Main Group Chemistry
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Lecture – 38
Chemistry of Group 14 Elements

Welcome to MSB lecture series on the chemistry of main group elements. In today's lecture, I will be discussing about halides of group 14 elements, and among group 14 element halides. So, far we discussed a few reactions, let me continue from where I had stopped in my previous lecture.

Now let us considered compounds having carbon halogen bonds, and here for example, I have taken one alkyl halide, you can see a the reactions of alkyl halides, especially some of the reactions with metals both main group and (Refer Time :01:05) elements to form a variety of compounds through oxidative addition, and one such important reaction is when this alkyl halide is treated with magnesium, it forms grignard reagent that is CH 3 Mg Br of course, I will be talking more details about grignard reagents, while discussing organometallic chemistry of main group elements.

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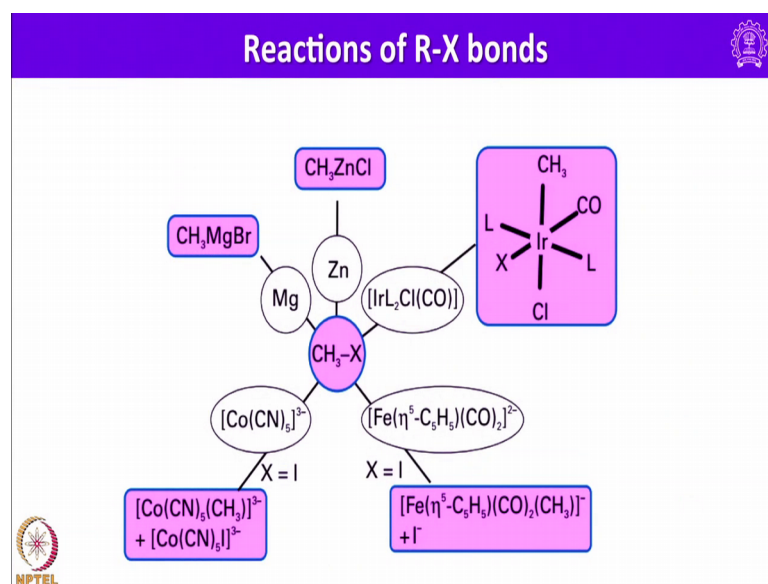
And now similar to grignard reagent, one can also form with zinc by oxidatively adding alkyl halide to zinc you can see, CH 3 ZnCl is shown here and of course, oxidative addition of alkyl halides to transfer metals is one of the important step in homogeneous

catalysis, also known as oxidative addition reactions. Of course, in order to perform oxidative addition reactions, metal should be electron rich and also it should be coordinatively unsaturated and since oxidative addition is a 2 electron process, metal should have 2 stable oxide states with a difference of 2 electrons, and also it should be able to increase its coordinates number by 2, in that case oxidative addition can be performed on a particular metal centre.

This is a preliminary step in homogeneous catalysis; in his case of course, when we talk about oxidative addition reactions, we come across 2 different type of oxidative addition reaction, one is the homoliptic addition of a molecule to the metal centre, through 3 centred concerted bond formations, that is called 3 centred concerted oxidative addition. The second one is nucleophilic oxidative addition reaction and consulted addition happens with those molecules, which have non polar bonds like CC bond or less polar like CH bond or HH bond, when we consider polar molecule such as methyl iodide in that case what happens? CH 3 carries a plus charge and x carries a minus charge, in that case when we take such molecules to the metal especially a square planar complex having 2 electrons in its d z square orbital. So, then, this CH 3 x of a polarizing CH 3 plus.
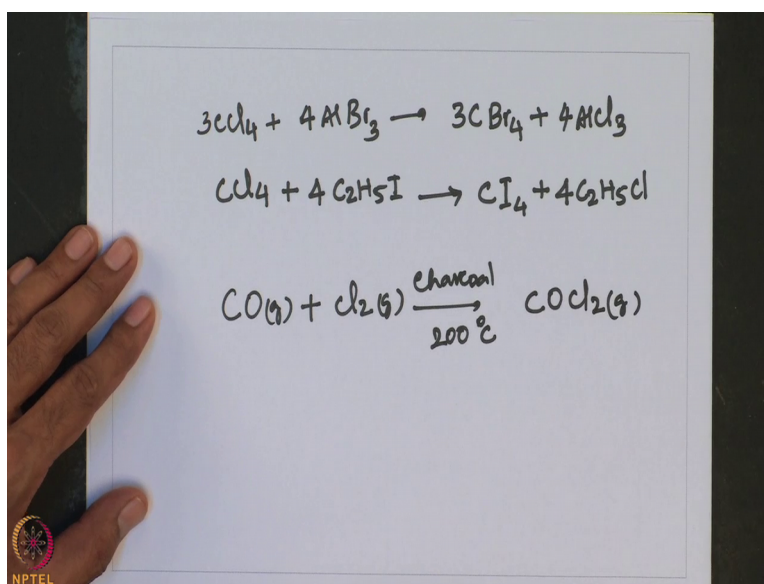
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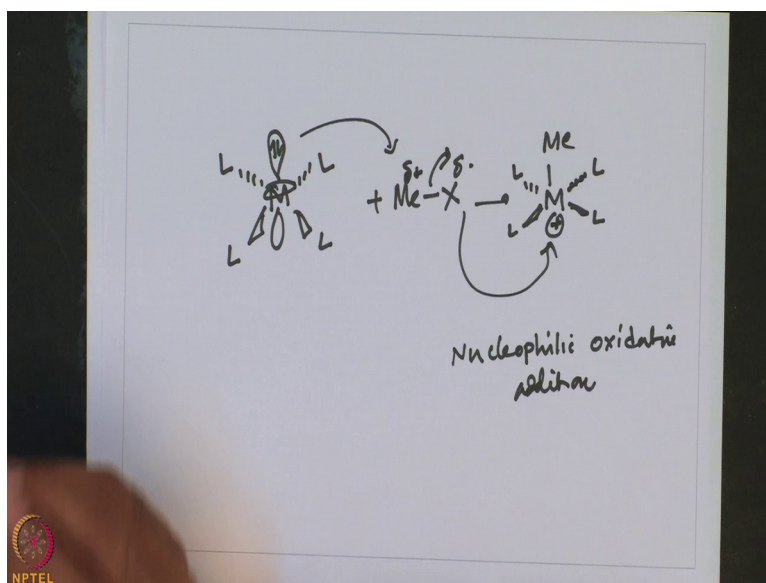
Here let me show that one, let us consider a typical square planar complex. So, it is a d z square we have 2 electrons are there, and when we add here M e X. So, this will be

