Main Group Chemistry
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Lecture – 47
Chemistry of Group 16 Elements

Welcome to MSP lecture series on main group chemistry. In fact, this is my 47th lecture in the series; today, I am going to start the chemistry of group 16 elements. The group 16 elements are the last group among S and P block elements to contain a true metal in polonium.

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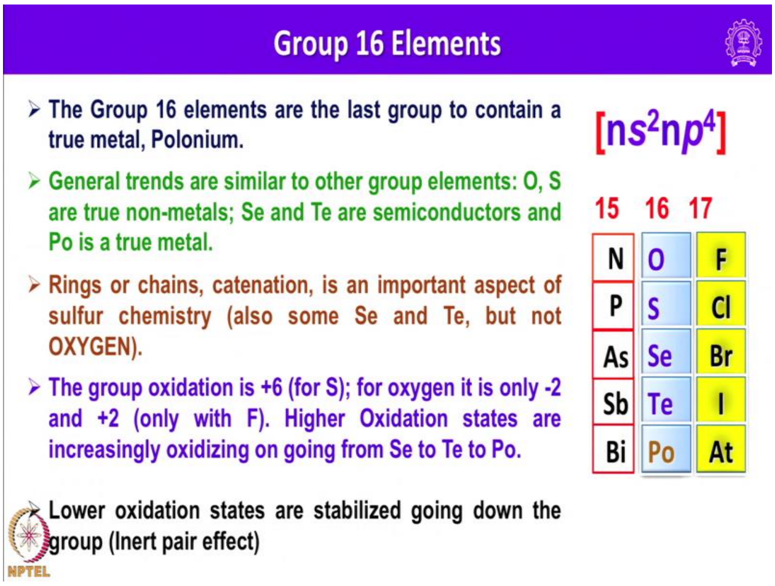

Group 16 Elements

- The Group 16 elements are the last group to contain a true metal, Polonium.
- General trends are similar to other group elements: O, S are true non-metals; Se and Te are semiconductors and Po is a true metal.
- Rings or chains, catenation, is an important aspect of sulfur chemistry (also some Se and Te, but not OXYGEN).
- The group oxidation is +6 (for S); for oxygen it is only -2 and +2 (only with F). Higher Oxidation states are increasingly oxidizing on going from Se to Te to Po.
- Lower oxidation states are stabilized going down the group (Inert pair effect)

$[ns^2np^4]$

15	16	17
N	O	F
P	S	Cl
As	Se	Br
Sb	Te	I
Bi	Po	At

We can see here in group 16 elements are also called as chalcogens, we have oxygen, Sulphur, selenium, tellurium and polonium. General trends are similar to other group elements oxygen and Sulphur or true non metals.

Whereas selenium and tellurium or semiconductors and polonium is a true metal, rings chains and catenation is an important aspect of Sulphur chemistry also to an extent in case of selenium and tellurium, but not oxygen. The group oxidation state is plus 6, for oxygen it is only minus 2 and plus 2 only when it reacts with fluorine. Higher oxidation states are increasingly oxidizing on going from selenium to tellurium to polonium because of inert pair effect, lower oxidation states are stabilized going down the group as I said it is essentially because of the inert pair effect.

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Who discovered Chalcogens?

Oxygen in 1773-74

Sulfur 1777

Selenium 1817

Tellurium 1782

Polonium 1898

Selenium was discovered in 1817 by two men that go by Johan Gottlieb Gahn and Jöns Jacob Berceius.

Carl Wilhelm Scheele

Joseph Priestley

Antoine-Laurent de Lavoisier

Gahn and Berceius

Franz- Joseph Müller

Merry Curie

Let us look into the discoveries of this Chalcogens of course, oxygen was identified and discovered by both Scheele and Joseph Priestley in 1773-74 and Sulphur was discovered in 1777 by Lavoisier and selenium was discovered in 1817 by 2 scientists called Gahn and Barceius and tellurium was discovered in 1782 by Joseph Muller whereas, polonium was discovered in 1898 by Merry Curie, and she isolated polonium from pitchblende while working with radium and other radioactive elements ok.

