Advanced Chemical Thermodynamic & Kinetics
Prof. Arijit Kumar De
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 17
Review of Chemical Kinetics – 4

All right; so, we will now discuss about kinetic measurements or how we can measure experimentally the reaction rates, again by reaction rates we mean here the rates of composite reactions. Now, the first method we will be discussing is titration based method, so may be some of you have already done it in practical courses.

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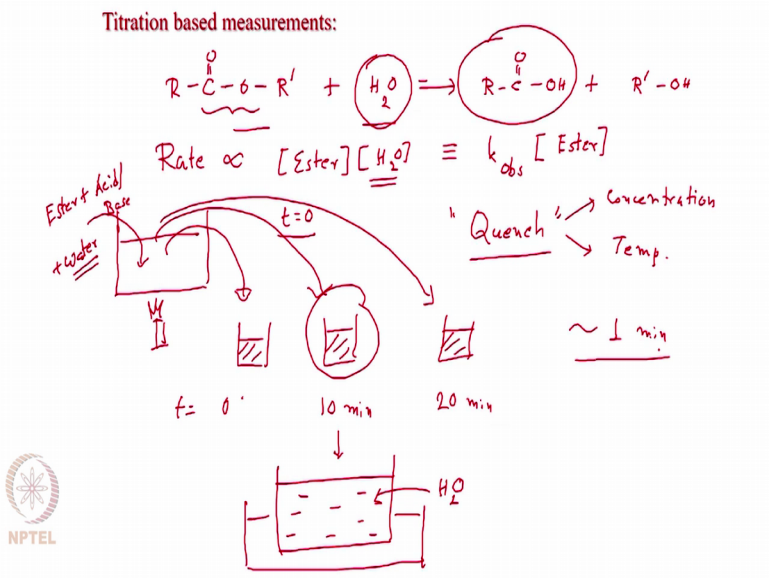

So, let us take an typical example for example, say we can actually discuss about, acid catalyzed or base catalyzed hydrolysis of esters where actually this ester bound is broken; or in one water molecule is inserted, and the reaction is overall that you get back your acid and the alcohol.

Now, this reaction is an example of bimolecular reaction, because you can see that at the rate determining step the two species will be involved. But, usually the water is present in is in large access, so what happens is that the observed rate that you find is proportional to concentration of ester times the concentration of water, but since the concentration of water is too large compared to the concentration of ester is practically it

behaves as if it is a first order reaction. So, this type of reactions we call as pseudo first order reaction.

Now, when people when you do this experiment in lab, what we do is that in order to give some activation energy of the reaction, particularly for the base catalyzed reaction you makes the ester, and acid or base together, and the medium is of course water. And this water is present in large access; and you put everything together and then you hit the so solution mixture, so that the reaction actually reaches at optimum rate.

Now, your t equal to 0 here is as soon as you mix it, but there is some physical error always involved. And in this case it is not much, because the kinetics of the reaction is very slow, the rate constant will be on the order of minutes. So, whatever error we made is perfectly fine for this reaction, but we will discuss of course, then the question arises that what will be the mixing procedure for reactions, which are even more faster, so that will discuss in a I mean is in the subsequent slides.

Now, first let us try to understand how do you analyze this reaction kinetics. Now, as soon as you mix it, and you heat it up the ester actually produces acid, and this acid you can actually titrate. So, what you can do, you can actually take the amount of the mixture at some regular interval. Suppose, we take it at close to some 0 time, so t equal to 0, then we take again the mixture say after 10 minutes something like that then you again take the mixture after say 20 minute something like that.

And then you take an equal volume of the mixture. So, if I have the equal volume, since the concentration is changing, so the amount will also change. And if you titrate this same volume, you will see the amount of acid is actually increasing which you can convert into the concentration of the acid, so how it is increasing.

Now, one interesting observation or what we shall point here is that moment you take this out, suppose after 10 minute I take out this mixture again, the same volume of the mixture. Now, within this reaction mixture, the reaction will still proceed meaning your titration takes some time to perform, but you do not want the reaction to happen during that during the period of titration. So, what you want is that you want a reaction mixture after 10 minutes, and immediately you want to stop it; you want to stop the reaction. So, this is known as generally you want to basically quench the reaction.

So, the question is how you can quench the reaction in this case. Now, this is very easy for this case. So, what you do is that you take out the same volume and then you dilute it, you actually pour it in some excess water, so that the reaction mixture become extremely dilute, so that now the ester molecules are and acid molecules are far apart. So, the reaction probability will be less because of collusion in this reaction.

