Chemical Kinetics and Transition State Theory
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Lecture 34
Prediction from potential energy surfaces – rotational vs vibrational energies

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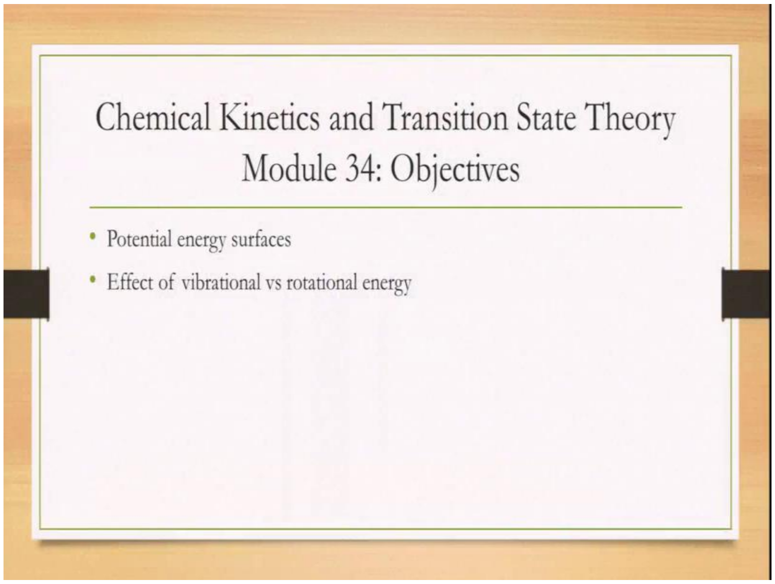

Chemical Kinetics and Transition State Theory
Module 34: Objectives

- Potential energy surfaces
- Effect of vibrational vs rotational energy

Hello and welcome to module 34 of Chemical Kinetics and Transition State Theory. So, we had previously briefly looked at molecular dynamics simulations as an alternate to calculating rate constants and looking at dynamics. Today, I want to just showcase the power of these kind of dynamics. We would not look at molecular dynamics, but the idea of a rolling spheres on potential energy surfaces.

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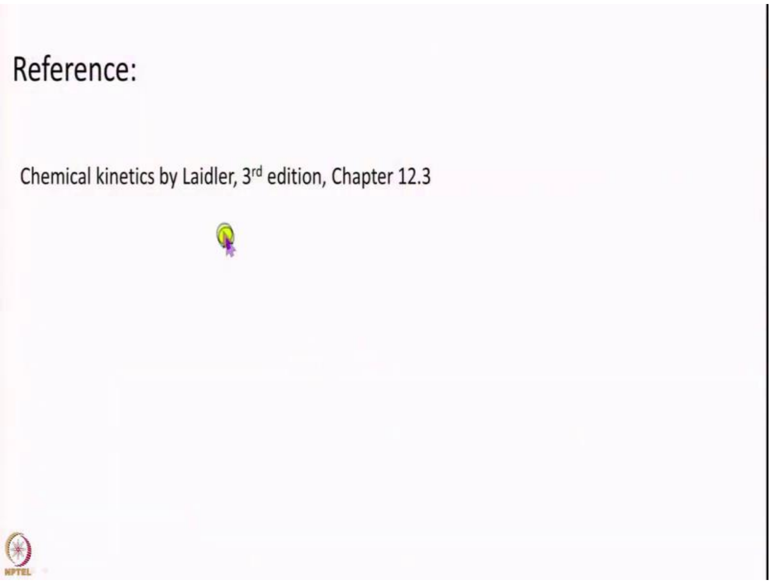

Reference:

Chemical kinetics by Laidler, 3rd edition, Chapter 12.3

So, the reference particularly that I will be looking at today is the Laidler's Third Edition Chapter 12.3.

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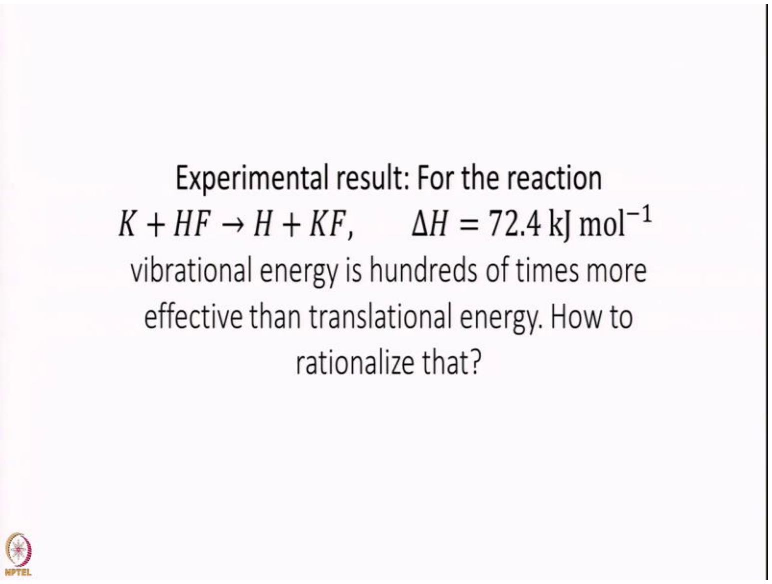