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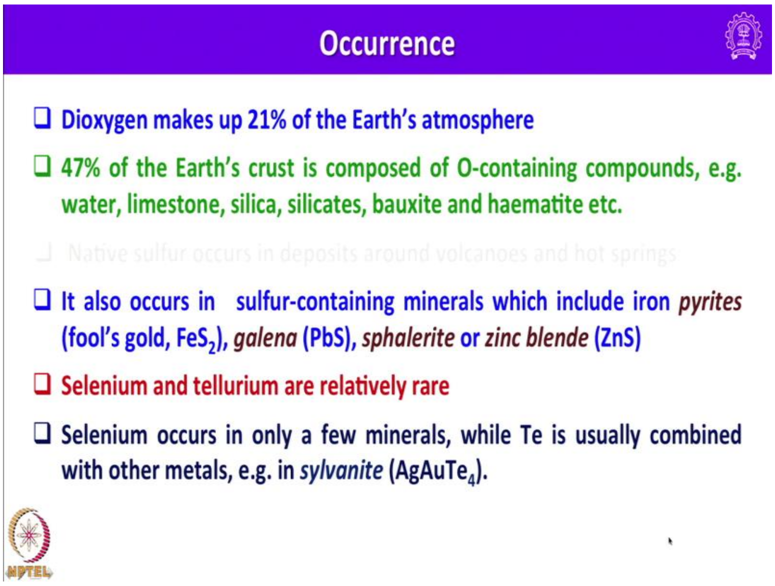

Occurrence

- ☐ **Dioxygen makes up 21% of the Earth's atmosphere**
- ☐ **47% of the Earth's crust is composed of O-containing compounds, e.g. water, limestone, silica, silicates, bauxite and haematite etc.**
- ☐ Native sulfur occurs in deposits around volcanoes and hot springs
- ☐ **It also occurs in sulfur-containing minerals which include iron *pyrites* (fool's gold, FeS_2), *galena* (PbS), *sphalerite* or *zinc blende* (ZnS)**
- ☐ **Selenium and tellurium are relatively rare**
- ☐ **Selenium occurs in only a few minerals, while Te is usually combined with other metals, e.g. in *sylvanite* ($AgAuTe_4$).**

And dioxygen makes up 21 percent of the Earth’s atmosphere, 47 percent of the earth’s crust is composed of oxygen containing compounds, example water, limestone, silica silicates, bauxites, hematite and several other minerals. It also occurs in Sulphur containing minerals, which include iron pyrites fools gold that is iron sulphide galena lead sulphide sphalerite or zinc blende zinc sulphide or zns.

Selenium and tellurium are relatively rare selenium occurs in only a few minerals while tellurium is usually combined with other metals for example, in sylvanite the composition of that one is AgAuTe4.

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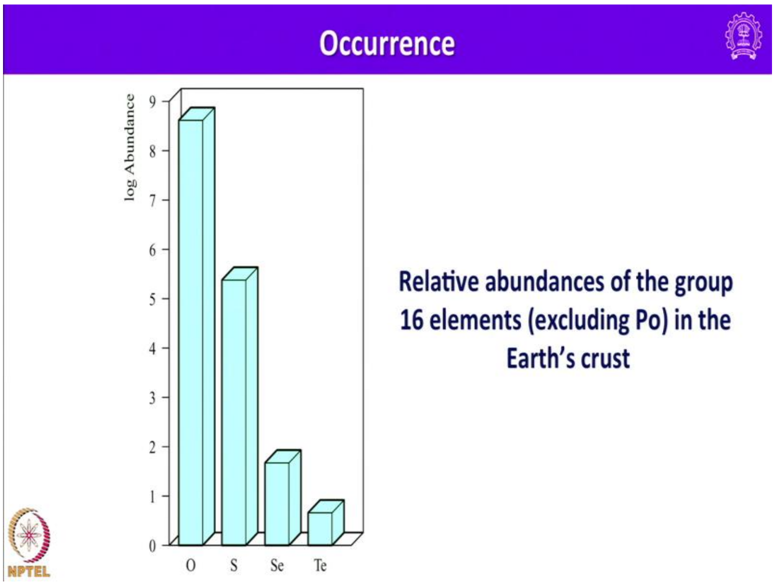

Occurrence

Relative abundances of the group 16 elements (excluding Po) in the Earth’s crust

So, this plot shows the relative abundance of group 16 elements excluding polonium in the earth’s crust.

