

Chapter # 5

Halogens And The Noble Gases

2004 - 2005

HALOGENS

Halogens include Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) and Astatine (At). Astatine is radioactive element.

Halogens (Greek hals means salt and gennan, means to form or generate)

ELECTRONIC CONFIGURATION

Halogens have seven electrons in their valence shell. Two electrons are present in s-orbital and five electrons are present in p-orbital. Their outer shell general configuration is $ns^2 np^5$.

Group VII-A:	
F ₉	$1s^2 2s^2 2p^6 2p_x^1 2p_y^1 2p_z^1$
Cl ₁₇	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
Br ₃₅	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p_x^1 4p_y^1 4p_z^1$
I ₅₃	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p_x^1 5p_y^1 5p_z^1$
At ₈₅	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p_x^1 6p_y^1 6p_z^1$

TRENDSPhysical State

F₂ and Cl₂ are gases, Br₂ is liquid while I₂ is solid

They attack the skin. Bromine cause burn that heals slowly.

Colour

F₂ is a yellow gas

Cl₂ is greenish yellow gas

Br₂ is reddish brown liquid

I₂ is grayish black solid

Odour

All halogens have pungent, irritating odour.

Atomic Radii

Atomic radii increases down the group due to increase in number of shells and shielding effect.

Density

Density increases down the group with increase in atomic mass

Melting Points/Boiling Points

M.P. and B.P. increases down the group. It is due to increase in atomic size down the group. With increase in atomic size, strength of Vanderwaal's forces increases. Thus m.p. and b.p. increases down the group.

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Ionization Energy

It decreases down the group due to increase in number of shells and shielding effect.

Electron Affinity

Halogens have large and negative electron affinities values. Thus they have great tendency to accept electrons. Their standard reduction potential are also large and positive.

Electronegativity

Halogens have large values of electronegativities. However, their electronegativities decreases down the group.

Intermolecular Forces

Halogens exist as separate molecules. These have weak Vandercaal's forces. The strength of these forces increases with increase in size down the group. Thus iodine has stronger forces than other halogens.

Note

- Elements with large electronegativity values exist as $-ve$ ions.
- Elements with small electronegativity values exist as $+ve$ ions
- Elements with intermediate electronegativity values exist as ions or molecules or in free elemental state.

Properties	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Electronic configuration	$[\text{He}]2s^2 2p^5$	$[\text{Ne}]3s^2 3p^5$	$[\text{Ar}]3d^{10} 4s^2 4p^5$	$[\text{Kr}]4d^{10} 5s^2 5p^5$
Physical appearance	Pale yellow gas	Greenish yellow gas	Red brown liquid	Shiny greyish black solid
Ionization energy (kJ mol^{-1})	1681	1251	1140	1008
Electron affinity (kJ mol^{-1})	-322	-349	-325	-295
Electronegativity	4.00	3.00	2.8	2.5
Ionic radius (pm)	136	181	196	215
Covalent radius (pm)	72	99	114	133
Melting point ($^{\circ}\text{C}$)	-220	-101	-7.2	114
Boiling point ($^{\circ}\text{C}$)	-188	-34.3	58.8	184.4
Density (g cm^{-3})	0.00181	0.00321	3.12	4.93
Oxidation states	-1	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7	-1, +1, +3, +5, +7
Bond energy (kJ mole^{-1}) (X-X)	154.30	242.67	192.46	150.6

Occurrence

Halogens do not exist in free state. Their common form of occurrence is as halide ions i.e. F^- , Cl^- , Br^- and I^-

These halides are water soluble and present in salt lakes and as underground salt beds.

Ores of Halogens

Fluorine	Fluorspar	CaF_2
	Cryolite	Na_3AlF_6
	Apatite	$[\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2]$
Chlorine	Halite (Salt beds, brine wells, sea water)	NaCl
	Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Bromine	Brine wells, sea water	NaBr , KBr , MgBr_2
Iodine	NaIO_3 , NaIO_4 deposits in Chile Brine wells	

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PECULIAR BEHAVIOUR OF F

Fluorine differs from its family members due to

- Small size of F atom and F⁻ ion
- High first ionization energy and electronegativity
- Low dissociation energy of F₂ molecule
- Valence shell restriction to an octet

Following are the important dissimilarities

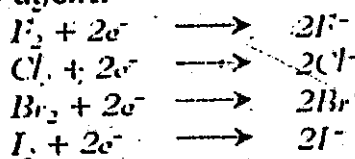
1. Lattice energy of halides
2. F has very small size. Thus it can form effective overlap with other elements except N, O and itself. Thus it can form shorter and stronger bonds
3. Ionic fluorides have very high lattice energies than other halides, thus these are stable. It is due to this reason that fluorides of Ca, Mg, Ba and Sr are insoluble in water.
4. F₂ molecule has very low dissociation energy. Thus it is very reactive, other halogens react very slowly under similar conditions.
5. Since valence shell of F is restricted to an octet. Therefore, many of its compounds show inertness e.g. CF₄, SF₆ etc.
6. Due to restriction to an octet, F shows only -1 oxidation state, while other halogens show variable oxidation states.
7. Only F reacts with noble gases directly like Xe and Rn to give fluorides.

