Chemical kinetics and transition state theory
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Lecture: 09
Kinetic theory of collisions: A Discussion

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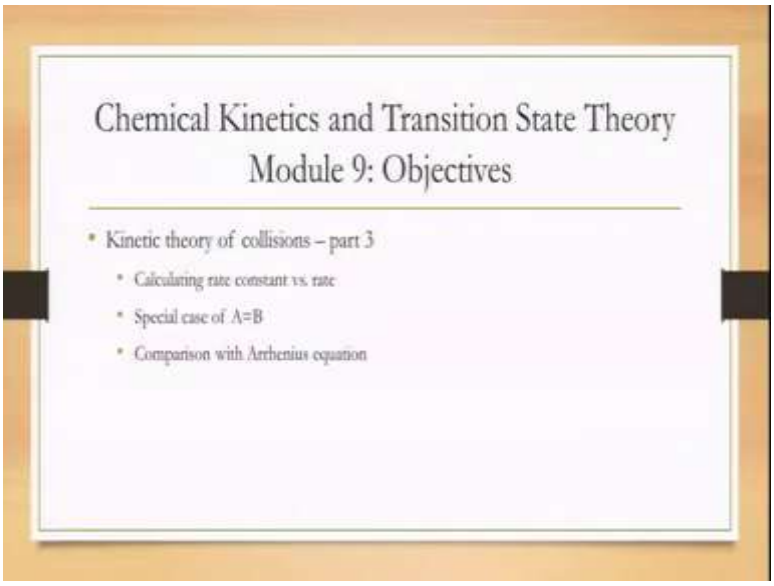

Chemical Kinetics and Transition State Theory
Module 9: Objectives

- Kinetic theory of collisions – part 3
  - Calculating rate constant vs. rate
  - Special case of A=B
  - Comparison with Arrhenius equation

Hello and welcome to Module 9 of Chemical Kinetics and Transition State Theory. So, this is the third instalment of kinetic theory of collisions. In the last two instalments, we had looked at the basic idea, which once again is assuming our reactants look like hard spheres, and they are colliding with each other. And we calculate the rate of the reaction is nothing but the rate of these collisions.

So, last module, we tried to figure out this thermal speed U as essentially the relative speed U and finding the thermal average and we did that by doing the center of mass transformation and all. Today, once we have a rate constant, we are going to analyze it a little bit, we are going to calculate the rate constant out of the rate we are going to look at a special case when A is equal to B when both reactions are identical and we will end with a comparison with the famous Arrhenius equation.

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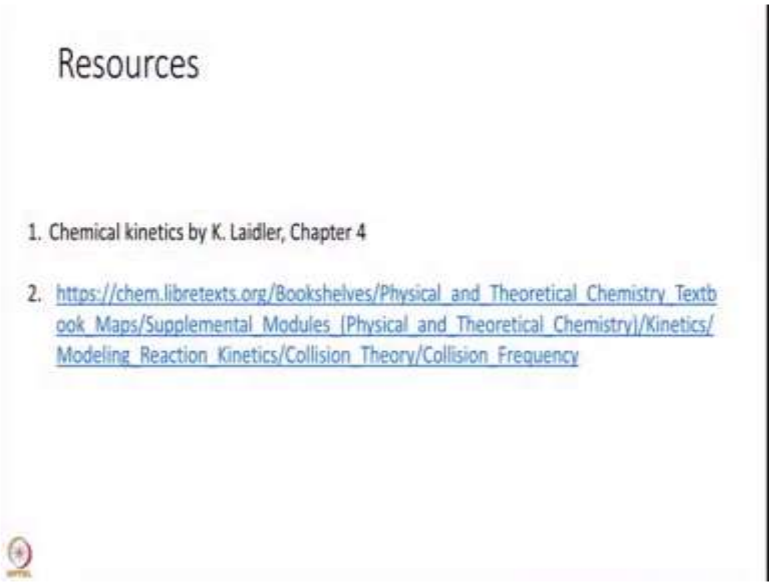
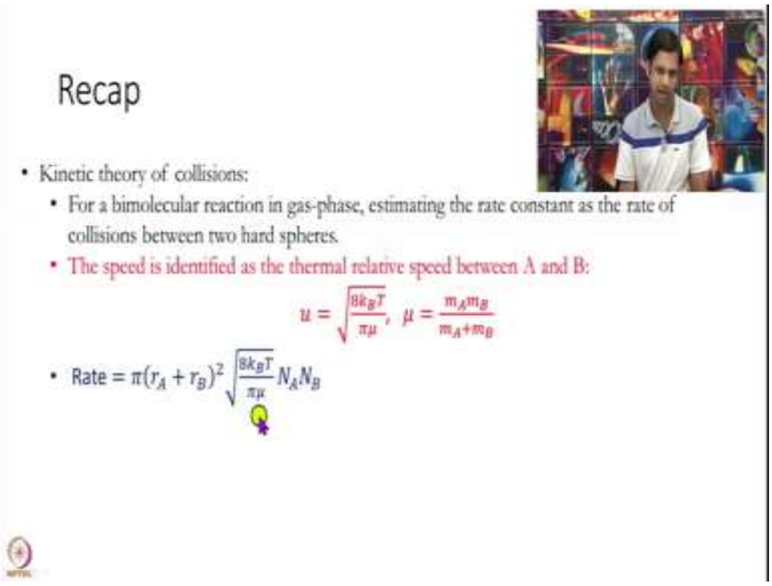