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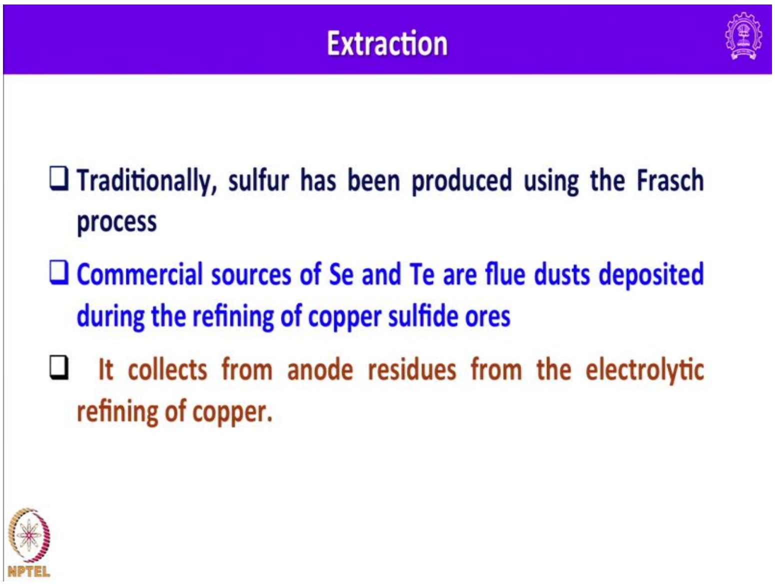

Extraction

☐ Traditionally, sulfur has been produced using the Frasch process

☐ Commercial sources of Se and Te are flue dusts deposited during the refining of copper sulfide ores

☐ It collects from anode residues from the electrolytic refining of copper.

So, let us look into the extraction of group 16 elements, traditionally Sulphur has been produced using the Frasch process I will tell you in a couple of minutes what is Frasch process. Commercial sources of selenium and tellurium are flue dusts deposited during the refining of copper sulphide ores and it collects from anode residues from the electrolytic refining of copper. So, what is Frasch process? So, superheated water is passed down a borehole which melts the Sulphur and allows it to be pumped to the surface by compressed air, Canada and the us or the largest producers of Sulphur in the world because they have large number of Sulphur springs, recovery of Sulphur from crude oil while refining and during natural gas production is now have greatest importance.

In natural gas the source of Sulphur is H 2 S which occurs in concentrations of up to 30 percent Sulphur is recovered by the reaction.

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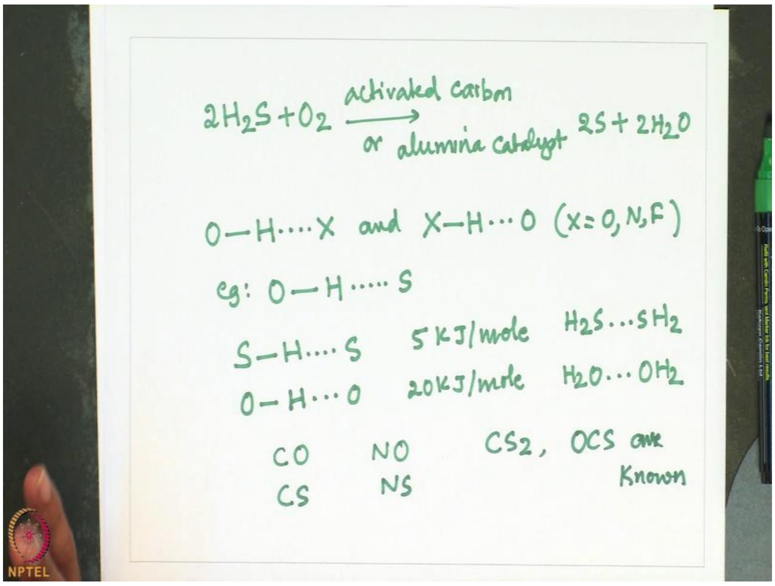

$$2H_2S + O_2 \xrightarrow[\text{or alumina catalyst}]{\text{activated carbon}} 2S + 2H_2O$$

