Chemical Kinetics and Transition State Theory
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Lecture 37
Problem Solving Session 5

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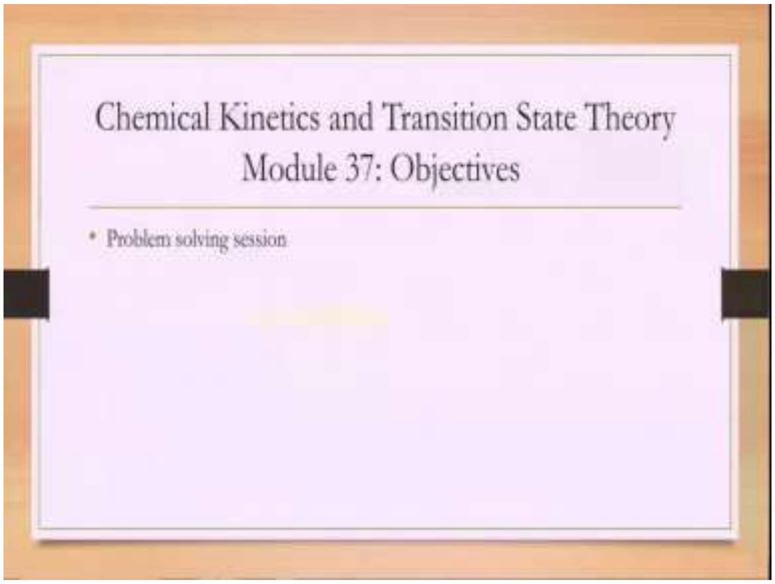

Chemical Kinetics and Transition State Theory
Module 37: Objectives

- Problem solving session

Hello, and welcome to module 37 of Chemical Kinetics and Transition State Theory. In last several modules, we have looked at a few concepts of molecular dynamics, and today is just a few problem solving session related to that.

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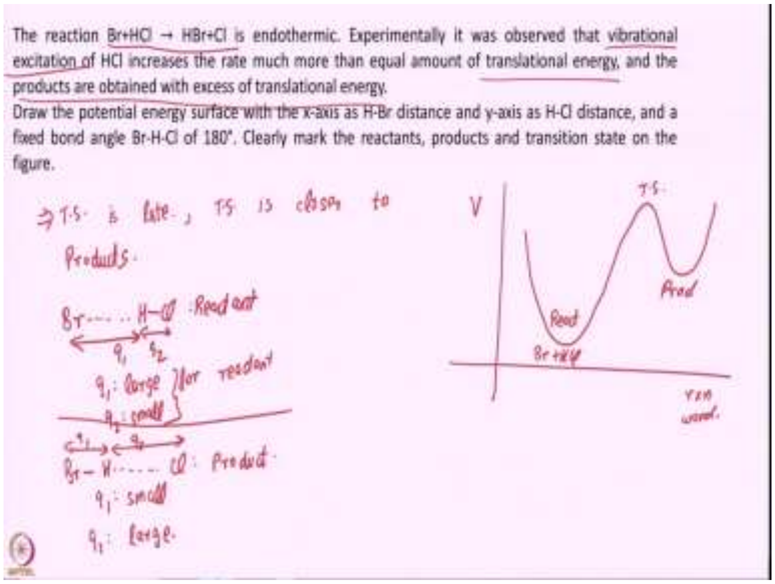

The reaction Br+HCl → HBr+Cl is endothermic. Experimentally it was observed that vibrational excitation of HCl increases the rate much more than equal amount of translational energy, and the products are obtained with excess of translational energy.

Draw the potential energy surface with the x-axis as H-Br distance and y-axis as H-Cl distance, and a fixed bond angle Br-H-Cl of 180°. Clearly mark the reactants, products and transition state on the figure.

⇒ T.S. is late, T.S is closer to Products.

Br.......H–Cl : Reactant

q_1 q_2

q_1 : large } for reactant
q_2 : small

q_1 q_2

Br – H....... Cl : Product

q_1 : small

q_1 : large.

So let us start with drawing potential energy surfaces. The problem states that for the reaction Br plus HCl going to HBr plus Cl. It is endothermic. We found that if we provide initially vibrational excitation to HCl that is much more conducive to the reaction compared to translational energy and the products are obtained with excess of translational energy. The part one asks you to draw a potential energy surface with respect to HBr distance and HCl distance.

