Unit

5

p-Block Elements II

5.1 Introduction

We have studied in standard 11, that the last electron is filled in p-orbital in the elements of groups 13 to 18. Hence, these elements are called p-block elements. The outermost electronic configuration of these elements is ns^2np^{1-6} (Except He; Electronic configuration of He is $1s^2$). The properties of the elements of p-block, depend on their atomic size, ionisation enthalpy, electron gain enthalpy and electronegativity. A large diversity is observed in properties of elements of p-block because of absence of d-orbital in the second period and presence of d- or/and f-orbitals in the electronic configuration of third to seventh period. In addition, diversity is also observed because of the presence of metals, non-metals and semimetal elements.

5.2 Elements of Group-15

Nitrogen, phosphorus, arsenic, antimony and bismuth are included in group 15. As the first element of the group is nitrogen, it is also known as **nitrogen group.** In any group if we move from top to bottom, non-metal to semimetal and then, increase in metallic properties is observed. Nitrogen and phosphorus are non-metals, arsenic and antimony are semimetals and bismuth is a metal element. Dinitrogen gas is present in air as 78 % by volume. Nitrogen element from the earth's crust is obtained in the form of sodium nitrate-$NaNO_3$ (Chile salt petre) and potassium nitrate-KNO_3 (Indian salt petre). Phosphorus element is obtained from apatite minerals $Ca_9(PO_4)_6 \cdot CaX_2$ (X = F, Cl, OH) e.g. fluorapatite $Ca_9(PO_4)_6 \cdot CaF_2$. Phosphorus is the important component in the constitution of animals and plants. It is present in living cell as well as in bones. Phospho-protein is present in eggs and milk. The important atomic and physical properties of the elements of this group are shown in table 5.1

Table 5.1 Atomic and Physical Properties of Group 15 Elements

Property	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic mass ($g\ mol^{-1}$)	14.01	30.97	74.92	121.75	208.98
Electronic configuration	$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
Ionisation enthalpy (I)	1402	1012	947	834	703
(Δ_iH) ($kJ\ mol^{-1}$) (II)	2856	1903	1798	1595	1610
(III)	4577	2910	2736	2443	2466
Electronegativity	3.0	2.1	2.0	1.9	1.9
Covalent radius (pm)	70	110	121	141	148
Ionic radius (pm)	171	212	222	76	103
Melting Point (K)	63	317	1089	904	544
Boiling Point (K)	77.2	554	888	1860	1837
Density ($g\ cm^{-3}$) (295 K)	0.879	1.823	5.77	6.697	9.808

5.2.1 Electronic configuration, occurrence, oxidation states :

Electronic configuration : The electronic configuration of valence shell of elements of group 15 is ns^2np^3. As the s-orbitals of these elements are completely filled and p-orbitals are partially filled, these elements are exceptionally stable.

Occurrence : The chief minerals of the elements of group-15 are shown in table 5.2

Table 5.2 Chief Minerals of Elements of Group 15

Elements	Structures of chief minerals and their names
Nitrogen	Approximately 78% in the form of free gas in the earth's atmosphere. Approximately 17% in animal and plant proteins, $NaNO_3$ (Chile salt petre); KNO_3 (Indian salt petre).
Phosphorus	Approximately 60% $Ca_3(PO_4)_2$ in bones and teeth, $Ca_9(PO_4)_6 \cdot CaF_2$ Fluorapatite; $Ca_9(PO_4)_6 \cdot CaCl_2$ Chlor aptatite; $Ca_9(PO_4)_6 \cdot Ca(OH)_2$ Hydroxyapatite.
Arsenic	As_4S_4-Rielger (Volcano regions); As_2S_3-Orpiment; $FeAsS_2$ Arsenopyrites.
Antimony	Sb_2S_3-Stibine; Sb_2O_4-Antimony ore.
Bismuth	Bi_2S_3-Bismuthine; Bi_2O_3-Bismite; $(BiO)_2CO_3$-Bismuthspar.

Oxidation State : The common oxidation states of elements of group-15 are –3, +3 and +5. The tendency to show –3 oxidation state decreases as we go down the group because of increase in the atomic size and metallic properties. Similarly the stability of +5 oxidation state also decreases as we go down in the group. When nitrogen element reacts with oxygen element, it shows +1 to +5 oxidation states. In certain oxoacids, phosphorus shows +1, +3, +4 and +5 oxidation states. The oxidation states of elements of group 15 are shown in table 5.3.

Table 5.3 Oxidation States of Elements of Group 15

Elements	N	P, As	Sb	Bi
Oxidation states	–3 to +5	–3, +3, +5	+3, +5	+3

5.2.2 Periodicity in physical and chemical properties :

(1) Periodicity in physical properties : It can be said on the basis of table 5.1, that in the elements of group 15 with the increase in atomic number, there is general tendency of increase in atomic size, decrease in ionisation enthalpy and decrease in electronegativity. Hence, the metallic property increases with atomic number.

(i) Atomic and Ionic Radii : Going down the group 15, atomic and ionic radii increase. There is remarkable increase in the atomic radii while moving from nitrogen to phosphorus; but there is slight increase in atomic radii while going from As to Bi; the reason for this, is that in heavy elements, d-or/and f-orbitals are present. (Table 5.1).

(ii) Ionisation Enthalpy : The value of ionisation enthalpy decreases while going down the group because of increase in atomic size. The order of the first ionisation enthalpy ($\Delta_i H_1$), second ionisation enthalpy ($\Delta_i H_2$) and the third ionisation enthalpy ($\Delta_i H_3$) is $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$ (Table 5.1). As the p-orbitals in elements of group 15 are half filled and so they possess characteristic stability. Hence, electron is not removed easily from these elements. Thus, in the same period, the values of ionisation enthalpy of elements of group 15 are more than the values of ionisation enthalpy of elements of group 14.

(iii) Electronegativity : Generally the atomic size increases with atomic number while going down the group, hence electronegativity decreases. The difference in electronegativities of heavier element is found to be less (Table 5.1).

The elements of this group are polyatomic. There are allotropes of all the elements of this group except nitrogen and bismuth.

(2) Periodicity in chemical properties :

(i) Reaction with hydrogen element : All the elements of group-15 form hydrides of the type MH_3 (where M= N, P, As, Sb or Bi) by combining with hydrogen. The stability of the hydride compounds decreases as we go from NH_3 to BiH_3 in the group, but its property as reducing agent increases. The order of basicity of these hydride compounds is $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

(ii) Reaction with oxygen element : All the elements of group-15 combine with oxygen and form two types of oxides M_2O_3 and M_2O_5. The oxides of the elements having higher oxidation state are more acidic than the oxides of the elements having lower oxidation states. The acidic character decreases as we move down the group. The M_2O_3 type oxides of nitrogen and phosphorus are acidic, oxides of arsenic and antimony are amphoteric and oxide of bismuth is basic. This shows the development in metallic property as we go down the group.

(iii) Reaction with halogen elements : The elements of group-15 react with halogens and form halide compounds of the type MX_3 and MX_5. As there are no d-orbitals in valence shell of nitrogen atom, it is not able to form pentahalide. Pentahalides are more covalent than trihalides. All the trihalides except the nitrogen element are stable; while only one trihalide of nitrogen element-NF_3 is stable. Trihalide compounds except BiF_3 are covalent compounds.

(iv) Reaction with metal elements : All the elements of group-15 combine with metal elements and form binary compounds like Ca_3N_2 (Calcium nitride), Ca_3P_2 (Calcium phosphide), Na_3As (Sodium arsenide), Zn_3Sb_2 (Zinc antimonide and Mg_3Bi_2 (Magnesium bismuthide). In these, the oxidation state of N, P, As, Sb and Bi is (–3).

5.3 Nitrogen

5.3.1 Preparation, Properties and Uses of Dinitrogen Gas :

(1) Preparation of Dinitrogen : Commercially, dinitrogen is prepared by liquefaction and fractional distillation of air. As the boiling point of dinitrogen is 77.2 K, it is first obtained during distillation. While, the boiling point of dioxygen is 90 K and so remains in the vessel. In the laboratory, dinitrogen gas can be prepared by the reaction of aqueous ammonium chloride with aqueous sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + 2H_2O(l) + NaCl(aq)$$

During this reaction, NO and HNO_3 are formed in smaller proportions. To remove them, the gas produced during the reaction is passed through the mixture of potassium dichromate and aqueous sulphuric acid. Dinitrogen gas can also be prepared by thermal decomposition of ammonium dichromate.

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{\Delta} N_2(g) + 4H_2O(l) + Cr_2O_3(s)$$

Very pure dinitrogen gas can be obtained by thermal decomposition of sodium or barium azide.

$$Ba(N_3)_2(s) \xrightarrow{\Delta} Ba(s) + 3N_2(g)$$

(2) Properties :

(i) Physical properties :

- Dinitrogen gas is colourless, odourless, tasteless and nonpoisonous.
- It possesses two stable isotopes ^{14}N and ^{15}N.
- It is sparingly soluble in water.
- It is inert at room temperature but its reactivity increases with the increase in temperature.

(ii) Chemical properties : At high temperature, it combines with certain metals and forms ionic nitrides while with non-metals it forms covalent nitrides.

e.g. $6Li(s) + N_2(g) \xrightarrow{\Delta} 2Li_3N(s)$

$$3Mg(s) + N_2(g) \xrightarrow{\Delta} Mg_3N_2(s)$$

$$2B(s) + N_2(g) \xrightarrow{\Delta} 2BN(s)$$

It reacts with dihydrogen and dioxygen and forms ammonia gas and nitric oxide gas respectively.

$$N_2(g) + 3H_2(g) \underset{\substack{200 \text{ bar pressure} \\ [FeO]}}{\overset{773 \text{ K}}{\rightleftharpoons}} 2NH_3(g)$$

$$N_2(g) + O_2(g) \overset{\Delta}{\rightleftharpoons} 2NO(g)$$

(3) Uses :

- Dinitrogen gas is useful in industry in the manufacture of ammonia gas and other nitrogen containing compounds.
- In the metallurgical processes to maintain inert atmosphere, in electric bulbs and preparation of nitric acid.
- The reactivity of oxygen in the air is decreased because of the presence of dinitrogen gas and so it becomes useful in respiration. Liquid dinitrogen is used as coolant in preservation of biological substances and food materials.

5.3.2 Distinction from other elements of group (Anomalous behaviour) :

(i) The diatomic molecule of nitrogen is in gaseous form as dinitrogen (N_2) while, other elements are in solid state in the form of M_4 molecule (except Bi).

(ii) Nitrogen element does not possess allotropes but other elements possess allotropes.

(iii) Nitrogen trioxide N_2O_3 and nitrogen pentoxide N_2O_5 are monomolecular (monomers); while the trioxides and pentoxides of other elements are bimolecular (dimers) e.g. P_4O_6, As_4O_6, P_4O_{10} and As_4O_{10}

(iv) The trihydride of nitrogen element (NH_3) is non poisonous while trihydrides of other elements are poisonous, (e.g. Phospine (PH_3), Arsine (AsH_3) etc).

(v) As nitrogen is non-metal, its oxide compounds possess acidic property.

(vi) The halides of nitrogen except NF_3 are explosive, while the halides of other elements are stable.

(vii) Because of the smaller size and higher electronegativity of nitrogen element, there is characteristic property of forming $p\pi$–$p\pi$ bond in it; while this property is not possessed by the other elements of the group. As a result, nitrogen element exists as dinitrogen gas having triple $N \equiv N$ bond; while other elements of the group possess P–P, As–As and Sb–Sb single bond. Bi forms metallic bond.

