Introduction to Chemical Thermodynamics and Kinetics
Dr. Arijit Kumar De
Department of Chemistry
Indian Institutes of Science Education and Research, Mohali

Lecture – 34
Chemical Kinetics: Mechanisms – Part 3

We will now consider first the unimolecular reaction and the model will consider for unimolecular reaction was perhaps provided by Lindemann and that is why it is called a Lindemann mechanism for unimolecular reaction.

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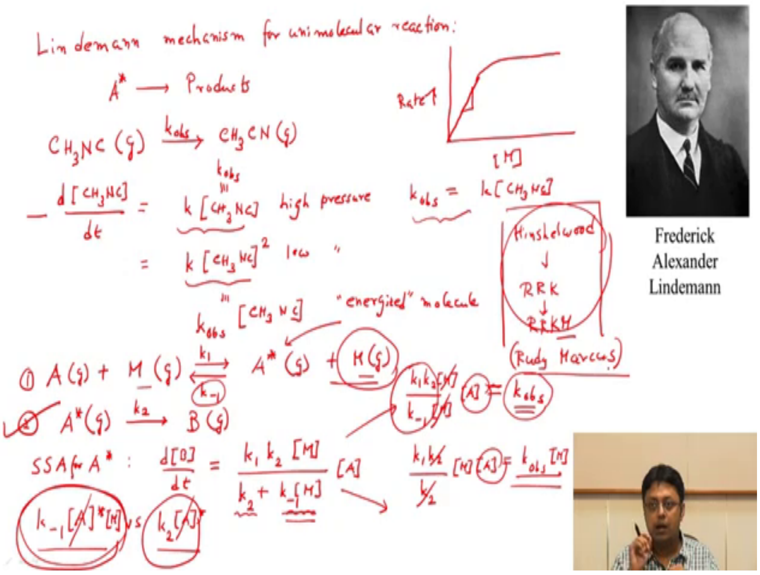

So, Lindemann mechanism sometimes it is also called Lindemann Christians and mechanism for unimolecular reaction; so, unimolecular elementary reaction.

So, as we said that a molecule is just decomposing into products, but it has to be some energized molecule. Because meaning actually what Lindemann said there should be some collision; if it is a collision in the activated unimolecular reaction; then the a bimolecular collision should precede the unimolecular reaction.

And then you can always write that to give you an example of the unimolecular reaction for example, this isomerization isocyanide to cyanide and you see some observed rate law. And the observed rate law which is nothing, but the if you just write it in terms of a reactant. So, I am using a negative sign; so, that is found to be minus k into or we can just write it as plus here, minus here does not matter CH 3 N C at high pressure and at low pressure it is; it just behaves as a bimolecular reaction, it is at low pressure.

So, usually the we write these this term which is minus k into C strain C as k observed in the sense that we take that rate and plot it versus the concentration of the pressure of the gas. But we do not plot the actual rate constant we actually drop the observed rate constant which is defined as minus k into CH 3 N C. We can actually write the minus sign in the other hand and just define that we observe like this. Which means at high pressure this will be nothing, but equal to k observed and at low pressure this thing will be nothing, but equal to k observed times the pressure of the gas this CH 3 N C.

Now, in order to understand the mechanism of Lindemann proposed that fine; you have a similar thing which you have discussed already; gas first say the reactant is A and it first collides with second gas molecule which can be the container also, which can be any other gas molecule also; to get and to basically generate an energized molecule. So, A star is nothing, but and energized molecule.

So, it has much more energy so, that it can decompose into the products plus the M of course, the way we are writing M here this is slightly different in the sense that this term has now a lower energy, but we are not writing it explicitly. And there is a first equilibrium for step 1 and in the step 2; then this energized molecule gives you the product with some rate constant.

Now, we have already told you that suppose it I am just writing it as B and we already told you that; what is the rate equation for this for this kind of reactions? And we can actually use the steady state approximation for A star and you can easily solve it. I am not solving it once again because we have already shown you what at how to solve it.

