7

P-Block Elements

The elements of groups 13 to 18 belong to p – block and have the general outer must electronic configuration ns^2np^{1-6}. For the elements of groups 13, 14,15,16,17 and 18 have 3, 4,5,6,7 and 8 electrons respectively in their outer most shells, while their inner shells are completely filled. The s sub shell have 2 electrons in each and the remaining 1,2,3,4,5 and 6 electrons are filled in their p – sub shells respectively. Students of class XI have read the elements of group 13 and 14.

ELEMENTS OF GROUP – 15

This group includes nitrogen (N), Phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). As we go through top to bottom in a group, the metallic properties increase. Thus, nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a typical metal.

Non metals : Nitrogen, phosphorus
Metalloids : Arsenic, antimony
Metal : Bismuth

OCCURRENCE

The elements of group 15, except phosphorus do not occur very abundantly in nature. Tough molecular nitrogen comprises 78% by volume of the atmosphere; it is not very abundant in the earth's crust. In the earth's crust, it occurs as sodium nitrate, $NaNO_3$ (called Chile saltpeter) and potassium nitrate (Indian Saltpeter). It is found in the form of proteins in plants and animals. Phosphorus occurred in minerals of the apatite family, $Ca_9(PO_4)_6.CaF_2$ (fluorapatite). In place of F in these minerals there may also Br, Cl or OH groups. These are the main components of phosphate rocks. Phosphorus is essential for life, both as in animals and plan as structural materials. It is present in bones as well as in living cells. About 60% bones and teeth are made by fluorapatite. Phospho-proteins are present in milk and eggs. Arsenic, antimony and bismuth are found many as sulphide minerals. The important atomic and physical properties of these group elements are given in the table –1.

Property	**N**	**P**	**As**	**Sb**	**Bi**
Atomic number	7	15	33	51	83
Atomic mass /$g.mol^{-1}$	14.01	30.07	74.92	121.75	208.98
Electronic Configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10}4s^2 4p^3$	$[Kr]4d^{10}5s^2 5p^3$	$[Xe]4f^{14}5d^{10}6s^2 6p^3$
Ionization enthalpy I,II,III ..H_2/kJ mol^{-1}	1402 2856 4577	1012 1903 2910	947 1798 2736	834 1595 2443	703 1610 2466
Electronegativity	3.0	2.1	2.0	1.9	1.9
(A^0) Covalent radius /(A^0)	0.70	1.10	1.21	1.41	1.48
Ionic radius (A^0)	1.7^a	2.12^a	2.22^a	0.76^b	1.03^b
Melting Point (K)	63^*	317^d	1089^e	904	544
Boiling Point (K)	77.2^*	554^d	888^f	1860	1837
Density (g cm^{-3}, 298K)	0.879^g	1.823	5.778^h	6.697	9.808

a = E^{-3} ionic radius, b = E^{+3} ionic radius, d= white phosphorus,

e = Gray phosphorus at 38.6 atm., f = sublimation temperature,

g = Density at 63K, h = gray form and * = molecular N_2

The electronic configuration of the elements of group 15 is ns^2np^3, where the s-orbital possess two electrons and the p–contains three electrons. The half filled p–orbital is responsible for extra stability of these elements.

The important trends of atomic and physical properties discussed below :

Ionisation Enthalpies

Ionization enthalpy decreases down the group due to gradual increase in atomic size of elements. The ionization enthalpy of group 15 elements is much greater than that of group 14 elements in the corresponding periods due to the extra stable half–filled p–orbital electronic configuration and the smaller size.

As expected, the successive ionization enthalpies of these elements increase in the order

$\Delta H_1 < \Delta H_2 < \Delta H_3$

Electronegativity :

The electro negativity value, decreases down the group with increasing atomic size. However, amongst the heavier elements, the difference is not that much pronounced.

Physical Properties :

All the elements of this group are poly atomic; nitrogen is a diatomic gas while all other elements are solids. The elements of group 15 are less metallic. However, on going down the group, the metallic character increases from N to Bi. The elements N and P are non-metallic, As and Sb are partly non-metallic while Bi is a metal. Due to increased nuclear charge and higher electro negativity, the elements of group 15 are less metallic than the corresponding elements of group 14. On moving down the group, the atomic size as well as the screening effect of the intervening electrons increases. As a result, the ionization enthalpy decreases and therefore, metallic character increases down the group. The melting points also increase down the group due to increase in atomic size. However, the unexpected decrease in the melting point of Sb and Bi is because of their tendency to form three covalent bonds instead of five covalent bonds, due to inter pair (ns^2) effect. As a result, the attraction among their atoms is weak and hence their melting points are low. Except nitrogen and bismuth, all other elements of this group show allotropic. For example:

Phosphorus exists as	:	White, black or red phosphorus
Arsenic exists as	:	yellow or grey arsenic
Antimony exists as	:	yellow or silver grey allotropic form

CHEMICAL PROPERTIES

Oxidation States :

The elements of group 15 have five electrons in their valence shell. They exhibit various oxidation states from –3 to +5. The tendency to exhibit -3 oxidation state decreases downs the group due to increase in size and metallic character. The elements have five electrons in the valence shell and therefore, require three more electrons to acquire the nearest Nobel gas configuration. But, the gain of three electrons is not energetically favorable because it requires very large amount of energy to gain three electrons and form M^{3-} ions. However, nitrogen being the smallest and most electro negative element the group forms N^{3-} ion and shows an oxidation state -3 in nitrides of some highly electro positive metals such as Mg_3N_2, Ca_3N_2, and AIN etc.

The other elements of this group form covalent compounds even with metals and show on oxidation state of -3 with metals, i.e. Ca_3P_2, Na_3AS etc. As evident from the decreasing electro negativities and decreasing ionization enthalpies, the tendency of the elements to exhibit -3 oxidation state decreases on moving down from P to Bi due to increase in size and metallic character.

In addition to, -3 oxidation state N and P show oxidation states of -2 in hydrazine (NH_2NH_2) diphosphine (P_2H_4) respectively. Nitrogen also shows an oxidation state of -1 in hydroxyl amine (NH_2OH) but P does not show this state.

The elements, of group 15 exhibit positive oxidation states of +3 and +5. However, on moving down the group, the stability of +5 oxidation states decreases while that of +3 oxidation state increases due to inert pair (ns^2) effect.

Because of energy considerations, these elements cannot lose all the five valence electrons. Therefore, the do not form M^{5+} ions and all pentavalent compounds i.e. PF_5, PCl_5, SbF_5, BiF_5 etc. are essentially covalent compounds. Nitrogen does not form compounds in +5 oxidation state such as NF_5, NCl_5 etc., because it does not have vacant d-orbital in its valence shell which can enable it to state (+5) decreases down the group. The, +5 oxidation state inert pair effect. The BiF_5 is only well characterized Bi (V) compound.

If may be noted that in case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution. For example,

$$3HNO_2 \rightarrow HNO3 + 2NO + H_2O$$

Chemical properties and Trends in Reactivity:

Anomalous Properties of Nitrogen :

Like first member of other groups, nitrogen differs from rest members of the group due to its smaller size, high electro negativity, high ionization enthalpy and non – availability of d - orbital in the valence shell.

Nitrogen has unique tendency to form $p\pi - p\pi$ multiple bonds with itself and with other elements having small size and high electro negativity (e.g. C and O). However, the heavier elements of this group do not form $p\pi - p\pi$ bonds because their atomic orbital are so large and diffuse that they cannot have effective overlapping. These differences between nitrogen and other members of the group result into "anomalous properties of nitrogen" Thus, nitrogen exists as a diatomic molecule with triple bonds (one σ and two π) between two atoms. On the contrary phosphorus, arsenic and antimony form single bonds as P-P, As-As and Sb-Sb while bismuth forms metallic bonds in elemental state. However, the single N-N bond is weaker than the single P-P bond because of high inter electronic repulsion of the non bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Therefore, nitrogen exists as gas while phosphorus exists as solid.

Since P-P single bond is much weaker then N≡N triple bond, therefore, phosphorus is much reactive then nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d-orbital in its valiancy shell. Nitrogen cannot for $p\pi$-$d\pi$ bonds whereas phosphorus and other heavier members of this group reading form $p\pi$-$d\pi$ multiple bonds, for examples $R_3P=O$, $R_3P=CH_2$, POX_3 etc.

Bond energies are given here :

Bond	C - C	N - N	P - P	As – As
Bond energy kJ mol^{-1}	353.3	163.8	201.6	147.4

Let us discuss some trends in chemical reactivity of group 15 elements and their compounds.

1. Reactivity towards Hydrogen :

All the elements of group 15 form gaseous tri hydrides of the formula EH_3, such as :

Properties	NH_3 Ammonia	PH_3 Phosphene	AsH_3 Arsine	SbH_3 Stibine	BiH_3 Bismuthine
M. Pt. (k)	195.2	139.5	156.7	185	-
B. Pt. (k)	238.5	185.5	210.6	254.6	290
E-H bond distance (PM)	101.7	141.9	151.9	170.7	-
H-E-H bond angle	107.8	93.6	91.8	91.3	-
E-H disso. energy	389	322	297	255	-

The hydrides show regular gradation in their properties. The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst the the hydrides.

Basicity also decreases in the order-

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

The reducing character depends upon the stability of the hydride. The greater instability of hydride, the greater is its reducing power. Nitrogen also forms a special hydride HN_3, which is called hydrazoic acid or azide.

(2) Reactivity towards Oxygen :

All the elements of group 15 for two types of oxides: E_2O_2 and E_2O_5. The oxide in the higher oxidation state of the element is more acidic in character than that the lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

(3) Reactivity towards Halogens:

Group 15 elements form two series of halides the type MX_3 and MX_5. The tri halides are formed by all the elements while pent halides are formed by all the elements except nitrogen. Nitrogen cannot form pentahalides due to the absence of vacant d – orbital in its outer most shell. Similarly, the last element, +5 oxidation state of Bi is ten stable than +3 oxidation state due to inert pair effect. Tri halides except BiF_3 are predominantly covalent in nature.

(4) Reactivity towards Metals:

All the elements of group 15 combine with metals to form their binary compounds in which the elements show -3 oxidation states. For example, calcium nitride (Ca_3N_2), sodium arsenide (Na_3As), zinc antimonite (Zn_3Sb_2), magnesium bismuthide (Mg_3Bi_2) etc.

Dinitrogen:

Nitrogen was discovered by Daniel Rutherford in 1772. It is the first member of group 15 of the periodic table. It has the electronic configuration $1s^2 2s^2 2p^3$ and therefore, has five electrons in its valence shell. In the molecular form, it exist as a diatomic molecule (N_2) having triple bond between nitrogen atoms (N=N). Therefore, it is also referred to as dinitrogen. It is a typical non – metal with high electro negativity next only to fluorine and oxygen.

Preparation :

In the laboratory dinitrogen is prepared by heating an aqueous solution containing an equivalent amount of ammonium chloride and sodium nitride.

$$NH_4Cl_{(aq.)} + NaNO_{2\,(aq.)} \longrightarrow N_{2\,(g)} + 2H_2O_{\,(l)} + NaCl_{\,(aq.)}$$

During the preparation, small amount of NO and HNO_3 are also formed in the reaction. These impurities can be removed by bubbling the fast through aqueous H_2SO_4 containing a small amount of $K_2Cr_2O_7$.

It can also be prepared by thermal decomposition of ammonium dichromate

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + 4H_2O + Cr_2O_3$$

Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium aside

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

And

$$2NaN_3 \longrightarrow 2Na + 3N_2$$

Properties :

Dinitrogen is a colorless, odorless, tasteless and non toxic gas. Nitrogen atoms have two stable isotopes. ^{14}N and ^{15}N. Its boiling paint is 77.2K. It has very low solubility in water [23.2 cm^3 per liter of water at 273K and 1 bar pressure].

Dinitrogen is chemically non reactive at room temperature. It is neither combustible nor it supports combustion because there is triple bond between the both of N atoms. The bond distance is 109.8 pm and bond dissociation enthalpy of 941.4 kJ mol^{-1}. However, reactivity increases rapidly with the rise in temperature. At higher temperature di nitrogen combines with some metals to form predominantly ionic nitrides and with non – metals to form covalent nitrides, for example :

$$6\,Li + N_2 \rightarrow 2\,Li_3N$$

$$3\,Mg + N_2 \rightarrow Mg_3N_2$$

$$2Al + N_2 \rightarrow 2AlN$$

Dinitrogen reacts with dihydrogen at about 772K under a pressure of 200 atm. In the presence of iron as catalyst (Haber process).

$$N_{2(g)}+3H_{2(g)} \overset{772K}{\underset{200\ atm}{\quad}} 2NH_{3(g)};\ \Delta H = -46.1\ KJ\ Mol^{-1}$$

Dinitrogen combines with di oxygen during lightning or at high temperature of about 2000K and form nitric oxide.

$$N_{2\,(g)} + O_{2\,(g)} \rightarrow 2NO_{(g)};\quad \Delta H = 135\ kJ\ mol^{-1}$$

Dinitrogen also combines with certain compounds on strong heating, for example, with calcium carbide at 1300K temperature-

$$CaC_2 + N_2 \rightarrow CaCN + C$$

Uses of Dinitrogen :

The main uses of dinitrogen are as follows:

(i) Dinitrogen is used in the manufacture of compounds like ammonia, nitric acid, calcium cyan amide, etc.

(ii) It is used in providing inert atmosphere is iron and steel industries.

(iii) Liquid nitrogen is used a refrigerant to preserve biological specimens, in freezing food stuffs and also in cryosurgery.

