

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

**Lecture – 54**  
**Chemistry of Group 18 Elements**

Welcome to MSB lecture series on the chemistry of main group elements, today I am going to discuss on group 18 elements. Of course, we have about 6 elements in the series started from helium, neon, argon, krypton, xenon and radon the valence shell electronic configuration is  $ns^2 np^6$ ; that means, octet is completed and in fact, most of the elements in the periodic table which come left in the groups have a tendency to have the electronic configurations of noble gases.

And this we call it as octet in case of s and p block elements; because all of them have a tendency to have  $s^2 p^6$  or  $ns^2, np^6$  electronic configuration. Noble gases or inert gases have that electronic configuration and as a result they are very very stable having very high ionization energy. So, the noble gases have also been called as the rare gases and as we know they are also called as inert gases.


(Refer Slide Time: 01:29)

**The Group 18 (Noble Gas) elements**

- The noble gases have also been called the rare gases, and the inert gases.
- None of the names is particularly suitable.
- With extensive chemistry, xenon is not inert, and argon is almost 30 times more abundant than carbon dioxide in air

|    |    |    |
|----|----|----|
|    | 17 | 18 |
|    |    | He |
| F  |    | Ne |
| Cl |    | Ar |
| Br |    | Kr |
| I  |    | Xe |
| At |    | Rn |

$[ns^2np^6]$



Of course now none of the names it appears are particularly a suitable with extensive chemistry xenon is not inert, and argon is almost 30 times more abundant than carbon dioxide in the air try to know a little bit more about this group 18 elements the greater

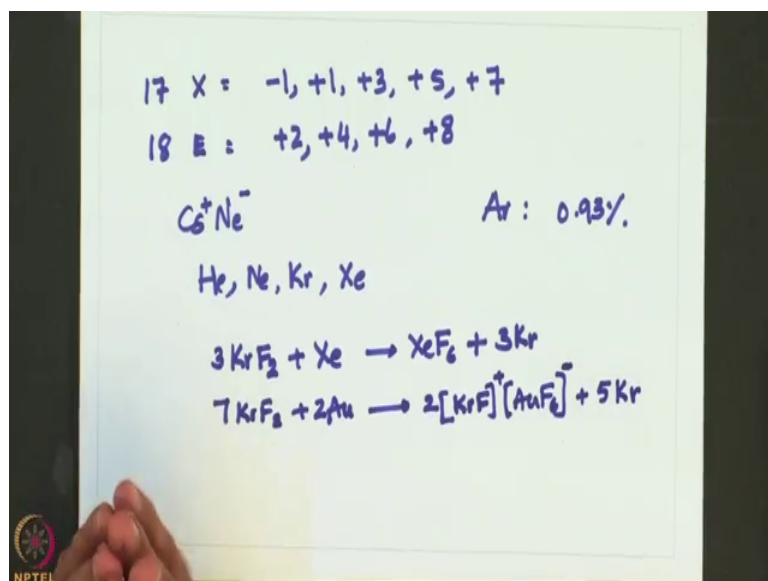
reactivity of xenon compounds compared to the other group 18 elements of course, only other element that known to react is krypton. So, xenon shows greater reactivity, and the stability of xenon compounds containing electronegative elements such as oxygen and fluorine, the reactivity of noble gas flow rates as fluoride ion donors and acceptors. In fact, it is known that inert gases are group 18 elements possess extremely high ionization energy, as a result initially it was assumed that they are not suitable for making chemical compounds the first xenon compound was synthesized in 1962.

Since then the chemistry of xenon is quite extensive, a few compounds of krypton have also been reported. The chemistry of main group gas compounds are analogous to those of heavier group 17 elements and VSEPR theory is a very powerful technique for rationalizing and predicting the shapes of many noble gas compounds, which have relatively large number of electron pairs in the valence shell of the central atom. Noble gases have filled shells that are  $ns^2 np^6$  completely filled having 8 electrons. So, in order to form chemical compounds, electrons must be promoted into the next shell.

So, depending on the number of electrons promoted compounds of the noble gases in oxide states plus 2 plus 4 plus 6 and plus 8 have all been synthesized, just if you recall the inter halogen compounds. Group 17 elements show plus 1 plus 3 plus 5 and plus 7 apart from minus 1 oxide state whereas, group 18 element shows plus 2 plus 4 plus 6 plus and plus 8 it is very simple if you just write the electronic configuration, and just promote 1 electron at a time to the higher shell.

You understand why inert gases are group 18 elements shows plus 2 plus 4 and plus 6 and plus 8 and so, on whereas, inter halogen compounds are halogens show plus 1 plus 3 plus 5 plus 7 it has to do with the electronic configuration, that is the  $ns^2 p^5$  plus  $ns^2 p^6$ . With increase in the atomic size the outer electrons are easily removed and there is a decrease in first ionization energy.

