

Physics of Functional Materials and Devices
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Lecture – 16, Week 4:
Bonds in molecules and solids

Welcome back. Let us continue our discussion on solids and till now we have seen that there are various ways to make solids, there are various types of solids and we have classified these solids into three broad sub classifications. Those are metals, insulators and semiconductors. We have also discussed about the theory which leads to this classification. Now, let us continue with our discussion and see what are the energies associated with these solids and how do they drive the stabilization of various types of solids. So, in today's lecture we will give you the introduction to bonds in molecules and solids.

Then we will talk about energies associated with solids. So, what do I mean by that? You can have energies which would lead to the stabilization of lattice or you will have energies which would lead to the stabilization of a molecule. So, there are various types of energies one should understand and those are relevant to this course and those are the binding energy, the dissociation energy, the ionization energy. We will also talk about electron affinity.

Most probably this is one term which many of you have not heard till now. The previous three you have heard. We will also talk about the sublimation energy, the energy linked to the condensation processes in solids or leading to solids and then cohesive and lattice energies. So, these are the typical energies about which you should have certain understanding to go further in this course. Then once we have a molecule formed there are various ways by which the atoms remain at their positions and that is leading to the condition where you will have to have various kinds of energies which would force these atoms to maintain certain distance and they will form certain ordered structures.

With these molecules in mind you will find that you can have different kinds of bonding. Bonding means the relationship between two atoms which are nearest to each other or you can also talk about the nearest neighboring atoms in a 3D lattice or molecule. So, we will talk about molecular bonds, we will talk about ionic bonds and we will talk about covalent bonds. And based on these three classifications of bonds you can have different types of materials. And finally, I will also introduce to you additional term that is the metallic bonds.

What is a bond? It is basically the attractive force that connects the distinct constituents. In our case we will mostly be talking about atoms. You can also talk in terms of ions or you can talk about in terms of any distinct constituents which are connected by an attractive force. And these bonds which we will be discussing would be mostly related to molecules

and how do these bonds ensure that the molecules are stable. These bonds once they form will ensure that the whole molecule is stable.

This stability can either be obtained by sharing of electrons or donating of electrons so that you can have the condition which satisfies the various requirements for charge neutrality that is the driving force behind any kind of sharing or donation of electrons. So, let us start with what we know till now. We know that there is a term which is called potential energy and it is basically described by the energy associated with the interactions between the particles. Now these particles let us say there is one particle shown by my right fist and then there is a left fist. Now these can interact by various fundamental forces.

Forces means they would be forces which would lead to attraction and if they come very near they would lead to repulsion. So basically these are the two forces. But what are these types of forces? These can be electromagnetic forces, they could be nuclear forces or they could be weak nuclear forces. But these forces would primarily lead to certain kind of attractive or repulsive actions. So potential energy in terms of force is defined as integral $\int_a^x -f dx$ where a is the zero level of the potential energy and this concept is basically used to understand the interaction between two particles.

So as I said if you have potential energy versus distance between nuclei curve. So you can have what? If two nuclei are very near to each other what they cannot go beyond a distance of closest approach then what will happen? They will undergo repulsion. But you know that the structure wants to stabilize at the minimum energy level so that you have certain distance between the atoms but the energy of the whole ordered lattice is minimized. So there is always a play between repulsive and attractive forces. We have seen earlier this is described by the 6-12 Lennard Jones potential and you stabilize a structure when these competing forces reach an equilibrium.

This is what is meant by the competing repulsive and attractive forces. So increasing stabilization and increasing destabilization means that if you are somewhere in this region of the potential energy curve or you are in this region of the potential energy curve what will happen? If you are in this region of the potential energy curve this will mean that you will easily be able to go back to the global minima or lower energy state. But if you are here then what is happening that you have very high energies associated and that would mean that the atoms are being forced to get further away from each other and you have higher energy which is forcing those atoms to move away from each other and that is why you are having certain level of destabilization of the lattice. And if you consider that the atoms are very much far away from each other then they do not interact. So based on these interactions there are set of energies which come into picture.