OXIDISING PROPERTIES

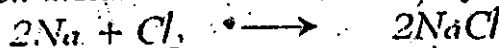
All free halogens are good oxidising agents.

Halogens have very high value of electron affinity and electronegativity.

Therefore these have tendency to accept electrons. Due to this reason these act as oxidising agent.



Thus elements of group IA and IIA reacts with halogens to form halides, in these reaction metals is oxidised and halogens are reduced.



Factors Affecting Oxidising Power

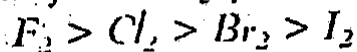
Following factors affect oxidising power

- Energy of dissociation
- Electron affinities of atoms
- Hydration energy of ions
- Heats of vaporization

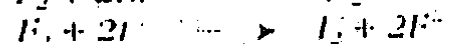
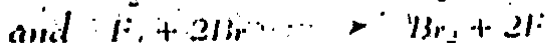
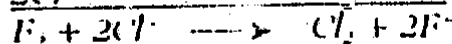
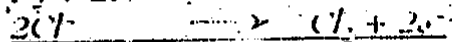
Trend In Oxidising Power

If a halogen has low energy of dissociation, high electron affinity and high hydration energy of its ions, then it will be a better oxidising agent. Thus oxidising power of F_2 is high due to low dissociation energy and high hydration energy of F^- ion.

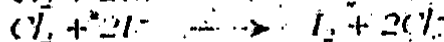
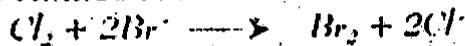
Thus general trend of oxidising power is

Relative Strength Of Oxidising Power Among Halogens

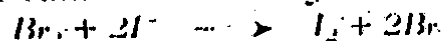
Due to difference in oxidising power, one halogen can oxidize other. Thus F_2 can oxidize all halide ions to molecular halogens.



Similarly Cl_2 oxidize both bromide and iodide ions.



Similarly Br_2 oxidize iodine only

Decolorization

F_2 and Cl_2 can oxidize coloured dyes to colourless substances e.g. litmus, universal indicators etc. during bleaching Cl_2 also act as oxidising agent.

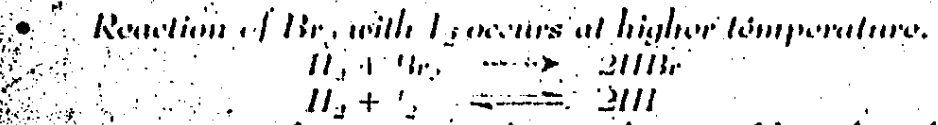
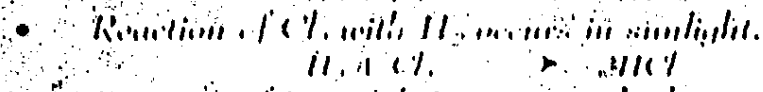
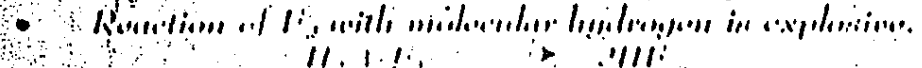
	F_2	Cl_2	Br_2	I_2
Standard reduction potential, E^0 (V)	+2.87	+1.36	+1.07	+0.54
$X_2 + 2e^- \longrightarrow 2X^-$				

COMPOUNDS OF HALOGENS

HALOGEN ACIDS (HYDRIDES)

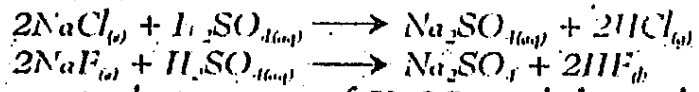
PREPARATION

All halogens react with hydrogen to form halogen acids.

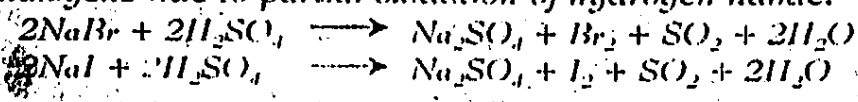


Reaction of I_2 is very slow and reversible. This direct method is only used for the preparation of HCl and HBr .

- HF and HCl can also be prepared by the reaction conc. H_2SO_4 with fluorides and chlorides.



- However, similar reaction of H_2SO_4 with bromides and iodides give free halogens due to partial oxidation of hydrogen halide.



PROPERTIES

1. They give fumes in moist air.
2. They are strong irritants.

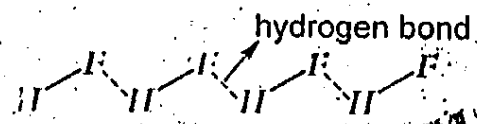
3. Physical State.

- HF is a colourless volatile liquid.
- HCl , HBr and HI are colourless gases at room T .