(iv) It is used in gas filled thermo meters used for measuring high temperature.

Ammonia :

Ammonia is the most important compound of nitrogen. It is present in small amounts in air and soil where it is formed by the decay of nitrogenous organic matter e.i. urea,

$$NH_2CONH_2 + 2H_2O \rightarrow (NH_4)_2\,CO_3$$

$$2NH_3+CO_2+H_2O$$

Ammonia is prepared in the laboratory by heating ammonium salt, NH_4Cl, or $(NH_4)_2SO_4$ with a strong alkli like NaOH.

$$NH_4Cl+NaOH \rightarrow NH_3+H_2O+NaCl$$

$$(NH_4)_2\,SO_4+2NaOH \rightarrow 2NH_3+2H_2O+Na_2SO_4$$

At industrial level, ammonia is manufactured by Haber's process which involves the following reaction :

$$N_{2(g)}+3H_{2(g)} \qquad 2NH_{3(g)};\quad \Delta H = -46.1\ kJ\ mol^{-1}.$$

In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of ammonia are a pressure of $200 x 10^5$ Pa, a temperature of 700 k and the use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

The schematic diagram for the production of ammonia by Haber's process is shown below :

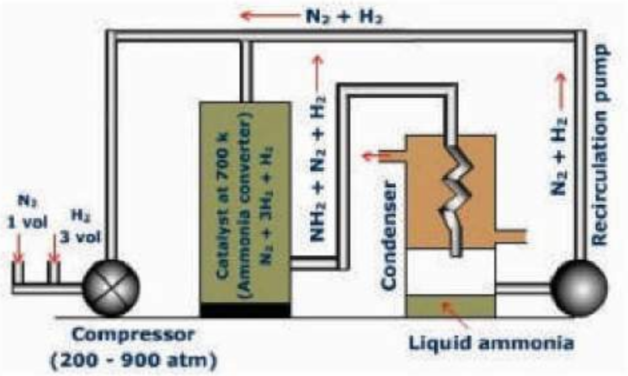
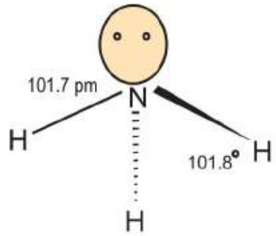


Fig. Haber's process of ammonia production

Structure and Properties :

Ammonia is expected to have a tetrahedral geometry because the central N–atom involves sp^3 hybridization. It has one position occupied by a lone pair. The lone pair distorts its geometry and the molecule has tri zonal pyramidal geometry with N–atom at the apex. The N – H bond length 101.7 pm and HNH bond angle is 107.8^0.



Ammonia is colourless gas with pungent order. It's freezing and boiling points are 198.4 K and 239.7 K respectively. In the solid and liquid states, it is associated through hydrogen bonding as in the case of water and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass. It is highly soluble in water and forms ammonium hydroxide. It is basic in nature due to the formation of OH^- ions.

$$NH_{3(g)} + H_2O_{\,(l)} \qquad NH_4^{+}{}_{(aq.)} + OH^{-}{}_{(aq.)}$$

The ammonium hydroxide acts as weak

base and forms salts with acidic compounds, such as NH_4Cl, $(NH4)_2SO_4$, CH_3COONH_4 etc. Ammonia itself is also acts as a base. e.g.

$NH_3 + HCl \rightarrow NH_4Cl$

$NH_3 + CH_3COOH \rightarrow CH_3COONH_4$

$$\underset{(aq.)}{ZnSO_4} + \underset{(aq.)}{2\,NH_4OH} \rightarrow \underset{(ppt.)}{Zn(OH)_2(\downarrow)} + \underset{(aq.)}{(NH_4)_2SO_4}$$

$$\underset{(aq.)}{FeCl_3} + \underset{(aq.)}{NH_4OH} \rightarrow \underset{(Brown\ ppt.)}{Fe_2O_3\,xH_2O} + \underset{(aq.)}{NH_4Cl}$$

The presence of a lone pair of electrons on the N – atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms linkage with metal ions and the formation of such complex compounds finds applications in detection of metal ions such as Cu^{+2}, Ag^{+} etc.

$$\underset{(blue)}{Cu^{+2}_{(aq.)}} + 4NH_{3\,(aq.)} \qquad \underset{(deep\ blue)}{[(Cu(NH_3)_4]^{2+}_{(aq.)}}$$

$$\underset{(colourless)}{Ag^{+}_{(aq.)} + Cl^{-}_{(aq.)}} \rightarrow \underset{(white\ ppt)}{AgCl_{(s)}}$$

$$\underset{(white\ ppt)}{AgCl_{(s)}} + 2\,NH_{3\,(aq.)} \rightarrow \underset{(colourless)}{[Ag(NH_3)_2]\,Cl_{(aq.)}}$$

Use of Ammonia :

It is commonly used for preparing various nitrogenous fertilizers such as ammonium nitrate, ammonium sulphate, ammonium phosphate and urea. Liquid ammonia is also used as a refrigerant. It is also used in the manufacture of nitric acid and sodium carbonate. Ammonia is an important reagent in laboratory.

Oxides of Nitrogen :

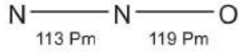
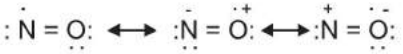
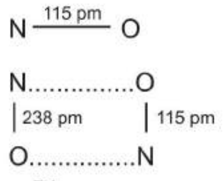
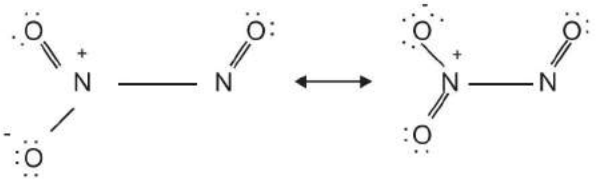
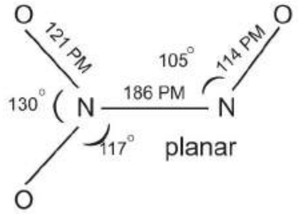
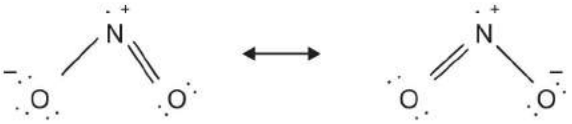
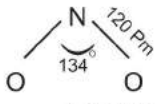
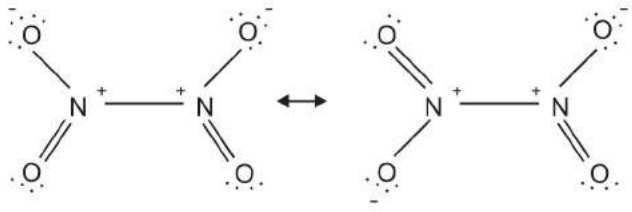
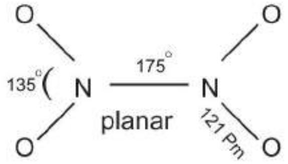
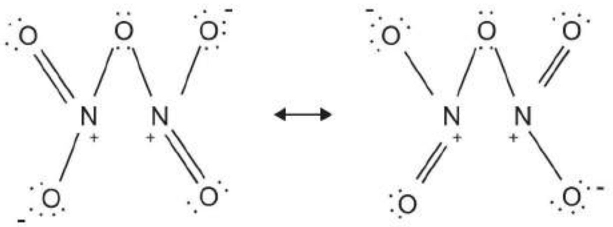
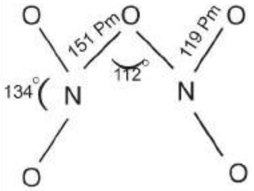
Nitrogen combines with more electro negative oxygen under different conditions to form a number of binary oxides which differ with respect to the oxidation state of nitrogen atom. They range from +1 to +5 oxidation states. The tendency to form pπ–pπ multiple bonds dictates the structures of oxides. The important oxides are given the following table (4) :

Table (4)

Name of Oxide	Formula	Oxidation state of nitrogen	General method of Synthesis	General nature
Dinitrogen oxide (Nitrogen - I oxide)	N_2O	+1	$NH_4NO_3 \xrightarrow{Temp.} N_2O + 2H_2O$	Colourless, neutral gas
Nitrogen monooxide (Nitrogen - II oxide)	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless, neutral gas
Nitrogen trioxide (Nitrogen - II oxide)	N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$	Blue, acidic solid
Nitrogen dioxide (Nitrogen - IV oxide)	NO_2	+4	$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$	Brown, acidic gas
Nitrogen tetraoxide (Nitrogen - IV oxide)	N_2O_4	+4	$2NO_2 \underset{Temp.}{\overset{Cold}{\rightleftharpoons}} N_2O_4$	Colourless, acidic solid or liquid
Dinitrogen pentaoxide (Nitrogen - V oxide)	N_2O_5	+5	$4HNO_3 + P_4H_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	Colourless, acidic solid

The resonating structures of various nitrogen oxides are given in the following table (5).

Table (5)

Resonating Structure	Structure
(1) **N_2O,** Nitrous oxide 	Linear 
(2) **NO,** Nitric oxide 	 Dimer
(3) **N_2O_3** Dinitrogen trioxide 	
(4) **NO_2** Nitrogen dioxide 	 Angular
(5) **N_2O_4** Nitrogen dioxide 	
(6) **N_2O_5** Dinitrogen pentaoxide 	

Nitric Acid (HNO_3) :

Nitrogen forms oxoacids such as $H_2N_2O_2$ (hyponitrous acid), HNO_2 (nitrous acid) and HNO_3 (nitric acid). Amongst them HNO_3 is the most important. It is very strong oxidizing agent and is a quite useful reagent. Nitrogen shows an oxidation state of, +5 in nitric acid.

Preparation :

In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

At industrial level, nitric acid is commonly manufactured by 'Ostwald processes of ammonia by atmospheric oxygen. The reaction is carried out at about 500K and $9x10^5$ Pa (9bar) pressure in the presence of Pt or Rh gauge as catalyst.

$$4NH_{3(g)} + 5O_{2\,(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

Nitric oxide (NO) thus forms combines with oxygen to form nitrogen dioxide.

$$2NO + O_{2\,(g)} \rightarrow 2NO_{2\,(g)}$$

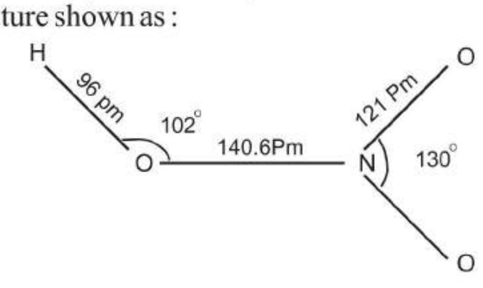
Nitrogen dioxide (NO_2) so formed dissolves in water to give nitric acid.

$$3NO_{2(g)} + H_2O_{\,(l)} \rightarrow 2HNO_{3(aq.)} + NO_{(g)}$$

The NO thus formed is recycled and the aqueous HNO3 can be concentrated by distillation up to about 68% by mass. This dilute nitric acid is further concentrated by dehydration with concentrated sulphuric acid to get, about 98% nitric acid.

Properties of Nitric acid :

Nitric acid is colourless liquid (f.p. 231.4K and B.P. 355.6K). Laboratory grade nitric acid contains about 68% of the HNO_3 by mass and has a specific gravity of 1.504 gm per ml. In the gaseous state, HNO_3 exists as a planer molecule with the structure shown as :



In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_{3\,(aq.)} + H_2O_{\,(l)} \rightarrow H_3O^+_{\,(aq.)} + NO^-_{3\,(aq.)}$$

With the exception of gold and platinum (noble metals), nitric acid attacks all metals forming a variety of products. The product depends upon the nature of metal, concentration of HNO_3 and temperature of reaction.

$$3Cu + 8HNO_3\,(dilute) \rightarrow 3Cu\,(NO_3)_2 + 4H_2O + 2NO$$

$$Cu + 4HNO_3\,(Conc.) \rightarrow Cu\,(NO_3)_2 + 2H_2O + 2NO_2$$

Zinc reacts with dilute nitric acid to give N_2O and with concentrated nitric acid to give NO_2

$$Zn + 10\,HNO_3\,(dilute) \rightarrow 4\,Zn\,(NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3\,(conc.) \rightarrow Zn\,(NO_3)_2 + 2H_2O + 2NO_2$$

Some metals (e.g. Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

The concentrated nitric acid also oxidizes non metals and their compounds, e.g. –

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2$$

(Iodic acid)

$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4\,NO_2$$

$$S_8 + 48\,HNO_3 \rightarrow 8\,H_2SO_4 + 48NO_2 + 12H_2O$$

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Brown Ring Test :

The familiar brown ring test for nitrates depends on the ability of Fe^{+2} to reduce nitrates to nitric oxide, which reacts with Fe^{+2} form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrate H_2SO_4 along the side of the inclined test tube to make a separate layer of H_2SO_4 at the bottom of test tube.

A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in the solution:

$$NO_3^- + 3Fe^{+2} + 4H^+ \rightarrow NO + 3Fe^{+3} + 2H_2O$$

$$[Fe\,(H_2O)_6]^{+2} + NO \rightarrow [Fe\,(H_2O)_5(NO)]^{+2} + H_2O$$

(Brown ring)

Uses of HNO_3 :

The major industrial use of nitric acid is in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosive and pyrotechnics. It is also used for the preparation of nitroglycerin, Trinitron toluene (an explosive) and other organic nitro compounds. Other major uses are in the pickling of stainless steel, etching of metals and as an oxidizer in rocket fuels.

