Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 31
Chemical Kinetics: Rate laws – Part 4

So, we will now consider the last part of this section on Chemical Kinetics. What we phenomenologically are describing, the reaction rates. And will now consider a very very interesting reaction, which is known as consecutive reaction.

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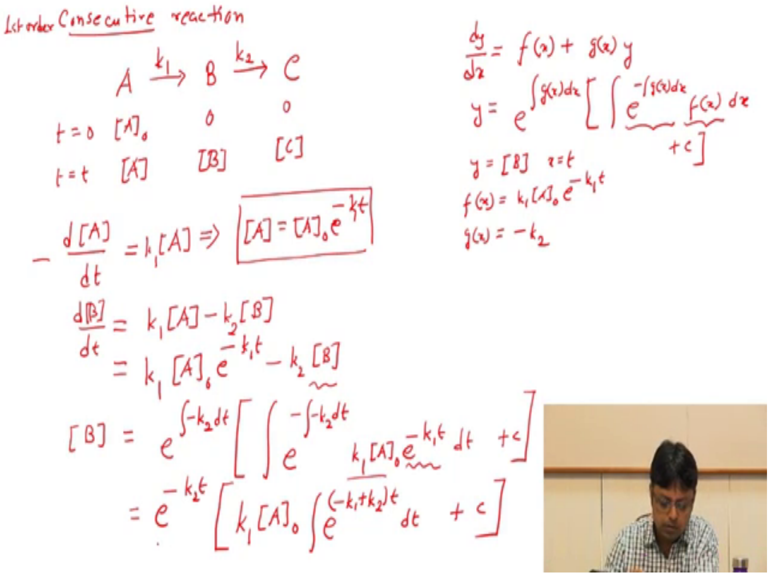

1st order Consecutive reaction

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

$t=0$ $[A]_0$ 0 0

$t=t$ $[A]$ $[B]$ $[C]$

$$-\frac{d[A]}{dt} = k_1[A] \Rightarrow \boxed{[A] = [A]_0 e^{-k_1 t}}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$= k_1[A]_0 e^{-k_1 t} - k_2 \underset{\sim}{[B]}$$

$$[B] = e^{\int -k_2 dt}\left[\int e^{-\int -k_2 dt}\, k_1[A]_0 \underset{\sim}{e^{-k_1 t}}\, dt + c\right]$$

$$= e^{-k_2 t}\left[k_1[A]_0 \int e^{(-k_1+k_2)t} dt + c\right]$$

$$\frac{dy}{dx} = f(x) + g(x)\,y$$

$$y = e^{\int g(x)dx}\left[\int \underbrace{e^{-\int g(x)dx}}\underbrace{f(x)}dx + c\right]$$

$y = [B]$ $x = t$

$f(x) = k_1[A]_0 e^{-k_1 t}$

$g(x) = -k_2$

So, consecutive reaction: consecutive as the name suggests, so it is basically, the reactions proceed in a sequential or in a consecutive order. So, A is forming something like B, and B is then forms C something like that.

And suppose all of the rates, we are now considering as first order. So, this is example of first order consecutive reaction, and also the stoichiometrics are all equal to 1. So, and let us assume, we call it as k 1 and k 2 the rate constants. And the question is, how A B and C vary with time? That we are going to solve. Now at time t, again as before, let us say that it was all A 0. So, we started with only A 0, B was 0, C was 0. At some arbitrary time, I have A B and C.

Now, first thing first, let us consider d A d t. Now d A d t is very easy to figure out, it is nothing but, d A d t will be nothing but, or minus d A d t will be nothing but k 1 into A. So, that solution is very easy. So, A will be, it is a first order, decay is nothing but A 0 into e to the power minus k 1 t. Now that is straight forward.

Now, for d B d t, will have some interesting situation, is, if you follow very carefully, it is forming at a rate k 1 into A, and it is decomposing at a rate k 2 into B. So, now, we have to integrate, but then we have to eliminate A and B. So, now we have a problem in, in this situation, because the B now contains A also. Now A already we have some form because, we have already solved the A, which is nothing but, A 0 into e to the power minus k 1 t minus k 2 into B.