Experimental result: For the reaction

$$K + HF \rightarrow H + KF, \qquad \Delta H = 72.4 \text{ kJ mol}^{-1}$$

vibrational energy is hundreds of times more effective than translational energy. How to rationalize that?

The question I want to focus on today is one, plain and simple. I want to look at this particular reaction K plus HF going H plus KF. It is an endothermic reaction, but an interesting experimental observation. For this reaction initial vibrational energy of the HF molecule is hundreds of time more effective for this reaction to happen than the translational energy of K and HF. How to explain that?

So, remember, rate theory or transition state theory specifically cannot explain that, because one of the assumptions of transition state theory is thermal equilibrium. So, we assume all translation, rotation, vibration all whatever it is, is at equilibrium and there is no sense of extra vibrational energy or extra translational energy. So, we have to think of something beyond rate theories for this problem to understand.

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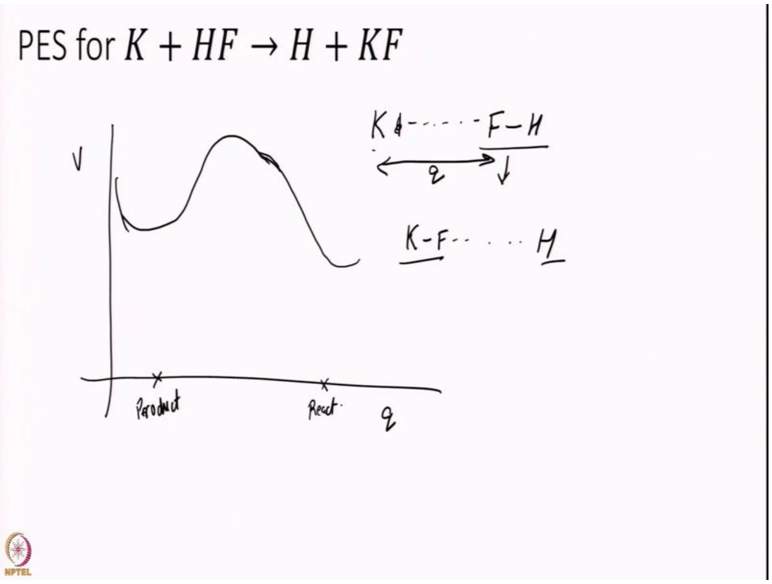

PES for $K + HF \rightarrow H + KF$

So let us start approaching and start thinking of these hills and ridges and valleys of energy surfaces. So let us start with drawing a one-dimensional energy surface. I really like one dimensional energy surfaces as you guys probably know already. So, I have the reaction which is K, let us say something like H, I will just write F first, we will see why, and the reaction that is happening is, I start with K plus FH going to KF plus H.

Let me just choose this distance q to be my reaction coordinate. So, when q is large, that is I am somewhere here, then I am reactant and when q is small, I am product. No big deal, it is just inverted, what is the big deal? So, I will get a reaction that will look something like, and remember it is endothermic, so it will look like this. It should be smoother than this, pardon my bad drawing.

Now, the question is looking at this energy surface, how do I explain the phenomena? How do I explain the difference between translational energy and vibrational energy? I cannot actually. For that we have to move to multi-dimensional potential energy surfaces. We will today think a bit carefully on how these multi-dimensional potential energy surfaces that actually I have drawn in multiple modules come about.