(viii) There are no d-orbitals available in the orbits of nitrogen element, its maximum bonding capacity is 4. As a result it cannot form $d\pi - p\pi$ bond. The other elements of this group are able to form this type of bond. e.g. $R_3P = O$ or $R_3P = CH_2$ where R is the alkyl group. Phosphorus and arsenic elements form $d\pi - d\pi$ bonds with tranistion metal elements in which the compounds of phosphorus and arsenic like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

5.3.3 Compounds of Nitrogen Element :

(1) Ammonia (NH_3) :

(i) Preparation : Ammonia gas is present in very less proportion in air. In addition ammonia gas is formed by the decay of nitrogen containing organic compounds like urea.

$$NH_2CONH_2(s) + H_2O(l) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

By reaction of ammonium salt with sodium hydroxide or calcium hydroxide, ammonia gas can be obtained.

$$(NH_4)_2SO_4(s) + 2NaOH(aq) \rightarrow 2NH_3(g) + 2H_2O(l) + Na_2SO_4(aq)$$

$$2NH_4Cl(s) + Ca(OH)_2(aq) \rightarrow 2NH_3(g) + 2H_2O(l) + CaCl_2(aq)$$

Industrially ammonia gas is manufactured by Haber's process.

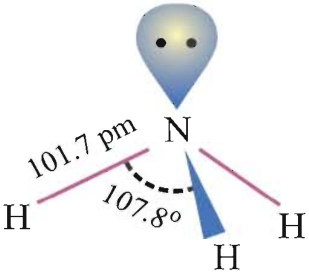
$$N_2(g) + 3H_2(g) \xrightleftharpoons[773\text{ K, [FeO]}]{200\text{ bar pressure}} 2NH_3(g) \quad \Delta_f H = -46.1\ \text{kJmol}^{-1}$$

According to Le Chatelier's principle 773 K temperature, 200 bar pressure and FeO as catalyst are used alongwith K_2O and Al_2O_3 in less proportions as **promoters.** By hydrolysis of magnesium nitride, ammonia gas is obtained.

$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(g)$$

(ii) Properties :

(A) Physical properties :



- Ammonia is a colourless gas with pungent smell.
- Its freezing point and boiling point are 198.4 K and 239.7 K respectively.
- Ammonia molecule possesses trigonal pyramidal structure in which three bonding and one nonbonding electron pairs are present.

(B) Chemical properties :

- Ammonia gas dissolves in water and forms ammonium hydroxide which acts as weak base.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- Aqueous solution of ammonia gas reacts with acid and forms ammonium salt.

$$NH_4OH(aq) + HCl(aq) \rightleftharpoons NH_4Cl(aq) + H_2O(l)$$

- Aqueous solution of ammonia gas forms hydroxides of metals by reaction with aqueous solutions of metal salts.

$$NH_4OH(aq) + ZnSO_4(aq) \rightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$$

- As nitrogen atom in ammonia molecule has got non-bonding pair of electron, it acts as a Lewis base. It forms co-ordinate covalent bond with metal ion and forms complex ion.

$$\underset{\text{(Blue)}}{Cu^{2+}(aq)} + 4NH_3(aq) \rightleftharpoons \underset{\text{(Dark Blue)}}{[Cu(NH_3)_4]^{2+}(aq)}$$

(iii) Uses :

- Ammonia gas is used in the formation of nitrogenous fertilisers like ammonium nitrate, urea, amonium phosphate and ammonium sulphate.
- It is also useful in preparation of certain important inorganic compounds like nitric acid.
- Liquid ammonia is used as refrigerant.

(2) Nitric acid (HNO_3) :

(i) Preparation : To prepare nitric acid in laboratory, sodium nitrate or potassium nitrate is heated with concentrated sulphuric acid in a glass retort.

$$NaNO_3(s) + H_2SO_4(aq) \xrightarrow{\Delta} NaHSO_4(aq) + HNO_3(aq)$$

Anhydrous nitric acid is obtained by distilling concentrated aqueous solution of nitric acid in presence of P_4O_{10}. Industrial production of nitric acid is carried out by catalytic oxidation of ammonia. This process is known as **Ostwald's method,** in which the following reactions are involved

$$4NH_3(g) + 5O_2(g) \xrightarrow[\text{500 K, 9 bar}]{[Pt\ (90\%) + Rh\ (10\%)]} 4NO(g) + 6H_2O(g)$$

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

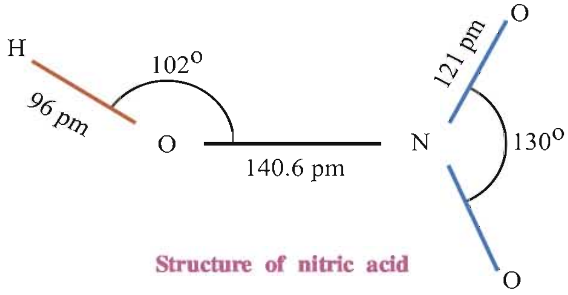
$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

The aqueous nitric acid obtained in this way is distilled and acid with 68.5 % by weight concentration can be obtained. To obtain nitric acid with 98 % concentration it is dehydrated with concentrated H_2SO_4.

(ii) Properties :

(A) Physical properties :

- Nitric acid is a colourless liquid.
- Its freezing point and boiling point are 231.4 K and 355.6 K respectively.
- Its density at 298 K temperature is 1.504 gram ml^{-1}.



Structure of nitric acid

- Nitric acid possesses planar structure in gaseous state.

(B) Chemical properties :

- Aqueous solution of nitric acid acts as a strong acid in which H_3O^+ and NO_3^- ions are present.

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

- Concentrated nitric acid is a strong oxidising agent. It reacts readily with metals except the noble metals like gold and platinum. Certain metals like Cr, Al do not dissolve in concentrated nitric acid because inert oxide layer is formed on these metals. Generally, nitrate salts are formed by reaction of metals with nitric acid. If dilute nitric acid is used in the reaction NO or N_2O are produced and if concentrated nitric acid is used NO_2 gas is produced.

$$4Cu(s) + 10HNO_3(dil., aq) \longrightarrow 4Cu(NO_3)_2(aq) + N_2O(g) + 5H_2O(l)$$

$$3Cu(s) + 8HNO_3(10 \text{ to } 30\ \%, aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

$$Cu(s) + 4HNO_3(con., aq) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

$$Zn(s) + 4HNO_3(con., aq) \longrightarrow Zn(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

- The non-metals and their compounds are oxidised by concentrated HNO_3.

$$I_2(s) + 10HNO_3(l) \longrightarrow \underset{\text{Iodic acid}}{2HIO_3(aq)} + 10NO_2(g) + 4H_2O(l)$$

$$C(s) + 4HNO_3(l) \longrightarrow CO_2(g) + 2H_2O(l) + 4NO_2(g)$$

$$S_8(s) + 48HNO_3(l) \longrightarrow 8H_2SO_4(aq) + 48NO_2(g) + 16H_2O(l)$$

$$P_4(s) + 20HNO_3(l) \longrightarrow 4H_3PO_4(aq) + 20NO_2(g) + 4H_2O(l)$$

- Aqueous solution of nitric acid gives ring test. This ring test is given by NO_3^- ion in aqueous solution, So nitric acid also gives this test

Ring test : Freshly prepared solution of ferrous sulphate is added to aqueous solution containing NO_3^- ion. Then after, concentrated sulphuric acid is added slowly from the inner wall of the test tube. (if required solution is cooled). **Brown coloured ring is observed near the surface where concentrated sulphuric acid and mixed solution meet. This ring is due to formation of nitroso complex.** The ring test is carried out during inorganic qualitative analysis for detection of NO_3^- ion.

$$NO_3^-(aq) + 3Fe^{2+}(aq) + 4H^+(aq) \longrightarrow NO(g) + 3Fe^{3+}(aq) + 2H_2O(l)$$

$$[Fe(H_2O)_6]^{3+}(aq) + NO(g) \longrightarrow \underset{\text{(brown)}}{[Fe(H_2O)_5(NO)]^{3+}(aq)} + H_2O(l)$$

(iii) Uses :

- The main use of nitric acid is made in preparation of fertilisers like ammonium nitrate and explosive substances like trinitrotoluene and nitroglycerine.
- It is used as oxidising agent in rocket fuels.

(3) Oxides of nitrogen :

Preparation, structure and properties of oxides of nitrogen : Nitrogen forms many oxide compounds in different oxidation states of nitrogen.Names of compounds of nitrogen oxides, molecular formula, oxidation states of nitrogen element, preparation and general properties are shown in Table 5.4.

Table 5.4 Oxides of Nitrogen

Name of oxide of Nitrogen	Molecular formula	Oxidation State of nitrogen element	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$	colourless gas neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + NaHSO_4 + 2H_2O + 2NO$	colourless gas neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO$	brown gas acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{heat}{\overset{cool}{\rightleftharpoons}} N_2O_4$	colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+ 5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	colourless solid acidic

Nitric oxide (NO) partially polymerises in liquid state because of presence of one unpaired eletrcon. It acts as dimeric molecule in solid state. Nitric oxide combines with oxygen and forms nitrogen dioxide.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Nitrogen dioxide in gaseous state forms compound having dimeric structure N_2O_4 by attaining equilibrium state as follows :

$$\underset{\text{(Brown-Paramagnetic)}}{2NO_2(g)} \rightleftharpoons \underset{\text{(Colourless-Diamagnetic)}}{N_2O_4(g)} \text{ (Dinitrogen tetroxide)}$$

Oxides of nitrogen, react with water and forms oxoacid compounds of nitrogen.

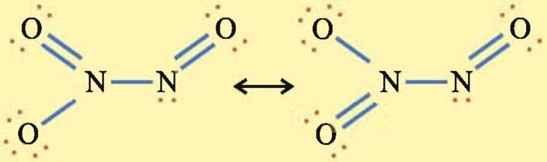
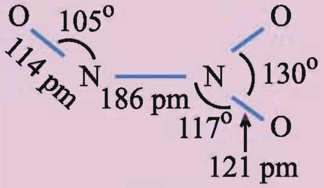
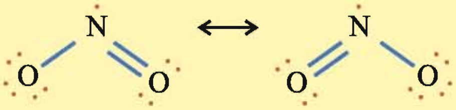
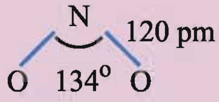
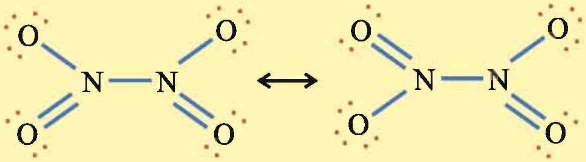
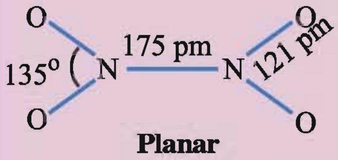
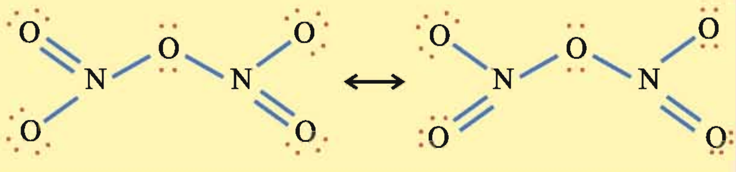
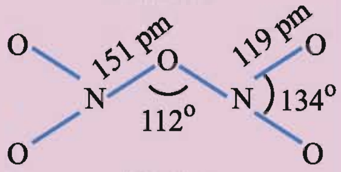
$$2NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$$

$$N_2O_3(g) + H_2O(l) \rightleftharpoons 2HNO_2(aq)$$

$$N_2O_5(g) + H_2O(l) \rightleftharpoons 2HNO_3(aq)$$

Because of this, N_2O_3 and N_2O_5 are called anhydrides of HNO_2 and HNO_3 respectively. The resonance structures of oxides of nitrogen and the information about their bonds are given in table 5.5

Table 5.5 Resonance Structures of Oxides of Nitrogen

Molecular formula	Resonance structure	Details about bond
N_2O	$N=N=\ddot{O} \leftrightarrow :N\equiv N-\ddot{O}:$	N − N − O 113 pm 119 pm **Linear**
NO	$:N=\dot{O}: \leftrightarrow :\dot{N}=O:$	N − O 115 pm
N_2O_3		 **Planar**
NO_2		 **Angular**
N_2O_4		 **Planar**
N_2O_5		 **Planar**