So, that is the equation. Now, how do you solve it? Now, for that we will use a standard integral, if say d y d x is something like f of x, where f is a function of x plus g of x into y, then we will use that y is e to the power integral g of x d x times integral e to the power negative of integral g of x d x times f of x d x. So, it is an integral of this, multiplied by this d x plus c, where c is the constant of integration.

Now, let us just use these standard integral, and try to figure out what are the terms here. So, here y is nothing but, the concentration of B and x is nothing but the time. And now, let us see what is f x; so this f x plus y into something. So, this is y. So, f x is nothing, but k 1 A 0 into e to the power minus k 1 t, and g x is just a constant which is minus k 2, you can see it is g x into y. So, you can just write the equation, you can just write it here, B is nothing but, you can follow it from here.

So, I will have e to the power integral g x d x. So, it will be e to the power integral minus k 2 d t, then in parentheses we will have integral of e to the power, now there is a minus sign already. So, I am writing it as, like this, minus k 2 d t and then f x f x is nothing but k 1 into A 0 into e to the power minus k 1 t and then I have d t into and then plus C.

Now, if we write it down, very carefully if you follow it, that I am keeping the C right now. So, e to the power minus k 2, k 2 is just a constant.

So, this will be nothing but e to the power minus k 2 into t, and inside bracket, I will have e to the power minus k 2 t, it will be plus k 2 t now, because there are 2 minus, and then I have e to the power minus k 1 t, but I could write it actually I could write them as together. So, and also there are some constants which I can see, k 1 into A 0, that I can take out of the integral, k 1 into A 0 into I have an integral of e to the power, remember it is now minus k 1 plus k 2 into t into d t, and then I will also have a constant of integration.

Now, you can easily figure that out, it is basically, we could write it as e to the power k 2 minus k 1 whichever way you like it. So, e to the power m x integration is nothing but, e to the power m x by c. So, this integral will be, we just write it here, it will be nothing but, e to the power, or we can write it in the next page. So, just remember it is e to the power minus k 2 t that is the first term.

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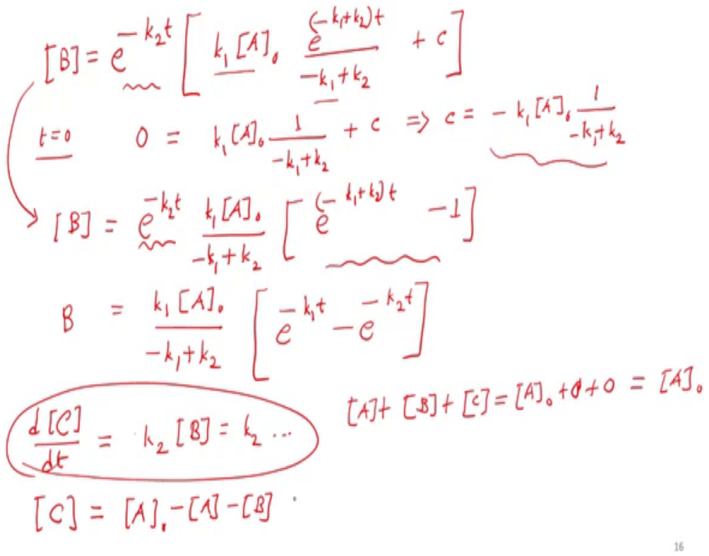

$$[B] = e^{-k_2 t}\left[k_1[A]_0 \frac{e^{(-k_1+k_2)t}}{-k_1+k_2} + c\right]$$

$$t=0 \qquad 0 = k_1[A]_0 \frac{1}{-k_1+k_2} + c \Rightarrow c = -k_1[A]_0 \frac{1}{-k_1+k_2}$$

$$[B] = e^{-k_2 t} \frac{k_1[A]_0}{-k_1+k_2}\left[e^{(-k_1+k_2)t} - 1\right]$$

$$B = \frac{k_1[A]_0}{-k_1+k_2}\left[e^{-k_1 t} - e^{-k_2 t}\right]$$

$$\boxed{\frac{d[C]}{dt} = k_2[B] = k_2 \ldots} \qquad [A]+[B]+[C] = [A]_0 + 0 + 0 = [A]_0$$

$$[C] = [A]_0 - [A] - [B]$$

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So, B is nothing but, e to the power minus k 2 t times. Now, this integral, inside I have some a constant k 1 into A 0. So, just write it, k 1 into A 0 times I will have the integrand, which is integration of this. So, it will be e to the power minus k 1 plus k 2 into t divided by minus k 1 plus k 2. So, it will be e to the power minus k 1 plus k 2 into t divided by minus k 1 plus k 2 plus I have a constant of integration which is C.