So, you just have to take the ds star dt that to equate it to 0 and then you can easily figure out what is the rate of the reaction? The rate of the reaction here is d B; d t that you can find as k 1 k 2 into M divided by k 2 plus k minus 1 into M into A and as before you can see here this we can actually now talk about the high pressure and the low pressure limit.

Now, in the high pressure in the low pressure limit what happens here is that you have a linear relationship. In the sense now the this term if it is linear then; obviously, this term should be much less than this term; which means k minus 1 into or you see basically a observed rate law is proportional to the concentration of the gas. And remember that the k observed was k times M; now you can say that if it is a very high pressure situation, then the collisional deactivation will be much more.

Now, what is the collisional deactivation step? This is basically that k minus 1 step. So, we have for the A star; there are two pathways one is the collisional deactivation where this is the rate for the collisional deactivation; k minus 1 into A star. And versus you have a reaction a reactive pathway for A star which is k 2 into A star sorry the collisional deactivation is also involve an M because M is sitting here.

So, now the question is which rate is faster? Now you can say at very high pressure when the pressure is fairly high the collisional deactivation is much more. So, this term will be more than this term; so, you can easily see that the rate will be nothing, but k 1 k 2 divided by; now the activation is more which is this k minus 1 into A star into M which means you can actually eliminate when you compare these two terms, you can actually eliminate the A term; A star term that we exactly did for the steady state approximation.

And in that case this term will now dominate and then what you have is nothing, but k 1 k 2 by divided by k 2 which is nothing, but sorry k 1; k 2 into M divided by k minus 1 into M into A and which is nothing, but now you can see that this M cancels. So, you have a combination of rate constant times A, but we say that that we call as k observed; so, this is nothing, but k observed.

So, at high pressure it is constant; it is not exactly a constant it is remember that the k observe we are saying that it is it includes the A inside that is a Lindemann actually treated this thing. And the at the very low pressure what will happen? The collisional deactivation a term which is this term will be much smaller than that k 2 term. So, we will have k 1, k 2 divided by k 2 into M into A and that you can easily write that I will have something like some rate constant which is k observed into M.

So, if I plot the rate of the reaction as a function of this M; we will see at low pressure region, it linearly proportional it is linearly proportional to this M. So, it will just rise like this, but at a high high pressure; you will see that it will be kind of constant where this rate or the rate constant is written in terms of a observed rate law, where the concentration of A or the reactant is already included or absorbed in the k observed.

But of course, the value of the k observe will be different, but from this slope actually you can easily calculate what is this composite rate constant? So, that way we can actually describe the variation of the unimolecular rate versus pressure. Now pressure of what? It is pressure of a in general any it can be a pressure of anything or you can actually insert an inert gas and also then I call it as M and then vary the pressure of the inert cut itself to study the unimolecular reaction.

You can consider it as a second body present there which is not reactive it is just increasing the pressure; which means actually it is increasing the coalition. And thereby it is controlling the amount which is by which the A star is formed and unsure and the amount by which the A star or the rate by which the A star is also deactivated.

So, it is controlling this activation and deactivation procedure of the A star without directly taking part in the reaction. Because in a reactive part all the A star forms the product which is that part? 2 here. So, that is how unimolecular reactions I mean the kinetics of the unimolecular reactions was explained by Lindemann.

Now, later on it was a I mean unimolecular reaction in has a very very important role in chemistry. It is extremely important in to describe many interesting situations for example, if I have an energized molecule how the energy flows within various vibrational degrees of freedom inside the molecule? And that is a fairly complicated problem to address and later on after Lindemann this was a kinetic model, but then people working on reaction dynamics took up this challenge and there are many interesting models that are developed.

The first advancement was done by American physicist cell in salute and then subsequently there a model came over a lot of people contributed the model is known as RRKM model and so, but that we will not discuss in here during this during this discussion on the reaction dynamics. We will not consider any unimolecular reaction dynamics because that is out of scope and that needs lot of understanding of classical statistical mechanics; particularly the understanding of the partition functions and many other things.

