

(HALOGEN & NOBLE GASES)

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Syllabus

Halogen & Noble Gases

Halogens: hydrohalic acids, oxides and oxyacids of chlorine, bleaching powder.

Noble gas : Isolation, Xenon fluorides, Xenon oxygen compounds.

Name : _____ Contact No. _____

HALOGEN & NOBEL GAS

GROUP 17 ELEMENTS : THE HALOGEN FAMILY

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17. These are collectively known as the halogens (Greek halo means salt and genes born i.e., salt producers). The halogens are highly reactive non-metallic elements.

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.

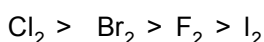
Electronegativity

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

Bond Energy :

F – F bond dissociation energy is less than that of Cl – Cl and Br – Br. It is due to larger inter electronic (electron - electron) repulsion between the non bonding electrons in the 2P orbitals of fluorine atom. then these in the 3p orbitals of chlorine atoms.

F – F	Cl – Cl	Br – Br	I – I
38 kcal/mol	57 kcal/mol	45.5 kcal/mol	35.6 kcal/mol



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 : $\text{Cl} - \text{Cl} > \text{Br} - \text{Br} > \text{F} - \text{F} > \text{I} - \text{I}$. 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 and 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

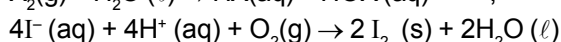
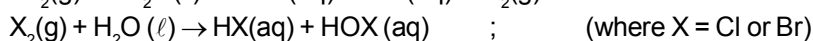
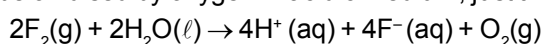
Oxidation states and trends in chemical reactivity

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.

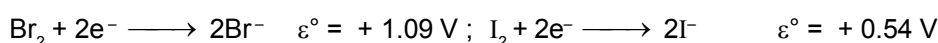
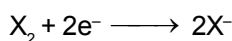
The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only -1 oxidation state.

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. F₂ 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.



Standard Reduction Potential (SRP) and Oxidising Power :



More the value of the SRP, more powerful is the oxidising agent. Hence the order of oxidising power is F₂ > Cl₂ > Br₂ > I₂

Hydration energy of X⁻ :

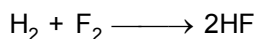
Smaller the ion, higher is the hydration energy.

F ⁻	Cl ⁻	Br ⁻	I ⁻	
515	381	347	305	in kJ/mol

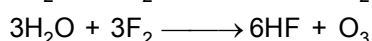
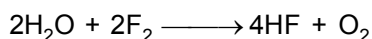
Anomalous behaviour of fluorine

Fluorine differs considerably from other halogens due to -

- (i) Small size
- (ii) High electronegativity.
- (iii) Non availability of d - orbitals in its valency shell.
- (iv) Low bond dissociation energy of F – F bond.
- (a) Boiling point of HF is the highest and for other increases down the group.
- (b) Due to hydrogen bonding HF is a liquid while HCl, HBr and HI are gases.
- (c) Fluorine, being the most electronegative gives SF₆ while other member do not form hexahalides with sulphur.
- (d) It exhibits oxidation state of only –1.
- (e) It is the strongest oxidising agent.
- (f) It liberates oxygen as well as ozone with water.
- (g) HF does not ionize while HCl, HBr and HF ionize in aqueous solution.
- (h) Solubility of salts :
 - (i) AgF is soluble in water while AgCl, AgBr and AgI are insoluble.
- (i) It combines with hydrogen with explosion at a low temperature and even in the dark. No other halogens combines so readily.



- (j) It liberates oxygen as well as ozone with water.



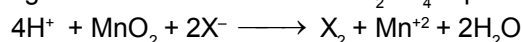
Comparison of [Cl₂, Br₂ and I₂]

S.No.	Property	Chlorine	Bromine	Iodine
1.	Physical State	Gas	Liquid	Solid
2.	Colour of Vapour	Greenish Yellow	Dark Red	Violet
3.	Action of H ₂ O	Decomposes into HCl & O ₂	Decomposes Slowly in Presence of Light	No action
4.	Oxidising Action	Strong	Good	Weak
5.	Bleaching Action	Moist Cl ₂ is a Good Bleaching Agent	Moist Br ₂ is a good Bleaching Agent	No Bleaching
6.	Action of Halides	Displaces Br ₂ & I ₂	Displaces I ₂	No Action
7.	Combination with H ₂	Explosive in Light Slow in Dark	Only on Heating	Heating + Catalyst

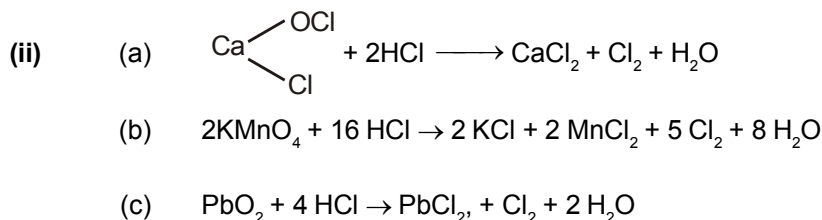
CHLORINE (Cl₂):

Preparation :

- (i) By heating chloride with concentrated H₂SO₄ in presence of MnO₂.



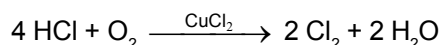
Bromides and iodides also liberate Br₂ and I₂ respectively with concentrated H₂SO₄ and MnO₂.



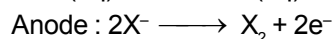
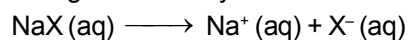
➤ These methods are exclusively used only for chlorine.

(iii) **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.



(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 manufacturing of sodium hydroxide.



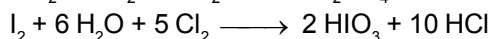
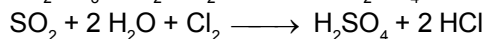
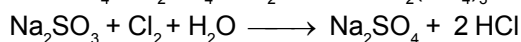
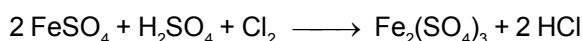
Properties :

(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.

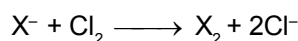
(ii) At low temperature it forms a hydrate with water having formula $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ which is infact a clathrate compound.

(iii) **Oxidising & bleaching properties :** Chlorine dissolves in water giving HCl and HOCl . Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

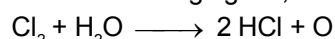
(a) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.



(b) Chlorine oxidises both Br^- and I^- to Br_2 and I_2 respectively.



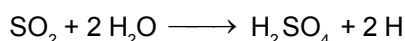
(c) It is a powerful bleaching agent ; bleaching action is due to oxidation.



Coloured substance + O → Colourless substance

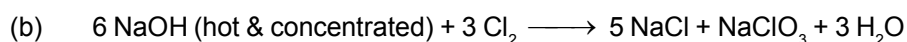
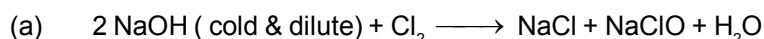
It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

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



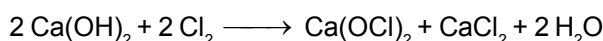
Reduced Colourless material $\xrightarrow{\text{O}_2 \text{ of air}}$ Coloured material.

(iv) **Reaction with NaOH :**



These reactions are also given by Br_2 and I_2 .

(v) **Reaction with dry slaked lime, Ca(OH)₂** : To give bleaching powder.



Uses : Cl₂ 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 CCl₄, CHCl₃, DDT, refrigerants, etc.
3. in the extraction of gold and platinum.

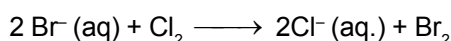
BROMINE (Br₂) :

Preparation :

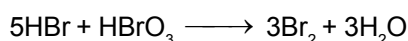
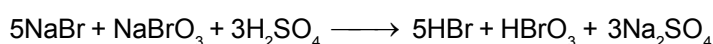
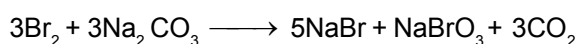
(i) **Common method** : $2 \text{NaBr} + 3\text{H}_2\text{SO}_4$ (concentrated) + MnO₂ $\xrightarrow{\Delta}$ Br₂ + MnSO₄ + 2NaHSO₄ + 2H₂O

(ii) **From Sea-water** :

NaCl is main component but NaBr is also present in some quantity in sea water. Cl₂ gas is passed through sea water when vapours of bromine are evolved.

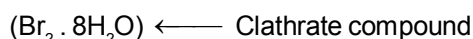


The Br₂ is removed by a stream of air since Br₂ is quite volatile. The gas is passed through a solution of Na₂CO₃ when the Br₂ is absorbed forming a mixture of NaBr and NaBrO₃. The solution is then acidified and distilled to give pure bromine.



Properties :

(i) Reddish brown liquid, fairly soluble in water. It also forms hydrate like Cl₂



(ii) Rest reactions are same as with Cl₂

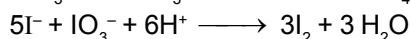
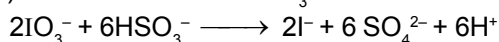
IODINE (I₂) :

Preparation :

(i) **Common method** : $2\text{NaI} + 3\text{H}_2\text{SO}_4$ (concentrated) + MnO₂ $\xrightarrow{\Delta}$ I₂ + MnSO₄ + 2NaHSO₄ + 2H₂O

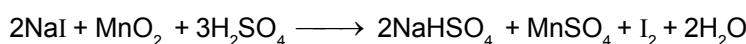
(ii) **From Caliche or Crude chile salt petre** :

The main source of iodine is NaIO₃ (sodium iodate) which is found in nature with NaNO₃ (chile saltpetre). NaIO₃ is present in small amount. After crystallisation of NaNO₃, the mother liquor left contains NaIO₃ (soluble). To this solution NaHSO₃ is added where upon I₂ is precipitated.



(iii) **From sea-weeds** :

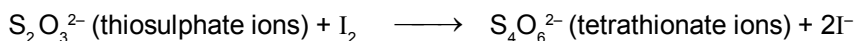
Certain marine plants absorb and concentrate I⁻ selectively in presence of Cl⁻ and Br⁻. Sea-weeds are dried and burnt in shallow pits, ash left is called kelp. Ash on extraction with hot water dissolves out chlorides, carbonates, sulphates and iodides of sodium and potassium. The solution on concentration separates out all leaving behind iodide in the solution. Solution is mixed with MnO₂ and concentrated H₂SO₄ in iron retorts. Liberated iodine is condensed in series of earthenware known as aludels.



