Main Group Chemistry
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Lecture – 51
Chemistry of Group 16 Elements

Welcome to MSB lecture series on the chemistry of main group elements. This is 51st lecture in the series, in my last lecture while speaking on group 16 halides, I gave information about one of the important sulphur tetrafluoride. Now, let me continue from where I had stopped similar to SF 4 disulfur dichloride S 2 C l 2 is a fuming orange liquid and which is toxic, and has a very repulsive smell it is manufactured by passing chlorine through molten sulfur.

And further chlorination yields disulfur dichloride it is manufactured by passing chlorine through molten sulfur other chlorination yields disulfur dichloride both are essentially used and this S C l 2 as well as S 2 C l 2 are used for the manufacture of SO C l 2 both SO l 2 and S 2 C l 2 are used for the manufacture of SOC l 2 and SO 2 C l 2 and which are essentially used in vulcanization of the rubber.

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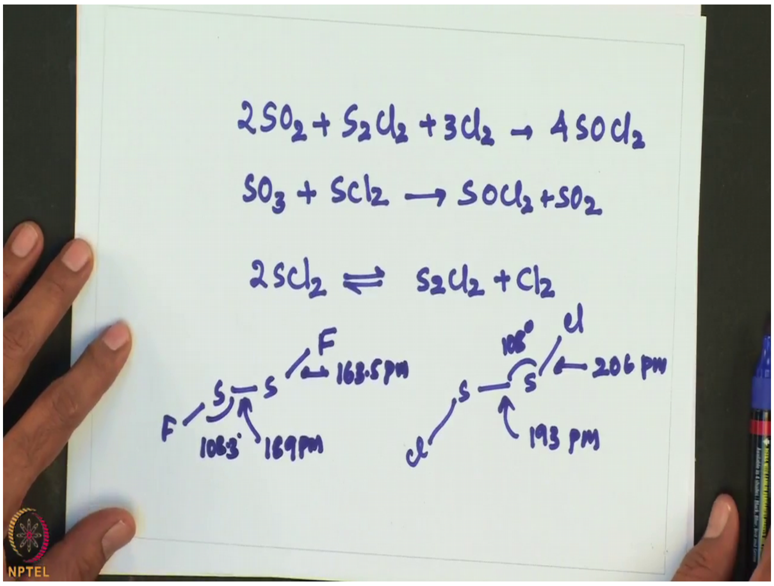

$$2SO_2 + S_2Cl_2 + 3Cl_2 \rightarrow 4SOCl_2$$

$$SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$$

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$$

So, sulfur dioxide when its treated with disulfur dichloride in presence of chlorine it gives SO C l 2 and of course, one can also make SO C l 2 starting from SO 3 and its treatment with S C l 2, 2 S C l 2 is unstable with respect to the equilibrium between disulfur dichloride and C l 2 ok. The structure of disulfur dichloride resembles that of S 2 F 2 while S C l 2 is a bent molecule I can write the structure here ok.

So, for example, this angle is 108 and this distance is 206 picometer whereas, SS bond distance is 193 picometer of course, as I said its very similar to S 2 F 2, and in this case this distance is 163.5 picometer and SS bond distance is little shorter 189 picometer, and then this angle is 108.3 ok.

Decomposition of both chlorides by water yields a complex mixture containing SSO 2 H 2 s y o 6 and h C l and H 2 C l 2 is also used for the formation of a s n ring, this thyonil chloride SO C l 2 and sulfural chloride SO 2 C l 2 are essentially colorless fluming liquids and SO C l 2 boiling point is 351 Kelvin and SO 2 C l 2 boiling point is 342 Kelvin.

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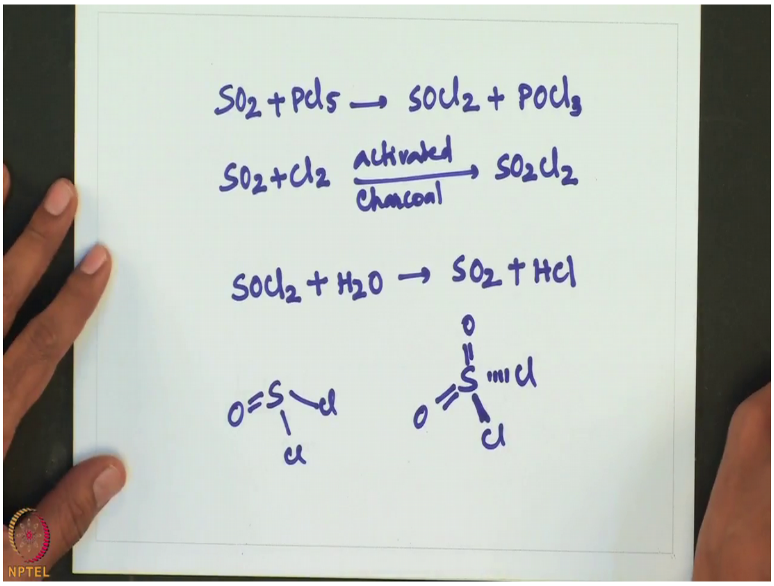

$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$

$SO_2 + Cl_2 \xrightarrow[\text{Charcoal}]{\text{activated}} SO_2Cl_2$

$SOCl_2 + H_2O \rightarrow SO_2 + HCl$

SO 2 un treatment with P C l 5 gives SO C l 2.

Of course through the formation of PO C l 3 and of course, when SO 2 is treated with the chlorine gas using activated charcoal SO 2, C l 2 or sulfural chloride is formed their ease of hydrolysis by water accounts for their fluming nature, what would happen if you add water to thionyl chloride? It liberates SO 2 and H C l. Both thionyl and sulfural chlorides are commercially available thionyl chloride is used to repair acyl chlorides and un anhydrous metals chlorides which are which are used in organo metallic synthesis, thionyl chlorides structure is like this, sulphueral chloride structure against like this.