So, we will skip that, but this is just to let you know that this R R K M model is one of the most celebrated theoretical models, which chemists often used. And this is a very beautiful mathematical development as well as of physical insight behind this model.

How actually unimolecular reactions take place, how the dynamics is take place? but; however, whatever it is that model that all this in solutes statement or the R R K M the extension to it.

Actually info before there R R K M there was this R R K Model and then there was a further refinement done by M which is a by Rudy Marcos and who gave the very interesting picture of these unimolecular reactions. And those are just in historical anecdotes, but this work is very famous and then, but the fundamental thing is that this kinetic model which Lindemann proposed is correct which means actually any unimolecular reaction.

For any unimolecular reactions to happen there should be a bimolecular reaction beforehand with some hard body or sorry it is a second body which is M here. And that collision with the molecule with M produces an energized molecule A star, but the collision activation and deactivation is controlled by the pressure of the M and that is for sure that is always hold; that is always held.

But the question right now is that how the A star is forming the product the second step. Now, all these models which I all the dynamical models which has just said the hints of treatment or R R K and R R K M; actually focuses on this part, once you have an energized molecule, How it will take part in that dissociation of the forming the products? The reason is think about it if you energize a molecule then there and suppose your energizing a big large molecule where there are many bonds.

Now, the question is how the bonds will break, which bond will break, can you predict it theoretically? And the R R K M theory says that fine once you dump some energy into the molecules, first what will happen the all the energy will be statistically redistributed equally to all the bonds. And then the weakest bond has the largest probability of breaking and that is a; that is not very correct assumption, but that is the essence of the R R K M theory. And then people start discussing what is the dynamics how or how to basically formulate write a rate constant and get an expression for the rate constant for this unimolecular reaction.

So, we will conclude our discussion on unimolecular reaction here and then we will proceed to catalysis. But before that I will give you an very brief introduction to the energy of activation. Now the Swedish chemist (Refer Time: 15:58) Arrhenius did a series of experiments to find this very interesting question what is the Temperature dependence of the rate constant; temperature dependence of rate constant?

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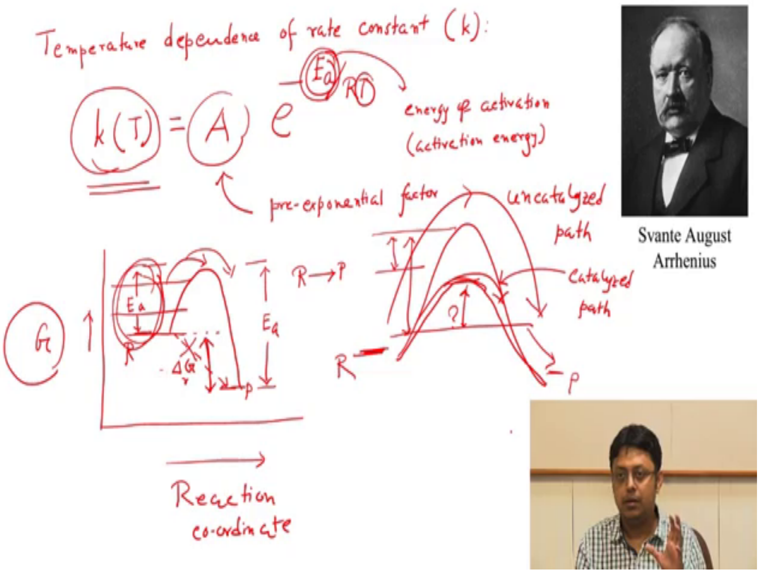

Temperature dependence of rate constant (k):

$$k(T) = A\, e^{-E_a/RT}$$

Now, rate constant so, far as we have described does not seem to have any temperature dependence. Because we just took it as a constant, but experimentally what Arrhenius found is that the k or the rate constant has a very strong temperature dependence. And that you found an exponential law and he found that it can be written as something like this where there is a factor we put the exponential which he called as the pre-exponential factor because it appears before the exponent.