Resources

1. Chemical kinetics by K. Laidler, Chapter 4
2. https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Modeling_Reaction_Kinetics/Collision_Theory/Collision_Frequency



Recap

- Kinetic theory of collisions:
  - For a bimolecular reaction in gas-phase, estimating the rate constant as the rate of collisions between two hard spheres.
  - The speed is identified as the thermal relative speed between A and B:

$$u = \sqrt{\frac{8k_BT}{\pi\mu}}, \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

  - $\text{Rate} = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}} N_A N_B$

So, again, the resources are the chapter 4 of the Ladler's book or you can look at this link chem libretexts dot org. Again, a quick recap, note that this kinetic theory of collisions is valid only and only for biomolecular reactions. We identify the thermal speed as this U 8 KT over pi mu. And this mu entered as a reduced mass MA MB over MA plus MB and we had gotten this final rate in the last module pi RA plus RB square, root 8 KT over pi mu into NA into NB.

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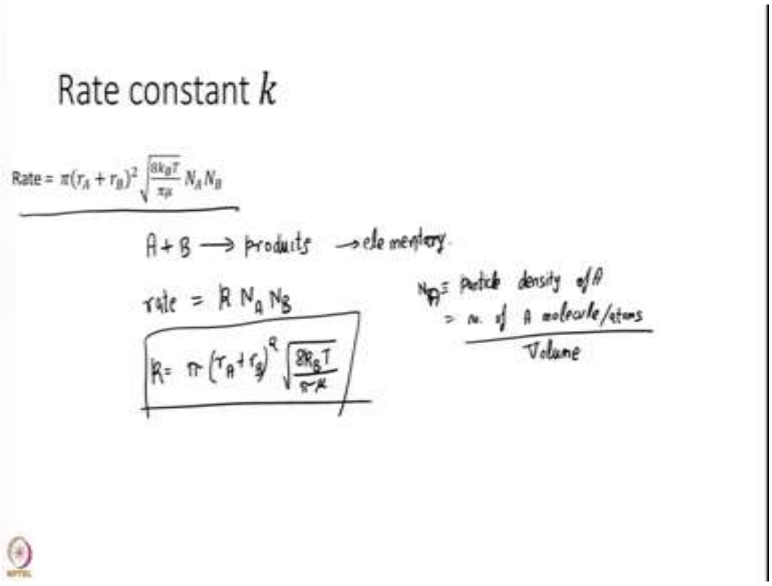

Rate constant k

$$\text{Rate} = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}} N_A N_B$$

$$A + B \longrightarrow \text{produits} \rightarrow \text{elementary}$$

$$\text{rate} = k N_A N_B$$

$$\boxed{k = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}}$$

$$N_A = \text{Particle density of } A = \frac{\text{no. of } A \text{ molecule/atoms}}{\text{Volume}}$$

So, first, let us simplify and calculate the rate constant. So, what is the difference between rate and rate constant? So again, let us write the reaction. Clearly, A plus B going to products. And remember, we are assuming this is elementary. This is one step nothing more is happening, A is coming and B is coming and they are colliding and giving these products.

