Main Group Chemistry
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Lecture – 49
Chemistry of Group16 Elements

Welcome to MSB lecture series on the chemistry of main group elements. In my previous lecture I was discussing about the chemistry of group 16 hydrides. So, let me continue the discussion on hydrides and related species.

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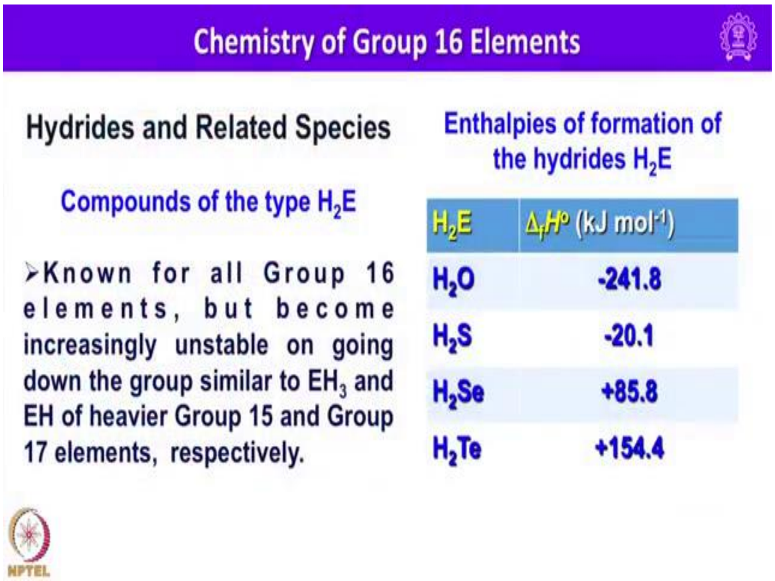

Chemistry of Group 16 Elements

Hydrides and Related Species

Compounds of the type H_2E

- Known for all Group 16 elements, but become increasingly unstable on going down the group similar to EH_3 and EH of heavier Group 15 and Group 17 elements, respectively.

Enthalpies of formation of the hydrides H_2E

H_2E	$\Delta_f H^o$ (kJ mol^{-1})
H_2O	-241.8
H_2S	-20.1
H_2Se	+85.8
H_2Te	+154.4

I have given the enthalpy of formation of various hydrides of group 16 elements ah, one can see clearly here H2O it is minus 241.8 kilo joules per mole; whereas, for hydrogen sulfide it is minus 20.1, in case of selenite it is plus 85.8.

Now, see in case of telluride it is plus 154.4, these values indicate the relative stability of this hydrides the stability of hydrides decreases down the group ; that means, this di hydrides of the type H2E are known for all group 16 elements, but become increasingly unstable on going down the group very similar to EH3 in case of group 15 elements and EH in case of group 17 elements like HCL HBR HI ok, in the trends are very similar.

The high boiling point of water is essentially due to the very strong hydrogen bonding, which gives complex structures in both solid and solutions states. In contrast to water

H2S H2Se and H2Te; that means, sulfur selenium and tellurium hydrides are highly toxic foul smelling gases, water undergoes self ionization with an equilibrium constant of 10 to the power of minus 14 at 55 degree centigrade that I showed you in my previous lecture.

Acids are substances which increase the concentration of H3O plus while basis increase the concentration of OH minus. So, water can act as acid as well as a base if you are curious to know the iupac name of H2O it is not water, H2O should be called as oxane and H2S should be called as sulphane and similarly H2Se should be selinane and H2Te should be called as tellurane ok.

Let us look into chalcogen anions, all the chalcogens form anions of say type e 2 minus whether it is a oxide sulfide solenoid or telluride by double de protonation of the hydrides that is H2E ok, a general method of preparation involves the direct combination of the elements with the metals.

