Main Group Chemistry
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Lecture – 50
Chemistry of Group 16 Elements

Hi once again welcome you all to the lecture series on main group elements. In my previous lecture I was discussing about chemistry of group 16 elements and I was discussing about oxy halides.

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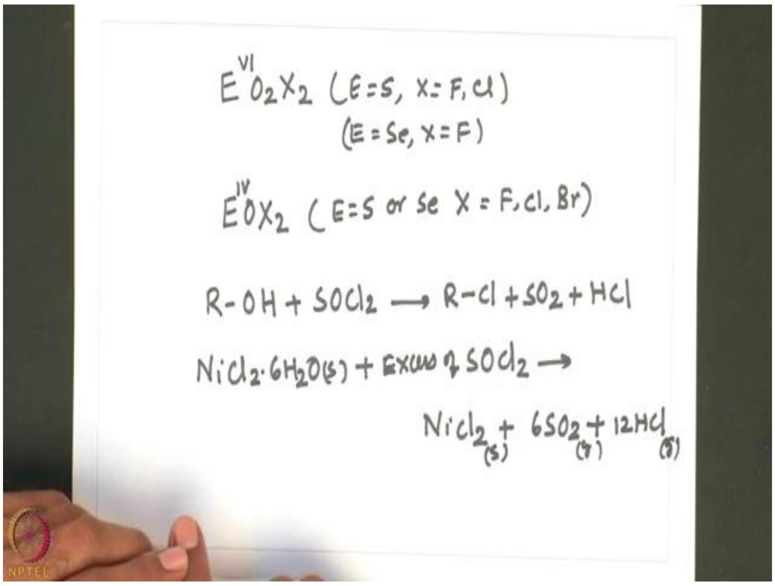

$E^{VI}O_2X_2$ (E = S, X = F, Cl)

(E = Se, X = F)

$E^{IV}OX_2$ (E = S or Se X = F, Cl, Br)

$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$

$NiCl_2 \cdot 6H_2O_{(s)} + \text{Excess of } SOCl_2 \longrightarrow NiCl_{2(s)} + 6SO_{2(g)} + 12HCl_{(g)}$

Let me continue from where I had stopped, oxy halides of sulfur selenium and tellurium are very important and they have general formula , where E equals sulfur X equals F and Cl and where E equals selenium this is with chalcogen in it is plus 6 oxide state , oxy chlorides with the chalcogen in it is 4 oxide state are also known there EOX 2 and here again when E equals sulfur or selenium for halides such as fluorine chlorine and bromine are known; that means, SOCl 2 and SOBr 2 are known on sulfural.

So, they are called sulfural halides and their thionyl halides in case of self sulfur. So, sulfural and thionyl halides and their selenium analogues are powerful hallucinating agents and find application in inorganic as well as organic chemistry. For example, in the preparation of chlorides from alcohols and anhydrous metal halides, these compounds are widely used let me write a couple of examples here; take a typical alcohol and treat with the thionyl chloride SOCl 2.

It forms R-Cl and in trans metallic chemistry for the preparation of anhydrous metal halides for their utility in organ metallic chemistry, one can generally treat the hydrated salts with excess of thionyl chloride. So, this is where the utility of sulfural and thionyl chloride comes into the picture. So, let us look into a couple of questions here , predict the shapes of molecules SOCl 2 and SO 2 Cl 2 and simply if you look into SOCl 2 that is in plus 4 state. So, we have here in this case 3 bonded pair and 1 lone pair, whereas in case of SO2Cl 2 we have 4 bonded pairs.

