Advanced Chemical Thermodynamics & Kinetics

Prof. Arijit Kumar De
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 25

Introduction to bimolecular reaction dynamics 01

Hello everyone. So in this lecture we will start our discussion on molecular reaction dynamics, meaning how reactions happen and what are the dynamics of reactions how molecules come close together and then they form the products; from reactant to product.

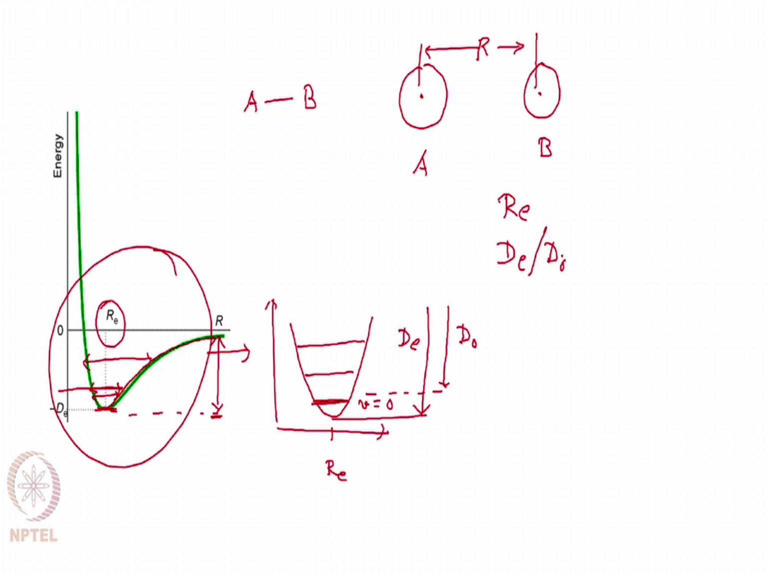
Now there are 2 approaches to understand this process. Fundamentally everything is based on collisions between your reactant molecules. But we already covered a great deal of the collision theory how reactions work in the earlier course and which can be found in any standard textbook. And briefly what you do there is you first calculate the number of collisions between say 2 species A and B per unit time and per unit volume and then what you would do is that those number of collisions will give you a reaction. But of course, not all collision gives a reaction because when they collide there is a pollution between 2 molecules we know that every reaction has an activation barrier.

So, you have to cross a certain amount of energy and then you very cleverly insert that concept introduce that concept that you have to cross this barrier energy barrier in order to the reaction to happen. And then what you do is that you use your collision theory as well as you use the Maxwell distribution of molecular speed you convert it to energy distribution, because, you have to consider a statistical distribution of energies among all these reactant species. And then you can arrive at a formula which we will discuss briefly when you compare with what we are going to do right now later so and that formula satisfactorily explains many gas phase reactions. Although it slightly actually always overestimates the actual rate constant that you get from using this formal and that what you actually get from experiments.

Now to understand how reactions work what we are going to do is that we were; we actually want a formula of rate constants, how it varies with temperature. And initially so as I said there are 2 approaches one is the collision based approaches and the other one which we are going to discuss is based on something which is based on potential energy surfaces. Now, what is potential energy surface and how it is connected to the reaction dynamics; that we are going to discuss. And so first we will understand what is potential energy surface.

Now potential energy surface means if I suppose have 2 atoms say let us start with atoms suppose if I bring 2 atoms closer together. So, how the potential energy between them is changing if a bond is being formed and that all of you know that we can form a diatomic molecule and the Vibra molecular potential energy looks like as an enharmonic potential energy surface which in the close to the ground state, you can approximate as a harmonic potential way.

(Refer Slide Time: 03:41)



Now, this is how it looks like. So this is a basically suppose if I have A and B 2 molecules and I am talking about the internuclear separation meaning let me draw it like this, suppose this is A atom and this is AB atom and we are talking about this distance which is known as the inter nuclear separation. Some separation between the nuclei of these 2 atoms which is plotted along this I mean which is along this direction along x axis. And along the y axis we are plotting the potential energy as they are brought closer together.

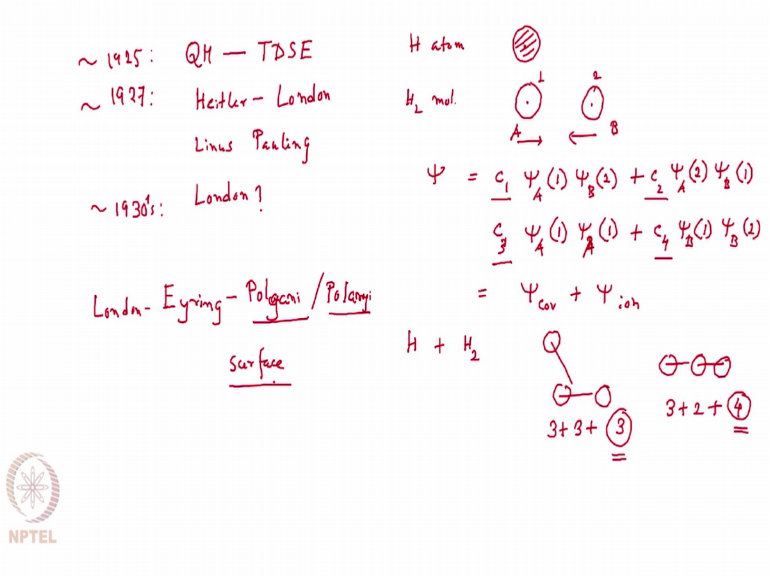
Now, we see that the potential energy falls and it goes to a minimum at a critical distance which we call as Re. So, Re is the known as the equilibrium bond distance between these 2 atoms which is between the 2 nuclei of these 2 atoms. And then if you further push this atom together what will happen that electrons in the atoms will try to repel each other and the potential energy again goes up. So, at this point we say that a bond has been formed between this diatomic molecules potential. But of course, this R equilibrium under or the bond length is not always constant at R equilibrium because the bond length always vibrates as we discussed.

