# 7. ELEMENTS OF GROUPS 16, 17 AND 18

**Can you recall ?**

- How does the valence shell electronic configuration of the elements vary in the p-block of periodic table ?
- Name the first element of groups 16, 17 and 18.

**7.1 Introduction :** You have learnt in Std. XI that in the p-block elements the differentiating electron (the last filling electron) enters the p-orbital of the outermost shell. Since maximum of six electrons can be accommodated in a p-subshell it gives rise to groups 13 to 18, in the p-block. In this chapter we shall study the properties of elements of groups 16, 17 and 18.

**7.2 Occurence :** The elements oxygen ($_8O$), sulfur ($_{16}S$), selenium ($_{34}Se$), tellurium ($_{52}Te$) and polonium ($_{84}Po$) constitute Group 16, called the oxygen family. Large number of metal ores are oxides or sulfides. Group 16 elements are also called **chalcogens** or ore forming elements.

Oxygen is the most abundant of all the elements on earth. Oxygen forms 20.95 % by volume of air and about 46.6 % by mass of earth's crust. Sulfur forms 0.034% by mass of the earths crust. It occurs mainly in combined forms as sulfates such as **gypsum** ($CaSO_4.2H_2O$), **epsom salt** ($MgSO_4.7H_2O$), **baryte** ($BaSO_4$) and sulfides such as **galena** ($PbS$), **zinc blende** ($ZnS$), **copper pyrites** ($CuFeS_2$).

Selenium and tellurium are also found as metal selenides and tellurides in sulfide ores. Polonium which is radioactive is a decay product of thorium and uranium.

Fluorine ($_9F$), chlorine ($_{17}Cl$), bromine ($_{35}Br$), iodine ($_{53}I$) and astatine ($_{85}At$) constitute Group 17. These are collectively known as **halogens** (Greek halo means salt, gene means born), that is, salt producing element.

Halogens are very reactive due to high electronegativities and hence they are not found in free sate. They occur in the form of compounds.

Fluorine occurs mainly as insoluble fluorides (**fluorspar** $CaF_2$, **cryolite** $Na_3AlF_6$, **fluorapatite** $3Ca_3(PO_4)_2.CaF_2$) and small quantities are present in soil, fresh water plants, and bones and teeth of animals. Sea water contains chlorides, bromides and iodides of Na, K, Mg and Ca. However it mainly contains NaCl (2.5 % by mass). The deposits of dried up sea beds contain sodium chloride and **carnallite**, $KCl.MgCl_2.6H_2O$. Marine life also contains iodine in their systems. For example, sea weed contains upto 0.5 % iodine and **chile saltpetre** contains upto 0.2 % of sodium iodate. Astatine, the last member of halogen family is radioactive and has a half life of 8.1 hours.

The elements helium ($_2He$), neon ($_{10}Ne$), argon ($_{18}Ar$), krypton ($_{36}Kr$), xenon ($_{54}Xe$) and radon ($_{86}Rn$) constitute the Group 18.

All the noble gases except radon occur in the atmosphere. Their abundance in dry air is ~ 1% (by volume) with argon as the major constituent. The main commercial source of helium is natural gas. Helium and neon are found in minerals of radioactive origin e.g. **pitchblende**, **monazite**, **cleveite**. Xenon and radon are the rarest elements of the group. Radon is a decay product of $^{226}Ra$.

**Table 7.1 : Condensed electronic configuration of elements of group 16, 17 and 18**

| Group 16 (Oxygen family) | | Group 17 (Halogen family) | | Group 18 (Noble gases) | |
|---|---|---|---|---|---|
| Element | Condensed Electronic Configuration | Element | Condensed Electronic Configuration | Element | Condensed Electronic Configuration |
| | | | | $_{2}He$ | $1s^2$ |
| $_{8}O$ | $[He]2s^22p^4$ | $_{9}F$ | $[He]2s^22p^5$ | $_{10}Ne$ | $[He]2s^22p^6$ |
| $_{16}S$ | $[Ne]3s^23p^4$ | $_{17}Cl$ | $[Ne]3s^23p^5$ | $_{18}Ar$ | $[Ne]3s^23p^6$ |
| $_{34}Se$ | $[Ar]3d^{10}4s^24p^4$ | $_{35}Br$ | $[Ar]3d^{10}4s^24p^5$ | $_{36}Kr$ | $[Ar]3d^{10}4s^24p^6$ |
| $_{52}Te$ | $[Kr]4d^{10}5s^25p^4$ | $_{53}I$ | $[Kr]4d^{10}5s^25p^5$ | $_{54}Xe$ | $[Kr]4d^{10}5s^25p^6$ |
| $_{84}Po$ | $[Xe]4f^{14}5d^{10}6s^26p^4$ | $_{85}At$ | $[Xe]4f^{14}5d^{10}6s^26p^5$ | $_{86}Rn$ | $[Xe]4f^{14}5d^{10}6s^26p^6$ |

## 7.3 Electronic configuration of elements of group 16, 17 and 18: :

The general electronic configuration of the group 16 elements is $ns^2np^4$ while that of group 17 elements is $ns^2np^5$. The group 18 elements are shown by $ns^2np^6$ configuration.

The elements of groups 16 and 17 repectively have two and one electrons less than the stable electronic configuration of the nearest noble gas.

Table 7.1 shows the condensed electronic configuration of the elements of group 16, 17 and 18.

## 7.4 Atomic and physical properties of elements of group 16, 17 and 18.

### 7.4.1 Atomic properties of Group 16, 17 and 18 elements :

These properties are given in Tables 7.2, 7.3 and 7.4.

**i. Atomic and Ionic radii :** In group 16, 17 and 18 atomic and ionic radii increase down the group, as a result of increase in the number of quantum shells.

Across a period atomic or ionic radii decrease with increasing atomic number, consequent to increase in ($Z_{eff}$) effective nuclear charge. Group 17 elements (Halogens) have the smallest atomic radii in their respective periods.

**ii. Ionisation enthalpy :** The group 16, 17 and 18 elements have high ionisation enthalpy. The ionisation enthalpy decreases down the group due to increase in the atomic size.

Across a period ionisation enthalpy increases with increase of atomic number. This is due to addition of electrons in the same shell. However the elements of group 16 have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods, owing to extra stable half filled electronic configuration of p-orbitals in elements of group 15.

**Table 7.2 : Atomic and physical properties of group 16 elements.**

| Element | Atomic number | Atomic mass g/mol | Atomic radius (pm) | Ionic radius $E^{2\ominus}$ (pm) | Ionization enthalpy ($\Delta_i H_1$) kJ/mol | Electro-negativity | Electron gain enthalpy kJ/mol | Density g /cm$^3$ | M.P. (K) | B.P. (K) |
|---|---|---|---|---|---|---|---|---|---|---|
| O | 8 | 16.00 | 66 | 140 | 1314 | 3.50 | -141 | 1.32 | 55 | 90 |
| S | 16 | 32.06 | 104 | 184 | 1000 | 2.44 | -200 | 2.06 | 393 | 718 |
| Se | 34 | 78.96 | 117 | 198 | 941 | 2.48 | -195 | 4.19 | 490 | 958 |
| Te | 52 | 127.60 | 137 | 221 | 869 | 2.01 | -190 | 6.25 | 725 | 1260 |
| Po | 84 | 210.00 | 146 | 230 | 813 | 1.76 | -174 | - | 520 | 1235 |

## Table 7.3 : Atomic and physical properties of group 17 elements

| Element | Atomic number | Atomic mass g/mol | Atomic radius (pm) | Ionic radius $E^{\ominus}$(pm) | Ionization enthalpy ($\Delta_i H_1$) kJ/mol | Electro negativity | Electron gain enthalpy kJ/mol | Density g/cm$^3$ | M.P. (K) | B.P. (K) |
|---|---|---|---|---|---|---|---|---|---|---|
| F | 9 | 19.00 | 64 | 133 | 1680 | 4.0 | -333 | 1.5 | 54.4 | 84.9 |
| Cl | 17 | 35.45 | 99 | 184 | 1256 | 3.2 | -349 | 1.66 | 172.0 | 239.0 |
| Br | 35 | 79.90 | 114 | 196 | 1142 | 3.0 | -325 | 3.19 | 265.8 | 332.5 |
| I | 53 | 126.90 | 133 | 220 | 1008 | 2.7 | -296 | 4.94 | 386.6 | 458.2 |
| At | 85 | 210 | - | - | - | 2.2 | - | - | - | - |

## Table 7.4 : Atomic and physical properties of group 18 elements.

| Element | Atomic number | Atomic mass g/mol | Atomic radius (pm) | Ionization enthalpy ($\Delta_i H_1$) kJ/mol | Electron gain enthalpy kJ/mol | Density g/cm$^3$ | M.P. (K) | B.P. (K) | Atmospheric content (% by volume) |
|---|---|---|---|---|---|---|---|---|---|
| He | 2 | 4.00 | 120 | 2372 | 48 | $1.8 \times 10^{-4}$ | - | 4.2 | $5.24 \times 10^{-4}$ |
| Ne | 10 | 20.18 | 160 | 2080 | 116 | $9.0 \times 10^{-4}$ | 24.6 | 27.1 | $1.82 \times 10^{-3}$ |
| Ar | 18 | 39.95 | 190 | 1520 | 96 | $1.8 \times 10^{-3}$ | 83.8 | 87.2 | 0.934 |
| Kr | 36 | 83.80 | 200 | 1351 | 96 | $3.7 \times 10^{-3}$ | 115.8 | 119.7 | $1.14 \times 10^{-4}$ |
| Xe | 54 | 131.30 | 220 | 1170 | 77 | $5.9 \times 10^{-3}$ | 161.3 | 165.0 | $8.7 \times 10^{-6}$ |
| Rn | 86 | 222.00 | - | 1037 | 68 | $9.7 \times 10^{-3}$ | 202 | 211 | - |

**iii. Electronegativity :** In a group (16, 17 and 18) the electronegativity decreases down the group.

* Oxygen has the highest electronegativity next to fluorine amongst all the elements.

* Halogens have very high electronegativity. Fluorine is the most electronegative element in the periodic table.

**iv. Electron gain enthalpy :** In the groups 16 and 17 electron gain enthalpy becomes less negative down the group.

However in group 16, oxygen has less negative electron gain enthalpy than sulfur due to its small atomic size.

* In group 17, fluorine has less negative electron gain enthalpy than that of chlorine. This is due to small size of fluorine atom.

* Group 18 elements (noble gases) have no tendency to accept electrons because of their stable electronic configuration ($ns^2np^6$) and thus have large positive electron gain enthalpy.