So, you call it as a pre-exponential factor and then there is some kind of energy that he called as energy of activation; which sometimes we call as activation energy, but it is not perfectly correct to call it as activation energy. Because activation energy is something different it has a statistical interpretation, but we will just call it as an activation energy. Now this activation energy or energy of activation; if we draw it in a potential energy diagram where basically we are talking about how the reaction Gibbs free energy is changing from going from say reactant to products.

So, suppose I have some reactant here and it is giving me some product; the product energy can be higher than the reactant, it can be lower than the reactant, but that we are not considering right now; it can be higher it can be lower let us say it is lower for the time being. So, we are considering a reaction where the reactant is going into product and we are just asking what are the energetics of it?

Now what thermodynamics told you is that whether this forward reaction is feasible or the reverse reaction is feasible; if the delta G of the reactive Gibbs free energy is negative then the reaction will be spontaneous at the forward reaction will be spontaneous that is what thermo dynamics told.

But thermodynamics did not tell how this reaction happens or at what rate the reaction happens. We could actually have a situation that fine it is lying at a higher energy, but let me just draw it slightly above say the reactant is sitting here and we have some difference in energy which is connected to the delta G r. So, this is basically the Gibbs free energy and this is the reaction free energy.

So, since it is a negative; so this reaction will be spontaneous, but the question is at what rate it will go or how the reaction will change? Is it something like that the reactant will eventually lose its energy and go to product. Now, Arrhenius said no actually it does not go like that it actually goes through a barrier which means there is a barrier that every reactant should cross before it forms product and this barrier is coming here. So, E a is nothing, but equivalent to this height of this barrier for the forward reaction.

Similarly, if you think about the reverse reaction; the reverse reaction in this case will have a much much larger barrier. So, it is all about the barriers to the reaction that actually controls the reaction. Now, we will give you an example or something very interesting that we discussed earlier, but we did not say it very clearly these thermodynamically and kinematically controlled product, but look at it here. So, if this barrier is very high enough it is coming as exponential minus; so, the reaction rate at the rate constant for this reaction will be very low. And if the reaction is actually if for a particular reaction if this barrier is smaller then the reaction rate will be faster.

Now, consider there is a fixed reaction which means there is a fixed activation energy. So, what we can do is that we can increase the temperature which means the average energy of the reactant will now increase; it will be here or it will be here; so that it can easily now cross the barrier. So, that is the entire concept; so, I have an energy of the reactant at room temperature and there is activation barrier. So, I have to cross this energy hill or sometimes that is called as a it is just like the crossing a mountain. And you cannot just it is just a mountain is there and you cannot go from reactant to the product by creating a tunnel through it.

So, you have to cross the mountain to go to the other side and that is the entire idea here. So, of course, when I say that this is not possible; this is actually possible this is not known as quantum mechanical tunneling, but we are not going to consider that right now. So, going from reactant to product you have to cross this mountain and then if you are energetically high; then you have to just spend a little bit energy to cross the mountain.

If you are energetically low; so then you have to apply lot of energy to you have to cross the mountain. So, the thermal activation is nothing, but basically pushing the reactant to the average number of molecules to a higher energy state so, that they can easily cross the barrier. The other way of looking at it is that fine I am not changing the temperature. So, all the molecules are sitting here, but can I actually modify the height of the barrier? Meaning; can I actually reduce the height of the barrier?

So, that is done by catalysis; so, catalysis is nothing, but it reduces the height of the barrier by providing some alternate pathway. So, the reaction does not follow now that this path which is known as the uncatalyzed path uncatalyzed path, but it now follows this path which is much less energetically and so, energetically much more favorable that is known as catalyzed path.

So, we are going to discuss that how the catalyzed path helps to proceed the reaction. Now you can easily imagine if E a is smaller, the reaction rate becomes faster at the same temperature. So, we discuss two different things one is the temperature dependence of the rate constant which Arrhenius I mean phenomenological he found. And he gave an equation which is known as Arrhenius equation and that that depends on exponentially with some energy, but there is a negative sign also.

