Introductory Organic Chemistry

Dr. Neeraja Dashaputre
Department of Chemistry
Indian Institute of Science Education and Research, Pune

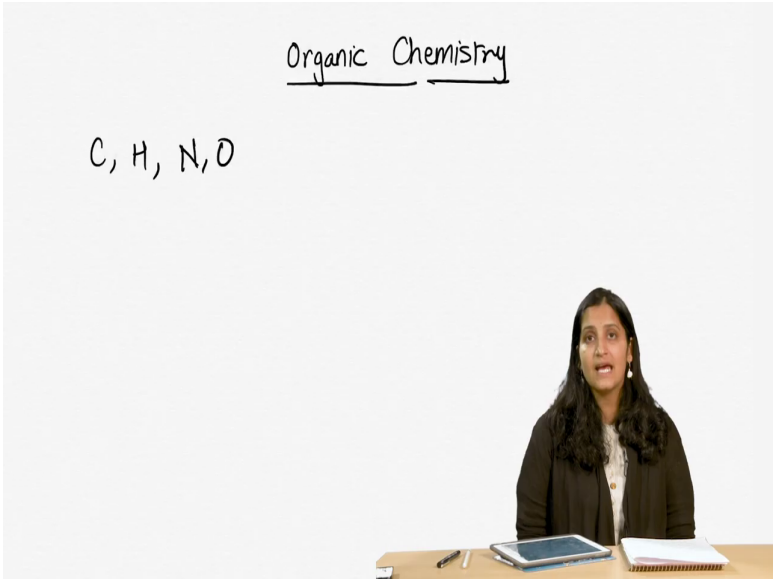
Lecture – 01
Introduction
Structure of atom and molecules

Welcome, in this course we are going to study the principles of Organic Chemistry. Like all sciences chemistry, in general has its unique place in the tools that we employ to study the universe around us. Organic chemistry came to be as a tentative attempt to understand the chemistry of life; chemistry of living beings, the molecules in our bodies, the molecules in nature.

In general chemists were very curious to know what organic matter consists of and organic chemistry began as a stream to understand it. Chemists in general are curious to know the structure and function of molecules around us and organic chemists in particular collaborate with mathematicians and physicists to understand the structure of molecules whereas, they collaborate with biologist to understand the functions that these molecules play in life processes.

In this course, what we are going to go over is the introductory organic chemistry meaning we will begin with the very basics of what molecules are the carbon compounds, functional groups and we will also go over their functions a little bit. So, we will have a little insight into the roles they play in the biological processes.

(Refer Slide Time: 01:33)

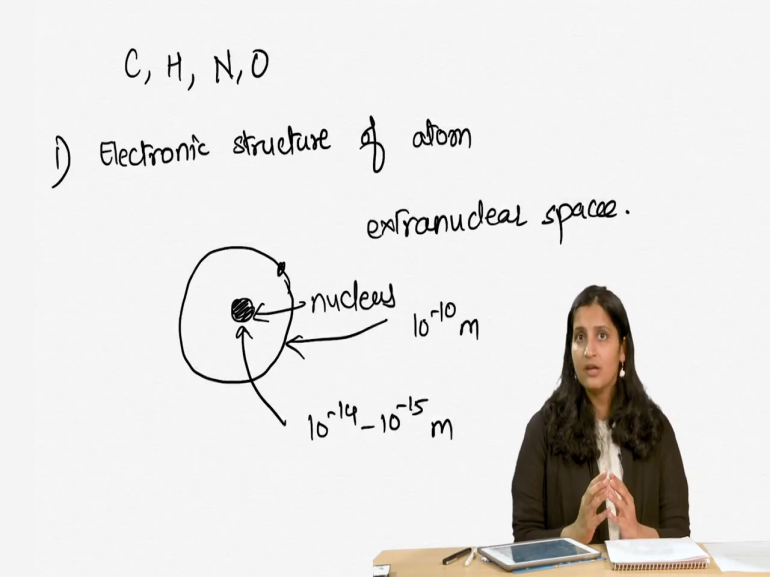


According to the simplest definition, organic chemistry is the study of carbon compounds. Most remarkable feature is that most of the carbon compounds around us contain only four elements; these are carbon, hydrogen, nitrogen and oxygen. A fun fact is that we have either synthesized or discovered more than 10 million molecules that only consist of carbon, hydrogen, nitrogen and oxygen.

So, as we begin this course, we are going to focus on these four elements and we are going to learn how carbon forms bonds with hydrogen, nitrogen and oxygen. But remember that there are other elements as well. So, we have boron, silicon we have phosphorus. These elements also form bonds with carbon, but for now, we will focus on the four elements as I talked about.

In the first week, we will lay the foundation to understand the structure of molecules and I am pretty sure that you must have gone over these principles in your introductory chemistry courses. So, you can just treat this as a revision. I am just doing this, so that we all have the basic foundation and we can build up on it as we progress in the course. So, the first thing we are going to cover is the electronic structure of atom.

