# Concepts of Chemistry for Engineering
### Professor Chidambar Kulkarni
### Indian Institute of Technology, Bombay
### Center of Distance Engineering Education Programme
### Lecture 67
# Salient features of H3 potential energy surface

Hello everyone, welcome to a module on intermolecular forces and potential energy surfaces. We are still discussing about potential energy surfaces. And in the previous lecture we had looked at the potential energy surface of H3 system in some detail. So, in this particular lecture we shall look at some of the salient features of the H3 system or the more generally A B plus C gives A plus BC system. But before we do that, let us just recap a memories on what we had discussed in the previous lecture.

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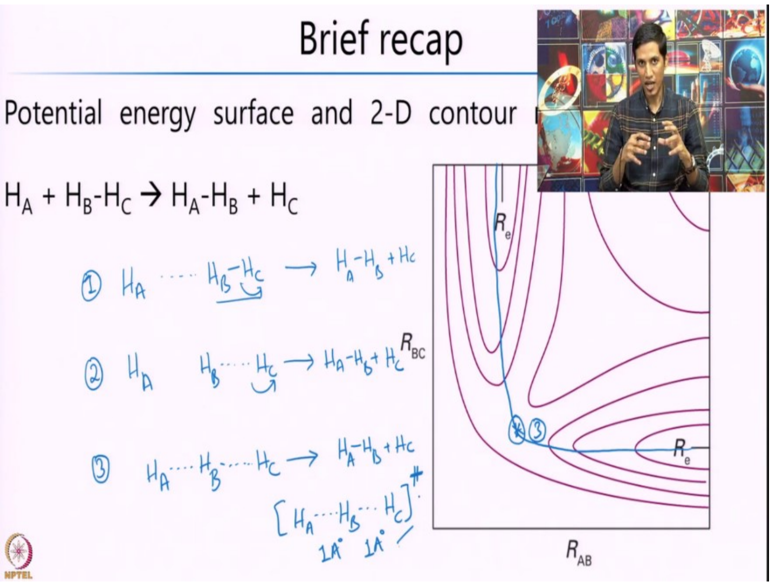

Brief recap

Potential energy surface and 2-D contour

$H_A + H_B\text{-}H_C \rightarrow H_A\text{-}H_B + H_C$

① $H_A \cdots H_B-H_C \longrightarrow H_A-H_B + H_C$

② $H_A \quad H_B \cdots H_C \longrightarrow H_A-H_B + H_C$

③ $H_A \cdots H_B \cdots H_C \longrightarrow H_A-H_B + H_C$

$[H_A \cdots H_B \cdots H_C]^{\neq}$

$\underset{1Å}{} \quad \underset{1Å}{}$ ✓

In the previous lecture, we had looked at the potential energy surface of H3 system, how does it look like and we would also see how does one map the H3 system three-dimensional surface onto a two-dimensional contour maps that is the one diagram which you see on the right-hand corner. And here we had said that the one could traverse different paths in this particular two-dimensional contour and that would tell me about the different trajectories which are possible for the given system.

So, just to put in perspective, we had said that one scenario is HA approaches HB, HC, and only on its close approach, this would break out and you would form HA, HB, plus HC, that is, this is HA, HB is the one which takes place whereas, this HB, HC bond remains constant and at almost the equilibrium bond distance between HA, HB, HC would break out and then you would end up in a product, this is one path we had said.

And the second one we are told was that these are the two extreme conditions that is in this case the HB, HC bond elongates first and HC almost leaves and then the HA comes and bonds that could also give you the HA, HB plus HC. And third scenario is what we had said is that both the approach of HA and the living of the HC would take place to almost the same extent throughout and that would give rise to this HA, HB and HC.

And we had drawn this as a plot something like this where you would go from here. So, this is what the scenario 3 would look like. And we said that the scenario 3 is the one, which would give rise to the product because that take goes over the saddle point or the transition point, which is marked with an asterisk sign here.

So, the important point to note is that, the at saddle point, or let us say, if I draw this at this point, what you would have is, you would have HA, HB and HC so this bond distances are roughly around one angstrom here, and both are equal, and they are roughly about one angstrom. And the barrier which one crosses, that is, I am starting with A here with interacting with an HB, then I will go up the hill that is at the saddle point and then I come down and fall into the product that is HA, HB.

