Chemical Kinetics and Transition State Theory
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Lecture No. 14
Critique of Kinetic Theory of Collisions

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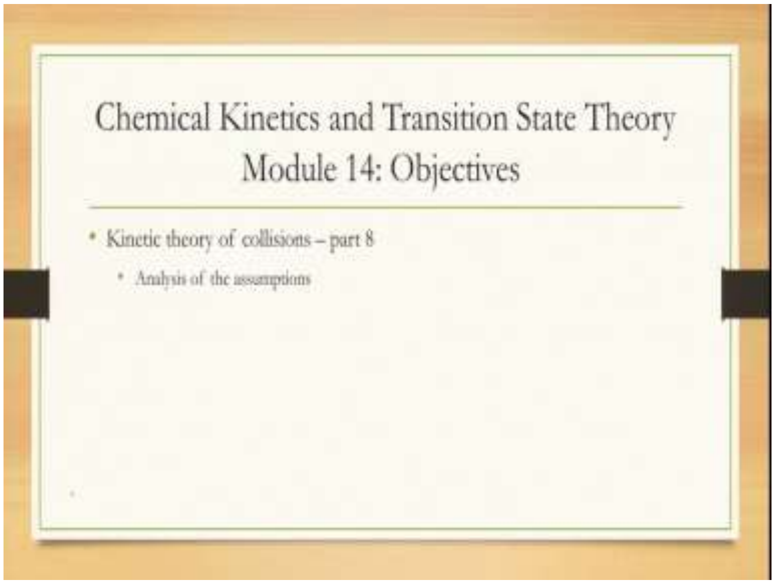

Chemical Kinetics and Transition State Theory
Module 14: Objectives

- Kinetic theory of collisions – part 8
    - Analysis of the assumptions

Hello and welcome to module 14 of Chemical Kinetics and Transition State Theory. In a series of modules, we have now developed the collision theory to calculate rate constants. We have solved several numerical problems; we have looked at the derivation very carefully and today is going to be the last module that specifically focusses on collision theory. So what I want to do today is end with an analysis of the assumptions that go into collision theory and essentially this module is one of the most important modules.

Because today when we will discuss when is collision theory applicable and when is it not. So if some experimentalist come to you and ask you okay I have done a reaction but I want to calculate the rate constant, will you apply collision theory to that or not? And that is the most important thing to do, so we will start and let us go over one by one of all the assumptions that we have made in deriving the rate equation.

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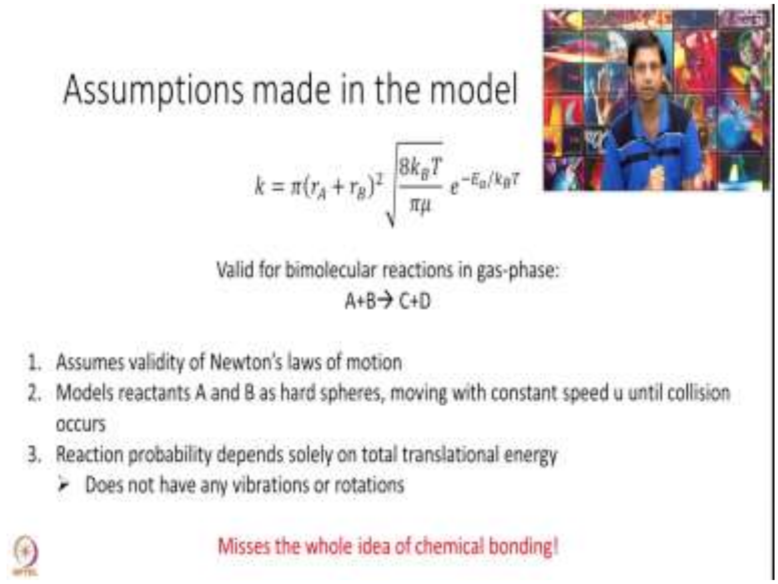

Assumptions made in the model

$$k = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, e^{-E_a/k_BT}$$

Valid for bimolecular reactions in gas-phase:
A+B→ C+D

1. Assumes validity of Newton's laws of motion
2. Models reactants A and B as hard spheres, moving with constant speed u until collision occurs
3. Reaction probability depends solely on total translational energy
   - ➢ Does not have any vibrations or rotations

Misses the whole idea of chemical bonding!

