Main Group Chemistry
Prof. M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture – 53
Chemistry of Group 17 Elements

Welcome to MSB lecture series on the chemistry of main group elements. In my last lecture I started discussion on oxides of halogens, I did mention about the oxides of fluorine and chlorine and you can see here in this one I have given the method of preparation for ClO 2 and also bromine and iodine oxides.

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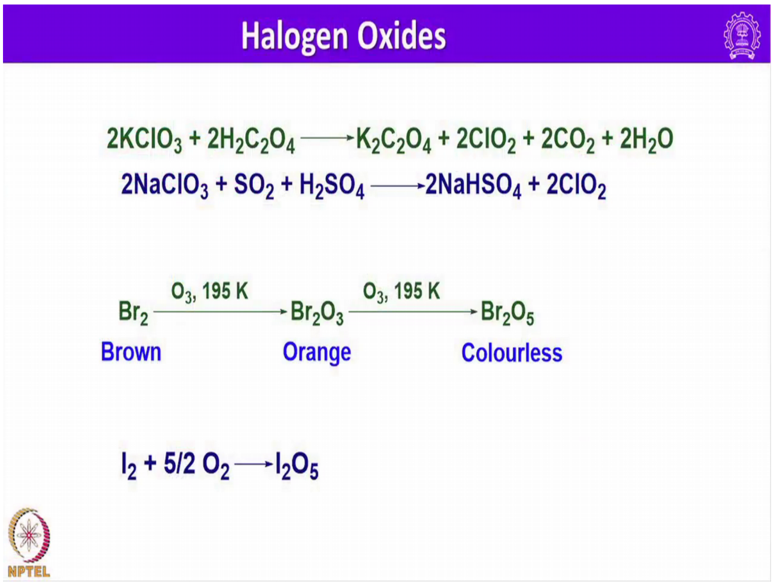

Halogen Oxides

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

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

$Br_2 \xrightarrow{O_3,\ 195\ K} Br_2O_3 \xrightarrow{O_3,\ 195\ K} Br_2O_5$

Brown Orange Colourless

$I_2 + 5/2\ O_2 \rightarrow I_2O_5$

So, one can see these things I had already discussed these things in my previous lecture the preparation. So, if you take bromine and pass ozone at 195 Kelvin, initially you get B r 2 O 3 and on further addition of one more equivalent of ozone it gives Br 2 O 5.

So, the course of this reaction can be monitored visually because of the color change and of course, iodine with oxygen it gives I 2 O 5. Br 2 O 5 is thermally unstable where as I 2 O 5 is stable up to 573 Kelvin, I 2 O 5 is a white hygroscopic solid prepared by dehydration of iodic acid the reaction is reversed when I 2 O 5 dissolves in water.

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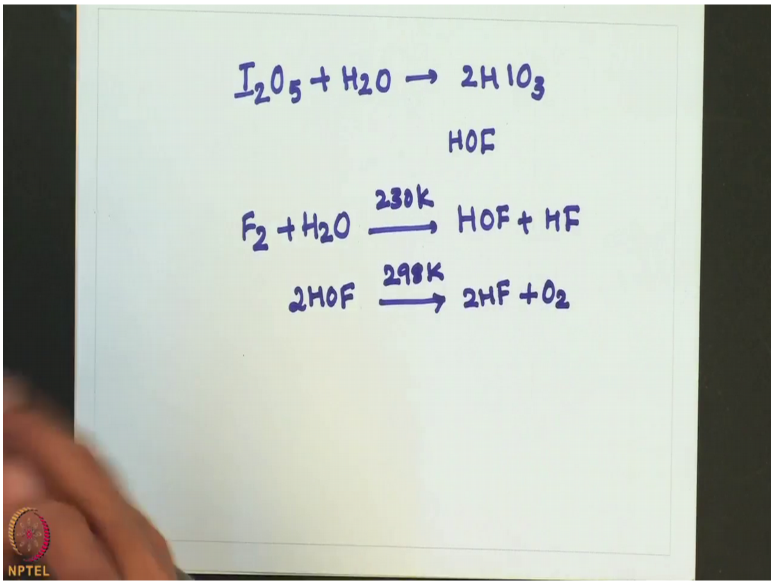

$I_2O_5 + H_2O \rightarrow 2HIO_3$

HOF

$F_2 + H_2O \xrightarrow{230K} HOF + HF$

$2HOF \xrightarrow{298K} 2HF + O_2$

For example, I 2 O 5 when its treated with water, it gives 2 H I O 3 now I 2 O 5 is used in analysis of carbon monoxide, in the solid state I 2 O 5 is structural related to B r 2 O 5 with a difference that it has a staggered conformation probably as a result of extensive intermolecular interactions where we have I 2 O interaction of course, that is more or less equal to 223 picometer the I O bond distance non bonded.

And if you are curious to know the structures of various halogen oxides here it is.

