Chemical Kinetics and Transition State Theory
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Lecture 26
Rate as a reflux across a dividing surface

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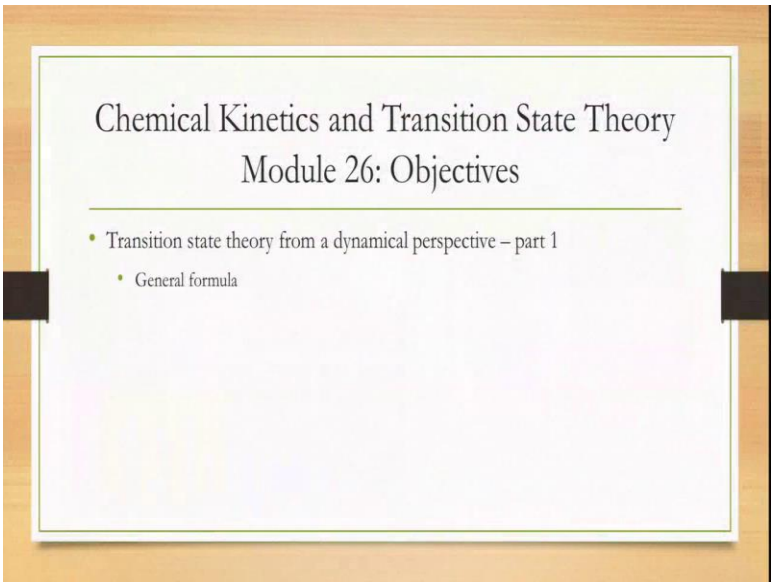

Hello, and welcome to module 26 of Chemical Kinetics and Transition State Theory. In today's module and the next module, we are going to look at a different way of deriving transition state theory. The derivation that we have done so far is from statistical mechanics. We look at the equilibrium constant and relate that to partition functions and we specifically make the five assumptions that we have discussed in the last several modules and we get a final expression, the very famous transition state theory expression. That derivation is perfectly correct.

But what I want to do in today's and the next module is to look at it from a different angle. What is missing in this derivation is any sense of dynamics. Remember what we are calculating is a rate constant and the rate is how fast is a reaction going. So, dynamics is very central to all of this. And that get somehow hidden into all this intricacies of equilibrium constant and partition functions. So, we want to bring the dynamics a little bit upside and elaborate where is this dynamics exactly hidden. So, in today's module, we are going to provide a much more general formula for rate constant, more general than transition state theory. And in the next module, we

are going to use that formula and make it a few more approximations and get the transition state theory result. So, without further ado let us begin.

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The resources, what book I am following is, one is this Steinfeld and Francisco and Hase. What I am covering today is not covered in that standard textbook of Laidler. You can also find the same thing in this excellent article by Bruce Mahan, Journal of Chemical Education. You can find the article here.

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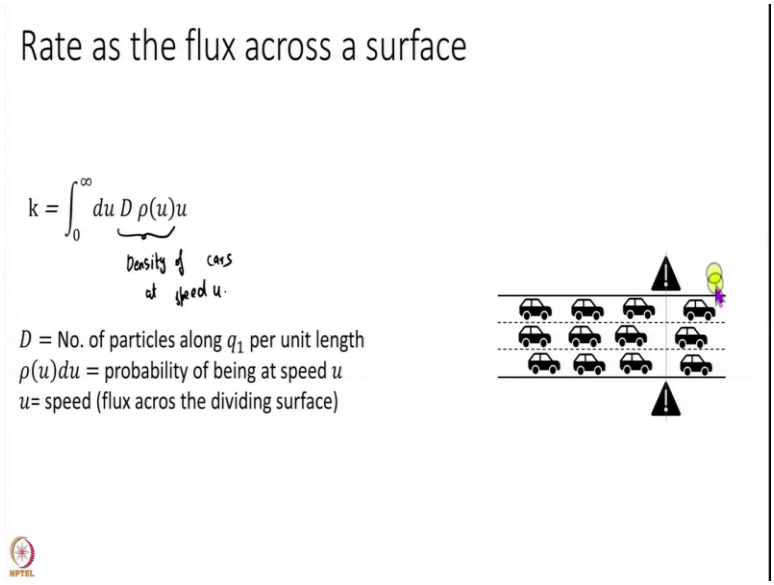

So, I will go back several modules and what we discussed in one particular module is, if you have a series of cars and the cars are going on some highway and I am standing at one given point and I am asking the question what is the rate at which cars will cross this dividing line. That we found is equal to this answer. This answer is the integral overall speeds, positive speeds, the density of cars multiplied by the probability that I am at that given speed.