(Refer Slide Time: 03:00)



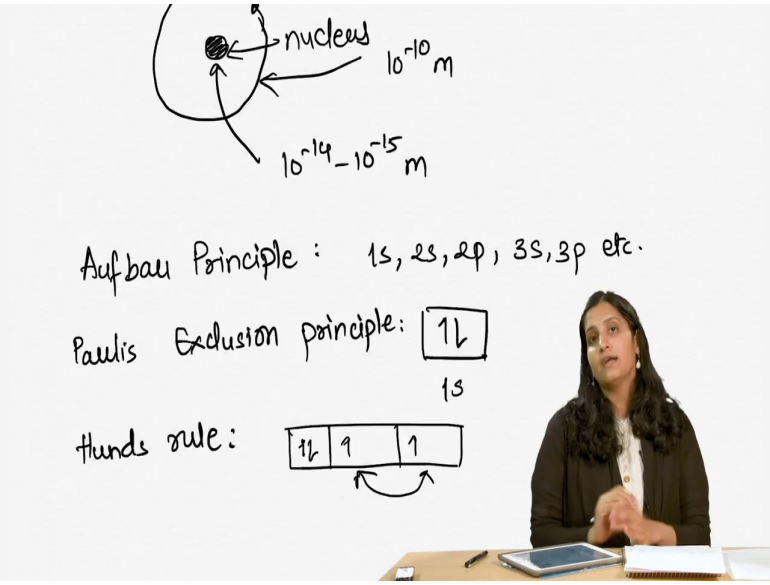
So, as we all know that atom also consists of subatomic particles like protons and neutrons and electrons. And the protons and neutrons are actually in the nucleus of the atom and the electron is revolving, or the electrons are revolving around this nucleus. So, just to draw a representational diagram, the nucleus consists of proton and neutrons whereas, the electrons can be found in the extranuclear space, but they are not found anywhere. In fact, we define shells; shells are defined as this the relative space around the nucleus where the probability of finding this electron is highest.

If we really start looking into the sizes, the nucleus has a diameter of around 10^{-14} to10^{-15} meters whereas, this extranuclear space in which the electrons can be found; that particular diameter goes to around 10^{-10} meters. So, you can imagine that the nucleus is a very compact, dense space inside the atom. In fact, that is where most of the mass of the atom is concentrated.

So, the nucleus is around $10^{-14 \text{ or } -15}$ meters and the electron can be found as upto 10^{-10} meters. So, if I have to give a right analogy, you can imagine that in a large football stadium, if you have a football placed in the middle that football is like the nucleus and the electron can be found anywhere in that stadium. That's the right size correlation of an atom. The shells are divided into sub-shells known as orbitals. The orbitals are denoted with a notation of s, p, d and f and we will look at these orbitals in detail when we go over molecular orbital theory. But for now what we know is that the subshells or the orbitals are also quantized energy, meaning the energy of electrons in a particular orbital is fixed.

For now, I want you to revise the shapes of s and p orbitals because these are the orbitals that will be mainly used when carbon forms bonds with other elements. So, s orbital is spherical in shape and p orbital becomes dumbbell in shape and in fact, there are three p orbitals, meaning you have px, py and pz orbitals available in which we can fill electrons. The other principles that govern the filling of electrons into the orbitals around the nucleus, so the first one is Aufbau's Principle.

(Refer Slide Time: 06:07)



The Aufbau principle states that that as we start filling electrons, they have to be filled such that they are filled in the order of increasing energy. Meaning as I start filling electrons into the orbitals, I must fill the first electron into the 1s orbital after that it comes as 2s and then 2p and so on.

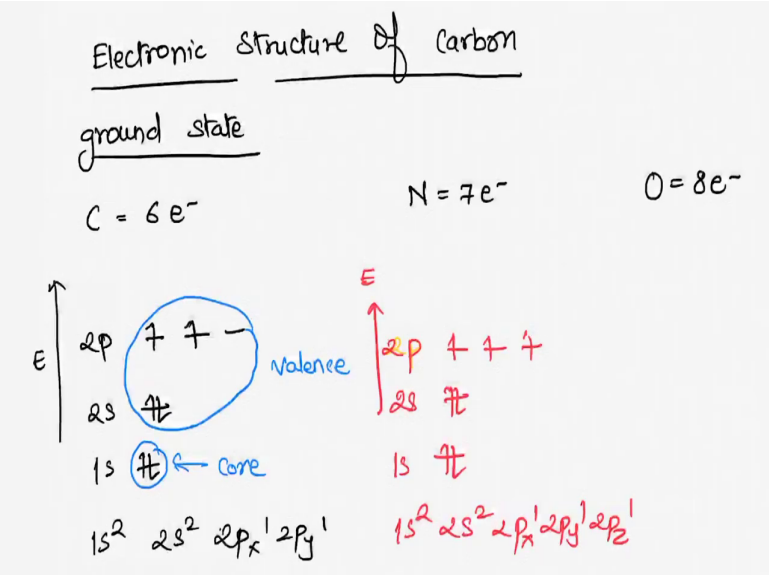
So, the general order of filling electrons into the orbitals goes as follows. The next thing we have to look at is Pauli's exclusion principle. So, Pauli's exclusion principle states that a particular orbital can only have two electrons in it and their spins must be paired with each other. So, you must have seen that the spins are represented with arrows going up and down, but typically what we say is that in any given orbital you can only put two electrons and that the spins must be paired. So, that is why we show that the arrows are going up and down. So, that is how let us say the two electrons in the 1s orbital will be represented.

