Chapter
5

GROUP VA AND VIA ELEMENTS

HALOGENS

The halogens, VIIA group of the periodic table consists of fluorine, chlorine, bromine, iodine and astatine. All these elements are **non-metals** quite similar in chemical properties. First four elements are more common halogens and Astatine is radioactive and its most stable isotope has half life of only 8.3 hours. Chemistry of astatine is not discussed here.

Table – Electronic configuration of halogens

Name	Symbol	At. Number	Electronic configuration
Fluorine	F	9	$1s^2, 2s^2, 2p^5$
Chlorine	Cl	17	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
Bromine	Br	35	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$
Iodine	I	53	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^5$
Astatine	At	85	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 5p^5$

NAME OF HALOGENS

Origin of Halogens:

With the exception of flourine, names of halogens are derived from Greek (Gk) words.

Name	Origin	Meaning
Halogen	Hals (Gk)	Salt
	Gen (Gk)	Producing
Flourine	Fluere (Land F)	Flow or flux (until AD 1500, the mineral fluorspar, CaF_2 was used as flux in metallurgy)
Chlorine	Chloros (Gk)	Greenish yellow
Bromine	Bromos (Gk)	Stench (Offensive odour, ill smell)
Iodine	Iodes (Gk)	Violet
Astatine	Astatos (Gk)	Unstable

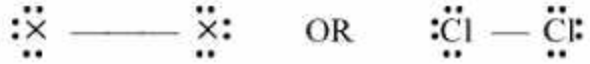
L = Latin, F = French, Gk = Greek

PHYSICAL PROPERTIES OF HALOGENS

Some common properties of halogens are given below:

(1) The electronic configuration of halogens is ns^2, np^5 one electron short from the octet.

(2) In the free elemental state, all halogens exist in diatomic molecules in which they complete octets by sharing their single unpaired electrons, e.g., F_2, Cl_2, Br_2, I_2.



(3) At room temperature and pressure, fluorine is pale yellow gas, chlorine is greenish yellow gas, bromine is red-brown coloured liquid and iodine is a metallic-appearing shiny grayish black solid. Bromine is the only non-metallic liquid.

(4) The halogens have irritating odours, and they attack the skin. Bromine is particularly nasty, it causes burns that heal slowly.

(5) Bromine and iodine have very high vapour pressure and even at room temperature, dark-red vapours are always present above the liquid bromine and violet vapours above the solid iodine.

(6) Halogens have high value of ionization potential due to their smaller size. However ionization potential decreases downward in a group, due to increase in the size of atom.

(7) Electron affinity values of halogens are large and negative, outer most shell of halogen can absorb one electron very easily.

(8) They have high value of standard reduction potentials and can easily be reduced.

(9) Halogens have high electronegativities.

F = 4.0, Cl = 3.0, Br = 2.8 and I = 2.5

(10) The intermoelcular attraction is greater in the larger molecules due to greater masses and greater polarizability. Due to their large size, the Van Der Waal's forces in iodine molecules are stronger than the smaller molecules and it exists in solid state.

(11) None of the halogens is found in free form. Most of the halogens exist in the form of negative ions due to their greater electronegativities.

Table – Physical properties of group VIIA

Properties	Flourine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Ionic radii (pm)	136	181	196	216
Covalent radii (pm)	72	99	114	133
Melting point (°C)	–220	–101	–7	+114
Boiling point (°C)	–188	–35	+59	+184
First ionization energy (kJ/mol)	1681	1251	1140	1008
Electron affinity, (kJ/mol)	–322	–349	–325	–295
Electronegativity	4.0	3.0	2.8	2.5
Bond energy (x-x) (kJ/mol)	154.80	242.67	192.46	150.6
Oxidation states	–I	–I, I, III, V, VII	–I, I, III, V, VII	–I, I, III, V, VII
Physical form at	Pale	Greenish	Red-brown	Shiny
Room temperature	Yellow gas	Yellow gas	Liquid	Greyish black solid

(12) Bond dissociation energy (to break X–X bond) decreases from Cl_2 to I_2 due increase in size of atoms. The bond dissociation energy of F_2 is less than Cl_2 due to large repulsive forces between the electrons in the small, highly electronegative fluorine atom.

OCCURRENCE

The halogens exist in nature primarily in the form of compounds. Their most common state is the halide ions F^-, Cl^-, Br^- and I^-. These halides are soluble in water and are found in sea, in salt lakes and underground beds of salts.

Element	Mineral	Formula
Flourine	Fluorspar Cryolite Apatite	CaF_2 Na_3AlF_6 $[CaF_2.3Ca_3(PO_4)_2]$
Chlorine	Halite (Salt beds, brine wells, sea water) Carnallite	NaCl $KCl.MgCl_2.6H_2O$
Bromine	Brine wells, sea water	NaBr, KBr, $MgBr_2$
Iodine	Deposits in chile brine wells	$NaIO_3$, $NaIO_4$

PECULIAR BEHAVIOUR OF FLUORINE

Fluorine has some difference in properties due to the following reasons:

(i) Small size of F atom and F^- ion.

(ii) High first ionization energy and electronegativity.

(iii) Low dissociation energy of F_2 as compared to Cl_2 and Br_2.

(iv) Restriction of valence shell to an octet.

Flourine has following peculiar properties:

(1) Bond of fluorine with other elements is shorter and stronger due to better overlap as compared to other elements like Cl, Br.

(2) Ionic fluoride like NaF, LiF have high lattice energy as compared to other halides.

(3) Fluroides of Ca, Mg, Ba, Sr are insoluble in water due to high lattice energy while other halides of these elements are water soluble.

(4) Due to low dissociation value of F_2 as compared to Cl_2 or Br_2 it has greater reactivity. Other halogens have low reactivity.

(5) Fluorine has only -1 oxidation state while other halogens have oxidation states -1, $+1$, $+3$, $+5$ and $+7$.

(6) Due to restriction of the valence shell, to an octet, many fluoro compounds are inert e.g., CF_4, SF_6, SiF_4.

(7) Fluorine is the only element which combines directly with noble gases, like xenon, krypton and radon forming their fluorides.

OXIDIZING PROPERTIES OF HALOGENS

All the free halogens (F_2, Cl_2, Br_2, I_2) act as oxidizing agents when they react with metals or non-metals. The reactant element acquires positive oxidation state in compound form.

On forming ionic compounds with metals, the halogen gain electrons and are converted into negative halide ions.

$$2Na + Cl_2 \longrightarrow 2Na^+Cl^-$$

The oxidizing power of halogens decreases with increase in atomic number. Fluorine has the highest oxidizing power and iodine the least. The order or decreasing power as an oxidizing agent is:

$$F_2 > Cl_2 > Br_2 > I_2$$

The oxidizing power of halogens depends upon the following factors:

(i) Energy of dissociation

(ii) Electron affinities of atoms

(iii) Hydration energy

(iv) Heats of vaporization (for Br_2 and I_2)

If a halogen has low energy of dissociation, a high electron affinity and a higher hydration energy of its ions, it will have a high oxidizing power.

Oxidizing power of F_2 is higher because it has low energy of dissociation and higher hydration energy of its ions. Due to the relative strength as oxidizing agents, it is possible for each free halogen to oxidize the ions of other halogens next to it, in the family.

Fluorine can oxidize all the halide ions to molecular halogens.

$$F_2 + 2e^- \longrightarrow 2F^-$$

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

$$F_2 + 2Cl^- \longrightarrow Cl_2 + 2F^-$$

In the similar way chlorine will oxidize both bromide and iodide ions, while bromine can oxidize only iodide, ion.

$$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$$

$$Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$$

Fluorine and chlorine can **oxidize various coloured dyes** to colourless substances. Colour of litmus or universal indicator can be decolourized when exposed to fluorine or chlorine. When chlorine acts are bleaching agent, it behave as oxidising agent.

COMPOUNDS OF HALOGENS

Hydrogen Halides, HX (Hydrides of Halogens):

Hydrogen halides are HF, HCl, HBr and HI.

Preparation:

(1) All halogens react with hydrogen to form halogen halides. e.g.,

$$H_2 + F_2 \longrightarrow 2HF$$

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$$H_2 + Br_2 \longrightarrow 2HBr$$

$$H_2 + I_2 \longrightarrow 2HI$$

The reaction of molecular hydrogen and flourine is very fast and explosive. With chlorine, molecular hydrogen reacts in the presence of sunlight. Bromine and iodine react with molecular hydrogen at a higher temperature. The reaction with iodine is very slow and reversible. Direct combination is used as a preparative method only for HCl and HBr.

