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

Lecture – 29
Chemical Kinetics: Rate laws – Part 2

All right so, let us now assume that, we have the similar equation, stoichiometric equation that, nu A plus nu A of A and nu B of B plus everything is going into products

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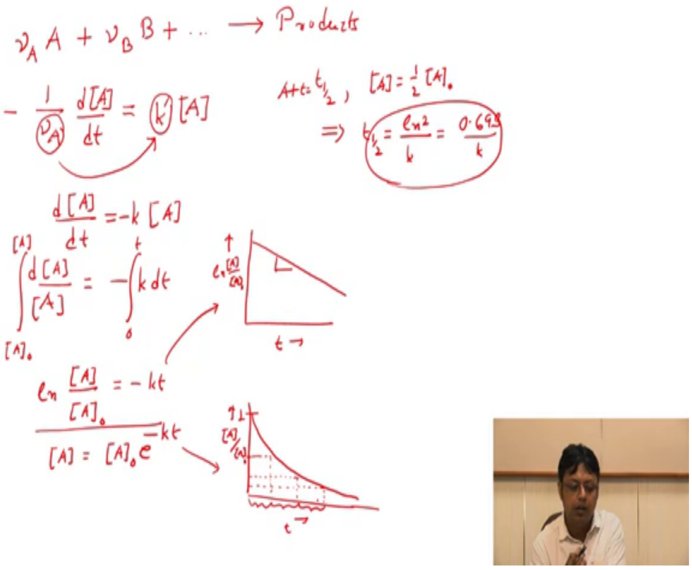

Now if we find that, the rate law, follows a first order with respect to A, then the rate, which we can write it as 1 by nu A d A d t with the negative sign, it is first order with respect to A, and the rate constant, I am writing as k prime, and then what you can also do is that, you can actually absorb this nu prime into k. And then, you can define, redefine a new rate constant, and then we can just write d A d t is nothing but, k into A with a negative sign. And then you can just arrange the terms, d A by A will be nothing but, minus k d t and then, you can integrate it, to get the integrated form of the rate law. And we are saying that, fine.

You go from 0 to sometime t, and initially suppose, I have a concentration like A 0, which is going to A. And you know this first order rate equation, what is the integrated form when you did the radioactivity.

So, that also follows the first order rate equation. So, you have l n A by A 0 is minus k t, or you can write it in terms of the exponential form where you will have A is nothing but, A 0 into e to the power minus k t. So, if you plot l n A by A 0 versus t, then you will have a linear slope, where a linear plot, where the slope will be equal to minus k.

So, this is a plot of l n A by A 0, and this is a plot of say versus t versus if you had plotted the other way, like you are plotting say A by A 0 versus t, and that is exponential plot. And initially at time 0, it will be 1, and then it decreases exponentially with time. Now ah, you can ask this question, fine, what about, what is the time at which the concentration drops to it is initial concentration, that we call as half life, you know that, and to get the half life, we just use this equation, and put that, put the condition at t equal to t half, the concentration drops to the half of this initial concentration. And you already know that, this t half will be nothing but, l n 2 by, by k which l n 2 is 0.693 by k.

So, for first order reaction, we see that, the half life is independent of the initial concentration, which is very important, which means, suppose this is 1, suppose this curve starts from 1. So, at what time it comes to 0.5? So, we say that fine, this is the time where it comes from 0.5, now suppose you start that, as your initial concentration which is 0.5 in this scale. And then you ask at what time it goes to 0.25? You will find that time is also the same time t half, or if you start with the 0.25, then you ask at what time it is goes to 0.125? You will find, that is also at the same time.

So, the t half is independent of the initial concentration. You could also start from a any arbitrary time, not like 1, 0.1, 0.25, you could just start from say 0.8, and ask this question at what time it goes to 0.4, if the if I start my initial time at when the concentration or the relative concentration was 0.8. So, this is very interesting and this happens only for the first order equation.