The third thing we have to look at is Hund's Rule. Now, there are two parts to the Hund's rule. The first part states that, that if orbitals of equal energy are available and you are filling

electrons into them and if there are not enough electrons to fill in all of them, then you must put one electron in each of the orbital before you put the second electron in any one of them. Just for example, if I have to fill the 3p orbital and if I have only four electrons to put in these p, 3p orbital, then I must put one-one electron each in these p orbitals and then only the fourth electron will be placed into one of them.

So, I put in one electron into all of these equal energy orbitals before I put in the second electron into any one of them. The second part of the Hund's rule states that, that the spins of the electrons that are put in these degenerate orbitals should be such that they are aligned with each other. So, for example, in this case these two electrons have an aligned spin as represented.

(Refer Slide Time: 08:49)



So, with all of these principles in mind, let us start writing the electronic configuration of carbon. We are going to write the ground state electronic configuration of carbon. Meaning we have written this configuration keeping in mind all the principles or all the quantum chemistry principles that we have seen before and that is how the carbon atom will exist in its lowest or the ground state electronic configuration way.

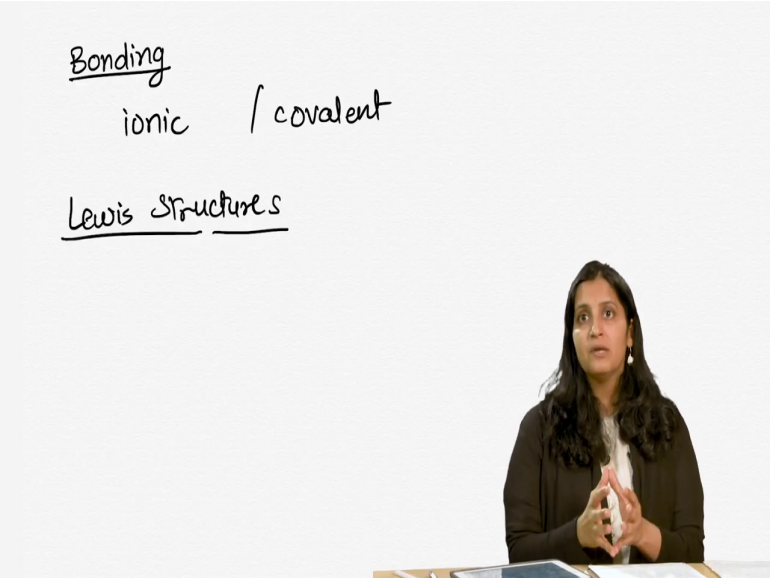
So, carbon has six electrons and using Aufbau's principle if I have to start filling these six electrons into the shells and subshells. The first two electrons go in 1s orbital; the next two electrons go in 2s orbital. Again remember I am following Pauli's exclusion principle here, so their spins are paired and then the next electrons start going in 2p orbital. Now, I have four

electrons; I have used four electrons, so there are two more electrons to be used. So, I will place them in the p orbitals as shown.

So, the electronic structure or electronic configuration of carbon becomes as $1s^2$, $2s^2$, and then $2px^1$, $2py^1$ right. Similarly, we can start writing the electronic configuration of nitrogen, again as I put it in the increasing order of energy, the 1s will have two electrons, 2s will have the next two, now nitrogen has total seven electrons. So, the 2p orbital will have one-one electron each in the x, y and z subshell. So, nitrogen becomes $1s^2$, $2s^2$, $2px^1$, $2py^1$ and $2pz^1$. You can try writing the electronic configuration of oxygen which has eight electrons in total in a similar manner.

Now if we see, let us look at carbon here, carbon has two core electrons and whereas, it has total four valence electrons. The valence electrons are the electrons that occupy the outermost shell of an atom and these are the electrons that take part in bond formation, bond breaking and any kind of chemical reactivity per say. So, chemists often focus more on the valence electron of a particular element when they have to study structure and function of its molecule.

(Refer Slide Time: 11:45)



So, now let us have a look at the bonding. Chemists often focus on the valence electrons because these are the electrons that take part in the bond formation. Now, bonding may be such that an element prefers forming ionic bonds such that in the case of NaCl or sodium chloride where cations and anions are formed or the element may prefer to share its electrons

with another element; such that in the case of let us say methane where carbon and hydrogen are sharing one-one electron to form a bond between carbon and hydrogen. So, this type of bonding is called as covalent bonding.

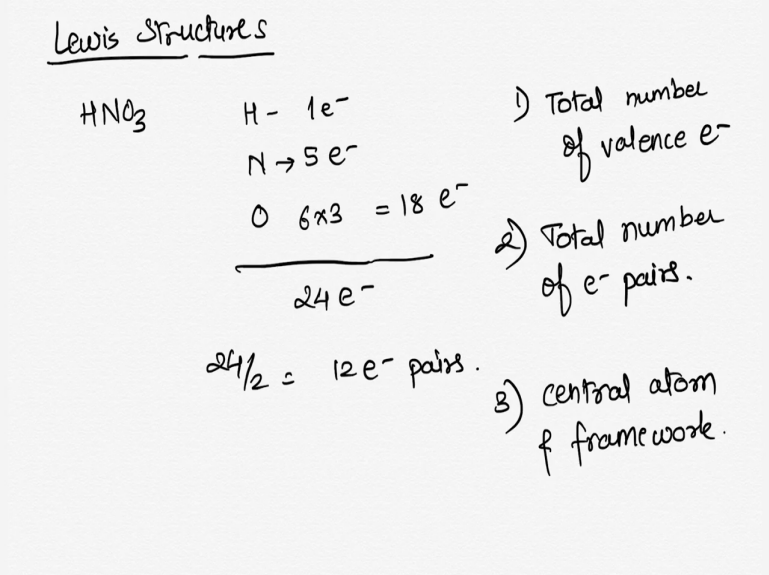
So, what I want you to revise is what are ionic bonds and what are covalent bonds. All bond formations are governed by the need to achieve the nearest noble gas configuration. So, for example, in the case of sodium; sodium has a configuration of $1s^2$, $2s^2$, $2p^6$ and $3s^1$. Its nearest noble gas that is neon has the configuration of $1s^2$, $2s^2$, $2p^6$. So, it is easier for sodium to just give up one electron and become Na^+ and achieve the nearest noble gas configuration of neon. On the other hand, it is much easier for chlorine to accept one electron to achieve the nearest noble gas configuration.

