THE HALOGENS

Section - 3

☐ Group - 17

Ionisation Energy

The ionization energies of halogens are very high, next only to the noble gases in each group. On moving down the group, the ionization enthalpies progressively decrease as the size of halogen increases from F to I

Electronegativity

Due to small size and higher nuclear charge, each halogen has the highest electronegativity in their respective periods. F is the most electronegative element (electronegativity of 4.0).
The electronegativity decreases down the group.

Electron Affinity

Halogens have large negative electron gain enthalpies. Down the group, electron affinity decreases as the size increases.

$$F < Cl > Br > I > At.$$

However, Cl is more eletronegative than F due to extremely small size of F as a result of which strong electron repulsions are present in the relatively compact 2p – orbitals of fluorine and thus its tendency to accept an electron decreases.

Oxidation States

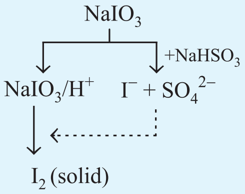
F shows O.S of only – 1 (being most electronegative) often halogens show oxidation states of ±1, +5 and +7.

Bond Dissociation Enthalpy

All elements form diatomic molecules. The bond dissociation energy decreases down the group since the atoms become larger which results in less effective overlap of orbitals.

$$F_2 << Cl_2 > Br_2 > I_2 .$$

However bond energy of F_2 is abnormally low due its very high reactivity. The small size of F atoms induces $e^- - e^-$ repulsion between the lone pairs of electrons on the two fluorine atoms.

Reaction with	F_2	Cl_2	Br_2	I_2
Preparation of Gas	Light - yellow gas	Yellow green gas	Brown liquid	Violet solid
	most reactive element known, strong O.A.	toxic, has pungent suffocating odour		Crystallizes as black flakes has slight lustre.
	Moisson was awarded Nobel Prize for his methods of preparing F_2 : $CaF_2 + \text{conc. } H_2SO_4 \longrightarrow HF$ $HF + KF \longrightarrow K^+[HF_2]^-$ $K^+[HF_2]^- + KF \xrightarrow{\text{electrolysis}} F_2 + K_2$	❐ Lab : $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$ ❐ Deacon's Process : It is then dried with CaO, P_4O_{10} or H_2SO_4 $HCl + O_2 \xrightarrow{CuCl_2} Cl_2 + H_2O$ ❐ Commercially it is also obtained by electrolysis of NaCl(aq) in the manufacture of NaOH or elect. of NaCl(ℓ) in the manufacture of Na	Obtained from Sea water and brine lakes by passing Cl_2 as follows : $Cl_2 + 2Br^- \longrightarrow Cl^- + Br_2$ $Br_2 + Na_2CO_3 \longrightarrow NaBr + NaBrO_3$ $\downarrow H^+$ $\underset{\text{pure}}{Br_2} \xleftarrow{CuCl_2} HBr + HBrO_3$	Chile saltpetre is mainly $NaNO_3$ but contains traces of $NaIO_3$. $NaIO_3.NaNO_3$ is crystallised out and left $NaIO_3$ is divided into two parts  Purification is done by sublimation.
H_2O	$\underset{(OA)}{F_2} + H_2O \longrightarrow 2H^+ + 2F^- + \frac{1}{2}O_2$ (spontaneous and strongly exothermic)	$Cl_2 + H_2O \underset{K^+}{\overset{\text{Cold OH}^-}{\rightleftharpoons}} ClO^- + Cl^-$ $Cl_2 + H_2O \xrightarrow{\text{hot OH}^-} ClO_3^- + Cl^-$	$Br_2 + H_2O \xrightarrow{OH^-} Br^- + BrO^-$	Sparingly soluble in water but dissolves if I^- are present (as soluble I_3^- forms) $I^- + I_2 \longrightarrow I_3^-$
NH_3	X_2 reacts with NH_3 to give N_2 and NH_4X (X = F, Cl, Br)			
Others	All halogens oxidise H_2S to S ; form SO_2X_2 with SO_2 ; trihalides with As, Sb, Bi ; penta halides (except I) with As, Sb, Bi.			
Uses	Used in making freon (CFC's)	❐ Used as a bleaching agent $Cl_2 + H_2O \longrightarrow HOCl$ ❐ and make poisonous gases like SO_2Cl_2	It is used to make flame retardant and in organic chemistry.	It is used to make tincture of iodine (I_2 + KI) and in titrations.

