Chemical Kinetics and Transition State Theory
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Lecture 43
Unimolecular decay – revisited

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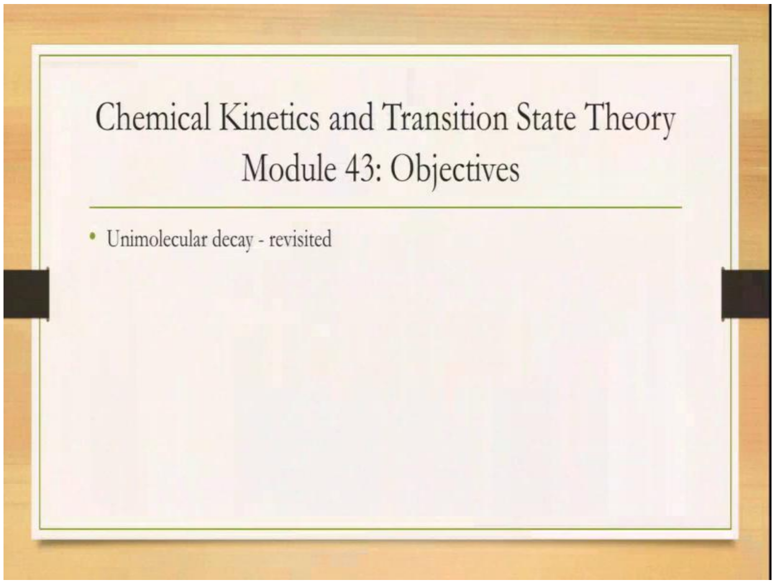

Chemical Kinetics and Transition State Theory
Module 43: Objectives

- Unimolecular decay - revisited

Hello, and welcome to module 43 of Chemical Kinetics and Transition State Theory. Today, we are going to discuss some neat application. We have been looking at microcanonical rate constants, that is rate constant at a given energy. Now you may ask why have we been looking at it at all.

So, we will look at the problem that was historically studied. Why these theories were originally developed, which is to understand unimolecular decay. So, this is something we discussed in our very first few modules and we will now today look at it in much more details that we understand rate constants a lot more now.

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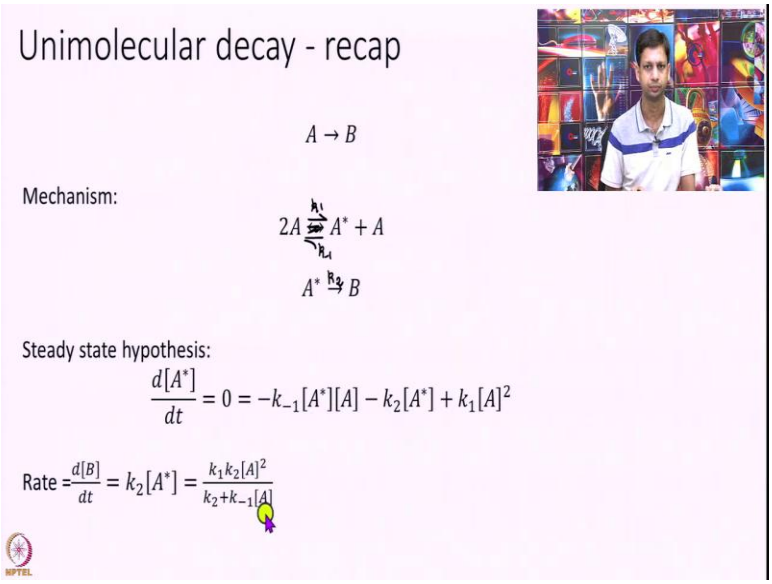

Unimolecular decay - recap

$$A \rightarrow B$$

Mechanism:

$$2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} B$$

Steady state hypothesis:

$$\frac{d[A^*]}{dt} = 0 = -k_{-1}[A^*][A] - k_2[A^*] + k_1[A]^2$$

Rate $=\frac{d[B]}{dt} = k_2[A^*] = \frac{k_1 k_2 [A]^2}{k_2 + k_{-1}[A]}$

So a quick recap, this is from module 2 or 3. I have a unimolecule decay, meaning I have only one A that is single handedly going to some products B, one reactant only. So this was very deeply studied in 1910s and 1920s. (())(1:25) seem to be the easiest problem to start investigating in chemical kinetics and people spend a lot of attention on it. So one mechanism that was proposed and that is what we discussed in our earlier modules is that rather than A directly going to B that is actually does not matches experiment at all.

