Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 43
Reaction dynamics – Part 6

All right; So, we discussed the Maxwell-Boltzmann distribution of molecular speed and from that we derived an expression for distribution of molecular energies. Now, that will be very useful. We are going to use that and, but before that let us just try to describe what is actually our notion of reactions. Now, reaction dynamics says that you can have two different pictures of this entire chemical reaction.

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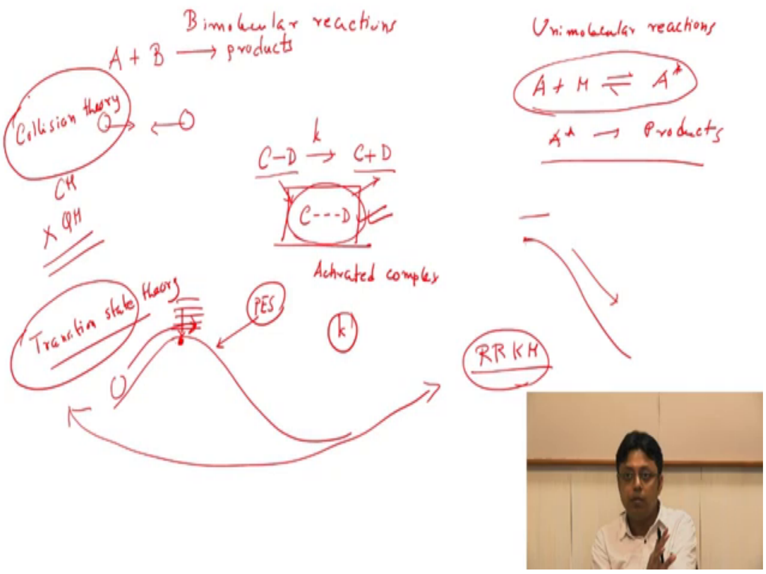

Suppose I have A plus B and going into say products and remember that we are describing here by reaction dynamics you are describing how an elementary reaction happens. Now, elementary reactions can be either unimolecular or by molecule, but even for a unimolecular reaction a by molecular collision persists.

Now, the question is so, when a collision happens then basically two molecules come close together and then they transfer some energy and then the reaction happens. Now, that we are going to discuss in detail. Now, here again we will be using classical mechanics of the collision not to the quantum mechanics of collision you can we are ignoring any quantum effect right now. An alternative approach or this approach is actually known as collision theory. An alternative approach is known as transition state theory which will not discuss here and that theory tells that this movement of these atoms or molecules are just like over a potential energy surface.

So, when you go from say higher energy to lower in it your lower energy to higher that you know that there is activation barrier. So, this is the energy barrier and it happens on our free energy surface which is known as potential energy surface or in a short form we write it as PES Potential Energy Surface.

Now, the theory tells that when at the right at the barrier top you can have situation suppose there is a the reaction is something like this, let us say we are having a breaking a bond say I have a C-D, and then or say something and then this in the reaction is something like that I am just breaking that C-D bond and it says that when this there will be a situation where basically this bond is neither broken nor former it is something like that.

So, that will happen right at the top of the barrier and if you can think that I have very very transiently living species which is which looks like that, then I can actually ask this question what is what are the properties of this basis and then I do not need to calculate how many collisions are happening and all this thing.

If I know actually this thing which is known as this transition instead now, the transition state the way I have described is not very rigorous we are very correct way actually transition state has a very deeper meaning it comes from classical mechanics and the transition set theory is a inherently classical theory and what I just said is better to call as something known as activated complex theory meaning you think about that there is a complex which is neither C-D or C plus D, but actually the bond is half broken.

So, that complex if you want to know the properties if I can calculate the properties I can calculate the rate constant for this reaction from C-D to C plus D. So, then actually you do not need to calculate any dynamics you have to just calculate the equilibrium or thermodynamic properties of this complex of this activated complex and that is the beauty of that theory and. So, that theory is known as transition state theory transition state model and this is for the bimolecular reactions bimolecular reactions and there also remember unimolecular reactions.

And, those unimolecular reactions we said that there will be a by molecular collision between A and M that will give me these a star and then this a star will give me the product and that was our Lindeman hypothesis a Lindeman model and now, that is actually collision driven just like by molecular collision, but now question is how the a star energized molecule is giving a product that also people think that ok, fine.

I have a similar thing like there is a transition state not a biomolecular transition state it is a transition state like thing and then actually it goes to the product and then you can actually think in the same way and then these different models that we talked about particularly the this sophisticated model which is RRKM which is developed by Rudy Marcus that actually agency only shows that the rate expression you get for a unimolecular reaction is exactly the same rate expression for the biomolecular transition state theory.

