



# CHEMISTRY

# p-BLOCK ELEMENTS (HALOGEN & NOBLE GASES)

## CONTENTS

Topic	Page No.
Theory	01 – 15
Exercise - 1	16 – 18
Exercise - 2	18 – 19
Part - I : Objective Questions	
Part - II : Assertion/Reasoning	
Exercise - 3	19 – 21
Part - I : JEE (Main) /AIEEE Questions	
Part - II : JEE (Adv.)/ IIT-JEE Questions	
Answer Key	22
JEE-MAIN Practice Test Paper	23 – 25
JEE-MAIN Test Paper Answers	26
JEE-MAIN Test Paper Solutions	26 – 27

### JEE (MAIN) SYLLABUS

Group - 17 : Preparation, properties and uses of chlorine and hydrochloric acid; Trends in the acidic nature of hydrogen halides; Structures of Interhalogen compounds and oxides and oxoacids of halogens.  
Group - 18 : Occurrence and uses of noble gases; Structures of fluorides and oxides of xenon.

### JEE(ADVANCED) SYLLABUS

Isolation/preparation and properties of the following non-metals : Halogens Preparation and properties of the following compounds :  
**Halogens:** Hydrohalic acids, oxides and oxyacids of chlorine, bleaching powder; Xenon fluorides.

# p-Block Elements (Halogens Family and Noble Gases)

## Introduction :

Group 13 to 18 of the periodic table of elements constitute the p-block. The p-block contains metals, metalloids as well as non-metals.

The p-block elements have general valence shell electronic configuration  $ns^2 np^{1-6}$ .

The first member of each group from 13–17 of the p-block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d-orbitals. The first member of a group also has greater ability to form  $p\pi-p\pi$  multiple bonds to itself (e.g.  $C=C$ ,  $C\equiv C$ ,  $N=N$ ) and to element of second row (e.g.  $C=O$ ,  $C=N$ ,  $C\equiv N$ ,  $N=O$ ) compared to the other members of the same group. The highest oxidation of p-block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding)

## Group 17 Elements : The Halogen Family

### Occurrence :

All halogens are very reactive & do not occur in free state.

Element	Abundance	Source
F	544 ppm (13 <sup>th</sup> most abundant element)	<ul style="list-style-type: none"> <li>Main Source : <math>\left[ \begin{array}{l} \text{Fluorspar (CaF}_2) \\ \text{or} \\ \text{Fluorite} \end{array} \right.</math></li> <li>Another Source : Fluoroapatite <math>[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]</math> (Mainly source of P)</li> </ul>
Cl	126 ppm (20 <sup>th</sup> most abundant element)	<ul style="list-style-type: none"> <li>Most abundant compound of Cl : NaCl</li> </ul>
Br	2.5 ppm	<ul style="list-style-type: none"> <li>Bromides occurs in sea water &amp; brine lakes</li> </ul>
I	0.46 ppm	<ul style="list-style-type: none"> <li>Iodides occurs in low conc. in sea water.</li> <li>Better source : Natural brines</li> <li>Impurities (<math>\text{NaIO}_3</math> &amp; <math>\text{NaIO}_4</math>) in Chile salt petre (<math>\text{NaNO}_3</math>)</li> </ul>
At	Radioactive & has a short half-life	<ul style="list-style-type: none"> <li>Do not occur in nature</li> </ul>

### Allotropy :

All the elements of halogen family generally do not show allotropy.

### Atomicity :

All halogens exist as diatomic ( $X_2$ ) molecule.



Atomic & Physical Properties :

S.NO.	Property	F	Cl	Br	I
1.	Atomic Number	9	17	35	53
2.	Atomic Mass/g mol <sup>-1</sup>	19	35.45	79.90	126.90
3.	Electronic configuration General electronic configuration=(ns <sup>2</sup> np <sup>5</sup> )	[He] 2s <sup>2</sup> 2p <sup>5</sup>	[Ne] 3s <sup>2</sup> 3p <sup>5</sup>	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>5</sup>	[Kr] 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>5</sup>
4.	Covalent Radius / pm (F < Cl < Br < I)	64	99	114	133
5.	Ionic Radius X <sup>-</sup> / pm (F < Cl < Br < I)	133	184	196	220
6.	Ionization enthalpy / (kJ mol <sup>-1</sup> ) (F > Cl > Br > I)	1680	1256	1142	1008
♦ Due to increase in atomic size, ionisation enthalpy decreases down the group.					
7.	Electron gain enthalpy / (kJ mol <sup>-1</sup> ) (Cl > F > Br > I)	- 333	- 349	- 325	- 296
♦ Maximum negative electron gain enthalpy in the corresponding period.					
♦ Negative electron gain enthalpy of fluorine < chlorine : Due to small size of fluorine atom. As a result, there are strong inter-electronic repulsions in the relatively small 2p orbitals of fluorine and thus, the extra electron (incoming) does not experience much attraction.					
8.	Distance X -X/pm (F <sub>2</sub> < Cl <sub>2</sub> < Br <sub>2</sub> < I <sub>2</sub> )	143	199	229	266
9.	Enthalpy of dissociation (X <sub>2</sub> )/kJ mol <sup>-1</sup> (Cl - Cl > Br - > F - F > I - I)	158.8	242.6	192.8	151.1
♦ Smaller enthalpy of dissociation of F <sub>2</sub> is due to relatively larger electrons-electrons repulsion among the lone pairs in F <sub>2</sub> molecule.					
10.	Electronegativity (F > Cl > Br > I)	4	3.2	3.0	2.7
11.	Melting point / K (F < Cl < Br < I)	54.4	172	265.8	386.6
12.	Boiling point / K (F < Cl < Br < I) (State at room temp.)	84.9 Gas	239.0 Gas	332.5 Liquid	458.2 Solid
13.	Δ <sub>Hyd</sub> H (X <sup>-</sup> ) / kJ mol <sup>-1</sup> (F > Cl > Br > I)	515	381	347	305
♦ Smaller the ion, higher is the hydration energy.					
14.	E <sup>0</sup> / V (SRP) ; X <sub>2</sub> (g) + 2e <sup>-</sup> → 2X <sup>-</sup> (aq) (F <sub>2</sub> > Cl <sub>2</sub> > Br <sub>2</sub> > I <sub>2</sub> ) (Order of oxidising power)	2.87	1.36	1.09	0.54
♦ More the value of the SRP, more powerful is the oxidising agent.					
15.	Colour (at room temp.)	Pale green yellow gas.	Greenish-yellow gas	Reddish brown liquid	Dark violet solid
16.	Oxidization state	-1	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7