Now, we can first, evaluate the constant. So, at t equal to 0, we can figure out, the B is 0, because we said that the initial concentration of B is 0. So, this thing is also 1 and so, what we have here is, k 1 into A 0. This is also 1, because this is now t is 0, minus k 1 plus k 2 plus C. So, I can easily evaluate what is C, C is nothing but negative of this entire number. So, it is minus k 1 into A 0, and we will have 1 divided by minus k 1 plus k. So, that is C.

So, we can easily rearrange now, what is B. So, B is nothing but, B means B at concentration of B at any time, any arbitrary time, it will be e to the power minus k 2 into t into, now I can take this entire factor as common, we can just take it out. So, it will be nothing but, but I will just take not the minus sign, I will just write k 1 into A 0 divided by minus k 1 plus k 2, and then inside bracket. So, I have taken this out, and this out, which was for C actually I will have minus 1 here, and inside bracket I have e to the power minus k 1 plus k 2 into t, or we can simplify it. I can actually now move this guy inside this bracket, and then I can get a nice form for minus k 1 plus k 2. So, let us do it.

So, if I multiply by e to the power minus k 2 t so, e to the power plus k 2 t cancels out here. So, the first term is e to the power minus k 1 t, and the second term is minus e to the power minus k 2 t. So, this is the expression for B, and for C we can actually proceed in the similar way, we can write d C d t and then write it in terms of B, because you remember that this d C d t will be nothing but, because C is forming.

So, it is forming at a rate of k 2 into B, and instead of B, you can write this B expression, but that is a very clumsy way of writing, instead, you can just instead of this way, you can just argue always at any point of time, since I have 1is to1 stoichiometry, at time 0, I and all the concentration was A 0, and A 0 is being converted to B, and B is being converted to C. So, at any point of time, if I had taken these concentrations, sum of concentration of A plus B plus C, that will be there sum of the initial concentration, which is A 0 plus 0 plus 0, which is nothing but A 0.

So, from there actually, you can easily figure out what is C, C will be nothing but, A 0 minus A minus B. And you can now, use the values of A and B, A already I resolved, that A was A 0 in to e to the power minus k 1 t, it is just a first order, and then B already we have this big expression. So, if you write it down the expression for C, will look like something like 1 minus e to the power minus, or we can actually write it in the next page, because we are going to plot all of them together.

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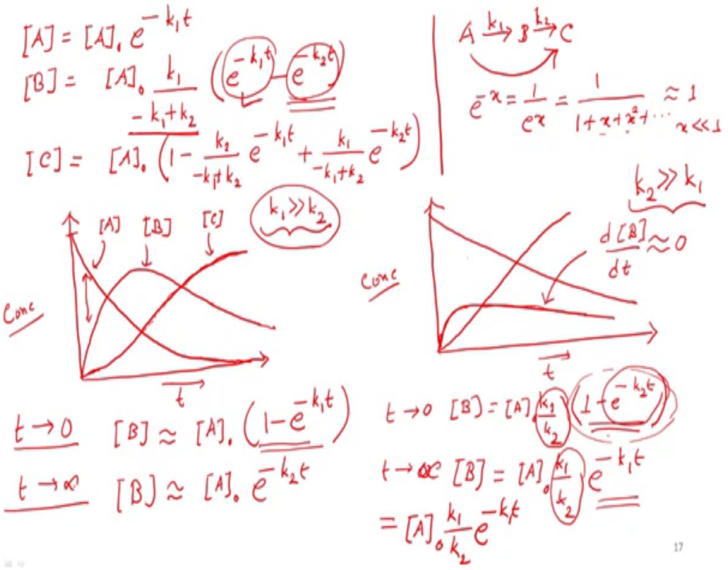

