# Main Group Chemistry
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## Lecture – 48
## Chemistry of Group 16 Elements

Welcome to the lecture series by MSV on main group elements. In my previous lecture I was discussing about Chalcogen halides, let me continue from where I had stopped sulfur does not react directly with iodine but in the presence of SbF5 a fluorine acceptor; it forms a cation of this type.

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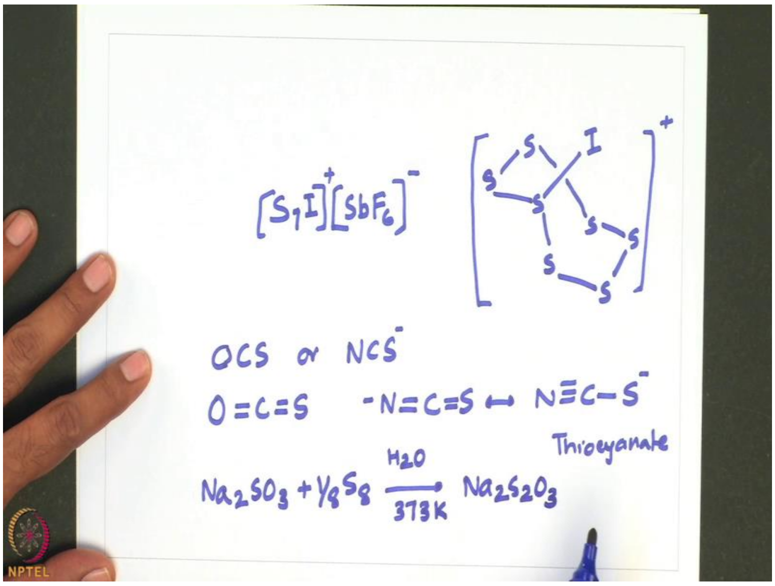

$[S_7I]^+[SbF_6]^-$

OCS or $NCS^-$

$O=C=S \qquad -N=C=S \leftrightarrow N\equiv C-S^-$

Thiocyanate

$Na_2SO_3 + \frac{1}{8}S_8 \xrightarrow[373\,K]{H_2O} Na_2S_2O_3$

So, this one is cationic, this is essentially having S 7 I plus SbF6 minus. Saturated hydrocarbons are dehydrogenated when heated with sulfur and further reaction with alkynes occurs; that means, when you do dehydrogenation of saturated hydrocarbons alkynes are formed.

These alkynes are formed these alkynes further react with sulfur, and application of this property comes in vulcanization of rubber in which soft rubber is toughened by cross linking of the isoprene chains making it suitable for use in for example, tyres. The reactions of sulfur with CO or cyanate yield c OCS or NCS while treatment with sulphides gives thiosulfates.

For example of course, the structure of this one is similar to CO 2 and can also write the thiocyanate structure or one can also write another possible structure like this, this is thiocyanate and sulfite gives thiosulfates for example, Na2SO3 reacts with one equivalent of sulfur. So, one eighth of sulfur in aqueous medium at 373 Kelvin to give Na2S2O3. So, oxidation of S 8 by AsF 5 or SbF5 with liquid. So, 2 yields salts containing cation such as S42 plus S 82 plus or even S 19 2 plus.

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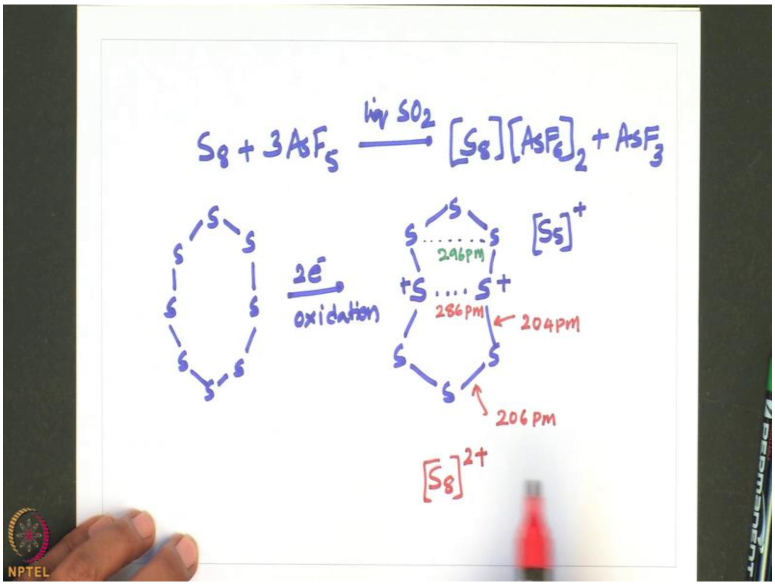

For example in the reaction of S 8 with AsF 5 in liquid sulfur dioxide. So, this is one such di cation, 2 electron oxidation of S 8 results in a change in ring conformation the red colored S 8 2 plus cation was originally reported as being blue, but the blue color is now known to arise from the presence of radical impurities such as S 5 plus. So, it is essentially not blue, it should be red the blue color originally noticed was essentially due to the presence of this radical impurity such as S 5 plus ok.