Also what you do, you do this reaction in an ice path so that your temperature goes down, and as you know that every reaction needs an activation energy. So, if I lower down the temperature, the reaction kinetics I mean there will be less probability of crossing the activation barrier; so the kinetics will be much slower. So, in general you do two types of quenching here; one is basically concentration quenching, because you diluted the reaction mixture, and secondly you also did temperature quenching.

So, you cool down the temperature so that you can arrest the reaction. So, after 10 minute if you do it, if you arrest the reaction so, you can approximate that whatever volume you are titrating, whatever volume of acid you are getting, and you can get back to the concentration that corresponds to the amount of acid or the concentration of acid after 10 minute of the progress. Similarly after 20 minute also, the story would be the same. And by quenching, you make sure that a reaction itself did not proceed during your measurement.

Now, as we just said that this mixing the time equal to 0 happens I mean ideally as soon as you mix all the reactants together. Now, in this case again the rate constant will be on the order of few tens of a minute or so, but in many cases you do not have this kind of luxury, because as soon as you mix the reaction actually proceeds. Now, with this method you can get roughly up to say 1 minute or few 10s of second to I mean 1 minute kind of resolution in your experiment. But we have most of the reactions are much more faster than then this particular example.

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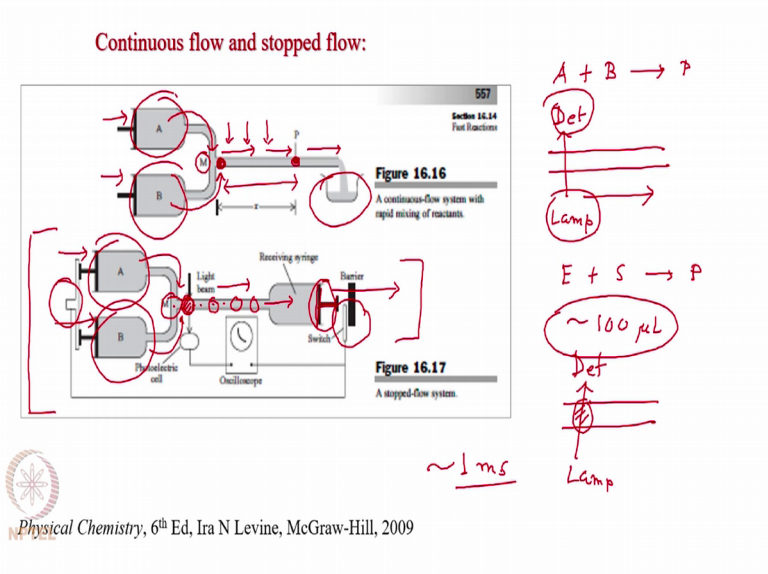

So, for these there are two methods which are developed these are usually called as flow methods. Now, we have two varieties of the flow method; one is known as a continuous flow method, and other one is known as a stopped flow method. Now, what is done in a continuous flow method? Suppose I am doing a reaction where the reactants are A and B; and I want to mix them, and some product is being formed let us say product B.

Now, what is shown in the upper figure is that A and B are initially kept in a vessel. And then there is a syringe as you can see here, so we put a force on this syringes; so that the reactants actually come, and they mix inside a mixing chamber which is known as which is shown here as M. And then this mixture actually continuously flow along this tube, and ultimately gets collected in this vessel.

Now, what is going to happen here as you can see right here, the reaction mixtures actually got mixed at a very early time. And then since they are flowing if I measure something here, the product concentration; then that distance is directly connected to the time interval, because they got mixed and then they had flown along the tube. So, if I measure at different different position of say product concentration, so I will get actually the concentration of the product at different time. So, if I am close to the right at the mixing chamber which is denoted here as M, I will get a very early product concentration, and if I go far away; I will get a very product concentration at a later time.

So, the experiment will be something like let us say I have tube here, and then I can actually do photometric experiment something like I can have a UV lamp, and then I can have a detector here. And then you can simply study the absorption, and you can actually look at a characteristic absorption of the product; you can also study the characteristic absorption of one of the reactants.

So, if you follow the reactant, that absorption will keep on decreasing with respect to time; if you follow the product, absorption band will increase with respect to time. And from that now you can actually from the intensity of absorption for products it is increasing; or for reactance it is diminishing. You can back calculate how much is the how much it gets converted into the concentration change, and from that you can calculate the kinetics. Now, the problem with this flow method is that with this method again is known as continuous flow method. And the problem here is that you need very large amount of sample, because the sample as you can see is ultimately wasted the mixture is being collected in a vessel.

