p-Block Elements (Nitrogen and Oxygen Family)

Introduction :

Group 13 to 18 of the periodic table of elements constitute the p–block. The p–block contains metals, metalloids as well as non–metals.

The p–block elements have general valence shell electronic configuration $ns^2\ np^{1-6}$.

The first member of each group from 13–17 of the p–block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d–orbitals.

The first member of a group also has greater ability to form $p\pi$–$p\pi$ multiple bonds to itself (e.g. C=C, C≡C, N≡N) and to element of second row (e.g C=O, C=N, C≡N, N=O) compared to the other members of the same group.

The highest oxidation of p–block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding)

Group 15 Elements : The Nitrogen family

Group 15 includes nitrogen phosphorus, arsenic, antimony and bismuth. As we go down the group, there is a shift from non-metallic to metallic through metalloidic character. Nitrogen and phosphorus are non-metal, arsenic and antimony metalloid and bismuth is a typical metal.

Electronic Configuration : The valence shell electronic configuration of these element is $ns^2\ np^3$. The s orbital in these element is completely filled and p orbitals are half- filled, making their electronic configuration extra stable.

Atomic and Ionic Radii : Covalent and ionic (in a particular state) radii increase in size down the group. There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed. This is due to the presence of completely filled d and / or f orbitals in heavier members.

Ionisation Enthalpy : Ionisation enthalpy decreases down the group due to gradual increase in atomic size. Because of the extra stable half- filled p-orbital electronic configuration and smaller size, the ionisation enthalpy of the group 15 element is much greater than of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies, as expected is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$

Electronegativity : The electronegativity value, in general, 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 polyatomic. Dinitrogen is a diatomic gas while all others are solids. Metallic character increases down the group. Nitrogen and phosphorus are non–metals, arsenic and antimony metalloids and bismuth is a metal. This is due to decrease in ionisation enthalpy and increase in atomic size. The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen, all the elements show allotropy.

ATOMIC & PHYSICAL PROPERTIES

Element		N	P	As	Sb	Bi
Atomic Number		7	15	33	51	83
Atomic Mass		14.01	30.97	74.92	121.76	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] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$
Covalent Radius / pm		70	110	120	140	150
Ionic Radius / pm a = M^{3-}, b = M^{+3}		171^a	212^a	222^a	76^b	103^b
Ionization enthalpy / (kJ mol^{-1})	I	1402	1012	947	834	703
	II	2856	1903	1798	1595	1610
	III	4577	2910	2736	2443	2466
Electronegativity		3.0	2.1	2.0	1.9	1.9

Chemical Properties :

Oxidation States and trends in a chemical reactivity :

The common oxidation states of these elements are –3, +3 and +5. The tendency to exhibit –3 oxidation state decreases down the group , bismuth hardly forms any compound in –3 oxidation state. The stability of +5 oxidation state decreases down the group. The only well characterised Bi (V) compound is BiF_5 .The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.

$Bi^{3+} > Sb^{3+} > As^{3+}$; $Bi^{5+} < Sb^{5+} < As^{5+}$

Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4 oxidation states in some oxoacids.

In the case of nitrogen, all oxidation states from +1 to +4 tend to disproportionate in acid solution.

For example, $3\ HNO_2 \longrightarrow HNO_3 + H_2O + 2\ NO$

Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid. However +3 oxidation state in case of arsenic , antimony and bismuth become increasingly stable with respect to disproportionation.

Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding. The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding (covalency) and hence , expand their covalence as in PF_6^- .

Anomalous properties of nitrogen :

Nitrogen differs from the rest of the members of this group due to its smaller size, high electronegativity, high ionisation enthalpy and non–availability of d orbitals. Nitrogen has unique ability to form $p\pi$–$p\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O). Heavier elements of this group do not form $p\pi$–$p\pi$ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Thus, nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms. Consequently, its bond enthalpy (941.1 kJ mol^{-1}) is very high. On the contrary, phosphorus, arsenic and antimony form metallic bonds in elemental state. However, the single N–N bond is weaker than the single P–P bond because of high interelectronic repulsion of the non–bonding electrons, owing to the small bond length. As a result the catenation tendency is weaker in nitrogen. Another factor which affects the chemistry of nitrogen is the absence of d orbitals in its valence shell. Besides restricting its covalency to four, nitrogen cannot form $d\pi$–$p\pi$ bonds as the heavier elements can e.g., $R_3P{=}O$ or $R_3P{=}CH_2$ (R = alkyl group). Phosphorus and arsenic can form $d\pi$–$p\pi$ bond also with transition metals when their compounds like $P(C_2H_5)_3$ and $As(C_6H_5)_3$ act as ligands.

(i) **Reactivity towards hydrogen :** All the elements of Group 15 form hydrides of the type EH_3 where E=N, P, As, Sb or Bi. Some of the properties of these hydrides are shown in Table. 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 all the hydrides. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Melting point / K	195.2	139.5	156.7	185	–
Boiling point / K	238.5	185.5	210.6	254.6	290
(E – H) Distance / pm	101.7	141.9	151.9	170.7	–
HEH angle (^{0})	107.8	93.6	91.8	91.3	–
$_fH^-$ / kJ mol^{-1}	– 46.1	13.4	66.4	145.1	278
$_{diss}H^-$(E – H) / kJ mol^{-1}	389	322	297	255	–

PROPERTIES OF HYDRIDES OF GROUP 15 ELEMENTS

(ii) **Reactivity towards oxygen :** All these elements form two types of oxides : E_2O_3 and E_2O_5. The oxide in the higher oxidation state of the element is more acidic than that of 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 is predominantly basic.

(iii) **Reactivity towards halogens :** These elements react to form two series of halides : EX_3 and EX_5 . Nitrogen does not form pentahalide due to non – availability of the d-orbitals in its valence shell. Pentahalides are more covalent than trihalides. All the trihalides of these elements except those of nitrogen are stable. In case of nitrogen, only NF_3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature. Halides are hydrolysed in water forming oxyacids or oxychlorides.

$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$

$SbCl_3 + H_2O \longrightarrow SbOCl\downarrow$ (orange) + 2HCl

$BiCl_3 + H_2O \longrightarrow BiOCl\downarrow$ (white) + 2HCl

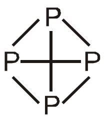
(iv) **Reactivity towards metals :** These elements react with metals to form their binary compounds exhibiting –3 oxidation state , such as , Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide) , Na_3As_2 (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

Solved Examples

Ex.1 Give reason(s) why elemental nitrogen exists as diatomic molecule whereas elemental phosphorus is a tetra-atomic molecule.

Sol. In the form of elemental nitrogen it exists as a diatomic molecule (N_2).

This is due to the fact that nitrogen can form pπ-pπ multiple bond (N≡N) because of small size of nitrogen atom. Heavier elements of this group do not form pπ-pπ bonds as their atomic orbitals are so large and diffuse that

$N \equiv N$ (N_2) ;

(P_4)

they cannot have effective overlapping. Further P–P single bond is stronger than N–N single bond. Hence phosphorus has tendency to under go catenation.

Ex.2 Why does $R_3P = O$ exist but $R_3N = O$ does not (R = alkyl group) ?

Sol. Because of inability of nitrogen to expand its covalency beyond 4.

Ex.3 Why does nitrogen show catenation properties less than prosphorus?

Sol. Because single P – P bond is stronger than single N – N bond.

Ex.4 Explain why NH_3 is basic while BiH_3 is only feebly basic ?

Sol. Lone pair of electrons is present in more concentrated spherical non directional s–orbital in BiH_3 whereas it is present in sp^3 hybrid orbital which is directional; due to decrease in bond (E – H) dissociation enthalpy down the group, BiH_3 acts as acid rather than a base.

Ex.5 Why are penta halides more covalent than trihalides ?

Sol. Higher the positive oxidation state of central atom more will be its polarising power which in turn increases the covalent character of bond formed between the central atom and the other atom.

DINITROGEN (N_2) :

Preparation :

(i) Laboratory method of preparation :

$NH_4Cl\ (aq) + NaNO_2 \longrightarrow (aq)\ N_2\ (g) + 2\ H_2O\ (1) + NaCl\ (aq)$

Small amounts of NO and HNO_3 are also formed in this reaction ; these impurities can be removed by passing the gas through aqueous suplhuric acid containing potassium dichromate. N_2 is collected by the downward displacement of water.

(ii) By heating ammonium dichromate : $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 \uparrow + 4H_2O + Cr_2O_3$

(iii) Very pure nitrogen ; $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$

Sodium azide also gives N_2 on heating.

(iv) Industrial method of preparation :

From liquefied air by fractional distillation : The boiling point of N_2 is –196°C and that of oxygen is –183°C and hence they can be separated by distillation using fractional column.