So, let me write the structures of those. So, this is S 8 2 electron oxidation leads to di cationic compound di cation, here essentially one of the resonance structure if I write. So, 2 sulfur S will have positive charge, and here it is really interesting to compare the bond parameters this distance is 296 picometre. This distance is 286 picometre and this distance is 204 picometre and this distance is 206 picometre.

So, this is one of the resonance structures of S 8 2 plus similarly let me write the structure of S 19 2 plus.

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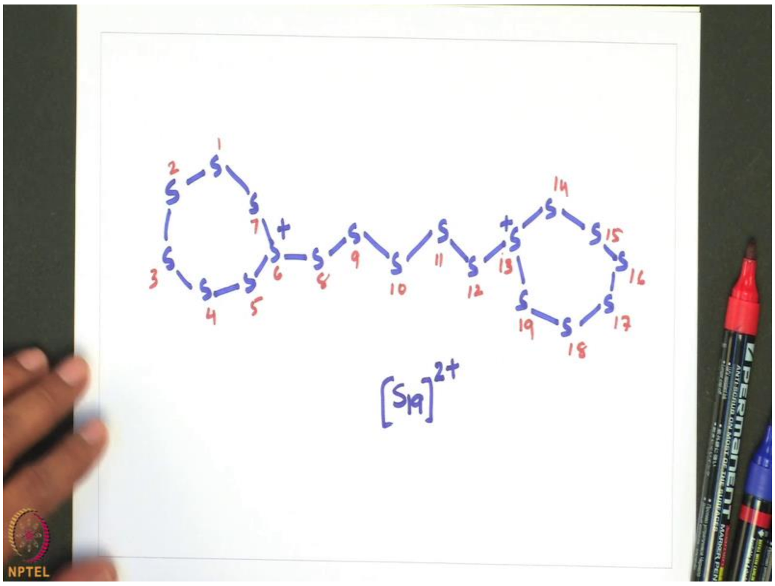

$[S_{19}]^{2+}$

So, this is essentially if I start numbering I can start numbering I can start somewhere does not matter 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 18, 19. So, it is essentially S 19 2 plus.

Ah selenium also possesses several allotropes crystalline red monoclinic selenium exists in 3 forms, each containing S 8 rings with the crowd confirmation very similar to S 8 and elemental selenium can be prepared by treaty, selenium chloride with triphenyl phosphine selenide.

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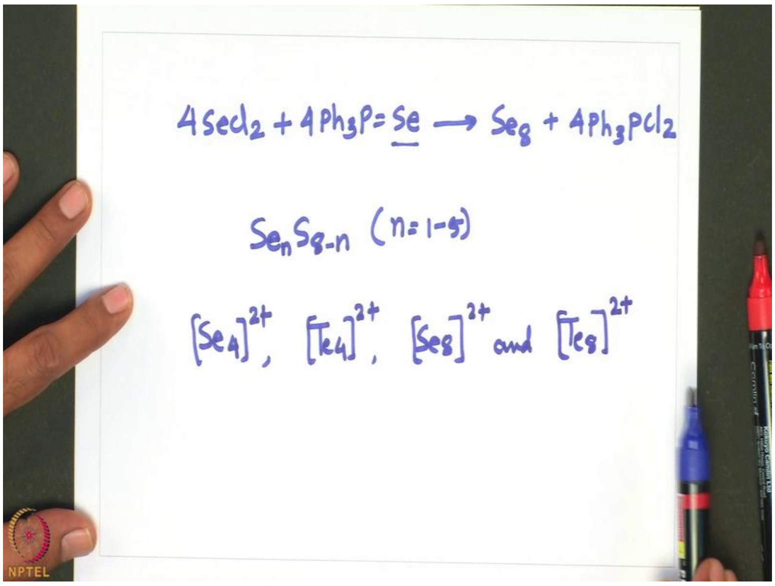

$$4SeCl_2 + 4Ph_3P{=}\underline{Se} \longrightarrow Se_8 + 4Ph_3PCl_2$$

$Se_nS_{8-n}$ $(n = 1\text{-}5)$

$[Se_4]^{2+}$, $[Te_4]^{2+}$, $[Se_8]^{2+}$ and $[Te_8]^{2+}$

For example 4 Secl 2 when its dealing with 4 equivalents of triphenyl phosphine selenide, it leads to the formation of Se 8. Now in this case if we substitute selenium with sulfur one can make a series of mixed chalcogen compounds of this type for example, S e n S 8 minus n 1 can prepare where n equals 1 to 5. So that means, this method gives a scope for the preparation of mixed chalcogen rings.

