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≡C, N≡N) and to element of second row (e.g C=O, C=N, C≡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

Electronic Configuration : All these elements have seven electrons in their outermost shell ($ns^2\ np^5$) which is one electron short of the next noble gas.

Atomic and Ionic Radii : The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge . Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

Ionisation Enthalpy : They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy decreases down the group.

Electron Gain Enthalpy : Halogen have maximum negative electron gain enthalpy in the corresponding period. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the extra electron (incoming) does not experience much attraction.

Electronegativity : They have very high electronegativity. The electronegativity decreases down the group. Fluorine is the most electronegative element in the periodic table

Physical Properties : Fluorine and chlorine are gases, bromine is a liquid whereas iodine is a solid. Their melting and boiling points steadily increase with atomic number. All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example, F_2, has yellow, Cl_2, greenish yellow, Br_2, red and I_2, violet colour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water. But are soluble in organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions. Except the smaller enthalpy of dissociation of F_2 compared to that of Cl_2. The X-X bond disassociation enthalpies from chlorine onwards show the expected trend : $Cl-Cl > Br-Br > F-F > I-I$.

The reason for the smaller enthalpy of dissociation of F_2 is the relatively larger electrons-electrons repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in case of Cl_2.

ATOMIC & PHYSICAL PROPERTIES

Element	F	Cl	Br	I
Atomic Number	9	17	35	53
Atomic Mass	19	35.45	79.90	126.90
Electronic configuration	[He] $2s^2\ 2p^5$	[Ne] $3s^2\ 3p^5$	[Ar] $3d^{10}4s^2\ 4p^5$	[Kr] $4d^{10}5s^2\ 5p^5$
Covalent Radius / pm	64	99	114	133
Ionic Radius X^- / pm	133	184	196	220
Ionization enthalpy / (kJ mol^{-1})	1680	1256	1142	1008
Electron gain enthalpy /(kJ mol^{-1})	– 333	– 349	– 325	– 296
Distance X -X/pm	143	199	229	266
Enthalpy of dissociation (X_2)/kJ mol^{-1}	158.8	242.6	192.8	151.1
Electronegativity	4	3.2	3.0	2.7
Melting point / K	54.4	172	265.8	386.6
Boiling point / K	84.9	239.0	332.5	458.2

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_2 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^- can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.

$$2F_2(g) + 2H_2O(\ell) \longrightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$$

$$X_2(g) + H_2O(\ell) \longrightarrow HX(aq) + HOX(aq) \;; \quad \text{(where X = Cl or Br)}$$

$$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(\ell)$$

Standard Reduction Potential (SRP)

$X_2 + 2e^- \longrightarrow 2X^-$

$F_2 + 2e^- \longrightarrow 2F^-$ E° = + 2.87 V ; $Cl_2 + 2e^- \longrightarrow 2Cl^-$ E° = + 1.36 V

$Br_2 + 2e^- \longrightarrow 2Br^-$ E° = + 1.09 V ; $I_2 + 2e^- \longrightarrow 2I^-$ E° = + 0.54 V

More the value of the SRP, more powerful is the oxidising agent. Hence the order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$
Since SRP is the highest for F_2 (among all elements of periodic table), it is a strongest oxidising agent.

Hydration energy of X^-

Smaller the ion, higher is the hydration energy.

F^-	Cl^-	Br^-	I^-	
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_2 and O_2F_2. However, only OF_2 is the thermally stable at 298 K. These oxide are essentially oxygen fluorides because of the higher electronegativity of flurorine than oxygen . Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 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_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

The bromine oxides, Br_2O, BrO_2, BrO_3 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 ℓ.p – ℓ.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 states 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 :

(i) By heating MnO_2 with concentrated hydrocloric acid.

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

(ii) By heating chloride with concentrated H_2SO_4 in presence of MnO_2.

$4H^+ + MnO_2 + 2X^- \longrightarrow X_2 + Mn^{+2} + 2H_2O$

(iii) $2KMnO_4 + 16\,HCl \longrightarrow 2\,KCl + 2\,MnCl_2 + 5\,Cl_2 + 8\,H_2O$

(iv) **Manufacture of chlorine :**

(a) Deacon's process : By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4\,HCl + O_2 \xrightarrow{CuCl_2} 2\,Cl_2 + 2\,H_2O$$

(b) Electrolytic process : Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is obtained as a by–product in many chemical industries e.g.; in mfg. of sodium hydroxide.