So I will give you some time. Pause the video and draw this potential energy surface. Hopefully, you have paused the video and tried this on your own. This is a very important concept for this course. Let us solve the problem together. So first let us gather information on what we have provided you. So if I draw a one dimensional energy surface, I have a surface that should look like this, where this is reactant and this is product.

The reaction is endothermic. This is a 1D surface. This is not a potential energy surface. I am just thinking. Now we are given extra information that the vibrational excitation is more, increases the rate more than a translational energy. This implies transition state is late. Meaning transition state is closer to products. That is what we had discussed earlier. So you can go back to that module and relook at it. If vibrational energy is more conducive that implies that the transition state is much closer to the product side.

Now, let us just make a few more inductions. So our problem is our reactant looks like this. What do I gain from this, q1 large for reactant and q2 is small at reactant. My product looks like this, where you have HBr and Cl is far separated away. So here q1 is small. This is q1. This is q2. And q2 is large. So for my reactant, I will have large q1 and small q2 and the opposite for product.

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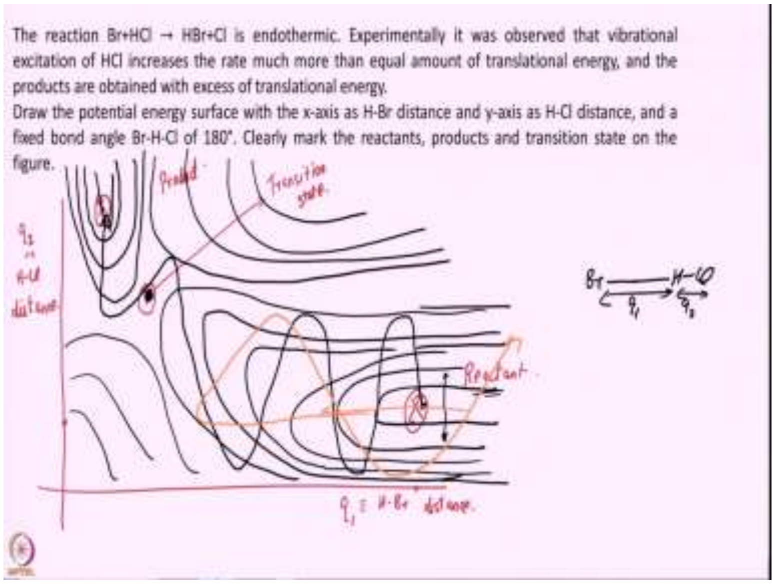

The reaction Br+HCl → HBr+Cl is endothermic. Experimentally it was observed that vibrational excitation of HCl increases the rate much more than equal amount of translational energy, and the products are obtained with excess of translational energy.

Draw the potential energy surface with the x-axis as H-Br distance and y-axis as H-Cl distance, and a fixed bond angle Br-H-Cl of 180°. Clearly mark the reactants, products and transition state on the figure.

So let us actually draw the energy surface with all this information now with me, HBr distance here that is what the question has asked me to do, q2 which is equivalent to HCl distance. Now where is my reactant on this? We analyzed q1 must be large and q2 must be small. So my reactant is somewhere here. Where has to be my product, q1 has to be small, q2 has to be large. This point must refer to product.

Now also remember we have argued that a transition state must sit closer to product than to reactant. So this is somewhere which is will be transition state. I will just change the color of my pen now. Otherwise things become confusing. So now let us draw energy surfaces first close to the reactant. Here if I increase q1 what will happen? Well, if you are increasing q, let me just draw this once more, this is q1, this is q2.

So Br is any way dissociated far away from the molecule. So if I increase q1 any further, I will just get flat potential energy surfaces. But if I increase q2, then the potential energy will change sharply, because q2 refers to the HCl bond. So, if I am, HCl is vibrating, well, of course, energy is changing. Now, as I decrease the value of q2, I will get these kind of surfaces now. Eventually, remember this is my transition state here.

So this thing has to curve around like this, qualitative figure and the same thing around the product, I will get surfaces that will look like this, the same argument, but the transition state is just sitting closer to the product. So that is your potential energy surface. And once more this, although is not part of the question.