5.4 Phosphorus

5.4.1 Allotropes of Phosphorus : The known allotropes of phosphorus are white (yellow), red and black. The white phosphorus prepared by industrial synthesis, is poisonous and wax like white substance in which discrete tetrahedral P_4 molecules are present. Red phosphorus is nonpoisonous and it is in polymeric form. The allotropes of phosphorus are shown in figure 5.1

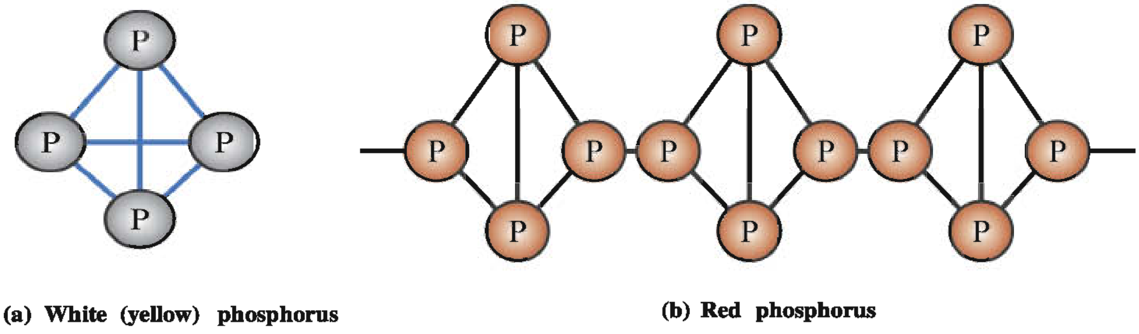

(a) White (yellow) phosphorus (b) Red phosphorus

Fig. 5.1 Allotropes of Phosphorus

White phosphorous is insoluble in water but soluble in solvent like carbon disulphide (CS_2). It glows in the dark. In the inert atmosphere, phosphorous undergoes redox reaction with boiling NaOH solution and forms phospine (PH_3).

$$P_4(s) + 3NaOH(aq) + 3H_2O(l) \longrightarrow PH_3(g) + \underset{\text{(Sodium hypophosphite)}}{3NaH_2PO_2(aq)}$$

The melting point of white phosphorus is 317 K. It is highly reactive and burns when kept open in air. Hence, it is stored in water. If white phosphorus is heated at 573 K in absence of air, it is changed to stable red form. The melting point of red phosphorus is 873 K. It is less soluble in solvent like CS_2 in comparison to white phosphorus and is less reactive. Hence, it does not burn when it comes in contact with air. The more reactivity of white phosphorus is due to its abnormal structure. Because of this, strain is generated in P_4 molecule. Hence, the bond angle is 60^0 in geometrical structure of P_4. Because of this, p-orbitals do not overlap head to head. As a result of this p–p bond is bent. Hence this bond is weak and reactive. As a result, white phosphorous bunrs as soon as it comes in contact with air.

Two froms of phosphorous found are α–black phsphorus and β–black phosphorus. α–black phosphorus is obtained by heating red phosphorus in closed tube at 803 K temperature. White phosphorus is heated under high pressure at 473 K to obtain β–black phosphorus.

5.4.2 Compounds of Phosphorus :

(1) Phosphine (PH_3) :

(i) Preparation : Phoshphine is obtained by reacting calcium phosphide with water or dilute hydrochloric acid.

$$Ca_3P_2(s) + 6H_2O(l) \longrightarrow 3Ca(OH)_2(aq) + 2PH_3(g)$$

$$Ca_3P_2(s) + 6HCl(aq) \longrightarrow 3CaCl_2(aq) + 2PH_3(g)$$

In laboratory, phosphine is prepared by reacting white phosphorus with concentrated NaOH in inert atmosphere

$$P_4(s) + 3NaOH(aq) + 3H_2O(l) \longrightarrow PH_3(g) + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2(aq)}$$

(ii) Properties :

(A) Physical properties :

- Phosphine is a colourless gas having smell like rotten fish and is very poisonous gas.
- It is sparingly soluble in water.

(B) Chemical properties :

- Phosphine explodes when it comes in contact with oxidising agents like HNO_3, Cl_2 and Br_2.
- If phosphine is absorbed in aqueous solution of copper sulphate or mercuric chloride, corresponding phosphide is formed

$$3CuSO_4(aq) + 2PH_3(g) \longrightarrow Cu_3P_2(g) + 3H_2SO_4(aq)$$

$$3HgCl_2(aq) + 2PH_3(g) \longrightarrow Hg_3P_2(g) + 6HCl(aq)$$

- Phosphine is a weak base. It gives phosphonium bromide (PH_4Br) by reaction with HBr.

$$PH_3(g) + HBr(g) \longrightarrow PH_4Br(g)$$

(iii) Uses :

- Becasue of spontaneous combustion property of phosphine, it is used in Holme's signals. By making a hole in the vessel containing calcium carbide and calcium phosphide is thrown into the sea and so the gas produced burns which works as signal.
- It is used in preparation of smoke screen.

(2) Phosphorus trichloride (PCl_3) :

(i) Preparation : Phosphorus trichloride is obtained by passing dry chlorine gas on white phosphorus at high temperature.

$$P_4(s) + 6Cl_2(g) \xrightarrow{\Delta} 4PCl_3(l)$$

Phosphorus trichloride is obtained by reaction of white phosphorus with thionyl chloride $(SOCl_2)$.

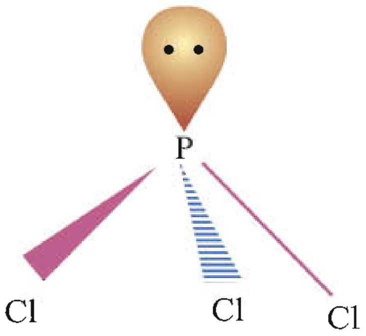
$$P_4(s) + 8SOCl_2(l) \longrightarrow 4PCl_3(l) + 4SO_2(g) + \underset{\text{Sulphur chloride}}{2S_2Cl_2(g)}$$

(ii) Properties :

(A) Physical properties :

- Phosphorus trichloride is a colourless fuming liquid.
- Its boiling point is 349 K.
- It is soluble in solvents like benzene, chloroform, ether, carbon disulphide
- Its shape is pyramidal.

(B) Chemical Properties :



Phosphorus trichloride

- Phosphorus trichloride forms fumes when it comes in contact with air or water-because the P–Cl bond present in PCl_3 is decomposed and is converted into the resulting product phosphorus acid (H_3PO_3).

$$PCl_3(l) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(aq)$$

- It reacts with organic compounds having –OH group. viz. CH_3COOH, C_2H_5OH as follows :

$$3CH_3COOH(l) + PCl_3(l) \longrightarrow 3CH_3COCl(l) + H_3PO_3(l)$$

$$3C_2H_5OH(l) + PCl_3(l) \longrightarrow 3C_2H_5Cl(l) + H_3PO_3(l)$$

(3) Phosphorus pentachloride (PCl_5)

(i) Preparation : Phosphorus pentachloride is obtained by reaction of white phosphorus with excess amount of dry chlolrine gas.

$$P_4(s) + 10Cl_2(g) \longrightarrow 4PCl_5(s)$$

Phosphorus pentachloride is obtained by reaction of white phosphorus with sulphuryl chloride (SO_2Cl_2).

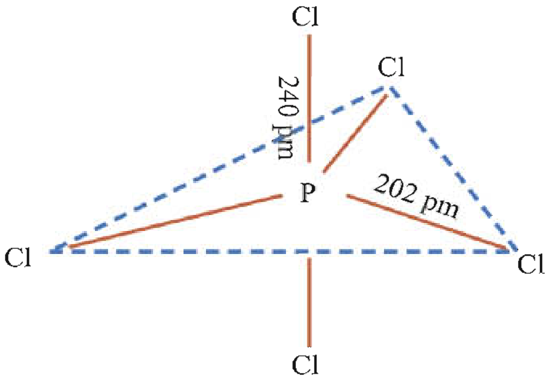
$$P_4(s) + 10SO_2Cl_2(l) \longrightarrow 4PCl_5(s) + 10SO_2(g)$$

(ii) Properties :

(A) Physical properties :

- Phosphorus pentachloride is yellowish white coloured solid substance.
- Its melting point is 440 K.
- PCl_5 possesses trigonal bipyramid shape in liquid and gaseous states.

(B) Chemical properties :



Structure of liquid or gaseous phosphorus pentachloride

- Phosphorus pentachloride is converted to phosphorus oxychloride by hydrolysis by moisture of air and finally phosphoric acid is formed.

$$PCl_5(s) + H_2O(g) \longrightarrow POCl_3(l) + 2HCl(g)$$

$$POCl_3(l) + 3H_2O(g) \longrightarrow H_3PO_4(aq) + 3HCl(aq)$$

- Phosphorus pentachloride sublimes on heating but decomposes when heated more.

$$PCl_5(s) \xrightarrow{\Delta} PCl_3(l) + Cl_2(g)$$

- It forms chloro compounds by reaction with organic compounds having –OH group.

$$CH_3COOH(l) + PCl_5(s) \longrightarrow CH_3COCl(l) + POCl_3(l) + HCl(l)$$

$$C_2H_5OH(l) + PCl_5(l) \longrightarrow C_2H_5Cl(l) + POCl_3(l) + HCl(l)$$

- On heating $PCl_5$with metal piece, it forms corresponding metal chlorides.

$$2Ag(s) + PCl_5(s) \xrightarrow{\Delta} 2AgCl(s) + PCl_3(l)$$

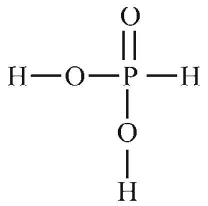
$$Sn(s) + 2PCl_5(s) \xrightarrow{\Delta} SnCl_4(s) + 2PCl_3(l)$$

(4) Oxoacids of phosphorus : Different oxoacids of phosphorus are obtained by reactions of phosphorus oxides with water.

$P_4O_6(s) + 6H_2O(l) \longrightarrow 4H_3PO_3(aq)$ Orthophosphorus acid

$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$ Orthophosphoric acid

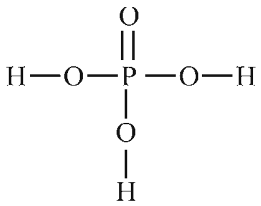
Orthophosphorus acid (H_3PO_3) is a weak diprotic acid because its only two hydrogen atoms are combined with oxygen atom. Hydrogen atom directly combined with phosphorus is not acidic because, the electronegativities of both P and H are same and so P–H bond is non polar. As all the three hydrogen atoms in orthophosphoric acid are combined with oxygen atom, it is a weak triprotic acid. In both these molecules, the other atoms around the phosphorus atom are arranged in tetrahedral shape. Also, the successive dissociation constants in both the molecules are decreasing by the approximate multiple of 10^5.



Orthophosphoric acid (H_3PO_3)

$Ka_1 = 1.0 \times 10^{-2}$

$Ka_2 = 2.6 \times 10^{-7}$



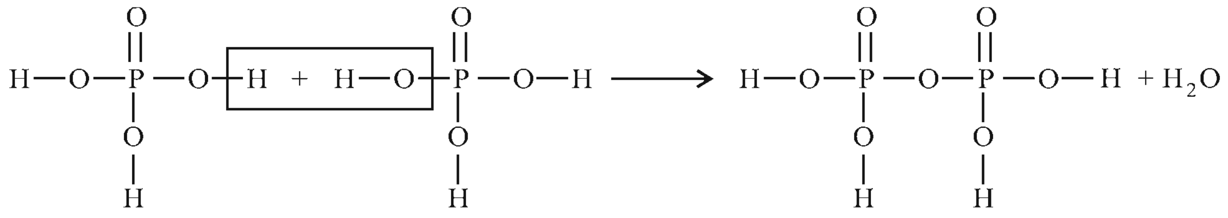
Orthophosphoric acid (H_3PO_4)

$Ka_1 = 7.5 \times 10^{-3}$

$Ka_2 = 6.2 \times 10^{-8}$

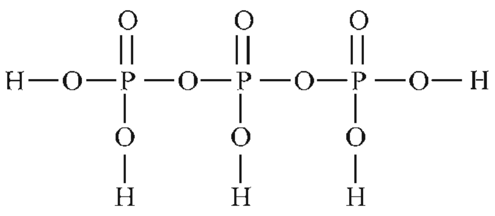
$Ka_3 = 4.8 \times 10^{-13}$

Diphosphoric acid ($H_4P_2O_7$) is also called pyrophosphoric acid which is obtained by removal of one molecule of water when two molecules of H_3PO_4 combine.

