

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 03 (Class XII, Semester 01)
Module Name/Title	P-block Elements (Group 17 elements): Part 4
Module Id	lech_10704
Pre-requisites	Knowledge about electronic configuration of elements of this block and variation of Atomic size, Ionization Enthalpy, Electron Gain Enthalpy and Electronegativity within the groups in the block, chemical bonding
Objectives	After going through this lesson, the learners will be able to understand the following: <ul style="list-style-type: none">• Anomalous behavior of fluorine• Hydrides, Oxides of group 17 elements and their properties.• Preparation and properties of chlorine.• Preparation and properties of hydrogen chloride.• Oxoacids of halogen and their properties.• Preparation and properties of Interhalogen compounds.
Keywords	Halogens, haloacids, hydrides, Interhalogen, hydrogen halides, chlorine oxoacids.

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11. Summary

Introduction- Fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are members of Group 17. These are collectively known as **halogens** (Greek *halo* means salt and *genes* means born i.e., salt producers). All halogens are non-metals and constitute the group of highly electronegative elements. They react with most of the metals to produce wide range of salts. Like s block elements, the elements of Group 17 show great similarity amongst themselves. This is the only group of the periodic table that contains elements in all the three states of matter at standard temperature and pressure. Astatine is a radioactive element.

OCCURENCE

Fluorine and chlorine are fairly abundant while bromine and iodine less abundant. Fluorine is present mainly as insoluble fluorides (fluorspar CaF_2 , cryolite Na_3AlF_6 and fluoroapatite $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ and small quantities are present in soil, river water, plants, bones and teeth of animals. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass). Even higher concentrations of chloride are found in the Great Salt Lake in Utah, which is 9% Cl^- ion by weight, the Dead Sea and in underground brine deposits. Most chloride salts are soluble in water, thus, chloride-containing minerals are usually only found in abundance in dry climates or deep underground. The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Like Cl, the largest natural source of bromine is oceans (concentration of Br: 65 ppm) where it is available in 1:300 Br:Cl mass ratio. Salt lake and

brine wells are richer in bromine than oceans. Concentration of Iodine in sea water is very less (0.05 ppm) though certain forms of marine life containing iodine in their systems become one source to extract iodine. Various seaweeds such as kelp, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate (NaIO_3). This element also exists in small amounts (0.02-1 %) in the mineral caliche, found in Chile, between the Andes.

Thyroid gland produces a growth regulating hormone, thyroxine, which is an iodinated amino acid. If the body is deficient in iodine, enlarging of thyroid glands is observed. Table salt is therefore enriched with 0.01% NaI to maintain the optimum iodine levels in body. Iodine also is a useful antiseptic when used as a solution of iodine (2-7%) containing some potassium iodide in water ethanol mixture.

2. General properties of Group 17 elements

Halogens display smooth variations in their atomic and physical properties.

2.1. Electronic Configuration

All these elements have seven electrons in their outermost shell (ns^2np^5) which is one electron short of the immediate next noble gas.

2.2. Atomic and Ionic radii

The halogens have the smallest atomic radii (Table 4.1) in their respective periods due to maximum effective nuclear charge. The atomic radius of fluorine like the other elements of second period is extremely small. Atomic and ionic radii increase from fluorine to iodine due to increasing number of quantum shells.

2.3. Ionization enthalpy

Being on the extreme right of the periodic table, halogens have very high ionisation enthalpy and have a little tendency to lose electron. The ionisation enthalpy as a regular group trend decreases down the group. Iodine though retaining its non metallic character do display some metallic properties.

2.4. Electron gain enthalpy

Halogens have maximum electron gain enthalpy in the corresponding periods. Halogens have the smallest size in their respective periods and have high effective nuclear charge on the

valence shell. They readily accept one electron to acquire a closed shell configuration. With increasing halogen atomic size, electron gain enthalpy decrease from Chlorine to Iodine. Fluorine however has lower electron gain enthalpy than chlorine.

2.5. Electronegativity- Electronegativities of these elements are very high though they decrease down the group. Fluorine is the most electronegative element in the periodic table.

2.6. Physical state

All the halogens exist as diatomic molecules. F_2 and Cl_2 are gases, Br_2 is a liquid and I_2 is a solid. Their melting and boiling points steadily increase with atomic number as the only force of attraction between the molecules is van der waals force increase with molecular size .

