Advanced Chemical Thermodynamics & Kinetics
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Lecture- 16
Review of Chemical Kinetics – 3

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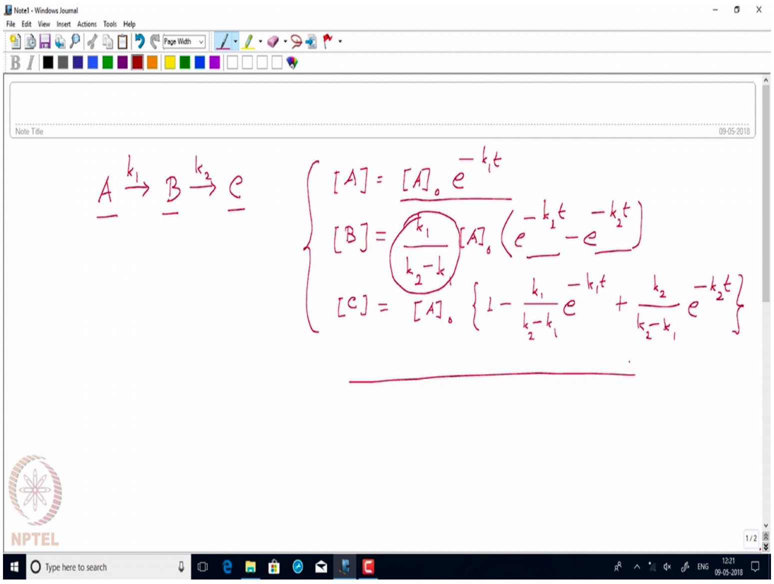

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$\left\{\begin{aligned} [A] &= [A]_0 e^{-k_1 t} \\ [B] &= \boxed{\frac{k_1}{k_2-k_1}} [A]_0 \left(e^{-k_1 t} - e^{-k_2 t}\right) \\ [C] &= [A]_0 \left\{1 - \frac{k_1}{k_2-k_1} e^{-k_1 t} + \frac{k_2}{k_2-k_1} e^{-k_2 t}\right\} \end{aligned}\right.$$

We will now discuss about consecutive reactions, as the name suggests consecutive reactions means, a reaction takes place in a consecutive fashion. So, A gives rise to B, which is known as an intermediate, and then the intermediate B gives rise to the product C. And let us define some rate constants k 1 and k 2. Now, in this case, this is consecutive irreversible reaction.

Now, solving this equation I mean for A is pretty straightforward, because A to B is just first ordered. So, you can always solve it right away A is A 0 e to the power of minus k 1 t. Now, solving the differential equation for B is little bit tricky, because B is being formed from A, and then it is being consumed to C, so that needs a particular integration. And you can always go to the YouTube lectures to see how this is solved. So, I am writing the answer here. So, if you solve these rate law for B, you will get the rate constant or the rate law something like k 1 by k 2 minus k 1 into A 0 times e to the power minus k 1 t minus e to the power minus k 2 t.

Similarly, you can also get a equation for C, which will be something like A 0 times, which will be 1 minus k 1 by k 2 minus k 1 e to the power minus k 1 t plus k 2 divided by k 2 minus k 1 e to the power minus k 2 t. So, these are the solved different I mean solution of the differential equation, these are the integrated rate laws. Now, using these equations, we can now plot the concentrations of A, B, and C with respect to time. Now, it will depend in this case.

