

INORGANIC CHEMISTRY

Topic: 3

Group VII A Elements

Long Answer Questions

1. Explain the general characteristics of Group VIIA elements.

Ans: Some physical properties of group 17 elements

Element	Atomic Radius (Å°)	Ionic Radius (Å°)	Ionization Energy (kJ mol ⁻¹)	Melting point (K)	Boiling point (K)	Electron affinity	Electro negativity
F	0.72	1.86	1681	53	85	332.6	4.0
Cl	0.99	1.81	1255	172	238	348.5	3.0
Br	1.14	1.95	1142	266	332	324.7	2.8
I	1.33	2.16	1007	386	456	295.5	2.5

1. Atomic and ionic radii

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. Among themselves, the atomic and ionic radii increase with increase in atomic number. This is due to increase in the number of electron shells.

2. Ionization energies

The ionization energies of halogens are very high. This indicates that they have very little tendency to lose electrons. However, on going down the group from fluorine to astatine, the ionization energy decreases. This is due to gradual increase in atomic size, which is maximum for iodine. Consequently, it has the least ionization energy in family.

3. Melting and boiling points

The melting and boiling points of halogens increase with increase in atomic number down the group.

Explanation:

The forces existing between these molecules are weak Van der Waals forces, which increase down the group. This is also clear from the change of state from fluorine to iodine. At room temperature, fluorine and chlorine are gases; bromine is a liquid while iodine and astatine are solids.

4. Electron affinities

(i) All these have maximum electron affinities in their respective periods. This is due to the fact that the atoms of these elements have only one electron less than the stable noble gas (ns^2np^6) configurations. Therefore, they may have maximum tendency to accept an additional electron.

(ii) In general, electron affinity decreases from top to bottom in a group. This is due to the fact that the effect of increase in atomic size is much more than the effect of increase in nuclear charge and thus, the additional electron feels less attraction by the large atom. Consequently, electron affinity decreases. .

(iii) Fluorine has unexpectedly less electron affinity than chlorine. Therefore, chlorine has the highest electron affinity in this group. The lower electron affinity of fluorine as compared to chlorine is due to very small size of the fluorine atom. As a result, there are strong inter-electronic repulsions in the relatively small 2p subshell of fluorine and thus the incoming electron does not feel much attraction. Therefore, its electron affinity is small. Thus, electron affinity among halogens varies as: $F < Cl > Br > I$.

Chlorine has the highest electron affinity in the periodic table.

5. Electronegativity

Halogens have large electronegativity values. The values decrease down the group from fluorine to iodine because the atomic size increases and the effective nuclear charge decreases. Fluorine is the most electronegative element in the periodic table.

6. Metallic or non-metallic character

Because of very high ionization energy values, all halogens are non-metallic in character. The non-metallic character decreases as we go down the group. Therefore, the last element, iodine is a solid with a metallic lustre and forms positive ions such as I^+ and I^{3+} .

7. Color

All the halogens are colored. The color of different halogens is given below:

Halogen	Fluorine	Chlorine	Bromine	Iodine
Colour	Light yellow	Greenish yellow	Reddish brown	Dark violet

Explanation:

The color of halogens is due to the fact that their molecules absorb radiations from visible light and the outer electrons are easily excited to higher energy levels. The amount of energy required for excitation depends upon the size of the atom. Fluorine atom is the smallest and the force of attraction between the nucleus and the outer electrons is very large. As a result, it requires large excitation energy and absorbs

violet light (high energy) and therefore, appears pale yellow. On the other hand, iodine needs very less excitation energy and absorbs yellow light of low energy. Thus it appears dark violet. Similarly, we can explain the greenish yellow color of chlorine and reddish brown color of iodine.

2. Write an essay on the chemical reactivity of halogens.

Like other groups, the candidates of this family show patterns in its electron configuration, especially the outermost shells resulting in trends in chemical behavior:

Z	Element	No. of electrons/shell
9	fluorine	2, 7
17	chlorine	2, 8, 7
35	bromine	2, 8, 18, 7
53	iodine	2, 8, 18, 18, 7
85	astatine	2, 8, 18, 32, 18, 7

Reactivity

Halogens are highly reactive, and as such can be harmful or lethal to biological organisms in sufficient quantities. This high reactivity is due to the atoms being highly electronegative due to their high effective nuclear charge. They can gain an electron by reacting with atoms of other elements. Fluorine is one of the most reactive elements in existence, attacking otherwise inert materials such as glass, and forming compounds with the heavier noble gases. It is a corrosive and highly toxic gas. The reactivity of fluorine is such that if used or stored in laboratory glassware, it can react with glass in the presence of small amounts of water to form silicon tetrafluoride (SiF_4). Thus fluorine must be handled with substances such as Teflon (which is itself an organo fluorine compound), extremely dry glass, or metals such as copper or steel which form a protective layer of fluoride on their surface.

The high reactivity of fluorine means that once it does react with something, it bonds with it so strongly that the resulting molecule is very inert and non-reactive to anything else. For example, Teflon is fluorine bonded with carbon.

Both chlorine and bromine are used as disinfectants for drinking water, swimming pools, fresh wounds, spas, dishes, and surfaces. They kill bacteria and other potentially harmful microorganisms through a process known as sterilization. Their reactivity is also put to use in bleaching. Sodium hypochlorite, which is produced from chlorine, is the active ingredient of most fabric bleaches and chlorine-derived bleaches are used in the production of some paper products. Chlorine also reacts with sodium to create sodium chloride, which is another name for table salt.

Hydrogen halides

The halogens all form binary compounds with hydrogen known as the hydrogen halides (HF, HCl, HBr, HI, and HAt), a series of particularly strong acids. When in aqueous solution, the hydrogen halides are known as hydrohalic acids. HAt, or "hydroastatic acid", should also qualify, but it is not typically included in discussions of hydrohalic acid due to astatine's extreme instability toward alpha decay.

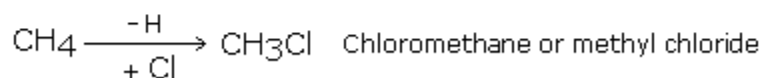
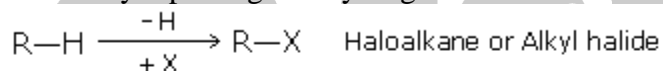
Interhalogen compounds

The halogens react with each other to form interhalogen compounds. Diatomic interhalogen compounds such as BrF, ICl, and ClF bear resemblance to the pure halogens in some respects. The properties and behaviour of a diatomic interhalogen compound tend to be intermediate between those of its parent halogens. Some properties, however, are found in neither parent halogen. For example, Cl₂ and I₂ are soluble in CCl₄, but ICl is not since it is a polar molecule due to the relatively large electro negativity difference between I and Cl.