**Try this...**

- Observe Table no 7.3 and explain the trend in following atomic properties of group 17 elements.

i. Atomic size, ii. Ionisation enthalpy, iii. electronegativity, iv. electron gain enthalpy

- Oxygen has less negative electron gain enthalpy than sulfur. Why ?

**Problem 7.1 :** Elements of group 16 generally show lower values of first ionisation enthalpy compared to the elements of corresponding period of group 15. Why ?

**Solution :** Group 15 elements have extra stable, half filled p-orbitals with electronic configuration ($ns^2np^3$). Therefore more amount of energy is required to remove an electron compared to that of the partially filled orbitals ($ns^2np^4$) of group 16 elements of the corresponding period.

**Problem 7.2 :** The values of first ionisation enthalpy of S and Cl are 1000 and 1256 kJ $mol^{-1}$, respectively. Explain the observed trend.

**Solution :** The elements S and Cl belong to second period of the periodic table.

Across a period effective nuclear charge increases and atomic size decreases with increase in atomic number.

Therefore the energy required for the removal of electron from the valence shell (I.E.) increases in the order $S < Cl$.

### 7.4.2 Physical properties of group 16, 17 and 18 elements :

**a. Group 16 elements (Oxygen family or chalcogens) :** Oxygen is a gas while other elements are solids at room temperature.

Oxygen and sulfur are nonmetals, selenium and tellurium are metalloids, while polonium is a metal. Polonium is radioactive with its half life of 13.8 days.

Melting and boiling points increase with increasing atomic number.

All the elements of group 16 exhibit allotropy.

**Problem 7.3 :** Why is there a large difference between the melting and boiling points of oxygen and sulfur ?

**Solution :** Oxygen exists as diatomic molecule ($O_2$) where as sulfur exists as polyatomic molecule ($S_8$).

The van der Waals forces of attraction between $O_2$ molecules are relatively weak owing to its much smaller size.

The large van der Waals attractive forces in the $S_8$ molecules can be noticed because of large molecular size. Therefore oxygen has low m.p. and b.p. as compared to sulfur.

**b. Group 17 elements (Halogen family) :**

Fluorine, chlorine are gases, bromine is a liquid and iodine is a solid at room temperature. $F_2$ is yellow, $Cl_2$ greenish yellow, $Br_2$ red and $I_2$ is violet, in colour.

Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water and are soluble in various organic solvents such as chloroform, carbon disulfide, carbon tetrachloride, hydrocarbons which give coloured solutions. Bond dissociation enthalpies of halogen molecules follow the order : $Cl - Cl > Br - Br > F - F > I - I$.

**Problem 7.4 :** Fluorine has less negative electron gain affinity than chlorine. Why ?

**Solution :** The size of fluorine atom is smaller than chlorine atom. As a result, there are strong inter electronic repulsions in the relatively small 2p orbitals of fluorine and therefore, the incoming electron does not experience much attraction. Thus fluorine has less negative electron gain affinity than chlorine.

**Problem 7.5 :** Bond dissociation enthalpy of $F_2$ (158.8 KJ $mol^{-1}$) is lower than that of $Cl_2$ (242.6 KJ $mol^{-1}$) Why ?

**Solution :** Fluorine has small atomic size than chlorine. The lone pairs on each F atoms in $F_2$ molecule are so close together that they strongly repel each other, and make the F - F bond weak (fig. 7.1) Thus it requires less amount of energy to break the F - F bond. In $Cl_2$ molecule the lone pairs on each Cl atom are at a larger distance and the repulsion is negligible. Thus Cl - Cl bond is comparitively stronger. Therefore bond dissociation enthalpy of $F_2$ is lower than that of $Cl_2$.

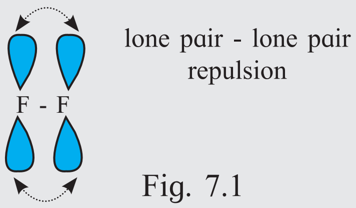


Fig. 7.1

**c. Group 18 elements (Noble gases) :**

Noble gases are monoatomic.

They are sparingly soluble in water.

Noble gases have very low melting and boiling points. Helium has the lowest boiling point (4.2 K) of any known substances.

**Problem 7.6 :** Noble gases have very low melting and boiling points. Why ?

**Solution :** Noble gases are monoatomic, the only type of inter atomic interactions which exist between them are van der Waals forces. Therefore, they can be liquified at very low temperatures and have very low melting or boiling points.

**Can you tell ?**

The first member of a group usually differs in properties from the rest of the members of the group. Why ?

## 7.5 Anamalous Behaviour

### 7.5.1 Anomalous behaviour of oxygen :

Oxygen shows the following anomalous properties compared to other members of group 16 :

**i. Atomicity :** Oxygen is a diatomic molecule ($O_2$) while others are polyatomic molecules. For example $P_4$, $S_8$.

**ii. Magnetic property :** Oxygen is paramagnetic while others are diamagnetic.

**iii. Oxidation state :** Oxygen shows -2, -1, and +2 oxidation states while other elements show, -2, +2, +4, +6 oxidation states. Oxygen can not exhibit higher oxidation state due to absence of vacant d orbitals.

**Use your brain power**

- Oxygen forms only $OF_2$ with fluorine while sulfur forms $SF_6$. Explain. Why ?

**iv. Nature of hydrides :** Hydride of oxygen ($H_2O$) is liquid at room temperature while hydrides of other members of the group are gases.

**Use your brain power**

- Which of the following possess hydrogen bonding ? $H_2S$, $H_2O$, $H_2Se$, $H_2Te$
- Show hydrogen bonding in the above molecule with the help of a diagram.

**v.** Common covalency of oxygen is 2. In rare cases it is four. But for the other members of the group 16 the covalency can exceed four.

The anomalous behaviour of oxygen is due to the following reasons.

i. small atomic size

ii. high electronegativity.

iii. absence of inner d-orbitals.

### 7.5.2 Anomalous behaviour of fluorine :

Fluorine, the first member of group 17, differs in properties from the other members of the group. The anomalous behaviour of fluorine is due to the following reasons.

i. small atomic size

ii. high electronegativity

iii. absence of d-orbitals in valence shell

iv. low F-F bond dissociation enthalpy

**Some anomalous properties of fluorine :**

i. Ionisation enthalpy, electronegativity, electrode potential are all higher for fluorine than expected trends shown by other halogens.

ii. Ionic and covalent radii, m.p., b.p. and electron gain enthalpy are quite lower than expected.

iii. Most of the reactions of fluorine are exothermic (due to the short and strong bond formed by it with other elements).

iv. It forms only one oxoacid (HOF) while other halogens form a number of oxoacids.

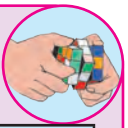
v. Hydrogen fluoride is a liquid (b.p. 293K) due to strong hydrogen bonding while other hydrogen halides are gases.

## 7.6 Chemical Properties of elements of groups 16, 17 and 18

**7.6.1 Oxidation state : i. The group 16 elements** have the valence shell electronic configuration $ns^2np^4$. They attain a noble gas configuration either by gaining two electrons, forming $E^{2\ominus}$ ions or by sharing two electrons, forming two covalent bonds. These elements, thus, show -2 and +2 oxidation states in their compounds.

Oxygen being highly electronegative, shows common oxidation state of -2 except two cases. In the case of $OF_2$, its oxidation state is +2 and in peroxides, it shows oxidation state -1 ($H_2O_2$, $Na_2O_2$). Other elements of the group exhibit +2, +4, +6 oxidation states with +4 and +6 being more common. The stability of higher (+6) oxidation state decreases down the group while the stability of the lower oxidation state (+4) increases down the group due to inert pair effect. Bonding in +4 and +6 oxidation states are primarily covalent.

**Try this...**



Complete the following tables

| Element | O | O | S | F |
|---|---|---|---|---|
| compound | $H_2O$ | $OF_2$ | $H_2S$ | HF |
| Oxidation state | -2 | ...... | ...... | ...... |
| Element | Se | Se | Te | Cl |
| compound | $SeO_2$ | $SeO_3$ | $TeF_6$ | HOCl |
| Oxidation state | ...... | +6 | ...... | ...... |

**ii. The group 17 elements** are represented by their valence shell electronic configuration as $ns^2np^5$. They attain noble gas configuration either by gaining one electron forming $E^{\ominus}$ ions or by sharing one electron forming one covalent bond.

All halogens exhibit -1 oxidation state. However Cl, Br and I exhibit +1, +3, +5 and +7 oxidation states as well. This is because they are less electronegative than F and possess empty d-orbitals in the valence shell and therefore, can expand the octet. The oxidation states +4 and +6 occur in the oxides and oxoacids of Cl and Br.

The fluorine atom has no d - orbitals in its valence shell and therefore cannot expand its octet. Thus fluorine being most electronegative exhibits mostly -1 oxidation state.

**iii. Group 18 elements (noble gases)** have stable valence shell electronic configuration $ns^2np^6$ with completely filled orbitals. Thus they have no tendency to gain or lose electrons, that is, they are zero valent and mostly exist as monoatomic gases. However, xenon has large atomic size and lower ionisation enthalpy compared to He, Ne, Ar and Kr. Hence xenon exhibits higher oxidation states. Its outermost shell has d-orbitals. The paired electrons of the valence shell can be unpaired and promoted to empty d-orbitals. The unpaired electrons are shared with fluorine or oxygen atoms and covalent compounds showing higher oxidation state such as $XeF_2$(+2), $XeF_4$ (+4), $XeF_6$ (+6), $XeO_3$ (+6) and $XeOF_4$ (+6) are formed.

### 7.6.2 Chemical Reactivity towards hydrogen:

**i. Group 16 elements :** The elements of group 16 react with hydrogen to form hydrides of the type $H_2E$. (Where E = O, S, Se, Te, Po).

For example, $H_2O$, $H_2S$, $H_2Se$, $H_2Te$ and $H_2Po$. Some properties of hydrides of group 16 are given in Table 7.5.

$H_2O$ is a colourless, odourless liquid, while $H_2S$, $H_2Se$, $H_2Te$ and $H_2Po$ are colourless bad smelling, poisonous gases at ambient conditions.

All hydrides have angular structures which involve $sp^3$ hybridisation of central atom (E).

The hydrides of group 16 elements are weakly acidic. The acidic character of the hydrides increases, while thermal stability decreases from $H_2O$ to $H_2Te$. This is due to decrease in the bond dissociation enthalpy of the H-E bond down the group (Table 7.5).

All hydrides except $H_2O$ possess reducing property which increases in the order $H_2S < H_2Se < H_2Te$.