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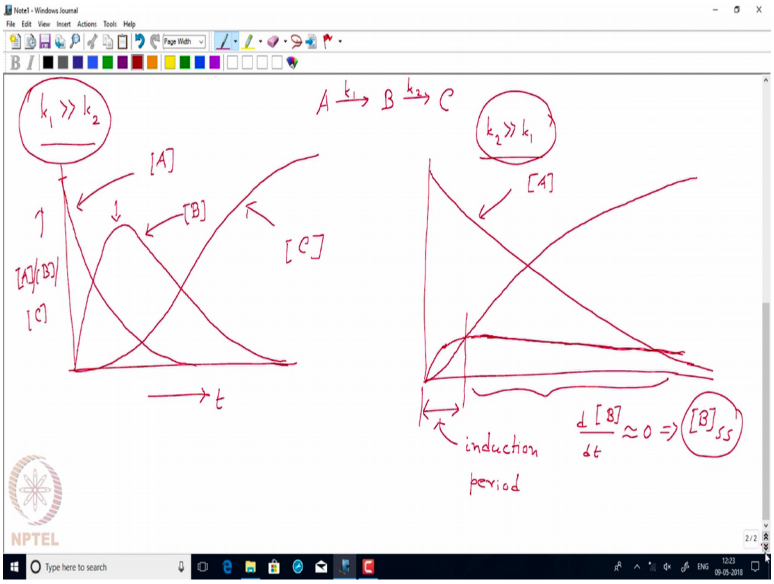

What are the relative magnitudes of k 1 and k 2, now let us first assume that k 1 is much greater than k 2. In this case what will happen, the concentration of A will fall readily with a rate constant, which is e to the power minus k 1 t which at which a rate. So, in this y-axis I am plotting the concentration of A or B or C, and I am plotting it against time so, this curve is for A. Now, for B, if you look at the equation for B, it is actually has two terms; e to the power of minus k 1 t, and e to the power of minus k 2 t. And in this case, k 1 is much greater than k 2.

So, you can approximate also this pre factor to be equal to nearly 1, because it will be k 1 divided by k 2 minus k 1. So, it will be close to minus 1. So, then you can make some approximation so, you can actually look at video for this earlier course, where the details are discussed. And then, you can show that the plot of the B will be something like this. So, the initial concentration of B first rises, and then false and then, C grows at a very very slow rate, and eventually the curve of C will be something like this.

So, you can qualitatively describe why what is the nature of that curve. So, as you see that the reaction goes this A is going to B, and then going to C. Since, k 1 is much faster than k 2. What will happen is that first the curve for A so the A will actually decompose into B very very quickly, because it is a it is actually forming B at a much higher rate, then B is forming C. So, the appearance of C happens much later time.

And in between what will happen, if A forms or A is converted into total into B, and as B is form is also called converting to C, but not at a much lower rate. So, we will have an accumulation of B in the reaction mixture, and this is what is happening. So, at this time, you can see the me actually reaches its maximum concentration. And then, since it is also forming C, eventually it will form C, and it will again become 0, and then the C curve slowly grows.

The interesting thing happens, when the opposite situation is there or actually the second rate constant k 2 is much higher than k 1. Now, in that case the curve for A will be much slower, because A now is decaying at a rate, which is e to the power minus k 1 t, and k is much k 1 is much smaller than k 2. Now, for B, this is a very interesting situation, because B is forming from A at a rate which is k 1, which is small, and it is decomposing first.

So, what will happen, initially the B will start forming at a much slower rate, which is e to the power it is a growth actually, and it goes as with the rate constant k 1 which is small. But then, as soon as it forms, and it has some significant little amount of concentration, it will actually keep on forming C. So, as soon as it is formed, it is decaying. So, what it will mean is that this initial concentration or B will be more or less kept constant over a long time, because some amount of B was formed initially that is that over a certain time, which is known as the induction period. And then, once that little amount B (Refer Time: 06:42) formed it is rapidly now forming C, because k 2 has a much higher value than k 1.

And what will happen, initially C formation will be slow, because there is no B, but as soon as B forms, C also forms rapidly. And C will form up like this. So, this period is called the induction period, when the formation of the intermediate is intermediate is being formed. And then, over this entire period of time, as you can see the concentration of B of course, it decreases, but it decreases ladder slowly.

So, we can say that the practically the concentration of the intermediate does not change over time or we can say that this concentration has reached a steady state concentration. Now, by steady state we mean, the concentration is not changing with time. Now, this steady state condition is extremely important, when we discuss the mechanism of a chemical reaction; we will see in a short while, how it is important.