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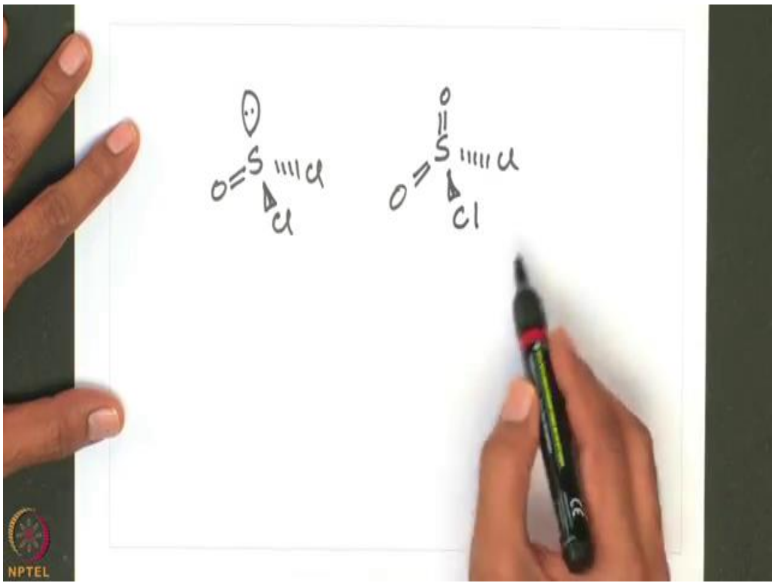

So, this has a pyramidal structure trigonal pyramidal structure whereas, SO 2 C l2 has tetrahedral structure ok. So, oxy acids of sulfur selenium and tellurium are known a wide range of axe acids and or their anions are known for group 16 elements, sulfur and selenium show coordination number up to 4 while tellurium tend to be 6 coordinate compounds with the S-S bonds are also quite known, sulfurous Salinas and tellurous acids having composition H 2 EO 3.

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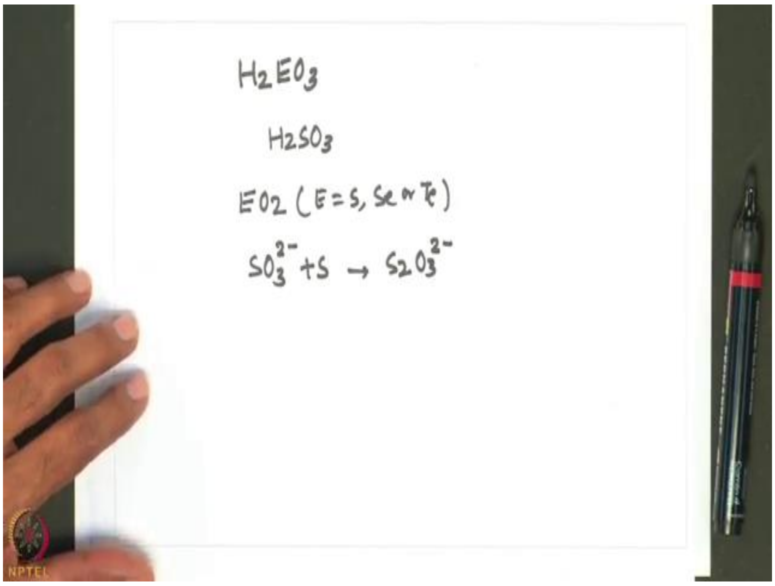

H_2EO_3

H_2SO_3

EO_2 (E = S, Se or Te)

$SO_3^{2-} + S \rightarrow S_2O_3^{2-}$

So, here when sulfur is there the sulfurous when selenium is there it is Salinas and when it is tellurium it is called tellurous acids, SO 2 is very soluble in water and dissolves largely without reaction forming an acidic solution known as sulfurous acid that is H 2 SO 3, the free acid has never been isolated and is either absent or present only in trace amounts of SO 2 solutions SeO 2 and TeO 2 behave very similarly. But are less acidic then H2SO3 a solution of EO2 , where E equals sulfur selenium or tellurium in aqueous hydroxide solution gives the corresponding EO3 2 minus HeO 3 anions. For example, SO 3 2 minus plus S gives S2O 3 2 minus ok.

Thiosulfate is widely used in redox titrations involving iodine in this reaction tetra thionate, that is S 4 O6 2 minus is formed which contains a chain of 4 sulfur atoms , tetra thionate is a member of unstable sulfur bridged poly thionates of composition ok, so where n can be.