Organohalogen compounds

RX where R is an alkyl group

Monohalogen derivatives of alkanes are called Haloalkanes or alkyl halides. They are formed by replacing one hydrogen atom in alkane.

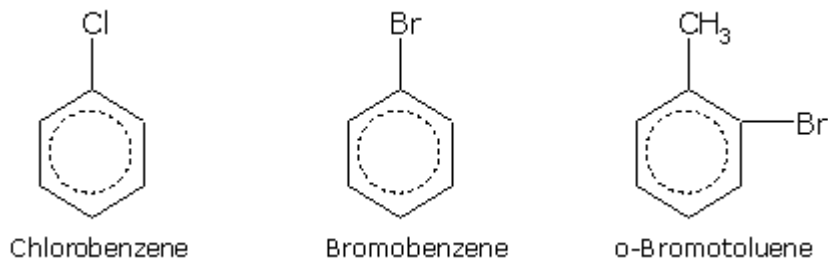


Haloarene

ArX where Ar is arene.

'X' is halogen atom (F, Cl, Br, I)

Haloarenes or aryl halides are halogen derivatives of aromatic hydrocarbons, which are derived by replacing hydrogen atom attached to the benzene ring by a halogen atom. Therefore, in haloarenes, the halogen atom (F, Cl, Br or I) is directly attached to the aromatic ring. For example,



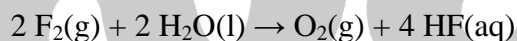
Many synthetic organic compounds such as plastic polymers, and a few natural ones, contain halogen atoms; these are known as halogenated compounds or organic halides.

Polyhalogenated compounds

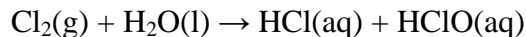
Polyhalogenated compounds are industrially created compounds substituted with multiple halogens. Many of them are very toxic and bioaccumulate in humans, and have a very wide application range. They include the much maligned PCBs, PBDEs, and PFCs as well as numerous other compounds.

Reactivity with water

Fluorine reacts vigorously with water to produce oxygen (O₂) and hydrogen fluoride (HF):



Chlorine has minimal solubility of 0.7g Cl₂ per kg of water at ambient temperature (21°C). Dissolved chlorine reacts to form hydrochloric acid (HCl) and hypochlorous acid, a solution that can be used as a disinfectant or bleach:



Bromine has a solubility of 3.41 g per 100 g of water, but it slowly reacts to form hydrogen bromide (HBr) and hypobromous acid (HBrO):



Iodine, however, is minimally soluble in water (0.03 g/100 g water @ 20 °C) and does not react with it.^[6] However, iodine will form an aqueous solution in the presence of iodide ion, such as by addition of potassium iodide (KI), because the tri iodide ion is formed.

3. Give an account on oxidising capacities of halogens.

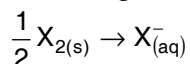
Ans: Oxidising power:

All the halogens are oxidising agents. Their oxidising power is high due to high EA values. The order of oxidising power is $F_2 > Cl_2 > Br_2 > I_2$

The order of S.R.P is $F_2 > Cl_2 > Br_2 > I_2$

All S.R.P. values are +ve. S.R.P. is a measure of the ability to undergo reduction.

Oxidising ability of halogens depends on the net energy change of the process,



THE OXIDISING ABILITY OF THE GROUP 7 ELEMENTS (THE HALOGENS)

This explores the trend in oxidising ability of the Group 7 elements (the halogens) - fluorine, chlorine, bromine and iodine. We are going to look at the ability of one halogen to oxidise the ions of another one, and how that changes as you go down the Group.

We are going to look at the reactions between one halogen (chlorine, say) and the ions of another one (iodide ions, perhaps). The iodide ions will be in a solution of a salt like sodium or potassium iodide. The sodium or potassium ions will be spectator ions, and are completely irrelevant to the reaction.

In the chlorine and iodide ion case, the reaction would be:



The iodide ions have lost electrons to form iodine molecules. They have been oxidised.

The chlorine molecules have gained electrons to form chloride ions. They have been reduced.

This is obviously a redox reaction in which chlorine is acting as an oxidising agent.

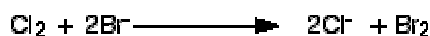
Fluorine

We'll have to exclude fluorine from this descriptive bit, because it is too strong an oxidising agent. Fluorine oxidises water to oxygen and so it is impossible to do simple solution reactions with it.



Chlorine, bromine and iodine

In each case, a halogen higher in the Group can oxidise the ions of one lower down. For example, chlorine can oxidise the bromide ions (in, for example, potassium bromide solution) to bromine:



The bromine appears as an orange solution.

As you have seen above, chlorine can also oxidise iodide ions (in, for example, potassium iodide solution) to iodine:



The iodine appears either as a red solution if you are mean with the amount of chlorine you use, or as a dark grey precipitate if the chlorine is in excess.

Bromine can only oxidise iodide ions to iodine. It isn't a strong enough oxidising agent to convert chloride ions into chlorine. (You have just seen exactly the reverse of that happening.)

A red solution of iodine is formed (see the note above) until the bromine is in excess. Then you get a dark grey precipitate.



Iodine won't oxidise any of the other halide ions (unless you happened to have some extremely radioactive and amazingly rare astatide ions - astatine is at the bottom of this Group).

To summarise

- Oxidation is loss of electrons. Each of the elements (for example, chlorine) could potentially take electrons from something else to make their ions (e.g. Cl^-). That means that they are all potentially oxidising agents.
- Fluorine is such a powerful oxidising agent that you can't reasonably do solution reactions with it.
- Chlorine has the ability to take electrons from both bromide ions and iodide ions. Bromine and iodine can't get those electrons back from the chloride ions formed.

That means that chlorine is a more powerful oxidising agent than either bromine or iodine.

- Similarly bromine is a more powerful oxidising agent than iodine. Bromine can remove electrons from iodide ions to give iodine - and the iodine can't get them back from the bromide ions formed.