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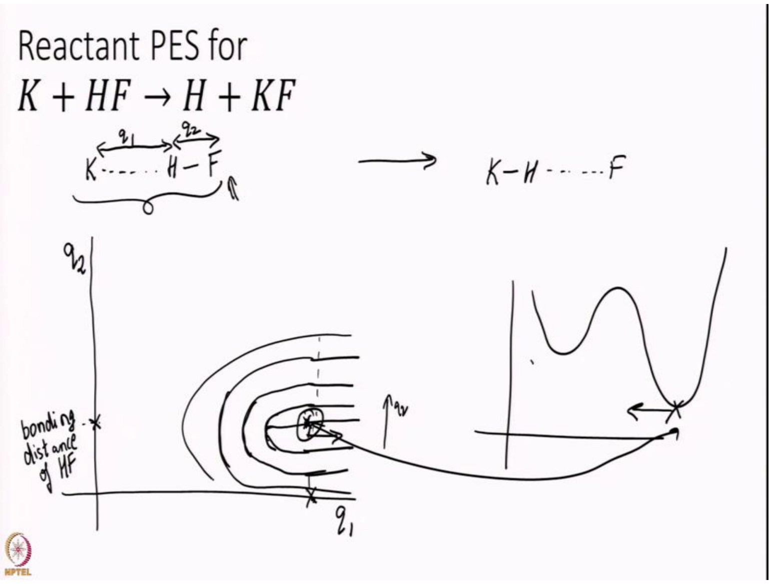

Reactant PES for

$K + HF \rightarrow H + KF$

So, let us get back to this same problem. I have K plus HF. So, I will write this as K HF, my apologies, I want to write this more clearly, F and I am going to K H. So let me just focus on this part first, just the reactant part. And now, in one dimension it is really not enough, I need at least two dimension for this phenomena to be explainable. So let me call this distance as q1 and this distance as q2. I have two distances now with me. Now you will see all the magic will appear.

So, I will have q1 here, I will have q2 here, and I will draw contour plots of the potential energy surface. So let us ask a few questions, if I am in this reactant state, well, I expect q2 to be small, by small I mean it is a bonding distance 1 angstrom or something whatever HF bond distance is and KH to be much larger than that. So q1 in the reactant configuration should be much larger and q2 should not be that large. It should not also be 0. It is some bonding distance. But this is, let us say, the bonding distance of HF, equilibrium distance of HF and some large distance of q1.

So, I get this point corresponding to, let us say, reactants. But I want to understand about this point, how does the energy surface look like? So let us move along q1 and q2 direction a little bit. So, if I fix q2 and I move q1, what do you expect will happen? So, by fixing q2, I have fixed HF bond distance and I am taking K and moving it farther apart let us say. So, I am let us say moving in the farther direction. What do you expect will happen?

Well, energy is not going to change much, K is anyway very far away. So, if you take it more far away, it is still not interacting. So, you get an energy surface that will be almost flat. So, my contour lines along the direction of q1 will look almost flat. So let me get rid of these arrows, which might be confusing. So, what I am drawing now are actually the contour lines.

What if I fix q1, but move F distance, q2 distance? So, I have fixed q1 K and H are rigid and I am moving F left and right, what will happen then. Well, you expect some kind of a harmonic post potential or a mass potential. So, along the q2 direction, you will have a gradient, a sharp gradient and this is simply the equilibrium, so this is the minima. So, we will get energy surfaces that will look like this close to the reactant well.

So, I get a harmonic oscillator like this here and as I am decreasing q1, well, slowly the potential will start changing. Initially, actually, you will see a maxima, which will eventually lead to the transition state. So, this is, I am trying to draw the same picture as I had drawn in the last figure. This point corresponds to the same point. So, as I move closer, initially the energy will increase. So that is why I get these kind of curves here. So, something like this.

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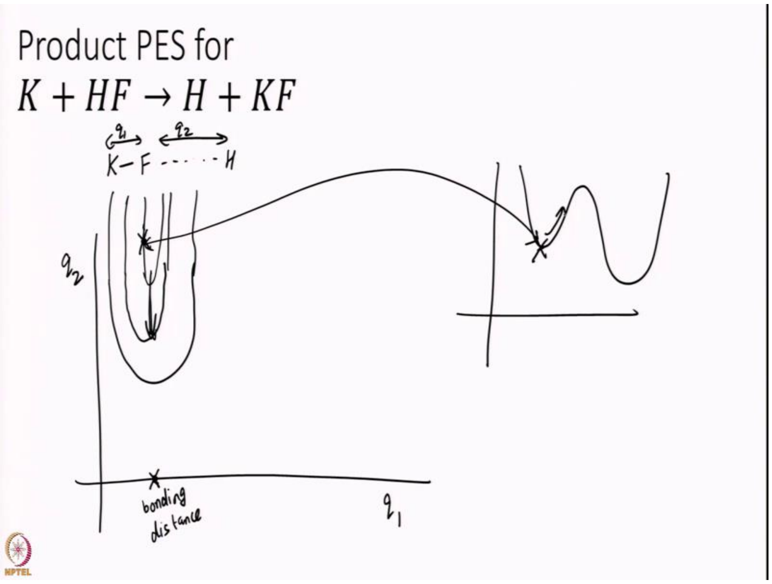

Product PES for

$K + HF \rightarrow H + KF$

So let us do the same analysis for the product. I have K, F, H, and this again is q1, same notation as last slide and this is q2. So, I want you to take a minute, pause the video and think how the product potential energy surface will look like, the contour lines of that. So please pause the video and draw these contour lines on your own.

