Introduction to Molecular Thermodynamics
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Lecture – 40
Rate of Chemical Reaction

Welcome, today we are going to discuss perhaps the most difficult topic that we have introduced in this course and that is the rate of a chemical reaction as we understand it by using the principles of molecular thermodynamics.

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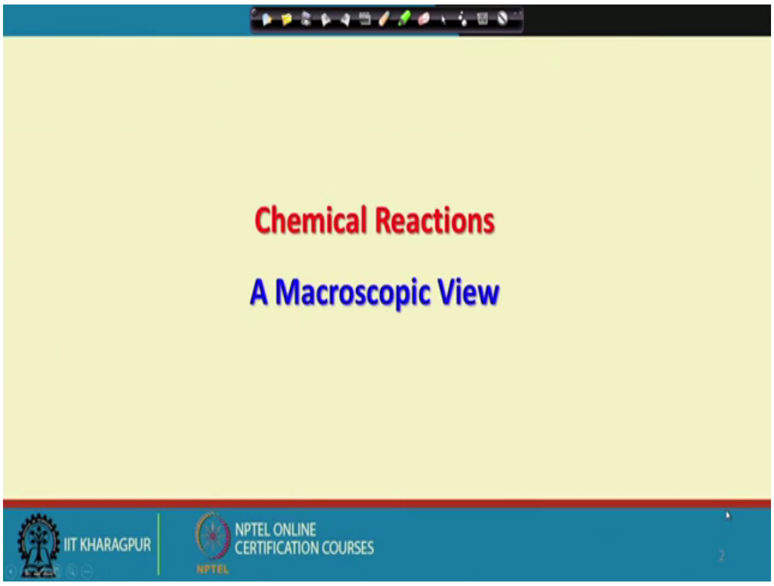
Chemical Reactions

A Macroscopic View

Now, as chemists, we always come across chemical reactions, but the view that we take of a chemical reaction is usually a macroscopic view.

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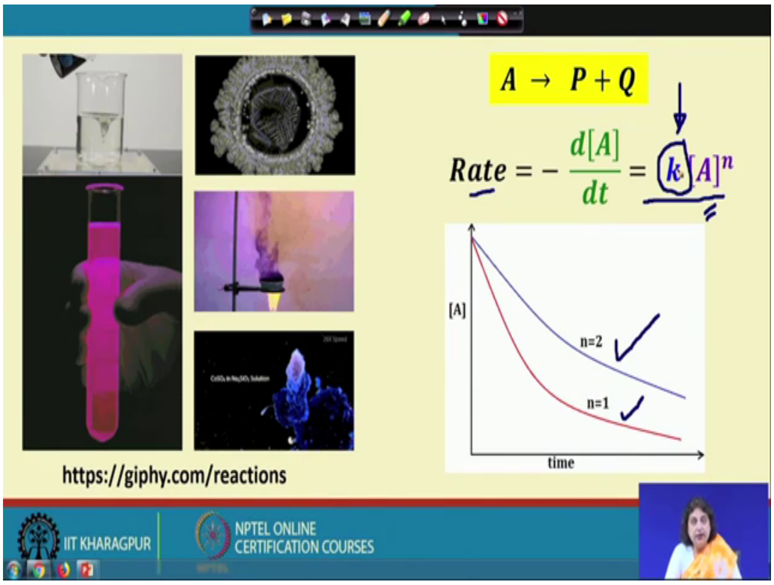

$A \rightarrow P + Q$

$$Rate = -\frac{d[A]}{dt} = k[A]^n$$

https://giphy.com/reactions

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So, when we go through the laboratory, we do see chemical reactions where you can see a variety of effects like the ones that have been highlighted over here. There may be a large amount of heat released; there may be a drastic change in color; accompanying the chemical change that you are observing through the chemical through your experiment. Now, if I want to find out the rate of such chemical reaction in that case the standard thing to do schematically is you write down a Stoichiometric chemical equation as shown here. And then you write the rate of the reaction as the rate at which the reactant A is degrading in time, so that the products P and Q are formed.

And in general what we find is in the experiments, it is found convenient to study if the rate depends on the concentration of the you know reactant which means that whether it is directly proportional to the concentration of the reactant A or it is proportional to the square of the concentration of the reactant A and so on and so forth. So, this quantity n, this is traditionally known as the order of the reaction.

And then what we do in the experiments is as follows. We try to for example, plot the change in concentration of A as a function of time and depending on what the order of the reaction is. You can have for the first order reaction a rapid decay in the concentration of A as it converts to P and Q, but if I have a second order reaction then the decay profile of a concentration of A in time is going to be different. So, then from this experimental data what one does is one finds out the slope of this curve and fits it to this equation and gives us the rate of the reaction. Now, in this rate of the reaction, the important quantity is this rate constant, which is a proportionality constant that tells me that the for the given reaction how the rate will be estimated for a given concentration of A.

So, the challenge of today’s lecture is if we can give a microscopic interpretation of this rate constant k. Because as you see here the rate that we are measuring we are doing using all the macroscopic equipments to do that; concentration of A is something like moles per liter, which once again is a macroscopic concentration, therefore, k is also a macroscopic quantity. And we are said to find out a microscopic interpretation of that.

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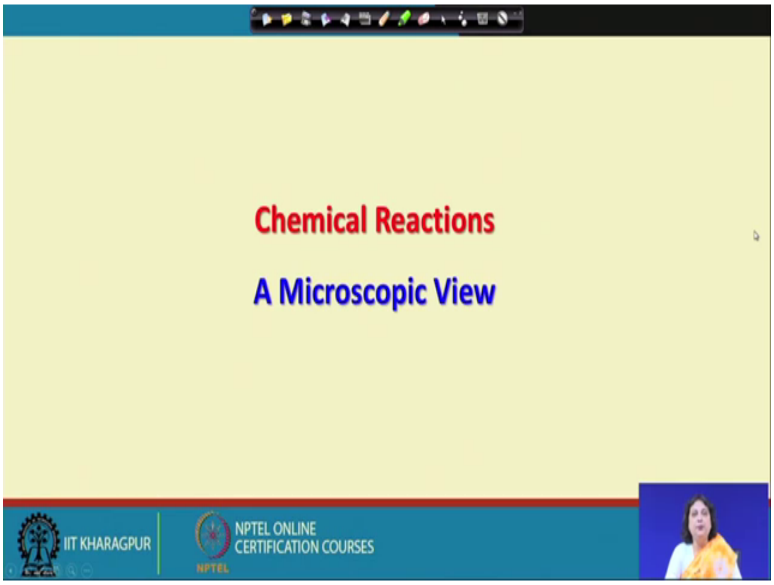

Chemical Reactions

A Microscopic View

Now, in order to do this; obviously, I need to set up the microscopic view of the chemical reactions.

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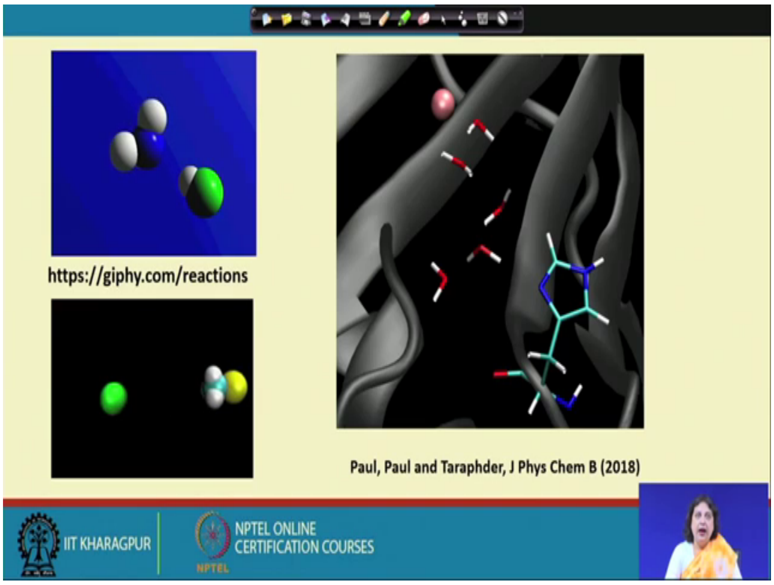
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Paul, Paul and Taraphder, J Phys Chem B (2018)

And when I do this we understand that as chemists we are usually we are usually familiar with a molecular picture like this associated with a chemical reaction. For example, here you see that this molecule appears approaches this molecule, and takes one atom from it, and leaves. On the other hand, in this particular case, as you see that the green molecule comes in and takes away a group like this is an NH 3, which was probably coordinated to the yellow atom and takes it away.

Or you can even have very complicated situations for example, in an enzyme catalyzed situation. So, this is a proton transfer reaction within an enzyme where you see that these water molecules are exchanging one proton between themselves. So, that one water molecule loses a proton and eventually this proton lands up on this particular nitrogen atom.

