Concepts of Chemistry for Engineering
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Lecture 65
Introduction to potential energy surfaces

Hello, everyone, welcome to the module on intermolecular forces and potential energy surfaces. In the last few lectures, we discussed about various intermolecular forces, and what are the consequences of those forces on the properties of gas molecules. Now we will move on and start looking at what do we mean by potential energy surfaces and how do we try to understand them. But before we get into potential energy surfaces themselves, let us just do a quick recap and try to see how intermolecular forces or potential energy surfaces are related with one another.

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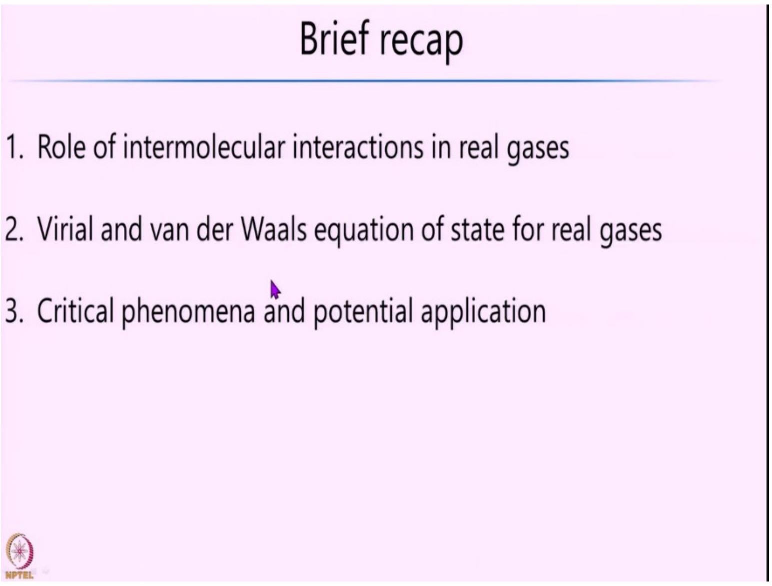

Brief recap

1. Role of intermolecular interactions in real gases
2. Virial and van der Waals equation of state for real gases
3. Critical phenomena and potential application

So, in the last few lectures, we have been looking at role of intermolecular interactions in real gases. Here, we had said that, because of the induced dipole, induced dipole or what are called as London dispersion or van der Waals interaction, real gases do experience an attractive force between them when they are at a close distance, the molecules are at a close distance. And in addition to a repulsive forces, which also come in when the molecules are really close to one another, actually contribute to a lot of the properties of real gases.

And we are trying to capture these properties using two formalisms or two kinds of methods. One is called as the virial equation of state and the second one was called as the van der Waals equation of state for real gases. In the van der Waals equation of state, we had tried to construct the equation using a very phenomenological arguments or very intuitive arguments based on the interaction between molecules. And we had also looked at some of the advantages and the limitations of van der Waals equation of state.

And, finally, we had seen what are called as critical phenomena or critical points which are associated with it, and some of the potential applications of these phenomena. For example, in selective and benign extraction of chemicals from a given mixture and this can be achieved by varying the temperature and pressure. And we have taking the example of supercritical carbon dioxide to illustrate this.

So, having learned this, and now let us try and jump into what are called as potential energy surfaces. But just to give you sort of a brief distinction between the two, what we looked at so far was interaction between molecules. And by that, I mean, there was actually no change in the bonding which was taking place.

So, the bonding was intact that is I had a molecule A and molecule B, which were actually floating around in solution, and they were interacting with one another. And this is what we were primarily concerned with, when we looked at intermolecular forces and the consequence of that on the properties of real gases.

Now, when we jump into potential energy surfaces, we shall actually go away from looking at intermolecular interactions and we shall actually look at the bonding or how when two atoms or ions come together, they actually bond to give rise to a covalent system. And that is what we would be primarily interested in.

And in this lecture, I will try to introduce to you what are called as potential energy surfaces. And in the subsequent lectures, we shall look at some of the examples to concretize the ideas built up in this lecture. With this now, let us begin by looking at intermolecular or interaction potential of diatomic molecules.

