Chemistry of Main Group Elements

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Lecture – 52

Chemistry of Group 17 Elements

Welcome to MSB lecture series on the chemistry of main group elements, let me start today the chemistry of group 17 elements. Group 17 elements are called halogens and they are the most electronegative elements in the periodic table, having a common oxidation state of minus 1.

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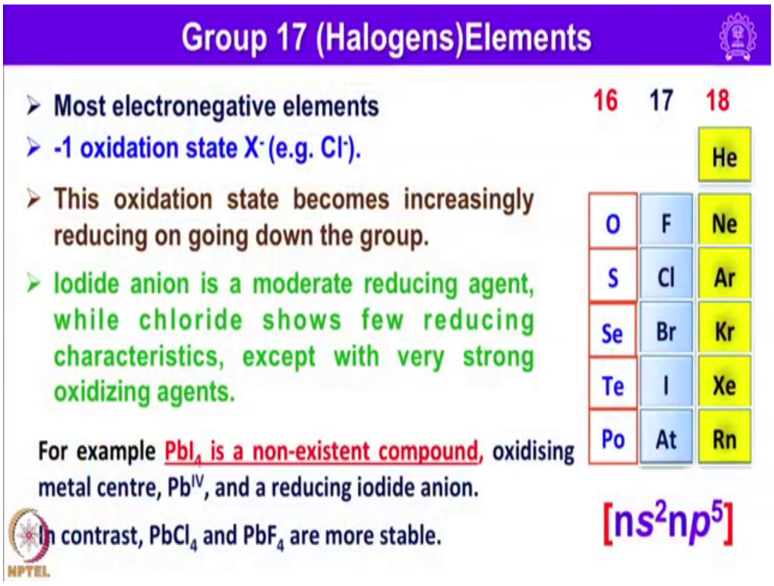

Group 17 (Halogens)Elements

- Most electronegative elements
- -1 oxidation state X^- (e.g. Cl^-).
- This oxidation state becomes increasingly reducing on going down the group.
- Iodide anion is a moderate reducing agent, while chloride shows few reducing characteristics, except with very strong oxidizing agents.

For example PbI_4 is a non-existent compound, oxidising metal centre, Pb^{IV}, and a reducing iodide anion.

In contrast, $PbCl_4$ and PbF_4 are more stable.

16	17	18
		He
O	F	Ne
S	Cl	Ar
Se	Br	Kr
Te	I	Xe
Po	At	Rn

$[ns^2np^5]$

So, this oxidation state becomes increasingly reducing on going down the group.

So, iodine anion is a moderate reducing agent, while chloride shows few reducing characteristics except with very strong oxidizing agents. For example, if we consider Pb I 4 is a nonexistent compound, because of the combination of highly oxidizing and highly reducing species. In contrast PbCl 4 and PbF 4 are moderately stable and besides minus 1 oxidation state, besides minus 1 out of oxidation state plus 1 plus 3 plus 5 and plus 7.

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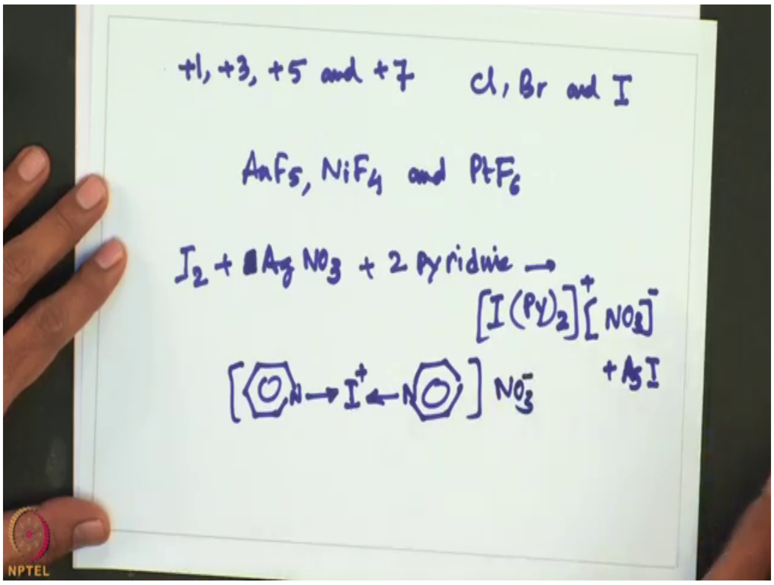

+1, +3, +5 and +7 Cl, Br and I

AuF_5, NiF_4 and PtF_6

$I_2 + AgNO_3 + 2$ pyridine $\rightarrow [I(Py)_2]^+[NO_3]^- + AgI$

States occur for chlorine, bromine, and iodine ok. Mainly in axi ions and also in inter halogen compounds; compounds in the highest oxygen states generally contain the electronic elements such as oxygen and fluorine for example, I F 7 or I O 4 minus, fluorine with its small size and high electro negativity coupled with the weakness of the ff bond it is able to stabilize the very highest ox states of elements such as Au F 5 Ni F 4 and Pt F 6.

So; that means, any metal or any main group element if it is the existing in its highest possible axi state ok. So, there is the role of fluorine in it ok. So, iodine forms solvated cat ions for example, iodine when its treated with Ag NO 3 with pyridine it forms a complex of this type, unless you the discovers of halogens Henry Moissan discovered fluorine in 1886, and William Scheele responsible for the discovery of many elements in the periodic table discovered chlorine in 1774.