Properties :

(i) N_2 is a colourless, odourless, tastless, non-toxic gas having very low solubility in water (23.2 cm^3 per litre water at 273 K and 1 bar pressure). It has two stable isotopes : ^{14}N and ^{15}N. It is neither combustible nor a supporter of combustion.

(ii) Li, Mg and Al on heating with N_2 form corresponding nitrides.

$6Li + N_2 \xrightarrow{\Delta} 2Li_3N$; $3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$; $2Al + N_2 \xrightarrow{\Delta} 2AlN$

(iii) Reaction with H_2 : At 200 atm and 773 K, and in the presence of iron catalyst and molybdenum promoter, N_2 combines with H_2 reversibly to form ammonia. The process is called Haber's Process and is the industrial method of manufacturing ammonia. The reaction is exothermic.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

(iv) Reaction with oxygen: When air free from CO_2 and moisture is passed over an electric arc at about 2000 K, nitric oxide is formed. This reaction is endothermic.

$$N_2 + O_2 \longrightarrow 2NO$$

Uses :

1. For providing an inert atmosphere during many industrial processes where presence of air or O_2 is to be avoided (e.g., in iron and steel industry, inert diluent for reactive chemicals).
2. For manufacture of NH_3 by the Haber's process.
3. For manufacture of HNO_3 by the Birkeland-Eyde process.
4. For manufacture of industrial chemicals containing nitrogen like calcium cyanamide.
5. Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

COMPOUNDS OF NITROGEN :

(1) Ammonia :

Preparation :

(i) Ammonia is present in small quantities in air and soil where it is formed by the decay of nitrogenous orgainc matter e.g., urea.

$$NH_2CONH_2 + 2\,H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2\,NH_3 + H_2O + CO_2$$

(ii) On a small scale ammonia is obtaned from ammonia salts which decompose when treated with caustic soda or lime.

$$2\,NH_4Cl + Ca\,(OH)_2 \longrightarrow 2\,NH_3 + 2\,H_2O + CaCl_2$$

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

(iii) On a large scale, ammonia is manufactured by Haber's process.

$$N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)\ ;\ \Delta_f H^- = -46.1\ kJ\ mol^{-1}$$

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 × 10^5 Pa (about 200 atm) , 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.

(iv) By hydrolysis of metal nitrides like AlN or Mg_3N_2

$$AlN + NaOH + H_2O \longrightarrow NaAlO_2 + NH_3$$

For drying, dehydrating agents like H_2SO_4 , P_2O_5 or $CaCl_2$ can not be used as these react with NH_3.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4\ ;\ 6NH_3 + P_2O_5 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$$

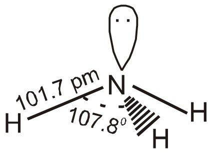
$$CaCl_2 + 8NH_3 \longrightarrow CaCl_2\,8NH_3\ (Adduct)$$

So quicklime (CaO) is used for drying of NH_3.

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

Properties :

Physical properties : Ammonia is a colourless gas with a pungent odour. Its freezing and boiling points are 198.4 and 239.7 K respectively. In the solid and liquid states , it is associated through hydrogen bonds and that accounts for its higher melting and boiling points than expected on the basis of its molecular mass. The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex. It has three bond pairs and one lone pair of electrons as shown in the structure.



Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH^- ions. $NH_3\,(g) + H_2O\,(1) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$

Chemical properties :

(i) It forms ammonium salts with acids , e.g., NH_4Cl , $(NH_4)_2\,SO_4$, etc. As a weak base , it precipitates the hydroxides of many metals from their salt solutions. For example ,

$$2\,FeCl_3\,(aq) + 3\,NH_4OH\,(aq) \longrightarrow \underset{\text{(brown ppt)}}{Fe_2O_3\,.\,xH_2O\,(s)} + 3\,NH_4Cl\,(aq)$$

(ii) The presence of lone pair of electrons on the nitrogen atoms of the ammonia molecule makes it a Lewis base. It donates the electrons pair and forms linkage with metal ions forming complex compounds.

$$Cu^{2+}\,(aq) + 4\,NH_3\,(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}\,(aq)$$

(blue) (deep blue)

$$\underset{\text{(colourless)}}{Ag^+ (aq) + Cl^{-1} (aq)} \rightleftharpoons \underset{\text{(white ppt)}}{AgCl (s)}$$

$$\underset{\text{(white ppt)}}{AgCl (s) + 2\,NH_3 (aq)} \longrightarrow \underset{\text{(colourless)}}{[Ag (NH_3)_2]Cl (aq)}$$

Test of ammonia/ammonium salts :

When NH_3 gas is passed into the colourless solution of Nessler's reagent a brown precipitate or coloration is formed. This is a test for NH_3 gas.

$$2K_2HgI_4 + 3KOH + NH_3 \longrightarrow H_2N{\cdot}HgO{\cdot}HgI \downarrow \text{(brown)} + 7KI + 2H_2O$$

Uses :

1. Liquid ammonia is used as a refrigerant.
2. For the production of ammonium fertilizers such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea etc.
3. For removing grease because NH_4OH dissolves grease.
4. For manufacture of HNO_3 by the Ostwald process.
5. As a laboratory reagent.
6. In the production of artificial rayon, silk, nylon etc.

Oxides of nitrogen :

Nitrogen forms a number of oxides, N_2O, NO, N_2O_3, NO_2 or N_2O_4 and N_2O_5, and also very unstable NO_3 and N_2O_6. All these oxides of nitrogen exhibit $p\pi$-$p\pi$ multiple bonding between nitrogen and oxygen.

Name	**Formula**	**Oxidation state of nitrogen**	**Common methods of preparation**	**Physical appearance and chemical nature**
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2\,H_2O$	colourless gas , neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4$ $\downarrow$ $Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas , neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N_2O_3	+ 3	$2\,NO + N_2O_4 \xrightarrow{250\,K} 2\,N_2O_3$	blue solid , acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2\,Pb(NO_3)_2 \xrightarrow{673\,K} 4\,NO_2 + 2\,PbO + O_2$	brown gas, acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2\,NO_2 \underset{\text{Heat}}{\overset{\text{cool}}{\rightleftharpoons}} N_2O_4$	colourless solid / liquid , acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N_2O_5	+ 5	$4\,HNO_3 + P_4O_{10} \longrightarrow 4\,HPO_3 + 2\,N_2O_5$	colourless solid, acidic

NITRIC ACID (HNO_3) :

Preparation :

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

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

(ii) On a large scale it is prepared mainly by Ostwald's process.

This method is based upon catalytic oxidation of NH_3 by atmospheric oxygen.

$$4\,NH_3\,(g) + 5\,O_2\,(g)\ (\text{from air}) \xrightarrow[500\ K\ ,\ 9\ bar]{Pt/Rh\ gauge\ catalyst} 4\,NO\,(g) + 6\,H_2O\,(g)$$

Nitric oxide thus formed combines with oxygen giving NO_2.

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

Nitrogen dioxide so formed, dissolves in water to give HNO_3.

$$3\,NO_2\,(g) + H_2O\,(\ell) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g)$$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

Properties :

Physical properties :

It is a colourless liquid. Freezing point is 231.4 K and boiling point is 355.6 K. Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

In the gaseous state, HNO_3 exists as a planar molecule.

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

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

(i) Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid , temperature and the nature of the material undergoing oxidation.

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

1. $4Zn + 10HNO_3\ (\text{dilute}) \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$

$Zn + 4HNO_3\ (\text{concentrated}) \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

2. $3Cu + 8HNO_3\ (\text{dilute}) \longrightarrow 2NO + Cu(NO_3)_2 + 4H_2O$

$Cu + 4HNO_3\ (\text{concentrated}) \longrightarrow 2NO_2 + Cu(NO_3)_2 + 2H_2O$

(ii) Concentrated nitric acid also oxidises non–metals and their compounds. Iodine is oxidised to iodic acid , carbon to carbon dioxide , sulphur to H_2SO_4 and phosphorus to phosphoric acid.

$$I_2 + 10\,HNO_3 \longrightarrow 2\,HIO_3 + 10\,NO_2 + 4\,H_2O$$

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

$$S_8 + 48\,HNO_3\ (\text{concentrated}) \longrightarrow 8\,H_2SO_4 + 48\,NO_2 + 16\,H_2O$$

$$P_4 + 20\,HNO_3\ (\text{concentrated}) \longrightarrow 4\,H_3PO_4 + 20\,NO_2 + 4\,H_2O$$

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+} to 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 concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicate the presence of nitrate ion in solution.

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

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

Uses :

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

Ex.6 Write the reaction of thermal decomposition of sodium azide.

Sol. Thermal decomposition of sodium azide gives dinitrogen gas. $2NaN_3 \longrightarrow 2Na + 3N_2$.

Ex.7 What happens when:

(a) NH_4Cl & $NaNO_3$ is heated strongly. (b) $(NH_4)_2CO_3$ is heated. (c) NH_4NO_2 is heated.