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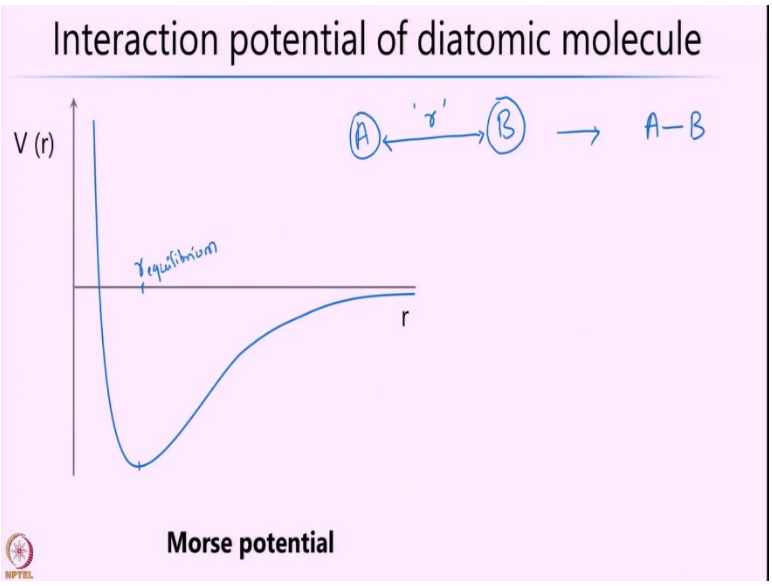
Interaction potential of diatomic molecule

Morse potential

Here, let us say, I have two atoms or ions which are interacting. For example, I have an atom or ion A, and similarly an atom or ion B, which are actually now interacting and they would ultimately give rise to a covalent system that is A, B. This is what I am trying to look at. How do A and B come together to form A, B covalent bond. So, if you look at the interaction potential or how does the energy of the system vary, as a function of this distance r, then one would end up in a diagram like this.

So, here, on the x axis, what I have is r, which is the distance between the two atoms or the ions, that is A and B. And on the y axis, I have the interaction potential of the system V of r. And I guess, you would already be reminded of something which we had looked at when we studied van der Waals equation of state in the previous lecture. That also had a very similar nature of the curve, where, at a very large distances, we had almost the 0 energy, which means the isolated energy of both the units A and B.

And as we come down along this line or as the constituents come closer to one another, they do interact, and they actually now form a covalent bond. And this, the length at which the energy is minimum is called as the equilibrium bond length or the equilibrium length, and it is labeled as r0 or we can call it r equilibrium this point.

And one, if we actually now go beyond this, I mean, if you try to even get the two units closer together even further, then they would actually repel because you are getting them because the Polly's exclusion principle and thus the energy would actually really go higher in energy.

So, this actually explains very nicely, how the interaction energy or interaction potential varies when I bring into atoms or ions, such as, A and B in this case. And this is, this potential is also called as Morse potential. So, the point to note is both, Morse potential and the Lennard Jones potential might look very similar in the nature of the curve, but they do have a very distinct and a different mathematical formula which describes them.

And another very key distinction is, the Morse potential is for a diatomic system where there is a covalent bonding takes place. Whereas, the van der Waals equation or the Lennard Jones potential is for two atoms, which are actually in a non-bonded interaction, that is, there is no bonding which is taking place between the two atoms or between the two molecules, such as, methane, and ethane or two any atoms, any molecule which we are trying to look at.

I hope, that distinction is clear. And so, this might look very simple and easy, how the interaction potential would look for a diatomic molecule. But now, things become actually far more complicated as we go away from diatomic molecules because, in reality, we do not just have diatomic molecules such as HF, H2, KI and many different systems, but we do have more different complex molecules to deal with in our life.

Like we deal with water, we do have amide bonds are many different kinds of molecular entities, which undergo reaction to form a covalent bond. So, how would one capture the interaction potential of such a system, which has more than two atoms in it? So, let us go ahead and see how we can do this.

So, in order to do that, we need to understand what are called as degrees of freedom and their association or their relationship with chemical reactions. So, I am sure, you all agree that if I take a system, which has n different atoms or ions and if I now look at what are the different degrees of freedom, I am sure you will all agree that the degrees of freedom is given by 3 n.

Because three comes from the three axes along which the system can freely undergo any kind of rotation, translation or vibration. So, you have x, y, and z direction, and each of the atom can go along these three accesses in the Cartesian coordinate or the similar accesses in a polar or spherical polar coordinates.