Now, in many cases you do not have that luxury. So, you suppose you are working with a very small particularly for biological samples, suppose you are working with a enzyme, and you are you want to study this enzyme substrate kinetics how it is giving rise to the product. Now, the question is how in these cases you will do this experiments? Usually, typically for enzyme catalyzed reaction, the amount you deal with is something like 100 microliter or even less; so it is less than 1 milliliter.

Now, the way is actually known as the stopped flow method which is a modified version of the continuous flow method. So, what is done here as you can see here, that I have the same similar mixing chamber like before, and the then their solutions actually come here; they mix here. And then they start flowing, and then they are actually collected in a receiving syringe.

And what happens is that you can see here if I just put a force here, I am actually mixing A and B. So, A and B are actually coming in the mixing chamber, and the mixture is flowing along the tube; and then it comes to the receiving chamber. Now, the receiving chamber also has a syringe, and as a result since I am putting a force here; this flow will cause this syringe to move in the other direction. And there is a circuitry, once it actually

reaches and touches this switch then as a back reaction, as a feedback this force will get stocked.

So, you force from one side, and the volume of the reactants move along the tube, and as a result the product is also being formed. And as soon as the volume at gets transferred substantial amount in that the receiving chamber. The receiving chamber syringe expands in the right hand direction, and then it stops the circuitry. So, what will happen as a result, that if you now look at the situation after the flow has stopped. Then you can think that if I fix my spectrophotometer at a particular position, and then take the spectrum overtime, then the flow actually has stopped everywhere. So, what we do here is that we mix the thing, and then in the earlier case, the difference is that in a earlier case it was continuously flowing.

And then I was saying that at a different locations, I have different locations basically maps into different time intervals, but in this case I have mixed and immediately I have stopped. So, stopping means now I have a mixed solution along the tube. So, I can actually choose one particular location along the tube, and then take my data over some interval of time. So, the difference here is that I will put the same thing lamp and the detector, but this time I will fix the position, I will not change the position.

Earlier time I have to actually scan, the lamp and the detector together along this tube, so that I can get a temporal information for special location. Here the flow has stopped, the mixing is completely done after certain time, as soon as the circuit is off and automatically in a in a feedback electronic circuitry, the flow is stopped. And then you start your measuring, and then you say that I can actually seat a particular region in space and then keep on detecting over time.

So, in a sense the stopped flow technique is a static technique. You started the flow, you mixed but immediately you stopped the flow, and now you look at a particular region in space over time. So, you are getting a direct temporal information and you do a direct time domain experiment, but in the earlier case you continuously make it flow, and then you make sure that your flow is converted to your time. The only precaution for this method says that particularly for the continuous flow method, that your velocity and should be very uniform. Otherwise you cannot calculate the amount of volume, if the

velocity has huge turbulence inside it, you cannot actually easily map; the concentration overtime to distance.

And the in the stop flow technique those are kind of eliminated, but again each method has its own limitation like in the stop flow the you have to make sure that the flow stops very quickly. So, the way it is drawn here in reality actually this volume of the mixing chamber as well as the receiving syringe is much smaller, because as I said that you only deal with something like say few hundreds of micro liters of the reaction volume. So, this is this kind of experiments which I said the earlier one, like the titration based experiments for slower kinetics.

And this continuous flow and stop flow kind of experiments are routinely done. And in the earlier case, I said that it gives you about few 10s of second to 1 minute resolution. And in this case stopped flow, you can get down to something like 1 millisecond resolution, 1 millisecond to 1 second, but usually chemical reactions are extremely fast, and most of the chemical reactions and as soon as you mix it just stops.

Now, the question is how one would handle this problem? Or how one wants to deal with this problem? Now, this problem has a very good analogy with developments in other areas that I will give you an overview. Now, this is known as the our race against time. So, over time the human race as struggled continuously to find better and better time resolution, so that they can capture, events which are faster for example, there was a very classic experiments where this it was asked or it was basically speculated, when a horse runs what happens, what is the motion of the horse.

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And this experiment was done in way back in 1872 or so, he was a generalist Eadweard Muybridge, and he was asked by the mayor in San Francisco that just make sure do an experiment, which actually proves when a horse actually runs; whether you get a situation or you get a moment at which all the 4 legs of the horse is in the air, or it is something like that the horse always touches the ground with at least one of its foot.