2.7. Colour

All halogens are coloured. F_2 has yellow, Cl_2 greenish yellow, Br_2 red and I_2 violet colour. This is due to the absorption in the visible region by the halogen molecules which results in the excitation of electrons in the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). Since the orbital energies of all halogens are different, different quanta of radiations are absorbed to give different colours.

Bromine and iodine are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

2.8. Oxidation states

All the halogens exhibit stable -1 oxidation state. Chlorine, bromine and iodine exhibit $+1$, $+3$, $+5$ and $+7$ oxidation states also. The higher oxidation states of chlorine, bromine and iodine are observed when these halogens are bonded to more electronegative fluorine and oxygen atoms forming compounds like interhalogens, oxides and oxoacids. The oxidation states of $+4$ and $+6$ are also displayed in the oxides and oxoacids of chlorine and bromine. Fluorine never displays a positive oxidation state as it is the most electronegative element in the periodic table. It does not show more than one negative oxidation state and is always univalent as it lacks d orbitals in its valence shell.

Table 4.1. Atomic and physical properties of halogens

Property	F	Cl	Br	I	At ^a
Atomic number	9	17	35	53	85
Atomic mass/g mol ⁻¹	19.00	35.45	79.90	126.90	210
Electronic configuration	[He]2s ² 2p ⁵	[Ne]3s ² 3p ⁵	[Ar]3d ¹⁰ 4s ² 4p ⁵	[Kr]4d ¹⁰ 5s ² 5p ⁵	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵
Covalent radius/pm	64	99	114	133	-
Ionic radius X ⁻ /pm	133	184	196	220	-
Ionisation enthalpy/kJ mol ⁻¹	1680	1256	1142	1008	-
Electron gain enthalpy/kJ mol ⁻¹	-333	-349	-325	-296	-
Electronegativity ^b	4	3.2	3.0	2.7	2.2
$\Delta_{\text{hyd}}H(X)/\text{kJ mol}^{-1}$	515	381	347	305	-
	F ₂	Cl ₂	Br ₂	I ₂	-
Melting point/K	54.4	172.0	265.8	386.6	-
Boiling point/K	84.9	239.0	332.5	458.2	-
Density/g cm ⁻³	1.5 (85) ^c	1.66 (203) ^c	3.19(273) ^c	4.94(293) ^d	-
Distance X - X/pm	143	199	228	266	-
Bond dissociation enthalpy /(kJ mol ⁻¹)	158.8	242.6	192.8	151.1	-
E ⁰ /V ^e	2.87	1.36	1.09	0.54	-

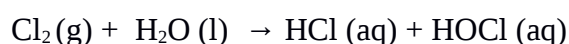
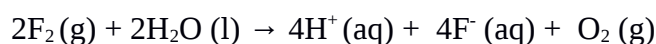
^a Radioactive; ^b Pauling scale; ^c For the liquid at temperatures (K) given in the parentheses; ^d solid; ^e The half-cell reaction is X(la) + 2e⁻ → 2X(aal).

2.9. Chemical reactivity

All halogens are chemically reactive. They react easily with both metals and non-metals to form ionic and covalent halides. The reactivity decreases down the group because of decreasing non metallic character and decreasing bond strengths.

2.10. Oxidising nature

All halogens act as oxidising agents. The oxidising strength decreases down the group with decreasing (X-X) bond strength and decreasing electron gain enthalpy. Fluorine is the strongest oxidising agent while iodine is the weakest oxidising agent. Conversely, I⁻ ion is the strongest reducing agent while F⁻ ion is the weakest reducing agent, The relative oxidising power of halogens can be shown by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine undergo disproportionation in water to form corresponding hydrohalic and hypohalous acids.

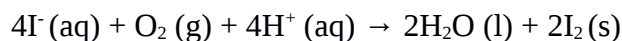


Hypochlorous acid



Hypobromous acid

The oxidation of water to oxygen by iodine is non spontaneous. In fact, I^- can be oxidised by oxygen to I_2 in acidic medium, which is just the reverse of the reaction observed with fluorine.