Phosphorus Allotropic Forms :

Phosphorus is widely distributed in nature and mainly occurs in the form of phosphate minerals in the crust of earth. Phosphorus exists in many allotropic forms.

Three main allotropic forms are:

(1) White Phosphorus

(2) Red Phosphorus

(3) Black Phosphorus

(i) White Phosphorus :

This allotrope is a translucent white waxy solid. It is poisonous, insoluble in water but soluble in carbon disulphide and glows in dark (chemiluminescence). It dissolves in boiling NaOH solution in an inert atmosphere giving PH_3

$P_4 + 3\ NaOH + 3H2O \rightarrow PH_3 + 3\ NaH_2\ PO_2$

(White phosphorus) (Sodium hyposulphite)

It can be obtained from phosphorite rock with coke and sand in an electric furnace at 1775K. It consists of P_4 units as shown in the figure:

White Phosphorash (Tetrahedral)

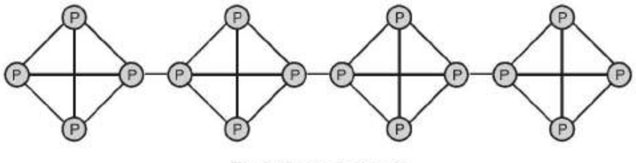
It ignition temperature is very low (303k) and therefore, it catches fire in air to form dense white fumes of P_uH_{10}.

$P_4 + 5O_2 \rightarrow P_4H_{10}$

It is soft waxy solid so that it can be cut with a knife. It's melting points is 317K and boils at 553K.

(ii) Red Phosphorus :

It can be obtained by heating white phosphorus in an inert atmosphere at 573K for several days. It is a hard crystalline solid without any smell. It possesses iron grey luster. This allotrope is non – poisonous in nature, insoluble in water as well as carbon disulphide and it does not glow in the dark. Red phosphorus is quite stable and its ignition temperature is quite high (543K). It, therefore, does not catch fire easily. Like white phosphorus, red phosphorus also exists as P4 tetrahedra but have polymeric structure consisting of P_4 tetra hedra linked together as shown below:



Red phosphorash
(Linear polymer of P_4)

Red phosphorus does not react with caustic alka lies. This property is made use in separating red phosphorus from white phosphorus. It can be converted in to white phosphorus by boiling it in an inert atmosphere and then condensing the vapours of white phosphorus formed under water.

(iii) Black Phosphorus :

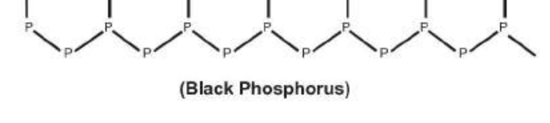
Black phosphorus has two forms; α-black phosphorus and β – black phosphorus. α-Black phosphorus formed by heating red phosphorus in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.

$$\text{Red phosphorus} \xrightarrow[\text{803K}]{\text{sealed tube}} \alpha\text{ - Black phosphorus}$$

β – Black phosphorus is obtained by heating white phosphorus at 473K under extremely high pressure (4000-12000atm) in an inert atmosphere.

$$\text{White phosphorus} \xrightarrow[\text{4000-12000 atm}]{\text{473K}} \beta\text{ -Black phosphorus}$$

It has a double layered crystal lattice. Each layer is made up of zig-zag chains with P-P-P bond angles 99^0 and bond distance P-P of 218pm, as shown below:



(Black Phosphorus)

It has black metallic luster and its melting point is 860K.

Phosphine :

Phosphine is a hydride of phosphorus (PH_3). It can be obtained by the action of water or dilute mineral acid on metallic phosphides like Na_3P, Ca_3P_2, AIP, etc.

$$CaP_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$

$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$$

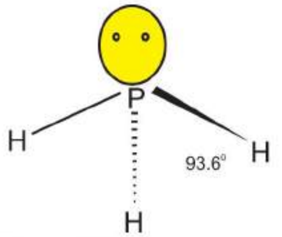
Phosphine is prepared in the laboratory by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2 or coal gas.

$$P_4 + 3NaOH + 3H_2O \rightarrow NaH_2PO_2 + PH_3$$

When pure, it is non – inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOh hives of Phosphine

$$PH_3 + HI \rightarrow PH_4I$$

$$PH_4I + KOH \rightarrow PH_3 + KI + H_2O$$



Properties of Phosphine:

It is a colourless gas with unpleasant smell of rotten fish or garlic and highly poisonous in nature. It explodes in contact with traces of oxidizing agents like HNO_3, Cl_2 and Br_2 vapours.

It is slightly soluble in water. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2. When absorbed in copper sulfate of $HgCl_2$ solution, the corresponding phosphides are obtained.

$$3\,CuSO_4 + 2PH_3 \rightarrow Cu_3 + 3\,H_2SO_4$$

$$3\,HgCl_2 + 2\,PH_3 \rightarrow Hg_3P_2 + 6\,H_4$$

Phosphene is weakly basic in nature like ammonia and gives phosphonium compounds with acids e.g.

$$PH_3 + HBr \_\_\_\_ PH_4Br$$

$$PH_3 + HI \_\_\_\_ PH_4I$$

Uses of Phosphine :

It is use in preparing "Holmes's signals" for the ships to know about the position of the rocks in sea. A mixture of calcium carbide and calcium phosphide is taken in a vessel. A hole is made in it and the vessel is immersed in the sea water near the rock. Calcium phosphide librates, phosphine while calcium carbide librates acetylene. Phosphine catches fire in air and lights up acetylene. This acts as a signal for the approaching ship. It is also used to prepare "Smoke screens" in warfare.

Halides of Phosphorus :

Phosphorus forms two types of halides i.e. phosphorus tri halides PX_3 (X=F, Cl, Br, I) and phosphorus pentahalides PX_5. With chlorine if forms:

I Phosphorus trichloride

II Phosphorus pentachloride

Phosphorus Trichloride :

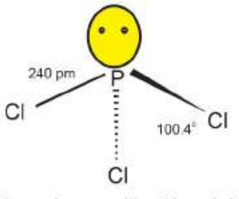
If is obtained by passing dry chlorine over heated white phosphorus:

$$P_4 + 6\,Cl_2 \rightarrow 4PCl3$$

It can also be obtained by the reaction of thionyl chloride with white phosphorus:

$$P_4 + 8\,SOCl_2 \rightarrow 4\,PCl_3 + 4\,SO_2 + 2\,S_2Cl_2$$

Phosphorus in PCl_3 under goes sp^3 hybridization. Three of the sp^3 hybrid overlaps with p-orbital of chlorine to form three P-Cl σ – bonds while the fourth sp^3 hybrid orbital contains a lone pair of electrons. Therefore, like PH_3, PCl_3 has pyramidal structure as shown below :



It is a colourless oily liquid and hydrolyses in the presence of moisture

$$PCl_3 + 3\,H_2O \rightarrow H_3PO_3 + 3HCl$$

It reacts with organic compounds

containing– OH group such as CH_3COOH, C_2H_5OH.

$$3\,CH_3COOH + PCl_3 \rightarrow 3\,CH_3COCl + H_3PO_3$$

$$3\,C_2H_5OH + PCl_3 \rightarrow 3\,C_2H_5Cl + H_3PO_3$$

Phosphorus Pentachloride :

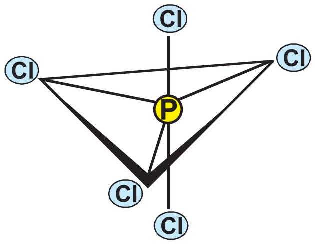
Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4\,PCl_5$$

It can also be obtained by the reaction of SO_2Cl_2 with white phosphorus

$$P_4 + 10\,SO_2Cl_2 \rightarrow 4\,PCl_5 + 10\,SO_2$$

In PCl_5, Phosphorus undergoes sp^3d hybridization and has tri zonal bi pyramidal structure as show below :



PCl_5 is a yellowish white powder and in most air, it hydrolysed into $POCl_3$ and it again hydrolyzed in phosphoric acid (H_3PO_4).

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

PCl_5 is thermally less stable than PCl_3. On heating it sublimes but decomposes on stronger heating into trichloride and chlorine.

$$PCl_5 \qquad PCl_3 + Cl_2$$

It reacts with compounds containing hydroxyl groups (-OH) to give the corresponding chloro- compounds in which each – OH group is replaced by a chlorine atom. For example,

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$

Finely divided metals on heating with PCl5 give corresponding chlorides.

$$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$$

$$Sn + 2\,PCl_5 \rightarrow SnCl_4 + 2\,PCl_3$$

It is used in the synthesis of some organic compounds, e.g. C_2H_5Cl, CH_3COCl. In the solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ octahedral.

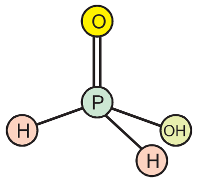
Oxoacids of Phosphorus :

Phosphorus forms a number of oxoacids. The important oxoacids of phosphorus with their formulas, methods of preparations and the presence of some characteristic bonds in their structures are given in the following table (6) :

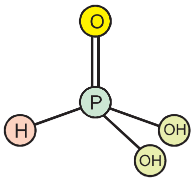
Name of oxoacid	Formula	Oxidation state of P	Characteristic bond & number	Synthesis
1. Hypophosphorus (Phosphine)	H_3PO_2	+ 1	One P - OH Two P - H One P = O	White P_4 + Base
2. Orthophosphorus (Phosphonic acid)	H_3PO_3	+ 3	Two P - OH One P - H One P = O	$P_2O_3 + H_2O$
3. Pyrophosphorus	$H_4P_2O_5$	+ 3	Two P - OH Two P - H Two P = O	$PCl_3 + H_3PO_3$
4. Hypophosphorus	$H_4P_2O_6$	+ 4	Four P - OH Two P = O One P - O	Red P_4 + Base

5. Orthophosphoric acid	H_3PO_4	+ 5	Three **P - OH** Two **P = O**	$P_4H_{10} + H_2O$
6. Pyrophosphoric acid	$H_4P_2O_7$	+ 5	Four **P - OH** Two **P = O** One **P-O-P**	Hot phosphoric acid
7. Metaphosphoric acid	$(HPO_3)_n$	+ 5	Three **P - OH** Three **P = O** Three **P-O-P**	Phosphoric acid + Br_2

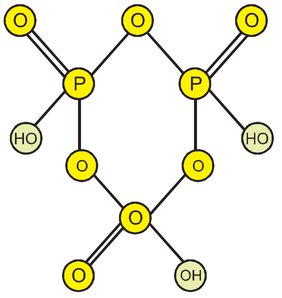
The structures of some important oxo acids are given below :



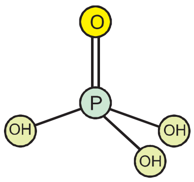
H_4PO_2



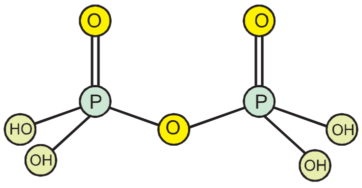
H_3PO_3



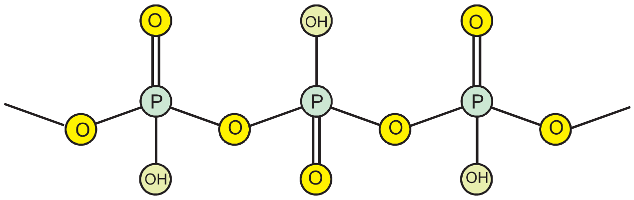
$(HPO_3)_3$



H_3PO_4



$H_4P_2O_7$



$(HPO_3)_3$

Structural Properties :

The basic structural and characteristic features of these phosphorus oxoacids are:

(1) All these acids contain phosphorus atom or atoms bonded tetrahedral to four other atoms or groups.

(2) These contain at least one P=O unit and one P-OH group. The P-OH group is ion sable giving proton. The number of P-OH groups determines the basicity of the oxoacid.

(3) Some oxoacids have one (or more) P-H groups and this bond is non ionisable.

(4) Some oxoacids have P-O-P or P-P bonds obtained by corner sharing of tetrahedral.

(5) Peroxoacids have P-O-O-H or P-O-O-P linkages.

(6) The oxoacids in which P has lower oxidation state (less than +5) contain in addition to P-OH and P=O bonds, either P-P (e.g., in $H_4P_2O_6$) or P-P (e.g., in $H_3 PO_2$) bonds but not both.

(7) These oxoacids in +3 oxidation state of P

tend to disproportionate to higher and lower oxidation states. For example,

$$4\,H_3PO_3 \rightarrow 3\,H_3PO_4 + PH_3$$

(+3) (+5) (+3)

(8) Acids which contain P-H bonds have strong reducing properties. For example, Hypo phosphorus acid is a good reducing agent because it contains two P-H bonds and therefore, reduces $AgNO_3$ to metallic silver.

$$4\,AgNO_3 + 2\,H_2O + H_3PO_2 \rightarrow 4\,Ag + 4\,HNO_3 + H_3PO_4$$

$$C_6\,H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6 + H_3PO_3 + N_2 + HCl$$

ELEMENTS OF GROUP - 16

The elements oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po) constitute group 16 elements of the periodic table. This group is sometimes known as group of “Chalcogens”. This name is derived from the Greek word for brass and points to the association sulphur and its congeners with copper. Most copper minerals contain either oxygen or sulphur and frequently the other members of the group.