So, this factor D into rho u is the density of cars at speed u, and u here is the speed which is nothing but the flux across my dividing surface. That is a technical language we use. So, this is what I call as my dividing surface. Dividing surface is nothing but a line that crosses the left to the right and u is telling me at what rate I am transitioning and D into rho u gives me the density and if I integrate overall speed, so I get the rate constant.

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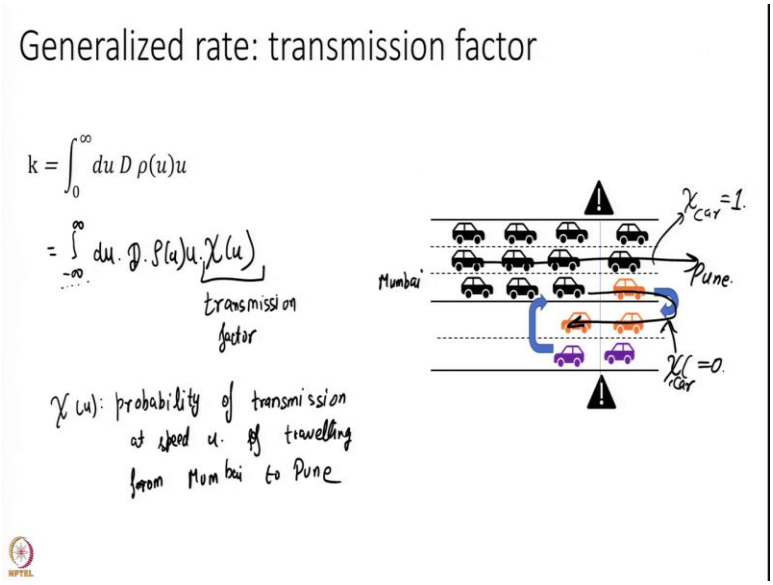

First thing I want to do today is to make this formula more general, in several aspects. First, in writing this formula, what I have actually assumed is I am integrating the speed only from 0 to infinite. So, I am assuming all cars are moving forward, one straight line. That may not be true though.

So, imagine there are some cars and some car moves forward, but suddenly realizes they have missed something and they turn around and come back, that can happen. So, this car is actually not contributing towards the rate. This car goes up and comes back. So, this formula has a problem then.

Or in other ways you can also imagine there is a car coming like this and it might have turned around this way and moved forward. So, cars can do funny business and so can our molecules. So, we have to make this a little bit more general and our way is, we hide all of this funny business in the following form. So, we hide all the funny business in the chi. And we call chi, the funny chi, the transmission factor. So, note now, I have changed the integral from minus infinite to plus infinite. I am saying let us look at all speeds. And at that given speed, chi of u tells me the probability of transmission at speed u.

So, let us just make things little bit more specific. Let us say here is Mumbai, let us say here is Pune. I am going from Mumbai to Pune. So, chi will tell me what is the probability of going from Mumbai to Pune if my car travels at speed u, transmission speed u of traveling from Mumbai to Pune. So, Mumbai can be my reactant in a chemical sense, Pune can be my product and this line can be my transition state at which I am counting the cars traveling through.

But the important thing is this chi is hiding all the dynamical information now. Chi is telling me, if a car is going forward, will it turn around in the future or not. So, for a car which behaves like this, for this particular car, chi will be 0. For this particular car, chi will be 1. That is the essential idea.