$[A] = [A]_0 e^{-k_1 t}$

$[B] = [A]_0 \frac{k_1}{-k_1+k_2}\left(e^{-k_1 t} - e^{-k_2 t}\right)$

$[C] = [A]_0 \left(1 - \frac{k_2}{-k_1+k_2} e^{-k_1 t} + \frac{k_1}{-k_1+k_2} e^{-k_2 t}\right)$

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

$e^{-x} = \frac{1}{e^x} = \frac{1}{1+x+x^2+\cdots} \approx 1 \quad x \ll 1$

$k_1 \gg k_2$

$k_2 \gg k_1$

$\frac{d[B]}{dt} \approx 0$

$t \to 0 \quad [B] \approx [A]_0 \left(1 - e^{-k_1 t}\right)$

$t \to \infty \quad [B] \approx [A]_0 e^{-k_2 t}$

$t \to 0 \quad [B] = [A]_0 \frac{k_1}{k_2}\left(1 - e^{-k_2 t}\right)$

$t \to \infty \quad [B] = [A]_0 \frac{k_1}{k_2} e^{-k_1 t}$

$= [A]_0 \frac{k_1}{k_2} e^{-kt}$

So, the equation for A was nothing but, A 0 into e to the power minus k 1 t, equation for B was, B 0 into e to the power, not B 0, and we will just we just solved it, it is a big one. So, we had it as in terms of A 0. So, it was A 0 into we have k 1 by minus k 1 plus k 2, if you remember that this equation into e to the power minus k 1 t minus e to the power minus k 2 t into e to the power minus k 1 t minus e to the power minus k 2 t, and for C using the material balance that A plus B plus C will always be equal to A 0, we can write it as, A 0 into 1 minus k 2 by minus k 1 plus k 2 into e to the power of minus k 1 t plus we will have k 1 into minus k 1 plus k 2 into e to the power minus k 2 into t.

Now, let us plot the, all these concentrations together on the same plot. So, y axis is the concentration of the species, and x axis is just the time. Now, let us suppose, we are considering, one particular situation, where k 1 is much larger than k 2. So, again this reaction was this, A is going to B, and B forming C with rate constants first order rate constants k 1 and k 2.

So, if k 1 is much greater than k 2, the plot will look like something like this. So, the A actually falls with a steep exponential decay, because k 1 is much larger, and then B actually, initially forms, because it is forming from A, and then it will further decay, because it is now decomposing into C, and C it will slowly rise.

Now, let us try to explain, why the curves are so like that. So, this is a curve for A, this is the curve for B, the intermediate, now B is called an intermediate, and this is the curve for C. So, it is as if it is going into C via B, and where B is the intermediate. So, this is the, only for the constant condition that k 1 is much larger than k 2, will see also the other condition in a minute.

Now, just think about it. So, a very simple, it is just decaying with minus k 1 into t, alright. So, let us now try to understand, what happens for these curves, when the time is very early time, or t tends to 0. Now remember that, all these exponential terms, you can write it as e to the power minus x, it is nothing but 1 by e to the power x, which is nothing but, 1 by 1 plus x plus x square that is all the way.

Now, usually, if all these terms are very small, x and x square and all these terms; so then you can think that, these terms we can ignore with respect to 1, and then you can actually write it to be equal to 1, if of course, x is much much less than 1. Now you see here, when t tends to 0, and also we have a condition like k 1 is much much larger than k 2. So, the concentration of the B will be proportional to, you can write it A 0 into k 1 by minus of k 1 because k 2 we are ignoring.

Now, e to the power k minus t and e to the power minus k 2 t; now, t is going to 0 and k 2 is also very very small, which means, now you can ignore the e to the power minus k 2 into t as you can just approximate it to be equal to 1, but e to the power k 1 t you cannot approximate because t is small, but k 1 is still large. So, I am just keeping it as e to the power minus k 1 t minus 1, which you can actually write it as, you can actually, you could use this minus sign and put it inside.

So, then it will be nothing but, now let us just write it. So, it will be nothing but, 1 minus e to the power minus k 1 t. Now think about it, what is happening, here it is 1 minus e to the power minus k 1 t. So, A is decreasing with A rate e to the power minus k 1 t, and B is raising with the same rate. So, that is why initially this B and b rates are exactly opposite.