So, the height of this barrier is typically about 10 kcal per mole or 10 kilocalories per mole. And what needs to be noted is that, this is much lower than the amount of energy needed to break the complete hydrogen bond by complete H2 bond. And also, this H3 system which is shown here is actually a transient system, and it actually does not exist or it or one can only identify it by what are called as femtosecond or transient spectroscopy. Other than that, it is very hard to actually isolate these species and look at them experimentally.

So, I hope, this sort of refreshes your memory back on to the potential energy surfaces, and also on to the different pathways or the trajectories which one can follow on a two-dimensional contour of the H3 system. So, having looked at this, now, what we shall go ahead and do is we shall look at a little more salient features of this particular system.

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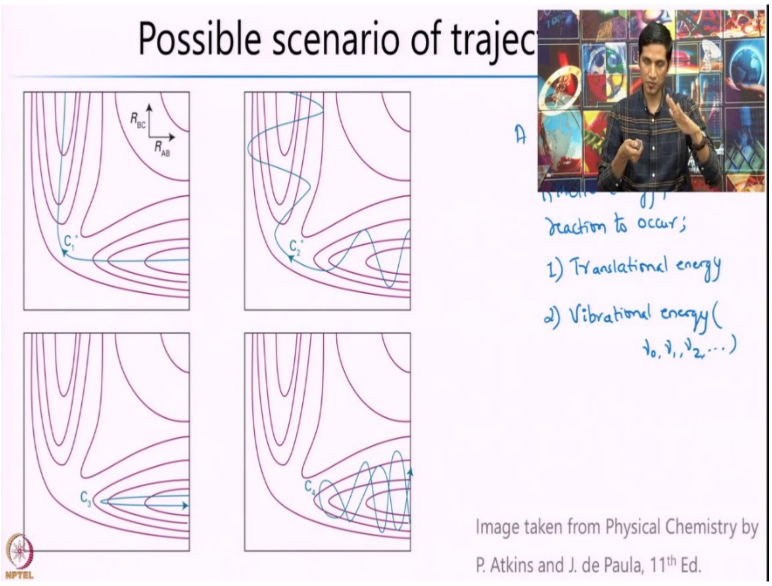

Possible scenario of trajec

A

reaction to occur;

1) Translational energy

2) Vibrational energy( $\nu_0, \nu_1, \nu_2, \ldots$)

Image taken from Physical Chemistry by P. Atkins and J. de Paula, 11th Ed.

And so, for that I have just drawn again shown you the same trajectory which we looked at in the previous slide that is, I have the HA, HB system where I am going from the reactant to the product that is AB going from BC. So, what is important here is that for a reactant to go to the product, it must have the enough amount of the kinetic energy to go and cross the barrier or the hill.

So, once it crosses the barrier or once it reaches the saddle point or the transition state region, then it would actually invariably go and fall onto the other side where it would lead to the formation of the product. But for it to go from the reactant side to the transition point, it should have enough of kinetic energy. I hope, you all agree with that.

If you agree with that, then the kinetic energy can come in different forms. One of the ways is that, it can have, the molecules can have just a translational energy, which is which will also contribute the kinetic energy or the molecules can actually exist in excited vibrational states, which would also be part of the kinetic energy. So, I will just write down the two components of it for the general AB system.

So, let us say I have A reacting with BC giving AB plus C this is the general reaction. So, the kinetic energy for the activation for reaction to occur can be divided into two parts. One is the translational energy of the molecules, and the two is the vibrational energy. So, that means, it could exist either in the mu 0 or mu 1 or mu 2 or the excited state so on and so forth.

So, these are the two primary ways in which the kinetic energy can be subdivided. And here what we said in the first case is that, we have a starting material that is BC at equilibrium bond length interacting with A and that would give rise to the product as shown here. So, now, let us look at a scenario where the kinetic energy is broken down into these two parts.

The first one is a scenario in which the ground state of the BC that is if you look at this, this one, what you see is that, it has, you actually see sort of wiggly lines. The wiggly lines represent that the BC bond is no longer in the ground state of the vibrational energy it is in some other excited state that is either the mu 1, mu 2 or higher excited states.

So, then what happens is, it would come in contact with a molecule of A which is approaching it, and that would interact and cross this the saddle point and go along this direction and lead to the product. Interestingly, in this case, what you observe is that the product which comes out is also in the excited state or will also be in the excited state, that is the AB would also be in a vibrational excited state rather than a ground state.