So, to summarize, consecutive reactions can be I mean can be solved an equation of the consecutive reactions differential equation can be analytically solved. And then, after you get all these solutions, you can actually try to plot them under two different conditions. One is for a condition, when the first rate constant, which is formation of the intermediate, is much faster than the decomposition of the intermediate. And that that condition gives in the an accumulation of the intermediate, because it is forming at a much faster rate, then it is being decomposed. On the other hand, if the opposite thing happens that the intermediate decomposes very quickly, so then you have a steady state condition after the induction period.

And this kind of steady state condition is extremely important for example, in many cases like, when we see say for example, in an enzyme catalysis reaction, when the enzyme works on a substrate forms an enzyme substrate concentration, and then actually we can say that a steady state has reached after the induction period. And this has been well studied for like practical examples will be say growth of bacteria in a culture medium, and so that also follows after certain induction period. Then suppose not only the growth of bacteria, particularly the enzyme degradation or an intermediate is involved in those cases, will see this kind of interesting kinetic behaviour of the intermediate.

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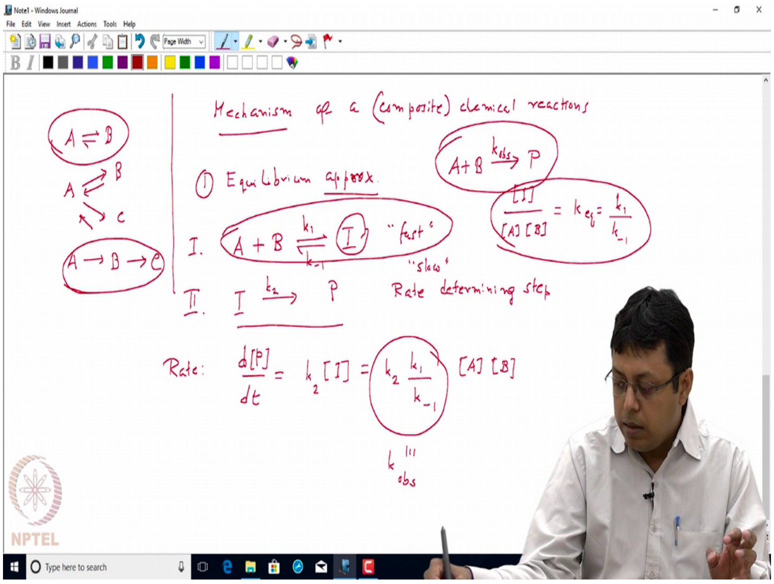

Mechanism of a (composite) chemical reactions

$A \rightleftharpoons B$

$A \rightleftarrows B$, $A \rightleftarrows C$

$A \rightarrow B \rightarrow C$

① Equilibrium approx.

$A + B \xrightarrow{k_{obs}} P$

I. $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I$ "fast"

$$\frac{[I]}{[A][B]} = k_{eq} = \frac{k_1}{k_{-1}}$$

II. $I \xrightarrow{k_2} P$ "slow" Rate determining step

$$\text{Rate: } \frac{d[P]}{dt} = k_2[I] = \underbrace{k_2 \frac{k_1}{k_{-1}}}_{k_{obs}^{III}} [A][B]$$

Now, we will talk more about this inter this steady state approximation, but will see it in a very different way. Now, this all these examples, which we give like irreversible reactions or say competitive reactions is going to two different products; it can be reversible also.

And then finally, to these consecutive reactions so, these reactions, the way we dealt with them is kind of elementary reactions, because we said that these are 3 basic elementary reactions, which will be using mostly the consecutive type and reversible type reactions, which will be using frequently to explain the overall rate law for a composite reaction, which is actually composed of many elementary reactions.

So, let us first give you an example of what are the how one should proceed this problem, which is known as the mechanism of a chemical reaction mechanism of a composite chemical reaction. So, the entire idea is that any composite reaction can be decomposed into a bunch of elementary reactions. So, almost all chemical reactions are way we see it in a laboratory or actually composite reactions.