(2) Hydrogen fluoride and hydrogen chloride can also be obtained by the action of concentrated sulphuric acid on fluorides and chlorides, but analogous reactions with bromides and iodides result in partial oxidation of the hydrogen halide to the free halogen.

$$2NaF + H_2SO_4 \longrightarrow Na_2SO_4 + 2HF$$

$$2NaCl_{(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + 2HCl_{(g)}$$

$$2NaBr_{(s)} + 2H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + Br_{2(l)} + SO_2 + 2H_2O$$

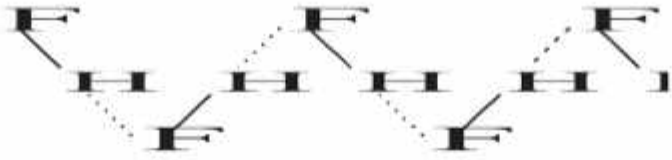
PROPERTIES OF HYDROGEN HALIDES

(1) HF is a colourless volatile liquid whereas other hydrogen halides (HCl, HBr, HI) are colourless gases at room temperature. They give fumes in moist air. They are strong irritants.

(2) **Hydrogen fluoride attacks glass** and has found applications as a non-aqueous solvent. It can be handled in teflon (polytetrafluorethylene) containers or if absolutely dry, in copper or stainless-steel vessels kept under vacuum.

(3) Pure liquid HF is strongly hydrogen bonded and is **viscous liquid**. Its viscosity is less than that of water due to the absence of a three-dimensional network of H-bonds which occur in H_2O. Hydrogen bonding is also responsible for the association of HF molecules in the vapour phase. Various test results indicate that gaseous HF consists of an equilibrium mixture of monomers and cyclic hexamers.

$$6HF \rightleftharpoons (HF)_6$$



Hydrogen bonding in HF

Chain polymers may also exist under certain conditions. Chains and rings of HF are of various sizes, some of these persist in the vapour phase as well. Some of the physical properties of hydrogen halides are given in table.

Table – Some physical properties of hydrogen halides

Property	HF	HCl	HBr	HI
M.P (°C)	–83.8	–114.2	–86.9	–50.8
B.P (°C)	19.5	–85.0	–66.7	–35.3
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)	–27.0	–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°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 vaporizaton** increase regularly from HCl to HI. The HF has much higher values for these properties due to hydrogen bonding. A very high boiling point of hydrogen fluoride is a major evidence of the presence of hydrogen bonding among its molecules. The relative volatility of HCl, HBr and HI reflects the strengthening of the van der Waal's forces due to increasing size of halogens. Since the dipole moment of molecules decreases from HCl to HI, probably dipole-induced dipole forces play an important role in the intermolecular binding of the heavier HX molecules.

(5) **The strength of the hydrogen halogen bond** is very high in HF. It decreases with increasing size of the halogen atom. The bond strength is reflected in the ease of dissociation of hydrogen halides at elevated temperatures.

(6) HF, HCl, HBr and HI act as reducing agents in the following order.

$$HF < HCl < HBr < HI$$

Hydrogen iodide is a stronger reducing agent. In redox reactions the hydrogen halides are oxidized to elemental halogens. e.g.,

$$2HI + S \rightleftharpoons I_2 + H_2S$$

(7) In water, hydrogen halides give hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids. Hydrofluoric acid is a weak acid due to limited ionization. The other three acids are very strong acids.

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

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

The strength of acids increases in the order of:

$$HF < HCl < HBr < HI$$

OXIDES OF HALOGENS

"The compounds which contain oxygen and halogens chemically combined together are called oxides of halogens."

Halogens do not react directly with oxygen. These halogen oxides are formed indirectly. Some oxides of halogens with their names are given below in the table.

Table – Oxides of halogen

Fluorine	Chlorine	Bromine	Iodine
Oxygen difluoride OF_2	Dichlorine monoxide Cl_2O	Bromine monoxide Br_2O	Iodine tetraoxide I_2O_4
Dioxygen difluoride O_2F_2	Chlorine dioxide ClO_2	Bromine dioxide BrO_2	Iodine iodate I_4O_9
Trioxygen difuloride O_3F_2	Chlorine heptaoxide Cl_2O_7	Bromine trioxide BrO_3	Iodine pentoxide I_2O_5

TRIOXYGEN DIFULORIDE (O_3F_2)

Preparation:

This oxide can be prepared when a mixture of fluorine and oxygen is subjected to the electric discharge.

$$2F_2 + 3O_2 \longrightarrow 2O_3F_2$$

Properties:

At 363°C, it is a dark red viscous liquid but turns to reddish brown solid at 350°C. on decomposition, it gives oxygen and other oxide of fluorine.

$$2O_3F_2 \longrightarrow 2O_2F_2 + O_2$$

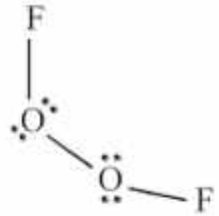
O_3F_2 reacts with F_2 in the presence of electric discharge to produce O_2F_2.

$$2O_3F_2 + F_2 \longrightarrow 3O_2F_2$$

Structure of OF_2 and O_2F_2 are shown below.



(OF_2)



(O_2F_2)

OXIDES OF CHLORINE

The oxides of chlorine are generally unstable. It is not possible to synthesize them by direct combination of the elements Cl_2 and O_2. They have extensive industrial use as commercial bleaching agents for wood, paper-pulp and for water treatment.

(1) Chlorine Dioxide ClO_2:

Preparation:

(a) It is prepared by reducing $NaClO_3$ with NaCl or SO_2 or CH_3OH in strongly acidic solution.

$$2ClO_3^- + 2Cl^- + 4H^+ \longrightarrow 2ClO_2 + Cl_2 + 2H_2O$$

(b) ClO_2 can also be prepared by the action of concentrated H_2SO_4 on $KClO_3$. This reaction is violent. To control the reaction, oxalic acid should be added.

$$2KClO_3 + H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O + 2CO_2 + 2ClO_2$$

Properties:

(1) It is pale yellow gas. ClO_2 explodes into Cl_2 and O_2 on warming.

(2) It is soluble in water and is stable in dark.

(3) It decomposes slowly in H_2O to HCl and $HClO_3$.

(4) It is a paramagnetic substance.

(5) It is used as an antiseptic, for purification of water and to bleach cellulose material.

(2) Chlorine Heptaoxide (Cl_2O_7):

Cl_2O_7 is an anhydride of perchloric acid ($HClO_4$). It can be obtained at $-10°C$ by dehydration of $HClO_4$ with P_2O_5.

$$2HClO_4 + P_2O_5 \xrightarrow{-10°C} Cl_2O_7 + 2HPO_3$$

(3) It is explosive in nature.

(4) It dissolves in H_2O.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

OXIDES OF BROMINE

Oxides of bromine are dark volatile liquids with low thermal stability.

(1) Bromine Monoxide Br_2O:

It can be prepared by the reaction of bormine vapours with mercuric oxide.

$$HgO + 2Br_2 \xrightarrow{50°C} HgBr_2 + Br_2O$$

Br_2O can also be prepared by treating the suspension of mercuric oxide in CCl_4 with bromine. It is stable in dark in CCl_4 at $-20°C$. It has oxidizing properties.

OXIDES OF IODINE

Out of all the oxides of iodine, only iodine, pentoxide I_2O_5 is important. The other compounds, I_2O_4 and I_4O_9 are salt like and are considered as iodine-iodates.

(1) Iodine Pentoxide (I_2O_5):

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

$$2HIO_3 \xrightarrow{240°C} I_2O_5 + H_2O$$

It is a white crystalline solid, stable up to 300°C. It has a polymeric structure. It is insoluble in organic solvents. It forms iodic acid with water.

$$I_2O_5 + H_2O \longrightarrow 2HIO_3$$

It reacts with H_2S, HCl and CO and acts as an oxidizing agent.

It is used for the quantitative analysis of CO.

$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

Reaction of chlorine with cold and hot NaOH (Disproportionation reaction):

"A reaction in which a species (molecule, atom or ion) is simultaneously oxidized and reduced, is called a "disproportionation reaction".

In cold (15°C) state chlorine will react with $NaOH_{(aq)}$ to form hypochlorite and chloride.

$$2NaOH_{(aq)} + Cl_{2(g)} \longrightarrow NaCl + NaClO + H_2O_{(aq)} \text{ (a)}$$

The reaction is a disproportionation reaction, because the zero oxidation state of chlorine atom in Cl_2 is converted to -1 in chloride and $+1$ in hypochlorite.