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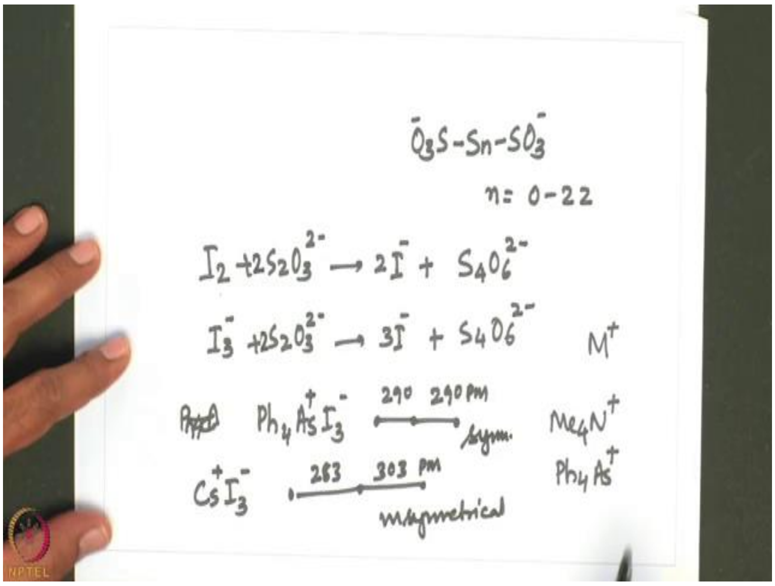

$^{-}O_3S-S_n-SO_3^{-}$

n: 0-22

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^{-} + S_4O_6^{2-}$

$I_3^{-} + 2S_2O_3^{2-} \longrightarrow 3I^{-} + S_4O_6^{2-}$

M^{+}

$Ph_4\overset{+}{As}I_3^{-}$ 290 290 pm symm.

Me_4N^{+}

$\overset{+}{Cs}I_3^{-}$ 283 303 pm unsymmetrical

Ph_4As^{+}

So, very interesting n can have anywhere between 0 to 22, how it reacts with iodine can be seen here for example, I2 when I stated with the S 2 O 3 2 minus; it I minus is formed through the formation of tetra thionate S 4 O 6 2 minus and this I 3 minus reacts with S 2 O 3 2 minus to give 3 I minus plus S 4 O 6 2 minus.

So, I3 minus anion is most commonly encountered during redox titrations involving iodine , where an excess of iodide ions is added to convert any iodine formed to the soluble I3 minus; the solubility of I 3 minus is dependent on the size of the catonium plus we are using here and to prosperate I 3 minus ion from solution large cat ions such as tri tetra methyl ammonium or tetra final arsenium are more preferred ok. The cat ions also has a market influence on the structure of the anion, the smaller cesium plus ion distorts the I3 minus ion; whereas, the larger cat ions such as triphenyl or sodium does not.

So, as a result you can see the structure will be little bit deformed, for example if we look into Ph4As I3 minus and if you suggest just look into the I3 minus here I3 minus or symmetric ii distance is 290 Pico meter very symmetrical. If you look into I3 containing a smaller cesium cat ion it is distorted , so in this case so this is 283 whereas this 1 is 303 Pico meter. So, this is unsymmetrical and this is symmetrical ok.

So, that indicates how cat ions have influence on the structure of anion, so oxo acids and their salts resemble the complicated system of phosphorus, there are structural analogues between sulfates and phosphates although fewer condenser sulfates are known. So, redox process involving sulfur oxo anions are often slow and thermodynamic data alone do not give a very good picture of their chemistry, compare similar situations for nitrogen and phosphorous containing oxo anions.

So, selenium and tellurium have a relatively simple oxo acid chemistry, other sulfur acids and their anions 1 can see for example, sulfuric acid H2SO4 1 of the OH groups may be replaced by a hydro peroxo group to give monoporoxo or sulfuric acid our OH group can also be replaced by a halogen or Nh 2 or NH or by an organic groups a methyl group. So that means, in sulfuric acid if we can replace OH group with other groups we can get different sulfur acids, thiosulfate anion has the same structure as sulfate. But with an action replaced by a thiosulfate over of the o group is replaced by, so for example.

