Advanced Chemical Thermodynamics & Kinetics
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Lecture - 15
Review of Chemical Kinetics - 2

So far we have discussed examples of reactions, which are actually irreversible in nature.

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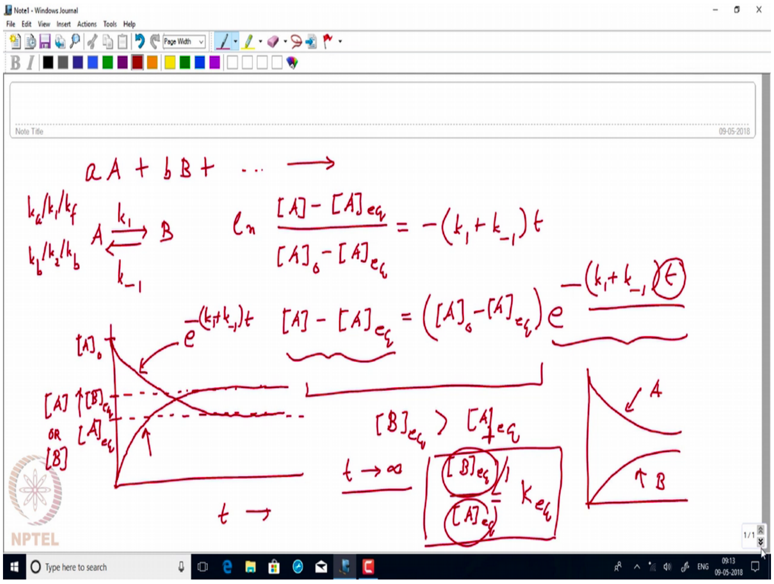

Something like I said that if you remember the very first example, which we took we wrote it like this, it is a irreversible in nature. Now, what happens, if the reaction is reversible, in principle all reactions are reversible in nature, you can actually see irreversibility under certain conditions, if the back reaction which is the reverse reaction is too slow or kinetically which means actually kinetically forbidden reaction, so then in case in that case you can see the irreversibility.

Otherwise, the most of the chemical reactions in which you studied in high school, a statement that chemical reactions are reversible in nature. And what happens, you also understood we also studied there that if you start a reaction sooner or later, and equilibrium is added.

Now, we will just talk about this equilibrium thing, how the equilibrium is added. Now, let me start with a very simple example, suppose A is going to B, and B is also giving back you A. And the stoichiometry, we are just taking here to be ones to one just to avoid complications, but it is not to complicate it, because you can always absorb the stoichiometry in your rate constant, and redefine a new rate constant.

Now, suppose for the forward reaction, I say that the rate constant is k 1 for the reverse reaction, I am just writing it as k minus 1. Some textbook actually use for forward reaction a notation like k a, and reverse reaction they write it as k b something like that or sometimes if they write it as k 1 for the forward reaction, and k 2 for the reverse reaction. Some textbook write k f, f for forward; and k b, b for backward something like that. So, I am just using 1 and minus 1 notation. Minus 1 means, it is a opposite direction; opposite in the sense that which we have chosen like A to B by our definition by our choice is the forward direction. Now, we can actually solve again in the similar way. And then, the integrated rate law looks like something like this, I will just describe what are the results, how the concentration of A or B actually changes with respect to time following this integrated rate law.

Now, suppose we started with an initial concentration of A, which was A 0. And then, the rate law will look like this. Again the derivation may be found in any standard text either the text might have the solution itself in the discussion or it might have it as a problem set, which you have to solve or you can actually go back and look at the you tube video lectures on Introduction to Chemical Thermodynamics course.

Now, look at it carefully. So, we can actually write it either in the logarithmic form or we could write it in the exponential form like A minus A equilibrium is basically A 0 minus A equilibrium times exponential minus k 1 plus k minus 1 into t. Now, here the question is how what is the equilibrium, so equilibrium is the equilibrium concentration of A.

Now, let us try to understand how the plots will look like. If I want to plot say A versus t or the concentration of A how it is varying with respect to time, following this equation. Now, as I know that initial concentration was A 0. We can quickly check if I put t equal to 0 in this equation, so this e to the power factor that goes to 1. So, I have basically A minus A equilibrium is basically A 0 minus A equilibrium. So, A is nothing but A 0, so that makes sense.

And with respect to time what I see here is that the concentration actually drops, but it drops exponentially of course, just like a first order reaction, but the rate constant is not just k 1, it is actually k 1 plus k minus 1. So, at the reverse reaction also contributes. And before that let us just try to understand; what is the final concentration of this thing.

