# Main Group Chemistry
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## Lecture – 12
## Structure and Bonding aspects: Valence Bond Theory

I once again welcome to MSB lecture series on main group chemistry. In my last lecture, I was discussing about the writing MO diagram for hetero diatomic molecules. So, let me continue from where I had stopped. So, let me write MO diagram for CO 2 molecules. You do not often come across the MO diagrams in standard textbooks for molecule such as CO 2, BH 3, H 2 O and all those things, at most you may see MO diagrams for NO, CO and not beyond that one.

So, that is the reason I am giving you some triatomic or poly atomic molecules and explain their bonding and analyzing from both valence bond point of view, VSEPR theory point of view as well as molecular orbital diagram and this can clearly give the idea about which one is more refined, which one will be which one is more informative. Of course, there is no doubt that molecular orbital theory gives the complete picture of a molecular including its reactivity everything.

So, let me continue with writing MO diagrams for CO 2.

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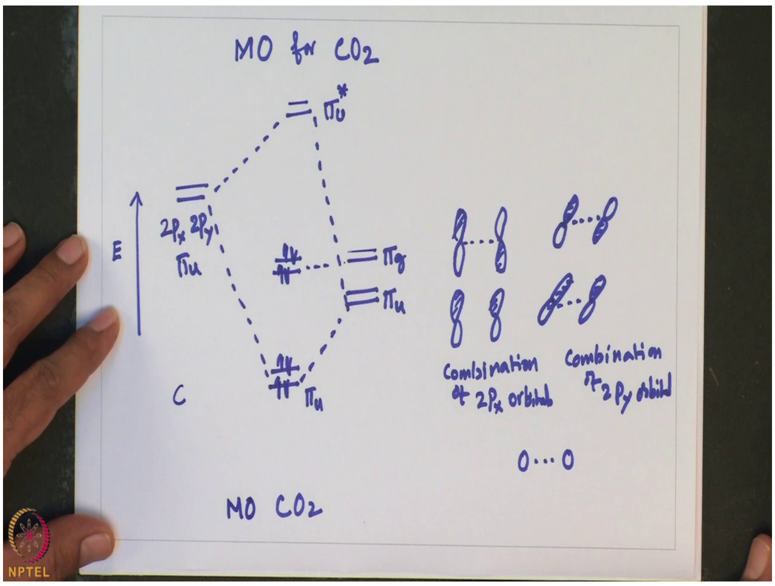

So, now, let me consider here 2p x and 2p y and then this is for carbon and then I am considering for oxygen pi g, pi u; you may be wondering what is this one. So, it essentially this is anti bonding, this is bonding. So, bonding is ungerade, whereas anti bonding is symmetric. So, gerade that is a reason this subscript is coming here and this is the combination of 2p x orbitals. Similarly, I will write combination of 2p y orbital. I have omitted p z because p z is involved in making sigma bond. So, I am just omitting that part that is very that is similar to most of the molecules we come across.

So, here combination of 2p y orbital, so, both represent O here and now, this is for CO 2 let me write here MO, the first one will be here this is pi u, two of them and then we have here almost non bonding because pi this both are pi u. So, that this remains as non bonding and now let me write here pi u you and connect them. So, now, we have to put these 8 electrons here. So, this is MO diagrams for CO 2 here this is for oxygen this is for CO 2. So, one should be able to write a simplified MO diagrams for CO 2 in this fashion.

So, now, let me write MO diagrams for another interesting molecules BF 3 and BF 3 is a Lewis acid, very strong Lewis acid. Of course, it is not stronger compared to BCl 3. So, those things also we can analysis after writing the MO diagram and while writing MO diagram I mentioned that to minimize complications all ligand orbitals are put together and considered as ligand group orbitals. So, now, we have to consider B, boron atom combining with 3 fluorine atoms and each fluorine is coming with 2s and 2p 4 orbitals. So, total of 12 orbitals are coming from fluorine and 4 orbitals are coming from boron and now, this 12 fluorine orbitals are together called ligand group orbitals molecules.