So, the question is as you see that the system is undergoing a series of transformations whereby it goes through a very large number of microscopic states. Therefore, if you want to find out that macroscopic rate constant, you need to take into account all these microscopic states that are available to the system.

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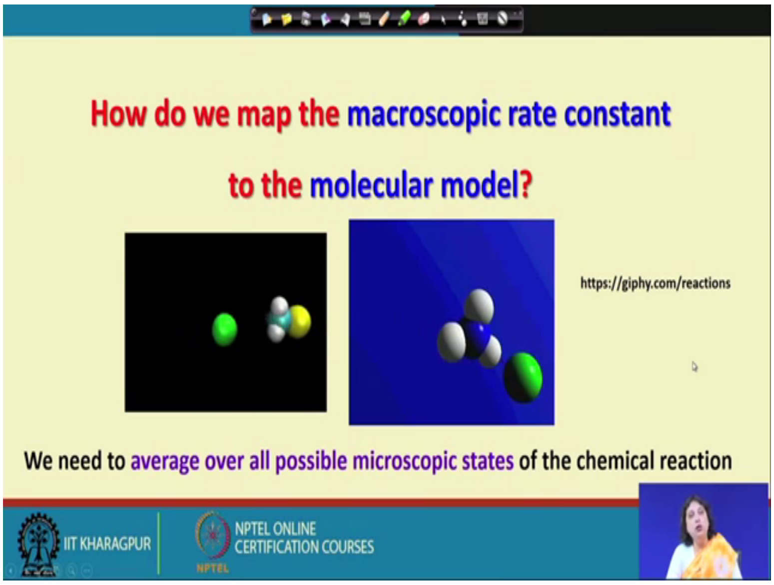

How do we map the macroscopic rate constant to the molecular model?

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We need to average over all possible microscopic states of the chemical reaction

Therefore, if we ask this question how do we map the macroscopic rate constant to the molecular model that we are usually using to understand them. The answer is we need to average over all possible microscopic states of the chemical reaction.

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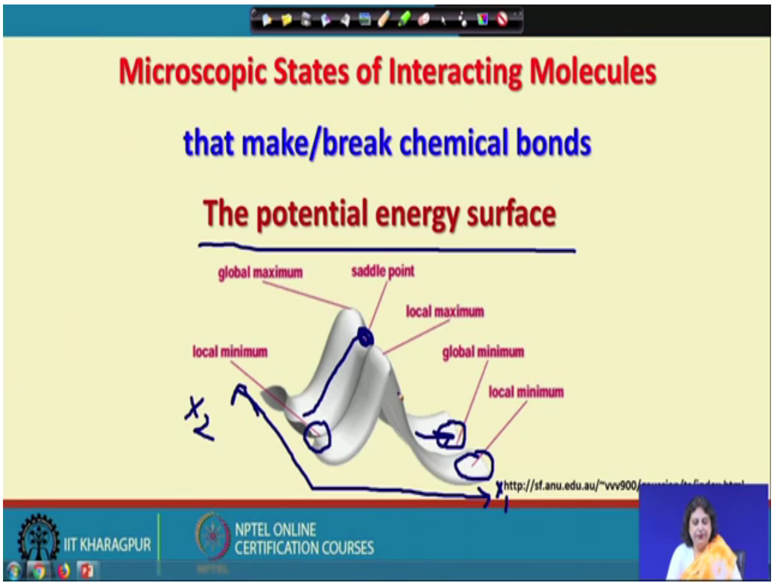

Microscopic States of Interacting Molecules

that make/break chemical bonds

The potential energy surface

And therefore, this brings us to the question of how do I model the microscopic states in a system where unlike the previous cases that we discussed, we do not have non interacting molecules. Right now, I have interacting molecules which participate in the making and the breaking of chemical bonds. And therefore, you understand that this problem has taken an enormously difficult proportion. And in this case with the development of quantum chemistry, we now know that the different microscopic states of these interacting molecules are represented in terms of what is known as a potential energy surface.

So, what is the potential energy surface, typically a potential energy surface in terms of two variables say x 1 and x 2 they would look like this ok. And now you see that this potential energy surface has a very complicated structure; it has some kind of what is called a local minimum, where the potential energy takes up the minimum value for certain values of x 1 and x 2. There may be other local minima like one here, but there can be global minimum where the potential energy of the system of this interacting system is the minimum amongst all the values of x 1 and x 2 available to it.

Now, a chemical reaction is observed or is modeled as a transition from one of these minimum by climbing this hill and going over to the minimum on the other side of the potential energy surface. Therefore, this top of the hill, which allows us to go from one side of the hill to the other is known as a saddle point which is the location of the so called transition state of the reaction.

Now, we are going to use many simple model systems to understand how such structures appear and how to interpret them so that we understand the task at hand that is the averaging over different microscopic states associated with the chemical reaction.

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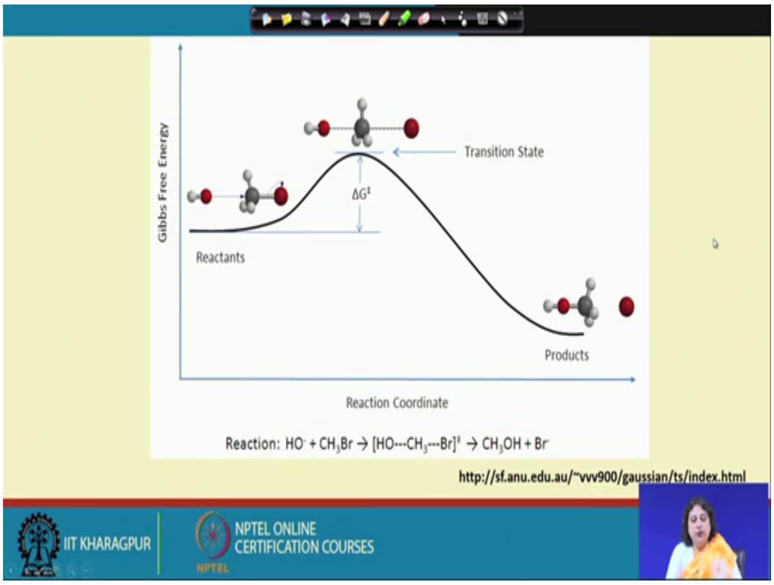

Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^‡ \rightarrow CH_3OH + Br^-$

http://sf.anu.edu.au/~vvv900/gaussian/ts/index.html

So, for this purpose, let me once again show you that well the task is I have a picture like this, where I can have something called a reaction coordinate that distinguishes between the reactant and the product state, and there is an energy barrier in between. And therefore, I would like to find out the energy surface such that the transition state is located at the maximum as the system passes from one minimum to the other minimum as the reaction progresses from the reactant to the product state.

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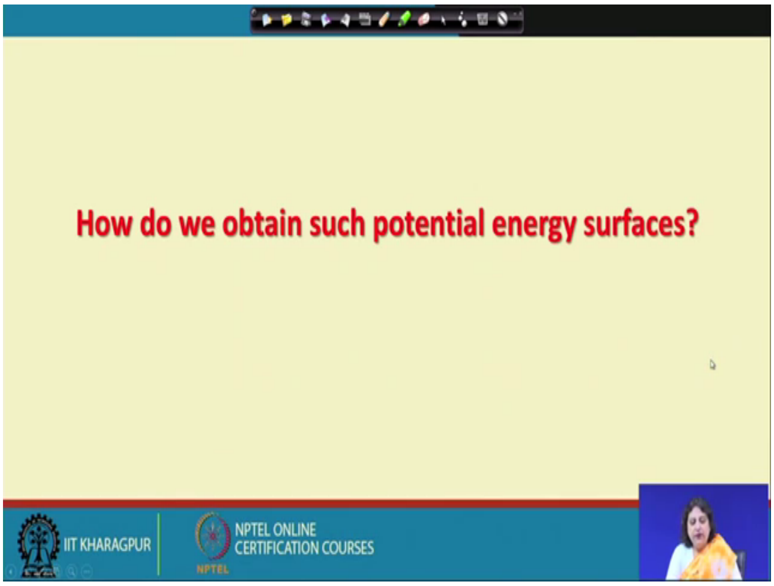

How do we obtain such potential energy surfaces?

Now, if I go ahead and try to ask this question how do we obtain such potential energy surfaces.