What was proposed is that two molecules of A collide with each other to give you A star plus A and this I was not able to put the equilibrium constant very well. So this is my creative way of writing. This is really equilibrium. This is k1 and this is k minus 1. And A star finally decomposes to give you B. That is our mechanism. I can build kinetics on top of it.

So I can find what is dA over dt, dA star over dt and dB over dt, then we make the steady state hypothesis which assumes dA star over dt is 0 and dA star over dt you can easily show is given by this expression. You get three terms, because A star appears three times, one is here, one is in the forward direction here and one in the backward direction.

So, you get a corresponding A star in these rate law equations. And the steady state hypothesis is that the intermediate population does not changes with time. So we set that to 0. And finally, the rate, which is nothing but dB over dt is equal to k2 into A star, B appears only here and then we use this equation to calculate A star and eliminate A star out and finally get rate as this. So this is something we studied a long time ago.

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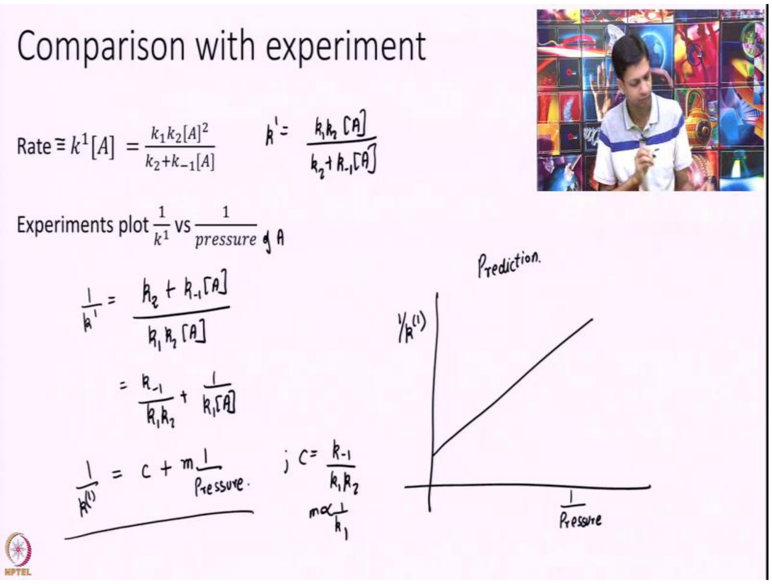

Comparison with experiment

Rate $\equiv k^1[A] = \frac{k_1 k_2 [A]^2}{k_2 + k_{-1}[A]}$ $k^1 = \frac{k_1 k_2 [A]}{k_2 + k_{-1}[A]}$

Experiments plot $\frac{1}{k^1}$ vs $\frac{1}{pressure}$ of A

$$\frac{1}{k^1} = \frac{k_2 + k_{-1}[A]}{k_1 k_2 [A]}$$

$$= \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 [A]}$$

$$\underline{\frac{1}{k^{(1)}} = c + m \frac{1}{Pressure}.} \quad ; c = \frac{k_{-1}}{k_1 k_2}$$

$$m \propto \frac{1}{k_1}$$

Now, finally, I can express rate as some k to concentration of A. This, let me define it this way only. It is this, is not elementary, but I can always define k1 as this. So I can calculate this k1 as then k1, k2A over k2 plus k minus 1 into A. I have divided by capital A on both sides. So clearly this k1 is not independent of concentration. It is not a number at a given temperature, depends on concentration of here. Clearly showing that A going to be is not elementary in this model.