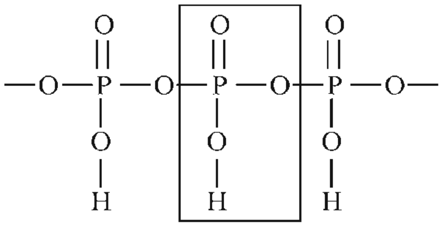


Pyrophosphoric acid

In trimetaphosphoric acid $H_5P_3O_{10}$ the HPO_3 unit is repeated three times. $(HPO_3)_n$ is known as polymetaphosphoric acid.

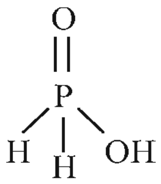


Trimetaphosphoric acid $H_5P_3O_{10}$



Polymetaphosphoric acid
(HPO_3 unit is repated)

In all the acids, the oxidation number of phosphorus is +5. Hypophosphorus acid is also called phosphonic acid. Its formula is H_3PO_2 and the oxidation number of phosphorous is +1.



Structure of H_3PO_2

5.5 Elements of Group-16

Oxygen, sulphur, selenium, tellurium and polonium elements are included in group 16. These elements are known as **oxygen group** elements or as **chalcogens.** The important atomic and physical properties are shown in table 5.6

Table 5.6 Atomic and Physical Properties of Elements of Group-16

Properties	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass (gm mol^{-1})	16.00	32.06	78.96	127.60	210.00
Electronic structure	[He]$2s^22p^4$	[Ne]$3s^23p^4$	[Ar]$3d^{10}4s^24p^4$	[Kr]$4d^{10}5s^25p^4$	[Xe]$4f^{14}5d^{10}6s^26p^4$
Ionisation Enthalpy (Δ_iH_1) (kJ mol^{-1})	1314	1000	941	869	813
Electronegativity	3.50	2.44	2.48	2.01	1.76
Covalent radius (pm)	66	104	117	137	146
Ionic radius (pm)	140	184	198	221	230
Melting point (K)	55	393	490	725	520
Boiling point (K)	90	718	958	1260	1235
Density (gm cm^{-3}) (298 K)	1.32	2.06	4.19	6.25	–

5.5.1 Electronic configuration, occurrence, oxidation states :

Electronic configuration : The electronic configuration of valence shell of elements of group 16 is ns^2np^4.

Occurrence : Oxygen element is the most abundant element available in highest proportion on the earth. Oxygen element possesses about 46.6% mass of earth's crust. In dry air oxygen is 20.9461% by volume. Sulphur present on the earth is about 0.03-0.1% by mass of earth's crust. It is available in combined forms i.e. sulphate compounds like gypsum ($CaSO_4 \cdot 2H_2O$), Epsom salt ($MgSO_4 \cdot 7H_2O$), Baryte ($BaSO_4$) and sulphide compounds like galena (PbS), zinc blende (Zns), copper pyrrites ($CuFeS_2$). Sulphur is also present in organic compounds present in eggs, proteins, garlic, onion, hair and wool. Selenium and tellurium are available as selenide and telluride compounds. Polonium is obtained by decay of minerals of thorium and uranium.

Oxidation states : There are six electrons in valence shell of elements of group-16 i.e. two electrons are less for completion of octet. Hence, the oxidation state of such elements is –2. The stability of –2 oxidation states of these elements decreases as we go down the group. Polonium does not show –2 oxidation state. The electronegativity of oxygen element is more and so it possesses –2 oxidation state but in OF_2 its oxidation state is (+2). The other elements of this group show +2, +4, +6, oxidation states. Sulphur, selenium and tellurium generally show +4 oxidation states in compounds with oxygen and +6 oxidation state in compounds with flluorine. As we go down from above in the group, the stability of +6 oxidation state decreases and stability of +4 oxidation state increases. Oxidation states of elements of group 16 are shown in Table 5.7.

Table 5.7 Oxidation states of Elements

Elements	O	S	Se	Te	Po
Oxidation state	–2, –1, +1, +2	–2, +2, +4, +6	–2, +2, +4, +6	–2, +2, +4, +6	+2, +4

5.5.2 Periodicity in physical and chemical properties :

(1) Periodicity in physical properties : On the basis of table 5.6, it can be said that there is general tendency of increase in atomic size, decrease in ionisation enthalpy, decrease in electronegativity with the increase in atomic number of elements of group-16. Hence, the metallic property increases with increase in atomic number.

(i) Atomic and Ionic radii : The atomic and ionic radii increase with increase in number of orbits in the elements when we go down the group. As an exception, the atomic radius and ionic radius of oxygen element is comparatively less than other elements (Table 5.6).

(ii) Ionisation Enthalpy : The value of ionisation enthalpy decreases with increase in aotmic number as we go down the group. The values of ionisation enthalpy of the elements of this group are comparatively less than those of the elements of corresponding period of group 15; because the elements of group 15 have half filled p-orbitals and so possess characteristic stability (Table 5.6).

(iii) Electronegativity : Amongst all the elements, after fluorine element, oxygen element has highest electronegativity. Generally, as we go down from above in the group as atomic number increases, atomic size increases and so electronegativity decreases (Table 5.6).

(2) Chemical properties :

(i) Reaction with hydrogen element : All the elements of group 16 form hydrides of the type H_2M (where M = S, Se, Te, Po). The acidic property of the hydride compounds increases on going from H_2O to H_2Te because as we go down from above in the group the value of dissociation enthalpy of M–H bond decreases.

(ii) Reaction with oxygen element : All the elements of group 16 form oxides of two types $-MO_2$ and $-MO_3$ when react with oxygen element (where M = S, Se, Te, Po). Ozone (O_3) and sulphur dioxide (SO_2) are in gaseous form and selenium oxide (SeO_2) is in solid form. The property as reducing agents of these dioxide compounds, decreases as we go from SO_2 to TeO_2. SO_2 is a reducing agent, while TeO_2 is an oxidising agent. All these oxides possess acidic nature.

(iii) Reaction with halogen elements : Elements of group 16 react with halogens and form MX_6, MX_4 and MX_2 type halide compounds, (where M = elements of group 16 and X = halogen element). The order of stability of halide compounds is $F^- > Cl^- > Br^- > I^-$. Amongst the hexahalide compounds, only hexafluoride compounds are found to be stable.

5.6 Oxygen

5.6.1 Preparation, Properties and uses of dioxygen gas :

(1) Preparation of Dioxygen gas : In laboratory, dioxygen (O_2) gas is prepared by following methods.

(i) By thermal decompositoin of oxygen containing elements like $KClO_3$ and $KMnO_4$ or by electrolysis of acidic water.

$$2KClO_3(s) \xrightarrow[{[MnO_2]}]{\text{Heat}} 2KCl(s) + 3O_2(g)$$

$$2H_2O(l) \xrightarrow{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

(ii) Dioxygen gas is obtained by thermal decomposition of oxides of certain metals.

$$2Ag_2O(s) \xrightarrow{\Delta} 4Ag(s) + O_2(g)$$

$$2HgO(s) \xrightarrow{\Delta} 4Hg(l) + O_2(g)$$

$$2Pb_3O_4(s) \xrightarrow{\Delta} 6PbO(s) + O_2(g)$$

$$2PbO_2(s) \xrightarrow{\Delta} 2PbO(s) + O_2(g)$$

(iii) Dioxygen gas is obtained by decomposition of H_2O_2 in presence of manganese dioxide.

$$2H_2O_2(l) \xrightarrow[\text{Heat}]{[MnO_2]} 2H_2O(l) + O_2(g)$$

For industrial production of dioxygen gas, first carbon dioxide and water vapour are removed from air. By liquefaction and fractional distillation of remaining air mixture dinitrogen and dioxygen gases are obtained.

(2) Properties :

(i) Physical Properties :

- Dioxygen is a colourless and odourless gas.
- It possesses three stable isotopes ^{16}O, ^{17}O and ^{18}O.
- It is paramagnetic.
- About 3.08 cm^3 of dioxygen gas dissolves in 100 cm^3 of water at 293 K temperature, which is sufficient to sustain life of marine and aquatic living beings.
- It is converted in liquid form at 90 K temperature and in solid form by cooling at 55 K temperature.

(ii) Chemical properties : Dioxygen gas reacts with most of metal elements except inert (e.g. Au, Pt) and noble gas elements. The reactions of dioxygen gas with certain metal elements, non-metal elements and other compounds are shown as below :

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$$

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

$$CH_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

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

$$4HCl(g) + O_2(g) \xrightarrow{[CuCl_2]} 2Cl_2(g) + 2H_2O(g)$$

(3) Uses :

- Dioxygen gas is useful in respiration reaction and combustion reaction.
- Dioxygen gas is useful in preparation of steel.
- Dioxygen gas is used in oxyacetylene flame. As very high temperature is obtained by this flame, it is used in welding work of metals.
- The cylinders of dioxygen gas are useful for treatment of patients in the hospital, mountaineers and divers going deep in the water as well as respiration process.

5.6.2 Distinction from other elements of group (anomalous behaviour) :

(i) Oxygen is in gaseous form at room temperature while other elements of the group are in solid form.

(ii) Oxygen exists as diatomic molecule (O_2) while other elements exists as polyatomic molecule.

(iii) Oxygen is a non-metal. With the increase in atomic number the metallic property of elements increases.

(iv) d-orbitals are not available in valence shells of oxygen atom. Hence, it possesses lower oxidation states (–2, –1, 1, 2). While in other elements, as d-orbitals are available, the expansion of valence orbit in elements is possible. Here, these elements possess higher oxidation states (–2, 2, 4, 6). (See table 5.7)

(v) Oxygen because of its smaller size and higher electronegativity, forms hydrogen bond with hydrogen atom in water. Hence, strong hydrogen bond is observed in water and not observed in H_2S.

5.6.3 Compounds of Oxygen :

(1) Simple Oxides : Oxygen combines with other elements and forms binary compounds called oxides. As noted earlier, oxygen element combines with most of the elements of periodic table. Certain elements combine with oxygen and form more than one compounds. Oxygen element is able to form both the types ionic and covalent type compounds. Simple oxide compounds are classified as acidic, basic and amphoteric on the basis of their properties.

The oxides which give acid by reaction with water are called acidic oxides e.g. SO_2, Cl_2O_7, CO_2, N_2O_5 etc.

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

Generally oxides of non metals are acidic.

The oxide compounds which give base by reaction with water are called basic oxides. e.g. Na_2O, CaO, BaO :

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

Generally oxides of metal are basic. Some oxides possess both the acidic and basic nature. These oxides are called amphoteric oxides. They react with both acid and base. Some oxides are such which possess neither of the acidic nor basic nature. These oxides are called neutral oxides. e.g. CO, NO and N_2O. Al_2O_3 reacts both with acid and base as shown below and so it is amphoteric oxide.

$$Al_2O_3(s) + 6HCl(aq) + 9H_2O(l) \rightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$

$$Al_2O_3(s) + 6NaOH(aq) + 3H_2O(l) \rightarrow 2Na_3[Al(OH)_6](aq)$$

(2) Ozone : Ozone is the allotrope of oxygen. Ozone is formed from oxygen in atmosphere in presence of sunlight at the height of 20 kilometer above sea level. This layer of ozone gas protects the earth from harmful effect of ultraviolet rays.