So, when sodium and chlorine form a bond, they form an ionic bond in which sodium has become Na^+ or a cation by giving up one electron and chlorine becomes chloride ion; Cl^- anion such that they both form an ionic bond because of electrostatic force of attraction. In the case of covalent bonding; for example, most of the carbon compounds are formed when carbon forms a covalent bond with another element. For example, in the case of methane; carbon is donating one electron and each of the hydrogen is donating one electron such that carbon has total eight electrons around it.

If you remember, we talked how carbon has four valence electrons. So, it needs four more electrons to have the noble gas configuration or have eight electrons in its outermost shell. So, in the case of methane, each of the carbon's electron gets paired up with one-one electron each from the hydrogen atoms and you have a covalent bond forming. The next thing that we have to look after are Lewis structures. So, Lewis structures are a way to represent the valence shell of an atom using dots where each of the dots represent an electron. The ability to draw Lewis structures is very critical for any organic chemist.

So, what I am going to do now is I am going to solve one or two problems of figuring out what is the correct Lewis structure of any given formula or of any given compound.

(Refer Slide Time: 15:06)



So, in the first one I am going to go over the Lewis structure of HNO_3 or nitric acid. Now, whenever we have to draw Lewis structure, we have to follow a particular set of instructions and we will go step by step into each one of them. The first one is that we have to figure out the total number of valence electrons present in that particular compound. So, I have hydrogen here which gives me one electron, nitrogen has total of five valence electrons; oxygen; each one of the oxygen has six valence electrons. So, I have 6 into 3 giving me 18 electrons in total. So, when I sum them up, it becomes as 24 electrons.

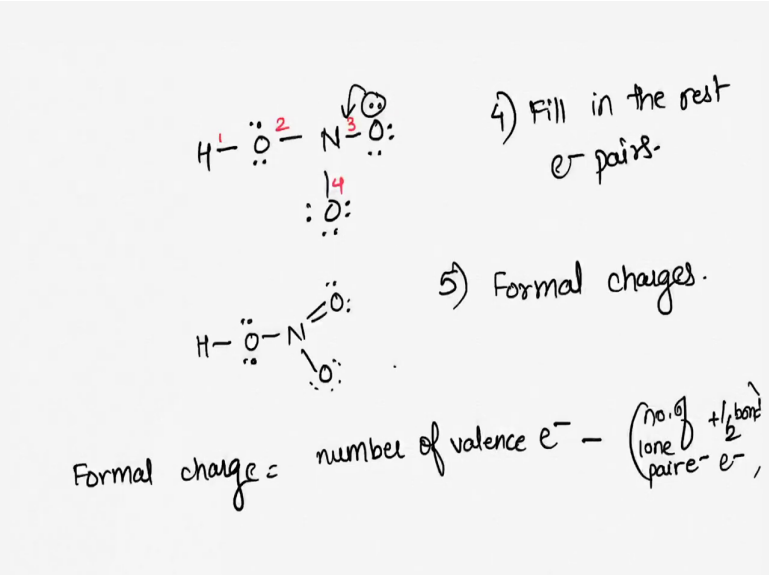
So, HNO_3, the total number of valence electrons present in HNO_3 are 24. Now, as we know electrons are going to form bond such that 2 electrons have to combine together. So, what we have to really figure out is how many electron pairs are available in HNO_3. So, first we figure out the total number of valence electrons and the second thing you figure out is the total number of electron pairs. In this case, I have 24 electrons, so I will have 24 by 2 that is 12 electron pairs, okay.

Now, the third step is a little bit tricky and it may need some practice or you may need to solve a couple of examples to really master this third step. The third step is figuring out the central atom and the kind of skeletal structure or framework for your molecule. So, I am going to write; decide the central atom and the framework. Typically, you put the element that forms maximum number of bonds in the center.

So, in our case, nitrogen; since typically nitrogen forms three bonds; nitrogen becomes the central atom and oxygen and hydrogen are connected to this particular nitrogen. So, in our

case nitrogen becomes the central atom and oxygen and hydrogens are connected to this particular nitrogen. We also follow all other rules that we know, meaning oxygen typically forms two bonds and hydrogen prefers to form only one bond.