Tellurium has only one crystalline form which is a silvery white metallic looking solid, selenium and tellurium are less reactive, but are chemically very similar to sulfur, this is also true in the case of cations such as Se 4 2 plus or tellurium 4 2 plus Se 8, 2 plus and tellurium 8 2 plus.

So; that means, they are more or less similar to sulfur. So, these are all poly chalcogen cations, you can see here of course, when it comes to oxygen its only one mono cationic O 2 plus is known and that too when its reacted with fluorine where is in case of sulfur.

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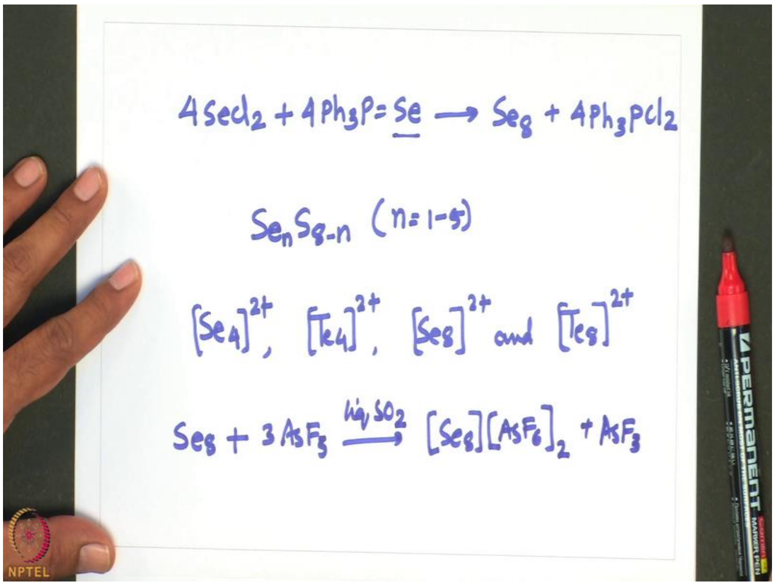

$$4SeCl_2 + 4Ph_3P{=}\underline{Se} \longrightarrow Se_8 + 4Ph_3PCl_2$$

$$Se_nS_{8-n} \ (n = 1\text{-}5)$$

$$[Se_4]^{2+}, \ [Te_4]^{2+}, \ [Se_8]^{2+} \text{ and } [Te_8]^{2+}$$

$$Se_8 + 3AsF_5 \xrightarrow{liq\ SO_2} [Se_8][AsF_6]_2 + AsF_3$$

You can see S 4 2 plus S 8 2 plus and to S 19 2 plus can be made, similarly in case of selenium one can make this species, in case of tellurium, tellurium 4 and tellurium 6 respectively in the plus 2 and plus 4 state are known, and this is for the tetra chalcogen di cation species the structure whereas, this one I already showed you S and Se 8 2 plus di cations, the salt I was telling you about in case of selenium, that can be readily made Se 8 di cationic salt can be made very similar to the sulfur analogue.

For example Se 8 when it is treated with 3 saf 5 in liquid sulfur dioxide it forms, Se 8 di cation through the fluorination of arsenium. So, the preparation of tellurium takes a slightly different method, here in the preparation of tellurium analogue that is Te 8 2 plus recent methods used metal halides such as recl 4 or wcl 6 as oxidizing agents.

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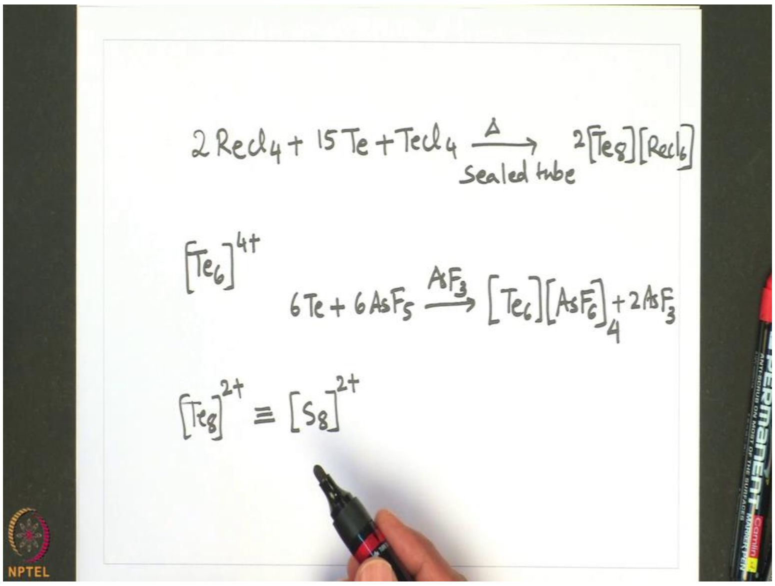

$$2ReCl_4 + 15Te + TeCl_4 \xrightarrow[\text{Sealed tube}]{\Delta} 2[Te_8][ReCl_6]$$

$$[Te_6]^{4+}$$

$$6Te + 6AsF_5 \xrightarrow{AsF_3} [Te_6][AsF_6]_4 + 2AsF_3$$

$$[Te_8]^{2+} \equiv [S_8]^{2+}$$

Let me write one such reaction here for example, rhenium tetrachloride when its treated with tellurium inference of tellurium tetrachloride, of this reaction has to be carried out in a sealed tube it leads to the formation of Te 8 di cation ok.