Property	HF	HCl	HBr	HI
Melting points ($^{\circ}C$)	-83.8	-114.2	-86.9	-50.8
Boiling points ($^{\circ}C$)	19.5	-85.0	-68.7	-35.2
Heat of fusion at M.P. (kJ/mol)	4.58	1.99	2.41	2.87
Heat of vaporization at B.P. (kJ/mol)	30.3	16.2	17.6	19.7
Heat of formation (kJ mol $^{-1}$ (ΔH_f))	-270.0	-92.0	-36.0	+26.0
Bond energy (kJ mol $^{-1}$)	566	431	366	299
H-X Bond length (pm)	92	128	141	160
Dissociation into elements at 1000 $^{\circ}C$ (%)	0	0.014	0.5	33
Dipole moment (Debye)	1.8	1.1	0.8	0.4

4. Melting Points, Boiling Points, Heats Of Fusion And Heats Of Vaporization.

- These increases regularly from HCl and HI . Thus HCl is more volatile than HBr , which is more volatile than HI . It is because, strength of Vanderwall's forces increases with increase in size of halogen atom. Thus HI has strong Vanderwall's forces than HBr , which has strong forces than HCl .
- HF has much higher values of these properties due to hydrogen bonding, e.g; it has very high b.p. which is an evidence of H-bonding in it.



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5. Dipole Moment.

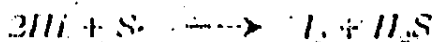
Dipole moment decreases from HCl to HI . Therefore, It may be said that dipole-induced dipole forces have an important role in intermolecular binding energy of heavier HX molecules.

6. Reducing Properties.

Halogen acids are good reducing agent. Their reducing strength is in the following order.



I_2 is a strong reducing agent. In redox reactions HI are oxidised to elemental halogens.



7. Bond Dissociation Energies.

Bond dissociation energy decreases with increase in size of halogen atoms.

Dissociation occurs in the following order.



Thus I_2 is dissociated more and HI is dissociated least.

8. Acidic strength.

In water, HX gives acid. These are hydrofluoric acid, hydrobromic acid, hydrochloric acid and hydroiodic acids.

- HF is a weak acid due to H-bonding effect.
- HCl , HBr and HI are strong acids.

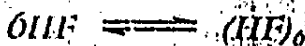
Acid strength increases in the following order



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PROPERTIES OF HF .

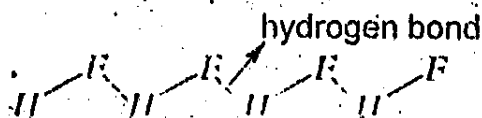
- HF is a colourless volatile liquid. HF attacks glass. It is handled in teflon (poly tetra fluoro ethylene) containers. In dry state, it can be stored in copper or stainless-steel containers under vacuum.
- HF is a strongly H-bonding viscous liquid.
- H-bonding in HF is less extensive than water. In H_2O , a three dimensional network of H-bonds is present.
- HF molecules exist as associated molecules in vapour phase as well due to H-bonding.
- Gaseous HF consists of an equilibrium mixture of monomers and hexamers.



- It is a strongly fuming liquid.
- It is used as non-aqueous solvent.

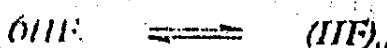
STRUCTURE OF HF

HF has a strong H-bonding structure.



Under certain conditions chain polymers may also exist. Chains and polymers of HF are of various sizes. Some of them even present in vapour phase as well.

In gaseous form, it exists as an equilibrium mixture of monomers and hexamers.



OXIDES OF HALOGENS

Generally halogens do not form oxides directly with oxygen. However by an indirect method following oxides can be prepared.

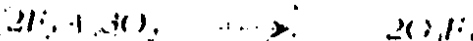
Fluorine	Chlorine	Bromine	Iodine
Oxygen difluoride (OF ₂)	Dichlorine monoxide (Cl ₂ O)	Bromine monoxide (Br ₂ O)	Iodine tetroxide (I ₄ O ₁₀)
Dioxygen difluoride (O ₂ F ₂)	Chlorine dioxide (ClO ₂)	Bromine dioxide (BrO ₂)	Iodine heptafluoride (I ₂ F ₇)
Tetraoxygen difluoride (O ₄ F ₂)	Chlorine hexoxide (Cl ₂ O ₆)	Bromine trioxide (BrO ₃)	Iodine pentoxide (I ₂ O ₅)
	Chlorine heptoxide (Cl ₂ O ₇)	Hexoxygen dibromide (Br ₂ O ₆)	

OXIDES OF FLUORINE

TRIOXYGEN DIFLUORIDE (O₃F₂)

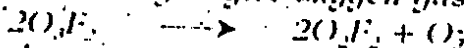
PREPARATION

It is prepared by passing electric discharge through a mixture of oxygen and fluorine.

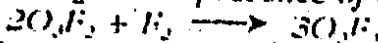


PROPERTIES

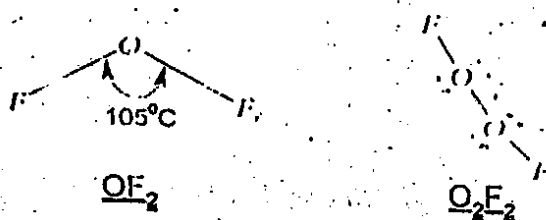
- At 365°C it is a dark red viscous liquid but turns to reddish brown solid at 350°C.
- It decomposes on heating to give oxygen gas and other oxides of fluorine.



- O₃F₂ reacts with F₂ in the presence of electric discharge to give O₂F₂.