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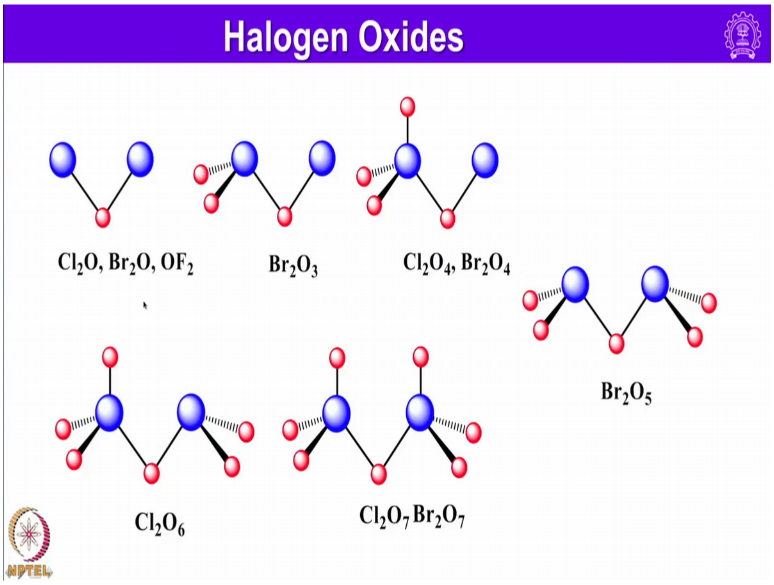

Halogen Oxides

And Cl 2 O B r 2 O have bend structure having 2 lone pairs where as B r 2 O 3 has this structure with 1 oxo bridge and Cl 2 O 4 B r 2 O 4 also have mixed valency with 1 oxygen bridge B r 2 O 5 1 oxygen bridging is there and C l 2 O 6 also mixed valency is therefore, chlorine and in case of C l 2 O 7 and B r 2 O 7 you can clearly see here both are in plus 7 state ok.

Let us look in to iodine oxides among all the halogen oxides those of iodine particularly in higher oxide states are the most stable. So, for example, if you take I 2 O 5 in which iodine is in plus 5 state, decomposes only at temperature greater than 300 degree centigrade and that is made by heating H I O 3. So, iodine oxides unlike the chlorine and bromine ones have polymeric structure, I have listed some oxy acids and here.

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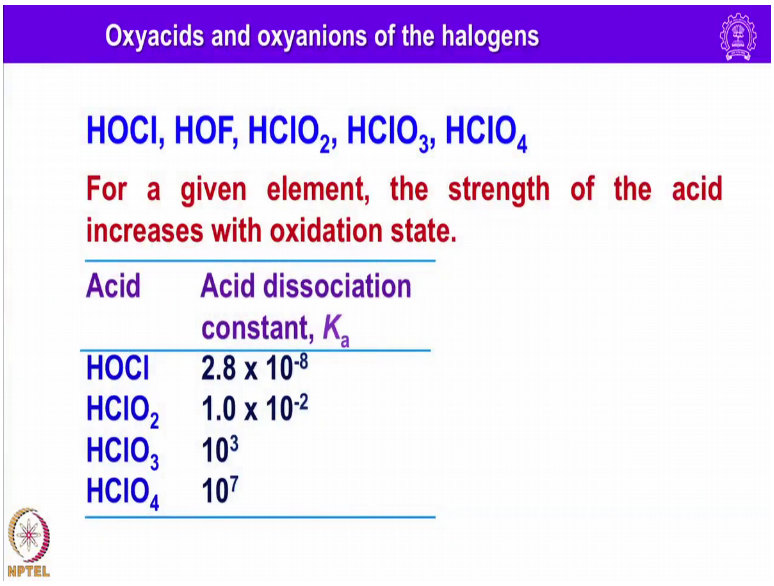

Oxyacids and oxyanions of the halogens

HOCl, HOF, $HClO_2$, $HClO_3$, $HClO_4$

For a given element, the strength of the acid increases with oxidation state.

Acid	Acid dissociation constant, K_a
HOCl	2.8×10^{-8}
$HClO_2$	1.0×10^{-2}
$HClO_3$	10^{3}
$HClO_4$	10^{7}

So, let us look into oxyacids and oxyanions of the halogens. If you see here I have given some oxy acids HOCl, HOF, HClO 2, HClO 3 and HClO 4 for a given halogen the strength of the acid increases with oxidation state for example, if you consider HClO 4 chlorine is in plus 7 oxygen state and also you can see acid dissociation constant this clearly indicates that per chloric acid is a strong acid compared to HOCl.

Halogens in their plus 7 oxy state or known for forming halic acids for example, h x o 4 per chloric acid we say or in general it is called halic acid where halogen is in plus 7 state and halite ions its or essentially plus 7 salts known for chlorine bromine and iodine ClO

4 B r O 4 and I O 4 chloric acid is a strong oxidizing agent, but least strongly oxidizing of all chlorine acids, the chloride anion can be used to crystallize large cations

For example when we make some coordination compounds having a chloride as a counter anion because of the difference in the size those complexes may not be stabilized, once if the chloride is replaced by per chloride that cation is stabilized and also it crystalizes very easily and chloride salts are quite explosive and shock sensitive, those who are working with per chloric acid or per chloride salts they have to be extremely careful and they have to take a very minuend quantity of those compounds, in few mode they have to give a little hammering and see whether they explored or not essentially these compounds are explosive and shock sensitive; chloride 7 slats are often referred to as per chlorides.