And preparation of Te 6 4 plus involves the reaction of tellurium with arsenic pentaflouride of course, inference of AsF3 and if you look into the structure of Te 8 2 plus this structure is very similar to that of sulfur , but in case of tellurium 8 if you use tungsten hexachloride the cation has the by cyclic structure ok.

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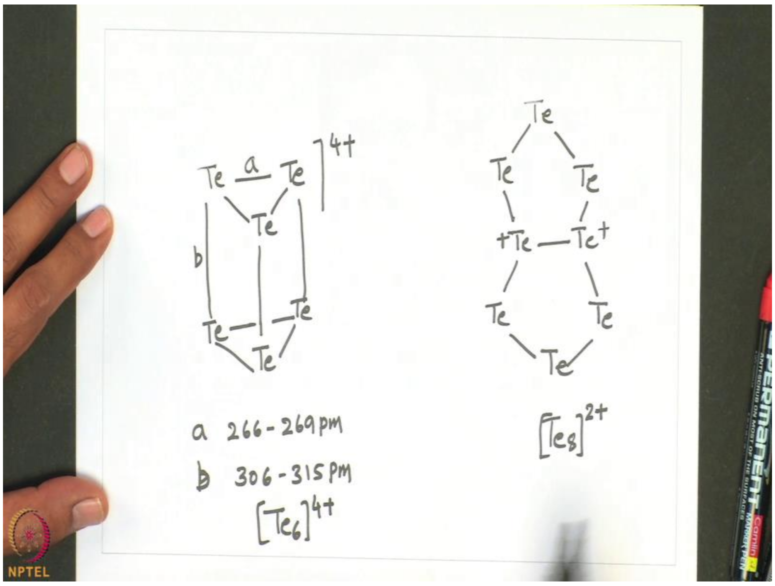

So, this is Te 8 2 plus, this is very similar to the sulfur and selenium analogue where as in case of tellurium 6 4 plus, it has a trigonal prismatic structure. So, here just if you look into this is a and this is b let me give the the a this tellurium; tellurium bond distance is in the range of 266 to 269 picometre whereas, these bond distances are in the range of little longer 306 to 315 picometre. So, this is your Te 6 4 plus.

Selenium and tellurium essentially consist of long spiral molecules with weak metallic interactions between adjacent chains, which break down into small rings and chains on melting. Polonium occurs naturally as a trace component of uranium ore pitchblende, but is made artificially by the radiation of 209 bismuth with neutrons.

Which eventually it gives 210 bismuth that eventually emits beta to give 209 polonium.

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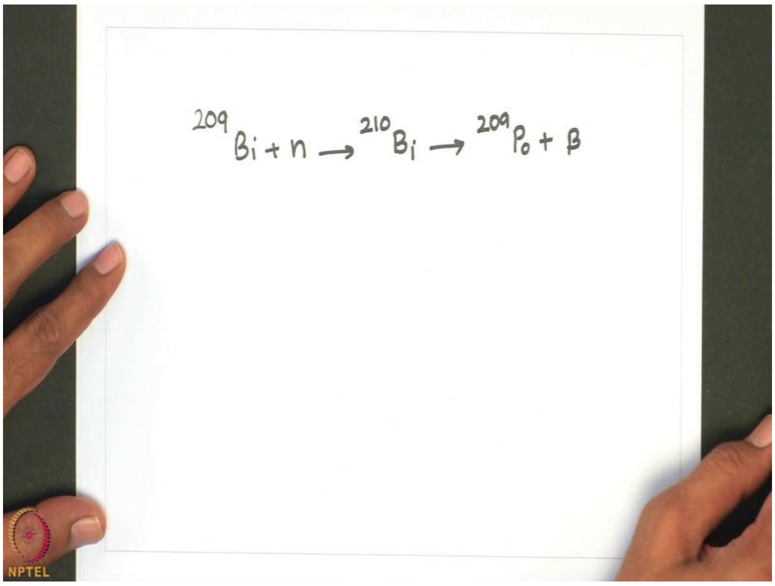

$^{209}Bi + n \rightarrow {}^{210}Bi \rightarrow {}^{209}Po + \beta$

So, this is the artificial method of preparation of polonium isotope 209.