So, around this equilibrium position will always see a vibration depending on the amount of energy that the molecule has, suppose the molecule act at a particular time has this much energy. So, the amplitude of the vibration will be something like this if we such a higher energy it will have a higher vibration. So, you have all these vibrational energy levels. And if you approximate with a harmonic oscillator you know that harmonic oscillator energy levels are equally spaced. So this is the energy and this is the bond distance and this distance I call it as a equilibrium bond distance.

Now, here the zero of energy the way it does curve on the left is shown, the zero of energy is a choice of zero of energy is very arbitrary. So, here it is chosen that when this act 2 atom are infinitely separated or far apart there is no interaction between them, at that point when R is going to infinity that energy it is chosen to be served. Now also there is something called dissociation energy basically tells you how much energy you have to supply in order to bond for the bond to break so that is known as D e. But De whatever when you measure this bond dissociation you always get something lower than D e, the reason is that this D e is measured from the bottom of this potential well. But you know that always for a harmonic oscillator or for an enharmonic oscillator even at the lowest quantum number v equal to 0 you have a 0 point energy.

So, you do not start from here when you measure that De rather you actually start from slightly above and that we call as D 0, so D 0 is always magnitude was lower than D e. Now these are all these details for a diatomic molecule. And then there is a very interesting history how all these quantum mechanics of molecules emerged and as you know that around 1925 the quantum mechanics was developed by independently Schrodinger and also later by Heisenberg and many others.

(Refer Slide Time: 07:25)



~1925: QM — TDSE

~1927: Heitler - London

Linus Pauling

~1930's: London ?

London - Eyring - Polyani / Polanyi

surface

H atom

H_2 mol.

$$\Psi = \underline{c_1}\,\psi_A(1)\,\psi_B(2) + \underline{c_2}\,\psi_A(2)\,\psi_B(1)$$

$$\underline{c_3}\,\psi_A(1)\,\psi_A(1) + \underline{c_4}\,\psi_B(1)\,\psi_B(2)$$

$$= \Psi_{cov} + \Psi_{ion}$$

$H + H_2$

Now do not so first quantum mechanics are basically the time dependent Schrodinger equation and it is a time independent version Kim, and then around 1927 or so 2 scientists Heitlar and Fresh London. Then they actually proposed something like suppose a quantum mechanics told that of what is the structure of atom.

Because, if you have a right some are studied some basic quantum mechanics you know that atoms and molecules energy levels are quantized. And what Schrodinger give is electronic structure up for the hydrogen atom and who which he could successfully explain the atomic spectrum which was observed experimentally and he basically rediscovered the board frequency condition. But, he showed that the quantum numbers actually come out very naturally as a solution of differential equation and moment you put some boundary conditions to it.

Now, after that Heitler and London asked; what is the change that happens when you talk about hydrogen molecule from hydrogen atom. So, let us say I have one hydrogen atom so and I just denote it like this. So, it has a nucleus and it has an electron cloud around it and then I am now talking about H 2 molecules and Heitler and London basically asked what happens if I just bring these 2 molecules closer together, what will be the energy of these 2.

Now, what they interestingly figured out there is a something called an exchange force that happens between these 2. In the sense that you can think that I have say atom A and atom B both are hydrogen atoms and I have say electron 1 and electron 2 what they should actually the total of a function can be written. Of course, as a product of the 2 individual atoms wave function and then they showed that I have electron 1 in A and electron 2 in B. But, there will be also another contribution that electron when the bonding is formed when the bond is formed or the bonding happens, so the electron 2 goes to atom A and 1 goes to atom B.

So, meaning actually there as if exchanging the electrons the atoms are exchanging the electrons. So, this was their formulation about the total wave function of the molecule and then eventually Linus Pauling subsequently said that you can also have something known as ionic contribution. Ionic contribution: in the sense the 2 electrons are in the same at all meaning suppose; if I let us say I am just writing these are basically the coefficients of the wave functions or the relative amplitude of these wave functions. And suppose I write it as C3 or whatever and then what I am saying that the both the electrons are basically I belong to atom A you can also think that both the electrons belong to atom B.

So, in that sense these 2 wave functions are called ionic wave functions. So, sometimes people write it as a psi covalent plus psi ionic something like that and the potential energy for this system will look exactly like what is a here. And with this ionic and covalent part covalent part of this wave function or covalent contributions of the wave function Claire longer than Pauling very accurately or may not accurately discussed and derive the energies and equilibrium bond distance very correctly. So, when you are it is when you actually compare all these theoretical results with experiment, you always compare with 2 things you always see what is the R e that you are calculating from your theory and match with your experiment. And the second thing is of course, the dissociation energy which you figured out experimentally what is the bond dissociation energy.

Now, after that the question was suppose I have hydrogen atom and from that I constructed hydrogen molecule and I know that how the inter atomic potential varies as a function of inter atomic distance or inter nuclear distance. Now the question is what happens if I actually bring and another atom to this system, meaning now I am talking about hydrogen atom and then bringing it together towards and hydrogen molecule. Now, this is a complicated problem because for if you think that if you talk about inter atomic potential, now if you have a 2 particle system the total number of degrees of freedom will be 6.