So, today let me just point out that this model is not complete. There are few issues with it. So in 1910s and 20s itself, some experimentalists had plotted 1 over k1 versus 1 over pressure of A. So let me massage my equation to have 1 over k1. So 1 over k1 is nothing but k2 plus k minus 1 of A.

Let me just simplify this and write this as k minus 1 over k1, k2 plus 1 over k1 A. And basically these experiments were done in gas phase. So pressure is proportional to concentration, just ideal gas law. So this is then equal to some constant. Let me call this C plus some m into 1 over pressure. C is nothing but k minus 1 over k1 k2 and m is nothing but proportional to 1 over k1, because pressure is proportional to concentration of A.

So, you see, what we have got is 1 over k1 is equal to some mx plus C where x is 1 over pressure. So my prediction is at a given temperature, if I plot 1 over k1 versus 1 over pressure, I should get a straight line. That is, this is an equation of a straight line.

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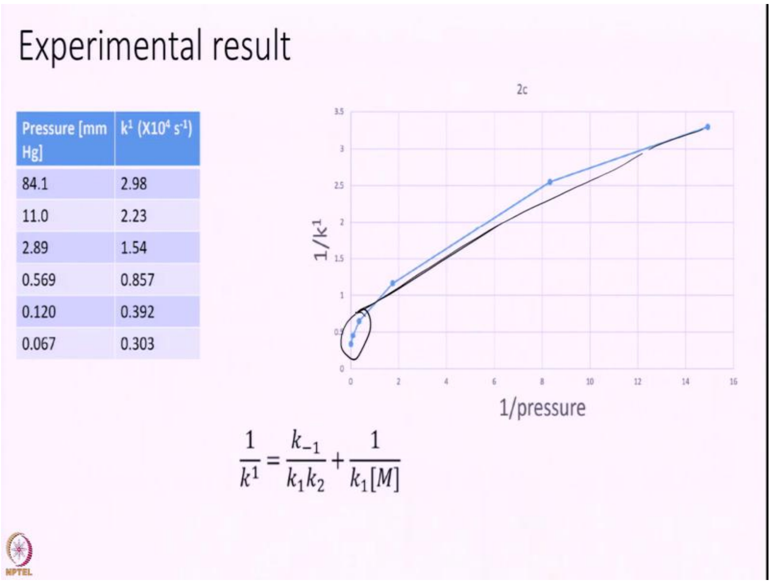

Experimental result

Pressure [mm Hg]	k^1 ($X10^4$ s^{-1})
84.1	2.98
11.0	2.23
2.89	1.54
0.569	0.857
0.120	0.392
0.067	0.303

$$\frac{1}{k^1} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1[M]}$$

This is the experimental result in front of you. So I have actually taken the data and plotted it on some graph. This is not a straight line. It is clearly deviating. So we have a problem. We get something that is reasonable. It is not completely off the charts. I mean, in some degree, I mean, this portion is starting to look like a straight line almost, but you see something happens here. So we have to try to understand it now. Why is it? What has went wrong in our model?

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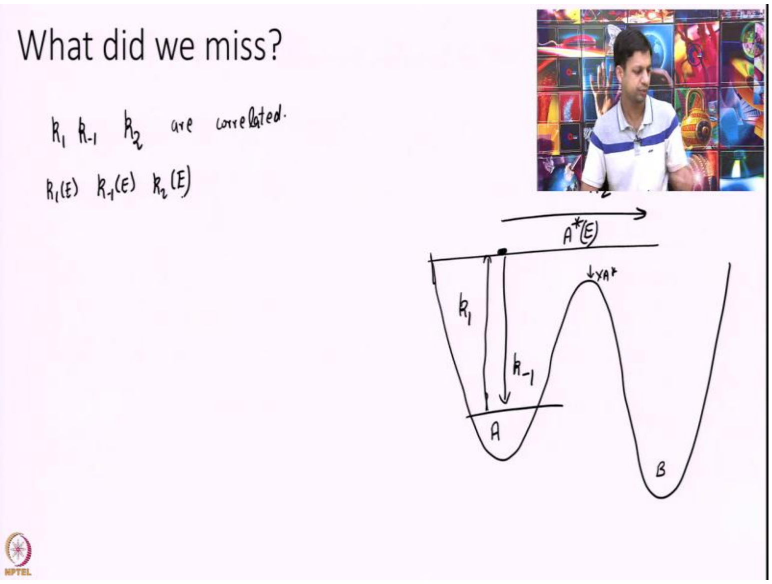