Now, we can actually vary the temperature you can increase the temperature to make the reaction more feasible. So, that basically increases the chances of crossing the reactant to the product side. However, we can also reduce the barrier out by itself by modulating the E a or the activation energy and that we can do by catalysis, where the it means that it is not actually crossing the old barrier that goes to the product, but it is it finds a new barrier in a catalyzed pathway that actually takes it to an alternate route to the product.

So, that is the interesting concept actually in catalysis; now we will not consider more on this pathways. Because that involves a lot of understanding on how these reactions of the molecules actually jump over a surface which is known as the potential energy surface; we will not discuss that, but rather we will discuss something else.

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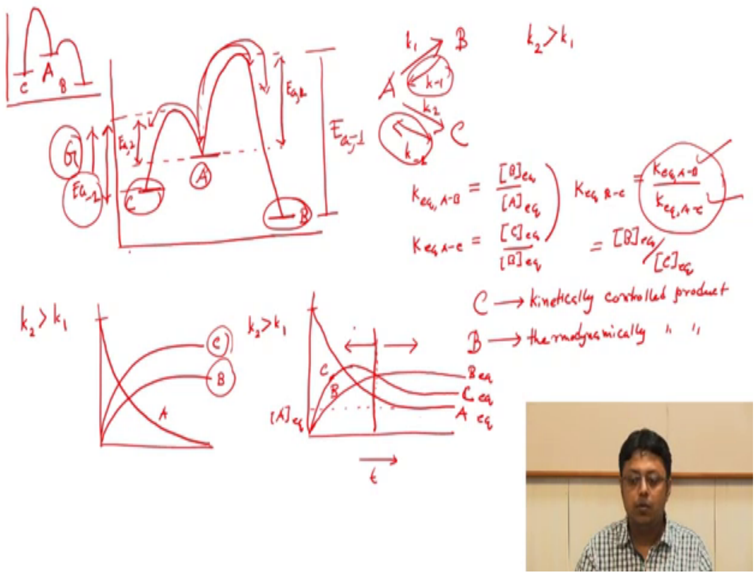

$K_{eq,A-B} = \frac{[B]_{eq}}{[A]_{eq}}$

$K_{eq,A-C} = \frac{[C]_{eq}}{[A]_{eq}}$

$K_{eq,B-C} = \frac{K_{eq,A-B}}{K_{eq,A-C}} = [B]_{eq}/[C]_{eq}$

C → kinetically controlled product

B → thermodynamically " "

We will first discuss to begin with how this reaction happened or just take an example of something which we had already discussed; say I have a competing faster reaction, but now I am making it a reversible computing faster direction.

So, I had rate constants earlier as k 1 and k 2; now I am imposing there also k minus 1 and k minus 2. So, what means that at equilibrium when the equilibrium is reached I know that there is a equilibrium between A and B. So, I can write it as equilibrium A B; so, that is nothing, but B by A of course, at their equilibrium concentration. There is also another equilibrium between A and C which means that it will be like C equilibrium by B equilibrium which means if we combine these two things; there is also an equilibrium established between B and C which can be given by the ratio of the equilibrium constants which is A B divided by A C equilibrium.

Now, how will you describe it? So, let us now go back again and think that fine these two steps does not exist the reverse steps. Just think that this is only irreversible transformation from A to B and then what will happen is that suppose the reactant is lying somewhere here; this is the energy diagram again versus the reaction coordinate, we call it as a reaction coordinate or this coordinate we call this call as reaction coordinate.

So, by reaction coordinate we mean that it discusses the progress of the reaction along some coordinate, but of course, it is not very easy to define that coordinate, but let us not discuss going to the details or what is a particular reaction coordinate. And here suppose this reactant which is A in this case goes to the product either B or goes to the product which is I think we the last class we took an example of C here ok. And then let us also assume that from A to B; it goes like this and for say I am sorry A to C it was like that and A to B; it is going like that.