This is because the BA bond which we started with is initially with an excited state and has enough energy to collide with A to give rise to the product. This is a simpler scenario. So, now let us look at another scenario where what happens is, I have the A coming and approaching the BC. Now, all of them are in the vibrational ground state. However, the approaching A does not have enough of translational energy. So, in that case, it will actually not be able to cross the barrier, it will never come and hit the saddle point. As a result, it would actually just sort of keep going back and forth in the reactant region.

As a result, you will no longer have the product formation in this connection. And the last scenario is, let us consider the BC which is this one in the vibrationally excited state. However, the collision energy of the vibrational excited state BC with A is actually not enough for it to actually cross or go along this saddle point. So, even in that situation it would actually keep doing a back and forth motion in the reactant region, as a result, one would not observe the formation of the product.

So, by looking at these different cases, I hope what we have learnt is that, the kinetic energy or the kinetic energy for the for crossing the, for processing the activation barrier can come in two different forms. It can come as a purely translational that is the case number 1 here to the extreme left it can be purely translational or it could also come in the form of excited state vibrations which could also help in crossing the transition state. So, both of these do contribute to crossing the transition state, and thus lead into the formation of the products.

So, having sort of learnt about the different contributions to the kinetic energy and the role in dictating the formation of the products. Now, let us look at two different kinds of potential energy surfaces, and they are namely called as attractive and repulsive potential energy surfaces. So, you must be wondering what is this attractive and repulsive he is talking about.

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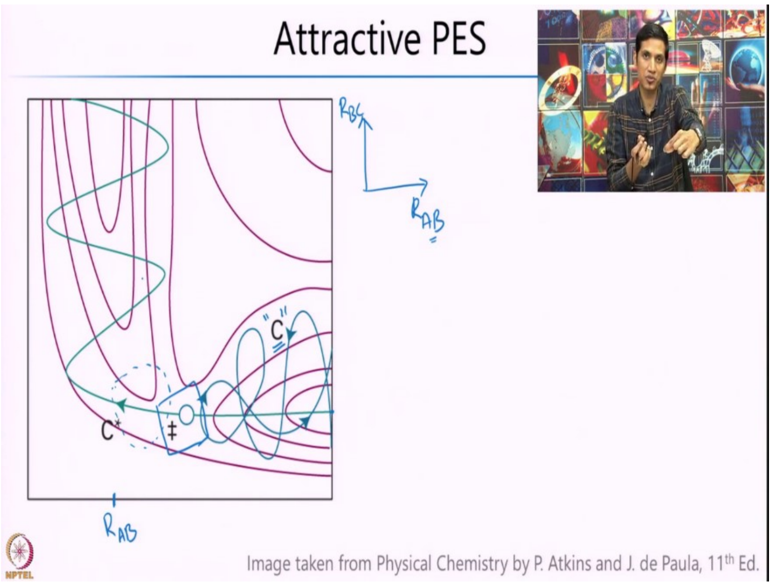

Attractive PES

Image taken from Physical Chemistry by P. Atkins and J. de Paula, 11th Ed.

So, let us try and understand what does the term attractive and repulsive mean here. So, I hope, you remember that this is rBC and this is rAB then AB is the product and BC is the reactant. So, here what we are looking at is the reactant, and this equilibrium bond length, this one is the rAB of the product.

And if we now look at the position of the transition state or the position of the saddle point along this along this two-dimensional contour map, what you see is that in this particular case of attractive potential energy surface, you see it lies somewhere here. Whereas, initially, when I talked about it was somewhere in this direction in this region. It was exactly at the middle of the both these mean equilibrium distances.

However, when you come to the attractive, you see that it has shifted slightly towards the right-hand side of the x axis. And when you go to the repulsive potential energy surface, you will see that it comes to the left of the equilibrium rAB. And the reason for this or the why we call this attractive and repulsive is because, if you now look at this particular position, now, it attains the or this is the saddle point or the highest energy point is now more closer to the reactants, that means, the position where you cross the highest energy barrier and fall into the product is now much more closer towards the reactant, that means, it is very easy to form the products or the reactants are both the reactants are easily coming in contact with one another to form the products.