**Chemical Properties**

**Oxidation states and trends in chemical reactivity**

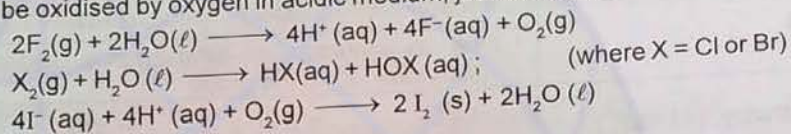
All the halogens exhibit -1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states also. The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms e.g., in interhalogens, oxides and oxoacids.

The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.

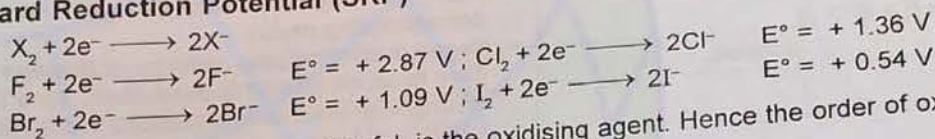
All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F<sub>2</sub> is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reactions of iodine with water is non-spontaneous.

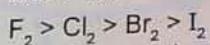
I<sup>-</sup> can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.



**Standard Reduction Potential (SRP)**



More the value of the SRP, more powerful is the oxidising agent. Hence the order of oxidising power is



Since SRP is the highest for F<sub>2</sub> (among all elements of periodic table), it is a strongest oxidising agent.

**Hydration energy of X<sup>-</sup>**

Smaller the ion, higher is the hydration energy.

F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	
515	381	347	305	in kJ/mol

**Anomalous behaviour of fluorine**

The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell. Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogens form a number of oxoacids. Hydrogen fluoride is liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

(i) **Reactivity towards hydrogen** : They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine with increasing atomic number. They dissolve in water to form hydrohalic acids. The acidic strength of these acids increases in the order : HF < HCl < HBr < HI. The stability of these halides decreases down the group due to decrease in bond (H-X) dissociation enthalpy in the order : H-F > H-Cl > H-Br > H-I.

(ii) **Reactivity towards oxygen** : Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF<sub>2</sub> and O<sub>2</sub>F<sub>2</sub>. However, only OF<sub>2</sub> is the thermally stable at 298 K. These oxide are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O<sub>2</sub>F<sub>2</sub> oxidises plutonium to PuF<sub>6</sub> and the reaction is used in removing plutonium as PuF<sub>6</sub> from spent nuclear fuel.

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogen vary from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones. Chlorine oxides, Cl<sub>2</sub>O, ClO<sub>2</sub>, Cl<sub>2</sub>O<sub>6</sub> and Cl<sub>2</sub>O<sub>7</sub> are highly reactive oxidising agents and tend to explode. ClO<sub>2</sub> is used as a bleaching agent for paper pulp and textiles and in water treatment. The bromine oxides, Br<sub>2</sub>O, BrO<sub>2</sub>, BrO<sub>3</sub> are the least stable halogen oxides and exist only at low temperature.

They are very powerful oxidising agents. The iodine oxides,  $I_2O_4$ ,  $I_2O_5$ ,  $I_2O_7$  are insoluble solids and decompose on heating.  $I_2O_5$  is very good oxidising agent and is used in the estimation of carbon monoxide.

- (iii) **Reactivity towards metals** : Halogen react with metals to form metal halides. For e.g., bromine reacts with magnesium to give magnesium bromide.
- (iv) **Reactivity of halogen towards other halogens** : Halogens combine amongst themselves to form a number of compounds known as interhalogen of the types  $AB$ ,  $AB_3$ ,  $AB_5$  and  $AB_7$ , where A is a larger size halogen and B is smaller size halogen.

### Solved Examples

- Ex.1** Although electron gain enthalpy of fluorine is less negative as compared to chloride, fluorine is a stronger oxidising agent than chlorine. Why?
- Sol.** It is due to : (i) low enthalpy of dissociation of F-F bond, (ii) high hydration enthalpy of  $F^-$ .
- Ex.2** Covalent radius of fluorine is 64 pm but the bond length is not equal to 128 pm and that is 143 pm and bond energy is found to be comparable to  $I_2$ .
- Sol.** This may be attributed to  $\ell.p - \ell.p$  repulsions due to small size of F atom.
- Ex.3** Why are halogens strong oxidising agents ?
- Ans.** (i) They have low bond dissociation energy, (ii) They have high electron affinity.
- Ex.4** Fluorine exhibits only -1 oxidation state whereas other halogens exhibit +1, +3, +5 and +7 oxidation state also. Explain.
- Sol.** Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have d orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states also.