**ii. Group 17 elements :** The elements of group 17 react with hydrogen to give hydrogen halides.

$$H_2 + X_2 \longrightarrow 2HX$$

(Where X = F, Cl, Br, I)

Some of the properties of hydrogen halides are given in Table 7.6.

Acidic strength of halogen acids increases in the order :

HF < HCl < HBr < HI

It is due to decreasing bond dissociation enthalpy of H-X bond in the order
HF > HCl > HBr > HI.

Thermal stability of hydrogen halides decreases in the order HF>HCl>HBr>HI. It is due to decrease in bond dissociation enthalpy of H-X bond down the group.

**Table 7.5 Properties of hydrides of group 16 elements**

| **Property** | **$H_2O$** | **$H_2S$** | **$H_2Se$** | **$H_2Te$** |
|---|---|---|---|---|
| m.p (K) | 273 | 188 | 208 | 222 |
| b.p (K) | 373 | 213 | 232 | 269 |
| H-E Bond length (pm) | 96 | 134 | 146 | 169 |
| $\Delta_{diss}H$ (H-E) kJ/mol | 463 | 347 | 276 | 238 |
| $\Delta_f H$ kJ/mol | -286 | -20 | 73 | 100 |
| HEH angle (°) | 104 | 92 | 91 | 90 |
| $pK_a$ | 14.0 | 7.0 | 3.8 | 2.6 |

**Table 7.6 Properties of hydrides of group 17 elements.**

| Property | HF | HCl | HBr | HI |
|---|---|---|---|---|
| m.p (K) | 190 | 159 | 185 | 222 |
| b.p (K) | 293 | 189 | 206 | 238 |
| Bond length (H-X) pm | 91.7 | 127.4 | 141.4 | 160.9 |
| $\Delta_{diss}H^0$ kJ/mol | 574 | 432 | 363 | 295 |
| pKa | 3.2 | -7.0 | -9.5 | -10.0 |

**iii. Group 18 elements (Noble gases) :**

Noble gases are chemically inert towards hydrogen due to their stable electronic configuration.

### 7.6.3 Reactivity towards oxygen :

**i. Group 16 elements :** All the elements of group 16 form oxides of the type $EO_2$ and $EO_3$ where E = S, Se, Te, Po.

**$EO_2$ type oxides,** Ozone ($O_3$) and sulfur dioxide ($SO_2$) are gases, while selenium dioxide ($SeO_2$) is solid. They are acidic in nature and react with water to form acids.

$SO_2 + H_2O \longrightarrow H_2SO_3$ (Sulfurous acid)

$SeO_2 + H_2O \longrightarrow H_2SeO_3$ (Selenious acid)

Reducing property of dioxides decreases from $SO_2$ to $TeO_2$. $SO_2$ is reducing while $TeO_2$ serves as an oxidising agent.

**$EO_3$ type oxides,** $SO_3$, $SeO_3$, $TeO_3$ are also acidic in nature. They dissolve in water to form acids.

$SeO_3 + H_2O \longrightarrow H_2SeO_4$ (Selenic acid)

$TeO_3 + 3H_2O \longrightarrow H_6TeO_6$ (Telluric acid)

**ii. Group 17 elements :** Elements of group 17 (Halogens) form many oxides with oxygen, but most of them are unstable.

Fluorine forms two oxides $OF_2$ and $O_2F_2$. However, only the $OF_2$ is thermally stable at 298 K. Both are strong fluorinating agents. $O_2F_2$ oxidises plutonium to $PuF_6$ and the reaction is used in removing plutonium as $PuF_6$ from spent nuclear fuel.

Chlorine oxides, $Cl_2O$, $ClO_2$, $Cl_2O_6$ and $Cl_2O_7$ are highly reactive oxidising agents and tend to explode.

$ClO_2$ is used as bleaching agent for paper pulp and textiles and in water treatment.

Bromine oxides, $Br_2O$, $BrO_2$, $BrO_3$ are the least stable halogen oxides (middle row anomaly). They are very powerful oxidising agents.

Iodine oxides, $I_2O_4$, $I_2O_5$ and $I_2O_7$ are insoluble solids and decompose on heating. $I_2O_5$ is a very good oxidising agent and used for the estimation of carbon monoxide.

The higher oxides of halogens are more stable than the lower ones.

**iii. Group 18 elements :** Noble gas elements are chemically inert and do not directly react with oxygen.

### 7.6.4 Reactivity towards halogens :

**i. Group 16 elements :** Elements of group 16 react with halogens to give a large number of halides of the types $EX_6$ , $EX_4$ and $EX_2$. (Where E = S, Se, Te)

**Hexahalides**, $SF_6$, $SeF_6$ and $TeF_6$ are formed by direct combination. They are colourless gases. They have $sp^3d^2$ hybridisation and possess octahedral structure. $SF_6$ is exceptionally stable halide for steric reasons.

Stability of halides decreases in the order fluorides > chlorides > bromides > iodides

**Tetrahalides**, $SF_4$, $SeF_4$, $TeF_4$, $TeCl_4$ have $sp^3$ hybridisation and thus trigonal bipyramidal geometry with one equatorial position occupied by a lone pair.

**Dihalides**, $SCl_2$, $SeCl_2$, $TeCl_2$ have $sp^3$ hybridisation and thus possess tetrahedral structure with two equatorial positions occupied by lone pairs.

Monohalides are dimeric in nature. For example, $S_2F_2$, $S_2Cl_2$, $Se_2Cl_2$ and $SeBr_2$. These dimeric halides undergo disproportionation.

$$2\ Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$$

**Internet my friend**

Find and draw the structures of $SeF_4$ and $SCl_2$.

**ii. Group 17 elements :**

Halogens (Group 17 elements) combine amongst themselves to form a number of compounds known as interhalogen compounds.

These are of following types : XX', $XX'_{3,}$ $XX'_{5,}$ $XX'_{7,}$

Where X is the halogen atom with larger size and X' is the halogen atom with smaller size. More details of interhalogen compounds are included in section 7.12.

**iii. Group 18 elements :** Group 18 elements (Noble gases) are chemically inert. Krypton and xenon, however react directly with fluorine to give their fluorides. For example,

$$Xe(g) + F_2(g) \xrightarrow[1\ atm]{673K} XeF_2(s)$$

Xenon fluorides $XeF_2$, $XeF_4$ and $XeF_6$ are crystalline and colourless which sublime readily at 298 K. They are powerful fluorinating agents.

### 7.6.5 Reactivity towards metals :

**i. Group 16 elements :** Elements of group 16 react with metals to form corresponding compounds.

e.g. $4Al + 3O_2 \longrightarrow 2Al_2O_3$

$Cu + S \longrightarrow CuS$

$Mg + Se \longrightarrow MgSe$

magnesium selenide

**Do you know ?**

Tellurium has the unusal property of combining with gold metal to form telluride.

$2Au + 3Te \longrightarrow Au_2Te_3$

(gold telluride)

**Internet my friend**

www.chemistry.explained.com

### ii. Group 17 elements :

Elements of group 17 (Halogens) react with metals instantly to give metal halides.

$2Na\ (s) + Cl_2\ (g) \longrightarrow 2NaCl\ (s)$

$Mg\ (s) + Br_2\ (l) \longrightarrow MgBr_2\ (s)$

magnesium bromide

Ionic character of halides decreases in the order MF > MCl > MBr > MI, where M is a monovalent metal.

The metal halides having metals in their higher oxidation states are more covalent than the ones having metals in lower oxidation state. 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.

**iii. Group 18 elements :** Noble gases do not directly react with metals.

## 7.7 Allotropy :

**Can you tell ?**

- What is allotropy ?
- What is the difference between allotropy and polymorphism ?

Elements of the group 16 exhibit allotropy. Oxygen has two allotropes $O_2$ and $O_3$ (ozone). Sulfur exists in a number of allotropic forms. Rhombic and monoclinic sulfur are the important allotropes of sulfur. Both are non metallic.

- Selenium exists in two allotropic forms red (non metallic) and grey (metallic).

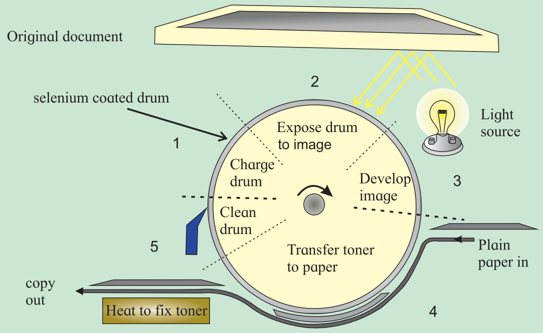
**Do you know ?**

Grey selenium allotrope of Se is a photoconductor used in photocells.

**Do you know ?**

The photocopying process.

A selenium-coated rotating drum is given a uniform positive charge (step 1) and is then exposed to an image (step 2). Negatively charged toner particles are attracted to the charged area of the drum (step 3) and the image is transferred from the drum to a sheet of paper (step 4). Heating then fixes the image and the drum is flooded with light and cleaned to ready the machine for another cycle (step 5). Figure of photocopying process using Se is as shown below :



- Tellurium exists in two allotropic forms (i) crystalline and (ii) amorphous.
- Polonium reveals two allotropic forms α and β (both metallic).

### 7.7.1 Allotropes of sulfur :

Sulfur exhibits numerous allotropic forms. However rhombic sulfur (α- sulfur) and monoclinic sulfur (β - sulfur) are the most important allotropes of sulfur (Table 7.7).

**Problem 7.7 :** Which form of sulfur shows paramagnetic behaviour ?

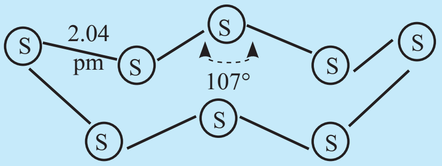
**Solution :** In vapour state, sulfur partly exists as $S_2$ molecule, which has two unpaired electrons in the antibonding $\pi^*$ orbitals like $O_2$. Hence it exhibits paramagnetism.

