DAY TWENTY SIX

p-Block Elements

(Groups 15 to18)

Learning & Revision for the Day

- Group- 15 Elements : Nitrogen Family
- Group-16 Elements : Oxygen Family
- Group -17 Elements : Halogens
- Group- 18 Elements : Noble Gases

Group-15 Elements : Nitrogen Family

Group 15th elements are nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids and bismuth is a typical metal.

Occurrence

Occurrence of the Group-15 elements are given in the following table:

Occurrence/ore and Abundance of Group VA Elements

Element	Abundance by weight (ppm)	Occurrence/Ore
N	19 (33rd most abundant)	Chile saltpetre -$NaNO_3$, saltpetre -KNO_3
P	1120 (11th most abundant)	Phosphorite $Ca_3(PO_4)_2$, Fluorapatite $Ca_5(PO_4)_3F$ or $3[Ca_3(PO_4)_2]\cdot CaF_2$, Hydroxyapatite -$Ca_5(PO_4)_3OH$ or $3Ca_3(PO_4)_2\cdot Ca(OH)_2$, chlorapatite $Ca_5(PO_4)_3Cl$ or $3[Ca_3(PO_4)_2]\cdot CaCl_2$.
As	1.8 (52nd most abundant)	Arsenopyrite -FeAsS, Realgar α - As_4S_4, Orpiment - As_2S_3, Arsenides such as NiAs, $NiAs_2$, $FeAs_2$
Sb	0.20 (64th most abundant)	Stibnite -Sb_2S_3
Bi	0.008 (71st most abundant)	Bismuthinite - , Bismite - Bi_2O_3

Trends in Physical and Chemical Properties

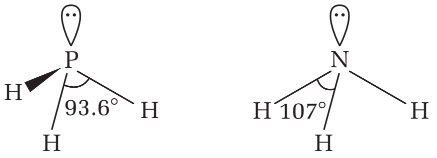
Some important physical and chemical properties of group-15 elements are as follows ;

Electronic Configuration

- The general electronic configuration of various elements of group 15 is ns^2np^3.
- Atomic and ionic radius increases down the group, however arsenic shows exceptionally low value of atomic volume.
- Ionisation energy of these elements is much higher due to increased nuclear charge and stable exactly half-filled electronic configuration.
- On moving down the group electronegativity decreases due to gradual increase in the atomic radius of the elements.
- On moving down the group, metallic character increases.
- All these elements show allotropy (except bismuth).

Oxidation States

- Elements of group VA exhibit **maximum oxidation state** of + 5 by losing all the five electrons in their outer most shell. + 3 oxidation state is shown when only *p*-orbital electrons are used in bonding or (–) 3 by using 3 electrons with less electronegative elements.
- On moving down, + 3 oxidation state becomes more stable due to inert pair effect. Nitrogen shows +5 to –3 oxidation states.
- General formula of hydrides of these elements is MH_3, e.g. NH_3, PH_3, AsH_3, SbH_3 and BiH_3.



All these hydrides are covalent in nature and have pyramidal structure (sp^3-hybridised).

Properties of Hydrides

Property	Down the group	Reason
Bond angle of MH_3	Decreases	As the size of central atom increases, electronegativity decreases, thus repulsion of bond pair and lone pair of central atom decreases.
Basic strength of MH_3	Decreases	As the size of central atom increases, electron density decreases.
Thermal stability of MH_3	Decreases	As the size of the central atom increases, its tendency to form stable *M*—H bond decreases.
Reducing character	Increases	As the stability of hydrides decreases the reducing character increases.
Melting and boiling point	Increases (except in N)	NH_3 has higher melting point and boiling point than PH_3 due to hydrogen bonding. As the molecular size increases van der Waals' forces increases.

- Elements of group VA form two types of **halides**, trihalides and pentahalides.
- Trihalides are mainly basic (Lewis bases) in nature and have lone pair of electrons (central atom is sp^3-hybridised) with pyramidal shape.
- Pentahalides are sp^3d-hybridised and trigonal bipyramidal in shape.

Properties of Halides

Property	Gradation	Reason
Stability of trihalides of nitrogen	$NF_3 > NCl_3 > NBr_3$	Large size difference between N and the halogens
Lewis base strength	$NF_3 < NCl_3 < NBr_3 < NI_3$	Decreasing electronegativity of halogens.
Bond angle among the halides of phosphorus	$PF_3 < PCl_3 < PBr_3 < PI_3$	Due to decreased bond pair-bond pair repulsion as these move away from P.

- All the elements of group VA form two types of **oxides**, i.e. M_2O_3 and M_2O_5 and are called trioxides and pentaoxides.

Properties of Oxides

Property	Gradation	Reason
Acidic strength of trioxides	$N_2O_3 > P_2O_3 > As_2O_3$	Electronegativity of central atom decreases
Acidic strength of pentaoxides	$N_2O_5 > P_2O_5 > As_2O_5 > Sb_2O_5 > Bi_2O_5$	Electronegativity of central atom decreases
Acidic strength of oxides of nitrogen	$N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$	Oxidation state of central atom increases
Stability of pentaoxides	$P_2O_5 > As_2O_5 > Sb_2O_5 > N_2O_5$	Stability of oxides of a higher oxidation state, i.e. M_2O_5 decreases with increasing atomic number due to inert pair effect

Dinitrogen (N_2)

Preparation

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

$$(NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

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

Properties

- Nitrogen does not react with alkali metals except Li but reacts with alkaline earth metals to give metal nitride.

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

- $N_2(g) + O_2(g) \xrightarrow{2000\text{ K}} 2\,NO(g)$
- $2B + N_2 \xrightarrow{\text{Heat}} 2BN$
- $CaC_2 + N_2 \xrightarrow{1273\text{ K}} CaCN_2 + C$

Uses

- Liquid N_2 is used as refrigerant.
- It is used in the manufacture of HNO_3, NH_3, $CaCN_2$ (calcium cyanamide) and other nitrogenous compounds.
- It is used for filling electric bulbs.