Occurrence :

Oxygen is most abundant of all elements. It occurs in the form as O2 and makes up 20.946% by volume of the atmosphere. Oxygen makes up 46.6% by weight of the earth's crust and is the major constituent of silicate minerals. It also occurs as metal oxide ores, and deposits of oxo salts such as carbonates, sulphates, nitrates, borates, etc.

Sulphur is the sixteenth most abundant element and constitutes 0.03-0.1% by mass of the earth's crust. It occurs in the combined forms as sulphite ores and sulphate ores such as galena PbS, Zinc blende ZnS, copper pyrites $CuFeS_2$ and sulphate minerals are gypsum $CaSO_4.2H_2O$, epsom salt $MgSO_4.7H_2O$, baryte $BaSO_4$ etc. It can also be present as H_2S in natural gas and crude oil and organosulphure compounds in far sands, oil shale and coal. Organic material such as eggs, proteins, garlic, onion, mustard, hair and wool also contain sulphur.

The other elements are comparatively rare. Selenium and tellurium occur as metal solenoids and tellurides in sulphide ores. Selenium and tellurium are found in anode mud or the anode slime deposited during the electrolytic refining of copper. Polonium is found only in traces (0.001ppm) in the earth's crust and it is also produces in the disintegration of uranium.

General Characteristics :

The important physical properties of the elements of group 16 are recorded in table (7) with their electronic configurations.

Table (7)

Properties	O	S	Se	Te	Po
1. Atomic number	8	16	34	52	84
2. Atomic wt. gm mol-1	16.00	32.06	78.96	127.60	210.00
3. Electronic Configuration	(He) $2s^2\ p^4$	(Ne) $3s^2\ p^4$	(Ar) $3d^{10}\ 4s^2\ p^4$	(Kr) $4d^{10}\ 5s^2\ p^4$	(Xe) $4F^{14}5d^{10}65^2\ p^4$
4. Covalent radius [a] (pm)	66	104	117	137	146
5. Ionic radius (pm) E^{-2}	140	184	198	221	230 [b]
6. Ionisation enthalpy (KJ Mol^{-1})	1314	1000	941	869	813
7. Electron affinity (KJ Mol^{-1})	-141	-200	-195	-190	-174
8. Electronegativity	3.50	2.44	2.48	2.01	1.76
9. Density (gm Cm^{-3})	1.32 [c]	2.06 [d]	4.19 [e]	6.25	-

10. M.Pt. (K)	55	393^{f}	490	725	520
11. B.Pt. (K)	90	718	958	1260	1235
12. Oxidation states	-2, -1, 1, 2	-2. 2, 4, 6	-2, 2, 4, 6	.-2, 2, 4, 6	2, 4

a = single bond, b = almost value, c = at m.pt., d = orthorhombic sulphur, e = hexagonal gray, f = monoclinic.

The general trends in characteristic properties are discussed below:

Electronic Configuration :

The elements of this group have six electrons in the outermost shell and have the general electronic configurations as ns^2np^4.

Atomic and Ionic Radii :

The atomic and ionic radii of the elements of group are smaller than those of the corresponding elements of group 15. As expected, these both radii increase on going down the group. The comparatively smaller atomic and ionic radii of group 16 elements compared to group 15 elements are due to the increased effective nuclear charge of group 16 elements.

Ionization Enthalpies :

Ionization enthalpy decreases drawn the group. It is due to increase in size. However, the elements of this group have lower ionization enthalpy values compared to those of Group-15 in the corresponding periods. This is due to the fact that Group 15 element have extra stable half filled p-orbital electronic configurations.

N (z=7) : $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ (half filled stable)

O (z=8) : $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ (Less stable)

Electron gain Enthalpy :

Because of the compact nature of oxygen atom due to its smaller size, it has less negative electron gain enthalpy than sulphur. However, from sulphur onwards have the value again becomes less negative up to polonium.

Electro Negativity :

The elements of group 16 have higher values of electro Negativity than the corresponding elements of group-15. Oxygen is the second most electronegative element next to fluorine. The electro negativity decreases on going down the group. The decrease in electro negativity downs the group id due to increase in size of the atoms.

Physical Properties :

Some of the most common physical properties of Group-16 elements are given in the above table. Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is sort lived (half life 13.8 days). All these elements exhibit allotropy. The melting and boiling points increase with increase in atomic number down the group. The large difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity, oxygen exists as diatomic molecule (O_2) whereas sulphur exists as polyatomic molecules (S_8). In this group, only sulphur has a strong tendency for catenation.

Chemical Properties :

Like other members of P-block elements present in second period, oxygen shows anomalous behavior. This is due to its small size, high electro negativity, high ionization enthalpy and absence of d-orbital in its valence shell. The typical effect of small size and high electro negativity is the presence of strong hydrogen bonding in water (H_2O) which is not present in H_2S and other hydrides of group 16 elements. Due to the absence of d-orbital in oxygen, its covalence is limited to four and in practice, rarely exceeds two. However, in case of other elements, the valence shell can be expanded using vacant d-orbital and hence covalence exceeds four. The stability of -2 oxidation state decreases down the group. Polonium hardly shows -2 oxidation states.

Since the electro negativity of oxygen is very high, it shows only negative oxidation state as -2 except in the case of OF_2 where its oxidation state is +2. Other elements of these group exhibits +2, +4, +6 oxidation states in their various compounds but +4 and +6 are more common in them. Sulphur, selenium and tellurium usually show +4 oxidation state in their compounds with oxygen and +6 with fluorine. The stability of +6 oxidation state, decreases down the group and stability of +4 oxidation state increases due to the "inert pair effect (ns^2)". Bonding in +4 and +6 oxidation states is primarily covalent.

(i) Reactivity with Hydrogen:

All the elements of Group-16 form hydrides of the type H_2E (E=O, S, Se, Te, Po). Some common properties of hydrides are given in table (8) :

Table (8)

Properties	H_2O	H_2S	H_2Se	H_2Te
M.Pt (K)	273	188	208	222
B.Pt (K)	373	213	232	269
H-E Distance (pm)	96	134	146	169
H-E-H Angle (θ)	104°	92°	91°	90°
H-E Disso. enthalpy $KJ\ mol^{-1}$	463	347	276	238
Disso. coefficient	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be explained in terms of decrease in bond enthalpy for the dissociation of H-E bond down the group. Owing to the decrease in enthalpy for the dissociation of H-E bond the group, the thermal stability of hydrides also decreases form H_2O to H_2Po. All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

(ii) Reactivity with Oxygen:

All the elements of group 16 form two main oxides EO_2 and EO_3 (E=S, Se, Te or Po). In addition, they form other oxides as given in table (9). Ozone (O_3) and sulphur dioxide (SO_2) are gases while selenium dioxide (SeO_2) is solid. Reducing property of dioxide decreases from SO_2 to TeO_2, SO_2 is reducing agent while TeO_2 is an oxidizing agent. Besides EO_2 type, sulphur, selenium and tellurium also form EO_3 type oxides (SO_3, SeO_3, TeO_3). Both types of oxides are acidic in nature.

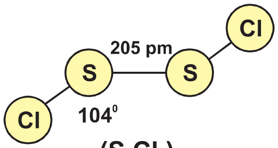
Table (9)

Oxide	S	Se	Te	Po
Monooxide	SO	-	TeO	PoO
Dioxide	SO_2	SeO_2	TeO_2	PoO_2
Trioxide	SO_3	SeO_3	TeO_3	-
Heptaoxide	S_2O_7	-	-	-
Other oxide	S_2O, S_2O_3, SO_4	-	-	-

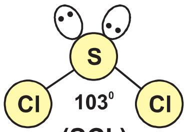
(iii) Reactivity towards the Halogens :

Elements of group -16 form a large number of halides of the type, EX_6, EX_4 and EX_2 where E is an element of the group and X is a halogen. The stability of the halides of this group decreases in the order $F^- > Cl^- > Bl^- > I^-$. Amongst hexahalides, hexafluoride are the only stable halides. All hexafluoride are gaseous in nature. They have octahedral structure. Sulphur hexafluoride, SF_6 is exceptionally stable for satiric reasons.

$$2SeCl_2 \longrightarrow SeCl_4 + Se$$



(S_2Cl_2)



(SCl_2)

Amongst tetra fluorides, SF_4 is gas, SeF_4 is a liquid and TeF_4 is a solid compound. All these fluorides have sp^3d hybridization and thus, have trigonal bipyramidal structures in which one of equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry.

All elements except selenium form dichlorides and dibromides also. These dihaledes are formed by sp^3 hybridization and thus, have tetrahedral structure. The well known monohalide are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo dir pro portion as given below :

$2SeCl_2 \rightarrow SeCl_4 + Se$.Insert Digram

Dioxygen :

Scheele was the first to prepare dioxygen by heating mercuric oxide in 1772. If occurs in three isotopic forms such as:

$^{16}_{8}O$	$^{17}_{8}O$	$^{18}_{8}O$
(Abundance 99.762%)	(Abundance 0.038%)	(Abundance 0.204%)

Out of the three isotopes, 18 isotopes are radioactive and are used in studying the mechanisms of organic reactions and other tracer techniques.

Dioxygen can be obtained in the laboratory by the following methods:

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

(ii) By thermal decomposition of the oxides of metals lower in the electrochemical series and higher oxides of some metals.

$$2AgO_{(s)} \rightarrow 4Ag_{(s)} + O_{2\,(g)}$$

$$2HgO_{(s)} \rightarrow 4Hg_{(l)} + O_{2\,(g)}$$

$$2Pb_3O_{4\,(s)} \rightarrow 6PbO_{(s)} + O_{2\,(g)}$$

$$2PbO_{2\,(s)} \rightarrow 2PbO_{(s)} + O_{2\,(g)}$$

(iii) Hydrogen peroxide is readily decomposed into water and di oxygen by catalysts such as finely divided metals and manganese di oxide:

$$2H_2O_2 \xrightarrow[\text{Pt,Ni}]{} 2H_2O_{(l)} + O_{2\,(g)}$$

On large scale it can be prepared from water or air. Electrolysis of water leads to the release of H_2 at the cathode and O_2 at the anode. However, at industrial level, dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

Properties of Dioxygen :

Di oxygen is a colourless, tasteless and odorless gas. It is slightly soluble in water and its solubility is about 3.08 cm^3 in 100 cm^3 of water at 293K. This solubility is just sufficient for the vital support of marine and aquatic life.

It can be liquefied to a pale liquid under pressure. It liquefies at 90K and freezes at 55K. Molecular oxygen is paramagnetic in spite of having even number of electrons and it can be explained by "molecular orbital theory."

The dioxygen is a quite stable in nature and its bond dissociation enthalpy is very high. Therefore, it is not very reactive as such :

$$O_2 \rightarrow O + O \quad ; \quad \Delta H = 493.4 \text{ kj mol.}^{-1}$$

Therefore, dioxygen reacts at higher temperature. However, once the reaction starts, it proceeds of its own. This is because the chemical reaction of di oxygen is exothermic and the heat produced during the reaction is sufficient to sustain the reaction.

Some of the reactions of dioxygen with metals, non-metals and other compounds are given below:

$$4\,Na + O_2 \rightarrow 2\,Na_2O$$

$$2\,Ca + O_2 \rightarrow 2\,CaO$$

$$2\,Mg + O_2 \rightarrow 2\,MgO$$

$$4\,Fe + O_2 \rightarrow 2\,Fe_2O_3$$

$$P_4 + 5O_2 \rightarrow P_4H_{10}$$

$$C + O_2 \rightarrow CO_2$$

$$2\,ZnS + 3O_2 \rightarrow 2\,ZnO + 2SO_2$$

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

Some compounds are catalytically oxidized, e.g.

$$2SO_2 + O_2 \quad \underline{V_2O_5} \quad 2SO_2$$

$$4\,HCl + O_2 \quad \underline{Cu\,Cl_2} \quad 2Cl_2 + 2H_2O$$

Uses :

(1) It is essential for life support respiratory system for living substances.

(2) Di oxygen is used in the oxy-hydrogen or oxy-acetylene torches which are used for welding and cutting of metals.

(3) It is used in metallurgical processes to remove the impurities of metals and non-metals by oxidations. It also used in making steel.

(4) It is essential in any burning processes.

(5) Liquid oxygen is used as a rocket fuel.

(6) Oxygen cylinders are widely used in hospitals, high attitude flying and in mountaineering.

(7) The combustion of fuels, e.g., hydrazine in liquid oxygen, provides tremendous thrust in rocket.

(8) It is used as an oxidizing agent and bleaching agent.

Simple Oxides :

The binary compounds of oxygen with other elements are called oxides. We have studied that oxygen combines with metals and non-metals to form their respective binary oxides. Oxide can be simple like MgO, Al_2O_3, etc. or mixed like Mn_2O_3, Fe_3O_4, Pb_3O_4 etc. On the basis of acid-base characteristics, the oxides may be classified into four classes.

(i) The oxides which combine with water to give acid are recognized as acidic oxides, like CO_2, SO_2, Cl_2O_7, N_2O_5, etc.

$$SO_2, + H_2O \rightarrow H_2\,SO_3 \text{ (sulphurous acid)}$$

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (Carbonic acid)}$$

$$N_2O_5 + H_2O \rightarrow HNO_3 \text{ (Nitric acid)}$$

$$Cl_2O_7 + H_2O \rightarrow 2HClO_4 \text{ (Perchloric acid)}$$

(ii) The oxides which combine with water to give basic solution are called basic oxides. These are mostly oxides of metals.

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$

$$Al_2O_3 + 3H_2O \rightarrow 2Al\,(OH)_3$$

The basic oxides react with acids to form salt and water.

