Combustion in Air Breathing Aero Engines
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Lecture – 06
Chemical Kinetics III

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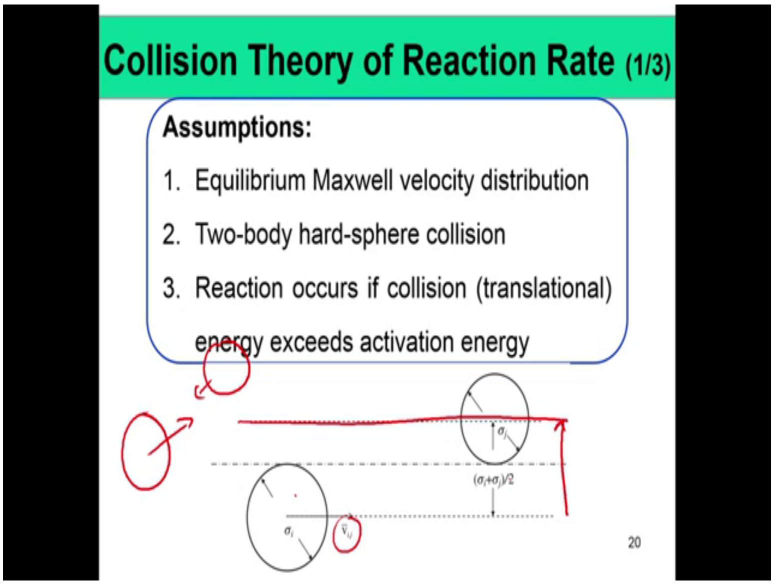

Collision Theory of Reaction Rate (1/3)

Assumptions:

1. Equilibrium Maxwell velocity distribution
2. Two-body hard-sphere collision
3. Reaction occurs if collision (translational) energy exceeds activation energy

So, as I said that determination of this rate constant is very, very important; and it is one of the most important tasks of chemical kinetics and combustion chemical kinetics, there are many high very famous combustion chemical kinetics who are involved in determining rate constants from theoretical calculations of course, by computation and theory.

So, we will talk about 2 basic methods by the coalitional theory of reaction rate and the transition state theory of reaction rate using these 2 basic theories we can essentially compute rate constant. These are not; these are very fundamental methods and some of these gives accurate and constants some of these does not give accurate rate constant, but it will give you a basic idea of how to estimate rate constant. But more importantly what this gives is that what is happening at the fundamental level. With this derivation of rate constant, we can understand that what is; how are these reactants actually going to form products, what is the mechanism. So, we always talk about this reacting with that, this reacting with this, but how does this reaction happen, and how do we develop a model to describe that those reaction rate constants.

So, for this collision theory of reaction rate we will talk about we will make several assumptions, we will assume that this molecules this which are like hard-spheres as you see in assumption 2 they follow this equilibrium Maxwell Boltzmann velocity distribution. And number three is that reaction occurs this is a very important assumption reaction occurs if collision energy exceeds the activation energy. And by collision energy we are only talking about translational energy that is too hard essentially like 2 molecules like 2 billiard balls, 2 billiard ball comes and collide and if the collision energy if they have sufficient kinetic energy associated with this translational energy and if translational energy large and greater than the activation energy of the reaction then the reaction happens.

You see, but first itself you see the basic inherent assumption is that even though reaction and formation of new molecules means arrangement and derangement of different electronic structure, here we are considering none of that that as long as the collision is hard and it exceeds certain activation energy, new molecules are being formed. And essentially this activity will be centered on finding the coalitional frequency, it is a number of in a given box how many collisions take place and that we will essentially you will see that you will associate that with the rate constant and it will give a very nice enlightening answer.

So, what is the requirement of collision? For collision of course, you see that this molecule comes and it must hit with this molecule. Of course, if they are head on collision is guaranteed, but if you replace this molecule with little bit offset this is still also guaranteed. So, the question is that; what is the limiting condition in which collision is guaranteed? The limiting condition you will see is this where this molecule comes in this way, let us consider instead of considering individual velocities of the molecules. So, we can consider that this molecule j of the species j is fixed and that of the species i is moving. And essentially the relative velocity with which the species i molecule approaches the species j molecule is essentially V i, j.