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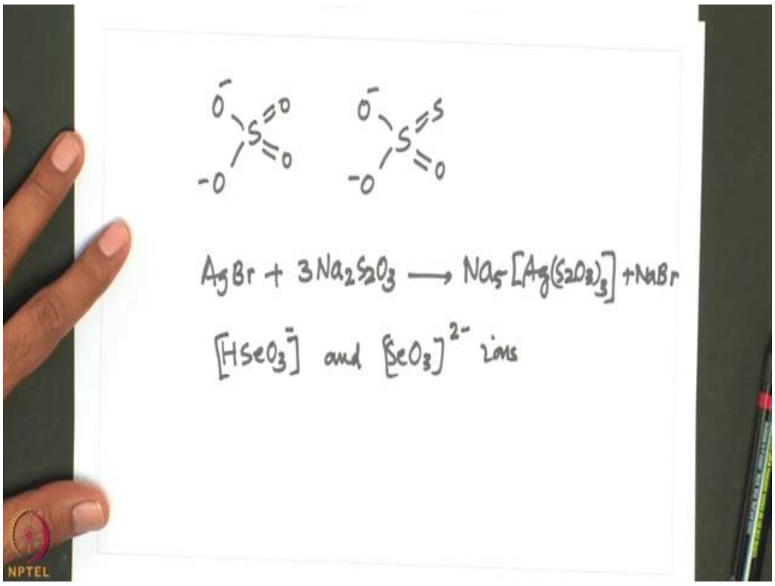

So, this is sulfate in thiosulfate basically what happens. So, this is 1 of the auction is replaced by sulfur, thiosulfate ion is a very good complexing agent for silver plus ions and sodium thiosulfate is used in photography for removing unchanged silver bromide from exposed photographic film. So, now nobody is using photographic film as we have entered into digital era; however, one should know how a photographic films were developed for example, AgBr are when it stated with sodium thiosulfate it was forming a silver complex , so that means, unchanged silver bromide was essentially removed using sodium thiosulfate.

So, most oxidizing agents including chlorine and bromine slowly oxidize S2 O3 to SO 4 thiosulfate into sulfate and thiosulfate is used to remove excess of chlorine in ditching process as well, Salinas acid H 2 Se O 3 may be crystallized from aqueous solution of SCO 2 and gives rise to 2 series of salts containing HSeO3 minus and SeO3 2 minus ions.

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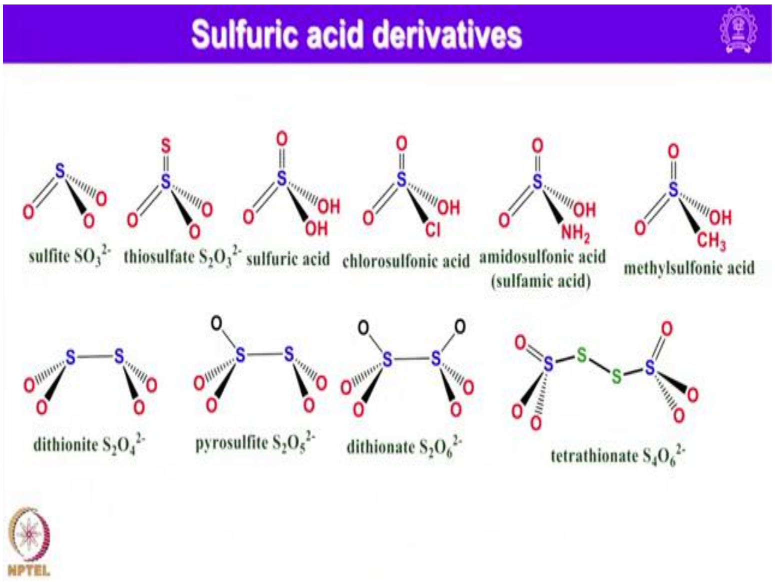

Sulfuric acid derivatives

sulfite SO_3^{2-}
thiosulfate $S_2O_3^{2-}$
sulfuric acid
chlorosulfonic acid
amidosulfonic acid (sulfamic acid)
methylsulfonic acid
dithionite $S_2O_4^{2-}$
pyrosulfite $S_2O_5^{2-}$
dithionate $S_2O_6^{2-}$
tetrathionate $S_4O_6^{2-}$

I will show you some of the sulfuric acid derivatives here, as I had mentioned if we replace OH with the chlorine we get chlorosulphonic acid; for example this is sulfide anion and this is from sulfate as I mentioned 1 of the action is replaced by sulfur is called thiosulfate S2 O3 2 minus and then this is sulfuric acid H2 SO 4 and if 1 of the OH group is replaced by chlorine it is called chlorosulphonic acid.