STRUCTURE OF OF₂ AND O₂F₂



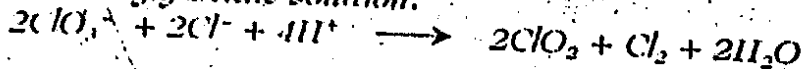
OXIDES OF CHLORINE

Oxides of chlorine are unstable. They are not prepared by direct reaction of chlorine and oxygen. These are used extensively for bleaching wood, paper-pulp in industry and for water treatment.

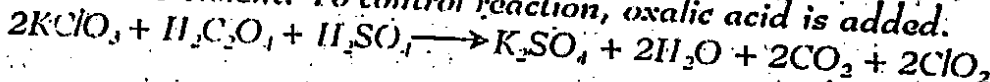
CHLORINE DIOXIDE (ClO₂)

PREPARATION

1. It is prepared by reducing NaClO₃ with NaCl or SO₂ or CH₃OH in strongly acidic solution.



2. It is also prepared by reacting conc. H₂SO₄ with KClO₃. This reaction is violent. To control reaction, oxalic acid is added.



PROPERTIES

- It is a pale yellow gas.
- On warming, it explodes into Cl₂ and O₂.
- It is soluble in water.
- It is stable in dark.
- It decomposes slowly in H₂O to HCl and HClO₃.
- It is paramagnetic.

USES

- It is used as antiseptic.
- It is used for purification of water.
- It is used to bleach cellulose material.

CHLORINE HEPTAOXIDE (Cl₂O₇)

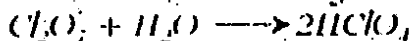
PREPARATION

It is prepared by dehydration of HClO₄ with P₂O₅ at -10°C. It is an anhydride of HClO₄.



PROPERTIES

- It is colourless oily liquid.
- It is explosive
- It slowly reacts with water to give HClO₄.



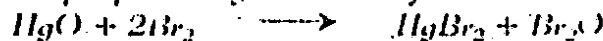
OXIDES OF BROMINE

These are dark volatile liquids. These have low thermal stability

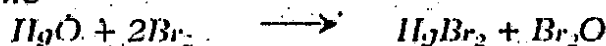
BROMINE MONOXIDE (Br₂O)

PREPARATION

1. It can be prepared by reaction of bromine vapours with mercuric oxide.



2. It can also be prepared by treating suspension of HgO in CCl₄ with bromine



PROPERTIES

- It is stable in dark in CCl₄ at -20°C
- It has oxidizing properties

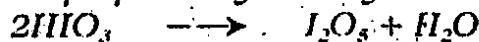
OXIDES OF IODINE

Only one oxide of iodine is important i.e. iodine pentoxide (I₂O₅). Other two oxides I₂O₄ and I₂O₆ are salt like compounds. They are considered as iodine-iodates.

IODINE PENTOXIDE (I₂O₅)

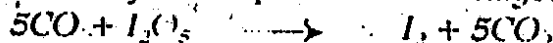
PREPARATION

It can be prepared by heating iodic acid at 240°C



PROPERTIES

- It is a white crystalline solid
- It is stable upto 300°C
- It has polymeric structure
- It is insoluble in organic solvents
- It reacts with water to give HIO₃
- It reacts with H₂S, HCl and CO as oxidizing agent
- It is used for the quantitative analysis of CO.



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OXYACIDS OF HALOGENS

Oxygen containing acids of halogens are called oxyacids.

General Features

- Stable oxyacids of fluorine do not exist. HOF has been prepared but is highly unstable.
- Most of the oxyacids of halogens are unstable compound. They generally exist only in aq. solution in the form of their salts. They cannot be isolated.

2004 - 2005

NOMENCLATURE OF OXYACIDS AND THEIR SALTS

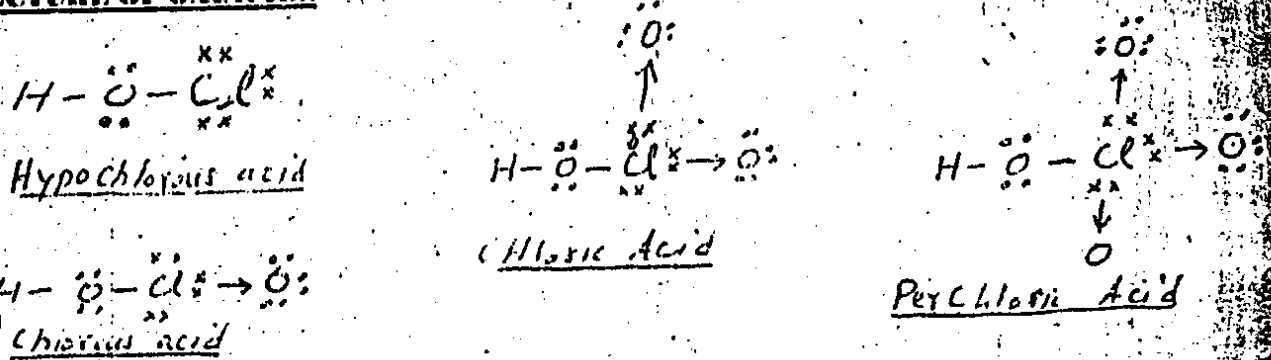
Following rules are used.