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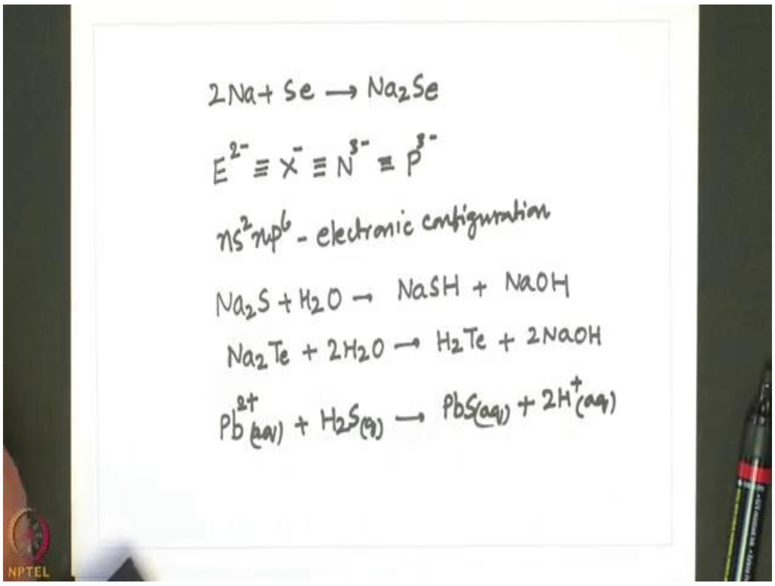

$2Na + Se \rightarrow Na_2Se$

$E^{2-} \equiv X^{-} \equiv N^{3-} \equiv P^{3-}$

ns^2np^6 - electronic configuration

$Na_2S + H_2O \rightarrow NaSH + NaOH$

$Na_2Te + 2H_2O \rightarrow H_2Te + 2NaOH$

$Pb^{2+}_{(aq)} + H_2S_{(g)} \rightarrow PbS_{(aq)} + 2H^{+}_{(aq)}$

For example 2Na plus selenium gives Na2 Se one can also prepare the telluride and also the sulfide ok. So, why they form di anions, by forming these ions the cholcogens attain noble gas electronic configuration it is very simple to start with all chalcogens have S2P4 electronic configuration by the addition of 2 electrons, the electronic configuration will become S2P6 that would be similar to the next inert gas electronic configuration.

So, E2 minus if we take this is isoelectronic with halide ions and also it is isoelectronic with the N3 minus and P3 minus. So, all of them have ns2 np6 electronic configuration ok; the tendency of formation of the corresponding anion is essentially to attain ns2np6 electronic configuration. So that means, next the question is why E2 minus anions become increasingly unstable going down the group, due to the increasing size the electrons are less tightly held so oxidation occurs more readily, as we go down the group the size of the atoms increases.

As a result added electrons are less firmly held by nucleus as a result that tend to be reducing nature, so they get oxidized ok. Many compounds containing E2 minus or water sensitive especially for group 1 and group 2 metals and the degree of hydrolysis is greater in the case of selenium and tellurium, for example if you take Na2S and if you treat with water it forms NaSH plus NaOH, similarly Na2 tellurium on treatment with water it forms telluride plus hydrogen tellurium hydrate plus 2NaOH.

Sulfides and selenides of soft polarizable heavy metals such as cadmium led mercury often occur naturally or moisture stable and prosperity readily when H2S or H2Se is passed through an accuse metal ions solution; for example, Pb2 plus in aqueous medium when it is treated with hydrogen sulfide Pb2 plus in aqueous medium when it is treated with hydrogen sulfide it forms Pbs plus 2H. Solid state chemistry of metal oxide sulfides and salinity is quite extensive and it is any discussion on these compounds is beyond the scope of this course ok. So, cationic (Refer Time: 07:28) ions that is H3e plus quite well known.

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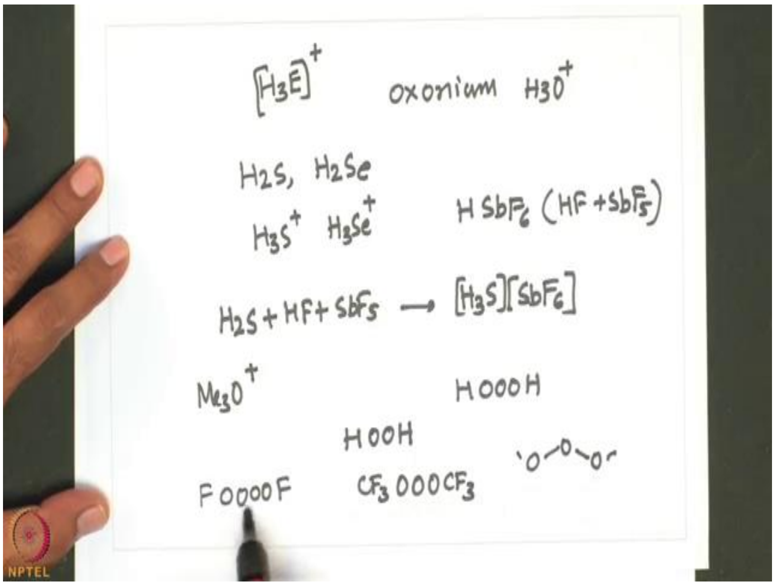