So, my rate, I can write essentially as K NA NB, you might be wondering why I am not using concentration of into it, it is really the same thing. It is a matter of change of units. Remember what is NA, NA is nothing but the particle density, which is the number of A molecules or atoms divided by the volume. Let me write the volume clearly. And similarly, B is defined as the number density of B. Well, that is effectively the same thing as concentration.

So as long as we are talking in the language of any NA NB, the rate will become equal to K into NA into NB. So, you can go back to the first module we discussed and go back to the definition of rate, which is D of the extent of reaction over DT, and you can identify that to be the same as this. It is the same thing. It is just a transformation. So, then you notice that the rate I calculated is this. So, if I compare these two, I can easily get.

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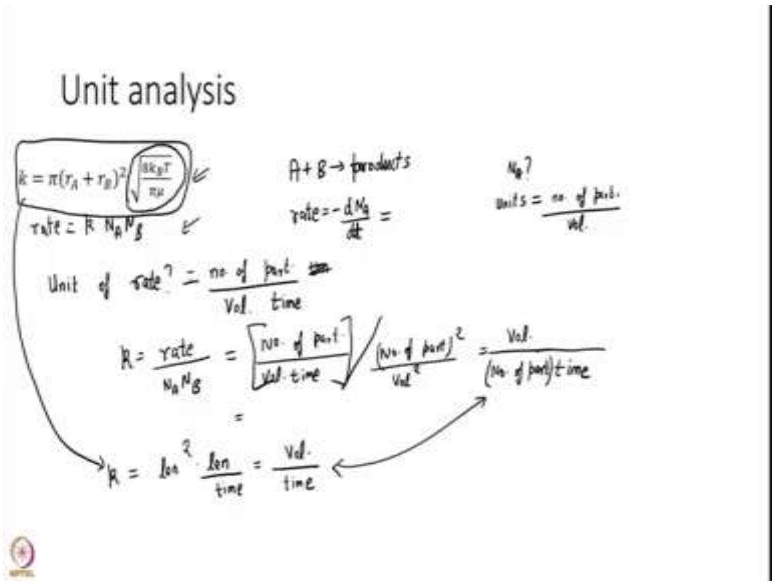

Unit analysis

$$k = \pi(r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}$$

rate = $k N_A N_B$

A + B → products

rate = $-\frac{dN_A}{dt}$ =

N_A?

units = $\frac{\text{no. of part.}}{\text{vol.}}$

Unit of rate? = $\frac{\text{no. of part}}{\text{Vol. time}}$

$$k = \frac{\text{rate}}{N_A N_B} = \left[\frac{\text{No. of part}}{\text{Vol. time}}\right] \Big/ \frac{(\text{No. of part})^2}{\text{Vol}^2} = \frac{\text{Vol.}}{(\text{No. of part})\,\text{time}}$$

=

$$k = \text{len}^2 \cdot \frac{\text{len}}{\text{time}} = \frac{\text{Vol.}}{\text{time}}$$

So, I have got this rate constant. And of course, the rate is K NA NB, I want to spend just a few minutes and just think of dimensions or units, just to make sure that our final result makes sense. There is no catastrophe that has happened in my whole proof. Everything is still logical everything is still sensible. That is always a good check. Anytime you have derived something, make sure that the end result is something that you can verify.

I mean, something that makes sense and one of the most important things that we often do is dimensional analysis. So, what is the first of all the unit of rate? Again my reaction is A plus B going to some products and the rate is minus D NA by DT. Again, you could have written concentration of A by DT that does not matter, it effectively is the same thing it just said transformation, if you write concentration of A then in our definitions here and here as well, this can be transformed to concentration.

So, the unit of this, what is the unit of NA then, the unit is nothing but the number of particles divided by volume. So, the unit of rate is nothing but D NA over DT. So, the number of particles divided by volume into time, time comes from DT. So, NA is number of particles by volume and T is time. So, far so good. So, K is rate divided by NA NB.