Let us look into oxoacids and their salts hypoflorus acid that is HOF to start with. So, fluorine is unique among the halogens in forming no spices in which it has a formal ox state other than minus 1. One should remember among all elements in the periodic table only fluorine can exists in only minus 1 oxygen state, and it can make any other element in the periodic table exists in higher oxygen states the only known oxo acid is hypoflorus acid thats HOF which is un stable it is obtained by passing F 2 over ice at 230 K elvin and condensing the gas reducer.

For example F 2 an it treated with H 2 O at 230 kelvin HOF is formed along with HF. At 298 kelvin HOF hypoflorus acid decomposes rapidly the strength of the oxoacids vary systematically with the number of oxy atoms on the central atom. If you look into per iodic acid H 5 I O 6 with iodic plus 7 state it is analogues of per chloric acid and of course, it is a very week acid with p k value of 13.29 the oxygen atoms in the conjugate base that is H 4 I O 6 minus are vary labile on account of the rapid equilibrium I have given the equation here.

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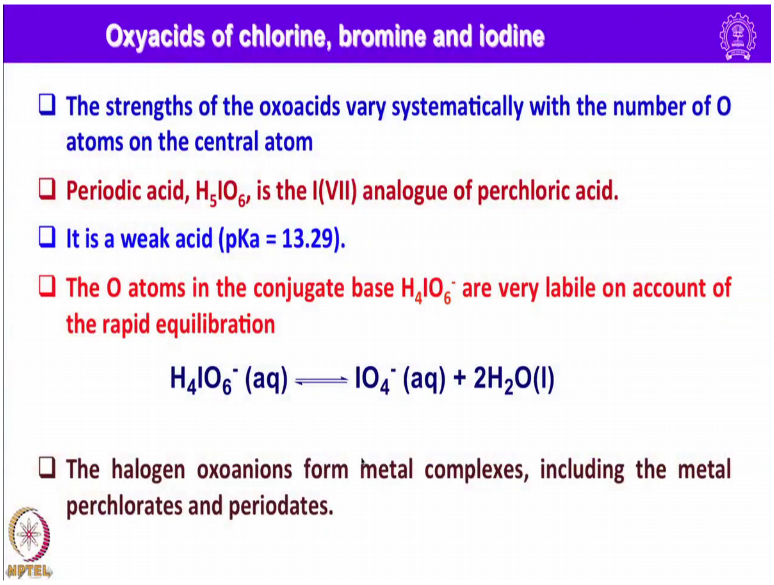

Oxyacids of chlorine, bromine and iodine

- The strengths of the oxoacids vary systematically with the number of O atoms on the central atom
- Periodic acid, H_5IO_6, is the I(VII) analogue of perchloric acid.
- It is a weak acid (pKa = 13.29).
- The O atoms in the conjugate base $H_4IO_6^-$ are very labile on account of the rapid equilibration

$$H_4IO_6^- (aq) \rightleftharpoons IO_4^- (aq) + 2H_2O(l)$$

- The halogen oxoanions form metal complexes, including the metal perchlorates and periodates.

The halogen oxyanions form metal complexes including the metal perchlorates and also periodates.

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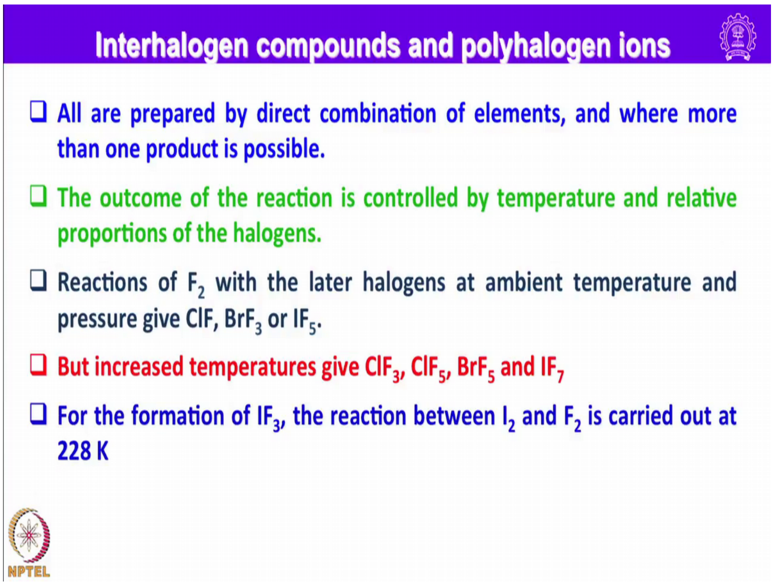