And for that the limiting condition which will guarantee a collision at least in some part here it will happen tangentially is that if these molecules if at least half of this molecules belong to a collision volume. What is a collision volume? The collision volume is essentially this hypothetical cylinder which has a radius given by this, I will elaborate this.

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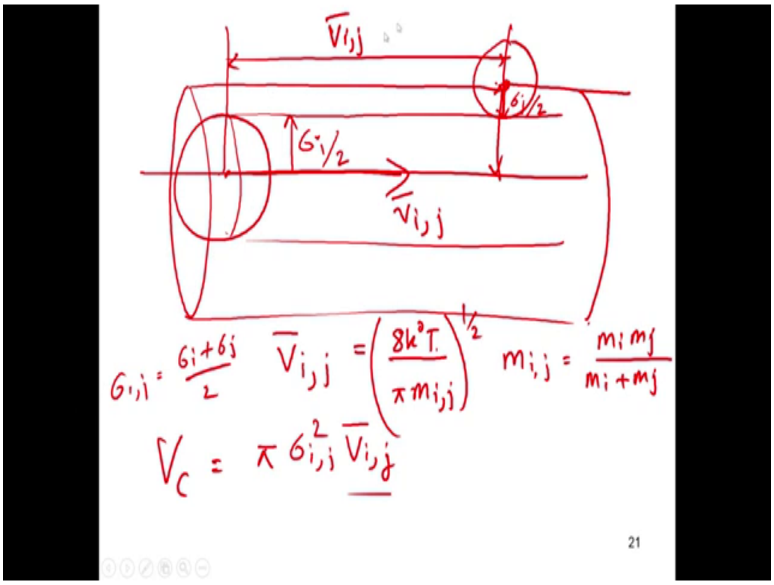

$$\sigma_{i,j} = \frac{\sigma_i+\sigma_j}{2} \quad \bar{V}_{i,j} = \left(\frac{8k^0T}{\pi m_{i,j}}\right)^{1/2} \quad m_{i,j} = \frac{m_i m_j}{m_i+m_j}$$

$$V_c = \pi \sigma_{i,j}^2 \underline{\bar{V}_{i,j}}$$

So, let us consider this as the centerline of my molecule i, and for collision to happen it the molecule j must be situated somewhere here. So, the center of this molecule j must lie within this domain within this volume which is this. And this is sigma i, this is sigma i by 2 because sigma i is the diameter of this molecule, sigma j by 2 is the sigma i is the diameter of the molecule, sigma i by 2 is the radius of this molecule, similarly sigma j by 2 is the radius of this molecule. So, the at least the center of the second molecule must be contained inside this collision volume for reaction to happen. And then this one is moving at a velocity V i, j which is the relative velocity.

What is V i, j? Now, V i, j cannot be arbitrary because as we have said that we assume that is equilibrium Maxwell Boltzmann distribution. So, then by Maxwell Boltzmann distribution V i, j has a definite form which it comes from essentially the distribution of the velocities and from the p d f of the velocity we can obtain the mean velocity which is equal to 8 k zero times T divided by pi times m i, j to the power of half. Whereas, m i, j is equal to m i m j divided by m i plus m j, it is called the reduced mass. And in this definition of course, you see that k 0 is the Boltzmann constant, T is the temperature, pi is pi, and m i, j is the reduced mass.

Now, so first let us assume find out the diameter of this collision volume. The diameter is of course, given by sigma i plus sigma j. What is the volume of this collision volume as such. The volume is given by is essentially the volume of the cylinder which is given say the V c is given by then pi sigma i j square, whereas sigma i j is essentially sigma i plus sigma j divided by 2 times V i, j average. So, what this collision volume means is that it means that in one second, these second molecule must be inside this collision volume with respect to the first molecule where does V i, j comes in V i, j is the distant covered in unit time. So, while this can be the separation in terms of their radius sigma i, j plus by 2 in terms of the center to center distance they can be separated only by V i, j in unit time, sorry let us average on unit time.

So, if there is has to be collision in one second, the criteria is that the second molecule has to be inside the collision volume of the with respect to the first molecule of i. And it has to be the distance between this 2 can be at most V i, j for collision to happen in unit time in a one second.