Now, this is the very complicated problem for that if you think that it was 1872, and then Muybridge actually did very very tedious experiment. So, what he did is that he made, he actually brought a series of cameras, and each camera I mean they there was no video camera available that time, and he place those video cameras at a regular interval in space on the track. And then he made all these cameras in a synchronized fashion, meaning one camera I will take the snapshot. And say after, one tenth of a second the second camera will take the snapshot something like that, and what it did is it a after lot of trial and error method; he basically collected a series of pictures of the horse.

Now, you can see here that this is the first frame, this is the second frame something like that. And interestingly you noticed this frame, where actually all 4 legs are in the air. So, when Eadweard Muybridge did all this collection of the frames. And then he what it did is that he projected it on to a white screen, and he basically was made a device, he was basically rolling the frames and while projecting; and if you do it very fast, you will see horse in motion. And that is exactly, what he produce. And this is the one of the first

example of video microscopy, but this is not a direct video microscopy remember that this was basically many synchronize static frames, and but with this he was he made it possible to visualize that actually during its motion the 4 legs come in to air at some instant.

Now, with this thing you can get something like which you cannot see, and there is a word like a blink of the eye. So, what you cannot see with the blink of the eye that you can visualize, but that means, actually it is something like millisecond resolution or so.

And then came another era where actually people talked about Stroboscopy. Now, what is Stroboscopy? Now, in the earlier case you see that how do see an object? You basically through light on it, and then the light reflects from the object; goes to into your eye or the detector which is the camera in this case, and it captures the frame. Now you take multiple frames, but the event which you are the way you are detecting is actually continuous, because light is continuously falling on the object and continuously coming to your eye.

Now, Stroboscopy has a very different idea. Stroboscopy tells that what happens instead of sending light continuously, if I actually send light as a flash, now we have seen flash lamp like in camera flash lamp; so which has on the order of say if you microseconds to 100 microseconds long. So, if you flash, send of flash to the on the object, then the object will be eliminated on the for a very short time. And then the reflection from the object or the scattering will also come for a short time, and then you can actually captured. So, then you do not need a camera with a very high shorter speed, you can actually have a continuous camera, but since your light exposure is short your events you capture is only on the order of very short period.

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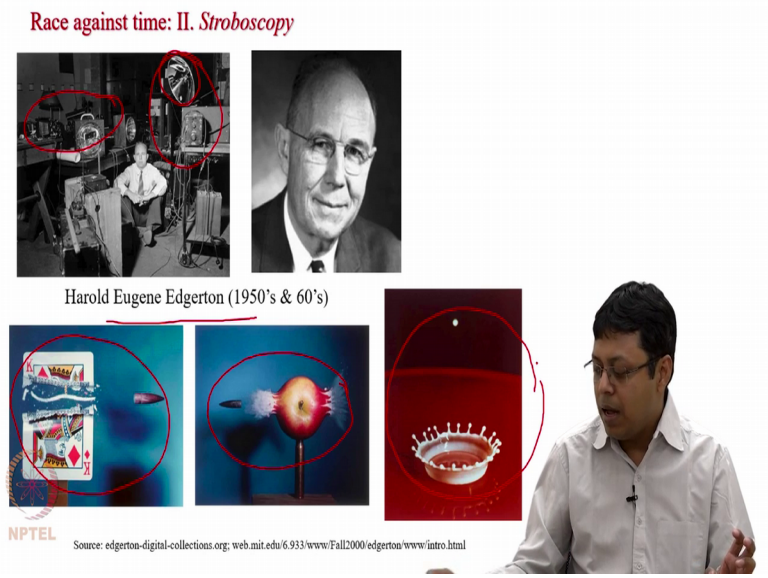

Now, this idea was put forward by an American engineer a Harold Edgerton, and this is basically the setup in as you can see in those days, there were big flash lamps which were available. And these are basically the capacitors of the flash lamps, and you just basically charge the capacitor, and then immediately you discharge it, and then you get a microsecond flash; and these are basically the concentrators which you have seen in photographic studios which actually focuses the light.

Now, with this kind of flash experiments Edgerton was able to collect extremely good images, which are otherwise aesthetically very beautiful. Now, you can see here this is a moment when bullet pierces through a card; this is a moment when the bullet actually pierces through an apple; and this is and picture what happens when a milk drop actually pulse on a surface which is red color, so, it be creates a very beautiful pattern.

