Chemical Kinetics and Transition State Theory
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Lecture No. 13
Kinetic Theory of Collision and Equilibrium Constant

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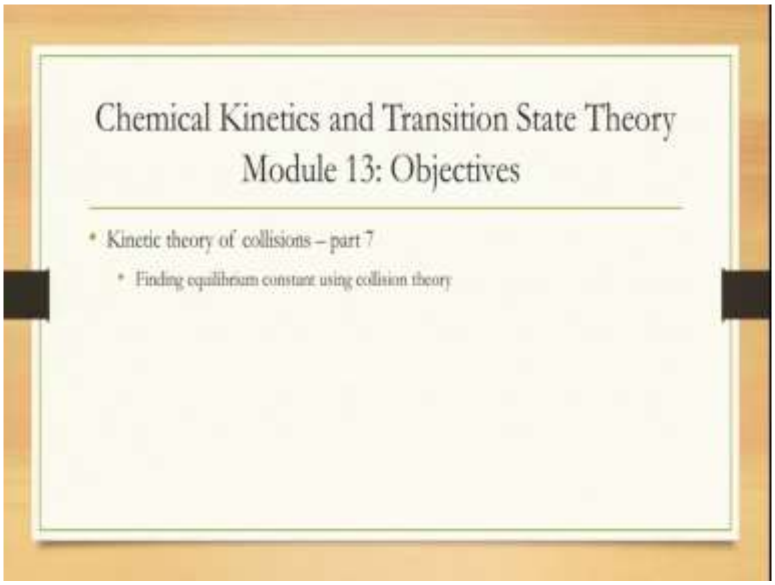

Hello and welcome to module 13 of Chemical Kinetics and Transition State Theory. We have discussed the collision theory quite deeply now over the last 7 or 8 modules and we are near the end of it. We are soon going to begin transition state theory. But before we do that, I want to spend little bit of time on one very interesting topic, which is what is called detailed balance or the idea of thermodynamic equilibrium. So it is a very interesting comment.

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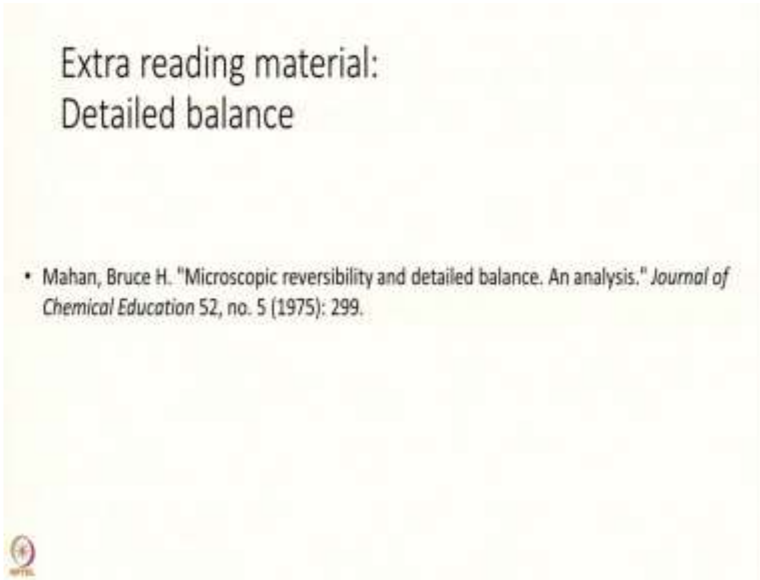

You can find a very beautiful paper written by Bruce Mahan in 1975, titled "Microscopic reversibility and detailed balance." What I am covering today in the next maybe 15 20 minutes, is a much simpler proof than this provided in this paper as applicable to collision theory. But for those who are interested can go to this paper and read the full proof, it is very readable and you have enough information to be able to go through this actually. So the more interested readers can look at this paper.