(Refer Slide Time: 17:42)



So, with all that in mind, I can draw the structure of HNO_3 or rather the skeletal structure of HNO_3 such that nitrogen is connected to each of the oxygens and one of the oxygen is connected to hydrogen that way hydrogen only forms one bond. Now, when we do this, the next thing you want to do is you want to figure out how many electron pairs you have used so far.

So, if I really count I have used 1, 2, 3 and 4 electron pairs so far. Whereas, I have 12 electron pairs with me. So, the next step to do is fill in the rest of the electron pairs, right. So, I have 8 more electron pairs to fill on this particular skeleton and one needs to remember that the electronegative atoms typically have a larger portion of electron density around them. So, what I am going to do is I am going to give most of the electron pairs to the three oxygens and then if anything remains we will put it on the nitrogen.

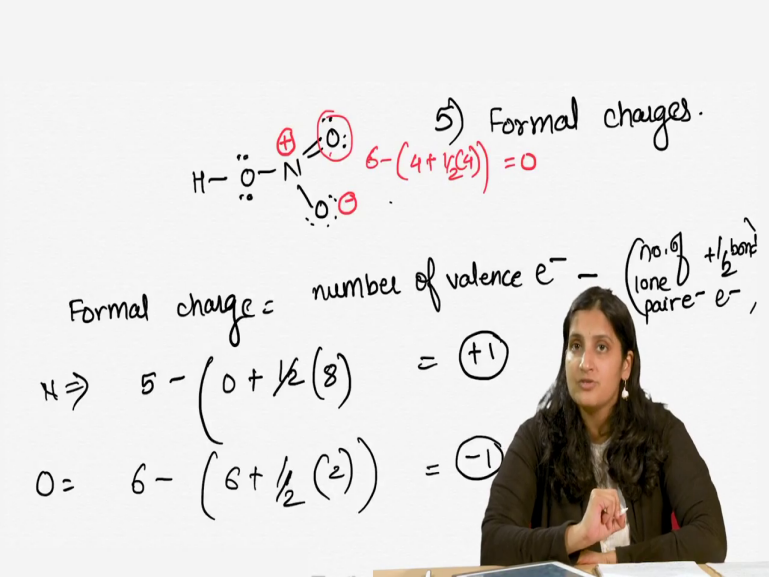
So, let us start completing the octet of each of these oxygens, so I have 1, 2, 3, 4, 5, 6, 7 and 8. So, that is the way I have distributed the eight electron pairs now. As you can see each of the oxygen has a complete octet meaning it has eight electrons in its outermost shell. The nitrogen; however, has only six electrons in its outermost shell and as we said that any element would prefer to have a complete octet because it gives it stability.

So, in order to give it a stability what I am going to do is, I am going to put one of the lone pairs of one of these oxygens such that it forms a bond with the nitrogen rather a double bond. So, the structure of HNO_3 now becomes; there is one thing missing which is the formal charge.

So, the 5th step actually talks about filling in the formal charges, okay. So, in this case, let us look at the charge on the central atom which is nitrogen. Now, formal charge can be given with the formula. So,

Formal Charge = No. of Valence electrons – (No. of lone pair electrons + 1/2 No. of bonding electrons)

(Refer Slide Time: 20:51)

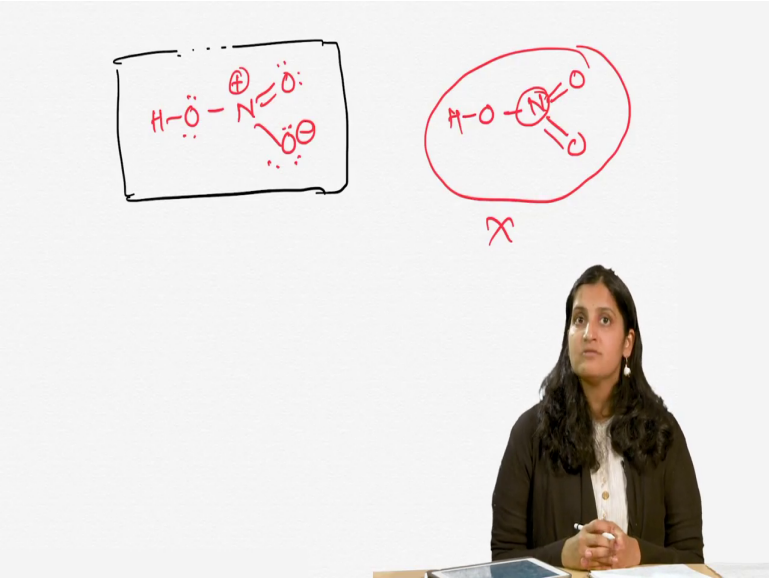


So, the formal charge on nitrogen; so, for nitrogen if I have to figure out the formal charge, the number of valence electrons is 5. So, nitrogen has 5 valence electrons and currently it has no lone pairs plus half the number of bonding electrons. So, if I see the total number of bonds nitrogen is forming; nitrogen is forming four bonds; so, it has 8 electrons. So, half of 8; so, 5 minus 4 will give me a charge of plus 1. So, nitrogen here will have a formal charge of +1.

On the other hand, if I see oxygen which is a single bonded oxygen; if I see the oxygen here, oxygen has 6 valence electrons minus the number of lone pair electrons. So, it has 3 lone pairs, so there are 6 electrons plus half the number of bonding electrons; now it is forming one bond. So, it has 2 electrons in it; so, 6 minus 7 which gives me a charge of -1.