Now, for that I can actually think that when t goes to infinity, so this entire thing becomes 0. So, by solving, we will see that A will be equal to A equilibrium. So, at a very very long time, actually it reaches the equilibrium concentration. Suppose, A equilibrium is somewhere here A equilibrium is a constant, if we do not change the temperature. So, A equilibrium will be constant.

So, what we just learned is that eventually the concentration will drop, but it will not drop to 0, it will just reach the equilibrium concentration of A. And the curve will look like something like this. So, it will be an exponential decay, and reaching exponentially to this asymptotic curve, where this decay is actually exponential, but it goes as e to the power minus k 1 plus k minus 1 into t, and which is very important.

Similarly, for the B expression also, we can have a similar expression like A, and B will also reach its equilibrium concentration. And suppose, B equilibrium is somewhere here, and if we start or if we assume that initially the B was at 0, so then we will see that the B also reaches with the same time constant to its equilibrium value. So, this is will also be something like it 1 minus e to the power minus k 1 plus k minus 1 t it is a exponential growth, but the time constants will be same.

So, the point here is that for an equilibrium reaction with two rate constants or two opposing rate constants k 1 and k minus 1, you will see that the way it reaches the equilibrium. It does not depend only on the forward rate constant or the reverse rate constant, it actually depends on the summation of these rate constants. And so in this plot actually, it will be plotted either the concentration of A or the concentration of B. So, this is a general plot.

Now, interesting thing to look here is here is that we assumed here that the B equilibrium is greater than A equilibrium at a very long time, the equilibrium concentration of B is higher than the equilibrium concentration of A, it need not be the situation, it may be reversed. And in those cases, the B equilibrium will lie lower than the equilibrium. So, the curves will look like something like this. This is for A, and this is for B.

So, the amount of the product in this case at a very very long time, when t goes to infinity in the long line long time limit is actually constant. And you can actually see the ratio can be connected to the equilibrium ratio of B and A, and which is nothing but your equilibrium constant which is the Thermodynamic equilibrium constant.

We have to be very careful, when we say Thermodynamic equilibrium constant, because strictly by definition, whenever you write a thermodynamic equilibrium constant, it is unit less. So, all these Bs and as are actually inherently, we have to assume that it is divided by unity unit concentration. Like if I express say B in terms of moles per liter, I have to divide by 1 mole per liter or the standard concentration unit, so that the k equilibrium becomes concentration less.

In this case, we took 1 is to 1 stoichiometry. So, naturally the concentration it is unit less, but it may be so that the reaction can have say the equilibrium constant expression can have B squared divided by A. In that case, to make it unit less, we have to first divide B by the equilibrium unit concentration, and then take the square so that everything becomes unit less.

Now, as you see that in this case, the A and the B either of them are I mean both of them basically approach their individual equilibrium concentration, it is it is not going to 0 or the entire A is not going to the B, which means the B is basically not going to the initial concentration of A, which is opposite to the first order reaction. And that is the importance of the equilibrium. So, equilibrium suggests ensures that everything actually checks finally to its equilibrium concentration.

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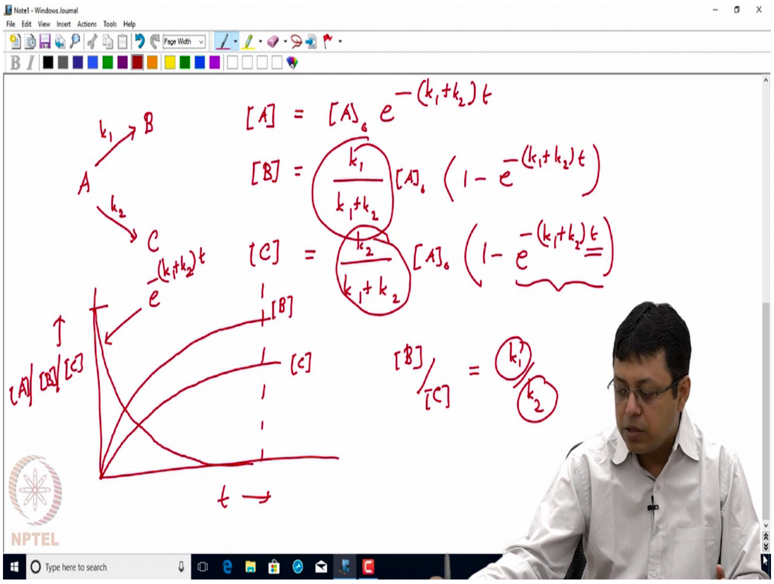