### CHLORINE ( $Cl_2$ ) :

#### Preparation :

S.No.	Method	Process	Comments
1.	Laboratory Preparation	$H_2SO_4 + NaCl \rightarrow HCl + NaHSO_4$ $4HCl + MnO_2 \rightarrow MnO_2 + 2H_2O + Cl_2 \uparrow$	<ul style="list-style-type: none"> <li>HCl is purified first through <math>H_2O</math> then through <math>H_2SO_4</math> to remove <math>H_2O</math> dried by <math>CaO</math> &amp; <math>P_4O_{10}</math></li> </ul>
2.	Commercially:		
(i)	By electrolysis of aq. NaCl solution in the manufacture of NaOH	$2NaCl + 2H_2O \xrightarrow{\text{Electrolyte}} 2NaOH + Cl_2 + 2H_2$ $2NaCl \xrightarrow{\text{Electrolyte}} 2Na + Cl_2$	
(ii)	Deacon's process	$4HCl + O_2 \xrightarrow[440^\circ C]{CuCl_2 \text{ Catalyst}} 2Cl_2 + 2H_2O + \Delta$	<ul style="list-style-type: none"> <li>Air is used to oxidize instead <math>MnO_2</math></li> <li>Reaction is reversible</li> <li>Conversion 65%</li> </ul>
(iii)	Electrolysis of Brine	<p><b>Reactions:</b></p> <p>At Anode : <math>2Cl^- \rightarrow Cl_2 + 2e^-</math></p> <p>At cathode : <math>Na^+ + e^- \rightarrow Na</math></p> <hr/> $2Na + 2H_2O \rightarrow 2NaOH + H_2$ <p>Side reactions may also occur if the products mix:</p> $2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$ $2OH^- + Cl_2 \rightarrow 2OCl^- + H_2$ (Hypochlorite) <p>At anode (small extent reaction) :</p> $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	

*p-Block Elements (Halogen & Noble Gases)*



**Properties :**

- (i) It is a greenish-yellow gas with pungent and suffocating odour. It is about 2-5 times heavier than air. It can be liquefied into greenish-yellow liquid which boils at 239 K. It is soluble in water.
- (ii) At low temperature it forms a hydrate with water having formula  $Cl_2 \cdot 8H_2O$  which is in fact a clathrate compound.

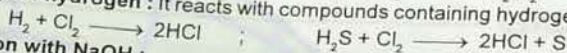
**Reaction with metals :**



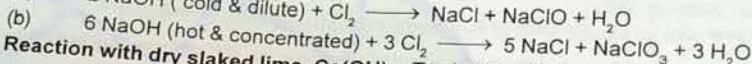
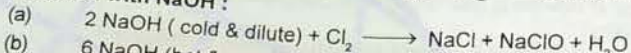
**Reaction with non-metals :**



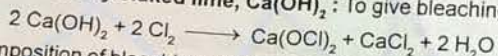
- (iv) **Affinity for hydrogen :** It reacts with compounds containing hydrogen and form HCl.



- (v) **Reaction with NaOH :**



- (vi) **Reaction with dry slaked lime,  $Ca(OH)_2$  :** To give bleaching powder.

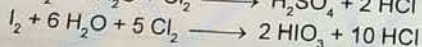
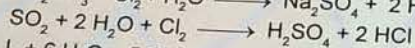
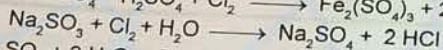
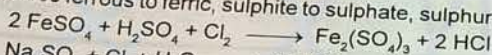


The composition of bleaching powder is  $Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O$

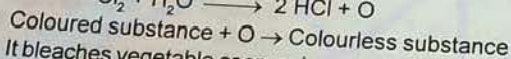
- (vii) **Oxidising & bleaching properties :**

Chlorine dissolves in water ( $Cl_2$  water is yellow) giving HCl (colourless) and HOCl (colourless). Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

- (a) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

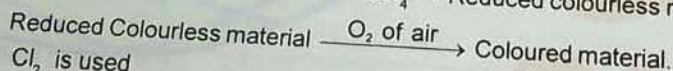
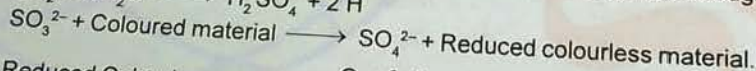
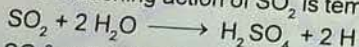


- (b) It is a powerful bleaching agent ; bleaching action is due to oxidation.



It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

- Note :** The bleaching action of  $SO_2$  is temporary because it takes place through reduction.



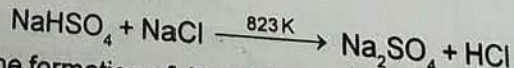
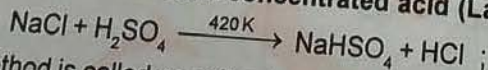
**Uses :**  $Cl_2$  is used

1. for bleaching wood pulp (required for the manufacture of paper and rayon), bleaching cotton and textiles,
2. in the manufacture of dyes, drugs and organic compounds such as  $CCl_4$ ,  $CHCl_3$ , DDT, refrigerants, etc.
3. in the extraction of gold and platinum.
4. in sterilising drinking water and
5. preparation of poisonous gases such as phosgene ( $COCl_2$ ), tear gas ( $CCl_3NO_2$ ), mustard gas ( $ClCH_2CH_2SCH_2CH_2Cl$ ).

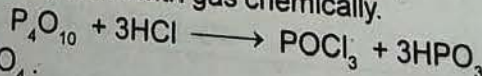
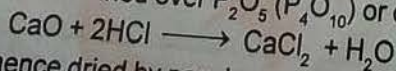
**HYDROGEN CHLORIDE (HCl) :**

**Preparation :**

By heating a halide with concentrated acid (Laboratory method) :



This method is called as salt cake method as it involves the formation of  $NaHSO_4$  (salt cake). HCl cannot be dried over  $P_2O_5$  ( $P_4O_{10}$ ) or quick lime since they react with gas chemically.



HCl is, hence dried by passing through concentrated  $H_2SO_4$ .



