Main Group Chemistry
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Lecture – 33
Chemistry of Group 14 Elements

Once again welcome to MSB lecture series on main group chemistry. In my previous lecture I started discussion on graphite and single layers of graphite is called graphene and how to generate carbon nanotubes from graphene. So, let me continue from where I had stopped; the structure of carbon nanotube also known as n c t can be imagined as a cylinder found by rolling a graphene sheet and then closing it on both sides by fullerene hemispheres. So that means, essentially if it is a graphene single sheet, graphene single sheet I had mentioned this is graphite, and then if I could take out very effectively single sheet this is nothing, but graphene and this graphene by folding and I can have a a cylinder it is called graphene cylinder. Graphene can be cut into thin strips or nanoribbons.

By lithographic techniques, these ribbons are described by their edges either zigzag or armchair. One can join the edges of nanoribbons together to form such nanotubes in several ways, it can also form multilayer carbon nanotubes in which one layer have pi interaction with another one. So, you can also have concentrate you know nanotubes of having different diameters.

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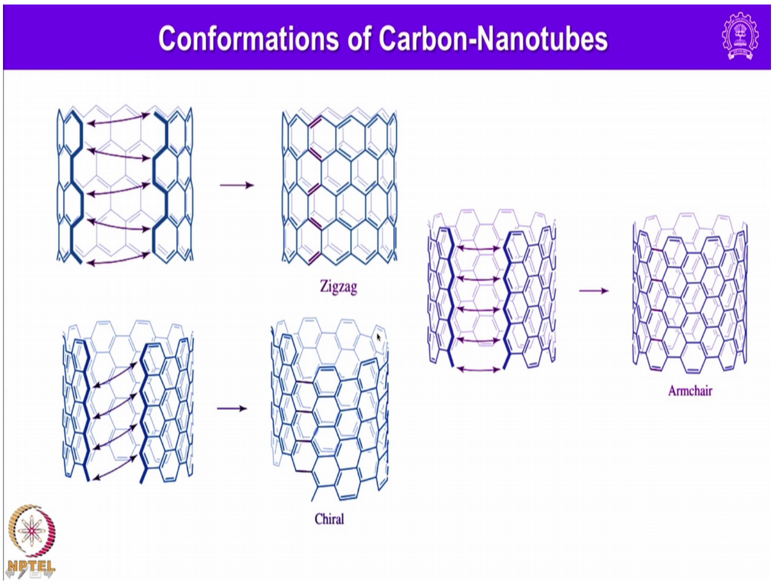

Conformations of Carbon-Nanotubes

So, you can see here carbon nanotubes here as I mentioned when we fold a graphite sheet, we can complete it by clipping this exposed carbon atoms in this fashion. This called zigzag or one can also make in this way this gives a chiral centre or one can also make like this armchair something like this. So, there are several ways in which the clipping of the edges can be performed ok.

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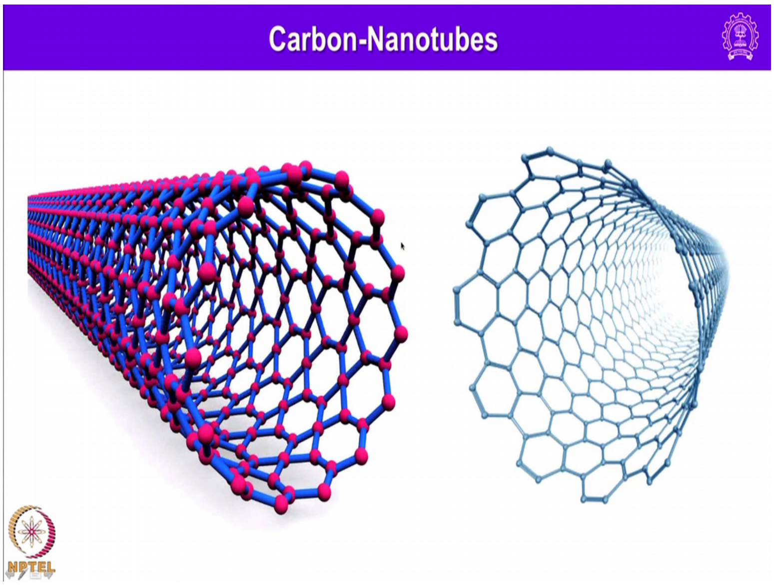

Carbon-Nanotubes

So, this is how a typical carbon nanotubes looks like, and if I could take a smaller nanotube put it inside you can see this one.

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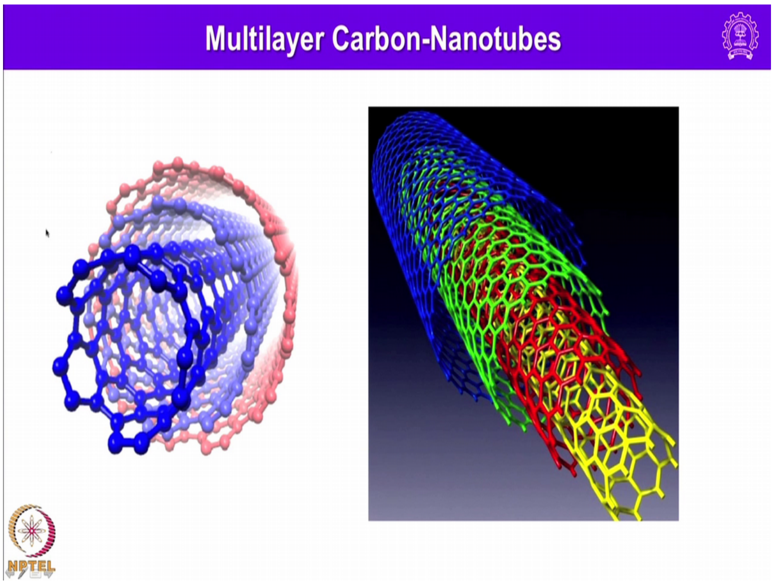

Multilayer Carbon-Nanotubes

One can play around this are called multilayer carbon nanotubes ok.

So, let us look into another important compound of graphene oxide.