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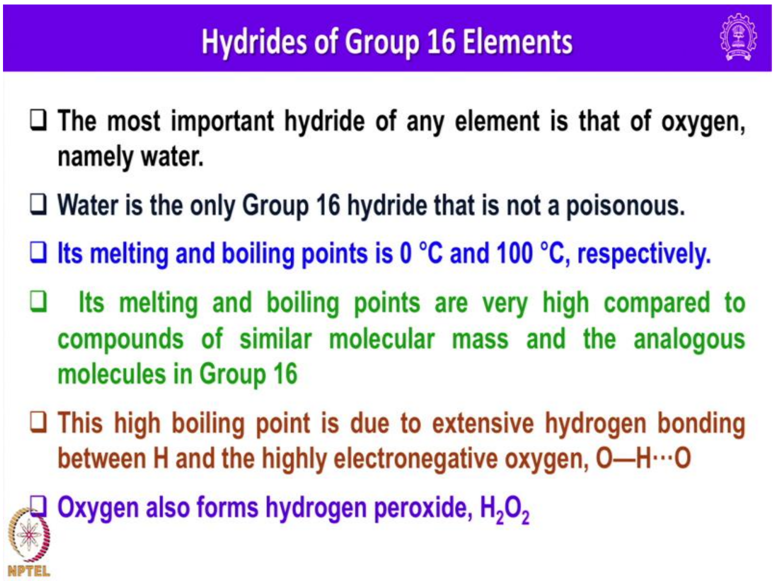

## Hydrides of Group 16 Elements

- The most important hydride of any element is that of oxygen, namely water.
- Water is the only Group 16 hydride that is not a poisonous.
- Its melting and boiling points is 0 °C and 100 °C, respectively.
- Its melting and boiling points are very high compared to compounds of similar molecular mass and the analogous molecules in Group 16
- This high boiling point is due to extensive hydrogen bonding between H and the highly electronegative oxygen, O—H···O
- Oxygen also forms hydrogen peroxide, $H_2O_2$

Now, let us look into the hydrides of group 16 elements, the most important hydride of any element is that of oxygen namely water or oxide. Water is the only group 16 hydride that is not at all poisonous, it is melting and boiling points are known 0 degree centigrade and 100 degree centigrade respectively, it is melting and boiling points are very high compared to compounds of similar molecular mass and the analogous molecules in group 16. This is essentially because of the strong hydrogen bonding, that we learnt when we are discussing about the chemistry of hydrogen in my earlier lectures, let me not going to the details, the high boiling point is due to extensive hydrogen bonding between hydrogen and highly electronegative oxygen.

Oxygen also forms hydrogen peroxide that is H2O2 a deuterium label in heavy water is indicated by writing 2 H 2 water or simply.

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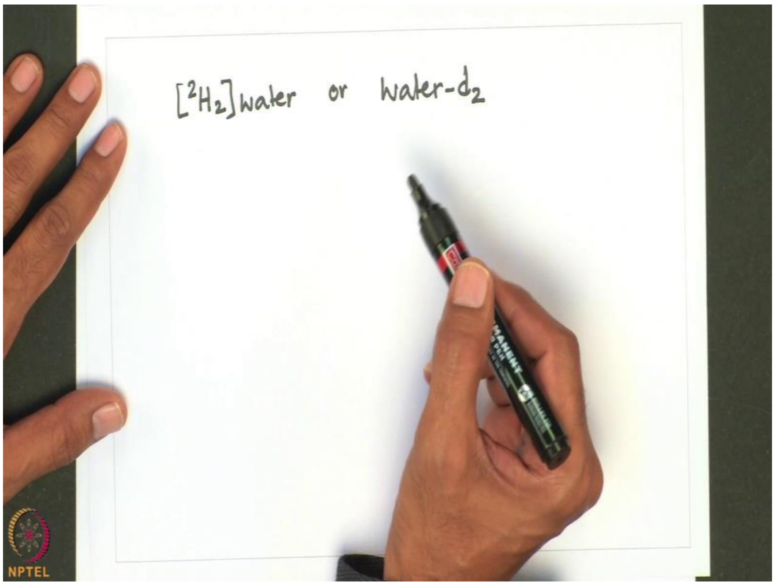

So, this indicates it is heavy water or D2O and similarly for other labelled compounds. Compounds in which hydrogen atoms have been replaced by d are used for a variety of purposes, example as solvents in NMR spectroscopy, the difference in boiling points indicates that intermolecular hydrogen bonding is stronger in D2O than in H2O yeah of course, the boiling point of d 2 is 101 degree centigrade, where as that of water is 100 degree centigrade, only one degree difference is there the major industrial use of D2O is as a moderator in nuclear reactors, d deuterium has a much lower cross section for neutron capture than hydrogen, and D2O is a suitable material for reducing the energies of fast neutrons produced in a typical nuclear fusion reaction. So, I have listed some of the properties of water and heavy water here.