Sol. (a) $NH_4Cl + NaNO_3 \longrightarrow NH_4NO_3 + NaCl$; $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

(b) $(NH_4)_2CO_3 \xrightarrow{\Delta} 2NH_3 + CO_2 + H_2O$ (c) $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

Ex.8 (A) Colourless salt + NaOH $\xrightarrow{\Delta}$ (B) gas + (C) alkaline solution

(C) + Zn (dust) $\xrightarrow{\Delta}$ gas (B) ; (A) $\xrightarrow{\Delta}$ $\underbrace{\text{gas (D)} + \text{liquid (E)}}_{\text{both triatomic}}$

Gas (B) gives white fumes with HCl. Identify (A) to (E) and write the chemical reactions involved.

Sol. $NH_4NO_3 + NaOH \xrightarrow{\Delta} NH_3 + NaNO_3 + H_2O$; $NH_3 + HCl \longrightarrow NH_4Cl$ (white fumes)

$NaNO_3 + 7NaOH + 4Zn \longrightarrow 4Na_2ZnO_2 + NH_3\uparrow + 2H_2O$

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

So, (A) = NH_4NO_3, (B) = NH_3, (C) = $NaNO_3$, (D) = N_2O and (E) = H_2O.

Ex.9 Anhydrous $CaCl_2$, P_4O_{10} or concentrated H_2SO_4 can not be used as drying agent for ammonia. Why ?

Sol. Ammonia cannot be dried using $CaCl_2$, P_2O_5 or concentrated H_2SO_4 because NH_3 reacts with all of these.

$CaCl_2 + 8NH_3 \longrightarrow CaCl_2\cdot 8NH_3$;$P_2O_5 + 6NH_3 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$

$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$; $CaO + H_2O \longrightarrow Ca(OH)_2$

Ex.10 NO_2 can not be dried by an alkali, why ?

Sol. NO_2 being acidic in nature is absorbed by alkali.

Ex.11 Illustrate how copper metal can give different products on reaction with HNO_3.

Sol. On heating with dil. HNO_3, copper gives copper nitrate and nitric oxide.

$3Cu + 8HNO_3$ (dil) $\xrightarrow{\text{Heat}} 3Cu(NO_3)_2 + 4H_2O + 2NO$ (nitric oxide)

With conc. HNO_3, instead of NO, NO_2 is evolved.

$Cu + 4HNO_3$ (conc) $\xrightarrow{\text{Heat}} Cu(NO_3)_2 + 2H_2O + 2NO_2$ (nitrogen dioxide)

PHOSPHORUS :

It occurs in nature in the form of stable phosphates. (Animal bones also contain calcium phosphate (58 %)). The important minerals are:

(i) Phosphorite, $Ca_3(PO_4)_2$ (ii) Chloraptite, $Ca_3(PO_4)_2CaCl_2$

(iii) Fluoraptite, $Ca_3(PO_4)_2CaF_2$ (iv) Vivianite, $Fe_3(PO_4)_2\cdot 8H_2O$ (v) Redonda phosphate, $AlPO_4$

Phosphorus Allotropic Forms :

Phosphorus is found in many allotropic forms , the important one being white , red and black.

White phosphorus :

Preparation :

$2Ca_3(PO_4)_2$ (f`rom bone-ash) + $10C + 6SiO_2 \xrightarrow{\Delta} 6CaSiO_3 + 10CO + P_4(s)$ (electric furnace method)

It is a translucent white waxy solid. It is poisonous , insoluble in water but soluble in carbon disulphide. Molecular formula is P_4. Ignition temperature is around 30ºC.

When exposed to air it undergoes oxidation which gradually raises it temperature and ultimately catches fire when the temperature exceeds 30ºC. That is why it is kept in water. White phosphorus is less stable and therefore , more reactive than the other solid phases under normal conditions because of angular strain in the P_4 molecule where the angles are only 60^0.

It glows in dark due to slow oxidation. This property is called phosphorescence (chemiluminescence).

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

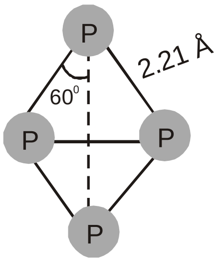


Fig White phosphorus

It consists of discrete tetrahedral P_4 molecule as shown in Fig.

Red phosphorus is obtained by heating white phosphorus at 573 K in an inert atmosphere of CO_2 or coal gas for several days. This red phosphorous may still contain some white phosphorus which is removed by boiling the mixture with NaOH when white phosphorus is converted in to PH_3 gas but red phosphorus remains inert.

$$P_4 + 3NaOH + 3H_2O \longrightarrow PH_3(g) + 3NaH_2PO_2$$

When red phosphours is heated under high pressure, a series of phase of black phosphorus are formed. Red phosphorus possesses iron grey lustre. It is odourless , non – poisonous and insouble in water as well as in carbon disulphide. Chemically, red phosphorus is much less reactive than white phosphorus. It does not glow in the dark. Ignition temperature is 260ºC. It is polymeric, consisting of chains of P_4 tetrahedra linked together in the manner as shown in Fig.

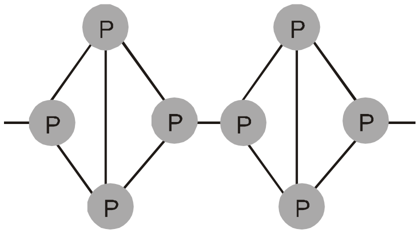
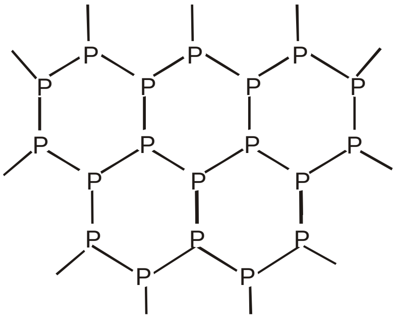


Fig. Red phosphorus

Black phosphorus has two forms α – black phosphorus and β – black phosphorus , α – Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystral. It does not oxidise in air. β – Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

β-black phosphorus is a good conductor of electricity whereas α-Black phosphorus is non-conductor.

β–black phosphorus has layered structure like graphite. The distance between the two layers is found to be 3.68 Å.



❍ **Density :** White phosphorus= 1.83 ; Red phosphorus = 2.20 ; Black phosphorus = 2.70 gm/cc ; As polymerisation increases compactness increases and therefore, density increases.

❍ Reactivity of the various allotropic forms of phosphorus towards other substances decreases in the order:
white > red > black, the last one being almost inert i.e. most stable.
Apart from their reactivity difference, all the forms are chemically similar.

COMPOUNDS OF PHOSPHORUS :

Phosphine :

Preparation :

(i) Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl.

$$Ca_3P_2 + 6\,H_2O \longrightarrow 3\,Ca(OH)_2 + 2\,PH_3$$
$$Ca_3P_2 + 6HCl \longrightarrow 3\,CaCl_2 + 2\,PH_3$$

(ii) In the laboratory, it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

$$P_4 + 3\,NaOH + 3\,H_2O \longrightarrow PH_3 + \underset{\text{(sodium hypophosphite)}}{3\,NaH_2PO_2}$$

Pure PH_3 is non inflammable but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours. For removal of impurify, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

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

Properties :

(i) It is a colourless gas with a slightly garlic or rotten fish smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

(ii) It is slightly soluble in water but soluble in CS_2 and other organic solvents. The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

(iii) When absorbed in copper sulphate or mercuric chloride, the corresponding phosphides are obtained.

$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2\downarrow \text{(black)} + 3H_2SO_4$$
$$3HgCl_2 + 2\,PH_3 \longrightarrow Hg_3P_2\downarrow \text{(brownish black)} + 6\,HCl$$

(iv) Phosphine on heating at 150ºC burns forming H_3PO_4

$$PH_3 + 2O_2 \longrightarrow H_3PO_4$$

(v) Phosphine is weakly basic and like ammonia, gives phosphonium compounds with acids e.g.,

$$PH_3 + HBr \longrightarrow PH_4Br$$

❍ Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous halogen acids (not in aqueous solution).

Uses :

The spontaneous combustion of phosphine is made to use in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

It is also used in the production of smoke screens. Calcium phosphide reacts with water producing phosphine which burns in air to give clouds of phosphorus pentaoxide and that acts as smoke screens.

Phosphorus Halides :

Phsophorus forms two types of halides , PX_3 [X = F , Cl , Br, I] and PX_5 [X = F , Cl , Br]

(a) Phosphorus Trichloride :

Preparation :

(i) It is obtained by passing dry chlorine over heated white phosphorus.

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

(ii) It is also obtained by the action of thionyl chloride with white phosphorus.

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

Properties :

(i) It is a colourless oily liquid and hydrolyses in the presence of moisture.

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

(ii) It reacts with organic compounds containing – OH group such as CH_3COOH , C_2H_5OH.