This all means that oxidising ability falls as you go down the Group.

4. Describe the preparation of Fluorine.

Ans: **FLUORINE**

Fluorine: Scheele discovered this element.

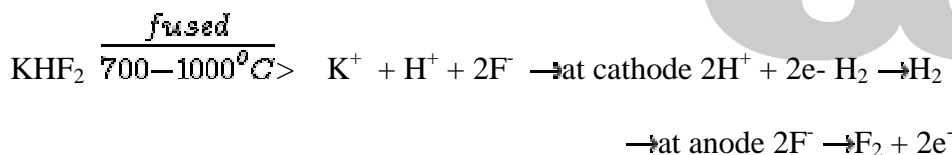
A. Occurrence: Fluorine is very reactive element. Hence it occurs in nature in the combined state only. Some of the important minerals of fluorine are:

Fluorspar (CaF_2); Cryolite (Na_3AlF_6 or $3\text{NaF} \cdot \text{AlF}_3$), Fluorapatite [$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$] .
Small quantities of fluorine are present as fluorides in the soil, river water plants, bones and teeth of animals.

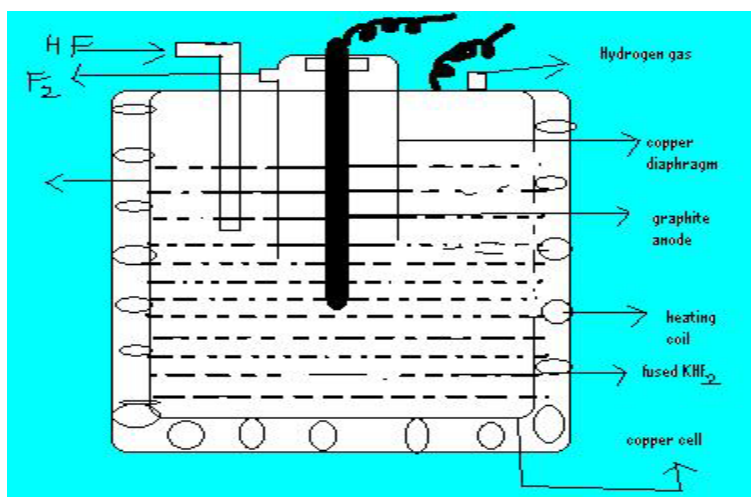
B . Preparation: The isolation of fluorine from its minerals was a huge challenge in chemistry. Many unsuccessful attempts were made to isolate fluorine for over six decades. Commercially several types of electrolytic cells are used for the preparation of fluorine. All these methods utilize the same Moissan's principle in fluorine isolation. The commonly used method is **Whytlaw Gray's method**.

Whytlaw Gray Method

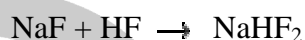
In this method electrolysis is carried out in an electrically heated copper cell. The electrolytic is fused potassium hydrogen fluoride (1 : 2; $\text{KF} \cdot \text{HF}$) the following reactions occur.



The copper vessel serves as cathode also. anode is made of graphite. The anode is surrounded by a copper diaphragm at the bottom. This diaphragm prevents the mixing of H_2 and F_2 which react explosively if they come into contact.



F₂, liberated at the anode is passed through the U - tube containing sodium fluoride. Hydrogen fluoride vapours accompanying fluorine as impurity are removed by NaF.



H₂ is liberated at the cathode. The corrosion of the cell by the action of F₂ is prevented by teflon coating given to various parts of the cell. the Fluorine obtained in this method is almost pure with traces of the HF present in it.

Other methods of preparation of fluorine are also known.

Abnormal Behaviour of Fluorine

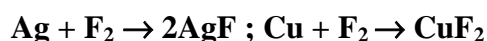
Fluorine differs considerably from halogens, the reasons are as follows:

- small size
- Highest electronegativity
- no d orbitals available in its valency shell
- low dissociation energy for F-F bond and
- 2 electrons only in the penultimate shell while other halogens have 8 electrons.

5. Write the chemical properties of Fluorine with relevant equations.

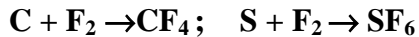
F₂ is most reactive and hence it is called as super halogen.

1) **With metals:** It reacts with all metals forming metal fluorides. It reacts with noble metals like Pt, Au, Ir also.



In case of reaction between Cu and F₂, the CuF₂ formed prevents further reaction between Cu and F₂.

2) **With non – metals:** It reacts with all non – metals directly except O₂ and N₂.

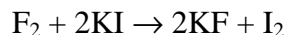
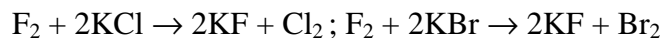


3) **With inert gases:** F₂ reacts with heavier inert gases like Kr and Xe.

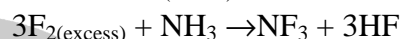
Compounds of Xe and F₂ : XeF₂, XeF₄, XeF₆

4) **With halides:** A lighter halogen or more electro-negative halogen displaces heavier halogen or less electronegative halogen from its salts.

Thus F₂ displaces and oxidise all other halides ions to their respective halogens.

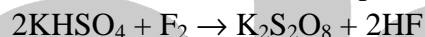


5) **With NH₃:** $3\text{F}_2 + 2\text{NH}_3(\text{excess}) \rightarrow \text{N}_2 + 6\text{HF}$



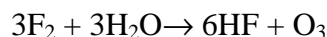
6) **With H₂S:** $4\text{F}_2(\text{excess}) + \text{H}_2\text{S} \rightarrow \text{SF}_6 + 2\text{HF}$

7) **With KHSO₄:** F₂ oxidises potassium bisulphate to potassium persulphate.



8) $\text{CH}_4 + 4\text{F}_2 \rightarrow \text{CF}_4 + 4\text{HF}$

9) **With water:** $2\text{F}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HF} + \text{O}_2$



Uses of F₂

- 1) In etching of glass HF is used (H₂SiF₆ is formed)
- 2) In Rocket fuels
- 3) In separation of isotopes of Uranium by atomolysis
- 4) SF₆ is used in high voltage electricity
- 5) NaF and Na₃AlF₆ are used as insecticides
- 6) Like DDT, DDFT is used as fungicide
- 7) Freon (CCl₂F₂) is used in refrigeration
- 8) Teflon, [(C₂F₄)_n] is used as anticorrosive plastic

6. What is the principle of preparation of Chlorine in the laboratory? Describe Nelosons method for its manufacture.

Ans:

Chlorine: It is available as chlorides in nature. In sea water 2.5 % NaCl is present by weight.