These are the binding or dissociation energy. Then you have ionization energy. Third is electron affinity. Then you have sublimation or condensation energy and finally you will

be understanding about the cohesive or lattice energy. The binding energy as we have been studying for many years now it is the energy that holds the nucleus of an atom together. Simple. And this is required to overcome the attractive forces that exist between protons and neutrons. We know that the binding energy of an atom is what that will define how stable the nucleus is. The more stable the nucleus the greater is the binding energy. This is what we have understood. Let us consider a case of atom A coming together with atom B to form certain kind of arrangement or a molecule.

Initially atom B is an independent entity, atom A is an independent entity. They are far away from each other. But when you are falling a forming a molecule which is AB that means these have to come together. But they will come together but they cannot go beyond a certain distance so that they start impinging each other's territories. That means you do not want to have the condition where the energy levels are facing a case of overlap.

So that cannot happen. You know from various rules this cannot happen. So you are having cases where atoms are far apart but then they slowly come together. The driving force could be any thermodynamic parameter as we have seen earlier that you can induce these movement of atoms from far apart condition to come together by increasing the heat. Then the motion of the atoms increase within a solution or if you are having some solid state reactions then you induce agitations and then these motions are there and then they are coming together or you can induce these kind of motions by changing pressure or you can induce these interactions by changing both temperature or pressure.

If I ask you a question which is the technique which gives you the way to change pressure and temperature together can you answer that? Yes, it is the hydrothermal technique. So slowly the atoms come together. When they come together there is an energy released when they come together and move from infinity to their equilibrium position. What is the equilibrium position? When they are moving together it is called attractive forces but when they come very close to each other they are repelled. So this is the repulsive force and then at one point they will stabilize and form a bond between them and that will be a stable structure AB and this distance is called the equilibrium distance.

So if you see these atoms they are not overlapping what I have done is basically you are having atom like this. So the atom is coming A and B they are coming like this. So if I take a cross section they are placed in this way. So they are not impinging. So I just drew this picture just to show that it is not as if they are overlapping each other you must understand they are like this and there is a gap between the two atoms.

So the binding energy is the energy which is released when atoms A and B are moved from infinity to their equilibrium position defined by $E_{\text{subscript B}}$. Now if you have the other case the atom AB is already formed you want to now go back to the condition that you want to have separate A and separate B. So that process is called dissociation and hence

the dissociation energy is the energy required to break a bond between two atoms in a molecule and completely separate them. So you need this energy to break the bond and convert the molecule back into its forming constituents. What would be the energy of dissociation? There was an energy which you associated for binding.

Now if I give the same energy for the atom, but somehow it has this energy has to do a reverse process then it will break the atom. Hence the dissociation energy is equal to the binding energy. And this will break the AB molecule into constituents A and B. So if you want to see it schematically you will again go back to the case of atom A and B as individual constituents which are again far apart. The next energy which we discuss is the ionization energy.

The ionization energy is the energy required to remove an electron from an atom or molecule and depending upon the type of atom or molecule the electron being extracted from them you need to provide different magnitude of energy. Some atoms will require higher amount of energies and some would require lower amount of energy. For example, the ionization energy for sodium is approximately 5.14 electron volt. So you will see that there is an atom, but when you provide this energy an electron is taken out of the atom.

This is just a schematic representation, an animation. Do not take into consideration the exact number of electrons which we have drawn. This is just a number. We have shown it to explain the phenomena. So if you change the number the name of the atom in the middle please ensure depending upon their atomic number you must have the right number of electrons.

Now contrary to what we have seen you can have the dissociation, you can have elimination of electrons. These are the two things which we have discussed in the previous two slides. Then comes the term electron affinity. You are having an affinity towards electron. What would it mean? It means the energy required to transfer an electron from infinity that means it is outside the periphery of the influence of the atom which is under consideration to the lowest feasible orbit in an atom or molecule.