Sodium hypochlorite which a produced in cold state in the above reaction decomposes forming sodium chloride and sodium chlorate at 70°C.

$$3NaClO_{4(aq)} \longrightarrow 2NaCl_{(aq)} + NaClO_{3(aq)} \text{ (b)}$$

The reaction (b) involves the disproportioantion of hypochlorite ion. To balance overall reaction in hot state, multiply equation (a) with 3 and then add (a) and (b).

$$6NaOH + 3Cl_2 \longrightarrow 3NaCl + 3NaClO + 3H_2O$$
$$3NaClO \longrightarrow 2NaCl + NaClO_3$$

$$6NaOH_{(aq)} + 3Cl_{2(g)} \longrightarrow 5NaCl_{(aq)} + NaClO_{3(aq)} + 3H_2O$$

The above two reactions (a) and (b) show that chlorine atoms are both reduced and oxidized.

OXYACIDS OF HALOGENS

Halogens form four kinds of oxyacids and their anions. No stable oxyacid of flourine (HOF) is known. Other halogens from oxyacids which cannot be isolated in pure form and are stable only in aqueous solutions in the form of their salts.

Names of Oxyacids and their Salts:

(1) Oxyacids in which central atom halogen has oxidation state +1 ends at **hypo-ous** acid and salt end as **hypo-ite**. e.g., HClO. (Hypochorus acid) NaClO sodium hypochlorite.

(2) Oxyacid in which central atom halogen has oxidation state +3 ends at **–ous** acid and salt ends at **–ite**. e.g., $HClO_2$ (chlorous acid) $NaClO_2$ (sodium chlorite).

(3) Oxyacid in which central atom halogen has oxidation state +5 ends at **–ic** acid and salt ends at **–ate**. e.g., $HClO_3$ (chloric acid) $NaClO_3$ (sodium chlorate).

(4) Oxyacids in which central atom halogen has oxidation state +7 ends at **per–ic** acid and salt ends at **per–ate**. e.g., $HClO_4$ (per chloric acid), $NaClO_4$ sodium per chlorate.

Table – Oxyacids of Cl, Br and I and anions of their salts

Oxidation state	Formula	Acids name	Anion	Name
+1	HClO	Hypochlorons acid	ClO^-	Hypochlorite
+3	$HClO_2$	Chlorous acid	ClO_2^-	Chlorite
+5	$HClO_3$	Chloric acid	ClO_3^-	Chlorate
+7	$HClO_4$	Perchloric acid	ClO_4^-	Perchlorate
+1	HBrO	Hypobromous acid	BrO^-	Hypobromite
+3	$HBrO_2$	Bromous acid	BrO_2^-	Bromite
+5	$HBrO_3$	Bromic acid	BrO_3^-	Bromate
+7	$HBrO_4$	Perbromic acid	BrO_4^-	Perbromate
+1	HIO	Hypolodous acid	IO^-	Hypoidoite
+3	HIO_2	Iodous acid	IO_2^-	Iodite
+5	HIO_3	Iodic acid	IO_3^-	Iodate
+7	HiO_4	Periodic acid	IO_4^-	Periodate

$HOCl$	$H-O-Cl$
$HClO_2$	$H-O-Cl=O$
$HClO_3$	$H-O-Cl(=O)=O$
$HClO_4$	$H-O-Cl(=O)(=O)=O$

Structure of oxyacids of chlorine is given below:

$HOCl$	hypochlorous acid	$H-\ddot{O}-\ddot{Cl}:$
OCl^{-1}	hypochlorite ion	
$HClO_2$ (or $HOClO$)	chlorous acid	$H-\ddot{O}-\ddot{Cl}=\ddot{O}:$
ClO_2^{-1}	chlorite ion	
$HClO_3$ (or $HOClO_3$)	chloric acid	$H-\ddot{O}-Cl(:O:)=\ddot{O}:$
ClO_3^{-1}	chlorate ion	
$HClO_4$ (or $HOClO_3$)	perchloric acid	$H-\ddot{O}-Cl(:O:)(:O:)=\ddot{O}:$
ClO_4^{-1}	perchlorate ion	

PROPERTIES OF OXYACIDS

(i) Acidic Strength of Oxyacids:

The acid strength increases with increase in the number of oxygen atom. As the oxidation state of the halogen increases, the bonding electrons are shifted away from the H-atom and the tendency for the molecule to lose a proton increases. This accounts for the change of strength of oxyacids. The oxyacids of halogens show their strength in the order given below:

$$HXO_4 > HXO_3 > HXO_2 > HXO$$

(ii) Thermal Stability:

Thermal stability of oxyacid molecules increase by increasing the number of oxygen atoms. Perchloric acid $HClO_4$ is more stable than $HClO$ hypochlorous acid.

(iii) Oxidizing Power of Oxyacids:

Oxidizing strength of oxyacid decreases by increasing oxidation number. HClO and $HClO_2$ are good oxidizing agent. Oxidizing strength is given in the following order.

$$HClO > HClO_2 > HClO_3 > HClO_4$$

(iv) Polarity:

In oxyacids the halogens serves as a central atom to which one or more oxygen atoms are covalently bonded. These bonds are polar in characters due to the electronegativity difference between halogen and oxygen.

(v) Relative Strength of Oxyacids of Different Halogens:

The oxyacids of chlorine are stronger than the corresponding oxyacids of bromine which are, in turn, stronger than the corresponding oxyacids of iodine. It is due to decrease in the electronegativity and increase in the size of the halogen. We will discuss perchloric acid ($HClO_4$) only at the stage.

PERCHLORIC ACID $HClO_4$

Preparation:

Perchloric acid ($HClO_4$) is commonly obtained in aqueous solution. Pure anhydrous compound can be prepared by distilling a mixture of perchlorate ($KClO_4$) and conc. H_2SO_4 under reduced pressure.

$$KClO_{4(s)} + H_2SO_{4(aq)} \xrightarrow{\Delta} KHSO_{4(s)} + HClO_{4(g)}$$

Properties:

(1) Perchloric acid is a colourless, hygroscopic liquid.

(2) At normal pressure it freezes at $-112°C$ and boils with decomposition at $90°C$.

(3) In the cold and dilute state perchloric acid is a very weak oxidizing agent but when hot and concentrated its oxidizing power is enhanced. Dissolving power of perchloric acid is enhanced due to its oxidizing strength. Perchloric acid is strongest of all the acid in an aqueous medium.

$$H_2O + HClO_4 \rightleftharpoons H_3O^+ + ClO_4^-$$

(4) Pure perchloric acid decomposes explosively when heated. That is why it is stored and used as 67% solution in water. Perchloric acid reacts with organic substances violently.

(5) Due to its oxidizing effect, acidic strength and solubility of its salts, it is considered as a valuable analytical reagent.

BLEACHING POWDER Ca(OCl)Cl

The chemical name of bleaching powder is calcium hypchlorite chloride. Formula of bleaching powder was given by **oddling**. It is mixed salt.

Preparation:

Bleaching powder can be manufactured by the action of chlorine on dry slaked lime using any one of the following methods:

(a) Hasenclever's method (old method)

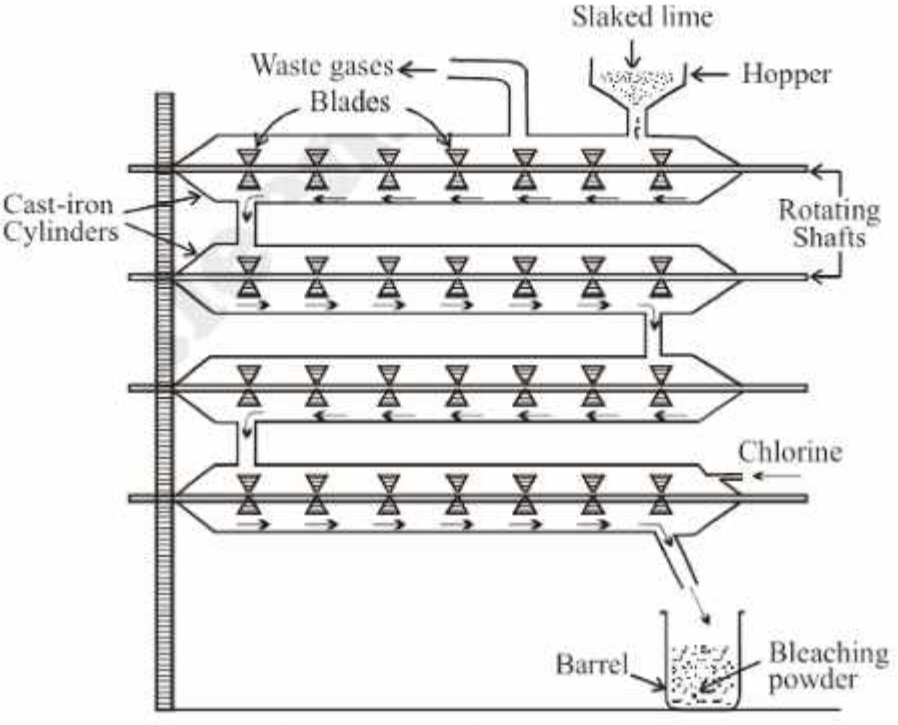
(b) Beckmann's method (modern method)

The reaction in both the cases will be:

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \xrightarrow{40^\circ C} \underset{\text{Bleaching powder}}{Ca(OCl)Cl} + H_2O$$

(1) Hasenclever's Method:

The apparatus used in this method consists of 4 to 8 iron cylinders placed one above the other horizontally. They are interconnected and provided with stirrers. The slaked lime is added in through a hopper in the upper cylinder and is transported from one cylinder to the other with rotating stirrers. Chlorine introduced into the lowest cylinder rises up and reacts with slaked lime to form bleaching powder which is collected through the outlet in the lowest cylinder.