So, the oxygen here has a charge of minus 1. If you look at any of the other elements which are the other two oxygens and the hydrogen they have a formal charge of 0 because their octet is complete and you can see for example, in the case of this particular oxygen here, the one on top. If I really want to calculate, the formal charge will be 6 minus it has 4 lone pair electrons plus half of 4, so; that means, the total formal charge on that particular oxygen will be 0.

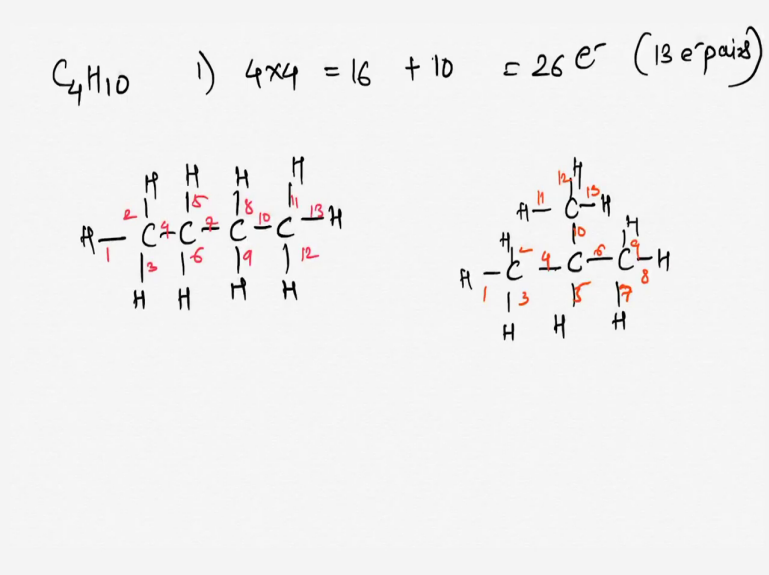
(Refer Slide Time: 22:36)



So, just to sum up the structure of HNO_3 becomes as follows, okay. Now, one might ask a question, why can I not form another double bond between nitrogen and oxygen; so, something like this. So, nitrogen is forming two double bonds with each of the oxygens and this. So, this becomes a wrong Lewis structure because if you really see the central atom nitrogen here is forming 5 bonds meaning it has 5 into 2 that is 10 electrons around it which is against the octet rule.

So, octet rules states that the second row elements can have up to 8 electrons in their outermost shell. Nitrogen cannot expand its octet to fill in the 10 electrons as we have shown here. So, this is not the right structure and in fact, we should stick with our earlier structure which is this one. The next Lewis structure, we will draw is of molecular formula C_4H_{10}.

(Refer Slide Time: 23:47)

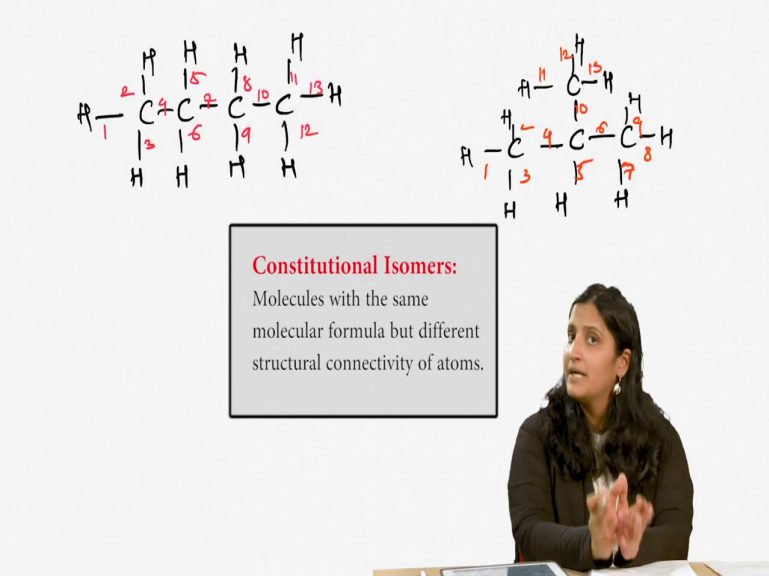


I just want to go over this particular example because as I said that the third step in drawing the Lewis structure which is figuring out the central atom and the framework might get tricky as we go on. So, I just want to go over this one, so that we clarify any doubts. So, C_4H_{10}, the first one is figuring out the total number of valence electrons and I have 4 carbon atoms. So, that is 4 into 4 is 16, plus 10 of these hydrogen atoms, so that will be total 26 electrons or 13 electron pairs, right.

Now, the third step is where I need to figure out the skeleton of this particular molecule. Now, there are various skeletons possible I am just going to draw two of them. So, you can think about it such that the 4 carbons are in one line such that they are forming bonds with each other and all the hydrogens are attached to these 4 carbons such that each carbon is forming 4 bonds, so that is one possibility. If I count the number of electron pairs, it becomes as 13. So, we are good we have filled in 13 electron pairs, but I can also draw the same molecule as this one and this is not a wrong representation of this particular compound.