1. Some common acid is arbitrarily called -ic acid. The name of its salt ends in -ate.
e.g. Chloric acid HClO_3 , Sodium chlorate NaClO_3 .
2. The acid in which halogen atom has oxidation state higher than -ic acid is called per-ic acid. Its salt is called per-ate salt.
e.g. perchloric acid HClO_4 , Sodium perchlorate NaClO_4 .
3. The acid in which halogen atom has oxidation state lower than -ic acid (one less oxygen atom) is called -ous acid. The name of its salt ends in -ite.
e.g. Chlorous acid HClO_2 , Sodium chlorite NaClO_2 .
4. The acid in which halogen atom has oxidation state lower than -ous acid is called hypo-ous acid. Its salt is called hypo-ite salt.
e.g. hypochlorous acid HClO , Sodium hypochlorite NaClO .

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Oxidation state of halogen	Formula of the oxyacids of halogens			General names of	
	Chlorine	Bromine	Iodine	Oxyacids	Salts of oxyacids
+1	HClO	HBrO	HIO	Hypo_ous acid	Hypo_ite
+3	HClO_2	-----	-----	___ acid	___ite
+5	HClO_3	HBrO_3	HIO_3	___ acid	___ate
+7	HClO_4	-----	$\text{HIO}_4, \text{H}_5\text{IO}_6$	Perhalic acid	Per_ate

STRUCTURE OF OXYACIDS



- It is clear that central atom in all oxyacids is halogen atom.
- One or more oxygen atoms are covalently bonded to the central halogen atom.
- Bond between hydrogen and oxygen atoms polar due to electronegativity difference.
- Ionizable hydrogen is directly attached with oxygen atom.

OXIDATION STATES OF HALOGEN AND PROPERTIES OF OXYACIDS

In oxyacids, halogens have following oxidation state,



Thus oxidation states of halogen increases from +1 to +7. Due to this increase following properties are observed.

Thermal Stability

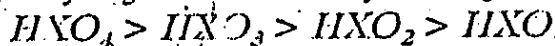
With increase in oxidation state, no. of oxygen atoms increases and thermal stability of acids also increases.

Acid Strength

Acid strength increases with increase in number of oxygen atoms.

Actually greater the number of oxygen atoms, greater the electron withdrawing effect. Thus bonding electrons are shifted away from hydrogen atom. Hence tendency to loose hydrogen increases. Therefore, strength of oxyacids increases with increase in number of oxygen atoms.

Thus strength of oxyacids is in the following order.



Oxidation Power

With increase in number of oxygen atoms, oxidation state of halogen increases and oxidizing power decreases.

Comparison Of Acid Strength Of Different Halogens.

Oxyacids of Cl are more acidic than Br, which are more acidic than that of iodine. It is due to decreases in electronegativity and increase in size of halogen atom from Cl to I.



PERCHLORIC ACID (HClO₄)

Preparation

It is commonly obtained in aq. solution

Pure anhydrous perchloric acid can be prepared by distillation of a perchlorate (KClO₄) with conc. H₂SO₄ under reduced pressure



Physical Properties

1. It is a colourless liquid
2. It is hygroscopic
3. At normal pressure it freezes at -112°C
4. It boils with decomposition at 90°C

Chemical properties

1. Cold and dilute perchloric acid is a very weak oxidizing agent
2. Hot and concentrated perchloric acid increases with increase in oxidizing strength
3. It is the strongest of all acids in aq. medium
4. Pure perchloric acid decomposes explosively on heating. That's why it is stored and used as 67% solution in water.
5. It reacts with organic compounds violently

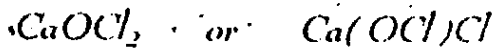
Uses

Due to its oxidizing effects, acid strength and solubility of its salts, it is used as an analytical reagent.

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BLEACHING POWDER

Its formula is



Bleaching powder is manufactured on industrial scale by following methods

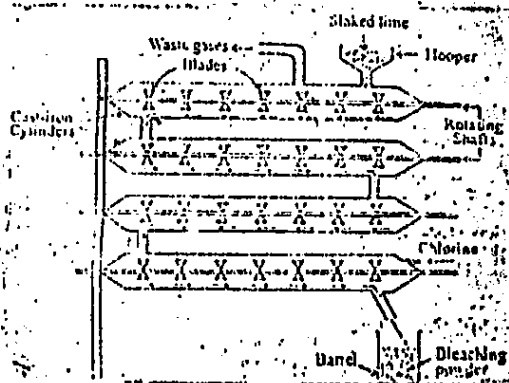
1. Hasenclever's method (Old Method)
2. Beckmann's method (Modern Method)

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1. HASENCLEVER'S METHOD

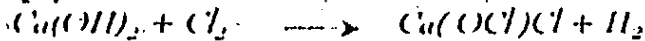
Construction

The apparatus consists of 4 to 8 iron cylinders. These are placed one above other horizontally. These are interconnected through pipe. These cylinders have stirrers. Upper cylinder has hopper to introduce lime. While lower cylinder has inlet for Cl₂ and an outlet to collect bleaching powder.



Working

The slaked lime is added through hopper in the upper cylinder. Lime is transported from one cylinder to other by rotating stirrers. Chlorine is introduced in the bottom cylinder. It rises up and reacts with the lime to form bleaching powder.

