

Group 17 Elements

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17. These are collectively known as the halogens (Greek halo means salt and genes means born i.e., salt producers). The halogens are highly reactive non-metallic elements. Like Groups 1 and 2, the elements of Group 17 show great similarity amongst themselves. That much similarity is not found in the elements of other groups of the periodic table. Also, there is a regular gradation in their physical and chemical properties. Astatine is a radioactive element.

Occurrence: Fluorine and chlorine are fairly abundant while bromine and iodine less so. Fluorine is present mainly as insoluble fluorides (fluorspar CaF₂, cryolite Na₃AlF₆ and fluoroapatite 3Ca₃(PO₄)₂.CaF₂) and small quantities are present in soil, river water plants and 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). The deposits of dried up seas contain these compounds, e.g., sodium chloride and carnallite, KCl.MgCl₂.6H₂O. Certain forms of marine life contain iodine in their systems; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

Electronic Configuration: All these elements have seven electrons in their outermost shell (ns²np⁵) which is one electron short of the next noble gas.

Atomic and Ionic Radii: The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. 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.

Ionisation Enthalpy: They have little tendency to lose electron. Thus they have very high ionisation enthalpy. Due to increase in atomic size, ionisation enthalpy decreases down the group.

Electron Gain Enthalpy: Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong interelectronic repulsions in the relatively small 2p orbitals of fluorine and thus, the incoming electron does not experience much attraction.

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

Physical Properties: Halogens display smooth variations in their physical properties. Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. Their melting and boiling points steadily increase with atomic number. All halogens are coloured. This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level. By absorbing different quanta of radiation, they display different colours. For example, F₂, has yellow, Cl₂ , greenish yellow, Br₂, red and I₂, violet colour. Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

One curious anomaly we notice is the smaller enthalpy of dissociation of F₂ compared to that of Cl₂ whereas X-X bond dissociation enthalpies from chlorine onwards show the expected trend: Cl – Cl > Br – Br > I – I. A reason for this anomaly is the relatively large electron-electron repulsion among the lone pairs in F₂ molecule where they are much closer to each other than in case of Cl₂.

Chemical Properties:

Oxidation states and trends in chemical reactivity:

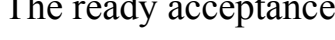
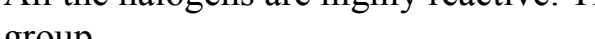
All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also as explained below:

Halogen atom in ground state (other than fluorine)	ns	np	nd	
	↑↓	↑↓↑↓↑		1 unpaired electron accounts for –1 or +1 oxidation states
First excited state	↑↓	↑↓↑↑	↑	3 unpaired electrons account for +3 oxidation states
Second excited state	↑↓	↑↑↑↑	↑	5 unpaired electrons account for +5 oxidation state
Third excited state	↑↑	↑↑↑↑	↑↑	7 unpaired electrons account for +7 oxidation state

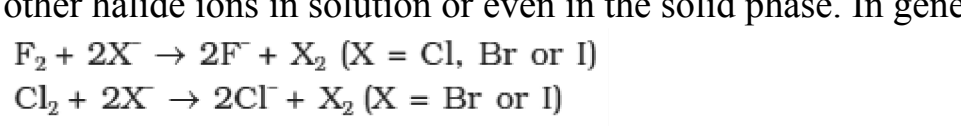
The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids. The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine. The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only –1 oxidation state.

All the halogens are highly reactive. They react with metals and non-metals to form halides. The reactivity of the halogens decreases down the group.

The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F₂ is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase. In general, a halogen oxidises halide ions of higher atomic number.



The decreasing oxidising ability of the halogens in aqueous solution down the group is evident from their standard electrode potentials which are dependent on the parameters indicated below:



The relative oxidising power of halogens can further be illustrated by their reactions with water. Fluorine oxidises water to oxygen whereas chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids. The reaction of iodine with water is nonspontaneous. In fact, I[–] can be oxidised by oxygen in acidic medium; just the reverse of the reaction observed with fluorine.