(Refer Slide Time: 04:46)



So, as a result there are many xenon compounds, but a few for krypton and none have been isolated so far argon inter halogen compounds halides show minus 1, plus 1, plus 3, plus 5, and plus 7 whereas, group 18 gases show plus 2, plus 4, plus 6, and also plus 8 oxidation states. I will come back to this one later all compounds tend to be strong oxidizing agents and the fluorides are also very powerful fluorinating agents.

The formation of anionic noble gas compounds such as cesium neonide with electropositive metal is an intriguing possibility though none has yet been isolated. Of course, this was reported in journal of chemical education in 1988, if you are curious to know that historical developments in noble gas chemistry.

(Refer Slide Time: 05:57)

- All compounds tend to be strong oxidizing agents, and the fluorides are also powerful fluorinating agents.
- The formation of anionic noble gas compounds (such as Cesium neonide,  $\text{Cs}^+\text{Ne}^-$ ) with electropositive metals is an intriguing possibility, though none has yet been isolated.

G. H. Purser, *J. Chem. Educ.*, 1988, 65, 119

- If you are curious to know the historical developments in noble gas chemistry.

See the ref.: P. Laszlo and G. I. Schrobilgen, *Angew. Chem. Int. Ed. Engl.* 1988, 27, 479.

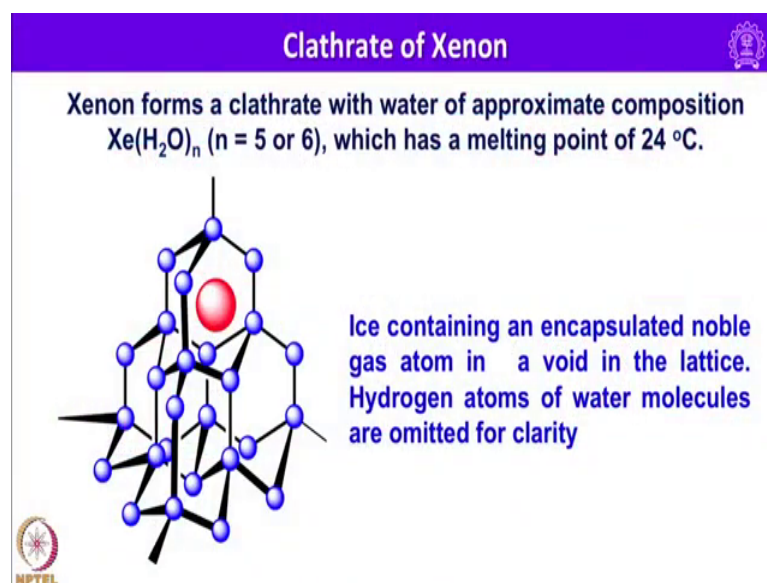


You can look into this article here, I have shown both the journal of chemical education as well as the Angew Chem international edition paper, in which you can look into the information if you are more curious to know about some of these unnamed noble gas compounds and also the historic development in noble gas chemistry. So, all of the elements exist as highly un reactive mono atomic gases with very low boiling points, argon is the most abundant comprising of 0.93 percent of the atmosphere, helium neon and krypton and xenon are trace constraints of air all isotopes of radon or radioactive and are formed naturally from the decay of heavy radioisotope.

Such as those of radium and uranium noble gas crow threads in 1920s and 1930s there was considerable interest in materials formed between noble gases, particularly those of argon, krypton and xenon and strongly hydrogen bonding compounds such as water and polyphenols. Later, it was shown that they are not actually chemical compounds, but their inclusion compounds known as clathrates; where the gas atoms occupy voids in the hydrogen bonded lattice of the host compound when the host is crystallized and their noble gas atmosphere.

For example, you take water or polyphenols and crystallize under a positive pressure of noble gases one can get inclusive compounds or noble gas clathrates; they are not actually in the compounds with a chemical bond ok.

(Refer Slide Time: 07:57)



So, for example, I have shown here a xenon forms a clathrate with water of approximate composition  $\text{Xe}(\text{H}_2\text{O})_n$ , time that is  $n$  equals 5 or 6 which has a melting point of  $24^\circ\text{C}$ . So, ice containing an encapsulated noble gas atom in a void in the lattice yeah it was I have shown here. So, hydrogen atoms of water molecules are omitted for clarity just I have shown here oxygen, and you can see here this group 18 element xenon sitting here in the void.

So, noble gas halides are quite well known, they are important class of compounds fluorine is the most electronegative element and is able to stabilize the highly oxidizing noble gas compounds, most of them are essentially fluorides. The worst majority of compounds are fluorides of xenon a few of krypton are also known as I said, though some chemistry of radon is known hampered by it is radioactivity and availability in very small or trace amounts.