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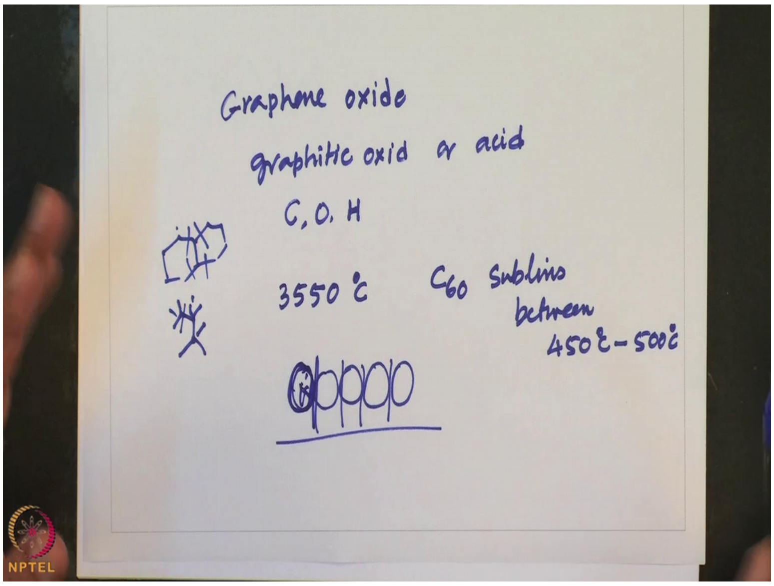

Graphene oxide

graphitic oxid or acid

C, O, H

3550 °C

C_{60} sublims between 450 °C - 500 °C

Graphene oxide formerly called graphitic oxide, oxide is also called graphitic oxide or graphitic acid or acid is a compound of carbon essentially carbon, oxygen and hydrogen in variable ratios by the oxidation of graphite or graphene using strong oxidizing agents, oxygenated functionalities are introduced in the graphite structure, which not only explain the layer separation, but also makes the material hydrophilic. You should remember graphene or graphite is hydrophobic, but adding this oxygenated functionalities one can make the material hydrophilic, graphite oxide is a multilayer system whereas, in a graphene oxide dispersion of few layers or monolayers flakes can we found; that mean dispersion of few layers or monolayer flakes can be found something like this.

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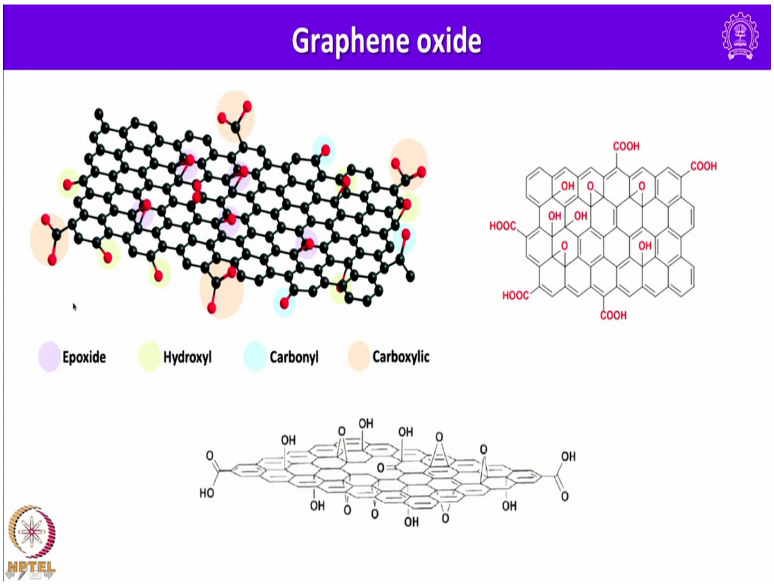

Graphene oxide

Of course one can also put epoxide here or hydroxyl groups can be added or carbonyl groups can be added or even carboxylic groups can be added and you can see here. And now this is how the dispersion of this groups can be visualised on a single graphene sheet; you can have all kind of oxygenated functionalities on the surface of graphene.

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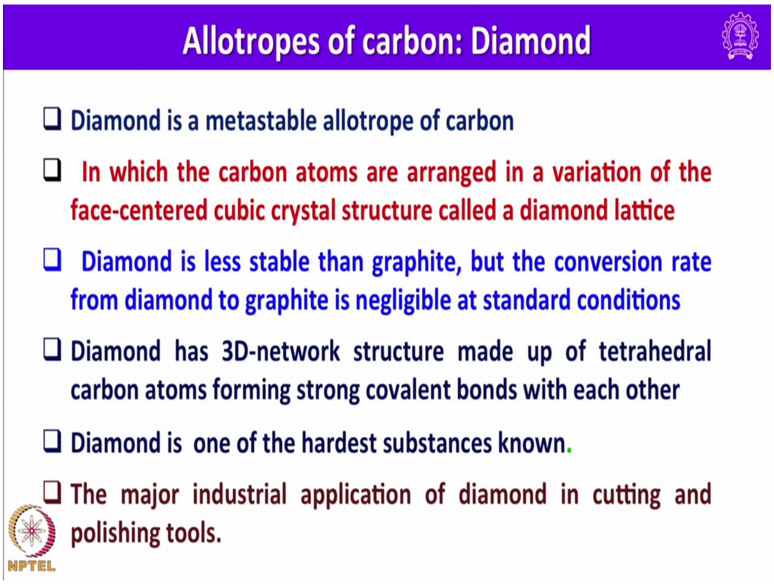

Allotropes of carbon: Diamond

- ☐ Diamond is a metastable allotrope of carbon
- ☐ In which the carbon atoms are arranged in a variation of the face-centered cubic crystal structure called a diamond lattice
- ☐ Diamond is less stable than graphite, but the conversion rate from diamond to graphite is negligible at standard conditions
- ☐ Diamond has 3D-network structure made up of tetrahedral carbon atoms forming strong covalent bonds with each other
- ☐ Diamond is one of the hardest substances known.
- ☐ The major industrial application of diamond in cutting and polishing tools.

Let us look into the other allotrope of carbon that is diamond. Diamond is a metastable allotrope of carbon, in which the carbon atoms are arranged in a variation of the face centred cubic crystal structure called a diamond lattice. In fact, in carbon what happens every carbon atom is tetrahedral and coordinated to another carbon atom, and this network is three dimensional in nature that leads to the formation of diamond. So, diamond is one of the hardest substance known, the major industrial application of diamond is in cutting and polishing tools.