essentially delta plus and delta minus. So, here essentially. So, this attacks here and then this goes here, and this leads to the formation of these are some ligands like triphenylphosphine, and now here positive charge is generated, now, this attacking here. So, this is a nucleophile, hence it is called nucleophilic oxidative addition, very important reaction in homogenous catalysis and also in organometallic chemistry.

So, of course, in that context alkyl halides are very very useful in a variety of cross coupling and carbon-carbon bond formation, and carbon hydrogen bond formation etc.

And let us look into carbon tetrachloride and carbon tetrachloride when it is heated with aluminium bromide, one can generate carbon tetra bromide and similarly one can also make carbon tetra iodide.

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$$3CCl_4 + 4AlBr_3 \longrightarrow 3CBr_4 + 4AlCl_3$$

$$CCl_4 + 4C_2H_5I \longrightarrow CI_4 + 4C_2H_5Cl$$

$$CO_{(g)} + Cl_{2(g)} \xrightarrow[200\,°C]{\text{charcoal}} COCl_{2(g)}$$

For example carbon tetrachloride on treatment with aluminium bromide, aluminium tribromide, it gives carbon tetrabromide plus aluminium chloride will be formed. Similarly if carbon tetrachloride is treated with 4 equivalents of ethyl iodide, it leads to the formation of carbon tetra iodide plus ethyl chloride. So, one can also make carbonyl halides likes $COCl_2$ that is also known as phosgene.

So, this can be essentially you know made by treating CO gas, with chlorine at over charcoal heated to 200 degree centigrade. CO gas plus c l 2 gas, charcoal it gives CO cl 2. Of course, it was used in the First World War chemical warfare it is very highly toxic

gas, and this is the large scale preparation method. So, CO gas is directly combined with chlorine over charcoal heated to 200 degree centigrade of course, this is a very good intermediate in organic reactions, a few of them I have shown here, carbonyl chloride or phosgene on treatment with water undergoes hydrolysis to give carbon dioxide on treatment with alcohol it gives.