$NaX\,(aq) \longrightarrow Na^+\,(aq) + X^-\,(aq)$

Anode : $2X^- \longrightarrow X_2 + 2e^-$

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 infact a clathrate compound.

(iii) **Reaction with metals :**

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$; $2Fe + 3Cl_2 \longrightarrow 2FeCl_3$

Reaction with non-metals :

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$; $S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$

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

$H_2 + Cl_2 \longrightarrow 2HCl$; $H_2S + Cl_2 \longrightarrow 2HCl + S$

(v) **Reaction with NaOH :**

(a) $2\,NaOH$ (cold & dilute) $+ Cl_2 \longrightarrow NaCl + NaClO + H_2O$

(b) $6\,NaOH$ (hot & concentrated) $+ 3\,Cl_2 \longrightarrow 5\,NaCl + NaClO_3 + 3\,H_2O$

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

$2\,Ca(OH)_2 + 2\,Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2\,H_2O$

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

(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.

$$2\ FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2\ HCl$$
$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2\ HCl$$
$$SO_2 + 2\ H_2O + Cl_2 \longrightarrow H_2SO_4 + 2\ HCl$$
$$I_2 + 6\ H_2O + 5\ Cl_2 \longrightarrow 2\ HIO_3 + 10\ HCl$$

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

$$Cl_2 + H_2O \longrightarrow 2\ HCl + O$$

Coloured substance + O → Colourless substance

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.

$$SO_2 + 2\ H_2O \longrightarrow H_2SO_4 + 2\ H$$
$$SO_3^{2-} + \text{Coloured material}\quad SO_4^{2-} + \text{Reduced colourless material.}$$
$$\text{Reduced Colourless material} \xrightarrow{O_2 \text{ of air}} \text{Coloured material.}$$

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) :

$$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl\ ; \qquad NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$$

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.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O\ ; \qquad P_4O_{10} + 3HCl \longrightarrow POCl_3 + 3HPO_3$$

HCl is, hence dried by passing through concentrated H_2SO_4 .

Properties :

(i) It is a colourless, pungent smelling gases with acidic tastes.

(ii) It is easily liqueflied 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 : $HCl(g) + H_2O(\ell) \longrightarrow H_3O^+(aq) + Cl^-(aq)$; $K_a = 10^7$

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 HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$$Au + 4\,H^+ + NO_3^- + 4\,Cl^- \longrightarrow [AuCl_4]^- + NO + 2\,H_2O$$

$$3\,Pt + 16\,H^+ + 4\,NO_3^- + 18\,Cl^-\ 3\,[PtCl_6]^{2-} + 4\,NO + 8\,H_2O$$

It reacts with ammonia forming white fumes of NH_4Cl

$$NH_3 + HCl \longrightarrow NH_4Cl$$

(iv) It decomposes salt of weaker acids.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$

Uses :

1. HCl is used in preparation of 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.

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	**HOF**	**HOCl**	**HOBr**	**HOI**
(Hypohalous acid)	(Hypofluorous acid)	(Hypochlorous acid)	(Hypobromous acid)	(Hypoiodous acid)
Halic (III) acid	–	HOClO	–	–
(Halous acid)	–	(chlorous acid)	–	–
Halic (V) acid	–	$HOClO_2$	$HOBrO_2$	$HOIO_2$
(Halic acid)	–	(chloric acid)	(bromic acid)	(iodic acid)
Halic (VII) acid	–	$HOClO_3$	$HOBrO_3$	$HOIO_3$
(Perhalic acid)	–	(perchloric acid)	(perbromic acid)	(periodic acid)

Some important order

(a) Acid strength

(i) HI > HBr > HCl > HF (ii) HOCl > HOBr > HOI (iii) $HClO_4 > HClO_3 > HClO_2 > HClO$

(b) Oxidising powder

(i) $F_2 > Cl_2 > Br_2 > I_2$ (ii) $BrO_4^- > IO_4^- > ClO_4^-$ (According to electrode potential)

(c) Order of disproportionations

$3\,XO^- \longrightarrow 2X^- + XO_3^-$ (hypohalite ion) ; $IO^- > BrO^- > ClO^-$

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_3	AB_5	AB_7
ClF	ClF_3	ClF_5	IF_7
BrF	BrF_3	BrF_5	

ICl	ICl_3	IF_5
IF	IF_3	

Preparation :

$Cl_2 + F_2$ (equal volumes) $\xrightarrow{473\ K}$ $2ClF$; $Cl_2 + 3F_2$ (excess) $\xrightarrow{573\ K}$ $2ClF_3$;

$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl$;

Diluted with water : $Br_2\ (g) + 3F_2 \longrightarrow 2BrF_3$

F_2 is diluted with N_2 : $I_2 + 3F_2 \xrightarrow{-78°C} 2IF_3$

F_2 is taken in freon : $Br_2 + 5F_2$ (excess) $\longrightarrow 2BrF_5$

Properties :

(i) These compounds may be gases, liquids or solids.
Gases : ClF, BrF, ClF_3 , IF_7 ; Liquids : BrF_3, BrF_5 ; Solids : ICl, IBr, IF_3, ICl_3.