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MAIN PHN - 5



*p-Block Elements (Halogen & Noble Gases)*

**Properties :**

- (i) It is a colourless, pungent smelling gases with acidic tastes.
- (ii) It is easily liquefied to a colourless liquid (b.p. 189 K) and freezes to a white crystalline solid (f.p. 159 K).
- (iii) It is quite soluble in water.  
 HCl ionises as below :  $\text{HCl(g)} + \text{H}_2\text{O (l)} \longrightarrow \text{H}_3\text{O}^+ \text{(aq)} + \text{Cl}^- \text{(aq)} ; K_a = 10^7$   
 It aqueous solution is called hydrochloric acid. High value of dissociation constant ( $K_a$ ) indicates that it is a strong acid in water.  
 When three parts of concentrated HCl and one part of concentrated  $\text{HNO}_3$  are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.  

$$\text{Au} + 4 \text{H}^+ + \text{NO}_3^- + 4 \text{Cl}^- \longrightarrow [\text{AuCl}_4]^- + \text{NO} + 2 \text{H}_2\text{O}$$

$$3 \text{Pt} + 16 \text{H}^+ + 4 \text{NO}_3^- + 18 \text{Cl}^- \longrightarrow 3 [\text{PtCl}_6]^{2-} + 4 \text{NO} + 8 \text{H}_2\text{O}$$
 It reacts with ammonia forming white fumes of  $\text{NH}_4\text{Cl}$   

$$\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}$$
- (iv) It decomposes salt of weaker acids.  

$$\text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

$$\text{NaHCO}_3 + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

$$\text{Na}_2\text{SO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2$$

**Uses :**

1. HCl is used in preparation of  $\text{Cl}_2$ , chlorides, aqua regia, glucose, (from corn starch).
2. It is used in medicines, laboratory as reagents, cleaning metal surfaces before soldering or electroplating.
3. It is used for extracting glue from bones and purifying bone black.

**BLEACHING POWDER :**

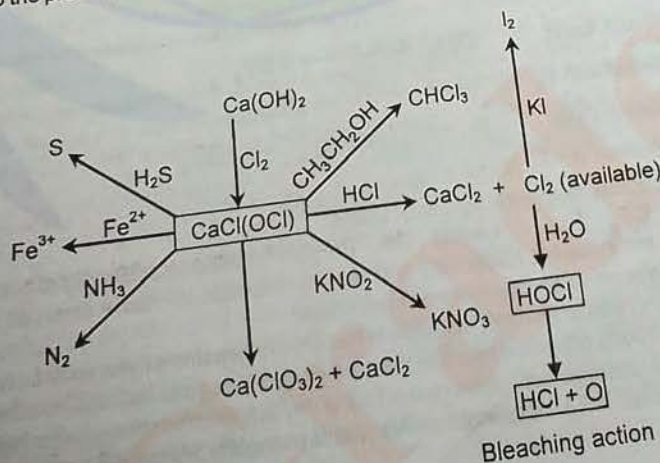
Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.  
 The composition of bleaching powder is  $\text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$ .

**PREPARATION:**



**Properties**

It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.







*p-Block Elements (Halogen & Noble Gases)*

**OXY-ACIDS OF Halogens :**

Fluorine forms only one oxoacid, HOF due to high electronegativity and small size. Other halogens form a number of oxoacids which are stable only in aqueous solutions or in the form of their salts. They can not be isolated in pure form.

Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (III) acid (Halous acid)	-	HOClO (chlorous acid)	-	-
Halic (V) acid (Halic acid)	-	HOClO <sub>2</sub> (chloric acid)	HOBrO <sub>2</sub> (bromic acid)	HOIO <sub>2</sub> (iodic acid)
Halic (VII) acid (Perhalic acid)	-	HOClO <sub>3</sub> (perchloric acid)	HOBrO <sub>3</sub> (perbromic acid)	HOIO <sub>3</sub> (periodic acid)

**Some important order**

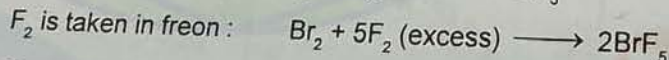
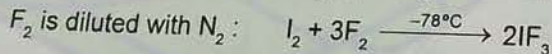
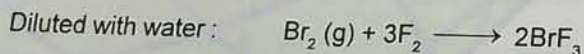
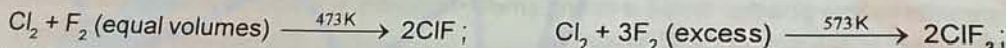
- (a) Acid strength  
(i) HI > HBr > HCl > HF    (ii) HOCl > HOBr > HOI    (iii) HClO<sub>4</sub> > HClO<sub>3</sub> > HClO<sub>2</sub> > HClO
- (b) Oxidising powder  
(i) F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>    (ii) BrO<sub>4</sub><sup>-</sup> > IO<sub>4</sub><sup>-</sup> > ClO<sub>4</sub><sup>-</sup> (According to electrode potential)
- (c) Order of disproportionations  
3 XO<sup>-</sup> → 2X<sup>-</sup> + XO<sub>3</sub><sup>-</sup> (hypohalite ion); IO<sup>-</sup> > BrO<sup>-</sup> > ClO<sup>-</sup>

**Interhalogen compounds :**

We know that halogen atoms have different electronegativity. Due to this difference in electronegativity the halogen atoms combine with each other and give rise to the formation of binary covalent compounds, which are called interhalogen compounds. These are of four types.

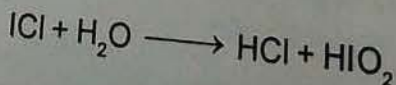
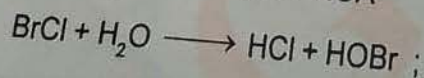
AB	AB <sub>3</sub>	AB <sub>5</sub>	AB <sub>7</sub>
ClF	ClF <sub>3</sub>	ClF <sub>5</sub>	IF <sub>7</sub>
BrF	BrF <sub>3</sub>	BrF <sub>5</sub>	
ICl	ICl <sub>3</sub>	IF <sub>5</sub>	
IF	IF <sub>3</sub>		

**Preparation :**



**Properties :**

- (i) These compounds may be gases, liquids or solids.  
Gases : ClF, BrF, ClF<sub>3</sub>, IF<sub>7</sub>;    Liquids : BrF<sub>3</sub>, BrF<sub>5</sub>;    Solids : ICl, IBr, IF<sub>3</sub>, ICl<sub>3</sub>.
- (ii) All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.
- (iii) The boiling points increases with the increase in the electronegativity difference between A and B atoms.
- (iv) Interhalogen compounds are more reactive than the parent halogens but less reactive than F<sub>2</sub>.
- (v) Hydrolysis : All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when AB), halite (when AB<sub>3</sub>), halate (when AB<sub>5</sub>), and perhalate (when AB<sub>7</sub>) anion derived from the larger halogen.