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

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

(b) Phosphorus pentachloride :

Preparation :

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

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

It can also be prepared by the action of SO_2Cl_2 on phosphorus.

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

Properties :

(i) PCl_5 is a yellowish white powder and in moist air , it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2\,HCl$$

$$POCl_3 + 3\,H_2O \longrightarrow H_3PO_4 + 3\,HCl$$

(ii) When heated it sublimes but decomposes on stronger heating.

$$PCl_5 \xrightarrow{\text{Heat}} PCl_3 + Cl_2$$

(iii) It reacts with organic compounds containing – OH group converting them to chloro derivatives.

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

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

(iv) PCl_5 on heating with finely divided metals give corresponding chlorides.

$$2\,Ag + PCl_5 \longrightarrow 2\,AgCl + PCl_3$$

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

It is used in the synthesis of some organic compounds , e.g., C_2H_5Cl , CH_3COCl.

Oxides of phosphorus :

(a) Phosphorus trioxide (P_2O_3) :

It is dimeric and has formula P_4O_6

Preparation :

It is prepared by burning phosphorus in a limited supply of oxygen.

$$P_4 + 3O_2 \text{ (limited supply of oxygen) } P_4O_6$$

Properties :

(i) It is colourless crystalline solid having melting point 23.8°C and boiling point 178°C.

(ii) It dissolves in cold water to form phosphorus acid and in hot water liberating PH_3.

$$P_4O_6 + 6H_2O \text{ (cold)} \longrightarrow 4H_3PO_3 \;; \qquad P_4O_6 + 6H_2O \text{ (hot)} \longrightarrow 3H_3PO_4 + PH_3$$

(iii) It burns in Cl_2 gas forming phosphorus oxytrichloride ($POCl_3$) and phosphoryl chloride (PO_2Cl)

$$P_4O_6 + 4Cl_2 \longrightarrow 2POCl_3 + 2PO_2Cl$$

(b) Phosphorus pentaoxide (P_2O_5) :

It is dimeric and has the formula P_4O_{10}.

Preparation :

It is obtained by burning phosphorus in excess air.

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

Properties:

(i) It is a white powder ,acidic in nature and is the anhydride of orthophosphoric acid.

(ii) It sublimes on heating at 250°C.

(iii) It dissolves in water with hissing sound forming metaphosphoric acid and finally orthophosphoric acid.

$$P_4O_{10} + 2H_2O \longrightarrow 4HPO_3 \;; \quad 4HPO_3 + 2H_2O \longrightarrow 2H_4P_2O_7 \;; \quad 2H_4P_2O_7 + 2H_2O \longrightarrow 4H_3PO_4$$

(iv) It dehydrates concentrated H_2SO_4 and concentrated HNO_3 to SO_3 and N_2O_5 respectively.

$$4HNO_3 + P_4O_{10} \xrightarrow{\text{distillation}} 4HPO_3 + 2N_2O_5 \;; \; 2H_2SO_4 + P_4O_{10} \xrightarrow{\text{distillation}} 4HPO_3 + 2SO_3$$

Uses:

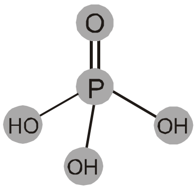
1. For drying acidic gases.
2. As a dehydrating agent
3. For the preparation of SO_3 and N_2O_5.
4. For the preparation of phosphoric acid.

Oxoacids of Phosphorus :

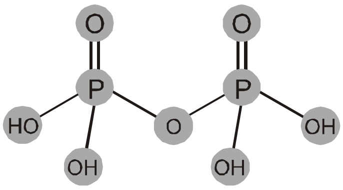
Phosphorus forms a number of a oxoacids as given in following **Table** :

Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous	H_3PO_2	+ 1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous	H_3PO_3	+ 3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+ 5	Three P – OH One P = O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+ 5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric	$(HPO_3)_3$	+ 5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2 , heat in sealed tube

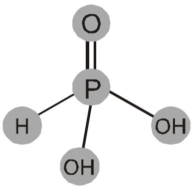
The structures of some of oxo-acids are as given below :



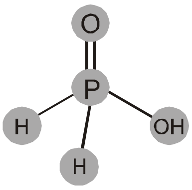
H_3PO_4
Orthophosphoric acid



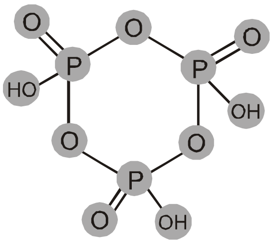
$H_4P_2O_7$
Pyrophosphoric acid



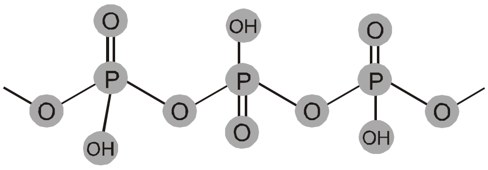
H_3PO_3
Orthophosphorous acid



H_3PO_2
Hypophosphorous acid



Cyclotrimetaphosphoric acid , $(HPO_3)_3$



Polymetaphosphoric acid , $(HPO_3)_n$

In oxoacids phosphorus is tetrahedrally surrounded by other atoms. All these acids contain one P=O and at least one P–OH bond. The oxoacids in which phosphorus has lower oxidation state (less than +5) contain in addition to P=O and P–OH bonds ,either P–P (e.g., in $H_4P_2O_6$) or P–H (e.g., in H_3PO_2) bonds but not both. These acids in + 3 oxidation state of phosphorus tend to disproportionate to higher and lower oxidation states. For example, orthophosphorus acid (or phosphorus acid) on heating disproportionates to give orthophosphoric acid (or phosphoric acid) and phosphine.

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

The acids which contanin P – H bond have strong reducing properties. Thus , hypophorous acid is a good reducing agent as it contains two P – H bonds and reduces , for example, $AgNO_3$ to metallic silver.

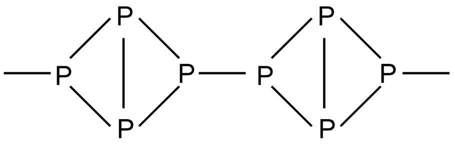
$$4\,AgNO_3 + 2\,H_2O + H_3PO_2 \longrightarrow 4\,Ag + 4\,HNO_3 + H_3PO_4$$

These P–H bonds are not ionisable to give H^+ and do not play any role in basicity. Only those H atoms which are attached with oxygen in P–OH form are ionisable and cause the basicity. Thus , H_3PO_3 and H_3PO_4 are dibasic and tribasic, respectively as the structure of H_3PO_3 has two P – OH bonds and H_3PO_4 three.

Solved Examples

Ex.12 Explain the high reactivity of white phosphorus as compared to red phosphorus.

Sol. The high reactivity of white phosphorus is due to an unusual bonding that produces considerable strain in the P_4 molecule. The P_4 molecule exists as a discrete molecule whereas the red phosphorus is a polymeric substance in which the tetrahedral, P_4 units are held by covalent bonds as shown in the following structure.



Ex.13 What happens ?

(a) When phosphine is heated at 150ºC .

(b) When phosphine is dissolved in water in presence of light.

Sol. (a) Phosphine on heating at 150ºC burns forming H_3PO_4

$$PH_3 + 2O_2 \longrightarrow H_3PO_4$$

(b) The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.

Ex.14 $P_4 + NaOH \xrightarrow{\text{warm}}$ Products.

Explain the reducing character of one of the products obtained by taking the example of silver nitrate.

Sol. $P_4 + 3\,NaOH + 3\,H_2O \longrightarrow PH_3 + 3\,NaH_2PO_2$ (sodium hypophosphite)

$3AgNO_3 + PH_3 \longrightarrow Ag_3P\downarrow$ (yellow) + $3HNO_3$. Ag_3P

$Ag_3P + AgNO_3 + 3H_2O \longrightarrow 3Ag\downarrow$ (black) + $3HNO_3 + H_3PO_3$

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

Ex.15 Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

Sol. The oxidation state of P in PCl_5 is +5. Since P has five electrons in its valence shell, therefore, it cannot increase its oxidation state beyond +5 by donating electrons, therefore, PCl_5 cannot act as a reducing agent. However, it can decrease its oxidation number from +5 to +3 or some lower value, therefore, PCl_5 acts as an oxidising agent. For example, it oxidises Ag to AgCl, Sn to $SnCl_4$ and H_2 to HCl.

$$2\overset{0}{Ag} + \overset{+5}{P}Cl_5 \longrightarrow 2Ag\overset{+1}{Cl} + \overset{+3}{P}Cl_3$$

$$\overset{0}{Sn} + 2\,\overset{+5}{P}Cl_5 \longrightarrow \overset{+4}{Sn}Cl_4 + 2\,\overset{+3}{P}Cl_3$$

$$\overset{+5}{P}Cl_5 + \overset{0}{H_2} \longrightarrow \overset{+3}{P}Cl_3 + 2\,\overset{+1}{H}Cl$$

Ex.16 What happens when

(a) PCl_5 is heated, (b) PCl_5 is reacted with heavy water, (c) H_3PO_3 is heated.