What did we miss?

k_1 k_{-1} k_2 are correlated.

$k_1(E)$ $k_{-1}(E)$ $k_2(E)$

So, what did we miss really? Our model seems pretty good. The model is still pretty good. There is something very fundamental and very nuanced point that we missed. So let me try to impress that upon you. Let us just, now we have started thinking in the language of energy surfaces. We have A here, we have B here, where is A star. That is the question you should start thinking. Pause the video and tell me where is A star. So think about it. I will give the answer in 5 seconds, 5, 4, 3, 2, 1.

A star is not this point. A star is simply an excited energy level here. Remember transition state is a very specific point on energy coordinate. There is one given potential energy. A star has, can have more energy than the transition state. A star can be many different possible structures. A star is not the transition state. But A star has some high energy E here. So the model that I have here is that this is k1, this is k minus 1 and once I get here, this is k2. So k1 pumps me up to the excited state, k2 will drive me to the product side and k minus 1 depletes my population in state energy E.

The settle point is the following. We have been taking these k, k1, k minus 1 and k2 independently. We are thinking of them as three independent numbers as a function of temperature. They are not independent. That is the point or correlated. What does it mean? It means the following. What is exactly k1? K1 effectively is that two molecules of A collide with each other giving me an energized product at a given energy E, not at a given temperature t. One collision will lead me to one energized state and this energized state can either go towards become a product or have another collision and become de-excited.

So k1, k minus 1 and k2 are better thought of as independent numbers, but functions of energy. Temperature is an ensemble average. But at a given energy, all these three things are happening. You go up to this energy E and that energy E you either go forward or you come down. So this is the very nuanced point. Start try thinking about this. It is really a matter of timescales at the end of the day. If everything goes, k2 was very, very fast, then it would not have mattered. But these three numbers are really interacting with each other. So we cannot just make these k1, k minus 1, and k2 as a function of temperature and get away with it.

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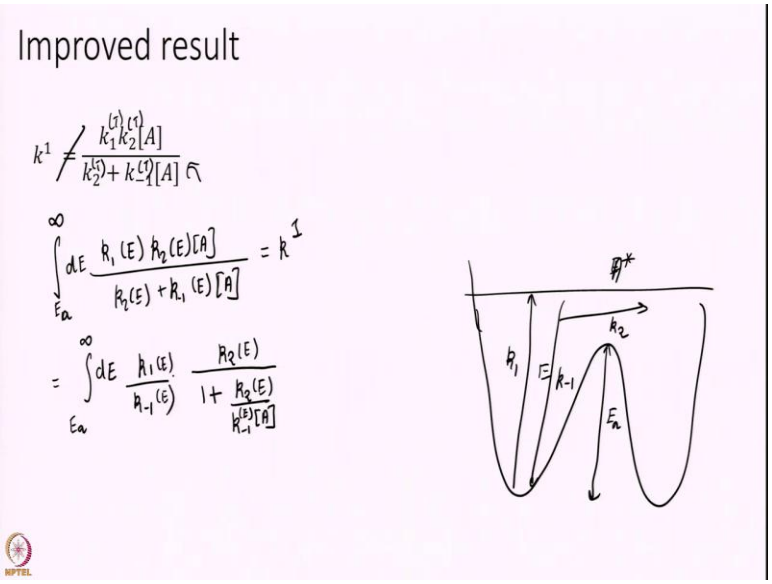