So, one is tetrahedral one is pyramidal in shape of course, here we have a lone pair so, this pyramidal whereas, SO 2 C l 2 is tetrahedral. So, let us look into the analogous compounds of selenium and tellurium, selenium and tellurium halides are simulate to those of sulfur, but there are some notable differences that tendency to form catanated compounds is markedly less in case of selenium and tellurium compounds.

Selenium and particularly tellurium halides in plus 4 (Refer Time: 06:07) state try to be polymeric for example, tellurium tetra fluoride is polymeric whereas, selenium tetra chloride, selenium tetra bromide, and also tellurium tetra chlorine tetra bromide or tetrameric I will be showing the structure in the next slide, selenium and tellurium halides have a greater tendency to form complex anions by addition of halide anions.

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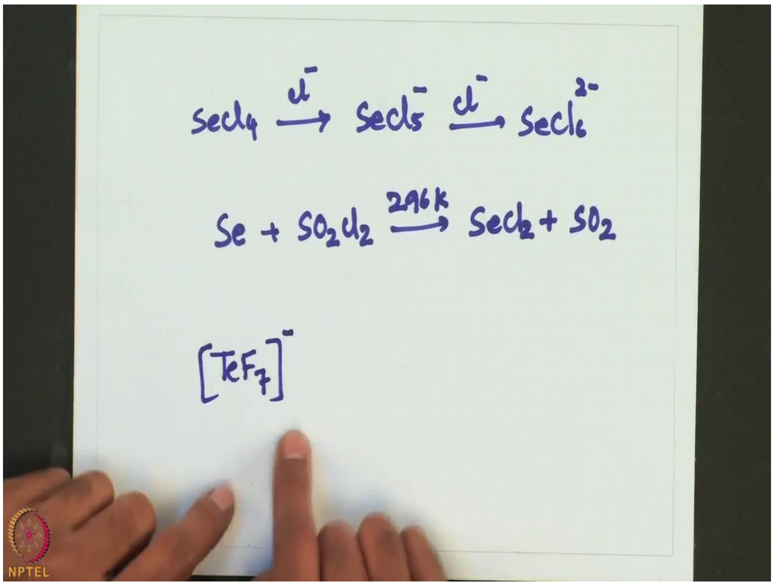

$$SeCl_4 \xrightarrow{Cl^-} SeCl_5^- \xrightarrow{Cl^-} SeCl_6^{2-}$$

$$Se + SO_2Cl_2 \xrightarrow{296\,K} SeCl_2 + SO_2$$

$[TeF_7]^-$

For example, if we consider S e C l 4 one can add to 1 or 2 fluorides to form minus or one can add another 1 to form S e C l 6 2 minus sings respectively. So, they form these kind of halide anions, selenium tetra fluoride is a very good flaunting agent and it is a liquid at 298 Kelvin, the isolation of dihalides of selenium and tellurium has only been achieved for selenium dichloride and selenium dibromide. Selenium dichloride is a thermally unstable red oil selenium dibromide is a red-brown solid.

For example, if you take selenium proud powder and treat with SO 2 C l 2 sulphurel chloride at 296 kelvin, it leads to the formation of selenium di chloride through the formation of SO 2. The tellurium fluorides are prepared similarly tellurium tetra fluoride from tellurium oxide and S F 4 or S e F 4 and tellurium hexa fluoride from the elements through direct combination that is by combining tellurium and florin.

Tellurium hepta fluoride ion has a pentagonal bipyramidal structure, all though in the solid state tellurium hepta fluoride ion has a pentagonal bipyramidal structure in the solid state; however, equatorial F o atoms deviates slightly from the mean equatorial plane you can see here in the slide this how selenium and tellurium tetra chloride and tetra bromide appear like.

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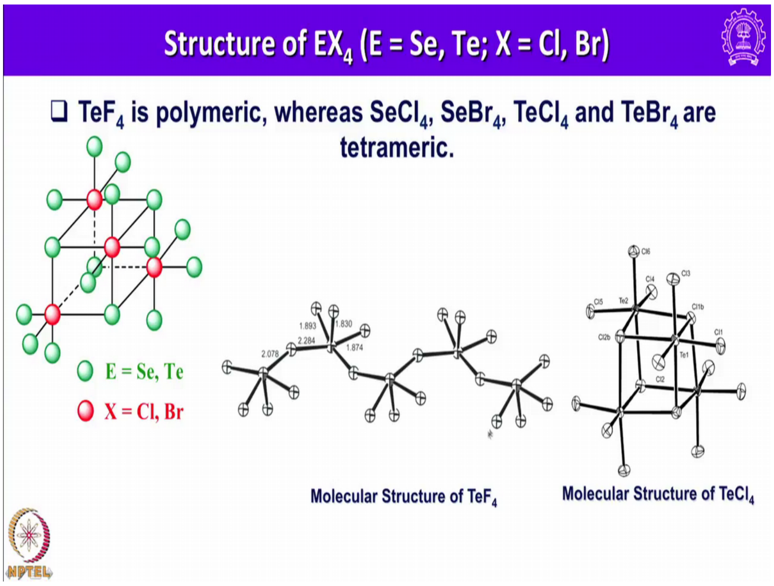

Structure of EX_4 (E = Se, Te; X = Cl, Br)

- ☐ TeF_4 is polymeric, whereas $SeCl_4$, $SeBr_4$, $TeCl_4$ and $TeBr_4$ are tetrameric.