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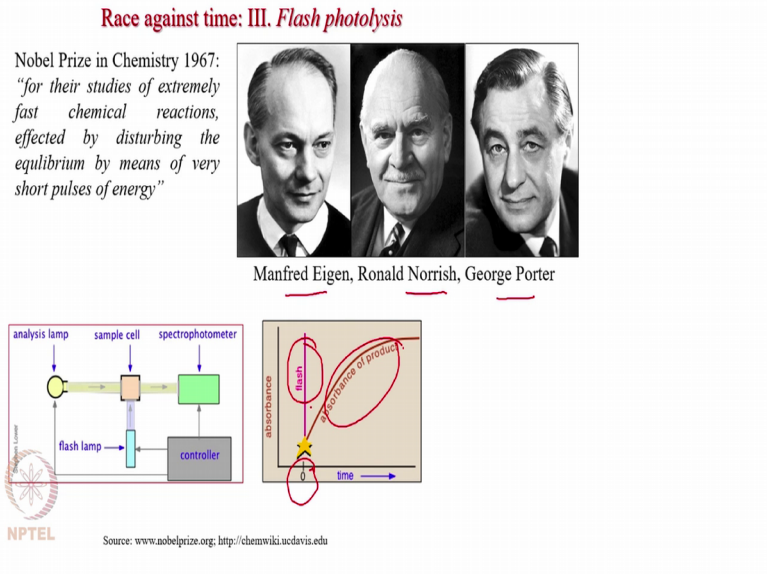

Now, this same idea of this flash lamp photography was actually picked up by chemists. And then basically they started something which is known as flash photolysis. Now, what they said is that the three gentlemen Manfred Eigen, Ronald Norrish and George Porter, they said that I will initiate a reaction with a very short burst of light, which I call as a flash. And in discuss it is a same flash, it is a microsecond of for few 10s of microsecond long flash and then what I will do, I will just see the formation of the product.

Now, you can connect it to the earlier discussion of the mixing, as I said that A and B are mixed together, and that mixing has to happen very quickly, because if the entire reaction happens during the course of mixing, then the stop flow or the flow method does not work at all. So, their point was that you can actually study with this method, what is known as photochemical reactions that has triggered by light. Now this triggering I am not actually doing it by continuous light, because if I continuously expose light, the reactions will be over during the exposer of the light.

So, I want to initiate the reaction with a very short pulse of light, meaning this short pulse or short burst of light is so short that I can think that the reaction does not proceed within the duration of the flash, it just initiates the thing. And then subsequently you observe their product. So, we have a setup, schematic of a setup here, and you have a

better picture in the next slide. All these wherever I have adopted the pictures are given the references at the bottom. So, you can go back and have a look at this references.

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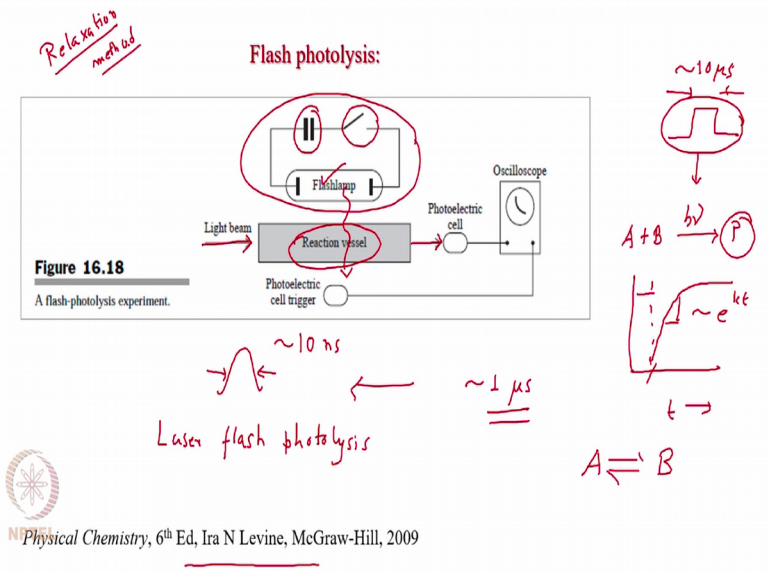

Now, what is shown here is that there is a flash lamp here, as you can see and it has a capacitor, as I said that it the capacitor has to be charged first, any flash lamp is nothing but a discharge tube. So, you have a rarefied gas in a vacuum tube, and then make a short circuit, you just make a connection of this open circuit. Then you have a discharge inside that tube, and depending on the amount of the gas and pressure of the gas and of course, the nature of the gas; you can actually generate a flash of a very short duration, and of a particular wave length.