**Table 7.7 Allotropes of sulfur**

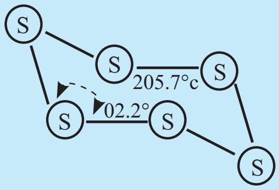
| | Rhombic Sulfur ($\alpha$ - Sulfur) | Monoclinic Sulfur ($\beta$ - Sulfur) |
|---|---|---|
| Color | Pale Yellow | Bright yellow solid |
| Shape | Orthorhombic crystals | Needle shaped monoclinic crystals |
| M. P. | 385.8 K | 393 K |
| Density | 2.069/ $cm^3$ | 1.989 / $cm^3$ |
| Solubility | Insoluble in water and soluble in $CS_2$ | Soluble in $CS_2$ |
| Stability | Stable below 369 K and transforms to $\beta$ - Sulphur above this temperature. | Stable above 369 K and transforms into $\alpha$ - Sulphur below this temperature. |
| Structure | $S_8$ molecules having puckered ring structure | $S_8$ molecules with puckered ring structure |
| Method of preparation | It is prepared by evaporation of roll sulphur in $CS_2$. | Rhomic sulphur melted in a dish and cooled till crust is formed. Two holes are made in the crust and remaining liquid is poured out to give needle shaped crystals of $\beta$ - Sulphur |

**Remember...**

Several modifications of sulfur containing 6-20 sulfur atoms per ring, have been synsthesised. In the $S_8$ molecule the ring is puckered and has a crown shape. In cyclo - $S_6$, the ring adopts the chair form. At elevated temperature (~ 1000 K), $S_2$ is the dominant species which like $O_2$ is paramagnetic.



Structure of $S_8$ ring in rhombic sulfur

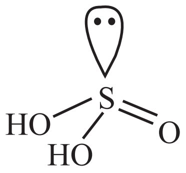


Chair form of $S_6$

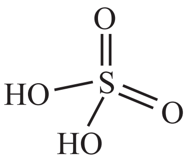
## 7.8 Oxoacids

**7.8.1 Oxoacids of sulfur :** Sulfur forms a number of oxoacids. Some of them are unstable and cannot be isolated. They are known to exist in aqueous solutions or in the form of their salts.

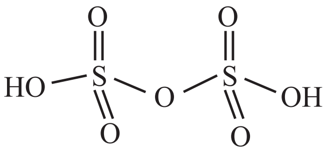
Some important oxoacids of sulfur and their structures are given below.



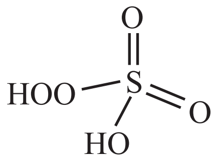
i. Sulfurous acid, $H_2SO_3$



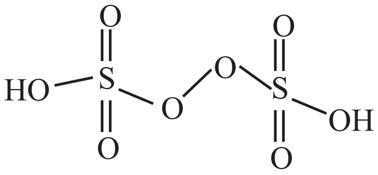
ii. Sulfuric Acid, $H_2SO_4$



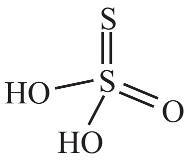
iii. Di or pyrosulfuric acid, $H_2S_2O_7$



iv. Peroxy monosulfuric acid, $H_2SO_5$



v. Peroxy disulfuric acid, $H_2S_2O_8$



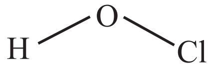
vi. Thiosulfuric acid, $H_2S_2O_3$

**7.8.2 Oxoacids of halogens : :**Halogens form several oxoacids (See Table 7.8). Only four oxoacids have been isolated in pure form: hypofluorous acid (HOF), perchloric acid ($HClO_4$), iodic acid ($HIO_3$), metaperiodic acid ($H_5IO_6$). The others are stable only in aqueous solutions or in the form of their salts.

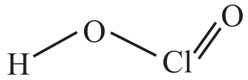
The acid strength of the halogen oxoacids increases with the increasing oxidation state of halogen. For example, acid strength increases from HClO, a weak acid ($K_a = 3.5 \times 10^{-8}$), to $HClO_4$, a very strong acid ($K_a >> 1$).

**Strucutres of oxoacids of chlorine :**

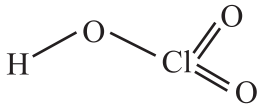
i. Hypochlorous acid, HOCl



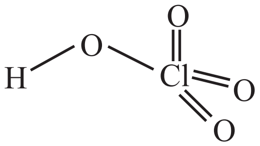
ii. Chlorous acid, HOClO or $HClO_2$



iii. Chloric acid, $HClO_3$



iv. Perchloric acid, $HClO_4$



## 7.9 Oxygen and Compounds of oxygen

### 7.9.1 Dioxygen

**a. Preparation**

**i. Laboratory methods :**

- By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_{3(s)} \xrightarrow[MnO_2]{Heat} 2KCl_{(s)} + 3O_{2(g)}$$

- By thermal decomposition of oxides of metals.

$$2Ag_2O_{(s)} \xrightarrow{\Delta} 4Ag_{(s)} + O_{2(g)}$$

$$2HgO_{(s)} \xrightarrow{\Delta} 2Hg_{(l)} + O_{2(g)}$$

Table 7.8 Oxoacids of halogens

| oxidation state of X | Generic name | Oxoacids of fluorine | Oxoacids of chlorine | Oxoacids of bromine | Oxoacids of iodine |
|---|---|---|---|---|---|
| +1 | Hypohalous acid (HXO) | HOF | HOCl | HOBr | HOI |
| +3 | Halous acid ($HXO_2$) | - | HOClO | - | - |
| +5 | Halic acid ($HXO_3$) | - | $HOClO_2$ | $HOBrO_2$ | $HOIO_2$ |
| +7 | Perhalic acid ($HXO_4$) | - | $HOClO_3$ | $HOBrO_3$ | $HOIO_3$ |

$$2PbO_{2(s)} \xrightarrow{\Delta} 2PbO_{(s)} + O_{2(g)}$$

- By decomposition of hydrogen peroxide in presence of catalyst such as finely divided metals and manganese dioxide.

$$2H_2O_{2(aq)} \xrightarrow[MnO_2]{\Delta} 2H_2O_{(l)} + O_{2(g)}$$

**ii. Electrolysis :** Dioxygen can be prepared on large scale by electrolysis of water, when hydrogen is liberated at cathode and oxygen at anode.

$$2H_2O \xrightarrow{\text{Electrolysis}} 2H_2 + O_2$$

**iii. Industrial method :** Dioxygen is obtained from air, by first removing carbon dioxide and water vapour. The remaining gases are liquified subsequently. This is followed by fractional distillation which gives dinitrogen and dioxygen.

### b. Physical properties :

- Dioxygen is colourless and odourless gas.
- Dioxygen is sparingly soluble in water, 30.8 $cm^3$ of $O_2$ dissolves in 1000 $cm^3$ of water at 293 K. A small amount of dissolved dioxygen is sufficient to sustain marine and aquatic life.
- It liquifies at 90 K and freezes at 55 K.
- Oxygen has three stable isotopes $^{16}O$, $^{17}O$ and $^{18}O$.
- Molecular oxygen, $O_2$ exhibits paramagnetism.

### c. Chemcial Properties :

**i. Reaction with metals :** Dioxygen directly reacts with almost all metals except Au, Pt to form their oxides.

$$2Ca + O_2 \longrightarrow 2CaO$$

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

**ii. Reaction with nonmetals :** Dioxygen reacts with nonmetals (except noble gases) to form their oxides.

$$C + O_2 \longrightarrow CO_2$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

**iii. Reaction with some compounds :**

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

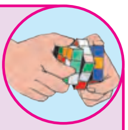
$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

$$4HCl + O_2 \xrightarrow[\Delta]{CuCl_2} 2Cl_2 + 2H_2O$$

### d. Uses

- Dioxygen is important for respiration to sustain animal and aquatic life.
- It is used in the manufacture of steel.
- It is used in oxyacetylene flame for welding and cutting of metals.
- Oxygen cylinders are widely used in hospitals, high altitude flying and mountaineering.
- It is used in combustion of fuels; for example, hydrazine in liquid oxygen provides tremendous thrust (energy) in rockets.

**Try this...**



Why water in the fish pot needs to be changed time to time ?

**Problem : 7.8**

Dioxygen is paramagnetic inspite of having even number of electrons. Explain.

**Solution :** Dioxygen is a covalently bonded molecule.

:Ö::Ö: or :Ö=Ö:

Paramagnetic behaviour of $O_2$ can be explained with the help of molecular orbital theory .

Electronic configuration of $O_2$

KK $\sigma(2s)^2$ $\sigma^*(2s)^2$ $\sigma(2p_z)^2$ $\pi(2p_x)^2$ $\pi(2p_y)^2$ $\pi^*(2p_x)^1$ $\pi^*(2p_y)^1$. Presence of two unpaired electrons explains paramagnetic nature of dioxygen.

**7.9.2 Simple Oxides :** A binary compound of oxygen with another element is called an oxide.

Oxides can be classified into

a. Acidic oxides  b. Basic oxides

c. Amphoteric oxides d. Neutral oxides

**a. Acidic oxides :** An oxide which dissolves in water to give an acid or reacts with a base to give a salt is called acidic oxide. For example, $SO_2$, $SO_3$, $CO_2$, $N_2O_5$, $Cl_2O_7$ etc.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$$

Generally, oxides of nonmetals are acidic oxides.

**b. Basic oxides :** An oxide which dissolves in water to give a base or reacts with an acid to give salt is called basic oxide. For example,

$Na_2O$, $CaO$, $BaO$ etc.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$BaO + 2HCl \longrightarrow BaCl_2 + H_2O$$

**c. Amphoteric oxides :** The oxide which reacts with a base as well as with an acid to give salt is called an amphoteric oxide. For example, $Al_2O_3$

$$Al_2O_{3(s)} + 6NaOH_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Na_3[Al(OH)_6]_{(aq)}$$

(Acidic)

$$Al_2O_{3(s)} + 6HCl_{(aq)} + 9H_2O_{(l)} \longrightarrow 2[Al(H_2O)_6]^{3\oplus}_{(aq)} + 6Cl^{\ominus}_{(aq)}$$

(Basic)

**d. Neutral oxides :** The oxides which are neither acidic nor basic, are called as neutral oxides. For example, $CO$, $NO$, $N_2O$ etc.

**7.9.3 Ozone :** Ozone ($O_3$) is an allotrope of oxygen. Oxygen in the upper atmosphere absorbs energy in the form of ultra-violet light and changes to atomic oxygen, which combines with molecular oxygen to form $O_3$.

$$O_2 \xrightarrow{\text{U.V. light}} O + O$$

$$O_2 + O \longrightarrow O_3$$

The layer of ozone protects the earth's surface from harmful ultraviolet (U.V) radiations. Hence, it is called as 'ozone umbrella'.

**a. Preparation of Ozone :** Ozone is prepared in the laboratory by passing silent electric discharge through pure and dry oxygen in an apparatus called ozoniser. As the conversion of oxygen to ozone is only 10%, the product is known as ozonised oxygen. It is an endothermic process.

$$3O_{2(g)} \rightleftharpoons 2O_3 \qquad \Delta H = +142 \text{ kJ/mol}$$

**b. Physical properties of ozone :**

i. Pure Ozone is a pale - blue gas, dark blue liquid and violet - black solid.

ii. Ozone has a characteristic smell. When inhaled in concentration above 100 ppm, it causes nausea and headache.

iii. It is diamagnetic in nature.