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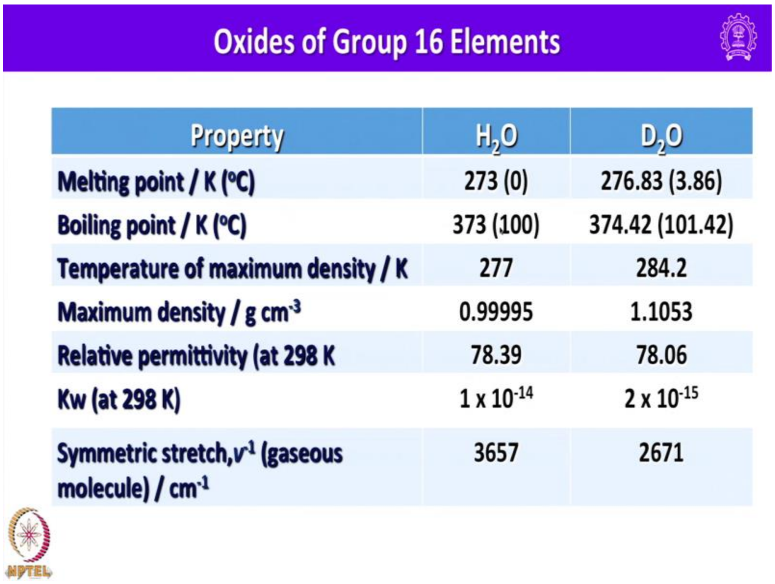

### Oxides of Group 16 Elements

| Property | $H_2O$ | $D_2O$ |
|---|---|---|
| Melting point / K (°C) | 273 (0) | 276.83 (3.86) |
| Boiling point / K (°C) | 373 (100) | 374.42 (101.42) |
| Temperature of maximum density / K | 277 | 284.2 |
| Maximum density / g $cm^{-3}$ | 0.99995 | 1.1053 |
| Relative permittivity (at 298 K | 78.39 | 78.06 |
| Kw (at 298 K) | $1 \times 10^{-14}$ | $2 \times 10^{-15}$ |
| Symmetric stretch, $v^1$ (gaseous molecule) / $cm^{-1}$ | 3657 | 2671 |

Of course boiling point, melting point little difference is there and the density also little bit difference is there.

And maximum density is 0.99995 in case of water whereas, in case of D2O its 1.10 relative permittivity also not much major difference is there. And hydrogen peroxide about hydrogen peroxide also I had already discussed its method of preparation while discussing the chemistry of hydrogen, H2O is the most well known peroxide which adopts gauche structure both in the gas phase and in the solid state owing to the repulsion of the lone pairs or the oxygen atoms. Hydrogen peroxide undergoes self ionization to water, but to a greater extent when compared to that of water.

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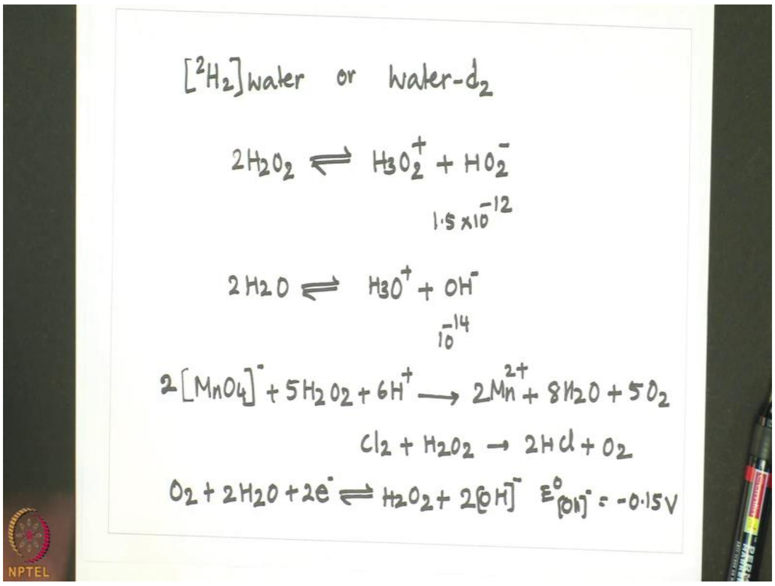

[$^2H_2$]water or water-$d_2$

$2H_2O_2 \rightleftharpoons H_3O_2^+ + HO_2^-$

$1.5 \times 10^{-12}$

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

$10^{-14}$

$2[MnO_4]^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$

$O_2 + 2H_2O + 2e^- \rightleftharpoons H_2O_2 + 2[OH]^-$ $E^o_{[OH]^-} = -0.15 V$

For example 2H2O2. So, here if you look into the equilibrium constant, this is 1.5 into 10 to the power of minus 12, in case of water. So, in case of water equilibrium constant is ten to the power of minus 14 ok.