But the point is, if I start with the reactants here and I through more vibrational excitation, you see it is just more conducive of hitting the transition state here like this. While if my initial conditions, let me choose another color, if my initial condition was more translational, then I can get lost and come back. Translational is just not more conducive. So, just a bit of extra information that we had discussed earlier.

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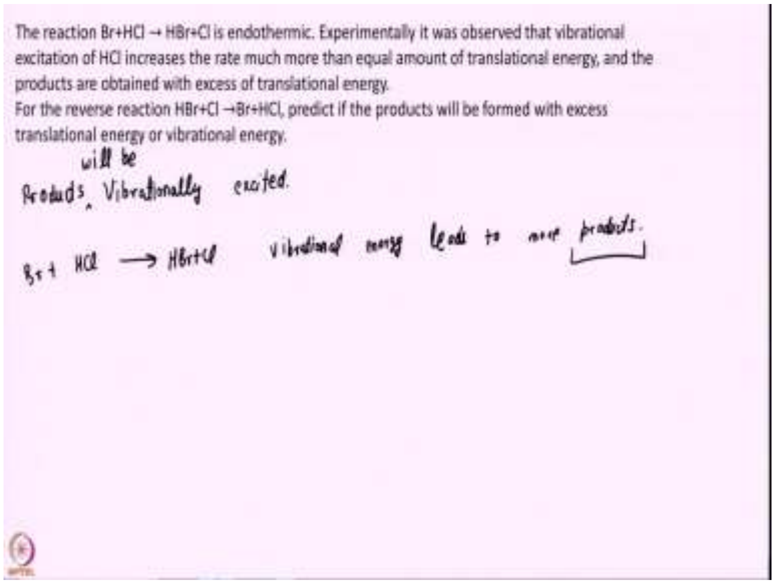

The reaction Br+HCl → HBr+Cl is endothermic. Experimentally it was observed that vibrational excitation of HCl increases the rate much more than equal amount of translational energy, and the products are obtained with excess of translational energy.
For the reverse reaction HBr+Cl →Br+HCl, predict if the products will be formed with excess translational energy or vibrational energy.

Products will be Vibrationally excited.

Br + HCl → HBr+Cl vibrational energy leads to more products.

The second part of this question asks for the reverse reaction now. HBr plus Cl going to Br plus HCl, predict if the products will be formed with excess translational energy or vibrational energy. So I will again request you to pause the video, think about it and answer on your own. Hopefully, you have paused the video and given it some thought. Let us discuss it now together.

So, well, I will argue it will come out vibrationally excited. Products will be vibrationally excited. Why? Because remember, for the forward reaction more vibrational energy was leading to more products. Vibrational energy leads to more products.

So if I reverse it and make the products or reactants, I am starting with the products now, and if I move to reactants, remember that Newton's laws are perfectly time reversible, I will end up in reactants having more vibrational energy. I just have more probability of that. So, therefore, products will be more vibrationally excited.

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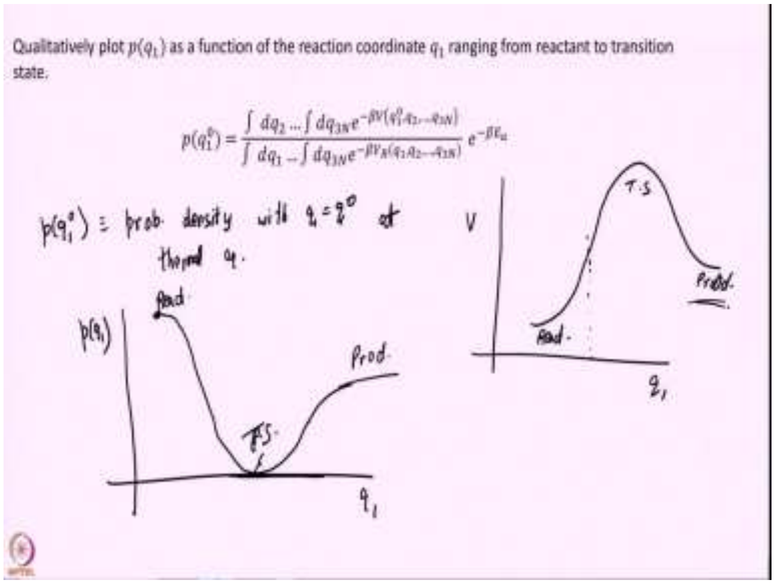