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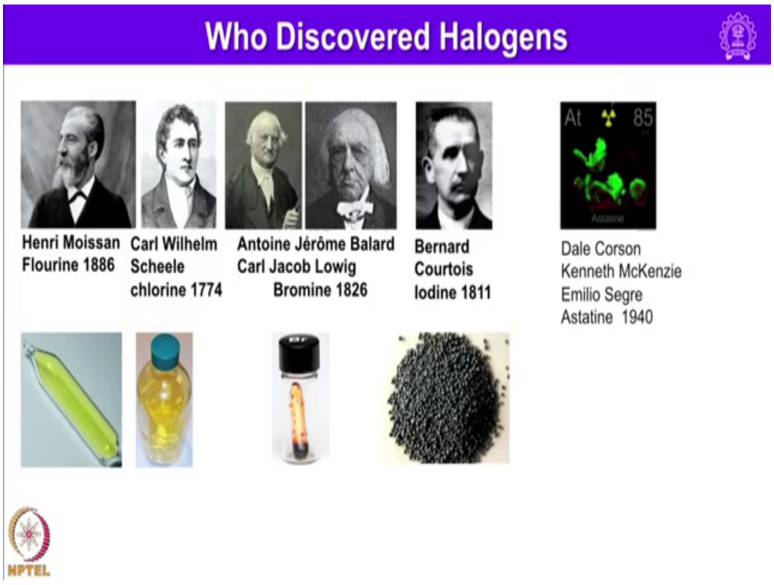

Who Discovered Halogens

Henri Moissan
Flourine 1886

Carl Wilhelm
Scheele
chlorine 1774

Antoine Jérôme Balard
Carl Jacob Lowig
Bromine 1826

Bernard
Courtois
Iodine 1811

Dale Corson
Kenneth McKenzie
Emilio Segre
Astatine 1940

Antonie Ballard and Carl Lowig discovered bromine in 1826 and Bernard Courtois discovered iodine in 1811, very recently in 1940 dale Carson Kenneth Mckenzie and Emilo Seger discovered astatine.

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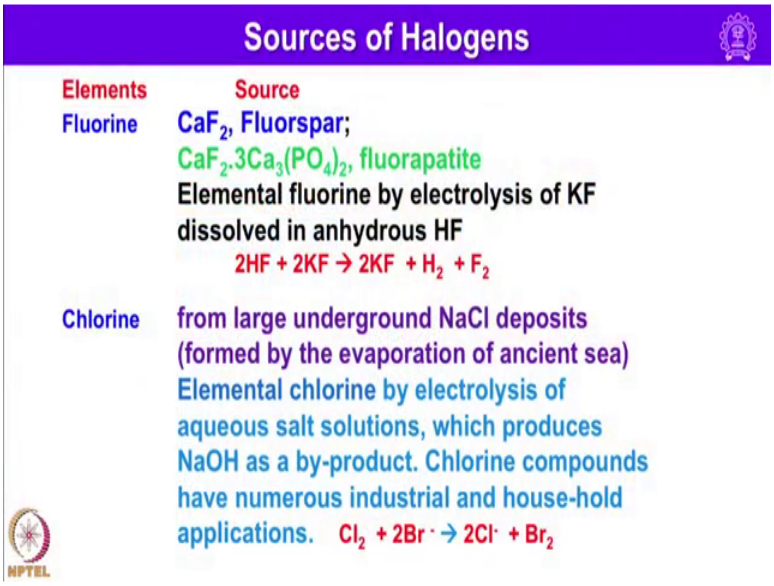

Sources of Halogens

Elements	Source
Fluorine	CaF_2, Fluorspar; $CaF_2.3Ca_3(PO_4)_2$, fluorapatite Elemental fluorine by electrolysis of KF dissolved in anhydrous HF $2HF + 2KF \rightarrow 2KF + H_2 + F_2$
Chlorine	from large underground NaCl deposits (formed by the evaporation of ancient sea) Elemental chlorine by electrolysis of aqueous salt solutions, which produces NaOH as a by-product. Chlorine compounds have numerous industrial and house-hold applications. $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

Let us look into the sources of halogens, fluorine sources are essentially calcium fluoride that is also called fluorspar and calcium fluoride having calcium phosphate, thus fluoro apatite. And essentially elemental fluorine is obtained by electrolysis of K F dissolved in anhydrous HF.

One can see that equations shown here this equation here, chlorine essentially obtained from large underground sodium chlorine deposits formed by the operation of ancient sea, and elemental chlorine by electrolysis of aqueous salt solutions which produce sodium hydroxide as a byproduct, chlorine compounds have numerous industrial and household applications. Bromine iron occurs in seawater of course, the concentration is very very low that is about 30 parts per million from which bromine is obtained by reaction with chlorine and sodium iodide NaIO 3.

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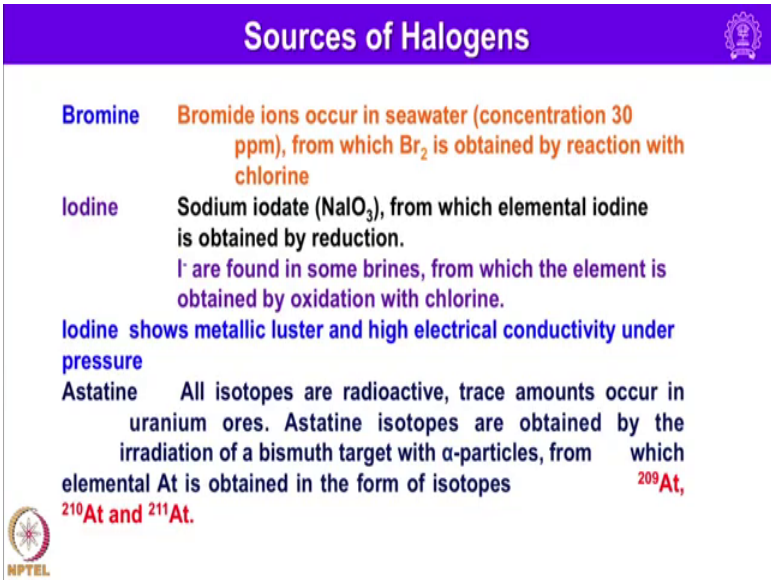

Sources of Halogens

Bromine Bromide ions occur in seawater (concentration 30 ppm), from which Br_2 is obtained by reaction with chlorine

Iodine Sodium iodate ($NaIO_3$), from which elemental iodine is obtained by reduction.

I^- are found in some brines, from which the element is obtained by oxidation with chlorine.

Iodine shows metallic luster and high electrical conductivity under pressure

Astatine All isotopes are radioactive, trace amounts occur in uranium ores. Astatine isotopes are obtained by the irradiation of a bismuth target with α-particles, from which elemental At is obtained in the form of isotopes ^{209}At, ^{210}At and ^{211}At.

From which elemental iodine is obtained by reduction, and iodides are found in some brains from which the element is obtained by oxidation with chlorine. Iodine shows metallic cluster and high electrical conductivity under pressure, and astatine is essentially radioactive and all its isotopes are also radioactive.