So, this will be number of particles divided by volume into time, divided by number of particles square, divided by volume square. So, if you simplify this, this will be equal to volume divided by number of particles into time. So, let us see the rate constant that I have got here. How does that look like? So, our K has the dimensions of pi does not have any dimension.

So, I am looking at this equation now, RA plus RB square that has dimensions of length square, and this thing is nothing but speed and speed is length divided by time. So, I have length Q, which is nothing but volume. So, the point is that this rate constant should be understood as eventually divided by the number of particles. So, we compared this with this.

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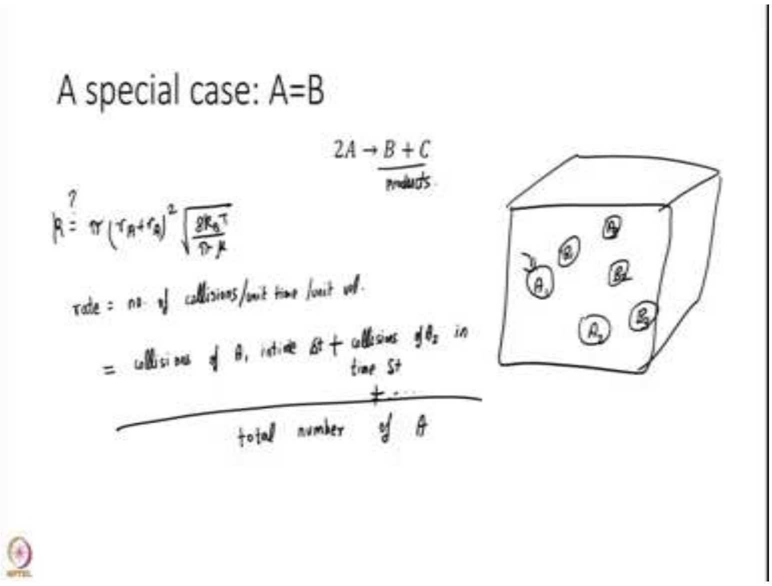

A special case: A=B

$$2A \rightarrow \underbrace{B + C}_{\text{products}}$$

$$k \overset{?}{=} \pi (r_A + r_B)^2 \sqrt{\frac{8k_BT}{\pi\mu}}$$

rate = no. of collisions/unit time/unit vol.

$$= \frac{\text{collisions of } A_1 \text{ in time } \delta t + \text{collisions of } A_2 \text{ in time } \delta t + \ldots}{\text{total number of } A}$$

The final thing, the next thing I want to compare is a somewhat special case if A is equal to B. so, I have 2 A going to some products. And so, A is reacting with itself. You might be a bit surprised perhaps but actually, we have seen such an example when we were discussing the isomerization of cyclohexane sorry, the isomerization of cyclopropane two propane, then we discuss this, 2A.

So, the question is, can I write K as the same pi of RA plus RA square into root 8 KT over pi mu? Actually, the answer is no. There is a little bit of a trick here. So, let us go back to the basics. What are we calculating? We are calculating the average number of collisions happening per unit time per unit volume. That is a definition of rate, number of collisions per unit time, per unit volume.

So, imagine you have this big box you have A here. Let us say you have a lot of A's and you have a lot of B’s. So, I am again going over back to the case when A and B are distinct. So, what I am doing is, I look at one particular A, I sit on A 1. And I wait for time DT, delta T, whatever. And I find the number of collisions A 1 had.

So, this essentially is an average quantity. Remember, all statistical mechanics is average. So, this we are calculating as collisions of A1 in time delta T. Well, plus collisions of A 2 in time, delta T, plus dot dot dot till the collisions of all A N, divided by total number of A. So, that is why we used NA, as a probability density. So, this is I mean, I am going back to the very basics. Now, let us do the same thing.