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$

(iii) The oxides which show acidic as well as basic character are called amphoteric oxides. These are the oxides formed by elements like Al, Zn, Sn, Pb etc., which are present on the border line between metals and non-metals. For example,

$$Al_2O_{3(s)} + 6\,HCl_{(aq.)} + 9\,H_2O\,(l) \rightarrow 2\,[Al(H_2O)_6]^{+3}{}_{(aq.)} + 6\,Cl^-{}_{(aq.)}$$

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

(iv) The oxides which neither react with acids nor with bases are called neutral oxides. These are neutral to litmus solution, for example, N_2O, NO, CO etc.

Ozone :

Ozone is an allotropic form of oxygen. It is present in the upper atmosphere (about 20 km above the surface of the earth). It is believed to be formed in the upper atmosphere by the action of ultraviolet (UV) radiations on oxygen as :

$$3O_2 + \text{ultraviolet} \rightarrow 2O_3\,, \quad \Delta H = 142.7 \text{ kj mol}^{-1}.$$

Therefore, ultraviolet rays, which are harmful to human beings, are absorbed by oxygen to form ozone. The layer of ozone thus formed also prevents the remaining ultraviolet rays to reach the earth's surface.

Preparation and Properties :

Pure ozone is a pole blue gas, dark blue liquid and violet black solid. It has characteristic smell and in small concentrations it is harmless. However, if the concentration rises above about 100 parks per million (ppm), breathing becomes uncomfortable resulting in headache and nausea.

When a slow dry stream is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen

$$3O_2 \rightarrow 2O_3 \text{ , } \Delta H\,(298K) = 142 \text{ KJ mol}^{-1}$$

Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition.

If the concentration of ozone, greater than 10 percent are required, a battery of ozonisers can be used, and pure ozone (B.P. 385K) can be condensed in a vessel surrounded by oxygen.

Ozone is thermodynamically unstable with respect to oxygen because it results in libration of heat (ΔH is negative) and increases in entropy (ΔS is Positive). These two factors reinforce each other resulting in large negative Gibb's free energy ($\Delta G = \Delta H - T\Delta S$) for its conversion into oxygen. Therefore, the high concentration of ozone can be dangerously explosive.

Ozone is one of the most powerful oxidizing agents with the liberation of oxygen and giving nascent oxygen (atomic oxygen).

$$O_3 \rightarrow O_2 + O \text{ (Nascent oxygen)}$$

For example, it oxidizes lead sulphite to lead sulphate and iodide ions to iodine.

$$PbS_{(s)} + 4O_{3(g)} \rightarrow PbSO_{4(s)} + 4O_{2(g)}$$

$$2I^-_{(aq.)} + H_2O_{(g)} + O_{3(g)} \rightarrow 2\,OH^-_{(aq.)} + I_{2(s)} + O_{2(g).}$$

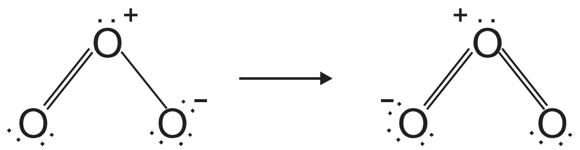
When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH9.2), iodine is librated which can be lit rated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

Nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust system of supersonic jet aero planes might be slowly depleting the concentration of the ozone layer in upper atmosphere.

$$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$

Another threat to this ozone layer is probably posed by the use of forms which are used in aero sol sprays and as refrigerants. Chlorofluorocarbons (CFS) are long lived molecules and diffuse into the stratosphere where they are decomposed by UV radiations to produce chlorine. These chlorine atoms react with ozone causing a decrease in its concentration at a faster rate than its forming from O_2.

The two oxygen – oxygen bond lengths in the ozone molecule are identical (128pm) and the molecule is angular as expected with bond angle of about 1170. It is resonance hybrid of two forms.



Uses:

It is used as germicide, disinfectant and for sterilizing water. It is also used for bleaching outs, ivory, flour, starch, etc. It acts as an oxidizing agent in the manufacture of potassium permanganate.

Sulphur and Allotropic Forms :

Sulphur exists in numerous allotropic forms of which three forms are the most important. These three main allotropic forms are :

(i) Rhombic sulphur (α-Sulphur)

(ii) Monoclinic sulphur (β-Sulphur)

(iii) Plastic sulphur (δ- Sulphur)

(i) Rhombic Sulphur :

It is the common form of sulphur and it

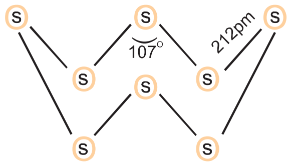
formed by slowly evaporating the solution of roll sulphur in CS_2, when octahedral crystals of sulphur appear. Its melting point is 385.8K and specific gravity is 2.06 gm cm^{-3}. It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. However, is readily soluble in CS_2. This is the most stable form of sulphur at room temperature and all other forms of sulphur change into this form on standing. It exists as S_8 molecules. The sulphur atoms are arranged in a puckered ring.

(ii) Monoclinic Sulphur :

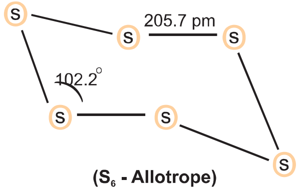
This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling till a crust is formed. Two holes are made in the crust and the remaining liquid poured out. On removing the crust, colourless needle shaped crystals of β-Sulphur are formed. Its melting pain is 393K and specific gravity is 1.98 gm-cm^{-3}. Monoclinic sulphur also exists as S_8 molecule with puckered ring structure like rhombic sulphur. However, the two forms differ in the symmetry of their crystals. It is stable above 369K and transforms in to a-sulphur below this temperature. Thus, at 369K both the forms are stable and coexist. This is called the transition temperature. Both rhombic and monoclinic sulphur have S_8 molecules and S_8 ring in both forms is puckered and has a crown shape.

(iii) Plastic Sulphur :

Plastic sulphur is obtained by pouring molten sulphur into cold water when a soft rubber like mass is obtained which is called plastic or δ-sulphur. It has no sharp melting point and has specific gravity of 1.95 gm. Cm^{-3}. It is amorphous form of sulphur. It is soft and elastic in the beginning but hardens on standing and gradually changes to rhombic sulphur. It is insoluble in CS_2 and is regarded as super cooled liquid. It exists as S_6.



(S_8 - Allotrope)



(S_6 - Allotrope)

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesized in the last few decades. At about 1000K, the sulphur can be obtained as S_2 like O_2 and the S_2 form is paramagnetic.

Sulphur Oxide :

It contains sulphur in +4 oxidation state and is formed together with a little (6.8%) sulphur trioxide when sulphur is burnt in air or oxygen.

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

In the laboratory, it is prepared by treating a sodium sulphite with dilute sulphuric acid.

$$Na_2SO_{3(s)} + H_2SO_{4(aq.)} \rightarrow SO_{2(g)} + Na_2SO_{4(aq.)} + H_2O_{(l)}$$

It may also be prepared by heating copper turnings with concentrated sulphuric acid

$$Cu_{(s)} + 2H_2SO_{4(aq.)} \rightarrow CuSO_{4(aq.)} + SO_{2(g)} + H_2O_{(l)}$$

Industrially, it is produced as a byproduct of roasting of sulphide ores such as iron pyrites or zinc bland.

$$4FeS_{(s)} + 11\,O_{2\,(g)} \rightarrow 2Fe_2O_{3(s)} + 8\,SO_{2(g)}$$

Properties :

Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water. It liquefies at room temperature under a pressure of two atmospheres and boils at 263K. It freezes at 197.5K, giving a white shown – like mass.

It is highly soluble in water, forms a solution sulphurous acid.

$$SO_{2(g)} + H_2O_{\,(l)} \rightarrow H_2SO_{3(aq.)}$$

It reacts readily with sodium hydroxide solution, forming sodium sulphite, which then reacts with more so2 to form sodium hydrogen sulphide.

$$2NaOH + SO_2 \rightarrow Na_2SO4 + H_2O$$

$$Na_2SO_4 + H_2O + SO_2 \rightarrow 2\,NaHSO_3$$

In its reaction with water and alkalis, the behavior of sulphur dioxide is very similar to that of carbon dioxide.

Sulphur dioxide reacts with chlorine in the presence of charcoal (which acts as catalyst) to give sulphuryl chloride, SO_2Cl_2. It is oxidized to sulphur trioxide by oxygen in the presence of vanadium pentaoxide catalyst.

$$SO_{2\,(g)} + Cl_{2\,(g)} \rightarrow SO_2Cl_{2\,(l)}$$

$$2\,SO_{2\,(g)} + O_{2\,(g)} \rightarrow 2\,SO_{3\,(g)}$$

When moist, sulphur dioxide behaves as a reducing agent. For example, it converts Fe^{+3} ions to Fe^{+2} ions and de colourises acidified potassium permanganate (VIII) solution, the latter reaction is a convenient test for the gas.

$$2\,Fe^{+3} + SO_2 + 2\,H_2O \rightarrow 2Fe^{+2} + SO_4^{-2} + 4H^{+}$$

$$5\,SO_2 + 2\,MnO_4^{-} + 2H_2O \rightarrow 5\,SO_4^{-2} + 4\,H^{+} + 2\,Mn^{+2}$$

Uses :

The main uses of SO_2 are as follows :

(1) Sulphur dioxide is used for the manufacture of important chemicals such as sulphuric acid, sodium hydrogen sulphite, calcium hydrogen sulphite etc. These bisulphites are used as preservatives for jams, pickles, jellies and squashes.

(2) It is used for refining of petroleum and sugar.

(3) It is used for bleaching delicate articles such as wool, silk, straw etc.

(4) It is used as an antichlor i.e. for removing excess chlorine from bleached articles.

(5) It is used as a disinfectant and a germicide.

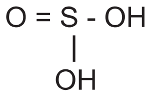
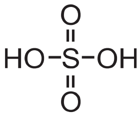
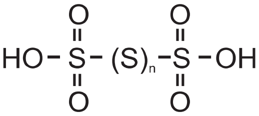
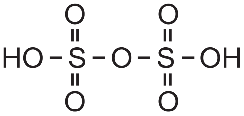
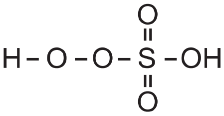
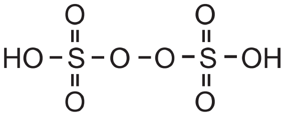
(6) Liquid SO_2 is used as a solvent.

(7) Liquid SO_2 is used as a refrigerant.

Oxoacids of Sulphur :

Sulphur, selenium and tellurium form a variety oxoacids of these, the oxoacids of sulphur are more numerous such as H_2SO_3, $H_2S_2O_3$, H_2S_2O4, $H_2S_2O_5$, cannot be isolated. They are known in aqueous solution or in the form of their salts. Some of oxoacids are shown in the following table (10).

Table (10)

S.No.	Formula	Name of acid	Oxidation state	Structure
1.	H_2SO_3	Sulphurous acid	+ 4	 $\mathrm{O=\underset{\underset{OH}{\mid}}{S}-OH}$
2.	H_2SO_4	Sulphuric acid	+ 6	 $\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$
4.	$H_2S_2O_4$	Dithonous acid	+ 3	 $\mathrm{HO-\overset{\overset{O}{\|}}{S}-\overset{\overset{O}{\|}}{S}-OH}$
5.	$H_2S_nO_6$ n = 2 to 5	Polythionic acid (S-S bonded)	–	 $\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(S)_n-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$
6.	$H_2S_2O_7$	Disulphuric acid (Olium)	+6	 $\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$
7.	H_2SO_5	Peroxomonosulphuric acid	+6	 $\mathrm{H-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$
8.	$H_2S_2O_8$	Peroxodisulphuric acid	+6	 $\mathrm{HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH}$

Sulphuric Acid :

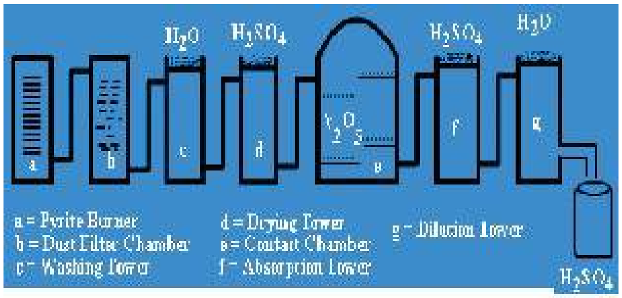
Sulphuric acid is one of the most important industrial chemicals worldwide because of its industrial applications; it is called the king of chemicals. It is manufactured by "contact process." The process involves the following steps :

(i) Sulphur dioxide is prepared by burning sulphur or iron pyrites in excess of air.

(ii) Sulphur dioxide is catalytically (V_2O_5) oxidized to SO_3 with atmospheric oxygen. The reaction is reversible as well as exothermic in nature. This is the key reaction far the process.

(iii) Sulphur trioxide (SO_3) is absorbed in about 98% H_2SO_4 to form oleum ($H_2S_2O_7$) or fuming sulphuric acid.