**Problem 7.9 :** High concentration of ozone can be dangerously explosive. Explain.

**Solution :** i. Thermal stability : Ozone is thermodynamically unstable than oxygen and decomposes into $O_2$. The decomposition is exothermic and results in the liberation of heat ($\Delta H$ is -ve) and an increase in entropy ($\Delta S$ is positive). This results in large negative Gibbs energy change ($\Delta G$). Therefore high concentration of ozone can be dangerously explosive.

Eq. $O_3 \longrightarrow O_2 + O$

**c. Chemical Properties :**

**i. Oxidising property :**

Ozone is a powerful oxidising agents as it easily decomposes to liberate nascent oxygen. ($O_3 \longrightarrow O_2 + O$).

Ozone oxidises lead sulfide to lead sulfate and iodide ions to iodine.

$$PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$$

$$2KI(aq) + H_2O(l) + O_3(g) \longrightarrow 2KOH(aq) + I_2(g) + O_2(g)$$

Ozone oxidises nitrogen oxide and gives nitrogen dioxide.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Hence the nitrogen oxide emitted from the exhaust systems of supersonic jet aeroplanes can bringforth depletion of ozone layer in the upper atmosphere.

**ii. Bleaching property :** Ozone acts as a good bleaching agent due to its oxidising nature.

$O_3 \longrightarrow O + O_2$

Coloured matter + O $\longrightarrow$ colourless matter

Ozone bleaches in absence of moisture so it is also known as dry bleach.

**iii. Reducing property :** Ozone reduces peroxides to oxides.

e.g. $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$BaO_2 + O_3 \longrightarrow BaO + 2O_2$

**Try this...**

a. Ozone is used as bleaching agent. Explain.

b. Why does ozone act as a powerful oxidising agent ?

**iv. Ozone depletion :** Thinning of ozone layer in upper atmosphere is called ozone depletion.

- The ozone ($O_3$) layer in the upper atmosphere, absorbs harmful UV radiations from the sun, thus protecting people on the earth.
- Depletion of ozone layer in the upper atmosphere is caused by nitrogen oxide released from exhausts system of car or supersonic jet aeroplanes.

$$NO\ (g) + O_3\ (g) \longrightarrow NO_2\ (g) + O_2\ (g)$$

- Depletion (thinning) of ozone layer can also be caused by chlorofluoro carbons (freons) used in aerosol and refrigerators and their subsequent escape into the atmosphere.
- The depletion of ozone layer has been most pronounced in polar regions, especially over Antarctica.
- Ozone depletion is a major environmental problem because it increases the amount of ultraviolet (UV) radiation that reaches earth's surface, thus causing an increase in rate of skin cancer, eye cataracts and genetic as well as immune system damage among people.

**Do you know ?**

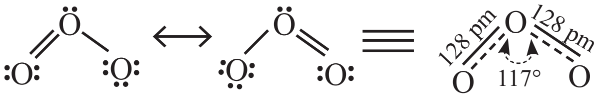
Ozone reacts with unsaturated compounds containing double bonds to form addition products called ozonides. Ozonides are decomposed by water or dilute acids to give aldehydes or ketones. This reaction is termed as ozonolysis.

**Internet my friend**

www.britannica.com

ozone depletion.

**d. Structure of Ozone :** Ozone ($O_3$) is an angular molecule. The two O — O bond lengths in the ozone molecule are identical, 128 pm and the O — O — O bond angle is about 117°. It is a resonance hybrid of two canonical forms.



**e. Uses of ozone :**

- Ozone is used for air purification at crowded places like cinema halls, tunnels, railways, etc.
- In sterilizing drinking water by oxidising all germs and bacteria.
- For bleaching ivory, oils, starch, wax and delicate fabrics such as silk.
- In the manufacture of synthetic camphor, potassium permanganate, etc.

## 7.10 Compounds of sulfur :

### 7.10.1 Sulfur dioxide

**a. Preparation :**

**i. From sulfur :** Sulfur dioxide gas can be prepared by burning of sulfur in air.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

**ii. From sulfite :** In the laboratory sulfur dioxide is prepared by treating aqueous solution of sodium sulfite with dilute sulfuric acid.

$$Na_2SO_3 + H_2SO_4(aq) \longrightarrow Na_2SO_4 + H_2O(l) + SO_2(g)$$

**iii. From sulfides : (Industrial method)**

Sulfur dioxide can be prepared by roasting zinc sulfide and iron pyrites.

$$2ZnS(s) + 3O_2(g) \xrightarrow{\Delta} 2ZnO(s) + 2SO_2(g)$$

$$4FeS_2(s) + 11O_2(g) \xrightarrow{\Delta} 2Fe_2O_3(s) + 8SO_2(g)$$

**b. Physical properties of $SO_2$**

i. Sulfur dioxide is a colourless gas with a pungent smell.

ii. It is poisonous in nature.

iii. $SO_2$ is highly soluble in water and its solution in water is called sulfurous acid.

iv. It liquifies at room temperature under a pressure of 2 atm and boils at 263 K.

**c. Chemical Properties :**

**i. Reaction with $Cl_2$ :** Sulfur dioxide reacts with chlorine in the presence of charcoal (catalyst) to form sulfuryl chloride.

$$SO_2(g) + Cl_2(g) \xrightarrow{\text{charcoal}} SO_2Cl_2(l)$$

**ii. Reaction with $O_2$ :** Sulfur dioxide is oxidised by dioxygen in presence of vanadium (V) oxide to sulfur trioxide.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

**iii. Reaction with NaOH :** Sulfur dioxide readily reacts with sodium hydroxide solution to form sodium sulfite.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

**iv. Reaction with $Na_2SO_3$ :** Sulfur dioxide reacts with sodium sulfite solution to form sodium hydrogen sulfite.

$$Na_2SO_3 + H_2O(l) + SO_2 \longrightarrow 2NaHSO_3$$

**v. Reducing property :** Sulfur dioxide acts as a reducing agent in the presence of moisture.

- Moist sulfur dioxide reduces ferric salts into ferrous salts.

$$2Fe^{3\oplus} + SO_2 + 2H_2O \longrightarrow 2Fe^{2\oplus} + SO_4^{2\ominus} + 4H^{\oplus}$$

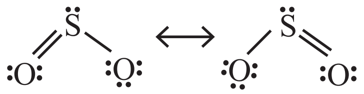
- Moist sulfur dioxide decolourises acidified potassium permanganate (VII) solution.

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

- Moist sulfur dioxide reduces halogens to halogen acids.

$$I_2 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HI$$

**d. Structure of $SO_2$ :** Sulfur dioxide is angular with O — S — O bond angle of 119.5°.



The S — O double bond arises from dπ - pπ bonding. It is a resonance hybrid of two canonical forms.

**e. Uses :** Sulfur dioxide is used

- In refining of petroleum and sugar.
- In bleaching wool and silk.
- As an anti-chlor, disinfectant.
- As a preservative.
- In the manufacture of $H_2SO_4$, $NaHSO_3$.
- Liquid $SO_2$ is used as a solvent to dissolve a number of organic and inorganic chemicals.

### 7.10.2 Sulfuric acid, $H_2SO_4$

**a. Preparation :** Sulfuric acid is manufactured by **Contact process**, which involves the following three steps.

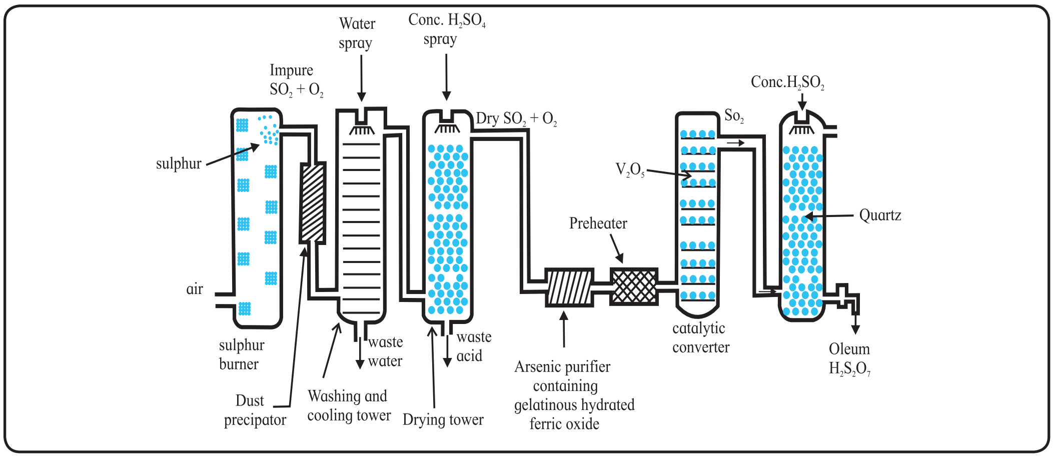


Fig. 7.1 : Flow diagram for manufacture of Sulfuric acid

i. Sulfur or sulfide ore (iron pyrites) on burning or **roasting in air** produces sulfur dioxide.

$$S(s) + O_2(g) \xrightarrow{\Delta} SO_2\,(g)$$

$$4FeS_2(s) + 11O_2(g) \xrightarrow{\Delta} 2Fe_2O_3(s) + 8SO_2(g)$$

ii. **Sulfur dioxide is oxidised catalytically** with oxygen to sulfur trioxide, in the presence of $V_2O_5$ catalyst.

$$2SO_2(g) + O_2 \xrightarrow{V_2O_5} 2SO_3(g)$$

The reaction is exothermic and reversible and the forward reaction leads to decrease in volume. Therefore low temperature (720K) and high pressure (2 bar) are favourable conditions for maximum yield of $SO_3$.

iii. **Sulfur trioxide gas** (from the catalytic converter) **is absorbed in concentrated $H_2SO_4$** to produce oleum.

Dilution of oleum with water gives sulfuric acid of desired concentration.

$$SO_3(g) + H_2SO_4 \longrightarrow \underset{\text{oleum}}{H_2S_2O_7}$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The sulfuric acid obtained by contact process is 96 - 98 % pure.

**b. Physical properties of $H_2SO_4$ :**

i. Sulfuric acid is a colourless, dense, oily liquid.

ii. It has a density (specific gravity) of 1.84 g/cm³ at 298 K.

iii. It freezes at 283 K and boils at 611 K.

iv. It is highly corrosive and produces severe burns on the skin.