And trace amount of astatine occurs in uranium ore and of course, uranium ore pitchblende is the source of many radioactive elements that we see in the periodic table. Astatine isotopes are obtained by the irradiation of bismuth target with alpha particles, from which elemental astatine is obtained in the form of isotopes such as 209, 210 and 211.

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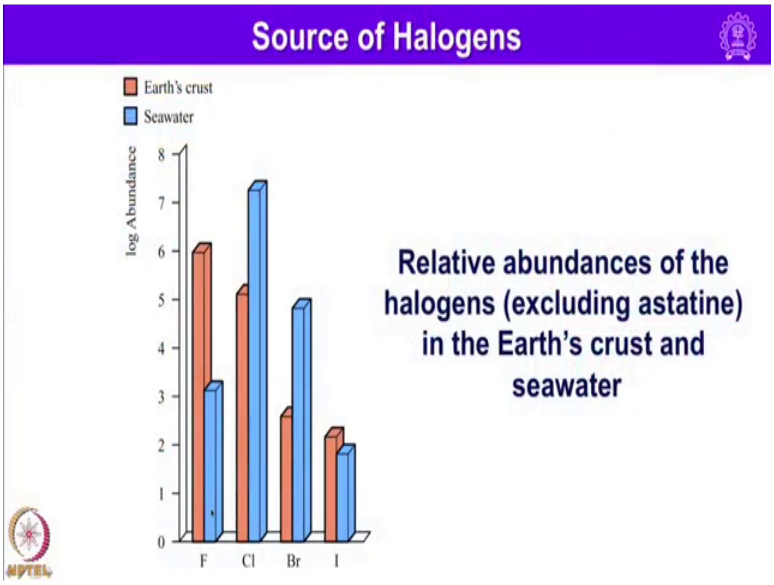

Source of Halogens

Relative abundances of the halogens (excluding astatine) in the Earth's crust and seawater

Let us compare the sources of halogens in both earth's crust and seawater. In sea water chlorine abundance is more whereas, in earth's crust fluorine abundance is more and most fluorine containing compounds are made using HF.

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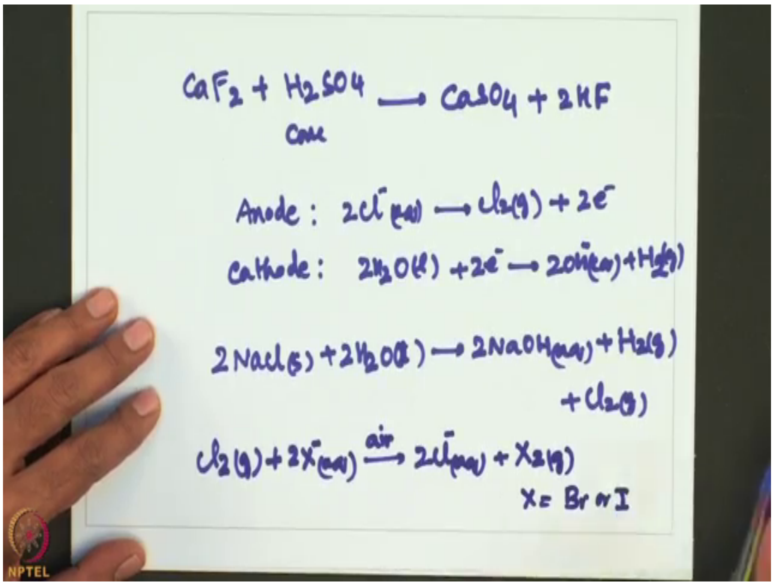

$$CaF_2 + \underset{conc}{H_2SO_4} \rightarrow CaSO_4 + 2HF$$

Anode : $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$

Cathode : $2H_2O(l) + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)}$

$$2NaCl_{(s)} + 2H_2O(l) \rightarrow 2NaOH_{(aq)} + H_{2(g)} + Cl_{2(g)}$$

$$Cl_{2(g)} + 2X^-_{(aq)} \xrightarrow{air} 2Cl^-_{(aq)} + X_{2(g)}$$

$X =$ Br or I

For example, calcium fluoride when it is treated with the concentrated sulfuric acid it gives calcium sulfate plus HF ok. Dyfluorine is strongly oxidizing and must be prepared industrially by electrolysis or electrolytic oxidation of F minus iron, the electrolyte is a mixture of anhydrous molten KF and HF, and the typical electrolysis cell contains a steel or a copper cathode with ungraphatized carbon anode and mono metal that is essentially a alloy of copper and nickel, that diaphragm with perforation below the surface of the electrolyte is used which essentially prevents the combination of H 2 and F 2 during the electrolytic process.

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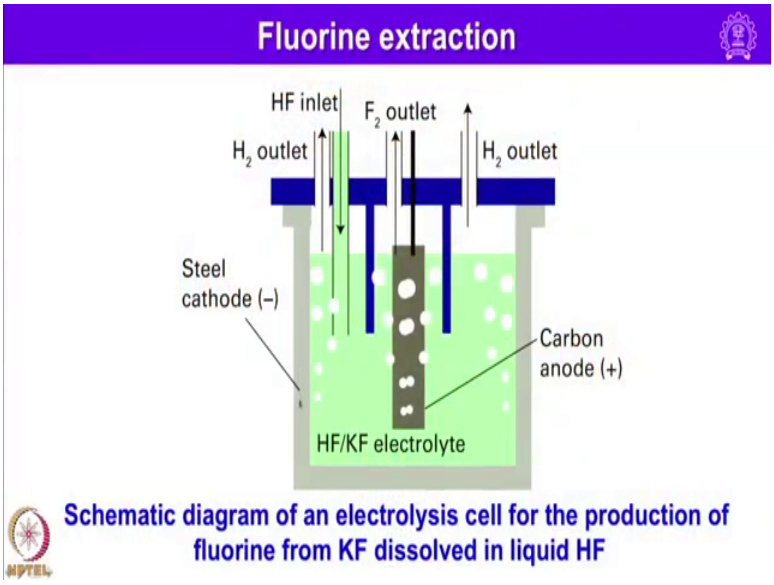

Fluorine extraction

Schematic diagram of an electrolysis cell for the production of fluorine from KF dissolved in liquid HF

A typical cell is shown here you can see here steel cathode and also we have ungraphatized carbon anode here. And of course, inlet is therefore, HF and outlets are therefore, both fluorine as well as hydrogen gas, and the commercial chlorine is produced by the electrolysis of aqueous sodium chloride solution in a chloroalkali cell. Let me write the half reactions involved in this reaction at anode is essentially 2 Cl minus giving Cl 2 plus 2 electrons, in at cathode 2 H 2 O plus 2 electrons gives 2 OH minus.