$[H_3E]^+$ oxonium H_3O^+

H_2S, H_2Se

H_3S^+ H_3Se^+ $HSbF_6$ $(HF + SbF_5)$

$H_2S + HF + SbF_5 \longrightarrow [H_3S][SbF_6]$

Me_3O^+ HOOOH

HOOH

FOOOOF CF_3OOOCF_3

For example hydronium so H3 e minus ions and of course when it is O it is called oxonium ion this is H3O plus.

So, cationic onium ions of this type are known, a typical example is oxonium H3O plus although H2S and H2Se have lower basicity compared to water ah, 1 can also make the corresponding H3S plus and H3Se plus, but by using very strong acids such as HSb F6 of course, hsbF6 can be prepared by treating HF with SbF5 ok. So, here H2S when it is treated with HF and SbF5 it forms H3S and spF6 ok. So, this is how the sulfonium cat ion can be generated organic days of these sulfonium salts are widely known; for example, Me3O plus salts are quite reactive and are widely used as reagents for transferring methyl groups or they are called methylating reagents.

Of course if you open any organic text books, you find the application of this Me3O plus as a methylating agent. All (Refer Time: 9:49) group containing compounds are oxidizing agents used as bleaching and stabilizing agents, no compounds are known which have greater than 2 auctions in a chain terminated by hydrogen atoms, such as HOOOH it is restricted only to HOOH that is hydrogen peroxide.

But related florin containing compounds having more than 2 oxygen atoms in a china are known, for example this is known you have F2O 4 and similarly CF3 these compounds are known, where we have something like 3 action atoms in a road here we have 4 oxygen atoms are there. In contrast sulfur selenium and tellurium hydrates and anions can have Te-Te bonds a number of hydrides are known which contain S-S or Se-Se linkages terminated by hydrogen are known ok.

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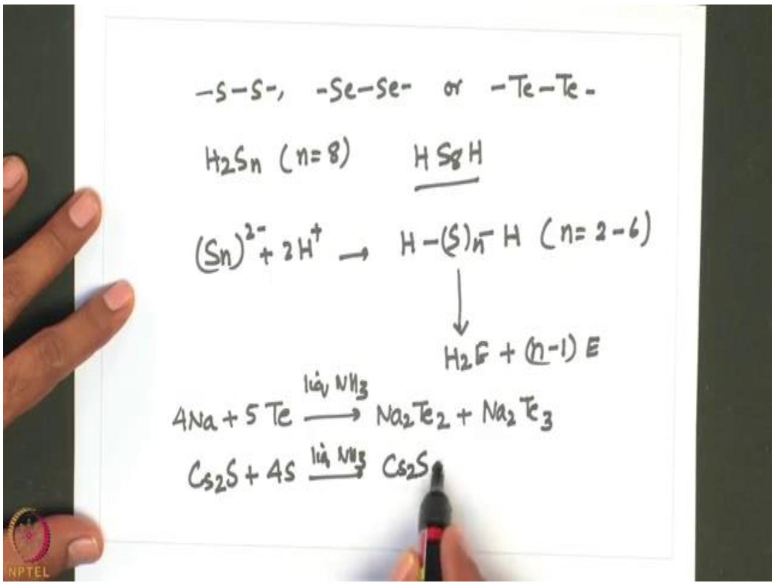

$-S-S-$, $-Se-Se-$ or $-Te-Te-$

H_2S_n $(n=8)$ $\underline{HS_8H}$

$$(S_n)^{2-} + 2H^+ \rightarrow H-(S)_n-H \quad (n = 2-6)$$

$$\downarrow$$

$$H_2E + (n-1)E$$

$$4Na + 5Te \xrightarrow{liq\ NH_3} Na_2Te_2 + Na_2Te_3$$

$$Cs_2S + 4S \xrightarrow{liq\ NH_3} Cs_2S$$

So, longest one is found for sulfur say H2Sn where n can be 8 so; that means, essentially HS8H something like this. Since sulfur has a strong tendency to form long chains and it is not unusual and polysulfane mixtures are also known for example, Sn 2 minus when it is treated with a 2H plus, so it can form ok. So, here as you said n can be anywhere between 2 to 6. So, polys; however, polysulfanes are unstable give the element and H2E.