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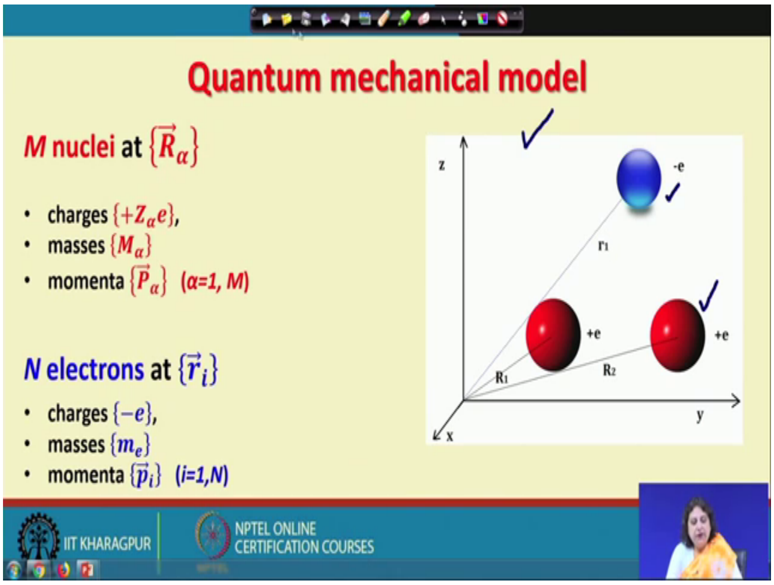

Quantum mechanical model

M nuclei at $\{\vec{R}_\alpha\}$

- charges $\{+Z_\alpha e\}$,
- masses $\{M_\alpha\}$
- momenta $\{\vec{P}_\alpha\}$ $(\alpha=1, M)$

N electrons at $\{\vec{r}_i\}$

- charges $\{-e\}$,
- masses $\{m_e\}$
- momenta $\{\vec{p}_i\}$ $(i=1,N)$

So, let us go back to the very qualitative consideration of the quantum mechanical model of such interacting systems. So, let us say that I have M nuclei located at the positions R capital R alpha, and with charges and masses and momenta specified for each of them. I can also have capital N electrons at their locations for a given macroscopic state with their respective charges, masses and momenta. And then the picture for a system like this is given here.

So, can you identify what kind of molecule is this? Obviously, this is H 2 plus where I have one hydrogen atom at the position one hydrogen nucleus at the position capital R 1, I have another hydrogen nucleus at the position R 2, and there is a single electron which is located somewhere here with a position vector small R 1 ok.

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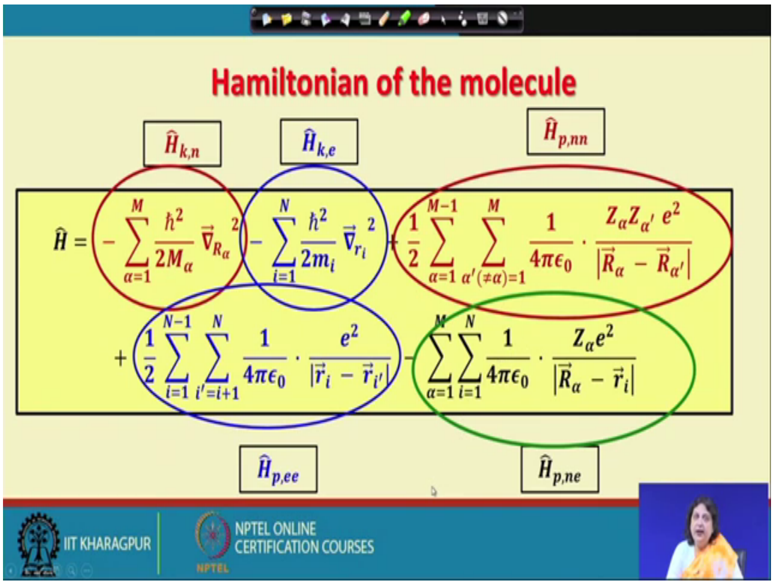

Hamiltonian of the molecule

$\hat{H}_{k,n}$ $\hat{H}_{k,e}$ $\hat{H}_{p,nn}$

$$\hat{H} = -\sum_{\alpha=1}^{M}\frac{\hbar^2}{2M_\alpha}\vec{\nabla}_{R_\alpha}^{\,2} - \sum_{i=1}^{N}\frac{\hbar^2}{2m_i}\vec{\nabla}_{r_i}^{\,2} + \frac{1}{2}\sum_{\alpha=1}^{M-1}\sum_{\alpha'(\neq\alpha)=1}^{M}\frac{1}{4\pi\epsilon_0}\cdot\frac{Z_\alpha Z_{\alpha'}\,e^2}{|\vec{R}_\alpha - \vec{R}_{\alpha'}|}$$
$$+\frac{1}{2}\sum_{i=1}^{N-1}\sum_{i'=i+1}^{N}\frac{1}{4\pi\epsilon_0}\cdot\frac{e^2}{|\vec{r}_i - \vec{r}_{i'}|} - \sum_{\alpha=1}^{M}\sum_{i=1}^{N}\frac{1}{4\pi\epsilon_0}\cdot\frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|}$$

$\hat{H}_{p,ee}$ $\hat{H}_{p,ne}$

So, if I now set up the Schrodinger equation for a system like this, what I would get is I have to start from the Hamiltonian of the molecule. So, the Hamiltonian of course, now requires many, many different terms to describe the contribution of kinetic energy as well as the potential energy of the different things present in the system.

So, initially I have this term which represents the Hamiltonian corresponding to the kinetic energy of the capital N nuclear is not in the system. Then I also have the part of the Hamiltonian, which represents the kinetic energy of all the capital N electrons in the system. And then I start having the potential energy terms.

So, this is the potential energy term for the interaction between the different nuclei present in the system. And this is the term where you have the interaction between the different electrons present in the system. And finally, I have one term which represents the interaction between the nucleus of having the charge Z alpha into e with an electron having the charge minus e and they are located at these two positions.

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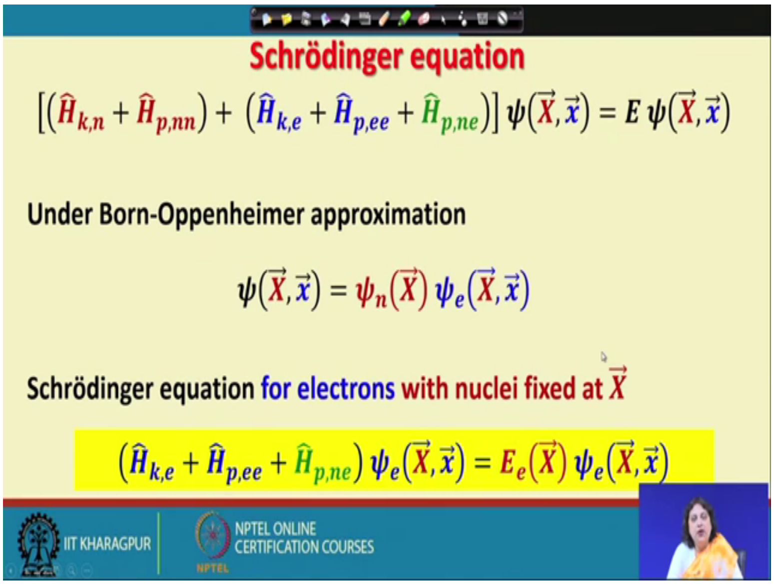

Schrödinger equation

$$[(\hat{H}_{k,n}+\hat{H}_{p,nn}) + (\hat{H}_{k,e}+\hat{H}_{p,ee}+\hat{H}_{p,ne})]\,\psi(\vec{X},\vec{x}) = E\,\psi(\vec{X},\vec{x})$$

Under Born-Oppenheimer approximation

$$\psi(\vec{X},\vec{x}) = \psi_n(\vec{X})\,\psi_e(\vec{X},\vec{x})$$

Schrödinger equation for electrons with nuclei fixed at $\vec{X}$

$$(\hat{H}_{k,e}+\hat{H}_{p,ee}+\hat{H}_{p,ne})\,\psi_e(\vec{X},\vec{x}) = E_e(\vec{X})\,\psi_e(\vec{X},\vec{x})$$

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Now, a simplified and compact notation of the Schrodinger equation to be solved then is given like this where this read capital X’s represent all the position coordinates of all the nuclear present in the system. And these blue small x’s represent the coordinates position coordinates of all the electrons present in the system. Now, under the Born-Oppenheimer approximation we know that the motion of the electrons and the nucleus they take place at very different time scales.

As a result of which we can actually solve the Schrodinger equation for the electrons by keeping the nuclei fixed at certain positions. So, this is exactly what we have done next. And we find that now the Schrodinger equation that I have to solve is given by an equation like this where capital X these positions are fixed.