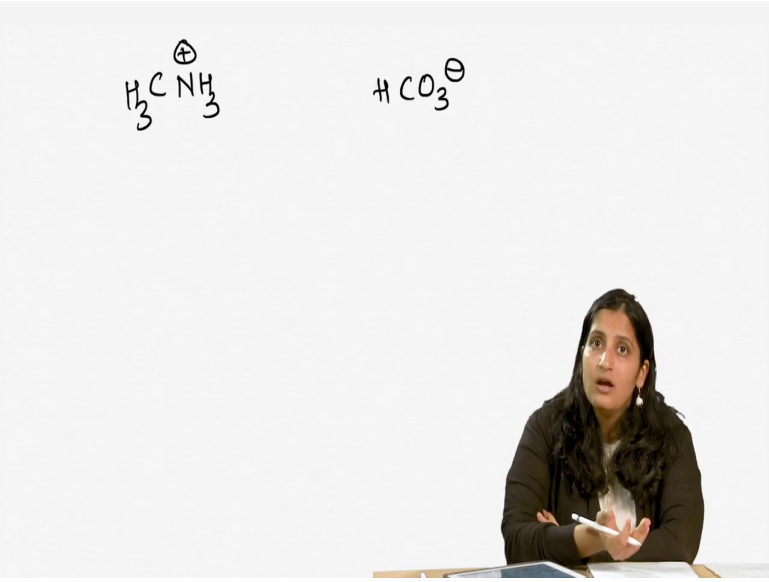
So, if you see in this particular second example, what I have done is that the three carbons are in one row and the one of the carbons is actually attach to the central carbon. So, now, if I count the number of electron pairs that have been used, that also comes down to 13. In fact, both of these structures are correct and in order to figure out which one of them is really correct, I may have to do some other chemical tests to figure out whether it is this first example or the second one. So, for now if you were asked to draw a Lewis electron dot structure of C_4H_{10}, any of these 2 molecules could be correct. In fact, the two structures that we have drawn here are butane and isobutane.

(Refer Slide Time: 26:29)



And these are isomers of each other meaning they have the same molecular formula, but different structural connectivity. So, both of the answers would be termed as right in our case.

(Refer Slide Time: 26:50)

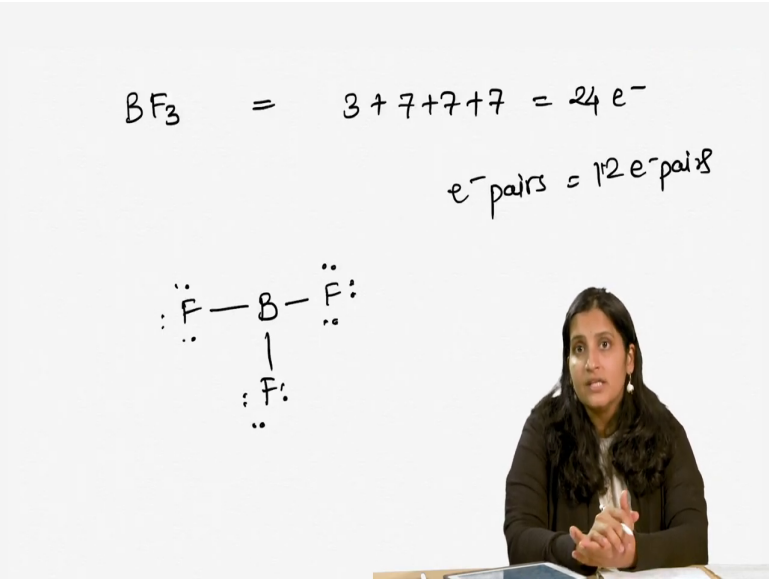


In fact, for practice, let us try drawing the two of these ions. So, the first one is going to be $CH_3NH_3^+$ and the second one is the bicarbonate ion which is HCO_3^-. Just a little trick when we are drawing the electron dot structure or the Lewis electron dot structure of ions which have a positive or a negative charge, we have to take those charges into account when we are counting the total number of valence electrons. Meaning in the case of HCO_3^- since there is a

negative charge on HCO_3, I will calculate the total number of valence electrons and we will add a plus 1 to the total number of valence electrons because of the presence of that negative charge.

In the case of $CH_3NH_3^+$ I will subtract one from the total number because I have to account for that positive charge. So, why do not you try these two molecules and try and draw their Lewis electron dot structure as a practice or as homework. So, we have always said that we wish to follow the octet rule such that each of the elements in a Lewis electron dot structure has 8 electrons around it, but in some cases you may find that there are exceptions to this rule.

(Refer Slide Time: 28:14)