Interhalogen compounds and polyhalogen ions

- All are prepared by direct combination of elements, and where more than one product is possible.
- The outcome of the reaction is controlled by temperature and relative proportions of the halogens.
- Reactions of F_2 with the later halogens at ambient temperature and pressure give ClF, BrF_3 or IF_5.
- But increased temperatures give ClF_3, ClF_5, BrF_5 and IF_7
- For the formation of IF_3, the reaction between I_2 and F_2 is carried out at 228 K

Now, let us look into the inter halogen compounds and also poly halogen ions. All this inter halogen compounds can be prepared by direct combination of elements and where more than 1 product is possible. So, when can (Refer Time: 08:12) when simply while combining 2 elements more than 1 product, the outcome of the reaction is controlled by temperature and relative proportions of the halogens; Reactions of fluorine with the later halogens at ambient temperature and pressure gives ClF BrF 3 and also I F 5.

But increased temperature gives higher halogen inter halogen compounds such as Cl F 3, C l F 5, BrF 5 and also I F 7. For the formation of I F 3 the reaction between I 2 and F 2 has to be carried out at 228 Kelvin; that means, they are sensitive to the stoichiometry as well as the reaction condition and temperature. Of course, inter halogen compounds can be classified into 3 categories neutral compounds, cationic compounds and also an ionic compound. When we talk about neutral compounds we have several examples that already I showed you.

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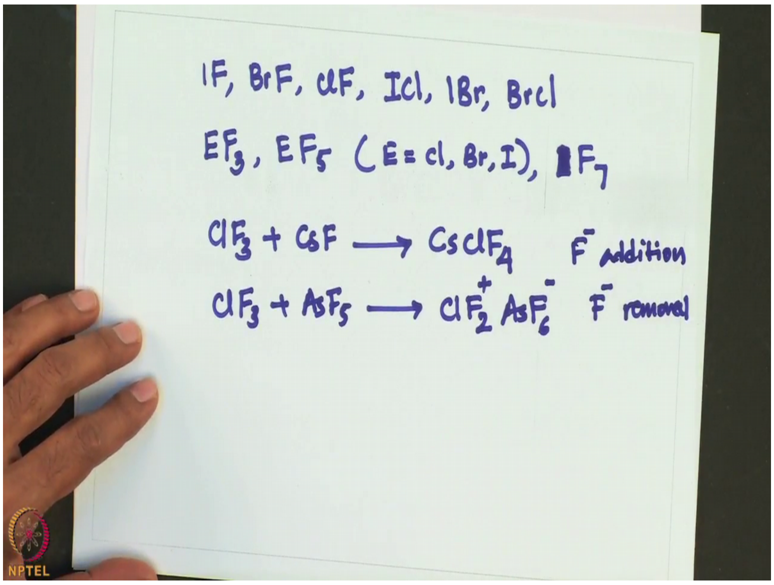

IF, BrF, ClF, ICl, IBr, BrCl

EF_3, EF_5 (E = Cl, Br, I), IF_7

$ClF_3 + CsF \longrightarrow CsClF_4$ F^- addition

$ClF_3 + AsF_5 \longrightarrow ClF_2^+ AsF_6^-$ F^- removal

However let me write some of them again for example, I F B r F C l F I C l I B r B r c l while writing these compounds make sure that the most electro negative will be coming on to the right side and the one that is in positive oxdates comes on the left side One can also write higher once E F 3 or E F 5 where E can be chlorine, bromine or iodine I F 7 I F 7 for the synthesis of inter halogen cationcations and anions we have to use different reagents.

So, here fluoride compounds are generally formed by addition or removal of fluoride from a parent neutral compound for example, one can add fluoride or one can remove fluoride; that means, one should think of reacting with fluoride donors or fluoride acceptor. For example, when we add fluorine to C l F 3 good fluoride donor is c (Refer

Time: 10:51) fluoride for example, C l F 3 when its treated with C s F fluoride it forms C s c l F 4. If we use a fluoride remover such as penta fluoroarsine so, this is F removal and F addition.

Addition and fluorine removal is equalant to the addition of F plus, which is not stable on its own. So, vigorous oxidation for example, using K r F 2 inert gas fluorides are very strong flaunting agents of a lower oxygen state compound can also be obtained for example, if you treat C l F 5.

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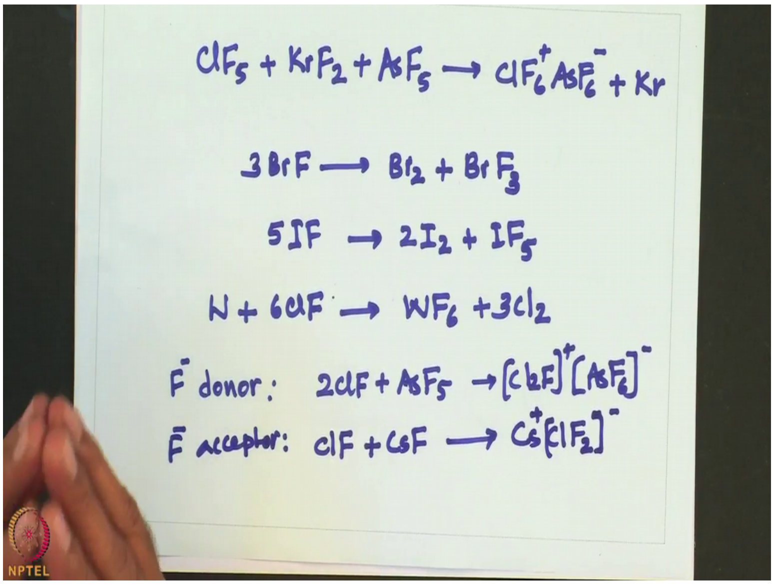