The rate equation that we derived is this. So the first big point is that it is valid only for bimolecular reactions; A plus B going to some products, product side might be anything, it might be C plus D or it might not be. But reactant side it has to be two A plus B, A can also be equal to B but it cannot be single molecular or it cannot be termolecular, it has to be bimolecular. So that is the whole regime of the model itself.

It assumes Newton's laws to be true. You think of these A and B moving classically, not only classically we assume essentially there is no potential energy as well, these particles we assume as big hard spheres which are colliding with each other. So essentially there is no interaction, these particles are not charge, these is no Coulomb force, there is no Lennard Jones force, there is no dispersion force, there is none of those forces.

It is a very simple minded model A and B two spheres, they move at a constant speed u until a collision happens, that is it. Another very big assumption in this model is what we introduce is a reaction probability at a given speed. So if you remember if you go through your modules carefully, we get this exponential term only by including this reaction probability, by introducing an appropriate reaction cross section.

But in that what we assume fundamentally is that this reaction cross section or the reaction probability depends solely on one number which is the translational energy. That is a assumption and today we will discuss the consequences of this assumption as well. So it does not have any vibrations or rotations by the way. Why? Because I have a perfect sphere, my molecule does not have bond to vibrate. So collision theory does not look into the structure of your reactants at all.

That is very important that actually transition state theory builds over, this missing factor. So that is the biggest limitation of collision theory, it does not have the idea of chemical bonding in it. Well that is a big drawback, is not it? Imagine if you go to an organic chemist, they really think in this language of electrons moving are outer, build, putting these arrows of how electrons are moving, how bonds are moving; none of that is built in this model.

All of that is completely missing. So we will see in the coming modules how to include that and that correct theory for including all of that is essentially transition state theory.

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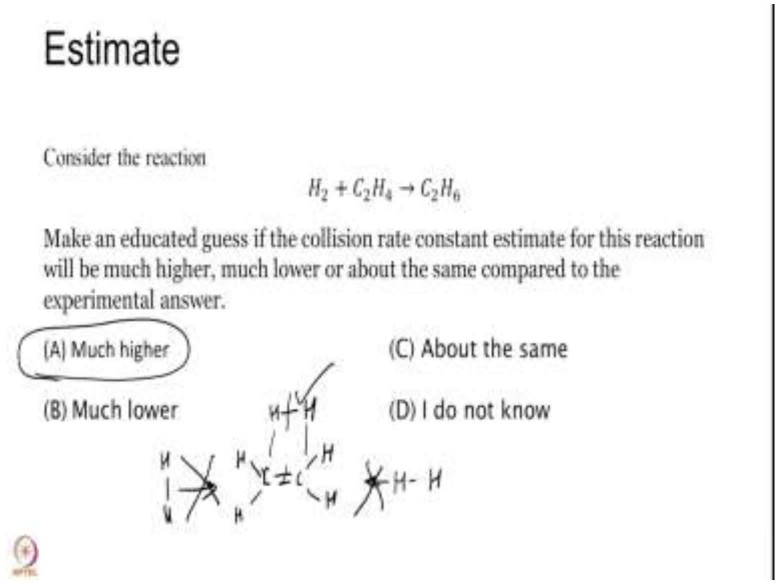

Estimate

Consider the reaction

$$H_2 + C_2H_4 \rightarrow C_2H_6$$

Make an educated guess if the collision rate constant estimate for this reaction will be much higher, much lower or about the same compared to the experimental answer.