Molecular Structure of TeF_4

Molecular Structure of $TeCl_4$

So, having a Cuban structure with alternate corners occupied by chalcogens and halogens and with each chalcogen is hexa coordinated. So, this is the structure of tellurium tetra fluoride, which has polymeric 1 dimensional polymeric structure through the bridging of one of the fluorine atom between 2 tellurium atoms. And this is the structure of tellurium tetrachloride this is very similar to what I have shown here.

Let us look into poly chalcogen cat ions oxygen with limited tendency towards catenation only forms O 2 plus, but the other group 16 elements particularly sulfur and selenium form a arrange of species sum of which are shown in the next slide, particularly sulfur and selenium form a range of species that I will show you in a minute.

So, these poly chalcogen cations are prepared by oxidation of the elements using strong oxidizing agents, in non aqueous solvents.

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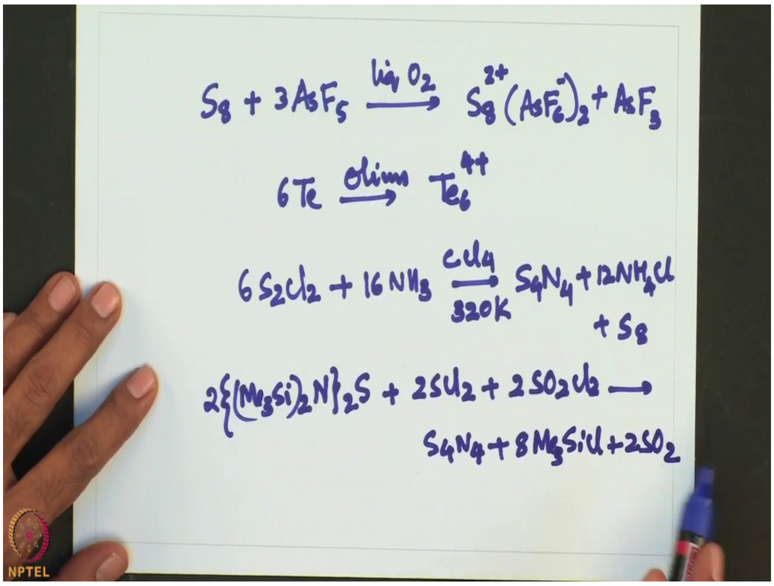

$$S_8 + 3AsF_5 \xrightarrow{liq\ O_2} S_8^{2+}(AsF_6^-)_2 + AsF_3$$

$$6Te \xrightarrow{oleum} Te_6^{4+}$$

$$6S_2Cl_2 + 16NH_3 \xrightarrow[320K]{CCl_4} S_4N_4 + 12NH_4Cl + S_8$$

$$2\{(Me_3Si)_2N\}_2S + 2SCl_2 + 2SO_2Cl_2 \longrightarrow S_4N_4 + 8Me_3SiCl + 2SO_2$$

for example if we take s 8 and treat this one with arsenic penta fluoride in liquid oxygen, it leads to the formation of a poly chalcogen cat ion the S 8 2 plus with A s F 6 minus being the counter an ion.

Similarly, a tellurium powder on treatment with olim it forms tellurium 6 in its plus 4 oxide state. So, this are poly chalcogen cations let us look into another importance set of compounds of sulfur that is sulfur nitrogen compounds, sulfur nitrogen chemistry is an area that has seen major development over the last few decades because of their utility as conducting polymers.

Tetra sulfur tetra nitrate one of the important sulfur nitrogen compounds that is S 4 N 4 can be readily prepared by treating S 2 Cl 2 with ammonia ok. So, one can also prepare starting from this reagent this (Refer Time: 12:02) amide sulfur plus 2 S C l 2 plus 2 SO 2 C l 2 gives S 4 N 4 plus 8 M e 3 S i C l plus 2 SO 2. So, S 4 N 4 undergoes hydration slowly by water, but rapidly when it is treated with warm alkali medium.

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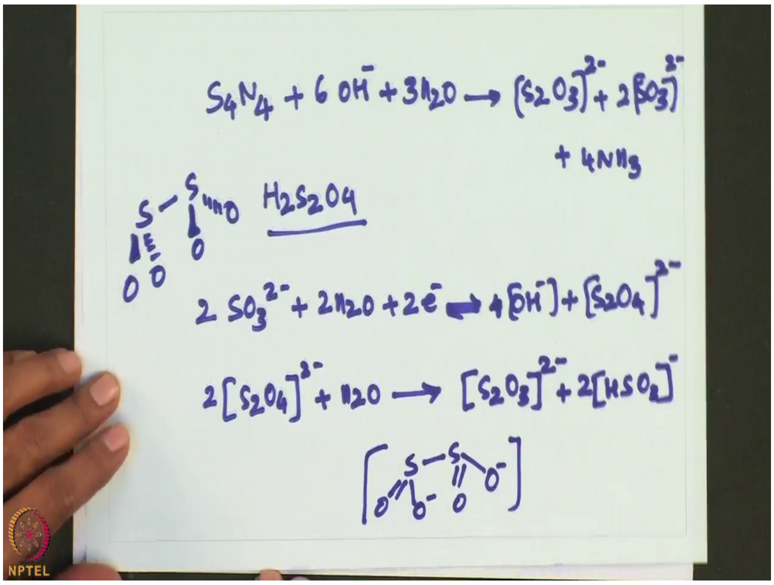

$S_4N_4 + 6\,OH^- + 3H_2O \rightarrow [S_2O_3]^{2-} + 2[SO_3]^{2-} + 4NH_3$

$H_2S_2O_4$

$2\,SO_3^{2-} + 2H_2O + 2e^- \rightarrow 4[OH^-] + [S_2O_4]^{2-}$

$2[S_2O_4]^{2-} + H_2O \rightarrow [S_2O_3]^{2-} + 2[HSO_3]^-$

The structure of S 4 N 4 is a cradle like ring in which pairs of S atoms are brought within the week bonding distance of one another.