Properties :

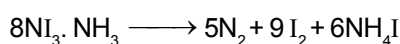
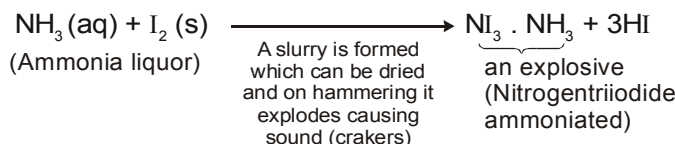
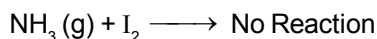
(i) It is a dark violet solid, undergoes sublimation, least soluble (among halogens) in water but much more soluble in KI(aq.) due to formation of KI_3 . It is soluble in organic solvents like $CHCl_3$, CCl_4 etc. to get violet solutions.

(ii) **Reaction with hypo :**

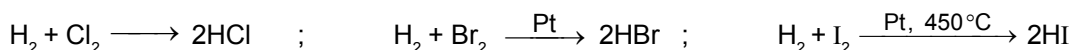


This reaction is the basis of iodometric titration, which is carried out for the estimation of iodine using starch indicator.

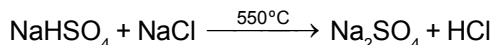
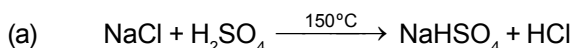
(iii) **Reaction with NH_3 :**

**HALOGEN ACIDS (HCl, HBr & HI) :****Preparation :**

(i) **By direct combination of elements :**

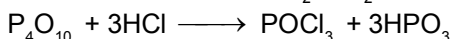
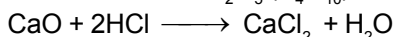


(ii) **By heating a halide with concentrated acid :**



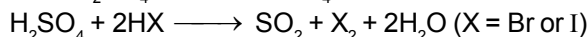
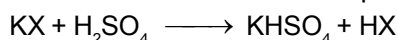
This method is called as salt cake method as it involves the formation of $NaHSO_4$ (salt cake).

HCl cannot be dried over P_2O_5 (P_4O_{10}) or quick lime since they react with gas chemically.

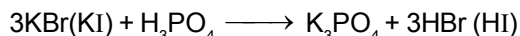


HCl is, hence dried by passing through concentrated H_2SO_4 .

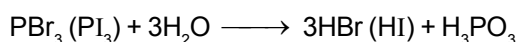
(b) HBr (or HI) cannot be prepared by heating bromide (iodide) with concentrated H_2SO_4 because HBr and HI are strong reducing agents and reduce H_2SO_4 to SO_2 and get themselves oxidised to bromine and iodine respectively.



Hence, HBr and HI are prepared by heating bromides and iodides respectively with concentrated H_3PO_4 .



(iii) **By reaction of P_4 (Laboratory Method) :**

**Properties :**

(i) These are colourless, pungent smelling gases with acidic tastes.

(ii) These are neither combustible nor supporter of combustion.

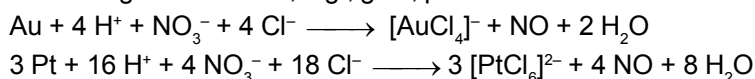
(iii) When perfectly dry, they have no action on litmus, but in presence of moisture, they turn blue litmus red, showing acidic nature. Among HX, HI is the strongest and HF is the weakest acid.

(iv) These are quite soluble in water.

HCl ionises as below : $HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq) ; K_a = 10^7$

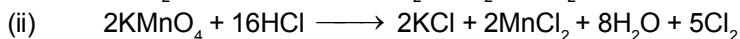
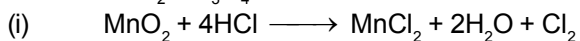
Its aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water.

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.

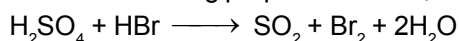


(v) **Reducing property and stability of hydrazides :**

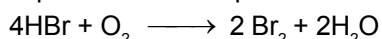
HCl : It is quite stable and hence is oxidised by strong oxidising agents like MnO_2 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, PbO_2 , Pb_3O_4 .



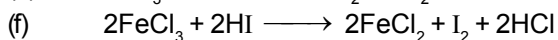
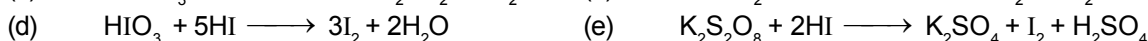
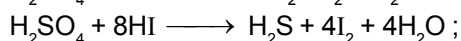
HBr : It is not very stable and hence more easily oxidised or acts as a strong reducing agent. In addition to above reducing properties of HCl, it also reduces H_2SO_4 to SO_2 which is not done by HCl.



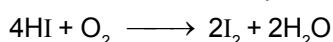
Aqueous HBr on exposure to atmospheric oxygen is oxidised to bromine (yellow)



HI : It is least stable hydrogen halide. It is readily oxidised and thus acts as a powerful reducing agent. In addition to reaction shown by HCl, it shows following reactions also.



➤ Aqueous solution of acid, if exposed to O_2 is oxidised to iodine.



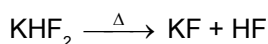
HYDROFLUORIC ACID [H_2F_2 , HF] :

Preparation :

H_2 and F_2 combine with each other very violently (even in dark) to form HF. So simple reaction cannot be used for its preparation, special methods are employed for its preparation.

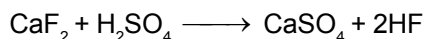
(i) **Laboratory Method :**

Anhydrous HF is obtained by heating dry potassium hydrogen fluoride in a copper retort connected with copper condenser.

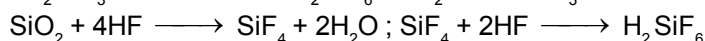


(ii) **Industrial Method :**

HF is prepared by heating fluorspar (CaF_2) with concentrated H_2SO_4 .



➤ Aqueous HF being corrosive to glass, is stored in wax lined bottles or vessel made of copper or monel. In glass or silica bottles, it attacks them as follows:



This action of HF on silica (silicates) is used for etching glass. The glass surface to be etched is coated with wax, the design, is scratched on glass through wax coating and this is then treated with 40% solution.

Properties :

(i) It is colourless, corrosive liquid with pungent smell with high boiling point due to hydrogen bonding.

(ii) Dry HF does not attack metals under ordinary conditions (except K), but in presence of water it dissolves metals with liberation of hydrogen gas.

(iii) It is a weak dibasic acid (due to strong HF bond) and forms two series of salt.



OXIDES OF CHLORINE :

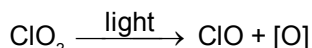
CHLORINE DIOXIDE (ClO₂):

Preparation :

- (i) $2 \text{NaClO}_3 + \text{SO}_2 + \text{H}_2\text{SO}_4 \xrightarrow{\text{traces of NaCl}} 2\text{ClO}_2 + 2\text{NaHSO}_4$
- (ii) $2\text{KClO}_3 + 2 \text{H}_2\text{C}_2\text{O}_4 \xrightarrow{90^\circ\text{C}} 2\text{ClO}_2(\text{g}) + 2\text{CO}_2(\text{g}) + \text{K}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$
- (iii) $2\text{AgClO}_3 + \text{Cl}_2 \xrightarrow{90^\circ\text{C}} 2\text{AgCl} \downarrow (\text{white}) + 2\text{ClO}_2 + \text{O}_2$

Properties :

- (i) Yellow gas at room temperature dissolves in water evolving heat and giving a dark green solution.



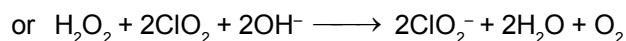
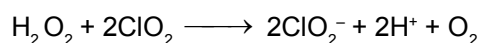
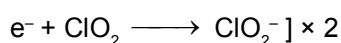
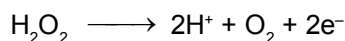
It kill bacteria better than Cl₂.

- (ii) **Reaction with ozone :** $2\text{ClO}_2 + 2\text{O}_3 \xrightarrow{\text{H}^+} \text{Cl}_2\text{O}_6 (\text{yellow solid}) + 2\text{O}_2$
dichlorine hexa oxide

In the reaction O₃ is behaving as an oxidising agent.

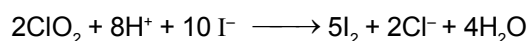
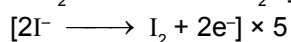
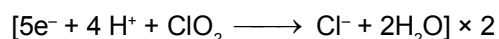
- (iii) **Reaction with alkaline H₂O₂ :**

In this reaction H₂O₂ acts as a reducing agent. It reduces ClO₂ into ClO₂⁻



- (iv) **Reaction with HI :**

In this reaction HI behaves as a reducing agent where it reduces ClO₂ into Cl⁻ and itself is oxidised to I₂.



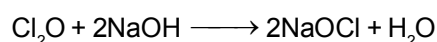
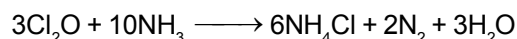
Dichlorine Monoxide (Cl₂O) :

Preparation :



Properties :

Cl₂O is yellow-brown gas very soluble in water.

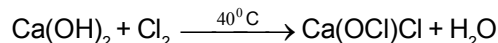


BLEACHING POWDER (CaOCl₂.H₂O)

Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

Ca(OCl)Cl

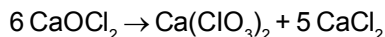
Preparation:



Properties

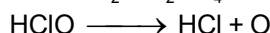
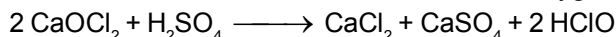
(i) It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.

(ii) On long standing, it undergoes auto-oxidation into calcium chlorate and calcium chloride.



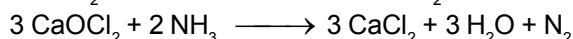
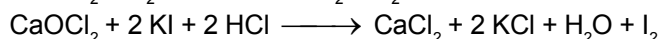
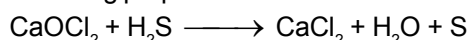
(iii) $2 \text{CaOCl}_2 \xrightarrow{\text{CoCl}_2} 2 \text{CaCl}_2 + \text{O}_2$

(iv) In presence of a little amount of a dilute acid, it loses oxygen.



