Concepts of Chemistry for Engineering
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Lecture No. 61 Intermolecular forces
Electrostatic and ion-dipole interaction

Hello everyone, welcome to the module on intermolecular forces and potential energy surfaces. In this particular module, we will try and look at what kind of forces exist between molecules and atoms, and what is the consequence of that on the bonding, as well as, the properties of the systems.

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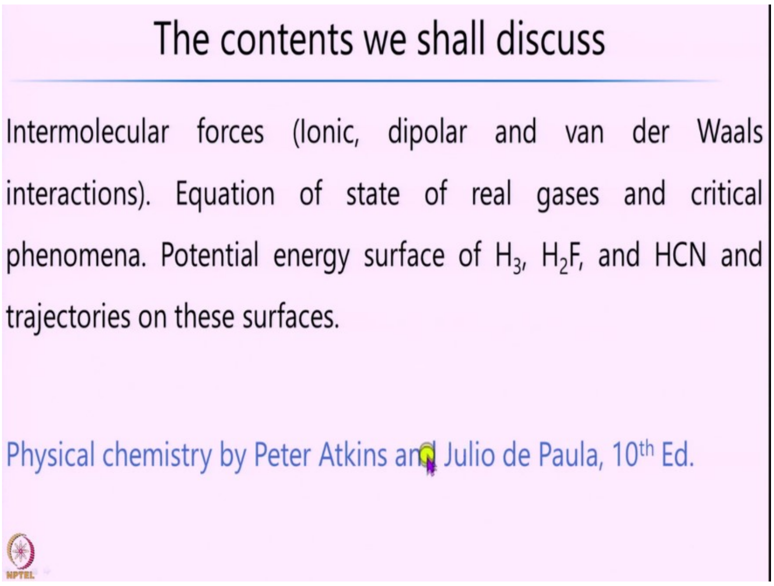

In this module, we would be discussing about the following contents, which you can see here. We shall begin by looking at intermolecular forces, namely, ionic, dipolar, van der Waals and to some extent hydrogen bonding, then, we shall look at the equation of state for real gas. And how does intermolecular forces actually play a role in going from an ideal gas to a real gas, and the critical phenomena.

Thereafter, we shall look at some of the potential energy diagrams of diatomic molecules such as H_3, H_2F, HCN and others. For this entire module, I would be mostly using the physical chemistry by Peter Atkins, and Julio de Paula, the 10th edition. And you can find more information about the contents I discuss in this particular book.

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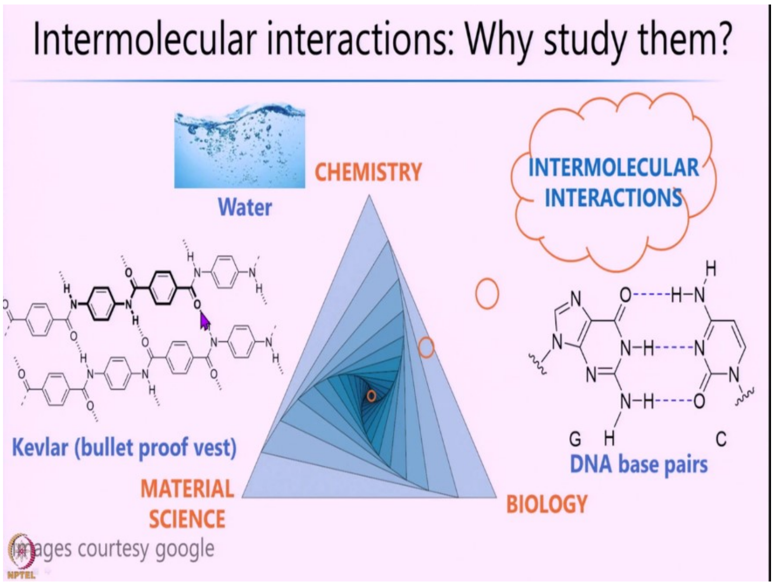

Now, let us begin by looking at intermolecular interactions. So, you must be wondering why are we even studying this topic or what is it of use to us or what is the relevance to us. So, to impress upon you the relevance of intermolecular interactions, I have shown here a triangle with the sort of a curved space which goes into the center of this strangle. And the three corners of the triangle represent are three different important disciplines which we come across, namely, chemistry, biology, and material science.