And similarly if we replace 1 of the OH group with the NH 2 it was called amidosulfonic acid and OH replaced by methyl group it is called methyl sulphonic acid and this is die thionate S2O4 2 minus and this is pyro sulfide S2O 5 2 minus and it is dithionate S2O6 2 minus and this is tetra thionate having 4S in a chain having S-S linkages; it is S4O6 2 minus and 2 minus can be seen here. So, let us look into the preparation of some of these compounds how these compounds are prepared.

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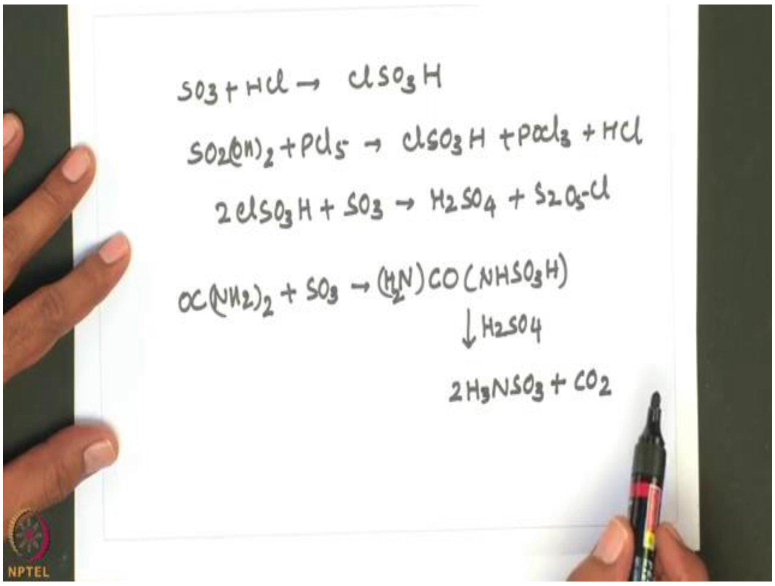

$$SO_3 + HCl \rightarrow ClSO_3H$$

$$SO_2(OH)_2 + PCl_5 \rightarrow ClSO_3H + POCl_3 + HCl$$

$$2ClSO_3H + SO_3 \rightarrow H_2SO_4 + S_2O_5Cl$$

$$OC(NH_2)_2 + SO_3 \rightarrow (H_2N)CO(NHSO_3H) \xrightarrow{H_2SO_4} 2H_3NSO_3 + CO_2$$

For example treat SO3 with HCl it gives chlorosulphonic acid or one can also I am writing in a different way this is essentially sulfuric acid I am writing in a different way to show the functionalities here, this is when it is treated with PCl 5 also it gives ClSO 3 H plus POCl 3 plus HCl and chlorosulphonic acid when you shield with SO 3 it gives H2SO 4 plus S2O5 Cl and sulphonic acid is produced industrial in 2 stages urea with a mixture of SO 3 and H2SO 4 or valium. For example, this is urea NH 2 CO NH 2 this is first treated with SO3 give NHSO 3 H and this 1 on further treatment with H2SO 4 forms 2H3NSO3 plus CO 2.

So, in this way approximately 1 million tons of amidosulfonic acid is produced every year and this chlorosulphonic acid is useful in detergents and also as chemical intermediate; for example, ROH plus ClSO3 H gives ROSO3 h plus HCl ok.

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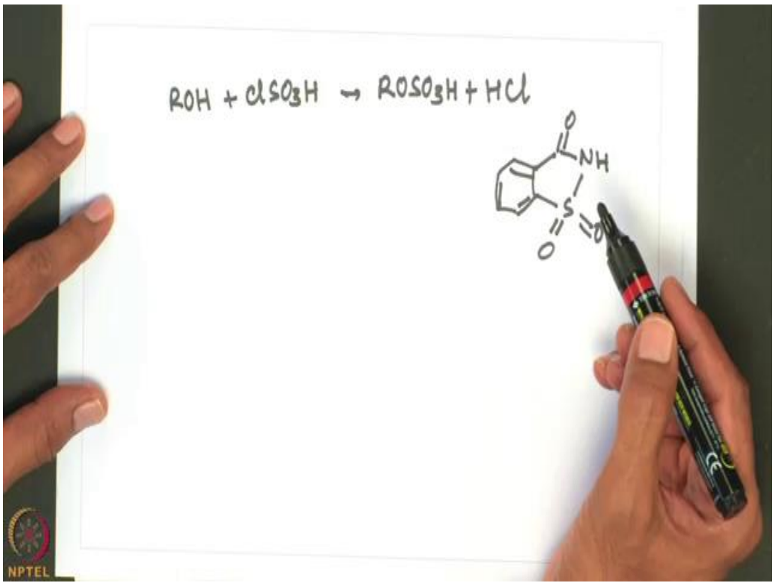