I will be showing you soon the s n bond distances in S 4 N 4 indicate delocalized bonding with pi contributions, the transfer of charge from s 2 n also occurs giving s delta plus and n delta minus polar bonds one can see here. So, this is how the structure of S 4 N 4 looks and also when the bond is polarized this is how you can see.

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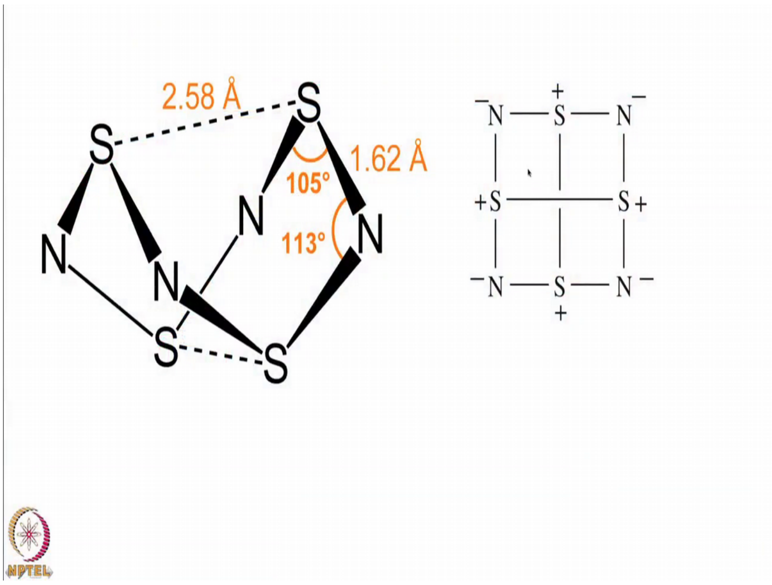

The weak interactions established between sulfur atoms. And S 4 N 4 is widely used to prepare a series of compounds a couple of compounds prepared from that one are shown here.

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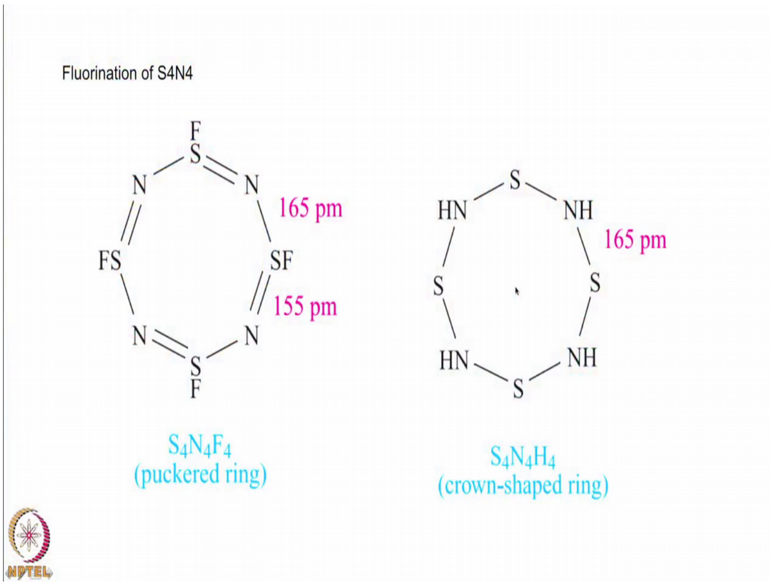

Fluorination of S4N4

$S_4N_4F_4$
(puckered ring)

$S_4N_4H_4$
(crown-shaped ring)

For example on fluorination of S 4 N 4 it gives a puckered ring of this type when S 4 N 4 is treated with SN C l 2 in ethanol it gives S 4 N 4 H 4 it also; obviously, crown shaped ring ok.

Now, let us look into dithionous acid that is H 2 S 2 O 4 ok. So, only its salts are known and this are very powerful reducing agents dithionite is prepared by reduction of sulphide in aqueous solution by zinc or sodium amalgam. So, in aqueous solution dithionite anion is oxidized by air, but in the absence of air it undergoes following reaction and if you are curious to know the structure this how the structure looks like S 2 O 4 minus or one can also write n this fashion. So, that you know where exactly the charge resides.

Now, let us look into 2 more axo acids of sulfur that is sulfurous and di sulfurous acids that is H 2 S 4 3 and H 2 S 2 O 5 neither sulfurous acid nor di sulfurous acid has been isolated as a free acid salts containing this sulfite ion that is S O 3 2 minus or well established under very good reducing agents.

For example, N a 2 S O 3 k 2 S O 3 which are commercially available S O 3 2 minus ion has a triagonal pyramidal structure with de localized bonding S 2 O 5 2 minus ion is the only known derived anion of di sulfurous acid, and possesses structure with a long week SS bond.