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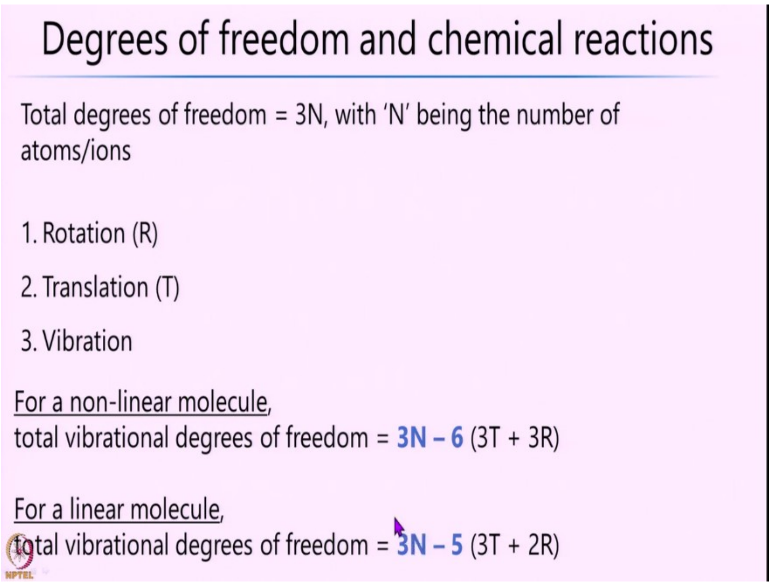

Degrees of freedom and chemical reactions

Total degrees of freedom = 3N, with 'N' being the number of atoms/ions

1. Rotation (R)
2. Translation (T)
3. Vibration

For a non-linear molecule,
total vibrational degrees of freedom = **3N – 6** (3T + 3R)

For a linear molecule,
total vibrational degrees of freedom = **3N – 5** (3T + 2R)

So, now, that means, that if I take any particular general system, then I would have 3N degrees of freedom to that system, where N being the number of atoms or ions in the constituting the system. And these 3N can further be divided into what are called as rotational or translational and vibrational degrees of freedom. So, that means the molecule has all these three ways in which it can actually move around. So, if this is the case, now let us go ahead and deconvolute or look at only the vibrational degrees of freedom. And I will come to that in a minute, why we are only interested in the vibration.

So, let us say, if I take a molecule which is nonlinear. For example, I have a molecule of a water or ammonia or any other subsystem, nonlinear system and the total number of vibrational degrees of freedom of such a system are given by 3N minus 6. So, I will tell you where this number 6 comes from. So, this 6 comes because the molecule can undergo three degrees of motion of translation.

That is, it can, if you take this as a molecule that can go under, it can translate along the one direction, one axis, other, as well as the next axis. So, along all the three axes, that is x, y, and z, the molecule can undergo translation. So, that gives me three degrees of freedom of translation. And now, the molecule can also undergo rotation along the three axes, that is x, y, and z. So, that gives me again three degrees of freedom which corresponds to rotation.

So, if I am interested in only the vibrational degrees of freedom, then all I need to do is, take the total degrees of freedom available to the molecule that is 3N in this case, and from this, I will subtract the contribution from the translation and the rotation, then what I will be left with is the vibrational degrees of freedom for a given system, which is nonlinear.

Similarly, one can also do this exercise for a linear molecule, and there is a slight difference. And what you find is that, the total vibrational degrees of freedom for a linear molecule is actually 3N minus 5, but not 3N minus 6. This is because you have the same three degrees of three translational degrees of freedom for a molecule along the x, y and z direction.

However, the degrees of freedom for rotation is now reduced by 1. This is because if you take a molecule which is actually linear, and if you actually rotate along this axis itself, then you do not see any change. So, you only have a rotation possible along the two orthogonal axis to this either this or this. If you rotate along the molecular axis, you do not see any change.

Thus, for a linear molecule, you only have two degrees of freedom for rotation. And now, if you do the same thing, that is, I take the total degrees of freedom for a particular system and subtract the translational and the rotational degrees for a linear molecule, which is totally 5. And then I would end up with 3N minus 5 degrees of freedom for a given system.

So, this looks, I think, at least intuitive or easy to understand. And you must be wondering, why is he telling us this or what is the relevance of this to the potential energy surfaces because that is what we started out by discussing. So, if you actually look at the degrees of freedom, and we are now currently only interested in the vibration, because if you think of chemical reactions, for a reaction to happen, let us say if I am holding a bond like this, for reaction to happen, that is either for this bond to break or for this bond to form between two atoms, the molecule should be vibrating.