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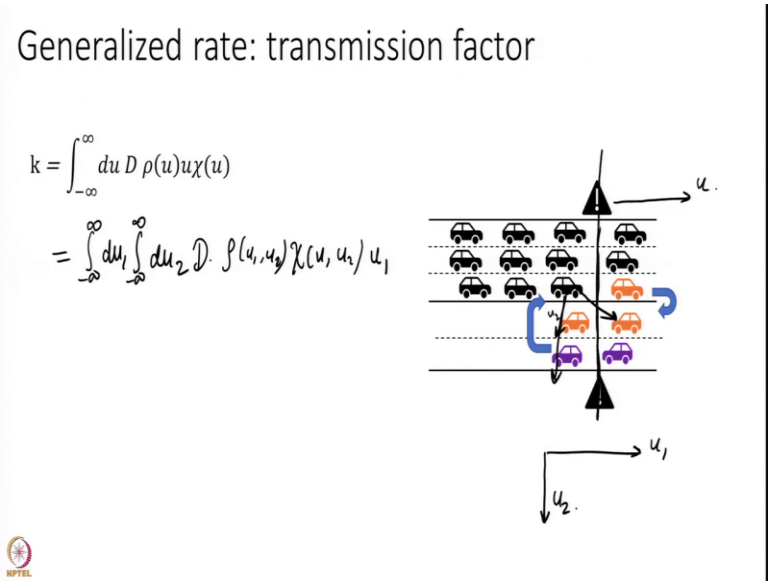

So, I have multiplied by chi, we have made some progress. How to calculate chi is a different business. But we are making the formula more general. We are trying to get to the most general

formula I can write. The second problem is, cars also do not necessarily move only in this direction, in the forward direction. Right now, I am writing everything in one direction, u. But your cars can do funny business once more. Some car might be traveling like this. Some car might be traveling like this, colliding with every other car, causing accidents. That is bad news but the cars can do that. Nothing stops them.

So, I have two directions now, one is u1 and the other component is u2. So, in two dimension I can write any velocity in two components. So, let us in general make sure that I have most general idea of u1 and u2. So, I will generalize this formula and integrate over both speeds along both directions. D rho of u1 comma u2, so there is some density of u1 comma u2, chi of u1 comma u2, chi will also depend on both, for example, a car which has the large u2 component, well, it is quite possible that it is going to turn around.

If it is anyway going in this way, they perhaps, it might turn around compared to a car with 0 u2 component. So, chi should depend on u2 as well, but this thing is simply u1, the flux, because remember this is my dividing line. This is the line at which I am sitting and counting the total cars passing through in the forward direction. That is what my aim is. How many cars per second go from left to right of this line, that is what I am calculating. So, that number remains u1, u2 does not contribute to this flux, u2 is parallel to this line.

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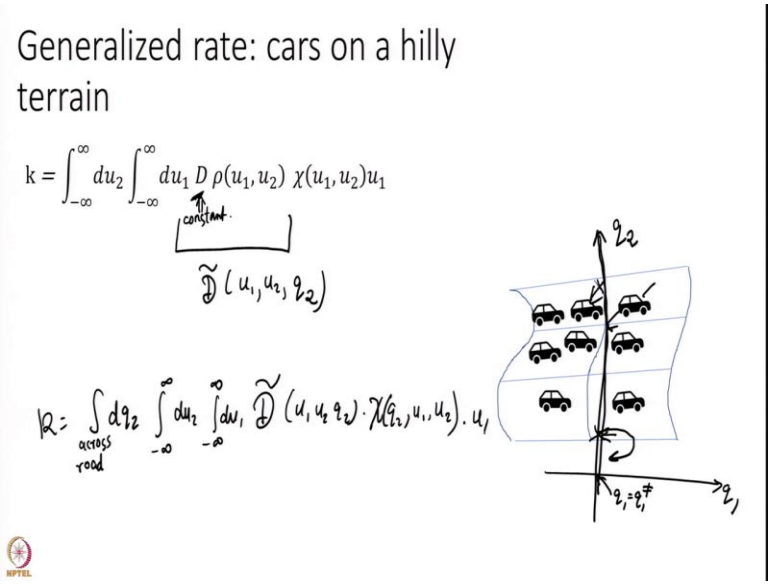

So, now I have a slightly more general formula with me. But there is still something missing. There is one factor that I have still missed and which is, that is density is I have assumed to be constant here that it is, all the cars are uniformly spread over all roads, but if you have ever travelled on a road, you will tell me that it is a bad approximation. More so for, imagine now, our dynamics happening on our, for reactants or our molecules, there the reaction is happening on a very hilly surface. So, now this is a very bad drawing perhaps of a hilly surface and this is my dividing line here now.