So, the idea is that all these fields would actually hinge very critically on the intermolecular interactions or the properties of molecules and the way they interact with one another. So, just to give you an example, if we say chemistry, then water is not ubiquitously found liquid, and we can use it and it is critical for life as well.

However, now if you ask the question, why is water a liquid at the certain particular range of temperatures and pressure, a major part of the reason stems from the fact that there are what are called as intermolecular interactions such as hydrogen bonds, which actually hold the molecules together, and this will give you the state of matter what we observe. So intermolecular interactions actually govern the properties of water to a large extent. And many systems in chemistry and not only water.

If you now come to biology, I am sure you are all aware of DNA and other biological molecules. And if you look at the DNA the base pairs such as the guanine and the cytosine, you do see that they are held together by intermolecular hydrogen bonding, as shown here with these dashed lines. So, these are the hydrogen bonds between oxygens and the hydrogens. So, this intermolecular hydrogen bond is very critical for the formation of these

GC or the AT base pairs and consequently, the formation of the DNA double helix, which is a very, very important biological macromolecule.

And not only DNA, many of the processes which take place in our body are mediated or take place through water called as proteins. And these proteins have a very well-defined tertiary structure and this structure is again primarily dictated by how molecules or how the chain of polypeptides fold on top of each other to give rise to the tertiary structure. This again at the end dictated by intermolecular forces, such as, either hydrogen bonding or other weak interactions, which we shall discuss in this module.

Finally, let us look at one example in material science or in application side. So, this particular structure which is called as Kevlar is used as a bulletproof vest, so you could wear it and it will protect you against bullets and also it is a very rough and a very resistant material towards wear and tear.

If you now go and look at the composition or the structure of this, all that you see is that you have benzene with an amide group which are actually connected in a linear fashion or in a chain and these chains are now interact with one another via hydrogen bonding, as shown here. You have the NHO hydrogen bond, which is taking place between two chains and these chains could also overlap on top of each other in a face-to-face manner. It is like keeping a pan-cakes on top of each other or you can think of them as a stack of books or a stack of pile.

So, this very simple interaction such as a NHO hydrogen bond, and the stacking interactions actually give rise to the exceptional resistance properties of this material Kevlar. As a result, it is used as a bulletproof vest. So, I hope, these examples actually give you an idea or give you a feel for what is the role of intermolecular interactions in our day-to-day life, as well as in various applications, and why one studies them.

So, to just reiterate again, so all of this, that is chemistry, material science and biology hinges very critically on the intermolecular interactions. And that would ultimately dictates many of the properties we observe. So, let us say if this, whatever I spoke till now sounds a bit abstract or sounds a bit disconnected, so let us take the following analogy and try to see if that makes a little more sense.

So, we can think of molecules like these ones here, that is the G or the C or the building blocks of the Kevlar or water molecules, as human beings like us, like you, me and others. So, and we as human beings interact with one another on a day-to-day basis, we are a part of a society, part of a family, part of an organization. And how well or how cohesive a society or an organization behaves, ultimately rests or depends on the way the individuals interact with one another.

That is, if I interact well with my colleagues or you interact well with your friends or the family members, that would lead you to a very cohesive family or a society or an institution. So, in the exactly similar analogy, the molecules or the way the molecules interact with one another are also are very important in dictating their properties.

With the only difference being that molecules are not as enigmatic as human beings they are still diverse and exotic, but they are still not as rich in terms of their interaction as human beings, but nonetheless, they are quite diverse, and to give a very rich array of properties, which one can harness. So, with this sort of introduction or a motivation to why one studies intermolecular interactions, now let us go ahead and try to learn a bit more about these kinds of interactions.