A schematic diagram of 'content process' is shown in the following figure :



Contact process for sulphuric acid production

The SO_2 produced is purified by removing dust and other impurities such as arsenic compounds. The key reaction is shown as follows :

$$2SO_2(g) + O_2(g) \overset{V_2O_5}{\rightleftharpoons} 2SO_2$$

$$\Delta H = - 196.6 \text{ KJ mol}^{-}$$

The condition for the maximum yield of SO_3 are derived by using Le Chatelier's as follows. The forward reaction is exothermic and therefore, low temperature favours the oxidation of sulphur dioxide. However, it is essential to have minimum temperature of 720K, called 'optimum temperature', to get the maximum yield of the product. Since the volume of the gaseous product is less than that of the gaseous reactants, high pressure should favour the oxidation of sulphur dioxide. But a very high pressure may cause the corrosion of the vessel in which oxidation is carried. Therefore, a pressure of 2 to 3 bar is sufficient for the oxidation. Dilution of oleum with water gives H_2SO_4 of the desired concentration. In the industry two steps are carried out simultaneously to make the process continuous one and also to reduce the cost.

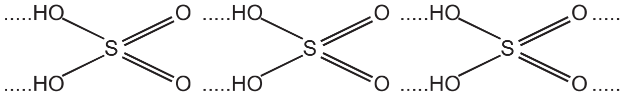
$$SO_2 + H_2SO_4 \underline{\qquad\quad} H_2S_2O_7$$

$$H_2S_2O_7 + H_2O \underline{\qquad} 2H_2SO_4$$

The sulphuric acid obtained by contact process in 96-98% pure.

Properties :

Pure sulphuric acid is viscous, colourless and dense languid with specific gravity of 1.84 at 298K. It freezes at 283K and boils at 611K. The high boiling point of sulphuric acid suggest that it is an associated molecule with inter molecular hydrogen bonding.



The sulphuric acid in concentrated form has strong affinity for water and the dissolution process is highly exothermic and produces a large quantity of heat during dissolution process. Concentrated sulphuric acid is diluted by adding acid to water not water to acid. Sulphuric acid forms hydrates such as H_2SO_4 H_2O and H_2SO_4 $2H_2O$ so that it is used as dehydrating agents.

The chemical reactions of sulphuric acid are as a result of the following characteristics :

(i) Low volatibility

(ii) Strong acidic character

(iii) Strong affinity for water and

(iv) Ability of act as an oxidizing agent.

In aqueous solution, sulphuric acid ionises in two steps :

$$H_2SO_4 + H_2O^+ \longrightarrow H_3O^+ + HSO_4^- \qquad K_1 = \text{Very high}$$

$$(Ka_1 > 10)$$

$$HSO_4^- + H_2O \longrightarrow H_3O^+ + SO_4^{-2} \qquad K_2 = 1.2 \times 10^{-2}$$

The larger value of Ka_1 (Ka_1>10) means that H_2SO_4 is largely dissociated into H^+ and $HSO\text{-}_4$. Greater the value of dissociation constant (Ka), the stronger is the acid.

The acid forms two series of salts, normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g. sodium hydrogen sulphate, $NaHSO_3$).

$$2Na + H_2SO_4 \longrightarrow Na_2SO_4 + H_2$$

$$Na + H_2SO_4 \longrightarrow NaHSO_4 + \frac{1}{2}H_2$$

Sulphuric acid can be used to manufacture more volatile acids from their corresponding salts, because of the lower volatility of it.

$$2MX + H_2SO_4 \longrightarrow 2HX + M_2SO_4$$

$[\, M = \text{Metal}; X = F, Cl, NO_3 \,]$

Concentrated sulphuric acid is a strong dehydrating agent. Many moist gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. It removes water content from organic compounds, it is evident by its charring action on carbohydrates.

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

(Charring)

Hot concentrated sulphuric acid is a moderately strong oxidizing agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidized by concentrated sulphuric acid, which is reduced to SO_2.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$3S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

Uses :

Sulphuric acid is a very important industrial chemical. A nation's industrial strength can be judged by the quantity of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilizers (e.g., ammonium sulphate, super phosphate)

Other uses are in :

1- Petroleum refining
2- Manufacture of pigments, paints and dyes tuff intermediates
3- Detergent industry
4- Metallurgical applications e.g. electroplating
5- In the manufacture of nitrocellulose products
6- As a laboratory reagent, and
7- Storage batteries

ELEMENTS OF GROUP - 17

Group 17 of the periodic table contains five elements :

Fluorine(F), chlorine(Cl), bromine(Br), iodine(I) and astatine(At). These are named as halogens. The name is derived from two Greek words 'halo' meaning sea salt and 'gens' meaning born i.e. sea salt produce because the first members occur as salt (chloride, bromide and iodides) in sea water. These are among the most reactive non metallic elements. The last member of the family, astatine is a radioactive element. Like groups 1 and 2, the group 17 show great similarity amongst themselves, thich is not found in the elements of other groups of the periodic table.

Occurrence :

The halogens are very reactive non=metals and therefore, do not occur in the free state. Fluorine and chlorine are fairly abundant while bromine and iodine less so. Fluorine is present mainly as insoluble fluorides (fluor-spar CaF_2, cryolite Na_3AlF_6 and fluoro apatite $Ca_3(PO_4)_2\, CaF_2$) and small quantities are present in soil, river water plants, bones and teeth of animals etc. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution (2.5% by mass).

Chlorine is twentieth most abundant white fluorine is thirteenth most abundant element is crustal socks. The dried and beds of inland takes and seas contain large deposits of sodium chloride (NaCl), carnalities ($KCl.\, MgCl_2\, 6H_2O$) and calcium chloride ($CaCl_2$)

The abundance of these elements in earth's crust are given below :

Table (11)

Element	Abundance in earth's crust (ppm)	Relative abundance
F	544	13
U	126	20
Br	2.5	47
I	0.46	62

Properties :

These elements have the general electronic configuration ns_2np_5. The important atomic and molecular properties of group-17 elements are given in table (12).

The general trends of some of the atomic, physical and chemical properties are discussed here :

Table (12)

Property	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Ato. Mass/g mol^{-1}	19	35.45	79.90	126.90	210
Elec. Configuration	$[He]2s^2p^5$	$[Ne]\ 3s^2p^5$	$[Ar]\ 4s^2p^5$	$[kr]\ 4d^{10}5s^2p^5$	$[Xe]\ 4f^{14}5d^{10}6s^2p^5$
Covalent Radius (pm)	64	99	114	133	-
Ionic Radius (pm)	133	184	196	220	-
Ionisation Enthalpy kJ mol^{-1}	1680	1256	1142	1008	-
Ele. Gain Enthalpy kJ mol^{-1}	-333	-349	-325	-296	-
Melting Pt.(K)	54.4	172.0	265.8	386.6	-
Boiling Pt(K)	84.9	239.0	332.5	458.2	-
Density (gcm^{-3})	1.5	1.66	3.19	4.94	-
Bond disso. enthalpy kJ mol^{-1}	158.8	242.6	192.8	151.1	-
Bond (x-x) distance (pm)	143	199	228	266	-
Electro negativity kJ mol^{-1}	4	3.2	3.0	2.7	2.2
Hydration Enthalpy kJ mol^{-1}	515	381	347	305	-

(1) Electronic Configuration :

The elements of this group have seven electrons in their outermost shell and the general electronic configuration is ns^2np^5, as shown in above table. There is one electron short of the nest noble gas configuration.

(2) Atomic and Ionic Radii :

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. Among themselves, the atomic and ionic radii increases with increase in atomic number. This is due to increase in number of electron shells.

(3) Ionisation Enthalpy :

Outermost shell of these elements have seven electrons and require only one electron to complete their octet so that they have very little tendency to lose electrons. Thus, the ionization enthalpies of halogens are very high. However, on going down the group from fluorine to astatine, the ionization enthalpy decreases as usual. This is due to gradual increase in atomic size which is maximum for iodine.

(4) Electron gain enthalpy :

These elements have highest electron affinity (or electron gain enthalpy) is their respective periods. This is due to the fact that the atoms of these elements have only one electron less than the stable nobel fas (ns^2np^6) configuration. Electron gain enthalpy of the elements of the group becomes less negative down the group. However, the negative electron gain enthalpy of fluorine is unexpectedly less than that of chlorine. It is due to small size of fluorine atom. As a result, there are strong inter electronic repulsions in the relatively small 2p orbital of fluorine and thus, the incoming electron does not experience much attractions. Therefore, chlorine has the highest negative electron gain enthalpy in this group.

(5) Electro negativity :

Halogens have large electro negativity values. The values decrease down the group from fluorine to iodine because the atomic size increases and the effective nuclear charge decreases. Fluorine is the most electro negative element in the periodic table.

Physical Properties :

Halogens display smooth variations in their physical properties. Fluorine and chlorine are gases, bromine is liquid and iodine is in solid state at atmosphere temperature and pressure. Melting and boiling points of these elements steadily increase with atomic numbers. All halogens are coloured. This is due to abruption of light 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, F_2, Has yellow, Cl_2, greenish yellow, Br_2, red and I_2, violet colour. Flourine and chlorine reacts or soluble in 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.

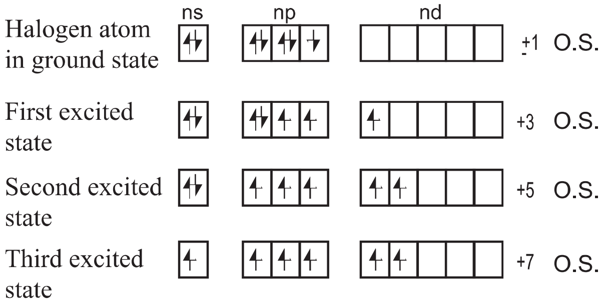
One can notice from the above table(12), that the bond dissociation enthalpy of F_2 is smaller than Cl_2, whereas x-x bond dissociation enthalpies from Cl_2 onwards show the excepted trend :

$Cl-Cl > Br-Br > I-I$

A reaction for this anomaly is the relatively large electron – electron repulsion among the lone pairs in F_2 molecule (due to smaller size) where they are much closer to each other than in case of Cl_2.

Chemical Properties :

The halogens are the most reactive elements as a family. They react readily with metals and non-metals to form halides. All the halogens show -1 oxidation state because these requires only one electron to complete their octate. Since fluorine is the most electro negative element, it always shows an oxidation state -1. It does not show any positive oxidation state. The other elements of this group also show positive oxidation states due to the presence of vacant d-orbital in their valency shells. As a result the outer s- or p- electrons can be promoted to the vacant d- orbital as per requirement and show +1, +3, +5 oxidation states as shown below :



These higher oxidation states are realized mainly when the halogen are in combination with the small and highly electro negative fluorine and oxygen atoms, e.g. in oxides, oxo acids and inter halogen compounds. The oxidation states of +4 and +6 occur in oxides and oxo acids of chlorine and bromine and +7 oxidation state occure in inter halogen compounds such as IF_7.

All the halogens are highly reactive while the reactivity decreases down the group. The readily acceptance of an electron is the reason for the strong oxidizing nature of halogens. F_2 is the strongest oxidizing halogen and it can oxidize easily to the other halide ions in solution or even in the solid phase. In general, a halogen oxidizes halide ions of higher atomic number.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 \ [X = Cl, Br, I]$$

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 \ [X = Br, I]$$

$$Br_2 + 2X^- \longrightarrow 2\,Br^- + X_2 \ [X = I]$$

The decreasing oxidizing power of the halogen as we go down the group is shown by their decreasing reducing potentials.

$$F_2 + 2e^- \longrightarrow 2F^- \quad : \quad E^0 = +2.87\ V$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \quad : \quad E^0 = +1.36\ V$$

$$Br_2 + 2e^- \longrightarrow 2Br^- \quad : \quad E^0 = +1.09\ V$$

$$I_2 + 2e^- \longrightarrow 2I^- \quad : \quad E^0 = +0.54\ V$$

Hence, F_2 is strongest oxidizing agent and the I_2 is weakest oxidising agent in this group. As we know that chlorine has the highest electron gain enthalpy, so gaseous cl atoms have minimum tendency to accept electrons and therefore, chlorine is expected to strongest oxidizing agent. However, chlorine is not strongest oxidizing agent, but fluorine is the strongest oxidizing agent. This can be explained with the help of Born Haber cycle. As we have learnt, electron gain enthalpy is the property of the isolated atoms in the gaseous state as :

$$X(g) + e^- \longrightarrow X^-(g)$$

$$\Delta \overset{0}{H}eg \ = \ \text{Electron gain enthalpy}$$

However, oxidizing power of halogen is a property in solutions as:

$$\frac{1}{2}X_2\ (s, l \text{ या } g) + e^- + nH_2O \xrightarrow{\Delta H} X^-(aq.)$$

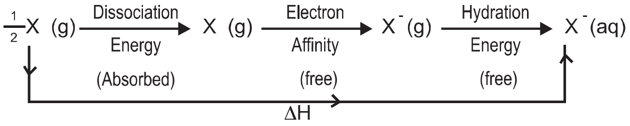
For gaseous F_2 and cl_2, the process may be thought to proceed as:

(i) $\frac{1}{2}X_2(g) \longrightarrow X(g)$; $\Delta \dot{H}dis$ = Dissociation (+)

(ii) $X(g) + e^- \longrightarrow X^-(g)$; $\dot{H}eg$ = Electron affinity (-)

(iii) $X^-(g) + nH_2O \longrightarrow X^-(aq)$; $\dot{H}hyd$ = Heat of hyd. (-)

This process may be expressed as :



The overall tendency for the change (oxidizing power) depends upon the net effect of the three steps. As we know that energy is needed to dissociate the halogen molecule into atoms. The enthalpy change for this step is positive. On the other hand, energy is released in step (ii) as well as step (iii) therefore enthalpy for these steps is negative. Now, although fluorine has less electron gain enthalpy, yet it is strongest oxidizing agent because of the following reasons :

(i) F_2 has low enthalpy of dissociation because of weak F-F bond.