3. Anomalous behaviour of fluorine

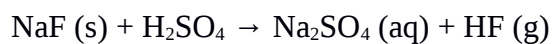
Fluorine being the smallest member of the group shows anomaly in many properties. These are:

- Ionisation enthalpy, electronegativity, and electrode potential values are exceptionally higher for fluorine
- Ionic and covalent radii for fluorine are exceptionally low which leads to very low melting and boiling points.
- In spite of having small orbital size suited for effective overlap, F-F bond dissociation enthalpy is exceptionally low. This is due to the repulsion between three pairs of non bonding electrons on each small bonded fluorine atom.
- In spite of being the most electronegative atom, the electron gain enthalpy of fluorine is lower than chlorine. The added electron, in fluorine atom to form F^- , encounters strong interelectronic repulsions from electrons already present in now extremely small 2p orbital of fluorine.
- Most of the reactions of fluorine are exothermic because of high strength of bonds formed between F and other elements. The high bond strengths are attributed to effective orbital overlap due to small size and high bond polarities resulting from large electronegativity differences between bonded atoms.
- Fluorine is always univalent and displays only -1 oxidation state.

4. Binary compounds of halogens with hydrogen (Hydrogen halides)

4.1. Preparation

All halogens react with hydrogen directly to give hydrogen halides though reactivity decreases down the group. Fluorine reacts violently with hydrogen even in dark, chlorine reacts in diffused sunlight, bromine reacts with hydrogen on heating while for iodine catalyst presence is also required. HF and HCl are prepared in laboratory by acidifying fluoride and chloride salt respectively with conc. sulphuric acid.



Conc.



Conc.

HBr and HI prepared by similar reaction will be contaminated with Br₂ and I₂ respectively.

4.2. Properties of hydrogen halides

4.2.1. Boiling point

Boiling point of HF is highest due to extensive intermolecular hydrogen bonding arising from high H-F bond polarity. For other hydrogen halides, with increasing size of the halogen atom boiling points show a regular increase due to increase in the magnitude of van der Waals forces of attraction.

4.2.2. Acidic strength

Hydrogen halides are also termed as halo acids because of their ability to ionise in water to give H⁺. The acid strength of these acids increases in the order: HF < HCl < HBr < HI. The bond (H-X) dissociation enthalpy of these halides, decreases down the group due to mismatch in orbital sizes of small hydrogen atom and large halogen atom leading to weak bonding. Thus hydrogen is easily released by larger halides.

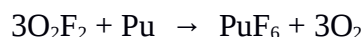
4.2.3. Stability

Stability of these halides decreases in the order HF > HCl > HBr > HI as it depends on bond enthalpy which decreases down the group.

5. Oxides of halogen

Halogens form many oxides with oxygen but most of them are unstable.

Fluorine combines with oxygen to form oxygen difluoride, OF₂ and oxygen monofluoride O₂F₂. These are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Only OF₂ is thermally stable at 298 K. Both are strong fluorinating agents. O₂F₂ oxidises plutonium to PuF₆ and the reaction is used in removing plutonium as PuF₆ from spent nuclear fuel.



The structure of OF₂ is similar to that of H₂O while that of O₂F₂ is similar to that of H₂O₂ involving sp³ hybridisation of O atoms. The bond angle in OF₂ is lower than that of H₂O. The

bond pair in OF_2 is closer to F atom and hence bond-pair –bond pair repulsion is decreased in OF_2 therefore decreasing the bond angle.

Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7. A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, $\text{I} > \text{Cl} > \text{Br}$. Iodide-oxygen bond is stable due to greater polarity of the bond while the stability of chlorine-oxygen bond is due to multiple bond formation involving d-orbital of chlorine atom. Bromine being in between lacks both these characteristics. The higher oxides of halogens tend to be more stable than the lower ones.

Chlorine oxides, Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 (table 4.2) are highly reactive, strong oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment. The bromine oxides, Br_2O , BrO_2 , BrO_3 are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents. The iodine oxides, I_2O_4 , I_2O_5 , I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

Table 4.2 –Structure of various oxides of chlorine

Name of chlorine oxide	Formula of chlorine oxide	Oxidation state of Cl
Cl_2O	Chlorine monoxide	+1
ClO_2	Chlorine dioxide	+4
Cl_2O_6	Dichlorine hexoxide	+6
Cl_2O_7	Dichlorine heptoxide	+7

6. Reactivity towards metals

Halogens react with all metals to form metal halides. The ionic character of the halides decreases in the order $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$ where M is a monovalent metal. **Reason-** This is due to corresponding decrease in electronegativity of the halogen from F to I. If a metal exhibits more than one oxidation state, the halides in higher oxidation state will be more covalent than the one in lower oxidation state. This is in accordance with Fajan's rule which states that higher the charge on the cation, higher is the polarising power and higher the covalent character in the ionic bond. For example, SnCl_4 , PbCl_4 , SbCl_5 and UF_6 are more covalent than SnCl_2 , PbCl_2 , SbCl_3 and UF_4 respectively.