So, one can make here methyl or alchoyl on early synthesis saccharine begins with the reaction of tolin with chloro sulfuric acid to give (Refer Time: 17:51) sulfonyl chloride derivative and this one is so prepared for the first time in 1879 ok, oxidation of the arthoa summer gives the benzoic acid derivative which is cyclized with ammonia and neutralized with the base to a upwards saccharin, chlorosulphonic acid has been used as an anti contrail agent in rayon model 147 with no constants drones and to produce smoke screens ok.

So, let us look into group 16 halides in contrast to the trend found in earlier groups, the stability of lowest out of state that is plus 2 of the central atom in the halides of the group 16 elements decreases down the group; oxygen difluoride is highly toxic and it is prepared by the reaction of NaOH and F2. So, all the OF 2 is firmly than hydra hypochlorous acid HYF pure OH 2 OF 2 can be heated at 470 Kelvin without decomposition.

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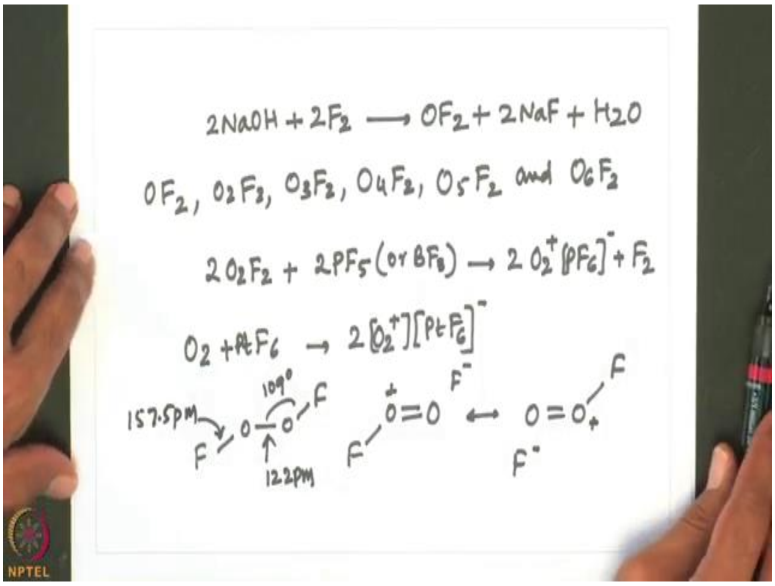

$2NaOH + 2F_2 \longrightarrow OF_2 + 2NaF + H_2O$

OF_2, O_2F_2, O_3F_2, O_4F_2, O_5F_2 and O_6F_2

$2O_2F_2 + 2PF_5 (\text{or } BF_3) \longrightarrow 2\,O_2^+[PF_6]^- + F_2$

$O_2 + PtF_6 \longrightarrow 2[O_2^+][PtF_6]^-$

But it reacts with many elements at or slightly above room temperature to form fluorides and oxides.

So, oxygen interestingly oxygen forms the 6 fluorides which are rare examples of compounds with oxygen in positive auction state, 1 should remember oxygen being the second most electronegative element can exist in plus auction state only when it is reacted with fluorine ah. It is interesting to know that we have several fluorides of this type having up to 6 oxygen atoms in a chain , for example OF2 is known O2F 2 is known O3F 2 is known O4F 2 is known O 5 F 2 and O 6 F 2 and they can also be prepared by treating sodium hydroxide with fluorine ah.

If we take O2F 2 analog of hydrogen peroxide and it is treated with 2 equivalents of PF5 phosphorus pentafluoride or BF3 it gives O2 plus and PF6 minus ion salt plus F2. So, by direct oxidation of O2 using PTF6 which 1 can prepare O2 plus cat ion, for example O2 plus PTF 6 gives 2 O2 PTF 6. In fact, this reaction led to the isolation of first a noble gas compound by Bartlett.