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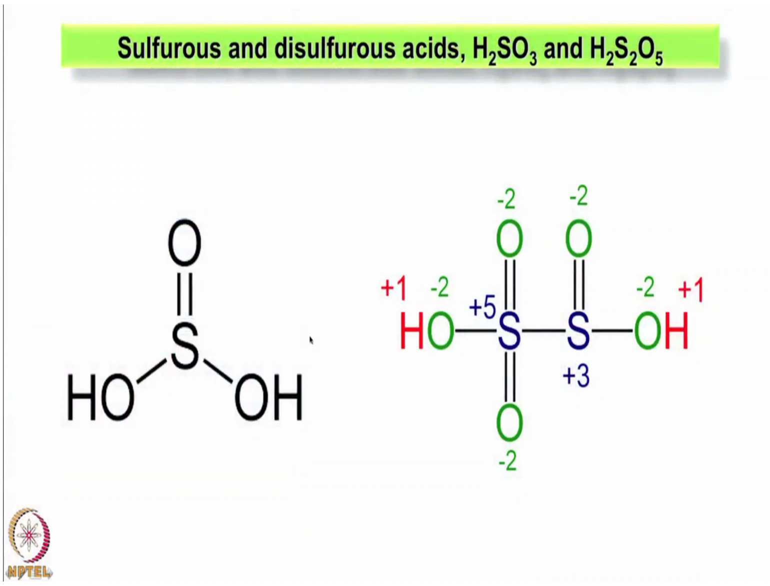

Sulfurous and disulfurous acids, H_2SO_3 and $H_2S_2O_5$

You can see here the structures I have shown this is sulfurous acid and this is di sulfurous acid and of course, here you can notice in the 2 different ox states of 2 sulfur atoms 1 is in plus 5 state, 1 is in plus 3 states since there is SS bond, it is a covalent bond. So, you should not count towards the oxide state. So, one should see here plus 2 plus 2, 4 and this 1 plus 5 and here plus 2 and plus 1. So, it is totally plus 3 for this one.

Whereas here ox state is plus 4 in case of disulfur sulfurous acid of course, lot of salts containing dithionite or no such salts can be isolated as crystalline solids which show the presence of a long SS bond, the anion possesses a staggered conformation in the solid state that thionite ion can be prepared by controlled oxidation of S O 3 2 minus.

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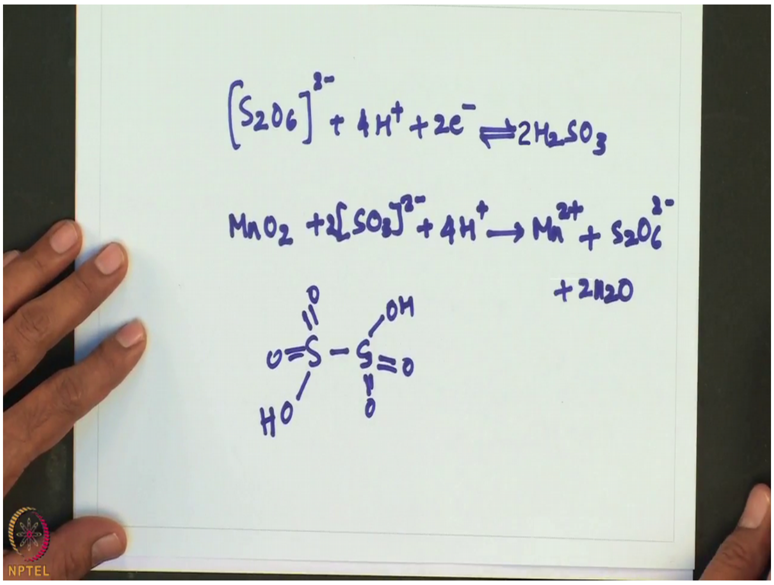

$[S_2O_6]^{2-} + 4H^+ + 2e^- \rightleftharpoons 2H_2SO_3$

$MnO_2 + 2[SO_3]^{2-} + 4H^+ \longrightarrow Mn^{2+} + S_2O_6^{2-} + 2H_2O$

So, that is S 2 O 6 2 minus plus 4 h plus 2 electrons will give H 2 S O 3 and M n O 2 on treatment with S O 3 2 minus and the acidic condition gives.

S 2 O 6 dithaionide anion and the structure of this dithionic acid looks like this S S and when you remove this it becomes S 2 O 6 2 minus of course, sulfuric acid is very important axo acid and it is manufactured and a o a large scale by contact process, you can find in any text book for the procedure.

The first stages of this process is conversion of SO 2 to S O 3 and formation of olium, the olium is finally, diluted with water to give sulfuric acid and pure sulfuric acid is a colorless liquid with a high viscosity caused by extensive intermolecular hydrogen bonding. In aqueous solution sulfuric acid acts as a strong acid, but the H S O 4 minus ion is a fairly weak acid.

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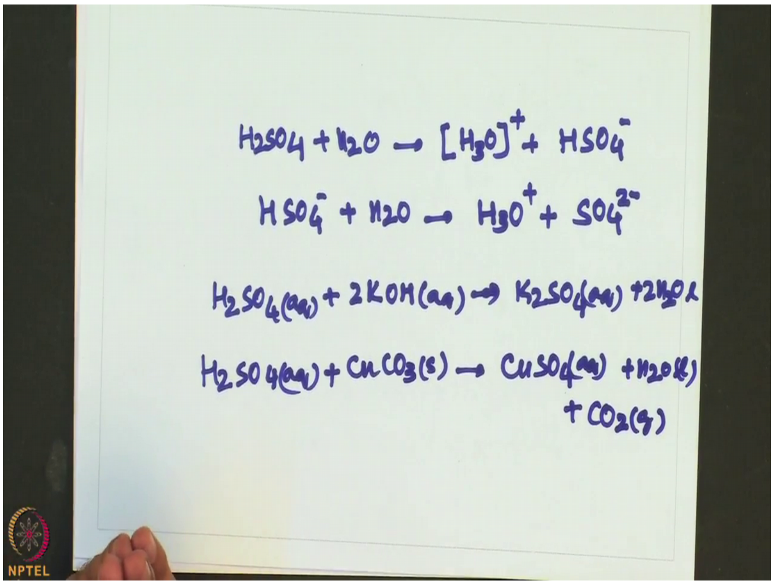

$$H_2SO_4 + H_2O \rightarrow [H_3O]^+ + HSO_4^-$$

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$$

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O\,l$$

$$H_2SO_4(aq) + CuCO_3(s) \rightarrow CuSO_4(aq) + H_2O(l) + CO_2(g)$$

So, dilute aqueous sulfuric acid typically 2 molar neutralizes bases and reacts with the electro positive metal lubricating H 2 H 2 S O 4 for example, H 2 S O 4 plus 2 K o H K 2 S O 4 plus 2 H 2 o H 2 S O 4 aqueous solution plus C u CO 3 gives C u S O 4. So, concentrated sulfuric acid is a good oxidizing agent and a powerful dehydrating agent it is reaction with HNO 3 is very important for organic nitration reactions ok.