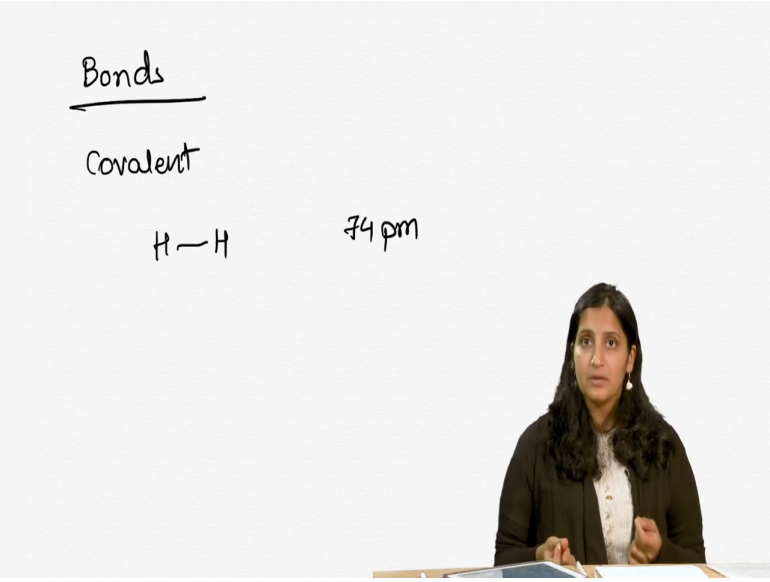


So, for example, when I have to draw a structure of boron trifluoride or BF_3, let us try drawing the structure here. So, if you have BF_3 boron has 3 electrons in its outermost shell or valence shell and each of the fluorine has 7 electrons. So, the total becomes 24 electrons and the next step is figuring out the electron pairs. So, the number of electron pairs becomes 12 electron pairs, right. Now, if I put the central atom as boron because it likes to form three bonds and each of the fluorine then forms bonds with the boron.

So, if we now count, I have used 3 electron pairs and I have 9 more electron pairs to fill. So, in this case, I can put them on fluorine because as you know fluorine is the most electronegative element, so it will have higher electron density around it. So, if you see in BF_3 boron has six electrons around it, each of the fluorine has 8 electrons around it and we have

used up all 12 electron pairs. In fact, the structure of BF_3 does exist where boron does not have a complete octet and this is an exception to the octet rule. Compounds like BF_3 or $AlCl_3$ where the central atom does not have a complete octet; typically show higher reactivity that is because their octet rule is not satisfied.

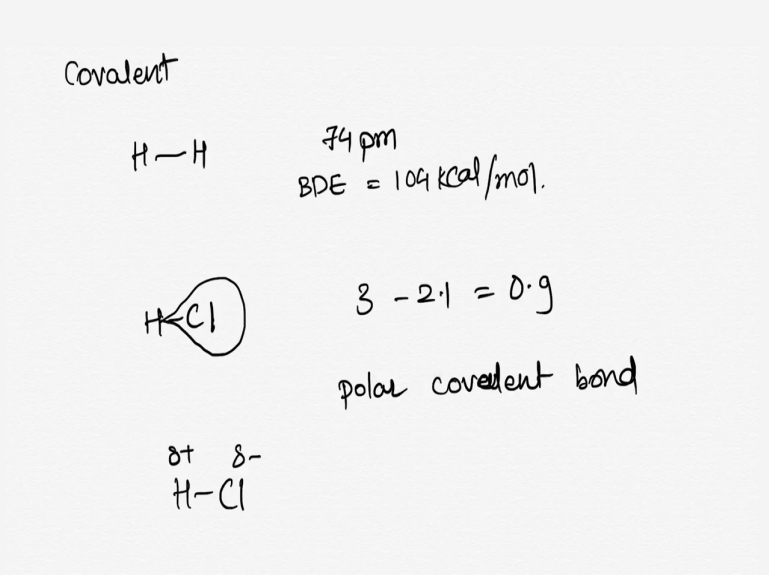
(Refer Slide Time: 29:52)



So, we have looked at covalent bonds. Now, let us look at a hydrogen-hydrogen covalent bond. In this particular bond, each of the hydrogen is donating one electron to form a pair of electrons that is shared between the two hydrogens. In fact, both the hydrogens hold an equal share of the electron density around them. The distance between the two hydrogen atoms is typically closer to 74 pm or you can also see what is the distance in typical Angstrom so, whereas, 1 pm is equal to 100 Å. As the two hydrogens pair to form a bond, a large amount of energy is released because of stabilization.

In the case of hydrogen-hydrogen bond, this particular energy is equivalent to about 104 kilocalories per mole. Different bonds are going to have a different amount of bond dissociation enthalpy and you can refer to the table given which talks about the bond dissociation enthalpy is of various covalent bonds.

(Refer Slide Time: 31:04)



Now, I want to point your attention to another covalent bond which exists as hydrogen chloride is formed. Now, in the case of hydrogen and hydrogen, both the hydrogens had equal electronegativity. So, the electron cloud was shared equally between both the elements. In the case of hydrogen chloride; however, as you can imagine, chlorine is much more electronegative than that hydrogen. So, it's pulling electron density away in that covalent bond.

In fact, chlorine shares or holds a large portion of the electron density or electron cloud and hydrogen holds a tiny portion. So, if I really have to represent, it is such that chlorine holds a large chunk of that electron density of the hydrogen and chlorine bond. This is because chlorine is much more electronegative. If you really see the difference in electronegativity of chlorine and hydrogen, it is 3 for chlorine and 2.1 for hydrogen so, which is around 0.9 units.

Whenever the electronegativity difference between the two elements is more than 0.5 units that particular bond is called as polar covalent bond. So, a polar covalent bond is still a covalent bond meaning the electron pair is shared between the two elements, but the electron density is not shared equally between the two elements. In the case of hydrogen chloride, hydrogen because it holds a very tiny portion of electron density has a partial positive charge on it and chlorine, on the other hand will have a partial negative charge on it. So, you will see these delta minus and delta plus signs on atoms or elements in various compounds and they represent the chunk of the electron density that they hold in formation of a particular bond.