(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_2.

(v) Hydrolysis : All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when AB), halite (when AB_3), halate (when AB_5), and perhalate (when AB_7) anion derived from the larger halogen.

$AB + H_2O \longrightarrow HB + HOA$

$BrCl + H_2O \longrightarrow HCl + HOBr$; $ICl + H_2O \longrightarrow HCl + HIO_2$

Uses :

(i) These compounds can be used as non aqueous solvents.
(ii) Interhalogen compounds are very useful fluorinating agents.
(iii) ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$U(s) + 3\ ClF_3\ (l) \longrightarrow UF_6\ (g) + 3\ ClF\ (g)$

Solved Examples

Ex.5 Name the compound which on electrolysis gives fluorine gas at anode.

Sol. Fused anhydrous potassium hydrogen fluoride (KHF_2)

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$; $KF + HF \longrightarrow K[HF_2] \xrightarrow{\text{electrolysis}} H_2 + F_2$

On Electrolysis : Cathode : $2H^+ + 2e^- \longrightarrow H_2(g)$
Anode : $2F^- \longrightarrow F_2 + 2e^-$

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 ?
(b) Chlorine water turns blue litmus red but solution becomes colourless after sometime.

Sol. (a) It forms H_2 gas. $Fe + 2\ HCl \longrightarrow FeCl_2 + H_2$.
Liberation of hydrogen prevents the formation of ferric chloride.

(b) Blue litmus change into red due to acidic nature ($Cl_2 + H_2O \rightarrow HOCl + HCl$) but it is bleaching agent also (oxidising agent),therefore, it decolourises the red litmus.

Ex.8 $CaOCl_2$ in aqueous solution changes to Cl_2 . What is the type of this change ?

Sol. $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$ Redox reaction.

Ex.9 Give appropriate reasons for each of the following :

(a) Addition of Cl_2 to KI solution gives it a brown colour but excess of Cl_2 turns it colourless.

(b) Perchloric acid is a stronger acid than sulphuric acid.

Sol. (a) Cl_2 being a stronger oxidising agent than I_2, first oxidises KI to I_2 which imparts brown colour to the solution. But when Cl_2 is passed in excess, the I_2 so formed gets further oxidised to HIO_3 (colourless)

$$2KI\,(aq) + Cl_2(g) \longrightarrow 2KCl\,(aq) + I_2(s)\ ;\ \ 5Cl_2 + I_2 + 6H_2O \longrightarrow 10HCl + 2HIO_3$$

(b) Oxidation state of Cl in $HClO_4$ is + 7 and that of S in H_2SO_4 is + 6. (Cl is more electronegative than S). As a result, ClO_3 part of $HClO_4$ can break the O–H bond more easily to liberate a proton than SO_2 part in H_2SO_4 . Thus $HClO_4$ is a stronger acid then H_2SO_4.

Ex.10 How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only.

Ans. $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$.

$H_2 + Cl_2 \longrightarrow 2HCl$.

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.

$$^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$

❍ 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^{-1})	2372	2080	1520	1351	1170
Density (at STP)/g cm^{-3}	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-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.

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 $O_2^+\ PtF_6^-$. He , then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol $^{-1}$) was almost identical with that xenon (1170 kJ mol $^{-1}$). He made efforts to prepare same type of compound with $Xe^+\ PtF_6^{\ -}$ by mixing Pt F_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 .

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 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 :

XENON–FLUORINE COMPOUNDS :

All fluorides of xenon are white solids. They are volatile, readily subliming at room temperature (298 K)

Compound	XeF_2	XeF_4	XeF_6
Melting point	129	117	49.6

They can be stored indefinitely in nickel or monel metal containers.