And let us look into poly axo acid although k plus salts are potassium salts of poly sulfuric acids are known they have been obtained by the reaction of S O 3 K 2 S O 4 the free acid cannot be isolated this salt is known ok.

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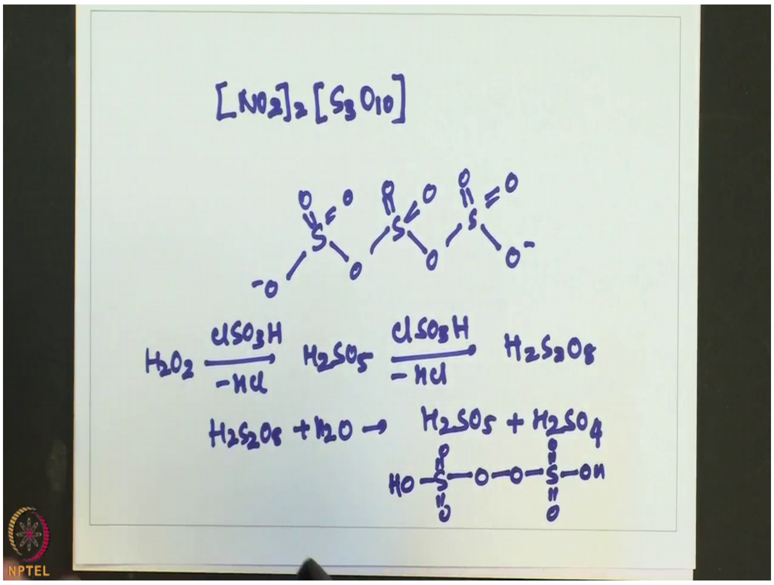

$[NO_2]_2[S_3O_{10}]$

$H_2O_2 \xrightarrow[-HCl]{ClSO_3H} H_2SO_5 \xrightarrow[-HCl]{ClSO_3H} H_2S_2O_8$

$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$

So, this has 2 negative charges dianion let me write the structure of this poly axoacid ok. Another important axoacid is paradox sulfuric acid that is H 2 S 2 O 8 and also one more is known H 2 S O 5, the reaction between code anhydrous H 2 SO 2 and chlorosulfunic acid yields paraxo mono sulfuric acid and also paraxo disulfuric acid. So, conversion of H 2 S 2 O 8 di sulfuric acid 2 mono sulfuric acid occurs by controlled hydrolysis, for example, H 2 o 2 chlorosulfuric acid a chlorosulfunic acid gives H 2 S O 5.

Again treatment with another equivalent of chlorosulfunic acid liberates 1 mole of h C l 2 form paraxo di sulfuric acid of course, H 2 S 2 O 8 on treatment with water gives H 2 S O 5 plus H 2 SO 4 both acids are crystalline solids at 298 kelvin and thio sulfuric acid and poly thionites are also quite well known, if you want to know that paraxo di sulfuric acid the structure looks like this paraxo di sulfuric acid means essentially you take HSO 3 2 HSO 3 minus and replace 2 h of hydrogen peroxide you get this peraxic di sulfuric acid ok.

So, one more thing is one should be familiar with a naming we used of sulfur (Refer Time: 24:43) of oxygen compounds in many cases sulfur annoys of auction compounds are known often indicated in the name.

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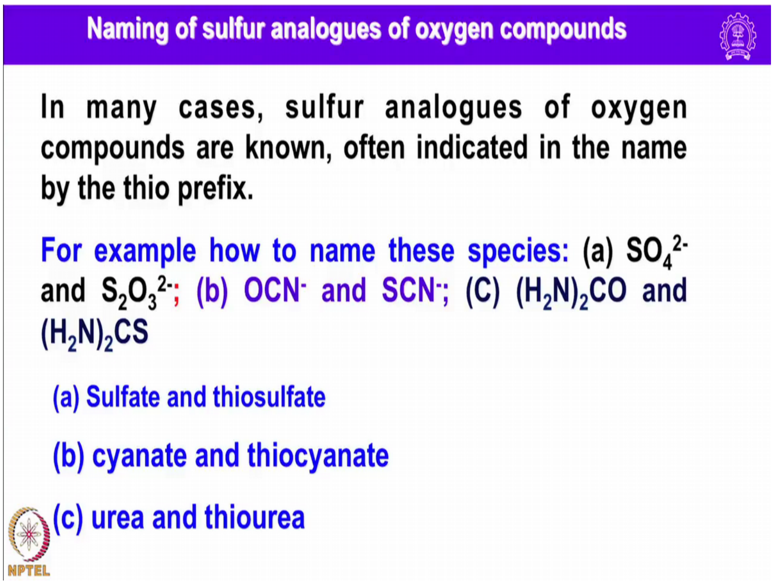

Naming of sulfur analogues of oxygen compounds

In many cases, sulfur analogues of oxygen compounds are known, often indicated in the name by the thio prefix.