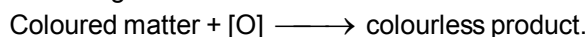
On account of the liberation of nascent oxygen, it shows oxidising and bleaching properties.

(a) Oxidising properties

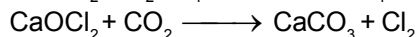
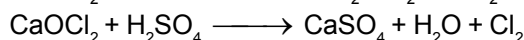
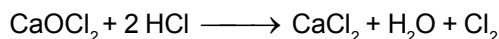


➤ It oxidises NO_2^- to NO_3^- , AsO_3^{3-} to AsO_4^{3-} and Fe^{2+} to Fe^{3+} (in acidic medium)

(b) Bleaching action

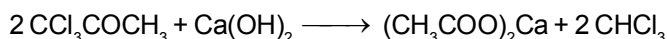


(v) When bleaching powder reacts with dilute acids or CO_2 it liberates chlorine which is known as available chlorine.



➤ HNO_3 is a strong oxidising acid to be avoided, here.

(vi) Bleaching powder converts acetone or ethyl alcohol into CHCl_3



OXY-ACIDS OF HALOGENS :

Oxidation state of halogens	Chlorine	Bromine	Iodine	Name of acid	Name of salt	
+1	HClO	HBrO	HIO	Hypohalous	Hypohalite	Stability and acidity
+3	HClO ₂	-	-	Halous	Halite	increases but
+5	HClO ₃	HBrO ₃	HIO ₃	Hallic	Halate	oxidising power
+7	HClO ₄	HBrO ₄	HIO ₄	Perhalic	Perhalate	decreases

—————→

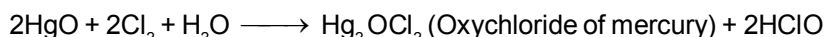
Acidity increases

HOX SERIES :

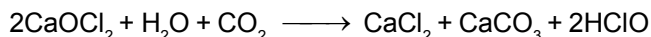
HYPO-CHLOROUS ACID [HClO] :

Preparation :

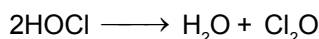
- (i) The acid is known only in solution, It is obtained by shaking precipitate of HgO with chlorine water.



- (ii) Commercially, it is obtained by passing CO_2 through suspension of bleaching powder and then distilling.

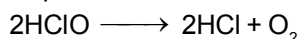


Maximum concentration obtained is 25% as in the process of distillation, the acid decomposes into its anhydrides, Cl_2O .

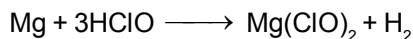


Properties :

- (i) It is a weak acid. Its concentrated solution is yellow in colour while dilute solution is colourless. It is unstable and decomposes.

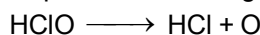


- (ii) It dissolves magnesium with evolution of hydrogen.



- (iii) With alkalis, it forms salts called hypochlorites.

- (iv) It acts as a powerful oxidising and bleaching agent. This is due to release of nascent oxygen easily.

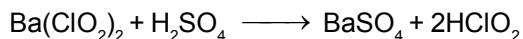


HXO₂ SERIES :

CHLOROUS ACID [HClO₂] :

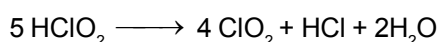
Preparation :

It is obtained in aqueous solution when barium chlorite suspension in water is treated with H_2SO_4 . The insoluble barium sulphate is filtered off.

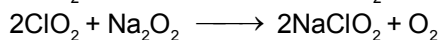
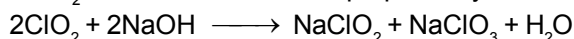


Properties:

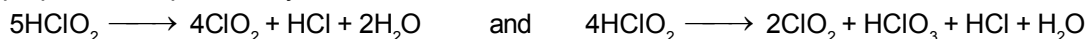
- (i) The freshly prepared solution is colourless but it soon decomposes to ClO_2 which makes the solution yellow.



- (ii) Salts of HClO_2 are called chlorite and prepared by one of the following methods.



Chlorites are used as bleaches. They are stable in alkaline solution even when boiled, but in acid solution they disproportionate, particularly when heated.

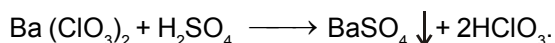


HXO₃ SERIES

CHLORIC ACID [HClO₃] :

Preparation :

This acid is only known in solution. The acid is prepared by the action of the dilute H_2SO_4 on barium chlorate.



After reaction, BaSO_4 is removed by filtration, and the filtrate is evaporated in vacuum till 40 percent solution is obtained. However, further concentration by evaporation leads to decomposition.



HBrO_3 can be prepared by similar method using $\text{Ba}(\text{BrO}_3)_2$.

Properties :

Concentrated acid is colourless and pungent smelling liquid. It decomposes in light. However, it is stable in dark. It acts as a strong oxidising and bleaching agent in light. Organic substances like paper, cotton, wool, etc., catch fire in contact with the acid.

- HClO_3 oxidises SO_2 to SO_3 : $\text{HClO}_3 + 3\text{SO}_2 \longrightarrow \text{HCl} + 3\text{SO}_3$
- HClO_3 when evaporates to dryness decomposes giving ClO_2 .
 $4\text{HClO}_3 \longrightarrow 4\text{ClO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$
- HBrO_3 is not very stable, but is known in solution, and as salts.
- HIO_3 is formed by oxidation of I_2 with concentrated HNO_3 or O_3 .
 $8\text{H}^+ + 10\text{NO}_3^- + \text{I}_2 \longrightarrow 2\text{IO}_3^- + 10\text{NO}_2 + 4\text{H}_2\text{O}$
- IO_3^- oxidises I^- to I_2 : $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$
- Iodic acid is reasonably stable and exists as a white solid.

PERCHLORIC ACID [HClO_4] :

Preparation:

- (i) It is the most stable oxy-acid of chlorine. Anhydrous HClO_4 is obtained by doing distillation of KClO_4 (potassium perchlorate), with 96-97.5% H_2SO_4 under low pressure at 90-160°C.
 $\text{KClO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{HClO}_4$
- (ii) An aqueous solution of the acid is obtained by reacting barium perchlorate with calculated quantity of dilute H_2SO_4 . The insoluble barium sulphate is removed by filtration.
 $\text{Ba}(\text{ClO}_4)_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 \downarrow + 2\text{HClO}_4$
- (iii) $4\text{ClO}_3^- \xrightarrow{\Delta} 3\text{ClO}_4^- + \text{Cl}^-$

Properties:

- (i) Anhydrous HClO_4 is a colourless liquid which turns dark on keeping. It fumes in moist air.
 - (ii) It is one of the strongest acid and ionises as follows :
 $\text{HClO}_4 \longrightarrow \text{H}^+ + \text{ClO}_4^-$
 - (iii) It dissolves most of the metals.
 $\text{Zn} + 2\text{HClO}_4 \longrightarrow \text{Zn}(\text{ClO}_4)_2 + \text{H}_2$
 - (iv) Hot concentrated acid (73%) behaves as a remarkable oxidising agent :
 $4\text{HClO}_4 \longrightarrow 2\text{Cl}_2 + 7\text{O}_2 + 2\text{H}_2\text{O}$
 - (v) $2\text{HClO}_4 + \text{P}_2\text{O}_5 \longrightarrow 2\text{HPO}_3 + \text{Cl}_2\text{O}_7$
- $\text{Mg}(\text{ClO}_4)_2$ is used in dry batteries and is also an effective desiccant called anhydron. KClO_4 is used in fire works and flares.

Some important order

- (a) Acid strength
 - (i) $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (ii) $\text{HOCl} > \text{HOBr} > \text{HOI}$
 - (iii) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$ (Order of stability of conjugate base $\text{ClO}^- < \text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$)
- (b) Oxidising powder
 - (i) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
 - (ii) $\text{BrO}_4^- > \text{IO}_4^- > \text{ClO}_4^-$ (According to electrode potential)
- (c) Order of disproportionations
 $3\text{XO}^- \longrightarrow 2\text{X}^- + \text{XO}_3^-$ (hypohalite ion) ; $\text{IO}^- > \text{BrO}^- > \text{ClO}^-$
- (d) Order of Stability $\text{HClO} > \text{HBrO} > \text{HIO}$

Pseudo halogens and pseudo halides :

A few ions are known, consisting of two or more electronegative atoms of which at least one is nitrogen, that have properties similar to those of halide ions. These ions are called pseudohalide ions, Pseudohalide ions are univalent and these form salts resembling halide salts.

The pseudohalide ions are :

Cyanide ions (CN⁻) : Isocyanide ion (NC⁻)
 Cyanate ion (OCN⁻) : Fulminate ion (ONC⁻)
 Thiocyanate ions (SCN⁻) : Isothiocyanate ion (NCS⁻)
 Selenocyanate ion (SeCN⁻) : Tellurocyanate ion (TeCN⁻)
 Azide ion (N₃⁻) : Azido carbon disulphide ion (SCSN₃⁻)

As the dimers of halide ions are called halogens, the covalent dimers of the pseudohalide ions are called halogens or halogenoids. The pseudohalogens known are :

Cyanogen (CN)₂ : Oxycyanogen (OCN)₂
 Thiocyanogen (SCN)₂ : Selenocyanogen
 (SeCN)₂
 Tellurocyanogen (TeCN)₂ : Azido carbon
 disulphide (SCSN₃)₂

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.