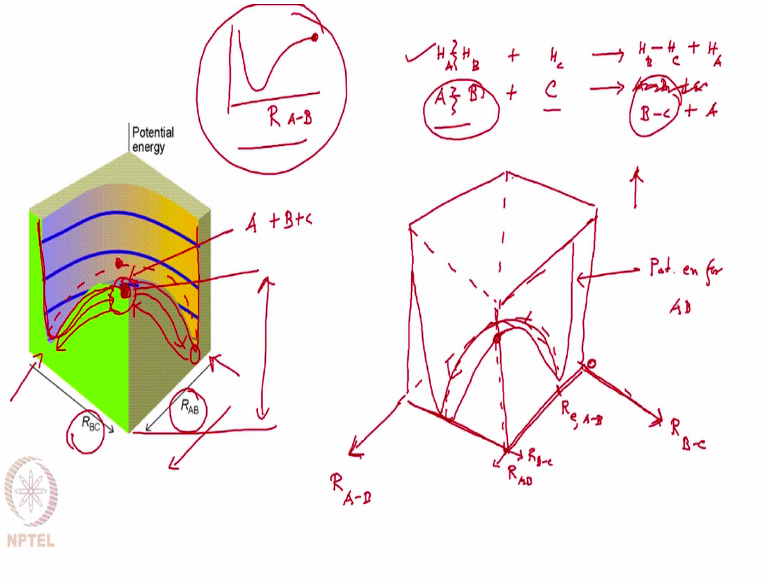
Now you can think that there will be 3 translational degrees of freedom of the 2 particle system as a whole well the center of mass of this 2 particle system moves, there will be some rotational motion but the rotation does not change the inter nuclear distance. So, there are the 2 kinds of rotation for a linear a because, it is diatomic molecule is a linear molecule and then can be vibration. So, it will be 2 there will be 3 translation 2 linear and one vibration because, the total degrees of freedom for a diatomic molecule 2 particle system is 6.

Now there is only one vibration but moment you keep a third molecule together the total degrees of freedom is 9. Now, 3 grows to translation 3 goes to rotation if it approaches as a non-linear fashion like 2 molecules of here. And the third molecule is coming like this, but if it is linear you will still have 2 rotation degrees of freedom. So, I will have 3 translation or 2 rotation or 3 translation and 3 rotation and in this case I have 3 vibrational degrees of freedom, in this case I will have 4 vibrational degrees of freedom. So, the number of degrees of freedom going to this inter atomic or thing which is connected to the vibration is actually increasing from 1 2 3 or 4 depending on what fashion you are bringing this third atom to this diatomic system.

Now, the question was even if I bring it like in a collinear fashion, how the potential is going to change and that was a question that fridge London asked I think sometime back in 1930s or so. And then it was very interesting there is a very interesting story and there was a there was a conference to honor Arnold Sommerfeld who actually was an atomic physicist and who contributed lot in our understanding and towards atomic structure and in that evening talk freeze; London actually gave this proposal or as this open question left this open question that what will be the potential energy diagram for a 3 particle system or 3 atomic system and around I mean in the sometime later.

So, 2 scientist Henry Eyring and Michael Polanyi, they actually I think it is Polanyi or this spelling will be Polanyi I will just check and update in the in the accompanying notebook So, Henry Eyring and Michael Polanyi so they actually I came up with the idea of the potential energy surfaces which together is known as London Eyring Polanyi surface our LEP surface. Now the question is what is how the potential energy surface will look like.

(Refer Slide Time: 15:55)



Now, you can think of this potential energy surface a very interesting with now on the left I have actually shown you how the potential energy surface look like. And let us try to understand from where it came from. Now, think about it I have fundamental to our understanding is the diatomic potential and already we know that that potential we look like something like this. If I vary the distance between A and B, say A and B are my 2 molecules something like that.

Now suppose, I am actually bringing a third atom which is C towards then A and B and then I can think about a reaction where this AB bond gets broken and this BC bond gets formed. So, I am talking about atom diatom reaction in a collinear fashion.So, what are the examples you can think about like this 2 hydrogen atoms are there and then 1 hydrogen atom is coming and then you are forming another hydrogen molecule and hydrogen atom. If you see that you look at this reaction it looks that as if there is nothing has happened because, it was H 2 plus Hand you are getting H 2 plus H again. But this is very different, because if you level these atoms it was A this was B and this was C. Now what happened is that you sorry in this case will have the instead of this BC bond here actually you will have BC plus A, because the A bond is breaking and then if you can level the hydrogen atoms it will be something like H B C and H A because the H A H B bond is getting broken.

So, this is also a reaction although apparently it does not look like a reaction because it is H plus H 2 giving you exactly the same thing H 2 plus H. Now the interesting thing is that so we are saying that there is already the atomic molecule and then another molecule another atom is approaching so that they form a bond. Now for this molecule AB I will have a diatomic potential like this, for this molecule BC also I will have diatomic potential like this and what we are going to do right now is to plot the potential energies among 2 different axes. Meaning I will have 2 different axis on one axis I will just plot the AB distance and in the other axis I will plot the BC distance.

Now, this is how we are going to draw it, so we are going to draw the same diagram but there are a few things that I want to discuss. So, that is why I am redrawing it just to make sure that the concepts are clear and let us just try to draw it. First let us say that so then draw it like this and first drawn hexagon like this. And then let us draw a surface like this ok. So, what you can see here I have say this surface of a cube and what I am saying here, on this surface I am basically drawing the potential energy for say AB molecule AB molecule in the sense that. Now look at this diagram and try to connect it with this diagram so this is potential energy for AB.