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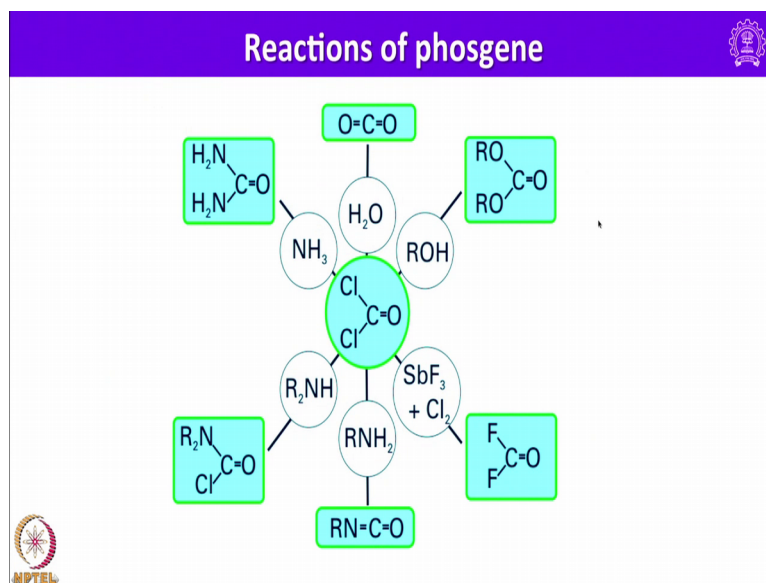
Anhydrides and also it can be fluorinated using antimony trifluoride, one can also generate RNCO by treating with a primary amine, with primary amine one can also substitute one to get this amide, one can also make urea by treating phosgene with ammonia. So, urea can also be made. So, these are the few reactions of phosgene, silicon and chlorine reacts to give Sicl 4 and SiF 4 can be obtained by fluorination of Sicl 4 using s b f 3 ,or by reaction of SiO 2 with calcium fluoride in acidic medium; that means, we take SiO 2.
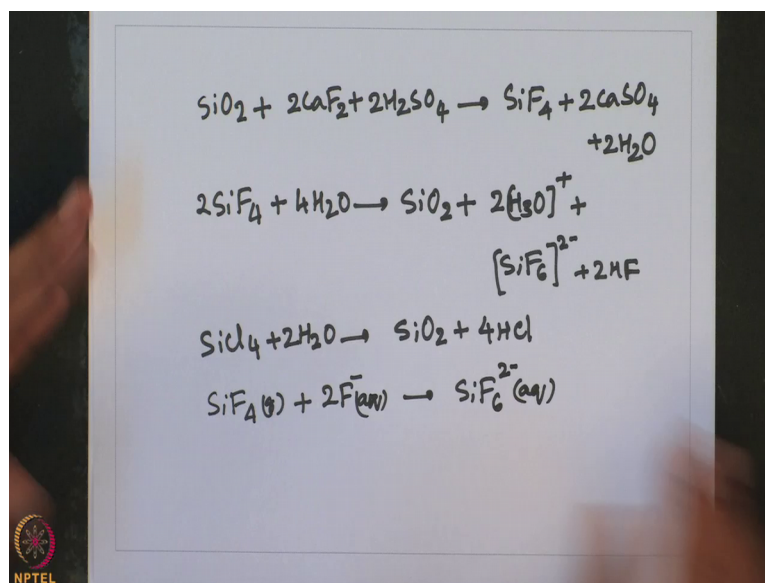
Treat this one with calcium fluoride in presence of sulphuric acid, to generate SiF 4 and of course, both silicon tetrafluoride and silicon tetrachloride or molecular having tetrahedral structures, they react readily with water, but SiF 4 is only partially hydrolyzed. For example, we take SiF 4 and reacts with water, besides formation of SiO 2, we also get hydronium ion plus hexafluro silicate plus 2 HF, but whereas, is in case of Sicl 4 complete hydrolysis occurs.

So, silicon halides are essentially mild acids and add 1 or 2 ligands to yield 5 or 6 coordinated complexes for example, if we consider again SiF 4 with fluorinating agents it gives SiF 6, 2 minus so; that means, here you can see how Louis acidity of halides can be explain, similarly germanium tetrahalides can also be prepared by direct combination of germanium with the corresponding halogens.

At 298 Kelvin germanium tetrafluoride is formed, germanium tetrafluoride is a colourless gas where as germanium tetrachloride is a colourless liquid, and germanium tetra iodide (Refer Time :10:48) or in solid and germanium tetra bromide melts at 299 Kelvin and of course, germanium forms stable dihalides as well, germanium difluoride like GeF 2.
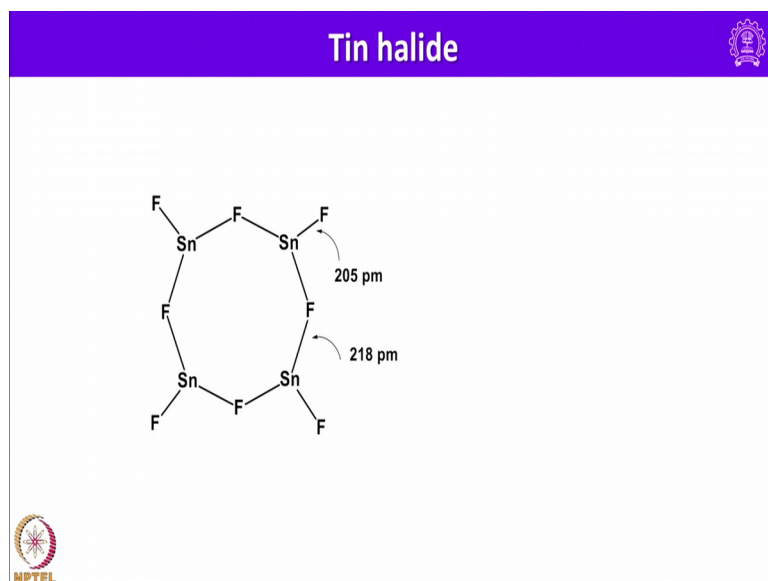
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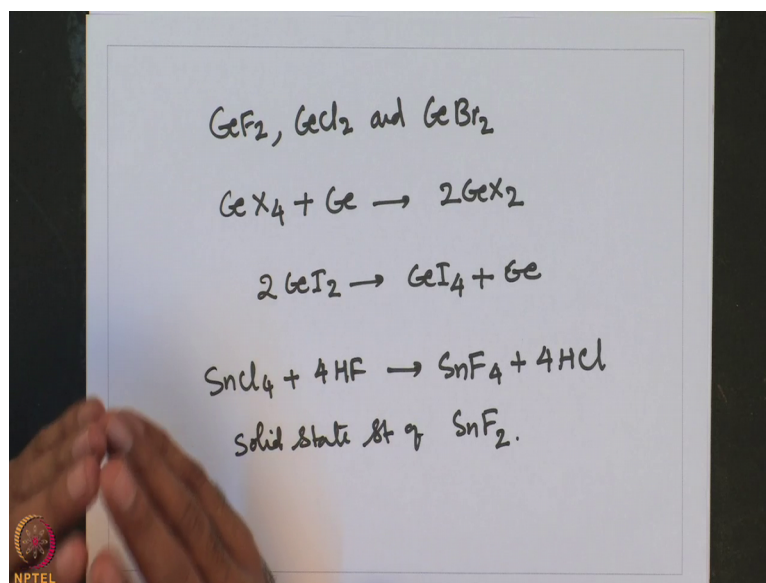
Or Gecl 2 and also GeBr 2. So, these are prepared when germanium tetrahalide is heated, germanium forms stable, germanium fluoride, germanium dichloride, germanium dibromide essentially they can be produced when germanium is heated with germanium tetrahalides. For example, if you take this one and if you heat this one with germanium.