(ii) F_2 has very high enthalpy of hydration because of smaller size of the F^- ion.

Let us discuss some general trends in reactivity of halogens :

(A) Reactivity with 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. Some of the properties of hydrogen of halides are given in table (13). The acidic strength of these acids varies in the order :

$$H-F < HCl < H-Br < H-I$$

The stability of these halides decreases down the group due to decrease in bond -

$$H-F > HCl > H-Br > H-I$$

Some properties of hydrogen halides are given here :

Property	HF	HCl	HBr	HI
Melting paint (K)	190	159	185	222
Boiling paint (K)	293	189	206	238
Bond distance (pm)	91.7	127.4	141.4	160.9
Bond diss. Energy (kj mol^{-1})	574	432	363	295
pKa - avlues	3.2	-7.0	-9.5	-10.0

(B) Reactivity with Oxygen :

Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is thermally stable at 298K.

These oxides are essentially oxygen fluorides because of the higher electro negativity of fluorine than oxygen. 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, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7. A combination of minetic 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 oxide, 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 a bleaching agent for paper pulp and textile and in water treatment. The bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents. The iodine oxides, I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

(C) Reactivity towards Metals :

Halogens react with metals to form metal halides. For example, bromine reacts with magnesium to give magnesium bromide.

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

The ionic character of the halides decreases in the order :

$$MF > MCl > MBr > MI$$

(D) Reactivity of halogens towards other halogens :

Halogens combine amongst themselves to form a number of compounds known as inter halogen compounds. Each halogen has tendency to combine with each other halogen. These inter halogen compounds are of type XX', XX'_3, XX'_5 and XX'_7 etc.

Chlorine :

Chlorine was the first of the halogens to be isolated and its common salt (NaCl) has been known from very early time. Chlorine was first prepared by C.W. Scheele in 1774 by the action of HCl on MnO_2. In 1810, Davy established its elementary nature and suggested the name chlorine on accounts of its colour (Greek : Chloros meaning yellowish green). Chlorine is very reactive does not occur in nature in free state.

Preparation :

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

(i) Chlorine is prepared easily by heating manganese dioxide with concentrated hydrochloric acid

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

(ii) By action of HCl on potassium permanganate or potassium dichromate :

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H2O + 5Cl_2$$

(iii) By Deacon's process, in which hydrochloric acid is oxidized by atmospheric air in the presence of CuCl2 (catalyst) at 723K.

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$

(iv) Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is librated at anode. It is also obtained as a by-product in many chemical processes.

At Cathode :

$$H^+ + e^- \rightarrow H$$

$$H + H \rightarrow H_2$$

At anode :

$$Cl^- \rightarrow Cl + e^-$$

$$Cl + Cl \rightarrow Cl_2$$

Properties :

It is a greenish yellow gas with pungent and suffocating odour. It is about 2-5 times heavier than air. It is poisonous gas which causes headache. It is soluble in water and its aqueous solution is called chlorine water. It is also soluble in organic solvents like carbon tetra chloride. It can be liquefied easily into greenish yellow liquid which boils at 239K and freezes at 171K.

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

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

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

$$Zn + Cl_2 \longrightarrow ZnCl_2$$

$$Sn + Cl_2 \longrightarrow SnCl_2$$
$$Cu + Cl_2 \longrightarrow CuCl_2$$
$$S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$$
$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$
$$2B + 3Cl_2 \longrightarrow 2BCl_3$$
$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$$

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

$$H_2 + Cl_2 \longrightarrow 2HCl$$
$$H_2S + Cl_2 \longrightarrow 2\,HCl + S$$
$$C_{10}H_{16} + 8Cl_2 \longrightarrow 16HCl + 10C$$

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

$$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$
$$\underset{\text{(excess)}}{NH_3} + \underset{\text{(excess)}}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

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

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

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

With dry slaked lime, it gives bleaching powder.

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

The composition of bleaching power is Ca $(OCl_2)\,CaCl_2.\,Ca(OH)_2.\,2H_2O$

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

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

Chlorine water on standing loses 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 and iodine acid respectively.

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$
$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$
$$SO_2 + 2H_2O + Cl_2 \longrightarrow 2H_2SO_4 + 2HCl$$
$$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$$

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

$$Cl_2 + H_2O \longrightarrow 2HCl + O \ \text{(Nascant oxygen)}$$

Coloured substance + O → Colourless substance.

Uses :

Some important uses of chlorine are as follows :

(1) Large quantity of chlorine are used industrially for bleaching wood pulp (required for manufacture of paper and rayon, bleaching of cotton, paper, wood, textile etc.

(2) It is used in the extraction of gold and platinum.

(3) It is used for the manufacture of dyes, drugs, refrigerants and organic compounds like $CHCl_3$, CCl_4, DDT etc.

(4) It is used in sterilization of drinking water.

(5) In the manufacture of poisonous gases like phosgene ($COCl_2$), tear gas (CCl_3NO_2) and mustard gas ($Cl\,CH_2\,CH_2S\,CH_2\,CH_2Cl$).

Hydrogen Chloride :

Hydrogen chloride is a major industrial chemical and is very familiar laboratory reagent. Glauber prepared this compound in 1648 by heating common salt with concentrated sulphuric acid. In 1810, Davy showed that it is a compound of hydrogen and chlorine.

Preparation :

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

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

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

HCl gas can be dried by passing through concentrated sulphuric acid which acts as dehydrating agent.

Properties :

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

$$HCl\ (g) + H_2O\ (l) \longrightarrow H_3O^+(aq) + Cl^-\ (aq)\ \ Ka = 10^7$$

High value of dissociation constant (Ka) indicates that it is strong acid in water. It react with NH_3 and gives white fumes of NH_4Cl.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

When three parts of concentrated HCl and one part of concentrated H NO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum. In aqua regia hydrochloric acid (which is reducing agent) is oxidized by nitric acid (which is an oxidising agent) to form nascent chlorine.

$$3HCl + HNO_3 \rightarrow NOCl + 2H_2O + 2\ Cl$$

(nascent chlorine)

$$Au + 3\ Cl \rightarrow AuCl_3 \qquad \text{(Auric chloride)}$$

$$Au + 4H^+ + NO^-_3 + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$$

Similaraly,

$$3\,Pt + 16H^+ + 4\,NO^-_3 + 18Cl^- \circledR\ 3\,PtCl_6^{-2} + 4\,NO + 8\,H_2O$$

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

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$

Uses : It is used :

(1) In the manufacture of chlorine and various chlorides.

(2) In dyeing, calico printing and tanning industry.

(3) In laboratory, as reagent.

(4) In the manufacture of various chemicals.

(5) In the preparation of aqua regia which is used to dissolve noble metals like gold.

(6) It is used in medicines.

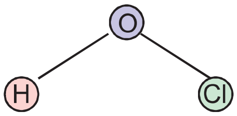
Oxoacids of Halogens :

Due to high electro negativity and small size, fluorine forms only one oxo acid, HOF known as fluoric (I) acid or hypo fluoric acid. Other halogens form several oxoacids. Most of them can not 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 table (14) :

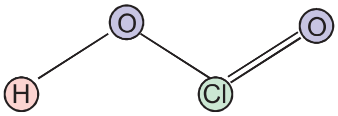
Table (14)

Halic(I) acid (Hypohalous acid)	H O F (Hypo fluolous acid	H O Cl (Hypochlorous acid)	H O Br (Hypobromous acid)	H O I (Hyporodous acid)
Halic (III) acid (Halous acid)	-	HO Cl O (Chlorous acid)	-	-
Halic(V) acid (Halic acid)	-	HO Cl O (Chlorous acid)	H O Br O2 (Bromic acid)	H O I O2 (Iodic acid)
Halic(VII) acid (Perhalic acid)	-	H O Cl O3 (Chloric acid)	HO Br O3 (Perbromic acid)	H O I O3 (Periodic acid)

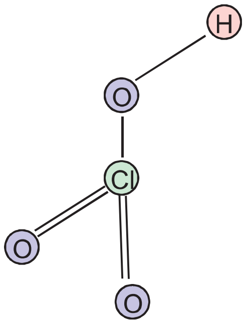
Structures of oxoacids of chlorine are as follows :



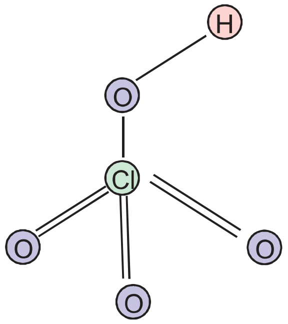
(Hypochloroush acid)



(Chloroush acid)



(Chloric acid)



(Perchloric acid)

Inter halogen Compounds :

The compounds containing two or more different halogen atoms are called inter halogen compounds. They may be represented by the general formula XX'_n, where X is a halogen of larger size and X' of smaller size and X' is more electro negative 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 IF_7 (having maximum number of atoms).

Preparation :

All inter halogen compounds are prepared by direct combination or by the reactions of halogen with other inter halogen compounds. For example,

$$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{437\ K} 2ClF$$

$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{273\ K} 2ClF_3$$

$$\underset{\text{(equal molar)}}{I_2 + Cl_2} \longrightarrow 2ICl$$

$$I_2 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow 2ICl_3$$

$$\underset{\text{(diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3$$

$$Br_2 + \underset{\text{(excess)}}{5F_2} \longrightarrow 2BrF_5$$

Properties :

Some properties of inter halogen compounds are given in the table (15).

Table (15)

Type	Formula	Physical state and colour	Structure
XX'_1	ClF	Colourless gas	Linear
	BrF	Pole brown gas	Linear
	IF	Unstable	Linear
	BrCl	Gas	Linear
	ICl	Ruby red solid (a – form)	Linear
	ICl	Brown red solid (b – form)	Linear
	IBr	Black solid	Linear

XX’$_3$	ClF$_3$	Colourless gas	Bent -T - shaped
	BrF$_3$	Yellow green liquid	Bent -T - shaped
	IF$_3$	Yellow powder	Bent -T - shaped
	ICl$_3$	Orange solid	Bent -T - shaped
XX’$_5$	IF$_5$	Colourless gas	Square pyramidal
	BrF$_5$	Colourless liquid	Square pyramidal
	ClF$_5$	Colourless liquid	Square pyramidal
XX’$_7$	IF$_7$	Colourless gas	Pentagonal bi - pyramidal

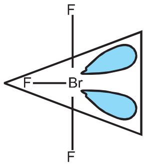
These are all covalent molecules and are diamagnetic in nature. The are volatile solid or liquid at 298K except CIF which is a gas. Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.

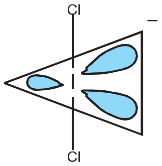
Their chemical reactions can be compared with the individual halogens. In general, inter halogen compounds are more reactive than halogens (except fluorine). This is because X-X' bond in inter halogens is weaker than X-X bond in halogens except F-F bond. All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypo halite (when XX_1), halite (when XX'_3), halite (when XX'_5) and per halite (when XX'_7)

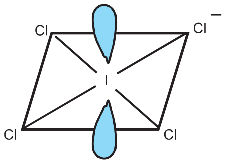
$$XX' + H_2O \rightarrow HX' + HOX$$

Their molecular structures are very interesting which can be explained on the basis of VSEPRT.

For example, the structure of BrF_3, $I\,Cl_2^-$ and $I\,Cl_4^-$ are shown as below :







Uses :

(1) The inter halogen compounds can be used as non-aqueous polar solvents

(2) Inter halogen compounds of fluorine are very useful fluorinating agents. For example, CIF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U.

$$U(s) + 3\,ClF_3\,(l) \rightarrow UF_6\,(g) + 3\,Cl\,F(g).$$

ELEMENTS OF GROUP - 18

The group 18 consists of elements helium (He), neon(Ne), orgon(Ar), krypton(kr), Xenon(Xe) and radon(Rn). It constitutes zero group of the periodic table. These gases at ordinary temperature do not have chemical reactivity and therefore, these were called inert gases. However, nowadays, a number of compounds of these gases, particularly of xenon and krypton have been prepared.

This shows that these gases are not completely inert. Consequently, these gases are called noble gases instead of inert gases which signifies that these gases have some reactivity. This name is analogous to noble metals like gold and platinum which show very low reactivity rather than complete inertness. Because of the low abundance of these gases on earth, they have been called rare gases.

Occurrence of Noble gases :

Due to the inert nature gases, they always occur in the free state. Except radon, all these gases are present in atmosphere in the atomic state. Their total percentage in dry air is about 1% by volume, of which argon (0.93%) is the major component.

Helium and sometimes neon are found in small quantities in minerals of radioactive elements such as monazite, clevite, pitch blende, etc. Helium, neon and argon are found in the water of certain springs. Radon is radioactive and does not occur in the free state because it decays very rapidly. Radon is obtained as a decay product of ^{226}Ra

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

The important atomic and physical properties of the Group 18 elements along with their electronic configurations are given in table (18). The trends in some of the atomic, physical and chemical properties of the group are discussed here.