Now, to understand the mechanism, we have basically two hypothesis or two approximations, which are frequently used. The first one is known as rate determining equilibrium approximation equilibrium approximation, where we approximate that there is a pre equilibrium, which exists between the reactants. Let us say I have some reactant, which is A plus B, which is forming our product or an intermediate, let us say I call it as I. And then, and this I eventually gives you the products, which is I denote as P.

So, what I am saying here, at the overall reaction let us say is a something like A pass B is going to product, and there is some rate constant, which is the observed rate constant, that is why I am writing it as suffix o b s, which is the observed experimental herbs of rate constant. And I am assuming the reaction actually happens, fire pre equilibrium followed by a step; and this step is nothing but the rate determining step. So, this step dictates the overall kinetics of the reaction, because this step is slow in nature. And we are assuming that this step is fast in nature, in the sense that there is a first pre equilibrium.

In the sense, as soon as I is formed, I also gives you brag the product. So, under that condition, this equilibrium you can think as if it is a separate equilibrium, although you cannot truly, because the I the intermediate is not only a part of the equilibrium, it is also part of the second step. So, we have basically two step here. So, the second step actually is forming the product, but since it is a slow step that we have approximated.

We can think that this equilibrium is kind of isolated. From this equilibrium, I can easily write that the concentration of I divided by concentration A and B is nothing but the equilibrium constant, which is the ratio of the forward and the reverse rate constant. So, we can readily say what is the rate of the reaction, the rate of the reaction for a multi step reaction will depend on the slowest step, because the slowest step creates as if it is the bottom line to the reaction.

Now, this rate determining step approximation it is not an approximation I mean it is the valid thing, where you say that if reaction is composed of many different steps, the overall reaction is at the rate of the overall reaction is actually controlled by the rate of the slowest step. Now, this is realized in many day to day phenomena. For example, if you have a highway and there are some I mean there are some different lengths and cars are going through the lens at different speeds, you will see the overall speed is actually dependent on the speed of that line, where actually the cars are moving with the slowest speed.

Again another example will be if you have a toll tax or something like that toll plaza, and then the cars or the velocity of the cars are slowed down, because you have to wait, pay the tax, and then go. And then, the overall speed is dependent how frequently the tax is being collected, and the cars are being led to go. So, this is a very general concept of kinetics.

In that case, I can write the overall rate of the reaction is rate of the product formation, which is in this case the d P dt. Since, these are all elementary steps I can directly write it as this is from the stoichiometry. I am writing it using the stoichiometry of the second equation, because it is an elementary reaction. So, this k 2 into the intermediate concentration and then, the intermediate concentration I can easily get from the equilibrium, and which will be nothing but k 2 times k 1 by k minus 1 into A into B.

Now, you see that the observed rate law is nothing but a combination of k 2, k 1, and k minus 1. Now, we could actually explaining this mechanism in a very very different way. And there will just use this concept which we just discussed, which is the steady state approximation.

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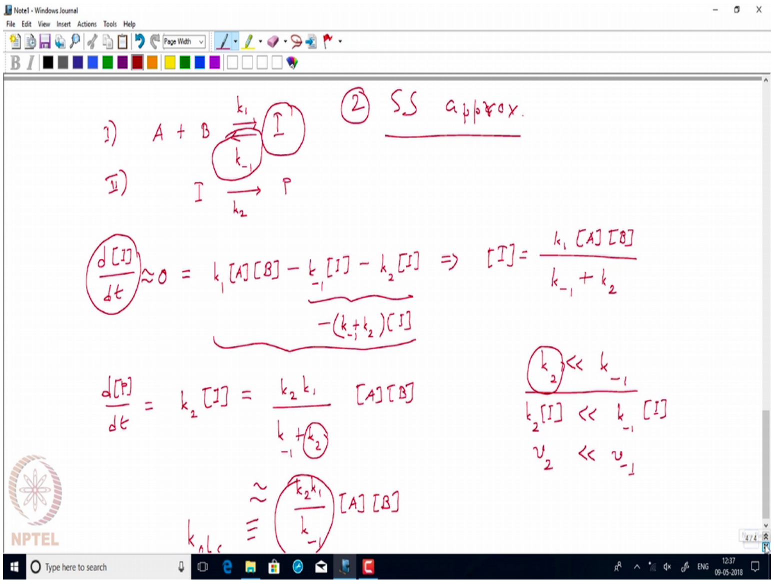

② SS approx.