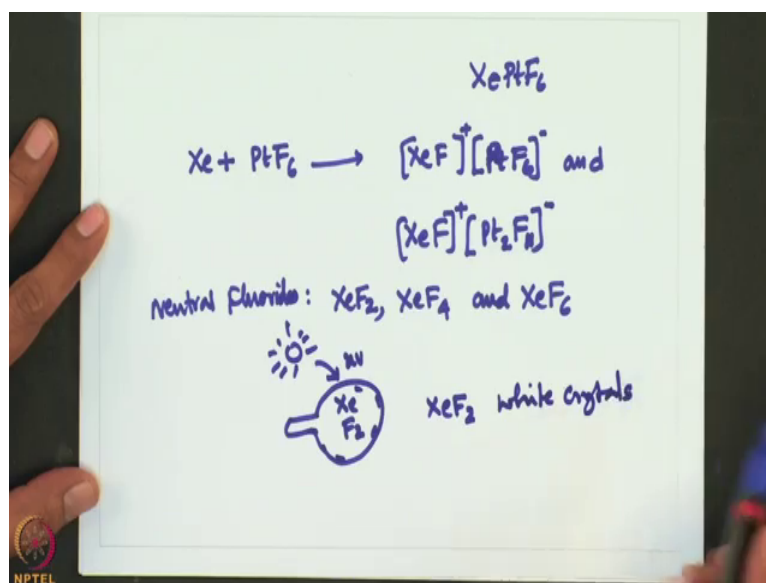
So, noble gases are used as lower temperature refrigerants, to provide an inert atmosphere and liquid xenon has found applications as an extremely unreactive solvent. So, let us look into krypton difluoride, only known halide is krypton difluoride, synthesized by passing an electrical discharge through fluorine krypton mixture.

So, krypton difluoride is a very powerful fluorinating agent and is more reactive than xenon difluoride. So, it will oxidize xenon to xenon hexafluoride and also a metallic gold to gold hexafluoride anion. Example  $3\text{KrF}_2 + \text{Xe} \rightarrow \text{XeF}_6 + 3\text{Kr}$ ;  $7\text{KrF}_2 + \text{Au} \rightarrow \text{AuF}_6^- + 7\text{Kr}$

2 plus 2 Au gives 2 KrF plus now krypton is in plus at 2 axon state Au F 6 minus plus 5 krypton, you can see here gold is in plus 5 oxidation state.

Now, let us look into xenon fluorides, a xenon fluoride is Xe PtF 6 was the first noble gas compound to be synthesized ok.

(Refer Slide Time: 10:50)



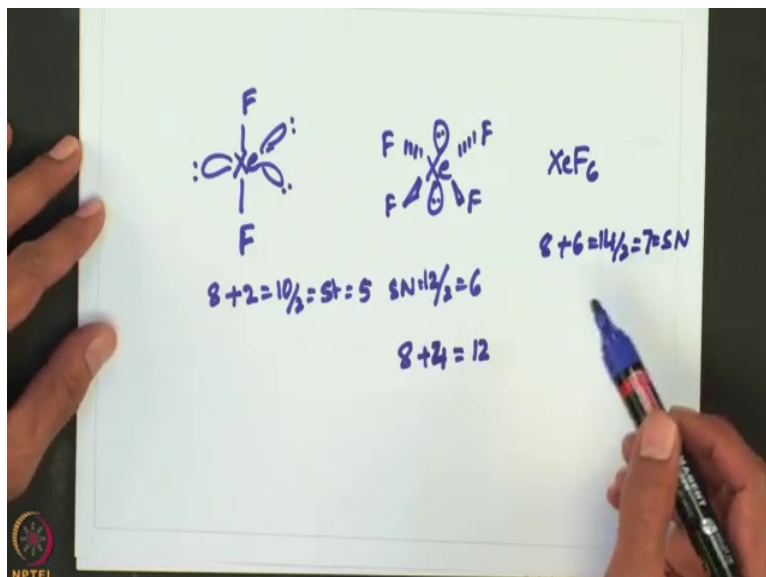
By reaction of xenon with strong oxidant such as PtF 6 and it was later shown to be probably a mixture of Xe F plus and P t F 6 minus. So, that is xenon plus P t F 6 which was shown as Xe F plus and P t F 6 minus and also Xe F plus and Pt 2 F 11 minus. So, xenon forms 3 neutral fluorides, xenon difluoride, xenon tetrafluoride and with xenon hexafluoride by the reaction of fluorine and xenon under different reaction conditions.

Simplest method involves exposing a fluorine xenon mixture in a dry glass bulb to sunlight colorless crystals of X e F 2 r deposited at the walls of the flask what you can do is you can take a tube like this sealed 1 containing xenon and F 2 shine UV light that is from sun.