$O-H\cdots X$ and $X-H\cdots O$ $(X = O, N, F)$

eg: $O-H\cdots S$

$S-H\cdots S$ 5 KJ/mole $H_2S\cdots SH_2$

$O-H\cdots O$ 20 KJ/mole $H_2O\cdots OH_2$

CO NO CS_2, OCS are known

CS NS

So, using activated carbon or alumina catalyst. So, let us look into the physical properties and bonding considerations in case of chalcogens, the trend in electronic ut values has important consequences as can be seen in the ability of OH bonds to form numerous strong hydrogen bonds.

In fact, and where x equals electronegative element such as oxygen nitrogen and fluorine. So, interactions are relatively strong hydrogen bonds those involving Sulphur are weak and typically involve a strong hydrogen bond donor with Sulphur acting as a weak acceptor.

For example, in case of S H S hydrogen bonds that is the calculated hydrogen bond enthalpy is approximately 5 kilo joules per mole which is so; that means, this kind of hydrogen bonding is responsible to hold 2 H 2 S together, which is very weak compared with what we come across in case of hydrogen and oxygen O H bonds. So, here it is approximately 20 joules per mole kilo joules per mole. So, this we come across in case of water molecules. So, this shows why water is a liquid with boiling point 100 degree centigrade whereas, H 2 S is a gas.

So, high oxidation state oxides often have no sulphide analogues, there are no stable Sulphur analogues of C O and NO for example, we know CO and NO, similarly we do not have the compounds like CS in free state and NS; however, CS 2 and OCS are known. So, the highest fluoride of oxygen is O F 2, but the latter elements form SF 6 SeF 6 and also tellurium hexafluoride.

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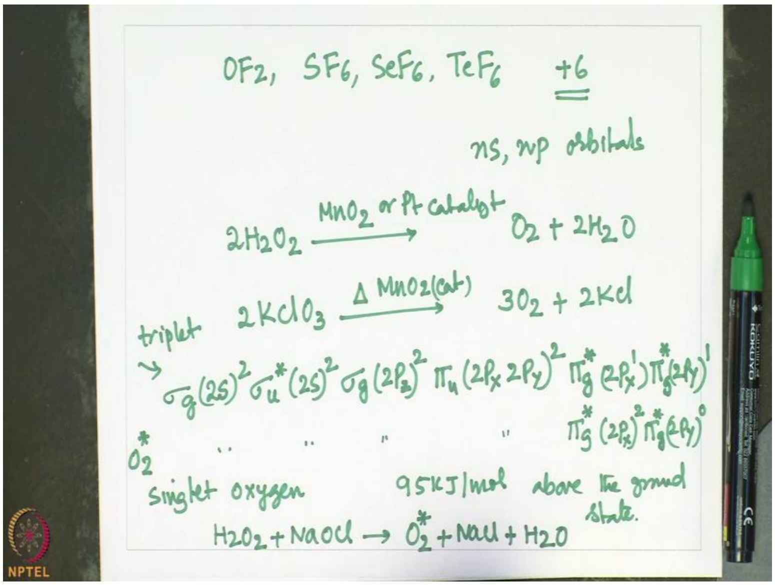

OF_2, SF_6, SeF_6, TeF_6 $\underline{\underline{+6}}$

ns, np orbitals

$2H_2O_2 \xrightarrow{MnO_2 \text{ or Pt catalyst}} O_2 + 2H_2O$

$2KClO_3 \xrightarrow{\Delta\ MnO_2(cat)} 3O_2 + 2KCl$

triplet

$\sigma_g(2s)^2\sigma_u^*(2s)^2\sigma_g(2p_z)^2\pi_u(2p_x\,2p_y)^2\pi_g^*(2p_x)^1\pi_g^*(2p_y)^1$

O_2^* .. .. " " $\pi_g^*(2p_x)^2\pi_g^*(2p_y)^0$

singlet oxygen 95 kJ/mol above the ground state.