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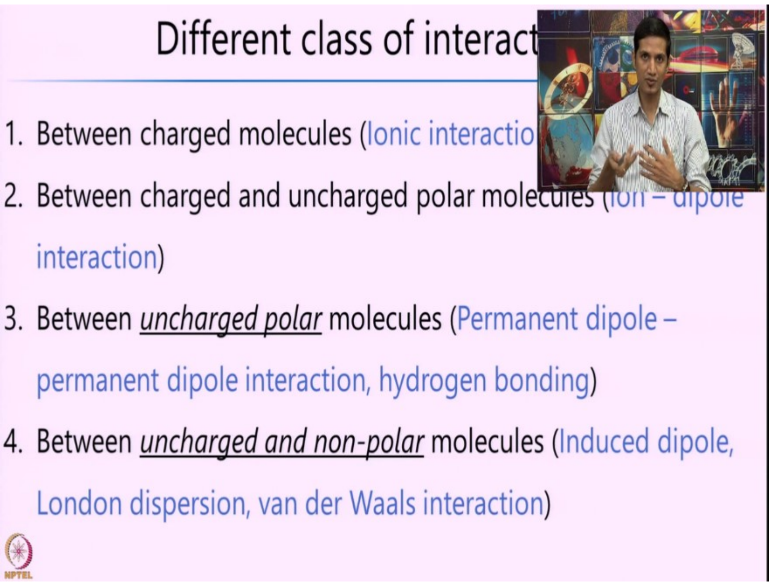

And so, there are different classes of intermolecular interactions, and I shall quickly classify them or name them. And the first one and the most obvious one is the interaction between charged molecules or ionic interaction. And you might be aware or familiar with what is called as columbic interaction, which is exactly same as the ionic interaction. And this typically takes place between two completely charged species that is either cation or an anion. These species could be either inorganic in origin or organic or different kinds of species.

And the next interaction is between a charged and uncharged, but a polar molecule. We shall see an example of this soon. And such interactions are called as ion-dipole interactions, because you have a cation or an anion interacting with the charged molecule, interacting with the uncharged but a polar molecule.

And the next one is between uncharged but polar molecules. That is, the two units which are interacting, both of them are uncharged that is they are neutral. However, they do have a finite amount of polarization or a dipole moment in them. And that would lead to what is called as a permanent dipole, permanent dipole interaction. And in some special cases, one would also invoke hydrogen bonding as a part of dipole-dipole interactions. And we shall look at that as well.

And finally, what I can go is I can go and take two molecules which are now completely uncharged and they are also not polar. That is, I am looking at uncharged and nonpolar molecules. For example, methane or ethane or any of the inert systems. In such systems people typically encounter what are called as induced dipole, induced dipole interactions or other words, London dispersions or also called as van der Waals forces. So, we shall look at each of these in a little more detail as we go along in this module.

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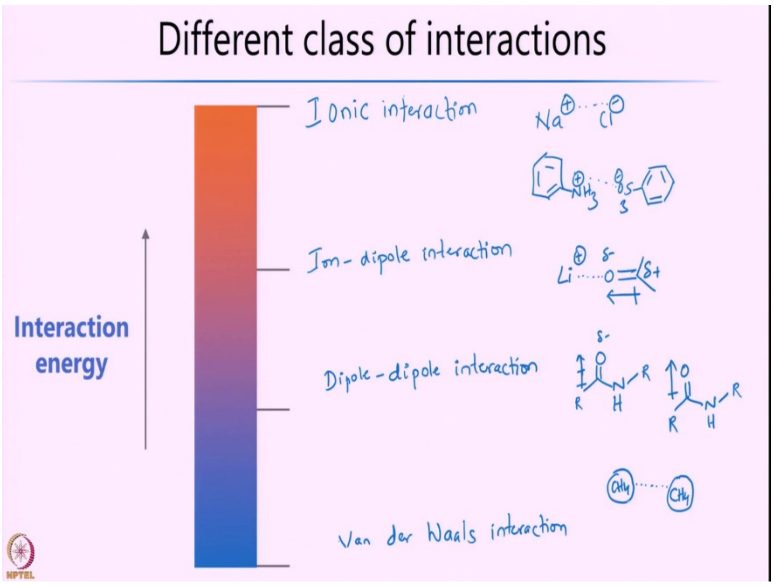

So, to give you a feel for this, I am trying to give you a little more visual classification of this. And here, I have shown you a graded spectrum, which is to show you that there is a wide array of interaction energies possible among the four different interactions, I told you in the last slide.