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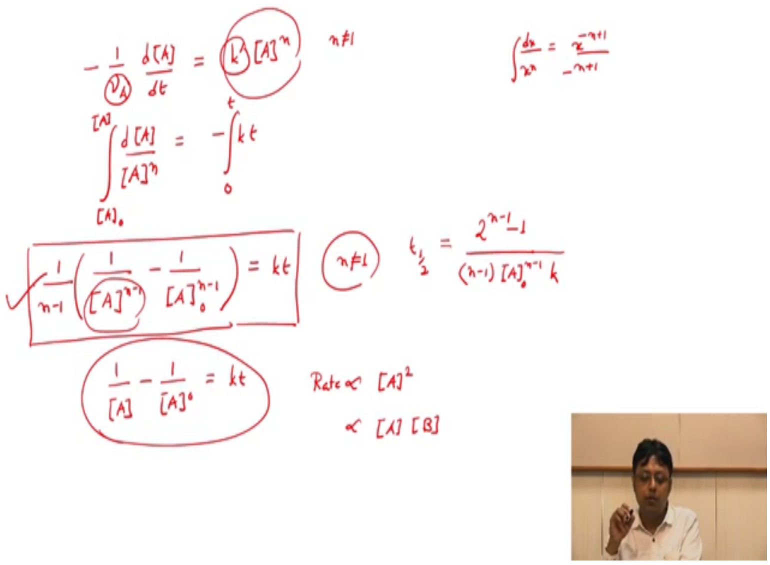

Now, for any, any, other equation where actually, you have a rate law, which is something like 1 over minus nu A into d A d t, suppose it varies with the A to the power n, where n is not equal to 1. So, then we can easily integrate it, and as before we can actually absorb the nu A inside k prime to redefine a new constant k, and we can just write it, d A by A to the power n integrated ah, that will give me minus k t and when time equal to 0, where using the same notation initial concentration was a 0 and time t it is A.

So, this integration is nothing but, l n 1 over x to the power n, is nothing but, not l n, integration of x to the power 1 over x to the power n, is nothing but x to the power minus n plus 1 divided by n plus 1, minus n plus 1. So, we can easily write it down, and you can also just write the, I mean you can rearrange the terms and you will figure out that the final form I am writing here. So, it will be 1 over A to the power n minus 1, minus 1 over A 0, we are writing A 0 like this, to the power n minus 1, that will be or we can also write it as 1 over n minus 1 here, that it will be equal to k t, of course this is true for n not equal to 1.

Now, this is true for any, order reaction like second order, third order something like that, provided to the second order, third order, or fourth order whatever we are saying, it, it is dependent only constant, the power is dependent only on one species, which means the molecularity is only 1.

Now, we could have a second order, if it is second order, for example this n equal to 2, then we will have a rate expression something like 1 over A minus 1 over A 0 is k t that is it.

Now we could ask, what will be the half life for any such reaction where, n naught is not equal to 1, you can easily figure that out, instead of A, I will just put here A 0 by 2 raise to n, n minus 1, and you can see here that the value will be 2 to the power n minus 1 minus 1 divided by n minus 1 into A 0 raise to n minus 1 into, of course you will have the rate constant here.

Now, you see here that this is true for again, n not equal to 1 which means, for second order it will be 1 over A 0, for third order it will be 1 over S 0 square, which means now the half life depends on the initial concentration. So, this is a very striking difference between the concentrations for the first order reaction with any other nth order reaction. Now, this equation we got, when actually the rate is proportional to the concentration of a squared, but you could have a second order reaction, where it will be something like A into B.

So, the 2 species are actually coming. So, the question is how will you solve it? Similarly, you could have a third order reaction when instead of A cube, it could actually be A into B square, or something like A into B into C. How will you solve those equations?

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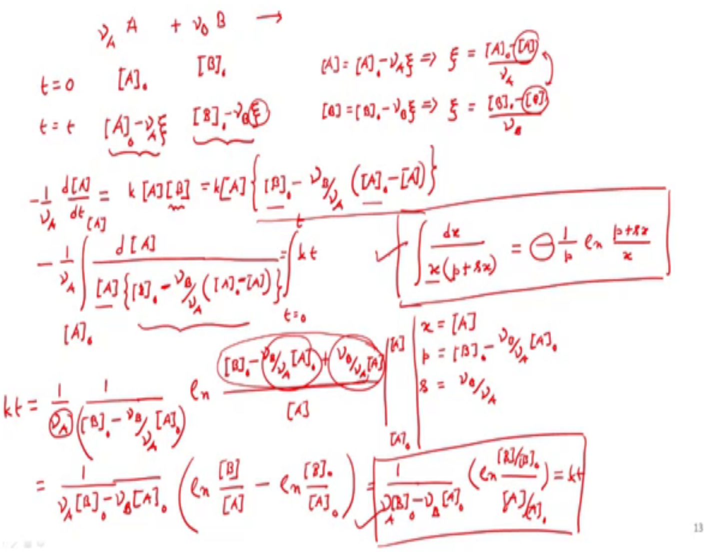