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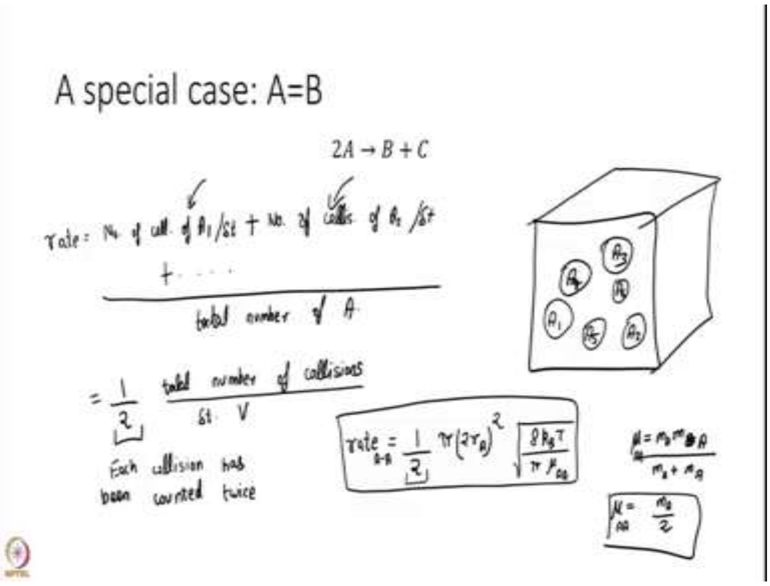

A special case: A=B

$2A \rightarrow B + C$

$$\text{rate} = \frac{\text{No. of coll. of } A_1/\delta t + \text{No. of colls. of } A_2/\delta t + \cdots}{\text{total number of } A}$$

$$= \underbrace{\frac{1}{2}}\, \frac{\text{total number of collisions}}{\delta t \cdot V}$$

Each collision has been counted twice

$$\boxed{\text{rate}_{A-A} = \underbrace{\frac{1}{2}}\, \pi (2r_A)^2 \sqrt{\frac{8k_BT}{\pi \mu_{AA}}}}$$

$$\mu = \frac{m_A m_A}{m_A + m_A}$$

$$\boxed{\mu_{AA} = \frac{m_A}{2}}$$

If A is equal to B, you will notice something very interesting will happen now. I have A 1, A 2, A 3 and B is the same, I have A 4, A 5, A 6. And I am looking at the collisions between A and A. So, when I do this averaging, number of collisions of A 1 in time DT plus number of collisions of A 2 in time delta T plus so on, divided by total number of A.

What you will notice is that I am counting the collisions twice because A 1 might have collided with A 2 that collision will appear here and the same collision will appear here. So, for every collision I will cannot count twice. If I am considering collision between same entities. So, this rate will be half of a total number of collisions per unit time per unit volume. Because why did this half appear?

Each collision has been counted twice. So, spend some time on it, think about it a little bit and you will immediately see that each collision is counted twice. So, in effect, my rate will be half of pi 2 RA square, it was RA plus RB and RM equal to RA into root 8 KT over pi mu and mu also becomes simplified mu is MA into MB, as so B again A divided by MA plus MB but B is nothing but A. So, this becomes NA over 2 for A with A.

So, always remember this factor of the half, when you are looking at bi-molecular reaction where A is colliding with itself.

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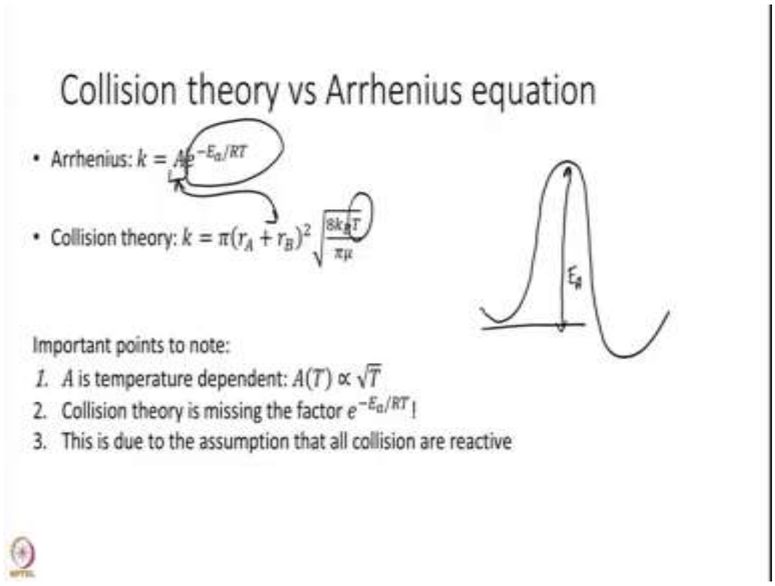