So, this one essentially decomposes to give the sulfide or the corresponding 1 plus elemental chalcogen. So, longer chain poly chalcogened anions of sulfur selenium and tellurium are prepared by reaction of an alkali metals with the element in non aqueous medium, we should remember strictly this reaction has to be carried out in liquid ammonia.

For example 4Na plus 5Te in liquid ammonia gives Na2Te2 plus Na2Te3, similar CCM sulfide when it is treated with sulfur in liquid ammonia it forms Cs2s5. Now just look into the inter chalcogen compounds that means, let us look into the dioxides of sulfur selenium and tellurium. In fact, di oxides of sulfur selenium tellurium and polonium are known they are essentially formed by heating the elements in a 1 typical example is S8 ok.

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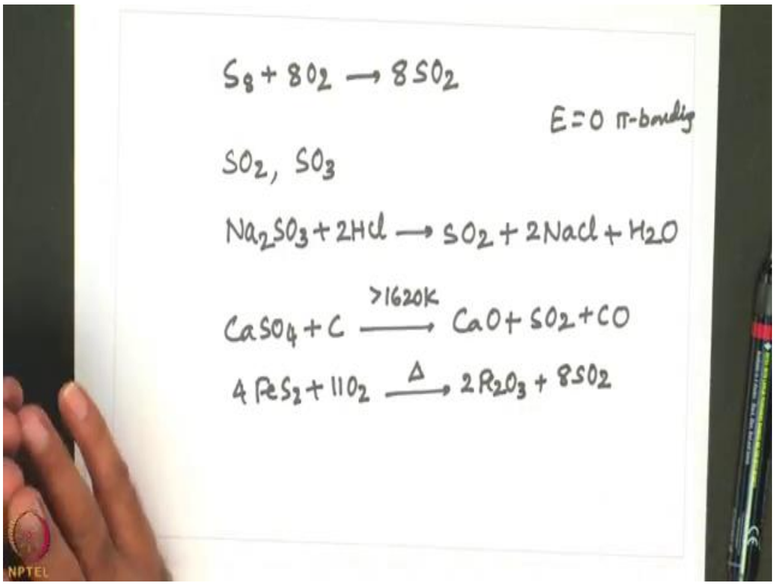

$S_8 + 8O_2 \rightarrow 8SO_2$

$E=O$ π-bondig

SO_2, SO_3

$Na_2SO_3 + 2HCl \rightarrow SO_2 + 2NaCl + H_2O$

$CaSO_4 + C \xrightarrow{>1620K} CaO + SO_2 + CO$

$4FeS_2 + 11O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 8SO_2$

This is a typical inter chalcogen compound. So, dioxides have different structures and So2 is a covalent substance and SeO2 has a infinite covalent chain structure in the solid state, I will be showing the structure later. But in gas phase t is very similar to SO2 whereas, tellurium oxide and polonium oxide have ionic structures this is again due to the increase in the metallic structures going down to the group and tendency for only the later elements to form E double bond x that is pi bonding.

So, heavier once the lack because of miss match of the orbital’s this double bonds owned effective ah, this is another region due to the increase in the metallic or ionic nature of the bonds in tellurium oxide as well as polonium oxide, the most important oxides of sulfur or SO2 and SO3 ; but there are also a number of unstable oxides sulfur dioxide is manufactured on a large scale by burning sulfur in the laboratory SO2 may be prepared by following reaction that I am going to write.