Hopefully, you have taken a break and you have drawn some figures. So let us draw it together. So, first of all, for the product configuration, my K, F distance is small. So K1 will be somewhere here, q1, I am sorry, I gave you a slightly wrong problem. So, you will have to change your page notation. Just take your page wherever you have drawn your energy surface and rotate by 90 degree. So q1 is small, so I get this as my bonding distance. And q2 is large, so, this is the product configuration. So, the 1D surface that we had drawn, this point is the same as this point.

Now, if I vary q2, if I make q2 larger, well, I am just taking H and taking it farther away. So, the energy is not really going to change. So, again, I will get straight contour lines like this. While if I change q1, I will, it will look like a harmonic oscillator. So, the energy will change sharply along q1. And again if, as q2 becomes smaller, your energy will change and you will get this kind of a minima or you will get the energy surfaces to increase in this direction. So, moving in this direction is the same as moving in this direction.

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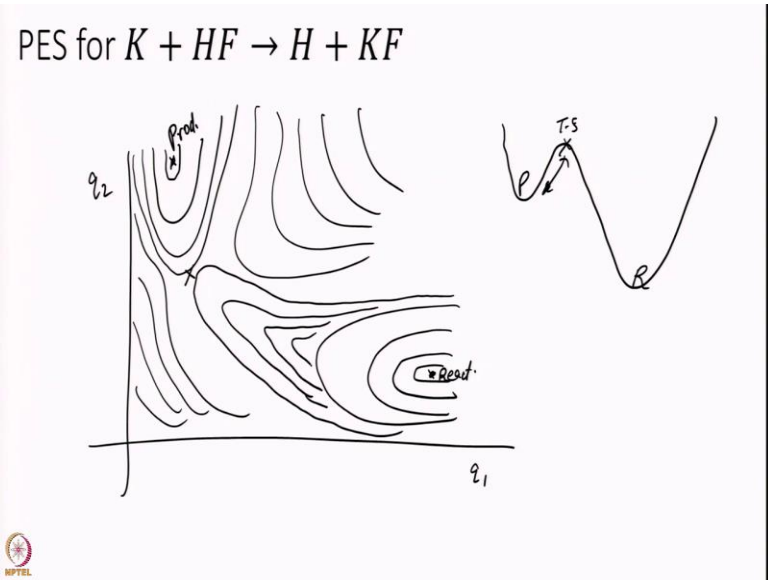

PES for $K + HF \rightarrow H + KF$

So let us put these two together and include the transition state as well now. So, I have q1, I have q2, I have the reactant surfaces that were looking like this. I have the product ones that are looking like this. Now, a one very important note and this is critical, it is endothermic. So, this point, this energy is much higher than this energy. This is reactant, this is product. Reactant is lower in energy.

So, your transition state will effectively be closer to product that is what you expect at least. Intuitively, your surface is look like this. So, you see your transition state will be closer generally. This is product, this is reactant, this is transition state. So, these surfaces will at some point start curving like this. Sorry, I have a slightly bad drawing, but I hope you get this idea.~~,~~

This curvature, let me just actually erase a few lines and redraw them, this curvature is extremely important in understanding our experimental result. So, this is how it will go, is going to look like. Reactant thing is going like this, it is turning around, this turn is extremely important in this, this like this.