Qualitatively plot $p(q_1)$ as a function of the reaction coordinate q_1 ranging from reactant to transition state.

$$p(q_1^0) = \frac{\int dq_2 \ldots \int dq_{3N} e^{-\beta V(q_1^0, q_2, \ldots q_{3N})}}{\int dq_1 \ldots \int dq_{3N} e^{-\beta V_R(q_1, q_2, \ldots q_{3N})}} e^{-\beta E_a}$$

$p(q_1^0) \equiv$ prob. density with $q_1 = q_1^0$ at thermal eq.

So let us look at the next question. We looked at this function p of q1, which was defined earlier. And if I go from q1 ranging from reactant to product, make a qualitative plot of p of q1. So I will again request you to pause the video and think on it on your own. I very much hope you have paused the video. This is an interesting qualitative question. And hope you have an answer. Let us do it together.

First of all, how does V looks like as a function of q1? That one is easy. That looks like this. This is a reactant. This is transition state. This is product. P is the probability density with q1 equal to q1 naught. So if I set a certain value of q1 and I am asking at thermal equilibrium what is the probability that I will be finding q1 equal to this q1 naught? So, what do you think?

If I plot q1 versus p of q1, well, I will get a plot that is the exact opposite now. I am much more probable to be found at the reactant. It has a lower potential and thermal equilibrium refers lower potential. You have an exponential function actually. So this is my reactant and this will be my transition state. I have hit 0, which I should not have, but it will be very close to 0, and this will be somewhere my product.

Once more, why, because the transition state is at a much higher energy. Therefore, at thermal equilibrium it is much less likely for me to be present there. I am much more likely to be the reactant. So that is why I must go from reactant to transition state in this fashion. I have drawn the product version as well corresponding to this, but that was not part of the question.

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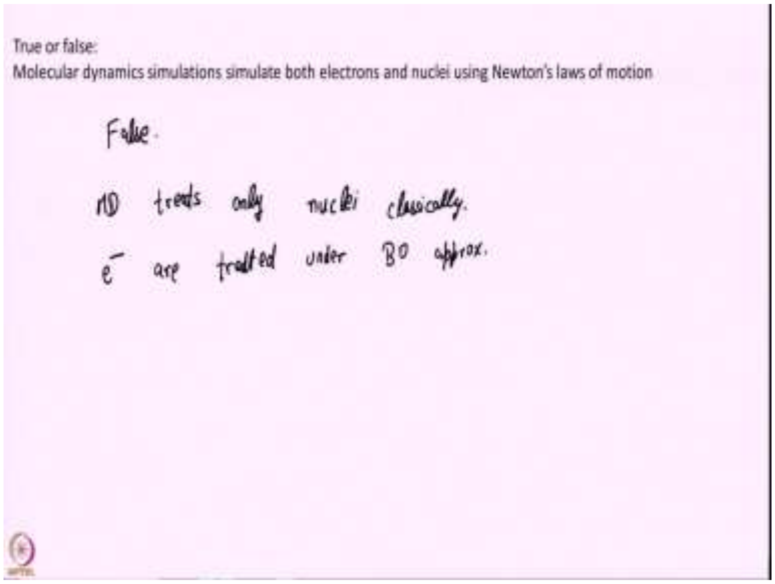

True or false:

Molecular dynamics simulations simulate both electrons and nuclei using Newton's laws of motion

False.

MD treats only nuclei classically.

e^- are treated under BO approx.

I have a few true, quick true and false questions. First one, molecular dynamics simulations simulate both electrons and nuclear using Newton's laws of motion, true or false? So think about it, pause the video and write your own answer. The correct answer is false. MD treats only nuclei classically. Electrons are treated under born-oppenheimer approximation, which is still quantum mechanical. So, molecular dynamics is not completely classical. Electrons still have retain their quantum mechanical nature.

