10 to the power minus 6 second or more; that is the limit; 10 to the power minus 6.

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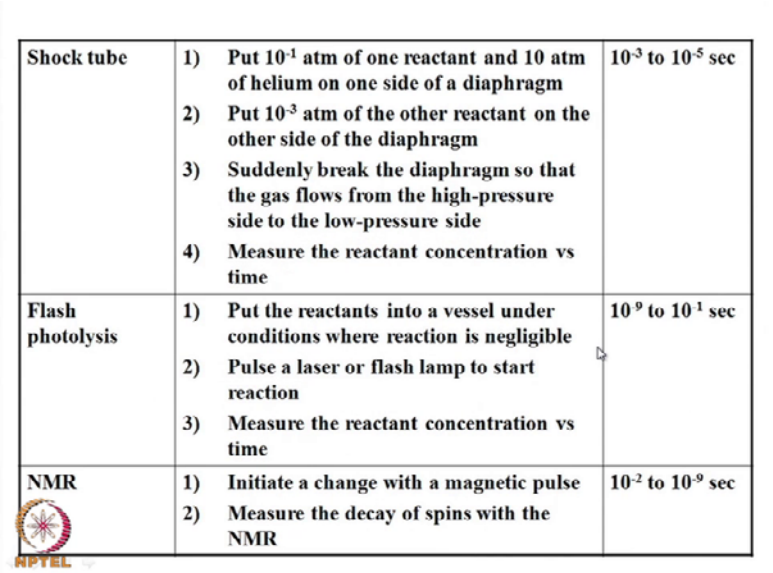

Shock tube; it takes it takes about 10 to the minus 3 to 10 to the power minus 5 second, and in that case, put 10 to the power minus 1 atom atmospheric pressure of one reactant and 10 atmospheric helium on the other side of the diaphragm. And put may be 10 to the minus 3 atmospheric pressure to other reactant on the other side of the diaphragm. Suddenly break the diaphragm so that the gas flows from high pressure side to the low pressure side. A huge heating and measure the reactant concentration versus time.

Flash photolysis; it is from 10 to the power minus 9 nanosecond to 10 to the minus 1 second; sub second. So, put reactant into vessel under conditions where reaction is negligible. Say it is consider reaction which does not generally occur in the ground state, may be in the excited state. I mean when out of out of two reactants, may be one is

excited and then it does the reaction. In that case, flash photolysis useful may be.

So, a pulse laser; in that case, a pulsed laser or flash lamp is used to initiate the reaction and measure the reactant concentration or may be the product concentration as well. In all the cases, as I told you that measure reactant concentration; maybe you can measure reactant concentration or may be product concentration, depending on your choice or may be depending on depending on the fact that which one is easier to do, easier to do whether it is easy or whether it is not easy.

NMR; initiate the change with a magnetic pulse and measure the decay of spins with NMR. That will give you the idea I mean 10 to the power minus 2 take it into I mean 10 to the minus 2 seconds to 10 to the minus 9 seconds.

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Conventional flow system	**1) Continuously feed reactants into a reactor** **2) Measure the steady state reaction rate**	**10^{-3} sec or more**
Molecular beam	**1) Direct beams of reactants toward each other in a vacuum system** **2) Measure the steady state reaction rate**	**10^{-13} to 10^{-9} sec**

So, and the conventional flow system continuously fed reactants into a reactor and measure the steady state reaction rate. And it is it is again it is the time constants at 10 to the power minus 3 seconds or more.