So, germanium tetrahalides are heated with germanium, it gives dihalides. Here x can be fluorine chlorine or bromine, but germanium di halides are unstable on heating they undergo disproportionation reactions for example, let me consider germanium di iodide reaction here. So, this is a typical disproportionation reaction, tin tetrafluoride can also be prepared starting from SnCl 4 and HF. For example, SnCl 4 when its treated with 4 equivalents of HF, it forms SnF 4 through formation of 4 equivalents of Hcl. So, this is one of the method used for the preparation of tin tetrafluoride.

So, at 978 Kelvin SnF 4 sublimes to give a vapour containing tetrahedral molecules, tin 2 fluoride is water soluble and can be prepared in aqueous medium the solid state structure of SnF 2 would be interesting. So, basically what happens, it undergoes cyclization to have a teramaric structure with each tin being trigonal bipyramidal, and of course, if it is trigonal bipyramidal we have to go for valence shell electron pair repulsion theory, to see all the discrete coordinated why it is trigonal bipyramidal that can be explained using a simple calculation. So, this how the structure looks like.

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So you can see here, in this one if you start counting the number of electrons here, tin if you consider tin is of course, S2 p 2. So, we have 4 electrons are there and 2 electrons are coming from 2 fluorine atoms.

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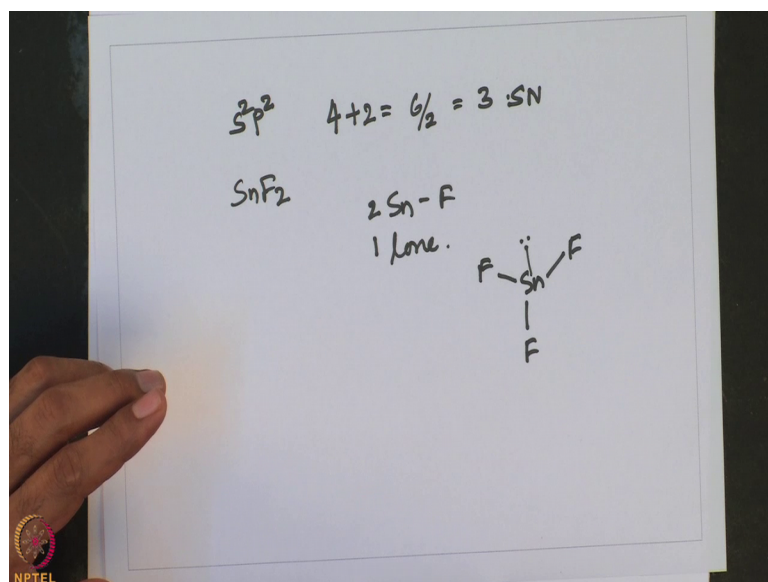
So, we have essentially 6 are there out of 6 basically what happens? We have 3 pairs are there this is the steric number, out of that one what we have is 2 bonded pairs are there if you consider SnF 2, two bonded pairs are there; that means, essentially we have 2 SnF bonds are there and one lone pair is there. So, this one lone pair is there, trigonal

pyramidal structure is there. So, in this one basically one lone pair will be projected upwards on this one. So, we have something like this here. So, we have something like this here. So, another loan pair will be here somewhere on each one because of the presence of a lone pair on this tin. So, it assumes the geometry trigonal bipyramidal. So, this lone pair will be somewhere here sitting on it.