[✓ (A) Much higher]

(B) Much lower

(C) About the same

(D) I do not know

So, let us start with one question. Consider this reaction of hydrogenation of C2H4 to give C2H6. So I am adding a hydrogen over the double bond to give me this molecule. Can you estimate, you just have to calculate, so just using your intuition of the assumptions that we have made, can you estimate if the rate constant as estimated by collision theory will be much more, much less or more or less the same as the experimental answer? So please pause the video, take a moment, reflect on the question and choose your answer.

Hopefully you are back, hopefully you paused the video, you thought about it. Let us discuss what one should expect, it is a colligative question, your answers might differ from mine. So well here now we have to really think of chemistry, I have C2H4 which essentially is this molecule and I have a H2 which is coming and adding here. Now the point is I am first assuming all of these as hard spheres, they do not look like spheres.

Let us assume I can just somehow still model them as sphere, I will just not look at them very carefully. But the point is that H2 must come in a very specific direction for a reaction to happen. This H2 has to come in this fashion, this bond has to break and this bond has to break. Now if H2 approached in this fashion, nothing would happen, what if H2 approached in this fashion, so this will not be reactive at all, this is the reactive one. Correct?

But collision theory considers all of them to be equally reactive; collision theory does not understand which direction the collision is happening from, all directions are equally good. Therefore, collision theory will grossly overestimate the rate of the reaction. So the correct answer will be, the collision theory answer is much higher than the experimental answer. Is that what you got?

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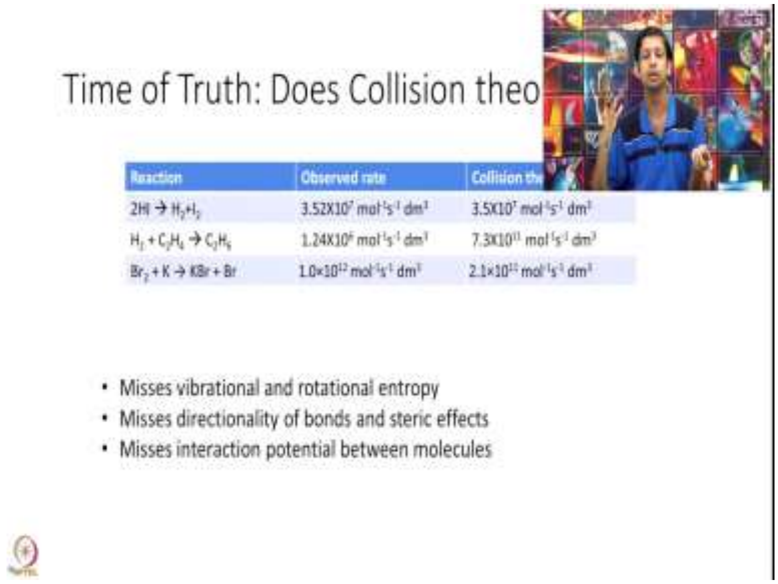

Time of Truth: Does Collision theo

Reaction	Observed rate	Collision th
$2HI \rightarrow H_2+I_2$	$3.52X10^7$ $mol^{-1}s^{-1}$ dm^3	$3.5X10^7$ $mol^{-1}s^{-1}$ dm^3
$H_2 + C_2H_4 \rightarrow C_2H_6$	$1.24X10^6$ $mol^{-1}s^{-1}$ dm^3	$7.3X10^{11}$ $mol^{-1}s^{-1}$ dm^3
$Br_2 + K \rightarrow KBr + Br$	1.0×10^{12} $mol^{-1}s^{-1}$ dm^3	2.1×10^{11} $mol^{-1}s^{-1}$ dm^3

- Misses vibrational and rotational entropy
- Misses directionality of bonds and steric effects
- Misses interaction potential between molecules

So let us look at a few specific examples. As one of the problems we had actually looked the reaction of H2 plus I2 going to 2HI, that was actually the problem that was originally studied by Trautz and Lewis in 1918 and it is a well fortunate or unfortunate, depending on your point of view that for that problem, collision theory works beautifully. It is really a coincidence though. We get the observed rate of 3.5 into 10 to the power of 7 liter mole in per second inverse and collision basic theory essentially gives you the same rate.