Now, think about it we said that if k 2 is greater than k 1 for that river irreversible path. So, we showed that that the time dresses like A will fall and then B and C will rise, but then the C will be higher than B the reason being the k 2 is much larger than k 1. Now what is k 2 and k 1? In Arrhenius picture k 2 is nothing, but the associated acting it is related to that associated activation energy for this path and k 1 was nothing, but the associated activation energy for this path.

So, this is related to so, it is the activation energy for path 1; just k 1 and this is activation energy for path 2. Now you see that since the activation energies are smaller for path 2 which means k will be larger because it goes as e to the power minus activation energy. So, this reactant can easily cross this barrier because the height of the barrier is smaller than it crosses this. So at a very early time if the reaction is totally controlled by kinetics, so you will see that the C will always dominate B and if it is irreversible then of course, A will go to 0.

Now, suppose we are imposing the reversibility situation; so, then what will happen? So, in a very long time A will of course, fall, but A not go to 0 because A will go to it eventually go to its equilibrium concentration. So, this is nothing, but this concentration is nothing, but A equilibrium and similarly B and C will rise. Now initially you might have a situation that C is rising ever B; the reason is C has to from going for A to C, you need a smaller activation energy; so the rate will be faster.

However, if you wet enough and allow the reverse reaction also to happen; now what is the reverse reaction? Reverse reaction activation energy is this; so, this is the activation energy for minus 2 and if you allow that to happen. So, then you see that for the reverse reaction of this actually it can easily come back here and then it can go to the B channel, but for the B to A reverse reaction the activation energy is very very high; so, it is minus 1.

So, once it goes into the B it cannot come back. So, what will happen initially you might have a increase in the reaction; in increase in the amount of C. So, if you follow the C by B ratio it will increase, but then as it reaches the equilibrium it may so, happen that it actually falls. And initially you might see the B actually goes like this, but eventually; it just takes over.

So, if you follow at this part or say below; this part which is the vertical line if I and this is the time profile. So, I see that the C is always above B because what I started with A; there is no B or C at the beginning. So, then as it is forming I see that of course, C is forming at a higher rate because the activation barrier is smaller and B activation barrier going from A to B barrier is higher; so, it is forming. Now, as C and B are forming more and more now they can also go back because of because there is a reversibility imposed in the reaction.

Now, C can go back to A very easily and A can also go to B, but B to A back reaction is not so, favorable because the activation barrier is very large. You can also think about this in terms of the equilibrium constant; what I have done I have written it I post the B much below than C; which means thermodynamically B is more stable than C.

And all this ratio B by C will be now controlled in the long time limit or in the thermodynamic limit, by the equilibrium constant. Now if A B equilibrium constant is higher than A C equilibrium constant then which means actually it is nothing, but the ratio B equilibrium by C equilibrium will see that we will have a more population and the amount of B will be more at equilibrium than C.

So, initially I might have that C is forming at a faster rate than B and I will see actually the C is higher than B, but eventually when that as the time progressed or if we allow enough temperature; if we increase the temperature, then these back reactions are also happen. Then the overall population will be dictated how stable is the product, how it is if it is more stable or less stable; that stability will control the total amount of the reaction, which will be controlled only by the reaction free energy for the individual parts. And the ratio will be controlled by their individual equilibrium constant rate ratios of the equilibrium constant.

So, this is a very interesting concept and in this case we call this C as kinetically controlled product. Because if you do it at low temperature or at a very short time; then you will see that C is forming more because the kinetics of forming C is very fast because that is followed as because k 2 is much larger than k 1. Initially it is working as if it is irreversible because there is no B and C to begin with; so, there is no question of reversibility at a very early time.

Now as I am progresses; so it is kinetically controlled product sometimes we call it as a KCP. And B as time progresses or if you allow enough temperature to the system then this reverse reaction also happens, but then everything is controlled by the equilibrium constant. And also you can think in the other way that B to B since B is actually energetically at the minimum position; the reverse reaction for B to A will be much much slower because the activation barrier is also very high.