Table (18)

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Atomic mass (g mol^{-1})	4.00	20.18	39.94	83.30	131.29	222.10
Electronic Configuration	IS$_2$	[He] 2s^2 2p^6	[Ne] 3s^2 3p^6	[Ar[3d^{10} 4s^2 4p6	[Kr] 4d^{10} 5s^2 5p^6	[Xe] 4f^{14} 5d^{10} 6s^2 6p^6
Atomic radius (pm)	120	160	190	200	220	-
Ionisation enthalpy (k J mol^{-1})	2372	2080	1520	1351	1170	1037
Electron gain enthalpy (k J mol^{-1})	48	116	96	96	77	68
Density (g cm^{-3})	1.8x10^{-4}	9.0x10^{-4}	1.8x10^{-3}	3.7x10^{-3}	5.9x10^{-3}	9.7x10^{-3}
Melting point (K)	-	24.6	83.8	115.9	161.3	202
Boiling Point (K)	4.2	27.1	87.2	11.7	5.0	211
Abundance%	5.24x10^{-4}	-	1.82x10^{-3}	0.934	0.3414x10^{-4}	8.7x10^{-6}

Electronic Configuration :

Except helium, the atoms of all noble fases have eight electrons in the valence shell. The general electronic configuration of noble gases (except He) may be expresses as ns^2p^6. On the other hand, helium has 1s^2 electronic configuration it is, therefore, reasonable to assume that inert nature of the noble faces is due to their stable electronic configurations.

Ionisation Enthalpy :

Due to stable electronic configuration these gases exhibit very high ionization enthalpy. However, it decreases down the group with increase in atomic size.

Atomic Radii :

In the case of noble gases, the atomic radii correspond to van der Waal's radii. As we go down the group, the van der Waal's radius increases due to the addition of new electronic shells.

Electron Gain Enthalpy :

Since noble gases have stable electronic configurations, they have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

Physical Properties :

1- All the noble gases are colourless, odourless and tasteless.

2- All the noble gases are mono atomic.

3- They have very low melting and boiling points because the only type of inter atomic inter actions in these elements is weak dispersion forces.

4- Due to smaller size, helium has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

Chemical Properties :

In general, noble gases are not very reactive. Their inertness to chemical reactivity is attributed to the following reasons :

(a) The noble gases have completely filled ns^2np^6 electronic configurations in their valence shells.

(b) They have very high ionization enthalpies. Therefore, they have neither tendency to gain nor to lose any electron and do not enter into chemical combinations.

These reactivity of noble gases has been investigated occasionally, ever since their discovery, but all attempts ot force them to react to form the compounds, we unsuccessful for quite a few years. In march 1962, Neil Barklett, then at the university of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+PtF_6^-$. He, then realized that the first ionization enthalpy of molecular oxygen (1175 KJ mol^{-1}) was almost identical with that of xenon (1170 KJ mol^{-1}). He made efforts to prepare same type of compound. $Xe^+PtF_6^-$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with must electronegtive elements like fluorine and oxygen, have been synthesised.

The compounds of kryptom are fewer. Only the difluorite (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g. RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

(a) Xenon-fluorine compounds :

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under appropriate experimental conditions.

$$\underset{\text{(in 2 : 1)}}{Xe + F_2} \xrightarrow[\text{673 K}]{\text{NI - Vessel}} Xe\,F_2(s)$$

$$\underset{\text{(in 1 : 5)}}{Xe + 2F_2} \xrightarrow[\text{6–7 bar}]{\text{873 K}} Xe\,F_4(s)$$

$$\underset{\text{(in 1 : 20)}}{Xe + 3F_2} \xrightarrow[\text{60 – 70 bar}]{\text{573 K}} XeF_6\,(s)$$

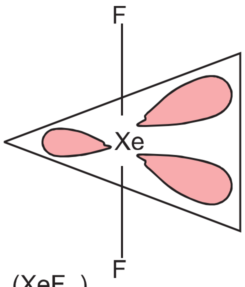
XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

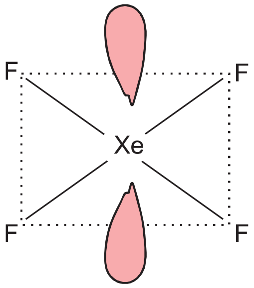
XeF_2, XeF_4 and XeF_6 are colourless crystalline solids ands sublime readily at 298K. They are strong fluorinating agents. These are readily hydrolysed even by traces of water. For example XeF_2 is hydrolysed to give Xe, HF and O_2.

$$2XeF_2\,(s) + 2H_2O\,(l) \longrightarrow 2Xe\,(g) + 4HF\,(aq) + O_2\,(g)$$

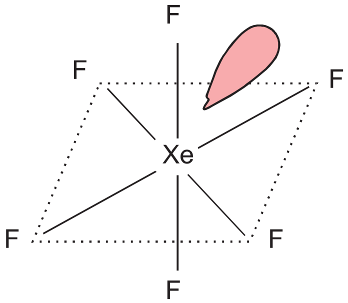
The structure of the three xenon fluorides can be deduced from VSEPRT and these are shown in the following fig. XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs and would thus, have a distorted octahedral structure as found experimentally in the gas phase.



(XeF_2)



(XeF_4)



(XeF_6)

Xenon fluorides react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+\,[PF_6]^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3^+]\,[SbF_6]^-$$

$$XeF_6 + NaF \longrightarrow [Na]^+\,[XeF_7]^-$$

$$XeF_6 + CsF \longrightarrow [Cs]^+[XeF_7]^-$$

(b) Xenon-oxygen compounds :

Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.

$$6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

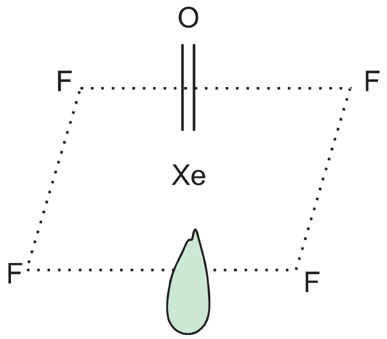
$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

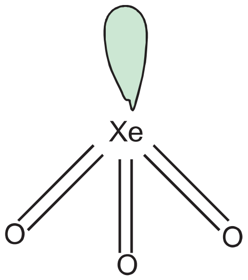
$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2H_2O \longrightarrow XeO_2F_2 + 4HF$$

XeO_3 is a colourless explosive solid and has a pyramidal molccular structure. $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.



($XeOF_4$)



(XeO_3)

Uses :

Helium is a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium finds use as cryogenic agent for carrying out various experiments at low temperatures. It is used to produce and sustain powerful superconducting magnets which form and essential part of modern NMR spectrometers and Magnetic Resounence Imaging (MRI) systems for clinical diagnosis. It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. Neon bulbs are used in botanical garden and in green houses.

Argon is used mainly to provide an inert atmosphere in high temperature. It is also used in the laboratory for handling substances that are air-sensitive.

There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

Exercise Questions

Multiple Choice Question :

1. The most abundant element in crustal rocks of the earth among group 15 is :

   (a) N (b) As (c) P (d) Sb

2. The brown gas formed when HNO_3 is reduced by metals is:

   (a) N_2O (b) N_2O_3

   (c) NO_2 (d) NO

3. The hydride of group 15 having largest bond angle is :

   (a) NH_3 (b) PH_3

   (c) AsH_3 (d) BiH_3

4. Out of all the halogen hydro acids, the weakest is :

   (a) HI (b) HBr

   (c) HF (d) HCl

5. The geometry of $XeOF_2$ is :

   (a) Pyramidal (b) T - Shaped

   (c) Octahedral (d) Tetrahedral

6. Which of the following has highest ionization enthalpy?

   (a) P (b) N

   (c) As (d) Sb

7. Which of the following oxide is strongly acidic?

(a) P_4H_{10} (b) SO_3

(c) Cl_2O_7 (d) Al_2O_3

8. Which of the following oxoacid is strongly acidic?

(a) HClO (b) $HClO_3$

(c) $HClO_2$ (d) HClO

9. The laughing gas is :

(a) Nitrogen oxide (b) Nitric oxide

(c) Nitrogen trioxide (d) Nitrogen pentaoxide

10. The halogen with highest negative electron gain enthalpy is ? :

(a) F (b) Cl

(c) Br (d) I

Very Short Answer Questions :

1. Why are pentahalides more covalent than tri halides?

2- Why is BiH_3 the strongest reducing agent amongst all the hydrides of group 15 ?

3- Why N2 is less reactive at room temperature ?

4- How does ammonia react with a solution of Cu^{+2} ?

5- What is the covalence of nitrogen in N_2O_5?

6- What happens when PCl_5 is heated ?

7- Write balanced equation for the hydrolyte reaction of PCl_5 with heavy water.

8- What is the basicity of H_3PO_4 ?

9- What happens when H_3PO_3 is heated ?

10- Why is H_2O a liquid and H_2S a gas ?

11- Why does O_3 act as a powerful oxidizing agent ?

12- Why is $Ka_2 << Ka_1$ for H_2SO_4 is water ?

13- Name two poisonous gases which can be prepared from chlorine gas;

14- Why is ICl more reactive than I_2

15- Why is helium used in diving apparatus?

16- Balance the following equation :

$XeF_6 + H_2O \rightarrow XeO_2F_2 + HF$

17- Why has it been difficult to study the chemistry of radon ?

18- Give the resonating structures of NO_2 and N_2O_5.

19- Why does $R_3P{=}O$ exists but $R_3N{=}O$ does not (R=alkyl group) ?

20- Explain why NH_3 is basic while BiH_3 is only feebly basic.

21- Give the disproportionate reaction of H_3PO_3.

22- Can PCl_5 act as an oxidizing as well as a reducing agent ?

23- Which aerosol deplete ozone ?

24- Describe the manufacture of sulphuric acid by contact process.

25- How is SO_2 an air pollutant ?

26- Why are halogens strong oxidizing agents ?

27- Write two uses of ClO_2.

28- Why are halogens coloured ?

29- Write the reactions of F_2 and Cl_2 with water.

30- Why do noble gases have comparatively large atomic sizes ?

Short Answer Questions :

1- Discuss the necessary conditions required to enhance the production of ammonia.

2- Why the bond angles in PH_4^+ is more than NH_3?

3- What happens, when white phosphorus is heated with concentrated solution of NaOH in the inert atmosphere of CO_2 ?

4- Give a list of major sources of sulphur.

5- Arrange the hydrides of group 16 in their thermal stability order.

6- Which of the following element does not react directly with oxygen ?

Zn, Ti, Pt, Fe.

7- Complete the following reactions –

$C_2H_4 + O_2 \rightarrow$ ………………..

$4\,Al + 3\,O_2 \rightarrow$ ………………..

8- How is O_3 estimated quantitatively ?

9- What happens when sulphur dioxide is

passed into aqueous solution of Fe (III) salt ?

10- Comment upon the nature of two S-O bonds formed in SO_2 molecule. Are the two S-O bond is this molecule equal.

11- Mention three areas in which H_2SO_4 plays an important role.

12- Write the conductions to maximize the yield of H_2SO_4 by contact process.

13- Considering the parameters such as bond dissociation enthalpy electron gain enthalpy and hydration enthalpy. Compare the oxidizing power of F_2 and Cl_2.

14- Give two examples to show the anomalous behavior of fluorine.

15- Sea is the greatest source of halogens. Comment.

16- Give the balanced chemical reaction when Cl2 reacts with hot and concentrated NaOH. Is it a disproportional reaction ? Explain.

17- Why the reactivity of nitrogen is different from phosphorus ?

18- Discuss the trends in chemical reactivity of group 15 elements.

19- Why does NH_3 form hydrogen bonds but PH_3 does not ?

20- How is nitrogen prepared in the laboratory ? Write the chemical equations of reactions involved.

21- How is ammonia manufactured industrially ?

22- Illustrate how copper metal can give different products on reaction with HNO_3.

23- The HNH angle value is higher than HPH, HAsH angles. Why?

24- Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

25- Write main differences between the properties of white phosphorus and red phosphorus.

26- Why does nitrogen show catenation properties less than phosphorus ?

27- Justify the placement of O, S, Se, Te and Po in the same group of periodic table in terms of electronic configuration, oxidation state and hydride formation.

28- Why is dioxygen a gas but sulphur a solid ?

29- Knowing the electron gain enthalpy values $O \rightarrow O^-$ and $O \rightarrow O^{-2}$ As -141 and +702 KJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{-2} species and not O^- ? (Hint: considers the lattice energy concept.)

30- Explain why in spite of nearly the same electro negativity, oxygen forms hydrogen bonding while chlorine does not.

31- How can you prepare Cl_2 from HCl and HCl from Cl_2 ?

32- What inspired N Bartlett for carrying out reaction between Xe and PtF_6 ?

33- What is the oxidation state of phosphorus in the following :

(i) H_3PO_3 (ii) PCl_3 (iii) Ca_3P_2

(iv) Na_3PO_4 (v) POF_3 ?

34- Write balanced equations for the following :

(i) NaCl is heated with sulphuric acid in the presence of MnO_2.

(ii) Cl_2 gas is passed into a solution of NaI in water.

35- How are XeF_2, XeF_4 and XeF_6 obtained ?

36- With what neutral molecule is ClO^- isoelectronic ? Is that molecule a Lewis base ?

37- Which of the following does not exists and why ?

(i) $XeOF_4$ (ii) NeF_2

(iii) XeF_4 (iv) XeF_6

38- Give the formula and describe the structure of noble gas species which is iso-structural with:

(i) ICl_4^- (ii) IBr_2^- (iii) BrO_3^-

39. List the uses of neon and organ gases.

Large Answer Questions :

1- Describe the general properties, electronic configuration, oxidation states, atomic sizes, ionization enthalpies and electro negativities of elements of group 15.

2- Arrange the every set of following in the order as shown their after the sets.

(i) F_2, Cl_2, Br_2, I_2 (Increasing order of bond dissociation enthalpies)

(ii) HF, HCl, HBr, HI (Increasing order of acid strength)

(iii) NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Increasing order of basic strength)