So, imagine that I have a hilly surface here and cars are travelling on this hilly surface with speeds u1 and u2 in forward and perpendicular direction. But when you have this rugged nature, well, some positions which are more smooth, more cars will accumulation. Cars would like to travel in that. And if some surface is very high and rugged, not good surface, then cars will avoid that region. So, this density will depend on where, on what point of this dividing surface I am looking at. So here you might have a less density, here you have more cars passing through.

So, what we are going to do, we are going to look at this D into rho and we will call this as D tilde which depends not only on u1 and u2, but also on coordinate q2. So, this I am calling as coordinate q2, this I am calling as coordinate q1. So, I am sitting at this point, let me call that as q1 equal to q1 dagger, in transition state theory again, linking to transition state theory where we use daggers. So, I am sitting at this q1 point, call it whatever else you want if you do not like dagger, this mile marker, and at that mile marker I am going across the road and finding the density at different points.

So, I write a more general formula now. I add another integral over q2 across the whole road, du2 overall speeds, du1 overall speeds, I call this D tilde u1 u2 q2, this full thing, D into rho. Now this chi also, let us be general, we never now. It might also depend on chi u2. So, imagine a car that is here. It might have a more tendency to be turning around compared to a car sitting here. If I am here, maybe I will feel a bit awkward traveling all this distance around. So it is,
chi might also depend on q2, but this is simply u1.

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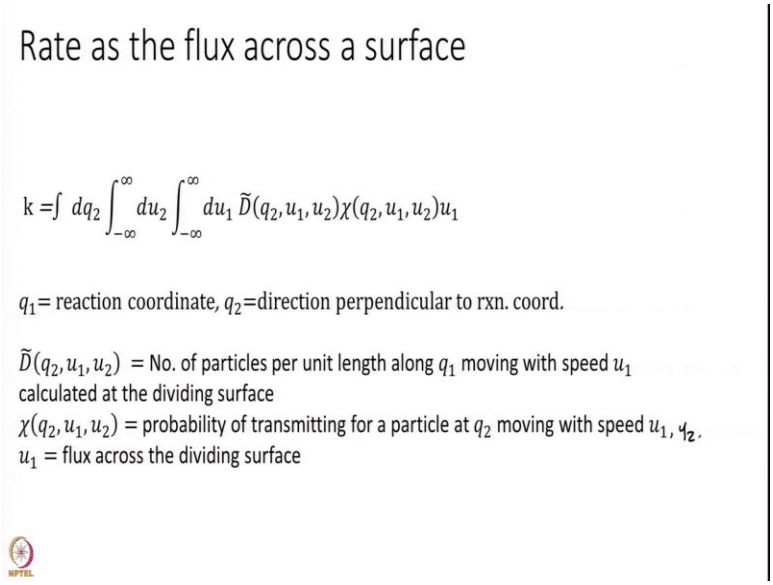