(i) Preparation : Ozone gas can be prepared in laboratory by the use of ozonizer of Siemens or Brodie. Ozone is obtained by passing cold and dry oxygen in presence of silent electric charge in Siemen's ozonizer.

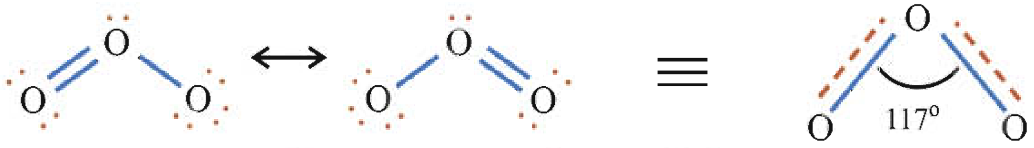
$$3O_2(g) \rightarrow 2O_3(g) \qquad \Delta H = 142.7 \text{ kJ mole}^{-1}$$

In industrial production the ozonizer of Siemens and Halteske is used in which 8000 to 10000 volt electromotive force is used between rods of aluminium. In electrolysis method, 95% ozone can be obtained at the anode by electrolysing acidic water using platinum electrodes and remaining 5% is oxygen gas.

(ii) Properties :

(A) Physical properties :

- Ozone possesses light blue colour in gaseous form, dark blue colour in liquid form and dark violet colour in solid form.
- Ozone possesses characteristic odour.
- Less proportion of ozone is not harmful but if its proportion, exceeds 100 ppm, then difficulty in respiration develops. As a result of this there is experience of headache and suffocation.
- The resonance structure of ozone are as shown below :



Resonance structures of ozone molecule

(B) Chemical Properties :

- Nascent oxygen [O] is released from decomposition of ozone. Hence, it is a strong oxidising agent.

  $O_3(g) \rightarrow O_2(g) + O(g)$

  Hence, ozone gas oxidises lead sulphide to lead sulphate and iodide ion to iodine.

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

  $2I^-(aq) + H_2O(l) + O_3(g) \longrightarrow 2OH^-(aq) + I_2(s) + O_2(g)$

- Nitric oxide coming out from the exhaust of supersonic jet planes, react with ozone and form nitrogen dioxide gas.

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

- In the same way, it forms oxo- acids by reaction with moisture containing sulphur, phosphorus and arsenic.

  $S(s) + H_2O(l) + 3O_3(g) \rightarrow H_2SO_4(aq) + 3O_2(g)$

  $2P(s) + 3H_2O(l) + 5O_3(g) \rightarrow 2H_3PO_4(aq) + 5O_2(g)$

  $2As(s) + 3H_2O(l) + 5O_3(g) \rightarrow 2H_3AsO_4(aq) + 5O_2(g)$

(iii) Uses :

- Ozone is used to sterilise drinking water.
- It is useful as bleaching agent for bleaching of different oils, flour and starch.
- It is useful as oxidising agent in production of potassium permanganate.

5.7 Sulphur

5.7.1 Allotropes of Sulphur :

Amongst the different alltropes of sulphur, yellow rhombic sulphur (α-sulphur) and monoclinic sulphur (β-sulphur) are very important. The stable form of sulphur at room temperature is rhombic sulphur. When it is heated at 369 K temperature it is converted into monoclinic sulphur.

Rhombic sulphur (α-sulphur) : Rhombic sulphur is of yellow colour. Its melting point is 385.8 K. On evaporation of solution of sulphur prepared in CS_2, rhombic sulphur is obtained. It is insoluble in water but soluble in organic solvents like benzene, alcohol.

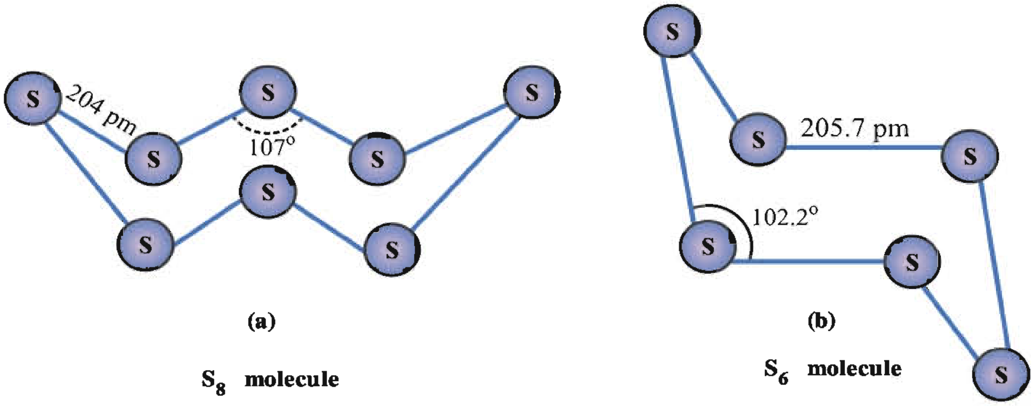


Fig. 5.2 Molecular structure of sulphur

Monoclinic sulphur (β-sulphur) : Monoclinic sulphur is soluble in CS_2. Its melting point is 393 K. When rhombic sulphur is melted in a dish and then cooled, monoclinic sulphur is obtained. Monoclinic sulphur is stable at temperature higher than 369 K and it is changed to rhombic sulphur at lower temperatures. As contrast to this, rhombic sulphur is stable at temperature lower than 369 K but is changed to monoclinic sulphur at higher temperature. At 369 K temperature, both the allotropes are stable. This temperature is called the **transition temperature.** Both these possess S_8 molecule. In both these forms S_8 molecule is in the form of a crown which is shown in fig 5.2 (a). In the last two decades, it has been possible to prepare sulphur molecules containing 6 to 20 atoms, as a result of rersearch. The cylic structure of S_6 molecule is of chair form which is shown in fig 5.2 (b).

5.7.2 Compounds of Sulphur :

(1) Sulphur dioxide (SO_2) :

(i) Preparation : When sulphur is combusted in air or oxygen gas, sulphur dioxide (with about 6 to 8% sulphur trioxide) is obtained.

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

In laboratory, sulphur dioxide gas is obtained by reaction of hydrochloric acid with sodium sulphite.

$$Na_2SO_3(s) + 2HCl(aq) \rightarrow SO_2(g) + H_2O(l) + 2NaCl(aq)$$

In industries, sulphur dioxide is obtained as a bye product during roasting of sulphide mineral.

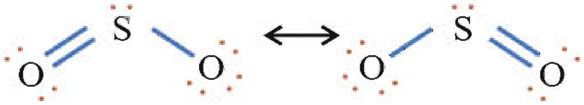
$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

Sulphur dioxide gas obtained this way is dried and stored in liquid state under pressure in steel cylinder.

(ii) Properties :

(A) Physical Properties :

- Sulphur dioxide is a colourless gas having intense smell and possessing burning effect.
- It is soluble in water in very high proportions.
- Its boiling point is 263 K. It gets liquefied at room temperature at 2 bar pressure.
- Sulphur dioxide molecule is angular. Its resonance structures are as follows :



Resonance structures of SO_2 molecule

(B) Chemical properties :

- Solution of sulphurous acid is obtained when sulphur dioxide is passed through water.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$

- It forms sodium sulphite in first step by reaction with NaOH which reacts with more proportion of sulphur dioxide and form sodium hydrogen sulphite.

$$2NaOH(aq) + SO_2(g) \rightarrow Na_2SO_3(aq) + H_2O(l)$$

$$Na_2SO_3(aq) + H_2O(l) + SO_2(g) \rightarrow 2NaHSO_3(aq)$$

- Sulphur dioxide reacts with chlorine gas in presence of catalyst and forms sulphuryl chloride (SO_2Cl_2). Sulphur trioxide is formed by oxidation in presence of vanadium pentoxide catalyst.

$$SO_2(g) + Cl_2(g) \rightarrow SO_2Cl_2(l)$$

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

It makes coloured acidic solution of $KMnO_4$ colourless. Thus it acts as a reducing agent.

$$5SO_2(g) + 2MnO_4^-(aq) + 2H_2O(l) \rightarrow 5SO_4^{2-}(aq) + 4H^+(aq) + 2Mn^{2+}(aq)$$

(iii) Uses :

- It is useful in purification of petroleum and sugar.
- It is also used to bleach wool and silk.
- To dissolve certain organic and inorganic substances liquid sulphur dioxide is used as solvent.
- Sulphur dioxide is useful in industrial production of sulphuric acid, sodium hydrogen sulphite, and calcium hydrogen sulphite.

(2) Sulphuric acid (H_2SO_4) :

(i) Industrial manufacture : Mainly the following steps are included in the manufacture of sulphuric acid by contact process.

(1) To obtain sulphur dioxide gas by combusting sulphur or sulphide mineral in air.

(2) To convert sulphur dioxide to sulphur trioxide with the help of oxygen in presence of vanadium pentoxide catalyst.

(3) Sulphur trioxide obtained this way is absorbed in concentrated sulphuric acid and so fuming sulphuric acid or oleum ($H_2S_2O_7$) is obtained.

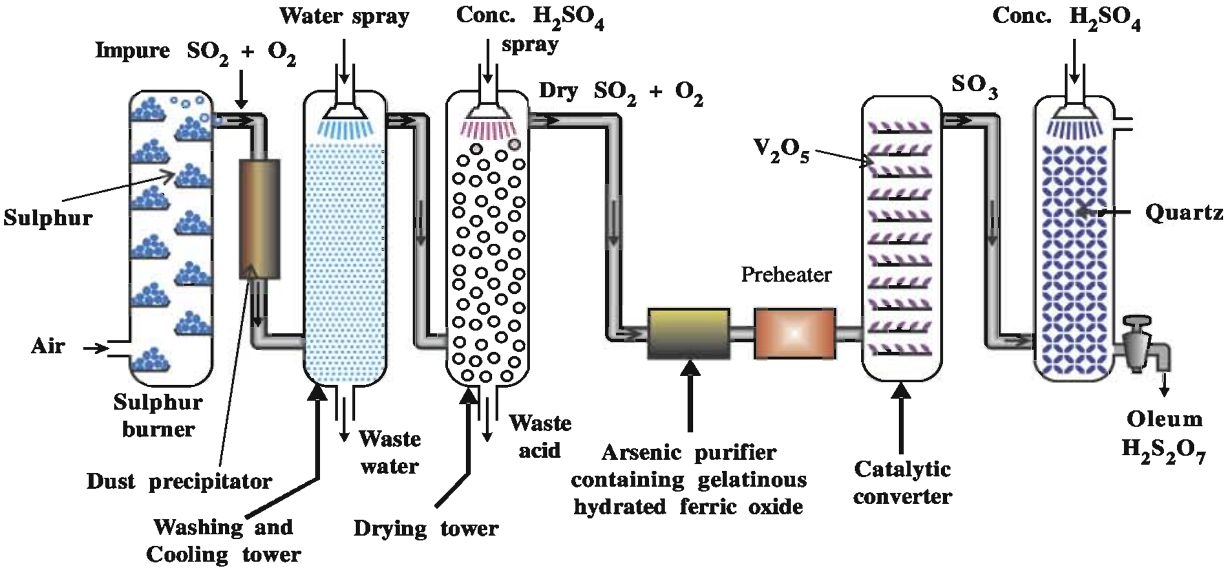


Fig 5.3 Industrial manufacture of sulphuric acid by contact process

First of all, arsenic compounds and other impurities are removed from sulphur dioxide gas and purification is carried out. The important step in production of H_2SO_4 by contact process is to prepare sulphur trioxide gas by catalytic oxidation in presence of vanadium pentoxide catalyst.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \qquad \Delta_rH = -\ 196.6\ \text{kJmole}^{-1}$$

This reaction is exothermic. The volume of the system decreases during forward reaction. Hence, to obtain more product, according to Le Chatelier's principle, lower temperature and higher pressure are required. But by decreasing the temperature very low, the rate of oxidation reaction decreases. In practice, this reaction is carried out at 2 bar pressure and 720 K temperature. Sulphur trioxide gas obtained in this way is absorbed in concentrated sulphuric acid. As a result fuming sulphuric acid or oleum ($H_2S_2O_7$) is obtained. Sulphuric acid of required concentration can be obtained by its dilution with water.