Note : I_2 is tested by starch indicator which turns blue. The bluish colour produced disappears on titration with $S_2O_3^{2-}$. This colour reappears after 2 – 3 minutes due to atmospheric oxidation.

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

$$2I^- + \frac{1}{2}O_2 + 2H^+ \longrightarrow I_2 + H_2O$$

Hydra - Acids

I Hydrofluoric acid [H_2F_2 or HF]

1. HF is a colourless, corrosive liquid with pungent smell. It attacks glass and is thus stored in wax bottles or gutta percha bottles.

$$SiO_2 + 6HF \longrightarrow [SiF_6]^{2-} + 2H^+ + 2H_2O \qquad \text{(This is also used for etching glass.)}$$

HF is kept in laboratory in KF giving $K^+[F-H-F]^-$ ions.

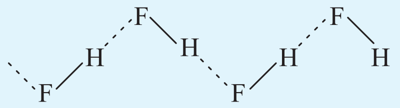
2. H_2 and F_2 combine with each other very violently even in dark to form HF. Thus special methods are employed in its preparation.

Industrially it is made by heating CaF_2 with strong H_2SO_4. The reaction is endothermic : hence the need for heating. SiO_2 impurities are removed from CaF_2 otherwise they consume much of HF produced.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF_{(aq)} \longrightarrow H_2[SiF_6]$$



H-bond in liquid H-F

3. Two thirds of HF produced are used to make chlorofluoro carbons (Freons) used as refrigerating fluids.

$$CCl_4 + 2HF \xrightarrow[SbCl_5]{\text{anhydrous conditions}} \underset{\text{freon}}{CCl_2F_2} + 2HCl$$

4. In liquid form HF is used as a non - aqueous solvent.

$$2HF(\ell) \rightleftharpoons [H_2F]^+ + F^-$$

II Hydrochloric acid [HCl]

1. At one time HCl was made exclusively by 'salt cake' method.

$$\underset{\text{Rock salt}}{NaCl} + conc.H_2SO_4 \xrightarrow{\Delta} HCl(g) + NaHSO_4$$

$$NaHSO_4 + NaCl \xrightarrow{\Delta} HCl(g) + Na_2SO_4$$

2. Highly pure HCl is made by bringing H_2 and Cl_2 in a special combustion chamber. (Direct combination is explosive)

$$Cl_2 + H_2 \longrightarrow 2HCl$$

3. In laboratory :

$$2NH_4Cl + \underset{\text{conc.}}{H_2SO_4} \longrightarrow 2HCl + (NH_4)_2SO_4$$

4. HCl cannot be dried over P_2O_5 or quick lime because it reacts with them :

$$CaO + HCl \longrightarrow CaCl_2 + H_2O$$

$$P_4O_{10} + 3HCl \longrightarrow POCl_3 + 3HPO_3$$

Hence it is dried by passing through conc. H_2SO_4

5. HCl(g) is colourless, weak reducing agent (is oxidised by strong oxidising agents like MnO_2, $KMnO_4$, $K_2Cr_2O_7$) and highly soluble in water.

6. Aqua Regia :

It is a fuming mixture of HCl and HNO_3 in the ratio 3 : 1. It can dissolve both gold and platinum while no other acid has that capability.

$$Au + NO_3^- + 4Cl^- + 4H^+ \longrightarrow AuCl_4^- + NO\uparrow + 2H_2O$$

$$Pt + NO_3^- + 6Cl^- + 2H^+ \longrightarrow PtCl_6^{2-} + NO\uparrow + 2H_2O$$

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

III HBr and HI

1. They are prepared by reaction of phosphoric acid on metal bromides or iodides (similar to salt cake process)

$$NaI + H_3PO_4 \longrightarrow HI + NaH_2PO_4$$

$$NaBr + H_3PO_4 \longrightarrow HBr + NaH_2PO_4$$

2. The usual laboratory process is :

$$\underset{\text{Red}}{2P} + 3Br_2 \longrightarrow 2PBr_3 \xrightarrow{+\,6H_2O} 6HBr + 2H_3PO_3$$

$$\underset{\text{Red}}{2P} + 3I_2 \longrightarrow 2PI_3 \xrightarrow{+6H_2O} 6HI + 2H_3PO_3$$