Ans : (a) $PCl_5 \xrightarrow{\Delta} PCl_3 + Cl_2$; (b) $PCl_5 + D_2O \longrightarrow POCl_3 + 2\,DCl$; (c) $4\,H_3PO_3 \xrightarrow{\Delta} 3\,H_3PO_4 + PH_3$

Ex.17 (i) Sodium salt of an acid (A) is formed on boiling white phosphorus with NaOH solution.

(ii) On passing chlorine through phosphorus kept fused under water, another acid (B) is formed.

(iii) Phosphorus on treatment with concentrated HNO_3 gives an acid (C) which is also formed by the action of dilute H_2SO_4 on powdered phosphorite rock.

(iv) (A) on treatment with a solution of $HgCl_2$ first gives a white precipitate of compound (D) and then a grey precipitate of (E). Identify (A) to (E) and write balanced chemical equations for the reactions at steps (i) to (iv).

Ans. (A) NaH_2PO_2 ; (B) H_3PO_3 ; (C) H_3PO_4 ; (D) Hg_2Cl_2 ; (E) Hg

Sol. The given changes are :

(i) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2$ (sodium hypophosphite) $+ PH_3$

Thus acid (A) is H_3PO_2, i.e., hypophosphorus acid.

(ii) $2P + 3Cl_2 + 6H_2O \longrightarrow 2H_3PO_3$ (phosphorus acid) + 6HCl

Thus, acid (B) is H_3PO_3

(iii) $P_4 + 20HNO_2 \longrightarrow 4H_3PO_4$ (C) $+ 20NO_2 + 4H_2O$

$P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4$ (C) (phosporic acid) $+ 10SO_2 + 4H_2O$

Thus, acid (C) is H_3PO_4

(iv) $H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$

$HgCl_2 + 2H \longrightarrow Hg_2Cl_2 \downarrow$ (D) (white) + 2HCl ; $Hg_2Cl_2 + 2H \longrightarrow 2Hg \downarrow$ (E) (grey) + 2HCl

---

Group 16 Elements : The Oxygen family

Oxygen, sulphur, selenium, tellurium and polonium constitute group 16 of the periodic table. This is sometimes known as group of chalcogens the ore forming elements because a large number of metals ores are oxides or sulphides.

Electronic Configuration : The elements of group 16 have six electrons in the outermost shell and have $ns^2\ np^4$ general valence shell electronic configuration.

Atomic and Ionic Radii : Due to increase in the number of shells , atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small .

Ionisation Enthalpy : Ionisation enthalpy decreases down the group. It is due to increase in size. However, the element of this group have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods. This is due to the fact that group 15 elements have extra stable half-filled p orbitals electronic configurations.

Electron Gain Enthalpy : Because of the compact nature of oxygen atom, it has less negative electron gain enthalpy than sulphur. However from sulphur onwards the value again becomes less negative upto polonium.

Electronegativity : Next to fluorine, oxygen has the highest electronegativity value amongst the elements. Within the group, electronegativity decrease with an increase in atomic number. This indicates that the metallic character increases from oxygen to polonium.

Physical Properties : Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). The melting and boiling points increase with an increase in atomic number down the group. The larger difference between the melting and boiling points of oxygen and sulphur may be explained on the basis of their atomicity; oxygen exist as diatomic molecules (O_2) whereas sulphur exists as polyatomic molecule (S_8).

Catenation : Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S_8). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.

- Selenium has unique property of photo conductivity and is used in photocopying machines and also a decolouriser of glass.

ATOMIC & PHYSICAL PROPERTIES

Element		O	S	Se	Te
Atomic Number		8	16	34	52
Atomic Mass		16	32.06	78.96	127.6
Electronic configuration		[He] $2s^2\ 2p^4$	[Ne] $3s^2\ 3p^4$	[Ar] $3d^{10}4s^2\ 4p^4$	[Kr] $4d^{10}5s^2\ 5p^4$
Covalent Radius / pm		74	103	119	142
Ionic Radius X^{-2} / pm		140	184	198	221
Ionization enthalpy / (kJ mol^{-1})	°	1314	1000	941	869
	°□	3388	2251	2045	1790
Electronegativity		3.5	2.44	2.48	2.01
Density/[g cm^{-3} (293 K)]		1.32	2.06	4.19	6.25
Melting point / K		54	393	490	725
Boiling point / K		90	718	958	1260

Chemical Properties :

Oxidation states and trends in chemical reactivity :

The elements of group 16 exhibit a number of oxidation states. The stability of -2 oxidation state decreases down the group. Polonium hardly shows -2 oxidation states. Since electronegativity of oxygen is very high, it shows only negative oxidation states as -2 except in the case of OF_2 where its oxidation states is + 2. Other elements of the group exhibit + 2 + 4 + 6 oxidation states but + 4 and + 6 are more common. Sulphur, selenium and tellurium usually show + 4 oxidation in their compounds with oxygen and +6 oxidations state with fluorine. The stability of +6 oxidation state decreases down the group and stability of + 4 oxidation state increases (inert pair effect). Bonding in + 4 and + 6 oxidation states are primarily covalent.

- HNO_3 oxidises sulphur to H_2SO_4 (S + VI) but only oxidises selenium to H_2SeO_3 (Se + IV) as the atoms are smaller and there is poor shielding of 3d electrons as a result the electrons are held more tightly with nucleus.

Anomalous behaviour of oxygen :

The anomalous behaviour of oxygen, like other member of p-block present in second period is due to its small size and high electronegativity. One typical example of effects of small size and high electronegativity is the presence of strong hydrogen bonding in H_2O which is not found in H_2S.

The absence of d orbitals in oxygen restricts its covalency to four and in practice, rarely increases beyond two. On the other hand, in case of other elements of the group, the valence shell can be expanded and covalence exceeds four.

(i) **Reactivity with hydrogen :** All the elements of group 16 form hydrides of the type H_2E (E = S, Se, Te, Po). Some properties of hydrides are given in Table. Their acidic character increases from H_2O to H_2Te.

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

TABLE : PROPERTIES OF HYDRIDES OF GROUP 16 ELEMENTS

Property	**H_2O**	**H_2S**	**H_2Se**	**H_2Te**
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H$/kJ mol^{-1}	-286	-20	73	100
Δ_{diss} H (H-E)/kJ mol^{-1}	463	347	276	238
Dissociation constant^a	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

(ii) **Reactivity with oxygen :** All these elements form oxides of the EO_2 and EO_3 types where E = S, Se, Te or Po. 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 while TeO_2 is an oxidising 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.

(iii) **Reactivity toward the halogens :** Elements of group 16 form a larger number of halides of the type EX_6, EX_4 and EX_2 where E is an element of the group and X is an halogen. The stabilities of the halides decrease in the order F > Cl > Br > I. Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. They have octahedral structure. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons.

Amongst tetrafluorides, SF_4 is a gas , SeF_4 liquid and TeF_4 a solid.

All elements except selenium form dichlorides and dibromides.The well known monohalides 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 disproportionation as given below :

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

Solved Examples

Ex.18 Identify the group 16(VI A) element that fits each of the following description is :
(a) the most electronegative, (b) semimetal, (c) radioactive, (d) the most abundant element in the earth's crust.

Ans. (a) Oxygen (b) Tellurium (c) Polonium (d) Oxygen

Ex.19 Elements of Group 16 generally show lower value of first ionisation enthalpy compared to the corresponding periods of group 15. Why ?

Sol : Due to extra stable half-filled p orbitals electronic configurations of Group 15 elements, larger amount of energy is required to remove electrons compared to Group 16 elements.

Ex.20 Give the names and formulae of the compounds in which sulphur exhibits an oxidation state of :
(a) – 2 (b) + 4 (c) + 6

Ans. (a) H_2S^{2-} (b) $S^{4+}O_2$ (c) $S^{+6}O_3$

Ex.21 Why is dioxygen a gas but sulphur a solid ?

Ans. Due to small size and high electronegativity, oxygen forms $p\pi - p\pi$ multiple bonds. As a result oxygen exists as diatomic (O_2) molecules. These molecules are held together by weak van der Waals forces of attraction which can be easily overcome by collisions of the molecules at room temperature. Therefore, O_2 is a gas at room temperature.

Sulphur, on the other hand, because of its bigger size and lower electronegativity, does not form pπ - pπ multiple bonds. Instead, it prefers to form S – S single bonds. Further, because of stronger S – S than O – O single bonds, sulphur has a much greater tendency for catenation than oxygen. Consequently, sulphur because of its higher tendency for catenation and lower tendency for pπ - pπ multiple bonds, forms octaatomic (S_8) molecules having eight-membered puckered ring structure. Because of bigger size, the forces of attraction holding the S_8 molecules together are much stronger which cannot be overcome by collisions of molecules at room temperature. Consequently, sulphur is a solid at room temperature.