So, tin halides will be interesting to look into the structure in gas phase it exists as a discrete monomeric species.

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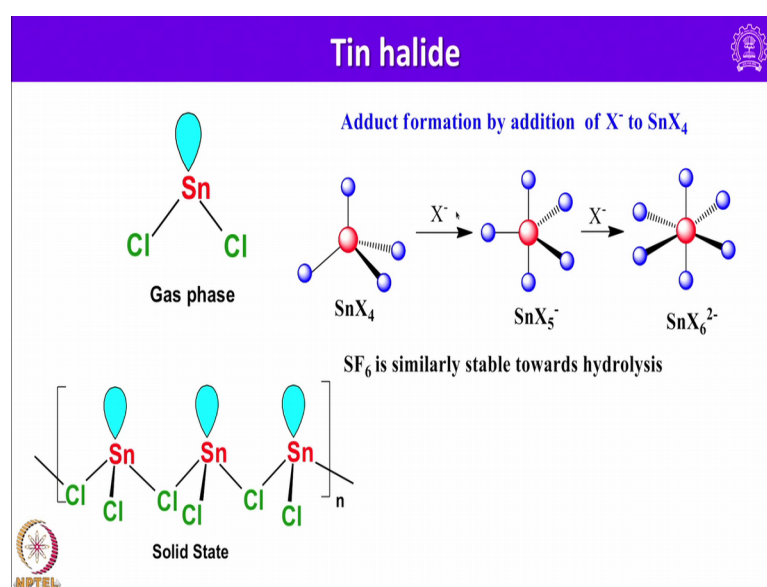
And also it is known for formation of the adducts like SnX 4 on addition of a halide it forms a trigonal bipyramidal molecule, and an addition of 1 more it will go to the octahedral geometry and it this is very similar to SF 6 or SiF 6 2 minus. And in solid state it has a one dimensional chain like structure like this again you can see here trigonal pyramidal with lone pair occupying one of this orbitals here.

Lead tetrachloride is essentially obtained as an oily liquid by the reaction of cold concentrated sulphuric acid on ammonium hexa chloro plumbate.

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$$(NH_4)_2[PbCl_6] \xrightarrow{H_2SO_4} PbCl_4 + 2NH_4Cl$$

$$Pb(NO_3)_2(aq) + 2NaCl(aq) \longrightarrow PbCl_2(s) + 2NaNO_3(aq)$$
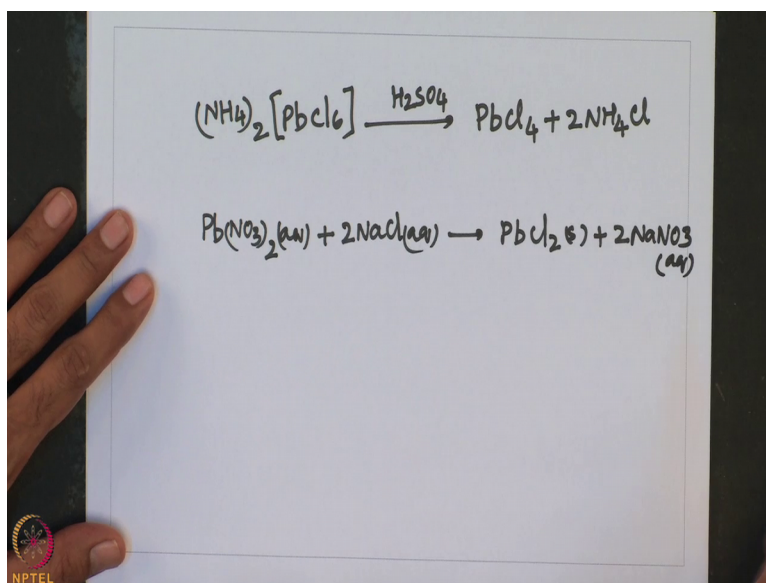
So, this how lead tetrachloride can be prepared by treatment of ammonium hexa chloro plumbate with cold concentrated sulphuric acid. P b c l 4 is hydrolysed by water, and decomposes to form P b c l 2 and gives c l 2 when gently heated. P b 2 plus halides are considerably more stable P b c l 2 for example, then there P b 4 plus analogs that is tetra halides and of course, tetrahalides are very oxidizing in nature. Of course, lead dichloride can also be prepared by mixing aqueous solution of soluble halide and soluble p b salts, for example, p b nitrate. Lead nitrate in aqueous medium when its treated with sodium chloride it forms P b c l 2. So, in the solid state lead chloride has a complicated structure with 9 coordinate P b centres.

So, let us look into one more type of silicon oxygen compounds doped with aluminium they are essentially called aluminosilicates.