Some Important Compounds of Nitrogen

Preparation and properties of nitrogen compounds are as follows:

1. Ammonia

- It is covalent compound. Due to the presence of lone pair of electrons, N-atom in NH_3 is sp^3 hybridised. it acquires pyramidal shape.
- It is prepared by the following methods :

$$\underset{\text{Urea}}{NH_2CONH_2} + 2H_2O \longrightarrow (NH_4)_2CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

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

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2\,NH_3 + 2H_2O + Na_2SO_4$$

On large scale, ammonia is manufactured by **Haber's process**.

$$N_2(g) + 3H_2(g) \underset{723\text{ K; Catalyst}}{\overset{200\text{ atm}}{\rightleftharpoons}} 2NH_3\,;\Delta H_f^\circ = -46.1\text{ kJ/mol}$$

Iron oxide is used as catalyst with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.

- NH_3 is basic in nature, has tendency to form hydrogen bond, therefore soluble in water and form NH_4OH or $NH_3(aq)$.
- Due to basic nature, NH_3 is a good complexing agent and reducing agent. e.g.

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

$$ZnSO_4(aq) + 2\,NH_4OH(aq) \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2(s)} + (NH_4)_2SO_4$$

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

$$\underset{\text{Colourless}}{Ag^+(aq) + Cl^-(aq)} \longrightarrow \underset{\text{White ppt.}}{AgCl(s)}$$

$$\underset{\text{White ppt.}}{AgCl(s)} + 2NH_3(aq) \longrightarrow \underset{\text{Colourless}}{[Ag(NH_3)_2]Cl(aq)}$$

- NH_3 is used in refrigeration due to its large heat of evaporation and in manufacture of HNO_3, $NaHCO_3$, ammonium compounds and nitrogenous fertilizers.

2. Nitric Acid (HNO_3)

It was earlier known as **aqua fortis**. It is prepared by the following processes.

- Laboratory preparation of HNO_3 is as follows:

$$NaNO_3(s) + H_2SO_4(aq) \longrightarrow NaHSO_4(aq) + HNO_3(aq)$$

- Ostwald process is the commercial process for manufacturing HNO_3.

$$4NH_3(g) + 5\,O_2(g) \xrightarrow[1100\text{ K}]{\text{Pt gauge}} 4NO(g) + 6H_2O(l)\,;\Delta H = -\text{ve}$$

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

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

- Anhydrous HNO_3 is a colourless fuming having pungent smelling liquid. It acquires yellow colour due to its decomposition.

$$4\,HNO_3 \xrightarrow{\text{Sunlight}} 4\,NO_2 + 2H_2O + O_2$$

- It has corrosive action on skin and causes painful sores.
- It is very strong acid and form salts on reaction with basic oxides, carbonates, hydroxides etc.

$$Na_2CO_3 + 2\,HNO_3 \longrightarrow 2\,NaNO_3 + H_2O + CO_2$$

- It acts as a strong oxidising agent.
- Non-metals such as C, S, P and I_2 are oxidised to carbonic acid, sulphuric acid, orthophosphoric acid and iodic acid respectively.

e.g. $C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + H_2O$

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

- Metalloids such as Sb is oxidised to antimonic acid, As to arsenic acid and Sn to stannic acid.

$$Sb + 5HNO_3 \longrightarrow H_3SbO_4 + 5NO_2 + H_2O$$

$$As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$$

$$Sn + 4\,HNO_3 \longrightarrow H_2SnO_3 + 4\,NO_2 + H_2O$$

- Oxidation of compounds

$$6\,FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 2\,NO + 4\,H_2O$$

NO is absorbed by $FeSO_4$ and a dark brown ring of nitroso ferrous sulphate is formed (ring test for nitrates).

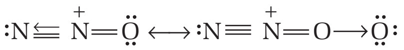
- Metals like iron, cobalt, nickel, chromium, aluminium become passive in conc. HNO_3 due to the formation of a thin protective film of oxide on the surface of the metal.

- HNO_3 is used in the manufacture of explosives such as TNT, picric acid, nitroglycerine, dynamite etc., fertilizers, such as NH_4NO_3, basic $Ca(NO_3)_2$ etc., artificial silk, dyes, drugs.

3. Oxides of Nitrogen

The structures of oxides of nitrogen are given below:

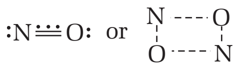
- **Nitrous oxide** (N_2O) or **Laughing gas**



$$:N\equiv\overset{+}{N}=\ddot{\underset{\cdot\cdot}{O}}\longleftrightarrow :N\equiv\overset{+}{N}=O\longrightarrow\ddot{\underset{\cdot\cdot}{O}}:$$

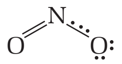
It is almost a neutral oxide.

- **Nitric oxide** (NO)



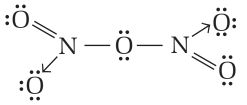
It is a neutral oxide.

- **Nitrogen dioxide** (NO_2)



It is an acidic oxide.

- **Anhydride of nitric acid** (N_2O_5)



It is highly acidic oxide.