DIOXYGEN (O_2) :

It differs from the remaining elements of the VIth group because of the following properties.

(A) small size (B) high electronegativity and (C) non-availability of d-orbitals.

Preparation :

(i) By thermal decomposition of oxides of metals.

$2\,HgO \xrightarrow{450^0C} 2\,Hg + O_2$; $2\,Ag_2O \xrightarrow{350^0C} 4\,Ag + O_2$

(ii) By thermal decomposition of oxygen rich compounds.

$KClO_3 \xrightarrow{\Delta} 2\,KCl + 3O_2$ (laboratory method)

(iii) $2H_2O_2(aq.) \xrightarrow{\text{finely divided metals and } MnO_2} 2H_2O(l) + O_2(g)$

(iv) **Industrial method :**

(a) Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

(b) Oxygen is obtained by liquification of air and then its fractional distillation.

Physical properties :

Colourless , odourless and tasteless gas. It is paramagnetic and exhibits allotropy. Three isotopes of oxygen are ${}^{16}_{8}O$, ${}^{17}_{8}O$ and ${}^{18}_{8}O$. Oxygen does not burn but is a strong supporter of combustion.

Chemical properties :

(i) Reaction with metals :

$2Ca + O_2 \longrightarrow 2CaO$; $4Al + 3O_2 \longrightarrow 2Al_2O_3$

(ii) Reaction with non-metals :

$P_4 + 5O_2 \longrightarrow P_4O_{10}$; $C + O_2 \longrightarrow CO_2$

(iii) Reaction with compounds :

$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$; $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$; $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

Note : It has been observed that its combination with other elements is often strongly exothermic which helps in sustaining the reaction. However, to initiate the reaction, some external heating is required as bond dissociation enthalpy of oxygen-oxygen double bond is high (493.4 kJ mol^{-1}).

Use :

1. Oxygen mixed with helium or CO_2 is used for artificial respiration.
2. Liquid oxygen (with combustion fuel hydrazine) is used as oxidising agent in rocket fuels.
3. Oxygen is used for production of oxy-hydrogen or oxy-acetylene flames employed for cutting and welding.

4. Pure dioxygen is used to convert pig iron into steel in the basic oxygen process which are kaldo and LD process.

OXIDES :

(i) Acidic oxides :

The covalent oxides of non-metal are usually acidic; dissolves in water to produce solutions of acids e.g., CO_2, SO_2 , SO_3, N_2O_5 , N_2O_3 , P_4O_6 , P_4O_{10}, Cl_2O_7, CrO_3 , Mn_2O_7 etc. They are termed as acid anhydride.

$$Cl_2O_7 + H_2O \longrightarrow 2\ HClO_4\ ;\ Mn_2O_7 + H_2O \longrightarrow 2\ HMnO_4$$

(ii) Basic oxides :

Metallic oxides are generally basic oxides. They either dissolve in water to form alkalies or combine with acids to form salts and water or combine with acidic oxides to form salts; e.g., Na_2O, CaO. CuO, FeO, BaO etc.

$$Na_2O + H_2O \longrightarrow 2\ NaOH\ ;\ CaO + H_2O \longrightarrow Ca(OH)_2\ ;\ CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

The metallic oxides with lowest oxidation sate is the most ionic and the most basic but with increasing oxidation sate the acidic character increases e.g., CrO is basic, Cr_2O_3 amphoteric and CrO_3 acidic.

(iii) Amphoteric Oxides :

Many metals yield oxides which combine with both strong acid as well as strong bases e.g., ZnO, Al_2O_3, BeO, Sb_2O_3, Cr_2O_3, PbO, SnO, SnO_2, Ga_2O_3 etc.

$$PbO + 2\ NaOH \longrightarrow Na_2PbO_2 + H_2O\ ;\quad PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$$

$$Cr_2O_3 + 2\ NaOH \longrightarrow Na_2Cr_2O_4 + H_2O;\quad Cr_2O_3 + 3\ H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3\ H_2O$$

OZONE (O_3) :

O_3 is an allotropic form of oxygen. At a height of about 20 Kms it is formed from atmoshperic oxygen in the presence of sunlight. This O_3 layer protects the earth's surface from an excessive concentration of ultra violet radiations.

Preparation :

It is prepared by passing silent electric discharge through a slow stream of pure and dry oxygen to prevent its decomposition.

$$O_2 \xrightarrow{\text{energy}} O + O$$

$$O_2 + O \longrightarrow O_3$$

$$3\ O_2 \rightleftharpoons 2\ O_3 \qquad \Delta H^{V}\ (298\ K) = +\ 142\ kJ\ mol^{-1}$$

The product is known as ozonised oxygen. If concentration of O_3 greater than 10% are required , a battery of ozonisers can be used , and pure ozone (bp 385 K) can be condensed in a vessel surrounded by liquid oxygen.

Properties :

Physical properties :

(1) It is a pale blue gas which forms a blue liquid and one solidification forms violet black crystals.

(2) It has a strong fish – like smell

(3) It is slightly soluble in water but more in turpentine oil or glacial acetic acid or CCl_4 .

(4) O_3 molecule is diamagnetic but O_3^- ion is paramagnetic (1 unpaired e^-)

(5) It is explosive and unstable with respect to O_2 as its decomposition into O_2 results in the liberation of heats and an increase in entropy.

Chemical Properties :

(1) As Oxidising agent : Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \longrightarrow O_2 + O$), it acts as a powerful oxidising agent.

In acidic medium : $O_3 + 2\,H^+ + 2e^- \longrightarrow O_2 + 2\,H_2O$ SRP = + 2.07 V.

In alkaline medium : $O_3 + H_2O + 2e^- \longrightarrow O_2 + 2\,OH^-$ SRP = + 1..24 V

Therefore , Ozone is a stronger oxidising agent in acidic medium.

With excess of potassium iodide solution buffered with a borate buffer, ozone liberates iodine which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

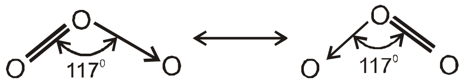
$$I^- \longrightarrow I_2$$
$$O_3 \longrightarrow O_2 + [O]$$
$$\underline{2\,KI + H_2O + [O] \longrightarrow 2\,KOH + I_2}$$
$$2\,KI + H_2O + O_3 \longrightarrow 2\,KOH + O_2 + I_2$$

It oxidises PbS to $PbSO_4$, MnO_4^{2-} to MnO_4^- (basic medium) and $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ (basic medium).

Note : With experimental facts it has been shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

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

Structure :



O – O B.L. = 1.28 Å

O–O bond length decreases in order : H_2O_2 (1.48 Å) > O_3 (1.28 Å) > O_2F_2 (1.22 Å) > O_2 (1.21 Å)

Uses :

It is used as a germicide, disinfectant and for sterilising water. It is also used for bleaching oil, ivory, flour starch etc. It acts as an oxidising agent in the manufacture of potassium permanganate.

Solved Examples

Ex.22 Write the allotropic forms of oxygen

Ans. Ordinary oxygen and ozone.

Ex.23 Ozone layer is being depleted. This is due to :

(A) NO emission from supersonic jets
(B) chloroflurocarbon used as aerosols
(C*) both (A) and (B)
(D) none of the above

Sol. (A) $O_3 + NO \longrightarrow NO_2 + O_2$

(B) $Cl_2CF_2 \longrightarrow {}^{\bullet}Cl + {}^{\bullet}CClF_2$; ${}^{\bullet}Cl + O_3 \longrightarrow ClO^{\bullet} + O_2$

$ClO^{\bullet} \longrightarrow Cl^{\bullet} + O^{\bullet}$; $ClO^{\bullet} + O^{\bullet} \longrightarrow {}^{\bullet}Cl + O_2$

Ex.24 In the following reaction explain which one is oxidising agent and which one is reducing agent ?

$$H_2O_2 + O_3 \quad 2\,O_2 + H_2O$$

Sol. Ozone is behaving as an oxidising agent and H_2O_2 is behaving as reducing agent.

$$2e^- + 2\,H^+ + O_3 \longrightarrow O_2 + 2\,H_2O$$

$$H_2O_2 \longrightarrow O_2 + 2\,H^+ + 2e^-$$

The above interpretations is further supported on the following grounds.
SRP of H_2O_2 is + 1.77 V while SRP of O_3 is + 2.07 V. Therefore , O_3 is stronger oxidising agent than H_2O_2 .

Ex.25 O_3 is a powerful oxidising agent. Write equation to represent oxidation of

(a) I^- to I_2 in acidic solutions,

(b) sulphur to sulphuric acid in the presence of moisture,

Ans. (a) $O_3 + 2I^- + 2H^+ \longrightarrow O_2 + I_2 + H_2O$

(b) $3O_3 + S + H_2O \longrightarrow H_2SO_4 + 3O_2$.