Collision theory vs Arrhenius equation

- Arrhenius: $k = Ae^{-E_a/RT}$
- Collision theory: $k = \pi(r_A + r_B)^2\sqrt{\frac{8k_BT}{\pi\mu}}$

Important points to note:

1. A is temperature dependent: $A(T) \propto \sqrt{T}$
2. Collision theory is missing the factor $e^{-E_a/RT}$!
3. This is due to the assumption that all collision are reactive

So, we have got a rate constant, K is equal to this pi RA plus RB square 8 KT over pi mu. Maybe a factor of half if you are more particular about A being equal to B or not. But let us take a broader picture are Arrhenius had went off earlier written a more general equation K is equal to A into E to the power of minus EA over RT. And this was found to be experimentally true.

So, we know this equation is more or less true, these two equations, now compare. That is the question. So, a few important points to note. First, we are relating this A with this quantity. So, the first thing to note is that A has this temperature dependence here. So, A is proportional to root T. So that is point number one. Second, which is the more important point, the collision theory so far is missing a critical factor, this exponential is a critical part.

That is what new Arrhenius looked at that patterns postulated that a transition state must exist, this transient species between the reactant and product must exist because of this exponential form and that is something missing here. So, in the next module, we will look at how to include that and the assumption we have made several assumptions so far. And the assumption that goes wrong is that we have assumed that all collisions are reactive so far.

And that of course cannot be true. Just think from the perspective of, How Arrhenius was thinking. Arrhenius was thinking of a transition state that looks like this. And so, Arrhenius said that you need a minimum activation energy for the reaction to happen, but what have we said in this collision theory, every collision is reactive at any energy.

So, these two molecules might be approaching very, very slowly coming out very, very slowly like this, they will still react. So, there is no sense of any activation energy here. What we have to build into this theory is, that molecules that are moving slower, should not react, molecules should react only if they have sufficient energy. So, that is the thing we are going to build in the next module.

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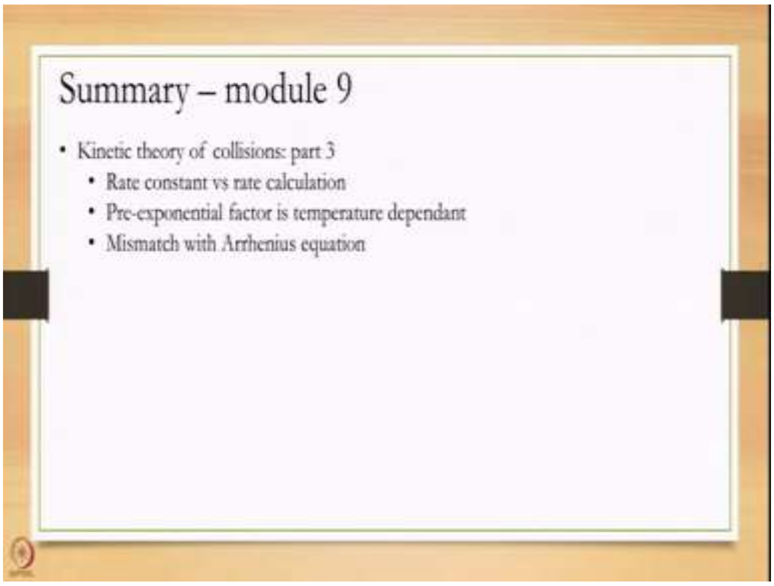

Summary – module 9

- Kinetic theory of collisions: part 3
  - Rate constant vs rate calculation
  - Pre-exponential factor is temperature dependant
  - Mismatch with Arrhenius equation

So, in this module, in summary, we have discussed the distinction between rate constant and rate. We have looked at special case, when a biomolecular reaction is happening or for reacting with itself. And finally, we have compared and analyzed with Arrhenius equation and two important points emerge.

One, the pre-exponential factor in the Arrhenius equation depends on temperature as square root of T. And the second is that, currently, the exponential itself is missing. So, we have to work on how to include that which we do in module number 10. Thank you very much.