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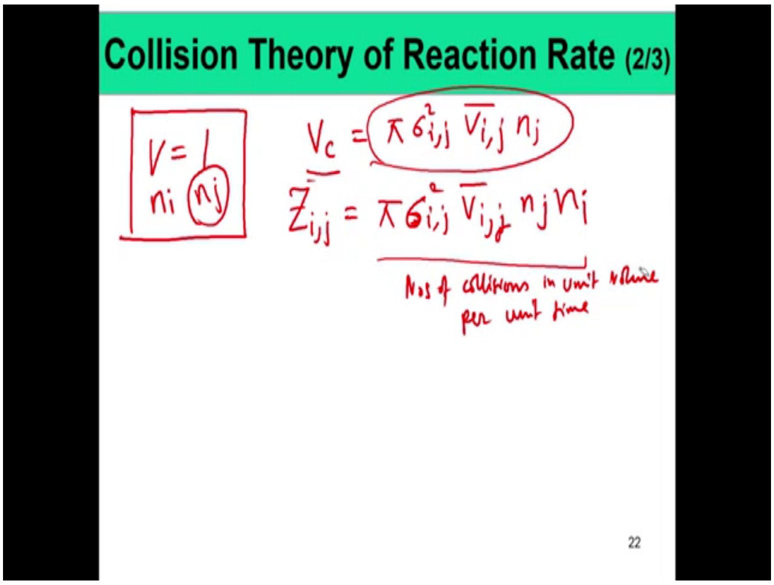

Collision Theory of Reaction Rate (2/3)

$$\boxed{\begin{matrix} V = 1 \\ n_i \; n_j \end{matrix}}$$

$$\underbrace{V_c} = \pi \sigma_{i,j}^2 \overline{V_{i,j}} n_j$$

$$Z_{i,j} = \underbrace{\pi \sigma_{i,j}^2 \overline{V_{i,j}} n_j n_i}_{\text{Nos of collisions in unit volume per unit time}}$$

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Now let us say will just remove all this. And let us say now we are considering a box of unit volume V equal to 1, which can be 1 cubic meter, 1 cubic centimeter etcetera. So, and this contains n i number of molecules of i, and n j number of molecules of j. So, you see in V c volume which was given by pi sigma i, j square times V i, j that was one collision and it involved collision between 2 molecules. So, basically for one molecule of i, there was another molecule of j that guaranteed this collision, but in this volume v equal to one there are n j molecules of j.

So, in this volume, now V c the total number of molecules of j that is present is nothing but pi sigma i, j square V i, j times n j. So, these many number of things can happen that was a limiting condition in V equal to 1, there can be n j molecules. So, in V equal to V c, there can be this many number of molecules of j; and as such this many number of collisions of of the molecules of j with one molecule of i. So, for one molecule of i, there are this many number of collisions happening. So, what is the total number of molecules of i now. N i, so the total number of collisions happening in one second is given by this pi sigma i, j square V i, j times n i n j and that we will represent by this frequency called Z i j which is the frequency of collision.

We can also think that this in a different way we can also think that volume V c is essentially swiping through our unit volume. So, in one volume as I said in V equal to one there are n j molecules present. So, inside this V c volume, there are in total this many number of molecules present. For so, there are for each one molecule of i, there are this many number of collisions, but we have n i molecules of i, so the total number of collisions between i and j is nothing but pi sigma i, j square times V i, j times n I n j. So, these are the number of collisions in unit volume per unit time. So, this is essentially called the collision frequency. Now, we will just do this little we will shift gears and go through this analysis, but in this analysis, the most important part is eventually this part, there is another conceptual part will which will see immediately.