So it is not that you will directly take the electron from infinity and put it in the k level. You can have cases where you will put them in l level or m level or n orbits. So this is the energy change associated with the addition of an electron to a neutral atom or molecule. So if you just take the case of chlorine what is happening? You had an additional electron coming to picture and when chlorine is gaining an electron energy released is approximately 3.62 electron volt. The next energy which comes into picture is called the sublimation energy. This is the energy required to change the substance from its solid to its gaseous or liquid state. Do you remember what is the process of sublimation? Sublimation is going directly from solid to gaseous state. Therefore what would be the

sublimation energy? It would be the energy required to change the substance from its solid state to a gaseous state.

Simple. Without going through the route of solid, liquid and then gas it is a direct process from solid to gaseous state. Therefore E_s is the energy required to move an atom from its position in the solid to infinity. That means you are allowing what kind of movement? You are having free movement of these atoms within the lattice. This is what it means. That is what you have the definition of gas.

What would be the next? If I have sublimation then I can also talk about condensation and this is the reverse process of sublimation. What would be the sublimation energy? This is the release of energy when vapor changes to solid and a condensation would just be in terms of magnitude would be equal to E_s , but if you also want to take the sign then $E_{\text{condensation}}$ would be $-E_s$. And sublimation and condensation energy is frequently expressed in joules per mole or kilojoules per mole. So these are the units for these energies. Once you have a structure there is a cohesion and that leads to the formation of the atom and this is driven by another energy that is called as cohesive energy.

And what would that energy would be? That energy is the energy needed right from the point the substance is most stable to the case when it completely separates into individual atoms or molecules. So this is the cohesive energy. So what will happen? Once you provide this energy the intermolecular bonds will break and you will have the individual molecules or atoms which were initially forming a stable structure. These forces may include hydrogen bonds or any other types of chemical bonds. They could be dipole interactions or London dispersion forces.

You have a material, you have arrangement which is ordered, then you have equilibrium positions, then if you have all these conditions what are you forming? You are basically forming a lattice and if there is a lattice that means if you see the case that there is a yellow colored ball, then there is a smaller white colored ball, then it is periodically arranged. So those are held together by certain form of energy. That is the energy required to separate a solid ionic compound which is made up of charged particles known as ions into its individual gaseous ions and if you are able to convert this compound to individual gaseous ions you break it, then it is giving you the lattice energy. This is a way to estimate how strongly the ions in the solid's crystal lattice attract one another. So the energy which has to be added to one stoichiometric unit of a crystal to separate its components into free ions is the lattice energy.

So stoichiometric means in the right concentration. So if you have again NaCl, then you have one Na and one Cl ions coming together. So the ratio is 1:1. So you cannot have NaCl₂. So stoichiometry means in the desired concentration and desired amount, then only you have a stable material and that is why you always talk in terms of stoichiometry.

So you will have the energy which is required to be added to this stoichiometric unit of a crystal to separate the components into free ions as the lattice energy. There are various types of bonds. You can have molecular bond, ionic, covalent or metallic bonds. As you know, what are molecular bonds? If you have dipole interaction in a molecule which acts as the source of origin of molecular bond formation. Now what do I mean with this? If you have unequal distribution of electrons amongst the atoms in a polar covalent case, then what will happen? This would mean that you will have a dipole moment within a molecule.

This dipole moment can lead to the condition that there is an interaction with the adjacent molecules to form a dipole-dipole interaction because there is unequal distribution of electrons between the two polar covalent atoms. Now these dipole interactions between the molecules leading to dipole moment is defined as $p = qr$ where q is the electrical charge and r is a vector which is directed from the negative towards the positive charge and p gives you the dipole moment. The ionic bonds are primarily formed by the electrostatic attractions between ions with opposing charges. These ions can you can consider as atoms or molecules with one or more electrons added or removed from them. If you take one electron or you impinge one electron, what are you doing? You are changing basically the net electrical charge and then you have a ionic condition.

When two atoms form an ionic bond, one of them gives one or more electrons to the other resulting in a formation of a positively charged cation and a negatively charged anion. So now you understand what are cations and what are anions. So if you have different types of cations interacting with different types of anions, you will have different kinds of materials being formed. Let us take the example of NaCl. What will happen in this case? You have Na plus as cation plus just one.