So, here the possibility of oxidation of water is there, that has to be suppressed by using an electrode material that has a high ore potential for ore to evolution then for Cl 2. So, does the oxidation of water is prevented. The best anode material for this type of reaction seems to be ruthenium oxide that is Reo 2, this process is the basis of the chloroalkali industry which produces sodium hydroxide on a very massive scale and this is the chlorine extraction cell here.

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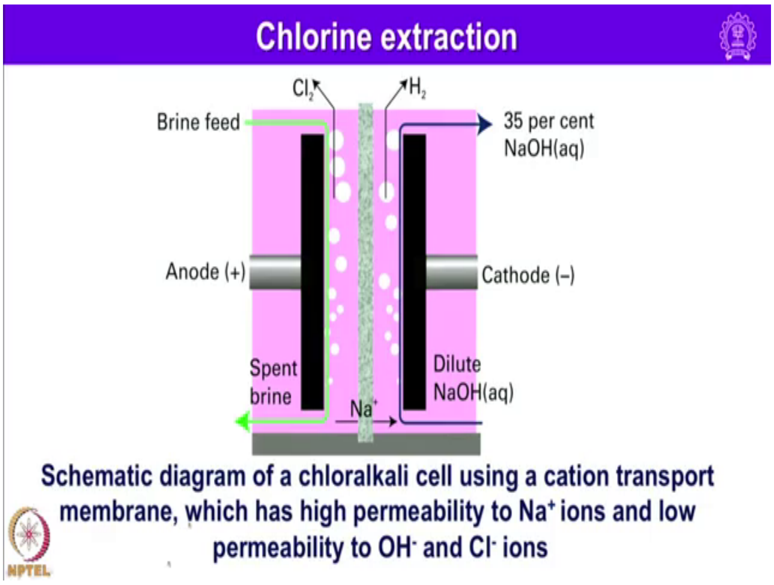

Chlorine extraction

Schematic diagram of a chloralkali cell using a cation transport membrane, which has high permeability to Na^+ ions and low permeability to OH^- and Cl^- ions

You can see here this schematic diagram represents the chloroalkali cell and of course, all the details are shown here. So, bromine is obtained by the chemical oxidation of bromide ions in seawater. A similar process is also used to recover iodine from certain natural brains that are rich in iodides.

The most strongly oxidizing halogen chlorine is used as the oxidizing agent in both processes. The resulting bromine and iodine are driven from the solution in a stream of air of course, here X equals bromine or iodine.

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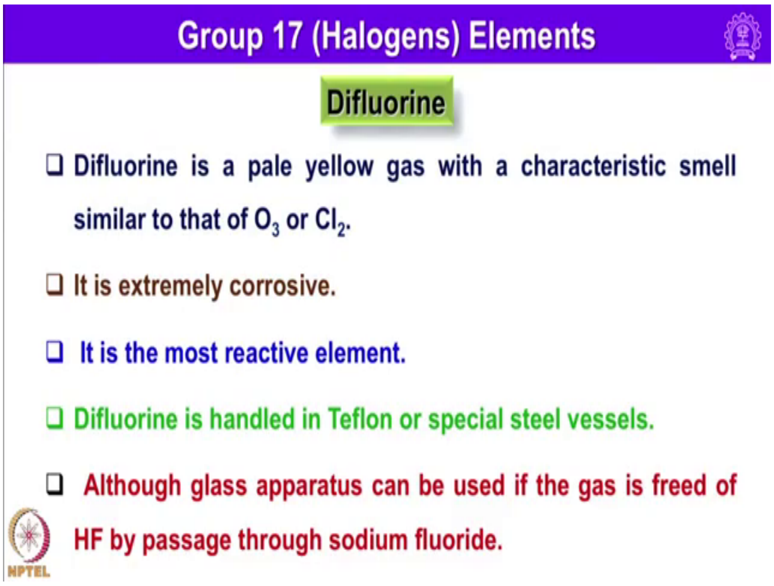

Group 17 (Halogens) Elements

Difluorine

- ❑ Difluorine is a pale yellow gas with a characteristic smell similar to that of O_3 or Cl_2.
- ❑ It is extremely corrosive.
- ❑ It is the most reactive element.
- ❑ Difluorine is handled in Teflon or special steel vessels.
- ❑ Although glass apparatus can be used if the gas is freed of HF by passage through sodium fluoride.

Let us look into the properties of group 17 elements, you know die fluorine is a pale yellow gas with a characteristic smell similar to that ozone our chlorine and its extremely corrosive and it is the most reactive element, and die fluorine is essentially handled in Teflon or special steel bezels.

One can also use glass operators provided F 2 is free from any dissolved HF gas in it. The synthesis of F 2 can be carried out in aqueous medium because F 2 decompose water liberating ozonized oxygen, F 2 is commercially available in cylinders so, there is no need to make it in laboratory.

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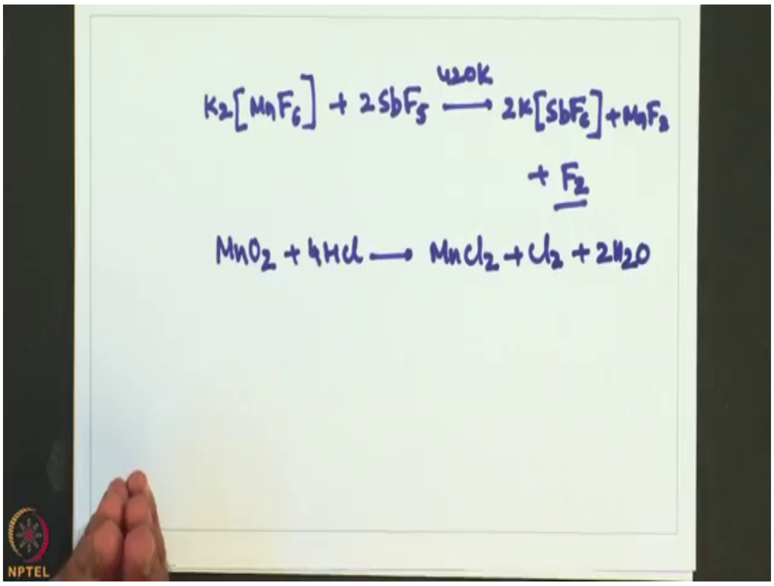

$$K_2[MnF_6] + 2SbF_5 \xrightarrow{420K} 2K[SbF_6] + MnF_3 + \underline{F_2}$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

The commercial method involves the treatment of K 2 M nF 6 with fluorine obstructing reagents such as antimony pentafluoride yeah die fluorine combines directly with all elements except oxygen, nitrogen and lighter noble gases and these reactions are very very violent in nature. The high reactivity of F 2 arises partly from the low bond dissociation energy, because 2 smaller atoms with high electron density makes this FF bond unstable.