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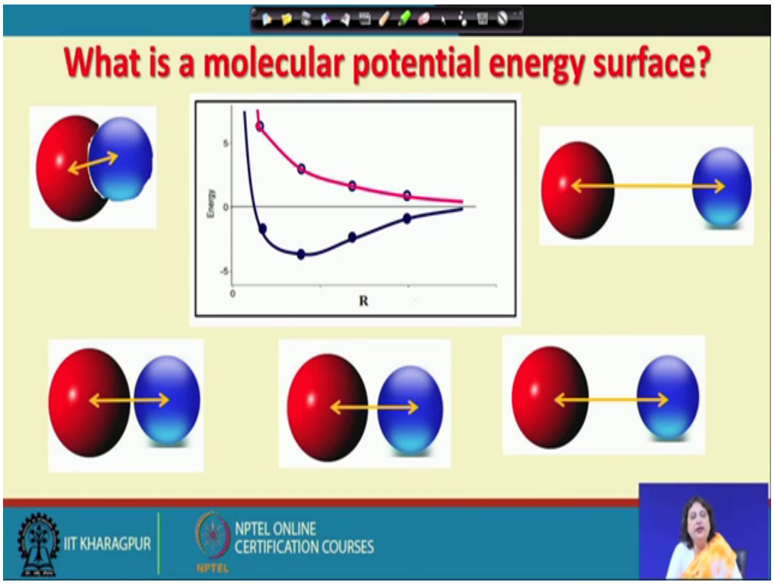

What is a molecular potential energy surface?

Now, when we solve these Schrodinger equations for a fixed value of X the results are something like this. So, by solving the Schrodinger equation, we get the energy Eigen states. So, let me say that if I fix the two this is a particular molecule that I am looking at, so it has one atom which is a red atom, another atom which is a blue atom. And the center to center distance is given by capital R.

Now, if I fix it at this particular value of R which corresponds to this value of R here, this is the ground electronic energy by obtained by solving the Schrodinger equation. And this is the first excited electronic energy that is obtained from the solving the same equation.

Now, as you understand that I can fix this relative separation of the two atoms at different values, for example, if I fix it at this value which is smaller than this before then let us say that this is a corresponding value of R. And these are the corresponding values of the ground and the first excited electronic state of this molecule. Now, this way we can actually generate all such energy values for different inter atomic separation within the molecule.

And as you understand that if the two atoms invade each other space then obviously, the energy is going to be very high and we have not shown it in this picture. So, by solving the Schrodinger equation what is it that we are getting now, what we are getting is we are now joining all the ground state electronic energies for the different geometries through this dark blue line, and all the first excited state electronic energies with this red line. So, the lower curve gives me the potential energy curve for this particular system and this is the ground state potential energy curve. And this is the first excited state potential energy curve obtained by solving the Schrodinger equation, and the first excited state solution of it at different geometries. So, this is possibly the simplest representation of a potential energy between the within a molecule, when I am changing their relative geometry.

Now, if I have a more complicated polyatomic molecule, you understand that in addition to R, I need to have many many more parameters. And in that case the potential energy curve does not remain a one-dimensional two-dimensional a curve, but in this case what I will get is a molecular potential energy hyper surface with a very large number of dimensions in the case of a complicated molecular system.

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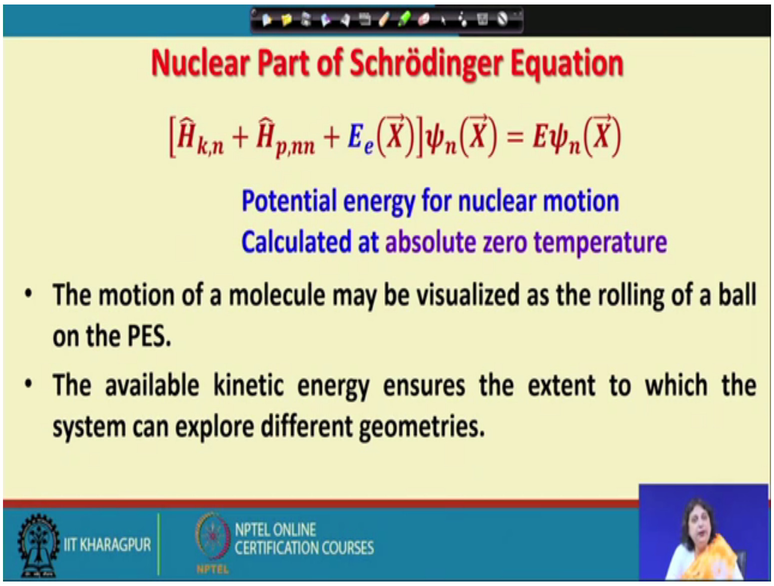

Nuclear Part of Schrödinger Equation

$$\left[\hat{H}_{k,n} + \hat{H}_{p,nn} + E_e(\vec{X})\right]\psi_n(\vec{X}) = E\psi_n(\vec{X})$$

Potential energy for nuclear motion
Calculated at absolute zero temperature

- The motion of a molecule may be visualized as the rolling of a ball on the PES.
- The available kinetic energy ensures the extent to which the system can explore different geometries.

Now, what is the use of this molecular potential energy surface. As you see if I write down the nuclear part of the Schrodinger equation, I find that this electronic energy actually plays the role of the potential energy on which the nuclear move ok. And therefore, here comes the importance of the electronic energies for fixed geometry of nuclei, fixed geometry of the nuclei because the solution of the electronic Schrodinger equation gives me the potential energy for nuclear motion.

But please remember there is no temperature in Schrodinger equation therefore, whatever have solved here it has been calculated at t equal to zero Kelvin. So, in

Schrodinger equation we are solving for the microscopic value of the microscopics description of the system at t equal to 0 Kelvin. Therefore, the potential energy surface that I get is valid description of the interaction between the different parts of the molecules at 0 Kelvin

Now, then obviously, the question is at a finite temperature, how do I represent the chemical reaction on the potential energy surface. This is in general visualized as a rolling of a ball on the potential energy surface that I will show to you later.

So, depending on the amount of thermal energy available to the system then the kinetic energy is high or low and that ensures the extent to which the system can explore different geometries. If you are at a very low temperature in the previous case, the two atoms cannot have large kinetic energy, and therefore, they will be forced to stay in close to each other thereby sampling only the geometry is near to the minimum of the potential energy surface.

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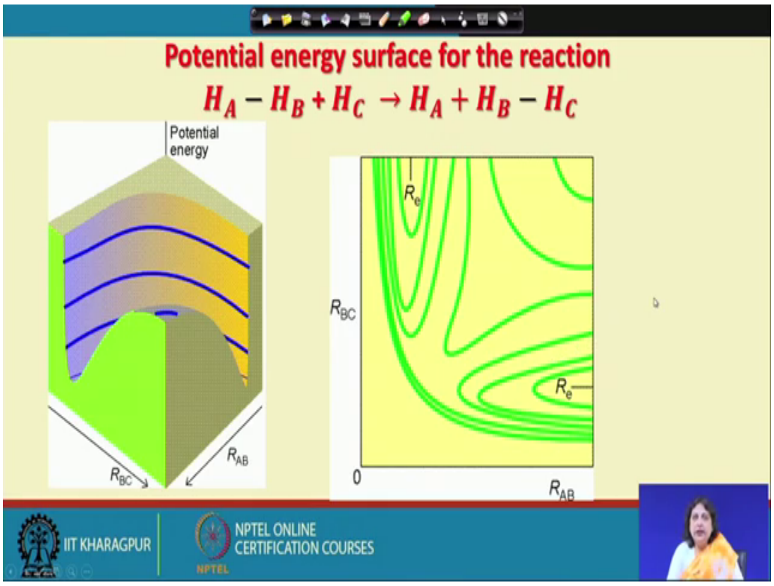

Potential energy surface for the reaction

$H_A - H_B + H_C \rightarrow H_A + H_B - H_C$

Now, let me take an example. So, this is a chemical reaction which is very simple. A hydrogen molecule interacting with an hydrogen atom. So, initially hydrogen atom A and B are bonded to each other and there is another atom C, which is coming close. And at the end of the reaction H A is isolated and a bond has been formed between H B and H C. Now, if I look at the potential energy surface that I get from here this is described in terms of two distances; one is the distance between the hydrogen atoms A and B, and another one is the distance between hydrogen atoms B and C.

So, as you see that in the reactant state A and B, these two must be having a minimum potential energy value indicating that there is a stable hydrogen stable chemical bond between them. And therefore, I see that this is where the reactant state for this reaction must be located. And under that condition, I must be having a large distance between B and C ok. So, here I have this R B C, it is going like this. So, since R B C increases in this direction, therefore at this point R A B is small, and R B C that is the distance between the hydrogen atoms B and C that is very large.

Now, as the system goes to this state, where there is a chemical bond between B and C. What do I expect? I expect a minimum in the in the potential energy corresponding to a small distance between B and C, so that exactly appears over here. And under such circumstances I must be having a large distance between the hydrogen atoms A and B. So, as you see as expected, this minimum appears at a very large value of R A B. And here as you see that we have connected equal energy points by these blue curves ok.