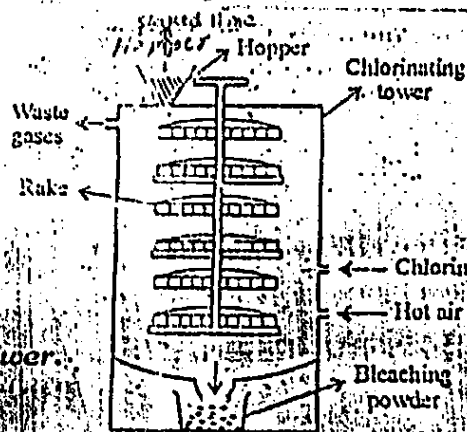


Bleaching powder is collected through outlet in the lower cylinder

2. BECKMANN'S METHOD

Construction

The apparatus consists of a cast iron tower. It has eight horizontal shelves. Each shelf has a rotating rake. There is hopper at the top. Bleaching powder is collected at the bottom. There are inlets for Cl₂ and hot air, at the base of tower.



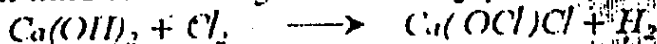
Working

Powdered slaked lime is introduced through hopper at the top with compressed air.

A mixture of hot air and Cl₂ is introduced through inlets at the base of tower.

Slaked lime is pushed down by rotating rakes while Cl₂ rises up. Thus apparatus works on counter current principle.

Slaked lime reacts to give bleaching powder



Bleaching powder is collected at the base of tower.

Due to counter-current principle maximum reaction takes place between Cl₂ with very little loss of Cl₂

Storage

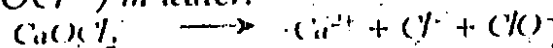
Bleaching powder is stored in airtight containers to avoid loss of chlorine

PHYSICAL PROPERTIES

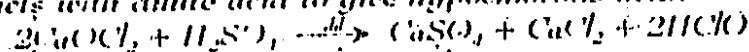
- It is a yellowish white powder
- It has strong smell of chlorine

CHEMICAL PROPERTIES1. As Oxidizing Agent

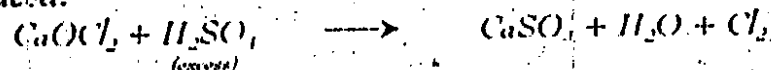
It is an oxidizing agent. This property is due to the generation of hypochlorite ion (OCl^-) in water.

2. Reaction with dilute acid

It reacts with dilute acid to give hypochlorous acid.

3. Reaction with excess acid

If excess of an acid (weak or strong) is added to bleaching powder, chlorine is produced.



The amount of chlorine liberated is called "available chlorine".

Available Chlorine

The amount of chlorine, which is set free during the reaction of bleaching powder with an acid, is called available chlorine.

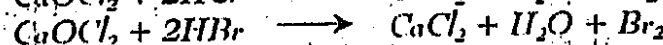
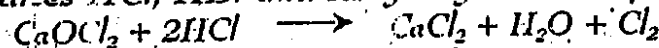
The activity of bleaching powder is measured in terms of available chlorine.

The average percentage of available chlorine in bleaching powder is 35-40%.

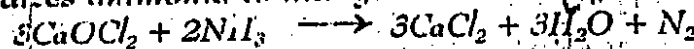
The bleaching action of bleaching powder is due to its oxidative character.

4. Reaction with HX

It oxidizes HCl, HBr and HI giving the corresponding halogens.

5. Reaction with NH_3

It oxidizes ammonia to nitrogen.

**USES:**

- It is used for the laboratory preparation of chlorine and oxygen.
- It is used in the manufacture of chloroform.
- It is used as a disinfectant and in the sterilization of water.
- It is used for making unshrinkable wool.
- It is used for bleaching cotton, linen and paper pulp.

Note

Delicate fabrics like wool, silk etc. cannot be bleached with it, since these could be damaged by chlorine

2004 - 2005

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COMMERCIAL USES OF HALOGENS AND THEIR COMPOUNDS

Uses of F

- It is used in the preparation of freon
Freons
 - ✓ Freons is commercial name of low molecular mass fluorochlorocarbons CCl_2F_2 , $CClF_3$
 - ✓ These are used as refrigerants and aerosol propellants.
- Fluorides in toothpastes build a protective coating on teeth.
- It is used to prepare Teflon
Teflon
 - ✓ Teflon is polytetrafluoroethylene compound. Its formula is $-(CF_2 - CF_2)-$
 - ✓ It is an important plastic. It is not attacked by strong acids, alkalis and oxidizing agents.
 - ✓ It is used to make corrosion proof parts of machinery
 - ✓ It is used as non-stick coating of cooking pans

Uses of Cl

- It is used in the manufacture of bleaching powder
- It is used in the manufacture of HCl , which is the cheapest industrial acid.
- It is used in the manufacture of antiseptics, insecticides, weed killers and herbicides
- It is used in the manufacture of polyvinyl chloride (PVC) plastic
- It is used in the manufacture of $CHCl_3$ and CCl_4 . These are used as solvents.
- It is used as disinfectant in swimming pool and water treatment plants.