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l) \text{ (Oleum)}$$

96 to 98% pure H_2SO_4 can be obtained by contact process.

(ii) Properties :

(A) Physical properties :

- Sulphuric acid is colourless, dense oily liquid.
- Its specific gravity at 298 K temperature is 1.84.
- Its freezing point is 283 K and boiling point is 611 K.
- It evolves heat when dissolved in water. Hence it is necessary to take utmost care when solution of sulphuric acid is prepared. For this, concentrated sulphuric acid is slowly added into water with constant stirring or ice is kept around the vessel.

(B) Chemical properties :

- The ionisation of sulphuric acid in aqueous solution takes place in two steps.

$$H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq) \quad Ka_1 > 10 \text{ (very high value)}$$

$$HSO_4^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + SO_4^{2-}(aq) \quad Ka_2 = 1.2 \times 10^{-2}$$

- The higher value of Ka_1, indicates that H^+ and HSO_4^- ions are obtained by its ionisation in more proportion. The higher value of Ka_1 indicates the more strength of acid.
- Sulphuric acid forms two types of salts-common sulphate (e.g. Na_2SO_4, $CuSO_4$) and acid sulphate or bisulphate or sodium hydrogen sulphate ($NaHSO_4$) by reaction with NaOH.
- It is used in preparation of other acids due to low volatility.

$$2MX(s) + H_2SO_4(l) \rightarrow 2HX(l) + M_2SO_4(aq)$$

(where M = metal ion, X = F^-, Cl^-, NO_3^-)

- Concenterated sulphuric acid is a strong dehydrating substance. Gases containing moisture when passed through concentrated H_2SO_4 they become dry. (These gases must not be reacting with H_2SO_4). It removes water from organic compounds.

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

By this charring reaction sugar becomes black.

Hot concentrated sulphuric acid acts as oxidising agent. Metals and non-metals are oxidised by concentrated H_2SO_4 and sulphuric acid is reduced and converted to SO_2.

$$Cu(s) + 2H_2SO_4(con.)(l) \rightarrow CuSO_4(aq) + SO_2(g) + 2H_2O(l)$$

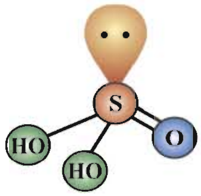
$$S(s) + 2H_2SO_4(con.)(l) \rightarrow 3SO_2(g) + 2H_2O(l)$$

$$C(s) + 2H_2SO_4(con.)(l) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$$

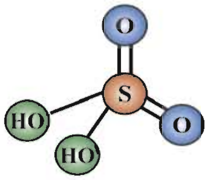
(ii) Uses :

- Sulphuric acid is an important industrial chemical.
- As sulphuric acid is very useful in preparation of most of the chemical substances like fertilizers, dyes, synthetic fibres, soap and detergent, it is called **'King of Chemicals.'**
- It is used as reagent in laboratory.

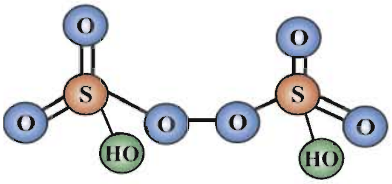
(3) Oxoacids of sulphuric acid : Sulphur forms different types of oxoacaid compounds - like H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x = 2 to 5), H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$.Here, we shall study only structrures of some oxoacids. They are shown below.



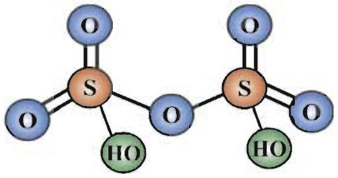
Sulphurous acid H_2SO_3



Sulphuric acid H_2SO_4



Peroxodisulphuric acid $H_2S_2O_8$



Pyrosulphuric acid (Oleum) $H_2S_2O_7$

5.8 Elements of group 17

Flourine, chlorine, bromine, iodine and astatine are the elements of group-17. These elements are collectively known as halogen elements. They are reactive non-metallic elements. As a whole more similarity is observed in the properties of the elements of this group. Astatine is a radioactive element. Important atomic and physical properties of the elements of this group are shown in table 5.8.

Table 5.8 Atomic and Physical Properties of Elements of group-17

Property	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Atomic mass (g mol^{-1})	19.00	35.45	79.90	126.90	210
Electronic configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$	$[Xe]4f^{14}5d^{10}6s^26p^5$
Ionisation enthalpy (Δ_iH_1) (kJ mol^{-1})	1680	1256	1142	1008	–
Electron gain enthalpy (kJ mol^{-1})	–328	–349	–325	–295	–
Electronegativity	4.0	3.2	3.0	2.7	2.2
Covalent radius (pm)	64	99	114	133	–
Ionic radius (pm)	133	184	196	220	–
	F_2	**Cl_2**	**Br_2**	**I_2**	**–**
Melting point (K)	54.4	172.0	265.8	386.6	–
Boiling point (K)	84.9	239.0	332.5	458.2	–
Density (g cm^{-3}) (298 K)	1.5	1.66	3.19	4.94	–

5.8.1 Electronic configuration, occurrence, oxidation states :

Electronic configuration : The electronic configuration of valence shell of elements of group-17 is ns^2np^5. They have one electron less for obtaining electronic configuration like their neighbouring inert elements.

Occurrence : The chief minerals of elements of group-17 are shown in table 5.9.

Table 5.9 Chief Minerals of Elements of Group-17

Elements	Structures and names of Chief Minerals
Fluorine	CaF_2–fluorspar, Na_3AlF_6–Cryollite, $Ca_9(PO_4)_6CaF_2$–Fluor apatite
Chlorine	NaCl–Sodium chloride, KCl–Potassium chloride, (in form of soluble salt)
Bromine	NaBr–Sodium bromide, KBr–Potassium bromide, $MgBr_2$–Magnesium bromide (in form of soluble salt)
Iodine	$NaIO_3$–Sodium iodate.

Oxidation state : Amongst the elements of this group flourine is the most electronegative element. As a result, its oxidation state is (–1) in all its compounds even then, going down from above in the group the tendency to attain positive oxidation state increases. e.g.Oxoacids of chlorine. Sometimes, the oxidation states of chlorine, bromine and iodine in their compounds are found to be –1, +1, +3, +5, +7.

5.8.2 Periodicity in Physical and Chemical Properties :

(1) Periodicity in physical properties : It can be said on the basis of table 5.8, that there is general tendency of increase in atomic size, decrease in ionisation enthalpy and decrease in electronegativity with increase in atomic number of elements of this group.

(i) Atomic and Ionic Radii : The atomic radii of elements of halogen group are the least in comparison to other elementes in the corresponding period; because halogen elements possess maximum effective nuclear charge. e.g. fluorine element of group 17 in second period possesses least atomic radius in comparison to all the elements. As we go down from above i.e. going from fluorine element to iodine element, atomic and ionic radii increase because of increase in principal quantum number in going from fluorine to iodine.

(ii) Ionisation Enthalpy : The values of ionisation enthalpy decrease with increase in atomic size while going down from above in the group.

(iii) Electron Gain Enthalpy : The value of electron gain enthalpy of halogen elements of the period is highest negative. The reason for this is that there is one electron less than the stable electronic configuration of elements of neighbouring noble elements. The value of electron gain enthalpy goes on being less negative as we go down from above in the elements of group 17; But table 5.8 shows that the value of electron gain enthalpy of Cl atom is more negative than the value of gain enthalpy of F-element. The reason for this is that new added electron takes place in 2p-orbital of F-element and in 3p-orbital of Cl element. You have studied in unit 3, std-11 (semester-I) that there is more electron repulsion in 2p-orbital than that in 3p-orbital and so electron enters into 3p-orbital very easily.

(iv) Electronegativity : The electronegativity of halogen elements is more. The electronegativity decreases as we move down from above in group 17. The electronegativity of fluorine element is maximum amongst all the elements in the periodic table.

(2) Periodicity in chemical properties :

(i) Reaction with hydrogen element : All the halogen elements react with hydrogen element, and form hydrogen halide compounds; but the tendency of reaction with hydrogen decreases as we move from fluorine to iodine element. These compounds dissolve in water and form hydrohalic acids. The order of acidic strength of these acid compounds is **HF < HCl < HBr < HI.** The stability of these halide compounds decreases with decrease in value of dissociation enthalpy of H-X bond. The order of stability of compounds is **HF > HCl > HBr > HI.**

(ii) Reaction with oxygen element : Halogen elementes react with oxygen element and form many oxides, and most of them are unstable. e.g. fluorine element forms two oxides OF_2 and O_2F_2. Amongst the two, OF_2 compound is thermally stable at 298 K temperature. In oxides that are formed by elements chlorine, bromine and iodine, the oxidation state of halogen elements is +1 to +7. The order of stability of oxides is **I > Cl > Br.**

(iii) Reaction with halogen elements : Halogen elements react with other elements of their group and form compounds called interhalogen compounds e.g. XX', XX'_3, XX'_5 and XX'_7 compounds, where X = higher volume halogen element and X' = halogen element of small size.

(iv) Reaction with metal elements : Halogen elements react with metal elements and form corresponding metal-halide compounds. e.g. Bromine element reacts with sodium metal and forms sodium bromide.

$$2Na(s) + Br_2(l) \longrightarrow 2NaBr(s)$$

The order of ionic character in metal halides is **MF > MCl > MBr > MI.**

5.8.3 Distinction of fluorine element from other elements of group (Anomalous behaviour) :

(i) Fluorine element has small size, more electronegativity, less value of dissociation enthalpy of F–F bond, so it shows anomalous behaviour from other elements. Ionisation enthalpy and electronegativity of element is more than the expectation, while value of atomic and ionic radii, melting point, boiling point and electron gain enthalpy are less in comparison to expected values of other elementes of this group.

(ii) Fluorine forms only one stable oxoacid: while other halogen elements form many oxoacids.

(iii) Because of the presence of strong hydrogen bond, hydrogen fluoride is in liquid state while other hydrogen halides are in gaseous state.

5.9 Chlorine

5.9.1 Preparation, Properties and Uses of Dichlorine Gas :

(1) Preparation : Dichlorine gas can be prepared by any of the following reactions :

(i) By reaction of manganese dioxide with concentrated HCl, dichlorine gas is formed.

$$MnO_2(s) + 4HCl(l) \longrightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$$

(ii) Chlorine gas is obtained by reaction of potassium permanganate with hydrochloric acid.

$$2KMnO_4(s) + 16HCl(l) \longrightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$$

(iii) Deacon's process : Chlorine gas can be obtained by oxidation of hydrogen chloride with oxygen of the air in presence of catalyst [$CuCl_2$].

$$4HCl(l) + O_2(g) \xrightarrow{CuCl_2} 2H_2O(l) + 2Cl_2(g)$$

(iv) Electrolysis method : Chlorine gas can be obtained by electrolysis of brine (saturated solution of NaCl), chlorine gas is deposited at the anode. Chlorine gas is obtained as a by-product in certain industries.

Chlorine gas can be prepared in laboratory by reactions (i) and (ii) and chlorine gas can be produced in industry by reactions (iii) and (iv).

(2) Properties :

(i) Physical properties :

- Chlorine is a suffocating and intense smelling gas.
- It is 2 to 5 times heavier than air.
- It can be converted to greenish yellowish coloured liquid.

(ii) Chemical properties : Chlorine gas is a strong oxidising agent and so reacts with metals and non-metals and forms corresponding chloride compounds.