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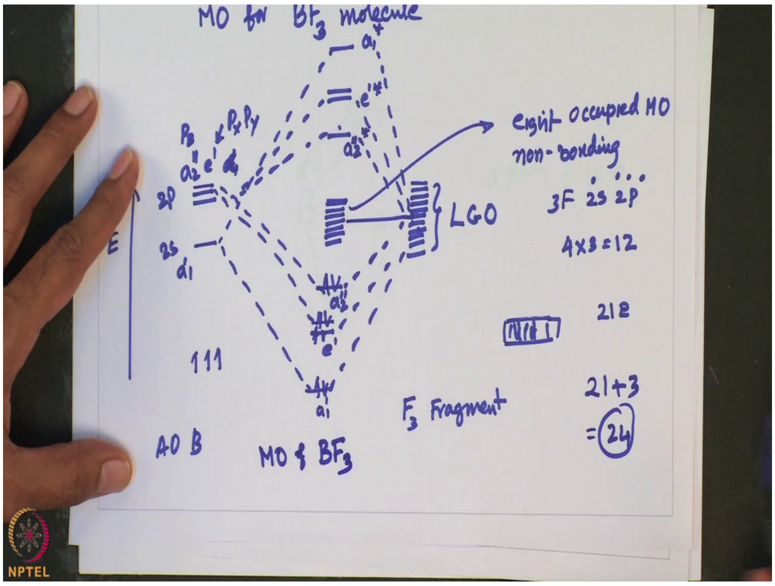


So, this one should remember all the time. So, here what we have is 2p and then 2s and then here we have ligand group orbitals are considered total there are 12 are there. So, these are all called ligand group orbitals. I had already mentioned how we are taking 12 here. So, each F as 2s and 2p that is 1, 1, 1, 1 – 4 orbitals are there and 4 into 3F are there. So, 3 we will get, totally 12 atomic orbitals of fluorine are participating in making BF 3 molecules.

So, while writing MO diagram, we are considering 12 fluorine atomic orbitals and 4 boron atomic orbitals the total of 16 atomic orbitals are involved in writing MO diagrams for BF 3. Out of this one, let us start writing and I would tell you about those. The first one is here. So, this is boron atomic orbitals 2p and 2s and here F 3 fragment. So, here the first one and then we have 2 and then we have 1 here and here we have 8, 1 2 3 4 5 6 7 8 they are essentially coming from here and they are essentially 8 and then we have 1 here and 2 here and 1 here. So, this is a 1 prime and this is e prime and this is a 2 double prime and this is non bonding and then a 2 double prime star and similarly e prime star and then a 1 star.

So, now, a 1, this one is a 1 and where here 2p x, let me write here. First, let me write here a 2 prime and e prime and a 1 prime and a 1 prime. So, this is a 1 prime is already I have given here. So, a 1 prime I have given 2s and this is p z and this is together p x and p y. So, this how it is. 2p has 2 type of orbitals, p x and p y forming e prime; whereas, a 2 double prime is p z. So, now, let me start connecting wherever it is there.

So, a 1, and then a 1 here and of course, all of them should be connected here and e and then e comes here and a 1 comes here and comes here and a 1 is here. So, e 1 goes here e 1 goes here. So, this is the MO diagrams writing is completed. So, now we have to write the electrons, we have to fill them. We know that, we have here 2s to 2p 1. We have 3 electrons are there, here we have about 5, 7, 21 electrons are there. From each one we have 7 electron s to p 5. So, out of that one electron comes here. So, 3 if it is something like this. So, this essentially makes covalent bond with this one.

So, we have like this 6 electrons; this 6 electrons whatever I have written it represents the BF 3 molecule. So, now, there is a small magnitude of pi bonding is there with one of the fluorine atoms. So, those 2 electrons will come here. So, due to this one what happens now, BF 3 has 8 electrons and also it has a pseudo octet electronic configuration. So, these 2 electrons are essentially coming from one of the pi orbitals of 2p x or 2p y, so, that comes. As a result what happens now, we have 8 electrons otherwise it will be very simple. It will be like having sp 2 hybridization and 3sp 2 having one electron each of boron interacting with 2p orbitals to form 3 covalent bonds.

Whereas, here the forth pair here. This is due to the pi bonding. Pi bonding from fluorine to boron that gives a pseudo octet electronic configuration to remove its electron deficiency. For this reason it is slightly less Lewis acidic compared to BCl 3, such provisions is not there in BCl 3. Now, remaining 8 occupied molecular orbitals there with essentially non bonding character that is a reason they are not interacted with any of the boron orbitals. We do not have a suitable symmetry one. So, they remains so; that means, now 8 means essentially we should have 16 electron. So, we should account for now 16 electrons let me go back to the Lewis dot structure here for BF 3.