Uses of Br

- It is used to manufacture ethylene dibromide ($C_2H_4Br_2$) which is added to leaded gasoline to prevent the deposition of lead oxide and lead sulphate in engine.
- It is used as fungicide
- It is used as $AgBr$ in photography

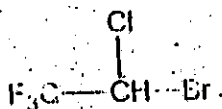
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Uses of I

- It is used in pharmaceutical industry
- e.g. It is used in the manufacture of tincture of iodine and iodex
- It is added as NaI or KI to table salt. This is done to provide iodine to the body. Such salt is called iodized salt. Diet with insufficient iodine leads to the enlargement of thyroid. This disease is called goiter.

Halothane

Its formula is



It is used as anesthetic

NOBLE GASES

Elements Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe) and Radon (Rn) that are placed in zero group or group VIIIA of periodic table are called noble gases.

These are also called inert gases or rare gases because they are chemically inert and present in very small amount in atmosphere (about 1%).

All these gases are colourless and odourless and exists as monoatomic gases.

These can be liquefied and solidified.

ELECTRONIC CONFIGURATION

Except He, all noble gases have complete octets. Thus they are chemically inert.

Elements	Atomic number	Electronic configuration
He	2	1s ²
Ne	10	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶
Ar	18	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰ 4p ⁶
Kr	36	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰ 4p ⁶ 5s ² 4d ¹⁰ 5p ⁶
Xe	54	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰ 4p ⁶ 5s ² 4d ¹⁰ 5p ⁶ 6s ² 4f ¹⁴ 5d ¹⁰
Rn	86	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰ 4p ⁶ 5s ² 4d ¹⁰ 5p ⁶ 6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶

OCCURANCE AND PROPERTIES

Noble gases are present in very small amount in air. These can be isolated from air by chemical methods or by fractional distillation of liquid air.

Air is an important commercial source of Ne, Ar, Kr and Xe

Helium (He)

- On earth He is present due to radioactive decay. It is present as α -particles which are doubly ionized helium atoms i.e. He⁺⁺.
- It can be isolated economically from natural gas by liquefaction method

Neon (Ne)

- It is present $\frac{1}{65000}$ th part of atmosphere. It is isolated during liquefaction of air.
- It glows red in gas discharge tube. It's colour is most intense in discharge tube of all the noble gases.
- Liquid Ne has 40 times more refrigeration capacity than liquid He

Argon (Ar)

- It is obtained as a by-product during liquefaction of air
- It is colourless, odourless gas
- It is very inert. It is not known to form any true chemical compounds

Krypton (Kr)

- Traces of Kr are present in air.
- It is colorless, odourless gas
- It is expensive
- It is identified by its brilliant green and orange spectral lines
- It's compound Krypton difluoride (KrF₂) can be prepared by various methods.

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Xenone (Xe)

- It is present in air to very small extent (0.08 ppm)
- It is obtained as by product during liquefaction of air
- Xe is available commercially in cylinders at high pressure
- It reacts with fluorine but not with H₂O
- It is slightly soluble in water (110ml / lit at 20°C)

Radon (Rn)

- Rn is formed by α -decay of radium from where it can be collected.

$${}^{226}\text{Ra} \longrightarrow {}^{222}\text{Rn} + {}^4\text{He}$$
- It is present to very small extent in air
- It is obtained as by product from liquefaction of air.

PHYSICAL PROPERTIES

Colour And Odour

All are colourless and odourless gases

Reactivity

They are chemically inert

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Ionization Energy

Due to complete shell, it is very difficult to remove electron from them. Thus they have high ionization energy. However ionization energy decreases down the group due to increase in atomic radii and shielding effect.

Melting Points, Boiling Points And Heats Of Vaporization

They have low values of m.p., b.p. and heats of vaporization. B.P. of He is lowest than any known substance.

B.P., M.P. and Heats of vaporization increases down the group with increase in atomic number.

It is because, strength of Vanderwaal's forces increases down the group with increase in atomic size

Solubility

They are very less soluble in H₂O. However, their solubility increases down the group due to increase in atomic size. It is because larger atoms are easily polarized by polar water molecules.

Property	He	Ne	Ar	Kr	Xe	Rn
At. Wt. (a.m.u)	4	20.18	39.95	83.8	131.3	222
M.P(°C)	-272	-249	-189	-157	-112	-71
B.P (°C)	-269	-246	-186	-153	-108	-61
Ionization energy (1 st) kJmol ⁻¹	2372	2081	1521	1351	1170	1037
Water solubility (ml/lit) at 20°C	13.8	14.7	37.9	73.00	110.9	---
Heat of vaporization kJmol ⁻¹	0.08	1.77	6.5	9.7	13.7	18.0

COMPOUNDS OF XENON

Xe reacts directly with F_2 to form different compounds. In these compounds oxidation state of Xe varies from +2 to +8. These compounds are stable

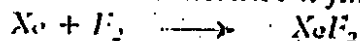
Oxidation state of xenon	Compound	Physical form	Melting Point ($^{\circ}C$)
+2	XeF_2	Colourless crystals	140
+4	XeF_4	Colourless crystals	114
+6	$XeOF_2$	Colourless crystals	90
	XeF_6	Colourless crystals	48
+8	$XeOF_4$	Colourless liquid	-28
	XeO_3	Colourless crystals	25 (Explodes)
	XeO_4	Colourless gas	-39.9 (Explodes on warming)