Occur naturally as clays minerals and rocks and zeolite aluminosilicates are widely used as molecular sieves catalyst and catalyst support materials. The molecular sieves are crystalline aluminosilicates having open structures with apertures of molecular dimensions and zeolites are aluminosilicates with tetrahedrally connected framework structures and based on corner sharing aluminate AlO_4 and silicate SiO_4 tetrahedras .

Zeolite can also be considered as pure silica framework with 1 or 2 silicon atom substituted by aluminium so; that means, here basically what happens when Si^{4+} is changed by Al^{3+}, it gives overall negative charge to the framework and this has to be balanced by a counter cation. So, basically what happens we are adding some counter cations in the form of alkali metals or alkaline earth metals, a simplified empirical formula for an aluminosilicate can be represented using the formula M.

$$M_{x/n}\left[(AlO_2)_x (SiO_2)_y\right].ZH_2O$$

aluminosilicate - Zeolite
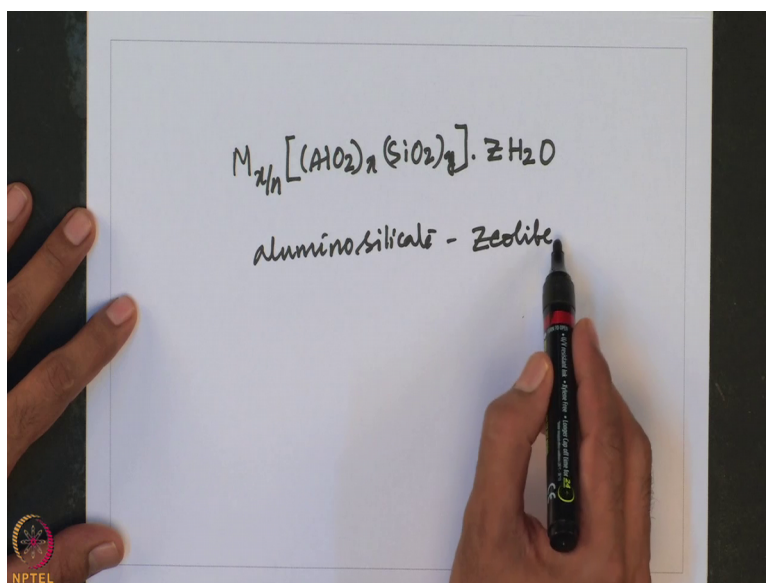
So, this is a typical molecular formula for aluminiosilicate, thus how zeolite, and essentially these structures I have a channels and cavities of different sizes, molecules of appropriate size maybe trapped in the holes and in this property that makes possible they are use as selective adsorbent, and also in the separation of different organic molecules especially you know ortha substituted, para substituted, meta substituted, aromatic compounds as well. And these essentially these kind of zeolites are called molecular sieves, in the hydrated state all the cavity contain water molecules. Of course, one can heat it to about 350 degree centigrade under vacuum to remove water molecules to generate anhydrous molecular sieves. So, this is how the typical zeolite looks like.

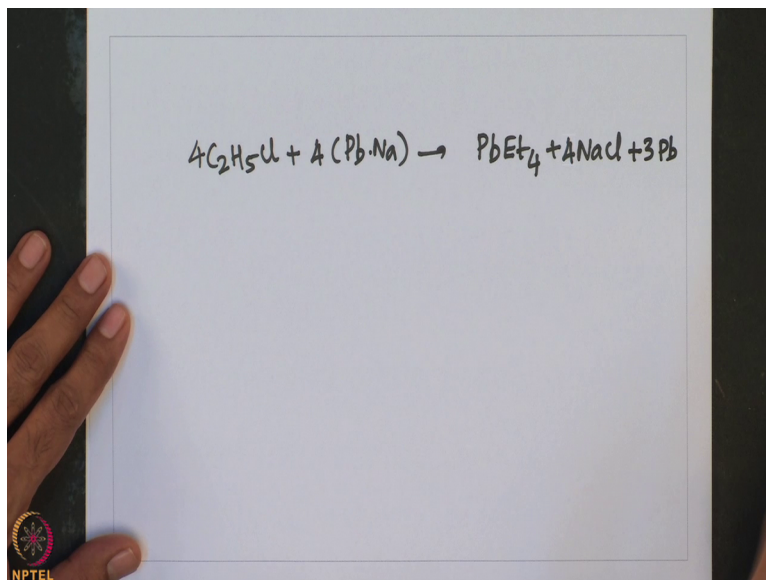(Refer Slide Time: 21:24)
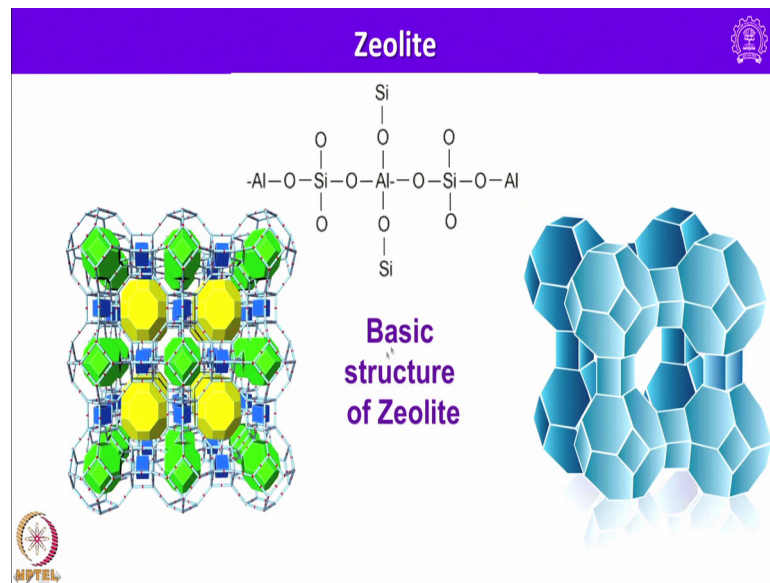
So this also this one unit we call it as sodalite structure, this how the cages in zeolite look like.