Phosphorus

Preparation and properties of white phosphorus are as follows:

Preparation

1. **Retort Process**

$$\underset{\text{Phosphorite}}{Ca_3(PO_4)_2} + 3H_2SO_4 \longrightarrow \underset{\text{Orthophosphoric acid}}{2\,H_3PO_4} + 3CaSO_4$$

$$H_3PO_4 \longrightarrow \underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O$$

$$4HPO_3 + 10C \longrightarrow P_4 + 10CO + 2H_2O$$

2. **Electrothermal Process**

Phosphorus is obtained from direct reduction of mineral phosphorite by carbon in the presence of silica.

$$2\,Ca_3(PO_4)_2 + 6SiO_2 + 10C \xrightarrow{1400\text{-}1500°C} 6\,CaSiO_3 + P_4 + 10\,CO$$

Allotropic Forms

Phosphorus exists in three allotropic forms, i.e. white or yellow, red and black (α- and β-) phosphorus. These forms are inter convertible.

$$\text{Black phosphorus} \xleftarrow[\text{under pressure}]{470\text{ K}} \underset{\text{White phosphorus}}{P_4} \xrightarrow{560\text{ K, inert atm}} \text{Red phosphorus}$$

- **White phosphorus** is transluscent, soft, poisonous, waxy solid, shows chemiluminescence and chemically more reactive.

$$P_4 + 5\,O_2 \longrightarrow P_4O_{10} \text{ or } 2P_2O_5$$

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3}$$

$$6Mg + P_4 \longrightarrow \underset{\text{Magnesium phosphide}}{2Mg_3P_2}$$

It acts as strong reducing agent.

$$P_4 + 10H_2SO_4 \longrightarrow 4\,H_3PO_4 + 10SO_2 + 4\,H_2O$$

- **Red phosphorus** is the stable form of phosphorus. It is odourless, non-poisonous and less reactive.

$$2\,P + 5Cl_2 \xrightarrow{\text{Heat}} 2PCl_5$$

$$2\,P + 3\,S \xrightarrow{\text{Heat}} P_2S_3$$

$$P + 3\,Na \longrightarrow Na_3P$$

It is a polymer consists of chains of P_4 tetrahedral linked together.

- **Black phosphorus** is obtained from white phosphorus.

White P $\xrightarrow[\text{high pressure}]{473\text{ K}}$ black phosphorus. It may occur in orthorhombic, rhombohedral and cubic form.

Uses

- Red phosphorus is used in match industry.
- Radioactive phosphorus is used in treatment of leukaemia and other blood disorders.
- Yellow phosphorus and zinc phosphide are used as a rat poison.

Compounds of Phosphorus

(Preparation and Properties)

1. Phosphine (PH_3)

- It is prepared by following methods.

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

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

$$P_4 + 3\,NaOH + 3H_2O \longrightarrow PH_3 + 3\,NaH_2PO_2$$

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

- It is a colourless gas with rotten fish like smell and is highly poisonous. It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.
- It forms phosphides when passed through the solutions of $CuSO_4$, $AgNO_3$ or $HgCl_2$.

$$3\,CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$$

- Phosphine is weakly basic $PH_3 + HBr \longrightarrow PH_4^+\,Br^-$.

2. Phosphorus Halides (PCl_3 and PCl_5)

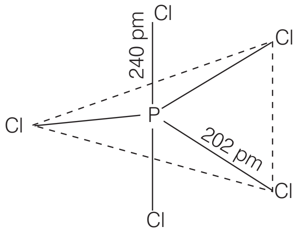
- Following methods the are used to prepare phosphorus halides.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$
$$P_4 + 10Cl_2 \longrightarrow 4PCl_5$$
$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$
$$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$$

- PCl_5 is a yellowish white powder and in moist air it gets hydrolysed to $POCl_3$ and finally gets converted to phosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

- PCl_5 in gaseous and liquid phases has sp^3d-hybridisation and its shape is trigonal bipyramidal.



The three equatorial P—Cl bonds are equivalent while the two axial bonds are longer than equatorial bonds.

- In solid state, PCl_5 exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which, the cation, $[PCl_4]^+$ is tetrahedral and the anion $[PCl_6]^-$ is octahedral.

3. Oxides of Phosphorus

Phosphorus trioxide and phosphorus pentoxide, of phosphorus exist in dimeric forms.

(i) **Phosphorus trioxide** (P_4O_6), is prepared from white phosphorus.

$$P_4 + 3O_2 \xrightarrow[\text{(limited supply of air)}]{\text{Burning}} P_4O_6$$

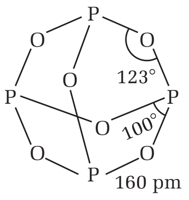
It is a poisonous waxy solid with garlic odour.

$$4P_4O_6 \xrightarrow{\text{Heat}} \underset{\text{Phosphorus tetraoxide}}{3P_4O_8} + 4P$$

$$P_4O_6 + 4Cl_2 \longrightarrow \underset{\text{Phosphorus oxychloride}}{2POCl_3} + \underset{\text{Metaphosphorus oxychloride}}{2PO_2Cl}$$

$$P_4O_6 + 6H_2O(\text{hot}) \longrightarrow 3H_3PO_4 + PH_3$$

Structure of P_4O_6 is as follows:



(ii) **Phosphorus pentoxide,** (P_4O_{10}) is obtained by burning of white phosphorus in free supply of air.

$$P_4 + 5O_2 \xrightarrow[\text{(free supply of air)}]{\text{Burning}} P_4O_{10}$$

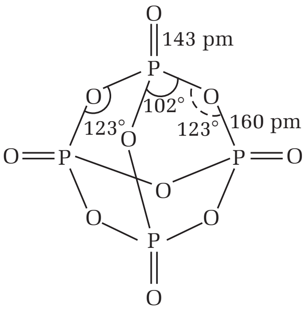
It is white crystalline, odourless solid which sublimes on heating.

$$P_4O_{10} \xrightarrow{2H_2O} \underset{\text{Metaphosphoric acid}}{4HPO_3} \xrightarrow{2H_2O}$$

$$\underset{\text{Pyrophosphoric acid}}{2H_4P_2O_7} \xrightarrow{2H_2O} \underset{\text{Orthophosphoric acid}}{4H_3PO_4}$$

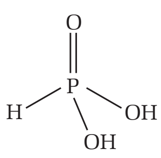
It is used as most effective dehydrating agent below 100°C.