Minerals:

- 1) Rock salt : NaCl
- 2) Horn silver : AgCl
- 3) Sylvine : KCl
- 4) Carnallite : $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

Preparation of Cl_2 in laboratory: It was prepared by scheele laboratory preparation: Oxidation of HCl with MnO_2
 $4\text{HCl} + \text{MnO}_2 \rightarrow \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$

Preparation of Chlorine by Nelson's cell method: It involves electrolysis of brine solution

Electrolyte: aqueous NaCl

Electrolytic cell : Iron tank

Anode : Graphite rod

Cathode : Iron tank

Asbestos lining: Separates anode from cathode

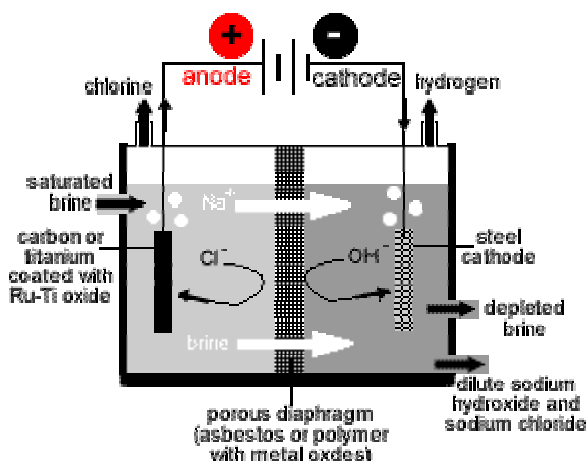
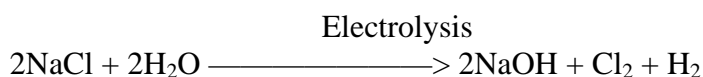
Product at anode : Cl_2

Products at cathode: H_2 , NaOH

Passage of steam : To keep the solution hot and clear the pores

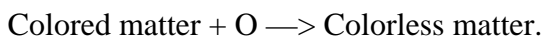
Possible impurities in NaOH: NaCl, NaOCl, NaClO_3

(ii) **Preparation:** On a commercial scale chlorine is prepared by electrolysis of an aqueous solution of sodium chloride (brine solution) (Nelson cell, Castner and Kellner's cell for the manufacture of NaOH) when Cl_2 is evolved at the anode and H_2 is evolved at the cathode.



7. Give the chemical properties of chlorine.

1. **Properties:** It combines with metals and non metals to form chlorides. it decomposes water forming HCl and HClO (hypochlorous acid) which is unstable and decomposes giving nascent oxygen which is responsible for oxidizing and bleaching action of chlorine.



The bleaching action is permanent and color is not restored on standing. However, it cannot be used for bleaching delicate articles such as straw, silk, wool etc. which are damaged by it.

Cl_2 oxidizes Br^- and I^- ions to Br_2 and I_2 respectively.



2. Reaction with alkalis:

It combines with alkalies forming hypochlorite and chlorate salts in cold and hot conditions respectively.



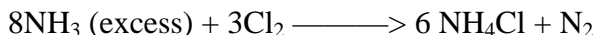
During these reactions, halogen is simultaneously reduced to X^- ion and is oxidized to either hypohalite (XO^-) or halate (XO_3^-) ion. Such reactions are called disproportionation reactions.

With slaked lime, Cl_2 gives bleaching powder (CaOCl_2)



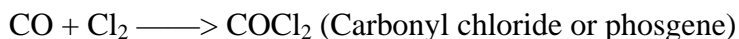
3. Reaction with ammonia:

With ammonia, Cl_2 reacts as follows:



4. Reaction with CO and SO_2 :

With SO_2 and CO , addition compounds are formed



Cl_2 is strong oxidizing agent. It oxidizes FeCl_2 to FeCl_3 , moist SO_2 to H_2SO_4 . SO_3^{2-} to SO_4^{2-} , thiosulfate to sulfate and sulfur.

8. Explain inter halogen compounds.

Ans: **Interhalogen Compounds**

Definition of interhalogen compounds:

"The binary diamagnetic compounds made by the direct combination of halogen elements among themselves under suitable conditions of temperature and pressure are called **Interhalogen** compounds." General formula is AX_n , $n=1,3,5$ or 7 . (In AX , A is central atom and X is bonded atom)

Main reason for the formation of **Inter halogen compounds** is the large electronegativity and size differences among the halogens.

Features of interhalogen compounds:

1. Fluorine never found as the central atom in these compounds. This is because, it never achieves a positive oxidation state and it cannot expand its coordination number beyond 4.
2. The halogen with the larger atomic number is the central atom in any **Inter halogen** compounds.
3. AX and AX_3 types of interhalogens are formed by halogens having nearly similar electronegativity. For example: ClF , BrF , IBr , ClF_3 , IBr_3 , BrF_3 , etc.,
4. AX_5 and AX_7 types of **Interhalogens** are formed by large atoms like Bromine and Iodine with the smaller atom like Fluorine.
5. For naming an **Interhalogen** compound, the less electronegative element is placed on to the left in formulae and naming is done straight forward.

Preparation of Interhalogen Compounds:

Interhalogen compounds are prepared either by,

- * The direct combination of the two halogens in a nickel tube or
- * The action of a halogen on a lower interhalogen such as fluorination of BrF_3 and IF_5 to form BrF_5 and IF_7 respectively.



Properties:

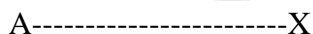
1. All Interhalogens are volatile, few are unstable.
2. All are polar due to difference in their electronegativity.
3. These are usually covalent liquids or gases due to small electronegativity difference among them.
4. Some compounds partially ionise in solution or fused state. For example,



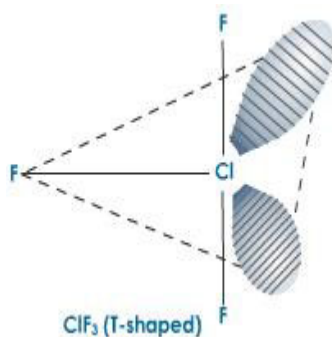
5. Interhalogen compounds are more reactive than normal halogens except Fluorine.