So, it gives Xe F 2 in the sides here as white crystals ok. The sunlight causes dissociation of the relatively weaker effect bond in F 2 to form f atoms which then react with xenon. With larger ratios of fluorine to xenon higher temperature and higher pressure one can make Xe F 4 as well as Xe F 6. If you are curious to know the structure and geometries

of xenon fluorides, of course, you can always use vsepr theory very effectively to arrive at the geometry and shapes of xenon fluorides.

(Refer Slide Time: 13:47)



For example if you take xenon difluoride it is linear whereas, the geometry is trigonal bipyramidal.

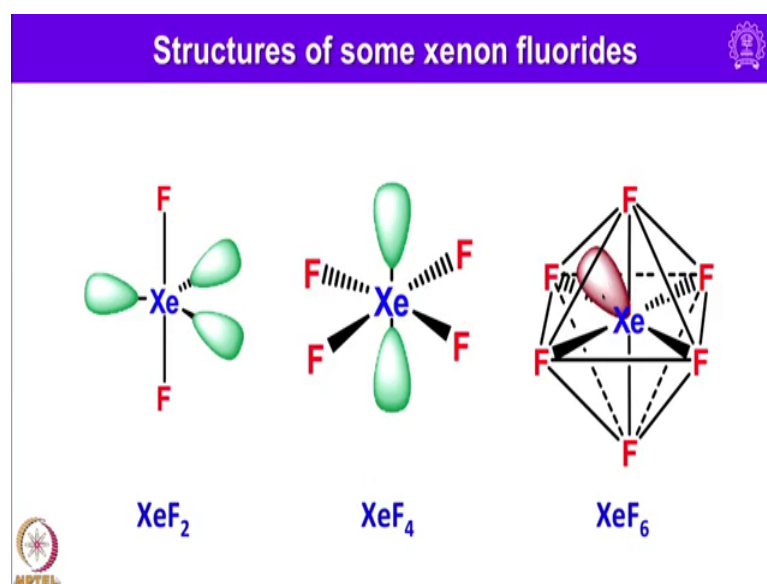
Basically, we have 8 electrons are coming from this 1 and 1 each 2 electrons are coming. So, we have 10 electrons by 2 because steric number is 5, 2 bonded pair and 3 lone pair best geometry would be trigonal bipyramidal ok. So, similarly 1 can write for Xe F 4. So, Xe F 4 if you take again 8 plus 4 12 electrons are there.

If 12 electrons is the steric number that is 2 equals 6 4 bonded pairs are there and they are have to be 2 lone pairs, and structure has to be octal hedral and the shape has to be planar. So, here 8 electrons are from xenon plus 2 electrons are from 4 electrons are from 4 fluorine atoms is 12. So, 12 with the total number of electrons there steric number is 6. So, you have this octahedral geometry and planar shape when you consider Xe F6.

So, here 8 plus 6 because 14 electrons are there 14 by 2 equals 7 is the steric number. So, here 1 lone pair is there. So, this one lone pair occupies 1 of the triangular faces of octahedral so; that means, essentially it becomes a capped octal hedral geometry, but here it is delocalizing oriented octahedral geometry as a result it appears slightly distorted octahedral structure. So, Xe F 6 is fractional in the gas phase. So, interchanging

between structures where the lone pair points through the center of any F e 3 triangle as I mentioned ok. So, since the lone pair is in a spherically in activist orbital what happens? It does not appear like typically a capped octahedral structure, but it appears like a slightly distorted octahedral molecule yeah.

(Refer Slide Time: 16:18)

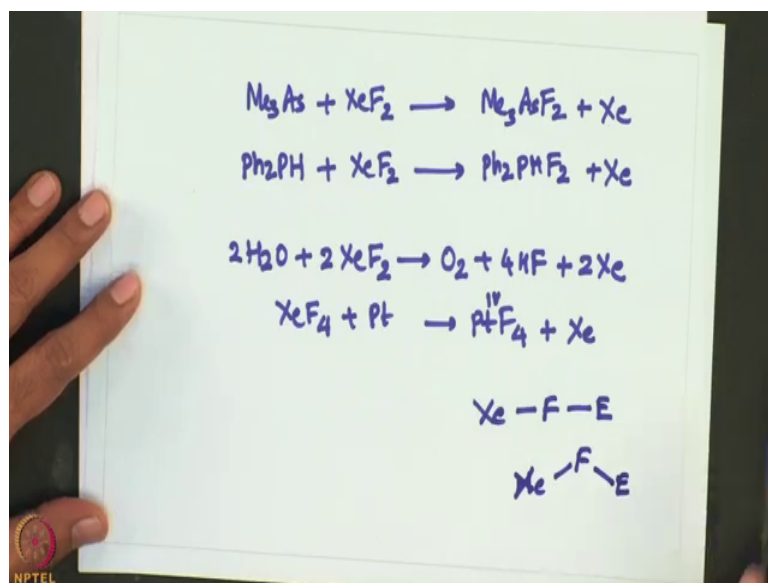


Of course I wrote I am showing you here the structures here you can see X e F 2 now also you can see X e F 4 and also you can see X e F 6 here this lone pair is represented here in this slope here. So, all of these xenon fluorides are powerful fluorinating agents, able to oxidize a wide range of compounds. In many cases X e F 2 is a very selective oxidant able to oxidize the central hetero atom of a main group compound like arsenic phosphorus and etcetera.