$ClF_5 + KrF_2 + AsF_5 \rightarrow ClF_6^+ AsF_6^- + Kr$

$3BrF \rightarrow Br_2 + BrF_3$

$5IF \rightarrow 2I_2 + IF_5$

$W + 6ClF \rightarrow WF_6 + 3Cl_2$

F^- donor: $2ClF + AsF_5 \rightarrow [Cl_2F]^+[AsF_6]^-$

F^- acceptor: $ClF + CsF \rightarrow Cs^+[ClF_2]^-$

With flaunting agents such as krypton dy fluoride in presence of fluorine acceptor such as A s F 5 it leads to the formation of C l F 6 plus and A s F 6 minus followed by the reduction of K r F 2 to give K r ok. The most stable of the (Refer Time: 12:47) molecules are essentially C l F and I c l at 298 Kelvin I b or dissociates somewhat its elements while B r C l e is substantially dissociated and bromine mono fluoride readily disproportionate to give bromine and bromine trifluoride for example, if you take 3 BrF and this gives B r 2 plus BrF 3.

Also iodine fluoride is unstable at room temperature, this also decomposers in this fashion 5 I F gives 2 I 2 plus I F 5. In general diatomic inter halogens exhibit property is intermediate between their parent halogens chlorine mono fluoride acts as a powerful flaunting agent and also as oxidizing agent for example, tungsten when its treated with chlorine mono fluoride C l F, it gives tungsten F 6 hexafluro tungsten plus 3 C l 2. Some of these compounds can behave as fluoride donors as well as fluoride acceptors for example, let us see is the fluoride donor property.

Let us take 2 C l F plus A s F 5. So, here we know that of course, the moment we treat with another reagent by looking to the nature of the reagent we should be able to tell whether fluoride donation is there or fluoride acceptor property is shown by inter halogen compounds. So, in this case we have a fluorine acceptor. So, it acts as a fluorine donor. So, in this case it gives C l 2 F plus and A s F 6 minus. Now C l F is there chlorine mono fluoride plus we have cesium fluoride. So, since cesium fluoride is a very good fluoride donor.

So, here essentially inter halogen compound should act as fluoride acceptor, it gives C s C l F 2 minus so; that means, by looking into the nature of the other reagent we should be able to conclude about the behavior of inter halogen compounds whether they act as donors or acceptors of fluoride ions. The structures of C l 2 F and C l F 2 minus can be rationalized using valiant shell and compression theory probably you can try at home, iodine mono chloride and mono bromide are less reactive than C l F, but F importance is the fact that in polar solvents I c l is a source of iodine plus and iodinates aromatic compounds.

So, this is where the application of this one in organ synthesis comes into the picture. The higher inter halogen compounds contain fluoride and or a extremely reactive exploding or reacting valiantly with water or organic compounds, despite these hazards they are very valuable flaunting agents example the highly reactive chlorine difluoride converts metals metal chlorides and metal oxides to corresponding metal fluorides. One of its main use is in nuclear fuel reprocessing for the formation of uranium hexafluoride.

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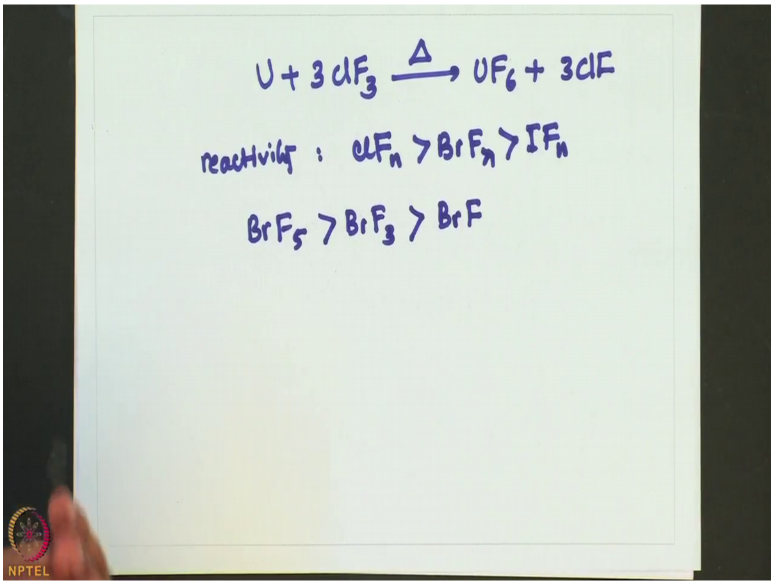

$$U + 3ClF_3 \xrightarrow{\Delta} UF_6 + 3ClF$$

reactivity : $ClF_n > BrF_n > IF_n$

$BrF_5 > BrF_3 > BrF$

So, here uranium on treatment with three equivalents of chlorine trifluoride, gives uranium hexafluoride along with chlorine mono fluorides, when we talk about reactivity decreases in the general order that is.