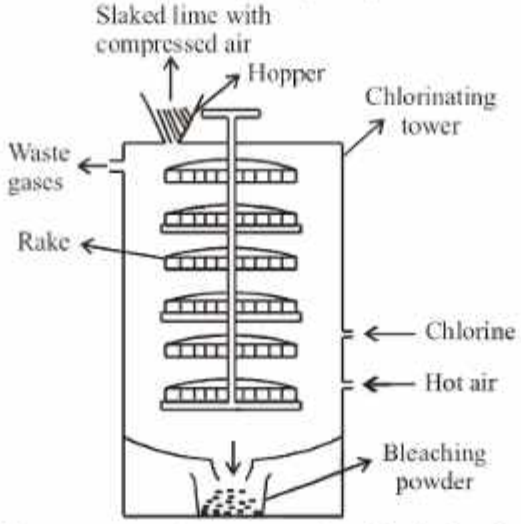
Hasenclever's method

(2) Beckmann's Method:

In this method a cast iron tower with eight horizontal shelves is used. In each shelf there is a rotating rake.

Powdered slaked lime is introduced through hopper at the top with compressed air. A mixture of hot air and chlorine are introduced from the base of the tower. The slaked lime is pushed down by the rotating rakes while chlorine rises up. Reaction between slaked lime and chlorine produces bleaching powder which is collected at the bottom of the tower.

$$Ca(OH)_2 + Cl_2 \xrightarrow{40^\circ C} Ca(OCl)Cl + H_2O$$



The apparatus works on **counter-current principle**. In counter-current principle reacting substances move in opposite directions and intermix together.

Thus maximum reaction of slaked lime and chlorine is brought about with very little loss of chlorine. Bleaching powder should always be packed in air tight containers to avoid the loss of chlorine.

Bleaching powder is a **yellowish white powder** with strong smell of chlorine.

CHEMICAL PROPERTIES OF BLEACHING POWDER

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

$$Ca(OCl)Cl \xrightleftharpoons{H_2O} Ca^{+2} + Cl^- + ClO^-$$

(2) With dilute acid it gives hypochlorous acid.

$$2Ca(OCl)Cl + \text{dil } H_2SO_4 \longrightarrow CaSO_4 + CaCl_2 + 2HClO$$

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

$$Ca(OCl)Cl + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2\uparrow$$

(b) Uses of Chlorine and its Compounds:

(1) Chlorine is used in the manufacture of **bleaching powder**.

(2) It is used as a disinfectant in swimming pools and water treatment plants.

(3) A number of antiseptics, insecticides, weed killers and herbicides are manufactured from chlorine.

(4) It is also used in the manufacture of hydrochloric acid, which is the cheapest industrial acid.

(5) Chlorine is also used in the manufacture of **polyvinyl chloride** (PVC) plastics.

(6) **Chloroform** and carbon tetrachloride are prepared from chlorine which are used as solvents.

(7) A salt of chlorine, sodium chloride is used in food and important ingredient of our diet.

(c) Uses of bromine and its Compounds:

(1) Ethylene dibromide ($C_2H_4Br_2$) is added to leaded gasoline to save the engine from lead oxide and lead sulphate deposits.

(2) Bromine is also used as **fungicide**.

(3) Silver bromide AgBr is used in **photography**. It is light sensitive compound.

(d) Uses of Iodine and its Compounds:

(1) The major applications of iodine are in pharmaceutical industry. It is used as disinfectant and germicide. Tincture of iodine and **iodex** are popular preparations of iodine. (I_2 in C_2H_5OH and H_2O containing KI is called tincture of iodine).

(2) Diet with insufficient iodide ion leads to an enlargement of the **thyroid** (Goiter). To ensure the presence of iodide ion the diet, sodium or potassium iodide is added to the common salt which is known as iodized salt.

(3) Deficiency of iodine in the body is cause of dwarfism.

NOBLE GASES

Introduction:

Noble gases are present in group VIIIA or the zero group of periodic table. Noble gases consist of helium, neon, argon, krypton, xenon and radon. All the elements of zero group are colourless and odourless gases. They exist in mono-atomic form. At low temperature and high pressure, they can be liquefied or solidified. These gases are also called rare gases. The noble gases are present in atmosphere and their percentage in atmosphere is less than 1%.

The amount of chlorine thus set free 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 percent. The bleaching action of bleaching powder is due to its oxidative character.

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

$$Ca(OCl)Cl + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

(5) It oxidizes ammonia to nitrogen.

$$3Cal(OCl)Cl + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$$

(6) It reacts with CO_2 to form $CaCO_3$ and Cl_2.

$$Ca(OCl)Cl + CO_2 \longrightarrow CaCO_3 + Cl_2$$

Uses:

(1) Bleaching powder is used for the preparation of Cl_2 and O_2.

(2) It is also used for the preparation of chloroform $CHCl_3$.

(3) It is used as disinfectant and for the sterlization of water.

(4) It is used for making unshrinkable wool.

(5) It is used to bleach cotton, linen and paper pulp. Delicate fabrics like wool, silk are not bleached with bleaching powder because they can be damaged by chlorine produced from bleaching powder.

(6) For the removal of poisonous gases from the atmosphere.

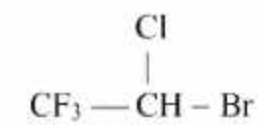
COMMERCIAL USES OF HALOGENS AND THEIR COMPOUNDS

(a) Uses of Fluorine and its Compounds:

(1) Fluorine is used for the preparation of Feons. **Freon** is the commercial name of low molecular mass fluorochlorocarbons, CCl_2F_2, $CClF_3$. These are being used as refrigerants and aerosol propellants.

(2) Fluorine is used to prepare **Teflon** $(-CF_2 - CF_2)_n$. It is a polymerized tetrafluoro ethylene compound. It is a valuable plastic which resists the action of oxidants, acids and alkalies. Corrosion-proof parts of machinery are made of it. It is used for coating the electrical wiring. Teflon is also used as a non-stick coating for cooking pans.

(3) **Halothane** is used as an anesthetic.



Halothane

(4) Fluorides in toothpastes build a protective coating on teeth.

(5) HF is used for etching glass.

(6) Sodium fluoro-acetate is rat poison.

Table – Electronic configuration of noble gases

Name	Symbol	Atomic number	Electronic configuration
Helium	He	2	$1s^2$
Neon	Ne	10	$1s^2, 2s^2, 2p^6$
Argon	Ar	18	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
Krypton	Kr	36	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$
Xenon	Xe	54	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6$
Radon	Rn	86	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6$

OCCURRENCE OR EXTRACTION OF NOBLE GASES

(1) The noble gases are isolated from air, either by fractional distillation or by some chemical method. The principal commercial source of Ne, Ar, Kr and Xe is air.

(2) **Helium** is present on earth as a result of radioactive decay. After hydrogen, it is the second most abundant element in the universe. α-particles are doubly ionized helium atoms He^{2+}. It is simple and economical to isolate the helium gas from certain natural gases by liquefaction method. In 1868, He was detected from the chromosphere of sun. The name helium is from the Greek word "Heilos" which means sun.

(3) **Neon** is $1/65000^{th}$ part of the atmosphere and it is also isolated during liquefaction of air in a discharge tube, neon glows reddish (of all the noble gases, the discharge of neon is the most intense at ordinary voltage and current). Liquid neon has over 40 times more refrigeration capacity than liquid helium.

(4) **Argon** was discovered by "Ramsay". It is a colourless and odourless gas. It is very inert and not known to form any true chemical compound. It is obtained as a by product during the liquefaction of air.

(5) Traces of **krypton** are present in air. It is a colourless, odourless and fairly expensive gas. It is characterized by its brilliant green and orange special lines. Its compound krypton difluoride (KrF_2) can be prepared by various methods.

(6) **Xenon** is present in the atmosphere to a very small extent (0.08 ppm). It is obtained as a by product during the fractional liquefaction of air. Xenon is available commercially in cylinders at high pressure. It reacts with fluorine but not with water. However it is slightly soluble in water to the extent of about 110 ml/litre at 20°C.