For example how to name these species: (a) SO_4^{2-} and $S_2O_3^{2-}$; (b) OCN^- and SCN^-; (C) $(H_2N)_2CO$ and $(H_2N)_2CS$

(a) Sulfate and thiosulfate

(b) cyanate and thiocyanate

(c) urea and thiourea

By a prefix called thio for example, I have shown some how to name this species SO 2 4 2 minus and if replace 1 of the O with s it becomes S 2 O 3 2 minus it becomes thio and then OCN minus is there and if replace O with S it becomes s c n minus and similarly urea if you replace O with sulfur it will become thio urea. So, you can name sulfate and thio sulfate cynate and thio cynate similarly urea and thio urea and phenol is there and (Refer Time: 25:25) it becomes O with S it becomes thio pennon so; that means, wherever oxygen is there you simply put the term thio it gives the analogues sulfur compound ok.

So, let us look into quickly uses of groups 16 compounds sulfamic acid is used as a precursor to make sweet tasting compounds.

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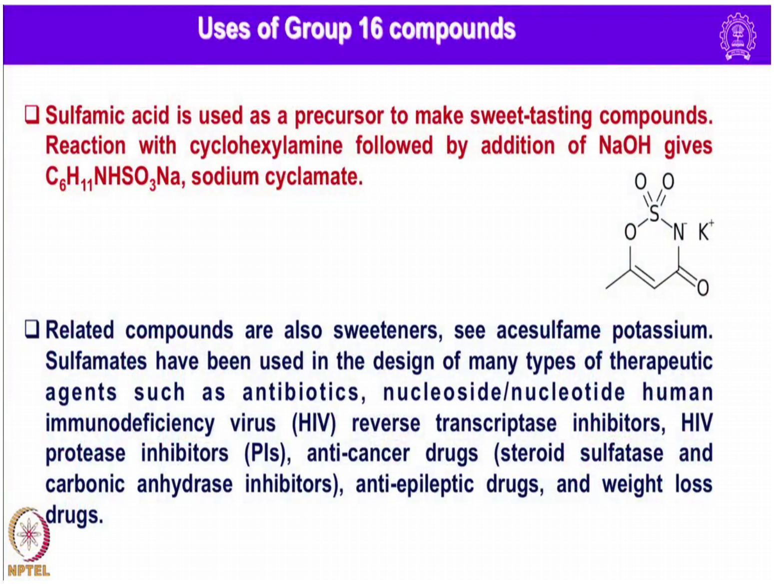

Uses of Group 16 compounds

- Sulfamic acid is used as a precursor to make sweet-tasting compounds. Reaction with cyclohexylamine followed by addition of NaOH gives $C_6H_{11}NHSO_3Na$, sodium cyclamate.

- Related compounds are also sweeteners, see acesulfame potassium. Sulfamates have been used in the design of many types of therapeutic agents such as antibiotics, nucleoside/nucleotide human immunodeficiency virus (HIV) reverse transcriptase inhibitors, HIV protease inhibitors (PIs), anti-cancer drugs (steroid sulfatase and carbonic anhydrase inhibitors), anti-epileptic drugs, and weight loss drugs.

Reaction with cyclohexylamine followed by addition of sodium hydroxide gives sodium cyclamate related compounds are also sweeteners. See acesulfame potassium I have shown here sulfamate have been used in the design of many types of therapeutic agents such as antibiotics nucleoside nucleotide human immunodeficiency virus, reverse transcriptase inhibitors and anti cancer drugs anti epileptic drugs ad weight loss drugs so, many of those things are used.

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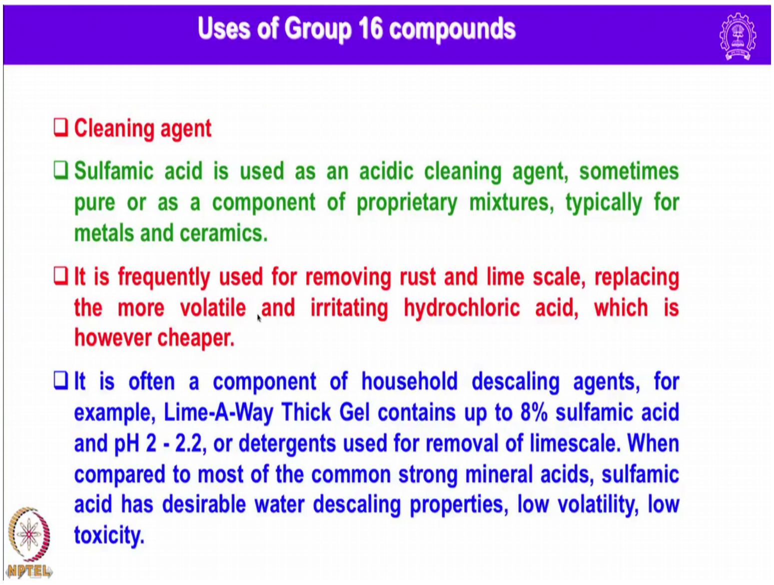

Uses of Group 16 compounds

- Cleaning agent
- Sulfamic acid is used as an acidic cleaning agent, sometimes pure or as a component of proprietary mixtures, typically for metals and ceramics.
- It is frequently used for removing rust and lime scale, replacing the more volatile and irritating hydrochloric acid, which is however cheaper.
- It is often a component of household descaling agents, for example, Lime-A-Way Thick Gel contains up to 8% sulfamic acid and pH 2 - 2.2, or detergents used for removal of limescale. When compared to most of the common strong mineral acids, sulfamic acid has desirable water descaling properties, low volatility, low toxicity.

And also they come very handy as cleaning agents sulfamic acid is used as in acidic cleaning agent, sometimes pure or as a component of preparatory mixture typically for metals and ceramics. It is frequently used for removing rust and lime scale replacing the more volatile and irritating hydrochloric acid which is; however, cheaper. It is often a component of house hold descaling agents for example, lime a way thick gel contains up to 8 percent of sulfamic acid and works in the range of P H 2 to 2 point 2 or in detergents used for removal of lime scale.