So, within a series having common halogens the compound with the highest value of n is the most reactive. For example, let us consider bromine series let us say we have B r F 5 we have B r F 3 and B r F. So, reactivity highest value of n so; that means, something like this so; that means, penta fluoro bromine is much more reactive than bromine mono fluoride.

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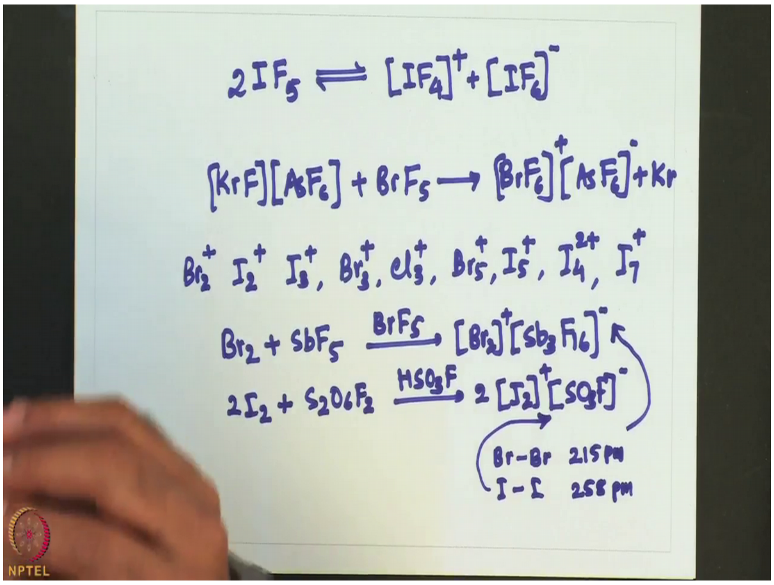

$$2IF_5 \rightleftharpoons [IF_4]^+ + [IF_6]^-$$

$$[KrF][AsF_6] + BrF_5 \longrightarrow [BrF_6]^+[AsF_6]^- + Kr$$

Br_2^+ I_2^+ I_3^+, Br_3^+, Cl_3^+, Br_5^+, I_5^+, I_4^{2+}, I_7^+

$$Br_2 + SbF_5 \xrightarrow{BrF_5} [Br_2]^+[Sb_3F_{16}]^-$$

$$2I_2 + S_2O_6F_2 \xrightarrow{HSO_3F} 2[I_2]^+[SO_3F]^-$$

Br–Br 215 pm

I–I 258 pm

So, in line with these trends is the use of I F I as a relatively mild flaunting agent in organic chemistry. So, as a result what happens 1 can use I F I as a relatively mild flaunting agent in organic chemistry. Some of these inter halogen compounds can also undergoes ionization for example, let us consider I F 5.

Although ClF 5 does not form stable complexes with alkyl metal fluorides at 298 kelvin, but does react with cesium fluoride or tetramethyl ammonium fluoride at low temperature to give salts containing ClF 6 plus ions. I F 6 plus can also be made by treating I F 7 with fluoride acceptors for example, if you take I F 7 treat with a fluoride acceptor such as arsenic penta fluoride or penta fluro arsine in it forms I F 6 plus cation.

ClF 6 plus and BrF 6 plus must made from cl F 5 or B r F 5 using in extremely powerful oxidizing agent because ClF 7 and B r F 7 are literally not know the use of KrF plus to oxidize bromine 5 and 7 is quite common for example, let us take KrF salt and treat this 1 with BrF 5 it leads to the formation of as I said B r F 6 plus and A s F 6 minus plus krypton.

So, this is how one can generate a cationic inter halogen ions. Let us look into poly halogen cations ok. So, we several homonuclear poly halogen cations are also known for example, B r 2 plus, I 2 plus I 3 plus B r 3 plus of course, C l 3 plus and B r 5 plus as well as I 5 plus of course, I 4 2 plus is also known, and I 7 plus exists, but it is not well characterized cations such as B r 2 plus I 2 plus can be obtained by oxidation of the corresponding halogen.

For example if you take B r 2 and if you treat this 1 with SbF 5 in presence of BrF 5 it gives B r 2 plus and Sb 3 F 16 minus o similarly iodine on treatment with S 2 O 6 F 2 in presence of HSO 3 F it gives minus.

So, in case of these compounds here Br distance is 215 picometer and in case of iodine compound corresponding iodine compound I distance is 258 picometer. The cations are paramagnetic and I 2 plus dimmers at 193 Kelvin to give I 4 2 plus the structure has been determined for the salt.

