Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 30
Chemical Kinetics: Rate laws – Part 3

Let us now discuss, what happens if the reaction is a reversible one, meaning, so far we have discussed irreversible nature of the reaction, like A plus B going into products.

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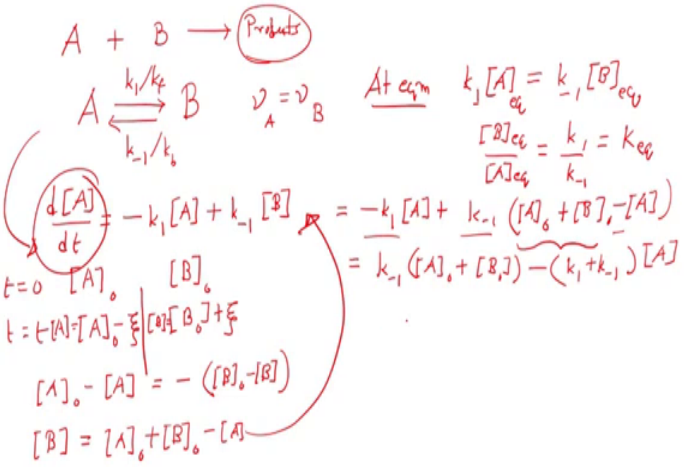

$A + B \longrightarrow \boxed{\text{Products}}$

$A \underset{k_{-1}/k_b}{\overset{k_1/k_f}{\rightleftharpoons}} B \qquad \nu_A = \nu_B$

At eqm $\quad k_1[A]_{eq} = k_{-1}[B]_{eq}$

$\dfrac{[B]_{eq}}{[A]_{eq}} = \dfrac{k_1}{k_{-1}} = K_{eq}$

$\dfrac{d[A]}{dt} = -k_1[A] + k_{-1}[B] = -k_1[A] + k_{-1}\left([A]_0 + [B]_0 - [A]\right)$

$= k_{-1}\left([A]_0 + [B]_0\right) - \left(k_1 + k_{-1}\right)[A]$

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

$t = t \quad [A] = [A]_0 - \xi \quad [B] = [B_0] + \xi$

$[A]_0 - [A] = -\left([B]_0 - [B]\right)$

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

So, let us now assume that, instead of going into reverse, irreversible, irreversibly into products. Let us have, we have two components A and say some product, that I am writing as C, the reason being, B actually we are using for reactant, we can also use a B, but just be careful that here, we are writing the B as the product for the forward reaction, and then B also can get back to A, which means the reaction is reversible.

Now, any reaction in principle is reversible in nature, but it depends, under what conditions, and reversible reactions can become our irreversible reaction, meaning, one of the directions like, the forward direction or the reverse direction will happen at a much more rate than the other direction.

So, the reaction will be essentially irreversible, but let us now consider that, both the forward and the backward reaction occurs at some appreciable rate. And also let us consider that, nu A and nu B are equal.

In the sense that, it is A and B are inter converting to each other with equal stoichiometry also, and the associated rate constants are say k 1 and k minus 1, some textbook write it as k 2, but we are just using the minus notation. So, k minus 1 is basically the reverse rate constant for the reverse reaction or the backward reaction, some, sometimes we write it as k f, in the sense it is a forward rate constant or rate constant for the forward reaction, and backward rate constant or rate constant for the backward or reverse reaction, sometimes written as k b or k r for the reverse reaction.

Now, we have to, before we begin, let us consider what the reaction mixture, initially content. So, suppose we mix some A and B together, and then what happens? the A starts converting into B. Now we could also start only from A, and then we suppose heat it up to make some B, and as we are making B, initially of course, the concentration of the B will be slow.

And so, more and more, with time more and more A will be consumed and to make B, and then the B concentration will increase, and then they will also, further react and then give back A. So, sooner or later this initial rate of A going to B will be very high, and B going to A will be slow. But sooner or later, these two rates will become equal, because you know that, rate constant is now, rate is nothing but rate constant times the concentration.

So, as the rate constants are fixed with respect to, if the temperature is fixed rate constants are also fixed, but if you vary the concentration, initially A was at a very high concentration. So, the rate for, rate of the reaction for A going to B was very high, but rate of the reverse reaction was slow, but as soon as the concentration builds up for B, then the reverse reaction also tries to be significant, and at a point will app appear, where basically the rate of the forward reaction and the rate of the reverse reaction becomes equal.