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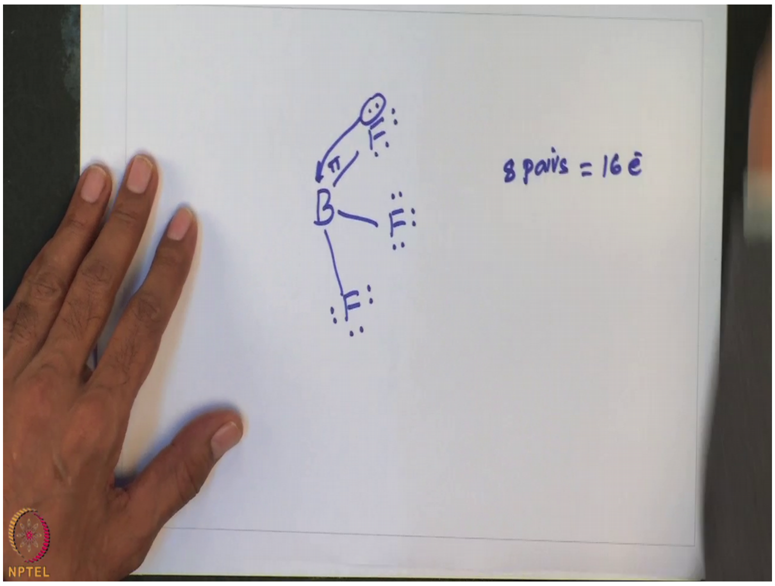


So, let me write again Lewis dot structure for BF 3. So, 3 electrons we have used now. We had now 2s 2, 2p 1, 3 electrons I have used for making the bonds and now, remaining electrons I write like this. So, total, because octet is satisfied for fluorine also 2, 4, 6 and 8. 2 electrons 2 ,4, 6 and 8. Now, one of the lone pair has gone through pi bonding. So, now, how many electrons are left now? We shall count, 1, 2, 3, 4, 5, 6, 7, 8 means 16. 8 pairs, that is, 16 electrons now. So, these 16 electrons essentially occupy here these 8 orbitals.

So, again very clearly if you have any doubt in your mind that how we have 8 orbitals here, of course, total of ligand group orbitals are 12. 3p orbitals and 1s orbitals; that means, 4 orbitals coming from each fluorine into 3 times 12 orbitals; out of 12, 4 are participating here and 4 are participating here, 4 bonding molecular orbitals and 4 anti bonding molecular orbitals, remaining 8 will be non bonding molecular orbitals. Essentially, whatever the electrons are there neutralized electrons of the 2p they remain here, this 16 electrons. So, total of 16 plus 8, 24 electrons. 24 electrons we have actually if we count the total electrons here, this is 21 plus 3. 21 electrons are coming from 3 fluorine atoms and 3 electrons are coming from boron we have a 24 electrons. All this 24 electrons are accounted in this MO diagrams.

Although it appears like complicated, once you understand how to write you should be able to write and also you can account for all the electrons present in the entire molecule and also you can correlate with this one with other bonding models we have used in the past. So, let me write one more important molecule MO diagram for that is SF 6.

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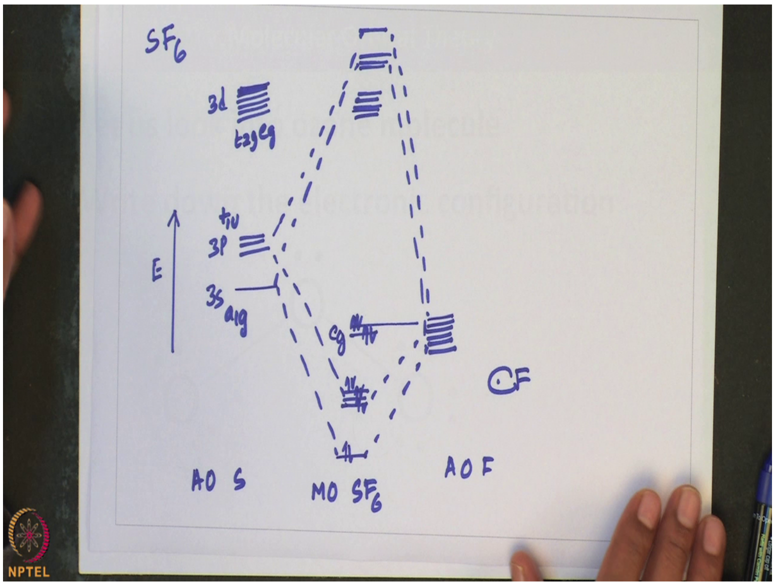