XENON FLUORIDES

There are three fluorides of Xenon i.e. XeF_2 , XeF_4 and XeF_6

XENON DIFLUORIDE (XeF_2)**Preparation**

It is prepared by direct reaction of Xe and F_2 . XeF_2 formed is immediately removed from reaction mixture. Otherwise it further reacts with F_2 to give XeF_4



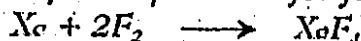
The reaction is completed in 8 hours

Properties

- It is a colourless crystalline solid
- Its m.p. is $140^{\circ}C$
- It is stored in Ni vessel
- It is a mild fluorinating agent

XENON TETRAFLUORIDE (XeF_4)**Preparation**

It is prepared by heating a mixture of Xe and F_2 in 1:5 ratio in Ni container under 0 atmospheric pressure for few hours

**Properties**

- It is a colourless crystalline solid
- Its m.p. is $114^{\circ}C$
- It can be stored in Ni vessel
- It is a strong fluorinating agent

XENON HEXAFLUORIDE (XeF_6)**Preparation**

It is prepared by heating a mixture of Xe and F_2 in the ratio 3:20 in a stainless vessel. The temperature is kept at $300^{\circ}C$ and pressure at 50 atm.

The yield of this reaction is 95%

**Properties**

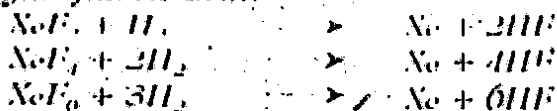
- It is colourless crystalline solid
- It is yellow in colour in liquid and gaseous state
- Its m.p. is $48^{\circ}C$
- It can be stored in Ni container

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CHEMICAL PROPERTIES OF XENON FLUORIDES

1. Reaction with H_2

Fluorides of xenon can be reduced with hydrogen at $400^\circ C$, to give Xenon and hydrofluoric acid.



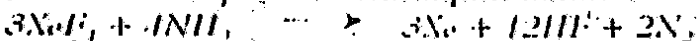
2. Fluorinating agents

Xenon tetra-fluoride is a good fluorinating agent. It can be used to prepare metal fluorides.



3. Reaction with NH_3

XeF_4 reacts with explosion with liquid ammonia.



4. Hydrolysis

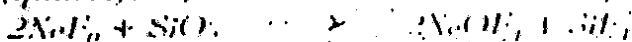
Hydrolysis of XeF_6 with small amount of water gives $XeOF_4$.



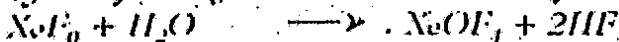
XENON OXYFLUORIDES

Preparation

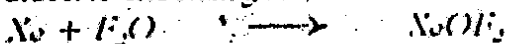
1. Xenon oxytetrafluoride, $XeOF_4$ is formed by a rapid reaction of XeF_6 with silica (quartz).



2. Hydrolysis of XeF_6 with small amount of water gives $XeOF_4$.



3. Xenon oxydifluoride $XeOF_2$ is obtained by reacting xenon oxygen difluoride in an electric discharge.



Properties of $XeOF_2$

- It is a colourless volatile liquid.
- It can be kept in nickel vessel.
- It reacts with water to give XeO_3 .

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OXIDES OF XENON

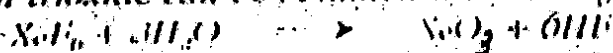
There are two oxides of xenon.

1. Xenon trioxide
2. Xenon tetraoxide

1. XENON TRIOXIDE (XeO_3)

Preparation

Xenon trioxide can be obtained when XeF_6 is hydrolysed slowly.



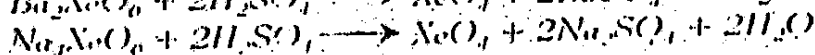
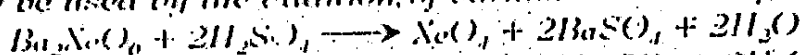
Properties

- It is crystalline solid.
- It explodes at very low temperature.
- It is weakly acidic
- Its aqueous solution is almost non conductor.

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2. XENON TETRAOXIDE (XeO₄)

It can be used by the addition of barium or sodium peroxide to conc. H₂SO₄.

APPLICATIONS OF THE NOBLE GASES

1. Helium is used in weather balloons, in welding and in traffic signal light.
2. A mixture of 80% helium and 20% oxygen is used for breathing by the sea divers.
3. Helium is used as a cooling medium for nuclear reactors.
4. Neon is largely used in making neon advertising signs, in high voltage indicators and TV tubes.
5. Neon and helium are used in making glass lasers.
6. Argon is used in electric light bulbs, in fluorescent tubes, in radio tube, and in Geiger counters (used to detect radioactivity).
7. Argon is also used for arc welding and cutting.
8. Krypton is used to fill fluorescent tubes and in flash lamps for high speed photography.
9. Xenon is used in bactericidal lamps.
10. Radon being radioactive is used in radiotherapy for cancer, and for earth quake prediction.

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