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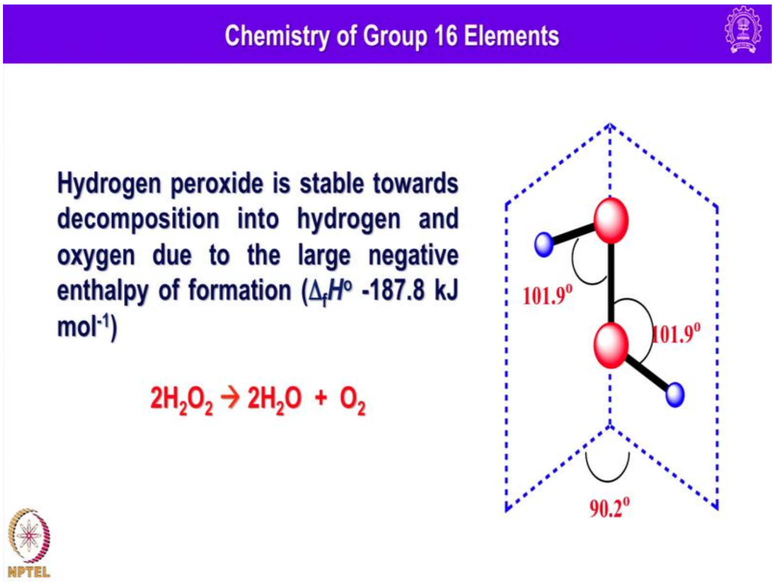

Chemistry of Group 16 Elements

Hydrogen peroxide is stable towards decomposition into hydrogen and oxygen due to the large negative enthalpy of formation ($\Delta_f H^o$ -187.8 kJ mol$^{-1}$)

$2H_2O_2 \rightarrow 2H_2O + O_2$

I will be showing, this how the structure of hydrogen peroxide looks like. So, hydrogen peroxide is a is stable towards decomposition into hydrogen and oxygen, due to the large negative enthalpy of formation you can see delta fH for hydrogen peroxide is minus

187.8 kilo joules per mol, as a result it does not decompose into oxygen and hydrogen instead what it does is it decomposes to water and oxygen.

So, industrial method of preparation of hydrogen peroxide involves the anthraquinone auto oxidation process, anthraquinone dissolved in an organic solvent is oxidized to anthraquinone and hydrogen peroxide is formed. The hydrogen peroxide is recovered by extracting the organic solution with water, the anthraquinone is then reduced back to the anthraquinone using hydrogen and a palladium complex or palladium metal as catalyst this process is repeated many times giving a catalytic cycle.

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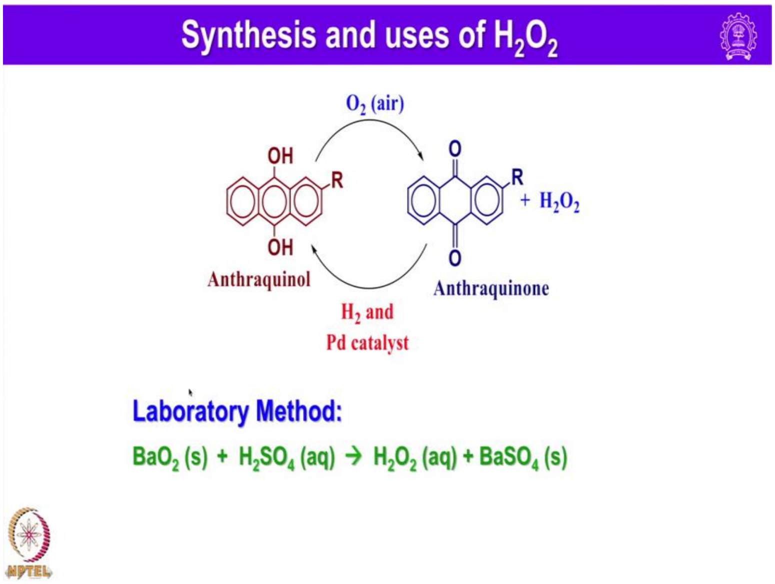

**Synthesis and uses of $H_2O_2$**

**Laboratory Method:**

$BaO_2 (s) + H_2SO_4 (aq) \rightarrow H_2O_2 (aq) + BaSO_4 (s)$

You can see here the auto oxidation of anthraquinone to form a anthraquinone and H2O2 is liberated and H2O2 is from organic phase to aqueous phase, and then anthraquinone is treated with hydrogen using palladium catalyst to regenerate anthraquinone to start the second cycle.

And in laboratory small scale preparation of hydrogen peroxide involves the reaction of barium peroxide with sulfuric acid that leads to the formation of barium sulphate and H2O2. Hydrogen peroxide is a very powerful oxidizing agent, it oxidizes iodide iodine. SO2 to H2SO4 in alkaline solution and chromium 3 compounds to chromium 6 compounds in fact, powerful oxygen such as MnO4 minus and cl 2 will oxidize H2O2 and in alkaline solution H2O2 is a good reducing agent.