Now, this is a three-dimensional picture. Most of the times it is found that it is much more easier to look at what is known as a contour diagram of this potential energy surface. So, in this potential energy surface contour diagram, as you see each minimum corresponds to this kind of contours with very small diameter. So, this is a minimum which is corresponding to this product state.

This is the minimum which corresponds to an equilibrium bond length between the hydrogen atoms A and B. Now, this blue lines now appear as these contours or curves in the two-dimensional space. And here you see that larger the diameter of the contour from some kind of a center which means that you are looking at higher energies. Therefore, this energy would appear here, but this energy would appear at a much lower value like this contour or this contour ok.

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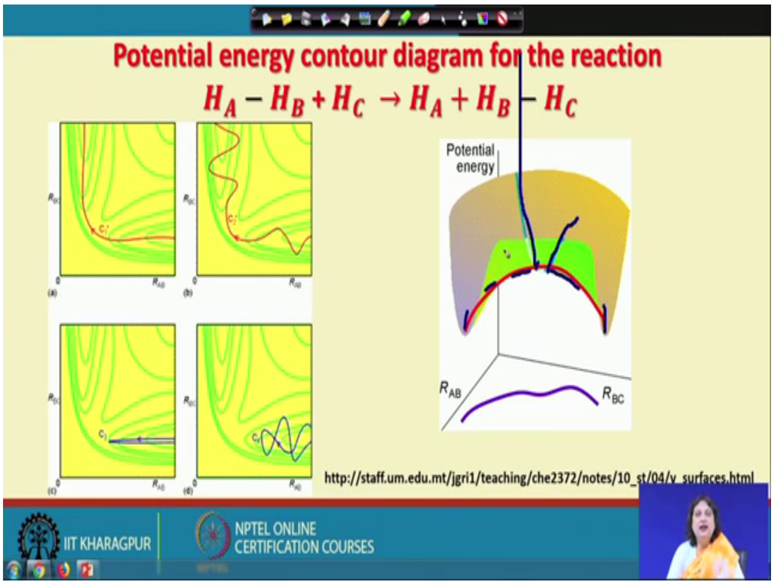

Potential energy contour diagram for the reaction

$H_A - H_B + H_C \rightarrow H_A + H_B - H_C$

http://staff.um.edu.mt/jgri1/teaching/che2372/notes/10_st/04/v_surfaces.html

Then the question is what happens when the reaction takes place? When the reaction takes place the system, for example, starts from the reactant well potential energy well from here then goes climbs up the energy hills. So, if you come from one this region to this region, you are going from lower energy to higher energy.

Then you pass through the saddle point and then you decay to the product state, but not always that the system when it attempts to scale this mountain of potential energy barrier, it will be able to do it just as cleanly as this. So, it gets it climbs up this way and then it goes this way and tries to find its path through the saddle point, and decays like this.

And many of the cases it so happens that the system is unable to climb the barrier at all because of the very high energy required for this. Now, if it so happens that at a given temperature the kinetic energy available to the system is not enough, then it attempts to scale the energy barrier, but once again falls back. And while doing this, it may fall back directly like this or it may try to rattle in that particular potential energy well and eventually go back to the minimum.

Now, once it is near this saddle point, so the saddle point is this region. Now, once it is near the saddle point it has two options. The first option that it has is I will go from this lower energy value through this direction through the saddle point and come here, so that is one kind of option it has. Or while it reaches the saddle point, instead of going here, it can try climbing in other directions like this or this, but as you see that the second direction requires a very large amount of energy. And a system as we know that is always trying to minimize the energy cost because it has limited thermal energy available to it.

As a result of this, I would say that in the plane R AB, R BC there will be only some combinations of R AB and R BC that will allow the system to pass from the reactant well to the product well. And those combinations of R AB and R BC which take the system from the reactant to the product well through a minimum energy path is called the reaction coordinate. So, if the system moves along the reaction coordinate, it undergoes a transition from the reactant to the product state through a minimum energy path ok. And in this particular case, the combination of R AB and R BC that gives you this minimum energy path is known as the reaction coordinate.

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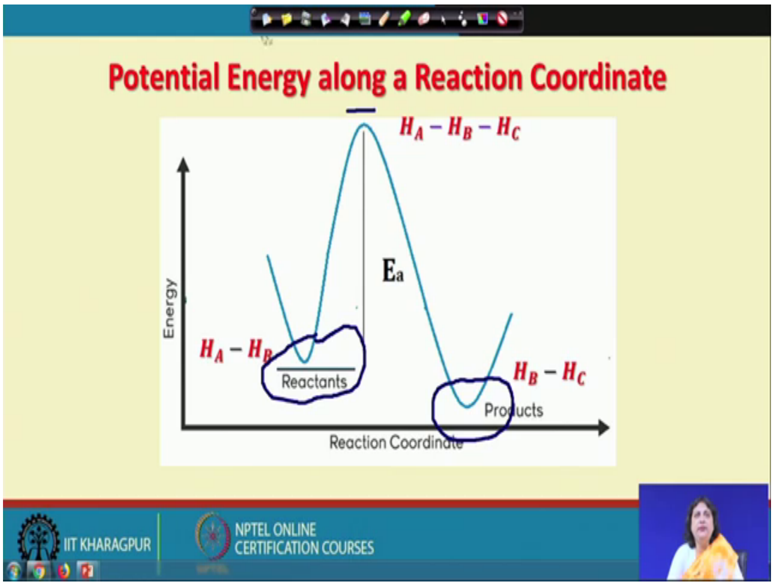

Potential Energy along a Reaction Coordinate

And therefore, once we have established what the reaction coordinate is then we can project the potential energy surface along this reaction coordinate. To get this very familiar one-dimensional potential energy profile that tells me that well I have here a potential energy well corresponding to the reactant where there is a stable chemical bond between the hydrogen atoms A and B.

There is another reactant well over here where there is a stable chemical bond between the hydrogen atoms B and C. And during the transition from this state to this state the system had to pass through a transition state here where A, A is still bonded to B, but it has started forming its bond to C. So, this is the hypothesis of a transition state or an activated complex.

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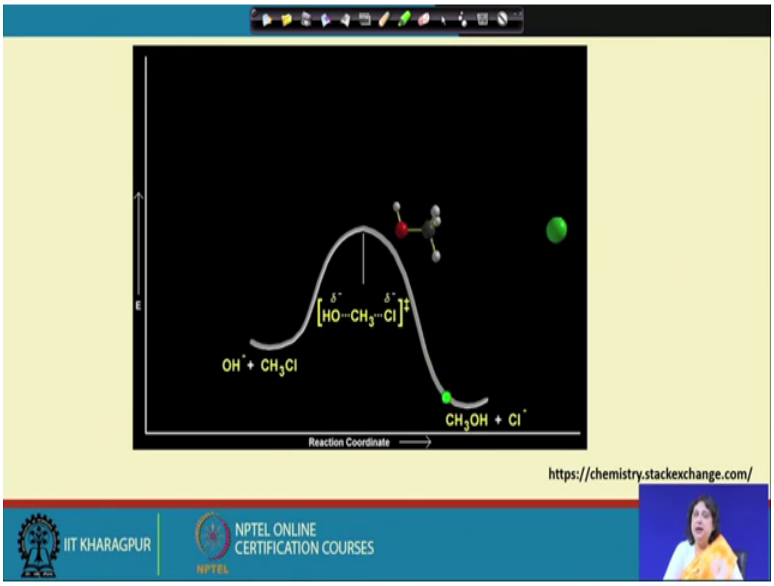

https://chemistry.stackexchange.com/

Now, within this molecular picture, then one tries to understand what happens when I adopt such a picture for the molecular model of the chemical reaction. So, as you see as the system samples many, many microscopic states accessible to a during the reaction this is how the chemical reaction is represented as a motion of a ball along the reaction coordinate starting from the reactant well and climbing the activation barrier and then finally relaxing to the product file.

So, this is the molecular picture and the many different ways that the system can do this is the array of molecular thermodynamics.