Actually not only that, as a function of temp as well, the rate mech is very well for this particular reaction. So that is the reason people were very excited about this theory, that at least we solved for one problem. And that itself by the way is a big achievement, at that point it is a first estimate of rate constant from a fundamental perspective, where we actually got the number without referring to anything experimental, from scratch, from (())(8:17) and some molecules.

What as it turns out, there are many other examples where this theory does not work. For most problems, you get things like where collision theory grossly overestimates the reaction rate. So this problem that we discussed in the last slide H2 plus C2H4, here I am giving you the actual numbers, the experimental weight is 10 to the power of 6. The collision theory answer is 10 to the power of 11, 5 orders of magnitude, 1 lakh times more.

So that is how bad collision theory can be and there are many, many more examples that collision theory will overestimate. There are also a small fraction of molecules or reactions, where collision theory also underestimate. I have given you one example where the collision theory answer is 10 to the power of 11 and the actual answer is 10 to the power of 12. So you have a factor of 5 underestimated. Well not as that as this one where you had 1 lakh factor, here the factor is 5 only, 5 is still somewhat large, we want better, we want to improve.

So today we will also discuss why can collision theory underestimate as well. So again just to reemphasize, collision theory misses vibrational and rotational entropy. This we will discuss in more detail in transition state theory. It has misses completely the idea of reaction, it has no sense of direction of bonds, how the electrons are distributed, that for a reaction to happen, the two reactants must come together in a specific form, that is completely missing here.

There are no steric effects here, where your molecule of interest might be hindered by this let us say some big organic group. Idea it is more common in organic chemistry, completely missing here. So these are the problems. And there (())(10:27) which is all kind of interactions, imagine if your reactants had a charge, even if it is a dipole movement.

Well you know these dipole movements will attract each other and because of that the idea of constant speed is a bad one, they will be accelerating or deaccelerating. And that or none of that is built into our model. So it is a very simple minded model from which you can get a first estimate think of it that way.

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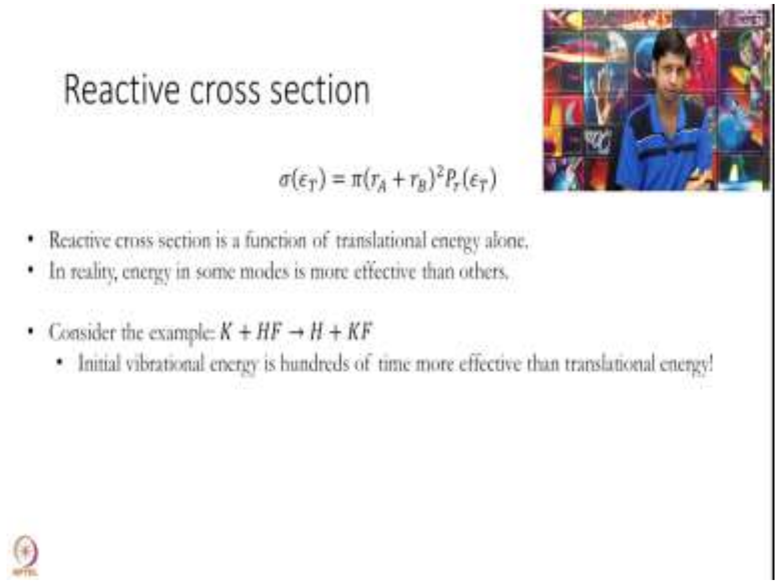

Reactive cross section

$$\sigma(\epsilon_T) = \pi(r_A + r_B)^2 P_r(\epsilon_T)$$

- Reactive cross section is a function of translational energy alone.
- In reality, energy in some modes is more effective than others.