Structures of Interhalogen Compounds:

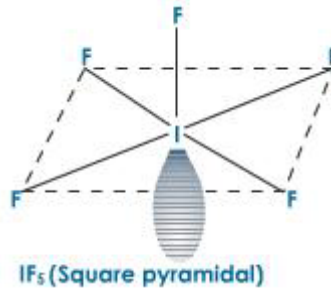
AX type: In AX type, A is the central atom and X is the bonded atom. In these type of compounds, both atoms share their electrons and form single covalent bond.



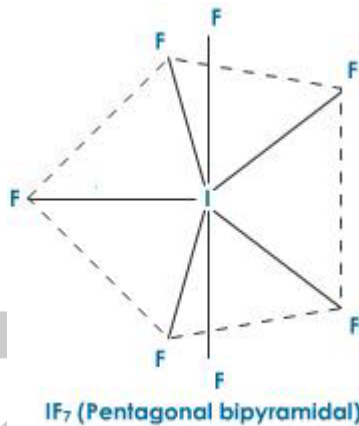
AX₃ type: In AX₃ type, A is the central atom and undergoes sp_3d_1 hybridisation in first excited state and gives 5 hybrid orbitals. Out of five, three are bonding electrons and two are lone pairs. Since sp_3d_1 hybridisation, it should be in Trigonal bipyramidal shape, but due to the presence of two lone pairs, structure is distorted to "T" shape.



AX₅ type: In AX₅, A undergoes Sp_3d_2 hybridisation. The shape of the molecule is distorted octahedral or distorted square pyramidal.



AX₇ type: A undergoes sp₃d₃ hybridisation, and the shape of the molecule becomes pentagonal bipyramidal.



SHORT ANSWER QUESTIONS

1. Explain the gradation in the properties of halogens with reference to

- i) Electronegativity ii) Oxidation states iii) Electron affinity

Ans: i) Electronegativity: The electronegativity values of all the halogens are very high. The most electronegative amongst the known elements is **Fluorine**. The electronegativity values decrease from **Fluorine to Iodine** because the sizes of the atoms increase gradually.

ii) **Oxidation states:** All halogens show '-I' oxidation state as they are strongly electronegative in nature. In addition to -I oxidation state, they (except F₂), show +I, +III, +V and +VII oxidation states.

Because of the absence of d – sublevel in the valency shell of fluorine, it does not exhibit higher oxidation states. Depending upon whether the electrons are promoted and on the no. of unpaired electrons present in corresponding excited state of the atom, different oxidation state are shown by these elements.

iii) Electron affinity: These elements possess highest electron affinities. Parallel to the high electronegativity values of the elements, the electron affinity values also vary. But **chlorine, in this group, has the highest electron affinity** in spite of fluorine being the most electronegative element.

The unexpected lower value of electron affinity for fluorine is due to its **small size**

2. Explain the oxidation states shown by halogens.

Ans: Oxidation states: All halogens show ‘-I’ oxidation state as they are strongly electronegative in nature. In addition to – I oxidation state, they (except F₂), show + I, + III, + V and +VII oxidation states.

Because of the absence of d – sublevel Fluorine does not show higher oxidation states. Chlorine, Bromine and Iodine have d – orbitals available in their valence shells.

Depending upon whether the electrons are promoted and on the no. of unpaired electrons present in corresponding excited state of the atom, different oxidation state are shown by these elements.

Element	Oxidation states
Flourine	-I
Chlorine	- I, + I, + III, + IV, + V, + VI, + VII
Bromine	- I, + I, + III, + IV, + V, + VI
Iodine	-I, + I, + III, + V, + VII

3. What is bond energy? Explain the bond energies of X₂.

Bond energy: The minimum amount of energy required to break one mole of a given kind of bonds is called its **bond energy**. Bond energies of halogens are given below.

Element	F ₂	Cl ₂	Br ₂	I ₂
Bond energy (kJmol ⁻¹)	159	243	193	157

Bond enthalpies (bond energies or bond strengths)

Bond enthalpy is the heat needed to break one mole of a covalent bond to produce individual atoms, starting from the original substance in the gas state, and ending with gaseous atoms.

So for chlorine, Cl_{2(g)}, it is the heat energy needed to carry out this change per mole of bond:

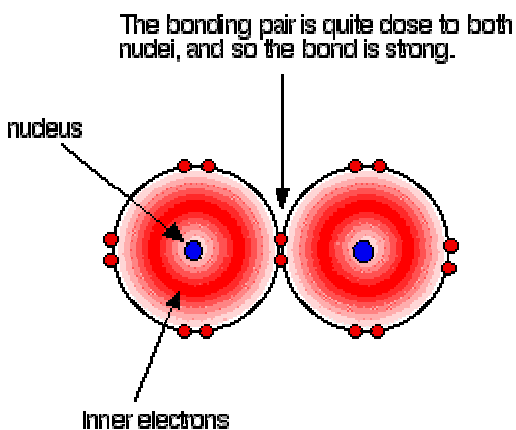


For bromine, the reaction is still from gaseous bromine molecules to separate gaseous atoms.



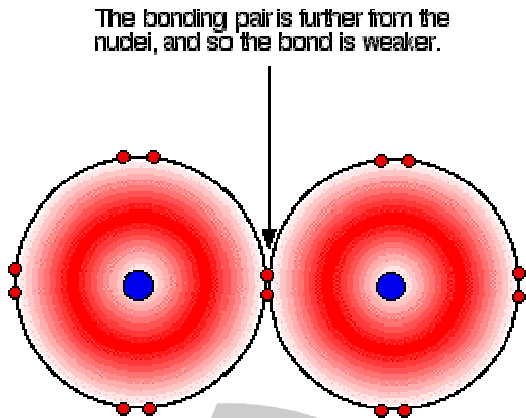
Bond enthalpy in the halogens, X_{2(g)}

A covalent bond works because the bonding pair is attracted to both the nuclei at either side of it. It is that attraction which holds the molecule together. The size of the attraction will depend, amongst other things, on the distance from the bonding pair to the two nuclei.