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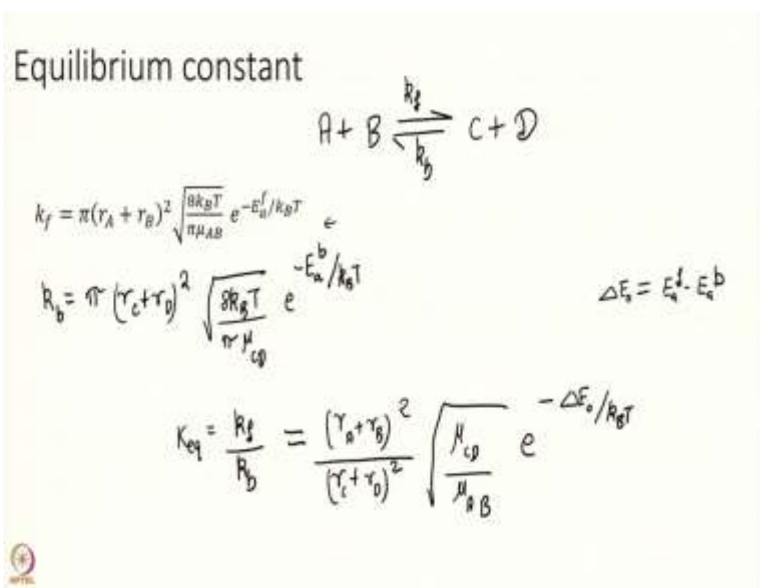

So what is it that I want today? What I am trying to calculate is not the rate constant today but equilibrium constant and something interesting pops out when we do that. So let us say, I have the wrong color of the pen somehow, I will change the color. I have A plus B and let us say the reaction is reversible it is C plus D. I have forward rate; I have a backward rate. Well what is the big deal? I can calculate both forward rate and backward rate using collision theory, I have assumed bimolecular on both sides.

If that is the case, my forward rate is given by this equation that we have derived and used multiple times in the last few several modules. But I can also write a backward rate as rc plus rd square, I do not know what their radii are, they might have changed. When the collision happens, some mass might transfer from A to B and the radii can change; root 8kT over pi mu cd e to the power of minus A and mu activation energy can also change, so I am keeping everything as general as I can and K equilibrium is k f over kb.

So this I just divide these two, when I do that you see the pi cancels, I have rA plus rB, I take in the square root, I have a lot of common terms 8kt over pi cancels and I get e to the power of minus what I will call as delta E naught over kT, where your delta E naught is simply Eaf minus Eab. So that is eventually the potential energy difference between reactants and products, delta E naught. I have some equation. Then I play around with this equation a little bit more let us see.

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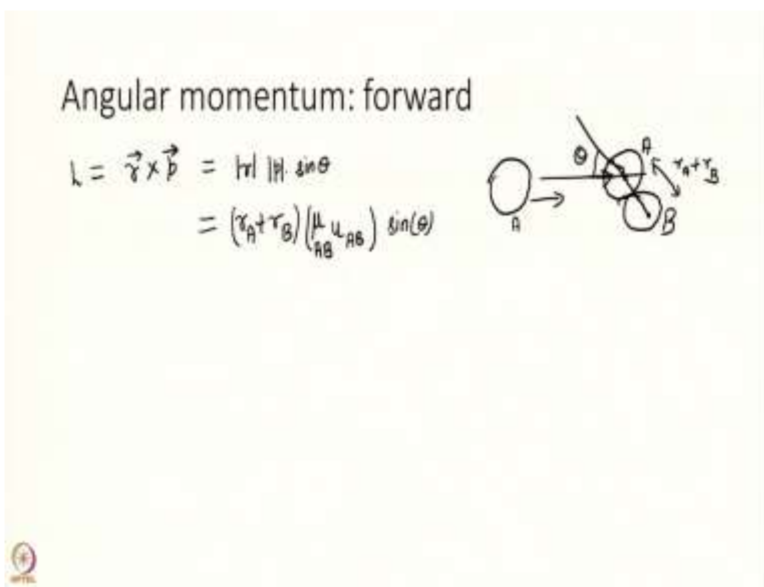

Remember what we are assuming here is Newton's Laws and Newton's Laws conserve what is called the angular momentum. So we are going to calculate forward angular momentum and the angular momentum of the products and equate those two. So let us see how we do that. We have A moving forward colliding with B, this two in general have different radii. So this is A, it has moved from here to here. This distance is rA plus rB and let us say this angle is theta and I am drawing straight lines apparently but this is a straight line.