7. Chlorine

Chlorine was first prepared in 1774 by Scheele by oxidising HCl with MnO₂, though he mistook it as a compound. In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, *chloros* means greenish yellow).

7.1. Preparation

In laboratory, Chlorine can be prepared by any one of the following methods:

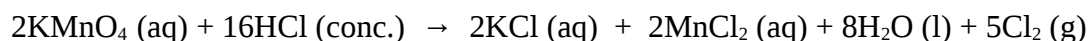
1) By heating manganese dioxide with concentrated hydrochloric acid.



HCl can be generated *in situ* by treating common salt with concentrated H₂SO₄

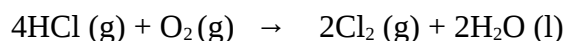
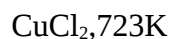


2) By the action of HCl on potassium permanganate



At industrial level, chlorine is manufactured by either of the following processes.

1) *Deacon's process*: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of CuCl₂ (catalyst) at 723 K.

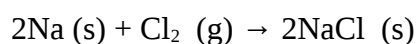
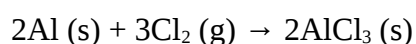


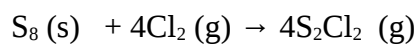
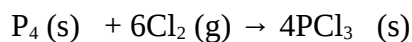
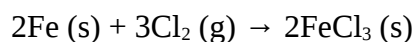
2) *Electrolytic process*: Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is also obtained as a by-product in many chemical industries.

7.2. Properties

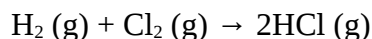
It is a greenish yellow gas with pungent and suffocating odour. It is about 2-5 times heavier than air. It can be liquefied easily into greenish yellow liquid which boils at 239 K. It has two natural isotopes ³⁵Cl and ³⁷Cl. It is soluble in water.

Chlorine reacts with a number of metals and non-metals to form chlorides.

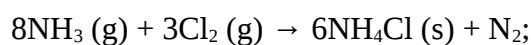




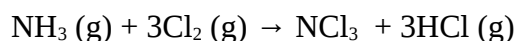
It has great affinity for hydrogen and form HCl



Excess ammonia reacts with chlorine to give nitrogen and ammonium chloride whereas when excess chlorine reacts with ammonia, nitrogen trichloride (explosive) is formed.

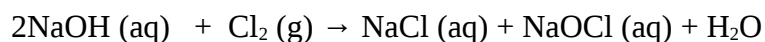


(excess)

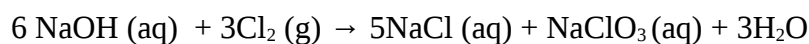


(excess)

Chlorine disproportionate in neutral and alkaline medium, the product formed depends on reaction conditions. With cold and dilute alkali chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkali it gives chloride and chlorate.

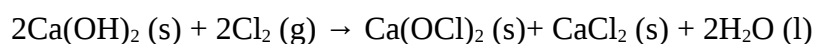


cold and dilute



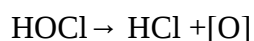
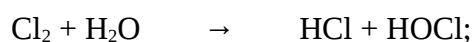
hot and conc.

With dry slaked lime it gives bleaching powder.

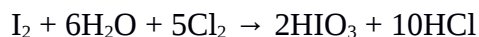
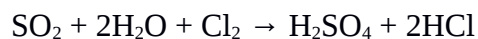
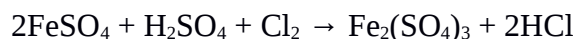


The composition of bleaching powder is $\text{Ca(OCl)}_2 \cdot \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O}$.

Aqueous solution of chlorine is called chlorine water. On standing chlorine water loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid thus formed, being unstable, decomposes to give nascent oxygen which is responsible for **oxidising property of chlorine water**.