Structure of P_4O_{10} is as follows :

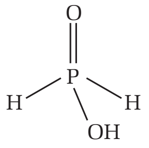


Oxoacids of Phosphorus

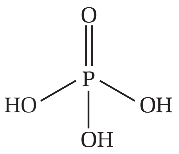
The structure of oxoacids of phosphorus are given below:



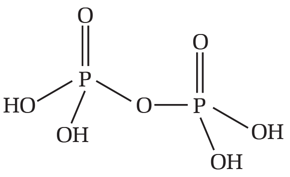
H_3PO_3
(Orthophosphorous acid)
sp^3, diprotic



H_3PO_2
(Hypophosphorous acid)
monoprotic, sp^3



H_3PO_4
(Orthophosphoric acid)
triprotic, sp^3



$H_4P_2O_7$
(Pyrophosphoric acid)
sp^3

Pyrophosphorus acid = $H_4P_2O_5$
Hypophosphoric acid = $H_4P_2O_6$

- H_3PO_3 on heating, disproportionates to give orthophosphoric acid and phosphine.

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

- The acids which contain P—H bond, have strong reducing properties, thus hypophosphorus acid is a good reducing agent as it contains two P—H bonds. e.g.

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

Group-16 Elements : Oxygen Family

16th group elements are oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po) known as **chalcogens** (due to ore forming nature).

Occurrence

Oxygen is the most abundant of all the elements on earth. Oxygen and sulphur are non-metals, selenium and tellurium are metalloids and polonium is radioactive metal. Sulphur occurs in combined state as PbS, ZnS, H_2S, $CuFeS_2$ etc. other elements like Se, Te and Po are present in traces.

Electronic Configuration

The general electronic configuration of group-16 members -ns^2, np^4.

Trends in Physical and Chemical Properties

Physical Properties

Physical properties of group-16 elements show following trends in their physical properties :

(i) **Ionisation Energies** On moving down the group from oxygen to polonium, the ionisation energy decreases because of increase in atomic size.

(ii) **Metallic Character** On moving down the group, the metallic character increases down the group from oxygen to polonium because of decrease in ionisation energy.

(iii) **Oxidation States** Group VIA elements show oxidation state of + 2, + 4 and + 6 due to the promotion of electrons to vacant *d*-orbitals. But down the group +4 oxidation state becomes more stable.

(iv) **Allotropy** Oxygen exists in two allotropic forms as O_2 and O_3 (ozone). Sulphur exists in a number of allotropic forms such as rhombic, monoclinic and plastic sulphur. Selenium has two common forms red (non-metallic) and white grey (metallic). Tellurium occurs in two allotropic forms, crystalline and amorphous. Polonium also exists in α- and β- forms (both metallic).

Chemical Properties

The main properties of group-16 elements are as follows :

- **Hydrides** All the elements of the oxygen family form stable hydrides of the type H_2M either by directly combining with hydrogen or by the action of acids on metal sulphides, selenides and tellurides.

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

H_2O is a liquid due to hydrogen bonding and others are colourless gases with unpleasant smell.

Compounds bond angle $H_2O > H_2S > H_2Se > H_2Te$
(all sp^3-hybridised) 104.5° 92.5° 91° 90°

- The decreasing bond dissociation enthalpy of the M—H bond is due to increase in the size of M which explains the increasing acidic character of hydrides down the group.
- **Halides** All the elements of the oxygen family form a number of halides.

Element	Fluorides	Chlorides	Bromides	Iodides
O	OF_2, O_2F_2	ClO_2, Cl_2O_7	—	—
S	S_2F_2, SF_4, SF_6	S_2Cl_2, SCl_2	S_2Br_3	—
Se	SeF_2, SeF_4, SeF_6	Se_2Cl_4, $SeCl_4$	$SeBr_2$, $SeBr_4$	—
Te	TeF_4, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
Po	—	$PoCl_2$, $PoCl_4$	$PoBr_2$, $PoBr_4$	PoI_4

- **Oxides** These form oxides of the type MO_2 and MO_3.

Oxide	S	Se	Te	Po
Monoxides	SO	—	TeO	PoO
Dioxides	SO_2	SeO_2	TeO_2	PoO_2
Trioxides	SO_3	SeO_3	TeO_3	PoO_3
Heptoxides	S_2O_7	—	—	—
Other oxides	S_2O, S_2O_3, SO_4	—	—	—

Some Important Compounds of Oxygen

Some important compounds of oxygen are as follows:

1. Dioxygen (O_2)

Dioxygen is a diatomic molecule of oxygen.

Preparation

- Laboratory method

$$2\,KClO_3 \xrightarrow[\Delta]{MnO_2} 2\,KCl + 3\,O_2$$

- It is manufactured from liquid air. Air is liquefied by making use of Joule Thomson effect. Liquid air is a mixture of liquid nitrogen and liquid oxygen.

  The difference in their boiling points is about 12.8°C, hence, they are easily separated by fractional evaporation.
- By electrolysis of water (acidified water)

$$H_2SO_4 \rightleftharpoons 2\,H^+ + SO_4^{2-}$$

$$\text{At cathode} \quad 2H^+ + 2e^- \longrightarrow H_2$$

$$\text{At anode} \quad 2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$$

Properties

- It' is a colourless, odourless, tasteless gas which is slightly soluble in water. Liquid oxygen exhibits paramagnetism.
- It is non-inflammable but a supporter of combustion.