$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

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

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

$$[B]/[C] = \boxed{k_1}/\boxed{k_2}$$

Now, I will give you another example of a different type of reaction, where it is known as opposing reaction, so where single reactant A is giving you two different products. So, I can actually call this rate constant that is a k 1, and this rate constant let us say as k 2. And in this case, now the integration of A is very straightforward, because it is just a first order in A it is a first order process giving rise to B, it is also another first order process, which is giving rise to C. So, the integration for the rate equation for A is pretty straightforward, it will be minus k 1 plus k 2 into t.

Now, what about B, now in a same way we can actually solve the integrated rate law for B, and you will find that it will be something like k 1 by k 1 plus k 2 into A 0 into e to the power minus, so with respect to time, the both the B and C will grow. So, any exponential growth we can actually show it like 1 minus e to the power minus k 1 plus k 2 into t.

And similarly, the concentration of the C will vary, instead of k 1 here I will have k 2 in the denominator, and everything else is just like the equation for B. So, the assumption of the initial condition was that only A was present, and that concentration at time 0 for A was A 0. And concentration at time 0 for B and C was 0.

Now, if I plot these concentration A, B or C A or B or say C versus time, now the profile for A is pretty straightforward, it will have a exponential decay, and it will go to 0 of course, because it is all irreversible reaction. And but remember that it falls with a time constant, which is not k 1 or k 2, it is actually k 1 plus k 2. Now, B and C will grow. And eventually, as you can see if I make this thing time to be infinity, so this part actually goes to 0. So, what we will have is basically A 0 the initial concentration times some factor, which is k 2 by k 1 plus k 2 in case of C or k 1 by k 1 by plus k 2 in case of B.

So, we will have exponential growth, and the final concentrations will be something like this. Let us say this is the curve for B, and this is the curve for C. Now, what we see is that at a very very long time, the ratio of B by C is nothing but k 1 by k 2. So, what it means is that the ratio of the B and C in the long time is dependent on their on the rates of how they were formed. So, these type of products are known as kinetically controlled product. Meaning the kinetics or the rates are actually controlling the absolute value of B and C in the long time limit

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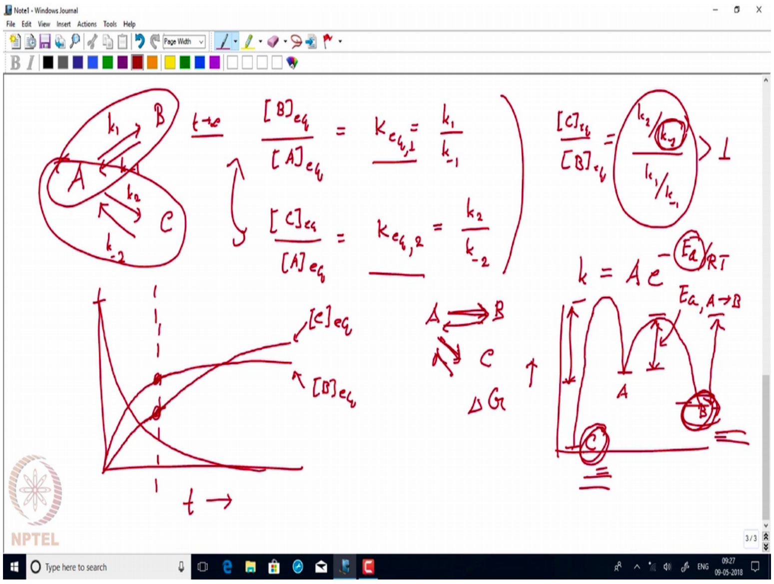

$$\frac{[B]_{eq}}{[A]_{eq}} = K_{eq,1} = \frac{k_1}{k_{-1}}$$

$$\frac{[C]_{eq}}{[A]_{eq}} = K_{eq,2} = \frac{k_2}{k_{-2}}$$

$$\frac{[C]_{eq}}{[B]_{eq}} = \frac{k_2/k_{-2}}{k_1/k_{-1}} > 1$$

$$k = Ae^{-E_a/RT}$$

Now, we can actually see the beauty, once we actually impose the condition that these reactions did not happen as irreversible reaction, but rather they had a reversibility. In the sense, all I am going to do is instead of writing it like A is going to B and C irreversibly, now imposing the condition A B also gives back to A, and C also gives back to A. So, I can actually think about the rate constant as k 1 and k minus 1, and for the A to C reaction and vice versa, I can say the rate constants k 2 and k minus 2.