Thus in the presence of moisture or in aqueous solution chlorine act as powerful oxidising agent. Some of the reactions in which exhibit this behaviour are as follows-

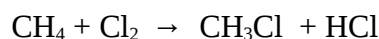


It also act as a powerful bleaching agent and bleaches vegetable matter or organic matter.

The bleaching action is due to oxidising power of chlorine in aqueous medium and is a permanent effect.

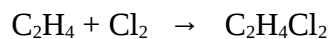
Chlorine reacts with saturated hydrocarbons to form substitution products and with unsaturated hydrocarbons to form addition products.

UV



Methane chloromethane (substitution)

Room temperature



Ethene dichloroethane (addition)

7.3. Uses

It is used (i) for bleaching wood pulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as CCl_4 , CHCl_3 , DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene (COCl_2), tear gas (CCl_3NO_2), mustard gas ($\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$).

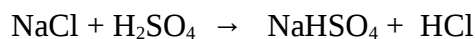
8. Hydrogen chloride

Glauber prepared this acid in 1648 by heating common salt with concentrated sulphuric acid. Davy in 1810 showed that it is a compound of hydrogen and chlorine.

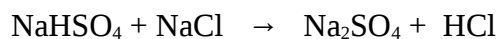
8.1. Preparation

In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.

420K



823K

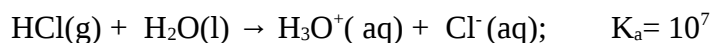


HCl gas is dried by passing through concentrated sulphuric acid.

8.2. Properties

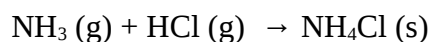
It is a colourless and pungent smelling gas. It is easily liquefied to a colourless liquid (b.pt. 189 K) and freezes to a white crystalline solid (f.pt. 159 K).

It is soluble in water and ionises as follows

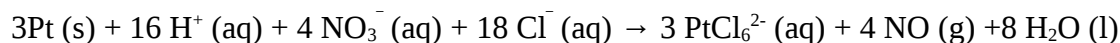
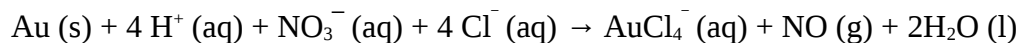


High value of dissociation constant (K_a) indicates that it is a strong acid in water.

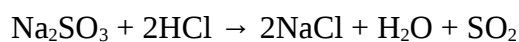
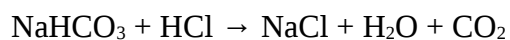
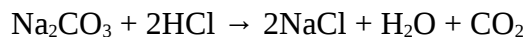
It reacts with NH_3 to give white fumes of NH_4Cl .



When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.



Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogen carbonates, sulphites, etc.



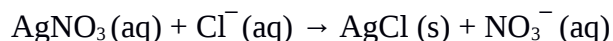
Active metals like Zn, Mg, Fe, Al liberate hydrogen gas from aqueous HCl



The salts of hydrochloric acid are called halides. The presence of Cl^- can be detected using *silver nitrate test* and *chromyl chloride test*.

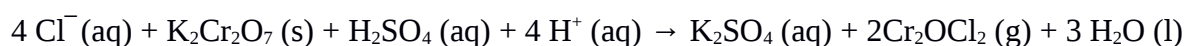
Silver nitrate test:

Aqueous solutions of soluble ionic chlorides, on treatment with AgNO_3 solution, precipitate chloride as white insoluble silver chloride AgCl which is soluble in excess ammonia solution.



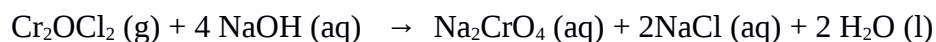
Chromyl chloride test:

Solid chloride salt on heating with solid potassium dichromate and conc. sulphuric acid generates a red brown gas, chromyl chloride. This gas on passing through NaOH solution, turns it yellow. Addition of lead acetate solution to this yellow solution produces a yellow precipitate of lead chromate.



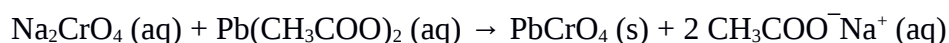
Chromyl chloride

(red brown)



Sodium chromate

(yellow soln.)



Lead chromate

(yellow ppt.)

8.3. Uses

It is used (i) in the manufacture of chlorine, NH_4Cl and glucose (from corn starch), (ii) for extracting glue from bones and purifying bone black, (iii) in medicine and as a laboratory reagent.