And that point equilibrium is attained, and once the equilibrium is attained for a particular temperature, if we do not disturb the system, the concentrations will not change, and we know that it is a dynamic equilibrium, meaning it is not like that is not forming B, and B is not forming A, they are interpreting still each other.

However, the net amount of A and B is unchanged, and at that equilibrium concentration, we know that, at equilibrium, rate of forward reaction which is k 1 into A, will be equal to the rate of the reverse reaction, which is k minus 1 into B, and then correspondingly the concentrations, if we write it as equilibrium concentration, we find that, this ratio B equilibrium divided by A equilibrium is nothing but, k 1 by k minus 1, it is a ratio of the rate constant, which is also a constant, which we termed as equilibrium constant.

Now, this equilibrium constant is not exactly the thermodynamic equilibrium constant, in the sense that we just took the ratios of the concentration, if we had written the thermodynamic equilibrium constant, we have to use the activities of the species, and then we have to write activity in terms of concentration, that concentration and with activity coefficient, and then also the concentrations has to be divided by the standard state, so that to make the k equilibrium dimensionless.

In this case also, it is dimensionless. Because, it is a 1 is to 1 stoichiometry, and the units just cancel out. Now, let us try to see, how will you write rate of the reaction. So, as before, I can write the rate of the reaction as, minus d A d t, but this minus I am not writing here, instead I am writing the minus here, k 1 into A, we could have written minus d A d t is, plus k 1 into A, but I am just writing in that way.

So, it is being consumed in the forward reaction, and it is being regained in the reverse reaction. So, that is the rate of the reaction, and at again, we can write it, that suppose at t equal to 0, we have say A 0, the initial concentration of A, and initial concentration of B, suppose was B 0, and at some arbitrary time, suppose the advancement is say some xi, and then will have A 0 minus xi, and here will have B 0 plus xi.

So, now you can see, if I just eliminate the xi. So, this is nothing but A at any time, and this is nothing but B at any time. And so, if we just eliminate the xi or equate the expression for the xi, with respect to A, and with respect to B, we will find that, at any point A 0 minus A, will be nothing but negative of B 0 minus B. That will always follow, because we just wrote it for any arbitrary time.

Now, it follows that, which means the B can be expressed in terms of A, and that is A 0. So, this is B, as you can see, plus we will have B 0, because that has a negative sign, and that we are going, taking the left hand side minus A. Now this expression you can put it back here, to get an expression of the rate, because since we wrote the rate in terms of the d A d t. So, we have to eliminate B, and write to B in terms of A.

So, we write it like this, minus k 1 into A plus k minus 1, and instead of A we are writing as A 0 plus B 0 minus A. I could rearrange it. So, we will have something like k minus 1, where I am writing the constant terms first, into A 0 plus B 0, and then the A dependent term, which are nothing but minus k 1. So, this minus k 1, and here I have plus k minus 1, but there is A minus in also. So, it will be k 1 by plus k minus 1 into A.

So, that is the expression for d A d t. Now we can proceed with that, because we have some constant minus something into A. And now, my left hand side have just d A d t, I can readily integrate it, but, before we integrate that, we can also simplify it. And we know that, at equilibrium what happens. At equilibrium we know that, like let us just turn the page, because we need some space here.

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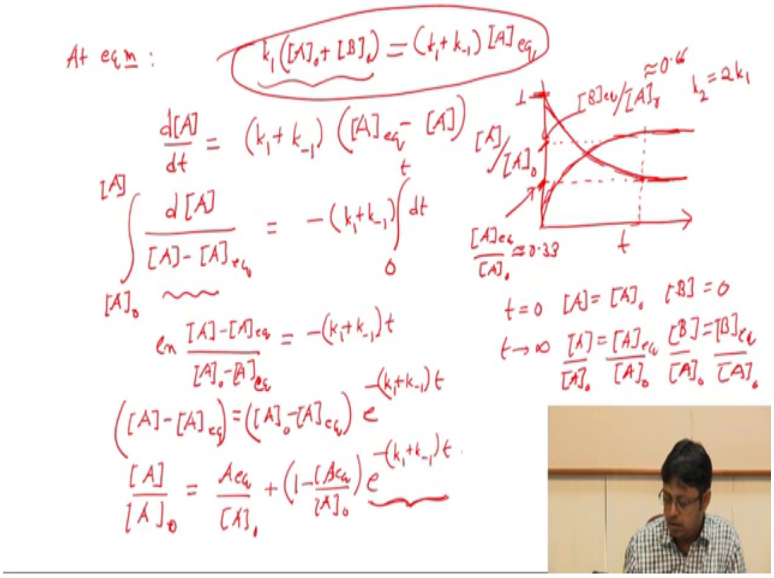