So, it is it will be very much not only kinetically or not only thermodynamically favored, it will be also kinetically inert. So, thermodynamically controlled products are also kinetically inert in the sense the back reaction is slow. So, B is called as thermo dynamically controlled product. So, in the long time or in the high temperature limit you will see that B is forming more than C.

So, you will see the C curve is down here and B curve is here and A is here. So, this is where basically everything has reached the equilibrium at a very very long time. Or you could achieve it in a very quicker time by increasing the temperature, by allowing there all the reverse reactions to happen. And then you can look at the rates and you can easily figure out that the B to A back conversion is very difficult.

Now, here what we also see that if two reactions are in equilibrium a common species the common species is A here; the B and C are also in equilibrium in principle because we showed that B equilibrium by C equilibrium is a constant. And; that means, it is going via a of course, because there is no direct interconversion of between B and C, but this example shows how the very simple concept which was put forward by Arrhenius in terms of the activation energy can tell the relative ratios of the product at a very early time, where actually kinetics controls or governs everything and at a later time their product I mean the thermodynamics controls everything.

Now, should not have this notion that the products which are kinetically controlled should not be thermo dynamical chemical, it can be both ways. Meaning I could have drawn the this thing in a very other different way like; I could have drawn this suppose this is the reactant and then I could have drawn the B here with a smaller barrier and then C here which is thermodynamical less stable with a larger barrier also.

So, here actually the barrier from going to A to C is higher. So, here B is both thermodynamic control as well as kinetic control; so, that actually depends. So, the way I have drawn here in the first picture; I showed that distinguishing feature what will be the thermal if one product is kinetically controlled and the other product is thermo dynamics controlled, but it may be the situation that the reaction favors a particular product; both thermo dynamically can as well as kinetically. So, from the very beginning you will see that it is only B that dominates and it will keep on dominating as the equilibrium is reached when the in the long time limit.

So, this depends on the relative energies and activation barrier of these individual paths. Now, the next thing that we are going to study is basically catalysis; now already we discussed that what is catalysis and what is a catalysis?

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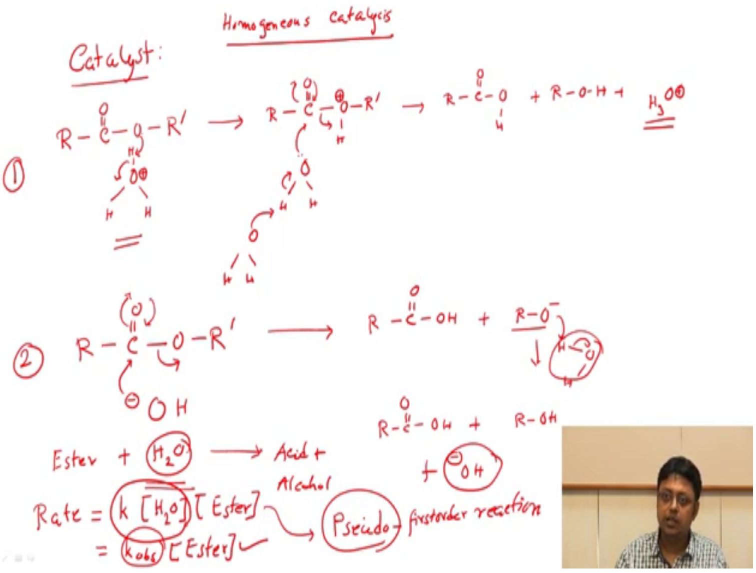

Now, the catalyst is a substance that does not take part in the reaction, but it is you know that it is basically regenerated during the after the reaction is over, but it takes part actively as a constituent in the reaction. And the particular way catalysis or range of catalysis or particularly the examples we are going to give are called homogeneous catalysis in the sense that the catalyst is in same phase as the reactant.

So, like for example, you are using a liquid solution where the this catalyst is in liquid phase as well as your reactants and products and everything are in liquid phase. So, that is known as homogeneous catalysis; now a catalyst by definition as we as we just said that it does not take part in the reaction; it takes part in the reaction, but it does not is not totally consumed there is no net consumption of the catalyst let us give you an example all of you know this thing like say I take an A star. So, A star say like this where R and R prime are just some alkyl group and so, this is an A star bond C O O and then we considered first the acid catalysis hydrolysis.