And another important part of this spectrum is that there is no clear-cut demarcation. That is, you do not have clear boundaries where one ends and other interaction begins. So, there is always a bit of fuzziness about these interactions. So, let us now go ahead and look at these different interactions and what are the different possible examples of them.

So, first, I shall look at what is called as the ionic interaction. And a very simple example of this is you can think of is a sodium plus and a chloride minus, which is an inorganic example where both ions are interacting with one another or you can also think of examples such as such as anilinium ion that is the cation form of the aniline interacting with an organic, let us say, organic salt such as SO_3 minus. So, this is also an example of ionic interaction. So, these are very easy to understand or to get a hang of. And the next is called as ion dipole interaction.

So, by dipole here, we mean, permanent dipole of a molecule and not something called as a induced dipole, which we shall come to later in this module. Let us say, I have a lithium ion or a sodium ion, and let us say it is interacting with the carbonyl group. So, you know that carbonyl has a delta plus delta minus, as shown here and that would give rise to a dipole moment, permanent dipole moment, but yet, the molecule as a whole is not charged. So, then these two systems can also interact, and that is an example of ion dipole interactions.

So, now let us come to a dipole-dipole interaction or permanent dipole, permanent dipole interaction to be more precise. So, in this case, one can take examples of say an amide, which has a let us generate dipole here or and you can also take another amide or a different molecule for the sake of convenience, I will take again another molecule of amide. So, then this would also have some sort of a dipole moment, which is along this direction. And then these two dipoles could actually interact in space.

So, this is again what I would want you to notice that these two molecules are now again neutral, but they have a definite amount of polarization built into them or a charge separation built into them, but they are not ionic yet. So, in this case, what we will have, is a permanent dipole permanent dipole interaction. And finally, we shall come to what are called as van der Waals interaction.

So, please note that the spelling of van der Waal is small v-a-a-n-d-e-r and capital W-A-A-L-S. Please do not confuse it with Walls, it is W-A-A-L-S. And this comes from a Dutch scientist called Johannes Diderik van der Waals. So, a classic example of this is that if I take a molecule like methane CH_4, interacting with another molecule of CH_4 or any such inert or non-charged and non-polarization built-in molecule, then you would have what are called as dispersion or London forces or van der Waals interactions built into these systems. So, now, having looked at broadly at these different class of interactions now let us go ahead in a bit more detail and look at them.

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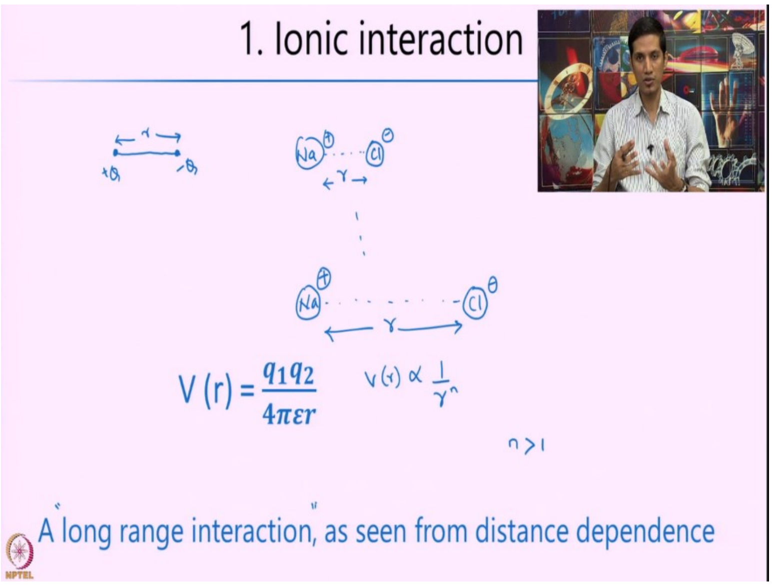

So, let us begin by looking at ionic interactions. So, for that, I will just take a point charge again. So, I have a point charge which is let us say, plus Q and minus Q, which is separated by distance r. And so, we know that the interaction potential of this kind of a system is given by columbic interaction, which I am sure you all would have studied in your 12 standards, that is, V of r is equal to q1 q2 divided by 4 pi epsilon r, where epsilon is the permittivity of the system and r is the distance between the two charges we are looking at and q1, q2, either small or capital are the charges of the individual ions we are looking at.