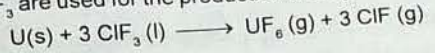




*p-Block Elements (Halogen & Noble Gases)*

**Uses :**

- (i) These compounds can be used as non aqueous solvents.
- (ii) Interhalogen compounds are very useful fluorinating agents.
- (iii)  $\text{ClF}_3$  and  $\text{BrF}_3$  are used for the production of  $\text{UF}_6$  in the enrichment of  $^{235}\text{U}$ .



**Pseudohalogens and Pseudohalides :**

A few ions are known, consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. They are therefore called pseudohalide ions. Pseudohalide ions are univalent, and these form salts resembling the halide salts. For example, the sodium salts are soluble in water, but the silver salts are insoluble. The hydrogen compounds are acids like the halogen acid HX. Some of the pseudohalide ions combine to form dimers comparable with the halogen molecule  $\text{X}_2$ . These include cyanogens  $(\text{CN})_2$ , thiocyanogen  $(\text{SCN})_2$  and selenocyanogen  $(\text{SeCN})_2$ .

Anion	Acid	Dimer
$\text{CN}^-$ cyanide ion	$\text{HCN}$ hydrogen cyanide	$(\text{CN})_2$ cyanogen
$\text{SCN}^-$ thiocyanate ion	$\text{HSCN}$ thiocyanic acid	$(\text{SCN})_2$ thiocyanogen
$\text{SeCN}^-$ selenocyanate ion		$(\text{SeCN})_2$ selenocyanogen
$\text{OCN}^-$ cyanate ion	$\text{HOCN}$ cyanic acid	
$\text{NCN}^{2-}$ cyanamide ion	$\text{H}_2\text{NCN}$ cyanamide	
$\text{N}_3^-$ azide ion	$\text{HN}_3$ hydrogen azide	

**Solved Examples**

**Ex.5** Name the compound which on electrolysis gives fluorine gas at anode.  
**Sol.** Fused anhydrous potassium hydrogen fluoride ( $\text{KHF}_2$ )  
 $\text{CaF}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{CaSO}_4 + 2\text{HF}$ ;  $\text{KF} + \text{HF} \longrightarrow \text{K}[\text{HF}_2]$   $\xrightarrow{\text{electrolysis}}$   $\text{H}_2 + \text{F}_2$   
 On Electrolysis : Cathode :  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$   
 Anode :  $2\text{F}^- \longrightarrow \text{F}_2 + 2\text{e}^-$

**Ex.6** Explain why fluorine forms only one oxoacid, HOF ?  
**Sol.** Due to high electronegativity and small size, it cannot act as central atom in higher oxidation state.

**Ex.7** (a) When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. why ?  
**Sol.** (a) It forms  $\text{H}_2$  gas.  
 $\text{Fe} + 2 \text{HCl} \longrightarrow \text{FeCl}_2 + \text{H}_2$ .  
 Liberation of hydrogen prevents the formation of ferric chloride.  
 (b) Blue litmus change into red due to acidic nature ( $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$ ) but it is bleaching agent also (oxidising agent), therefore, it decolourises the red litmus.

**Ex.8**  $\text{CaOCl}_2$  in aqueous solution changes to  $\text{Cl}_2$ . What is the type of this change ?  
**Sol.**  $\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{Cl}_2$  Redox reaction.

**Ex.9** Give appropriate reasons for each of the following :  
**Sol.** (a) Addition of  $\text{Cl}_2$  to KI solution gives it a brown colour but excess of  $\text{Cl}_2$  turns it colourless.  
 (b) Perchloric acid is a stronger acid than sulphuric acid.  
 (a)  $\text{Cl}_2$  being a stronger oxidising agent than  $\text{I}_2$ , first oxidises KI to  $\text{I}_2$  which imparts brown colour to the solution. But when  $\text{Cl}_2$  is passed in excess, the  $\text{I}_2$  so formed gets further oxidised to  $\text{HIO}_3$  (colourless)  
 $2\text{KI}(\text{aq}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{KCl}(\text{aq}) + \text{I}_2(\text{s})$ ;  $5\text{Cl}_2 + \text{I}_2 + 6\text{H}_2\text{O} \longrightarrow 10\text{HCl} + 2\text{HIO}_3$   
 (b) Oxidation state of Cl in  $\text{HClO}_4$  is + 7 and that of S in  $\text{H}_2\text{SO}_4$  is + 6. (Cl is more electronegative than S). As a result,  $\text{ClO}_3$  part of  $\text{HClO}_4$  can break the O-H bond more easily to liberate a proton than  $\text{SO}_2$  part in  $\text{H}_2\text{SO}_4$ . Thus  $\text{HClO}_4$  is a stronger acid than  $\text{H}_2\text{SO}_4$ .

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**MAIN PHN - 8**





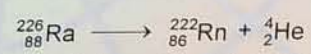
*p-Block Elements (Halogen & Noble Gases)*

- Ex.10** How can you prepare  $Cl_2$  from HCl and HCl from  $Cl_2$ ? Write reactions only.  
**Ans.**  $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$   
 $H_2 + Cl_2 \rightarrow 2HCl$
- Ex.11** Write two uses of  $ClO_2$ .  
**Ans.** (i)  $ClO_2$  is a powerful oxidising agent and chlorinating agent. Large quantities of  $ClO_2$  are used for purifying drinking water.  
 (ii) It is an excellent bleaching agent. Its bleaching power is about 30 times higher than that of  $Cl_2$  and is used for bleaching flour to make white bread, wood pulp and cellulose.