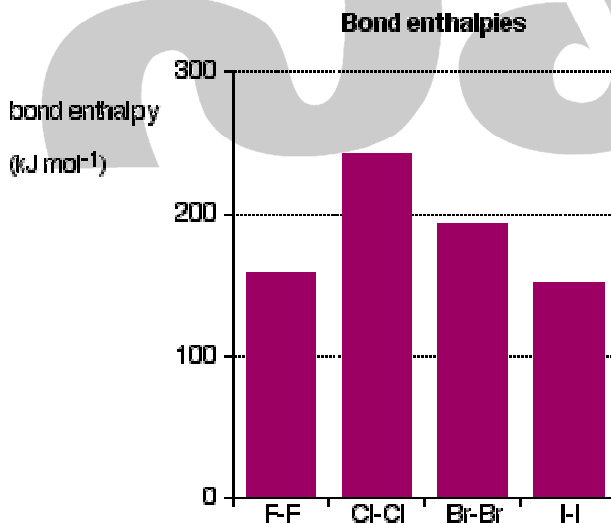


As with all halogens, the bonding pair will feel a net pull of 7+ from both ends of the bond - the charge on the nucleus offset by the inner electrons. That will still be the same whatever the size of the halogen atoms.

As the atoms get bigger, the bonding pair gets further from the nuclei and so you would expect the strength of the bond to fall.



So ... are the actual bond enthalpies in line with this prediction?

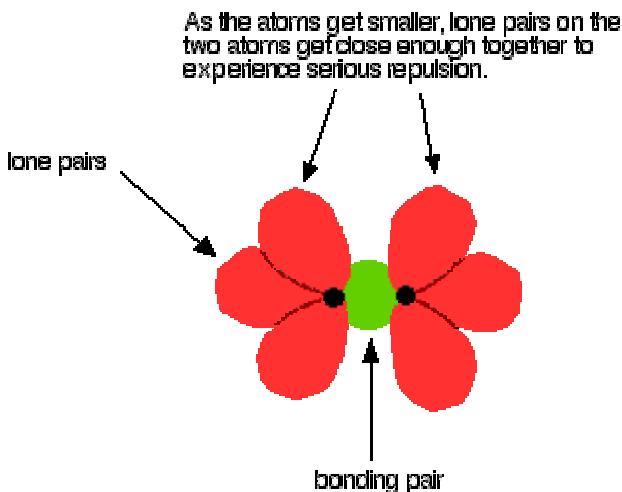


The bond enthalpies of the Cl-Cl, Br-Br and I-I bonds fall just as you would expect, but the F-F bond is way out of line!

Because fluorine atoms are so small, you might expect a very strong bond - in fact, it is remarkably weak. There must be another factor at work as well.

As well as the bonding pair of electrons between the two atoms, each atom has 3 non-bonding pairs of electrons in the outer level - lone pairs. Where the bond gets very short

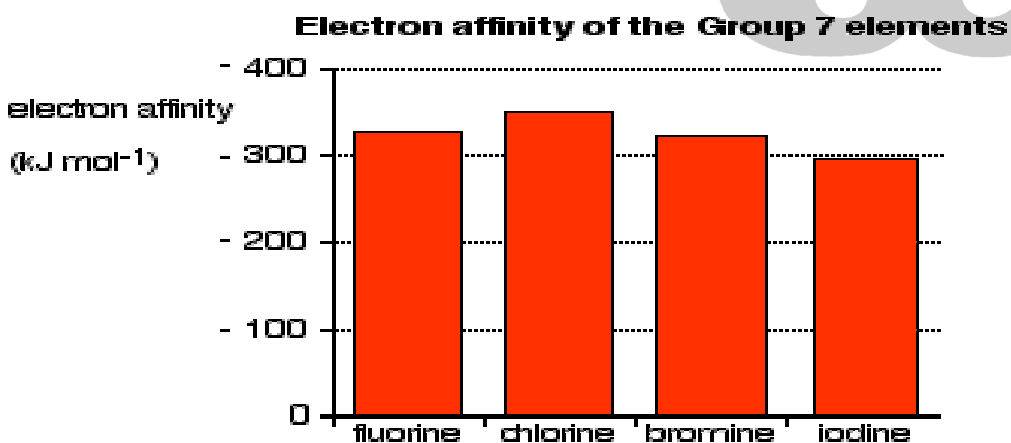
(as in F-F), the lone pairs on the two atoms get close enough together to set up a significant amount of repulsion.



In the case of fluorine, this repulsion is great enough to counteract quite a lot of the attraction between the bonding pair and the two nuclei. This obviously weakens the bond.

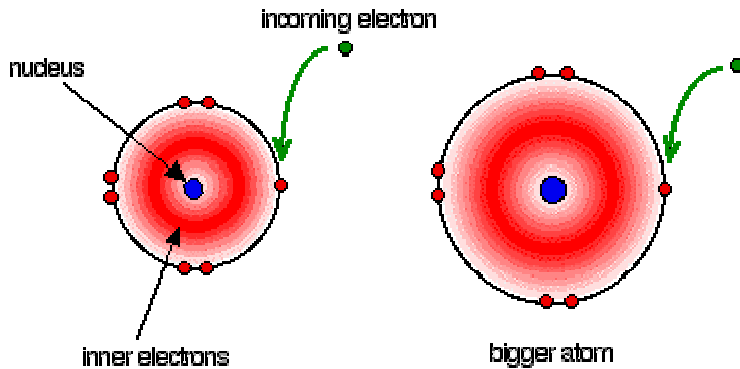
4 What is the order of electron affinities of halogens? Explain.

The first electron affinities of the Group 7 elements



Notice that the trend down the Group isn't tidy. The tendency is for the electron affinities to decrease (in the sense that less heat is given out), but the fluorine value is out of line.

The electron affinity is a measure of the attraction between the incoming electron and the nucleus. The higher the attraction, the higher the electron affinity.



In the bigger atom, the attraction from the more positive nucleus is offset by the additional screening electrons, so each incoming electron feels the effect of a net $7+$ charges from the centre - exactly as when you are thinking about atomic radius or electronegativity.

As the atom gets bigger, the incoming electron is further from the nucleus and so feels less attraction. The electron affinity therefore falls as you go down the Group.

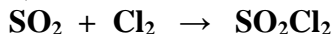
But what about fluorine? That is a very small atom, with the incoming electron quite close to the nucleus. Why isn't its electron affinity bigger than chlorine's?

There is another effect operating. When the new electron comes into the atom, it is entering a region of space already very negatively charged because of the existing electrons. There is bound to be some repulsion, offsetting some of the attraction from the nucleus.