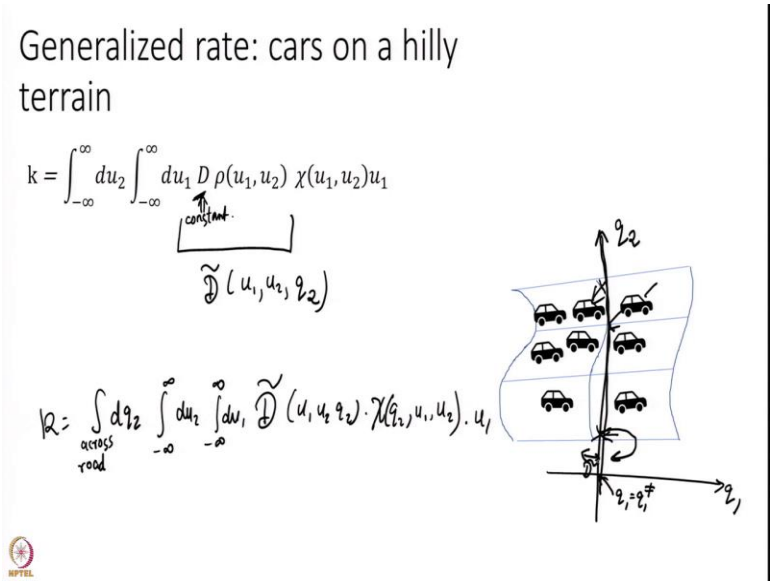

So, we arrive at a much more general formula in two dimension. Remember, roads are only two dimension, we are not making our cars go in more than two dimensions, they are not flying around. But for this at least two dimension, we have the as general formula as we can get following Newton's law by the way, this is quantum mechanical. We still have positions and speeds.

So here, q1 is my reaction coordinate, q2 is a direction perpendicular to reaction coordinate, D tilde is the number of particles per unit length along the direction q1. So, let me just go back one slide. I am sorry, I went forward. So, if I am sitting here and along this direction is where D is

measured. So, the number of cars in a unit length along the direction of q1 that is my D tilde at various values of q2, u1 and u2 and chi is the probability of transmitting if I am traveling at speed u1 comma u2 and u1 is what is the flux. And if flux founds too fancy, u1 is telling me essentially the rate of transmission.

So now, I want to connect this to our molecular transition state theory. If we actually understand this formula that I had written you understand all of rate, all of kinetics, all of rate theories. That is all, all rate theories are, they are just an integral of flux across a dividing surface. So, we have to just carefully think on what dividing surfaces mean in chemical dynamics. So, imagine a reaction now.

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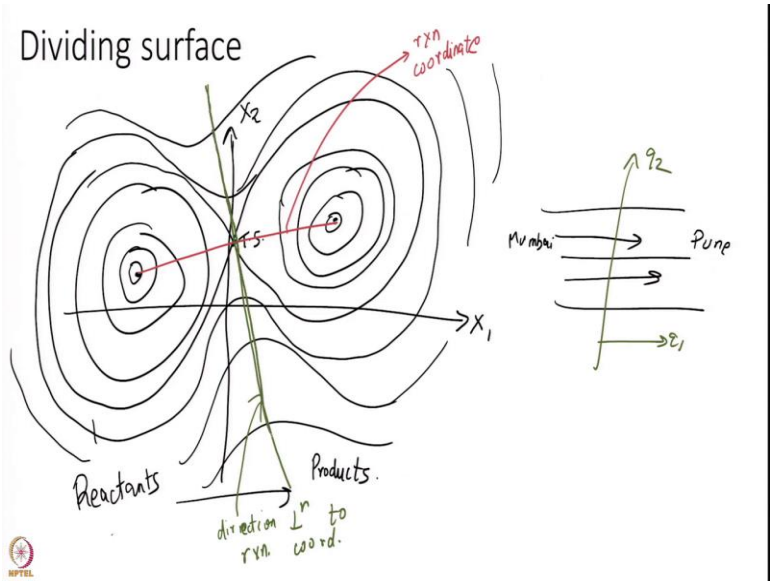

So, what we have our drawing so far, we had these roads with cars traveling like this and here was my Mumbai, here was my Pune. Well, in the language of reactants, what I have are energy surfaces. Let me just redraw that. So, imagine I have some coordinate space, just to start with a drawing in two dimensions only. And let us say here is my reactants and reactants appear as this in terms of contour plots. Here is my, let us say, some product in general. So, they are given by some energy surface. And if you have a reactant or a product typically you will have a minimum, a bowl shape like this.

And the transition state, I am sorry, that should have happened. Something like this, this point is the transition state. I am just bad at drawing this contour. This contour should never touch each

other. So, you get energy surfaces that look like this. And I am going from this reactant to product, so this is my reaction coordinate. And I am sitting at the transition state and if I draw a surface that is parallel, that is perpendicular to the reaction coordinate, this is called, this is essentially my q2. So, this was q2 and this was q1. This is my direction perpendicular to reaction coordinate.

So, what I want to do is to do an integral over this green line effectively. So, I set a transition state, I find my reaction coordinate, I find the direction that is perpendicular to my reaction coordinate and I integrate over that. I find the flux of my trajectory is going from reactant to product across this green line. That is what I have to calculate.