- Consider the example: $K + HF \rightarrow H + KF$
  - Initial vibrational energy is hundreds of time more effective than translational energy!

So let us just discuss a bit more, one important point that we raised is that the reaction cross section that we had introduced earlier is a factor of only translational energy. That is incorrect experimentally speaking. You have many more factors on which this reaction cross section can depend on, so one simple example I can give you is this reaction of K plus HF going to H plus KF. Now this is one example where you can see the difference in different kinds of energy.

So I put the initially a little bit more energy into vibration of HF, so HF is a bond, it has, it is vibrating and initially let us say I put in little bit laser or otherwise some more energy into this HF, the reaction will proceed thousand times faster compare to if I had put this energy in translational energy. So the reaction cross section is not just a function of total energy, it depends very selectively on how this energy is partitioned.

So energy can come in different forms and these different forms effect the reaction differently. So again this is a big failure of collision theory.

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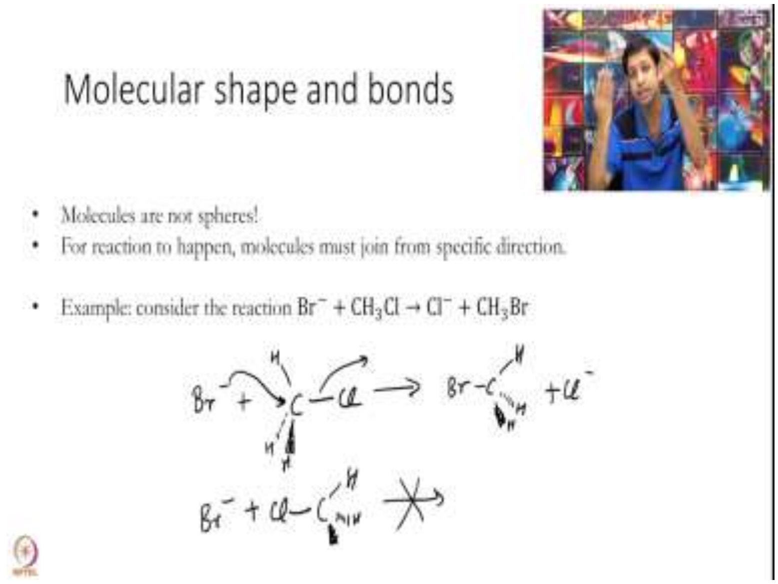

Molecular shape and bonds

- Molecules are not spheres!
- For reaction to happen, molecules must join from specific direction.

- Example: consider the reaction $Br^- + CH_3Cl \rightarrow Cl^- + CH_3Br$

The next thing I want to just point out once more just to reemphasize is, because it is such an important point, there is no notion of molecular shapes or bonds in collision theory. So just let us look at one of the simple examples that we study as an SN2 reaction for example, you can cook up your own reaction. So, just I am bad at organic chemistry, so please pardon me for my bad drawing skills here, so this reaction essentially happens as Br minus attach the carbon opposite to Chlorine and this Chlorine dissociates for this give you essentially this gets inverted like this.

Now if you think about this let us say reaction, actually you can think of spherical shape as a good approximation to be honest, Br minus is an atom, atoms are thought of a spheres. And even this molecule CH3Cl, well you have a central carbon surrounded by these atoms and they can perhaps think of this as a sphere, not a bad model.

But what is a bad model is assuming all directions to be same, Br minus has to come from a very, very specific direction, if Br minus let us came in this fashion, orientation really matters here, you will not get any reaction. So Br minus must come opposite to Chlorine, that is the idea of an SN2 reaction, none of that is present in a collision theory.