In the case of fluorine, because the atom is very small, the existing electron density is very high. That means that the extra repulsion is particularly great and lessens the attraction from the nucleus enough to lower the electron affinity below that of chlorine.

9. Give the reactions of Cl_2 with a) SO_2 b) NaOH c) Iron metals.

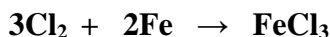
1) Chlorine reacts with sulphur dioxide to form sulphuryl chloride.



2) Cl_2 reacts with hot and cold NaOH as follows;

- $\text{Cl}_2 + \text{NaOH (Cold, dil)} \rightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$
- $\text{Cl}_2 + \text{NaOH (Hot, Conc.)} \rightarrow \text{NaCl} + \text{NaClO}_3 + \text{H}_2\text{O}$

3) Iron metal reacts with chlorine to form FeCl_3 .



10. Write the names and formulae of oxoacids of chlorine.

The names of the oxyanions of the halogens use the endings -ite and -ate to indicate low and high oxidation numbers and the prefixes hypo- and per- to indicate the very lowest and very highest oxidation numbers, as shown in the table below. Each of these ions can be converted into an oxyacid, which is named by replacing the -ite ending with -ous and the -ate ending with -ic.

Oxyanions and Oxyacids of Chlorine

Oxidation State of the Chlorine	Oxyanions		Oxyacids	
	Compound	Name	Compound	Name
+1	ClO ⁻	hypochlorite	HClO	hypochlorous acid
+3	ClO ₂ ⁻	chlorite	HOClO	chlorous acid
+5	ClO ₃ ⁻	chlorate	HOClO ₂	chloric acid
+7	ClO ₄ ⁻	perchlorate	HOClO ₃	perchloric acid

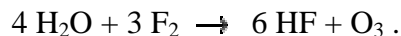
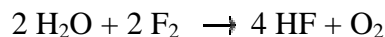
11. How does F₂ react with i) H₂O ii) NaOH. Give equation for them.

Reactions of Fluorine:

Fluorine is a very reactive element and therefore reacts with a large number of substances. Following are some reactions of fluorine

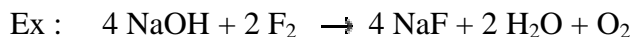
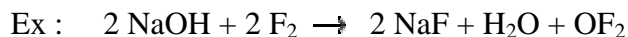
(1) Reaction with Water (H₂O) :

Fluorine produces ozonized oxygen on reaction with H₂O .



(2) Reaction with alkalis:

Cold, dilute alkalis (2 % solution) react with fluorine and produce fluorides and oxygen difluoride.



(**Note:** If excess of fluorine is passes through an alkali , ozonizes oxygen and HF may be formed).

12. What is available chlorine? Give chemical equation which determine the same.

Bleaching powder liberated free chlorine on reaction with dilute acids or when exposed to atmosphere where it reacts with carbon di oxide and moisture evolving chlorine .



The evolved chlorine is called “available chlorine’ and is usually 30 to 35 % by weight of the powder> the strength of the bleaching powder is evaluated on the basis of this available chlorine.

Commercially prepared chlorine is seldom pure and contains a small amount of unreacted slaked lime and hence the % of available chlorine is lower than as per the formula of bleaching powder. There are many uses of bleaching powder.

13. What are different classes of interhalogen compounds?

The compounds containing two or more halogen atoms are called inter halogen compounds. Each halogen combines with every other halogen to form interhalogen compounds. For e.g., ClF, ICl₃, BrF₅ etc.

They are of two types:

(i) Neutral molecules containing two or more halogen atoms. For e.g., ICl, BrF₅, IF₅, IF₇ etc.

(ii) Negatively charged interhalogen anions or polyhalide ions such as

ICl₂⁻, ICl₄⁻, I₃⁻ and positively charged interhalogen cations such as ICl₂⁺, ICl₄⁺ etc.

The different (types of) interhalogens of the type AX (diatomic), AX₃ (tetra atomic), AX₅ (hexa atomic) and AX₇ (octa atomic) are given below:

AX	AX ₃	AX ₅	AX ₇
ClF	ClF ₃	ClF ₅	-
BrF, BrCl	BrF ₃	BrF ₅	-
ICl, IBr	ICl ₃	IF ₅	IF ₇

Some characteristics of inter halogen compounds are:

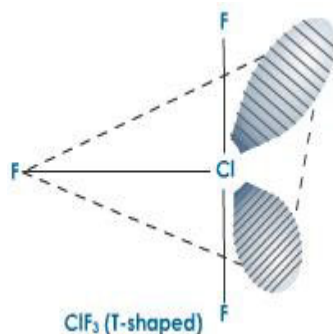
- (i) They are covalent compounds.
- (ii) They are more reactive than the constituent halogens. It is because A-X bond is relatively weaker than X-X bond.
- (iii) They are very good oxidising agents.
- (iv) Their melting and boiling points increase with the increase in the difference of electronegativity.
- (v) Chlorofluoro hydrocarbons are known as **Freons** and are used as refrigerants. For e.g., Freon-11 is CCl₃F, Freon-12 is CCl₂F₂, Freon-13 is CClF₃ etc.

14. Name the hybridisation involved in interhalogen compounds.

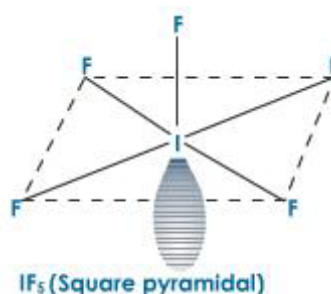
AX type: In AX type, A is the central atom and X is the bonded atom. In these types of compounds, both atoms share their electrons and form single covalent bond.



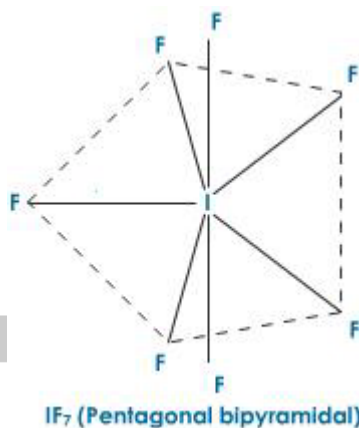
AX₃ type: In AX₃ type, A is the central atom and undergoes sp₃d₁ hybridisation in first excited state and gives 5 hybrid orbitals. Out of five, three are bonding electrons and two are lone pairs. Since sp₃d₁ hybridisation, it should be in Trigonal bipyramidal shape, but due to the presence of two lone pairs, structure is distorted to "T" shape.