I will be discussing about the group 18 chemistry especially that of xenon and krypton, when I proceed to the chemistry of group eighteen elements; the structures of some of these oxy fluorides can be seen here 1 can also write like this and here this angle is 109 and this lower bond distance is 122 picometer and this OF up on distance is 157 point 5 picometer ah. The fluorides of sulfur such as the SF 4 S2F 2 can be prepared from the reaction of SCl2 and HgF 2 at elevated temperature.

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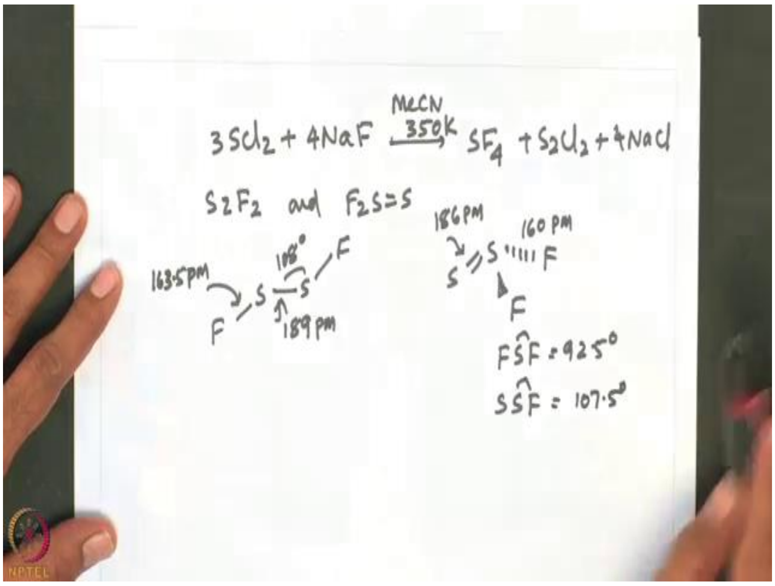

For example sulfur chloride when it is treated with fluorinating agent such as sodium fluoride in astro nitrile at 350 Kelvin gives SF4 ok. So, both SF4 and SF6 are highly stable disulfur di fluoride exists as 2 isomers that is S2F2 and F2S double bond ok.

So, I will write the structure these 2 structure like isomers , this angle is 108 and this is 189 picometer and this FS bond distance is 163.5 picometer other structure is and here it is 160 picometer and here it is S-S bond distance is 186 picometer and here FSF angle is 92.5 degree whereas, the SSF angle is 107.5 degree most of the people who have learned vsepr theory are quite familiar with the structure of SF4 and also I had discussed with the structure of SF4 while dealing with the structure and bonding concepts in earlier lectures; however, let me write the structure of SF4 here ok.

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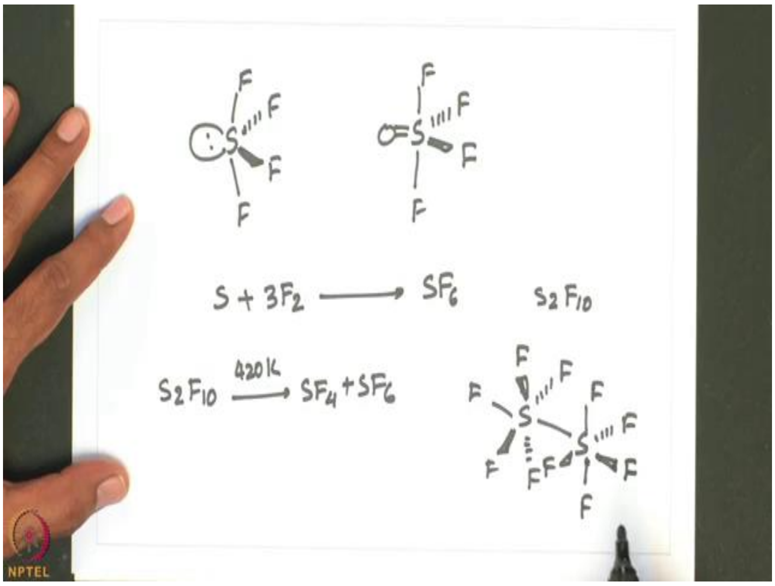

$S + 3F_2 \longrightarrow SF_6$

S_2F_{10}

$S_2F_{10} \xrightarrow{420K} SF_4 + SF_6$

See this is the see saw type structure and also SOF4 has trigonal by pyramidal structure ok.