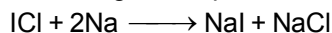
AB	AB ₃	AB ₅	AB ₇
ClF	ClF ₃	ClF ₅	IF ₇
BrF	BrF ₃	BrF ₅	
ICl	ICl ₃	IF ₅	
IF	IF ₃		

Properties :

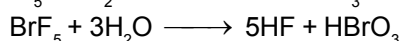
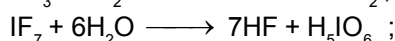
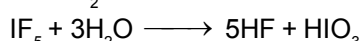
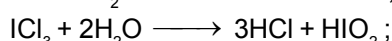
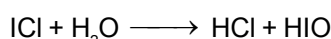
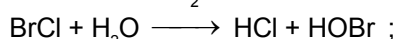
- (i) These compounds may be gases, liquids or solids.
 Gases : ClF, BrF, ClF₃, IF₇; Liquids : BrF₃, BrF₅; Solids : ICl, IBr, IF₃, ICl₃.
- (ii) Interhalogens containing fluorine are colourless but inter halogens consisting of heavier halogens are coloured. The intensity of colour increases with increase in the molecular weight of the compounds.
- (iii) All interhalogens are covalent molecules and are diamagnetic in nature since all the valence electrons present as bonding or non-bonding electrons are paired.
- (iv) The boiling points increases with the increase in the electronegativity difference between A and B atoms.
- (v) Thermal stability of AB type interhalogen compounds decreases with the decrease in electronegativity difference between A and B atoms. IF > BrF > ClF > ICl > IBr > BrCl.

➤ More polar is the A – B bond more is the stability of interhalogen.

- (vi) Interhalogen compounds are more reactive than the parent halogens but less reactive than F₂.



- (vii) Hydrolysis : All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when AB), halite (when AB₃), halate (when AB₅), and perhalate (when AB₇) anion derived from the larger halogen.

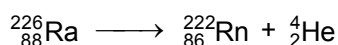


GROUP 18 ELEMENTS : (THE ZERO GROUP FAMILY)

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 $\text{Ar} > \text{Ne} > \text{Kr} > \text{He} > \text{Xe}$.

ISOLATION

Except He, non-radioactive noble gases are commercially isolated from air by two methods.

(i) Fractional Distillation of Liquid air (Claude's Method) :

Due to difference in b.p. the various constituents of air are separated from each other.

(ii) Dewar's Coconut Charcoal Adsorption Method :

- O_2 and N_2 are removed by means of compound formation.
- The principle of this method is that the adsorption capacity of these gases at low temperature by coconut charcoal increases with increases in their atomic weights.
- Thus He has the lowest and Xe has the maximum adsorption capacity.

Adsorption of Inert Gases :

- Done on coconut. Gas particles are adsorbed in surface of coconut charcoal
- Larger the size, more will be the adsorption so maximum adsorption of Xe at highest temp.

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 and 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	$1s^2$	$[\text{He}] 2s^2 2p^6$	$[\text{Ne}] 3s^2 3p^6$	$[\text{Ar}] 3d^{10} 4s^2 4p^6$	$[\text{Kr}] 4d^{10} 5s^2 5p^6$
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 of xenon (1170 kJ mol^{-1}). He made efforts to prepare same type of compound with $Xe^+ PtF_6^-$ 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.

➤ If Helium is compressed and liquified it forms He(I) liquid at 4.2 K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K, which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity.

Clathrate compounds :

Inert gas molecules get trapped in the cages formed by the crystal structure of water.

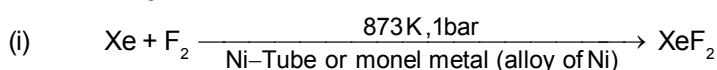
During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clathrate compounds.

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.

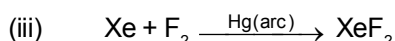
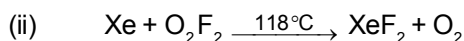
COMPOUNDS OF XENON :

XENON DIFLUORIDE (XeF_2):

Preparation:



➤ Volume ratio should be 2 : 1 otherwise other higher fluorides tend to form.



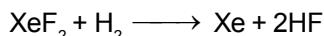
(iv) Recently discovered method :

$K^+ [AgF_4]^-$ [potassium tetrafluoroargentate (III)] is first prepared and this is reacted with BF_3 .

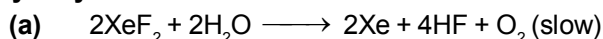


Properties :

- (i) Colorless crystalline solid and sublimates at 298 K.
- (ii) Dissolves in water to give a solution with a pungent odour. Much soluble in HF liquid.
- (iii) This is stored in a vessel made up of monel metal which is a alloy of nickel.
- (iv) **Reaction with H_2 :** It reacts with hydrogen gas at 400°C

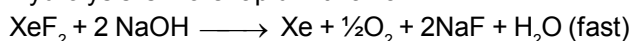


(v) **Hydrolysis :**



The above is neither a cationic hydrolysis nor an anionic hydrolysis as seen in ionic equilibrium. It is a covalent compound and hydrolysis is like that of PCl_5 .

(b) Hydrolysis is more rapid with alkali.

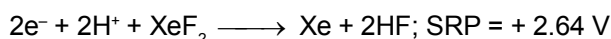


The reaction (a) is slower probably due to dissolution of XeF_2 in HF.

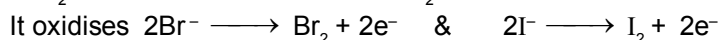
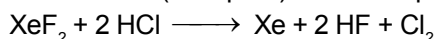
(vi) **Oxidising properties :**

Higher the value of SRP better is the oxidising property of the species.

The standard reduction potential for XeF_2 is measured to be + 2.64 V. Therefore, it acts as a strong oxidising agent.

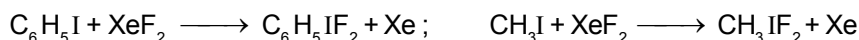


This oxidises halides (except F⁻) to their respective halogens.



- Similarly it can oxidise BrO₃⁻ (bromate) which are themselves good oxidising agents to BrO₄⁻ (perbromate ions) and Ce³⁺ to Ce⁴⁺ ion.

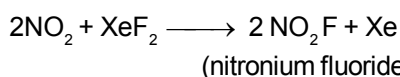
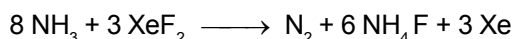
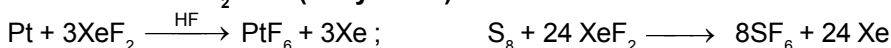
- (vii) **Oxidising as well as fluorinating properties** : It can act as strong oxidising agent as well as fluorinating agent.



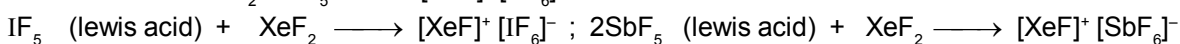
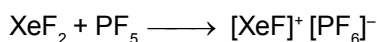
- CH₃IF₂ exists as CH₃⁺IF₂⁻, IF₂⁻ is analogous to I₃⁻

- F₃⁻ can not be formed as it has no d-orbitals to attain sp³d hybridisation.

- (viii) **Reactions of XeF₂ + HF (anhydrous)** :



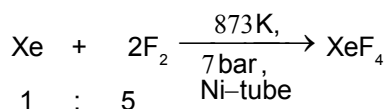
- (ix) **Formation of addition compounds** : XeF₂ reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



- Similar behaviour is shown by PF₅ and AsF₅

XENON TETRAFLUORIDE (XeF₄) :

Preparation :



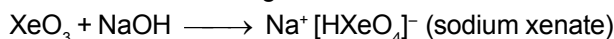
Properties :

- (i) It is a colorless crystalline solid and sublimes at 298 K.
 (ii) It undergoes sublimation, soluble in CF₃COOH. It undergoes hydrolysis violently hence no moisture must be present during its preparation.

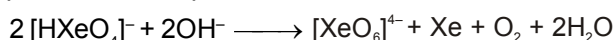
- (iii) **Reaction with H₂O** : $6 \text{XeF}_4 + 12 \text{H}_2\text{O} \longrightarrow 4 \text{Xe} + 2\text{XeO}_3 + 24 \text{HF} + 3\text{O}_2$

- XeO₃ is white solid and explosive compound (dry), soluble in water (well behaved in water)

- XeO₃ reacts with NaOH forming sodium xenate

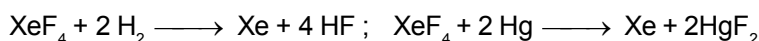


- It disproportionates into perxenate ion in basic medium.

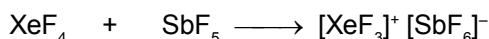


Xenic acid (H₂XeO₄) is a very weak acid.

- (iv) **Oxidising properties of XeF₄** :

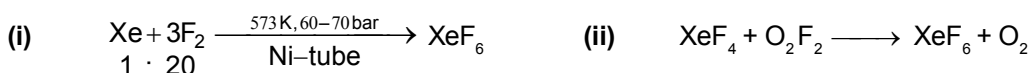


- (v) **Addition reactions** : XeF₄ reacts with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.



XENON HEXAFLUORIDE (XeF₆) :

Preparation:



EXERCISE # 1

PART - I : OBJECTIVE QUESTIONS

* Marked Questions are having more than one correct option.

Group 17th

- The halogens are :
(A) transition elements (B) inner-transition elements
(C) noble elements (D) representative elements
- Astatine is the element below iodine in the group VIIA of the periodic table. Which of the following statements is not true for astatine ?
(A) It is less electronegative than iodine.
(B) It will exhibit only -1 oxidation state.
(C) Intermolecular forces between the astatine molecules will be larger than that between iodine molecules.
(D) None of these.
- H₂O is oxidised to O₂ by :
(A) ClO₂ (B) H₂O₂ (C) H₂O (D) F₂
- Oxidising action increases in the following order :
(A) Cl₂ < Br₂ < I₂ < F₂ (B) Cl₂ < I₂ < Br₂ < F₂ (C) I₂ < F₂ < Cl₂ < Br₂ (D) I₂ < Br₂ < Cl₂ < F₂
- Which of the following hydrogen halide is most volatile.
(A) HCl (B) HF (C) HI (D) HBr
- Which can do glass etching ?
(A) HIO₄ (B) HF (C) HNO₃ (D) SiF₄
- Which of the following pairs is not correctly matched ?
(A) A halogen which is liquid at room temperature – Bromine
(B) The most electronegative element – Fluorine
(C) The most reactive halogen – Fluorine
(D) The strongest oxidising agent – Iodine
- Hydrogen bonding does not play role in the boiling point of :
(A) NH₃ (B) H₂O (C) HI (D) HF
- Fluorine does not show positive oxidation states because -
(A) It is most electronegative element
(B) It forms only anions in ionic compounds
(C) It cannot form multiple bonds
(D) It shows non-bonded electron pair repulsion due to small size
- When iodine reacts with NaF, NaBr and NaCl -
(A) It gives mixture of F₂, Cl₂ and Br₂ (B) It gives chlorine
(C) It gives bromine (D) None of the above
- Which one of the following is wrongly matched ?
(A) ClO₃⁻, sp³ pyramidal (B) ClO₄⁻, sp³ tetrahedral
(C) ICl₄⁻, sp³d² square planar (D) ICl₂⁻, dsp² trigonal bipyramidal