3. HBr is not very stable and acts as a strong reducing agent while HI is least stable and thus a more powerful reducing agent.

$$2HNO_3 + 2HI \longrightarrow 2NO_2 + I_2 + 2H_2O$$

$$2HNO_2 + 2HI \longrightarrow 2NO + I_2 + 2H_2O$$

$$HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$$

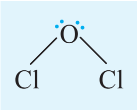
$$H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + 2H_2O$$

Oxides

There is only a small difference in electronegativity between the halogens and oxygen and thus the bonds in oxides are largely covalent. Most halogen oxides are unstable and tend to explode when subjected to shock. Stability of oxides increases down the group and higher oxidation states are more stable than lower oxidation states.

I Dichloro oxide [Cl_2O]

Cl_2O is a yellow - brown gas which condenses to an orange liquid (bp = 2°C). It is the anhydride of hypochlorous acid (HClO).



1. It is prepared by passing dry chlorine over freshly precipitated mercuric oxide.

$$HgO + \underset{\text{dry}}{2Cl_2} \longrightarrow HgCl_2 + Cl_2O.$$

2. It is soluble in water $Cl_2O + H_2O \rightleftharpoons \underset{\text{Golden solution}}{2HOCl(aq)}$

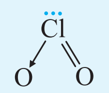
3. It explodes in presence of NH_3 or a reducing agent or on heating.

$$3Cl_2O + 10NH_3 \longrightarrow 2N_2 + 6NH_4Cl + 3H_2O$$

4. It is a strong oxidising agent.

$$Cl_2O + 2HCl \longrightarrow 2Cl_2 + H_2O$$

II Chlorine Dioxide [ClO_2]



It is a yellow gas, condenses to deep red liquid, explodes above –40°C and in presence of reducing agents. It is paramagnetic being an odd electron molecule but DOESNOT dimerise as the odd electron is delocalised.

1. It explodes when mixed with reducing agents. The safest laboratory preparation is from sodium chlorate and oxalic acid as this automatically dilutes the gas with CO_2.

$$2NaClO_3 + 2(COOH)_2 \longrightarrow 2ClO_2 + 2CO_2 + (COONa)_2 + 2H_2O$$

2. $ClO_2 + H_2O \longrightarrow \underbrace{HClO_3 + HClO_2}_{\text{dark green solution}} + \text{heat}$

3. It is used to manufacture $NaClO_2$ which is used for bleaching paper and textiler.

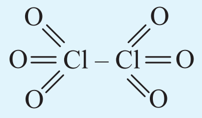
$$2ClO_2 + 2NaOH + H_2O_2 \longrightarrow 2NaClO_2 + O_2 + 2H_2O$$

$$2ClO_2 + 2NaOH \longrightarrow \underset{\text{Chlorite}}{NaClO_2} + \underset{\text{Chlorate}}{NaClO_3} + H_2O$$

4. ClO_2 is a powerful oxidising agent and a bleaching agent and is used to purify water.

III Dichlorine Hexoxide [Cl_2O_6]

It is a dark red liquid which freezes at –180°C to a yellow solid. It is diamagnetic in nature due to absence of unpaired electrons and exists as a dimer. The structure is guessed to be as shown but the exact structure is unknown.



[The exact structure is unknown]

1. It is obtained from ClO_2 and O_3.

$$ClO_2 + O_3 \longrightarrow ClO_3 + O_2$$

$$2ClO_3 \rightleftharpoons Cl_2O_6$$

2. Hydrolysis with water or alkali gives chlorate and perchlorate

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

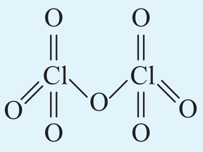
$$Cl_2O_6 + 2NaOH \longrightarrow \underset{\text{Chlorate}}{NaClO_3} + \underset{\text{perchlorate}}{NaClO_4} + H_2O$$

3. It is a strong oxidising agent which explodes on contact with grease.

4. Reaction with anhydrous HF is reversible :

$$Cl_2O_6 + HF \rightleftharpoons FClO_2 + HClO_4$$

IV Dichlorine Heptoxide [Cl_2O_7]