But not the organic substituents bonded to it for example, if methyl or phenyl groups are there they are not getting fluorinated only the central atom is getting fluorinated let me write couple of examples.



(Refer Slide Time: 17:00)



For example if I take trimethyl arsine, and treat with the  $\text{XeF}_2$  only here arsine is getting fluorinated to form penta valent penta coordinated trimethyl difluoride arsine. Similarly, if diphenyl phosphine is treated with xenon difluoride; again here phosphorus getting fluorinated.

So, we get  $\text{Ph}_2\text{PHF}_2$  so, the plus xenon.  $\text{XeF}_2$  also oxidizes water to oxygen while  $\text{XeF}_4$  can oxidize platinum metal  $\text{PtF}_4$ . So, why we say a oxidation of oxygen in water? Because if we just look into water oxygen is in 2 minus state, and in when it is decomposed and we get oxygen is in 0 valence state essentially it is oxidized oxidation of oxygen if water is dissociated that broken off.

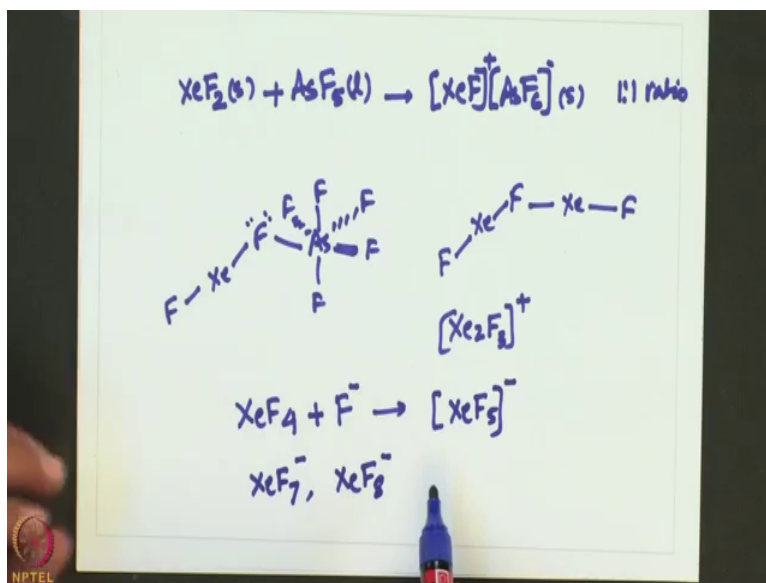
So, here xenon difluoride oxidizes water to oxygen while  $\text{XeF}_4$  can oxidize even platinum metal to platinum tetra fluoride. Similarly if you take  $\text{XeF}_4$  and treat this one with platinum metal it gives platinum  $\text{PtF}_4$  with platinum is in plus 4 state plastic xenon. Noble gas fluorides can react with fluoride and donors as well as acceptors, and the chemistry is quite extensive. So, noble gas fluorides react with strong fluoride and acceptor such as group 15 pentafluoro they reduce of arsenic antimony bismuth and also tantalum ruthenium and platinum xenon difluoride forms the greatest number of compounds.

By this type of reaction followed by  $\text{XeF}_6$  and  $\text{XeF}_4$  and  $\text{KrF}_2$  krypton difluoride forms many similar compounds, while transferring the fluorides can be fully transferred

to the Lewis acid that is  $\text{XeF}_2$  for example,  $\text{XeF}_2 + \text{AsF}_5 \rightarrow [\text{XeF}]^+[\text{AsF}_6]^-$  (s) 1:1 ratio  
 species, but in most cases fluorine is only partially transferred resulting in compounds having X-F-E bridges so, fluoride bridges.

So, here we have a fluoride bridge so; that means, essentially something like this in all these compounds where there is a partial transfer of fluoride. So, different types of cations and anions are formed depending on the stoichiometry of noble gas fluoride.