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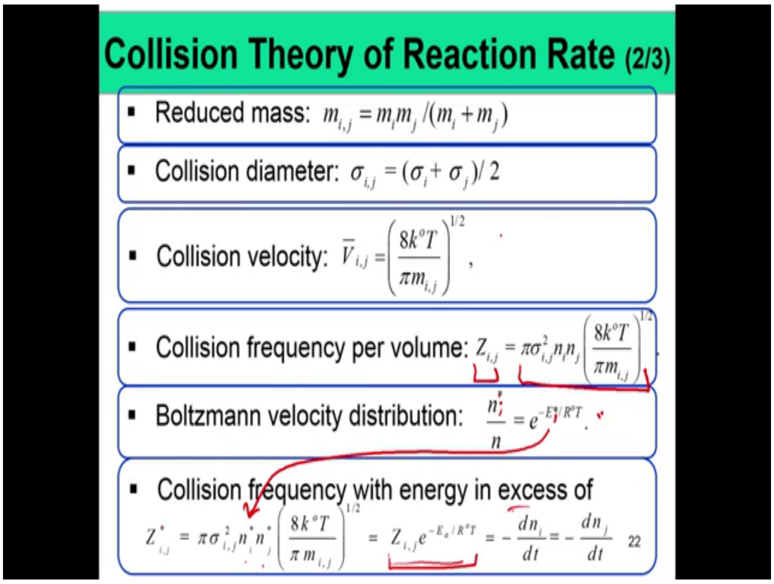

Collision Theory of Reaction Rate (2/3)

- Reduced mass: $m_{i,j} = m_i m_j / (m_i + m_j)$
- Collision diameter: $\sigma_{i,j} = (\sigma_i + \sigma_j)/2$
- Collision velocity: $\bar{V}_{i,j} = \left(\frac{8k^{o}T}{\pi m_{i,j}}\right)^{1/2}$,
- Collision frequency per volume: $\underbrace{Z_{i,j}}_{} = \underbrace{\pi\sigma_{i,j}^2 n_i n_j \left(\frac{8k^{o}T}{\pi m_{i,j}}\right)^{1/2}}_{}$.
- Boltzmann velocity distribution: $\frac{n_i^*}{n} = e^{-E_i^*/R^{o}T}$.
- Collision frequency with energy in excess of

$$Z_{i,j}^* = \pi\sigma_{i,j}^2 n_i^* n_j^* \left(\frac{8k^{o}T}{\pi m_{i,j}}\right)^{1/2} = \underbrace{Z_{i,j}e^{-E_a/R^{o}T}}_{} = -\frac{dn_i}{dt} = -\frac{dn_j}{dt}$$

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So, what we have found is that we have defined this reduced mass m i, j is equal to m i times m j divided by m i plus m j. We have defined a collision diameter sigma i, j is equal to sigma i plus sigma j divided by 2. And we have defined about this collision velocity which comes from the Maxwell Boltzmann distribution which is given by V i, j is equal to V i, j mean is equal to 8 k 0 T divided by pi m i, j to the power of half. And we have obtained the collision frequency per unit volume given by Z i, j is equal to pi sigma square n i n j times the mean V i, j which is nothing, but eight k zero t divided by pi m i, j to the power of half.

Now, so there are in total per unit volume this many number of collisions happening per unit time, but all collisions do not have sufficient energy. Remember the postulate the assumption number three that only those collisions which have an energy exceeding a will result in reaction. So, how many molecules how many numbers of molecules does exceed this energy E a that is given by Boltzmann distribution which says that this n i times n star by n is essentially given by e to the power of minus E star by R 0 T. So, we can define find out the collision frequency of those molecules which have got energy in excess of E a.

So, we define that collision frequency is given by this Z i, j star and these are those molecules those number of molecules which have energy exceed of exceeding E a n i star and n j star. And that is essentially if you substitute this guy into here for n i star and n j star, you will find with this. Now, what is the collision frequency Z i, j which results in reaction Z i, j star that is nothing, but your minus of d n i d t is equal to minus of d n j d t going back to the generalized formula for species consumption rate that we have defined. So, then we can equate this to this, and we can essentially using that we can equate this with this as we see.