Xenon difluoride

$$Xe + F_2 \ (2 : 1 \text{ mixture}) \xrightarrow[\text{sealed nickel tube}]{873\text{K, 1 bar}} XeF_2 .$$

It is soluble in water, giving solution 0.15 M at 0ºC. The solution which have pungent smell due to XeF_2 are powerful oxidizing agents.

$$XeF_2(aq) + 2H^+ + 2e^- \longrightarrow Xe + 2HF(aq) \ ; \ E^o = + 2.64 \text{ V}$$

$$XeF_2 + H_2 \longrightarrow 2 \text{ HF} + Xe$$

Hydrolysis is slow in water due to dissolution of XeF_2 in HF formed, but is rapid in basic solution.

$$2Xe F_2 + 2H_2O \longrightarrow 2 \text{ Xe} + 4HF + O_2$$

$$XeF_2 + 2OH^- \longrightarrow Xe + \frac{1}{2}O_2 + 2F^- + H_2O$$

It acts as fluoride ion donor XeF_2 (Lewis base) + PF_5 (Lewis acid) $[XeF]^+ [PF_6]^-$

Xenon tetrafluoride

$$Xe + 2F_2 \ (1 : 5 \text{ mixture}) \xrightarrow[\text{sealed nickel tube}]{873\text{ K, 7 bar}} XeF_4$$

XeF_4 reacts violently with water, giving dangerously explosive XeO_3.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2 \text{ } XeO_3 + 24 \text{ HF} + 3O_2$$

XeF_4 can act as F^- acceptor as well as F^- donors and thus form anionic species in reactions such as :

$$XeF_4 + NaF \longrightarrow Na^+ \ XeF_5^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ \ [SbF_6]^-$$

Xenon hexafluoride

$$Xe + 3F_2 \ (1 : 20 \text{ mixture}) \xrightarrow[\text{sealed nickel tube}]{573\text{K, 60–70 bar}} XeF_6$$

$$XeF_4 + O_2 F_2 \longrightarrow XeF_6 + O_2$$

XeF_6 reacts violently with water but slow hydrolysis with atmospheric moisture giving XeO_3.

$$XeF_6 + 6 \text{ } H_2O \longrightarrow XeO_3 + 6HF \text{ (complete hydrolysis)}$$

With small quantities of water, partial hydrolysis takes place.

$$XeF_6 + H_2O \longrightarrow XeOF_4 \text{ (colourless liquid)} + 2HF$$

$$XeF_6 + 2 \text{ } H_2O \longrightarrow XeO_2F_2 + 4HF$$

XeF_6 reacts with fluoride ion donors to form fluoroanions.

$$XeF_6 + MF \longrightarrow M^+ \ [XeF_7]^- \qquad (M = Na, K, Rb \text{ or } Cs)$$

XENON–OXYGEN COMPOUNDS :

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6\,XeF_4 + 12\,H_2O \longrightarrow 4\,Xe + 2\,XeO_3 + 24\,HF + 3\,O_2$$

$$XeF_6 + 3\,H_2O \longrightarrow XeO_3 + 6\,HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2 .

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2\,HF$$

$$XeF_6 + 2\,H_2O \longrightarrow XeO_2F_2 + 4\,HF$$

XeO_3 is a colourless explosive solid and has a pyramidal molecular structure. $XeOF_4$ 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 handls ing substances that are air–sensitive.

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

Solved Examples

Ex.15 Does the hydrolysis of XeF_4 at – 80ºC lead to a redox reaction ?

Sol. $XeF_4 + H_2O \xrightarrow{-\,80^\circ C} XeOF_2 + 2HF$.

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 :

(i) $XeF_2 + H_2 \rightarrow$; (ii) $XeF_6 + H_2O \rightarrow$; (iii) $XeF_6 + SbF_5 \rightarrow$.

Sol. (i) $XeF_2 + H_2 \rightarrow Xe + 2HF$

(ii) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

(iii) $XeF_6 + SbF_5 \rightarrow [XeF_5]^+ [SbF_6]^-$ [Addition ionic product is formed]

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.

Sol. **(i)** The standard reduction potential of fluorine is maximum.

$$:\underset{\cdot\cdot}{\ddot{F}}\cdot + e^- \longrightarrow :\underset{\cdot\cdot}{\ddot{F}}:^-$$

Thus, it cannot be oxidised by any other reagent. F^- ion is very stable due to small size and high electronegativity of fluorine atom.

(ii) In anhydrous state, HCl is a covalent molecule. In aqueous solution, HCl combines with water molecule to form H_3O^+ and Cl^- ions.

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

(iii) F-does not have empty d-orbital liked other halogen. The formation of X_3^- ions involves sp^3 d-hybridizaion.