$$\nu_A A + \nu_B B \longrightarrow$$

$$t=0 \qquad [A]_0 \qquad [B]_0$$

$$t=t \qquad \underbrace{[A]_0-\nu_A\xi} \qquad \underbrace{[B]_0-\nu_B\xi}$$

$$[A]=[A]_0-\nu_A\xi \Rightarrow \xi=\frac{[A]_0-[A]}{\nu_A}$$

$$[B]=[B]_0-\nu_B\xi \Rightarrow \xi=\frac{[B]_0-[B]}{\nu_B}$$

$$-\frac{1}{\nu_A}\frac{d[A]}{dt}=k[A][B]=k[A]\left\{[B]_0-\frac{\nu_B}{\nu_A}([A]_0-[A])\right\}$$

$$-\frac{1}{\nu_A}\int_{[A]_0}^{[A]}\frac{d[A]}{[A]\underbrace{\left\{[B]_0-\frac{\nu_B}{\nu_A}([A]_0-[A])\right\}}}=\int_{t=0}^{t}kt$$

$$\boxed{\int\frac{dx}{x(p+sx)}=-\frac{1}{p}\ln\frac{p+sx}{x}}$$

$$x=[A]$$

$$p=[B]_0-\frac{\nu_B}{\nu_A}[A]_0$$

$$s=\frac{\nu_B}{\nu_A}$$

$$kt=\frac{1}{\nu_A}\frac{1}{\left([B]_0-\frac{\nu_B}{\nu_A}[A]_0\right)}\ln\frac{[B]_0-\frac{\nu_B}{\nu_A}[A]_0+\frac{\nu_B}{\nu_A}[A]}{[A]}\Bigg|_{[A]_0}^{[A]}$$

$$=\frac{1}{\nu_A[B]_0-\nu_B[A]_0}\left(\ln\frac{[B]}{[A]}-\ln\frac{[B]_0}{[A]_0}\right)=\boxed{\frac{1}{\nu_A[B]_0-\nu_B[A]_0}\left(\ln\frac{[B]/[B]_0}{[A]/[A]_0}\right)=kt}$$

Now, what we are going to do right now is that, we are saying that fine, let us start with the our old stoichiometric equation, sorry, it will be just a nu A A plus nu B B is going to product and at time 0, I call this as A 0 and B 0 and at time equal to t, we are saying that, fine, let us assume that the advancement of this reaction is psi. So, the amount which is reduced for A, will be minus nu A into psi, amount reduced for B, because both are reactant, remember, that will be minus nu B into psi, because that will be proportional to the stoichiometric number. So now, what we can write is that, the problem here is that, if I write d A d t or minus 1 over nu A d A d t. So, the problem will face is that, it is now some rate constant into A into B.

So, the B is appearing here. So, I have to write B in terms of A, otherwise I cannot solve it. I can actually write it very easily. So, this is ah, this is A right now, and this is B. So, let us just write it first. So, A is nothing but, A 0 minus nu A into psi, and B is nothing but B 0, or instead of, since we are solving the A, we will just keep it as A because, that is a, that is a variable here. So, not variable the variable is t, but that will integrate anyway. So, writing it as k into A, and instead of B, we are just writing it as B 0, remember B 0 is a constant, minus, I can write it as a nu B into psi.

But what is the value of psi here. Let us see. So, what I am saying here, I know that A is A 0 minus mu A into psi. So, which means psi is nothing but, A 0 minus A divided by nu A, and similarly you can write for B as B 0 minus nu B into psi, and you can ask this question, what is psi here? Psi is nothing but, B 0 minus B divided by nu B. So, you can now equate these 2 equations and write B in terms of A. So, that is what we are going to do, and if you do that so, you can easily figure out that, I am skipping the steps.

So, it will be nothing but, nu B divided by nu A times A 0 minus A. So now, I have a equation which depends only on A, remember that B 0 is a constant, just like A 0. So, B 0 is not a problem. So, now, I can rearrange the terms, and then try to integrate, and then let us see how to do this integration. So, I will have 1 over nu A, and then we can just write d A divided by this entire thing, which is A times, it is basically B 0 minus nu B by nu A times A 0 minus A, and ah, then we have ah, k t here and then you, will integrate.

So, as before we will just integrate, we will say that at t equal to 0, the initial concentration was A 0, and at time t the concentration was A. Now to solve this equation, you can actually use a standard integral, which is d x divided by x into p plus s x, that you can write it as, minus 1 over p l n p plus s x divided by x. So, that integral you can directly use, which I have provided here. And you just, I do not have to identify what are the x a p and s here.

So, x is nothing but, the concentration of A that you are integrating. And ah, you can see it here, A appears are just like x appears here, and then p plus s x. So, p is nothing but ah, the constant, and you can see the constant is nothing but B 0. If I just write this thing, and it is nothing but B 0 minus nu by nu B by nu A into A 0, that part is the p, and then you have a s, s is nothing but if you expand it so, I will have the third term as, A times nu B by nu A, there is a minus sign here, and there is also a minus sign here. So, that is plus. So, s is nothing, but nu B by nu A.