**Do you know ?**

Sulfuric acid dissolves in water with the evolution of a large quantity of heat. Hence care must be taken while preparing solution of sulfuric acid from concentrated sulfuric acid. Concentrated $H_2SO_4$ must be added slowly to water with constant stirring by keeping the beaker in water bath.

**c. Chemcial Properties :**

**i. Acidic Property :** Sulfuric acid ionises in aqueous solution in two steps.

$$H_2SO_4(aq)+H_2O(l) \longrightarrow H_3O^{\oplus}(aq)+HSO_4^{\ominus}(aq) \qquad K_a > 10$$

$$HSO^{\ominus}_4(aq)+ H_2O(l) \longrightarrow H_3O^{\oplus}(aq) + SO_4^{2\ominus}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

The greater value of $K_a$ ($K_a$>10) means that $H_2SO_4$ is largely dissociated into $H^{\oplus}$ and $HSO_4^{\ominus}$ ions. Thus $H_2SO_4$ is a strong acid.

**ii. Reaction with metals and nonmetals (oxidising property) :** Metals and nonmetals both are oxidised by hot, concentrated sulfuric acid which itself gets reduced to $SO_2$.

$$Cu + \underset{\text{(Conc.)}}{2H_2SO_4} \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$\underset{\text{(Conc.)}}{S + 2H_2SO_4} \longrightarrow 3SO_2 + 2H_2O$$

$$\underset{\text{(Conc.)}}{C + 2H_2SO_4} \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

**Remember...**

Oxidizing properties of sulfuric acid depend on its concentration and temperature. In dilute solutions, at room temperature, $H_2SO_4$ behaves like HCl, oxidizing metals that stand above hydrogen in the e.m.f. series.

$$Fe\ (s) + 2\ H^{\oplus}\ (aq) \longrightarrow Fe^{2\oplus}\ (aq) + H_2\ (g)$$

Hot, concentrated $H_2SO_4$ is a better oxidizing agent than the dilute, cold acid. It oxidises metals like copper.

**iii. Dehydrating property :** Concentrated sulfuric acid is a strong dehydrating agent.

Sulfuric acid removes water from sugar and carbohydrates. Carbon left behind is called sugar charcoal and the process is called charring.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$$

**iv. Reaction with salts :** Concentrated sulfuric acid decomposes the salts of more volatile acids to the corresponding acid

e.g. $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

**Problem 7.10 :** What is the action of concentrated $H_2SO_4$ on (a) HBr (b) HI

**Solution :** Concerntrated sulfuric acid oxidises hydrobromic acid to bromine.

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

It oxidises hydroiodic acid to iodine.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

**d. Uses :** Sulfuric acid is a very important industrial chemical. It is used

- In the manufacture of fertilizers. For example, ammonium sulfate, superphosphate, etc.
- In the manufacture of pigments, paints and dyestuff intermediates.
- In petroleum refining.
- In detergent industry.
- In metallurgy, for cleaning of metals electroplating and galvanising.
- In storage batteries.
- As a laboratory reagent.
- In the manufacture of nitrocellulose products.

## 7.11 Chlorine and compounds of chlorine

**7.11.1 Chlorine :** Chlorine was discovered by Scheele, a German Swedish chemist in 1774 by the action of HCl on $MnO_2$. In 1810, Davy established its elementary nature and suggested the name chlorine on account of its colour.
(Greek, Chloros = greenish yellow).

**a. Preparation :**

1. Chlorine can be prepared by the oxidation of hydrochloric acid with any of the following oxidising agents.

**i. Manganese dioxide :**

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

**ii. Potassium permanganate :**

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

2. Chlorine can also be prepared by the action of concentrated sulfuric acid on a mixture of sodium chloride (common salt) and manganese dioxide. The reaction takes place in two steps.

$$4NaCl + 4H_2SO_4 \longrightarrow 4NaHSO_4 + 4HCl$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

---

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow 4NaHSO_4 + MnCl_2 + 2H_2O + Cl_2$$

**b. Manufacture of chlorine :**

**i. Deacon's process :**

Chlorine is manufactured by the oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ as catalyst at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

**ii. Electrolytic process :**

By the electrolysis of brine (concentrated NaCl solution), chlorine is liberated at the anode.

$$NaCl \rightleftharpoons Na^{\oplus} + Cl^{\ominus}$$

Cathode: $2H_2O + 2e^{\ominus} \longrightarrow H_2 + 2OH^{\ominus}$

$Na^{\oplus} + OH^{\ominus} \longrightarrow NaOH$

Anode : $Cl^{\ominus} \longrightarrow Cl + e^{\ominus}$

$Cl + Cl \longrightarrow Cl_2$

**c. Physical Properties of Chlorine :**

i. Chlorine is a greenish-yellow gas having pungent and suffocating odour.

ii. It is poisonous in nature.

iii. It can be easily liquified into a greenish yellow liquid, which boils at 239 K.

iv. It dissolves in water to give chlorine water.

v. It is 2-5 times heavier than air.

**d. Chemical properties of chlorine :**

**i. Reaction with metals :** Chlorine reacts with metals to form chlorides.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

$$2Na + Cl_2 \longrightarrow 2NaCl$$

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

**ii. Reaction with nonmetals :** Chlorine reacts with nonmetals to form their chlorides.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

$$S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$$

**iii. Affinity for hydrogen :** Chlorine has great affinity for hydrogen. It reacts with hydrogen and compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

**iv. Reaction with $NH_3$ :** Chlorine when reacted with excess of ammonia gives ammonium chloride and nitrogen.

$$\underset{(Excess)}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

Excess of chlorine reacts with ammonia to give nitrogen trichloride (explosive).

$$NH_3 + \underset{(Excess)}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

**v. Reaction with alkali :** Chlorine reacts with cold and dilute alkali to produce a mixture of chloride and hypochlorite. When reacted with hot concentrated alkali, chloride and chlorate are produced.

$$\underset{(Cold\ and\ dilute)}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

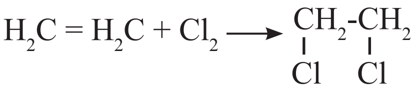
$$\underset{(Hot\ and\ conc.)}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

Chlorine when reacted with dry slaked lime gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

**vi. Reaction with hydrocarbons :** Chlorine reacts with saturated hydrocarbons to give substitution products and with unsaturated hydrocarbons gives addition products.

$$\underset{Methane}{CH_4} + Cl_2 \xrightarrow{U.V} \underset{Methylchloride}{CH_3Cl + HCl}$$



$$\underset{Ethene}{H_2C = H_2C} + Cl_2 \longrightarrow \underset{1,2\text{ - Dichloroethane}}{\underset{Cl\quad\ Cl}{CH_2\text{-}CH_2}}$$

Ethene 1,2 - Dichloroethane

**vii. Oxidising property :** Chlorine oxidises ferrous salts to ferrric salts and sulfites to sulfates.

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

It oxidises sulfur dioxide to sulfur trioxide and iodine to iodate. In presence of water they form sulfuric acid and iodic acid respectively.

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$$

**viii. Bleaching Property :** Chlorine requires the presence of moisture (water) for bleaching. It liberates nascent oxygen from water which is responsible for its oxidising and bleaching property

$Cl_2 + H_2O \longrightarrow HCl + HOCl$

$HOCl \longrightarrow HCl + [O]$

Chlorine bleaches vegetable matter or coloured organic matter in the presence of moisture to colourless matter.

Coloured organic matter + [O] ⟶ Colourless organic matter

**e. Uses :**

Chlorine is used

- For purification (sterilizing) of drinking water.
- For bleaching wood pulp required for manufacture of paper and rayon, bleaching cotton and textiles.
- For extraction of metals like gold and platinum.
- In the manufacture of dyes, drugs and organic compounds such as $CCl_4$, $CHCl_3$, DDT, refrigerants, etc.
- In the preparation of poisonous gases such as phosgene ($COCl_2$), tear gas ($CCl_3NO_2$), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

**Try this...**

i. Give the reasons for bleaching action of chlorine.

ii. Name the two gases used in war.

**Do you know ?**

Bleaching by chlorine is permanent. It bleaches cotton fabrics, wood pulp, litmus, etc. However chlorine is not used to bleach delicate materials such as silk, wool etc. as it is a strong bleaching and oxidising agent. This dual action will damage the base material.

### 7.11.2 Hydrogen Chloride :

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

**a. Preparation :** In the laboratory, hydrogen chloride is prepared by heating sodium chloride (common salt) with concentrated sulfuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{420\ K} Na_2SO_4 + HCl$$

HCl gas can be dried by passing it through concentrated sulfuric acid.

**a. Physical properties of HCl**

i. Hydrogen chloride is a colourless and pungent smelling gas.

ii. It can be easily liquified to a colourless liquid (b.p. 189 K) which freezes to a white crystalline solid (m.p. 159 K)

iii. It is highly soluble in water.

**Chemical properties :**

**i. Acidic property :** Hydrogen chloride is highly soluble in water and ionises as follows :

$$HCl\ (g) + H_2O\ (l) \longrightarrow H_3O^{\oplus}\ (aq) + Cl^{\ominus}\ (aq)$$

$$K_a = 10^7$$

The aqueous solution of HCl gas is called hydrochloric acid. High value of dissociation constant ($K_a$) indicates that it is a strong acid in water.

**ii. Reaction with $NH_3$ :** Hydrochloric acid reacts with ammonia and gives white fumes of ammonium chloride.

$NH_3 + HCl \longrightarrow NH_4Cl$

**iii. Reaction with noble metals :** When three parts of concentrated HCl and one part of concentrated $HNO_3$ are mixed, aqua regia is formed.

Noble metals like gold, platinum get dissolved in aqua regia.

$$Au + 4\,H^{\oplus} + NO_3^{\ominus} + 4Cl^{\ominus} \longrightarrow AuCl_4^{\ominus} + NO + 2H_2O$$

$$3Pt + 16\,H^{\oplus} + 4NO_3^{\ominus} + 18Cl^{\ominus} \longrightarrow 3PtCl_6^{2\ominus} + 4NO + 8H_2O$$

**Can you recall ?**

- Which type of bonds do halogens form with other elements?
- Does $BrF_5$ obey the octet rule?
- What is the oxidation state of Br in $BrF_5$?
- How many electrons do halogens require to complete their octet ?
- What is the shape of $CIF_3$?

## 7.12 Interhalogen compounds

We have seen that all halogen molecules are diatomic. They form binary compounds with hydrogen, with oxygen they form oxyacids, and with halogens they form interhalogen compounds.

Although all halogens belong to the same group they have different electronegativites. Due to this difference in electronegativity two or more halogen atoms combine to form species which may be ionic or neutral. The neutral molecules are called **Interhalogen compounds**. For example, CIF, $BrF_3$.