12. Which of the following possess the highest bond energy ?
 (A) F_2 (B) Cl_2 (C) Br_2 (D) I_2
13. Elements of which one of the following groups will form anions most readily ?
 (A) oxygen group (B) nitrogen group (C) halogens (D) alkali metals
14. The strongest reducing agent is :
 (A) F^- (B) Cl^- (C) Br^- (D) I^-
15. The most powerful oxidising agent is :
 (A) fluorine (B) chlorine (C) bromine (D) iodine
16. Which one of the hydric acid does not form any precipitate with $AgNO_3$?
 (A) HF (B) HCl (C) HBr (D) HI
17. Which of the following is the strongest acid ?
 (A) HBr (B) HF (C) H_2S (D) PH_3
18. Which of the following has highest bond strength :
 (A) HI (B) HCl (C) HF (D) HBr
19. On heating $KClO_3$ we get :
 (A) $KClO_2 + O_2$ (B) $KCl + O_2$ (C) $KCl + O_3$ (D) $KCl + O_2 + O_3$
20. T-shape molecule are -
 (A) ClF_3 (B) ICl_3 (C) BrF_3 (D) All of these
21. Of the following statements -
 (a) Cl_2 gas is dried by using conc. H_2SO_4
 (b) Fluorine have highest oxidising power
 (c) Oxidising power of halogens follow the order $I_2 > Br_2 > Cl_2$
 (d) HI is the strongest acid among HI, HBr, HCl
 (A) a, b and d are corrects (B) a, c are corrects
 (C) b, c are corrects (D) c, d are corrects
22. Which of the following statements about the halogen is correct ?
 (A) They are all diatomic and forms univalent ions
 (B) They are all diatomic and forms divalent ions
 (C) All shows variable oxidation state
 (D) All
23. Volatile nature of halogen is because -
 (A) Halogen molecules are bonded by strong forces
 (B) Halogen molecules are bonded by electrostatics force
 (C) The forces existing between the discrete molecule are only weak vander waal's force
 (D) Halogen molecules are more reactive
24. Hydrogen fluoride is a liquid unlike other hydrogen halides because -
 (A) F atom is small in size (B) HF is a weakest acid
 (C) HF molecule are hydrogen bonded (D) Fluorine is highly reactive
25. The property of halogen acids, that indicated incorrect is -
 (A) $HF > HCl > HBr > HI$acidic strength (B) $HI > HBr > HCl > HF$reducing strength
 (C) $HI > HBr > HCl > HF$bond length (D) $HF > HCl > HBr > HI$ thermal stability
26. I_4O_9 is a/an -
 (A) Covalent compound (B) Coordinate compound
 (C) Ionic compound (D) Double salt

27. Bleaching powder is an example of -
 (A) An acidic salt (B) A complex salt (C) A double salt (D) A mixed salt
28. Which of the following pairs is not correctly matched -
 (A) A halogen which is liquid at room temperature-Bromine
 (B) The most electronegative element - Fluorine
 (C) The most reactive halogen-Fluorine
 (D) The strongest oxidising agent - Iodine
29. Which of the following has the greatest reducing power -
 (A) HBr (B) HI (C) HCl (D) HF
30. When iodine is dissolved in CCl_4 , the colour that result is -
 (A) Brown (B) Bluish green (C) Violet (D) Colourless
31. ClO_2 is the anhydride of :
 (A) HOCl (B) HClO_2 (C) HClO_3 (D) HClO_2 and HClO_3
32. ClO_3 is the mixed anhydride of :
 (A) HClO_2 and HClO_3 (B) HClO_3 and HClO_4 (C) HClO_2 and HClO_4 (D) HClO_2 and HClO_3
33. Concentrated H_2SO_4 cannot be used to prepare HBr from NaBr, because it ;
 (A) reduces HBr (B) oxidises HBr
 (C) disproportionates HBr (D) reacts slowly with NaBr
34. The following acids have been arranged in order of decreasing acid strength. Identify the correct order.
 ClOH (I), BrOH (II), IOH (III)
 (A) $\text{I} > \text{II} > \text{III}$ (B) $\text{II} > \text{I} > \text{III}$ (C) $\text{III} > \text{II} > \text{I}$ (D) $\text{I} > \text{III} > \text{II}$
35. Which one of the following is not a pseudohalide ?
 (A) CNO^- (B) RCOO^- (C) OCN^- (D) NNN^-
36. Which of the following is weakest oxidising agent ?
 (A) F_2 (B) Cl_2 (C) Br_2 (D) I_2
37. Fluorine reacts with water to give :
 (A) oxygen and hydrogen fluoride (B) HOF and O_3
 (C) hydrogen fluoride and HOF (D) No reaction
38. F_2 is formed by reacting K_2MnF_6 with :
 (A) SbF_5 (B) MnF_3 (C) KSbF_6 (D) MnF_5
39. Which of the following is not oxidised by MnO_2 ?
 (A) F^- (B) Cl^- (C) Br^- (D) I^-
40. Chlorine acts as a bleaching agent only in presence of :
 (A) dry air (B) moisture (C) sunlight (D) pure oxygen
41. Which reaction is possible -
 (A) $\text{I}_2 + 2\text{NaBr} \longrightarrow \text{Br}_2 + 2\text{NaI}$ (B) $\text{I}_2 + 2\text{NaCl} \longrightarrow \text{Cl}_2 + 2\text{NaI}$
 (C) $\text{Br}_2 + 2\text{NaCl} \longrightarrow \text{Cl}_2 + 2\text{NaBr}$ (D) $\text{Cl}_2 + 2\text{NaBr} \longrightarrow \text{Br}_2 + 2\text{NaCl}$
42. Which has maximum pH in aqueous solution -
 (A) NaClO (B) NaClO_2 (C) NaClO_3 (D) NaClO_4
43. Which one of the following is the strongest oxidising agent -
 (A) HClO (B) HClO_2 (C) HClO_3 (D) HClO_4

44. The solubility of iodine in H_2O may be increased by the addition of -
 (A) $Na_2S_2O_3$ (B) $CHCl_3$ (C) KI (D) CS_2
45. When thiosulphate ion is oxidised by iodine, the new product formed is :
 (A) SO_3^{2-} (B) SO_4^{2-} (C) $S_4O_6^{2-}$ (D) $S_2O_6^{2-}$
46. Iodine is liberated from KI solution when treated with :
 (A) $ZnSO_4$ (B) $CuSO_4$ (C) $NiSO_4$ (D) $FeSO_4$
47. Concentrated HNO_3 reacts with I_2 to give :
 (A) HI (B) HOI (C) HIO_3 (D) $HOIO_3$
48. Bleaching powder is obtained by the interaction of chlorine and :
 (A) dilute solution of $Ca(OH)_2$ (B) concentrated solution of $Ca(OH)_2$
 (C) dry calcium oxide (D) dry slaked lime
49. Which amongst the following reactions cannot be used for the respective preparation ?
 (A) $2KBr + H_2SO_4$ (conc.) $\longrightarrow K_2SO_4 + 2HBr$ (B) $NaCl + H_2SO_4$ (conc.) $\longrightarrow NaHSO_4 + HCl$
 (C) $NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$ (D) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$
50. In the preparation of HBr or HI , NaX ($X = Br, I$) is treated with H_3PO_4 and not by concentrated H_2SO_4 since,
 (A) H_2SO_4 makes the reaction reversible
 (B) H_2SO_4 oxidises HX to X_2 (Br_2, I_2)
 (C) Na_2SO_4 is water soluble and Na_3PO_4 is water insoluble
 (D) Na_3PO_4 is water insoluble and Na_2SO_4 is water soluble
51. HBr and HI can reduce H_2SO_4 , HCl can reduce $KMnO_4$ and HF can reduce :
 (A) $K_2Cr_2O_7$ (B) $KMnO_4$ (C) H_2SO_4 (D) none of these
52. The strongest acid amongst the following is :
 (A) $HClO_4$ (B) $HClO_3$ (C) $HClO_2$ (D) $HClO$
53. The isoelectronic pair is :
 (A) Cl_2O, ICl_2^- (B) ICl_2^-, ClO_2 (C) IF_2^+, I_3^- (D) ClO_2^-, ClF_2^+
54. Which one is the anhydride of $HClO_4$?
 (A) Cl_2O (B) ClO_2 (C) Cl_2O_6 (D) Cl_2O_7
55. The reaction, $3ClO^-$ (aq.) $\longrightarrow ClO_3^-$ (aq.) + $2Cl^-$ (aq.)
 is an example of :
 (A) oxidation reaction (B) reduction reaction (C) disproportionation (D) decomposition reaction
56. The chemical name of bleaching powder is -
 (A) Calcium hypochlorite (B) Calcium chlorohypochlorite
 (C) Calcium chlorate (D) Calcium perchlorate
57. Which one of the following is the strongest acid -
 (A) $SO(OH)_2$ (B) $SO_2(OH)_2$ (C) $ClO_2(OH)$ (D) $ClO_3(OH)$
58. Chlorine acts as a bleaching agent only in the presence of -
 (A) Dry air (B) Sun light (C) Moisture (D) Pure oxygen
59. Antichlor is a compound -
 (A) Which absorbs chlorine (B) Which removes Cl_2 from a material
 (C) Which liberates Cl_2 from bleaching powder (D) Which acts as a catalyst in the manufacture of Cl_2