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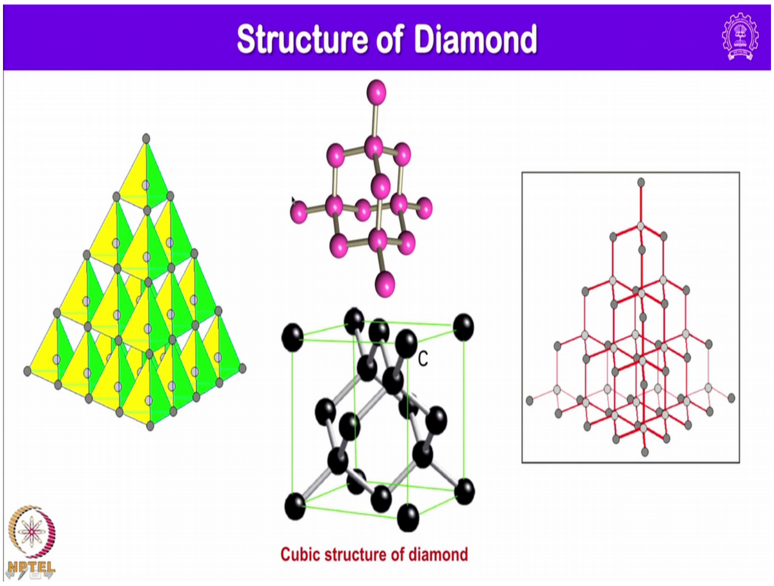

Structure of Diamond

Cubic structure of diamond

And this how the diamond looks like. So, every carbon atom is binding in a tetrahedral fashion to neighbouring carbon atom and this network grows in three dimension to give this kind of structure here, cubic structure of diamond can be seen here in this diagram.

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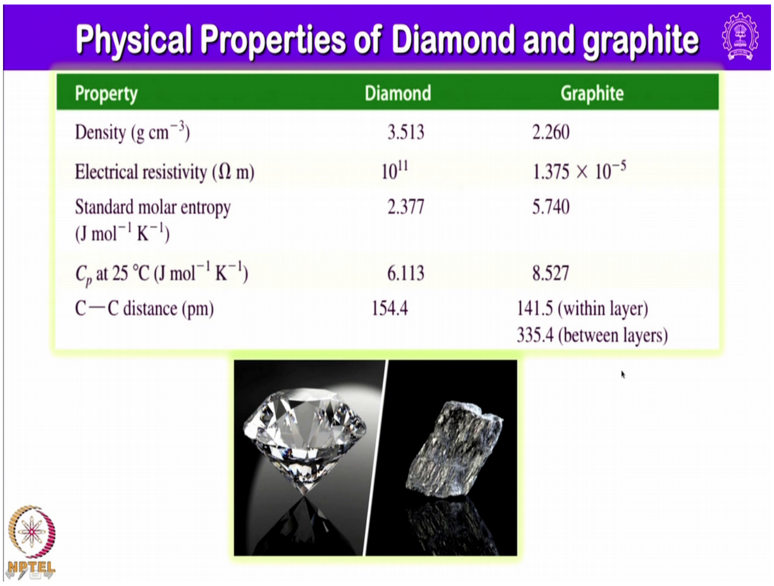

Physical Properties of Diamond and graphite

Property	Diamond	Graphite
Density (g cm^{-3})	3.513	2.260
Electrical resistivity (Ω m)	10^{11}	1.375×10^{-5}
Standard molar entropy (J mol^{-1} K^{-1})	2.377	5.740
C_p at 25 °C (J mol^{-1} K^{-1})	6.113	8.527
C—C distance (pm)	154.4	141.5 (within layer) 335.4 (between layers)

Let us look into the difference between graphite and diamond density is more in case of diamond its 3.513 whereas, graphite 2.26, and electrical resistivity is remarkable in case of diamond 10 to the power of 11 whereas, in case of graphite you can see that and standard molar entropy is 2.37, 7 in case of diamond whereas, in case of graphite its 5.740 joules per mole per Kelvin, and carbon carbon distance is much longer in case of diamond its 154 picometre whereas, in case of graphite it is 141.5 within the layer and between the layer the separation is 335 picometre.

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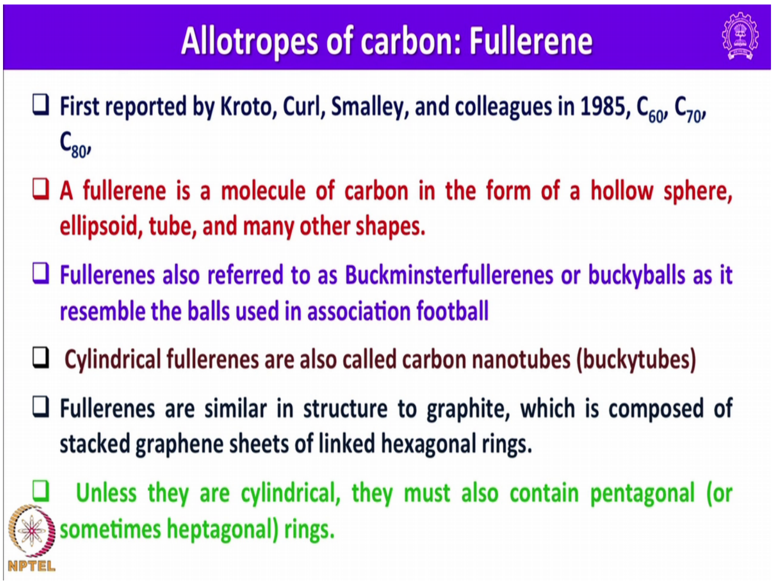

Allotropes of carbon: Fullerene

- First reported by Kroto, Curl, Smalley, and colleagues in 1985, C_{60}, C_{70}, C_{80},
- A fullerene is a molecule of carbon in the form of a hollow sphere, ellipsoid, tube, and many other shapes.
- Fullerenes also referred to as Buckminsterfullerenes or buckyballs as it resemble the balls used in association football
- Cylindrical fullerenes are also called carbon nanotubes (buckytubes)
- Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings.
- Unless they are cylindrical, they must also contain pentagonal (or sometimes heptagonal) rings.