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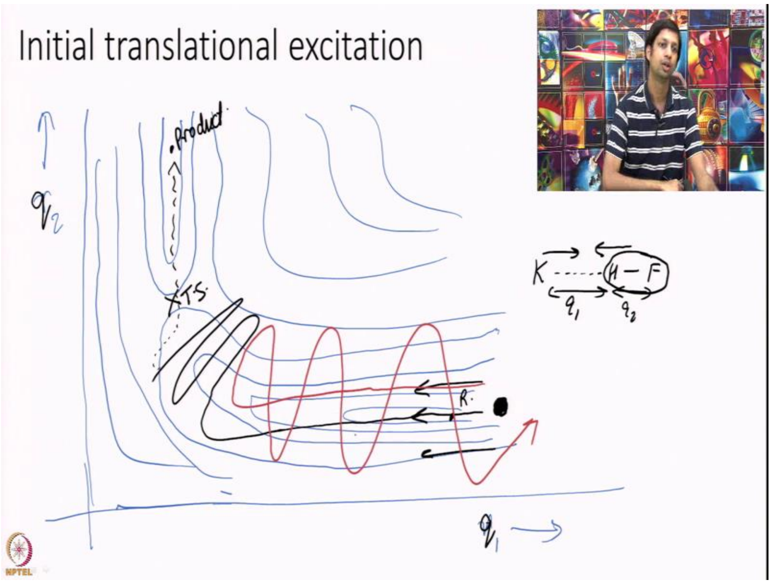

Initial translational excitation

So, this is what I have drawn and let us start thinking about dynamics on this energy surface. What I mean by dynamics on this energy surface is we are really going to think of marbles rolling on this energy surface. So, you have a minima here, some kind of a minima here. You have a maxima here, this is my transition state and this is my product. By the way, sorry, I could not find a good figure online.

So, I just drew it on my own. This is my reactant. So, I wanted to distinguish between initial translational energy versus initial vibrational energy. So, what does initial translational energy on this energy surface mean on this context of r1 and r2? Sorry, I you have been calling it q1 and q2. So again, let me just look at my notation K plus HF, K, H, F, q1, q2.

Initial translational energy means these to K and this whole HF are approaching each other very fast. Think of this K and think of HF as one entity and I am colliding them together like this. When that happens, see q2 then does not have a lot of energy in it. Q2 is not really moving. it is the HF as a whole that is moving. So, it is dynamics mostly along q1.

So, I literally want you to think on this complex energy surface. I have taken a little ball here, think of a marble if you wish and I have rolled this marble like this on this energy surface and I have thrown it straight forward. I have taken this marble here and taken this marble and just given it an initial kick along q1. So just kick the marble like this along q1. And I want you to think. This is very intuitive now, you can actually use a computer to simulate it but you do not have to. If you have this kind of a complex energy surface, complex all I mean is it has all these ridges and curves and turns arounds. What do you expect to happen? So, think about it.

Your intuition is good enough, we have everyday intuition. You see, since my energy surface is curving around, this thing is going to come up here and if the energy is not super high, well, it is going to do this kind of dynamics. And when that happens, sometimes if it is exactly right it might move in this direction. But if it is not too good, then maybe I will come here and hit and maybe I can also turn around like this. So, this does not seems very effective way of transferring energy. You see.

Because this translational energy that is coming in is become converted into vibrational energy. The motion, this, remember, this motion that you are seeing, oscillating motion along q2, this kind of motion, is exactly what vibration is. Your q2 is increasing, your q2 is decreasing, your q2 is increasing, your q2 is decreasing. Q2 increasing and decreasing means HF is vibrating.

So, this is just a bad, this translational energy just seems like a bad idea. Your molecules will come in and before they even reach the transition state, they will collide with these walls of your energy surfaces and there is some chance they might just turn around.

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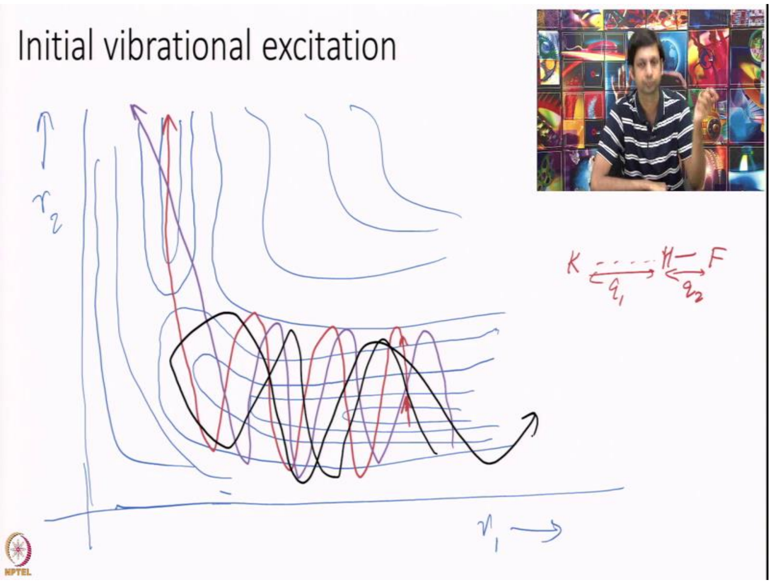
Initial vibrational excitation

What happens for initial vibrational excitation though? Initial vibrational excitation means along q1, I do not have a lot of energy. I have some energy, but not a lot. But I have a lot of energy along q2, where q2 again refers to the vibrational motion. So, I am sending the initial particle kicked in this direction. I put the, my cancha, my marble here and I kick it like this along q2. So, when that happens, your energy, your trajectory will move along like this. And you see this is just more conducive on passing through the transition state, it just helps.