I) $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I$

II) $I \xrightarrow[k_2]{} P$

$$\frac{d[I]}{dt} \approx 0 = \underbrace{k_1[A][B] - \underbrace{k_{-1}[I] - k_2[I]}_{-(k_{-1}+k_2)[I]}} \Rightarrow [I] = \frac{k_1[A][B]}{k_{-1}+k_2}$$

$$\frac{d[P]}{dt} = k_2[I] = \frac{k_2 k_1}{k_{-1}+k_2}[A][B]$$

$$\approx \frac{k_2 k_1}{k_{-1}}[A][B]$$

$$k_{obs} \equiv \frac{k_2 k_1}{k_{-1}}$$

$k_2 \ll k_{-1}$

$k_2[I] \ll k_{-1}[I]$

$v_2 \ll v_{-1}$

Here we considered the same thing the same kinetic equation like A and B, initially forms a product. And the product sorry an intermediate, and this intermediate also gives back to A and B. But here, the approximation is slightly different, where tools who are going to say is that this intermediate is under steady state, so that the concentration of the intermediate does not change with time that we are going to approximate here. And then, in the second step as before, so this is the first step; and this is the second step. And in the second step, I will have a direct formation of the product with a rate constant k 2.

Now, what is happening here is let us find out what are the terms that involves this d I dt. So, if I see the first step the product is being formed at a rate constant with the rate constant k 1, so it is a by molecular reaction; these are all elementary reactions that is why from stoichiometry directly writing it. And it is also being decomposed with the rate, which is k minus 1. And then, it is also decomposing in the second step into the product. So, if I collect the terms, I can easily see that the intermediate concentration is nothing but if I take this as common, it will be minus k minus 1 plus k 2 into I.

So, if I take the I on the other side, because this entire thing is 0. And then, I will be nothing but k 1 and into A into B and divided by k minus 1 plus k 2. And then, the rate of product formation as before is nothing but k 2 into I, which is nothing but k 2 into k 1 divided by k minus 1 plus k 2 into A into B.

Now, you see that the rate laws, which we derived using the equilibrium approximation and the second approximation, which we already told as steady state approximation are slightly different. You see here that in the final rate law I have k observed is k 2 k 1 by k minus 1 whereas, in the steady state approximation, I have an extra k 2 here. So, if we assume that this k 2 is much smaller than k minus 1, then again it reduces to our earlier rate law, which you which we got from equilibrium approximation.

Now, we will see what is the connection, what does it mean that k 2 is much smaller than k minus 1? Now, if you think in a deeper way, so let us just multiply both sides by intermediate concentration, which is basically k 2 into I is much smaller than k minus 1 into I. So, what it means is that, the rate or the velocity of the process 2 is much smaller or much slower than the velocity of this reverse reaction.

Now, if you remember our original steady state approximation, the way we arrived at in the case of consecutive reaction, where we have A is going to B; B is in this case in our new notation, the B is nothing but that intermediate; and that intermediate is forming C. The steady state is achieved, when the intermediate is rapidly removed. Here we are saying that fine, we can actually rapidly remove the B from the mixture, but it need not be the k 2 has to be higher than k 1 it can be the reverse reaction k minus 1 can also be higher than k 2.

So, somehow you have to remove the intermediate from the reaction mixture, as soon as it is formed either it is giving product or it is giving back to the reactant. In this case the approximation says that if I think in the other way that it is giving me back the reactant, then also I call it as a steady state. And then, I see the equilibrium approximation and the rate determining approximation, both actually give the same expression for the observed rate law, which is a composite rate constant observed rate constant.