$O_3Cl - O - ClO_3$

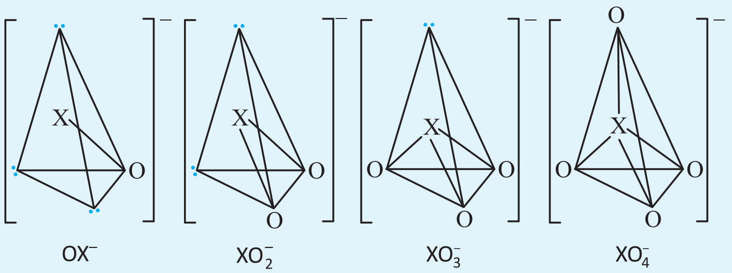
It is a colourless oily liquid which is moderately stable and less reactive than others. It is the only exothermic oxide of Cl and the anhydride of perchloric acid $HClO_4$.

It is anhydride of perchloric acid and made by dehydrating perchloric acid with P_2O_5 or H_3PO_4.

$$2HClO_4 \xrightarrow{P_4O_{10}} Cl_2O_7$$

Oxo Acids

Four series of oxo acids are known (HOXO, $HOXO_2$, $HOXO_3$ and HOX_4). The structure of the ions formed from these oxoacids are:



OX^- XO_2^- XO_3^- XO_4^-

Structures of the oxoacids

- In general, for any series of oxoacids, the acid with most oxygen (i.e. highest oxidation state) is most dissociated. This is because, the more oxygen atoms are bonded, the more the electrons will be pulled away from the O – H bond and thus weaking the bond. [Note that plainly ClO_4^- ion is larger than OCl^- ion and so hydration energy of ClO_4^- is less than that of OCl^-. This suggests HOCl to be a stronger acid but the reverse is true. The reason is the bond energies discussed above]

  Thus the acidic character follows the trend :

  $HClO_4 > HClO_3 > HClO_2 > HClO$

  Similarly,

  $H_2SO_4 > H_2SO_3$; $HNO_3 > HNO_2$

- The thermal stability of the oxyhalide ion increases from ^-OCl to ClO_4^-.

  $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$

  This is due to the increase in the number of oxygen atoms.

- Among the hypohalous acids (HXO) stability order is :

  $HClO > HBrO > HIO >> HFO.$

  Oxoacids of F are exceptionally unstable because all the oxoacid ions except those of F are stabilised by pπ – dπ bonding between full 2p orbitals on O and empty d orbitals on the halogen atoms.

HOCl/HClO **Hypochlorous acid**	**$HClO_2$** **Chlorous acid**	**$HClO_3$** **Chloric acid**	**$HClO_4$** **Perchloric acid**
General Characteristics			
❐ Very weak acid ❐ Only known in aqueous solution. NaOCl is well known. ❐ Unstable	❐ Weak acid (stronger than HClO) ❐ Only exists in solution	❐ Known as salts and in aqueous ❐ Not very stable and detonates if heated. $HClO_3 \longrightarrow ClO_2 + H_2O + O_2$	❐ One of the strongest acids known. ❐ Both salts and acids are well known, can infact be isolated in anhydrous form ($HClO_4 . 2H_2O$)
Preparation			
❐ Shake halogen with freshly precipitated HgO $2HgO + H_2O + Cl_2 \longrightarrow HgO.HgCl_2 + 2HOCl$ ❐ NaOCl is made industrially by electrolysis of cold brine (NaOH solution) or by : $X_2 + OH^- \xrightarrow[<RT]{cold} XO^- + X^-$	❐ $Ba(ClO_2)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + HClO_2$ $BaSO_4$ is filtered off. ❐ Chlorites are made from ClO_2 and NaOH or ClO_2 and Na_2O_2 (See Chlorine Dioxide).	❐ $Ba(ClO_3)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_3$ $BaSO_4$ is filtered off. ❐ Chlorates are formed by : $X_2 + OH^- \xrightarrow{hot} XO_3^- + X^-$	❐ $Ba(ClO_4)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HClO_4$ ❐ $NaClO_3 + H_2O \xrightarrow{electrolysis} NaClO_4 + H_2$
Reactions			
❐ $\underset{+I}{3XO^-} \xrightarrow{hot} \underset{+V}{2XO_3^-} + \underset{-I}{X^-}$ ❐ $2HClO \xrightarrow{-H_2O} Cl_2O$	❐ $ClO_2^- \xrightarrow{OH^-}$ stable ❐ $ClO_2^- \xrightarrow[\Delta]{OH^-} Cl_2O + Cl^-$ makes solution yellow ❐ $2HClO_2 \xrightarrow{-H_2O} Cl_2O_3$	❐ $ClO_3^- \xrightarrow{400°C}$ stable ❐ $ClO_3^- \xrightarrow{low\ temp} ClO_4^- + Cl^-$ ❐ $2HClO_3 \xrightarrow{-H_2O} Cl_2O_5$	$2HClO_4 \xrightarrow[-H_2O]{P_2O_5} Cl_2O_7$
Uses			
used in bleaching and as a disinfectant (especially NaOCl)	Chlorites are also used as bleaches	Chlorates are used to make fire works, matches. $NaClO_3$ is a powerful weedkiller. Solid $NaClO_3$ has also been used to make bombs.	Half of perchlorates is used as NH_4ClO_4 in shuttle launch. $KClO_4$ is used in fireworks and flared.