Let me write a couple of these equations for you. So, this indicates the reducing nature of H2O2. Hydrogen sulphide is more toxic than hydrogen cyanate, but because H2S has a very characteristic odor of rotten eggs, it can be easily recognized. So, in the laboratory H2S was historically prepared by reaction of FeS in a chips operators.

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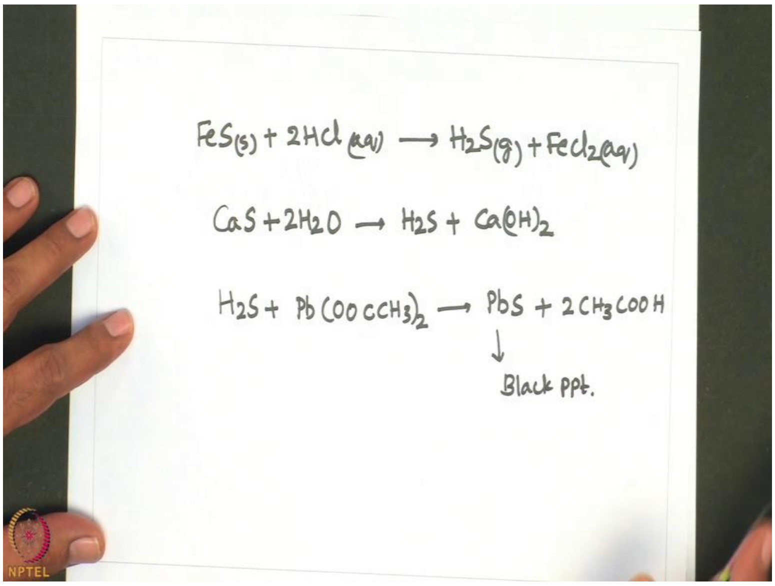

$$FeS_{(s)} + 2HCl_{(aq)} \longrightarrow H_2S_{(g)} + FeCl_{2(aq)}$$

$$CaS + 2H_2O \longrightarrow H_2S + Ca(OH)_2$$

$$H_2S + Pb(OOCCH_3)_2 \longrightarrow \underset{\substack{\downarrow \\ \text{Black ppt.}}}{PbS} + 2CH_3COOH$$

That method involves the treatment of FeS with aqueous Hcl. Hydrolysis of calcium or barium sulphides also produces pure hydrogen sulphide for example, if you take calcium sulphide and treat this one with water, it gives H2 S and calcium hydroxide. In aqueous solution the hydrides behave as weak acids a qualitative test for H2S is its reaction with aqueous lead acetate forming block precipitate that is essentially due to the formation of pbs.

For example H2S plus Pb that acetate gives lead sulphide plus acetic acid. So, this is black phosphate. Hydrogen selenide may be prepared by the reaction of Al2Se3 and a similar reaction can be used to make tellurium hydride.

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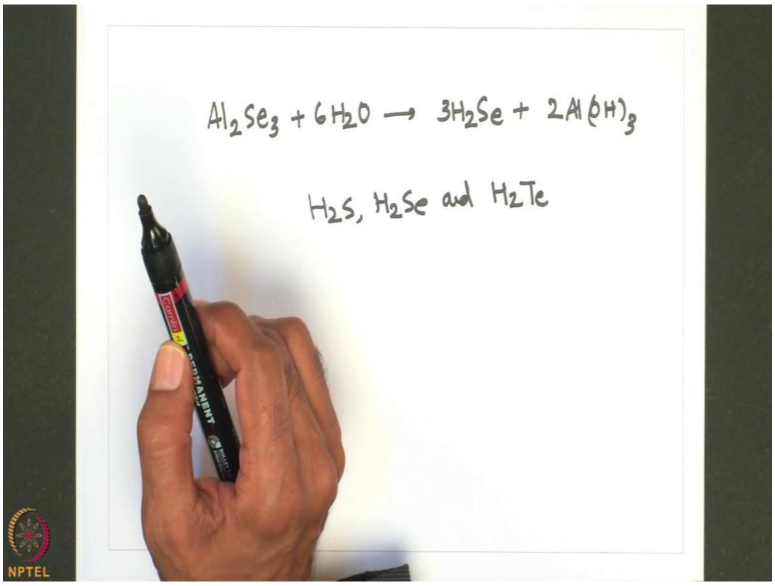

$Al_2Se_3 + 6H_2O \rightarrow 3H_2Se + 2Al(OH)_3$

$H_2S$, $H_2Se$ and $H_2Te$

As well let me give the preparation of hydrogen selenide or selenium hydride. The enthalpies of formation of H2S H2Se and H2Te indicate that the sulphide can be prepared by direct combination of H2 and sulfur it is more stable with respect to the decomposition into its elements then H2Se or H2 tellurium; that means, selenium or tellurium hydrides.

Let me stop at this stage, in my next lecture, I will be continue the chemistry of group 16 elements, until then have a pleasant reading of inorganic chemistry.

Thank you.