So, A is forming B, and B is farming, B is getting formed, and then B is actually decomposing at a very slow rate that is why the decay of the B is not very significant, right now, at least at the initial part.

So, it is as if C is just not there, because C going from B to C, the rate constant k 2 is much much smaller, but however, at a very longer time, what will happen, you can think that this B, we still have the same condition. So, k 1 is much larger than k 2. So, the, this will be just minus A 0, because there is a minus sign. Now if you take the other limit. So, you can actually set, e to the power minus k 2 t, this term to be 0, now because t is very large, and then you can totally ignore that term, and then you can, you can actually not, not this term sorry, it is e to the power k 1 t term, that you can totally ignore, because k 1 is large and t is also large. So, it is going to e to the power minus infinity. So, it is, you can totally ignore it. It is 0, and then you have the second term which is e to the power minus k 2 into t.

So, together you can write it there is a minus sign also here. So, this minus sign, and that minus sign, you can together write it as, e to the power minus k 2 t. So, in a long time B is decaying with it is own rate constant, which is basically B is forming into C, and at that rate, C is also growing you can see that. Now let us consider the other limit. So, these are basically, the 2 limits for this condition, but we can also think about when k 2 is much much greater than k 1, and then we will see that there is a very very interesting situation, if k 2 is much much greater than k 1, let me first plot it, and then again qualitatively, not qualitatively, quite quantitatively trying to, try to describe, why the nature of the curve is like that, in that case it will decrease very very slowly, but the concentration of the B will rise, and then will become very very steady and then, but rise a little and then will have a C which will first go and then grow.

Now, what is happening here, again we can approximate, that at t tends to 0. Now remember that k 2 is much much greater than k 1. So, I will have always in the look at the B equation. So, the B equation will be, A 0 divided by k 1 by k 2, because I am ignoring now, k 1 with respect to k 2, and then inside parentheses, I have e to the power minus k 1 t, and e to the power minus k 2 t. Now we will follow the same logic, if k 2 is very large, you can think that k 1 is very small. So, e to the power minus k 1 t can be approximated to be equal to 1 because k 1 into t is a very small number. And if x is a very small number, e to the power minus x is 1, and then minus we have e to the power minus k 2 t.

Now, think about it. So, this is also an growth, just like the earlier case; however, look at it very carefully. So, when we have this kind of situation. So, the initially the B will rise, of course,, but then sooner or later, what will happen is that, we have it just 1 minute, you will have k 2 is much greater than k 1. So, that is why we are ignoring this term, making it to be 1, that is perfect and when t is very large, then B as before will be, A 0 into k 1 by k 2, and then we will have e to the power minus k 1 t, because now what is happening this k 2 into t is very large. So, e to the power of it is almost e to the power minus infinity. So, that is going to almost 0 and then we will have just e to the power minus k 1 t.

Now, let us look at the nature of the curve, think about B. So, B is actually now growing as e to the power minus k 2 into t, not as e to the power minus k 1 into t. So, A is earlier A was forming into B, and that was basically the driving force, but here you can see that, A set B is actually decaying with e to the power minus k 2 t. So, the growth of the B was initially, it is 1 minus e to the power minus k 2 t, but the growth is not very large, why? Because you see there is a factor, which is k 1 by k 2, since k 1 is much less than k 2. So, this curve did not rise to a very great height. So, it just raised a little bit, and then trying to decay, and in the very long limit, you can see, I have a very very small factor which is always there, k 1 by k 2, and then I have e to the power minus k 1 t, but what is k 1? k 1 is a very small number.

So, the decay will be also very very slow. So, under this condition, we can say, that the intermediate concentration is, such a way it is varying, that it is almost 0, which means the intermediate is not varying over time, remember that we, we do not have space here. So, let me just write it as here. So, it is at A 0 to k 1 by k 2 into e to the power of minus k 1 t, that is ok. I am just removing this part, because my, picture is blocking that section.