And so, one thing to note in this particular example is that here, the V of r is goes as 1 by r or is proportional to 1 by r, and this 1 by r dependence is what is typically called as a long-range interaction or what we, what people mean by that is that if I take a molecule. Let us say I have a sodium ion and I have a chloride ion, and I have certain interaction energy between them.

And what I can do is, I can keep on increasing this distance r between the two ions. So, then I could end up in a situation where I have sodium plus and a chlorine, which is still far away from here. So, this is the r.

So, even at much larger separation between the two interacting ions, one can, in principle, have a significant amount of interaction between them, because the V of r goes as 1 by r. If it were the interaction potential were going as the higher powers of r, that is, if I put a n here, and if let us say the n was greater than 1, as n becomes greater than 1, then the interaction strength decays rapidly, so you will have the two interacting species, the moment you take them apart, the interaction strength between them actually goes out very rapidly.

For in this case, since the interaction strength goes as 1 by r, which is actually that means that the both the systems are interacting even when you pull them apart to a larger distance. We call this a long-range interaction as shown here. And these become important when you are trying to understand or trying to look at intermolecular interactions in an assembly or more than one molecules at a time.

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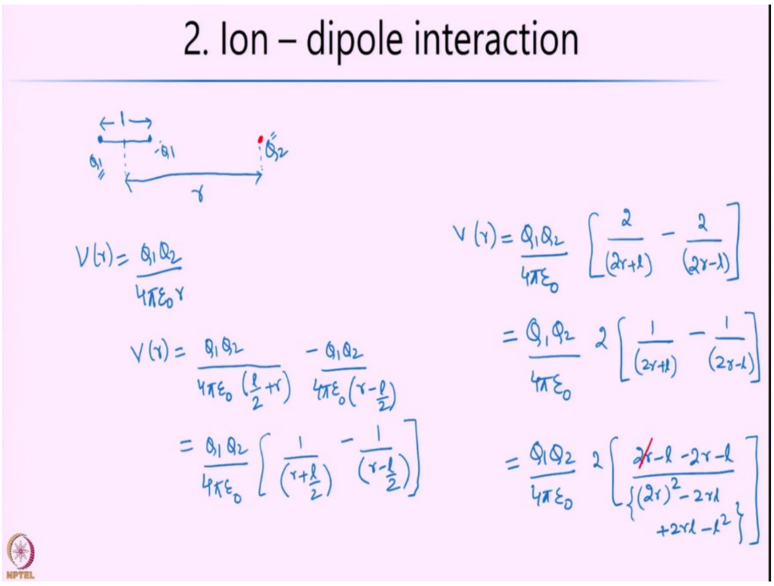

Now, let us go ahead and try to look at an ion dipole interaction. So, for this, what we shall again consider is a point dipole. So, I am going to make a dipole here. I shall put in charge here that is the ion. So, now, let us say the distance between this is l between the two charges in a dipole. And let us call this Q2, and from the center of this dipole to this charge let us have, let us call this distance r.

So, now, what I can do is I can use the same interaction potential which I showed you previously to look at what would be the form of this interaction potential between an ion and a dipole. So, let us first write down V of r is equal to Q1 Q2 divided by 4 pi epsilon naught r, this is for a typical interaction between two charges, this is what we saw on the previous slide.

Now, let us try and apply this to the present case here. So, what can happen is the Q1 can interact with Q2 and minus Q1 can also interact with Q2. So, now, I will write both the forms and add them up to give me a V for the or the potential for the entire system. So, V of r would be Q1 Q2 divided by 4 pi epsilon naught, and now the r would be l by 2, because I am going from this Q1 till the Q2, so it will be l by 2 the half the length of l plus the r, so, it will be l by 2 plus r.