9. Oxoacids of Halogens

Being univalent and most electronegative atom, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens capable of displaying positive oxidation states form several oxoacids, Most of which exist only in aqueous

solutions or in the form of their salts and are not isolable in pure state. The oxoacids of halogens are given in Table 4.3 and their structures are given in Fig. 4.1.

Table 4.3. Oxoacids of Halogens

Halic (I) acid (Hypohalous acid)	HOF (Hypofluorous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (III) acid (Halous acid)	-	HOClO (chlorous acid)	-	-
Halic (V) acid (Halic acid)	-	HOClO ₂ (chloric acid)	HOBrO ₂ (bromic acid)	HOIO ₂ (iodic acid)
Halic (VII) acid (Perhalic acid)	-	HOClO ₃ (perchloric acid)	HOBrO ₃ (perbromic acid)	HOIO ₃ (periodic acid)

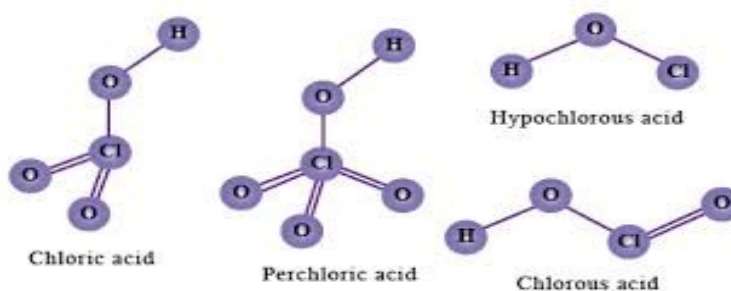


Fig 4.1 Structures of oxoacids of chlorine

9.1. Properties

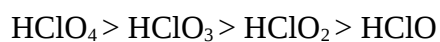
These oxidation states of halogens in these acids are: +1 in HOX, +3 in HOXO, +5 in HOXO₂, +7 in HOXO₃. All are monobasic acid as one ionisable OH group is present in all the acids.

For oxo acids of similar composition, the acid strength decreases with decrease in electronegativity of the halogen



The polarity of O-H bond is affected by attached halogen. As the electronegativity of the halogen decreases from Cl to I, electron withdrawal from O-X bond towards X decreases thus decreasing O-H bond polarity also.

For same halogen, the strength of oxoacid increases with increase in oxidation state of halogen.



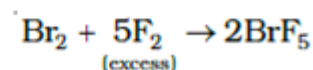
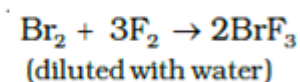
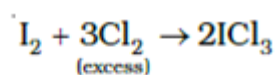
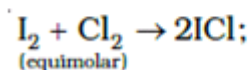
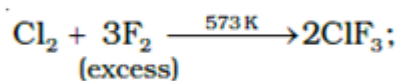
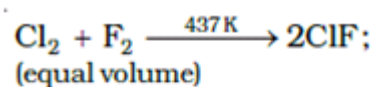
Higher positive oxidation state of the halogen leads to greater polarisation of attached O-H bond thus increasing its acidity.

10. Interhalogen Compounds

When two different halogens react with each other, compounds formed are called interhalogens. They can be assigned general compositions as XX' , XX_3' , XX_5' and XX_7' where X is halogen of larger size and X' of smaller size and X is less electronegative than X'. As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride has maximum number of atoms as the ratio of radii between I and F is maximum. That is why only iodine generates interhalogen with maximum number of fluorine atoms, IF_7 .

10.1. Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions, For e.g.,



10.2. Properties

Some properties of interhalogens are enlisted in table 4.4.

The heavier halogen is always present as central atom.

They are essentially covalent compounds because of small electronegativity difference.

They have even number of halogen atoms and are diamagnetic in nature.

They are volatile solids or liquids at 298 K except ClF , BrF , ClF_3 , IF_5 and IF_7 (Table 4.4) which are gas. Their m.pt. and b.pt. are a higher than corresponding halogens because of polar bonds..

In general, interhalogen compounds are more reactive than halogens (except fluorine). The $X-X'$ bond in interhalogens is weaker than $X-X$ bond in halogens except $F-F$ bond due to mismatch in the size of overlapping orbitals. The polarity of $X-X'$ bond provides the attacking sites on the molecule.