Bleaching Powder :

Bleaching powder is actually written as $Ca(OCl)_2.Ca(OH)_2 . CaCl_2 . 2H_2O$. It is a pale yellow powder having a strong smell of chlorine and soluble in water. However, a clear solution is never formed due to the presence of impurities.

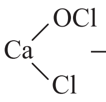
Preparation :

It is made by passing Cl_2 into slaked lime.

$$3Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)Cl + H_2O$$

Chemical Properties :

1. Bleaching action

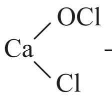


$$\xrightarrow[\text{(slight amount)}]{H^+\text{(dilute)}} CaCl_2 + HClO$$

$$HClO \longrightarrow HCl + [O]$$

Coloured matter + [O] $\longrightarrow$ Colourless product.

While,



$$\xrightarrow[\text{(excess amount)}]{H^+} CaCl_2 + Cl_2\uparrow$$

2. Oxidising action

$$CaOCl_2 + H_2S \longrightarrow CaCl_2 + H_2O + S$$

$$CaOCl_2 + Pb(NO_3)_2 + 2NaOH \longrightarrow CaCl_2 + PbO_2 + 2NaNO_3 + H_2O.$$

3. It converts acetone into chloroform.

Halogen Halides

I. Inter Halides

$$\underset{\text{halogen}}{A} + \underset{\text{halogen}}{X} \longrightarrow AX, AX_3, AX_5, AX_7 \text{ (inter halides) where X is smaller than A.}$$

Interhalogen compounds are covalent and have physical properties intermediate of A and X. They are more reactive than halogens (except F_2) as A – X bond is weaker than X – X bond.
[*Draw the structures of all four kind of interhalides*]

1. ICl(l) is conducting as it ionises :

$$3ICl \rightleftharpoons [I_2Cl]^+ + [ICl_2]^-$$

Addition of $AlCl_3$ in molten ICl greatly increases conductivity as it increases the ionisation by forming $[AlCl_4]^-$ and $[I_2Cl]^+$ ions.

$$AlCl_3 + 2ICl \longrightarrow [I_2Cl]^+ + [AlCl_4]^-$$

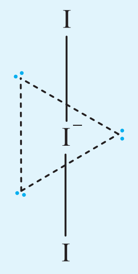
2. ICl_3 exists as dimer I_2Cl_6 with two Cl bridges

$$[I_2Cl_6] \rightleftharpoons [ICl_2]^+ + \underset{\text{Square planar}}{[ICl_4]^-} \quad \text{and is thus conductive.}$$

3. Hydrolysis of interhalides :

$$AX_n + H_2O \longrightarrow HA + HXO_{\frac{n+1}{2}} \ (n = 1, 3, 5, 7)$$

II. Poly Halides



The most impostant polyhalide is I_3^-. It has very long, weak bonds with bond order 0.5 and is linear in shape. I_2 is only slightly soluble in water. Its solubility is greatly increased if some iodide ions are present. This is due to the formation of the polyhalide I_3^-.

$$I_2 + I^- \rightleftharpoons I_3^-$$

III. Pseudo Halides

These are univalent ions with at least one N atom, that have properties similar to those of the halide ions. Examples are CN^-, SCN^-, N_3^-, OCN^-.