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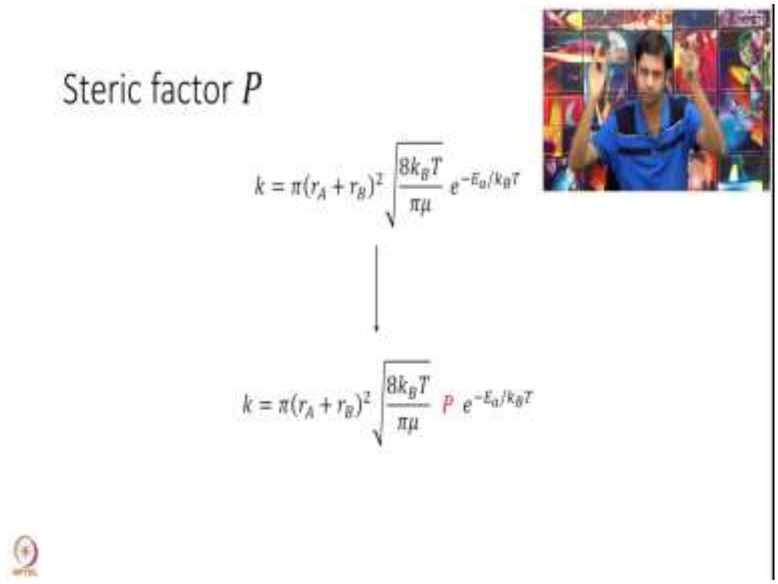

Steric factor P

$$k = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, e^{-E_a/k_BT}$$

$$\downarrow$$

$$k = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}\, P\, e^{-E_a/k_BT}$$

So, one way people try to improve on this is by introducing what is called the steric factor. So this is an ad hoc factor, we just say that our collision rate look like this, this is what we derived, but to get it right you must multiply it by P. So P is number that you can calculate experimentally, but P is usually not dependent on temperature, so that is the advantage of using this.

So at one temperature perhaps you calculate this P as the measured rate versus the collision theory rate, you can find the ratio and then you can use the same P for different temperatures. So that is one way of correcting it, but it is not very satisfactory. Yeah because it is ad hoc, it is not from an atomistic perspective which is has been our aim.

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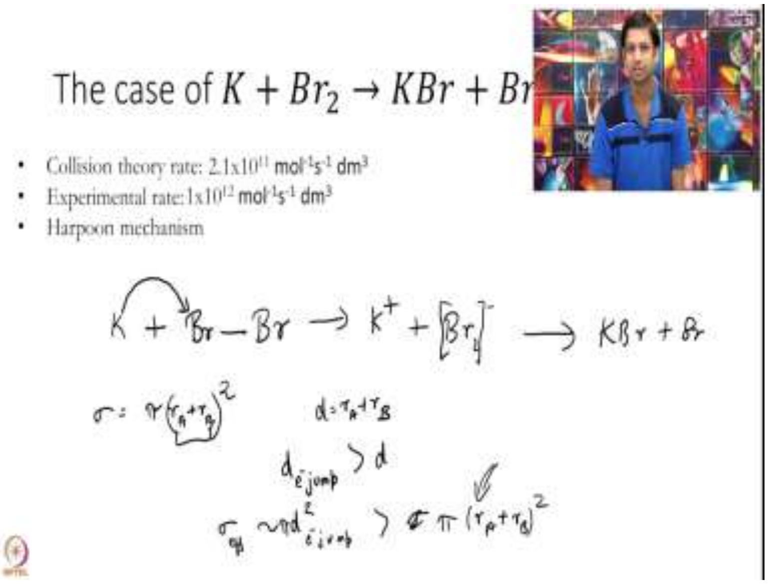

The case of $K + Br_2 \rightarrow KBr + Br$

- Collision theory rate: 2.1×10^{11} mol^{-1}s^{-1} dm^3
- Experimental rate: 1×10^{12} mol^{-1}s^{-1} dm^3
- Harpoon mechanism

$$K + Br-Br \rightarrow K^+ + [Br_2]^- \longrightarrow KBr + Br$$

$$\sigma = \pi\underbrace{(r_A+r_B)}^2 \qquad d = r_A + r_B$$

$$d_{\bar{e}\,jump} > d$$

$$\sigma_{eff} \sim \pi d^2_{\bar{e}\,jump} > \cancel{\sigma}\ \pi(r_A+r_B)^2$$

Let us finally discuss this example, it is a very interesting case of K plus Br2 going to KBr plus Br. In this case it is the opposite, collision theory underestimates where a correct reaction rate. What happens here is something very interesting and cool, I just wanted to highlight that. I have K and I have Br2, this reaction happens under what is called harpoon mechanism.