An interhalogen compound is a compound formed by combination of atoms of different halogens. The interhalogen compound is regarded as the halide of the more electropositive halogen. A given halogen forms an interhalogen compound only with the halogen having lesser electronegativity.

**Do you know ?**

The ions formed by combination of different halogens are called **polyhalide ions** or interhalogen ions, For example, $K^{\oplus}[Cl_3^{\ominus}]$, $[NH_4]^{\oplus}$ $[I_5]^{\ominus}$, which contain $Cl_3^{\ominus}$ and $I_5^{\ominus}$ ions.

**Use your brain power**

- Chlorine and fluorine combine to form interhalogen compounds. The halide ion will be of chlorine or fluorine ?
- Why does fluorine combine with other halogens to form maximum number of fluorides ?

**Table 7.9 Various types of interhalogen compounds**

| Element | Fluoride | Chloride | Bromide | Iodide |
|---|---|---|---|---|
| Chlorine | CIF, $CIF_3$, $CIF_5$ | - | - | - |
| Bromine | BrF, $BrF_3$, $BrF_5$ | BrCl | - | - |
| Iodine | IF, $IF_3$, $IF_5$, $IF_7$ | ICl, $ICl_3$ | IBr | - |

**Do you know ?**

ICl Iodine monochloride in glacial acetic acid called Wijs solution is used in determination of iodine value of an oil.

### 7.12.1 Classification : Depending on their composition, interhalogen compounds are classified into four types.

| Type | Example |
|---|---|
| XX' | CIF, BrF, BrCl, ICl, IBr |
| $XX'_3$ | $CIF_3$, $BrF_3$, $IF_3$ |
| $XX'_5$ | $CIF_5$, $BrF_5$, $IF_5$ |
| $XX'_7$ | $IF_7$ |

In the general formula $XX'_n$. X is the halogen having larger size and is more electropositive. X' is the halogen having smaller size and more electronegativity.

### 7.12.1 General characteristics of interhalogen compounds

1. The compound is considered as the halide of X. For example, ClF. Here the halogen having larger size is chlorine, it is more electropositive than F and hence the interhalogen compound is named as chlorine monofluoride. (n) is the number of atoms of X' attached to X.

As the ratio [radius of X : radius of X'] increases the value of n also increases.

2. Interhalogen compounds have even number of atoms 2, 4, 6, 8. For example, $ClF_3$ has 4 atoms.

3. The properties of interhalogen compounds are generally intermediate between those of the halogens from which they are made.

4. The central halogen exhibits different oxidation states in different interhalogen compounds.

5. Number of X' atoms in the compounds is always odd.

6. They are all diamagnetic .

**Use your brain power**

- What will be the names of the following compounds : ICl, BrF.
- Which halogen (X) will have maximum number of other halogen (X') attached?

**Do you know ?**

XX' compounds are more reactive than $X_2$ or $X'_2$. In the X-X' bond X' is more electronegative than X, while in $X_2$ and $X'_2$ both atoms have same electronegativity, hence the X-X' bond energy is less than the X-X or X'-X' bond energy.

**Use your brain power**

- Which halogen has tendency to form more interhalogen compounds?

**Use your brain power**

- Which will be more reactive ?

a. $ClF_3$ or ClF, b. $BrF_5$ or BrF

- Complete the table

| Formula | Name |
|---|---|
| ClF | Chlorine monofluoride |
| $ClF_3$ | ………. |
| ………. | Chlorine pentafluoride |
| BrF | ………. |
| ………. | Bromine pentafluoride |
| ICl | ………. |
| $ICl_3$ | ………. |

Table 7.10 : States of Interhalogen compounds at 25°C

| XX' | |
|---|---|
| ClF | Colorless gas |
| BrF | Pale brown gas |
| BrCl | Gas |
| ICl | Ruby red solid (α- form)<br>Brown red soid (β - form) |
| IBr | Black solid |
| $XX_3'$ | |
| $ClF_3$ | Colorless gas |
| $BrF_3$ | Yellow green liquid |
| $IF_3$ | Yellow powder |
| $ICl_3$ | Orange solid dimerises to form ($I_2Cl_6$ having Cl - bridges) |
| $XX_5'$ | |
| $IF_5$ | Colorless gas at R. T. but solid below 77 K |
| $BrF_5$ | Colorless liquid |
| $ClF_5$ | Colorless liquid |
| $XX_7'$ | |
| $IF_7$ | Colorless gas |

### Methods of Preparation of Interhalogen compounds

| Method | $XX'$ | $XX'_3$ |
|---|---|---|
| 1.Direct combination | Both in equal volumes<br>$Cl_2 + F_2 \xrightarrow[\text{Cu-vessel}]{523\ K} 2ClF$<br>$I_2 + Cl_2 \xrightarrow[\text{boil}]{HCl + HNO_3} 2ICl$<br>$Br_2 + Cl_2 \longrightarrow 2BrCl$ | $Cl_2 + 3F_2\,(\text{excess}) \longrightarrow 2ClF_3$<br>$Br_2 + 3F_2 \longrightarrow 2BrF_3$<br>$I_2 + 3Cl_2(\text{excess}) \longrightarrow 2ICl_3$ |
| 2.Reaction of halogen with interhalogen compounds. | $Br_2 + BrF_3 \longrightarrow 3BrF$ | $Br_2 + ClF_3 \longrightarrow 2BrF_3 + BrCl$ |
| Special reaction for ICl | $I_2 + KClO_3 \xrightarrow{\Delta} ICl + KIO_3$ | ------- |

**Use your brain power**

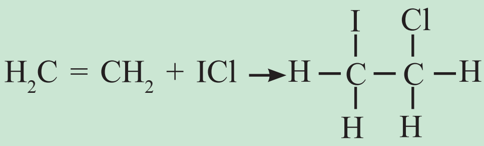
In the above special reaction for ICl, identify the oxidant and reductant. Denote oxidation states of the species.

**Do you know ?**

ICl in liquid state, undergoes autoionization like water, to form a cation and an anion.

$$2\ ICl \rightleftharpoons \underset{\text{(solvent cation)}}{I^{\oplus}} + \underset{\text{(solvent anion)}}{ICl_2^{\ominus}}$$

### Some Properties of Interhalogen compounds

| | Reaction/Property | $XX'$ | $XX'_3$ |
|---|---|---|---|
| 1 | Thermal stability | $ClF > ICl > IBr > BrCl > BrF$ | |
| 2 | Hydrolysis gives oxoacids | $BrCl + H_2O \longrightarrow HOBr + HCl$<br>$5ICl + 3H_2O \longrightarrow HIO_3 + 5HCl + 2I_2$ | $2ICl_3 + 3H_2O \longrightarrow HIO_3 + 5HCl + ICl$ |
| 3 | Disproportionation/ Autoionisation | $5BrF \longrightarrow 2Br_2 + BrF_5$ | $2ClF_3 \rightarrow ClF_2^{\oplus} + ClF_4^{\ominus}$<br>$ICl_3 \xrightarrow{341\ K} ICl + Cl_2$ |
| 4 | Flourination | --------- | $U + ClF_3 \longrightarrow UF_6(l) + ClF(g)$ |
| 5 | Addition across olefins |  $H_2C = CH_2 + ICl \rightarrow H-\underset{H}{\overset{I}{C}}-\underset{H}{\overset{Cl}{C}}-H$ | |

### Uses of interhalogen compound

| $XX'$ | $XX'_3$ |
|---|---|
| ICl is used to determine iodine value of oils | For Preparation of polyhalides |
| As catalyst for oxidation of As(III) | As fluorinating agent |
| For Preparation of polyhalides | As nonaqueous solvent |

**Table 7.11 Structures of some Interhalogen Compounds**

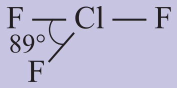
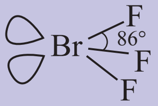
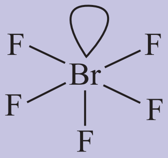
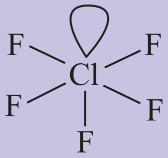
| Formula | Name | Structure | Shape |
|---|---|---|---|
| ICl | Iodine monochloride | $:\ddot{\underset{..}{Cl}}-I-\ddot{\underset{..}{Cl}}:$ | Linear |
| $ClF_3$ | Chlorine trifluoride |  | Bent T- shaped |
| $BrF_3$ | Bromine trifluoride |  | Bent T- shaped |
| $BrF_5$ | Bromine pentafluoride |  | Square pyramidal |
| $ClF_5$ | Chlorine pentafluoride |  | Square pyramidal |

**Table 7.12 Oxidation states of central halogen atom in interhalogen compounds.**

| O.S. central Halogen | No. of lone pairs of electrons | Examples |
|---|---|---|
| +7 | 0 | $IF_7$ |
| +5 | 1 | $ClF_5$, $BrF_5$,<br>$IF_5$ |
| +3 | 2 | $ClF_3$, $BrF_3$,<br>$IF_3$, $I_2Cl_6$ |
| +1 | 3 | ClF, BrF, IF,<br>BrCl, ICl,<br>IBr |

## 7.13 Compounds of Xenon

**Can you recall ?**

- What is the correlation between ionization energies and reactivity of elements?
- Trends in ionization energy down a group.

We have studied earlier in this chapter that group 18 elements have very high ionisation energies and due to this property they are unreactive. Each noble gas atom has a completely filled valence electron shell which makes it inert.

The first ionization potential decreases down the group, hence heavier noble gases Kr, Xe and Rn can form compounds due to low ionization energy.

**Do you know ?**

First true compound of noble gas was made in 1962 by Neil Bartelt and Lohman.

$$Xe + 2[PtF_6] \rightleftharpoons [XeF]^{\oplus} [Pt_2F_{11}]^{\ominus}$$

Only Xenon reacts directly with fluorine to form Xenon fluorides.

**Remember...**

$XeF_2$, $XeF_4$, $XeF_6$ are stable fluoride of xenon.

Xenon also forms compounds with oxygen, such as $XeO_3$, $XeOF_2$, $XeOF_4$, $XeO_2F_2$.