Another important allotrope of carbon is fullerene, it was first reported by a three scientists Kroto curl and Smalley in 1985, and they showed the presence of C60, C 70 as well as C 80. a fullerene is a molecule of carbon in the form of a hollow sphere resembling a football or it can be in the form of an ellipsoid or a tube and can take many other shapes. Fullerenes also referred as buckminsterfullerenes or buckyballs as it resembles the ball used in association football. Cylindrical fullerenes are also called carbon nanotubes buckytubes, fullerenes are similar in structure to graphite which is composed of stacked graphene sheets of linked hexagonal rings unless they are cylindrical, they must also contain pentagonal or sometime heptagonal rings as well you can see here fullerene.

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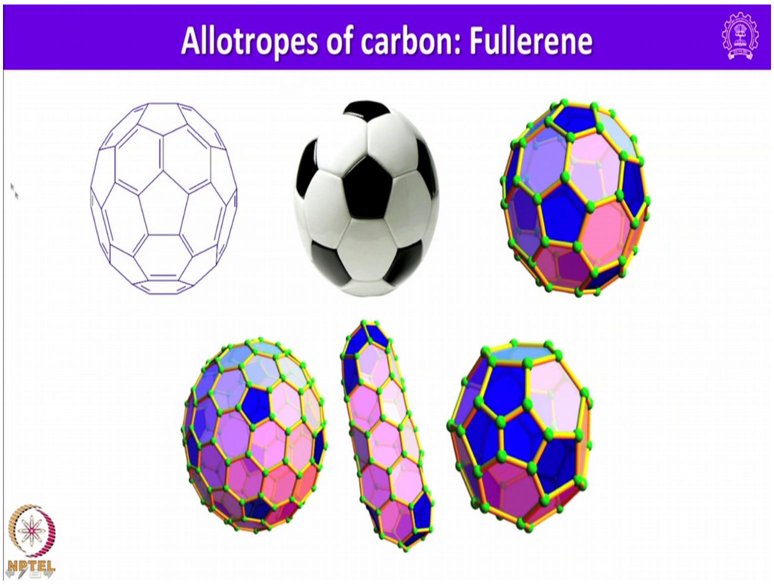
Allotropes of carbon: Fullerene

So, it is made up of hexagonal as well as pentagonal rings and also you can see here it is made up of 6 membered as well as 5 membered rings. So, just let us look into one point here, the melting point of diamond and graphite are greater than 3550 degree centigrade, but carbon 60, sublimes between 450 degree centigrade to 500 degree centigrades why is this difference? Melting point of diamond or graphite is greater than 3550 degree centigrade, only carbon carbon atoms are there in C 60 also only carbon carbon atoms are there though hydrogen atom are anything else, but here its sublimes at between 450 to 500 degree centigrade. So that means, here one should remember what is the meaning of melting point? And in case of graphite or diamond melting point means the cleavage of all the bonds associated with diamond ok.

So; that means, we have to strip of all the carbon and we have to take individual carbon atoms, when you achieve the separation of each carbon atoms it indicates we achieved melting point. Whereas, in case of C 60, C 60 is a molecule something like this and in solid state they are arranged in this fashion, through weak interactions in melting point what happens essentially we are separating them. So, they are held by weak interactions as a result its sublimes at 450 degree centigrade whereas, in case of graphite if you have something like this. If it continues the every bond has to be broken and same thing is too in case of a tetrahedral carbon atom. So, here essentially we have to cleave all we have to strip of all carbon atoms from each other to achieve its melting same thing is too in case of fullerene essentially we have to take out this because this itself is a molecule ok.

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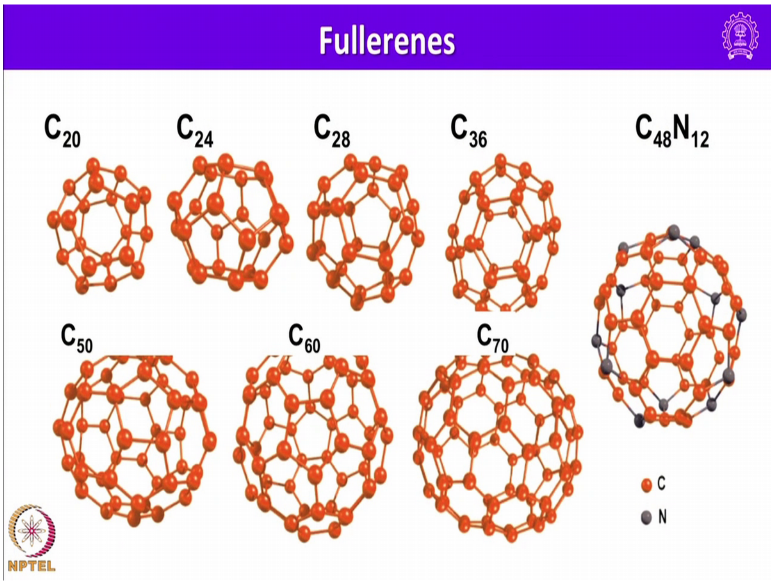

Fullerenes

So, this is the difference between the melting point, in case of diamond graphite and fullerene. So, I have shown you some fullerenes C 20 and C 24, C 28, C 36 and also here this essentially fullerene in which 12 carbon atoms are replaced by 12 nitrogen atoms this is a C 48 N 12 it is a hetero fullerene and C 50, C 60 and C 70 they are some of the important fullerenes.

And let us look into the reactivity of fullerenes, fullerenes are formed when an electric arc is discharged between carbon electrodes in an inert atmosphere, although C 60 exhibits a small degree of aromatic character its reaction tend to reflect the presence of localised double and single bonds. For example, if that is the case if any olefin having a double bond undergoes addition reaction, you can anticipate similar addition reactions in case of fullerene also.

In fact, it undergo addition reactions the (Refer Time: 11:17) like nature of C 60 is reflected in the range of reactions, such as the addition of an oxygen atom to give an epoxide or addition of ozone at 257 Kelvin to yield an intermediate ozonide like C 60 O 3 or reaction of C 60 with free radicals also can readily occur. So, polyhedral fullerenes undergo reversible multi electron reduction and form complexes with d block organometallic compounds, and also without osmine in tetraoxide let me show you some of these reactions here.