Angular momentum is defined to be r cross p, r here so this thing is nothing but magnitude of r magnitude of p into sin theta, where theta is the angle between r and p. And I am finding the angular momentum at the point of collision. I can do it before as well, it does not matter, actually you are going to get the same answer, angular momentum is after all a conserved quantity.

So r is rA plus rB, that is your r, that is the distance between the two centers, p is a mass, for mas remember I should use mu, the reduced mass into u, because u is the relative speed and for relative speed again we derived all of this in detail, you get the relative mass. And at the reactant side it is mu AB and let me call this as u AB sin theta. So this is the forward angular momentum.

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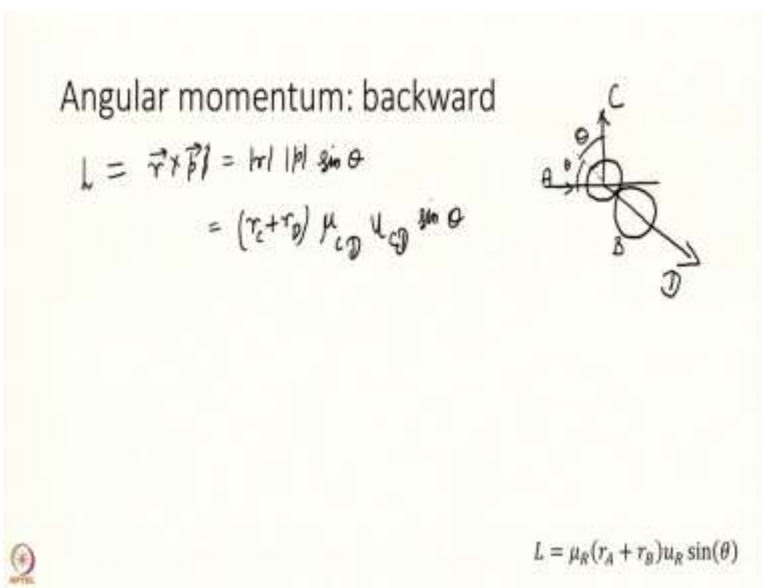

I can do the same thing in the backward side as well. So what I mean by the backward side, right after the collision has happened, the mass transfer has happened, I have this as, so this came like this as A here, this is B right now and after the collision this goes like this and it becomes D, this A gets reflected like this as C.

So if this is theta the reflection will be equal according to Newton's Laws. So the angular momentum right after collision, when the mass transfer has happened, my radii have changed, so again in collision theory effectively we are assuming all this is happening instantly, I go from radii rA and rB to rC and rD and masses mA and mB to mC and mD.

So I can write the same kind of angular momentum now as r cross p which is mod r mod p and sin theta, that angle is the same theta. This r is now rC plus rD, the distances have changed and p has become mu CD u CD sin theta. So my speeds have changed, my masses have changed, my radii have changed, so I calculate the new angular momentum, that is alright.