So, there is a deep connection, but to understand that you need to know a lot of classical statistical mechanics how this works, how to calculate the number of states in this region or you had to basically figure out what is the density of states and then you have to multiply with the probability of crossing or occupying that occupying those states and then you can actually do kinetics.

So, there are two approaches what I just said one is basically the dynamical approach which is the you calculate the dynamics either in classical dynamics or quantum dynamics or sometimes into a mixed or a classical plus quantum and the second approach is that you completely get rid of dynamics you just look at the region of the potential energy surface and just look at the equilibrium properties of that region.

And then you will be done then you have to just do time independent calculations and then you will be done with the rate constant and for a unimolecular reaction there are also statistical theories and which are very much which very much resemble the transition state theory which is also statistical in nature. Now, we will only consider the collision theory a very very simple model of collision theory.

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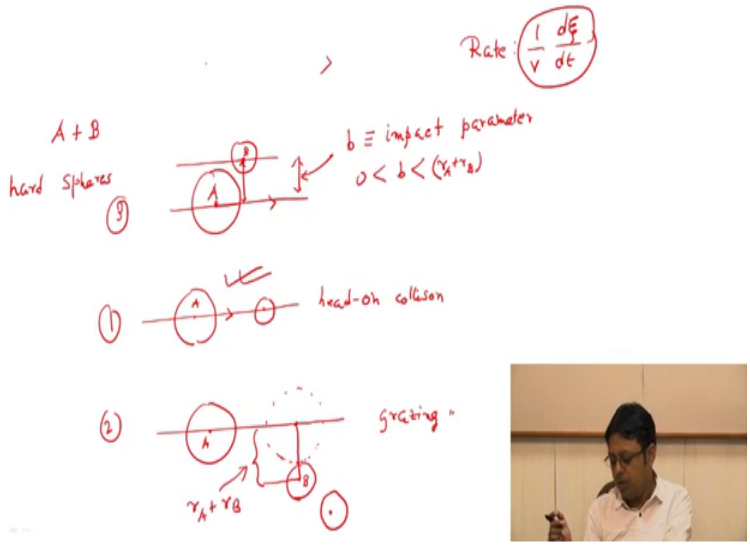

Now, how to calculate the number of collisions? Now, suppose a molecule is moving from say left to right and then I am asking this question how many collisions it make per unit time per unit volume, ok. So, that will be definitely connected to our rate because rate is nothing, but how many reactions are happening remember per unit time per unit volume because if you the way we describe the rate if you remember at the very beginning it is basically the advancement of the reaction which means rate of advancement of the reaction with respect to either products or reactant whatever it is and per unit volume that was rate.

So, if you ask this question how many collisions are happening per unit time per unit volume and suppose I am talking about collision between two molecules which are A and B and right now, we are thinking these molecules having some dimension and meaning they are not just like point masses, but they have some size, but to make the model very simple. We are considering them to be spheres and this what kind of spheres these are hard spheres. In the sense that if there are two spheres touch they will just touch at the surface there they will not penetrate each other.

So, these are called hard sphere it is just like say two billiard balls on a billiard table they are just they just collide and they just fly upper or suppose two hard balls like two cricket balls and which cannot actually penetrate each other something like that very very much classical in nature. And, then suppose this is the molecule of B and suppose this is the molecule of A.

Now, think about it if this mark this molecule suppose is moving now why I am considering only one molecule is or one particular A molecule is moving is that this is all relative velocity everything is moving, but then you can think that if there are two things moving you can actually think one of them is as if it is fixed and the other thing moving with a relative velocity with respect to the other. So, that is very well known.

So, we are using this concept of relative velocity and then you can see that collision between these two will happen only when they sent it to center distance vertical distance is actually less than the addition of the radii of the two molecules. In the sense that what I just said is that think about three different situation suppose this molecule is moving and there is a second molecule suppose I am calling this as that is the bigger molecule as A and the smaller one is B. So, if it moves like this then it just collides right I mean bang on the second molecule. So, this is something known as a head on collision.

So, there, but you can have a situation another extreme situation where this guy is moving like this at some other point it is basically here. However, the second molecule was just lying here, so, their surfaces just touch. So, this is one extreme where it will be just this is like this it is just coming and this is just touched and went a fly flew apart, but if it is even away the molecules which are even further away they will not collide with this a molecule. So, all the B molecules which are lying within a distance and how do you get the distance this is nothing, but you can easily see it is basically the radius of our a molecule and radius of B molecule, if it is within that distance then only they will collide.