So, if in water say for example, now in water what will have is you have; if you add acid in water the active form is nothing, but this. So, hydroxyl ion; so, then what you can have that this proton can be captured and you can have a situation like this, you have R C double bond O O H or prime with a positive sign; it is. Now what you can have in the second step you can have actually the in the median the water is also present.

And then the water lone pair oxygen here basically the lone pair of the oxygen attacks can actually attack this carbonyl center. And then after opening and reopening in organic chemistry language, it can give you the product like R C O O H; you can see that and then you have R O H.

So, and then of course, this proton also leaves and it can be taken up by a another water molecule. And you can have this proton can be taken up and you can have actually H 3 O plus again regenerated. So, that is the catalyst here which actually started the reaction, but in the net reaction as you can see; one molecule of water got just consumed and that is the overall thing in this industry action.

So, it is just addition of one water molecule; however, we see that it is catalyzed by hydroxyl (Refer Time: 41:15) actually the catalyzed by proton, but the active species is a C O plus because H plus never exist in H 2 O; water has x as a base and then forms a conjugate acid which is H 3 O plus. Similarly could also think about this reaction being preceded fire and base catalysis where I have instead of H 3 O plus O H minus and O H minus directly attached takes center. And you can have situation like R C O O H and then you have basically O minus. And then you can have a harder addition of water in the sense that a proton can be abstracted from water. Because this is a very strong base and then you will have R O H plus O H minus and then you can see this O H minus is regenerated.

So, I will have R C O H and in an effect actually this water is consumed. So, that is also another example of sorry you know to write it as here this is plus O H minus. So, this O H minus is regenerated and you can see that we have just given you an example of acid catalyzed hydrolysis of the A star as well as the base catalyzed hydrolysis of the A star. So, these are two different pathways by the way; so, the base catalysis if I remember correctly is the is actually a slower process than the acid catalyzed reaction.

So, if you will do this experiment you take something like say it ethyl acetate and then you put some acid heat it warm it up and you will see that this acetic acid is generated in the mixture. And that acid you can titrate again some unknown volume of alkali and try to figure out how much as it is being produced in the reaction. And then you can actually find a rate constant also of the hydrolysis of this reaction. And then you will figure out that just adding water it does not hydrolyze maybe at warming up it may hydrolyze, but just by adding acid it the rate actually increases by whole a lot and for base catalyzed it is a little bit slower than at acid catalysis.

So, you need also to elevate the temperature and one more interesting thing for this particular example since I gave this example is that when you have the ester and you have the water basically hydrolysis is nothing, but addition of water and then you get some acid plus alcohol back from the A star. Then the question is the water the distraction it is kind of an elementary reaction because in the rate determining step; the water actually attached and that step controls the entire step of the intercourse of the rate of the entire course of the reaction. And then you can always suggest that this water molecule are these actual addition of water at the attack of the water on this ester.

Since this is the rate determining step the rate will be more or less proportional to the concentration of these two, but. So, it will be something like these into ester the observed rate law; however, water is in present in very large excess because when you do this experiment; you put a lot of water here. So, the concentration of water does not change much which means this concentration of water is almost constant and then you say that it is a bimolecular reaction actually.

But it appears that as if it is a not bimolecular sorry it is a secondary it is actually a second order reaction, but it looks like that it is a first order reaction which actually only depends on the concentration of the ester and the observed rate log is actually known as it is it is a first order rate law, but it is not exactly first order because it is a second order. So, this kind of reactions we call as Pseudo first order reaction Pseudo first order reaction.

So, it is not actually first order, but we made a condition in such a way that one of the component is in large excess. So, if that concentration does not change; so, they bimolecular not by molecules in the second order reaction actually behaves as a first order reaction.

Now, in the next lecture on the next on under this lecture in the next topic, we will discuss about enzyme kinetics.