So, in the laboratory SO2 can be prepared by treating Na2SO3 with 2HCl that leads to the formation of SO2 plus 2NaCl plus H2O some other methods utilized in the preparation of SO2 or essentially calcium sulfate when it is treated with carbon at 1620 Kelvin it forms CaO plus SO2 plus CO or treatment of FeS2 with oxygen these to the formation of Fe2O3 plus 8SO2.

Essentially here the roasting of sulfide is essentially to convert into the corresponding oxide. So, that carbon can be used as a reducing agent to get pure metal.

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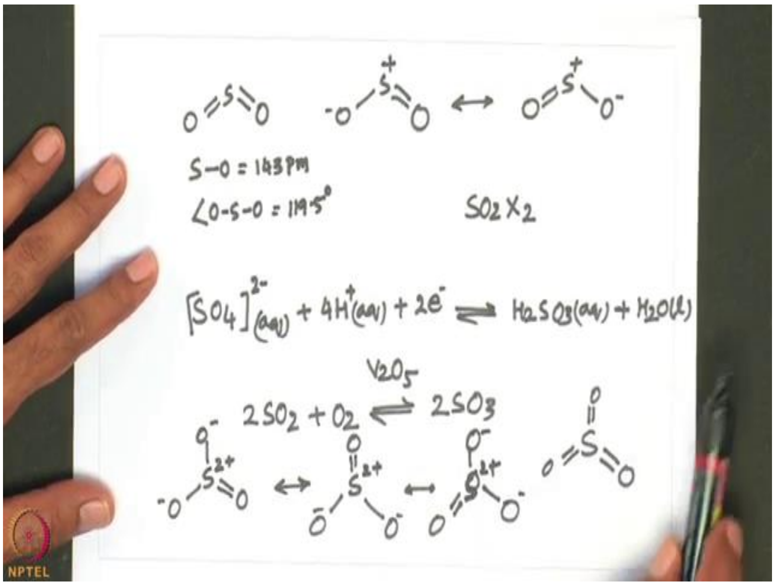

The structure of sulfur dioxide I am sure you are all familiar with it and 1 can also write like this ok. So, here a SO bond distance is 143 picometres, whereas, this angle is OSO angle is 119.5 5 degrees. So, sulfur dioxide reacts with oxygen fluorine chlorine in case of florin and chlorine it gives oxy halides, such as SO2 X2 in aqueous solution it is converted into only a small extent to form sulfurous acid aqueous solutions of H2SO3 contain significant amount of dissolved SO2.

Ah oxidation of SO2 by atmospheric oxygen is very slow, but is essentially catalyzed by vanadium pent oxide. So, in the manufacture of sulfuric acid gaseous SO3 is removed from the reaction mixture by a passage through concentrated sulfuric acid, in which it dissolved to form oleum on a small scale SO3 can be prepared by heating oleum and SO3 structure is something like this. Of course, 1 can also write resonant structures SO3 reacts with h x to form HSO3 X, where X equals F or Cl or it can react with Lewis base to form an adduct, where l equals a typical leis base it can be pyridine or py pph3 with H2O it forms H2S O4.

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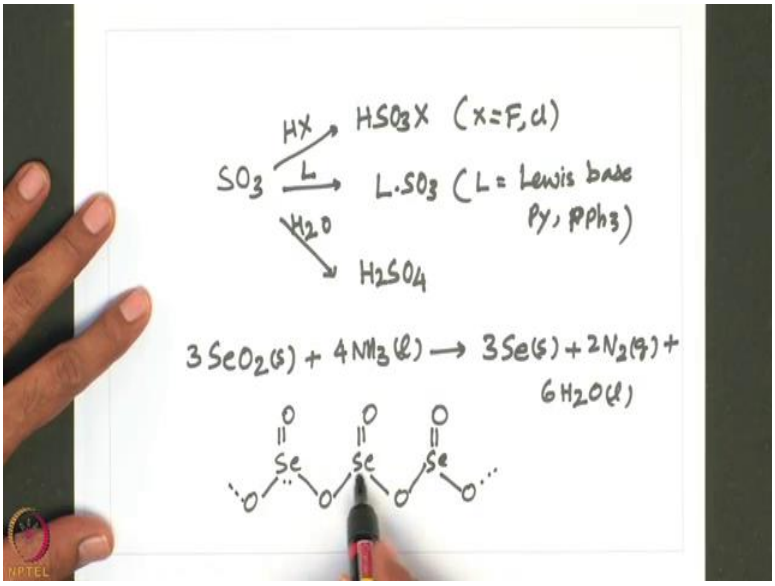