So, you can have an intermediate situation also which I have drawn here. So, this is one extreme situation head on collision this is known as sometimes the raising collision. So, this is just touching this thing and this is some kind of intermediate situation or more general thing were the distances are such a way like it is coming and it is colliding, but not at centered I mean like on face to face. So, it is just touching and colliding and something like that. So, this distance we call it as something we write it as B and this B we write it as impact or call it as impact parameter. So, B can vary from 0, when this will be 0 you can see it in this situation it is 0 because this centre to centre are there is no difference actually they are just on lying on our same line.

So, there is no difference in that center to center vertical distance or it can be maximum it can be 0 minimum and it can be maximum to r A plus r B, if it is more than that then actually you do not get any collision.

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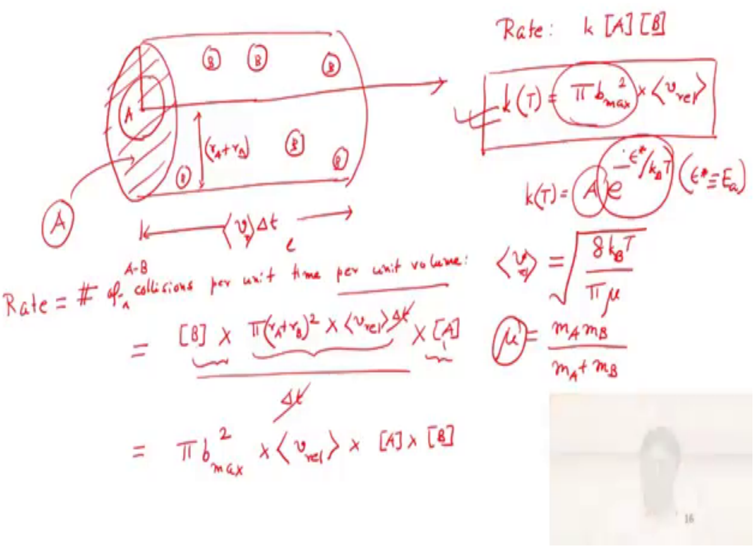

Rate: $k\,[A]\,[B]$

$$k(T) = \pi b_{max}^2 \times \langle v_{rel} \rangle$$

$$k(T) = A e^{-\epsilon^*/k_BT} \quad (\epsilon^* \equiv E_a)$$

Rate = # of A-B collisions per unit time per unit volume:

$$= \frac{\underbrace{[B]} \times \underbrace{\pi(r_A+r_B)^2 \times \langle v_{rel} \rangle \cancel{\Delta t}} \times \underbrace{[A]}}{\cancel{\Delta t}}$$

$$= \pi b_{max}^2 \times \langle v_{rel} \rangle \times [A] \times [B]$$

$$\langle v \rangle = \sqrt{\frac{8 k_B T}{\pi \mu}}$$

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

So, long story short if this molecule moves from say left to right it will collide with those molecules which are lying within a distance r A plus r B from this line of approach. So, we can say that we can think of a cylinder like this what the radius of the cylinder is nothing, but r A plus r B and we can say all the B molecules which are lying within this cylinder will be hit by this molecule in an interval delta t then the length of the cylinder must be the v into delta t where v is the speed of this molecule because this molecule sweeps v into delta t distance in delta t time.

So, all we have to calculate we already know the volume of the cylinder, this is the length and the volume will be length times the cross section and we know the radius we can easily figure out the cross section, but not here that this v, what is this v? v is down the relative velocity because I am considering only this particular molecule which is a molecule is moving and making a collision with all the B molecules that are lying within this cylinder and there are also A molecule.

So, within this cylinder, but A plus B it will not give any reaction. So, I am saying that ok, fine so, all the A plus B collision is giving reaction or instead of v I have to take the relative velocity here. So, that is why I am writing v suffix r and also it is not only one relocate velocity because the mole there will be many molecules. So, I have to take an average of the relative velocity and that is a more accurate way of describing it.

So, these are number of collisions we can easily figure out these number of collisions number of say I should say that number of A-B collisions, per unit time per unit volume. How do you calculate that now you have to basically write it like the if the cross sectional area is A. So, we can easily figure it out. So, the suppose the number of. So, it will be just equal to the number of molecules those are sitting inside number of B molecules sitting inside that volume. So, suppose for that we need to know the density of the B molecule. So, I am writing it as rho B times the following.

Now, the volume here is the area. Area is pi r A plus r B square. So, that is the area and then I have to also get the volume. So, the volume will be v relative I can write r or re l into delta t. So, this is the length and this is the area, this is basically the length area times l is the volume that is what I am doing and this is basically this number what I just wrote is tells me that this many this is the volume and this is the density of B molecules those many B molecules are present in that area and that volume of the cylinder.

So, this particular molecule will make coalition with those many molecules and then we have to also calculate per unit time. So, I have to divide it by delta t. So, the delta t would cancel, but this is for one particular molecule.