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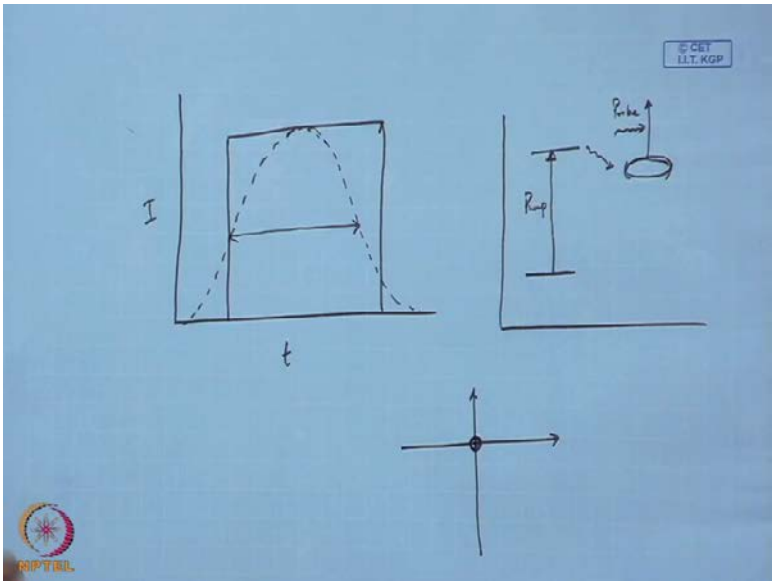

Molecular beam; direct beams of reactants towards each other, I mean like that say we have got a beam of molecule say, one is doing this way, another is going this way. So, there is the there is a interaction at this point.

So, reaction is happening at this point. So, and you can study how much of reaction is taking place maybe by using a suitable detector over here. Again here, the time constants are like 10 to the power minus 13 to 10 to the power minus I mean 13 to 10 to the power minus 9 second. So, I mean we have now seen the time constants and various also the various a base basics of various techniques to follow mainly the fast reactions.

So, it looks like that in some cases, it looks like that in some cases, this flow techniques are not useful because of the slowness I mean because of the fastness of the process. In some cases may be flash photolysis could be useful. Not always flash photolysis is useful. If excited state reaction is taking place, may be say excited state intra molecular proton transfer may be excited state hydrogen atom transfer. In that case, these light induced detection processes or light induced processes like flash photolysis are very useful.

So, let us again come back to what we have we have learnt today. So, we started with I mean important of chemical kinetics in our life, and why do we need to study chemical kinetics because we want to know how some reactants are depleted, may be how we are growing in height. So, there must be you know definitive chemical process that that is happening I mean the process is going on with time. So, it must have some kinetics.

Now in case of conventional process I mean conventional processes for studying reactions where the reaction is not very fast, you can use conventional techniques like say titration, but for studying fast reactions, you have to you have to adopt a method I mean adopt ways by which you can compete with the fastness of the process; like whenever you want to catch a train which has just started to you know started to move, what you have to do? You have to you have to run and the moment your speed is I mean close to the speed of the train, then you can get into it. Otherwise it is difficult.

So, like that your methods should compete with the speed of the reaction. I mean if your method is very slow, then during your measurement, you may miss many thing. The details of the process may be missed, but if you can if you can follow, if you can detect very fast, then may be details of the processes can be achieved.

So, one method was you know I like I talked about is the flow technique. Then it is the modified version is the stopped flow technique. Then we talked about I mean given just idea about this flash photolysis. Another version was the pulsed radiolysis. Relaxation method is also a very important thing; that is, it relies on the fact that that you have to you have to perturb the system; that is, an equilibrium system such that a new equilibrium is established. So, during establishment of new equilibrium, you can follow how faster how slow it is equilibrate it to a new description. And we have compared an another method was a shock method, preferably for gases reaction it is it is used, and we have compared various methods and they are you know time constraints.

So, in the next lecture, we will talk about this in a little detail of the technique which is called the flash photolysis and also the laser flash photolysis. And there, we will have you know chance to know a little about flash photolysis, I mean little about flash photolysis, laser flash photolysis and what is a laser, and what is the difference between a

laser and laser light or laser source with the simple light. So, that we will try to cover in the in the next lecture. So, till then, have a nice time. Thank you.