As a result you F F bond dissociates readily even an exposure to u v light. When we look into these properties of chlorine dye bromine and iodine, dye chlorine is a pale green yellow gas with a characteristic odder inhalation of chlorine causes irritation of the respiratory system, and liquid chlorine birth the skin and synthesis of chlorine involves the treatment of M n O 2 with HCl.

And of course, dye bromine is a dark orange volatile liquid, the only liquid nonmetal at 298 Kelvin and often it is used as say aqueous solution called bromine water, skin contact with liquid bromine results in burns; one has to be extremely careful while handling liquid bromine. Bromine vapor has an unpleasant smell and causes eye and respiratory irritation.

At 298 Kelvin iodine forms dark purple crystals, which sublime readily at 1 bar pressure into your purple vapor. Chemical reactivity decreases steadily from chlorine to iodine notably in the reactions of halogens with hydrogen white phosphorus and sulfur and many metals. The observed colors of the halogens arise from an electronic transition from the highest occupied by star molecular orbital to the lowest unoccupied sigma star molecular orbital.

If you recall the mo diagrams, that I wrote for first row demerit species now there for example, if we consider oxygen we have 2 unpaired electrons in the pi star anti bonding orbital whereas, in case of halogens we have 3 unpaired electrons are there and here the gap between pi star and sigma star. Pi star is essentially highest occupied molecular orbital and sigma star is essentially lowest unoccupied molecular orbital between which the gap is small and the electron transition can readily occur, as a result some of these halogens are colored in nature. The homo lumo energy gap decreases from fluorine to iodine; that means, transition is very facile when you go from fluorine to iodine ok.

Solutions of I 2 in donor solvents such as pyridine, ether or ketones are brown or yellow because of formation of adducts, that I showed in a couple of minutes back. Even benzene acts as a donor forming charge transfer complexes with iodine as well as bromine. In dichloromethane solution triphenyl phosphine dibromide ionizes to give salt of this type.

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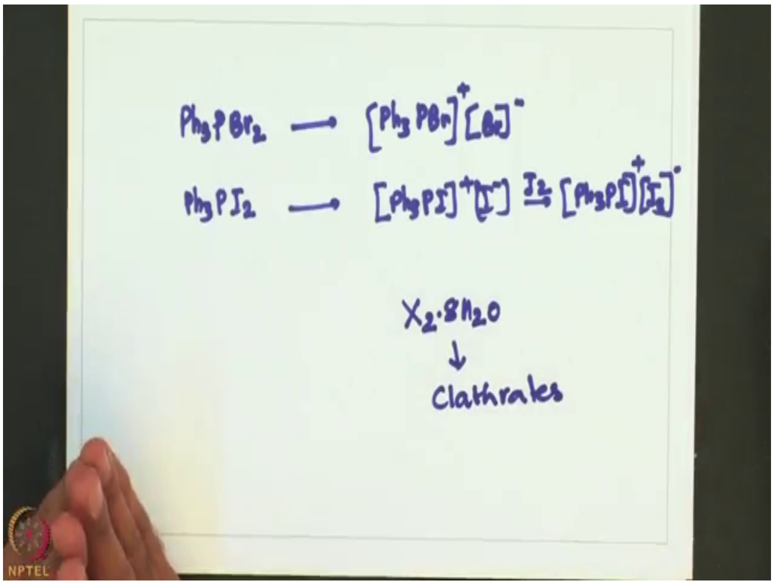

$Ph_3PBr_2 \longrightarrow [Ph_3PBr]^+[Br]^-$

$Ph_3PI_2 \longrightarrow [Ph_3PI]^+[I]^- \xrightarrow{I_2} [Ph_3PI]^+[I_3]^-$

$X_2 \cdot 8H_2O$

↓

Clathrates

For example if you consider Ph 3 P Br 2, this ionizes to give Ph 3 P Br plus and minus. Similarly iodine also forms iodine minus of course, in presence of access of iodine, it can also leads to the formation of I 3 minus or can given I 5 minus.

The nature of products from reaction of P r 3 and I 2 r dependent on the solvent and the r group; on phosphine solid state structure determination exemplify products of this type. For example, I will show you in the next slide you can see this has been isolated where between 2 phosphines we have 5 iodine atoms.

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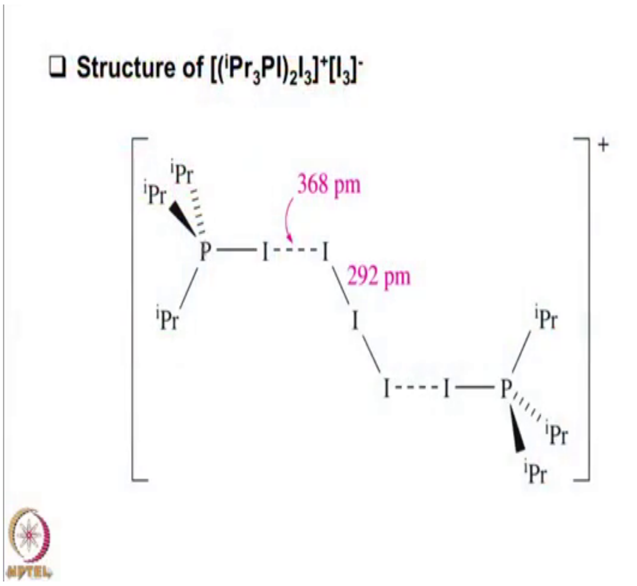

❑ **Structure of $[(^iPr_3PI)_2I_3]^+[I_3]^-$**

So, essentially this is I 3 plus and again I 3 minus the composition or structural formula can be written in this fashion. So, let us look into the clath rates, die chlorine, die bromine and die iodine are sparingly this soluble in water. By freezing aqueous solutions of chlorine and bromine, solid hydrates of approximate composition X 2 8 H 2 O may be obtained these crystalline solids are essentially known as clath rates.