What I have drawn, of course, is a much more convenient trajectory, but even if I do not choose it to be this convenient, if I draw a different version, you see, I can still be able to pass on like this. So, I can draw, well, not all of them are going to be perfectly reactive. What color to choose now? We choose black. Maybe someone of them might come and hit the surface like this and return back. That is possible, I am not denying it.

But now compared to translational energy, I am much better off. I am much better equipped to take this curvature. You have a road that is turning around like this and if you are, initially you had this oscillation with you, you can just turn much better. So now we understand why initial vibrational energy for this reaction is just so much more conducive for this reaction to happen compared to translational energy.

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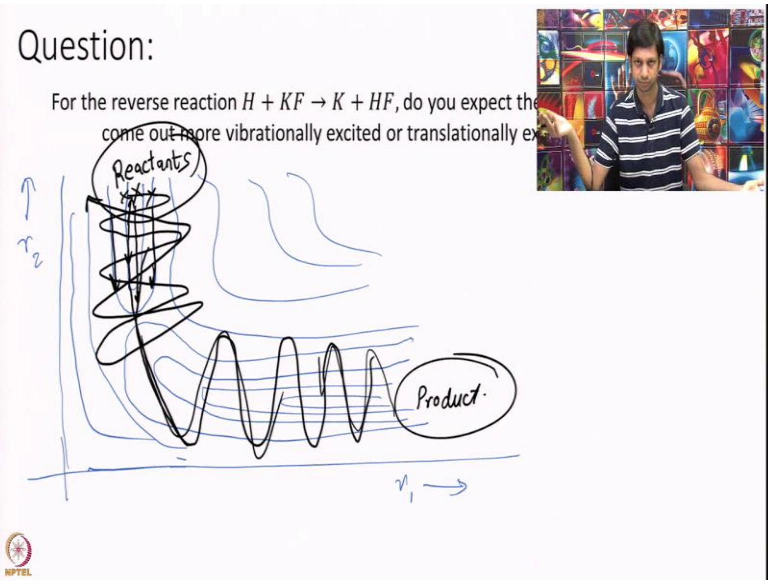

Question:

For the reverse reaction $H + KF \rightarrow K + HF$, do you expect the
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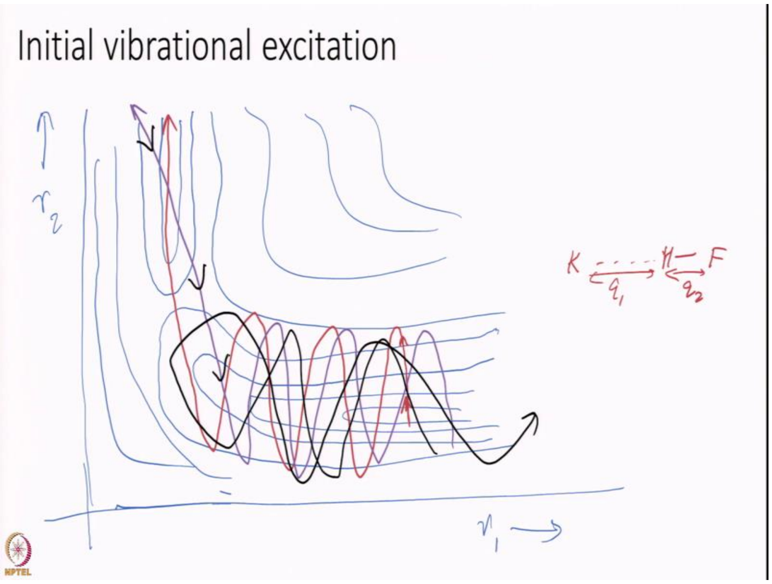

Initial vibrational excitation

So, I have a question for you now. For the reverse reaction, so far, we were looking at K plus HF going to H plus KF. I want to think of the reverse reaction. Of course, it is exothermic now, H plus KF going to K plus HF. Do you think the products are going to come out more vibrationally excited or do you think they will come out more translationally excited? So, it is a conceptual question. Pause the video and think about the answer.