- O=O, bond dissociation energy is high, therefore it reacts with metals or non-metals after external heating to start the reaction.

$$N_2 + O_2 \xrightarrow{3300\text{ K}} 2\,NO$$

$$4Na(s) + O_2(g) \xrightarrow{\text{Room temperature}} 2\,Na_2O(s)$$

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

Uses

- In oxyacetylene and oxyhydrogen flames.
- Liquid O_2 is used as a rocket fuel.
- For life support systems, e.g. in hospitals and in water diving for divers, for miners and mountaineers.
- As an oxidising and bleaching agent.

2. Ozone (O_3)

Ozone is a triatomic molecule of oxygen. It is formed in the upper layer of atmosphere by the action of UV rays from sun on oxygen. It prevents the UV rays from entering the earth's atmosphere. CFCs, common refrigerants deplete the ozone layer.

Preparation

It is prepared in ozoniser by subjecting dry and cold dioxygen to the action of silent electric discharge.

$$3O_2(g) \xrightleftharpoons{\text{Silent electric discharge}} 2\,O_3(g)$$

Properties

- It is pale-blue gas with pungent odour. It is diamagnetic and poisonous.
- Ozone is unstable;

$$2O_3 \xrightarrow{\text{Heat}} 3\,O_2$$

- It acts as a powerful oxidising agent. It liberates iodine from neutral KI solution and the liberated I_2 turns starch paper blue.

$$2\,KI + H_2O + O_3 \longrightarrow 2KOH + I_2 + O_2$$

$$I_2 + \text{Starch} \longrightarrow \text{Blue colour}$$

- Alkaline KI is oxidised to potassium iodate and periodate.

$$KI + 3O_3 \longrightarrow \underset{\substack{\text{Potassium}\\ \text{iodate}}}{KIO_3} + 3O_2$$

$$KI + 4O_3 \longrightarrow \underset{\substack{\text{Potassium}\\ \text{periodate}}}{KIO_4} + 4O_2$$

$$H_2S + O_3 \longrightarrow H_2O + S + O_2$$

- Mercury loses its meniscus in contact with ozone (tailing of mercury).

$$2\,Hg + O_3 \longrightarrow Hg_2O + O_2$$

Uses

- As a germicide and disinfectant for sterilising water.
- As a bleaching agent for oils, ivory wax and delicate fibre.
- For detecting the position of double bond in unsaturated compounds. In destroying odours coming from cold storage room, slaughter houses and kitchen of hotels.

Sulphur

Allotropic-forms

Allotropic forms of sulphur are as follows:

(i) **Rhombic Sulphur** (α-sulphur) It is common crystalline form of sulphur, yellow in colour. Melting point 114.5°C and specific gravity 2.06. Its crystals are prepared by evaporating sulphur solution in CS_2. It is insoluble in water but readily soluble in CS_2.

(ii) **Monoclinic Sulphur** (β -sulphur) It is stable above 95.6°C. Its crystals are amber-yellow in colour, melting point 119°C, specific gravity 1.98. It is insoluble in CS_2. It is prepared by melting rhombic sulphur in a dish followed by cooling till crust is formed.

$$\text{Rhombic sulphur} \xrightleftharpoons{95.6^\circ C} \text{Monoclinic sulphur.}$$

At 95.6°C both the forms are stable. This temperature is called transition temperature. S_8 rings in both the forms are puckered and has a crown shape.

(iii) **Plastic Sulphur** It is obtained by pouring boiling sulphur into cold water. It is amber-brown in colour, specific gravity 1.95 and insoluble in CS_2.

(iv) **Milk of Sulphur** It is obtained by boiling milk of lime with sulphur and decomposing the products formed with HCl. It is used in medicines.

(v) **Colloidal Sulphur** It is prepared by passing H_2S through a solution of an oxidising agent such as nitric acid etc.

$$2HNO_3 + H_2S \longrightarrow 2NO_2 + 2H_2O + S$$

colloidal sulphur changes into ordinary form on heating.

Compounds of Sulphur

(Preparation and Properties)

Sulphur Dioxide (SO_2)

Preparation

- It is mostly prepared by burning of sulphur in air or oxygen.

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

- Inlaboratory, it is prepared by treating a sulphite with dilute sulphuric acid.

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

- Industrially, it is produced as a by-product of the roasting of sulphide ores.

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

After drying, gas is liquefied under pressure and stored in steel cylinders.

Properties

(i) It is a colourless gas with pungemnt smell of burning sulphur.

(ii) It is highly soluble in water and it forms a solution of sulphurous acid when passed through water.

$$SO_2(g) + H_2(l) \rightleftharpoons \underset{\text{Sulphurous acid}}{H_2SO_3(aq)}$$

(iii) It reacts with sodium hydroxide solution to form sodium sulphite, which on reaction with more SO_2 form sodium hydrogen sulphite.

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

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

(In reaction with water and alkalies, the behaviour of SO_2 is very similar to CO_2)

(iv) SO_2 reacts with chlorine to produce sulphuryl chloride, SO_2, Cl_2 in the presence of charcoal (which acts as catalyst).

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

It is further oxidised to sulphur trioxide by oxygen in the presence of vanadium (V) oxide as catalyst.

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

(v) Moist sulphur dioxide behaves as a reducing agent.

It converts Fe^{3+} ions to Fe^{2+} ions.

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

Uses

(i) Used in refining petroleum and sugar.

(ii) As an antichlor, disinfectant and preservative.

(iii) In bleaching wool and silk.

(iv) Liquid SO_2 is used as a solvent.

(v) Preparation of industrial chemicals like H_2SO_4, $NaHSO_3$, $CaHSO_3$, etc.

Sulphuric Acid (H_2SO_4)

Sulphuric Acid (H_2SO_4) is also known as **King of acids**.

Preparation

- Sulphuric acid is one of the most important industrial chemical worldwide. It is manufactured by contact process which involves three steps:
- Burning of sulphur ores in air to generate SO_2.
- Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5).

$$2\,SO_2(g) + O_2(g) \xrightarrow[\text{2 bar, 720 K}]{V_2O_5} 2SO_3(g)$$

- Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$)

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

Properties

- Concentrated sulphuric acid is a strong dehydrating agent.