So, these crystalline solids consists of hydrogen bonded structures with X 2 molecules occupying cavities in the lattice, a clath rate is essentially a host guest compound a molecular assembly, in which the guest molecules occupy the cavities in the lattice of host species ok.

So, let us look into the hydras of group 17 elements, all the hydrogen halides that is H X are gases at 298 Kelvin with the sharp acid smells, direct combination of hydrogen with halogens to form H X can be used synthetically only in case of chloride and bromide.

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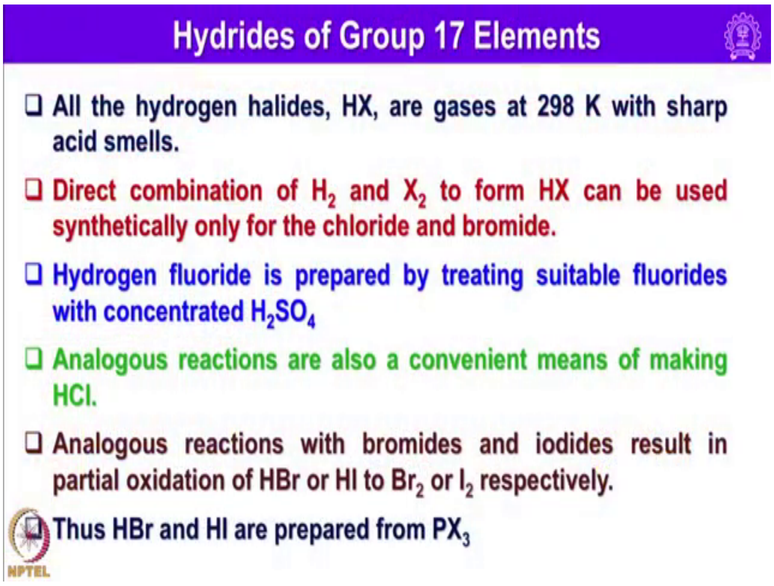

Hydrides of Group 17 Elements

- All the hydrogen halides, HX, are gases at 298 K with sharp acid smells.
- Direct combination of H_2 and X_2 to form HX can be used synthetically only for the chloride and bromide.
- Hydrogen fluoride is prepared by treating suitable fluorides with concentrated H_2SO_4
- Analogous reactions are also a convenient means of making HCl.
- Analogous reactions with bromides and iodides result in partial oxidation of HBr or HI to Br_2 or I_2 respectively.
- Thus HBr and HI are prepared from PX_3

So, hydrogen fluoride is prepared by treating suitable flow rates with concentrated sulfuric acid, analogous reactions are also a convenient means of making HCl, analogues reactions with bromides and iodides result in partial oxidation of HBr 2 HI, HBr, HI, 2 B r 2 r I 2; respectively. A HBr and HI r prepared from corresponding phosphorus trihalides, let me give the synthetic procedure for this halides.

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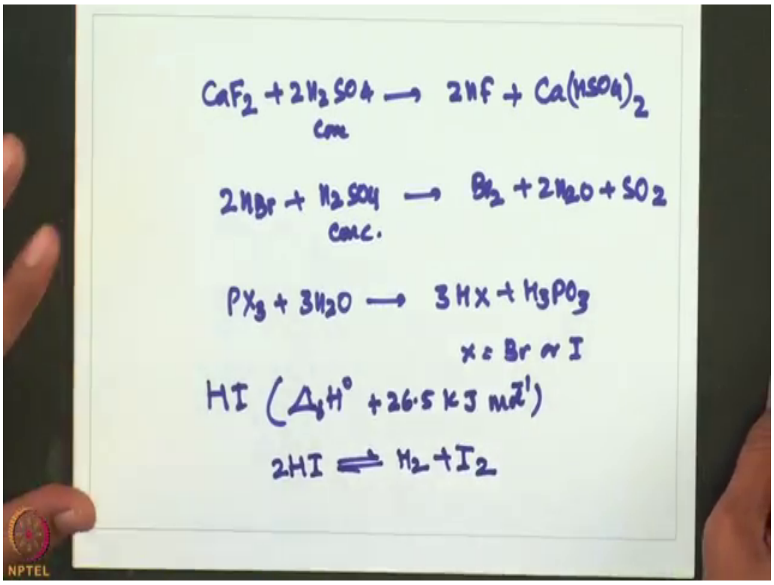

$CaF_2 + \underset{Con}{2H_2SO_4} \longrightarrow 2HF + Ca(HSO_4)_2$

$2HBr + \underset{Conc.}{H_2SO_4} \longrightarrow Br_2 + 2H_2O + SO_2$

$PX_3 + 3H_2O \longrightarrow 3HX + H_3PO_3$

$X = Br$ or I

$HI\ (\Delta_f H^\circ\ +26.5\ kJ\ mol^{-1})$

$2HI \rightleftharpoons H_2 + I_2$

For example a CaF 2 when its treated with constant sulfuric acid gives 2 HF of course, Ca HSO 4 twice, similarly 2 HBr plus H 2 SO 4 is Br 2 plus 2 H 2 O plus SO 2 plus PX 3 plus 3 H 2 O gives 3 HX plus H 3 PO 3 where X equals bromide or iodide.

Hydrogen halides are known and stability of this hydrogen halides decreases down the group going to the increasing mismatch in atomic sizes for example, if you consider HF we have 1 s hydrogen and 2 p fluorine, when we go further it becomes 3 p 4 p and 5 p and steadily the size of these orbits are increasing, due to the mismatch of the over lapping orbital's the stability decreases down the group and it is expected and H I is rather unstable for example, delta HF is positive is plus 26.5 kilo joules per mole and HI exists in equilibrium H 2 and I 2 so, always ok.