Ex.26 Give the important applications of O_3 .

Sol. (A) As a germicide and disinfectant for sterilising water and improving the atmosphere of crowded places.
(B) For detecting the position of double bond in the unsaturated organic compounds.
(C) In mfg. of artificial silk, synthetic camphor, $KMnO_4$ etc. It is also used for bleaching oil, ivory, flour starch etc.

SULPHUR (S) :

Allotropic Forms Of Sulphur :

Sulphur forms numerous allotropes of which the **yellow rhombic** (α - sulphur) and **monoclinic** (β - sulphur) forms are the most important. The stable forms at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

Rhombic sulphur (α - sulphur) :

This allotrope is Syellow in colour , melting point 385.8 K and specific gravity 2.06. Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2. It is insoluble in water but dissolved to some extent in benzene, alcohol and ether. It is readily soluble in CS_2 .

Monoclinic sulphur (β - sulphur) :

Its melting point is 393 K and specific gravity 1.98. It is soluble in CS_2. This form of sulphur is prepared by melting rhombic sulphur in a dish and cooling till 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. It is stable above 369 K and transforms into α - sulphur below it . Conversely, α - sulphur is stable below 369 K and transforms into β - sulphur above this. At 369 K both the forms are stable. This temperature is called transition temperature.
Both rhombic and monoclinic sulphur have S_8 molecules these S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape. The molecular dimensions are given in figure.

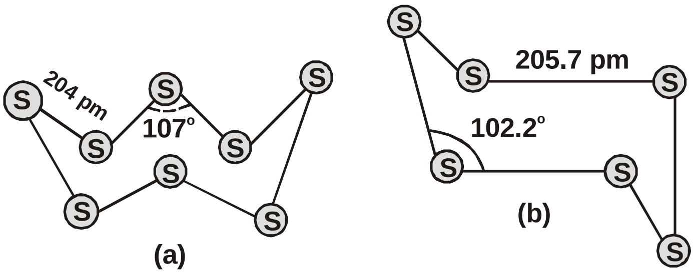


Fig. : The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in the last two decades. In cyclo- S_6, the ring adopts the chair form and the molecular dimension are as shown in fig. (b).

- Sulphur melts to form a mobile liquid. As the temperature is raised the colour darkens. At 160ºC C_8 rings break, and the diradicals so formed polymerize, forming long chains of up to a million atoms. The viscosity increases sharply, and continues to rise up to 200ºC. At higher temperatures chains break, and shorter chains and rings are formed, which makes the viscosity decrease upto 444ºC, the boiling point. The vapour at 200ºC consists mostly of S_8 rings, but contains 1-2% of S_2 molecules. At elevated temperature (~1000 K), S_2 is the dominant species and is paramagnetic like O_2, and presumably has similar bonding. S_2 gas is stable upto 2200ºC.

COMPOUNDS OF SULPHUR :

Sulphur Dioxide:

Perparation :

(i) Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

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

(ii) In the laboratory it is readily generated by treating a sulphite with dilute sulphuric acid.

$$SO_3^{2-}(aq) + 2H^+ (aq) \longrightarrow H_2O(l) + SO_2(g)$$

(iii) Industrially it is produced as a by- product of the roasting of sulphide ores.

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

The gas after drying is liquefied under pressure and stored in steel cylinders.

Properties :

(i) Sulphur dioxide is a colorless gas with pungent smell and is highly soluble in water. It liquefies at room temperature under a pressure of two atomsphere and boils at 263 K.

(ii) Sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2 SO_3 (aq)$$

(iii) It reacts readily with sodium hydroxide solution, forming sodium sulphite which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

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

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2 NaHSO_3$$

(iv) In it reaction with water and alkalies, the behaivour of sulphur dioxide is very similar to that of carbon dioxide.

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

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

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{V_2O_5} 2SO_3(g) \qquad \text{Addition reactions}$$

(v) When moist, sulphur dioxide behaves as a reducing agent. For example it converts iron (III) ions to irons (II) ions and decolourises acidified potasssium permanganate (VII) solution; the latter reaction is a convenient test for the gas.

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

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

(vi) Bleaching action :

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$$

$$\text{coloured matter} \underset{\text{Air oxidation}}{\overset{H^+}{\rightleftharpoons}} \text{colourless matter}$$

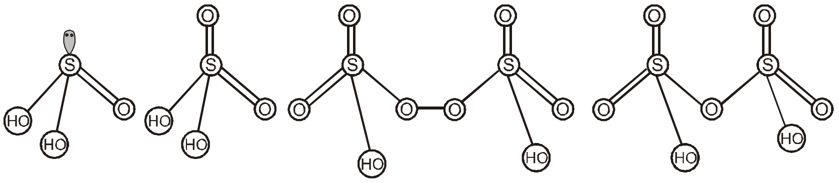
❖ Bleaching is through reduction but it is temporary.
It is a more powerful reducing agent in alkaline medium than in acidic medium.

Uses :

Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti- chlor, disinfecatant and preservation. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

OXYACID OF SULPHUR

Sulphur forms a number of oxoacid such as H_2SO_3, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_2O_6$ (x = 2 to 5,) H_2SO_4, $H_2S_2O_7$, H_2SO_8. Structures of some important oxoacids are shown in figure.



Sulphurous acid (H_2SO_3) Sulphuric acid (H_2SO_4) Peroxodisulphuric acid ($H_2S_2O_8$) Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Fig. Structures of some important oxoacids of sulphur

SULPHURIC ACID (H_2SO_4) :

Manufacture :

Sulphuric acid is manufactured by the contact process which involves three steps :

(i) burning of sulphur or sulphide ores in air to generate SO_2

(ii) conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5), and

(iii) absorption of SO_2 in H_2SO_4 to give Oleum ($H_2S_2O_7$)

The SO_2 produced is profiled by removing dust and other impurities such as arsenic compounds.

The key step in the manufacture of H_2SO_4 is the catalytic oxidation of SO_2 with O_2 to give SO_3 in the presence of V_2O_5 (catalyst).

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)\ D_rH\,\Theta = -196.6\ \text{kJ mol}^{-1}.$$

The reaction is exothermic reversible and the forward reaction leads to a decrease in volume. Therefore, low temperature and high pressure are the favourable conditions for maximum yield. But the temperature should not be very low other wise rate of reaction will become slow.

In practice the plant is operated at a pressure of 2 bar and a temperature of 720 K. The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. 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 a continuous one and also to reduce the cost.

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

The sulphuric acid obtained by Contact process is 96-98% pure.

Properties :

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a larger quantity of heat. The chemical reaction of sulphuric acid are as a result of the following characteristics : (a) low volatility (b) strong acidic character (c) strong affinity for water and (d) ability to act as an oxidising agent in aqueous solution,

(i) Sulphuric acid ionises in two steps.

$$H_2SO_4(aq) + H_2O(\ell) \longrightarrow H_3O^+ (aq) + HSO_4^- (aq) \text{ ; } Ka_1 = \text{very larger } (K_{a1} > 10)$$

$$H_2SO_4^-(aq) + H_2O(\ell) \longrightarrow H_3O^+ (aq) + SO_4^{2-} (aq) \text{ ; } Ka_2 = 1.2 \times 10^{-2}$$

The larger value of K_{a1} ($K_{a1} > 10$) means that H_2SO_4 is largely dissociated into H^+ and HSO_4^-. Greater the value of dissociation constant (K_a) the stronger is the acid.

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

(b) Decomposes carbonates and bicarbonates in to C.

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2 \text{ ; } NaHCO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + CO_2$$

(c) Sulphuric acid, because of its low volatility can be used to manufacture more volatile acid from their corresponding salts.

$$2MX + H_2SO_4 \longrightarrow 2HX + M_2SO_4 \text{ (X = F, Cl, NO}_3\text{) ; } NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

(M = Metal)

(ii) Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passing them through sulphuric acid, provided the gases do not react with the acid. Sulphuric acid removes water from organic compound; it is evident by its charring action on carbohydrates.

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O \text{ ; } H_2C_2O_4 \xrightarrow[-H_2O]{H_2SO_4} CO + CO_2$$

(iii) Hot concentrated sulphuric acid is moderately strong oxidising agent. In this respect it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to SO_2.

$$Cu + 2H_2SO_4 \text{(concentrated)} \longrightarrow CuSO_4 + 2H_2O$$

$$3S + 2H_2SO_4 \text{(concentrated)} \longrightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4 \text{(concentrated)} \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

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 also in many industrial processes .The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). Other uses are in : (i) petroleum refining (ii) manufacture of pigment, paints and dyestuff intermediates (iii) detergent industry

(iv) metallurgical applications (e.g., cleansing metal before enameling, electroplating and galvanising) (v) storage batteries (vi) in the manufacture of nitrocellulose products and (vii) as a laboratory reagent.

Solved Examples

Ex.27 Which allotropic form of sulphur is stable at room temperature ?