And that light which is coming that actually initiates the reaction, and the reactions are already kept in the vessel, but a reaction does not happen all of a sudden, because it needs photon to initiate the reaction. So, the flash actually initiates the reaction and as soon as you initiate, suppose I had already mixed A and B together; and it gives me product in the presence of light. And as soon as I give this light, in the form of a say microsecond flash is something like say on the order of say 10 microsecond reaction initiates and the product p forms.

Now, again everything has a timescale the product p will form overtime. And then what I can do is that I can actually simultaneously pass a light beam, and do some absorption or emission based experiment as I just outlined in the previous flow technique. And then

one can see in the directly in the oscilloscope or in some detector, how the product actually gets form. So, suppose this is the time at which I started light flash. And then all of a sudden I will see that the product concentration will rise, and then it will reach at a equilibrium.

So, from the timescale, I can actually calculate what is the timescale of formation of the product something like that. So, you can also see the other picture, so at this point as you can see, the flash was initiated; this is my time 0, and then the absorbance of the product actually increases. And it reaches to the maximum value, and from the growth or the slope of this curve, you can actually find out the kinetics.

Now, again this method at its own limitation, because it depends on what is the width of the your flash lamp. Now, usually you can go with this flash photolysis technique, down to 1 microsecond or so. Now, eventually what Norrish and Porter developed instead of using flash lamp, flash photolysis, they actually improved it to something known as a laser flash photolysis. So, instead of a capacitor based microsecond flash, they actually used a laser pulse to photolysis these experiment and where you can actually use a laser pulse of few 10s of nanosecond duration something like that.

So, with this technique they were able to detect events, which were a much shorter something like 10 nanoseconds or 100 nanoseconds or so. And that is why when this gentleman were given the Nobel prize in chemistry 1967, the citation says for their studies on extremely fast chemical reactions that were not, I mean possible to study with the flow techniques or stopped flow techniques. And also you see that they are writing here, they are by effected by disturbing the equilibrium by means of a very short pulse of energy.

Now, this energy they showed eventually, it can be an electronic pulse also. Like if you have an electron transfer reaction you can think of I will trigger it with some flash; not a light flash, but with a electrical flash, something like you can actually send, bunch of electrons with an electron gun something like that. But another point to look at here very carefully, it say that the effect by disturbing the equilibrium, this is very very important.

So, what is happening here is that we already discussed, what is the what happens if I have a reaction, something like that A is going to B and B is also giving back you the reactant. And then you show to that in a very long time limit, both an A and B are

actually reaches that equilibrium value, A does not go to 0, because it always reaches it equilibrium value, because it is a reversible reaction.

So, the overall idea in flash photolysis type of experiments is that you all of a sudden, you had a mixture and all of a sudden, you disturb that mixture. Initially A and B suppose were in a thermodynamic equilibrium, and all of a sudden you start the reaction to proceed. So, you are disturbing the equilibrium, and you are basically moving this entire mixture from equilibrium to perform equilibrium. And then slowly again the product forms, and it comes and establishes a new equilibrium, so that is why you see kind of growth, in the product.

And you can think that initially I had an equilibrium of the only between the reactants. And then of course, there are not reacting they are just thermodynamic equilibrium. And then all of a sudden you make them react, because now you are disturbing this entire system, your pushing it far from the equilibrium. And then you are seeing that how basically the product is form.

Now, this general concept is known as relaxation methods. So, by relaxation method you mean that you start with a mixture and then you create some disturbance, where the entire mixture actually goes from far from the equilibrium position. And then it relaxes back to the equilibrium something like say for example, you can also instead of doing a electronic flash or say photoflash. You could also do a temperature flash, something like you can actually send huge change in I mean a heat pulse, so that the temperature actually changes all of a sudden.

And then you reaction initiates, and then again the system thermal equilibrates and goes back to the new equilibrium. In this case always you have to remember that is, it does not go back to the old equilibrium, because a reaction is happening. So, it goes gives you the the product back, but the overall idea is that there was an equilibrium you disturb it, and then you establish a new equilibrium, and you watch overtime, how this new equilibrium is established.

So, as is shown here that the product goes, I mean or product basically accumulates overtime and that is a new equilibrium, where you have predominately product in the mixture. So, again these are collectively known as a relaxation methods. And we have

many different methods like temperature jump experiments, flash photolysis, all fall under, all fall under this relaxation methods.