So, the melting and boiling point increase down the group, with the exception of HF which has a very high boiling point due to extensive hydrogen bonding. In fact, even in gaseous phase HF retains this hydrogen bonding.

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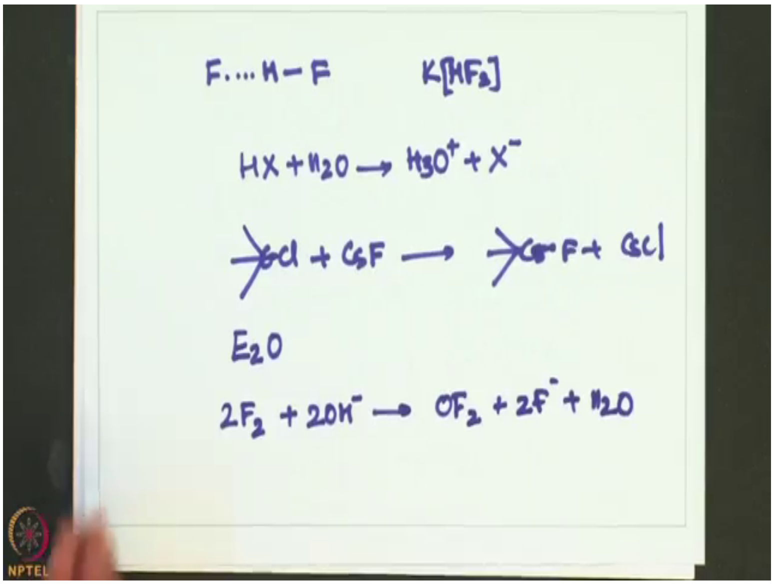

$F \cdots H-F$ $K[HF_2]$

$HX + H_2O \longrightarrow H_3O^+ + X^-$

$CCl + CsF \longrightarrow CF + CsCl$

E_2O

$2F_2 + 2OH^- \longrightarrow OF_2 + 2F^- + H_2O$

So, this F HF unit is always linear about the hydrogen and also occurs in the so, called hydrogen fluoride salts such as K HF 2 is linear and also it is observed in salts such as K HF 2 ok. The hydrogen halides dissolve in water to give highly acidic solutions and HCl HBr H I all are very strong acids and are essentially fully dissociated in dilute solution; however, HF is a much weaker acid that is again due to the extensive hydrogen bonding and one can see in this slide the structure of HF in the solid state.

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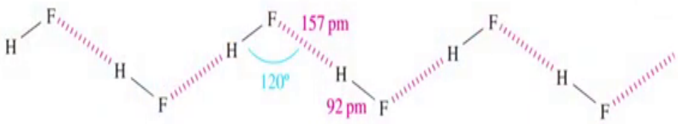

The structure of HF in the solid state

And this kind of structure is also retained even in the gaseous phase ok.

Let us look into metal halides, all the halides of the alkali metals have sodium chloride or cesium chloride structures, and cesium fluoride is the best choice of alkali metal fluoride to effect the hydrogen exchange reaction; that means, its a good fluorinating agent for example, if we take CCl and if you treat this cesium fluoride ok. Cesium fluoride is the best choice of alkali metal fluoride to affect the halogen exchange reaction and; that means, cesium fluoride is a very good fluorinating agent.

If you take this CCl bonded compound and treat with CCl fluoride florin exchange takes place to form fluorinated compound along with cesium chloride. A few other mono halides possess this sodium chloride as a simpler structure for example, silver fluoride as well as silver chloride, these compounds exhibit significant covalent character that is true in case of coopers chloride, cuprous bromide, cuprous iodide and also silver iodide which possess the (Refer Time: 23:36) structure.

So, let us look into halogen oxides, all halogens form oxides those of iodine is are the most stable while those of bromine tend to be the least stable and of course, all oxides of halides are oxidizing agents and die hydrogen monoxides of this type are known for example, E 2 O is O F 2 plus 2 F minus plus H 2 O F 2 is the most stable and is a very powerful oxidizing agent it can even oxidize water to oxygen and O F 2 explorers when mixed with halogens, but a spark is required to ignite mixtures of O F 2 and hydrogen or carbon monoxide.

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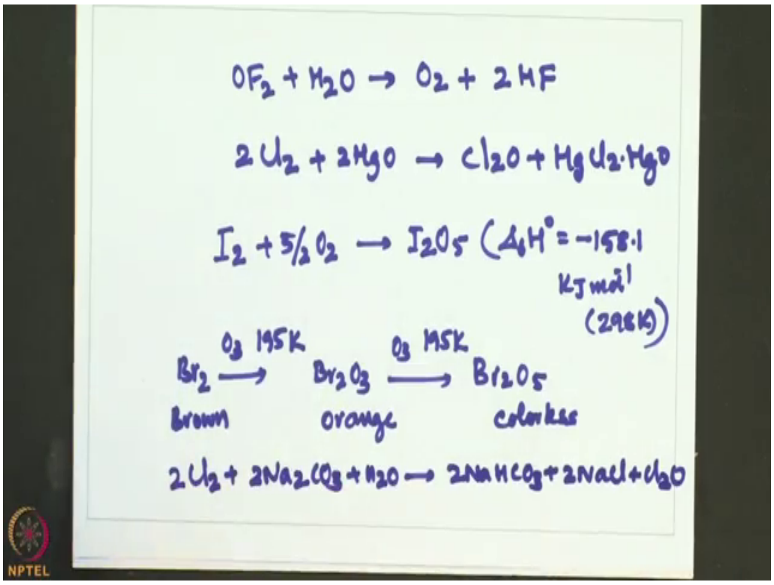

$$OF_2 + H_2O \rightarrow O_2 + 2HF$$

$$2Cl_2 + 2HgO \rightarrow Cl_2O + HgCl_2 \cdot HgO$$

$$I_2 + 5/2\,O_2 \rightarrow I_2O_5 \; (\Delta_f H^\circ = -158.1 \text{ kJ mol}^{-1} \; (298K))$$

$$\underset{\text{Brown}}{Br_2} \xrightarrow{O_3 \; 195K} \underset{\text{orange}}{Br_2O_3} \xrightarrow{O_3 \; 195K} \underset{\text{colorless}}{Br_2O_5}$$

$$2Cl_2 + 2Na_2CO_3 + H_2O \rightarrow 2NaHCO_3 + 2NaCl + Cl_2O$$

For example if you take O F 2 and treat with water, water is oxidized to oxygen through the liberation of HF. Similarly if you consider Cl 2 plus 2 H g O, this is the method for the preparation of Cl 2 O through the formation of Hg Cl 2 Hg O.