**Group 18 Elements : The Zero Group Family**

Group 18 consists of six elements: helium, neon, argon, krypton, xenon and radon. All these are gases and chemically unreactive. They form very few compounds. Because of this they are termed noble gases.

**Occurrence :** All the noble gases except radon occur in the atmosphere. Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent. Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite. The main commercial source of helium is natural gas. Xenon and radon are the rarest elements of the group. Radon is obtained as a decay product of  $^{226}Ra$ .



- Most abundant element in air is Ar. Order of abundance in the air is  $Ar > Ne > Kr > He > Xe$ .

**Electronic Configuration :** All noble gases have general electronic configuration  $ns^2np^6$  except helium which has  $1s^2$ . Many of the properties of noble gases including their inactive nature are ascribed to their closed shell structures.

**Ionisation Enthalpy :** Due to stable electronic configuration these gases exhibit very high ionisation enthalpy. However, it decreases down the group with increases in atomic size.

**Atomic Radii :** Atomic radii increase down the group with increase in atomic number.

**Electron Gain Enthalpy :** Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have larger positive values of electron gain enthalpy.

**Physical properties :** All the noble gases are mono-atomic. They are colourless, and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces. Helium has the lowest boiling point (4.2K) of any known substance. It has a unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

**ATOMIC & PHYSICAL PROPERTIES**

Element	He	Ne	Ar	Kr	Xe
Atomic Number	2	10	18	36	54
Atomic Mass	4	20.18	39.10	83.80	131.30
Electronic configuration	$1s^2$	$[He] 2s^2 2p^6$	$[Ne] 3s^2 3p^6$	$[Ar] 3d^{10} 4s^2 4p^6$	$[Kr] 4d^{10} 5s^2 5p^6$
Atomic Radius (pm)	120	160	190	200	220
Ionization enthalpy / (kJ mol <sup>-1</sup> )	2372	2080	1520	1351	1170
Density (at STP)/g cm <sup>-3</sup>	$1.8 \times 10^{-4}$	$9.0 \times 10^{-4}$	$1.8 \times 10^{-3}$	$3.7 \times 10^{-3}$	$5.9 \times 10^{-3}$
Melting point / K	-	24.6	83.8	115.9	161.3
Boiling point / K	4.2	27.1	87.2	119.7	165.0

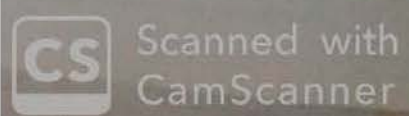
**Chemical Properties :**

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons :

- (i) The noble gases except helium ( $1s^2$ ) have completely filled  $ns^2 np^6$  electronic configuration in their valence shell.
- (ii) They have high ionisation enthalpy and more positive electron gain enthalpy.



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The reactivity of noble gases has been investigated occasionally ever since their discovery, but all attempt to force them to react to form the compounds were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as  $O_2 \cdot PtF_6$ . He, then realised that the first ionisation enthalpy of molecular oxygen ( $1175 \text{ kJ mol}^{-1}$ ) was almost identical with that xenon ( $1170 \text{ kJ mol}^{-1}$ ). He made efforts to prepare same type of compound with  $Xe \cdot PtF_6$  by mixing  $PtF_6$  and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Only the difluoride ( $KrF_2$ ) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g.,  $RnF_2$ ) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

**Clathrate compounds :**

Inert gas molecules get trapped in the cages formed by the crystal structure of water. During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clathrate compounds. There are no chemical bonds. They do not possess an exact chemical formula but approx it is 6 water molecules : 1 inert gas molecule. The cavity size is just smaller than the atom of the noble gas. Such compounds are also formed by the other organic liquids like dihydroxybenzene (for example quinol). The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities. Clathrate provides a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

**Solved Examples**

**Ex.12** Name the noble gas which (a) is most abundant in atmosphere, (b) has least boiling point.

**Sol.** (a) Argon.  
(b) Helium; Exists as mono-atomic molecules and are held together by weak van der Waal's forces. These van der Waal's forces increase with the increase in atomic size of the atom, and therefore, the boiling points increases from He to Rn. Hence He has least boiling point.

**Ex.13** Which idea led for the discovery of xenon fluorides ?  
**Sol.** Neil Bartlett obtained an orange yellow solid from the reaction of xenon with  $PtF_6$  to have  $Xe^+[PtF_6]^-$ . He noticed earlier that  $O_2$  with  $PtF_6$  reacts to give  $O_2^+[PtF_6]^-$  and since ionisation enthalpies of  $O_2$  and Xe were close to each other ( $Xe = 1170, O_2 = 1175 \text{ kJ mol}^{-1}$ ), he could succeed to prepare  $Xe^+[PtF_6]^-$  from Xe and  $PtF_6$ .

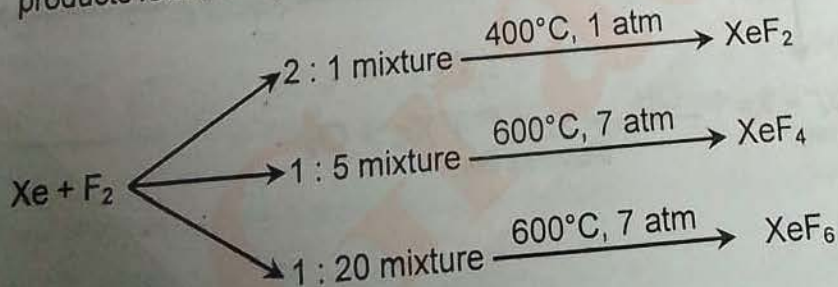
**Ex.14** Why do noble gases have comparatively large atomic size ?  
**Sol.** (i) They exist as monoatomic molecules and, therefore, radius is measured as van der Waal's radius,  $r_{\text{van der Waal}} > r_{\text{covalent}}$ .

(ii) They have completely filled valance shells. As all electrons are paired there are inter electronic repulsions. This leads to expand the electron cloud.