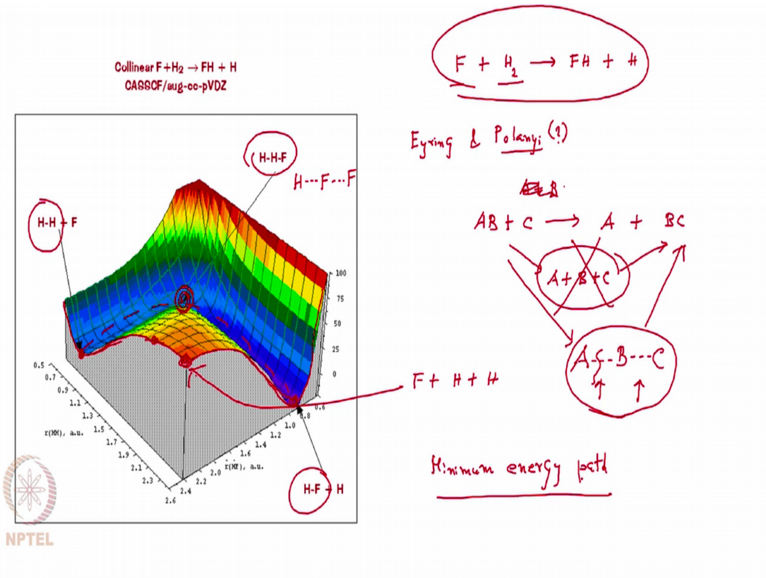
So, the energy is increasing in the vertical direction what is this axis. So, this axis now is basically the distance between A B. So, this is the 0 distance when there will be huge repulsion and this is basically the equilibrium bond distance for the AB molecule. So, along this axis actually plotting our A B. Similarly on the other axis I can plot the other potential energy surface which is basically the BC thing and suppose the BC also has some it is a similar potential energy something like this. So, along this direction I am plotting R B C so the parallel to this is this, so I can say that this is basically showing you the BC bond vibrations. And then you can say that fine how the potential energy looks like when I am in between.

Now, you see the drawing on your left which is a more accurate or more I mean more picture as drawing and what it shows is that I have a potential energy like this for the BC vibration. And I have a potential energy like this which are diatomic potential which is the AB vibration and together suppose the there is actually surface when I am varying R

AB and R BC together ok. But now, this is again this is a collinear reaction so that is why we are talking about only 2 distances it is something like ABC, so it is suppose C is at the middle either you can vary this guy AB and you can vary this thing.

When you reach at this point which is at this point you can think that here the along this R AB the bond has basically dissociated which were actually I am here. So, it is a potential minimum and then it goes towards the right, so at a very awesome distance you can see that it is basically A plus B isolated. But if you follow the BC bond vibration according to that this bond corresponds to B plus C because the BC one has totally dissociated. So, here this point on this energy surface is known as basically 3 isolated atoms together you can have a better picture in here.

(Refer Slide Time: 22:21)


Collinear F+H_2 → FH + H
CASSCF/aug-cc-pVDZ

So, here actually instead of H plus H 2 they actually reacted with something like F plus H 2, this is not a symmetric reaction like H plus H 2 this is a kind of asymmetric collinear at demand diatomic reaction. But it is still collinear atom which is fluorine atom and diatomic molecule which is H 2 that kind of reaction and of course the potential energy will be slightly different, because as you can see that H F has a much deep potential energy than basically H 2 ok. So, it is kind of a symmetric there is asymmetry in the picture but the picture is the same.

Now, the question is with the question Eyring and Polanyi was asking after they had basically came up with the idea of potential energy surface and still not with the spilling.

So, then they asked this question fine what is the path followed when this reaction happens, this kind of reaction or in any general when this kind of reaction happened I have initially probably started with AB.

So, I have AB plus C and how I am getting this reaction. So, during the course of the reaction what happens now you can think I can actually break the AB bond completely, so that I had A plus B plus C, and then I can actually join the BC together. So, the path will be something like that I was here and then I come to here and then I come to here at this point where actually I have A plus B plus C. In this case it is a plus H plus H and then again I form a molecule here let us actually show it on the other diagram. So, one path could be like this and then going to the other way. So, we are actually talking about AB to BC a reaction. So, that we have to start from here and then we go from here and then end up in here.

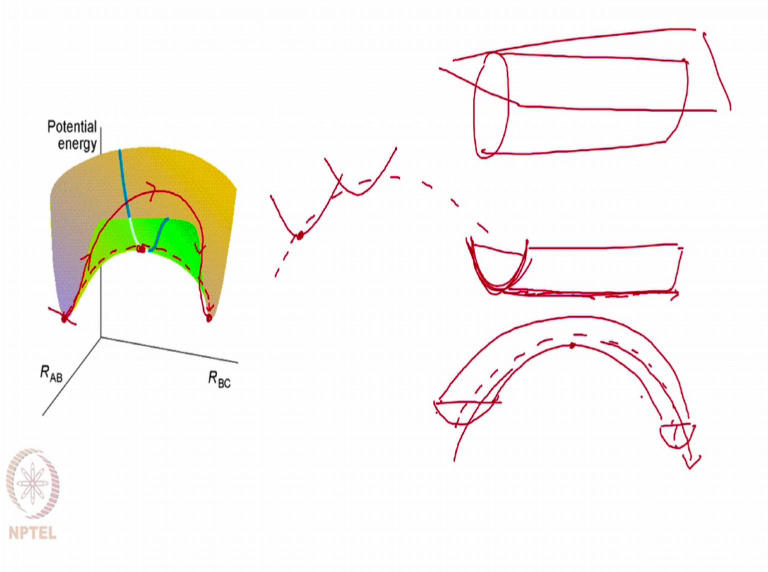
So, we are starting from the AB well and then going to the BC well through intermediate where actually you dissociate it all the atoms together. So, basically you had A plus B plus C but this will be very much energetically unfavorable because, as you can see here on the potential energy surface you could actually use some other alternate path. Where the energy is not so high because, as you can see this is a very high energy, what we could alternately do and what Eyring and Polanyi are good is that you could actually follow a path which is much less in energy. And then you could actually go from this portion say this was our starting point to this portion of this surface.