Now, we have already studied the what happens for equilibrium. Now, considering A B equilibrium, we know that in the long time the ratio is all these the ratio of the products will be nothing but B equilibrium by A equilibrium, which is related to the equilibrium constant, which is also related to their rate ratio of the rate constants. And similarly, in the when this is we are discussing, when the it is a very long time for the equilibrium has reached.

Similarly, for this equilibrium A to C, we can also say that the long time ratio will be dictated by something like this, which is the equilibrium I mean this is for the second equilibrium. And we can also write it as the ratio of the individual rate constant. Now, we can actually ask this question, what will be the final ratio of C and B. You can just take the ratio using these two equations, which we have written here. And then, we will find a beautiful thing that it is basically ratio of the equilibrium constants, which is nothing but k 2 by k minus 2 divided by k 1 by k minus 1.

Now, you see that it is not simply k 2 by k 1. As we just saw earlier, where actually did not consider any reversibility and here. So, now the back reactions are also important, and it may so happen that although in this case I have B is higher than C, because k 1 is higher than k 2. It might so happen that this thing the overall thing may be positive. Meaning, although k 1 is greater than k 2 the overall thing k 2 by k minus 2 and k 1 by k minus 1 may adjust themselves. In such a way, that they can be more than 1, in that case actually in the long time, C will dominate.

Now, if I want to plot it this situation, it will be something like this A will be always exponentially decaying, and B initially will be forming at a higher rate than C. But then, eventually what will happen is that the C will reach its equilibrium concentration, whereas the B concentration will be lower. So, this is basically C equilibrium, and this is suppose B equilibrium.

So, we see that at time at a at a early time, it may so happen that we are only forming where suppose we start only from A, and then you are forming B in one channel, and you are forming C in the another channel. Now, then as soon as the B forms after certain time, the reverse reaction rate also increases, because you remember that the rate is nothing but rate constant times the concentration.

So, initially if they then if there is no B or C only the k 1 and k 2 will dominate all only the forward processes, this rate and this rate will dominate. But later, when in the reaction mixture, you have sufficient amount of B and C, then the reverse reactions also proceed, and then you can have a situation that the entire thing might change. So, the equilibrium ratios might be very different. So, in this case, we said that these products are thermodynamically control, because everything is dictated by the ratio of the equilibrium constant or if it is a higher equilibrium constant, that product will be formed.

Now, we can cost this entire thing in the energy level diagram. Now, what is an energy level diagram? All of you know that the rate constant is connected by (Refer Time: 18:19) equation, which says that for any rate constant I will have some energy, which is known as activation energy, which is kind of an experimentally determined quantity, and which can be connected to the minimum energy that is required for a reaction to happen.

Now, for any reaction say A to B, we can say that there is an activation energy. In the sense that suppose, this is the energy of the A ok. And this is suppose the energy of the product B, now these does not happen all the energetically, B is more favorable by energy we always mean the Gibbs free energy for the reaction. And we say here that A to B, there is an activation barrier, in the sense that you have to cross certain amount of energy, you have supply certain amount of energy for the reaction to happen. In this case, this is the activation energy for A to B. Similarly, when B actually forms, it also has an activation energy, which is activation energy for the reverse reaction.

Now, what we have said that in the earlier example of kinetically controlled product is that at a very early time. What is happening is something like this, I had A here, and then I was forming both B and C, suppose B were had an activation energy, which is something like this much amount, but C had an activation energy, which is much higher. So, as you can see that the activation energy for this reaction A to C is much higher, which means actually the rate will be much slow. Because, if you remember that rate constant is actually proportional to minus e to the power e to the power minus E a by RT, where if I have a higher activation energy or higher E a will have actually less amount of the rate constant, and the value of the rate constant will be less.

So, what it means is that the kinetics of the activation barrier is controlling the product ratio. However, it may so happen that in a longer time, as the B accumulates, the reverse reaction also happens, and initially suppose it is going from A to C had a very high barrier, but then thermodynamically C is more stable than B, the way I have drawn here.

As you can see the in the free energy diagram, the position of C, and the free energy for the product C product C is much more stable than the product B.

So, what we can say here is that as soon as initially, so everything is dictated by the activation energy for the forward reactions. In this case, the activation energy (Refer Time: 21:18) per going for A to B is smaller. So, B will form more as you can see at this up to this time, which is shown as the dotted line here. So, the B is actually lying higher than C. But, as time progresses the reverse reaction also takes place.