At eq$\underline{m}$:

$$\boxed{k_1([A]_0+[B]_0)=(k_1+k_{-1})[A]_{eq}}$$

$$\frac{d[A]}{dt}=(k_1+k_{-1})([A]_{eq}-[A])$$

$$\int_{[A]_0}^{[A]}\frac{d[A]}{[A]-[A]_{eq}}=-(k_1+k_{-1})\int_0^t dt$$

$$\ln\frac{[A]-[A]_{eq}}{[A]_0-[A]_{eq}}=-(k_1+k_{-1})t$$

$$([A]-[A]_{eq})=([A]_0-[A]_{eq})e^{-(k_1+k_{-1})t}$$

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

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

$t\to\infty$ $\frac{[A]}{[A]_0}=\frac{[A]_{eq}}{[A]_0}$ $\frac{[B]}{[A]_0}=\frac{[B]_{eq}}{[A]_0}$

So, we know that, at equilibrium [Noise], the forward and reverse set are equal. So, if I plot the d A d t, or if I just ask the question, what is d A d t or d B d t, each of them will be 0.

So, d A d t will be 0, which will be nothing but, the constants term, which is this term, minus this term, but instead of A, will write A equilibrium, which is the equilibrium concentration of A. So, we get that minus, sorry not minus, it will be k 1 times A 0 plus B 0 minus k 1 plus k minus 1 into A equilibrium, because it is the equilibrium concentration. So, this term, this constant term is nothing but, we can just say from here directly is this.

So, we can just rewrite the equation for d A d t, d A d t was first term was this constant, constant term, but instead of the constant term, I will write it as k 1 plus k minus 1, and the second term remember was, k 1 plus k minus 1 into A. So, together we can write it as A equilibrium minus A. So, that is a much simpler version of this, of this rate, and then, what we can write is, we can now integrate it. So, d A divided by, I am just writing it as, A minus A equilibrium, and with a negative sign here, k 1 plus k minus 1 into d t. And we can again integrate, that at time equal to 0, we have the initial concentration as A 0, and time equal to t, you have A.

So, that integration is nothing but a logarithmic integration. So, we will have l n. So, this integration will be l n, we can actually write it directly between the limits A and A 0. So, it will be A minus A equilibrium divided by A 0 minus A equilibrium, which is nothing but, minus k 1 plus k minus 1 into t. And we can write it in the exponential form, which is A minus, sorry this is k equilibrium, A minus A equilibrium is nothing but, A 0 minus A equilibrium into e to the power of minus k 1 plus k minus 1 into t.

So, then we can actually plot it like this. Suppose we have, with respect to time, we are plotting the A 0 minus A equilibrium, or you can plot A by A 0, we can actually plot A by A 0 also. So, the A by A 0 will be nothing but, if we just follow here, that will have, if I just divide both sides by A 0.

So, we will have A by A 0, will be nothing but, A equilibrium by A 0 plus 1 minus A equilibrium by A 0 into e to the power minus k 1 plus k minus 1 into t, something like that, we can easily figure out.

Now, one time is equal to 0. So, this term is equal to 1, and then we also see that is that time is equal to A 0 itself. So, A by A 0 will be nothing but equal to 1, and with respect to time, it will just fall, now when time is equal to infinity. So, then you can easily see, that this term actually will be 0, that time the exponential term very, very long time, and so, the concentration will get is nothing but, A by A 0 will be A equilibrium by A 0.

So, that A equilibrium by A 0, since everything is scaled with respect to A 0, will have some value. So, it will exponentially decay and reach some value, which is the equilibrium value of is A 0, A sorry, this will be nothing but, A equilibrium by A 0. So, this is the long time behavior, and similarly the B concentration will increase. Now initially, if you think that the B concentration is 0. So, it will start from 0. Although we did not take the B to be 0, but we can always put B 0 to be 0, and then that will increase, and that will also reach an equilibrium value for B.