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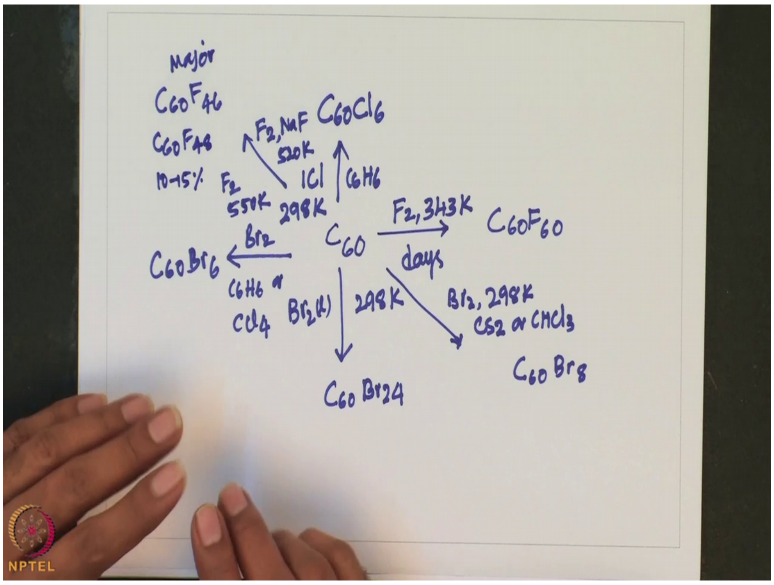

Let me write some reactions of C 60 for example, if it is treated with F 2 343 Kelvin for days it forms C 60 F 60.

Similarly, I Cl is added in benzene at 298 Kelvin, it forms C 60 Cl 6 and if you treated with bromine liquid at 298 K, it forms C 60 Br 24 or with controlled addition of Br 2 at 298 Kelvin only in benzene or carbon tetrachloride, it can give you C 60 Br 6. So that means, by controlling the amount of bromine we are using, we can either make C 60 Br 24 or one can make C 60 Br 6. Similarly one can also use Br 2 at 298 Kelvin in carbon disulphide or CHCl 3 chloroform to get C 60 Br 8, one can also take fluorine with sodium fluoride at 520 Kelvin or directly F 2 at 550 Kelvin, one can get C 60 F 46 this is the major product along with this one can anticipate C 60 F 48 in about 10 to 15 percent yield. So, this indicates some of these reactions of C 60 with halogens.

One can also perform as I mentioned addition reactions for example, I would mention something like this C 60 one can conveniently mention like this.

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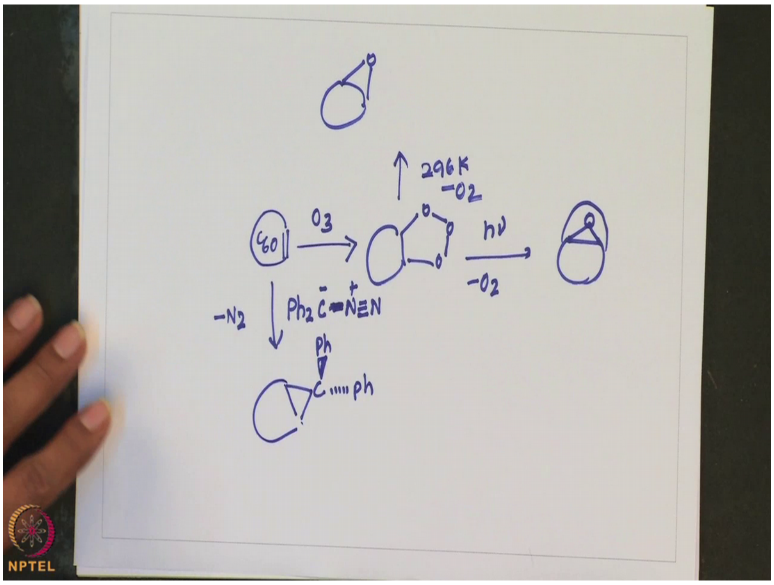

So, this one simply if you add ozone, one can generate something like this, something like this and of course, once after making this one if it is exposed to u v light O2 comes out to form oxide epoxide or one can take this one and treat with heated to 296 Kelvin O2 can come out here also and one can also get now it will be something like it will be part of it will be it opens up one c c bonded forms or it can be simply an epoxide something like this it can form and taking C 60 directly, let us say if you treat this one with this reagent. So, N 2 will come out here. So, here one can see addition reaction happening here.

So, it is di ozone compound can be taken and added. So, that you can carry out several reactions of course, one can also add carbonyls also and to it.

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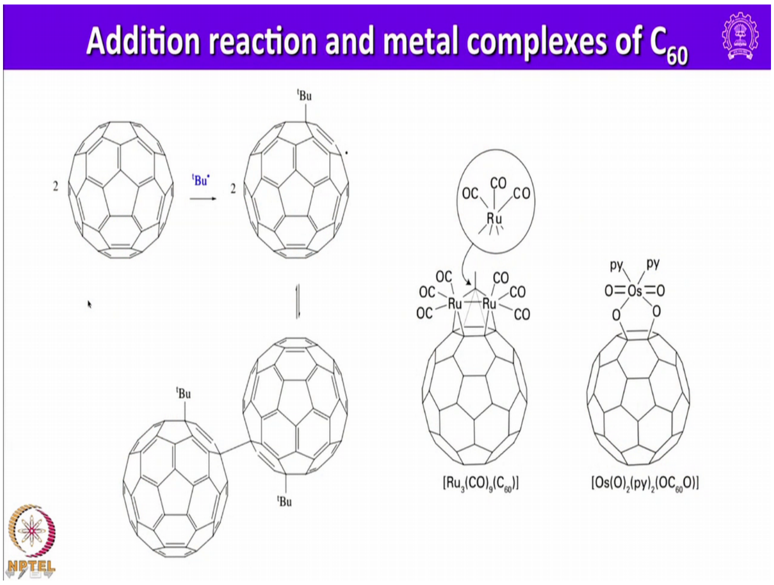

Addition reaction and metal complexes of C_{60}

You can see here some of these reactions are shown here in this one, you can take this radicals and you can add it here or you can take RuCO 3 fragment, Ru if you take Ru three CO 12 you can do addition reaction in this fashion, and also one can treat this one with osmium tetroxide in presence of pyridine to form a compound of this type. So, this are all reactions are very similar to react in some of the species with a single alkene; that means, essentially they resemble the reaction with an alkene or as simple as ethylene molecule.