So, iodine is the only hydrogen to form an oxide which is thermodynamically stable with respect to decomposition into its elements ok. Chlorine and bromine oxides are hazardous materials with a tendency to explore, chlorine oxides although not difficult to prepare all are liable to decompose explosively. For less is known about the oxides of bromine, which are very unstable than those of chlorine as well as iodine, although one can prepare B r 2 O 3 and B r 2 O 5 using convenient synthetic groups ok. For example, if you take B r 2 and treat with ozone at 195 Kelvin it can form B r 2 O 3 which are further treatment with ozone at the same temperature.

It gives B r 2 O 5 and formation of this one can be concluded visually by looking into the color initially it is brown and it changes to orange, and eventually B r 2 O 5 is form its colorless bromine 5 centers are trigonal pyramidal and in B r 2 O 5 and B r O 2 groups are eclipsed. So, die chlorine monoxide Cl 2 O is obtained as a yellow brown gas by auction of Cl 2 on mercuric oxide or moist sodium carbonate. So, other reaction I wrote let me write the another method here yeah ok.

So, this Cl 2 O liquefies at minus 277 Kelvin and explores violently on warming it hydrolyzes to hypochlorous acid and its formed lady unheeded of this acid. For example, if you take Cl 2 O plus water it gives 2 H O Cl ok.

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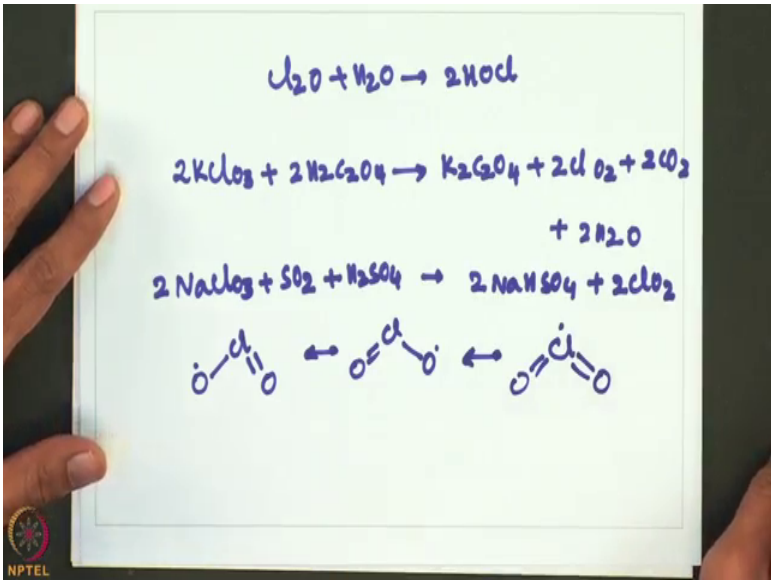

$$Cl_2O + H_2O \rightarrow 2HOCl$$

$$2KClO_3 + 2H_2C_2O_4 \rightarrow K_2C_2O_4 + 2ClO_2 + 2CO_2 + 2H_2O$$

$$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2NaHSO_4 + 2ClO_2$$

Chlorine dioxide Cl O 2 is a yellow gas and is produced in the highly dangerous reaction between potassium chloride KClO 3 and constantly sulfuric acid one has to be extremely careful in performing this reaction if one has to do it or you can also start from N a Cl O 3 I the presence of SO 2 and sulfuric acid and one can also write in the following structures, these are the possible resonance structures for Cl O 2. Cl O 2 to is a yellow gas explosive in high concentration and prepared by the reduction of KClO 3 in acidic solution and this also paramagnetic molecule ah.

You saw having one unpaired electron because of de localization of the unpaired electrons over the entire molecule, it shows little tendency to undergo dimerization ; however, in the solid state it forms lose dimers with a ClO distance of about 270 pico meter of course, the normal Cl O bond distance is 147 pico meter and Cl O 2 is commercially an important bleaching and sterilizing agent, it dissolves unchanged in water, but is slowly hydrolyzed to HCl and HCl O 3 involving ClO radical, ozone reacts with Cl O 2 a 273 Kelvin to form Cl 2 O 6 a dark red liquid which is also made by following reaction that I am going to write now.

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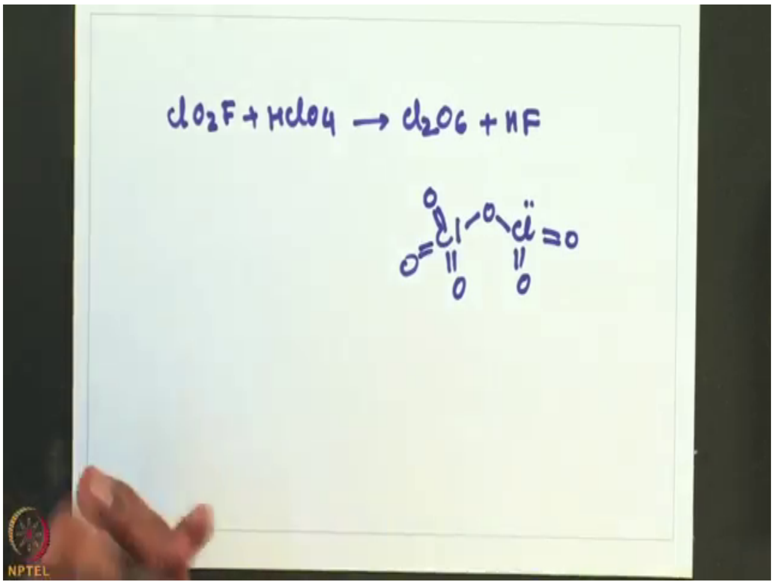

$ClO_2F + HClO_4 \rightarrow Cl_2O_6 + HF$

Of course, if you are curious to know the structure of Cl 2 O F this how it looks like we have a oxygen bridge here.

So, let me stop here and in my next class I will continue from here, I need a another lecture to complete group 17 elements, then I will move on to group 18 chemistry until then have a pleasant reading of main group chemistry.

Thank you very much.