So, which will be nothing but, the B equilibrium, but we are scaling everything with respect to A 0. So, it will be B equilibrium by A 0. Now suppose that we, we know that the equilibrium concentrations will be given by the ratio of the rate constants, and suppose we take a ratio that k 2 is say twice of k 1, which means the at equilibrium the ratio of B is to 1, or B equilibrium divided by equilibrium will be 2, or B equilibrium by A 0 divided by equilibrium by A 0 also be equal to 2.

So, you can think that, and this is a normalized plot, because everything is normalized with respect to A 0. So, the initial concentration was 1, which is totally we started with A only, and then. So, basically at time 0, the way we have written it, A is nothing but A 0, and B is nothing but 0, and at time is equilibrium, which means when at a very very long time. So, this A has attained the equilibrium concentration, and B has also attend the equilibrium concentration, and their ratio is 2, B equilibrium by A equilibrium is 2.

But we are plotting not exactly A; we are plotting A by A 0, and, everything divided by A 0, but that does not matter, because the ratio will still be the same, because A 0 just a constant.

So, you can think that, if it is 2 is to 1, then, this value will be nothing but, 0.33, about 0.33, and this value will be nothing but, about say 0.66 or so, because if we add at any time, A equilibrium plus B equilibrium, you can see the mass balance here, that we wrote earlier that, at any point this should hold. So, initial concentration of B 0, we took to be 0. So, at any point, if say, at equilibrium point so, this B equilibrium plus A equilibrium will be a 0.

So, we see that, if we have 0.33 and 0.66, then the ratio 2 is also maintained, and 0.33 plus 0.66 is 0.99 which is roughly equal to 1. So, that where the curves will look like, but it might have an opposite situation, meaning A can be also higher in proportion, but that will be set by the equilibrium constant, which is a function of temperature alone.

So, as long as we are not changing the temperature of the system, the equilibrium constant is kept constant. And we will see the similar ratios for A and B, which is given by the, dictated by the temperature. So, the system has a system of A and B, have now acting equilibrium, in the very very long time limit.

And the time concept is also, interesting here, as we just discussed, because it will happen only at the long time, the reason being, you can easily figure out, that only at in long time initially, only the A was forming into B, and then slowly as the B concentration increases, the rate of the reverse reaction also increases, and then at some point the match, and once they start matching, then there will be no change, because it has reached equilibrium point, which is in according to this plot, is happening say somewhere here.

So, after this time, basically the slopes have become 0. So, as you see the slope, initial slope was very high here, but the slope of the d A d t curve is changing, and the d B d t curve was also rising, and they, that is also changing. So, then at, after equilibrium has attained the slopes are 0. So, basically there is no change, and that is exactly what we used in this condition, that at equilibrium, we made it to be 0, and that is how we established this condition.

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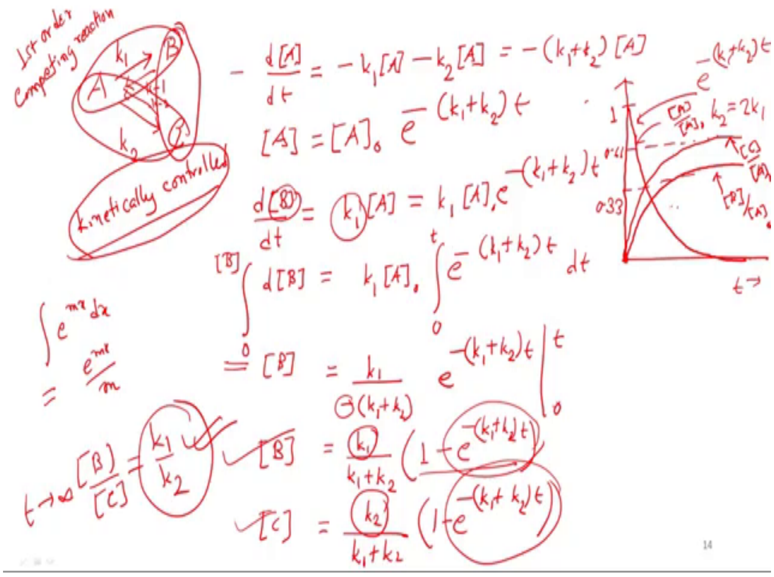

Now, let us think about another interesting situation, where we have some species A is going into B, but it can also go to another species which is C, and these are called competing reactions because, there are two competing pathways, where A can go in to B, A can go in to C. So, it is called competing reaction, and of course, this is a first order, in the sense that, we are assuming that the reaction A to B is first order with some rate constant k 1, and A to C is also first order with some rate constant k 2.