AX₅ type: In AX₅, A undergoes Sp₃d₂ hybridisation. The shape of the molecule is distorted octahedral or distorted square pyramidal.



AX₇ type: A undergoes sp₃d₃ hybridisation, and the shape of the molecule becomes pentagonal bipyramidal.



VERY SHORT ANSWER QUESTIONS

1. Write the names of all the VIIA group elements.

Ans: VIIA group elements are Flourine (F), Chlorine (Cl), Bromine(Br), Iodine(I) and Astatine(.At).

2. List out the atomic numbers and the corresponding electronic configuration of halogens.

Element	Atomic No.	Electronic configuration
F	9	[He] 2s ² 2p ⁵
Cl	17	[Ne] 3s ² 3p ⁵

Br	35	[Ar] 3d ¹⁰ 4s ² 4p ⁵
I	53	[Kr]4d ¹⁰ 5s ² 5p ⁵

3. List out the atomic numbers and the corresponding electronic configuration of halogens.

Ans. In the periodic table, the most electronegative element is Fluorine.

Electronegativity value of Fluorine is 4.0 on Pauling scale

4. Name the element with highest E.A., and give its value.

Ans. "Chlorine" has the highest E.A.,

E.A., of chlorine is $\Delta H = -349 \text{ KJ/mol}$.

5. Why is the E.A., of Cl₂ greater than of F₂?

Ans. Lower E.A., of 'F₂' is due to its small size. The addition of an electron to the fluorine atom produces a high electron density in a relatively compact 2p - subshell. Therefore, there is a strong repulsion between them. Consequently, fluorine has a least tendency to accept an extra electron, hence lower E.A.,

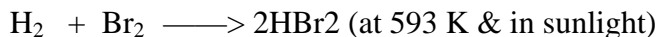
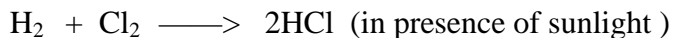
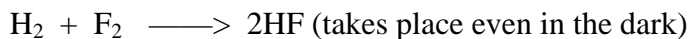
6. What is the order of oxidising capacity of halogens? Give an example to prove the order?

Ans: Order of oxidising power of halogens is

Fluorine > Chlorine > Bromine > Iodine

Proof for the above order:

Reaction conditions of halogens with hydrogen.





7. Give the oxidation states of Cl₂. Explain with the proper electronic configuration.

Negative Oxidation State of Chlorine:

Chlorine is in Group 17 with the electronic configuration of [Ar] 3s², 3p⁵. It requires only one electron to complete its octet so it tends to gain one electron. It has got the highest electron gain enthalpy of all the halogens. So it easily gains one electron and forms Cl⁻

This oxidation state is seen in many of the chlorine compounds. With metals they form only -1 oxidation state. Some of the examples of compounds with chlorine having -1 oxidation state are sodium chloride, potassium chloride, Magnesium chloride, lead (II) chloride, Tin (IV) chloride, Cesium chloride, Calcium chloride, Barium chloride.

Positive Oxidation State of Chlorine:

Chlorine has got empty 3d orbitals. So it can expand its octet. Chlorine with other electronegative elements forms a variety of compounds. When it reacts with more electronegative elements like fluorine, oxygen it forms positive oxidation numbers. It can form +1, +3, +5 and +7 oxidation states. With oxygen it also forms +4 and +6 oxidation numbers.

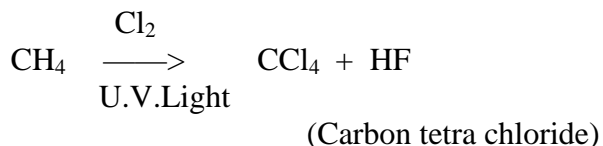
HOCl is a compound in which chlorine is in +1 oxidation number. HClO₂ has chlorine in +3 oxidation number. HClO₃ has chlorine in +5 oxidation number and HClO₄ has chlorine in +7 oxidation number.

8. What happens when methane reacts with (i) F₂ and (ii) Cl₂.

Ans: i) F₂ reacts with methane to form HF. Direct fluorination is not possible.



ii) Cl₂ reacts with methane to form CCl₄ as the final substituted product.



9. From the structures of interhalogen compounds predict their magnetic behaviour.

Ans. From the structures of interhalogen compounds, it is clear that there are no unpaired electrons.

Interhalogen compounds are diamagnetic in nature.

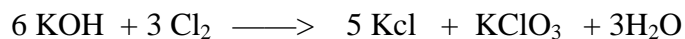
10. Give any three names of oxoacids of chlorine and give the oxidation state of chlorine in them.

Ans:

S.No.	Oxoacid	Oxidation state of chlorine
1	Hypochlorous Acid (HOCl)	+1
2	Chlorous acid (HClO ₂)	+III
3	Chloric acid (HClO ₃)	+V

11. Name the product formed in the reaction of hot and conc. KOH with a current of Cl₂.

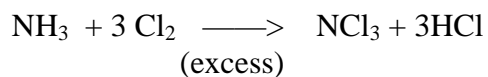
Ans. Hot and conc. KOH react with Cl₂ and produce “**Potassium chloride**” and **Potassium chlorate**”

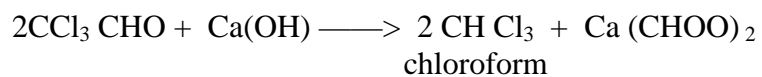
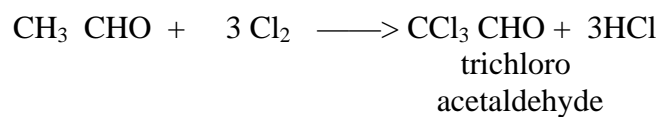


(hot & conc.)

12. Write the balanced equation (s) for the reaction of Cl₂ with NH₃.

Ans: i) With **excess of Cl₂**, NH₃ gives Nitrogen trichloride





19. Give any two uses of bleaching powder.

Ans: Bleaching powder is used

- i) In the sterilization of water
- ii) In the preparation of chloroform
- iii) As an oxidising and chlorinating agent.

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