Now, does we see how one can actually use these two approximations, which are frequently used. One is known as equilibrium approximation, where we say that equilibrium or a pre equilibrium exists between the reactants and the intermediate, which can be isolated from the rest of the equations where are the reactions, where the intermediate is eventually forming the product, because it is a fast equilibrium.

And the other approximation we said that there is no such equilibrium, but what is happening due to the fine balance between the different rate constant, the intermediates concentration does not change or the intermediate concentration has reached a steady state. And, we see the connection is that the reverse reaction, which is the k, which has the rate constant k minus 1. If I make that very fast, that also gives me the same steady state approximation.

So, there is a slight (Refer Time: 22:03) often students do not get this thing very correctly or understand it very correctly that when we talk about the consecutive reaction, we say that it is a irreversible consecutive reaction; A is going to B, B is going to C. And then, when you do the approximations instead of the first step being irreversible, we write it as a reversible. So, A is going to B; B is going back to A, and then B is also giving me C, which is the product. Then we say that just like in the irreversible consecutive reaction, the removal of B at the intermediate has to be fast than the formation. In this case, instead of k 2 being higher, we can actually make k minus 1 to be higher than the k 2.

Now, you see here if I make that condition that k 2 is much smaller than k minus 1, which means k 2 is actually small, which means again that the second step k 2 is the rate constant for the second step, it is not smaller, which again tells you that that is actually the rate determining step, which is the earlier approximation. So, that is the connection between the equilibrium approximation or rate determining step approximation, and the steady state approximation. And the connection is that, when you make this condition that the back reaction in the first step is much faster than any other step. Then only you can show that these two approximations are the same approximations.

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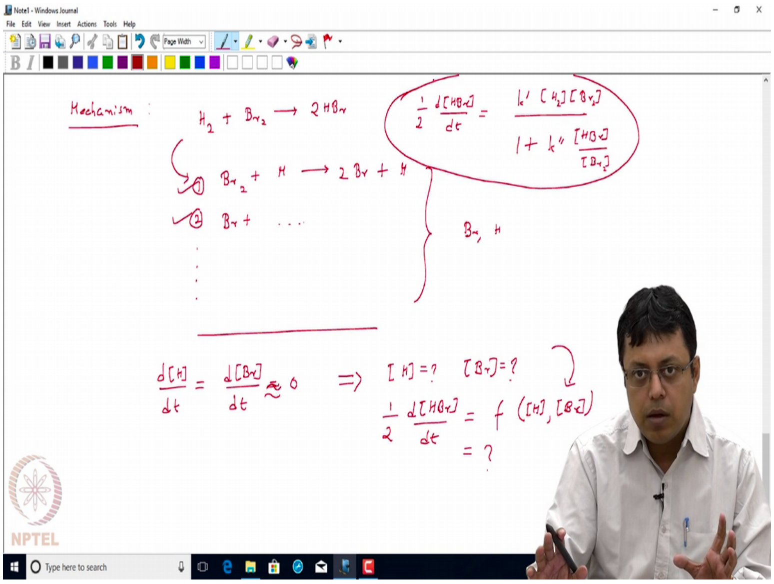

Mechanism :

$H_2 + Br_2 \longrightarrow 2HBr$

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k'[H_2][Br_2]}{1 + k''\frac{[HBr]}{[Br_2]}}$$

① $Br_2 + H \longrightarrow 2Br + H$

② $Br + \ldots$

Br, H

$$\frac{d[H]}{dt} = \frac{d[Br]}{dt} \approx 0 \Rightarrow [H] = ? \quad [Br] = ?$$

$$\frac{1}{2}\frac{d[HBr]}{dt} = f([H], [Br])$$

$= ?$

And then, using this approximation, we use we can actually explain many other things and many other composite reactions, so which are usually covered under the mechanism of chemical reactions. And usually in textbook will get a great variety of this mechanism of the chemical reaction. For example, we gave you an example of this reaction H 2 plus B r 2 is giving 2 HB r, and the rate of the reaction which we can express as in terms of say product, which is d HB r dt was found to be extremely complicated. And, if you remember, it was something like 1 rate constant times H 2 into B r 2 and then divided by 1 plus another rate constant, and then we had the HB r, the product concentration divided by B r 2.