$H_2O_2 + NaOCl \rightarrow O_2^* + NaCl + H_2O$

So; that means, basically with fluorine we have of 2 to whereas, in case of Sulphur SF 6 is known and also in case of selenium SeF 6 is known and also in case of tellurium with Sulphur selenium and tellurium mean pus 6 oxidation state ok.

The coordination numbers above 4 for Sulphur selenium and tellurium can be achieved using a valence set up n S and np orbitals. So, dioxygen is obtained industrially by the liquefaction and fractional distillation of air and is stored and transported as a liquid. So, convenient laboratory preparation of oxygen or the electrolysis of aqueous alkali using nickel electrodes and decomposition of hydrogen peroxide, a mixture of potassium chlorate and Mn O 2 used to be sold as oxygen mixture and the thermal decomposition of many other oxo salts such as kno 3, kmno 4 and k 2 S 2 O 8 produce oxygen.

Sold at. So, these are some of the important methods of preparation of oxygen. So, dioxygen is a colorless gas, but condenses to a pale blue liquid or solid at very lower temperature and it is paramagnetic nature due to the presence of 2 unpaired electrons. So, in all phases oxygen is paramagnetic with a triplet ground state the 2 unpaired electrons have the same spin with the valence electron configuration one can write like this I am sure your all familiar of writing this one ok.

So, this indicates that paramagnetic nature of dioxygen. So, in this state O 2 is a very powerful oxidizing agent; however, a single state oxygen that is. So, this is singlet state here both the electrons are paired. So, we have a situation like this it comes up to here it is essentially same if I write. So, only in this case what basically happens is.

And so, here both are paired this is called singlet oxygen whereas, as this one is triplet oxygen the singlet oxygen with a valence electron configuration of this one lies only about 35 kilo joules per mole above the ground state. So, this indicates this excited state can be generated photochemically by a radiation of O 2 in the presence of an organic dye as sensitizer or non photochemically by reaction involving H2 O2 plus Naocl, it generates singlet oxygen plus Nacl plus H 2 O ok.

So, this is one of the method of preparation of singlet oxygen. So, another important compound of oxygen is ozone. Ozone is usually prepared in up to 10 percent concentration by the action of a silent electrical discharge between 2 concentric metalized troops, in an operators called Ozonizer, you can find this instrument in any organic textbook because many of these compounds are used in ozonolysis.

And many ozonolysis reactions involved this ozonizer operators, the action of UV radiation on oxygen or heating oxygen above 2750 kelvin followed by rapid quenching also produces ozone. In each of these process oxygen atoms are produced and combined with oxygen molecules to form ozone, pure ozone can be separated from reaction mixture by fractional liquefaction, the liquid is blue and boils at 163 kelvin to give a blue gas with a characteristic electric smell and molecules of O 3 are essentially bent.

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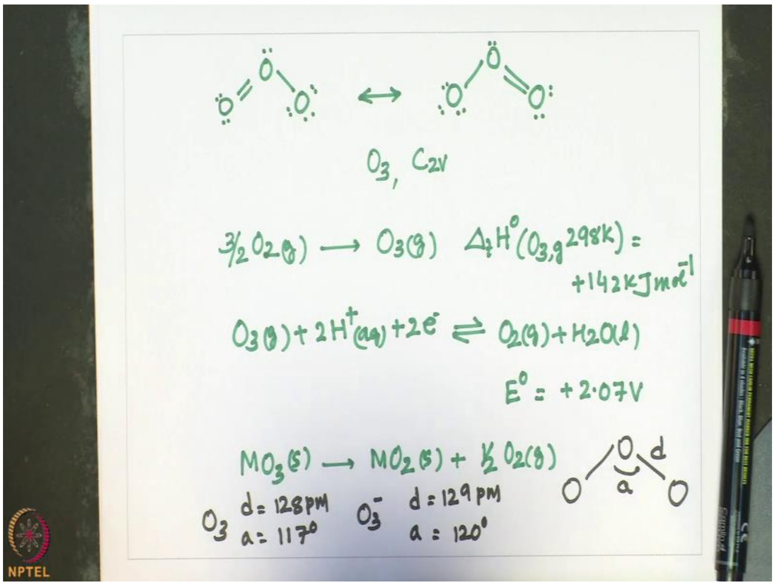