So, instead of totally dissociated the atoms you could actually do what is that when the BC bond is being formed the AB bond is being broken. So, the AB bond is not completely broken when the BC bond is getting formed and vice versa. So, what they say that this path that going to ABC it does not occur, because it really is a very highly energetic path, rather what you have is that you have a kind of intermediate although we will make a distinction that it is not an intermediate.

Why it is not an intermediate you have formed something like ABC kind of a duct, where neither the AB bond is broken completely not the BC bond has formed completely. So, it is partially broken AB bond and partially broken BC bond and then you eventually break the AB bond and form the BC bond and that structure lies somewhere here which is shown like H H F here. But we will use a kind of dotted thing here because it is not exactly H H F H bonded to because, them it is not it is a loose bonding a loose interaction.

Now, if I follow this path I will energetically favored their reaction because, I am to dissociate that AB completely and then forming the BC actually is a much more energetic process. So, this path is a minimum energy path and the they said Eyring and Polanyi that the reaction will proceed through an minimum energy path from say AB to BC, so that is how we got the concept of minimum energy path. Now along this minimum energy path you will encounter a point where I have a situation that it is right at the middle.; in the sense that when I am traversing this potential energy surface. So, I am making sure that every time actually my energy is minimum across the motion let me give you a more better example.

(Refer Slide Time: 27:57)



So, this is another way of looking at the path where we are talking about, so actually I am traversing from say AB to BC and on the potential energy surface I could actually go from here to here. So, that is a much more energetic path I am not doing that rather what I am doing is that I am just following a minimum much more less energetic path which is like this. So, there is a curved surface like this and what I am doing is that I am actually following the minima of this curved surface.

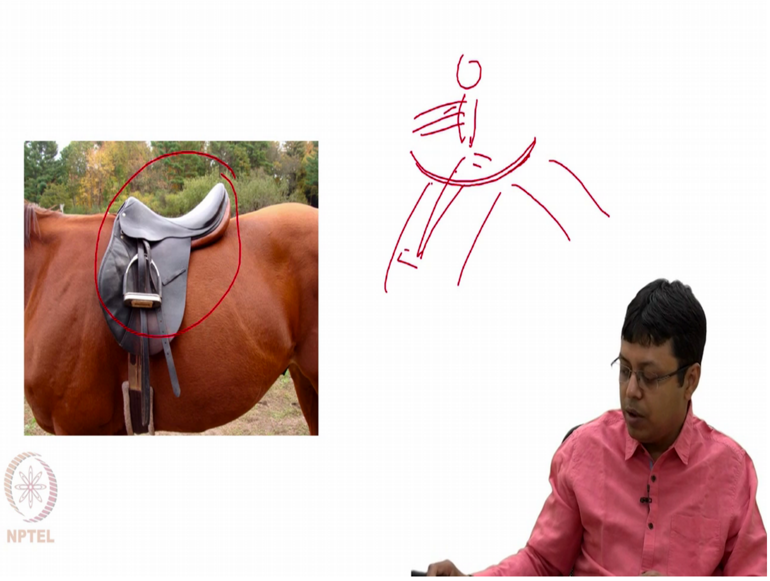
But there is the interesting thing when you go along this curved surface, suppose I am drawing it once again suppose this is a surface. What you see here is that minima in the sense that at any point, if you look curved you will see that you are sitting at the minima in the potential energy in the other direction. Other direction means along this direction along say I am moving in this direction when in the other direction I always say that I am sitting at the minimum of the potential energy surface.

So, that is why it is called a minimum energy path, but then at certain point you can see that this path has a maximum energy, but it is maximum along the path where we are doing this rare where we are basically proceeding for the reaction to happen. But that path is always minima in the other direction, so this means this is a surface you can think of like this you take a tube suppose I take a tube something like that.

Now I am saying that you cut the tube along this along this length you just cut it into a half like this and what will look like is something like this is what will be left to it. So, you have a tube. And then you cut it and then what I am saying now you bend the tube, so if you bend the cube now you look like something like this let me press draw it so it will be like this.

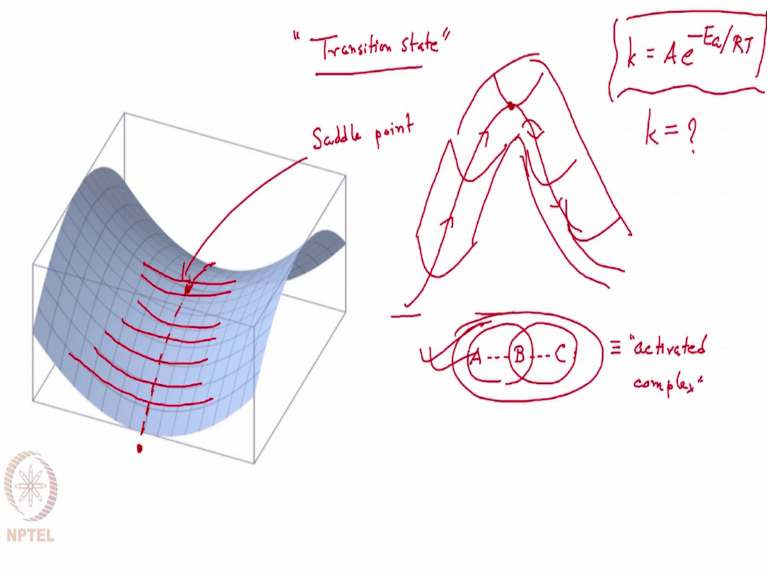
Now, you see that if I now move along this tube, what I am seeing here is that at every point I am at the minima, because I am actually following this bottom of the tube. But now as since I have bend it the actually I am going through a maxima along my direction of movement, so it is minima in the sense that you are at the bottom of the tube because the tube has a surface like this. So this is the surface and you are always at the minima of with respect to that I mean that energy in that is in that direction. But then I bend the tube and I am saying that I am going like this so you will hit a point, where actually you are maxima along your direction of movement but you were at the maximum. But you are at the minimum along the other direction but this point is known as a saddle point.