And now let us look at how minus Q1 interact with Q2. So, it will be minus Q1 Q2 divided by 4 pi epsilon naught. Now, if you look at the distance between the minus Q1 that is a point and the Q2 it is r minus l by 2. Because the entire r is this, and if we subtract l by 2 from that, then I would end up on the minus Q1. So, this can be written as I will take out Q1 Q2, r plus l by 2 minus 1 divided by r minus l by 2. So, now, let us look at this particular this part and see if we can simplify this further.

So, V of r is equal to Q1 Q2 divide by 4 pi epsilon naught and the 2 goes up so then I would have 2 divided by 2r plus l minus 2 divided by 2r minus l. So, this what I could do is I can take out the 2 outside of the bracket, so then I have I am left with and then I will, I am left with the following that is 2r plus l and 2r minus l.

So, then what you can do is you can try and simplify this part in the bracket, so then I would write Q1 Q2 divided by 4 pi epsilon naught 2 divided by 2l, sorry, so this is 2r minus l, so this will be 2r minus l and minus of 2r and minus l divided by 2r square and minus 2rl plus 2rl and minus l square. So, now these two terms would cancel, and similarly, these two terms would get cancelled.

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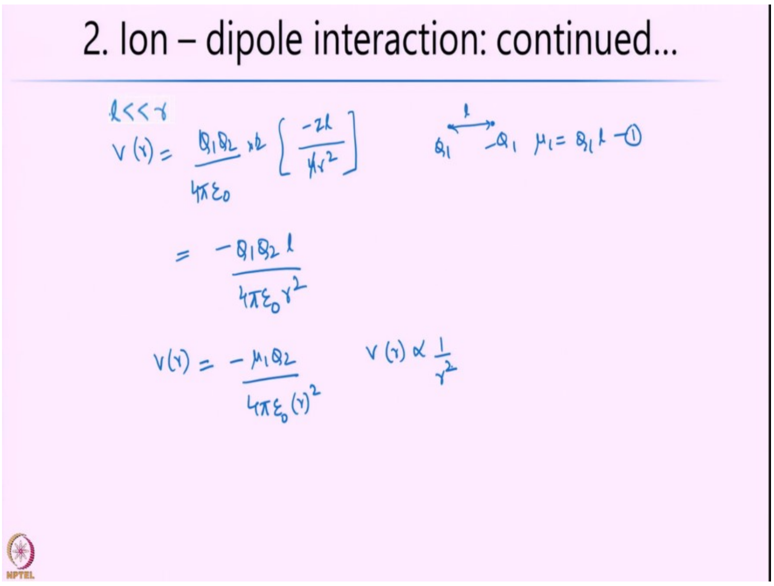

So now what we will be left with is that V of r is equal to Q1, Q2 divided by 4pi epsilon naught and a factor of 2 and Vn minus 2l divided by r square divided by 4r square. So, then what would happen is that I have the 4, 4 gets cancelled that is this, this gets cancelled and one can write this simply as minus Q1, Q2 l divided by 4 pi epsilon naught r square. And I hope you remember that the dipole moment between the two charges that is Q1 and minus Q1 with the separation of l is given by mu 1 is equal to Q1 times l.

So, if we put that plug this in, into this particular V of r we would be left with V of r is equal to minus mu 1 times Q2 divided by 4pi epsilon naught r square. So, the key thing is that V of r is now proportional to 1 by r square which is which states that the interaction between an ion and a dipole is actually now goes as 1 by r square which is, which has a power higher compared to interaction between just two ions or just two point charges. So, this would fall down more rapidly compared to interaction between two ions.

So, now, what we will do is, we shall look at the angle dependence of this particular thing. We should look at the angle dependence of the ion dipole interaction and that would be that if the two charges are at if the ion and the dipole are at an angle theta, then one would have a cos theta term to account for the angular dependence between the charges as well as the and the point dipole. With this, we shall stop here. And in the next class we shall look at a permanent dipole, permanent dipole interaction and van der Waals interaction in detail. Thank you.