So, SF 6, if we just recall the explanation of bonding in SF 6 using VSEPR theory or valence bond theory, so, VSEPR theory, we will be our giving a geometry of octahedral where 6 electrons from 6 fluorine atoms and 6 electrons from the valence orbitals of sulfur it 12 electrons, we will make 6 bonded pair and these bonded pairs are directed towards to the 6 kernels of an octahedral. So, it has a octahedral geometry.

So, now, let us look into the explanation using molecular orbitals theory, how this electrons are arranged here. 3s 3p and 3d 5, so, of course, they have t2 g and e g symmetry and they have t 1 u symmetry and this one is a 1 g symmetry. So, that is not important here and now, we are using again 6 fluorine orbitals where considering, so, now I am not considering all again very similar to what I did in case of BF 3 just for the explanation I am considering only 6 orbitals that are participating in bonding. So, remaining will remain as non bonding.

So, here essentially, this represent the fluorine orbitals having one electron in the 2p, so, that means, we have 2s 2p 5 that I am considering only that one. So, now, here the first one and then we have t 1 u and then we have here 2 and then this essentially remains and then we have 1, 2, 3 and 1.

So, here and then 3. So, now, we can place the electrons here. We have here, yeah, 6 electrons and 6 electrons are there. I can place here 6 electrons here and so, total of 12 electrons are placed here. So, that means, here if you just look into atomic orbitals of s atomic orbitals of F and this is molecular orbitals of SF 6. So, if we just see here the energy of 3d orbitals are too high to interact with f orbitals. So, that essentially it indicates d orbitals are not participating in the formation of SF 6 molecules and it is essentially a high prevalent molecule and here, if you see these 4 electrons are coming from f essentially remains as non bonding here.

So, this is how you can write the structure whereas, in case of valence bond theory we depicted SF 6 having sp 3, d2 hybridization and these sp 3, d 2 having one electron each will interact with 2p orbitals of fluorine to form 6 covalent bonds they are disposed towards 6 kernels of an octahedral. But, here if you just look into MO diagram the energy of 3d orbitals are too high to interact with f orbital, as a result 4 electrons coming from f having essentially e g symmetry, do not really interact with e g of this one they remain as non bonding. So, this is how one can write the MO diagrams and compare this with other bonding theories.

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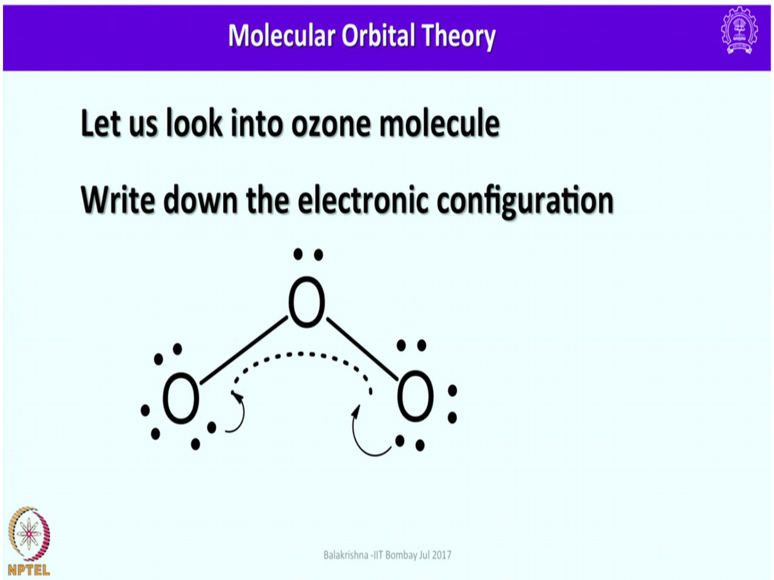


So, let us look into ozone molecule and ozone molecule, one can write down the electronic configuration. I have shown there, we can see clearly. Here, 6 electrons are there and it has 4 electrons and 6 electrons, that means, here essentially the octet of this 2 terminal oxygen atoms are satisfied whereas, this one as only 6 electrons. So, here what happens, one of the electron from this one oxygen, another electron from this one essentially getting delocalized over O-O-O bond and hence, it is stabilizes once. You put these 2 electrons here, you can see all 3 oxygen atoms will be having octet.