So, let us look into the catenation, catenation is very very common for carbon then for silicon germanium and tin among group 14 elements, the much higher c c bond enthalpy is compared with those of silicon silicon germanium germanium and tin; tin means that the formation of compounds containing bonds between carbon atoms is thermodynamically more favourable, then analogous compounds having silicon silicon germanium germanium or tin tin bonds on descending group 14. So, orbital overlap becomes less efficient as well the well as orbital size increases and they become more and more diffuse as the principal quantum number increases, for this reason what happens is catenation is less pronounce among heavier group 14 elements the back bones of saturated hydrocarbons are composed of c c bonds, that is their formation depends on catenation being favourable. An additional factor that favours the formation of hydrocarbon is the strength of CH bonds. So, stronger than s i h germanium hydrogen or tin h bond carbon hydrogen bond is much stronger than any of the hydrogen bonds of the group 14 elements.

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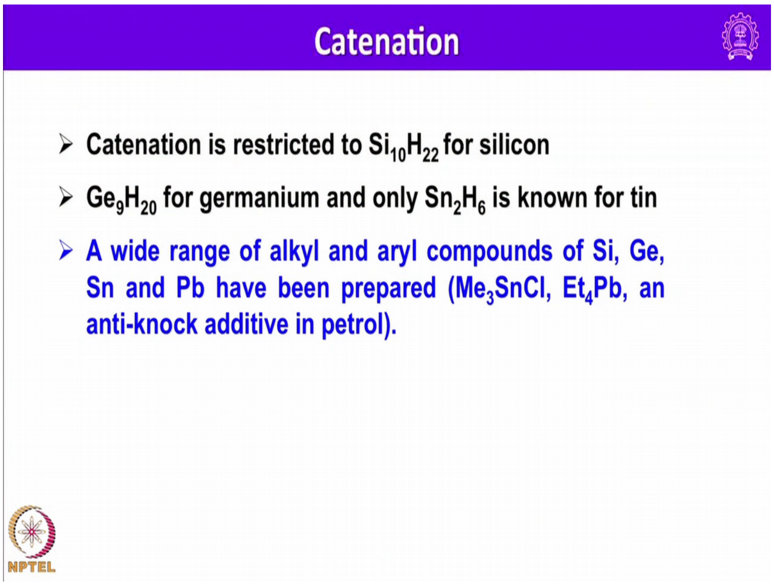

Catenation

- Catenation is restricted to $Si_{10}H_{22}$ for silicon
- Ge_9H_{20} for germanium and only Sn_2H_6 is known for tin
- A wide range of alkyl and aryl compounds of Si, Ge, Sn and Pb have been prepared (Me_3SnCl, Et_4Pb, an anti-knock additive in petrol).

So, when we will look into the catenation, catenation can leads to all kind of polymers in case of carbon whereas, in case of silicon it is restricted to having 10 silicon atoms in the chain for example, Si 10H 22 for silicon, and in case of germanium one can go up to only 9 germanium atoms in a chain germanium G e nine H 20, for germanium and in case of tin only dimeric compound is known very similar to ethane and of course, in case of lead with great difficult using very bulky groups one can kinetically controlled and make a dimeric species having some multiple bond character something like this.

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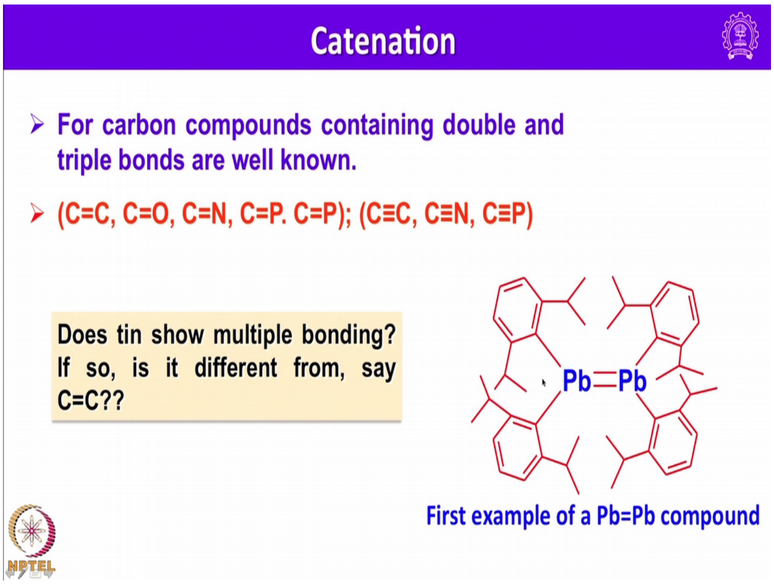

Catenation

- For carbon compounds containing double and triple bonds are well known.
- (C=C, C=O, C=N, C=P. C=P); (C≡C, C≡N, C≡P)

Does tin show multiple bonding? If so, is it different from, say C=C??

First example of a Pb=Pb compound

Of course here the structure of this one is very interesting, and I will be explaining the structure of this one how this P b P b distance it is not actually a double bond.

But it has a double bond character it is not a conventional pi bond that we come across in case of carbon carbon, it is a different one that I would be explaining those things when I go to the organometallic chemistry of group main group compounds and especially while comparing the bonding of tin compounds with lead and other silicon compounds having more than one bond or bonded main group elements. So, this is one example of a dimeric lead compound of course, you can see here this P b P b double bond is stabilized by very bulky groups we have two (Refer Time :20:40) isopropyle phenyl groups this is kinetically this P b P b bond is stabilized.