60. HCl cannot form H_2Cl_2 , while HF can form hydrogen bonds -
 (A) Fluorine is more reactive
 (B) HF is more reactive
 (C) Fluorine atom is small and can form hydrogen bonds
 (D) None
61. The ion that cannot undergo disproportionation is -
 (A) ClO_4^- (B) ClO_3^- (C) ClO_2^- (D) ClO^-
62. $\text{Cl}_2 \xrightarrow{\text{Cold and dilute NaOH}}$ (A) + NaCl + H_2O
 $\text{Cl}_2 \xrightarrow{\text{Hot and conc. NaOH}}$ (B) + NaCl + H_2O
 Compounds (A) and (B) are -
 (A) NaClO_3 , NaClO (B) NaOCl_2 , NaOCl (C) NaClO_4 , NaClO_3 (D) NaOCl, NaClO_3
- 63.* Which is / are true statement(s) ?
 (A) Basic nature of X^- is in order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$
 (B) HI is strongest acid of HF, HCl, HBr and HI
 (C) The ionic character of M—X bond decreases in the order M—F > M—Cl > M—Br > M—I
 (D) Among F, Cl, Br and I, F has the highest enthalpy of hydration.
- 64.* Electrolysis of aqueous solution of Brine (NaCl) gives :
 (A) Cl_2 (B) H_2 (C) NaOH (D) None
- 65.* Which of the following salts will evolve halogen on treatment with conc. H_2SO_4 ?
 (A) NaCl (B) KI (C) NaBr (D) none of these
- 66.* Iodine reacts with hypo to give :
 (A) NaI (B) Na_2SO_3 (C) $\text{Na}_2\text{S}_4\text{O}_6$ (D) Na_2SO_4
- 67.* Select the correct order of acidity :
 (A) $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ (B) $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$
 (C) $\text{HClO} < \text{HBrO} > \text{HIO}$ (D) $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$
- 68.* Which of the following product(s) is/are obtained when Cl_2O_6 reacts with KOH ?
 (A) KCl (B) KClO_2 (C) KClO_3 (D) KClO_4
- 69.* Which of the following product(s) is/are obtained when Cl_2O reacts with NH_3 ?
 (A) NO_2 (B) N_2 (C) NCl_3 (D) NH_4Cl

Group 18th

1. The formation of $\text{O}_2^+ [\text{PtF}_6]^-$ is the basis for the formation of xenon fluorides. This is because :
 (A) O_2 and Xe have comparable sizes.
 (B) both O_2 and Xe are gases.
 (C) O_2 and Xe have comparable ionisation energies.
 (D) O_2 and Xe have comparable electronegativities.
2. Which of the following gaseous molecules is monoatomic ?
 (A) chlorine (B) helium (C) oxygen (D) nitrogen
3. Which one of the following noble gases is not found in atmosphere ?
 (A) Rn (B) Kr (C) Ne (D) Ar
4. The inert gas abundantly found in atmosphere is :
 (A) Ar (B) Kr (C) He (D) Xe

5. The inert gases can be isolated and separated by -
 (A) Electrolysis of their compounds (B) Fractional distillation of liquid air
 (C) Adsorption on charcoal (D) Both (B) and (C)
6. Hybridisation involved in the structure of XeF_2 -
 (A) sp^3d^2 (B) dsp^2 (C) sp^3d (D) sp^3
7. Which of the following noble gas was reacted with PtF_6 by Bartlett to prepare the first noble gas compounds-
 (A) He (B) Xe (C) Ar (D) Kr
8. Molecular shapes of SF_4 , CF_4 and XeF_4 are -
 (A) The same, with 2, 0 and 1 lone pairs of electrons respectively
 (B) The same, with 1, 1 and 1 lone pairs of electrons respectively
 (C) Different, with 0, 1 and 2 lone pairs of electrons respectively
 (D) Different, with 1, 0 and 2 lone pairs of electrons respectively
9. Of the following species, one which is non-existent :
 (A) XeF_6 (B) XeF_5 (C) XeF_4 (D) XeF_2
10. Maximum number of compounds are known in the case of :
 (A) neon (B) xenon (C) krypton (D) argon
11. Which inert gas has abnormal behaviour on liquefaction ?
 (A) Xe (B) He (C) Ar (D) Kr
12. Helium is added to oxygen used by deep sea divers because :
 (A) It is less soluble in blood than nitrogen under high pressure
 (B) It is lighter than nitrogen
 (C) It is readily miscible with oxygen
 (D) It is less poisonous than nitrogen
13. Helium oxygen mixture is used by deep sea divers in preference to nitrogen oxygen mixture because-
 (A) Helium is much less soluble in blood than nitrogen
 (B) Nitrogen is much less soluble in blood than helium
 (C) Due to high pressure deep under sea nitrogen and oxygen react to give poisonous nitric oxide
 (D) Nitrogen is highly soluble in water
14. Which of the following two are isostructural -
 (A) XeF_2 , IF_2^- (B) NH_3 , BF_3 (C) CO_3^{2-} , SO_3^{2-} (D) PCl_5 , ICl_5
15. Hybridization and structure of XeF_4 is -
 (A) sp^3d , trigonal bipyramidal (B) sp^3 , tetrahedral
 (C) sp^3d^2 , square planar (D) sp^3d^2 , hexagonal
16. Number of lone pairs of electrons on Xe atoms in XeF_2 , XeF_4 and XeF_6 molecules are respectively -
 (A) 3, 2 and 1 (B) 4, 3 and 2 (C) 2, 3 and 1 (D) 3, 2 and 0
17. The ease of liquefaction of noble gases decreases in the order -
 (A) He > Ne > Ar > Kr > Xe (B) Xe > Kr > Ar > Ne > He
 (C) Kr > Xe > He > Ar > Xe (D) Ar > Kr > Xe > He > Ne
18. The forces acting between noble gas atoms are -
 (A) van der Waals forces (B) Ion-dipole forces
 (C) London dispersion forces (D) Magnetic forces

19. XeF_4 on partial hydrolysis produces -
 (A) XeF_2 (B) XeOF_2 (C) XeOF_4 (D) XeO_3
20. The first compound of noble gases prepared by N-Bartlett was -
 (A) $\text{Xe}^+[\text{Pt F}_6]^-$ (B) XeF_4 (C) XeF_6 (D) XeOF_4
21. Which one of the following is a correct pair with respect to molecular formula of xenon compound and hybridization state of xenon in it -
 (A) XeF_4 , sp^3 (B) XeF_2 , sp (C) XeF_2 , sp^3d (D) XeF_4 , sp^2
22. Hydrolysis of XeF_4 and CaNCN gives respectively :
 (A) XeO_3 and CaCO_3 (B) XeO_2 and CaCN_2 (C) XeOF_3 and CaCN_2 (D) XeOF_2 and CaCO_3
23. Consider following properties of the noble gases.
 I : They readily form compounds which are colourless.
 II : They generally do not form ionic compounds.
 III : Xenon has variable oxidation states in its compounds.
 IV : the smaller He and Ne do not form clathrate compounds.
 Select correct properties.
 (A) I, II, III (B) II, III, IV (C) I, III, IV (D) All
24. Which one of the following configuration represents a noble gas ?
 (A) $1s^2 2s^2 p^6, 3s^2$ (B) $1s^2 2s^2 p^6, 3s^1$ (C) $1s^2 2s^2 p^6$ (D) $1s^2 2s^2 p^6, 3s^2 p^6, 4s^2$
25. Among the following molecules, (i) XeO_3 (ii) XeOF_4 (iii) XeF_6 those having same number of lone pairs on Xe are :
 (A) (i) and (ii) only (B) (i) and (iii) only (C) (ii) and (iii) only (D) (i), (ii) and (iii)
26. XeF_6 on complete hydrolysis gives :
 (A) Xe (B) XeO_2 (C) XeO_3 (D) XeO_4
27. The product of the reaction between one mole of XeO_3 and two mole of XeF_6 is :
 (A) XeO_2F_2 (B) XeOF_4 (C) XeO_3F_2 (D) XeO_4
28. $[\text{HXeO}_4]^- + \text{OH}^- \longrightarrow [\text{X}] + [\text{Y}] + \text{O}_2 + \text{H}_2\text{O}$
 The products [X] and [Y] in unbalanced reaction are :
 (A) $[\text{XeO}_6]^{4-}$ & Xe (B) $[\text{XeO}_6]^{4-}$ & XeO_3 (C) XeO_3 & Xe (D) H_2XeO_4 & Xe
- 29.* Which of the following is/are properties of helium?
 (A) It is chemically inert. (B) It has very high thermal conductivity.
 (C) It has extremely low boiling point. (D) It has very low viscosity.
- 30.* Select the correct statement(s) regarding the fluorides of xenon.
 (A) All three fluorides are decomposed by water, XeF_2 slowly and, XeF_4 and XeF_6 rapidly.
 (B) All three fluorides are powerful oxidising agents.
 (C) XeF_4 and XeF_6 can act as fluoride ion acceptors as well as fluoride ion donors.
 (D) All three fluorides are volatile, readily subliming at room temperature (298 K).

EXERCISE # 2

PART - I : MIXED OBJECTIVE

Single choice type

- Which of the following is a mixed anhydride
(A) P_4O_{10} (B) SO_3 (C) Cl_2O_6 (D) SO_2
- The correct order of pseudohalide, polyhalide and interhalogen are :
(A) BrI_2^- , OCN^- , IF_5 (B) IF_5 , BrI_2^- , OCN^- (C) OCN^- , IF_5 , BrI_2^- (D) OCN^- , BrI_2^- , IF_5
- Which of the following is a false statement-
(A) Halogens are strong oxidizing agent (B) Halogens show only (-1) oxidation state
(C) HF molecules form intermolecular H-bonds (D) Fluorine is highly reactive
- Consider the following perchlorate ion in acidic medium
 ClO_4^- (I), BrO_4^- (II), IO_4^- (III)
Arrange these in the decreasing order of oxidizing power.
(A) I > II > III (B) I > III > II (C) II > I > III (D) II > III > I
- Which of the following reactions will give bleaching powder –
(A) $CaCl_2 + H_2O$ (B) $CaO + HCl$ (C) $Ca(OH)_2 + Cl_2$ (D) $ClO_2 + Ca(OH)_2$
- The boiling point and melting point of inert gases are –
(A) Low (B) High (C) Very high (D) Very low
- The ease of liquefaction of noble gases increases in the order –
(A) He < Ne < Ar < Kr < Xe (B) Xe < Kr < Ne < Ar < He
(C) Kr < Xe < He < Ne < Ar (D) Ar < Kr < Xe < Ne < He
- Noble gases can be separated by –
(A) Passing them through some solution
(B) Electrolysis of their compounds
(C) Adsorption and desorption on coconut charcoal
(D) None
- I_4O_9 is an –
(A) covalent bond (B) coordinate compound
(C) ionic compound (D) double salt
- Cl_2 $\xrightarrow{\text{Cold and dilute NaOH}}$ (A) + NaCl + H_2O
 Cl_2 $\xrightarrow{\text{Hot and conc. NaOH}}$ (B) + NaCl + H_2O
Compounds (A) and (B) are -
(A) $NaClO_3$, $NaClO$ (B) $NaOCl_2$, $NaOCl$ (C) $NaClO_4$, $NaClO_3$ (D) $NaOCl$, $NaClO_3$
- When chlorine water is added to an aqueous solution of sodium iodide in the presence of chloroform, a violet colouration is obtained. On adding more of chlorine water and vigorous shaking, the violet colour disappears. This shows the conversion of.....into.....
(A) I_2 , HIO_3 (B) I_2 , HI (C) HI, HIO_3 (D) I_2 , HIO
- A greenish yellow gas reacts with an alkali hydroxide to form a halate which can be used in fireworks and safety matches. The gas and the halate are –
(A) Br_2 , $KBrO_3$ (B) Cl_2 , $KClO_3$ (C) I_2 , $NaIO_3$ (D) I_2 , KIO_3