O_3, C_{2v}

$\frac{3}{2}O_2(g) \longrightarrow O_3(g)$ $\Delta_f H^\circ(O_3, g, 298K) = +142 kJ mol^{-1}$

$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$

$E^\circ = +2.07V$

$MO_3(s) \longrightarrow MO_2(s) + \frac{1}{2}O_2(g)$

O_3 d = 128pm a = 117°

O_3^- d = 129 pm a = 120°

So, this is how ozone structure looks like. So, of course, one can also write another resonance structure also for this one. It has C 2 v cemetery ozone absorbs strongly in the UV region its presence in the upper atmosphere, of the earth is essential in protecting the planets surface from over exposure to UV radiation coming from sun ozone is highly endothermic, the pure liquid is dangerously explosive and the gas is very powerful oxidizing agent.

So, here that is O 3 gas a 298 kelvin is plus 142 kilo joules per mole, and O 3 plus 2 H plus in aqueous medium takes 2 electrons in a reversible fashion to form O 2 plus H 2 O. So, here E 0 for this reaction is plus 2 plus 2.07 volts ok.

So, ozone forms ozonides with group 1 and 2 elements, they are prepared by passing gaseous ozone over the powdered hydroxide such as M O H or if it is alkali metal, M O H twice if it is alkaline earth metal at temperature below minus 10 degree centigrade, the ozonides are red brown solids that decompose on warming.

For example MO 3 is ozonide it gives M O 2 plus half O 2. So, ozonide iron is angular like ozone, but with a slightly larger bond angle, this if we just compare if I write a and this d, I can write here for ozone d the oo distance is 128 picometre and the angle a is 117 whereas, in case of ozonide this is slightly longer 129 picometre and the angle is 120.

This shows the difference very minute difference in the bond parameters of ozone and ozonide. So, potassium ozonide is an unstable red salt which contains the paramagnetic ozonide iron.

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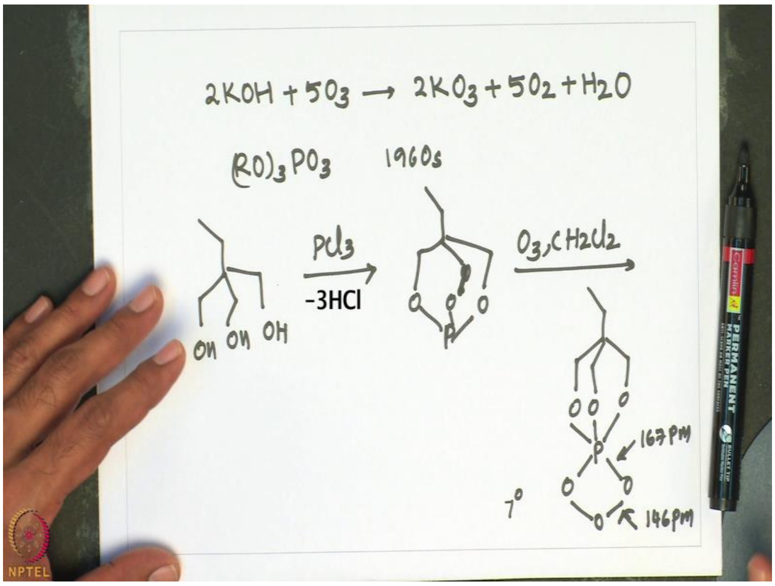

And phosphite ozonides having this composition RO 3 PO 3 have been known since 1960s and or made in c 2 as precursors to singlet oxygen, the ozonides are stable only at very low temperatures its only with the use of modern low temperature crystallographic facilities, the structural data is available for some of this gaseous species.