What happens actually is that when this K and Br2 comes somewhat close to each other, an electron actually jumps from K to Br, so this first goes to K plus plus Br2 minus, and this eventually reacts to give KBr plus Br. So what is the big deal? The point is the radii at which electron transfers is much larger than the radii of K plus Br2.

So if you remember, your sigma was pi rA plus rB square. So this distance d, but electron jump happens, d at which electron jump happens is much larger than d. And once the electron jump happens, these become charged and then it accelerates each other very fast, so the reaction will happen very fast. So in effect, the sigma effective is actually closer to d electron jump square.

The d at which the electron is jumping which is in much greater than sigma of just this pi of rA plus rB square, sorry I forgot a pi here. So that is the reason that the collision theory which is approximating this as a rate is lesser than the actual rate. As an assignment problem, you will see how to estimate this using a very ad hoc calculation. So that I will leave to in assignment in a how to calculate this d electron jump approximately, but in general it is hard to calculate these numbers, for this one it works out very well.

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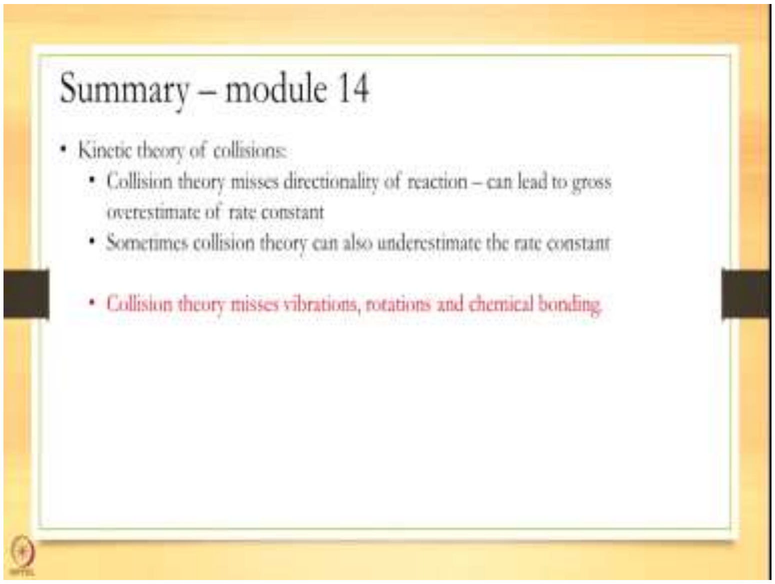

Summary – module 14

- Kinetic theory of collisions:
  - Collision theory misses directionality of reaction – can lead to gross overestimate of rate constant
  - Sometimes collision theory can also underestimate the rate constant
  - Collision theory misses vibrations, rotations and chemical bonding

So with this we end our chapter on collision theory. From next time on, we will start building towards transition state theory. For collision theory there are few things you should keep in mind in terms of when is it valid and when is it not valid. What we have approximated in collision theory is that these are perfectly hard spheres moving at constant speed, there is no potential in between these molecules, there is no sense of bonding in between these molecules.

So it is a crude approximation, but none the less it is the first theory that gives a rate constant from an atomistic picture. Not only that, I have been decimating collision theory a lot today, so let me advocate for it a little bit as well. It is none the less a good qualitative picture to keep in mind.

You can think of these atoms coming together somehow and reacting, the details have went wrong a little bit. But it is still presenting a good way to start thinking about reactions. So next time let us try to build on transition state theory to get rid of the problems that collision theory faces. Thank you very much.