(Refer Slide Time: 20:28)

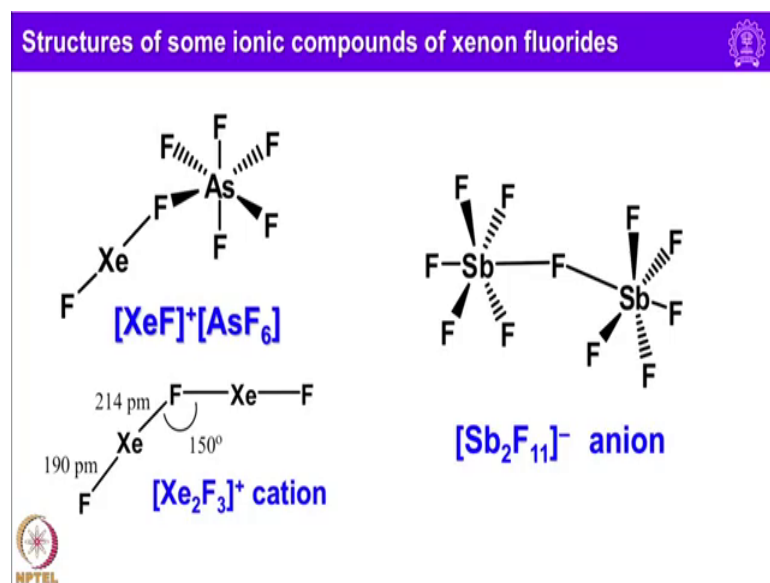


For example  $\text{XeF}_2$  taking solid and treat this one with again fluoride acceptor it gives  $\text{XeF}^+ \text{AsF}_6^-$  this is solid of course, this 1 is to 1 ratio ok.

So, what would happen when 1 is to 2 ratio is used. So, we can have more of them for example, I will write some of the structures here yeah F you can see here partial transferring is there and this is  $\text{Xe}_2\text{F}_3^+$ ,  $\text{AsF}_6^-$  and also. So, we can also have a diametric species  $\text{Sb}_2\text{F}_{11}^-$  anion noble gas fluorides can act as fluoride acceptors or donors to give anions or cations I already mentioned let me show you a couple of reactions here.

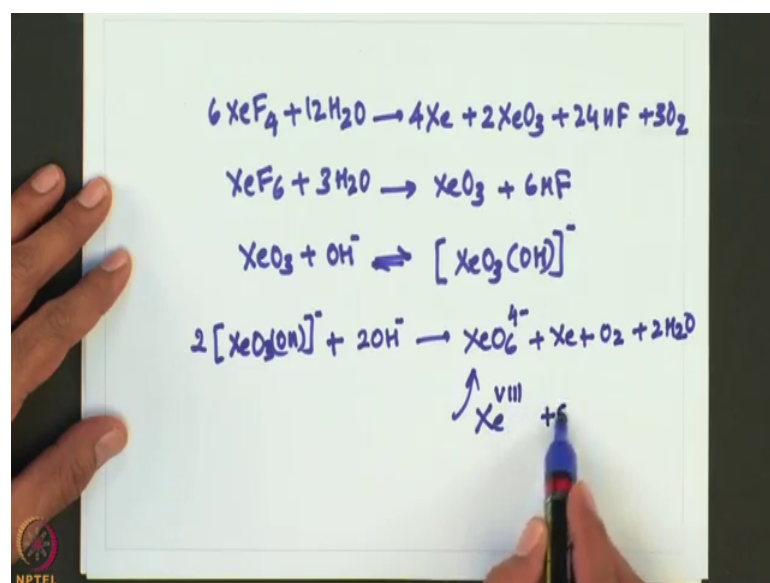
For example,  $\text{XeF}_4$  when it is treated with fluoride ion donors such as cesium fluoride it forms xenon pentafluoride anion similarly  $\text{XeF}_7^-$  minus  $\text{XeF}_8^-$  minus are known they are obtained from  $\text{XeF}_6$  and  $\text{XeF}_7$  by adding 1 or 2 fluoride ions the structures I have shown here for  $\text{XeF}^+ \text{AsF}_6^-$ .

(Refer Slide Time: 22:34)



Now, so Xe 2 F 3 plus and here this for Sb 2 F 11 anion so, always whenever this halides are bridging you should never write in the straight and it should be at an angle, that angle will be much closer to the tetrahedral angle because each bridging die bridging halide ion has 2 lone pairs intact on it for example, in this case you have 1 lone pair here and 1 lone pair here. So, xenon action coupons are also quite known they result from the hydrolysis of the fluorides such as the Xe F 4 and Xe F 6 for example, let us take xenon tetra fluoride and try to add water to hydrolyze it.