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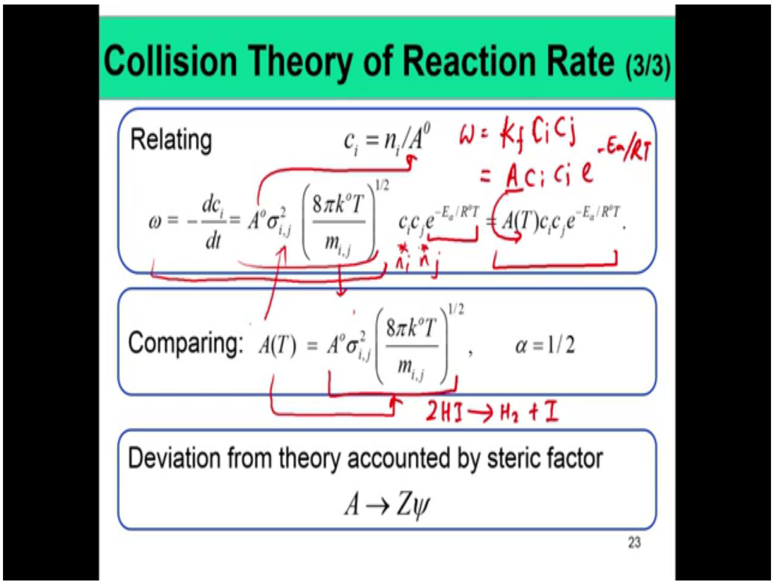

Collision Theory of Reaction Rate (3/3)

Relating $c_i = n_i/A^0$

$$\omega = -\frac{dc_i}{dt} = A^o\sigma_{i,j}^2\left(\frac{8\pi k^o T}{m_{i,j}}\right)^{1/2} c_i c_j e^{-E_a/R^oT} = A(T)c_i c_j e^{-E_a/R^oT}.$$

$\omega = k_f c_i c_j$

$= A c_i c_j e^{-E_a/RT}$

$n_i^* \; n_j^*$

Comparing: $A(T) = A^o\sigma_{i,j}^2\left(\frac{8\pi k^o T}{m_{i,j}}\right)^{1/2}$, $\alpha = 1/2$

$2HI \rightarrow H_2 + I$

Deviation from theory accounted by steric factor

$$A \rightarrow Z\psi$$

And now we can relate n i with the concentration, because n i is the number of molecules of i which if you divide by the Avogadro number which is the total number of molecules present in unit volume or a given volume as such we can find out the concentration. And then as such we can relate d c i dt to omega that is the reaction rate and we find that the reaction rate is given by this. This as you see this comes from the mean V i, j this comes from the diameter of the collision volume comes from the conversion factor between c and n concentration and numbers. And c i, j c j comes from n i and n j, n i n j star and this comes from the fact that only those molecules only those collisions which have an energy exceeding E a can result in reactions. And if you summarize this what you will get is a very nice looking relation which is A T times c i c j and e to the power of minus E a by R 0 T.

Now, does not this look this looks very similar to our expression of omega is equal to the which we have obtained by the Arrhenius law as A times which is omega was like this, k for this, k f times c i c j and that is equal to A times e to the power of if we put c i c j now c i c j e to the power of minus E a by R T. So, this frequency factor, if we compare between this one and the A T that has been obtained which is essentially this you find that the frequency factor is given by this formula. So, you see that this collision theory nice as a very nice correlation with the Arrhenius law as such and the law of mass action.

So, now but now unfortunately in some cases for example, if you consider something like a reaction involving say hydrogen iodide decomposition of 2 H I something like 2 H I something like if you see this reaction, if you see say 2 H I goes to H 2 plus I. Now, if you compare the sigma for sigma H I, and if you find out the mass of the reduced mass of H and I and if you find the k 0 and A 0 if you find that the reactions rate has a very nice the reaction rate obtained from this has a very nice relationship with accidental obtained reaction rates. But this is not does not this is not always the case. The prime reason you see that we have made very simplified assumption. We have made we have assumed that as soon as there is head on collision that is enough to guarantee reaction, but reaction is much more as I said reaction means the change of the orbital structure the electronic structure change is during reaction. So, one molecule one species become some other species.

So, the electronic structure change and also there can be other components of energy involved also not only translation there can be rotational energy involved there can be vibrational energy involved and also the molecules need not be hard-spheres. In fact, most molecules say the hydrocarbon molecules, methane, ethane, propane, butane all of this and even higher on they have large complicated chain like structures. So, this assumption that this 2 hard-spheres collide and immediately react when the E a is greater than when the translational coalitional energy is greater than E a that is a little bit too limiting an assumption and as such it does not obey the theory all the time. But it gives you a very clear idea of how to approach this problem and what is essentially happening. And the deviation of this theory can be accounted from this steady factor that is equal to Z times i, but we will not go into this here.