$SO_3 \xrightarrow{HX} HSO_3X$ (x = F, cl)

$SO_3 \xrightarrow{L} L \cdot SO_3$ (L = Lewis base Py, PPh$_3$)

$SO_3 \xrightarrow{H_2O} H_2SO_4$

$3SeO_2(s) + 4NH_3(l) \longrightarrow 3Se(s) + 2N_2(g) + 6H_2O(l)$

In fact, when we cut onion irritation will be there and tears comes in the eyes, It is essentially because when we cut onion a chemical called propane thionious oxide is released. So, that will react with another enzyme to form SO3 that is liberated, when SO3 start moving towards eyes moisture in the eyes will react with SO3 to form H2SO4 and then this H2S 4 starts irritating our eyes ah, in order to delude this 1 eyes produces more and more tears and this is because of the formation of sulfuric acid while cutting onion, so that tears comes and of course, 1 can avoid this 1 by cutting onions and putting in water for sometime or keeping a candle next to the place where onion is being cut.

So, that what happens this flame essentially deflect SO3 ways. So, that it does not reach our eyes the structure of tetra halides is given here.

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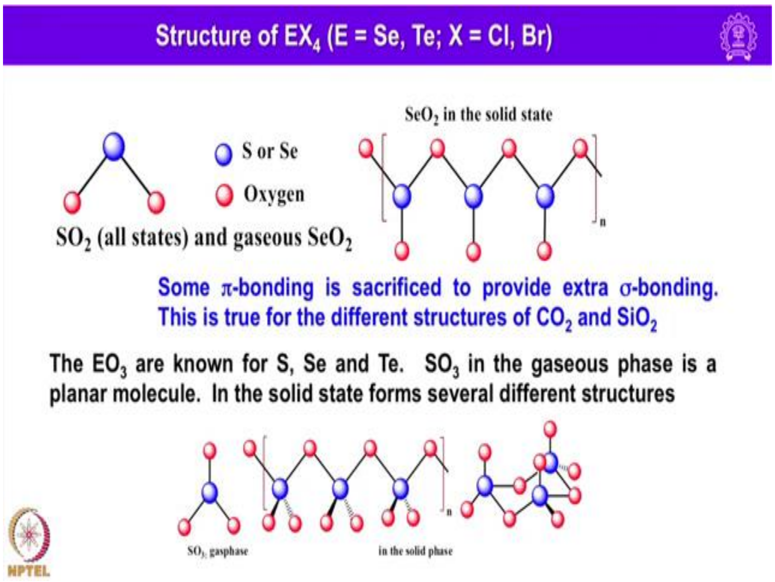

Structure of EX_4 (E = Se, Te; X = Cl, Br)

Some π-bonding is sacrificed to provide extra σ-bonding. This is true for the different structures of CO_2 and SiO_2

The EO_3 are known for S, Se and Te. SO_3 in the gaseous phase is a planar molecule. In the solid state forms several different structures

You can see here this is for SO2 and this is for SeO2 as I said it has a chain structure in the solid state, this how oxygen bridging occurs and it has a chain structure, some pi bonding is sacrifice to provide extra sigma bonding this is true for different structures of CO2 and SiO2 as well EO3 are known for sulfur selenium and tellurium that is SO3 SeO3 and TeO3 are known, SO3 in the gaseous place is a planar molecule. In the solid state forms several different structures that you can see here in the solid state it have this structure and also it can have a structure like this.

So, the dioxide of selenium tellurium polonium can be prepared by direct reaction of the elements selenium dioxide is a wide solid that sublimes at 315 degree centigrade, it has a polymeric structure in the solid state, it is thermodynamically less stable than SO2 and tellurium oxide and is reduced to selenium on the reaction with the Nh3 N2H4 are aqueous 4S2. Let me write the equation for example, 3SeO2 when it stated with ammonia liquid ammonia ok. It is used as an oxidizing agent in organic chemistry and the structure of selenium oxide will be something like this, so it continues of course we should remember it has a lone pair as well here.