(7) **Radon** is the α-decay product of the radium. Radon is present to a very small extent in the atmosphere and it could be obtained as a by product from the liquefaction of air. However the small quantities of this gas which are usually needed can be collected from the radioactive decay of radium isotopes.

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

PHYSICAL PROPERTIES OF NOBLE GASES

(1) The noble gases have valence shells which are closed octets (except He). Due to closed shells their ionization energy values are very high.

(2) They have low boiling points. The boiling point of helium is the lowest of any known substance. Their boiling points increase with increasing atomic number down the group.

(3) The very low values of melting and boiling points and low heats of vaporization show that noble gases have weak forces of attraction between their atoms. As there are no ordinary electron pair interaction, these weak forces must be of the van der Waal's type.

(4) The solubility of the noble gases in water increases with increasing atomic number. This is because the bigger atoms are more readily polarized by water molecules.

Table – Some physical properties of noble gases

Property	He	Ne	Ar	Kr	Xe	Rn
At. mass (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}) kJ mol^{-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 kJ mol^{-1}	0.08	1.77	6.5	9.7	13.7	18.0

COMPOUNDS OF XENON

Xenon reacts directly with fluorine only. The known oxidation state of Xe in its compounds range from +2 to +8. The compounds are stable and can be obtained in large quantities. Some important compounds of Xe are given in the table. The first compound of Xe (Xenon Hexafluroplatinate) was prepared by N-Bartlet in 1962 in Chicago University.

Table – Compounds of Xenon

Oxidation state of xenon	Compound	Physical form	Milting point (°C)
+2	XeF_2	Colourless crystals	140
+4	XeF_4	Colourless crystals	114
	$XeOF_2$	Colourless crystals	90
+6	XeF_6	Colourless crystals	48
	$XeOF_4$	Colourless liquid	–28
	XeO_3	Colourless crystals	25 (Explodes)
+8	XeO_4	Colourless gas	–39.9 (Explodes on warming)

(a) FLOURIDES OF XENON

Three known fluorides of Xenon are XeF_2, XeF_4 and XeF_6.

XeF_2 can be prepared by direct interaction of the elements. The compound formed should be removed immediately from the reaction zone, otherwise further reaction with F_2 will give XeF_4. The reaction is completed in about **8 hours**. XeF_2 is a crystalline solid. It is stored in nickel vessels. XeF_2 is a mild fluorinating agent.

$$Xe + F_2 \longrightarrow XeF_2$$

XeF_4 can be prepared by heating a mixture of **Xe and F_2 in 1 : 5** ratio in a nickel container under **6 atmospheric** pressure for a **few hours**. It can be stored in nickel vessels. Its properties are similar to that of **XeF_2** but it is a strong fluorinating agent.

$$XeF_2 + F_2 \longrightarrow XeF_4$$

XeF_6 require more severe conditions. **Xe and F_2 are taken in 3 : 20 ratio** in a stainless steel vessel and heated to **300°C at 50 atmospheric** pressure. More than 95% conversion to XeF_6 takes place. XeF_6 is a crystalline solid. It is colourless in the solid state but yellow in liquid and gaseous forms.

$$XeF_4 + F_2 \longrightarrow XeF_6$$

CHEMICAL REACTIONS OF FLUORIDES OF XENON

(1) Fluorides of xenon can be reduced with hydrogen at 400°C giving xenon and hydrofluoric acid.

$$XeF_2 + H_2 \longrightarrow Xe + 2HF$$

$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$$

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

(2) Xenon tetra-fluoride is a good fluorinating agent and can be used to prepare metal fluorides as follows.

$$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$$

(3) Reaction occurs with explosion when XeF_4 is brought in contact with liquid ammonia.

$$3XeF_4 + 4NH_3 \longrightarrow 3Xe + 12HF + 2N_2$$

(4) Hydrolysis of XeF_6 with small amount of water gives $XeOF_4$.

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

XENON OXYFLUORIDES

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

$$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$$

$XeOF_4$ is colourless volatile liquid. It can be kept in nickel vessel. It reacts with water to give XeO_3.

Xenon oxydifluoride $XeOF_2$, is obtained when xeon reacts with oxygen difluoride in an electric discharge.

$$Xe + F_2O \longrightarrow XeOF_2$$

OXIDES OF XENON

There are two oxides are xenon:

(1) Xenon trioxide

(2) Xenon tetraoxide

(1) Xenon Trioxide XeO_3:

Xenon trioxide can be obtained when XeF_6 is hydrolysed slowly.

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

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

(2) Xenon Tetraoxide XeO_4:

It is obtained by the addition of barium or sodium perxenate to conc. H_2SO_4.

$$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$$

$$Na_4XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2Na_2SO_4 + 2H_2O$$

USES OF NOBLE GASES

(1) Helium is used in weather balloons. It is twice in density than hydrogen and safe to use.

(2) A mixture of 80% helium and 20% oxygen is used for breathing by the sea divers. Helium is less soluble in blood than nitrogen.

(3) Helium is used as a cooling medium for nuclear reactors.

(4) He is used for the treatment of asthama by mixing with oxygen.

(5) Neon is largely used in making neon advertising signs, in high voltage indicators and TV tubes.

(6) Neon and helium arc is used in making glass lasers.

(7) Argon is used in electric light bulbs, in fluorescent tubes, in radio tubes, and in Geiger counters (used to detect radioactivity).

(8) Argon is also used for arc welding and cutting.

(9) Krypton is used to fill fluorescent tubes and in flash lamps for high speed photography.

(10) Kr_{85} is used for the measurement of thickness of sheets of metals and plants.

(11) Xenon is used in bactericidal lamps.

(12) Liquid Xe is used in the bubble chamber for the detection of gamma photons and neutral mesons.

(13) Radon being radioactive is used in radiotherapy for cancer, and for earth quake prediction.

(14) Radon is used for the photography of interior of opaque objects.

EXERCISE

Q.1 Fill in the blanks:

(i) The halogen with the highest electronegativity is ————.

(ii) HI is ———— agent.

(iii) The only halogen acid which is not a strong acid is ————.

(iv) Tincture of ———— is a common antiseptic.

(v) The halogen with the lowest melting and boiling points is ————.

(vi) Bleaching powder is prepared from ———— and ————.

(vii) ———— is the halogen which causes burns on the skin which heal slowly.

(viii) ———— is used for making unshrinkable wool.

(ix) A mixture of ———— and ———— is used for breathing by the sea divers.

(x) Noble gas used to fill fluorescent tubes is ————.

ANSWERS

(i)	fluorine	**(ii)**	reducing	**(iii)**	HF
(iv)	iodine	**(v)**	fluorine	**(vi)**	Cl_2, slaked lime
(vii)	bromine	**(viii)**	bleaching powder	**(ix)**	80% He, 20% O_2
(x)	argon and krypton				

Q.2 Indicate True or False:

(i) HF is used for etching glass.

(ii) HI is weaker reducing agent as compared to HF.

(iii) Bleaching powder is completely soluble in water.

(iv) The formula of perchloric acid is $HClO_3$.

(v) On warming, aqueous KOCl disproportionates as follows.

$$3KOCl \longrightarrow 2KCl + KClO_3$$

(vi) α-particles emitted by radioactive elements are ions of radon.

(vii) Radon is the only one of the noble gases that is radioactive.

(viii) The molecules of the noble gases are all monoatomic.

(ix) Argon is used to fill electric bulbs.

(x) The noble gas which is present in the largest amount in atmosphere is krypton.