Now, this reaction is thought to be composed of many many steps, first actually these bromine atom gets collides with some another atomic bromine or hydrogen or the wall of the container to give bromine radicals. And then, this bromine radical actually initiates the, a chain of reaction so, these things are called chain reactions. And we can actually divide this entire equation by many such steps; each of these steps are actually elementary reaction.

So, what we do ultimately is that we find out what are the intermediates. And in this case, the intermediates are radical intermediates, which are bromine and iodine. And what we do is that we apply the steady state condition for each of these intermediates, which is the for the bromine and iodine bromine and the hydrogen atom, and we make under steady state condition, we say that this will be 0. And you figure out from all these equations, what are the kinetic equations. And from that, we figure out what is the concentration of H, and what is the concentration of bromine, then we find out the rate law, which is half d HB r dt. And, we write it as a function of hydrogen radical and bromine radical concentration, and from these values we just incorporated here to find what is the final expression.

And if you work out through all these mathematics, you will figure out that you get back to this equation, after certain approximation. So, this is done or this is given at this particular example as a problem in many textbook, but we derived it in the earlier lecture, which will get it on YouTube.

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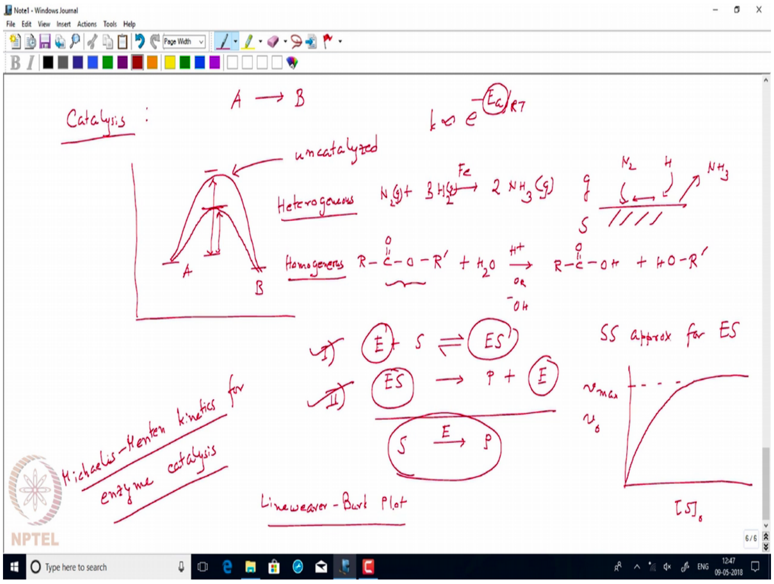

Now, also as a final note of this topic, we also discuss often catalysis. And already we give an example of catalysis, which is heterogeneous catalysis, when you discuss the (Refer Time: 27:04) adsorption isotherm, but we did not discuss catalysis as such. Now, catalysis means actually so, if I have suppose A is going to B, and we have some kind of activation energy, so the rate is dependent on this particular activation energy, now this if this is for the energetics for an un catalyzed reaction.

For a catalyzed reaction, the rate of the reaction will be faster, the reason is the catalyst actually provides an alternative route; it actually binds to the substrate, and then again gets regenerated, so that is why it is catalyst it does not stoichiometrical take part in the reaction, but in an effect it actually reduces the activation energy. And as you know the rate constant is proportional to exponential minus activation energy by RT, in a result what happens reduction of activation energy increases the rate of the reaction. So, the reaction is said to be catalyzed, the rate actually increases.

There are many examples we usually divide the catalysis into two parts. One is heterogeneous catalysis, where the catalyst and the reaction are in different phases like for example, there are many gas phase reactions, the most notable is the catalysis for production of ammonia, which is known as ever process, where actually we use iron catalyst, and you know that this iron nano particles these are solids, whether this species nitrogen, hydrogen, and ammonia, they are all gaseous bases.