When compared to most of the common strong mineral acids sulfamic acid has desirable water, descaling properties and low volatility with low toxicity. And it forms water soluble salts of calcium and pyric ion importantly sulfurium acid is preferable in house hold usage in comparison to hydrochloric acid for its intrinsic safety.

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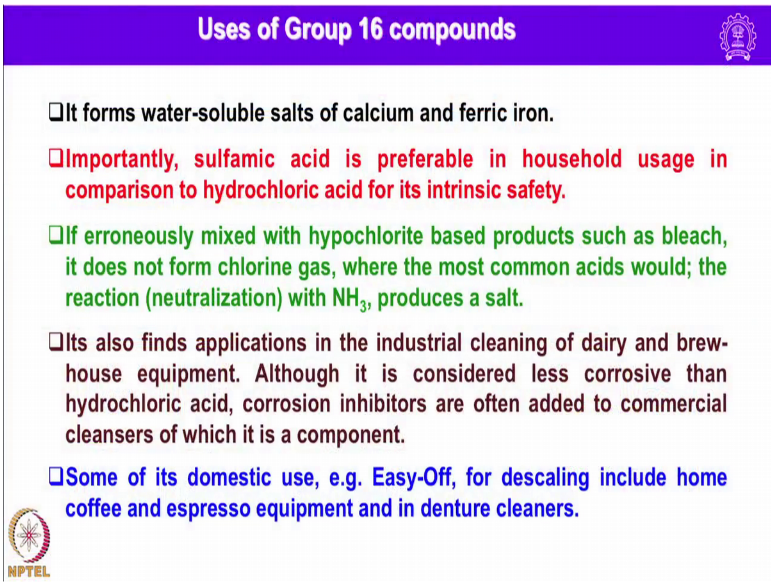

Uses of Group 16 compounds

❑It forms water-soluble salts of calcium and ferric iron.

❑Importantly, sulfamic acid is preferable in household usage in comparison to hydrochloric acid for its intrinsic safety.

❑If erroneously mixed with hypochlorite based products such as bleach, it does not form chlorine gas, where the most common acids would; the reaction (neutralization) with NH_3, produces a salt.

❑Its also finds applications in the industrial cleaning of dairy and brew-house equipment. Although it is considered less corrosive than hydrochloric acid, corrosion inhibitors are often added to commercial cleansers of which it is a component.

❑Some of its domestic use, e.g. Easy-Off, for descaling include home coffee and espresso equipment and in denture cleaners.

If erroneously mixed with hydrochloride based on products such as bleach it does not form chlorine gas, we has a most common acids wood the reaction with n h 3 produces a salt it is also finds application in the industrial cleaning of dairy and brew house equipment. Although it is considered less corrosive then hydrochloric acid corrosion inhibiters are often used to commercial cleaners of which it is a one of the important component.

So, let me conclude the overall group 16 chemistry. We learned in the last few lectures group 16 includes true non metals semiconductors and true metal in polonium. In fact, polonium is the last metal among the P block elements. So, in group 17 we do not have any metal and of course, group18 consists of only net gases action shows a maximum possible plus 2 state with most alto negative elements such as florin other elements hyper valiant compounds to show group of state of plus 6 minus 2 ox state is the stable oxide state.

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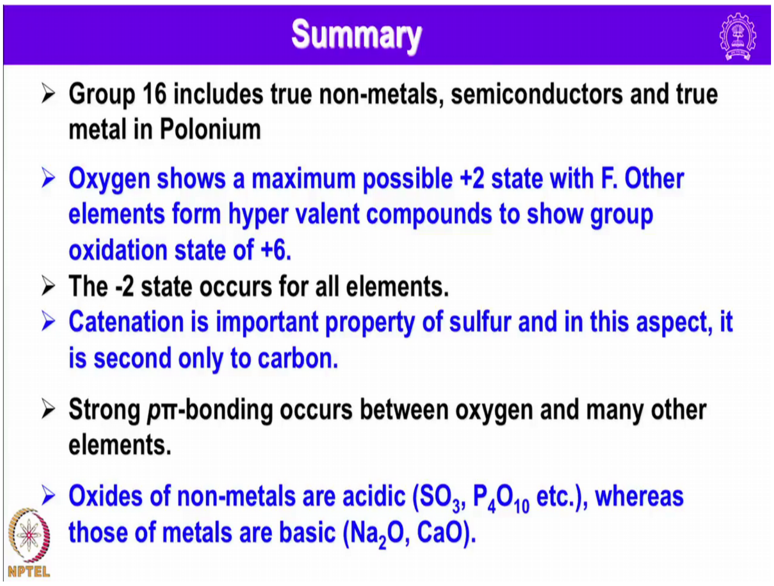

Summary

- Group 16 includes true non-metals, semiconductors and true metal in Polonium
- Oxygen shows a maximum possible +2 state with F. Other elements form hyper valent compounds to show group oxidation state of +6.
- The -2 state occurs for all elements.
- Catenation is important property of sulfur and in this aspect, it is second only to carbon.
- Strong $p\pi$-bonding occurs between oxygen and many other elements.
- Oxides of non-metals are acidic (SO_3, P_4O_{10} etc.), whereas those of metals are basic (Na_2O, CaO).

For all elements catenation is very very important property of sulfur and in this aspect it is only second to carbon.

Strong p pi bonding between oxygen and many other elements oxides of non-metals are acidic like S O 3 P 4 O 10 etcetera whereas, those of metals are essentially basic we know the difference between the properties of N a 2 O C a o with S O 3 or P 4 O 10; or CO 2 with these I completed the chemistry of group 16 elements. In my next lecture, I will be starting discussion on group 17 elements until then have a very present reading of main group elements.

Thank you very much.