So, tellurium dioxide occurs naturally as the mineral telluride, beta telluride has a layer structure in which TeO4 units form diamonds synthetic telluride consists of.

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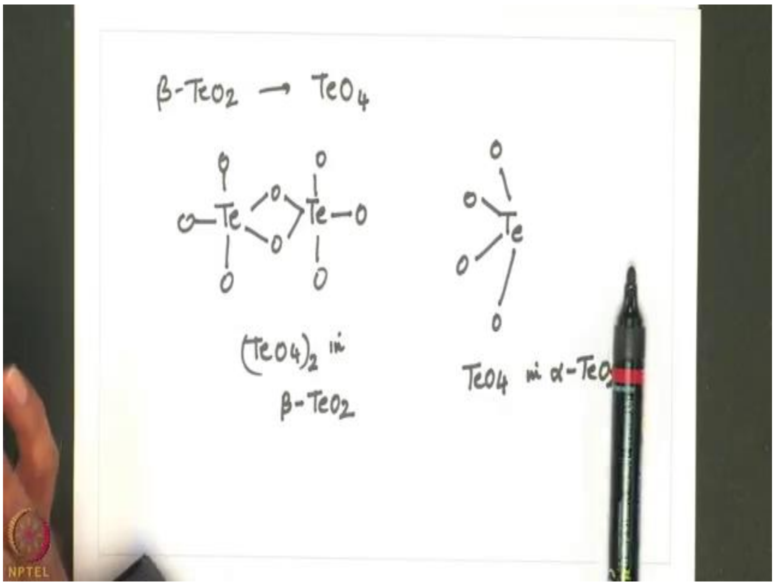

Similar TeO4 units that share world sees to form a 3 dimensional rutile like structure, that is rutile is TeO4 something like this ok. So this TeO4 twice in beta telluride ok. So, in case of alpha telluride the structure is slightly different this is in alpha telluride TeO4 ok.

So, polonium dioxide exists as yellow form with the fluoride structure and the red triagonal form. So, selenium trioxide unlike SO3 or TeO3 is thermodynamically less stable that the dioxide, it is a wide hygroscopic solid and sublimes at 100 degree centigrade and decomposes at 165 degree centigrade in the solid state the structure Is based on Se4O12 tetra moronic let me write it.

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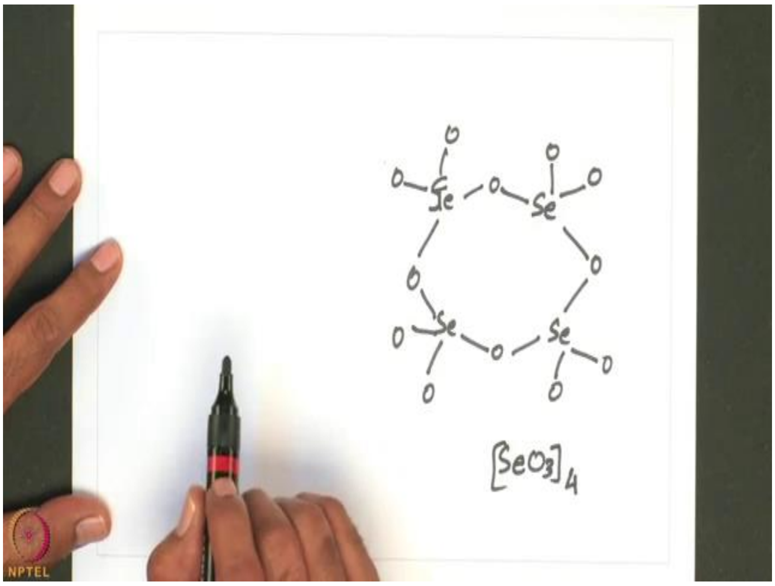

But it is monomeric in the vapor phase, it has something like this. So, SeO3 4 times. So, TeO3 is more stable made by heating alpha TeO3 or tellurium OH6 times in oxygen hexahydroxide tellurium ok. Tellurium trioxide exists as the l o alpha TeO3 which is prepared by dehydration of TeOH 6 times. So, also we have oxy halides in case of sulfur selenium and tellurium. So, let me discuss the oxy halides of heavier group 16 elements in my next lecture, until then have a pleasant reading of group 16 chemistry.

Thank you.