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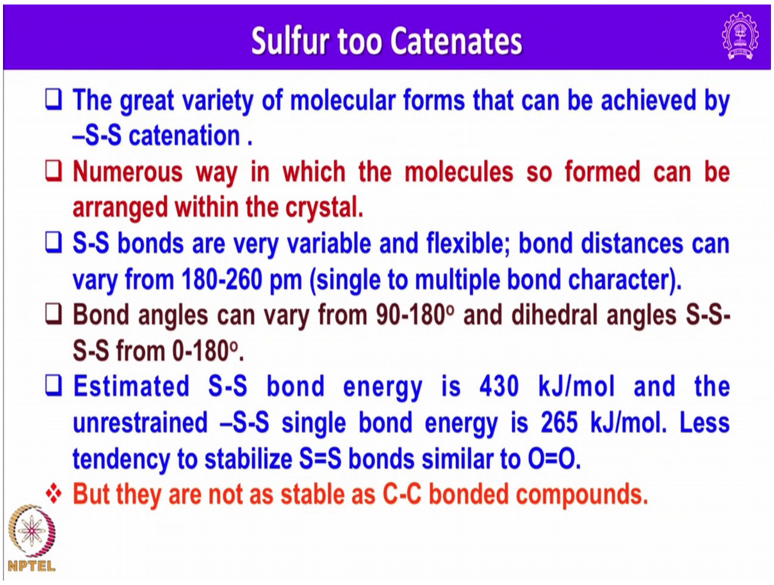

Sulfur too Catenates

- ❑ The great variety of molecular forms that can be achieved by –S-S catenation .
- ❑ Numerous way in which the molecules so formed can be arranged within the crystal.
- ❑ S-S bonds are very variable and flexible; bond distances can vary from 180-260 pm (single to multiple bond character).
- ❑ Bond angles can vary from 90-180° and dihedral angles S-S-S-S from 0-180°.
- ❑ Estimated S-S bond energy is 430 kJ/mol and the unrestrained –S-S single bond energy is 265 kJ/mol. Less tendency to stabilize S=S bonds similar to O=O.
- ❖ But they are not as stable as C-C bonded compounds.

So, sulphur too catenates of course, when we look into the catenation another element in the main group are among the elements in the periodic table, that forms a larger number of catenated compounds in sulphur the first one is carbon second one is sulphur of course, I will be discussing more about the sulphur chemistry, when I start discussion on group 16 elements never the less let me compare its catenetic abilities, since we are talking about catenation of carbon.

So, the great variety of molecular forms can be achieved by sulphur sulphur bond formation or catenation of S-S. Numerous way in which the molecules, formed can be arranged within the crystal S-S bonds are very variable and flexible, bond distances can vary from 180 to 260 picometre some there is some elasticity is there in the S-S bond in catenated compound, because of single to multiple bond character. Bond angles can also vary from 90 to 180 that is another interesting feature, not only the bond angles even dihaderal angle can also vary from 0 to 180, and estimated S-S bond energy is 430 kilo joules per mole, and the unrestrained S-S single bond energy is 265 kilo joules per mole. So, less tendency to stabilize S-S bond similar to O-O bond and, but they are not as stable as carbon carbon bonded compound, never the less it shows moderately stable catenated compounds.

So, catenated halides are another important class of compounds similar to extensive range of hydrocarbons diverse range of halocarbons are known, especially chloro compounds fluoro compounds as well as fluoro chloro compounds together, best example being polytetrafluoroethane.

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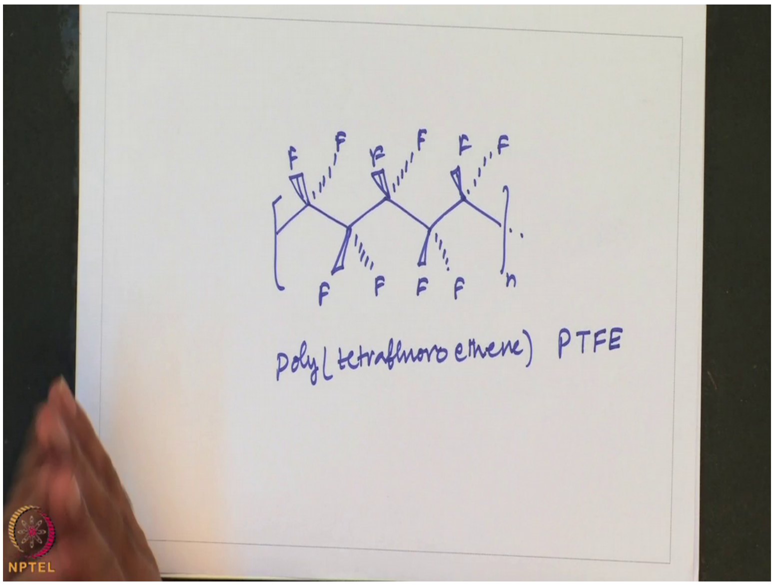

That is also called PTFE in extremely stable polymer finding numerous applications and this PTFE has something like this the structure, it goes and all are flowing atoms this is called poly tetra fluoro ethane. So, PT; for silicon a large number of higher halides are known containing changes of silicon atoms analogous to the polysilanes, germanium tin and lead form few analogous of the silicon compounds because of the lowest stability of E-E bonds, going down the group and the increase stability of the divalent halides.

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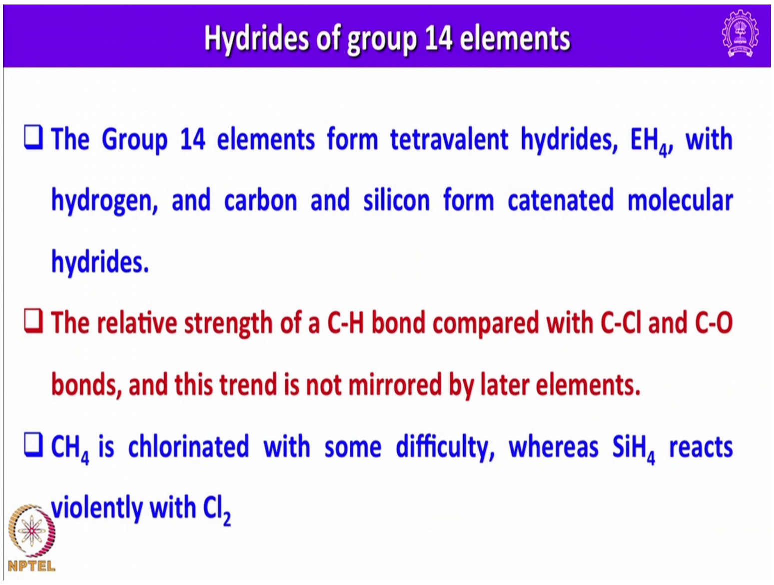

Hydrides of group 14 elements

❑ The Group 14 elements form tetravalent hydrides, EH_4, with hydrogen, and carbon and silicon form catenated molecular hydrides.