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

- Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids.

$$S + 2\,H_2SO_4\text{ (conc.)} \longrightarrow 3SO_2(g) + 2\,H_2O$$

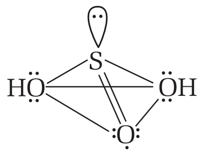
$$C + 2\,H_2SO_4\text{(conc.)} \longrightarrow CO_2 + 2\,SO_2 + 2\,H_2O$$

Uses

- In the manufacture of fertilisers.
- Petroleum refining.
- In the manufacture of pigments, paints and dyestuff.
- Detergent industry
- Metallurgical application.
- Storage batteries.
- As a laboratory reagent.

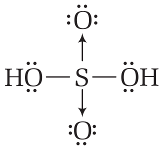
Structure of Oxoacids of Sulphur

(i) Sulphurous acid (H_2SO_3)



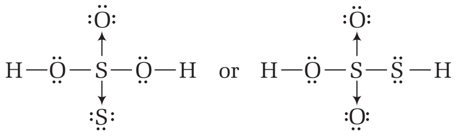
Reducing agent

(ii) Sulphuric acid (H_2SO_4)



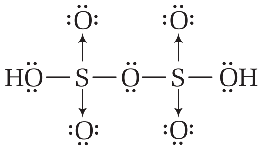
Strong dehydrating agent

(iii) Thiosulphuric acid ($H_2S_2O_3$)



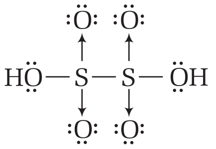
Reducing agent

(iv) Pyrosulphuric acid ($H_2S_2O_7$)



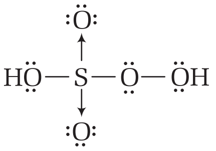
Strong oxidising agent

(v) Dithionic acid ($H_2S_2O_6$)



Oxidising agent

(vi) Peroxomonosulphuric acid (H_2SO_5)



(Caro's acid)

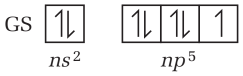
Strong oxidising agent

Group-17 Elements : Halogens

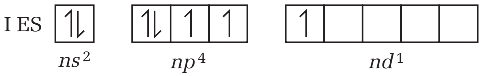
Group-17 elements are also called **Halogens**. Group-17 members are fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Astatine is a radioactive element. The halogens are highly reactive non-metallic elements. Fluorine is most electronegative atom and strong oxidising agent.

General Electronic Configuration

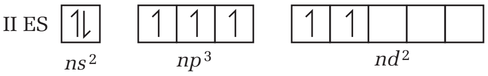
- General configuration and oxidation state of halogens:



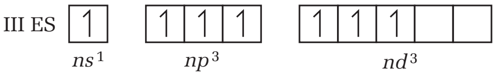
(1 unpaired electron accounts for –1 or +1 oxidation state)



(3 unpaired electrons account for +3 oxidation state)



(5 unpaired electrons account for +5 oxidation state)



(7 unpaired electrons account for +7 oxidation state)

Trends in Physical and Chemical Properties

Oxidation States

- Ground state and excited state in fluorine will be same due to the absence of d-orbitals and oxidation state of fluorine is always −1. All the halogens are highly reactive. Halogens are strong oxidising agent and their oxidising power decreases down the group.

$$\underset{\text{Oxidising power decreases}}{F_2 > O_2 > Cl_2 > Br_2 > I_2}$$

e.g. $F_2 + 2X^- \longrightarrow 2F^- + X_2$ (X = Cl, Br and I)

$$2F_2(g) + 2H_2O(l) \longrightarrow 4HF(aq) + O_2(g)$$

$$X_2(g) + H_2O(l) \longrightarrow HX(aq) + HOX(aq)$$

(where, X = Cl or Br)

The reaction of I_2 with water is non-spontaneous. However, I^- can be oxidised by oxygen in acidic medium.

$$4I^-(aq) + 4H^+(aq) + O_2(g) \longrightarrow 2I_2(s) + 2H_2O(l)$$

Except fluorine all other may show +1, +3, +5 and +7 oxidation states.

- Bond dissociation enthalpy of halogens :

$$Cl — F > Cl_2 > Br_2 > F_2 > I_2$$

- Fluorine shows anomalous behaviour because of its very small size and high electronegativity. F_2 has less bond enthalpy than Cl_2 and Br_2 and the absence of d-orbitals in valence shell.

Compounds of Halogens

Some important compounds of halogens are as follows

Chlorine (Cl_2)

This is the second member of group-17 elements.

Preparation

- $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ (Lab. method)
- $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacon's process)
- Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode (electrolytic process). It is also obtained as a byproduct in many chemical industries.

Properties

- It is a greenish-yellow gas with pungent and suffocating odour. It is soluble in water.
- $8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$
- $NH_3 + \underset{\text{Excess}}{3Cl_2} \longrightarrow \underset{\text{Explosive}}{NCl_3} + 3HCl$
- $\underset{\text{Cold and dil.}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
- $\underset{\text{Hot and conc.}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$
- With dry slaked lime it gives bleaching powder.

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

1. Hydrogen Chloride (HCl)

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

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

$$NaHSO_4 + NaCl \xrightarrow{823\ K} Na_2SO_4 + HCl$$

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

- It is a colourless and pungent smelling gas. Its aqueous solution is called hydrochloric acid.
- When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua-regia is formed which is used for dissolving noble metals. e.g. gold, platinum.

2. Interhalogen Compounds

- When two different halogens react with each other, interhalogen compounds are formed.
  These compounds are covalent and diamagnetic in nature. They are volatile solids or liquids except ClF which is a gas at 298 K. Interhalogen compounds are more reactive than halogens (except fluorine).
- The XY_3 type compounds have bent T-shape, XY_5 type compounds have square pyramidal shape and IF_7 has pentagonal bipyramidal structure.