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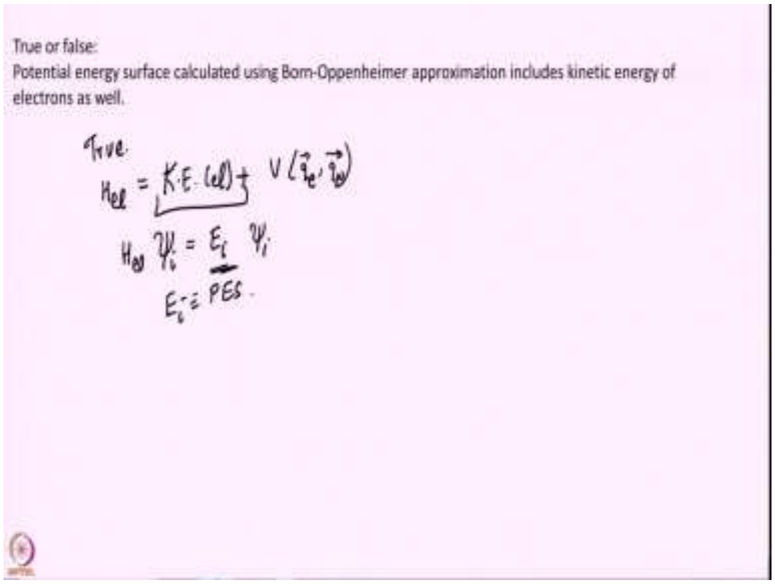

True or false:

Potential energy surface calculated using Born-Oppenheimer approximation includes kinetic energy of electrons as well.

True.

$$H_{el} = \underbrace{K.E.(el)} + V(\vec{r}_e, \vec{r}_N)$$

$$H_{el}\psi_i = \underline{E_i}\,\psi_i$$

$$E_i = PES.$$

True or false, potential energy surface calculated using BO approximation includes kinetic energy of electrons as well. Take your time and answer your question true or false. The correct answer is true. So, remember, born-oppenheimer surface is an eigenfunction of H electronic which is kinetic energy of electrons plus the potential energy of electrons comma nuclei and we solve H electronic psi i equal to Ei psi i and Ei is your potential energy surface. So this Ei actually has the contributions from kinetic energy of electrons.

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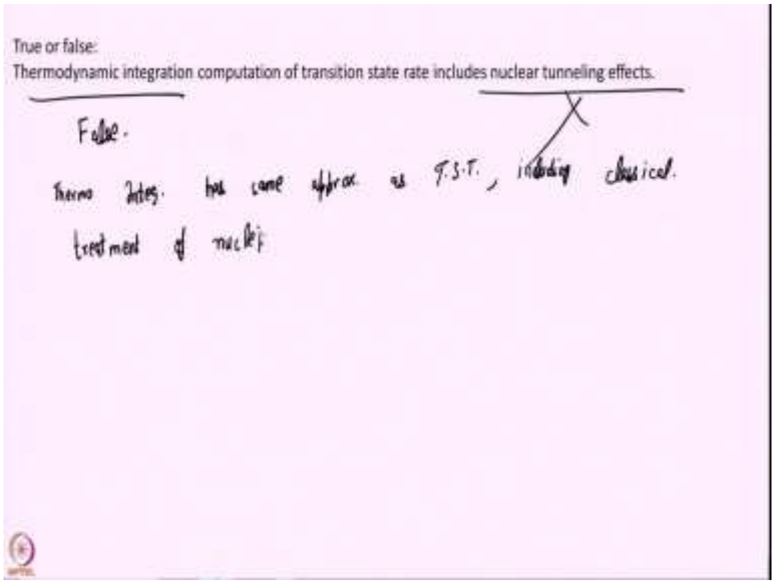

True or false:

Thermodynamic integration computation of transition state rate includes nuclear tunneling effects.

False.

Thermo Integ. has same approx as T.S.T., including classical treatment of nuclei

True or false, thermodynamic integration computation of transition state rate includes nuclear tunneling effects. Again, take your time, think about it and answer true or false. The correct answer is false. Thermodynamic integration is still treating nuclei classically. Integration has the same approximations actually as transition state theory including classical treatment of nuclei. So, nuclear tunneling effects are not included. So, with that, I will end here. Thank you very much.