You can see here how this RP 3 PO 3 is made I will show you. So, when this trihydroxy alcohol is treated with Pcl 3. So, on treatment of this phosphite with ozone in dichloromethane list to the formation of phosphorus ozonide.

So, in the PO 3 ring PO distance is 167 picometre and O O bond distance is 146 picometre and of course, ring is close to the planar structure with a dihedral angle of about 7 degrees. This 4 member PO 3 is a more or less a planar molecule and it has a planar geometry with a dihedral angle of 7 degree.

So, O 2 on exposure to electric discharge it forms O 3. So, extremely reactive and it is a non-linear allotrope, O 3 is a very important component in the stratosphere where it is produced by the reaction of oxygen atoms following by dissociation of O 2 molecules with oxygen molecule, that involves the following sequence of reactions.

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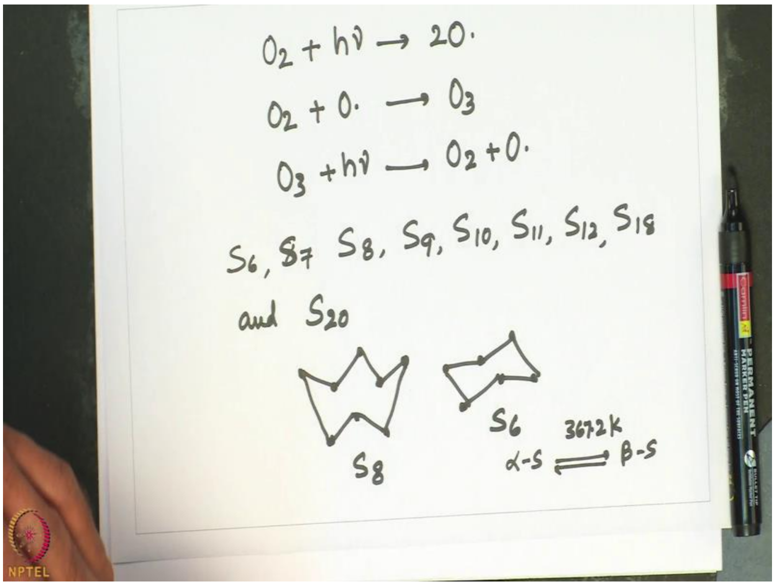

$O_2 + h\nu \rightarrow 2O\cdot$

$O_2 + O\cdot \rightarrow O_3$

$O_3 + h\nu \rightarrow O_2 + O\cdot$

$S_6, S_7\ S_8, S_9, S_{10}, S_{11}, S_{12}, S_{18}$ and S_{20}

$\alpha\text{-S} \xrightleftharpoons{367.2\,K} \beta\text{-S}$

So, O 2 gives essentially radicals. So, this radical combines with the oxygen to form O 3 and of course, O 3 on exposure to UV light forms O 2 plus 4. So, this continues and there is a steady formation of ozone in the stratosphere.

So, ozone itself is photolyzed by UV radiation wavelengths, which O 2 cannot absorb thus give you protection from the harmful effects of short wavelength ultraviolet radiations that is emitted from sun. So, let us look into the Sulphur; Sulphur occurs naturally in several forms as the element in sulphate minerals such as gypsum, gypsum is you know CA2 SO4, 2 H 2 O and in sulphide minerals such as pirate Fes2cus galena PBS elemental Sulphur occurs in underground deposits and is extracted by Frasch process I did mention about Frasch process a few minutes back. It also obtained in relatively large amounts from the crude oil processing, Sulphur exist in numerous allotropes exhibiting different chain and ring structures allotropes of known structures include S 6, S 7, S 8, S 9, S 10, S 11, S 12, S 18 and S 20.