ANSWERS

(i)	True	**(ii)**	False	**(iii)**	False	**(iv)**	False	**(v)**	True
(vi)	False	**(vii)**	True	**(viii)**	True	**(ix)**	True	**(x)**	False

Q.3 Multiple choice questions. Encircle the correct answer:

(i) Which of the following hydrogen halide is the weakest acid in solution:

(a) HF **(b)** HBr

(c) HI **(d)** HCl

(ii) Chlorine heptaoxide (Cl_2O_7) reacts with water to form:

(a) Hypochlorous acid **(b)** Chloric acid

(c) Perchloric acid **(d)** Chlorine and oxygen

(iii) Hydrogen bond is the strongest between the molecules of:

(a) HF **(b)** HCl

(c) HBr **(d)** HI

(iv) Which halogen will react spontaneously with Au(s) to produce Au^{3+}:

(a) Br_2 **(b)** F_2

(c) I_2 **(d)** Cl_2

(v) The anhydride of $HClO_4$ is:

(a) ClO_3 **(b)** ClO_2

(c) Cl_2O_5 **(d)** Cl_2O_7

(vi) Bleaching powder may be produced by passing chlorine over:

(a) Calcium carbonate **(b)** Hydrated calcium sulphate

(c) Anhydrous calcium sulphate **(d)** Calcium hydroxide

(e) Magnesium hydroxide

(vii) Which is the strongest acid:

(a) HClO **(b)** $HClO_2$

(c) $HClO_3$ **(d)** $HClO_4$

(viii) Which halogen occurs naturally in a positive oxidation state:

(a) Fluorine **(b)** Chlorine

(c) Bromine **(d)** Iodine

(ix) An element that has a high ionization energy and tends to be chemically inactive would most likely to be:

(a) An alkali metal **(b)** A transition element

(c) A noble gas **(d)** A halogen

(x) Which of the following represents the correct electronic configuration of the outermost energy level of an element of zero (VIIIA) group in the ground state:

(a) s^2p^2 **(b)** s^2p^4

(c) s^2p^5 **(d)** s^2p^6

ANSWERS

(i)	(a)	**(ii)**	(c)	**(iii)**	(a)	**(iv)**	(d)	**(v)**	(d)
(vi)	(d)	**(vii)**	(d)	**(viii)**	(d)	**(ix)**	(c)	**(x)**	(d)

Q.4 What is bleaching powder? How it is prepared commercially? Give its uses.

Ans. **Bleaching Powder:** Preparation and uses see in text book.

Q.5 (a) Discuss the oxides of chlorine.

(b) What are disproportionation reactions? Explain your answer with an example.

Ans. Descriptive questions. See text book for details.

Q.6 Discuss the system of nomenclature used for oxyacid of halogens. Support your answer with examples.

Ans. Descriptive question. See text book for details.

Q.7 (a) How the halogen acids are ionized in water?

(b) Why HF is weaker acid than HCl?

Ans.

(a) Halogen acids ionize in water and form halide ions and hydronium ions. e.g.,

$$HF + H_2O \longrightarrow H_3O^+ + F^-$$

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

$$HBr + H_2O \longrightarrow H_3O^+ + Br^-$$

$$HI + H_2O \longrightarrow H_3O^+ + I^-$$

(b) In case of halogen acids:

$$\text{Acidic strength} \propto \text{Ionization}$$

HF due to strong hydrogen bonding has less ionization and HCl ionizes more than HF. HF is weaker acid than HCl.

Q.8 In the following sets, arrange the substances in order of the property indicated. Give reasons:

(a) Increasing acidic character

$HClO$, $HClO_2$, $HClO_3$, $HClO_4$

(b) Increasing oxidizing power

F_2, Cl_2, Br_2, I_2

Ans.

(a) The order of increasing acidic character of given acids is as following:

Reason: In case of oxyacids of halogens the acidic strength increases with the increase in the number of oxygen atoms or oxidation sate. As the oxidation state of the halogen increases, the bonding electrons are shifted away from the H-atom and tendency of the molecule to lose a proton increases which ultimately increase the acidic character.

(b) The order of increasing oxidizing powder of halogens is given as:

$$I_2 < Br_2 < Cl_2 < F_2$$

Reason: Oxidizing power of halogens depends upon:

(i) Energy of dissociation.

(ii) Electron affinity of atoms.

(iii) Hydration energy of ion.

(iv) Heat of vaporization.

If a halogen atom has low dissociation energy, high electron affinity and high hydration energy of its ions, it will have high oxidizing power.

Q.9 What happens when bleaching powder reacts with the following reagents dil. H_2SO_4, excess of conc. H_2SO_4, NH_3, HI and CO_2.

Ans. **With dil. H_2SO_4:**

$$2CaCOCl_2 + \text{dil. } H_2SO_4 \longrightarrow CaSO_4 + CaCl_2 + 2HClO$$

With conc. H_2SO_4:

$$CaOCl_2 + H_2SO_{4(conc.)} \longrightarrow CaSO_4 + H_2O + Cl_2$$

With NH_3:

$$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$$

With CO_2:

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

With HCl:

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

Q.10 Discuss the various commercial uses of halogens and their compounds.

Ans. Descriptive question. See text book for details.

Q.11 What are noble gases? Explain their inertness on the basis of their electronic configuration.

Ans. Descriptive question. See text book for details.

Q.12 Write notes on the followings:

(i) Oxyfluorides of xenon.

(ii) Applications of noble gases.

Ans. Detailed question. See text book.

Q.13 Short questions.

(i) What is "iodized salt"?

(ii) What are Freons and Teflon?

(iii) Arrange the following ions in order of increasing size:

F^-, Cl^-, I^-, Br^-

(iv) Why iodine has metallic luster?

(v) Which halogen sublimes to violet vapours?

(vi) Which halogen is used as an antiseptic?

(vii) Which halogen is used in water treatment to kill bacteria?

(viii) Name the gas, which is used for earthquake prediction.

(ix) Name the gas, which is used in bactericidal lamps.

Ans.

(i) Mixture of NaCl and trace amount of KI is known as "iodized salt.

(ii) **Freon** is commercial name of low molecular mass fluorochloro carbons CCl_2F_2, $CClF_3$. They are used as refrigerants and aerosol propellants teflon $(-CF_2-CF_2-)_n$ is poly tetrafluoro ethylene. It is valuable plastic which resist the action of oxidants, acids, alkalies corrosion proof parts of machinery are made of it. It is used as non-stick coating for cooking pans and for coating the electrical wiring.

(iii) Ionic radii increases downward from top to bottom in a group. The order is:

$$F^- < Cl^- < Br^- < I^-$$

(iv) Metallic luster is due to excitation of electrons. When excited electrons come back they emit radiations. Due to bigger size, electrons of iodine excite at room temperature and it appears as lustrous greyish black solid.

(v) Among halogens iodine sublimes to violet vapours.

(vi) Chlorine.

(vii) **Chlorine** is a disinfectant and used to kill bacteria. It is used as disinfectant in drinking water and also in swimming pools.

(viii) **Radon** is the gas which is used for earth-quake prediction and for photography of opaque objects.

(ix) **Xenon** is used in bactericidal lamp.

DO YOU KNOW?

(1) The name halogens is derived from the Greek word "Halos" which means salt and genes means "born".

(2) Astatine was discovered in 1940. It is radioactive and its half-life is 8.3 hours.

(3) Fluorine and chlorine are gases, Br_2 is a liquid and I_2 is a solid.

(4) Order of oxidizing power of halogens is:

$$F_2 > Cl_2 > Br_2 > I_2$$

(5) HF is the weakest of all the halogen acids.

(6) ClO_2 is yellow pungent gas. It is paramagnetic in nature.

(7) The formula of bleaching was given by Oddling.

(8) Bleaching powder is used in making unshrinkable wool.

(9) The amount of chlorine which is let free during the reaction of bleaching powder with acid is called "available chlorine".

(10) Poly tetra fluoro ethylene is called "Teflon".

(11) Filament of electric bulb is made of Tungeston (W).

(12) The first compound of Xe (Xe Pt. F_6) was prepared by N-Bartlet in 1962 in the University of Chicago.

(13) Xenon is used in bactericidal lamps.

(14) Silver bromide is light sensitive. It is used in photography.

(15) $AgNO_3$ is called "Lunar caustic".

(16) Bleaching powder is mixed salt.

CHAPTER 5

THE HALOGENS AND THE NOBLE GASES

MULTIPLE CHOICE QUESTIONS

1. Which of the following hydrogen halide is the weakest acid in solution:

(a) HF **(b)** HBr

(c) HI **(d)** HCl

2. Hydrogen bonding is the strongest among the molecules of:

(a) HCl **(b)** HF

(c) HI **(d)** HBr

3. Which of the following halogen is in solid form at room temperature:

(a) I_2 **(b)** F_2

(c) Br_2 **(d)** Cl_2

4. Which of the halogens is most easily reduced:

(a) I_2 **(b)** Br_2

(c) F_2 **(d)** Cl_2

5. What is the reason for lowest bond dissociation energy of F_2 among the halogens:

(a) Low I.E **(b)** Absence of d-orbitals

(c) Low lattice energy of salts **(d)** Repulsion among non-bonding electrons

6. Which silver salt is sparingly soluble in H_2O:

(a) AgF **(b)** AgBr

(c) AgCl **(d)** AgI

7. All the halogens are coloured. The intensity of the colour depends on:

(a) Valence electron **(b)** Atomic number

(c) Atomic mass **(d)** None of these

8. Which of the following is the strongest acid:

(a) HClO **(b)** $HClO_2$

(c) $HClO_4$ **(d)** $HClO_3$

9. Oxidation state of Ca in Ca(OCl)Cl (bleaching powder) is:

(a) +3 **(b)** +4

(c) +2 **(d)** +1

10. Which of the following has greater volatility:

(a) CH_3F **(b)** CH_3Cl

(c) CH_3Br **(d)** CH_3I

11. Among fluorides of xenon which is a mild flourinating agent:

(a) XeF_2 **(b)** XeF_4

(c) XeF_6 **(d)** All

12. Which one is used for etching of glass:

(a) HBr **(b)** HF

(c) HCl **(d)** HI

13. Astatine (radioactive element) has a half-life:

(a) 4 hrs **(b)** 10 hrs

(c) 8.3 hrs **(d)** 4.3 hrs

14. Which halogen occurs naturally in positive oxidation state:

(a) Flamine **(b)** Chlorine

(c) Bromine **(d)** Iodine

15. The anhydride of $HClO_4$ is:

(a) ClO **(b)** ClO_2

(c) ClO_3 **(d)** Cl_2O_7

16. Bleaching powder is not used for bleaching:

(a) Cotton **(b)** Costly fabrics

(c) Limen **(d)** Paper pulp

17. Consider the following reaction

$$6NaOH + 3Cl_2 \xrightarrow[\text{State}]{\text{Hot}} 5NaCl + NaClO_3 + 3H_2O$$

the type of above reaction is:

(a) Addition reaction **(b)** Disproportionation reaction

(c) Displacement reaction **(d)** Decomposition reaction

18. Cl_2O_7 react with H_2O to form:

(a) Hypochlorous acid **(b)** Chloric acid

(c) Perchloric acid **(d)** Cl_2 and O_2

19. Halogen used in toothpaste, it builds protecting covering:

(a) F **(b)** Cl

(c) Br **(d)** I

20. Which of the following react with H_2 in dark:

(a) F_2 **(b)** I_2

(c) Cl_2 **(d)** Br_2

21. Which of the following is used in radiotherapy:

(a) Rn **(b)** Xe

(c) Kr **(d)** Ar

22. Who reported the first noble gas:

(a) Cavendish **(b)** Frankland

(c) William Ramsay **(d)** Rayleigh

23. Which noble gas does not obey octet rule:

(a) Ne **(b)** He

(c) Ar **(d)** Kr

24. Which is the most polarised noble gas:

(a) Kr **(b)** Xe

(c) He **(d)** Rn

25. XeF_2 molecule is:

(a) Tetrahedral **(b)** Linear

(c) Pyramidal **(d)** Trigonal planar

answers

1.	(a)	**2.**	(b)	**3.**	(a)	**4.**	(c)	**5.**	(d)
6.	(c)	**7.**	(b)	**8.**	(c)	**9.**	(c)	**10.**	(a)
11.	(a)	**12.**	(b)	**13.**	(c)	**14.**	(d)	**15.**	(d)
16.	(b)	**17.**	(b)	**18.**	(c)	**19.**	(a)	**20.**	(a)
21.	(a)	**22.**	(c)	**23.**	(b)	**24.**	(b)	**25.**	(b)

SOLVED EXERCISE

Q.1 Fill in the blanks:

(i) The halogen with the highest electronegativity is ————.

(ii) HI is ———— agent.

(iii) The only halogen acid which is not a strong acid is ————.

(iv) Tincture of ———— is a common antiseptic.

(v) The halogen with the lowest melting and boiling points is ————.

(vi) Bleaching powder is prepared from ———— and ————.

(vii) ———— is the halogen which causes burns on the skin which heal slowly.

(viii) ———— is used for making unshrinkable wool.

(ix) A mixture of ———— and ———— is used for breathing by the sea divers.

(x) Noble gas used to fill fluorescent tubes is ————.

answers

(i)	fluorine	**(ii)**	reducing	**(iii)**	HF
(iv)	iodine	**(v)**	fluorine	**(vi)**	Cl_2, slaked lime
(vii)	bromine	**(viii)**	bleaching powder	**(ix)**	80% He, 20% O_2
(x)	argon				

Q.2 Indicate True or False:

(i) HF is used for etching glass.

(ii) HI is weaker reducing agent as compared to HF.

(iii) Bleaching powder is completely soluble in water.

(iv) The formula of perchloric acid is $HClO_3$.

(v) On warming, aqueous KOCl disproportionates as follows.

$$3KOCl \longrightarrow 2KCl + KClO_3$$

(vi) α-particles emitted by radioactive elements are ions of radon.

(vii) Radon is the only one of the noble gases that is radioactive.

(viii) The molecules of the noble gases are all monoatomic.

(ix) Argon is used to fill electric bulbs.

(x) The noble gas which is present in the largest amount in atmosphere is krypton.

answers

(i)	True	**(ii)**	False	**(iii)**	False	**(iv)**	False	**(v)**	True
(vi)	False	**(vii)**	True	**(viii)**	True	**(ix)**	True	**(x)**	False

Q.3 Multiple choice questions. Encircle the correct answer:

(i) Which of the following hydrogen halide is the weakest acid in solution:

(a) HF **(b)** HBr

(c) HI **(d)** HCl

(ii) Chlorine heptaoxide (Cl_2O_7) reacts with water to form:

(a) Hypochlorous acid **(b)** Chloric acid

(c) Perchloric acid **(d)** Chlorine and oxygen

(iii) Hydrogen bond is the strongest between the molecules of:

(a) HF **(b)** HCl

(c) HBr **(d)** HI

(iv) Which halogen will react spontaneously with Au(s) to produce Au^{3+}:

(a) Br_2 **(b)** F_2

(c) I_2 **(d)** Cl_2

(v) The anhydride of $HClO_4$ is:

(a) ClO_3 **(b)** ClO_2

(c) Cl_2O_5 **(d)** Cl_2O_7

(vi) Bleaching powder may be produced by passing chlorine over:

(a) Calcium carbonate **(b)** Hydrated calcium sulphate

(c) Anhydrous calcium sulphate **(d)** Calcium hydroxide

(vii) Which is the strongest acid:

(a) HClO **(b)** $HClO_2$

(c) $HClO_3$ **(d)** $HClO_4$

(viii) Which halogen occurs naturally in a positive oxidation state:

(a) Fluorine **(b)** Chlorine

(c) Bromine **(d)** Iodine

(ix) An element that has a high ionization energy and tends to be chemically inactive would most likely to be:

(a) An alkali metal **(b)** A transition element

(c) A noble gas **(d)** A halogen

(x) Which of the following represents the correct electronic configuration of the outermost energy level of an element of zero (VIIIA) group in the ground state:

(a) s^2p^2 **(b)** s^2p^4

(c) s^2p^5 **(d)** s^2p^6

answers

(i)	(a)	**(ii)**	(c)	**(iii)**	(a)	**(iv)**	(d)	**(v)**	(d)
(vi)	(d)	**(vii)**	(d)	**(viii)**	(d)	**(ix)**	(c)	**(x)**	(d)

Q.4 What is bleaching powder? How it is prepared commercially? Give its uses.

Ans. **Bleaching Powder:** Preparation and uses see in text book.

Q.5 (a) Discuss the oxides of chlorine.

(b) What are disproportionation reactions? Explain your answer with an example.

Ans. Descriptive questions. See text book for details.

Q.6 Discuss the system of nomenclature used for oxyacid of halogens. Support your answer with examples.

Ans. Descriptive question. See text book for details.

Q.7 (a) How the halogen acids are ionized in water?

(b) Why HF is weaker acid than HCl?

Ans.

(a) Halogen acids ionize in water and form halide ions and hydronium ions. e.g.,

$$HF + H_2O \longrightarrow H_3O^+ + F^-$$

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

$$HBr + H_2O \longrightarrow H_3O^+ + Br^-$$

$$HI + H_2O \longrightarrow H_3O^+ + I^-$$

(b) In case of halogen acids:

$$\text{Acidic strength} \propto \text{Ionization}$$

HF due to strong hydrogen bonding has less ionization and HCl ionizes more than HF so, HF is weaker acid than HCl.

Q.8 In the following sets, arrange the substances in order of the property indicated. Give reasons:

(a) Increasing acidic character

$HClO$, $HClO_2$, $HClO_3$, $HClO_4$

(b) Increasing oxidizing power

F_2, Cl_2, Br_2, I_2

Ans.

(a) The order of increasing acidic character of given acids is as following:

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

Reason: In case of oxyacids of halogens the acidic strength increases with the increase in the number of oxygen atoms or oxidation sate. As the oxidation state of the halogen increases, the bonding electrons are shifted away from the H-atom and tendency of the molecule to lose a proton increases which ultimately increase the acidic character.

(b) The order of increasing oxidizing powder of halogens is given as:

$$I_2 < Br_2 < Cl_2 < F_2$$

Reason: Oxidizing power of halogens depends upon:

(i) Energy of dissociation.

(ii) Electron affinity of atoms.

(iii) Hydration energy of ion.

(iv) Heat of vaporization.