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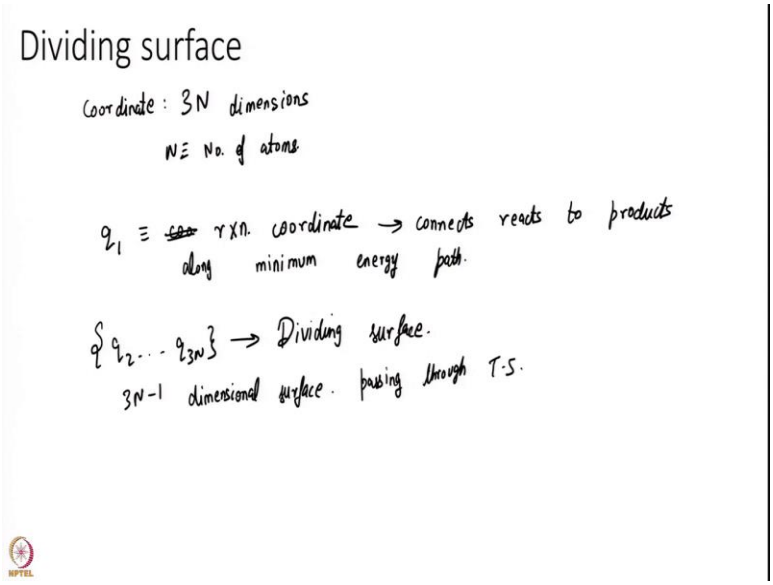

I just want to make things more general because, as you know, our coordinates, I have to change my color back to black, so I have the coordinate space of 3N dimensions, not two, in general, where N is number of atoms. So, each atom has x, y, z, so I get 3N number of coordinates.

So, I cannot draw an energy surface for you in 3N dimensions, it is not easy to visualize, it is perhaps impossible. But the idea, mathematically the idea is the same. I have q1, one coordinate that I will call the reaction coordinate, reaction coordinate is always only one. That is the coordinate that connects reactants to products along minimum energy path. That is one coordinate. Every other coordinate constitutes my dividing surface.

So, I really have to be integrating the flux or this rate across a 3N minus 1 dimensional surface passing through transition state. So, transition state is one point. I draw a surface of 3N minus 1 dimensions, do not even try to visualize it, you cannot, you can visualize a surface only in 3D. But imagine this huge surface that is separating the reactant from the product and I am simply sitting at this surface and trying to see how many trajectories per second go from reactant side to product side. That is what I have to calculate.

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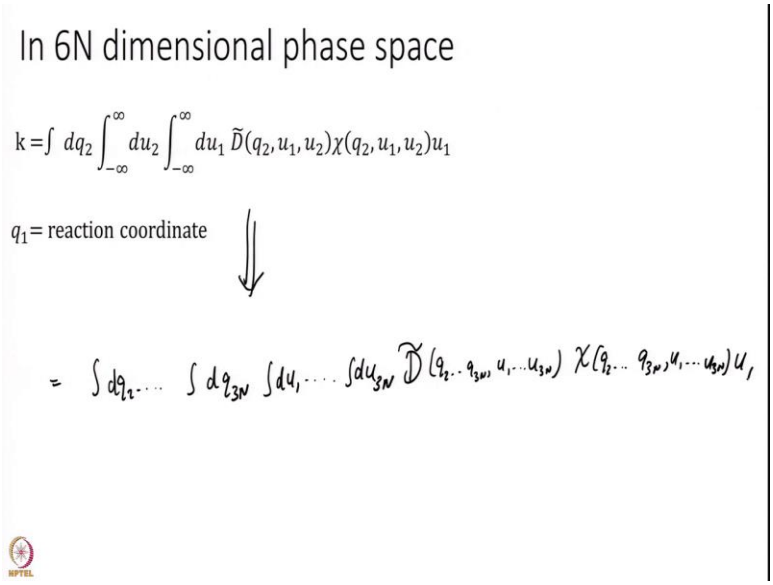

So, in short, this is the formula I had in 2D. I take this formula and I generalize it. I integrate from dq2 to dq3N and I integrate overall speeds, D tilde of q2 to q3N, u1 to u3N chi q2 to q3N u1 to u3N into u1. So, it is a straight forward generalization. Earlier I, for example, I showed you how it works in q2 space only because it is easier to see, but the really it is q2 to q3N and all speeds.