All of these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (when XX'_3), halate (when XX'_5) and perchalate (when XX'_7) anion derived from the heavier halogen.



The stability of interhalogen compound increases as the size of the central atom increases.

Interhalogen compounds of fluorine are good fluorinating agent and hence fluorinate metals, non metals, metal oxides and metal halide.

10.3. Structure of Interhalogen Compounds

The XX_3 compounds have the bent 'T' shape, XX_5 compounds have square pyramidal and IF_7 has pentagonal bipyramidal structures (Fig 4.2). For e.g.; in BrF_3 , the central atom Br has seven electrons in the valence shell ($4s^2 4p^5$). Three of these will be utilised in bonding with three fluorine atoms leaving behind four electrons not involved in bonding. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid. The two lone pairs being bulky, will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions. The axial fluorine atoms experiencing greater repulsions from two equatorial lone pairs will be bent towards the equatorial fluorine in order to minimise the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'

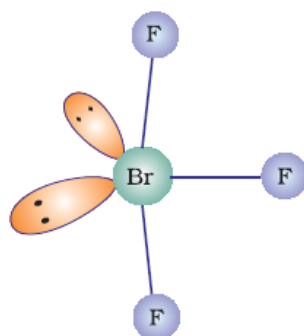


Fig 4.2 Structure of BrF_3

Table 4.4. Properties of Interhalogen compounds

Type	Formula	Physical state and colour	Structure
XX' ₁	ClF	colourless gas	–
	BrF	pale brown gas	–
	IF ^a	detected spectroscopically	–
	BrCl ^b	gas	–
	ICl	ruby red solid (α-form)	–
		brown red solid (β-form)	–
XX' ₃	IBr	black solid	–
	ClF ₃	colourless gas	Bent T-shaped
	BrF ₃	yellow green liquid	Bent T-shaped
	IF ₃	yellow powder	Bent T-shaped (?)
XX' ₅	ICl ₃ ^c	orange solid	Bent T-shaped (?)
	IF ₅	colourless gas but solid below 77 K	Square pyramidal
	BrF ₅	colourless liquid	Square pyramidal
XX' ₇	ClF ₅	colourless liquid	Square pyramidal
	IF ₇	colourless gas	Pentagonal bipyramidal

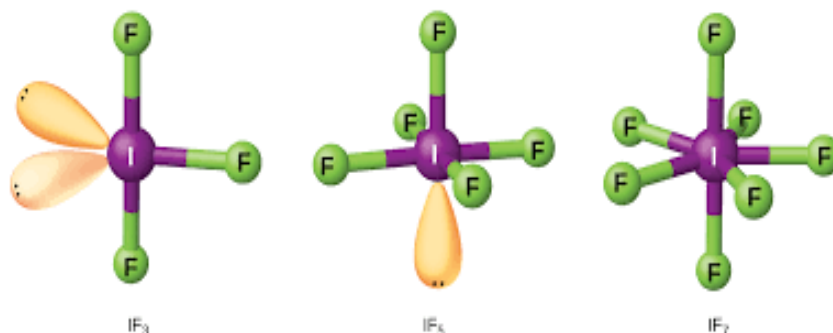
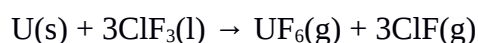


Fig 4.3. Structure of some Interhalogen Compounds

(Image source: <https://opentextbc.ca/chemistry/chapter/18-11-occurrence-preparation-and-properties-of-halogens/>)

10.4. Uses

These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents. ClF₃ and BrF₃ are used for the production of UF₆ in the enrichment of ²³⁵U.



11. Summary

Group 17 of the periodic table consists of F, Cl, Br, I and At, collectively known as halogens. These elements are highly electronegative and reactive and as such they are found in the combined state only. The common oxidation state of these elements is -1 . Though Cl, Br and I display positive oxidation states with ease.. They show regular gradation in physical and chemical properties. They form oxides, hydrogen halides, oxoacids. Halogens in a unique way combine with one another to form interhalogen compounds of the type XX'_n ($n = 1, 3, 5, 7$) where X' is lighter than X . In the oxoacids, halogen is the central atom linked to one ionisable OH bond and variable number of pi bonded oxygen atoms. F, Cl and I have their presence in living systems also.