(Refer Slide Time: 31:13)



Saddle means actually, if you have seen horse riding competition or something like that, you will see that there is a beautiful structure on the surface of the on the top of the horse so it is a sitting arrangement. So, that actually there rider does not fall so basically you will have an arrangement like this. So, that somebody who is actually riding the horse will not fall because, his or her legs will be on the 2 sides of the horse. So, you will have a structure like this, so that the legs are actually on 2 sides. But when you are moving I mean along the length of the horse you also have a curved surface which is like this so that you do not move horizontally.

(Refer Slide Time: 32:03)



So, we have a better picture here so this is known as a saddle. So the reaction when it happens it is something like this I was in AB and I am following a path like this and then I see that at every point I am at the minima. In the sense that it is just in the same inner analogy like that a curved tube there is a curved surface, and I am going through the minima of the curved surface. But then I am reaching at a point where I see that I am maxima along this dotted line, but I am at a minimum along this solid horizontal line.

So, that is what we actually when you drew this potential energy surfaces or let us say the activation energy we said that we need a minimum energy and we always draw this path. So, this path is the minimum energy path but you have to always remember that in all the direction you were actually at a minimum position and then you reach to a point where you are maximum along your direction this is the direction of motion. But every time you are at the minima of this surface of this in any other direction

So, in our tube analogy the tube is bent like this something like that. So, this point is known as a saddle point on the potential energy surface and the chemical species which Eyring and Polanyi talked about is a species which looks like something like this, where actually neither the AB bond has been completely broken not the BC bond has been completely formed. And then they said that the reactance actually goes through a state which they called as transition state.

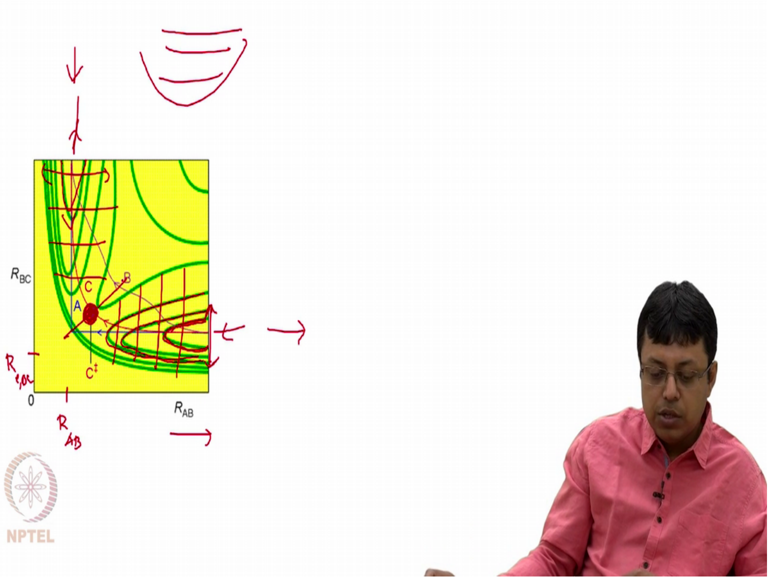
Now, all we are going to do is to discuss about this transition state how the knowledge of the transition state helps you to understand the reaction dynamics. So, what they said is that around the transition state you form a kind of complex which they termed as activated complex, will emphasize later why it is not an intermediate. They call it as an activated complex in the sense that you activate the reactants. And then, as if you form a complex where actually some bonds are weakly formed or in a state of being broken, which will eventually break as I cross this path and that is lying and a maxima in the direction of the reaction. But in all of the direction it is actually at sitting at the minimum of the potential in the surface.

So, I am on a saddle point geometry and that state is very short lived and that state they called as a transition state and then they kind of visualize the transition state like this or a diatom diatomic collinear reaction. Where actually one bond is getting formed and one bond is getting from that state this intermediate state. And then they said that I can actually calculate this rate constant which actually Arrhenius form empirically, through a series of experiment that this is the expression for the rates constant and then they said in order to calculate the rate constant all we need to know is basically the properties of this complex or the properties of this activated complex. Because there as I said there are 2 ways you can actually solve the entire process or the dynamics of the entire process by something known as collision theory and then you can also do it by this theory which is known as transition state theory.

Now, in the collision theory the problem is that for an atom diatomic reaction or something like this a moment you keep on increasing the number of atoms and all possible geometries of collision. Then actually if you want to really calculate the rate constant you have to solve equations of motion for each and every atom and molecules which are the reactants. Now that is a very tedious job because you can do classical mechanics you can use quantum mechanics. But whatever you use your complexity is still the same because, it is a huge number of atoms and molecules you are telling them and here the trajectories you are dealing with.