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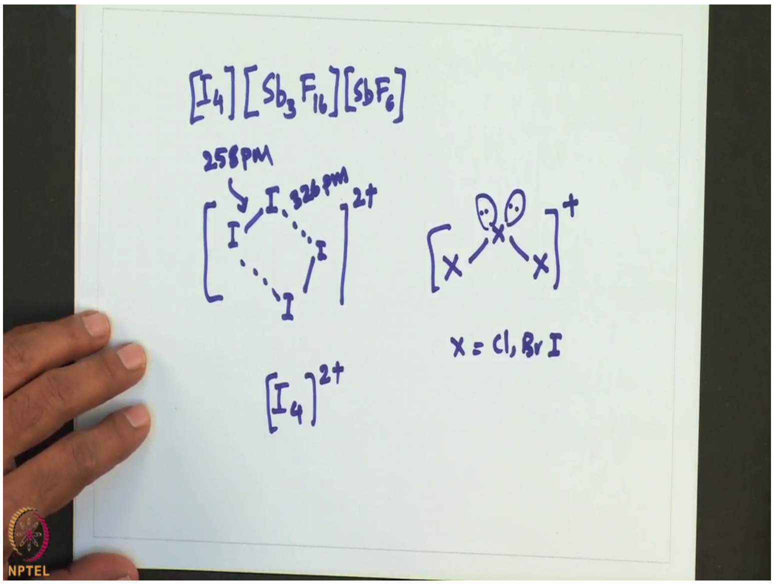

I 4 S b 3 F 16 S b F 6 here there is a significant cation anion interaction in this there the cation C l 3 plus B r 3 plus and I 3 plus are bent as expected from v s e p r theory and the x x bond lengths are similar to those in gaseous x 2.

For example you consider I 2 there is some interaction like this and here it is 3 26 pico meter whereas, this distance is 258 picometer in this of course, this is I 4 2 plus, in case of show a this 1 where x can be chlorine, bromine or iodine plus.

Of course here one can see the lone pairs will be there. So, it is a bend structure (Refer Time: 25:05) speed that is all and B r 3 plus I 3 plus can be synthesized again using A s F 5.

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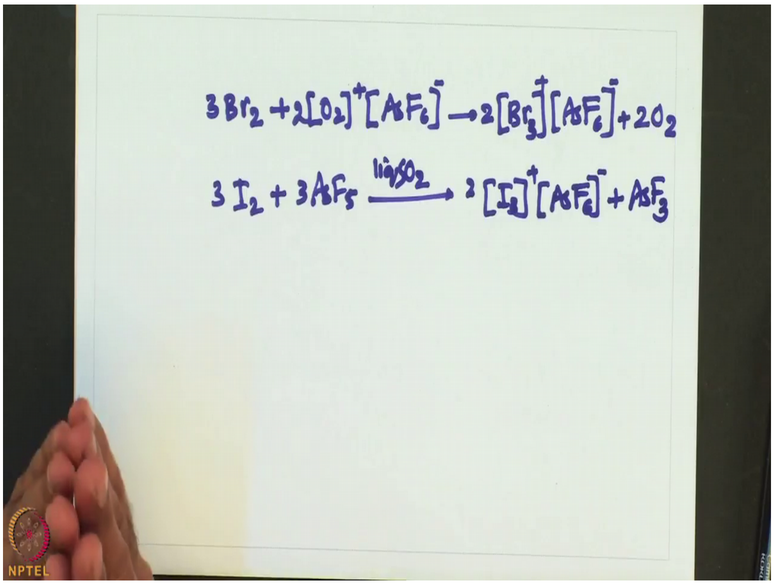

$$3Br_2 + 2[O_2]^+[AsF_6]^- \rightarrow 2[Br_3]^+[AsF_6]^- + 2O_2$$

$$3I_2 + 3AsF_5 \xrightarrow{liq.SO_2} 2[I_3]^+[AsF_6]^- + AsF_3$$

For example 3 Br 2 plus gives 2 o 2 or 3 I 2 plus 3 S F 5 in liquid sulfur dioxide it gives I 3 plus A s F 6 minus plus A s F 3 ok. Uses of higher concentrations of I 2 in the reaction between I 2 and A s F 5 reaction leads to the formation of I 5 plus as 1. So, even using extremely power full oxidizing agents such as O 2 plus it has not possible for to obtain the free C l 2 plus ion by oxidizing C l 2 of source here because of little higher electro negativity its seems it not possible ok.

So, I have given the some examples of both cations and anions of interhaolgen species.