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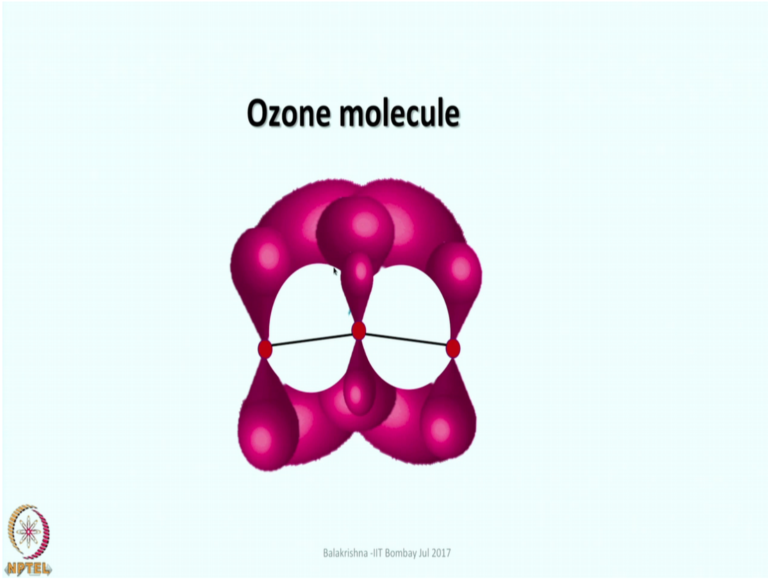


So, this how you can write MO diagram, you can show the interaction of orbitals to form this kind of 3 centered 2 electron bond to satisfy its octet. So, now, let us summarize all the bonding concepts we came across.

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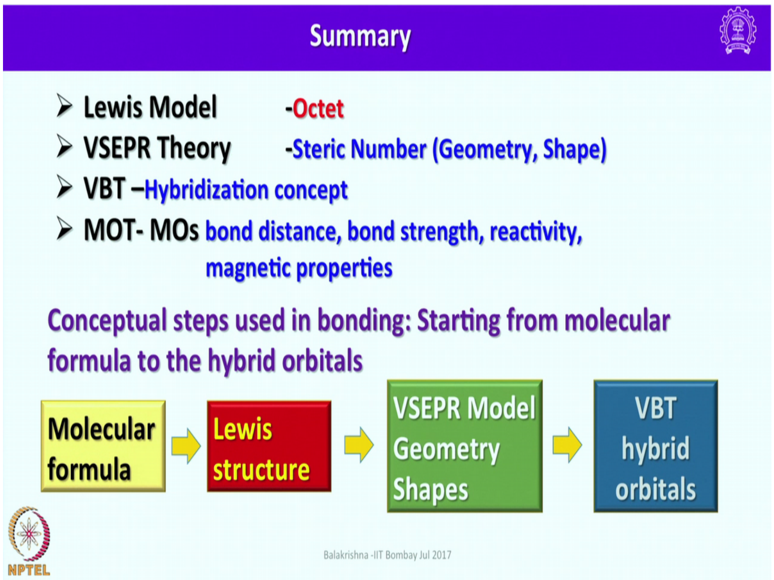


First, we began with Lewis model. Lewis model gives emphasis for s2 p6 electronic configuration; that means, octet each and every element has a tendency to have main group elements, I am referring to have s2 p6 electronic configuration so that they can have next inert gas electronic configuration at in the stability. So, the octet model is given important, whereas VSEPR theory gives emphasis for steric number and steric number is nothing, but the number of bonded pairs, but number of lone pairs and how we essentially we can dispose this steric numbers from the central atom away from each other to minimize interaction that results in a particular standard geometry.

And, when we do not consider lone pairs we get the shape of the molecule and then valence bond theory talks about hybridization concept. It is fantastic it can explain everything about a molecule especially when it comes from the main group elements. Only the problem is with the coordination compounds, where it cannot explain spectral properties color magnetic properties and other things relative strength of the legends and molecular orbitals theory essentially gives all aspects related to a molecule, that means, bond distances; you can talk about bond distances, you can correlate the bond distance and bond strengths and reactivity, magnetic properties without any problem without any flaw.