So, rather than what you can do is that you can actually think about a potential energy surface and you can go to a particular point in the potential energy surface, you can visualize or get the structure on this potential energy surface. And then you can actually talk about the properties of the of the system which is basically at the transition state or at the saddle point and those properties by properties will mean the statistical properties which we already studied. And those properties if I know then I can actually calculate the rate constant and that was the entire argument of Eyring and Polanyi. So, now we will see how and why basically this activated how one can actually get an expression for the rate constant using this using this concept of potential energy surface.

(Refer Slide Time: 37:53)



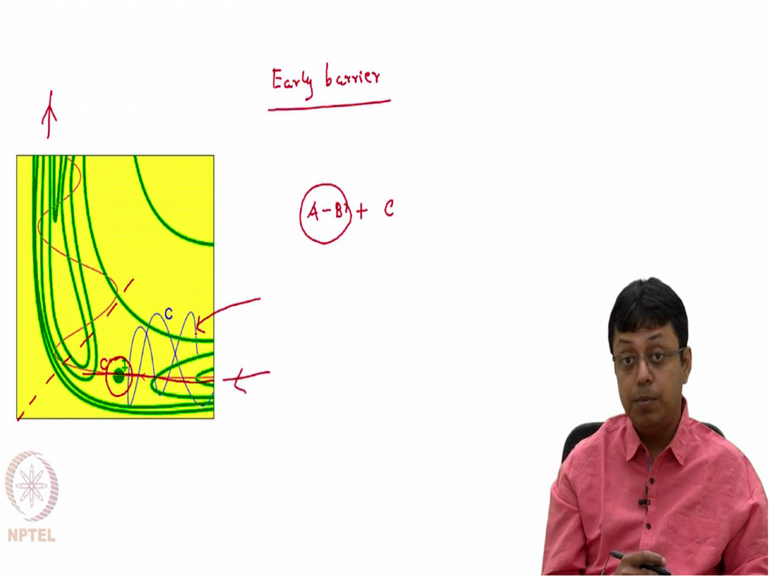
But before that which is known as actually also the transition state theory or in Eyring and Polanyis language it is also known as activated complex theory. Now before that what do we have drawn so far if you look at it here, like say for example we have drawn it along AB and along BC but and it is a true dimensional picture. But we could draw it actually along in a different way. So this is known as a projection diagram where basically you had on the z axis you had the energy and then you are actually taking a projection of everything onto the x y plane and x y plane; remember there was only distance. So, the energy you show all this isoenergetic surface you show as a line and this kind of diagram is known as contour diagram.

Now, you can see that all the points along this green line one particular green line has the same energy and this energy is actually increasing so this is a different line. So, moment you go from this line to that line to set, this particular line to that line your energy is increasing and this is the reaction path coming from here to go into here. So, I started from in this case actually the way it is shown it is basically BC to AB. Now in our convention actually the reaction should be in the other direction AB into BC. So because if you remember that this is the R AB distance and this is suppose the equilibrium R AB distance which corresponds to the vibration here. So, in the potential energy surface if you remember that there was something like this, and I am taking a projection that is why you are saying all this lines here. And then this is the BC form and suppose this is the equilibrium distance for BC where see these vibrations along BC just like the AB vibrations here.

So, the AB is going to BC means actually the direction of the arrow from will be from here to here in our convention or you can think of the reverse reaction also the way it is shown here. Now the point here when you traverse this production in surface you heat a maxima which is shown here, and the red spot and this maxima is I mean like it is along the path of the reaction. But in any other direction like the direction which I am drawing like this vertical arrow I mean or horizontal the solid red arrows in every direction you are at the minimum. So, which means at this red point you are right at the top along the direction movement and you are at the minima in the all other orthogonal direction.

So, you can think that this is for a very symmetric reaction you can have an interesting situation where this barrier actually sits.

(Refer Slide Time: 40:56)

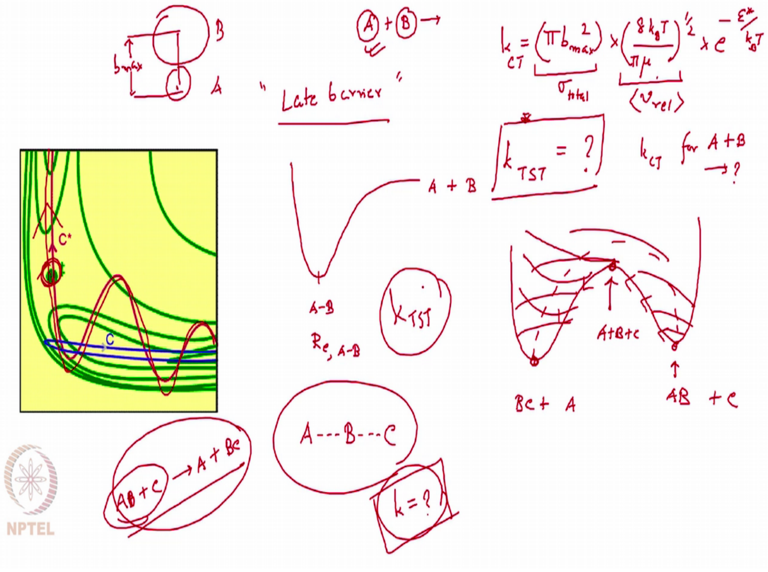


Slightly before the symmetric point meaning the saddle point is actually offering slightly before, now you can think what this is called actually early barrier. All of these are very advanced topics I am just giving you a flavor how the potential energy surface gives you a concept of early barrier a lead barrier. So, if the barrier is very early so then suppose you know all you have to do is to cross the barrier

Now, what you can do is that suppose you have the AB molecule initially and the C, now there is a relative kinetic energy between these 2 spaces every molecule and C atom. Now this total energy between of the system you can partition as a relative kinetic energy and the vibration energy of the AB, meaning I can have a low kinetic energy, but very high vibration in that AB; now which will help for this particular reaction if I am going from here to here and if I encounter the barrier right before. So then it is better that I cross the barrier first why because if you have a very high vibrational energy you can think like.