**COMPOUNDS OF XENON :**

**(i) XENON FLUORIDES :**  
**PREPARATION :**

Xenon reacts directly with fluorine when the gases are heated at  $300-600^\circ\text{C}$  in a sealed nickel vessel and the products formed depend on the Xe /  $F_2$  ratio.



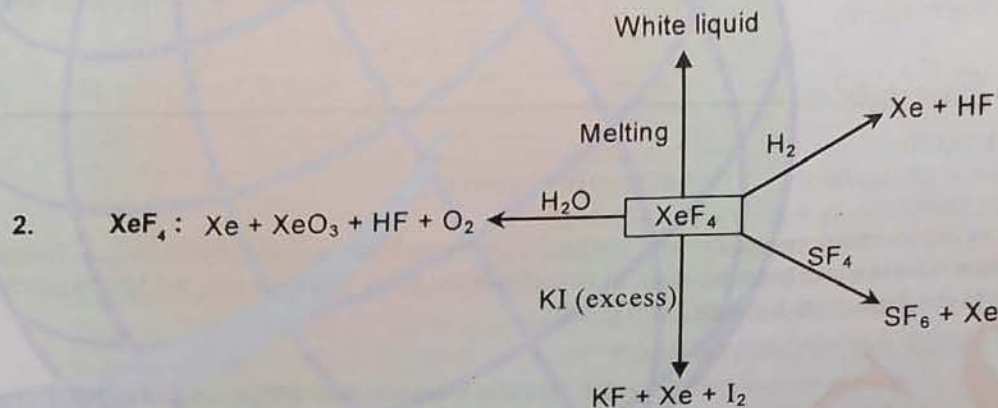
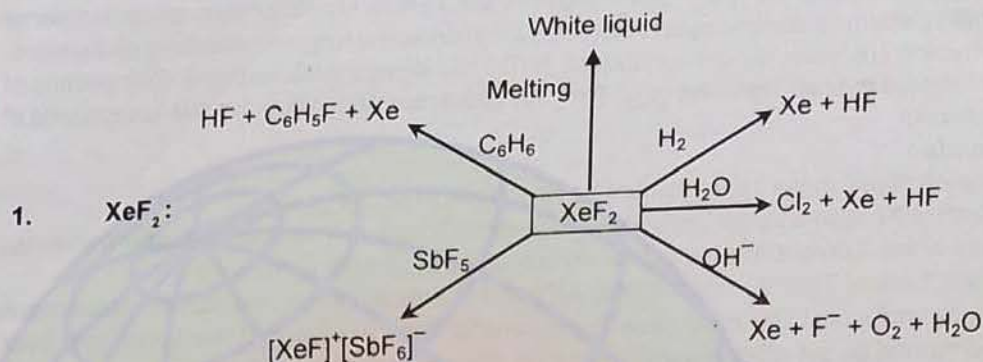


*p-Block Elements (Halogen & Noble Gases)*

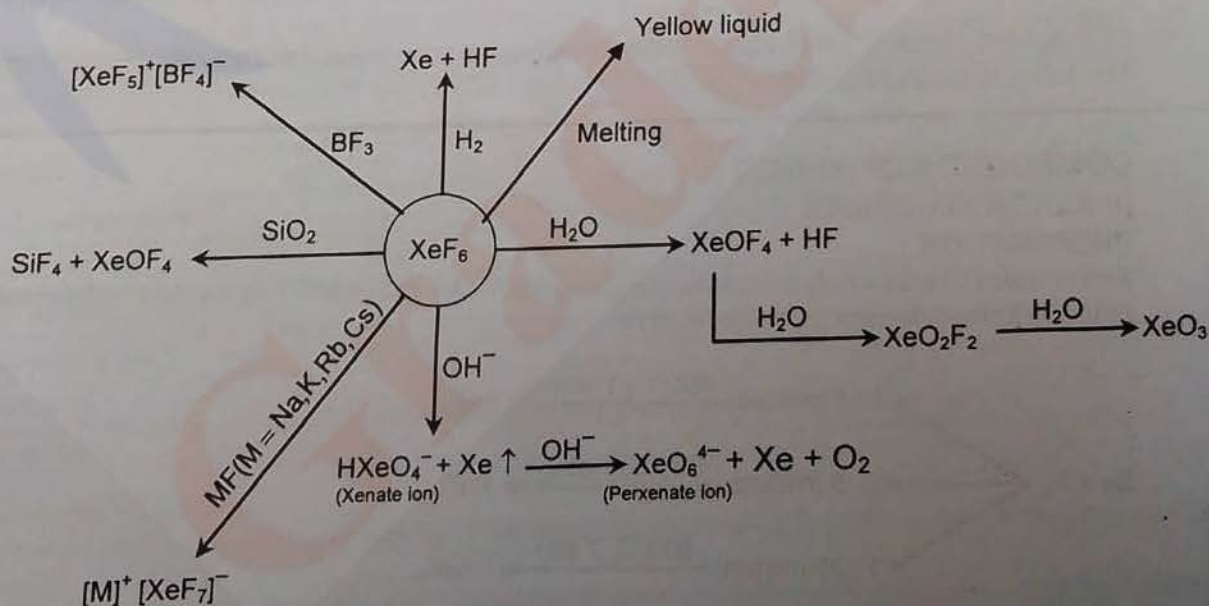
**PROPERTIES :**

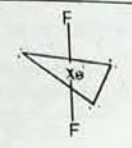
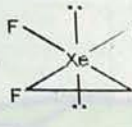
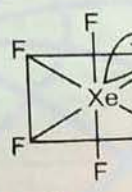
These are colourless (white) solids. They can be sublimed at room temperature and can be stored indefinitely in nickel or monel (an alloy of nickel) containers.