(Refer Slide Time: 23:28)

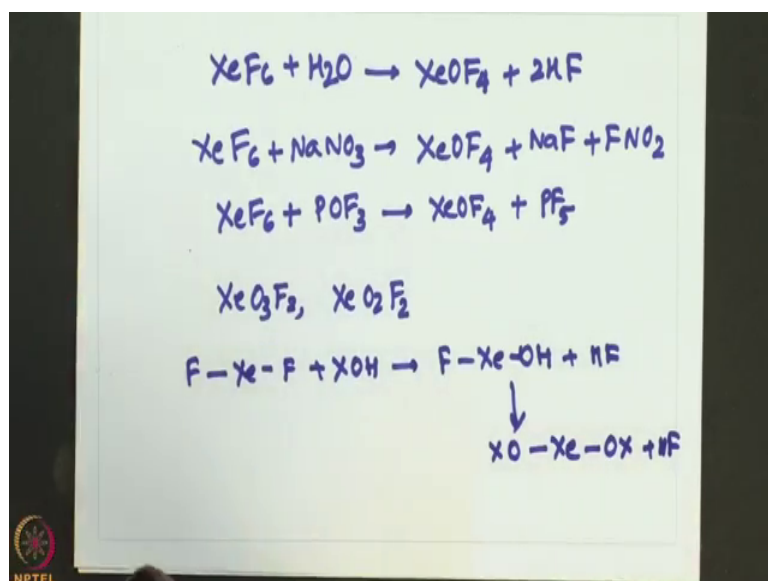


Similarly, if you take a Xe F<sub>6</sub> and treat this 1 with water; that undergoes hydrolysis to form xenon oxide plus 6 HF.

So, in this in both of course, here xenon is in plus 6 oxidation state ok. So, XeO<sub>3</sub> is a highly explosive white solid, soluble in the water in strong alkaline solution XeO<sub>3</sub> behaves as a weak acid giving xenate 6 anion. So, for example, XeO<sub>3</sub> when it is treated with OH minus it gives xenate anion.

So, xenate anion is unstable in aqueous solution and undergoes a disproportionation reaction to give xenon gas and the xenate anion with xenon in plus 8 oxygen state and that is the XeO<sub>6</sub><sup>4-</sup> which contain xenon in plus 8 oxygen state for example, if you take XeO<sub>3</sub> OH anion in aqueous solution it forms XeO<sub>6</sub><sup>4-</sup> plus xenon plus O<sub>2</sub> plus 2 H<sub>2</sub>O. So, here xenon is in it is essentially xenon is in plus 8 oxidation state the controlled reaction of xenon hexafluoride with water will gives xenon oxy fluoride.

(Refer Slide Time: 25:59)

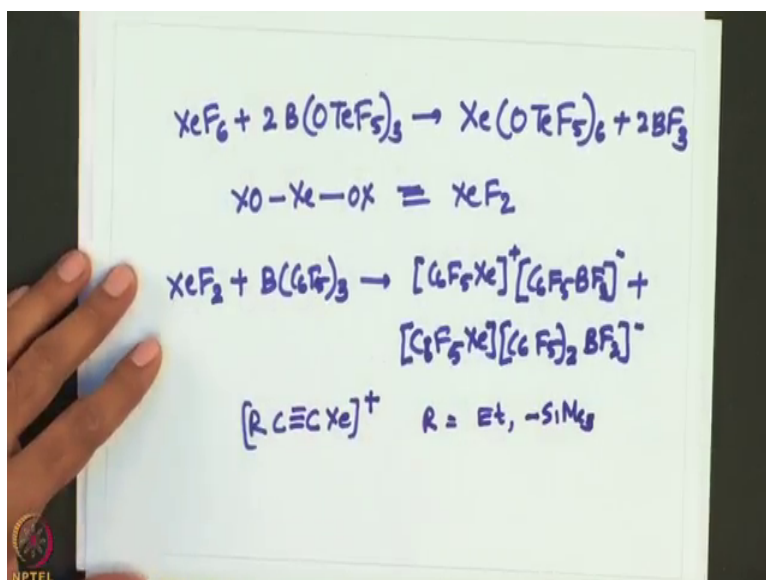


Now, for example, Xe F<sub>6</sub> plus water 1 equivalent of water gives Xe o F<sub>4</sub> plus 2 HF Xe F<sub>6</sub> also reacts with sodium nitrate to give xenon oxy fluoride plus N a F plus FNO<sub>2</sub> or reaction of Xe F<sub>6</sub> with phosphorus oxy fluoride gives Xe OF<sub>4</sub> plus PF<sub>5</sub> phosphorus is getting reducer the reaction of Xe F<sub>6</sub> with Na<sub>4</sub> Xe O<sub>6</sub> gives the oxy fluoride Xe O F<sub>4</sub> and XeO<sub>3</sub> F<sub>2</sub> and also Xe O<sub>2</sub> so; that means, using 1 of these methods 1 can also prepare a XeO<sub>3</sub> F<sub>2</sub> and XeO<sub>2</sub> F<sub>2</sub>.