If a halogen atom has low dissociation energy, high electron affinity and high hydration energy of its ions, it will have high oxidizing power.

Q.9 What happens when bleaching powder reacts with the following reagents dil. H_2SO_4, excess of conc. H_2SO_4, NH_3, HI and CO_2.

Ans. **With dil. H_2HO_4:**

$$2CaCOCl_2 + \text{dil. } H_2SO_4 \longrightarrow CaSO_4 + CaCl_2 + 2HClO$$

With conc. H_2SO_4:

$$CaOCl_2 + H_2SO_{4(conc.)} \longrightarrow CaSO_4 + H_2O + Cl_2$$

With NH_3:

$$3CaOCl_2 + NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$$

With CO_2:

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

With HCl:

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

Q.10 Discuss the various commercial uses of halogens and their compounds.

Ans. Descriptive question. See text book for details.

Q.11 What are noble gases? Explain their inertness on the basis of their electronic configuration.

Ans. Descriptive question. See text book for details.

Q.12 Write notes on the followings:

(i) Oxyfluorides of xenon.

(ii) Applications of noble gases.

Ans. Detailed question. See text book.

Q.13 Short questions.

(i) What is "iodized salt"?

(ii) What are Freons and Teflon?

(iii) Arrange the following ions in order of increasing size:

F^-, Cl^-, I^-, Br^-

(iv) Why iodine has metallic luster?

(v) Which halogen sublimes to violet vapours?

(vi) Which halogen is used as an antiseptic?

(vii) Which halogen is used in water treatment to kill bacteria?

(viii) Name the gas, which is used for earthquake prediction.

(ix) Name the gas, which is used in bactericidal lamps.

Ans.

(i) Mixture of NaCl and trace amount of KI is known as "iodized salt.

(ii) See text book.

(iii) Ionic radii increases downward from top to bottom in a group. So, the order is:

$$F^- < Cl^- < Br^- < I^-$$

(iv) Metallic luster is due to excitation of electrons. When excited electrons come back they emit radiations. Due to bigger size, electrons of iodine excite at room temperature and it appears as lustrous greyish black solid.

(v) Among halogens iodine sublimes to violet vapours.

(vi) Chlorine.

(vii) **Chlorine** is a disinfectant and used to kill bacteria. It is used as disinfectant in drinking water and also in swimming pools.

(viii) **Radon** is the gas which is used for earth-quake prediction.

(ix) **Xenon** is used in bactericidal lamp.

DO YOU KNOW?

1. The name halogens is derived from the Greek word "Halos" which means salt and genes means "born".
2. Astatine was discovered in 1940. It is radioactive and its half-life is 8.3 hours.
3. Fluorine and chlorine are gases, Br_2 is a liquid and I_2 is a solid.
4. Order of oxidizing power of halogens is:

   $$F_2 > Cl_2 > Br_2 > I_2$$

5. HF is the weakest of all the halogen acids.
6. ClO_2 is yellow pungent gas. It is paramagnetic in nature.
7. The formula of bleaching powder was given by Oddling.
8. Bleaching powder is used in making unshrinkable wool.
9. The amount of chlorine which is set free during the reaction of bleaching powder with acid is called "available chlorine".
10. Poly tetra fluoro ethylene is called "Teflon".
11. Filament of electric bulb is made of Tungeston (W).
12. The first compound of Xe (Xe Pt. F_6) was prepared by N-Bartlet in August 1962 in the University of Chicago.
13. Xenon is used in bactericidal lamps.
14. Silver bromide is light sensitive. It is used in photography.
15. $AgNO_3$ is called "Lunar caustic".

SHORT QUESTIONS

Q.1 What is iodized salt?

Ans. Some amount of iodide ions are added to NaCl. Usually NaI or KI is added for this purpose. Deficiency of iodine in the body causes goiter which is enlargement of thyroid gland.

Q.2 Which halogen is used as antiseptic and water treatment to kill bacteria?

Ans. Iodine is used as antiseptic in the form of iodine tincture and iodex. Chlorine is disinfectant and used to kill the pathogenic bacteria and used for water chlorination and sterilization.

Q.3 Why HF is weak acid while HI is strong acid?

Ans. Strength of an acid depends upon the ionization constant (Ka) of the acid. Due to greater difference in electronegativity. HF has less ionization than HI. HI is the strongest acid among halogen acid. The order of acid strength is

$$HI > HBr > HCl > HF$$

% ionization of HF = 10% and that of HI = 92%.

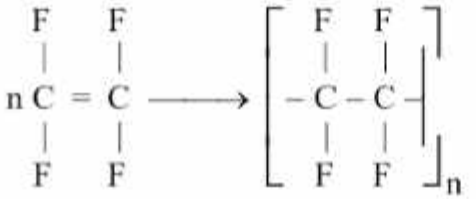
Q.4 F_2 is gas while I_2 is solid at room temperature, why?

Ans. In the groups of periodic table, atomic radii increases from top to bottom. As the size of atom increases, the polarizability also increases. Due to greater distortion of electrons and polarizability, intermolecular forces increases and melting point also increases.

Q.5 What is Freon and Teflon?

Ans. Fluorochlorocarbons are called freons. For example CF_2Cl_2 are used as refrigerant and aerosol propellants. Their use is decreasing now-a-days because they cause depletion in ozone layer.

Teflon is a polymer of tetrafluoroethene. Teflon is used as non-stick coating in pans. It is also used to insulate the electric wires.



Q.6 What is disproparationation reaction? Explain.

Ans. The reaction in which same substance is oxidised as well as reduced is called disproportionation reaction. When cold Cl_2 reacts with conc. NaOH oxidation number of chlorine changes from zero to −1 and +5.

$$Cl_2 + 2NaOH \xrightarrow{dil.} NaCl + NaClO + H_2O$$

$$3Cl_2 + 6NaOH \xrightarrow{Conc.} 5NaCl + NaClO_3 + 3H_2O$$

Q.7 How the activity of bleaching powder is measured?

Ans. The activity of bleaching powder is measured by the available chlorine. The average % of available chlorine in bleaching powder is 35–40%.

Q.8 What are the uses of noble gases?

Ans. (i) He is used in weather ballons.

(ii) He is used as a cooling medium for nuclear reactors.

(iii) Neon is used in making neon advertising signs, in high voltages indicators and TV tubes.

(iv) Neon and helium are used in making glass lasers.

(v) Argon is used in electric light bulbs, in fluorescent tubes, in radio tubes.

(vi) Argon is used for are welding and cutting.

(vii) Krypton is used to fill fluorescent tubes.

(viii) Xenon is used in bacterial lamps.

(ix) Radon is used in radiotherapy for cancer and for earth-quake prediction.

Q.9 What are the uses of halogen?

Ans. (i) Fluorine is used for the preparation of freons.

(ii) Fluorine is used to prepare teflon.

(iii) Chlorine is used in the manufacture of bleaching powder.

(iv) Chlorine is used as disinfectant in swimming pools and water treatment plants.

(v) Bromine is used as fungicide.

(vi) The major applications of iodine are in pharmaceutical industry. It is used as disinfectant and germicide.

Q.10 Complete and balance.

Ans. $3XeF_4 + 4NH_3 \longrightarrow 3Xe + 12HF + 2N_2$

$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$

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

$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$

$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$

$Na_4XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2Na_2SO_4 + 2H_2O$

$$XeOF_4 + 3H_2 \xrightarrow{300^\circ C} Xe + H_2O + 4HF$$

Q.11 Formula of ores of halogens.

Ans.

Fluorspar	CaF_2
Cryolite	Na_3AlF_6
Apatite	$CaF_2 \cdot 3Ca_3(PO_4)_2$
Halite	$NaCl$
Carnalite	$KCl \cdot MgCl_2 \cdot 6H_2O$
Sodium iodate	$NaIO_3$
Sodium periodate	$NaIO_4$

Q.12 Complete and balance the following.

Ans.

$$2HClO_4 + P_2O_5 \xrightarrow{-10^\circ C} Cl_2O_7 + 2HPO_3$$

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

$$HgO + 2Br_2 \xrightarrow[CCl_4]{50^\circ C} HgBr_2 + Br_2O$$

$$2KClO_3 + H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2CO_2 + 2ClO_2 + 2H_2O$$

$$I_2O_5 + H_2O \longrightarrow 2HIO_3$$

$$2HIO_3 \xrightarrow{240^\circ C} I_2O_5 + H_2O$$

$$5CO + I_2O_5 \longrightarrow 5CO_2 + I_2$$

$$Cl_2 + 2NaOH \xrightarrow{dil.} NaCl + NaClO + H_2O$$

$$3Cl_2 + 6NaOH \xrightarrow{Conc.} 5NaCl + NaClO_3 + 3H_2O$$