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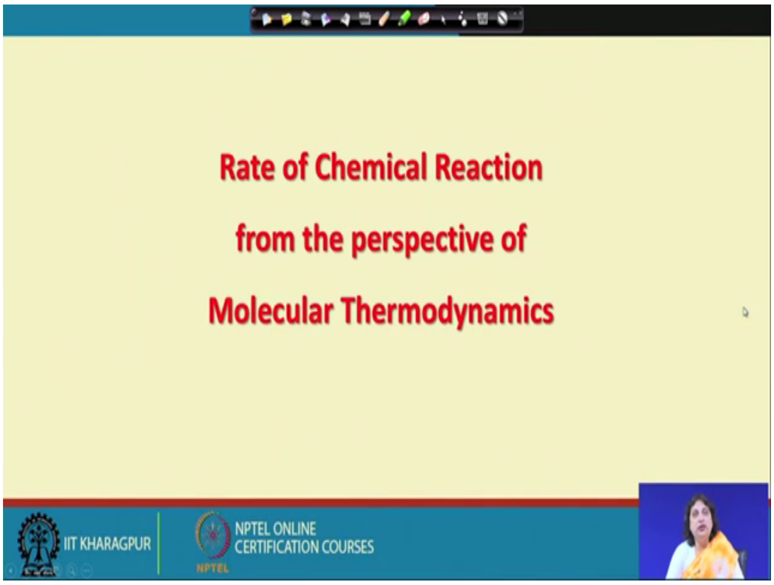

Rate of Chemical Reaction

from the perspective of

Molecular Thermodynamics

So, let us now quickly discuss how to get the rate of chemical reaction from the perspective of molecular thermodynamics.

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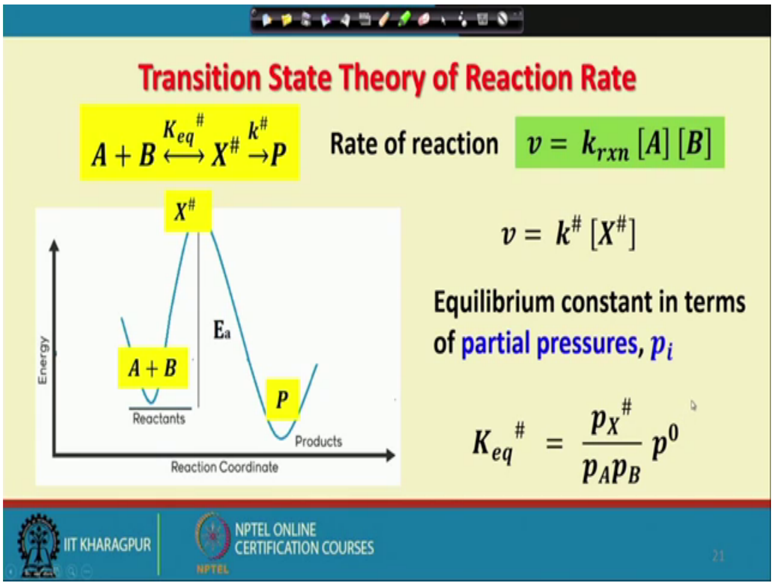

Transition State Theory of Reaction Rate

$A + B \overset{K_{eq}^{\#}}{\longleftrightarrow} X^{\#} \overset{k^{\#}}{\rightarrow} P$

Rate of reaction $v = k_{rxn}[A][B]$

$v = k^{\#}[X^{\#}]$

Equilibrium constant in terms of partial pressures, p_i

$$K_{eq}^{\#} = \frac{p_X^{\#}}{p_A p_B} p^0$$

And in this context, we are going to use the same potential energy profile along the reaction coordinate. And we are going to consider this very simple kinetics scheme which is A and B reacting with each other. And while doing so they rapidly establish an equilibrium to produce the transition state or the activated complex X dagger which subsequently decays into the product P. Therefore, in this picture what I have is this minimum corresponds to the two reactants A and B. And then this maximum corresponds to the formation of the activated complex X dagger. And finally, the second minimum in this profile corresponds to the product or the products here there is only one product P.

So, once we have established this kind of a picture, in that case the rate of the chemical reaction can be given by this rate constant multiplied by the concentration of A into concentration of B, but please remember concentration of A is given in terms of moles per liters. So, all the quantities that I see here are macroscopic quantities, but the picture that I am associating here is a microscopic one.

So, what I am going to do is I am going to write down according to this my kinetic scheme valid at the molecular level, what can be v, v is going to be proportional to the concentration of the activated complex. And the v is therefore, given by k dagger into the concentration of the activated complex. So, k dagger is the rate constant with which X dagger decays into the product.

Now, with this we can also write down if there is an equilibrium between A and B the molecules of A and molecules of B forming with the molecules of the activated complex. This can be written down in terms of partial pressures like this. So, I am now assuming that this is a gas phase reaction where the total system is maintained at a given temperature T and at a standard pressure p naught ok.

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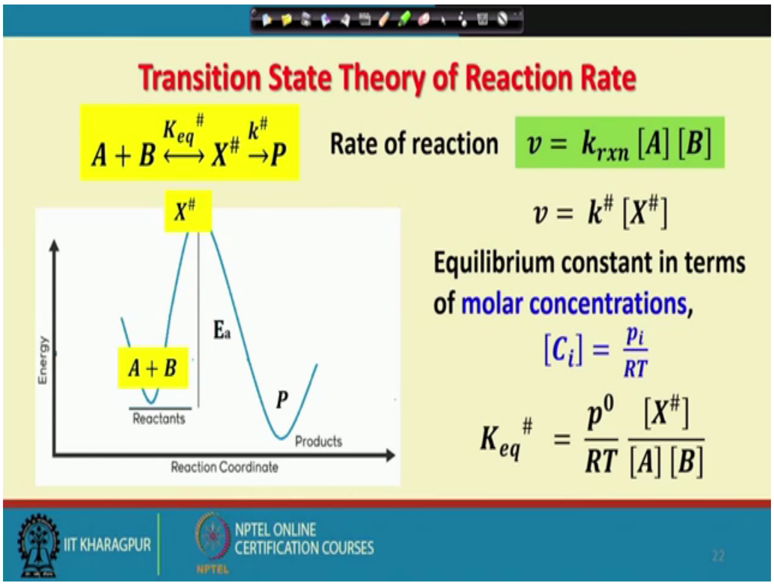

Transition State Theory of Reaction Rate

$$A + B \overset{K_{eq}^{\#}}{\longleftrightarrow} X^{\#} \overset{k^{\#}}{\rightarrow} P$$

Rate of reaction $v = k_{rxn}[A][B]$

$$v = k^{\#}[X^{\#}]$$

Equilibrium constant in terms of molar concentrations,

$$[C_i] = \frac{p_i}{RT}$$

$$K_{eq}^{\#} = \frac{p^0}{RT}\frac{[X^{\#}]}{[A][B]}$$

So, under such condition I can also say that well since I am my all my rate laws are written in terms of the concentration of the species, I will replace the partial pressures in terms of molar concentrations. And if I do that then I can write down the equilibrium constant for the formation of the activated complex like this. So, this is done in terms of things that we know very, very well from our initial knowledge of physical chemistry.

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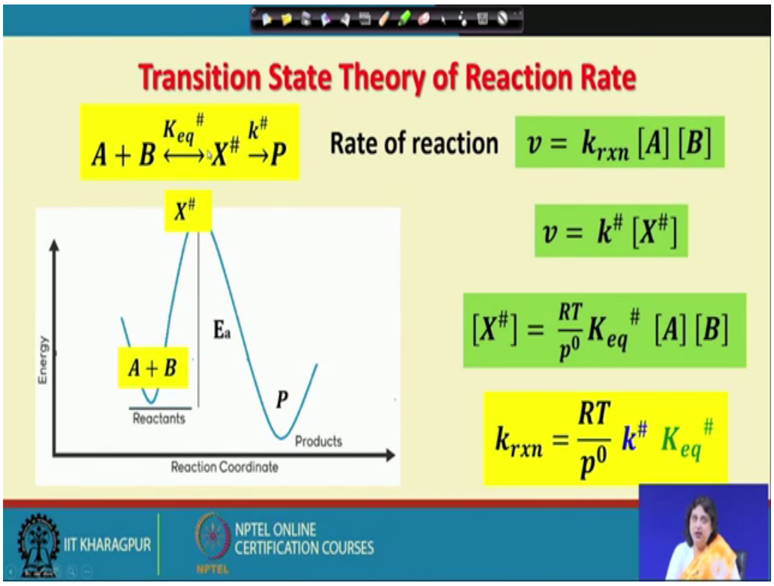

Transition State Theory of Reaction Rate

$$A + B \overset{K_{eq}^{\#}}{\longleftrightarrow} X^{\#} \xrightarrow{k^{\#}} P$$

Rate of reaction $v = k_{rxn}[A][B]$

$$v = k^{\#}[X^{\#}]$$

$$[X^{\#}] = \frac{RT}{p^0} K_{eq}^{\#} [A][B]$$

$$k_{rxn} = \frac{RT}{p^0} k^{\#} K_{eq}^{\#}$$

Now, we will go further and then say that well from the equilibrium constant, I can rewrite the concentration of the activated complex. And now combining these three equations, I can write down k reaction is a quantity which depends on this constant k dagger and the equilibrium constant k equilibrium dagger.

So, the task of molecular thermodynamics is evaluation of this rate constant small k dagger and this equilibrium constant K equilibrium dagger given the scheme as shown here.