Whereas, when you go to the repulsive part, you will see that you need to bring both the reactants at a far closer distance for them to actually undergo an interaction and then give rise to the product. So, having looked at what do we mean by this attractive and repulsive potential surfaces now, let us see a couple of trajectories on this diagram.

Let us say I am starting with the trajectory C here, which is this trajectory, which you are seeing here. What I do is, I am starting from a vibrationally excited state of the BC and it goes on, and then it encounters the other reactant A, but then, it now actually falls back into the reactants and it does not really end up in the product.

However, if it had purely a translational energy in the kinetic energy is purely translational, then let us see what could be the profile. So, in that case, I would go along this green line. I hope you all can see this here that I am going along this green line here. And since it is purely translational, it is going to go and hit the transition state or the saddle point.

And once it hits that it is almost out downhill. So, now we could go along the same path. But now because the system is not symmetric or the transition point or the saddle point is asymmetric actually what will happen is, the product would go actually go and bounce on the surfaces of the potential energy surface.

So, if you can think of a well, if the now the reactant come and cross the saddle point, now they are going to go and hit the wall of this potential energy surface, and then they bounce back, and then finally trickle down to the final product. As a result, the product one obtains is also in the excited state. So, I hope, this gives you an idea of an attractive potential energy surface.

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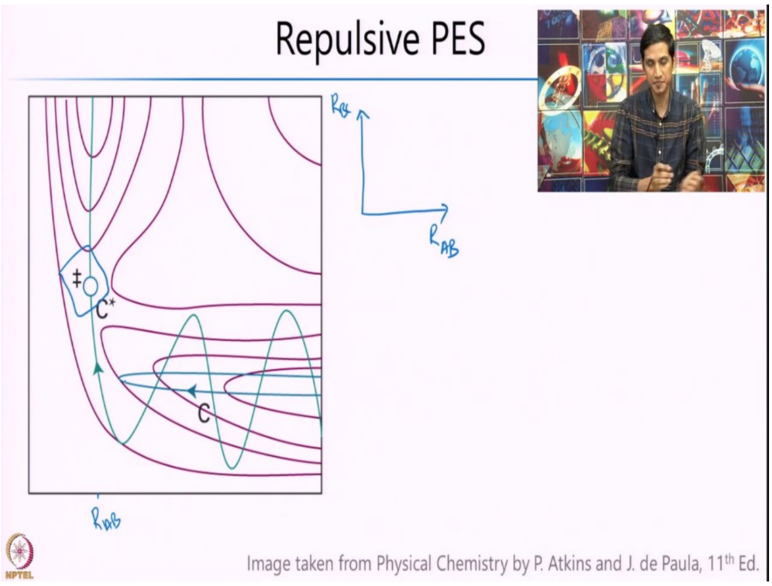

Repulsive PES

Image taken from Physical Chemistry by P. Atkins and J. de Paula, 11th Ed.

Now, let us go ahead and look at a repulsive potential energy surface. In this case, what you see is at again, I will just draw the same picture that you have the rBC and the rAB. Now, you see that the saddle point is actually at a much closer internuclear distance of rAB.

And here, again, one can do the same exercise, that is I can think of the kinetic energy for the reaction to be completely translational. So, if that is the case, I would have a scenario in which the path C would be followed, that is, I go along this line, it is purely transitional. It would go but it would now actually hit higher energy surface wall. And that would actually not lead me to any of the products, it would, that would mean I would still be in the reactant space that is the right-hand side.

However, if I start with the higher energy or higher vibrationally excited state, that is the green curve here or the green trace or the C star trace, then what I would say is that it would actually start bouncing off from the walls. And as a result of this, it can actually cross this the corner which it has, which it encounters.

That is the reason, why, in the repulsive potential energy surfaces, having the molecules in the vibrational excited state would actually result in the formation of the product because then that would go through the saddle point and that would ultimately give rise to the formation of the products.

And here, again, as you can imagine, once you hit the saddle point, you are just going sort of down the hill or down the lane. As a result, the products you would encounter are in the ground state compared to the attractive potential energy surfaces where the products you encountered were in the vibrational excited state.

So, these are sort of the opposite sides of the spectrum one can think of like that. So, this I hope, this sort of gives you an idea of what are repulsive and attractive potential energy surfaces. And with this, we shall stop this lecture. And in the next lecture, we shall look at a couple of more examples of potential energy surfaces. Thank you.