So, then I can actually write a, use this integration or integral. So, I will have a minus sign here. So, I already had a minus sign here, that will be plus. So, it will be 1 over nu A and then 1 over p, p was nothing but B 0 minus nu B by nu A into A 0, and times I have l n p plus s x, what is p? P is B 0 minus nu B by nu A into A 0 that is the p. And p plus s x is nothing but what we have written in the so this entire part.

So, that was p, and then I had nu B by nu A into A and it is divided by x, x is nothing but A. Now remember this is just the integral. So, I have to ah, evaluate it between A equal to A 0 and A equal to A. And that should be equal to, the right hand side integration is pretty straightforward, that should be equal to k t. So, k t is nothing but this. So, I can now simplify it. So, this term actually if I just multiply it with this entire thing. So, I will have 1 divided by nu A B 0 minus nu B A 0 and then I have to take the upper and lower limits.

So, in the upper limit, when I am writing A has A. So, you remember that, what was this entire thing. This entire thing was ah, we, we actually, replaced it. If you remember that it was replaced for B. So, this was the expression for B, it was k into B, and the entire thing was actually B. So, it is nothing but B by A minus for, the lower limit, if I put A as A 0.

So, then you see that these two terms will cancel, and then I will only have B 0 by A 0. So, we can again rearrange it a little bit. So, which will be nothing but, 1 over nu A B 0 minus nu B A 0. And then, we will have l n ah, we have B by B 0 divided by A by A 0 that is equal to k t.

So, that will be the integrated form for a second order reaction, where it is first order with respect to each of these, each of the reactants. So, you can see that moment we go from first order to a nth order reaction, where the nth order is only with respect to one particular reactant, we have a form like this we already discussed. And then for a second order, we, we see that, we have a very different way of solving, we have to use a standard integral otherwise we cannot solve it. And then you can also ask this question as, as a, as a, homework problem, you can try solving this.

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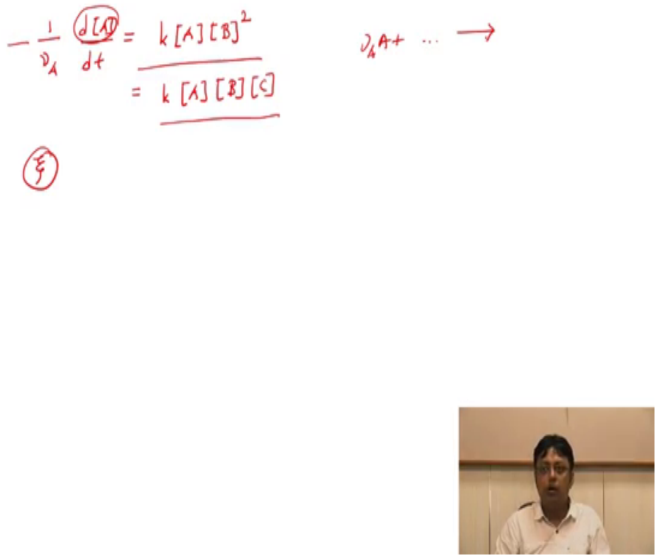

$$-\frac{1}{\nu_A}\frac{d[A]}{dt} = k[A][B]^2$$

$$= k[A][B][C]$$

$$\nu_A A + \cdots \rightarrow$$

If I have a general equation like A plus B plus C whatever, and if I have a situation like this, 1 over nu A d A d t, how actually, what will be the solution, if I have say k into A into B square suppose, can be A square into B, but that mathematically the same, or if it has something like k into A into B into C, and the procedure is the same. You can first solve this one you do not need to solve the A B C problem.

But the procedure is the same, you just have to eliminate psi from the B equation and A equation, and then equate them, and then write B in terms of A, or C in terms of A.

So, everything you have to write it in terms of A, because you were writing your rate equation as d A d t, if you had written as d B d t, you write everything in terms of B, and then choose some initial concentration which are constants, but then at the end of the day, you have to have some kind of ah, you need to know how to integrate that particular complicated form, because you need to use a standard integral, a standard triple, and find out, figure out actually, what is this integral, and then use it and solve it. Now, in the next part, we will discuss some special reactions like what happens. So far, we are actually considering only nu A A plus nu B B all these things going into the product as an irreversible reaction, but what happens if we include reversibility. And then, we will also discuss some special reactions like competing reactions, which are in general account, the opposite reaction and the consecutive reaction those things we will discuss.