Hopefully, you paused the video. This is an important conceptual question, if you have not paused the video, this is your second turn to do it, think about it. Let us move on though. Well, I will redraw my energy surfaces. So, for the reverse reaction, what it means is that this is now my reactants and this is now products. So, I am starting my trajectories here.

Well, what we learned so far is that starting here, if I had more vibration, I could have went to this side easier. Well, remember that molecular dynamics are invertible. So, if I am starting here, it would make sense for these trajectories to come here and start vibrating then. I am just literally taking the trajectories that I had drawn here and I am taking the arrow backwards. So, for each trajectory, I invert the arrows. That is your reverse reaction, which means that the products will come out more vibrationally excited. And again, I have, since I have reversed, sorry, these are my new products.

And additional information, now the translational energy will be much more effective for the reverse reaction. You can see it very clearly here. So, if I give translational energy like this, then I can go through this transition state very easy. And after I pass through the transition state, I will take this curved road and my trajectories are going to bend around and do this vibrational motion. But initially, if I had provided vibrational energy, then you will come here and you see you have a good chance of returning back like this.

So now the thing has completely reversed. Initial translational energy is more effective if I start in this region and when I end up in the product region, I expect I will be more vibrationally excited.

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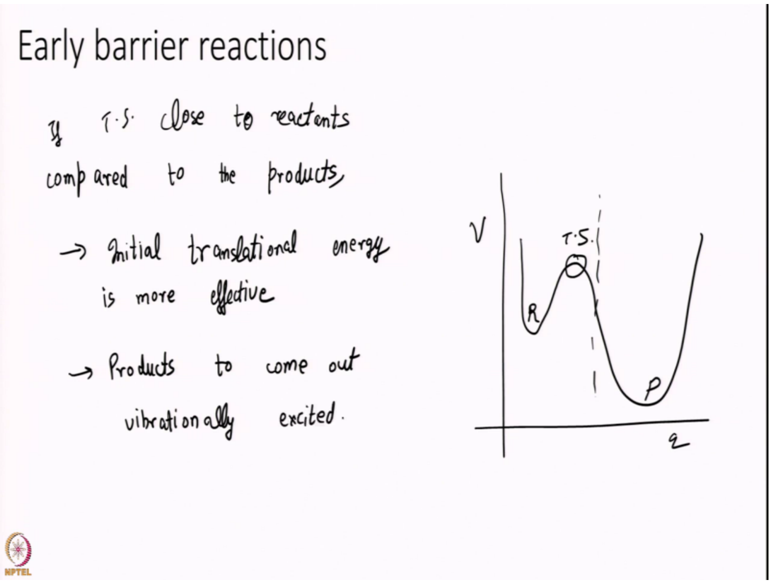
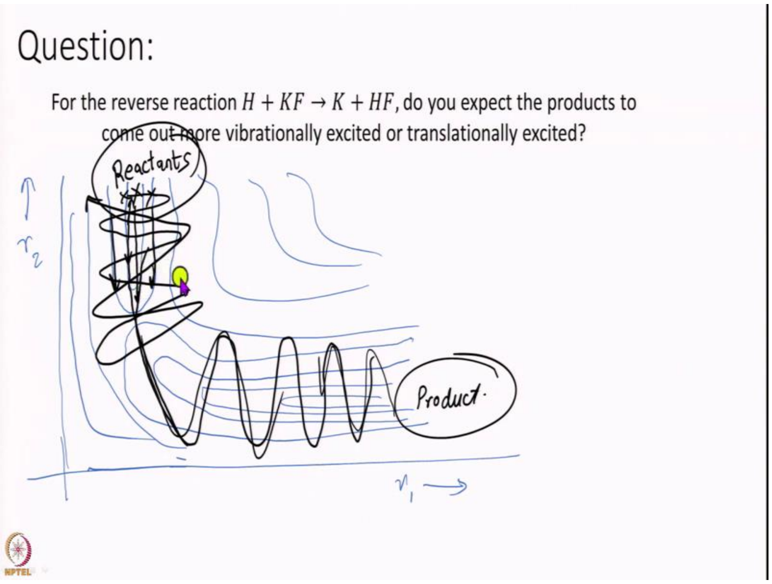


Early barrier reactions

If T.S. close to reactants compared to the products,

→ Initial translational energy is more effective

→ Products to come out vibrationally excited.



Question:

For the reverse reaction $H + KF \rightarrow K + HF$, do you expect the products to come out more vibrationally excited or translationally excited?