### 7.13.1 Xenon fluorides

**a. Preparation of Xenon Fluorides** : Xenon fluorides are generally prepared by direct reaction of xenon and fluorine in different ratios and conditions, such as temperature, electric discharge and photochemical reaction.

i. $Xe + F_2 \xrightarrow[\text{Ni tube, 400}^{0}\text{C}]{\text{sealed}} XeF_2$

iv. $Xe + F_2 \xrightarrow[\text{5-6 atm}]{\text{Ni tube, 400}^{0}\text{C}} XeF_4$
1 : 5

v. $Xe + 2F_2 \xrightarrow[\text{-80 }^{0}\text{C}]{\text{electric discharge}} XeF_4$

vi. $Xe + 3F_2 \xrightarrow[\text{low temp.}]{\text{electric discharge}} XeF_6$

**b. Important chemical reactions of $XeF_2$**

i. **Hydrolysis :** $XeF_2$ undergoes hydrolysis to form HF

$$2XeF_2 + 2H_2O \longrightarrow 4HF + 2Xe + O_2$$

ii. **Reaction with $PF_5$ :** $XeF_2$ forms adducts on reaction with $PF_5$.

$$XeF_2 + PF_5 \longrightarrow XeF_2.PF_5$$

### 7.13.2 Xenon trioxide

**a. Preparation of Xenon trioxide ($XeO_3$) :**

Fluorides of Xenon react with water to form $XeO_3$.

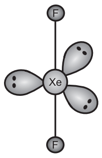
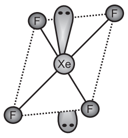
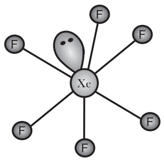
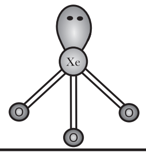
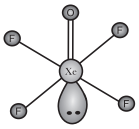
$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12\ HF + 1\tfrac{1}{2}\ O_2$$

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

**7.13.3 Oxyfluorides of Xenon :** Xenon forms the following oxyfluorides :

$XeOF_2$, $XeO_2F_2$, $XeO_3F_2$, $XeO_2F_4$, $XeOF_4$

Table 7.13 : Structure of Xenon Compounds

| Sr. No. | Formula | Oxidation state of Xe | Structure |
|---|---|---|---|
| 1. | $XeF_2$ | +2 | Linear<br><br> |
| 2. | $XeF_4$ | +4 | Square planar<br><br> |
| 3. | $XeF_6$ | +6 | Distorted octahedral<br><br> |
| 4. | $XeO_3$ | +6 | Trigonal pyramidal<br><br> |
| 5. | $XeOF_4$ | +6 | Square pyamidal<br><br> |

**a. Preparation**

i. Partial hydrolysis of Xenon fluorides yields different oxyfluorides.

$$XeF_4 + H_2O \xrightarrow{80\ ^0C} XeOF_2 + 2HF$$

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

ii. Reaction of Xenon oxyfluoride with $SiO_2$ or hydrolysis yields xenon dioxydifluoride.

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

$$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$$

**Use your brain power**

What are the missing entries ?

| Formula | Name |
|---|---|
| $XeOF_2$.................... | Xenon mono oxyfluoride |
| ......................... | Xenon dioxydifluoride |
| $XeO_3F_2$ | ......................... |
| $XeO_2F_4$ | ......................... |

**Table 7.14 : Uses of helium, neon and argon**

| Element | Uses |
|---|---|
| Helium | i. Mixture of He and $O_2$ is used for artificial breathing of asthma patients.<br>ii. Mixture of He and $O_2$ is used for respiration by sea divers.<br>iii. For filling balloons, a mixture of helium (85%) and hydrogen (15 %) is used.<br>iv. Helium is used for producing inert atmosphere required for welding purpose and metallurgy of some metals.<br>v. Liquid helium is used for producing low temperature required for research.<br>vi. In low temperature gas thermometry, for production of lasers.<br>vii. Used to pressurize fuel tanks of liquid fueled rockets.<br>viii. Used as shielding gas for arc welding.<br>ix. In supersonic wind tunnels.<br>x. Helium nucleus is used as a bombarding particle for disintegration of atoms.<br>xi. Used for magnetic resonance imaging. |
| Neon | i. In Neon discharge lamps and signs. These signs are visible from the long distances and also in mist or fog.<br>ii. Mixture of Ne and He is used in certain protective electrical devices such as voltage stabilizers and current rectifiers.<br>iii. For production of lasers.<br>iv. In fluorescent tubes. |
| Argon | i. For produc312ing inert atmosphere in welding and steel production.<br>ii. Mixture of 85 % Ar and 15 % $N_2$ is filled in electric bulb to increase life of filament.<br>iii. In filling fluorescent tubes and radio valves.<br>iv. It is mixed with neon to get lights of various colors. |

## Exercises

### 1. Select appropriate answers for the following.

i. Which of the following has highest electron gain enthalpy ?
A. Fluorine B. Chlorine
C. Bromine D. Iodine

ii. Hydrides of group 16 are weakly acidic. The correct order of acidity is
A. $H_2O > H_2S > H_2Se > H_2Te$
B. $H_2Te > H_2O > H_2S > H_2Se$
C. $H_2Te > H_2Se > H_2S > H_2O$
D. $H_2Te > H_2Se > H_2O > H_2S$

iii. Which of the following element does not show oxidation state of +4 ?
A. O B. S C. Se D. Te

iv. HI acid when heated with conc. $H_2SO_4$ forms
A. $HIO_3$ B. $KIO_3$
C. $I_2$ D. KI

v. Ozone layer is depleted by
A. NO B. $NO_2$
C. $NO_3$ D. $N_2O_5$

vi. Which of the following occurs in liquid state at room temperature ?
A. $HIO_3$ B. HBr
C. HCl D. HF

vii. In pyrosulfurous acid oxidation state of sulfur is
A. Only +2 B. Only +4
C. +2 and +6 D. Only +6

viii. Stability of interhalogen compounds follows the order
A. BrF > IBr > ICl > ClF > BrCl
B. IBr > BeF > ICl > ClF > BrCl
C. ClF > ICl > IBr > BrCl > BrF
D. ICl > ClF > BrCl > IBr > BrF

ix. BrCl reacts with water to form
A. HBr B. $Br_2 + Cl_2$
C. HOBr D. HOBr + HCl

x. Chlorine reacts with excess of fluorine to form.
A. ClF B. $ClF_3$
C. $ClF_2$ D. $Cl_2F_3$

xi. In interhalogen compounds, which of the following halogens is never the central atom.
A. I B. Cl C. Br D. F

xii. Which of the following has one lone pair of electrons ?
A. $IF_3$ B. ICl
C. $IF_5$ D. $ClF_3$

xiii. In which of the following pairs, molecules are paired with their correct shapes ?
A. $[I_3]$ : bent
B. $BrF_5$ : trigonal bipyramid
C. $ClF_3$ : trigonal planar
D. $[BrF_4]$ : square planar

xiv. Among the known interhalogen compounds, the maximum number of atoms is
A. 3 B. 6 C. 7 D. 8

### 2. Answer the following.

i. Write the order of the thermal stability of the hydrides of group 16 elements.

ii. What is the oxidation state of Te in $TeO_3$ ?

iii. Name two gases which deplete ozone layer.

iv. Give two uses of $ClO_2$

v. What is the action of bromine on magnesium metal ?

vi. Write the names of allotropic forms of selenium.

vii. What is the oxidation state of S in $H_2SO_4$.

viii. The $pK_a$ values of HCl is -7.0 and that of HI is -10.0. Which is the stronger acid ?

ix. Give one example showing reducing property of ozone.

x. Write the reaction of conc. $H_2SO_4$ with sugar.

xi. Give two uses of chlorine.

xii. Complete the following.

1. $ICl_3 + H_2O \longrightarrow$ ........ + ...... + ICl
2. $I_2 + KClO_3 \longrightarrow$ ....... + $KIO_2$
3. $BrCl + H_2O \longrightarrow$ ....... + HCl
4. $Cl_2 + ClF_3 \longrightarrow$ ........
5. $H_2C = CH_2 + ICl \longrightarrow$ .......
6. $XeF_4 + SiO_2 \longrightarrow$ ....... + $SiF_4$
7. $XeF_6 + 6H_2O \longrightarrow$ ........ + HF
8. $XeOF_4 + H_2O \longrightarrow$ ....... + HF

xiii. Match the following

| A | B |
|---|---|
| $XeOF_2$ | Xenon trioxydifluoride |
| $XeO_2F_2$ | Xenon monooxydifluoride |
| $XeO_3F_2$ | Xenon dioxytetrafluoride |
| $XeO_2F_4$ | Xenon dioxydifluoride |

xiv. What is the oxidation state of xenon in the following compounds.

$XeOF_4$, $XeO_3$, $XeF_6$, $XeF_4$, $XeF_2$.

### 3. Answer the following.

i. The first ionisation enthalpies of S, Cl and Ar are 1000, 1256 and 1520 kJ/mol$^{-1}$, respectively. Explain the observed trend.

ii. "Acidic character of hydrides of group 16 elements increases from $H_2O$ to $H_2Te$" Explain.

iii. How is dioxygen prepared in laboratory from $KClO_3$ ?

iv. What happens when

a. Lead sulfide reacts with ozone ($O_3$).

b. Nitric oxide reacts with ozone.

v. Give two chemical reactions to explain oxidizing property of concentrated $H_2SO_4$.

vi. Discuss the structure of sulfure dioxide.

vii. Fluorine shows only -1 oxidation state while other halogens show -1, +1, +3, +5 and +7 oxidation states. Explain.

viii. What is the action of chlorine on the following

a. Fe    b. Excess of $NH_3$

ix. How is hydrogen chloride prepared from sodium chloride ?

x. Draw structures of $XeF_6$, $XeO_3$, $XeOF_4$, $XeF_2$.

xi. What are inter-halogen compounds ? Give two examples.

xii. What is the action of hydrochloric acid on the following ?

a. $NH_3$    b. $Na_2CO_3$

xiii. Give two uses of HCl.

xiv. Write the names and structural formulae of oxoacids of chlorine.

xv. What happens when

a. $Cl_2$ reacts with $F_2$ in equal volume at 437 K.

b. $Br_2$ reacts with excess of $F_2$.

xvi. How are xenon fluorides $XeF_2$, $XeF_4$ and $XeF_6$ obtained ? Give suitable reactions.

xvii. How are $XeO_3$ and $XeOF_4$ prepared ?

xviii. Give two uses of neon and argon.

xix. Describe the structure of Ozone. Give two uses of ozone.

xx. Explain the trend in following atomic properties of group 16 elements.

i. Atomic radii ii. Ionisation enthalpy

iii. Electronegativity.

### 4. Answer the following.

i. Distinguish between rhombic sulfur and monoclinic sulfur.

ii. Give two reactions showing oxidising property of concentrated $H_2SO_4$.

iii. How is $SO_2$ prepared in laboratory from sodium sulfite? Give two physical properties of $SO_2$.

iv. Describe the manufacturing of $H_2SO_4$ by contact process.