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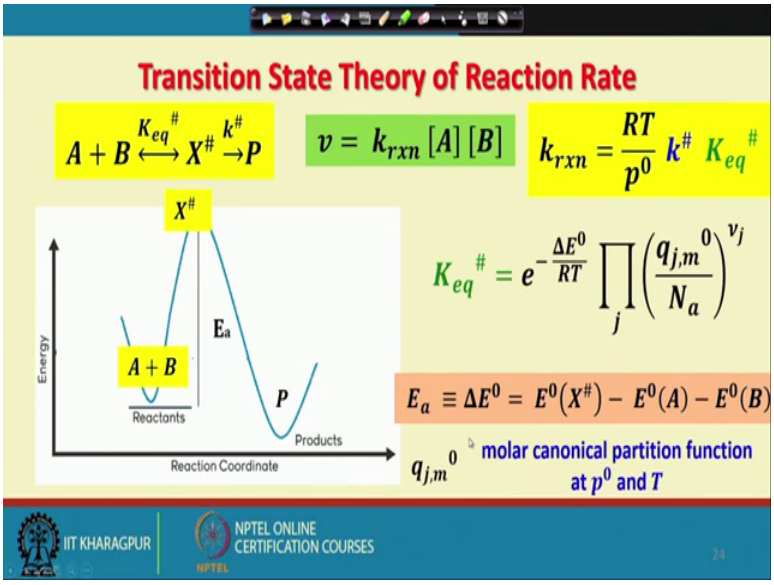

Transition State Theory of Reaction Rate

$A + B \overset{K_{eq}^{\#}}{\longleftrightarrow} X^{\#} \overset{k^{\#}}{\rightarrow} P$

$v = k_{rxn}[A][B]$

$k_{rxn} = \frac{RT}{p^0} k^{\#} K_{eq}^{\#}$

$$K_{eq}^{\#} = e^{-\frac{\Delta E^0}{RT}} \prod_j \left(\frac{q_{j,m}^0}{N_a}\right)^{\nu_j}$$

$E_a \equiv \Delta E^0 = E^0(X^{\#}) - E^0(A) - E^0(B)$

$q_{j,m}^0$ molar canonical partition function at p^0 and T

Now, this is something for which we can use what we have learned before for chemical equilibrium between ideal gases. So, this is given in terms of an expression like this. We have seen this before, but the difference here is now the different components of the reaction these are present at different energies and that is the reason why this additional exponential term appears.

So, what are these E naught and q j m naught. So, what I find here is E a that is the activation energy as shown here this is nothing but the E naught that I have shown here and that is the 0 Kelvin potential energy of the activated complex minus the same energy for the reactant A minus the same energy from the reactant B.

Therefore, if I know this potential energy profile from the solution of Schrodinger equation, I can find out E a. At the same time, I see that I am using these q j terms for each component in the reaction mixture this is nothing but the molar canonical partition function for the jth component at a given temperature T, where the total volume of the gas corresponds to the standard pressure P.

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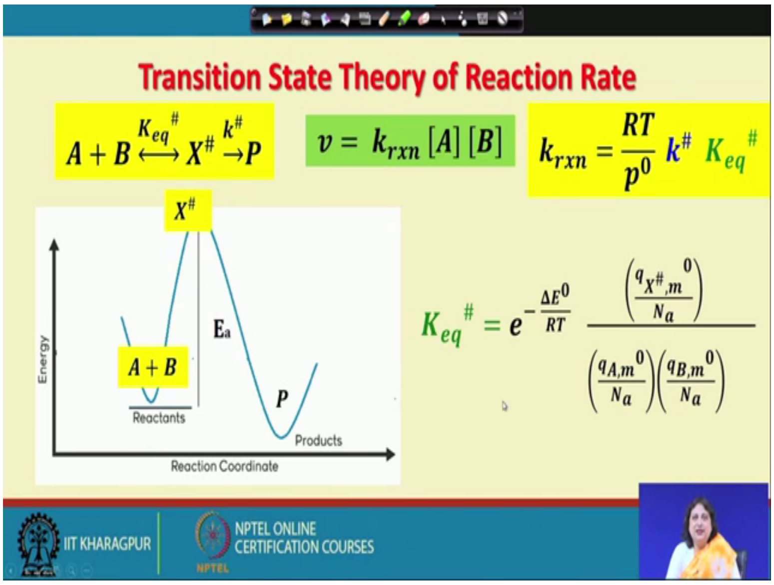

Transition State Theory of Reaction Rate

$A + B \overset{K_{eq}{}^{\#}}{\longleftrightarrow} X^{\#} \overset{k^{\#}}{\rightarrow} P$

$v = k_{rxn}[A][B]$

$k_{rxn} = \frac{RT}{p^0} k^{\#} K_{eq}{}^{\#}$

$$K_{eq}{}^{\#} = e^{-\frac{\Delta E^0}{RT}} \frac{\left(\frac{q_{X^{\#},m}{}^0}{N_a}\right)}{\left(\frac{q_{A,m}{}^0}{N_a}\right)\left(\frac{q_{B,m}{}^0}{N_a}\right)}$$

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So, using these two notations, what we can do is we can rewrite the K equilibrium like this. And now I understand that I can further simplify this algebraic equation.

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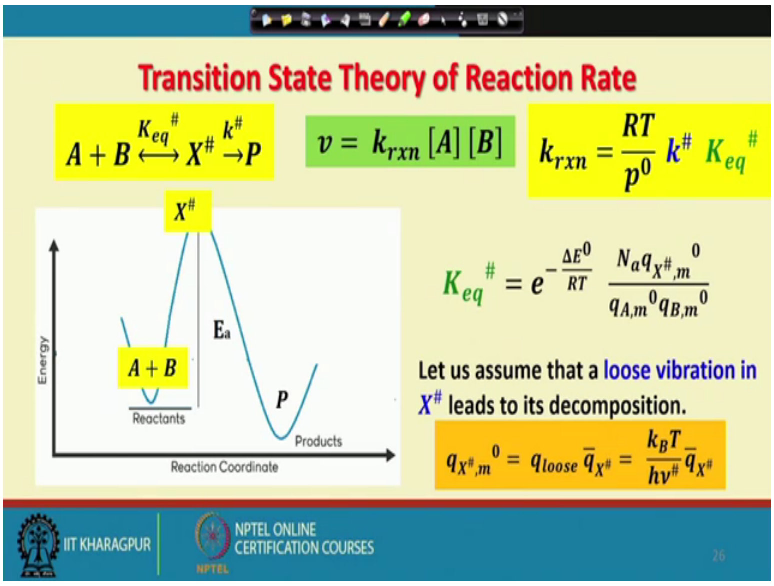

Transition State Theory of Reaction Rate

$A + B \overset{K_{eq}{}^{\#}}{\longleftrightarrow} X^{\#} \overset{k^{\#}}{\rightarrow} P$

$v = k_{rxn}[A][B]$

$k_{rxn} = \frac{RT}{p^0} k^{\#} K_{eq}{}^{\#}$

$$K_{eq}{}^{\#} = e^{-\frac{\Delta E^0}{RT}} \frac{N_a q_{X^{\#},m}{}^0}{q_{A,m}{}^0 q_{B,m}{}^0}$$

Let us assume that a loose vibration in $X^{\#}$ leads to its decomposition.

$$q_{X^{\#},m}{}^0 = q_{loose}\bar{q}_{X^{\#}} = \frac{k_B T}{h\nu^{\#}}\bar{q}_{X^{\#}}$$

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And have an expression of q equilibrium in terms of this in not then Avogadro number and the molar partition functions for the three components in the equilibrium mixture X dagger A and B. Now, let us assume that the difference the system when it forms this activated complex, there is a it has several bonds in it. And one of these bonds is executing a very loose vibration ok, and this loose vibration it is so weak that it leads to the decomposition of that particular bond. If that happens is very easy to say that X dagger which is which may be comprised of many, many atoms, but one vibrational mode of that atom is loose. And that is becoming loose as the system more that is loose and that bond is broken as the system goes from the reactant to the product state across the transition state.

As a result I can write that the this q naught of x dagger this is q loose that is the vibrational partition function corresponding to the loose vibrational mode multiplied by the vibrational partition function for the rest of the vibrational modes for the complex X dagger where because of strong bonds present within X dagger.

They are not undergoing any loose vibration. Now, a loose vibration means a very small value of the intrinsic angular frequency of vibration. And under such condition, it can be very easily shown that q loose is going to be given by this particular expression it is k B T by h nu dagger. And therefore, under such assumption I say that I am actually able to find out what the molar partition function standard molar partition function for the activated complex is in terms of a loose vibrational mode.