So one electron is lost whereas chlorine minus means an electron is gained. What is the nature of bonding? The ionic bond in NaCl is therefore leading to the stabilization of NaCl, but the origin of that lies in the electrostatic interaction between the ions that means Na plus and Cl minus. So this is an interaction between Na plus, Na minus separated by a distance and you have the dipole moment and that is driving the stabilization of the whole lattice. Now how does the bond attain stability? You have an electron cloud of two sub-shells which start to overlap. So the electron cloud associated with sodium or electron cloud associated with chlorine.

Now there would be one electron cannot be distinguished from the other electron. So you have these lot many electrons. If they are coming together, then what will happen? You will have strong repulsive forces which would act and hence these would lead to the cases where the arrangements are such that there are some repulsive forces which would drive the case where the distance between the ions to shrink or increase until an case where equilibrium distance between Na^+ and Cl atoms or ions are obtained so that you can have a stable NaCl molecule. At this point, the electrostatic attraction force balance the strong

repulsive forces. This we have seen that during the formation of material there is attraction and then there is repulsion.

So the equilibrium position is such that the electrostatic attractive forces balance the repulsive forces and because of the Pauli's exclusion principle, no electron can have four equal quantum numbers. Hence some electrons must be excited to higher energy levels. This process requires lot of energy and that is why you have the sub-shells which are occupied by different number of electrons. The next you have the formation of covalent bonds and covalent means that I do not give you an electron, you do not give me an electron. What we will do is we will share an electron or we will share certain electrons so that when I need stable condition I will use that electron or that those number of electrons and same is for the next atom which is coming together with the first atom.

So there is sharing of electrons. Covalent bonds tend to occur in non-metal atoms such as hydrogen, oxygen, carbon. They can be found in many molecules including water, methane, glucose, mostly formed of combination of hydrogen and carbon. And you can see the typical example of H_2O . What is happening? Two hydrogen atoms and the oxygen atoms share the electrons to form a stable molecule. To complete these outer shells the hydrogen atoms or the oxygen atom they share their electrons while the oxygen atom shares electron with the hydrogen atoms.

So you have the sharing of the, you can clearly see certain number coming from hydrogen and another coming from oxygen. So oxygen 6 to become stable you need 8, hydrogen 1 to have the first shell as stable. How many electrons you need? You need 2. So 1 comes here from the oxygen this hydrogen is stable. Then at some point you share the other electron this shell of hydrogen is stable.

Oxygen needs 2 then both these hydrogen share their electron when oxygen needs to be stable and hence they have the sharing concept. Similarly, you can talk about the sharing of electrons in chlorine, hydrogen or any other gases. The main properties of covalent bonds are they are strong, very strong hence they lead to high melting points and very high mechanical strength. But they are poor conductors of heat and electricity because once you have shared these electrons and you have gone to a stable orbit then you do not have any delocalized electrons that means you do not have any free charge carriers which can move and carry energy or charge from one place to the other within the material and therefore they become poor heat and electricity conductors.

Finally the metallic bonds. These are the bonds which are associated in a way that the valence electrons of metal atoms in a metallic bond are delocalized. This means that they are not bound to any particular atom and are therefore free to move freely in the entire metal lattice. If you take this condition that an atom is not tightly bound to any of the delocalized electrons then you are talking about the case of metallic bond. This is what we

have just discussed. And if there is unrestricted movement within the metal lattice then what will happen if there is unrestricted movement of charges.

What will happen they can carry energy or charge. If you are carrying energy you can have high thermal conductivity. If you are carrying charge you can have high electrical conductivity and therefore metals can conduct electricity and heat effectively because of these delocalized electrons. So let me conclude what have we seen today. We have seen the energies associated with the formation of stable materials or lattices and why they should be understood because if you take different types of atoms bring them together to form a new molecule then the electrons which become available are in different number and based on that you can have different types of bonds and those bonds would lead to the formation of systems which can have metallic character or semiconductor like behavior or insulating properties and that is the reason why you should understand these energies. These are the references which were used for preparing the lecture that I have presented today and I thank you once again for attending this lecture.