Only when the molecules are vibrating or when the molecules are actually undergoing some sort of a torsion or a distortion, then you would have a chemical reaction take place and that would lead to a change in a potential energy. However, if you just have a molecule from one position going into another patient or just rotating along an axis in the system, then you will not have a significant contribution towards a chemical reaction.

That is the reason why we are particularly interested about vibration, because generally vibrational degrees of freedom are the ones, which constitute or which actually are the dominant degrees of freedom, which lead to a chemical reaction, when molecules actually come and collide with one another.

So, I hope, this idea of vibrational degrees of freedom being connected to chemical reactions is clear. That is, you can think of the atoms as actual like springs, which are actually vibrating around or moving around and if the two units which are moving around come and hit one another, then when because of this vibration, the change in the bond order is what would lead you to your chemical reaction.

So, I hope, this idea of vibrational degrees of freedom being connected to chemical reactions is clear. So, with this, we shall now go ahead and try and look at slightly more complex systems. But if you want to actually understand the previous example, which we learned, you can do a very simple exercise that is if you now go to this linear molecule case, which I told you that is you take 3N minus 5, and now, put N is equal to 2 in this then you would end up with one degree of freedom. And that is exactly what we saw when we took two molecules which are actually linear in the previous slide when we talked about atom A, atom or ion A and atom or ion B. There only coordinate was the distance between the two units.

So, I hope, this gives you an idea about the vibrational degrees of freedom and their connection to chemical reactions. Now, let us go ahead and look at the potential energy surface for a multi-atomic system or for a system which has more than two atoms in it.

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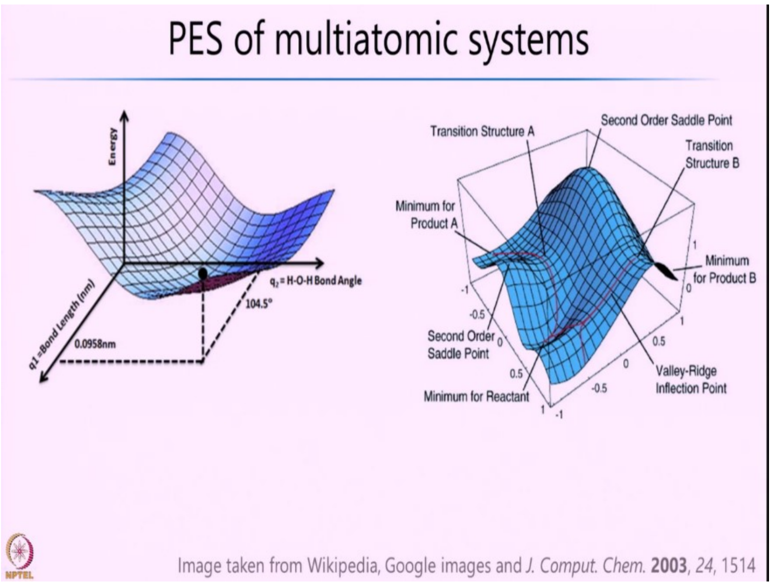
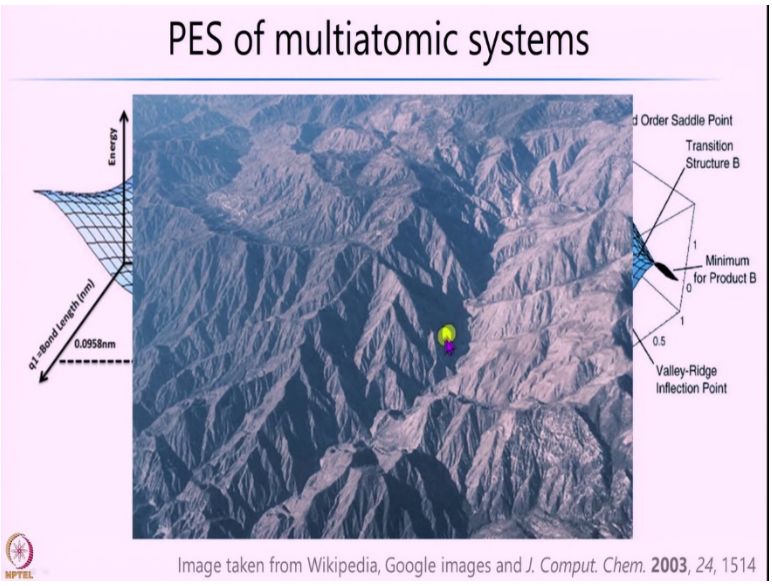