Ans. Rhombic sulphur

Ex.28 Out of following forms of sulphur which one is paramagnetic in nature and why ? S_8 ,S_6 and S_2

Ans. Sulphur exist as S_2 in vapour state which has two unpaired electrons in the anti-bonding π^* orbitals like O_2

Ex.29 SO_2 and Cl_2 both are used as bleaching agent. What factors cause bleaching ?

Sol. $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H.$

$Cl_2 + H_2O \longrightarrow 2HCl + O.$

Bleaching action of SO_2 is due to H (that causes reduction) and that of Cl_2 is due to O (that causes oxidation).

Ex.30 Why concentrated H_2SO_4 can not be used for drying H_2 ?

Ans. As hydrogen catches fire due to heat liberated when water is absorbed by acid.

Ex.31 Describe the changes which occur on heating sulphur .

Ans. S_8 (melt) $\underset{\angle 160^\circ C}{\overset{\text{at } 160^\circ C}{\rightleftharpoons}}$ S_8 ring break and diradical so formed polymerises to forms long chain polymer and viscocity starts to increase $\xrightarrow{\text{At } 200^\circ C}$ Viscosity further ↑ $\xrightarrow[\text{boiling point}]{\text{At } 444^\circ C}$ viscosity ↓ shorter chains and rings are formed $\xrightarrow{\text{At } 600^\circ C}$ in vapour state exist as S_2 molecules (paramagnetic like O_2).

MISCELLANEOUS SOLVED EXAMPLES

1. Ammonia can not be prepared by :

(1) heating NH_4NO_3 or $(NH_4)_2 Cr_2O_7$

(2) heating of NH_4Cl or $(NH_4)_2CO_3$

(3) heating of $NaNO_3$ or $NaNO_2$ with zinc dust or aluminium and sodium hydroxide

(4) reaction of AIN or $CaCN_2$ with H_2O

Sol. Except (1) all gives ammonia because

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$; $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$ **Ans. (1)**

2. What happens when ?

(i) Ammonia reacts with $KMnO_4$ (neutral medium)

(ii) A mixture of NO and NO_2 is passed in Na_2CO_3 solution.

(iii) Aqueous solution of $NaNO_3$ is heated with zinc dust and caustic soda.

(iv) CaO in water reacts with white phosphorus.

Sol. (i) $2NH_3 + 2KMnO_4 \longrightarrow 2KOH + 2MnO_2 + N_2 + 2H_2O$

(ii) $Na_2CO_3 + NO + NO_2 \longrightarrow 2NaNO_2 + CO_2$.

(iii) $4Zn + 7NaOH + NaNO_3 \longrightarrow NH_3 + 4Na_2ZnO_2 + 2H_2O$

(iv) $3CaO + 8P + 9H_2O \longrightarrow 3Ca(H_2PO_2)_2 + 2PH_3$

3. Evaluate the following Assertion & the Reason there of

Assertion : HNO_3 is stronger acid than HNO_2.

Reason : In HNO_3 there are two nitrogen to oxygen bonds where as in HNO_2 there is only one

(1) Both (A) and (R) are correct and (R) is the correct explanation of (A).

(2) Both (A) and (R) are correct and (R) is not the correct explanation of (A).

(3) (A) is correct but (R) is incorrect.

(4) (A) is incorrect but (R) is correct.

Sol. **Assertion :** Conjugate base of HNO_3, the NO_3^- is more stable (charge dispersion on three oxygen atoms) than conjugate base of HNO_2 , the NO_2^- (charge dispersion on two oxygen atoms).

Reason : There are three nitrogen to oxygen bonds in HNO_3 and two in HNO_2.

4. Write balanced equation for the following :

Manufacture of phosphoric acid from phosphorus.

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

or

$P_4 + 5O_2 + \rightarrow P_4O_{10}$; $P_4O_{10} + 6H_2O\ (g) \rightarrow H_3PO_4$.

5. Complete and balance the following :

(i) $P_4O_{10} + PCl_5 \longrightarrow$ (ii) $CuSO_4 + NH_3 \longrightarrow$

Sol. (i) $P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3$ (ii) $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]\ SO_4$

6. Why does H_3PO_3 act as a reducing agent but H_3PO_4 does not ?

Sol. H_3PO_3 contains one P–H bond (i.e. reducing hydrogen) and hence acts as a reducing agent but H_3PO_4 does not contain a P–H bond.

7. (i) An organic iodide (A) on heating with a solution of KOH gives a gas (B) and the solution of compound (C).

(ii) The gas (B) on ignition in air gives a compound (D) and water.

(iii) Copper sulphate is finally reduced to the metal on passing (B) through its solution.

(iv) Precipitate of compound (E) is formed on reaction of (C) with copper sulphate solution. Identify (A) to (E) and give chemical equations for steps (i) to (iv).

Ans. (A) PH_4I ; (B) PH_3; (C) KI; (D) P_4O_{10}; (E) Cu_2I_2

Sol. (A) is PH_4I. The given changes are :

(i) $\underset{(A)}{PH_4I} + KOH \longrightarrow \underset{(C)}{KI} + \underset{(B)}{PH_3} + H_2O$

(ii) $\underset{(B)}{4PH_3} + 8O_2 \longrightarrow \underset{(D)}{P_4O_{10}} + 6H_2O$

(iii) $4Cu^{2+} + PH_3 + 4H_2O \longrightarrow H_3PO_4 + 4Cu\downarrow + 8H^+$

(iv) $2CuSO_4 + 4KI \longrightarrow \underset{(E)}{Cu_2I_2} + 2K_2SO_4 + I_2$

8. What happens when

(a) $K_2Cr_2O_7$ is strongly heated

(b) Silent electric discharge is passed through pure and dry O_2

(c) Reaction between formaldehyde and hydrogen peroxide is carried out in dark.
(d) Conc. H_2SO_4 is made to react with phosphorus pentaoxide

Sol. (a) $4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

(b) $3O_2 \xrightarrow[\text{electric discharge}]{\text{silent}} 2O_3$

(c) $2HCHO + H_2O_2 \longrightarrow 2HCOOH + H_2$

yellow coloured light is emitted

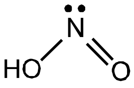
(d) $H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

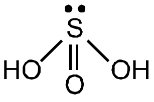
9. In the following reaction, $A + 2B + H_2O \longrightarrow C + 2D$

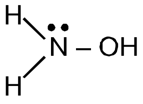
($A = HNO_2$, $B = H_2SO_3$, $C = NH_2OH$). Identify D.

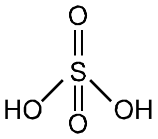
Draw the structures of A, B, C and D.

Sol. $\underset{(A)}{HNO_2} + \underset{(B)}{2H_2SO_3} + H_2O \longrightarrow \underset{(C)}{NH_2OH} + \underset{(D)}{2H_2SO_4}$

(A) 

(B) 

(C) 

(D) 

10. **Assertion :** Ozone is a powerful oxidising agent in comparison to O_2.

Reason : O_3 molecule is diamagnetic but O_3^- is paramagnetic.

(1) Both (A) and (R) are correct and (R) is the correct explanation of (A).
(2) Both (A) and (R) are correct and (R) is not the correct explanation of (A).
(3) (A) is correct but (R) is incorrect.
(4) (A) is incorrect but (R) is correct.

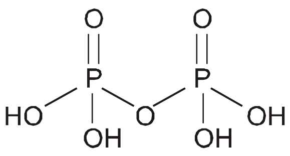
Sol. **(A) :** Higher SRP value of ozone than oxygen.

(R) : In ozone all electrons are paired. But O_3^- is an odd electron species. **Ans.** (2)

11. Match the oxy-acids of phosphorus listed in column-I with type of bond(s) listed in column-II.

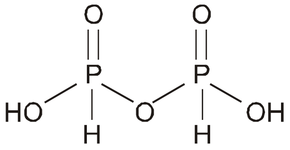
Column I **(Oxy acids of phosphoros)**	**Column II** **(Characteristic bonds)**
(1) $H_4P_2O_7$	(p) P—P bond (s)
(2) $H_4P_2O_5$	(q) P—O—P bond (s)
(3) $H_4P_2O_6$	(r) P—H bond (s)
(4) $(HPO_3)_n$ (cyclic)	(s) Three or four P—OH bonds

Ans. (1 - q, s ; 2 - q, r ; 3 - p, s ; 4 - q, s)

Sol. (1) $H_4P_2O_7$ 

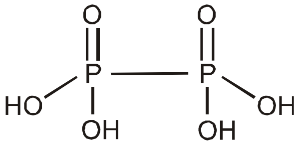
One P—O—P bond and four P—OH bonds

(2) $H_4P_2O_5$



Two P—H bond and one P—O—P bond

(3) $H_4P_2O_6$



Four P—OH bonds and one P—P bond

(4) $(HPO_3)_3$ (cyclic)