(where X = Cl or Br)



Anomalous behaviour of fluorine: Like other elements of p-block present in second period of the periodic table, fluorine is anomalous in many properties. For example, ionisation enthalpy, electronegativity, and electrode potentials are all higher for fluorine than expected from the trends set by other halogens. Also, ionic and covalent radii, m.p. and b.p., enthalpy of bond dissociation and electron gain enthalpy are quite lower than expected. The anomalous behaviour of fluorine is due to its small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell. Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements). It forms only one oxoacid while other halogens form a number of oxoacids. Hydrogen fluoride is a liquid (b.p. 293 K) due to strong hydrogen bonding. Other hydrogen halides are gases.

(i) Reactivity towards hydrogen: They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine. Hydrogen halides dissolve in water to form hydrohalic acids. The acidic strength of these acids varies in the order: HF < HCl < HBr < HI. The stability of these halides decreases down the group due to decrease in bond (H–X) dissociation enthalpy in the order: H–F > H–Cl > H–Br > H–I.

(ii) Reactivity towards oxygen: Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF₂ and O₂F₂. However, only OF₂ is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O₂F₂ oxidises plutonium to PuF₆ and the reaction is used in removing plutonium as PuF₆ from spent nuclear fuel. 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, I > Cl > Br. The higher oxides of halogens tend to be more stable than the lower ones. Chlorine oxides, Cl₂O, ClO₂, Cl₂O₆ and Cl₂O₇ are highly reactive oxidising agents and tend to explode. ClO₂ is used as a bleaching agent for paper pulp and textiles and in water treatment. The bromine oxides, Br₂O, BrO₂ , BrO₃ are the least stable halogen oxides (middle row anomaly) and exist only at low temperatures. They are very powerful oxidising agents.

The iodine oxides, I₂O₄ , I₂O₅, I₂O₇ are insoluble solids and decompose on heating. I₂O₅ is a very good oxidising agent and is used in the estimation of carbon monoxide.

(iii) Reactivity towards metals: Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.



The ionic character of the halides decreases in the order MF > MCl > MBr > MI where M is a monovalent metal. 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. For example, SnCl₄, PbCl₄, SbCl₅ and UF₆ are more covalent than SnCl₂, PbCl₂, SbCl₃ and UF₄ respectively.

(iv) Reactivity of halogens towards other halogens: Halogens combine amongst themselves to form a number of compounds known as interhalogens of the types XX' , XX₃' , XX₅' and XX₇' where X is a larger size halogen and X' is smaller size halogen.

Chlorine

Chlorine was discovered in 1774 by Scheele by the action of HCl on MnO₂. In 1810 Davy established its elementary nature and suggested the name chlorine on account of its colour (Greek, chloros = greenish yellow).

Preparation

It can be prepared by any one of the following methods:

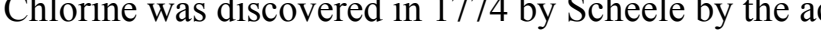
(i) By heating manganese dioxide with concentrated hydrochloric acid.



However, a mixture of common salt and concentrated H₂SO₄ is used in place of HCl.



(ii) By the action of HCl on potassium permanganate.



Manufacture of chlorine

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

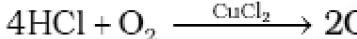
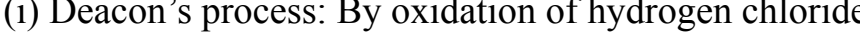


(ii) Electrolytic process: Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode. It is also obtained as a by–product in many chemical industries.

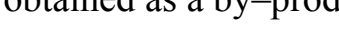
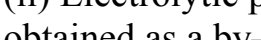
Properties

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 is soluble in water.

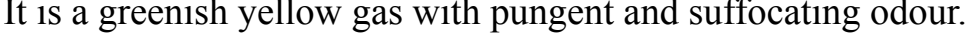
Chlorine reacts with a number of metals and non-metals to form chlorides.



It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

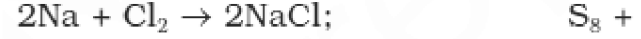


With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.



(excess) (excess)

With cold and dilute alkalis chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalis it gives chloride and chlorate.

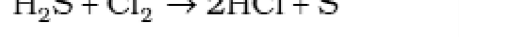


(cold and dilute)



(hot and conc.)

With dry slaked lime it gives bleaching powder.

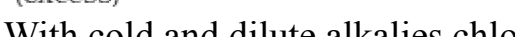


The composition of bleaching powder is Ca(OCI)₂.CaCl₂.Ca(OH)₂.2H₂O.

Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons. For example,



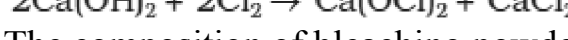
Methane



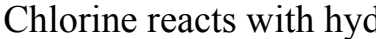
Ethene

Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

(i) It oxidises ferrous to ferric and sulphite to sulphate. Chlorine oxidises sulphur dioxide to sulphur trioxide and iodine to iodate. In the presence of water they form sulphuric acid and iodic acid respectively.



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



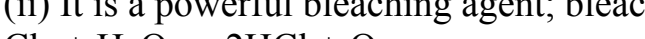
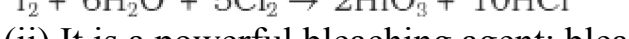
Uses: It is used (i) for bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as CCl₄, CHCl₃, DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene (COCl₂), tear gas (CCl₃NO₂), mustard gas (ClCH₂CH₂SClCH₂CH₂Cl).

Hydrogen Chloride

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

Preparation:

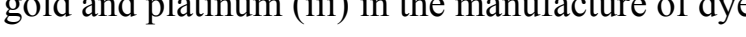
In laboratory, it is prepared by heating sodium chloride with concentrated sulphuric acid.



HCl gas can be dried by passing through concentrated sulphuric acid.

Properties

It is a colourless and pungent smelling gas. It is easily liquefied to a colourless liquid (b.p.189 K) and freezes to a white crystalline solid (f.p. 159 K). It is extremely soluble in water and ionises as follows:



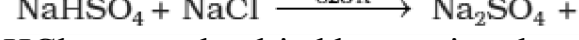
Its aqueous solution is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water. It reacts with NH₃ and gives white fumes of NH₄Cl.



When three parts of concentrated HCl and one part of concentrated HNO₃ 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, hydrogencarbonates, sulphites, etc.

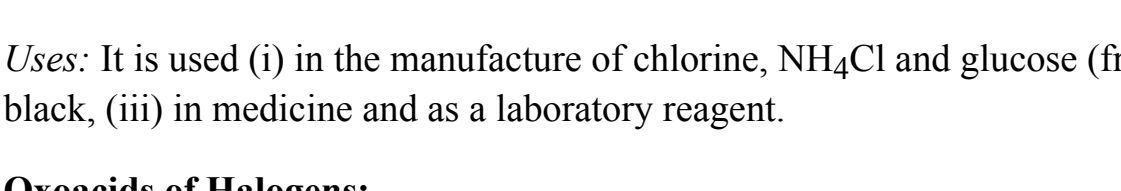


Uses: It is used (i) in the manufacture of chlorine, NH₄Cl and glucose (from corn starch), (ii) for extracting glue from bones and purifying bone black, (iii) in medicine and as a laboratory reagent.

Oxoacids of Halogens:

Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids. Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts. The oxoacids of halogens are given in the following Table and their structures are given in the following figure.

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



Interhalogen Compounds

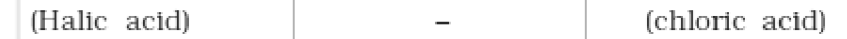
When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX' , XX₃' , XX₅' and XX₇' where X is halogen of larger size and X' of smaller size and X is more electropositive than X'. As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is IF₇ (having maximum number of atoms).

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.,



(equal volume)



(excess) (diluted with water)



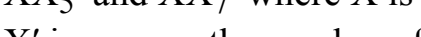
(equimolar)

Properties: Some properties of interhalogen compounds are given in the following Table

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 ₅ ^c	orange solid	Bent T-shaped (?)
	IF ₅	colourless gas but solid below 77 K	Square pyramidal
	BrF ₅	colourless liquid	Square pyramidal
	ClF ₅	colourless liquid	Square pyramidal
XX ₇	IF ₇	colourless gas	Pentagonal bipyramidal

These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids at 298 K except ClF which is a gas. Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.

Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because X–X' bond in interhalogens is weaker than X–X bond in halogens except F–F bond. All 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 perhalate (when XX'₇) anion derived from the larger halogen.



Their molecular structures are very interesting which can be explained on the basis of VSEPR theory . The XX₃ compounds have the bent 'T' shape, XX₅ compounds square pyramidal and IF₇ has pentagonal bipyramidal structures

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 ²³⁵>U