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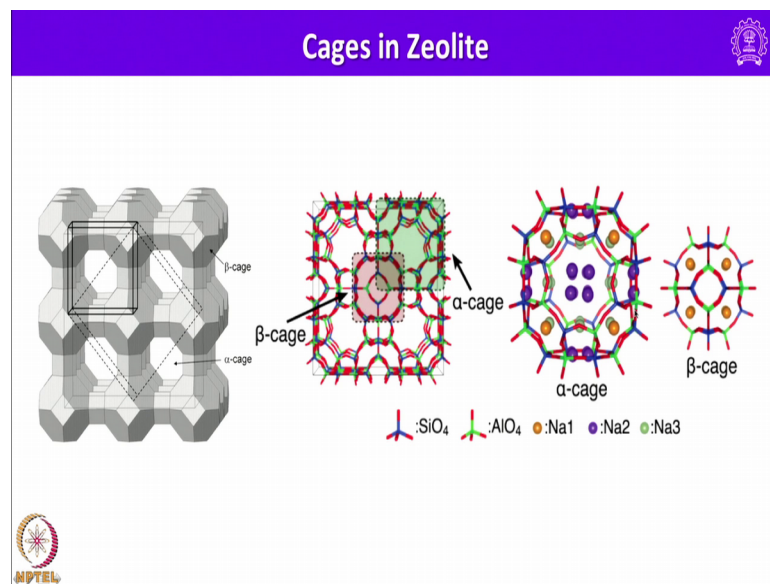
So, let us look into one important compound tetraethyl lead. Tetraethyl lead was essentially prepared by the reaction of ethyl chloride with sodium lead alloy.

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$$4 C_2H_5Cl + 4(Pb \cdot Na) \longrightarrow PbEt_4 + 4NaCl + 3Pb$$

So, earlier it was used as a anti compound as an additive in the petrol that was used in automobiles to improve the quality of gasoline. Of course, of looking into its toxic effect and also its impact on atmosphere, it was banned in 1985, and it is no longer used anywhere as an additive and instead less toxic compounds are added as antiknock into the gasoline or automobile fuel.

Another important compounds are freons; they are nothing, but chlorofluorocarbons are also called CFCs, they are used as freons; they are unreactive non toxic are widely used as refrigeration fluids, and also as the propellant in eurosoles. In the upper atmosphere freons undergo a photolytic reaction and producer free chlorine atoms or radicals they decompose ozone and as a result what happens it depletes the ozone in atmospheric ozone layer. For example, the type of reactions that happens in upper atmosphere, that is responsible for the depletion of ozone can be seen in this reaction here.

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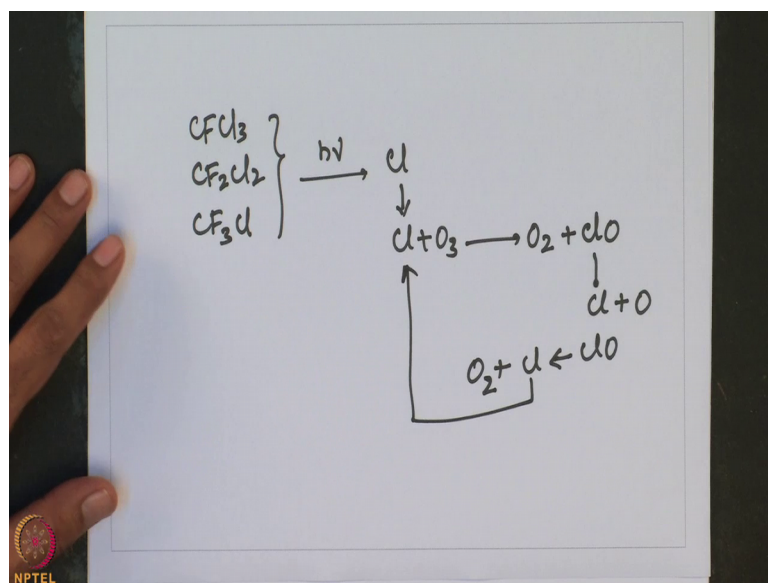
CFC 3, CF 2 c l 2 or CF 3 cl are essentially called freons are fluoro chlorofluorocarbons. So, they on exposing to sunlight they generate radicals, and this radical will react with ozone very rapidly to form oxygen molecule and c l o. And this one what happens is it generates c l plus o and also c l o can also generate c l plus o 2. So, like this and then this c l again goes here and again involves in further decomposition of ozone. So, because of this one now a days the usage of fluoro chloro carbon has been discouraged, alternates are used as refrigerants. So, now before I conclude let me look into couple of questions here is a question you can see that one complete the following chemical reactions.