(iv) The weakest acidic nature of HF is due to following three factors :
(a) Strong H–F bond as the dissociation energy is high.
(b) Large heat of dehydration dues to hydrogen bonding.
(c) Low value of electron affinity.

3. Xenon has closed shell configuration but is known to give compounds with fluorine.

Ans. Xe has relatively lower ionisation energy among inert gases and thus the outermost shell electrons of Xe are excited to d-subshell and thereby showing unpaired electronic structure. Therefore Xe shows covalent bonding with fluorine showing sharing of electron pair.

4. The boiling points of noble gases increase with increase in atomic number. Why ?

Ans. Van der Waal's forces of attraction among molecules increase with the increase of atomic masses. Thus, higher energy is required to separate these molecules as to get gaseous state. Hence, the boiling points increase with increase of atomic masses.

5. **Assertion :** All interhalogens are paramagnetic.
Reason : AB type of interhalogen undergoes hydrolysis giving a halide ion derived from the smaller halogen and a hypohalite ion derived from the larger halogen.
(1) Both (A) and (R) are correct and (R) is the correct explanation of (A).
(2) Both (A) and (R) are correct and (R) is not the correct explanation of (A).
(3) (A) is correct but (R) is incorrect.
(4) (A) is incorrect but (R) is correct.

Sol. **(A) :** All valence electrons present as bonding or non-bonding electrons are paired.
(R) : $AB + H_2O \longrightarrow HB + HAO$ **Ans.** (4)

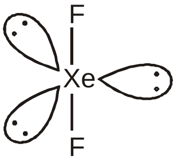
6. **Assertion :** Fluorine with sodium hydroxide solution does not undergo disproportionation reaction.
Reason : Fluorine has the highest SRP value, therefore, it is completely reduced only.
(1) Both (A) and (R) are correct and (R) is the correct explanation of (A).
(2) Both (A) and (R) are correct and (R) is not the correct explanation of (A).
(3) (A) is correct but (R) is incorrect.
(4) (A) is incorrect but (R) is correct.

Sol. $2F_2 + 2NaOH\ (dil.) \longrightarrow OF_2 + 2NaF + H_2O$
$2F_2 + 4NaOH\ (conc.) \longrightarrow O_2 + 4NaF + 2H_2O$ **Ans.** (1)

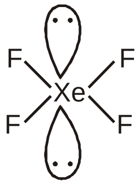
7. Match the compounds listed in column-I with characteristic(s)/type of reaction(s) listed in column-II.

Column –I	**Column –II**
(1) XeF_2	(p) Undergoes hydrolysis with water.
(2) XeF_4	(q) Acts as oxidising agent.
(3) XeF_6	(r) Undergoes addition reaction.
(4) XeO_3	(s) Has lone pair(s) of electrons.

Ans. (1 – p, q, r, s) ; (2 – p, q, r, s); (3 – p, q, r, s) ; (4 – q, s)



Sol. (1) $XeF_2 + 2H_2O \xrightarrow{\text{Hydrolysis}} 2Xe + 4HF + O_2$
$XeF_2 + 2HCl \longrightarrow Xe + 2HF + Cl_2$
as oxidising agent
$XeF_2 + PF_5 \xrightarrow{\text{Addition reaction}} [XeF]^+\ [PF_6]^-$



(2) $6XeF_4 + 12H_2O \xrightarrow[\text{Disproportionation}]{\text{Hydrolysis}} 4Xe + 2XeO_3 + 24HF + 3O_2$
$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$
as oxidising agent.
$XeF_4 + SbF_5 \xrightarrow{\text{Addition reaction}} [XeF_3]^+\ [SbF_6]^-$

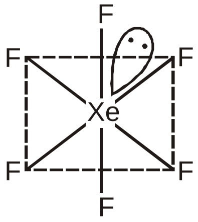
(3) $XeF_6 + 3H_2O \xrightarrow{\text{Hydrolysis}} XeO_3 + 6HF$

$XeF_6 + 3H_2 \longrightarrow 6HF + Xe$

as oxidising agent

$CsF + XeF_6 \xrightarrow{\text{Addition reaction}} CsXeF_7$

$XeF_6 + PtF_6 \xrightarrow{\text{Addition reaction}} [XeF_5]^+ [PtF_6]^-$



(4) $XeO_3 + OH^- \rightleftharpoons HXeO_4^-$

$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$

$XeO_3 + 6H^+ + 6e^- \longrightarrow Xe + 3H_2O$ (E = 2.10 V)

acts as oxidising agent.