PES of multiatomic systems

Image taken from Wikipedia, Google images and *J. Comput. Chem.* **2003**, *24*, 1514



PES of multiatomic systems

Image taken from Wikipedia, Google images and *J. Comput. Chem.* **2003**, *24*, 1514

So, here what is shown is a potential energy surface for a triatomic system that is particularly water. And in this what you have is, one of the axis is that is typically the vertical axis is energy and the other two axes in this case the x and the y are in one case, it is the length bond length of the O-H and the other one is the bond angle, which is the again the two degrees vibrational degrees of freedom.

That is, you have the bond length, which can actually stretch or you have the if you think of this intersection as oxygen and the two hydrogen this bond angle can actually change. So, what one can do is, you can take at every point or every change in the bond length and the bond angle, and you can look at the energy of the system.

And if you now plot the energy of the system at each of the different angles and the bond length, then you would end up in this, so called, hypersurface. And in this hypersurface the point which corresponds to the minimum is corresponds to this angle of about 104.5 degrees and about point 0.0958 nanometers as the bond length.

So, this is how one goes about constructing the potential energy surface for a multi atomic system. That is, you keep one of the accesses as constant that is the energy of the system. And then you take many different accesses, which each of which corresponds to either a bond length or a bond angle or any different kinds of vibrations. And then, you look at how with each change in either bond length, bond angle or a vibration or bending the energy of the system varies.

And if you plot that, you would get a surface, which looks something like this, which is a hypersurface. And in this way, once you get a surface like this, you can actually extract many, many information out of this. So, this still looks okay to understand for our triatomic system. But let us say if I go to multi atomic system, which is even, which would look even more complex.

So, here, on the right-hand side is shown a potential energy surface for a system with more than three atoms. And where what you see is actually that, please ignore these labels because they have finer details which we need not get into right now. And what you see is that there are actually there are hills, and there are different valleys in this.

And this is a what is called as a potential energy surface or a N dimensional hypersurface for a given system, where each of the accesses would represent some of the one other change in the coordinate that is it could be again, a change in the bond length or bond angle or any of the other vibrational degrees of freedom. And you are looking at N how does the energy of the system change when you change all these different parameters or vibrational degrees of freedom.

So, I can understand that this might look a bit daunting to understand or figure out. So, to make it easy, let us take an example of a mountain range, which we are all familiar with. If you look at this image from a Google image, what you see from a top view, you see that there is a this is a beautiful mountain range and here you see lots of valleys and hills and various kinds of pathways, which go through. This is exactly how a potential energy surface would look like for a real system.

So, you can imagine mountain range as a potential energy surface. And the various valleys and hills actually correspond to each of the states, that is, it could be intermediate, it could be a transient species or it could be a transition state or it could be many different kinds of species.

So, the best way to visualize a potential energy surface is to think of it as a mountain range, where you have different kinds of let us say lanes going through one another. And we will go dive into this in a bit more detail and see what are the important informations one can understand or extract from such a potential energy surface.

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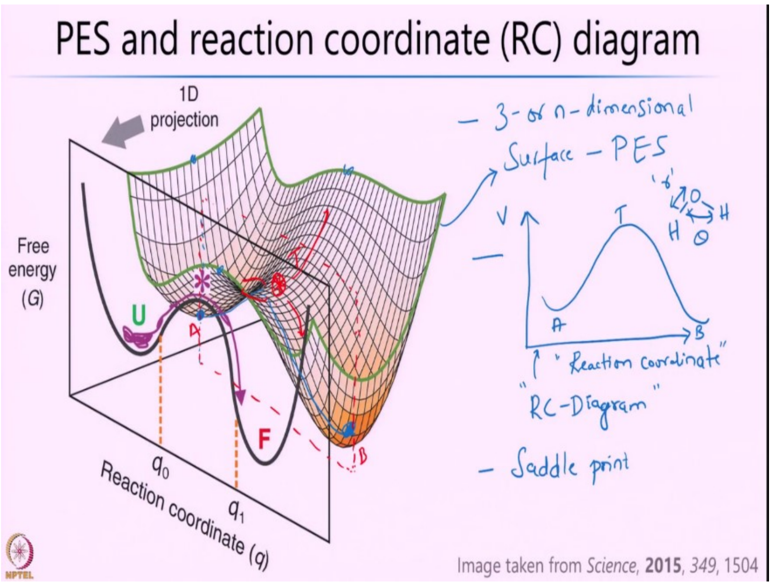