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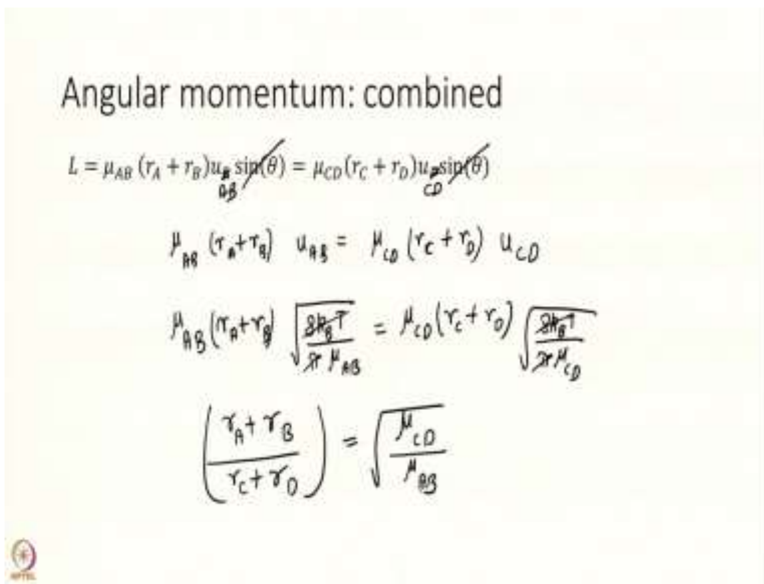

But angular momentum, however you want to transfer masses, whatever you do, angular momentum is none the less a conserved quantity. So I equate the two angular momentums that I have calculated, this should have been AB, this should have been CD. So this theta terms cancels and I get mu AB rA plus rB u AB equal to mu CD rC plus rD u CD. And as is common I am going to take essentially a thermal average here.

Instead of u AB I will write the thermal speed of AB which is root, this is what we do really in collision theory, pi mu AB this is equal to mu CD rC plus rD, some terms will cancel 8kT over pi, 8kT over pi and I will get rA plus rB divided by rC plus rD this is equal to, you will notice I have a full mu here and a root mu, I can simplify all of that and this will become to mu CD over mu AB. A very powerful relation, the radii have to be related, they cannot be arbitrary because angular momentum is conserved.

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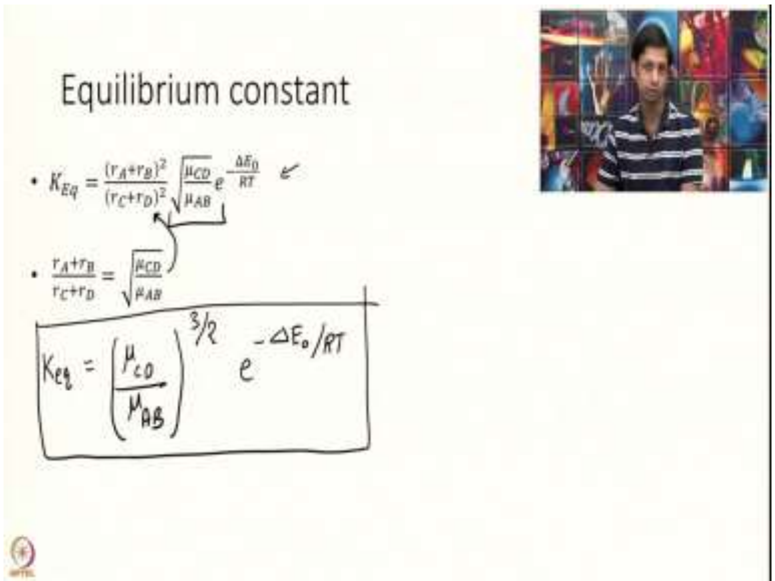

So earlier I had derived K equilibrium to be this big equation rA plus rB square all this thing, just few slides ago and now we have found a relation between the radii. So I am going to substitute this equation here, so this will become equal to mu CD over mu AB and you notice I have a square root of mu CD over mu AB here, so this become to the power of 3 half.

So according to collision theory, your equilibrium constant is given by this. It is actually independent of the radii. If you could tell me the masses, if you tell me the reactants and you tell me the products and you tell me the difference between the potential energy between the reactants and products, I can calculate you the equilibrium constant.

By the simple proof but a very, very powerful, it goes somewhat deep and once we discuss transition state theory and partition functions, this we will revisit then in the language of partition functions. So there is more about this that we come to later.