Now, you can easily figure out, what is the kinetics of the integrated rate law with respect to A, that we can write as minus d A d t, remember that nu is 1 in this case. So, the stoichiometry, you are taking just 1 is to 1, the d A d t is nothing but, minus k 1 into A, for this path, where A is forming the B, minus k 2 into A, where the other path, where basically A is forming C. So, it is nothing but, minus k 1 plus k 2 into A.

Now, you can easily integrate it out, it is a first order rate equation. So, it is nothing but A 0, where A 0 is the initial concentration of A times e to the power minus k 1 plus k 2 into t. Now we can plot it, but before we plot it, let us see, what is the concentration? How the concentration of B and C varies?

Now, d B d t will be nothing but, k 1 into A, because that is formed from A with a rate constant, which is k 1 and A, we just solved, A is nothing but A 0 into e to the power minus k 1 plus k 2 into t.

So, you can easily integrate it. So, d B will be nothing but, so this is a integration with respect to that, yeah. So, we can write it like this, d B is nothing but, k 1 into A 0, we remember A 0 as a constant, into e to the power minus k 1 plus k 2 into t d t. And we can assume that, at time 0, the initial concentration of B was 0, and at some time, arbitrary time t, initial concentration of B was just B.

So, my left hand side integration will be just B, and right hand side. So, it is integration of e to the power m x d x. So, that is nothing but, e to the power m x divided by m. Here m is minus k 1 plus k 2. So, you can just write it, k 1 divided by minus k 1 plus k 2. And this will be, into e to the power minus k 1 plus k 2 into t, evaluated between the limits 0 and t, and that limit if you see at 0, it is e to the power 0 is 1, and that is a lower limit, and the upper limit will be just e to the power minus k 1 plus k 2 into t.

So, it is e to the power minus k 1 plus k 2 into t minus 1, but that minus 1, we can actually introduce the minus sign inside, and write it, like k 1 plus k 2 into, we are writing the lower limit first, e to the power of minus k 1 plus k 2 into t. And this is the concentration of B, similarly for the concentration of C, you can easily figure out, that C will be nothing, the rate equation instead of if we write C here, the k 1 will be just replaced by k 2.

So, this will be nothing but, k 2 into k 1 plus k 2 into 1 minus e to the power minus k 1 plus k 2 into t. So, if you know plot the 3 terms, which are A B and C, in the same plot, you can see that, if I start with say A, and again, suppose I am plotting by A by A 0, or, something like that.

So, that will start from 1, because I have normalized it, as a function of time. So, I will have a very steep drop, why steep? Because, the stiffness is because it is an exponential decay, but the exponential constant is nothing but, k 1 plus k 2, it is a k 1 plus k 2 means, actually it is a joint contribution of k 1 plus k 2, because A is decomposing into A as well as into B.

So, it has two pathways; however, when the B rises, B will rise at the rate which is k 1 t, you can easily see that B equation of B.

So, it is 1 minus exponential minus, which is basically exponential growth. So, in the very long limit, you can always see that in the very short limit on t was equal to 0. So, you will have, basically 1 minus 1, which is 0. So, for C also it is 0. So, the initial concentration will took to be A 0, because all the initial concentration, we suppose that it is on the A 0, and remember that initial concentration of B was 0. And similar argument, we also provided for initial concentration of C, and which means they will both start from here, but as time progresses, you can think that at a very very large limit, this even t goes to infinity.

So, this term goes to 0, both these terms. So, I will just have 1. So, I will just have B concentration to be k 1 divided by k 1 plus k 2 and C concentration as k 2 divided by k 1 plus k 2.