3. Oxoacids of Halogens

Higher oxoacids of fluorine such as HFO_2, HFO_3 do not exist because fluorine is most electronegative and has the absence of *d*-orbitals. $HBrO_2$ and HIO_2 are less stable.

Decreasing order of acidic nature

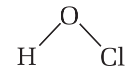
$$\underset{\text{(Hypofluorous acid)}}{HOF} > \underset{\text{(Hypochlorous acid)}}{HOCl} > \underset{\text{(Hypobromous acid)}}{HOBr} > \underset{\text{(Hypoiodous acid)}}{HOI}$$

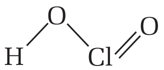
$$\longrightarrow \underset{\text{(Chloric acid)}}{HOClO_2} > \underset{\text{(Bromic acid)}}{HOBrO_2} > \underset{\text{(Iodic acid)}}{HOIO_2}$$

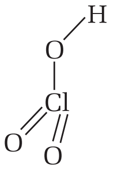
$$\longrightarrow HOClO_3 > HOClO_2 > HOClO > HOCl$$

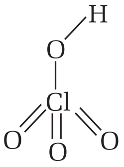
$$\longrightarrow HClO_4 > HBrO_4 > HIO_4$$

Structures of oxoacids of halogens are shown below:


Hypochlorous acid


Chlorous acid


Chloric acid


Perchloric acid

Pseudohalide ions are stronger ligands than halide ions, and these can function as ambidentate ligands as they are made up of two hetero atoms.

4. Oxides of Halogens

Fluorine forms two oxides, OF_2 and O_2F_2, but only OF_2 is thermally stable at 298 K. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used for removing plutonium as PuF_6 from spent nuclear fuel.

- Chlorine forms a number of oxides such as, Cl_2O, Cl_2O_3, Cl_2O_5, Cl_2O_7, ClO_2. ClO_2 is used as a bleaching agent for paper pulp, textiles and in water treatment.
- Br_2O, BrO_2, BrO_3 are the least stable bromine oxides and exist only at low temperatures. They are very powerful oxidising agents.
- The iodine oxides, i.e. I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

Group 18 Elements : Noble Gases

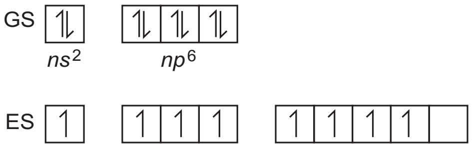
- Elements of group 18 are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) (radioactive).
- All of these are gases and chemically unreactive. Down the group their ionisation enthalpy decreases, therefore Xe reacts with oxygen and fluorine and forms different compounds. Xenon and radon are the rarest elements of the group. First prepared noble gas compound by Neil Bartlett in 1962 is $XePtF_6$.

Occurrence

On account of their inert nature, the noble gases always occur in the free state. Argon is the most abundant noble gas in the atmosphre while radon is not present in atmosphere. He, Ar and Ne are also found as constituents of dissolved gas of certain spring water.

Electronic Configuration

General electronic configuration of group-18 elements are (ns^2np^6) (except helium).



Trends in Physical and Chemical Properties

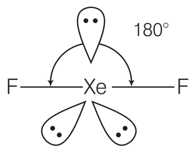
- Ionisation energy of group-18 elements is highest in each period.
- Atomic radii of group-18 elements is largest in each period (due to van der Waal's radii).
- Electron gain enthalpy of group-18 elements is (+)ve and therefore have no tendency to gain electrons.
- $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$
- $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
- $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
- Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.
- XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents.

- XeF_6 is extremely reactive. It cannot be stored in glass or quartz vessels as it readily reacts with SiO_2 present in glass.

Summary of Stable Compounds of Xe

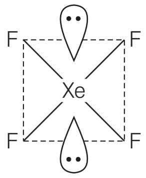
Compound	Oxidation state of Xe	Hybridisation	No. of lone pair(s) of electrons	Shape
XeF_2	+2	sp^3d	3	Linear
XeF_4	+4	sp^3d^2	2	Square planar
XeF_6	+6	sp^3d^3	1	Distorted octahedral
$XeOF_2$	+4	sp^3d	2	T-shaped
XeO_2F_2	+6	sp^3d	1	Distorted trigonal bipyramidal
$XeOF_4$	+6	sp^3d^2	1	Square pyramidal
XeO_3	+6	sp^3	1	Pyramidal

- **Molecular Structures of Xenon Compounds**



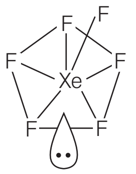
XeF_2

(Xe atom in 1st excited state)



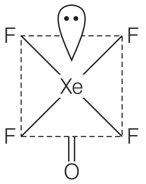
XeF_4

(Xe atom in 2nd excited state)



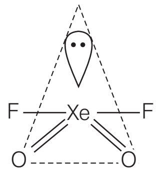
XeF_6

(Xe atom in 3rd excited state)



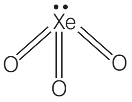
$XeOF_4$

(Xe in 3rd excited state)



XeO_2F_2

(Xe in 1st excited state)



XeO_3

(Xe in 1st excited state)

Uses

- He is used in filling balloons for meteorological observations. It is used in gas cooled reactor to produce powerful super-conducting magnets and as a diluent for oxygen in diving apparatus.
- Ne is used in discharge tubes and fluorescent bulbs.
- Ar is used in filling bulbs and to produce inert atmosphere in various metallurgical operations.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Among the members of VA group (N, P, As, Sb and Bi), which of the following properties shows an increase as we go down from nitrogen to bismuth?