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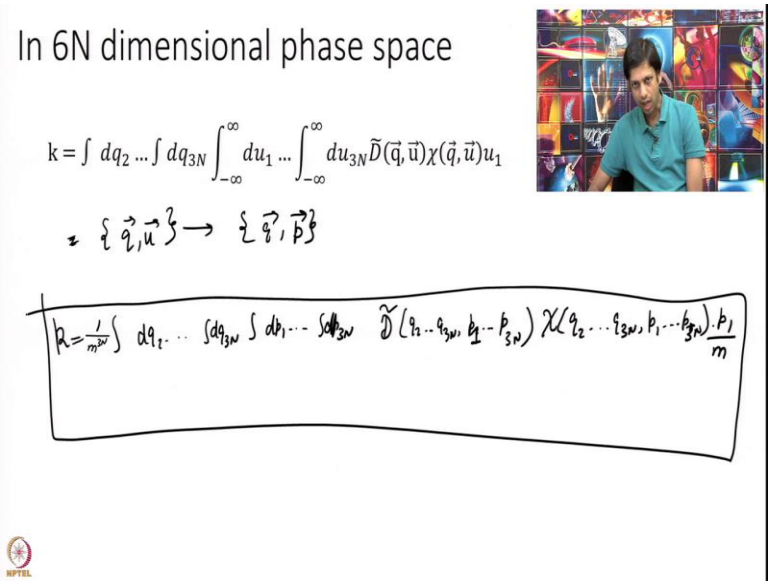

And just one remark, the point is we really in statistical mechanics integrate over q, p space. So, I want to go from this q, u space to q, p space, momentum space. So that is straightforward. I just write this in p space instead, this integral. So, I am integrating overall momenta instead of speeds.

This D, which would depend on q2 to q3N, p1 to p3N, what is that, do not know what that symbol even is, we will correct the symbol, chi q2 to q3N, p1 to p3N and the u1 is nothing but p1 over m, because of p equal to m u. So, this is my more general formula.

And this formula actually is, makes very few assumptions. All I have really assumed is that a dividing surface exists and classical mechanics, only two assumptions have made. No idea about equilibrium, no idea that you have no re-crossing assumption, all that is not made, only two assumptions have made, that the trajectories are classical and the dividing surface does exist over which I am integrating.

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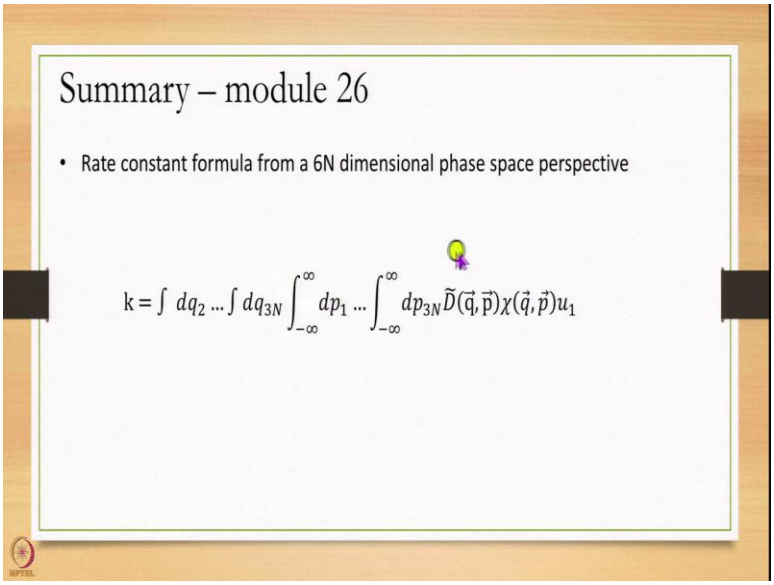

So, we have this more general formula with us today. And what we are going to do in the next module is to use this formula and make a few more assumptions that are needed to get to transition state rate. Thank you.