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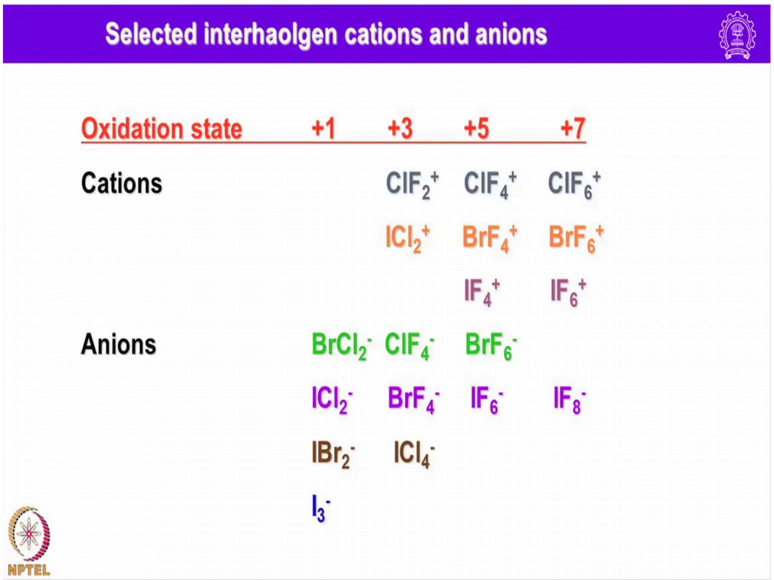

Selected interhaolgen cations and anions

Oxidation state	+1	+3	+5	+7
Cations		ClF_2^+	ClF_4^+	ClF_6^+
		ICl_2^+	BrF_4^+	BrF_6^+
			IF_4^+	IF_6^+
Anions	$BrCl_2^-$	ClF_4^-	BrF_6^-	
	ICl_2^-	BrF_4^-	IF_6^-	IF_8^-
	IBr_2^-	ICl_4^-		
	I_3^-			

One can see the existence of these cations and anions in plus 1 plus 3 plus 5 as well as plus 7 oxidation states for example, you can see here c l F 2 plus C l F 4 plus and C l F 6 plus and similarly I C l 2 B r F 4 B r F 6 plus and I F 4 plus I F 6 plus and of course, in case of anions also we can see here.

Of course, by just looking to the charge, considering the minus 1 for peripheral species you should be able to determine the oxidation state of the central haolgen atom or central halide ion.

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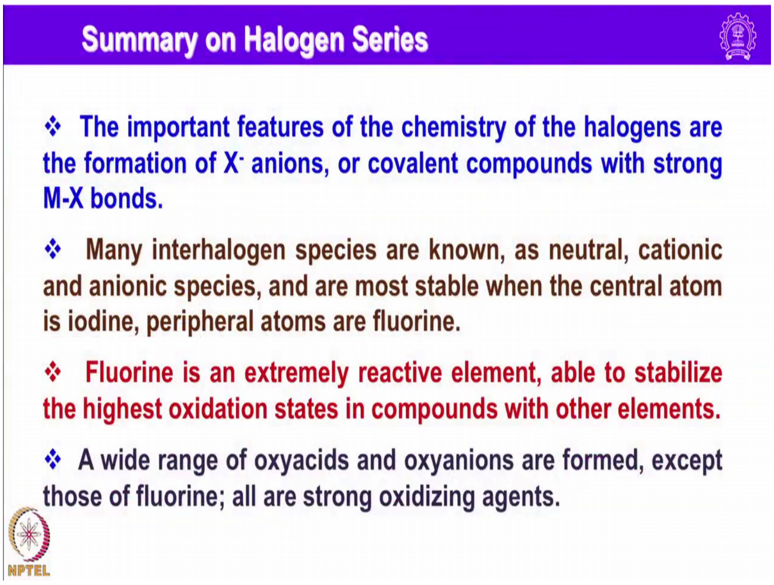

Summary on Halogen Series

- ❖ The important features of the chemistry of the halogens are the formation of X^- anions, or covalent compounds with strong M-X bonds.
- ❖ Many interhalogen species are known, as neutral, cationic and anionic species, and are most stable when the central atom is iodine, peripheral atoms are fluorine.
- ❖ Fluorine is an extremely reactive element, able to stabilize the highest oxidation states in compounds with other elements.
- ❖ A wide range of oxyacids and oxyanions are formed, except those of fluorine; all are strong oxidizing agents.

So, let me summaries the chemistry of group 17 elements, the important feature of the chemistry of the halogens or the formation of halide anions or covalent compounds with string M to X bonds, where m can be a main group element or a trans element many inter halogens species are known as neutral cationic and anionic species and are most stable when the central atom is iodine and peripheral atoms are fluorine; that means, I F 3, I F 5 I F 7 are much more stable compared to ClF 3 of BrF 3 like that.

Interhaolgen compounds are ideal examples to arrive at various geometries using valence electron pair repulsion theory of course, while discussing valence shell electron pair repulsion theory, I have given several examples of interhaolgen spices.

Fluorine is an extremely reactive element able to stabilize the highest of oxdation states in compounds with other elements. A wide range of oxoacids and oxyanions are formed except those of fluorine all are strong oxidizing agents this I conclude that the discussion on the chemistry of group 17 elements.

in my next lecture I will be discussing the chemistry of group 18 elements, only 2 more aspects will be left they chemistry of group 12 elements. That is zinc cadmium, mercury and then the organometallic chemistry of main group elements with this thank you very much and see you in my next lecture.