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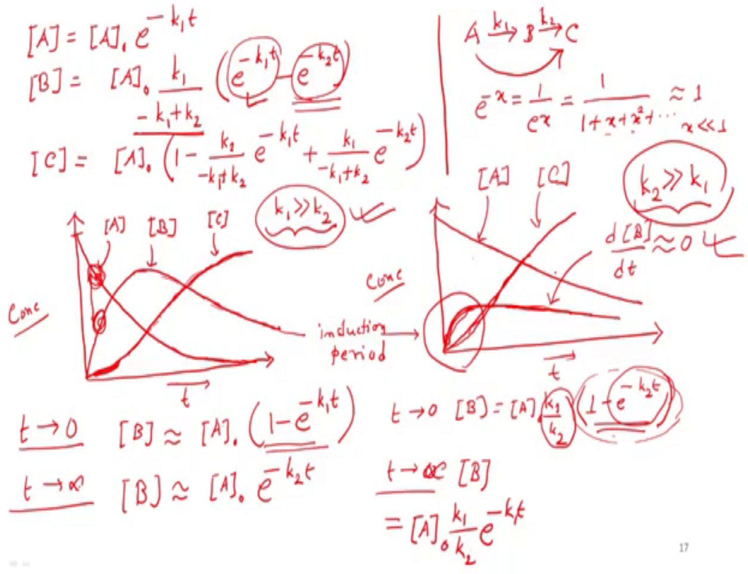

$[A] = [A]_0 e^{-k_1 t}$

$[B] = [A]_0 \frac{k_1}{-k_1+k_2}\left(e^{-k_1 t} - e^{-k_2 t}\right)$

$[C] = [A]_0 \left(1 - \frac{k_2}{-k_1+k_2} e^{-k_1 t} + \frac{k_1}{-k_1+k_2} e^{-k_2 t}\right)$

$k_1 \gg k_2$

$t \to 0 \quad [B] \approx [A]_0 \left(1 - e^{-k_1 t}\right)$

$t \to \infty \quad [B] \approx [A]_0 e^{-k_2 t}$

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

$e^{-x} = \frac{1}{e^x} = \frac{1}{1+x+x^2+\cdots} \approx 1 \quad x \ll 1$

$k_2 \gg k_1$

$\frac{d[B]}{dt} \approx 0$

$t \to 0 \quad [B] = [A]_0 \frac{k_1}{k_2}\left(1 - e^{-k_2 t}\right)$

$t \to \infty \quad [B] = [A]_0 \frac{k_1}{k_2} e^{-k t}$

So, we can write it, and then C actually grows, and A, look at the A curve, the curve of A actually decays much slowly, because A is nothing but, e to the power minus k 1 t, but now k 1 is much small. So, a decay is very slow, and B, not B, the C actually grows with a rate, which is k 2 into t, and k 2 is large. So, that is why, I see actually grows much at a, much higher rate than this curve, where actually initially C did not grow much.

So, we have a period where actually C, now builds up this period, and that period is known as induction period. So, during the induction period, the concentration of B is just building up, when not B, the product C is building up, when actually B was rising, but then all of A sudden, the B becomes almost steady condition, and why it is steady state? It is we can actually easily, see it from the curve, which decays at a very very slow rate, e to the power minus k 1 t, and in a very long time limit, in that t tends to infinity limit, and under this condition, where k 2 is much much greater than k 1.

So, that we see that the nature of the curves in a consecutive reaction, varies greatly if you take k 1 much much greater than k 2, or k 2 much much greater than k 1, and we can actually now, have a very very interesting analogy between these two rates.

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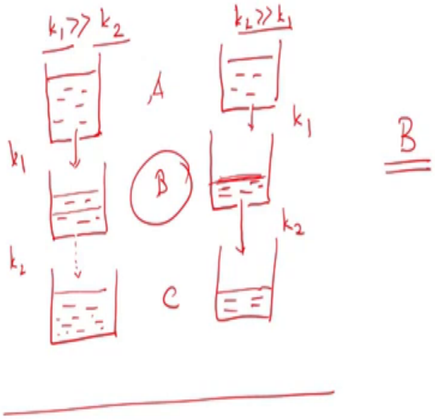

So, what is happening suppose, I have a bucket, I have actually 3 buckets, and I am basically, suppose this is A, initially I pour some water here, and then the bucket B and bucket C are empty, this is A this is B this is C.