❑ The relative strength of a C-H bond compared with C-Cl and C-O bonds, and this trend is not mirrored by later elements.

❑ CH_4 is chlorinated with some difficulty, whereas SiH_4 reacts violently with Cl_2

Let us look into the hydrides of group 14 elements. The group 14 elements form tetravalent hydrates CH 4 with hydrogen and carbon and silicon form catenated molecular hydrides so; that means, we can see catenated hydrates as well of course, hydrocarbons are especially catenated hydrides, in case of silicon also we can expect that one having a chain length of 10. Having up to 10 silicon atoms in the chain and each one is having two hydrogen atoms. The relative strength of a CH bond to compared to CCl and CO bond and this trend is not mirrored by later elements CH 4 is chlorinated with some difficulty whereas, SiH 4 reacts violently with chlorine ok.

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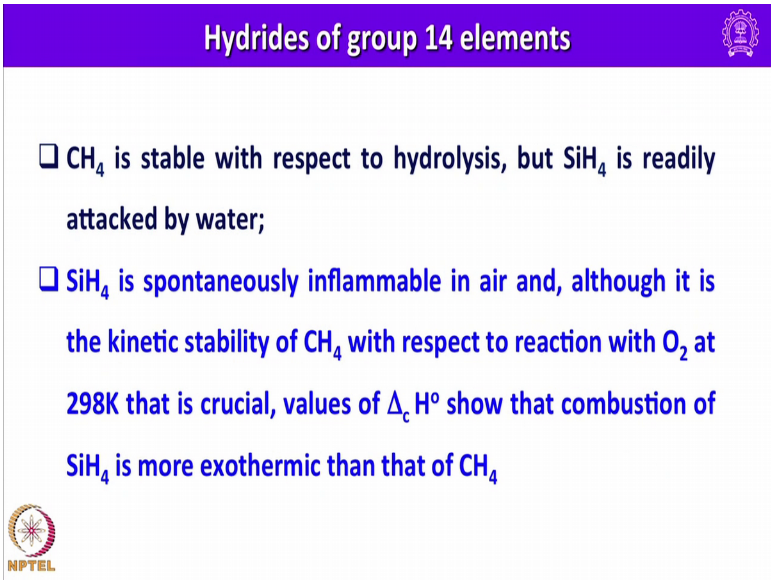

Hydrides of group 14 elements

❑ CH_4 is stable with respect to hydrolysis, but SiH_4 is readily attacked by water;

❑ SiH_4 is spontaneously inflammable in air and, although it is the kinetic stability of CH_4 with respect to reaction with O_2 at 298K that is crucial, values of $\Delta_c H^\circ$ show that combustion of SiH_4 is more exothermic than that of CH_4

CH 4 is very stable with respect to hydrolysis, but SiH 4 is readily attacked by water, here the reactivity of SiH 4 is purely kinetic. SiH 4 is spontaneously inflammable in air and although it is the kinetic stability of CH 4 with respect to reaction with oxygen at 298 Kelvin that is crucial the values of delta CH 0 shows that the combustion of SiH 4 is more exothermic than that of CH 4 as I said it is one is exothermic another one is kinetic, I will I shall explain later when I talk about the reactivity of S i Cl 4 with respect to CCl 4. CCl 4 is not prone to hydrolysis whereas, S i Cl 4 can undergo readily hydrolysis.

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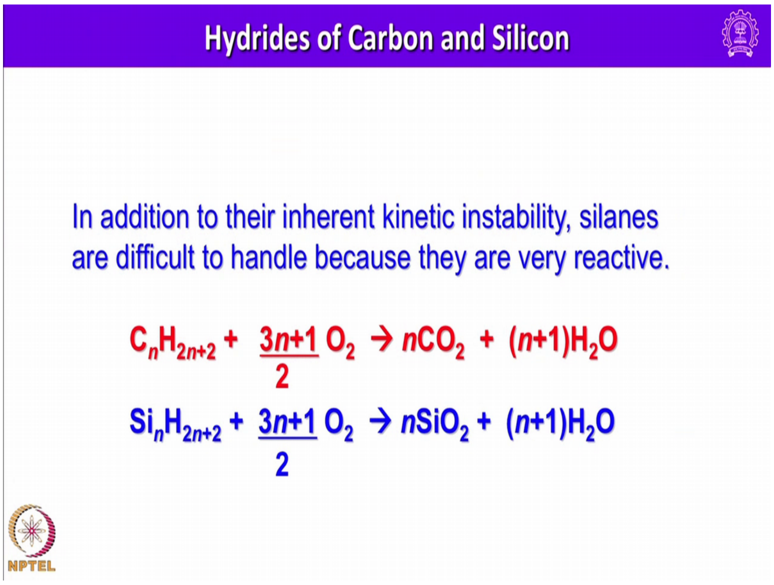

Hydrides of Carbon and Silicon

In addition to their inherent kinetic instability, silanes are difficult to handle because they are very reactive.

$$C_nH_{2n+2} + \frac{3n+1}{2} O_2 \rightarrow nCO_2 + (n+1)H_2O$$

$$Si_nH_{2n+2} + \frac{3n+1}{2} O_2 \rightarrow nSiO_2 + (n+1)H_2O$$

So, in addition to their inherent kinetic instability, silanes are difficult to handle because they are very reactive. For example, if you take here this is the typical reaction of a carbon hydride or hydro carbon react with oxygen to give water and carbon dioxide, similarly if we compare the reaction of a silane with oxygen it gives silica that is SiO 2 plus water. So in fact, both the reactions are thermodynamically favour to proceed towards the right.

The major differences not apparent in the stoichiometric reaction is the energy of activation, which causes the paraffins to be kinetically inert in contrast to the relative silanes. Further complications with silanes arise from lack of conventional synthesis and difficulties in separation; however, compounds n equals 1 to n equals 8 have been isolated including straight chain as well as branched chain silanes Of course, more details are given in this book. I will stop at this stage and I will continue the discussion on hydrides of group 14 elements in my next lecture, until then have a pleasant reading of inorganic chemistry.

Thank you very much.