There are also many other A molecules those are also moving and we can get it how many A molecules are also other a molecules are also giving the collision. Then we have to also calculate how what are the other A molecules present in that volume, but that we have to just multiply by the density of the A molecules because there A there is a volume and I am just multiplying by the density then I am getting the total number.

So, thus I get the total number of collisions within this volume. Now, when I say that it is per unit volume there is a confusion because this volume is not a unit for this volume is has something it is pi r A plus r B square into v relative something like that into delta t that was the interval, but think about it like if you consider one say I am using 1 decimeter cube or 1 liter as my unit volume.

Now, within that 1 liter volume what is happening is that. So, there are some molecules and those molecules when they are colliding they are actually leaving those in this area and the other molecules are also coming into this area. So, all these collisions what is happening you can actually track one particular molecule and that will also give you the same number. So, what we are saying is that the particular molecule actually leaves that area always in that unit time, but then the other molecules are also coming in.

So, in a statistical ground we can say that this is actually per unit volume because what we calculate is up to this point this is basically the number of molecules per which actually collides with that I mean when it moves actually to the per unit time those are the number of collisions if which one particular A molecule makes with all other B molecules and if we want to calculate also the number of A-B collisions then we have to multiply it by the number of A molecules, but I know that the number of A molecules per unit volume is nothing, but the density of A molecules. So, that is the number. So, what we get is nothing, but instead of rho we could also write it could also write it as B and A because that was our original notation and then what we get here is pi.

Now, r A plus r B you know that this is nothing, but the maximum value of B or the impact parameter that I am writing at as B max square times I have relative velocity an average of the relative velocity why average because they are the distribution of velocities for A molecules distribution of velocities for B molecules. So, there will be a distribution of A relative velocities also, but you can easily show that distribution will also follow the Maxwell-Boltzmann distribution and then I will have A into B. Now, this will be if all collisions give you the reaction. So, that will be nothing, but equal to your rate.

So, and we know that rate of the reaction for a bimolecular elementary reaction can be written as some rate constant into A into B then with comparison of this equation we find that k has the form of pi B max squared times v relative velocity or the average of the relative velocity. Now, we see that if this is very far from the Arrhenius expression where we found that k of T is something a pre exponential factor into E to the power minus epsilon by k B T, now that is missing because the reason is this actually comes instead of epsilon you can write E A I think we are writing is as E A, but we could also write it as something like say epsilon and epsilon star because we are using epsilon for maximum distribution. So, epsilon e whatever we write it it is just the energy and instead of epsilon A, I am writing right now as epsilon star.

Now, when you calculate when you when you made this model we said that this is basically the number of collisions and all collisions are keeping your reactions then actually this will happen because if all collisions give me a reaction remember then the idea is that the activation barrier is 0. So, e to the power minus 0 by k B T that is actually 1, then actually there is no surprising that I will get something.

So, this actually this expression which you just got is very interesting this basically tells me the value of A or the pre exponential factor and it tells me, ok. So, it is basically pi B max square and times B relative velocity and this is very interesting. So, this immediately tells me that A is also temperature dependence why because the relative velocity is also temperature dependent.

Now, this relative velocity in the average velocity value we already know it is 8 k B T by pi m square root of that. When I write the relative velocity for when you write the relative velocity between two particles you have to consider one thing that then you considered one particle fixed and as if the second particle is moving at a speed which is the relative speed between them, by the way when I talk about when I say relative velocity it is basically magnitude of the velocity it is not exactly velocities you should call it as a relative speed always keep that in mind, but at time to time I just call it as a velocity, but it is just v or it is actually just the magnitude of the velocity the speed.

Now, this relative velocity or speed actually speed think about it when I grant it then actually the mass will be replaced by not the mass of the molecules, but it will be replaced by the radius mass. Now, you can easily show how it appears you can show that the move if the two particles are moving in some direction.

Then you can resolve this two particle movement into two different frame of reference one is that called the center of mass frame of reference; well as if the two particle together other their joint mass is moving and the other one is a relative frame, where you can show that as if on one something a fictitious mass which is having a reduced mass where mu is giving given by this formula it is basically the mass of A mass of B divided by mass of A plus mass of B. So, a fictitious particle of mass mu is moving.

So, that is exactly what we are doing. It is a relative frame as if one is fixed and the other one is moving. Now, strictly speaking it is a fictitious mass moving, but we will not go into those details we are saying that ok, fine as if one is fixed and relative to that other guy is moving and then again you can show that the mass will be replaced by the reduced mass, this is basically called a relative frame.

Now, the question is how will incorporate this activation parameter. For that we have to make a choice that all collisions will not give me reactions, only those collisions which have energy which is slightly above some threshold energy will give me reaction.