PES and reaction coordinate (RC) diagram

– 3- or n-dimensional Surface – PES

– Saddle print

Image taken from *Science*, **2015**, *349*, 1504

So, now, let us go ahead and look got three important ideas in this potential energy surface, what are called as potential energy surface and reaction coordinate diagram and another term called a saddle point or transition state. So, to understand that, here I have shown you this rather simple looking potential energy surface from a paper in science, where what you have is, you have an energy minimum, which is, you can see it here.

I hope, you can see this energy minimum wave which is a dip, and then you actually come up in energy and then you actually again fall down into another valley, where the energy is even lower, and then you on either side of this you have the energy which goes up.

So, if you take a three-dimensional or n-dimensional hypersurface, like this, that is what people typically call it as a potential energy surface. So, I will just write it down here, so that it is easier to remember. So, let us say 3 or n-dimensional surface is called a potential energy surface.

So, this is point number 1, and that is what we are having currently here. This is what we are I am trying to show. And now, what you can do is, you would say that, let us say the molecules are in this particular valley here somewhere, and they are trying to come up through this and traverse this path, and then go down the hill and end up in this particular valley.

So, then you would say that I am interested in only looking at this particular pathway and I am not because this is the one which is the energetically the least expensive for the molecules to undergo. And I am not looking at actually what happens here or what happens here or let us say, what happens here.

So, if that is the case, then what I would do is, I would actually take this hypersurface and I would actually make a cut or a slice of it along this plane. So, I could actually make a slice along this plane, I will use a different ink. So, I will, if I just cut it along this plane, then what I am doing is I am taking a, I had a three-dimensional n-dimensional surface, I have cut it into a two-dimensional surface or in other words I have mapped the three-dimensional surface into a two-dimensional graph. And in this what we typically look at is the following.

So, you will have something like this. You will have the energy, the potential energy V and this is what is called as a reaction coordinate, and one would have something like this. You had a let us say A going to B via some T. And what the important thing to note is, this reaction coordinate is one of the element, that is, it could be either one or more than one or combination of one element.

That is let us say, if I am looking at a molecule of water, for example, so I can look at the change in this bond length r and I can also look at this theta which is the angle which is making the angle between the H O and H. So, this reaction coordinate could be one or more than one of these bond lengths or bond angles which are changing, which are now mapped from a three-dimensional surface into a two-dimensional surface. So, that is the distinction between what is called as reaction coordinate diagram and potential energy surfaces.

So, this is a two-dimension, so, this is what is called as RC diagrams. The one which I have just drawn up. So, I hope, this distinction is clear between a potential energy surface and the reaction coordinate diagram. I will again repeat, a potential energy surface is a 3 or n-dimensional hyper surface in which you look at how does the energy of the system change as the function of the different vibration degrees of freedom that is 3N minus 5 or 3N minus 6 based on the system.

Whereas, a reaction coordinate diagram is a two-dimensional slice of a potential energy surface to represent the important steps which a reaction in which you are interested in. So, reaction coordinate diagram is typically a two-dimensional slice of a n-dimensional potential energy surface. So, now we shall look at one important point, which is called as a saddle point.

So, if I actually were to look at this point here, and the on the potential energy surface, that is, the atom or the system is trying to come from A to say B and it going through the point let us say T, that is what we have represented here. And if you actually look a bit carefully at T, what you see is that at T there is a, it has a very unique feature that is on two sides of T you have the energy which is decreasing that is towards A and towards B. Whereas, if you go orthogonal to A and B on the other two sides the energy is increasing.

That is, if you go along this path or if you come along this path the energy increases. Whereas, if you go along this and this which is going back to the reactant or going to the product, you have a lowering of the energy of the total system. So, such points which actually resemble like a saddle on a horse, if you ever sat on the horse, I am sure you will realize that the both of your legs would come down on either side, and the places you are sitting would look something like this, where your legs are on either side here.

So, this is what is called a saddle, and this point is called as a saddle point, and this invariably represents a transition state of a chemical reaction. So, with this brief introduction to potential energy surfaces, we shall stop here. And in the next few lectures, we shall take a few examples to understand the potential energy surfaces in a bit more detail. Thank you.