Improved result

$$k^1 \neq \frac{k_1^{(T)} k_2^{(T)}[A]}{k_2^{(T)} + k_{-1}^{(T)}[A]}$$

$$\int_{E_a}^{\infty} dE \, \frac{k_1(E)\, k_2(E)[A]}{k_2(E) + k_{-1}(E)[A]} = k^1$$

$$= \int_{E_a}^{\infty} dE \, \frac{k_1(E)}{k_{-1}(E)} \, \frac{k_2(E)}{1 + \frac{k_2(E)}{k_{-1}^{(E)}[A]}}$$

So, what we actually do? This is back to our expression of k1. We so far were thinking of these as independent numbers as a function of temperature at a given temperature. This is a bad approximation. The correct way to think about it is that we have this graph with us. This is let us say Ea, E star is somewhere here, A star.

This is let us say energy E. This is k1. This is k minus 1. And this is k2. We are going to calculate these things at a given energy and then integrate them over all possible energies. And the energies, of course, will range from Ea to infinite. You cannot have energy less than Ea, because then no reaction can happen. K2 will be 0 below energy Ea.

So, that is our new novel idea. This is what RR and K did. So we discussed this RRK theory earlier, Rice, Ramsperger and Kassel and that was their major breakthrough. They said, you have been calculating these numbers as a function of temperature, but that is not correct. You should be calculating them as a function of energy and integrating over all possible energies.

So, we have this. I will massage this a little bit to get into a form that is better to understand. I will divide both numerator and denominator by k1 A, sorry, k minus 1 A. So I am dividing by, let me write, k minus 1 A. So I will get k1 over k minus 1 into k2 divided by 1 plus k2 over k minus 1. And all these things are function of energy. I am not writing them as explicitly, I think, but it should be understood now.

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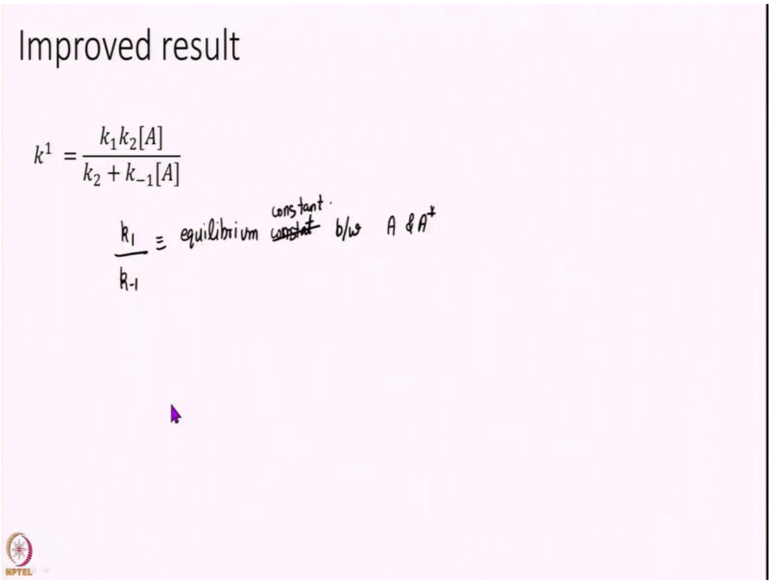
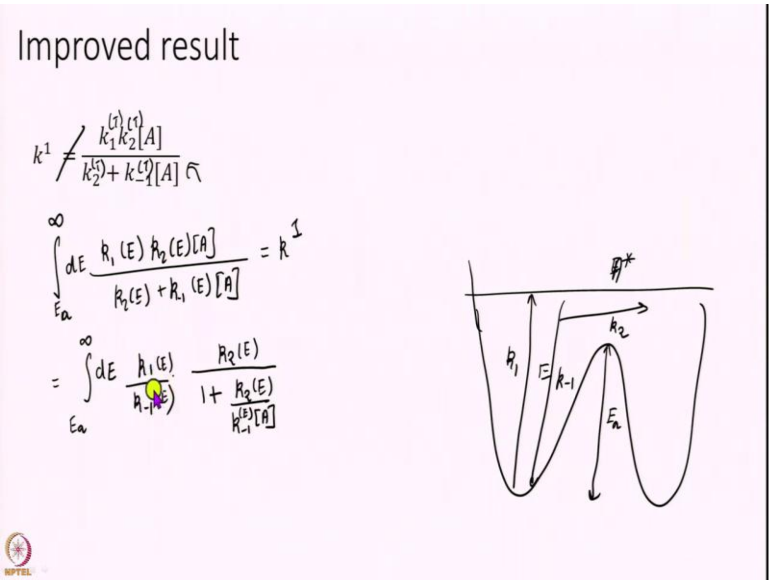