So, it occurs on a surface, where I have first nitrogen, it gets adsorbed to the surface; and then hydrogen gets absorbed, and then they react the absorption is react between them, and then the ammonia comes out. So, this is called as heterogeneous catalysis, because this is a solid, and this is reaction between solid and the gas.

Similarly, you can think of (Refer Time: 29:11) phase catalysis, which is known as homogeneous reaction, homogeneous catalysis, examples are acid base catalysis. For example, you can have any ester R C O O say R prime, and then water can actually hydrolyse these ester bond and you can get the acid and the alcohol back, which is nothing but the addition of a water, but this is catalyzed either by H plus and or basically any acid or by an OH minus (Refer Time: 29:53) base. So, this is these are the examples of homogeneous catalysis.

So, catalysis is defined as heterogeneous or homogeneous catalysis. One very important example for under homogeneous catalysis is in enzyme catalysis, where actually the enzyme bounds to a substrate to give you the enzyme substrate complex. And this enzyme substrate complex eventually gives you the product plus the free enzyme back. So, the enzyme is a catalyst, it does not take part in the stoichiometry the overall stoichiometry is the substrate, going to the product.

As you see if you follow carefully, this is nothing but the way I have written it the entire reaction substrate going to product catalyzed by enzyme is using two steps, which we just discussed. In the first step, the enzyme binds with the substrate, to gives you the enzyme substrate complex and in the second step, the enzyme substrate complex gives you the product.

And then, you can actually use the steady state approximation for the intermediate and in this case, the intermediate is the enzyme substrate complex. And then, you get very beautiful discussion based on the work by Michaelis and Menten. And, you talk about Michaelis Menten kinetics will not cover Michaelis Menten kinetics in this course, because it is well covered in the textbook, so Michaelis-Menten kinetics for enzyme catalysis. So, you can always go back and have a look, how it looks like.

And then, so if I usually it is plotted as the initial substrate concentration versus the initial velocity, and then something like this, this is your initial substrate concentration. And then, you see that it actually reaches to a maximum (Refer Time: 32:07) which we call as V max. So, all these discussion you get it in any standard textbook.

And then, people talk about the alternate representation of the Michaelis Menten kinetics, which is known as the Line weaver Burk Plot, so which instead of V 0 and S 0, there in plot actually 1 over the reciprocals 1 over V 0 and 1 over S 0, and then you get a linear plot and these plots are known as Lineweaver-Burk Plot. And these plots are very very interesting, when you discuss enzyme inhibition, because there you show how basically the enzyme inhibition is a competitive or non-competitive one.

In the sense, that the enzyme and the inhibitor, and the substrate are competing for the same site of the enzyme or they are competing for different to different sites of the enzymes. So, those things are also covered in the YoyTube lectures of this preceding course.

Now, what we have done so far, we have given you an overview of how basically this overview of the introduction to chemic kinetics, what are the rate laws, what is the definition and how one can think about the integration of the rate laws, and then what are the specific type of reactions like equilibrium, (Refer Time: 33:36) consecutive, and then how a multi step reaction or a composite reaction can be decomposed into many single step reactions, so that we can actually explain the observed rate law in by doing all these maths, but we need some approximations.

And often we use two there are two approximations; so one is known as equilibrium approximation or rate deterministic approximation, and the other one is known as steady state approximation. And these two approximations are equivalent, if you imply or if you if you just apply certain conditions and then, we talked about little bit about the enzyme catalysis; there also you use the steady state approximation to get the final rate for the product formation.

And now, will discuss the more advanced topics on chemical kinetics; how one can actually think about reactions, were actually the product significantly alters the rate of the reaction. So, these are known as basically feedback reactions or the oscillatory reactions, but the product gives a positive or negative feedback to the reaction.

We also talked about the methods other methods of solving the coupled differential equation for these particular cases, and before that will give you a brief overview of how the kinetics all these all these experimentally determined things are arrived and this rate law, which means actually how you do the experiment. So, I will give you an overview about the kinetics measurement first how one can determine experimentally the rate law for a composite reaction.