It is very interesting to look into the structures and geometries and shapes of these molecules you can try these things at home. So, other xenon oxygen compounds can be formed from xenon fluoride xenon tetra fluoride or xenon hexafluoride by substitution of 1 or more fluorides by reaction of strong oxy acids, such as triflic acid, trifluoromethanesulfonic acid with the elimination of HF 1 example I will show you.

So, for example,  $\text{XeF}_6$  with  $\text{XOH}$  gives  $\text{XeOF}_5$  plus  $\text{HF}$  ok. So, of course, this can also give  $\text{XeO}_3$  plus  $\text{HF}$  alternately fluoride exchange yields analogous products. So, let me give you a couple of more reactions here.

(Refer Slide Time: 28:21)



For example  $\text{XeF}_6$  plus this boron compound  $\text{OTeF}_5$  thrives gives  $\text{Xe(OTeF}_5)_6$  plus  $2 \text{BF}_3$ .

So, the compounds have similar shapes to the fluorides for example, if we consider this  $\text{XeO}_3$ . So, this is very similar to  $\text{XeF}_2$  having linear geometry xenon and krypton compounds with bonds 2 elements other than 1 f are also known for example,  $\text{XeF}_2$  when it is treated with  $\text{C}_6\text{F}_5\text{B}$ , it gives  $\text{C}_6\text{F}_5\text{Xe}$  plus  $\text{C}_6\text{F}_5\text{BF}_3$  minus plus  $\text{C}_6\text{F}_5\text{Xe}$  and  $\text{C}_6\text{F}_5$  twice  $\text{BF}_2$  minus so; that means, all current species of the type also known ok.



Where R can be a range of non flaunted groups such as where (Refer Time: 00:00) can be where ethyl group or SiMe 3 group extensive organic chemistry is avoided yeah with these kind of compounds.

(Refer Slide Time: 30:25)

Few xenon compounds containing other elements are:

$$[\text{C}_6\text{F}_5\text{Xe}]^+ + \text{Cl}^- \longrightarrow \text{C}_6\text{F}_5\text{XeCl}$$

The  $[\text{C}_6\text{F}_5\text{Xe}]^+$  cation in MeCN solution get solvated to give  $[\text{C}_6\text{F}_5\text{Xe}(\text{NCMe})]^+$ ; which has a linear geometry




So, you can see here in this slide how this compound reacts with chloride to form a neutral compound and also 1 can also see the formation of xenon to carbon bond here in this one pentachlorophenol derivative ok.

(Refer Slide Time: 30:38)

### Uses of Noble gas elements

- Helium is used as an inert gas and as a light source in lasers and electric discharge lamps; liquid helium is a very low temperature refrigerant.
- Being very light and non-inflammable, He is used to inflate the tyres of large aircraft, and in balloons including weather balloons.
- Liquid He is an important coolant and is used in highfield NMR spectrometers
- Argon is also used in laboratory inert atmosphere ('dry' or 'glove') boxes for handling airsensitive compounds.
- Neon, krypton and xenon are used in electric discharge signs




So, let me talk about the uses of noble gas elements before I summarize helium is used as an inert gas and as light source in lasers and electric discharge lamps liquid helium is a very low temperature refrigerant, being very light and nonflammable helium is used to inflate the tails of large aircraft and in balloons including weather balloons liquid helium is an important coolant and is used in high field NMR spectrometer, argon is also used in laboratory inert atmosphere or dry boxes for handling air sensitive compounds, neon, krypton and xenon are also used in electric discharge science.

(Refer Slide Time: 31:19)

**Summary on Inert gas elements series**

- Only Xenon shows extensive chemistry and forms compounds such as  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$
- Xenon fluorides act as fluorinating agents and react with both donor and acceptors.
- Xenon compounds undergo hydrolysis reactions
- Compounds containing bonds from Xe to F, O, N and Cl are known and well characterized
- Few compounds of Kr and Rn in their +2 oxidation states are known.
- Compounds of Kr are more reactive than Xe.



So, let me summarize the overall chemistry of group 18 elements only xenon shows extensive chemistry and forms compounds such as xenon difluoride, tetra fluoride and hexafluoride xenon fluorides act as fluorinating agent react with both donor and acceptors xenon compounds; undergo hydrolysis reactions to form oxy fluorides. Compounds containing bonds from xenon to fluorine, oxygen, nitrogen, chlorine and also carbon are well characterized. Few compounds for krypton and radon in their plus 2 other states are also known compounds of krypton are much more reactive than xenon.

So, with this I conclude the chemistry of group 18 elements in my next lecture, I will be discussing about the chemistry of group 12 elements that is zinc, cadmium, mercury and proceed to the organic chemistry of main group elements. Until then have a present reading of the chemistry of main group elements.

Thank you very much.