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$

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

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$

$$S_8(s) + 4Cl_2(g) \rightarrow 4S_2Cl_2(l)$$

- As it has very strong attraction towards hydrogen, it forms HCl by combination with dihydrogen gas or compounds containing hydrogen.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

$$H_2S(g) + Cl_2(g) \rightarrow 2HCl(g) + S(s)$$

- In the reaction of chlorine gas with excess amount of ammonia, ammonium chloride and dintrogen gas are formed. If proportion of dichlorine gas is more in this reaction, nitrogen trichloride (explosive substance) is obtained.

$8NH_3(g) + 3Cl_2(g) \rightarrow 6NH_4Cl(s) + N_2(g)$

(excess)

$NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(g) + 3HCl(g)$

(excess)

- It gives mixture of chloride and hypochlorite by reaction with cold and dilute alkali, while it gives chloride and chlorate by reaction with hot and concentrated alkali.

$2NaOH(aq) + Cl_2(g) \rightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$

(Cold and diluted))

$6NaOH(aq) + 3Cl_2(g) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$

(Hot and concentrated)

- It forms bleaching powder by reaction with slaked lime.

$2Ca(OH)_2(aq) + 2Cl_2(g) \rightarrow Ca(OCl)_2(aq) + CaCl_2(aq) + 2H_2O(l)$

The composition of bleaching powder is $Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O$.

- Dichlorine gas reacts with saturated hydrocarbons in presence of sunlight and gives substituted product but reacts with unsaturated hydrocarbons giving addition product.

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Dichlorine gas}}{Cl_2} \xrightarrow{UV} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$\underset{\text{Ethene}}{C_2H_4} + \underset{\text{Dichlorine gas}}{Cl_2} \xrightarrow{\text{Room temperature}} \underset{\text{1,2-Dichloroethane}}{C_2H_4Cl_2}$$

- If chlorine water is kept for a long time, it loses its yellow colour because of formation of HCl and HOCl. The hypochlorous acid (HOCl) formed this way gives nascent oxygen which is responsible for its oxidation and bleaching property.

$2FeSO_4(s) + H_2SO_4(l) + Cl_2(g) \rightarrow Fe_2(SO_4)_3(s) + 2HCl(l)$

$Na_2SO_3(s) + Cl_2(g) + H_2O(l) \rightarrow Na_2SO_4(aq) + 2HCl(aq)$

(3) Uses :

- Dichlorine gas is used for bleaching the wood pulp used in preparation of paper and jute.
- Chlorine gas is useful in extraction of gold and platinum, and preparation of medicines, dyes and organic compounds.
- It is used in preparation of poisonous gases like phosgene ($COCl_2$), tear gas (CCl_3NO_2) and mustard gas [$ClCH_2CH_2SCH_2CH_2Cl$].

5.9.2 Preparation of Hydrogen Chloride Gas, Properties and Uses :

(1) Preparation : Hydrogen chloride can be prepared in the laboratory by reaction between sodium chloride and concentrated sulphuric acid.

$$NaCl(s) + H_2SO_4(aq) \xrightarrow{420\ K} NaHSO_4(aq) + HCl(g)$$

$$NaHSO_4(aq) + NaCl(s) \rightarrow Na_2SO_4(aq) + HCl(g)$$

By passing this HCl gas from concentrated sulphuric acid, it becomes dry.

(2) Properties :

(i) Physical properties :

- It is colourless gas with pungent smell.
- It is converted into colourless liquid (b.p.189 K) and in white crystalline solid substance (f.p. 159 K).
- It is highly soluble in water.

(ii) Chemical properties :

- The aqueous solution of hydrogen chloride is called hydrochloric acid.
- As hydrogen chloride is completely ionised in water, it acts as a strong acid.

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

- Hydrochloric acid gives white fumes of NH_4Cl by reaction with ammonia gas.

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

- For dissolving noble metals like gold, platinum etc. mixture of three parts of HCl and one part of HNO_3 (which is called aquaregia) is used.

$$Au(s) + 4H^+(aq) + NO_3^-(aq) + 4Cl^-(aq) \rightarrow AuCl_4^-(aq) + NO(g) + 2H_2O(l)$$

$$3Pt(s) + 16H^+(aq) + 4NO_3^-(aq) + 18Cl^-(aq) \rightarrow 3PtCl_6^{2-}(aq) + 4NO(g) + 8H_2O(l)$$

- It decomposes salts of weak acid.

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

(iii) Uses :

- Hydrogen chloride gas; is useful in the production of glucose and ammonium chloride.
- It is useful as a reagent in laboratory.

5.10 Preparation, Properties and Uses of Interhalogen Compounds

When two different halogen elements react with each other and form the compounds, they are called **interhalogen compounds** e.g. XX', XX'_3, XX'_5 and XX'_7 compounds, where X = halogen elements with bigger size, X' = halogen elements with smaller size.

(1) Preparation : Interhalogen compounds are obtained by direct reaction of halogen elements with each other.

$$\underset{\text{Equal volume}}{Cl_2(g) + F_2(g)} \xrightarrow{473\ K} \underset{\text{Chlorine fluoride}}{2ClF(g)}$$

$$Cl_2(g) + \underset{\text{excess}}{3F_2(g)} \xrightarrow{573\ K} \underset{\text{Chlorine trifluoride}}{2ClF_3(g)}$$

$$I_2(s) + \underset{\text{Equal mole}}{Cl_2(g)} \rightarrow \underset{\text{Iodine chloride}}{2ICl(s)}$$

$$I_2(s) + \underset{\text{excess}}{3Cl_2(g)} \rightarrow \underset{\text{Iodine trichloride}}{2ICl_3(g)}$$

$$Br_2(g) + 3F_2(g) \rightarrow \underset{\text{Bromine trifluoride}}{2BrF_3(l)}$$

$$Br_2(g) + \underset{\text{excess}}{5F_2(g)} \rightarrow \underset{\text{Bromine pentafluoride}}{2BrF_5(l)}$$

(2) Properties : Some properties of Interhalogen compounds are given in table 5.10.

Table 5.10 Some Properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure (shape)
XX'	ClF	colourless gas	–
	BrF	pale brown gas	–
	IF	detected spectroscopically	–
	BrCl	gas	–
	ICl	ruby red solid (α-from)	–
		brown red solid (β-form)	–
	IBr	black solid	–

XX'_3	ClF_3 BrF_3 IF_3 ICl_3	colourless gas yellow green liquid yellow powder orange solid	Bent T-shaped Bent T-shaped Bent T-shaped Bent T-shaped
XX'_5	IF_5 BrF_5 ClF_5	colourless gas but solid below 77 K colourless liquid colourless liquid	Square pyramidal Square pyramidal Square pyramidal
XX'_7	IF_7	colourless gas	Pentagonal bipyramidal

(i) Physical properties : Most of the interhalogen compounds are in volatile solid or liquid form. Some compounds are in gaseous form. (Table 5.10).

(ii) Chemical properties : Generally interhalogen compounds are more reactive than their corresponding halogen elements (Except fluorine) because the X–X' bond in interhalogen compounds is relatively weak in comparison to X–X bond. By hydrolysis of interhalogen compounds halide ion is formed from smaller size from them and hypohalite (for XX'), halite (for XX'_3), halate (for XX'_5) and perhalate (for XX'_7) ions are formed from bigger size halogen.

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

(3) Uses :

- Interhalogen compounds are used as non-aqueous solvent.
- They are very good fluorinating reagents.
- ClF_3 and BrF_3 are used to obtain U^{235} for concentration of UF_6.

$$U(s) + 3ClF_3(l) \rightarrow UF_6(g) + 3ClF(g)$$

5.11 Oxoacid Compounds of Halogen Elements

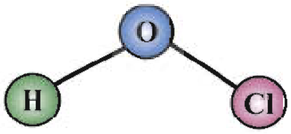
Fluorine forms only one oxoacid because of smaller size and more electrnegativity of fluorine element. HOF is called fluoric (I) acid or hypofluorous acid. Other halogen elements form oxoacid compounds in more number. Most of the compounds cannot be separated in pure form. They are stable as aqueous solutions or in the form of salts. The oxoacid compounds of halogen elements are shown in table 5.11.

Table 5.11 Oxoacid Compounds of halogens

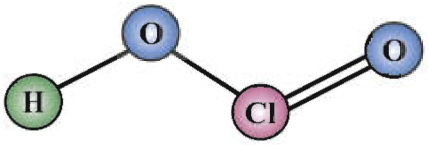
Halic (I) acid **(Hypohalus acid)**	**HOF (Hypoflourous acid)**	**HOCl (Hypochlourous acid)**	**HOBr (Hypobromous acid)**	**HOI (Hypoiodous acid)**
Halic (II) acid (Halous acid)	–	HOClO (Chlorous acid)	–	–
Halic (V) acid (Halic acid)	–	$HOClO_2$ (Chloric acid)	$HOBrO_2$ (Bromic acid)	$HOIO_2$ (Iodic acid)
Halic (VII) acid (Perhalic acid)	–	$HOClO_3$ (Perchloric acid)	$HOBrO_3$ (Perbromic acid)	$HOIO_3$ (Periodic acid)

The strength of oxoacids of halogens increases with the increase in oxidation state of halogen e.g. HClO is a very weak acid, in which oxidation state of Cl element is (+1). $HClO_4$ is a very strong acid in which oxidation state of Cl element is (+7).

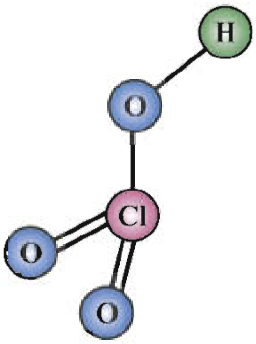
Here we will have structures of some of the oxoacids which are shown below :



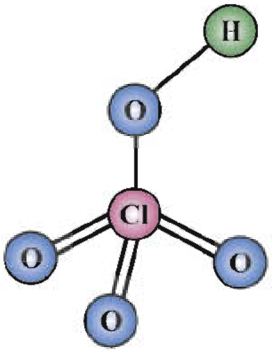
Hypochlorous acid



Chlorous acid



Chloric acid



Perchloric acid

5.12 Elements of Group 18

In this group six elements helium, neon, argon, krypton, xenon and radon are present. These elements are also known as, **'Inert gases'** or **'Noble gases'.** These elements are not considered as metals or non metals. All these elements are in gaseous form at the room temperature and are chemically inert. Hence they form very few compounds. The atomic and physical properties of the elements of this group are shown in table 5.12.

Table 5.12 Atomic and Physical Properties of group 18 Elements

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Atomic mass ($g\ mol^{-1}$)	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Ionisation enthalpy (Δ_iH) ($kJ\ mol^{-1}$)	2372	2080	1520	1351	1170	1037
Electron gain enthalpy ($kJ\ mol^{-1}$)	48	116	96	96	77	68
Atomic radius (pm)	120	160	190	200	220	–
Melting point (K)	–	24.6	83.8	115.9	161.3	202
Boiling Point (K)	4.2	27.1	87.2	119.7	165.0	211
Density ($g\ cm^{-3}$) (298 K)	1.8×10^{-4}	9.0×10^{-4}	1.8×10^{-3}	3.7×10^{-3}	5.9×10^{-3}	9.7×10^{-3}

5.12.1 Occurrence, Electronic Configuration, Oxidation States :

Electronic configuration : Except helium ($1s^2$) the elements of group 18 have their electronic configuration in valene orbits is ns^2np^6. Except helium, all the elementes have outermost orbit completely filled with electrons. Hence, these elements are chemically inert.

Occurrence : All the noble gases except radon are available from atmosphere. Helium is obtained mostly in nature. It is available from natural gas. Argon is 1% by volume in dry air.

Oxidation state : Xe possesses +2, +4, +6, or +8 oxidation states in its compounds.

5.12.2 Periodicity in Physical and Chemical Properties :

(1) Periodocity in physical properties : On the basis of table 5.12 it can be said that general tendency of increase in the atomic size, decrease in ionisation enthalpy with increase in atomic number in elements of group-18 is observed.

(i) Atomic radii : As we go down in the group from above, the atomic radii increases with increase in atomic number.