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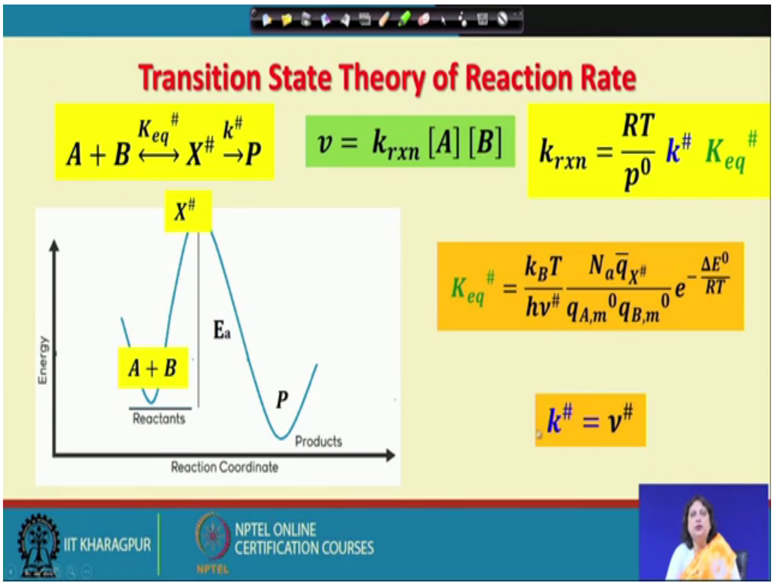

Transition State Theory of Reaction Rate

$$A + B \overset{K_{eq}^{\#}}{\longleftrightarrow} X^{\#} \overset{k^{\#}}{\rightarrow} P$$

$$v = k_{rxn}[A][B]$$

$$k_{rxn} = \frac{RT}{p^0} k^{\#} K_{eq}^{\#}$$

$$K_{eq}^{\#} = \frac{k_B T}{h\nu^{\#}} \frac{N_a \bar{q}_{X^{\#}}}{q_{A,m}{}^0 q_{B,m}{}^0} e^{-\frac{\Delta E^0}{RT}}$$

$$k^{\#} = \nu^{\#}$$

Now, under such condition then I know how to write down the equilibrium constant and it is this angular frequency with which X dagger would decay into the product. Therefore, k dagger is also nu dagger. And this is of course, valid if the system once it reaches the transition state immediately decays through the product and never comes back to the reactant state.

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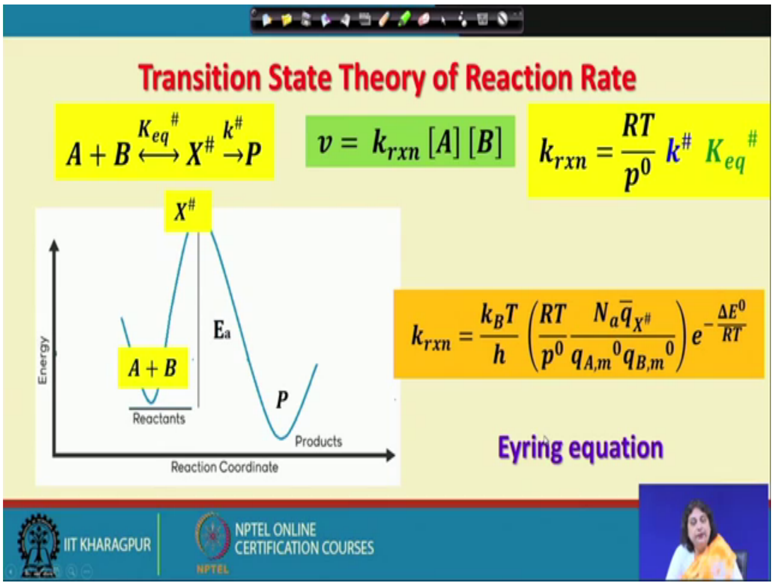

Transition State Theory of Reaction Rate

$$A + B \overset{K_{eq}^{\#}}{\longleftrightarrow} X^{\#} \overset{k^{\#}}{\rightarrow} P$$

$$v = k_{rxn}[A][B]$$

$$k_{rxn} = \frac{RT}{p^0} k^{\#} K_{eq}^{\#}$$

$$k_{rxn} = \frac{k_B T}{h}\left(\frac{RT}{p^0}\frac{N_a \bar{q}_{X^{\#}}}{q_{A,m}{}^0 q_{B,m}{}^0}\right) e^{-\frac{\Delta E^0}{RT}}$$

Eyring equation

Now, if I combine these two conditions then what I get is a molecular expression for the rate constant k reaction in terms of the molecular quantities like q bar x tagger, q A m naught q B m naught etcetera, etcetera and this is the Eyring equation.

So, what we have learnt from here is the k reaction can indeed be mapped onto the experimentally known result of Arrhenius equation. We have retrieved this exponential term which includes the activation barrier and we have a pre exponential term that depends on the molecular nature of the participants in the reaction.

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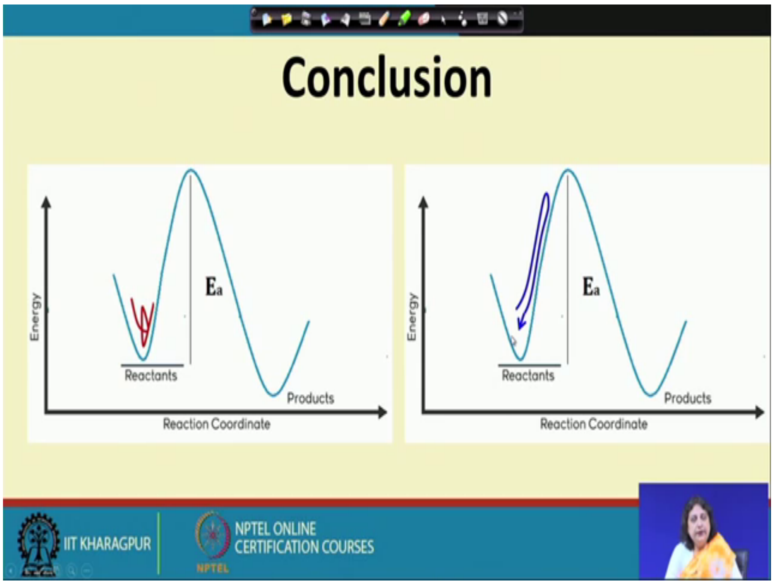

Conclusion

So, to conclude, first of all in order to understand the microscopic states of the reaction, we have introduced a one-dimensional potential energy profile for the reaction. Then we realize that for a certain amount of kinetic energy available to the system with the thermal energy available to the system, it is most probable that most of the system reactant molecules will remain here executing small amplitude motion within the reactant well.

Now, what happens is it is much system having a high potential energy and scaling this barrier is a less probable process, because the probability of a system being found here is E to the power of minus beta e, and therefore, with increasing value of E, the probability decreases. So, what happens is with some accessible amount of kinetic energy the system tries to climb back, and then it comes back again ok.

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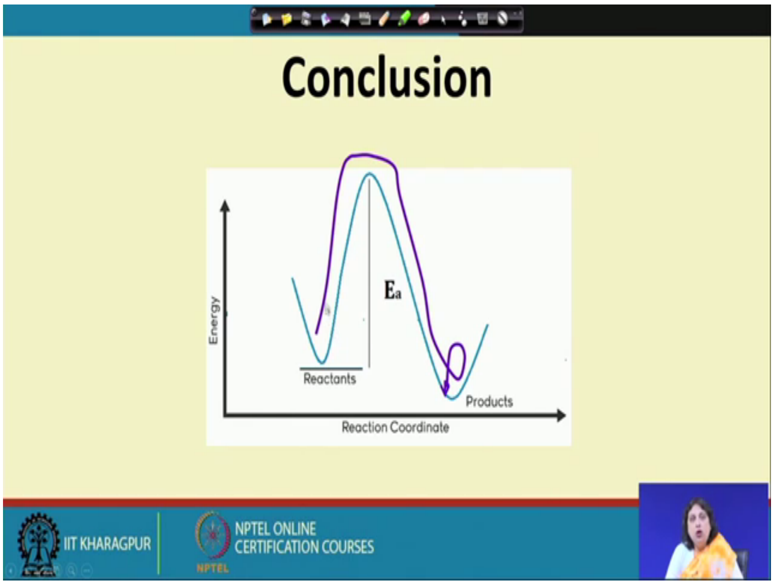

Conclusion

And then finally under certain conditions very rarely what happens is a trajectory a system can start from the reactant well and then according to transition state theory, it crosses the barrier and eventually it settles in the product well. Therefore, if I want to calculate the rate constant for this kind of a reaction, I must take into account, what this potential energy profile is what, what are the mechanisms through which the system can climb.

The barrier, cross the barrier and then settle into the product and all such barrier crossing events needs to be taken into account for the averaging to calculate the rate constant of the reaction.

Thank you.