Among the sulfur fluorides SF6 stands out for it is high stability and chemical inertness, it can be made by burning S in florin and is commercially available widely used as electrical insulator the preparation of SF6 from S and you have to produce a small quantity of S2F 10 as well and the yield can be optimized by controlling the reaction conditions, molecules of S2F 10 have the staggered structure; it disproportionate when heated and is a powerful oxidizing agent.

For example, S2F 10 when it is heated to 420 Kelvin it forms SF4 plus SF6. Now if you are curious to know the structure of S2F10 here it is , sulfur forms a wild range of halides particularly with fluorine in oxide states ranging from low fractional positive auction states to group auction state of plus 6 mono halides.

Such as S2 have structures similar to H2O2, but S2F 2 has been found to exist in 2 isomeric form that other day I showed you ah; besides this S2Cl2 and S2Br2 are the smallest members of a series of chloro and bromo sulfates of the type SnX2 sulfance with up to 8 sulfur atoms in the chain with S-S bonds are known, very similar to HS and H called as poly sulfanes are formed by direct combination of the elements.

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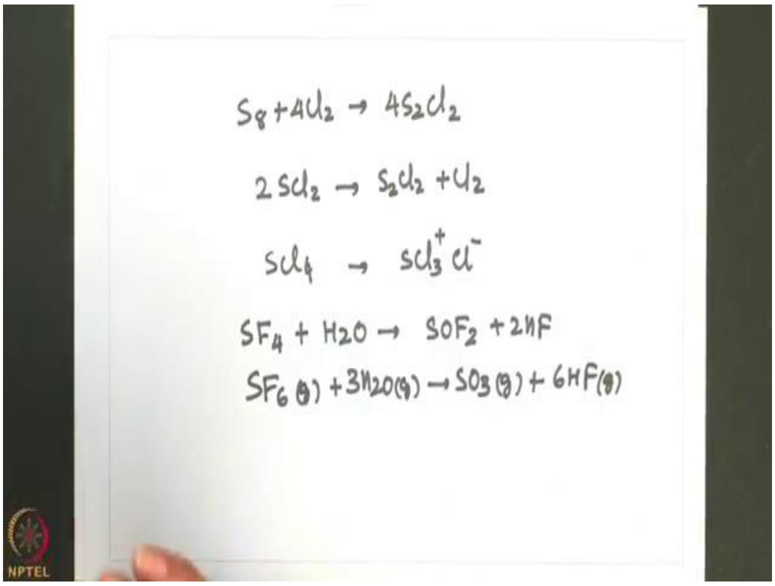

$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$

$2SCl_2 \rightarrow S_2Cl_2 + Cl_2$

$SCl_4 \rightarrow SCl_3^+ Cl^-$

$SF_4 + H_2O \rightarrow SOF_2 + 2HF$

$SF_{6(g)} + 3H_2O_{(g)} \rightarrow SO_{3(g)} + 6HF_{(g)}$

Quickly let me write S8 plus 4Cl2 gives 4S 2 Cl2, 1 the stable species is bent SCl2 which disproportionate to give S2Cl 2 and Cl 2. So, SCF 2 is even less stable. For example, SCl2 it disproportionate to give S2Cl 2 plus Cl 2 sulfur 4 are restricted own that SF4 and SCl4 and in solid state SCl 4 is thought to exist in ionic form such as SCl4 is thought to exist in the form of SCl 3 plus and Cl minus, let me write quickly the hydrolysis reaction of SF4 it gives SOF 2 plus 2HF SF 6 ok.

So, SF 6 is kinetically inert because it is coordinately un saturated having 6 coordination number having octahedral geometry; however, under drastic conditions it undergoes hydrolysis and Sf bonds can be broken under normal circumstances SF6 is stable. So, let me stop at this stage and continue in my next lecture remaining portions of the chemistry of group 16 elements.

Thank you very much.