More than one choice type

बहु विकल्पी प्रकार

13. Which of the following product(s) is/are obtained in the following reaction
 $\text{KBrO}_3 + \text{F}_2 + \text{KOH} \longrightarrow \text{product(s)}$
(A) KBrO_4 (B) KF (C) HOF (D) Br_2
14. Which statement is correct about halogen ?
(A) They are all diatomic and form univalent ions
(B) Helogen have the smallest atomic radii in there respective periods
(C) They are all diatomic and form diatomic ions
(D) They are all reducing agents
15. Which of the following will not displace the halogen from the solution of the halide ?
(A) Br_2 added to NaI (B) Br_2 added to NaCl (C) Cl_2 added to KCl (D) Cl_2 added to NaF
16. Cl_2 reacts with hot aqueous NaOH to give :
(A) NaCl (B) NaClO_3 (C) NaClO_2 (D) NaClO_4
17. Thermal decomposition product (s) of XeF_6 is /are :
(A) Xe (B) XeF_2 (C) XeF_4 (D) F_2
18. Which of the following statements(s) is /are true for XeF_6 ?
(A) Its partial hydrolysis gives XeOF_4 .
(B) Its reaction with silica gives XeOF_4
(C) It is prepared by the reaction of XeF_4 and O_2F_2
(D) Its reaction with XeO_3 gives XeOF_4 .

MATCH THE COLUMN

19. Match the following .

Column - I

- (A) $\text{ClO}_2 \longrightarrow \text{Cl}_2\text{O}_3$
(B) $[\text{Al}(\text{OH})_4]^- \longrightarrow \text{Al}(\text{OH})_3 \downarrow$
(C) $\text{P}_4 \longrightarrow \text{PH}_3 + \text{H}_2\text{PO}_2^-$
(D) $\text{XeF}_2 \longrightarrow \text{Xe}$

Column - II

- (p) Boiling with NaOH solution.
(q) On passing ozone.
(r) Reaction with hydrogen.
(s) On passing CO_2 gas.

20. $\text{Na}_2\text{S}_2\text{O}_3$ may react with the compounds given in column (I). $\text{Na}_2\text{S}_2\text{O}_3$ exhibits the properties of the type given in the column (II)

Column - I

(reactant)

- (A) Chlorine (Cl_2)
(B) Silver bromide
(C) Hydrochloric acid
(D) Iodine (I_2)

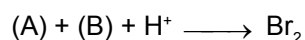
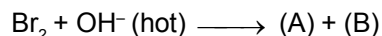
Column - II

(type of property shown)

- (p) Complexing reagent
(q) Disproportionation
(r) Only as reductant
(s) An-antichlor

PART - II : SUBJECTIVE QUESTIONS

1. Identify (A) and (B).

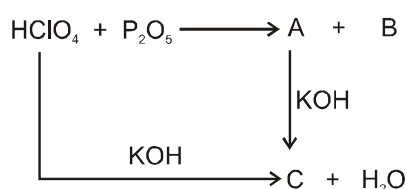


(A) gives yellow precipitate with AgNO_3 which is completely soluble in concentrated NH_3 solution.

2. (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.

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

4. Identify A, B and C in the following



5. 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.
 (c) HI can not be prepared by heating NaI with concentrated H_2SO_4 .

6. Name the noble gas which

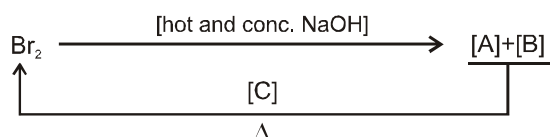
(A) is most abundant in atmosphere.

(B) has least boiling point.

7. What is the utility of the clathrate compounds?

8. Does the hydrolysis of XeF_4 at -80°C lead to a redox reaction?

9. Identify [A] [B] and [C] and gives the complete chemical reactions involved.



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

EXERCISE # 3

PART - I : IIT-JEE PROBLEMS (PREVIOUS YEARS)

* Marked Questions are having more than one correct option.

Group 17th

1. Give an example of oxidation of one halide by another halogen. Explain the feasibility of reaction. [JEE 2000 (M), 2/100]
2. The set with correct order of acidity is : [JEE 2001 (S), 3/35]
(A) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ (B) $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$
(C) $\text{HClO} < \text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2$ (D) $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$
3. The reaction, $3\text{ClO}^-(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq}) + 2\text{Cl}^-(\text{aq})$ is an example of : [JEE 2001 (S), 3/35]
(A) oxidation reaction (B) reduction reaction
(C) disproportionation reaction (D) decomposition reaction
4. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y'. [JEE 2002 (S), 3/90]
(A) $\text{X} = \text{CO}_2$, $\text{Y} = \text{Cl}_2$ (B) $\text{X} = \text{Cl}_2$, $\text{Y} = \text{CO}_2$ (C) $\text{X} = \text{Cl}_2$, $\text{Y} = \text{H}_2$ (D) $\text{X} = \text{H}_2$, $\text{Y} = \text{Cl}_2$
5. Reaction of Br_2 with Na_2CO_3 in aqueous solution gives sodium bromide and sodium bromate with evolution of CO_2 gas. The number of sodium bromide molecules involved in the balanced chemical equation is [JEE 2011, 4/80]
- 6.* Which of the following hydrogen halides react(s) with $\text{AgNO}_3(\text{aq})$ to give a precipitate that dissolves in $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$? [JEE 2012, 4/210]
(A) HCl (B) HF (C) HBr (D) HI

Paragraph

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry.

7. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is [JEE 2012, 3/198]
(A) Cl_2O (B) Cl_2O_7 (C) ClO_2 (D) Cl_2O_6

Group 18th

Paragraph for Question Nos. 1 & 2

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6. XeF_4 reacts violently with water to give XeO_3 . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

1. Argon is used in arc welding because of its : [JEE 2007 (P-I), 4/81]
(A) low reactivity with metal (B) ability to lower the melting point of metal
(C) flammability (D) high calorific value
2. The structure of XeO_3 is : [JEE 2007 (P-I), 4/81]
(A) linear (B) planar (C) pyramidal (D) T-shaped

3. XeF_4 and XeF_6 are expected to be : [JEE 2007 (P-I), 4 /81]
 (A) oxidizing (B) reducing (C) unreactive (D) strongly basic
4. All the compounds listed in **Column I** react with water. Match the result of the respective reactions with the appropriate options listed in **Column II**. [JEE 2010, (P-II) 8/79]

Column I	Column II
(A) $(\text{CH}_3)_2\text{SiCl}_2$	(p) Hydrogen halide formation
(B) XeF_4	(q) Redox reaction
(C) Cl_2	(r) Reacts with glass
(D) VCl_5	(s) Polymerization
	(t) O_2 formation

Paragraph for Question Nos. 05 to 06

The reactions of Cl_2 gas with cold-dilute and hot-concentrated NaOH in water give sodium salts of two (different) oxoacids of chlorine, **P** and **Q**, respectively. The Cl_2 gas reacts with SO_2 gas, in presence of charcoal, to give a product **R**. **R** reacts with white phosphorus to give a compound **S**. On hydrolysis, **S** gives an oxoacid of phosphorus, **T**.

5. **R**, **S** and **T**, respectively, are : [JEE_Advanced_2013, P-II]
 (A) SO_2Cl_2 , PCl_5 and H_3PO_4 (B) SO_2Cl_2 , PCl_3 and H_3PO_3
 (C) SOCl_2 , PCl_3 and H_3PO_2 (D) SOCl_2 , PCl_5 and H_3PO_4
6. **P** and **Q**, respectively, are the sodium salts of : [JEE_Advanced_2013, P-II]
 (A) hypochlorous and chloric acids (B) hypochlorous and chlorus acids
 (C) chloric and perchloric acids (D) chloric and hypochlorous acids

PART - II : AIEEE PROBLEMS (PREVIOUS YEARS)

Marked Questions are having more than one correct option.

1. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. This is due to : **[AIEEE 2003]**
(1) strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke.
(2) strong affinity for water, conc. HCl pulls moisture of air towards self. The moisture forms droplets of water and hence the cloud.
(3) conc. HCl emits strongly smelling HCl gas all the time.
(4) oxygen in air reacts with emitted HCl gas to form a cloud of chlorine gas.
2. Which one of the following statements regarding helium is incorrect ? **[AIEEE 2004]**
(1) It is used to produce and sustain powerful superconducting magnets
(2) It is used as a cryogenic agent for carrying out experiments at low temperatures
(3) It is used to fill gas balloons instead of hydrogen because it is lighter and non-inflammable
(4) It is used in gas-cooled nuclear reactors
3. Which among the following factors is the most important in making fluorine the strongest oxidizing halogen? **[AIEEE-2004]**
(1) Hydration enthalpy (2) Ionization enthalpy (3) Electron affinity (4) Bond dissociation energy
4. The correct order of the thermal stability of hydrogen halides (H – X) is : **[AIEEE 2005]**
(1) HI > HBr > HCl > HF (2) HF > HCl > HBr > HI
(3) HCl < HF < HBr < HI (4) HI > HCl < HF < HBr
5. Which of the following chemical reactions depicts the oxidizing behaviour of H₂SO₄? **[AIEEE 2006]**
(1) $2\text{HI} + \text{H}_2\text{SO}_4 \rightarrow \text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O}$ (2) $\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$
(3) $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$ (4) $2\text{PCl}_5 + \text{H}_2\text{SO}_4 \rightarrow 2\text{POCl}_3 + 2\text{HCl} + \text{SO}_2\text{Cl}_2$
6. What products are expected from the disproportionation reaction of hypochlorous acid? **[AIEEE 2006]**
(1) HClO₃ and Cl₂O (2) HClO₂ and HClO₄ (3) HCl and Cl₂O (4) HCl and HClO₃
7. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence : **[AIEEE 2007, 3/120]**
(1) $\text{GeX}_2 < \text{SiX}_2 < \text{SnX}_2 < \text{PbX}_2$ (2) $\text{SiX}_2 < \text{GeX}_2 < \text{PbX}_2 < \text{SnX}_2$
(3) $\text{SiX}_2 < \text{GeX}_2 < \text{SnX}_2 < \text{PbX}_2$ (4) $\text{PbX}_2 < \text{SnX}_2 < \text{GeX}_2 < \text{SiX}_2$
8. Identify the incorrect statement among the following. **[AIEEE 2007, 3/120]**
(1) Cl₂ reacts with excess of NH₃ to give N₂ and HCl.
(2) Br₂ reacts with hot and strong NaOH solution to give NaBr, NaBrO₄ and H₂O.
(3) Ozone reacts with SO₂ to give SO₃.
(4) Silicon reacts with NaOH_(aq) in the presence of air to give Na₂SiO₃ and H₂O.
9. Which one of the following reactions of Xenon compounds is not feasible ? **[AIEEE 2009, 4/144]**
(1) $3\text{XeF}_4 + 6\text{H}_2\text{O} \rightarrow 2\text{Xe} + \text{XeO}_3 + 12\text{HF} + 1.5\text{O}_2$ (2) $2\text{XeF}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Xe} + 4\text{HF} + \text{O}_2$
(3) $\text{XeF}_6 + \text{RbF} \rightarrow \text{Rb}[\text{XeF}_7]$ (4) $\text{XeO}_3 + 6\text{HF} \rightarrow \text{XeF}_6 + 3\text{H}_2\text{O}$
10. Which of the following exists as covalent crystals in the solid state ? **[JEE Mains_2013]**
(1) Iodine (2) Silicon (3) sulphur (4) Phosphorus

EXERCISE # 4

NCERT QUESTIONS

1. Why are halogens strong oxidising agents?
2. Explain why fluorine forms only one oxoacid, HOF.
3. Explain why in spite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.
4. Write two uses of ClO_2 .
5. Why are halogens coloured?
6. Write the reactions of F_2 and Cl_2 with water.
7. How can you prepare Cl_2 from HCl and HCl from Cl_2 ? Write reactions only.
8. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6 ?
9. What are the oxidation states of phosphorus in the following :
(i) H_3PO_3 (ii) PCl_3 (iii) Ca_3P_2 (iv) Na_3PO_4 (v) POF_3 ?
10. Write balanced equations for the following :
(i) NaCl is heated with sulphuric acid in the presence of MnO_2 .
(ii) Chlorine gas is passed into a solution of NaI in water.
11. How are xenon fluorides XeF_2 , XeF_4 and XeF_6 obtained?
12. With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?
13. How are XeO_3 and XeOF_4 prepared?
14. Arrange the following in the order of property indicated for each set :
(i) F_2 , Cl_2 , Br_2 , I_2 - increasing bond dissociation enthalpy.
(ii) HF , HCl , HBr , HI - increasing acid strength.
(iii) NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 - increasing base strength.
15. Which one of the following does not exist?
(i) XeOF_4 (ii) NeF_2 (iii) XeF_2 (iv) XeF_6
16. Give the formula and describe the structure of a noble gas species which is isostructural with :
(i) ICl_4^- (ii) IBr_2^- (iii) BrO_3^-
17. Why do noble gases have comparatively large atomic sizes?
18. List the uses of neon and argon gases.

ANSWERS

EXERCISE # 1

PART - I

Group 17th

- | | | | | | | |
|------------|-----------|-----------|------------|-----------|-----------|-----------|
| 1. (D) | 2. (B) | 3. (D) | 4. (D) | 5. (A) | 6. (B) | 7. (D) |
| 8. (C) | 9. (A) | 10. (D) | 11. (D) | 12. (B) | 13. (C) | 14. (D) |
| 15. (A) | 16. (A) | 17. (A) | 18. (C) | 19. (B) | 20. (D) | 21. (A) |
| 22. (A) | 23. (C) | 24. (C) | 25. (A) | 26. (C) | 27. (D) | 28. (D) |
| 29. (B) | 30. (C) | 31. (D) | 32. (B) | 33. (B) | 34. (A) | 35. (B) |
| 36. (D) | 37. (A) | 38. (A) | 39. (A) | 40. (B) | 41. (D) | 42. (A) |
| 43. (A) | 44. (C) | 45. (C) | 46. (B) | 47. (C) | 48. (D) | 49. (A) |
| 50. (B) | 51. (D) | 52. (A) | 53. (D) | 54. (D) | 55. (C) | 56. (B) |
| 57. (D) | 58. (C) | 59. (B) | 60. (C) | 61. (A) | 62. (D) | 63.* (BC) |
| 64.* (ABC) | 65.* (BC) | 66.* (AC) | 67.* (ABD) | 68.* (CD) | 69.* (BD) | |

Group 18th

- | | | | | | | |
|-------------|-------------|---------|---------|---------|---------|---------|
| 1. (C) | 2. (B) | 3. (A) | 4. (A) | 5. (D) | 6. (C) | 7. (B) |
| 8. (D) | 9. (B) | 10. (B) | 11. (B) | 12. (A) | 13. (A) | 14. (A) |
| 15. (C) | 16. (A) | 17. (B) | 18. (A) | 19. (B) | 20. (A) | 21. (C) |
| 22. (A) | 23. (B) | 24. (C) | 25. (D) | 26. (C) | 27. (B) | 28. (A) |
| 29.* (ABCD) | 30.* (ABCD) | | | | | |

EXERCISE # 2

PART - I

- | | | | | | | |
|---|--|-----------|------------|---------|----------|----------|
| 1. (C) | 2. (D) | 3. (B) | 4. (D) | 5. (C) | 6. (D) | 7. (A) |
| 8. (C) | 9. (C) | 10. (D) | 11. (A) | 12. (B) | 13. (AB) | 14. (AB) |
| 15. (BCD) | 16. (AB) | 17. (BCD) | 18. (ABCD) | | | |
| 19. (A - q) ; (B - s) ; (C - p) ; (D - p,r) | 20. (A - r, s) ; (B - p) ; (C - q) ; (D - r) | | | | | |

PART - II

- $$\text{Br}_2 + \text{OH}^- (\text{hot}) \longrightarrow \text{Br}^- + \text{BrO}_3^-$$

$$\text{Br}^- + \text{BrO}_3^- + \text{H}^+ \xrightarrow{\text{distillation}} \text{Br}_2$$
- (a) It forms 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.
- $$\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Cl}_2$$

Redox reaction.
- $$\text{HClO}_4 + \text{P}_2\text{O}_5 \longrightarrow \text{Cl}_2\text{O}_7 + \text{HPO}_3$$

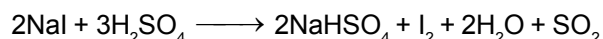
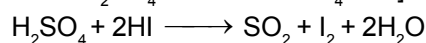
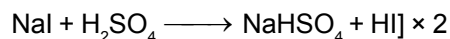
$$\downarrow \text{KOH}$$

$$\text{KClO}_4 + \text{H}_2\text{O}$$
- (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)

$$2\text{KI} (\text{aq}) + \text{Cl}_2 (\text{g}) \longrightarrow 2\text{KCl} (\text{aq}) + \text{I}_2 (\text{s}) ; 5\text{Cl}_2 + \text{I}_2 + 6\text{H}_2\text{O} \longrightarrow 10\text{HCl} + 2\text{HIO}_3$$

(b) Oxidation state of Cl in 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 than H_2SO_4 .

(c) HI is a stronger reducing agent. It, therefore, reduces H_2SO_4 to SO_2 and itself gets oxidised to I_2 .



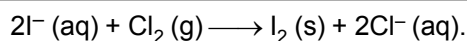
6. (A) Argon.
 (B) Helium ; Exists as mono-atomic molecules and are held together by weak van der Waal's forces. These van der Waal's forces increase with the increase in atomic size of the atom, and therefore, the boiling points increases from He to Rn. Hence He has least boiling point.
7. It can be used to separate mixture of inert gases containing say He and Xe. Process is much cheaper than say distillation as a means of separation.
8. $\text{XeF}_4 + \text{H}_2\text{O} \xrightarrow{-80^\circ\text{C}} \text{XeOF}_2 + 2\text{HF}$.
 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.
9. [A] = Br^- ; [B] = BrO_3^- ; [C] = concentrated H_2SO_4
10. 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.

EXERCISE # 3

PART - I

Group 17th

1. $2\text{KI}(\text{aq.}) + \text{Cl}_2 \longrightarrow 2\text{KCl}(\text{aq.}) + \text{I}_2$
 In the reaction Cl_2 oxidises iodide ion (-1 oxidation state) to I_2 (0 oxidation state). Cl_2 has higher oxidation potential than I_2 and thus oxidises iodide to iodine getting itself reduced to chloride ion. Similarly,
 $2\text{I}^- (\text{aq.}) \longrightarrow \text{I}_2 (\text{s}) + 2\text{e}^-$
 $\text{Cl}_2 (\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^- (\text{aq.})$



2. (A) 3. (C) 4. (C) 5. 5 6.* (ACD) 7. (A)

Group 18th

1. (A) 2. (C) 3. (A) 4. (A - p, s) ; (B - p, q, r, t) ; (C - p, q) ; (D - p)
 5. (A) 6. (A)

PART - II

1. (4) 2. (3) 3. (4) 4. (2) 5. (1) 6. (4) 7. (3)
 8. (2) 9. (4) 10. (2)