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With balanced equations for example, if you take tin and treat with excess of iodine, what happens? Beryllium carbide treat with water, carbon tetrachloride with water, diethyl dichlorosilane reacts with lithium aluminium hydride one can give the products.

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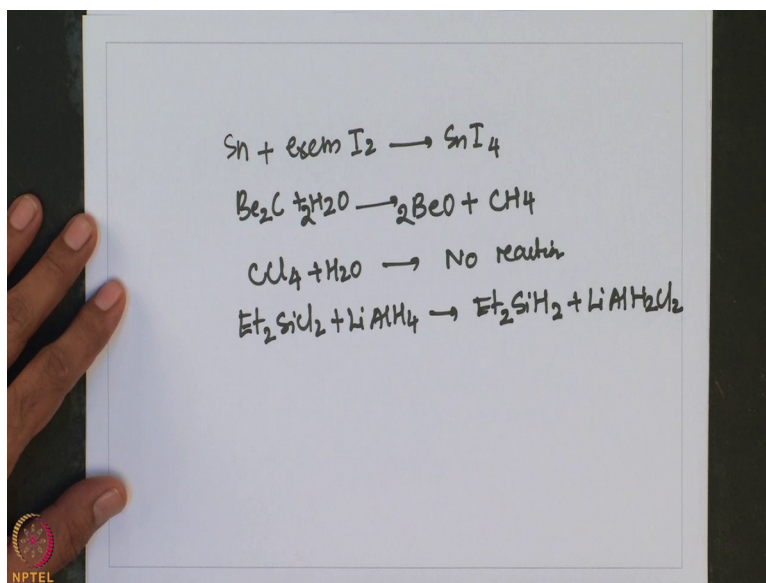
Here for example, tin with excess of iodine, it forms S n I 4, and beryllium carbide with water of course, one has 2 equivalents of water it gives CH 4, you take here 2 equivalents of water and under normal circumstances CC l 4 with water no reaction no hydrolysis, and diethyl dichlorosilane with lithium aluminium hydride leads the formation of diethyl silane. So, this is how one can complete the reactions using a balanced chemical equation.

So, let me summarise the chemistry of group 14 elements, group 14 members lie in the centre of the main group elements and show remarkable differences from the lightest element carbon to the heaviest main group metal lead.

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That means, always you can anticipate this kind of anomaly between the first element and rest of the elements, that we are observing all through p block elements and as well as s block elements, the plus 4 oxide state dominates the chemistry of carbon and silicon where as in case of heavier once plus 2 oxide state comes into the picture and especially in case of lead because of inert pair effect, lead is more stable in its plus 2 state; Hydrocarbons with carbon in minus 4 oxide state are thermodynamically unstable, and are an important class of compounds and has constituted organic chemistry. Germanium tin and lead form compounds with both plus 2 as well as plus 4 oxide states, but lead 4 plus compounds are oxidising P b o 2 is a very powerful oxidising agent, and inert pair effect dominates in lead.

P pi bonding and catenation are important for carbon and less important for heavier elements. For silicon SiO bond is very strong resulting in a wide range of polymeric oxides with numerous applications we come across all kind of minerals that are present in earth crust which accounts for 90 percent are essentially coming from silicate minerals ok.

Lastly while discussing in one of my previous lecture, I did mention that carbon tetrafluoride and carbon tetrachloride are thermodynamically unstable, with respect hydrolysis that is very much true, but just now I wrote a equation where I stated that CC l 4 does not hydrolysis, that is true it is because of the kinetic inertness, we come across in

case of CCl 4. Under normal circumstances it does not react with water, only under drastic conditions it undergoes hydrolysis, where as in case of silicon tetrachloride hydrolysis is very fissile, because it can increase its coordination number from 4 to 6, as a result its possible, where as in case of carbon tetrachloride it is not very easy to increase its coordination number, when water essentially comes and coordinates to CC l 4 prior to hydrolysis.

As a result, its kinetically prevented from undergoing hydrolysis, otherwise strictly speaking from thermodynamic point of view both carbon tetrafluoride and carbon tetrachloride are unstable with respect to hydrolysis. With this I conclude the chemistry of group 14 elements. So, in my next lecture, I will be discussing the chemistry of group 15 elements until then have a pleasant reading of inorganic chemistry.

Thank you very much.