And what happens, ultimately at the end of the day, everything is dictated by the ratio of the equilibrium constants. And that will be dictated, how the product is thermodynamically is stable. In this case, in C stable more than B, we expect the long time concentration for C or the equilibrium concentration of C will be more than B. Also a point to note here is that if you see carefully, for the reverse reaction B to A and C to A.

Now, way I have drawn it since actually C is much more stable, it is actually lying much below in the energy level diagram energy scale than B. Now, which means actually the reverse reaction activation energy from C to A is much higher. So, C to A will be much much smaller, so which means actually this k minus 2 will be very very small, so which actually makes this overall ratio much more than 1, so that C equilibrium is greater than k B equilibrium.

So, so this kind of diagram is very important to understand how basically in a short time scale. We can have when that reactions are I mean you can approximate it as irreversible reaction irreversible opposing reaction, that A is going to B, and A is going to C. And then, moment you add the or includes the condition, that B and C can also come back to give you the give you back the product A, then you see the beauty that everything is now reach equilibrium. And the equilibrium at equilibrium the concentrations will be slowly dependent on their equilibrium constants, which are actually combination of all this forward and reverse rate constant; there are four rate constants.

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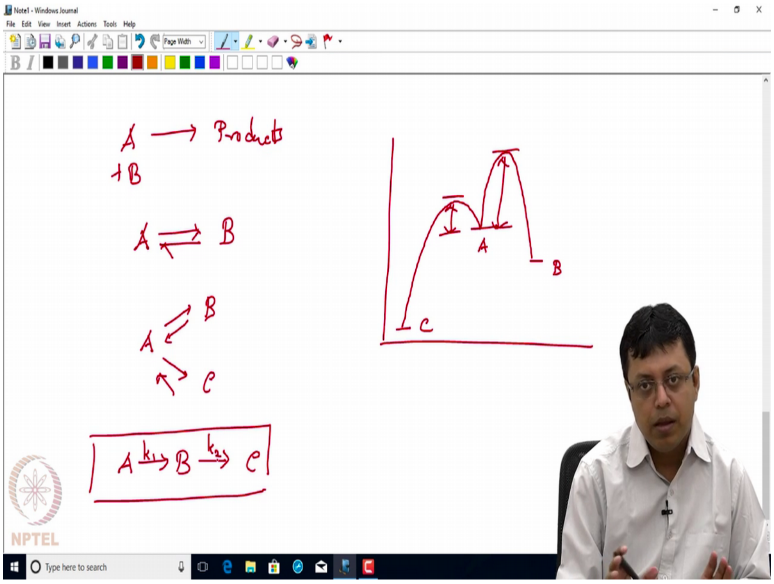

And so, let me summarize this part. So far whatever we just explained irreversible reaction A plus B is going to product something like that. And then, eventually we said that instead of irreversibility what happens, if we just include reversibility of the reactions, and we saw that how the ratios actually reach the equilibrium concentrations.

Then we said that what will happen, if we have two competing channels in the reaction, and you showed that initially everything will governed by their rate constants of the kinetics, which are connected to the activation barrier. So, the smaller activation barrier will have the higher rate constant, and that product will be favored. But eventually with time as B and C gets accumulated, the reverse reaction will also happen. And then, everything will be dictated as the ratio of the equilibrium concentration will be dictated, how thermodynamically they are stable.

And the example, which we give remember that the way we showed it is that the kinetically controlled product, which is B is not thermodynamically controlled product, which is C. And that is why the crisis actually reverse, initially B was higher, but eventually the C takes off. And for this other case, you can also have a situation, where the one of the products let us say C is both kinetically and thermodynamically favored.

In that case, when I am going from A to say C, the activation barrier is smaller as well as C is much more stable. When I am going to A to B, the activation barrier is higher, as well as B is thermodynamically less stable than C, as you can see the position of C is much at the at the bottom. And also the activation barrier for going from A to C is smaller than going from B to A to B.

So, in this case C is both kinetically, as well as thermodynamically controlled product. Meaning from the very beginning, you will see the C to B form. In the next part, we will consider another class of interesting reactions, which are known as consecutive reaction, which is something like A is giving intermediate which is B, and B is subsequently giving an intermediate C, and we will considered all these consecutive reactions are very important. So, consider it in some detail.

Again we will not solve the equations, which are integrated rate equations. You can always go back and look at a standard text of the YouTube videos of the preceding course.