So, they are going to be a constant in the asymptotic time limit, when the time is very large, when the entire A has decayed. Let me just draw the A curve once again. So, it will be, if I want to show it, it will be much more steeper. So, it decays much earlier, and then this B actually gets converted to, sorry, A gets converted into B, and A also gets converted into C. So, let me just draw it once again.

o, this was my, this was the axis, and I am plotting here, A by A 0, or B by B 0, or C by C 0, everything, the concentration versus C 0. And then, the concentration for C, suppose is here, and we can easily argue that, just like the earlier case, that if k 2 is like twice k 1, then you see that, the concentration of B will be just twice the concentration of C, and if we are plotting something like, this is a plot of say B by A 0, we are normalizing everything with respect to A 0.

So, this is say C by A 0, and this plot we say for A by A 0. So, then as before we can argue that this will reach something like 0.33 because, it is a normalized curve, this was 1 and this B, sorry, concentration of C will reach 0.66. So, their ratio is just like 2 is to 1, and the ratio is dictated by the ratio of k 1 and k 2 because, as we just said that at t equal to infinity, or t tends to infinity, the ratio of B by C will be nothing but, k 1 by k 2, or C by B will be k 2 by k 1.

When t tends to infinity so, that ratio is now maintained. So, this is not a reversible reaction remember; however, this is an irreversible reaction, because A is completely decaying and to 0, actually in the long time limit, and B and C are formed, but B and C formed, and then the final concentration B and C are maintaining a ratio, and that ratio is maintained by the ratio of their rate constant.

So, this kind of situation is known as kinetically controlled, in the sense that, the kinetics is controlling everything; Now, when we discuss the Arrhenius rate equation, or how the rate constant depends on the, on their, on their, on their, relative rates? Or how the relative rates actually control the products?

Here actually, it is a very interesting situation, but when we discuss the Arrhenius concept that, if I vary the temperature, how the rate constant changes? And there, we can see that, that is also another way of thinking of products, that the relative stability of the products might be very different.

In the sense that B can be actually more stable than C here. So, in the long time limit, we will see that, that situation might be, might get reversed; So, that we will discuss, when we have a very, something elementary concept of activation energy. So, for the time being, here, it is a concept what we guys develop. So, here C is known as a, it is known as kinetically controlled product or the reaction.

It is better to call that these reaction e say, e is actually kinetically controlled, means actually, the rate constant of that species, that species will be high in the long time limit, or the concentration of that particular species will be higher in that long time limit, which had formed at a first order rate, because all the ratios are now given by k 1 k 2, which are actually rate constants.

So, the initial rates of the reactions of the rate, rate constants are actually dictating, the final distribution of the product, and that is why, it is called the kinetics is basically governing everything. There is also another thing called thermo dynamical control product, and we will also see, how these two are interrelated, and how we can actually plot it in an free energy diagram, but that we will discuss, when we discuss the Arrhenius equation, and such kind of reactions which we just described are called as kinetically controlled reactions.

Further reaction to be, thermodynamically controlled, we have to have 2 equilibrium established between them. So, there will be our reverse reaction also, which is k minus 1, and there is another reverse reaction k minus 2. So, k minus 1 is the rate at which B is forming A, and k minus 2 is the rate at which C is forming A. So, under this condition, we will see that C and B can also come back to A, and then A necessary we will not go to 0, actually I will never go to 0, because there is a equilibrium.

And then you can see that, if these two are in equilibrium, and these two are also in equilibrium, then you can actually show that B and C are also in equilibrium, it is through A.

So, B cannot directly interconvert B and C that cannot directly inter convert. So, B can convert to A and to C, and similarly C can convert t A and to B, but which means that they are inter-convertible and, but then we can show very nicely, that we can actually control the ratio of B by C, by temperature also, and in a very interesting case, we can show that in the very long time limit, this curve may actually get reversed, in the sense that, in a very early limit when the kinetics actually controls everything.

Now, C will dominate B, but then at a later time, then we will see that B actually dominates the C. So, there are curves actually switches, and how temperature can be an effective parameter, in that switch, we can will discuss at that point. So, in the following section, which we are going to discuss, in the next section, we will consider another interesting kind of reactions, which are known as consecutive reaction, and then we will end our first part, which is basically the reaction kinetics.

So, we consider different models, and then that will be our last particular model or last example, where we have, some reactions happening in, in a consecutive fashions, and how to get an integrated rate law for the consecutive reaction, that we will discuss in the next section.