Suppose I am climbing a mountain like this and then how do I do it so it is just a straight uphill thing. So, I just better go straight like this because if I have too much vibration vibrations to occur across the motion, then I may actually may not have enough energy to cross the mountain because, I have too much vibration not too much translational energy along this direction. So, I will just bounce back from the surface which is this blue trajectory which is shown here so and for an only barrier it is better that the reactants have much more relative kinetic energy.

(Refer Slide Time: 42:44)



$$k_{CT} = \underbrace{\left(\pi b_{max}^2\right)}_{\sigma_{total}} \times \underbrace{\left(\frac{8 k_B T}{\pi \mu}\right)^{1/2}}_{\langle v_{rel} \rangle} \times e^{-\frac{E^*}{k_B T}}$$

$$\boxed{k_{TST} = ?}$$

k_{CT} for A + B → ?

The opposite will happen for a laid barrier when the barrier is right here. So, there are actually what you are saying is that you are crossing the barrier you were crossing the midpoint, but then you encounter the saddle point and this is very interesting if you have a high kinetic energy what can happen is that the barrier is here. So, basically you have to take a curved thing, because your barrier is not that straight you have to go like this and then you will hit the barrier. So, how do you do that one thing is that if you go straight with a very high kinetic energy, you might actually hit the wall and come back because you have to go towards left for the foot to cross the barrier. So, what you can do if you come initially with a very high vibration then after crossing this thing you can actually convert this vibrational energy into a translational energy.

So, this type of barrier is known as late barrier and for a late barrier reaction it is better that the reactants initially have higher vibrational energy than where kinetic energy. But these are all the details which will not go further our aim is very different our aim is to use this potential energy surface concept to understand how reactions occur. We started with a diatomic potential and where we said that the potential energy varies some and harmonically like this and what you can think atoms are totally dissociated. And here you can see for a minimum energy at the equilibrium bond length you can have a diagram potential like this.

Next we said that if we have 3 bodies together like AB is varying also simultaneously I am varying BC and then I said that ok. So, the potential energy now for a 2 body system as you see it is just a line it is a linear potential, but for a 3 body system if you consider it as a collinear thing. So, then you have 2 degrees of freedom because you have the AB distance and the BC distance and then as a result the potential energy look like a surface.

So, this surface we kind of try to draw and then we said that ok. So, there is a surface like this and then one possibility from going to from here say where I have AB bound AB, because it is a molecule and in the other point it is basically BC plus A. I could actually go through this path, but that is a very very high energetic path where in between I create A plus B plus C all the atoms dissociated.

But rather I could actually have this energy going from this path which is actually a minimum energy path because you see that everywhere along this path you are lined on the minima of the potential energy across your motion. So, again the tube analogy is the is the much better analogy you can think of it like I have a tube, and then I cut the tube, and I bend the tube, and then you can actually try to visualize the reaction path. So, what will do is that; we will give you a video demonstration of this tube surface, so that actually you can get a better idea of the potential energy surfaces and so.

So, the next task we are left to it is to understand how one can calculate the statistical properties of this complex which is the activated complex. And using those statistical properties how one can calculate the rate constant for the reaction, let us say AB plus C going to A plus BC. So, it is atom diatom kind of reaction and how one can get an understanding of this thing and moment we know how to do it we will try to actually solve a problem a very very simple problem and try to actually compare this with the collision theory.

Now, if you go back and have a look at the rate constant one obtained from the collision theory, you will see that it is written something like pi B max squared. Where suppose if I have 2 molecules A and B suppose this is B this is A. And now I am talking about to say collision I am just changing the notation right now, this always said atom the atom of reaction. But now I am talking about even simpler thing reaction between side 2 atoms A and B something like that or 2 molecules does not matter. So, the B max is defined as this parameter which is basically the addition of their radius. So, that is B max and then it will be multiplied by their relative velocities and relative velocity the expression which is obtained from Maxwell Boltzmann distribution of molecular speed is this 8 k b t by pi mu. Where mu is the reduced mass of the system and times you will have a Boltzmann kind of factor which is e to the power of minus epsilon star by k b t, where epsilon star is the minimum energy that the collision should have to cross this barrier.

You can actually have look at the derivation which is done in the earlier and of course, you get their YouTube videos or you can actually have it in your standard textbook also, sometimes this is called as the collisional cross section the total collision and cross section and this is as we said it is basically the relative average velocity. And this is the Boltzmann factor

So, if we have an expression so this is from the collision theory. So, I am just saying it is a rate constant obtained from collision theory. And then we will see what is the rate constant often from the transition state theory and these 2 should be should give me the same results. So, we try to solve a problem where actually will get similar results, you can actually we should get the collision theory expression for a reaction where actually say 2 molecules are colliding and giving you something. Now, when I say it is a 2 molecule it can be atom and diatom also. So A and B notation is this arbitrary do not get confused with this AB plus C in notation and the A plus B notation. So, our AB in the old notation is basically A in the new moderation something like that.

So, we will just try to solve it once we get to know; what is the expression for k or what is the expression for the k transition state theory and use this expression for to calculate bimolecular reaction rate constants.

Thank you.