Improved result

$$k^1 = \frac{k_1 k_2[A]}{k_2 + k_{-1}[A]}$$

$\frac{k_1}{k_{-1}} \equiv$ equilibrium ~~constat~~ constant b/w A & $A^\ddagger$



Improved result

$$k^1 \neq \frac{k_1^{(T)} k_2^{(T)} [A]}{k_2^{(T)} + k_{-1}^{(T)} [A]}$$

$$\int_{E_a}^{\infty} dE \, \frac{k_1(E) \, k_2(E) [A]}{k_2(E) + k_{-1}(E) [A]} = k^1$$

$$= \int_{E_a}^{\infty} dE \, \frac{k_1(E)}{k_{-1}(E)} \, \frac{k_2(E)}{1 + \frac{k_2(E)}{k_{-1}^{(E)} [A]}}$$

Just a quick point, this quantity that we had now, k1 over k minus 1, this represents the equilibrium constant between A and A star. So that is the reason that I massage my question to have the form which has k1 over k minus 1, because that is an easier quantity to calculate.

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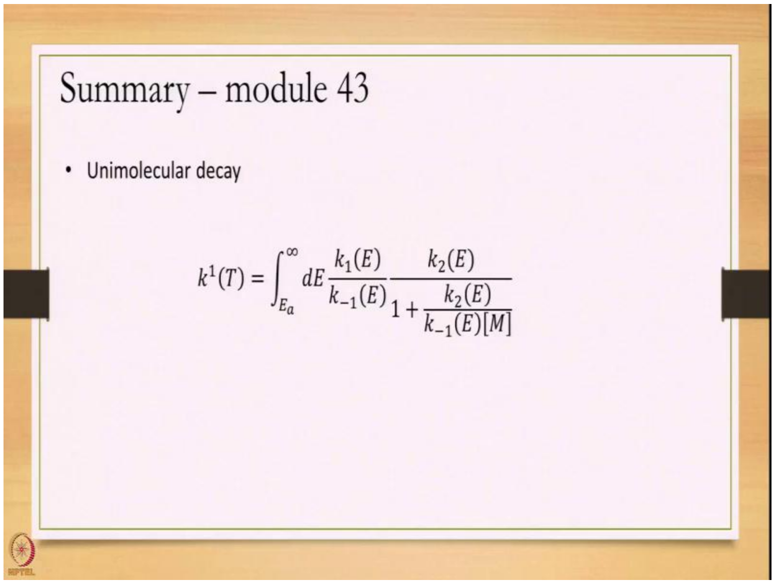

Summary – module 43

- Unimolecular decay

$$k^1(T) = \int_{E_a}^{\infty} dE \, \frac{k_1(E)}{k_{-1}(E)} \, \frac{k_2(E)}{1 + \frac{k_2(E)}{k_{-1}(E)[M]}}$$

So, now, the question becomes, how do we calculate these quantities? How do we calculate this k1 and k minus 1 and k2? There are two different treatments that we will look at. One is what these R, R and K have done. This was in early, this was in late 1920s, ‘27 and ‘28. And then we will follow it up with even better treatment that came with Marcus, RRKM, and see what even improved treatment can be. So this is where the two theories that we discussed for microcanonical rate constant will be used. Thank you very much.