CN^- resemble Cl^- closely in the following ways :

1. It forms an acid HCN and the dimer $(CN)_2$ just like HCl and Cl_2
2. It forms insoluble salts with Ag^+, Pb^{2+}, Hg^{2+} and soluble salts with Na^+.
3. $$(CN)_2 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} CN^- + OCN^-$$

$$\begin{tikzcd} CuSO_4 + CN^- \arrow[r] & Cu_2(CN)_2 + (CN)_2\uparrow \arrow[d, "\text{excess } CN^-"] \\ & {[Cu(CN)_4]^{3-}} \end{tikzcd}$$

and $$3ICN \rightleftharpoons [I_2CN]^+ + [I(CN)_2]^-$$

(*Replace* CN^- *by* Cl^- *and compare the above reactions with those of* Cl^-).

IN-CHAPTER EXERCISE-C

1. *Give reason for the following :*

(a) *HF exists as dimeric molecule i.e.* H_2F_2 *or HF has higher viscosity or high boiling point.*

(b) *When blue limus is dipped into a solution of hypochlorous acid, it first turns red and then later gets decolourised.*

(c) *In preparation of HI from alkali iodide,* H_3PO_4 *is preferred in place of* H_2SO_4.

(d) *Fluorine is better oxidant than chlorine.*

(e) *The brown colour of an acidified dilute solution of iodine in aqueous KI is intensified by the addition of nitrite but it is discharged by the addition of a sulphite.*

(f) *It is not possible to obtain* F_2 *by electrolysis of aqueous HF, aqueous NaF or anhydrous HF.*

(g) *A mixture of KF and HF is electrolysed to increase the conductivity of anhydrous HF.*

2. *Write balanced equations for :*

(a) *reaction between HF and* (i) CCl_4 (ii) SiO_2 (iii) KF

(b) *reaction between* Cl_2 *and* (i) SO_2 (ii) H_2 (iii) $NaOH$

3. *Find A, B, C, . . . in the following reactions :*

(a) $MnO_2 + HCl \longrightarrow A(g) \xrightarrow{\text{hot NaOH}} B + C$; $B \xrightarrow[\Delta]{OH^-} C + D(g)$. *D is a yellow triatomic gas.*

(b) $HCN + CuSO_4 \longrightarrow A(g) + B \xrightarrow{\text{excess } CN^-} \text{complex } C$

(c) *Red phosphorus* $\xrightarrow{Br_2} A \xrightarrow{H_2O} B(g) \xrightarrow{\text{conc. } H_2SO_4} Br_2$ **(d)** $CH_3-CH=CH_2+ICl \longrightarrow$

4. H_2SO_4 *is a weaker acid than HCl, yet HCl is evolved when conc* H_2SO_4 *is added to NaCl. Explain.*

5. *HF can be prepared by the action of* H_2SO_4 *on NaF. Explain why HBr cannot be prepared by the action of the same acid on NaBr.*

Choose the correct alternative. Only One choice is correct.

6. *HBr and HI reduce sulphuric acid, HCl can reduce* $KMnO_4$ *and HF can reduce :*

(A) H_2SO_4 **(B)** $KMnO_4$ **(C)** $K_2Cr_2O_7$ **(D)** *None of these*

7. *Chlorine acts as a bleaching agent only in presence of*

(A) *dry air* **(B)** *moisture* **(C)** *sunlight* **(D)** *pure* O_2

8. *Bromine can be liberated from potassium bromide solution by the action of :*

(A) *iodine solution* **(B)** *chlorine water* **(C)** *sodium chloride* **(D)** *potassium iodide*

9. *Which of the following species is not a pseudo halide ?*

(A) CNO^- **(B)** $RCOO^-$ **(C)** OCN^- **(D)** NNN^-

10. *Identify the order of decreasing acid strength of*

I. *ClOH* **II.** *BrOH* **III.** *IOH*

The correct choice is :

(A) $I > II > III$ **(B)** $II > I > III$ **(C)** $III > II > I$ **(D)** $I > III > II$

***11.** *Which of the following regarding oxides of chlorine is(are) true ?*

(A) ClO_2 *on passing through aqueous NaOH form* $NaClO_2$ and $NaClO_3$

(B) Cl_2O_6 *on passing through NaOH gives* $NaClO_3$ *and* $NaClO_4$

(C) ClO_2 *on reaction with* O_3 *gives* Cl_2O_6

(D) Cl_2O *is a neutral oxide*