So, these are all some of the important cyclic systems having different Sulphur atoms in the ring. Forms more allotropes and polymorphs than any other element next to carbon among P block elements or in the entire periodic table for that matter, and S 8 and S 6 are important cyclic compounds.

Of course you can start 1 2 3 4 5 6 7 8 this is S 8, similarly this is S 6 the most common form is rhombic Sulphur S 8 the alpha form understand the state of the element and it occurs naturally as large yellow crystals in volcanic areas at 367.2 kelvin the alpha form transfers reversible into monoclinic Sulphur or beta form, that is alpha Sulphur changes to beta Sulphur at 367.2 kelvin reversibly.

Both alpha and beta forms contain S 8 rings there is also a monoclinic polymorph of S 8 rings, which has a different packing arrangement in the crystal structure; some molten Sulphur contains numerous ring and chain forms of Sulphur of different sizes depending on the conditions at the melting point Sulphur melting point is 115 degree centigrade. Sulphur is a yellow low viscosity liquid comprising mainly S 8 rings with traces of other rings ranging in size from S 6 to S 30, further heating initially decreases the viscosity of the molten Sulphur, but then it increases above 150 degree centigrade reaching a maximum at 170 degree centigrade due to the formation of high molecular mos rings and chains at the boiling point of Sulphur is 444 degree centigrade at boiling point Sulphur vapors consists mainly of S 7.

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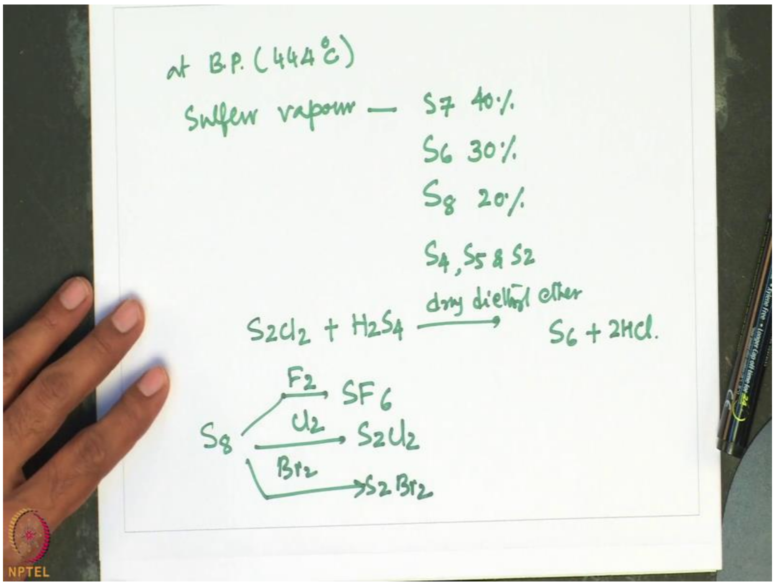

at B.P. (444°C)

Sulfer vapour — S_7 40%

S_6 30%

S_8 20%

S_4, S_5 & S_2

$$S_2Cl_2 + H_2S_4 \xrightarrow{\text{dry diethyl ether}} S_6 + 2HCl.$$

$$S_8 \xrightarrow{F_2} SF_6$$

$$S_8 \xrightarrow{Cl_2} S_2Cl_2$$

$$S_8 \xrightarrow{Br_2} S_2Br_2$$

But that is 444 degree centigrade, Sulphur vapor conserve of S 7 about 40 percent, S 6 30 percent and S 8 20 percent and smaller amounts of S 4 S 5 and S 2. So, Rhombohedral Sulphur there is gamma form compresses S 6 rings and is obtained by ring closer reaction.

For example S 2 cl 2 on treatment with H 2 S 4 in ether very dry di ethyl ether from S 6 plus 2 Hcl. So, Sulphur is a very reactive element. So, it can combine with F 2 to form

SF6 Cl2 to form S 2 Cl 2 Br 2 to form S 2 Br 2. So, these are some of the important highlights of Sulphur, let me stop here and continue in my next lecture more information about group 16 elements, until then have a pleasant reading of main group chemistry.

Thank you very much.