So, molecular orbitals theory is more refined and it is more informative compared to any of the bonding theories we come across and conceptual steps one can use in bonding can begin from the molecular formula, one should write first molecular formula and then write Lewis structure and then try to use VSEPR model to predict geometry and shape then go for valence bond theory using hybridization concept and then eventually proceed to molecular orbitals theory to know about this molecules.

For example, now if I ask a question, why atoms combine? You can say simply to form molecules and then if I ask again why molecules are formed, because atoms are combined; that means, essentially why atoms combine to form molecules. The reason is very simple some atoms have a tendency to lose electrons from their valence shell and some elements have a tendency to gain electrons into their valence shell; that means, when they have tendency to lose electrons they become positively charged, they are called cat ions. When they have a tendency to gain an electron essentially they will be having one extra electron they are called anions or they form anions usually non metals and once when they have ability to share their valence electrons they form a covalent bond. So, ions formed by main group elements are usually isoelectronic with the one of the nearest noble gases.

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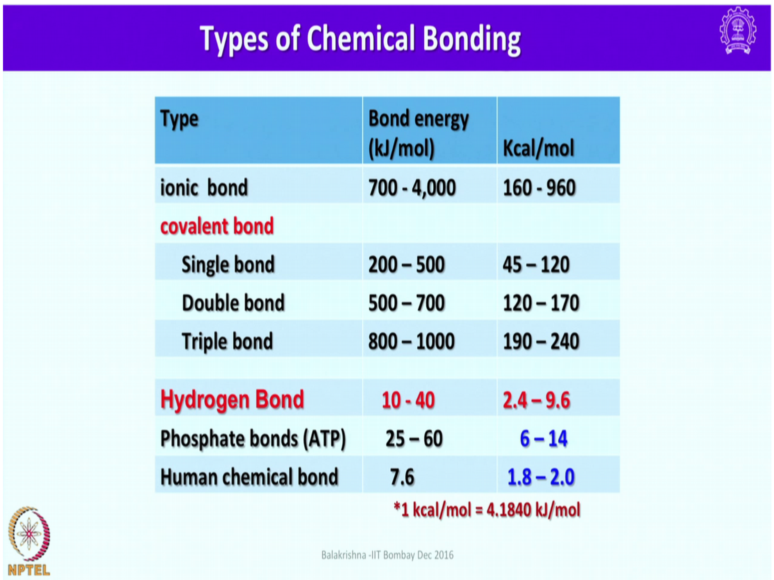

## Types of Chemical Bonding

| Type | Bond energy (kJ/mol) | Kcal/mol |
|---|---|---|
| ionic bond | 700 - 4,000 | 160 - 960 |
| covalent bond | | |
| Single bond | 200 – 500 | 45 – 120 |
| Double bond | 500 – 700 | 120 – 170 |
| Triple bond | 800 – 1000 | 190 – 240 |
| Hydrogen Bond | 10 - 40 | 2.4 – 9.6 |
| Phosphate bonds (ATP) | 25 – 60 | 6 – 14 |
| Human chemical bond | 7.6 | 1.8 – 2.0 |

*1 kcal/mol = 4.1840 kJ/mol

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So, now, I have given some bond energy for all kind of bonds here. We have ionic bond, covalent bonds; again, covalent bonds we have single bond, double bond, triple bond like we come across in methane, ethylene or alkyne and again we have a hydrogen bond and phosphate bonds in ATP and also, there is some values also given for human chemical bond. You can see ionic bonds are much more stronger the energy is anywhere between 700 to 4000 kilo joules per mole or you can convert them into kilo calories per mole. Essentially, 1 kilo calories per mole are equal to 4.1840 kilo joules per mole. I repeat again, 1 kilo calories per mole are equal to 4.1840 kilo joules per mole. So, you can always use that one for conversion and single bonds will be having energy anywhere between 200 to 500 kilo joules per mole, whereas, double bonds will have anywhere between 500 to 700 and triple bonds have energy between 800 to 1000 kilo joules per mole.

And, when we look into individual hydrogen bond, anywhere they have energy between bond energy 10 to 40 kilo joules per mole and phosphate bonds have anywhere between 25 to 60 and human chemical bonds also they have given a value it stays around 7 to 6 kilo joules per mole.