So, I just want to make things a little bit more concrete. This is true for a wide variety of reactions, not only for this K plus HF going to HK plus F, not only for this specific reaction we have looked at. So, for all reactions, in general, this is a rule of thumb, exceptions exist, but our intuition at least is, if I have a early barrier, early barrier really means that if I draw my energy surface along some reaction coordinate, my transition state is much close to the reactants compared to the products.

So, if transition state close to reactants compared to the products, what do I expect then? Initial translational energy is more effective. So, this is exactly this problem, where my transition state here, was closer to reactants than this was to product. In this case translational energy is more effective compared to vibrational energy. And I expect products to come out vibrationally excited.

So again, this is a rule of thumb, exceptions exist, and do not end up mugging this rule up. Use your brains. If you see a new reaction, you must always ask, how will balls roll on this kind of an energy surface.

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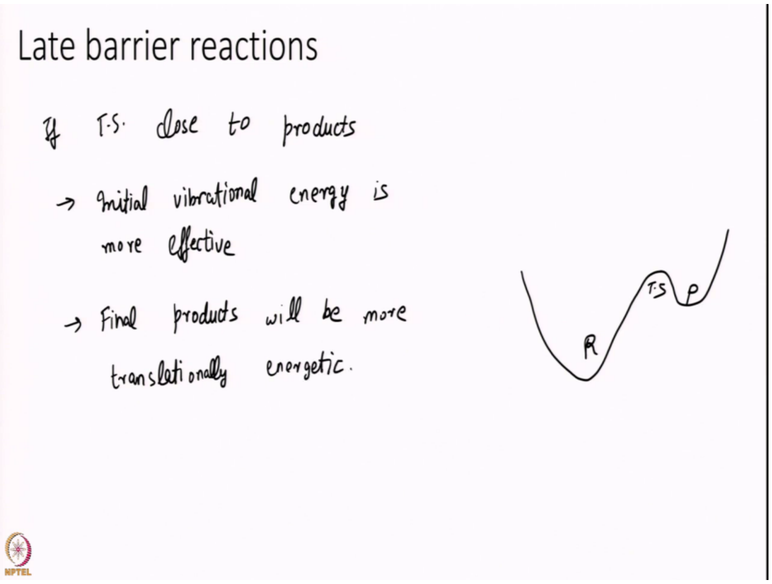

Late barrier reactions

If T.S. close to products

→ Initial vibrational energy is more effective

→ Final products will be more translationally energetic.

For a late barrier reaction, I will make the appropriate conclusions. So, if this looks like this. This is my transition state, this is reactant, this is product. Well, for this, if transition state close to products initial vibrational energy is more effective, just the reverse, the problem that we discussed for the most part of this module. And final products will be translationally excited, will be more translationally energetic.

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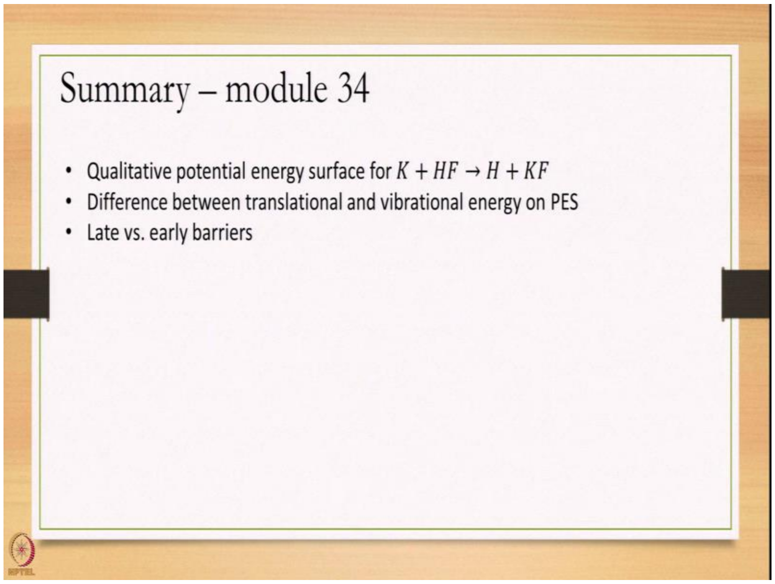

Summary – module 34

- Qualitative potential energy surface for $K + HF \rightarrow H + KF$
- Difference between translational and vibrational energy on PES
- Late vs. early barriers

So, in summary, what we have looked today is how to use this information of balls rolling on energy surfaces to think of dynamics and we have looked at a very specific, somewhat simpler example, of H K plus HF going to KF plus H and try to understand how translational and vibrational energy can change the rate of the reaction. Thank you very much.