(ii) Ionisation enthalpy : Very high values of ionisation enthalpy because of stable electronic configuration of group 18 is observed. As we go down in the group the value of ionisation enthalpy decreases with increase in atomic number.

(iii) Electron gain enthalpy : Because of the stable electronic configuration of the elements of this group, they have no tendency to accept the electrons. Hence, the values of the electron gain enthalpy of these elements is more positive.

5.13 Xenon-Fluorine Compounds

Xenon element forms three compounds with fluorine viz. XeF_2, XeF_4 and XeF_6. To obtain these compounds, xenon is to be reacted with fluorine under definite conditions.

$$Xe(g) \quad + \quad F_2(g) \xrightarrow{673\ K,\ 1\ bar} XeF_2(s)$$

excess

$$Xe(g) \quad + \quad 2F_2(g) \xrightarrow{873\ K,\ 7\ bar} XeF_4(s)$$

1:5 proportion

$$Xe(g) \quad + \quad 3F_2(g) \xrightarrow{573\ K,\ 60\text{-}70\ bar} XeF_6(s)$$

1:20 proportion

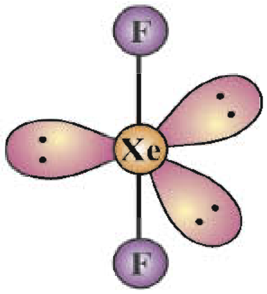
By reaction of XeF_4 and O_2F_2 at 143 K temperature, XeF_6 is obtained.

$$XeF_4(s) + O_2F_2(g) \rightarrow XeF_6(s) + O_2(g)$$

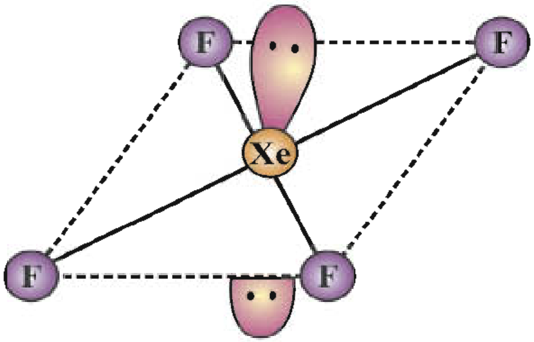
XeF_2, XeF_4, XeF_6 are colourless crystalline solid substances. They sublime easily at 298 K temperature. They are strong fluorinating agents. In very small amount of water they get hydrolysed e.g.

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

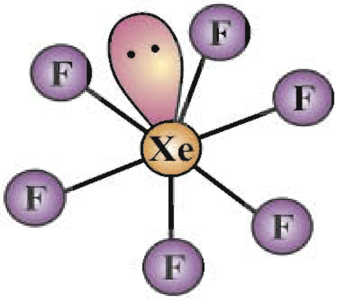
The structures of some important xenon fluorine compounds are shown below :



XeF_2
(Linear)



XeF_4
(Square planar)



XeF_6
(Distorted octahedral)

5.14 Xenon-Oxygen Compounds

Xenon trioxide XeO_3 is formed by hydrolysis of XeF_4 and XeF_6 with water.

$$6XeF_4(s) + 12H_2O(l) \rightarrow 4Xe(g) + 2XeO_3(s) + 24HF(aq) + 3O_2(g)$$

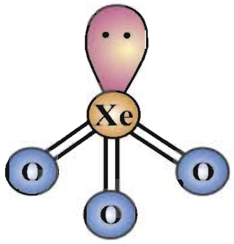
$$XeF_6(s) + 3H_2O(l) \rightarrow XeO_3(s) + 6HF(aq)$$

Because of partial hydrolysis of XeF_6 oxyfluoride compounds of Xenon $XeOF_4$ and XeO_2F_2 are formed.

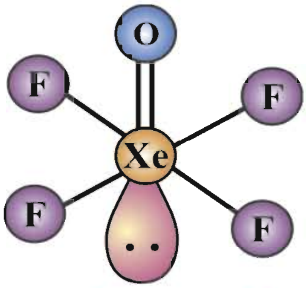
$$XeF_6(s) + H_2O(l) \rightarrow XeOF_4(l) + 2HF(aq)$$

$$XeF_6(s) + 2H_2O(l) \rightarrow XeO_2F_2(l) + 4HF(aq)$$

XeO_3 is a colourless explosive solid substance. It possesses trigonal pyramidal structure. $XeOF_4$ is a colourless volatile liquid. It possesses square pyramidal structure. The structure of XeO_3 and $XeOF_4$ are shown bellow :



XeO_3 Trigonal pyramidal



$XeOF_4$ Square pyramidal

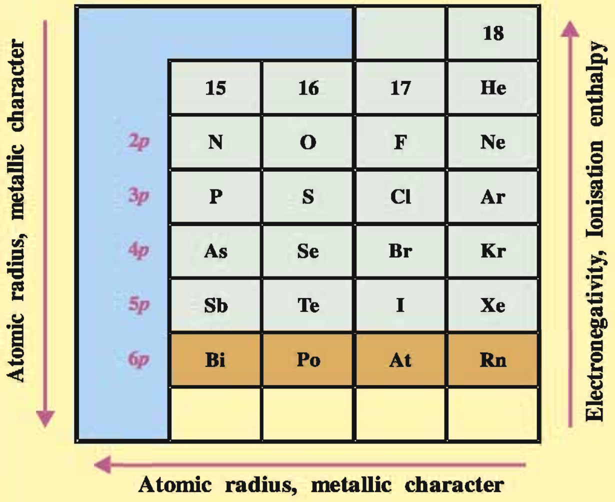
SUMMARY

The elements of groups 13 to 18 in the periodic table are known as p-block elementes. The general electronic configuration of these elements is ns^2np^{1-6}. We have studied about the elements of groups 15, 16 ,17 and 18 in this unit.

General introduction of elements of groups 15, 16, 17, 18

	group 15	group 16	group 17	group 18
Common name/ Identification	**Nitrogen group**	**Chalogens or Oxygen group**	**Halogen Group**	**Noble Gas Group**
Electronic configuration of valence shell	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Oxidation state	N –3, to +5	O –2, –1, +1, +2	F –1	Ne –
	P, As –3, +3, +5	S, Se, Te –2, +2, +4, +6	Cl, Br, I –1, +1, +3, +5, +7	Xe +2, +4, +6, +8
	Sb, Bi +3, +5	Po +2, +4	– –	– –

The periodicity in properties of elements of groups 15,16,17,18.



The first element of group 15, differs in many aspects from the other elements in the group. The reason for which is its smaller size, the capacity of formation of pπ–pπ triple bond between, nitrogen atoms and the nonavailability of d–orbitals. As we go down from above in the group, variations are found in properties. Dinitrogen (N_2) can be prepared in the laboratory as well as on commercial level. The oxides of nitrogen element are N_2O, NO, N_2O_3, N_2O_4 and N_2O_5 which possess resonance forms. Ammonia and nitric acid are compounds of nitrogen. Phosphorus element exists as P_4 molecule. It has many allotropes. It forms hydrides, halides and oxoacid compounds.

Polonium element of group 16 is radioactive. Oxygen forms metal oxides with metals. Ozone is a strong oxidising agent. Sulphur element possessess different allotropes. Out of these α and β allotropes are very important. Sulphur element combines with oxygen and forms oxide compounds like SO_2 and SO_3. Out of the different oxoacids of sulphur, sulphuric acid is very important. It is called 'King of Chemicals.'

Astatine element of group 17 is radioactaive. As these elements require one electron to have stable electronic configuration, they are very reactive. As a result of this, the elements of this group are not available in free state, but are availalbe in the combined state as negative ions. The elements of this group form oxides, hydrogen halides, interhalogen compounds and oxoacid compounds.

Radon element of group 18 is radioactive. As the octet structure is complete in all the elements of this group they are chemically inert. Xenon element of this group, under specific reaction conditions combine with fluorine and oxygen elements and form fluoride and oxide compounds.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) How many groups are there in p-block element ?

(A) 3 (B) 4 (C) 5 (D) 6

(2) What is the molecular formula of chilie salt petre ?

(A) KNO_3 (B) $NaNO_3$ (C) $Ca(NO_3)_2$ (D) $Ba(NO_3)_2$

(3) For the presence of which of the following ions, ring test is useful ?

(A) NO^- (B) NO_3^- (C) NO_2 (D) N_2O

(4) Which of the following groups of four elements is called chalcogens ?

(A) Nitrogen, phosphorus, arsenic and antimony

(B) Oxygen, sulphur, selenium and tellurium

(C) Fluorine, chlorine, bromine, iodine

(D) Helium, neon, argon, krypton.

(5) Which of the following electronic configurations is the general electronic configuration of elements of group 16 ?

(A) ns^2np^3 (B) ns^2np^4 (C) ns^2np^6 (D) ns^2np^5

(6) Which of the following oxoacids of chlorine is most stable ?

(A) $HClO_3$ (B) $HClO$ (C) $HClO_4$ (D) $HClO_2$

(7) Which of the following orders with reference to stability is correct ?

(A) $HF > HBr > HCl > HI$ (B) $HI < HCl < HBr < HF$

(C) $HF > HCl > HBr > HI$ (D) $HF > HI > HCl > HBr$

(8) Which of the following is the interhalogen compound ?

(A) XeF_4 (B) IF_7 (C) $NaCl$ (D) CaF_2

(9) What is the molecular formula of oleum ?

(A) H_2SO_3 (B) H_2SO_5 (C) $H_2S_2O_7$ (D) $H_2S_2O_8$

(10) In which of the following oxides of nitrogen, the oxidation state of nitrogen element is (+4) ?

(A) N_2O_3 (B) N_2O_4 (C) N_2O_5 (D) N_2O

2. Write the answers of following questions in short :

(1) Mention the important allotropes of phosphorus.

(2) Mention the oxidation state of underlined elements in the following compounds.

(i) $\underline{Cl}_2O$ (ii) $\underline{Cl}O_2$ (iii) $K\underline{Br}O_3$ (iv) $Na\underline{Cl}O_4$

(3) Draw resonance formulas of NO_2.

(4) Write molecular formula of four oxoacids of sulphur element.

(5) Mention the name and molecular formula of the oxoacid of fluorine element.

(6) Write reaction for preparation of phosphorus trichloride.

(7) Mention two uses of sulphur dioxide gas.

(8) Which allotrope of phosphorus is stored in water ?

(9) Mention the transistion temperature for the two allotropes of sulphur-rhombic and monoclinc.

(10) Write molecular formula of polymetaphosphoricacid.

3. Write answers of the following :

(1) The values of ionisation enthalpy of elements of group 15 are more than the values of ionisation enthalpy of the group 14 in the same period, why ?

(2) Write two chemical properties of ammonia gas.

(3) Write ring test for the detection of nitrate ion.

(4) Mention the interconversion of sulphur allotropes.

(5) What is meant by interhalogen compounds ? Mention its types and give one example of each.

(6) Write reaction of chlorine gas with ammonia gas.

(7) Write two examples of oxide compounds of phosphorus with water.

(8) Write two examples of each of xenon-fluorine and xenon-oxygen compounds.

(9) Mention oxidation states of elementes of group 16.

(10) Write two reactions of preparation of dioxygen gas.

4. Give answers of the following in detail :

(1) Discuss the reactions of elements in group 15 with hydrdogen element, oxygen element, halogen elements and metallic elements.

(2) Explain the anomalous behaviour of nitrogen element from other elements of group 15.

(3) Discuss preparation, properties and uses of nitric acid.

(4) Write a short note on 'oxides of nitrogen'.

(5) Discuss preparation, properties and uses of dioxygen gas.

(6) Discuss the industrial production of sulphuric acid by contact process.

(7) Write names, molecular formulas and structural formulas of four oxoacids of sulphur.

(8) Discuss chemical properties of hydrogen chloride.

(9) Write preparation and properties of phosphorus.

(10) Discuss preparation, properties and uses of ozone gas.

●