Chemical properties:



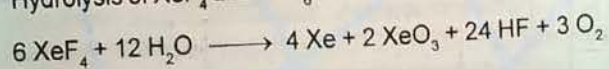
3.  $\text{XeF}_6$  :



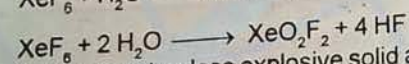
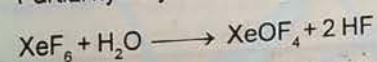
Compounds	Structures	Hybridisation	Geometry	Shape
XeF <sub>2</sub>		sp <sup>3</sup> d	trigonal bipyramidal	linear
XeF <sub>4</sub>		sp <sup>3</sup> d <sup>2</sup>	octahedral	square planar
XeF <sub>6</sub>		sp <sup>3</sup> d <sup>3</sup>	pentagonal bipyramidal	distorted octahedron

**(ii) XENON-OXYGEN COMPOUNDS :**

Hydrolysis of XeF<sub>4</sub> and XeF<sub>6</sub> with water gives XeO<sub>3</sub>.



Partial hydrolysis of XeF<sub>6</sub> gives oxyfluorides, XeOF<sub>4</sub> and XeO<sub>2</sub>F<sub>2</sub>.



XeO<sub>3</sub> is a colourless explosive solid and has a pyramidal molecular structure. XeOF<sub>4</sub> is a colourless volatile liquid and has a square pyramidal molecular structure.

**USES :**

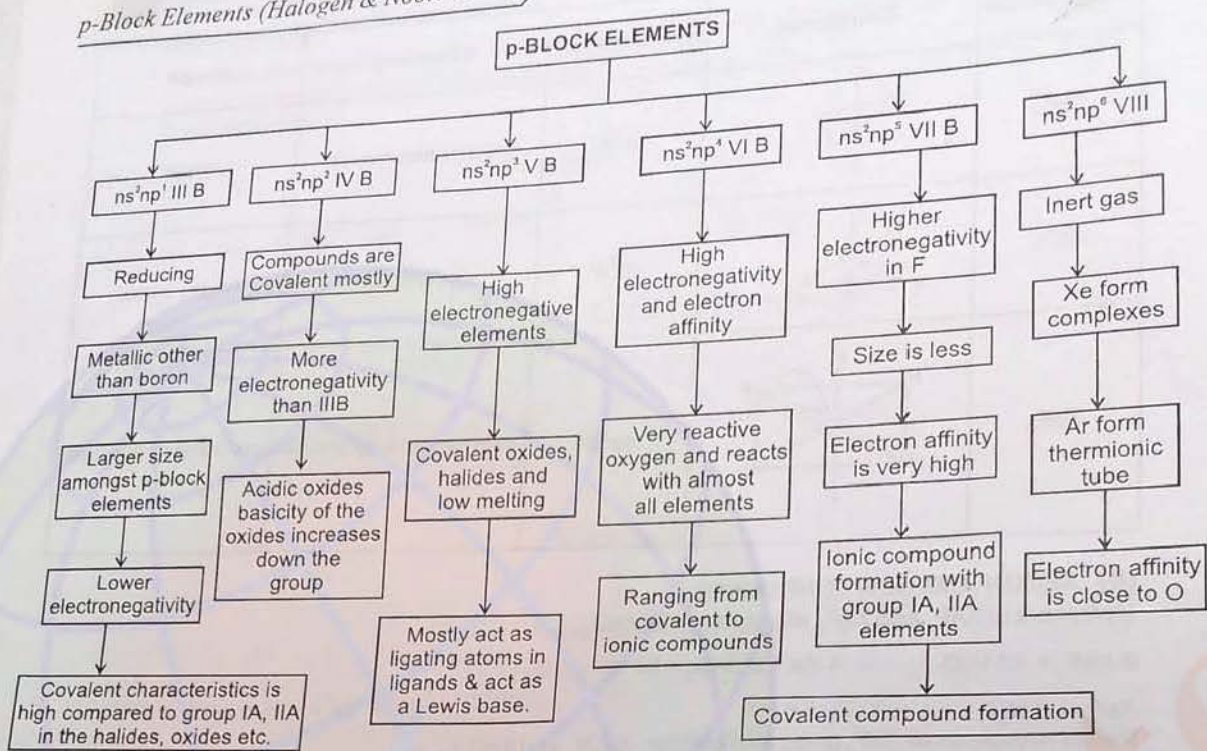
Helium is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium (b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical gardens and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

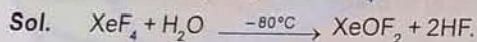
Xenon and Krypton are used in light bulbs designed for special purposes.

*p-Block Elements (Halogen & Noble Gases)*



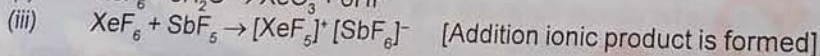
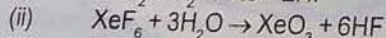
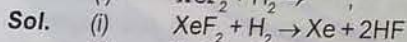
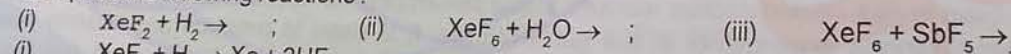
**Solved Examples**

**Ex.15** Does the hydrolysis of  $XeF_4$  at  $-80^\circ C$  lead to a redox reaction ?



The oxidation states of all the elements in the products remain the same as it was in the reacting state. hence, it is a not redox reaction.

**Ex.16** Complete the following reactions :



**MISCELLANEOUS SOLVED EXAMPLES**

1. Why anhydrous HF liquid is not electrolysed alone to get  $F_2$ ?

**Sol.** Anhydrous HF is only slightly ionized and is, therefore a poor conductor of electricity Thus a mixture of KF and HF is electrolysed to increase the conductivity.

2. Explain the following with proper reason :

(i) Fluorine cannot be prepared from fluorides by chemical oxidation.

(ii) Anhydrous HCl is a bad conductor of electricity while aqueous HCl is a good conductor.

(iii) Fluorine does not form  $F_3^-$  (polyhalide) ion.

(iv) HF has a greater electronegativity difference and more ionic character than HCl, HBr and HI but it is the weakest acid.

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