Now, suppose I punch a hole here, in the sense that, I punched a hole like this, which means, I have k 1 much much greater than k 2, means the water is pouring here in the B, but B also has a hole, but that hole is much smaller. So, what will happen water will first filling the B, and then slowly, this will come to filling the C. So, in the long term, of course, everything will be C, but in the very early time, you will see that, it is only filling up B, but slowly B also transfers that water, but at a much low rate, because now that k 2 is much slower than k 1, and that is what exactly you saw, that A 1 is filling here, A 1 is decaying, and B is actually growing with the same rate.

But after some time, actually it starts decaying, when actually A also has completely consumed, and then B is only decaying, and then C also rises at the same rate, like the B is decaying. Similarly on the other extreme, when I have k 2 much greater than k 1, what will happen? I have a small hole here, the water is coming, and then it is filling here, but as soon as it is filled, I have a very very larger hole here, immediately the water gets passed and fills the C. So, what I have C here that this water level will be a little bit high always, but as soon as it is filled in, that actually gets passed to the other bucket, because now k 2 is much larger than k 1.

So, you see that initially the B has rise, but then it just does not change, because as soon as it is filled in, it is decaying, and quickly the C actually takes over, it just goes above B very quickly, and A actually is decaying very very slowly, the reason is, A has a very small hole. So, this is a nice analogy, you can think off, for a consecutive reaction that water is being transferred from one bucket to the other bucket and eventually to C.

So, eventually all the water will be transferred from A to C, but through an intermediate bucket which is the B bucket. So, this B is an intermediate, and in many many chemical and biological reactions, these intermediates has to be studied to understand the reaction mechanism, and the kinetics of the intermediate is very very important, where we can actually understand the, how the intermediate varies with respect to time, and we see that under conditions like, when the first rate is larger than the second rate, or the second rate constant is larger than the first rate constant, we can have very very different situation.

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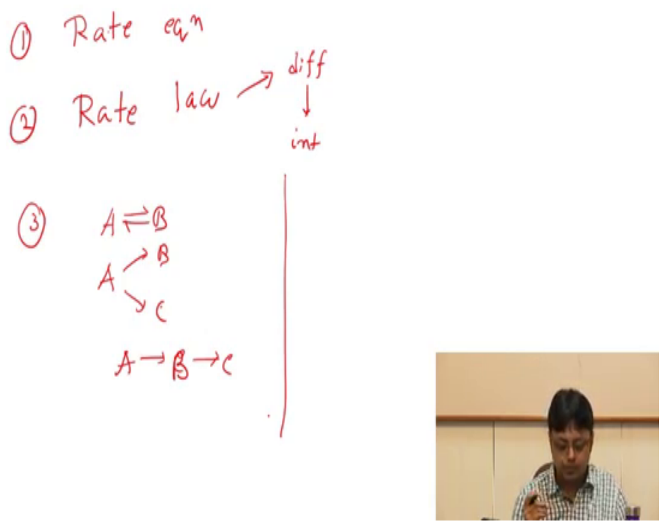

① Rate eqⁿ

② Rate law ↗ diff ↓ int

③ $A \rightleftharpoons B$

$A \to B$, $A \to C$

$A \to B \to C$

So, to summarize what we actually studied, in this entire section of the first part of chemical kinetics, we just defined, how we can express the rate equation, we also discussed how you can express the rate equation as a function of the concentrations, that we call as Rate law, and then we integrated it, we wrote it in a differential form, and we showed how to integrate into a rate law for various reactions like, first order, second order, and nth order, second order with 2 different species, and many other ways.

And then we talked about interesting situations, if we have reversible reaction, or if we have competing reactions like this, or at last we also talked about the consecutive reactions.

So, in the next lecture we will discuss about mechanism. So, we will use all these concepts which we have built in so far. And then we will see, how using these concepts of the rate constant we can actually propose a mechanism of a reaction, or a composite reaction, beam which is actually can be split into many elementary reactions, and if we add up the overall rate constant or the rate law, actually mimics what we observe experimentally.

So, we can actually propose many different mechanisms, and meaning that many different mechanisms can explain the same reaction, but we will choose actually very intelligently, which one actually can be, the most common, or most reliable mechanism. And we will use some approximation, how to do it, we will use two approximation steady state, and equilibrium approximation, a rate determining setup approximation, which we will be discussing in detail in the next lecture.

Thank you.