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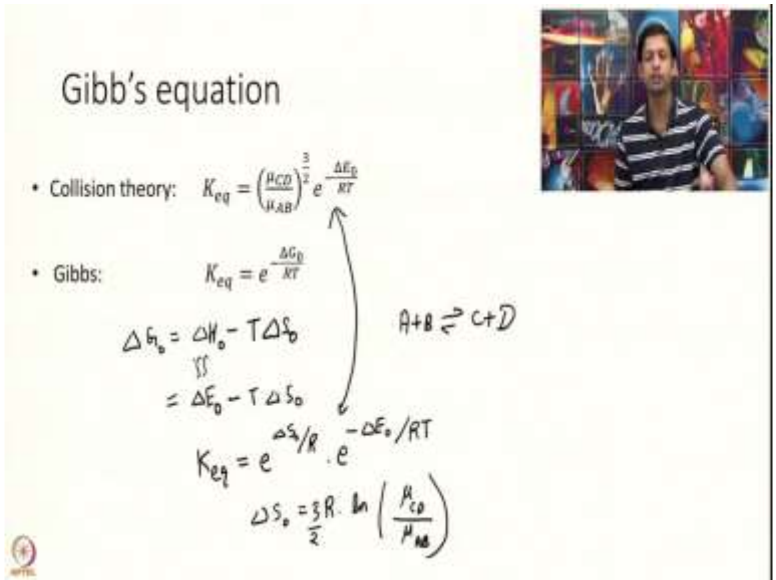

One comment that I do want to make today itself is relation with Gibb's equation. So Gibb's much earlier had written an equation that relates the equilibrium constant with the free energy and Van't hoff's equation actually comes out of this. So let us relate, I have a equilibrium constant from collision theory and the equilibrium constant from Gibb's equation. Let us do I little bit of our thermodynamics. So that is how delta G is defined.

In our case we have A plus B going to C plus D. In this case, what is the, and this we will examine in more detail delta X naught you can basically convert to delta E naught. You have to be a bit careful, factor of RT and pv might be there, so I will leave that to you. But let us just ignore constant factors right now, let us say this is delta E naught.

So if I put it in the Gibb's equation, you will see this is equal to and if I compare these two equations, I get something interesting, I get delta S naught is R into ln of, 3 half mu CD over mu AB. So actually collision theory is also commenting on change of entropy. Simple theory just particles colliding and the power of thermodynamics is can come in and you can use all these equations in thermodynamics and comment a lot more.

So I will end with this today and again this in a few more modules, once we have a better idea of transition state theory, we will come back to this.

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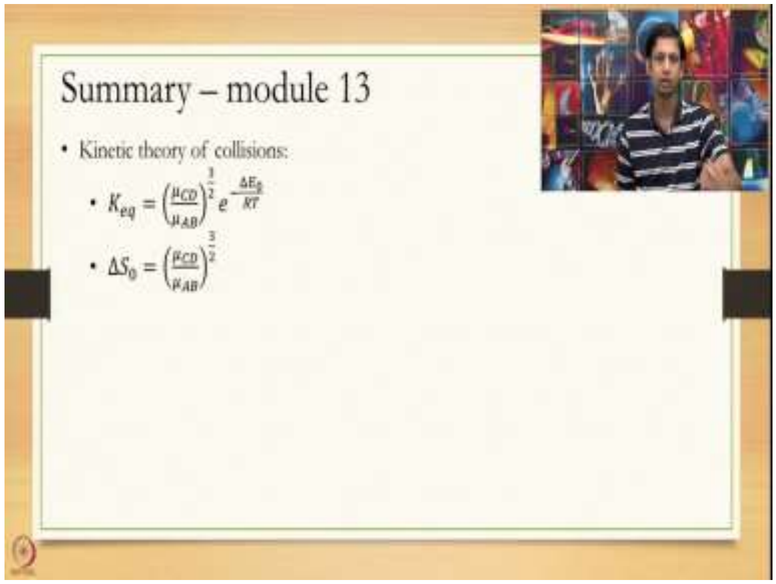

In summary, what we have done today is looked at deriving the equilibrium constant from collision theory and commented on the change of entropy of a reaction based on collision theory. So this is not a, we will see actually that this is, there is a mistake here and transition state theory is going to correct that mistake. Thank you very much.