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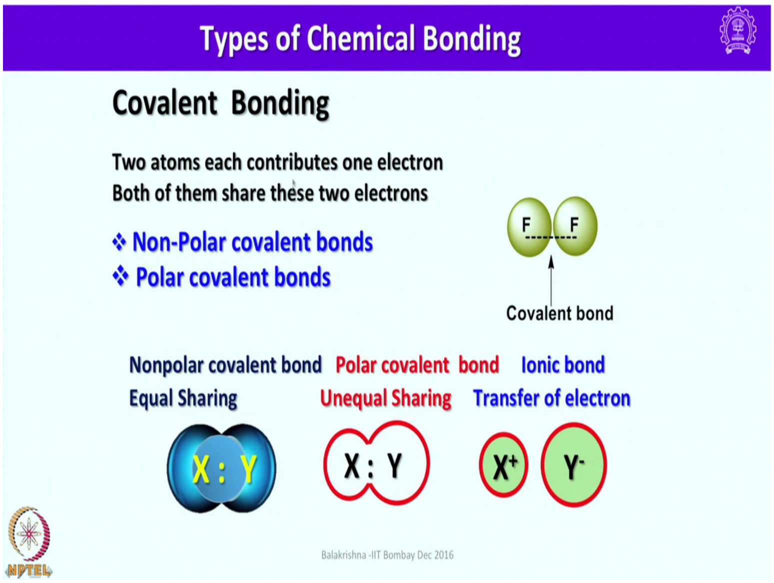


So, now, covalent bonds I have shown. 2 atoms each contribute one electron. Both of them share these 2 electrons, for example, you can see covalent molecule such as F 2 and again, when you make covalent bond we have polar covalent bonds as well as non polar covalent bond and if the electro negativity difference between the 2 atoms is minimum or in case of homo diatomic molecule it is essentially non polar covalent bond. When the electro negativity difference is larger that results in polar covalent bond electro negativity is too much larger then that results in ionic bonding. So, those all the 3 category of bonding I have shown here in this one.

So, non polar covalent bonds equal sharing and polar covalent bond unequal sharing, this happens when the electro negativity difference is marginal or little more and whereas, ionic bond transfer of electron it happens between the most electro negative elements with most electro positive elements; that means, alkaline earth metals are alkaline metals with halides is an ideal example for them.

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| | | | | | | | kJ/mol |
|---|---|---|---|---|---|---|---|
| H—H | 432 | N—H | 391 | I—I | 149 | C = C | 614 |
| H—F | 565 | N—N | 160 | I—Cl | 208 | C ≡ C | 839 |
| H—Cl | 427 | N—F | 272 | I—Br | 175 | O = O | 495 |
| H—Br | 363 | N—Cl | 200 | | | C = O* | 745 |
| H—I | 295 | N—Br | 243 | S—H | 347 | C ≡ O | 1072 |
| | | N—O | 201 | S—F | 327 | N = O | 607 |
| C—H | 413 | O—H | 467 | S—Cl | 253 | N = N | 418 |
| C—C | 347 | O—O | 146 | S—Br | 218 | N ≡ N | 941 |
| C—N | 305 | O—F | 190 | S—S | 266 | C ≡ N | 891 |
| C—O | 358 | O—Cl | 203 | | | C = N | 615 |
| C—F | 485 | O—I | 234 | Si—Si | 340 | F—F | 154 |
| C—Cl | 339 | | | Si—H | 393 | F—Cl | 253 |
| C—Br | 276 | | | Si—C | 360 | F—Br | 237 |
| C—I | 240 | | | Si—O | 452 | Cl—Cl | 239 |
| C—S | 259 | | | | | Cl—Br | 218 |
| | | | | | | Br—Br | 193 |

*1 kcal/mol = 4.1840 kJ/mol



And, then I have also listed some bond energies here, bond enthalpies in this table. You can see here lot of interesting data is available we shall discuss all these things as and when we come across when I start discussing the chemistry of main group elements group wise.

Once, the bonding concept is over now, more or less I have completed the structure and bonding concepts. In my next lecture I will be discussing about the chemistry of hydrogen, once that is done I will be proceeding to the chemistry of main group elements by group wise, that is, alkali metals and alkaline earth metals then group 13 elements like that I continue until I complete group 18 that is inert gas chemistry. So, let me stop at this juncture and I wish you a pleasant chemistry reading.

Thank you very much.