(a) Electronegativity
(b) Acidic nature of the pentoxide
(c) Stability of – 3 oxidation state
(d) Reducing character of hydrides

2 Elements of group-15 form compounds in +5 oxidation state. However, bismuth forms only one well characterised compound in +5 oxidation state. The compound is

(a) Bi_2O_5 (b) BiF_5
(c) $BiCl_5$ (d) Bi_2S_5

3 Correct order of decreasing thermal stability is as

(a) $NH_3 > PH_3 > AsH_3 > SbH_3$
(b) $PH_3 > NH_3 > AsH_3 > SbH_3$
(c) $AsH_3 > PH_3 > NH_3 > SbH_3$
(d) $SbH_3 > AsH_3 > PH_3 > NH_3$

4 The following are some statements related to VA group hydrides,

I. Reducing property increases from NH_3 to BiH_3.
II. Tendency to donate lone pair decreases from NH_3 to BiH_3.
III. Thermal stability of hydrides decreases from NH_3 to BiH_3.
IV. Bond angle of hydrides decreases form NH_3 to BiH_3.

The correct statements are

(a) I and IV (b) I, III and IV
(c) I, II and IV (d) I, II, III and IV

5 Ammonia, on reaction with excess of chlorine, gives

(a) NCl_3 and HCl (b) N_4 and NH_4Cl
(c) NCl_3 and NH_4Cl (d) N_2 and HCl

6 Which of the following does not give oxygen on heating?
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(a) $Zn(ClO_3)_2$ (b) $K_2Cr_2O_7$

(c) $(NH_4)_2Cr_2O_7$ (d) $KClO_3$

7 Which of the following is not known?

(a) NI_3 (b) NCl_3
(c) NCl_5 (d) $SbCl_3$

8 Which of the following is the most explosive?

(a) NCl_3 (b) PCl_3
(c) $AsCl_3$ (d) All of these

9 Match the reactions of metals with dilute HNO_3 (in Column I) with the compounds obtained (in Column II).

	Column I		Column II
A.	Mg + dil. HNO_3	1.	NO
B.	Zn + dil. HNO_3	2.	H_2
C.	Sn + dil. HNO_3	3.	N_2O
D.	Pb + dil. HNO_3	4.	NH_4NO_3

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	2	1	4	3
(c)	2	3	4	1	(d)	3	4	2	1

10 The correct order of N - compounds in its decreasing order of oxidation states is **➞ NEET 2018**

(a) HNO_3, NH_4Cl, NO, N_2 (b) HNO_3, NO, NH_4Cl, N_2
(c) HNO_3, NO, N_2, NH_4Cl (d) HNO_4Cl, N_2, NO, HNO_3

11 On heating compound (*A*) gives a gas (*B*) which is a constituent of air. This gas when treated with 3 moles of hydrogen (H_2) in the presence of a catalyst gives another gas (*C*) which is basic in nature. Gas (*C*) on further oxidation in moist condition gives a compound (*D*) which is a part of acid rain. Identify compound (*D*).

(a) HNO_2 (b) HNO_3 (c) H_2SO_4 (d) HCl

12 Maximum bond angle at nitrogen is present in which of the following? **➞ CBSE-AIPMT 2015**

(a) NO_2 (b) NO_2^- (c) NO_2^+ (d) NO_3^-

13 On heating lead (II) nitrate gives a brown gas *A*. The gas *A* on cooling changes to colourless solid *B*. Solid *B* on heating with NO changes to a blue solid *C*. Identify *C*.

(a) NO_2 (b) N_2O_4 (c) N_2O_5 (d) N_2O_3

14 Which is the most thermodynamically stable allotropic form of phosphorus?

(a) Red (b) Yellow
(c) White (d) Black

15 The substance used in Holme's signals of the ship is a mixture of

(a) $CaC_2 + Ca_3P_2$ (b) $Ca_3(PO_4)_2 + Pb_3O_4$
(c) $H_3PO_4 + CaCl_2$ (d) $NH_3 + HOCl$

16 In solid state, PCl_5 is a

(a) covalent solid
(b) octahedral structure
(c) ionic solid with $[PCl_6]^+$ octahedral and $[PCl_4]^+$ tetrahedral
(d) ionic solid with $[PCl_4]^+$ tetrahedral and $[PCl_6]^-$ octahedral

17 Consider the sequence of oxides : Na_2O, SiO_2, P_4O_{10}. Which factor decreases from Na_2O to SiO_2 and also from SiO_2 to P_4O_{10}?

(a) Covalent character
(b) Melting point
(c) pH when mixed with water
(d) Solubility in aqueous alkali

18 Sodium pyrophosphate is represented by which of the following formula?

(a) $Na_2P_2O_4$ (b) $Na_4P_2O_5$ (c) $Na_4P_2O_7$ (d) $Na_2P_2O_5$

19 Strong reducing behaviour of H_3PO_2 is due to **➞ CBSE-AIPMT 2015**

(a) presence of one —OH group and two P—H bonds
(b) high electron gain enthalpy of phosphorus
(c) high oxidation state of phosphorus
(d) presence of two —OH groups and one P—H bond

20 Which of the following compound is tribasic acid?

(a) H_3PO_2 (b) H_3PO_3 (c) H_3PO_4 (d) $H_4P_2O_7$

21 Which is the correct statement for the given acids? **➞ NEET 2016, Phase I**

(a) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid
(b) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid
(c) Both are triprotic acids
(d) Both are diprotic acids

22 Which of the following statements is not valid for oxoacids of phosphorus? **➞ CBSE-AIPMT 2012**

(a) Orthophosphoric acid is used in the manufacture of triple superphosphate
(b) Hypophosphorus acid is a diprotic acid
(c) All oxoacids contain tetrahedral four coordinated phosphorus
(d) All oxoacids contain at least one P ═ O unit and one P—OH group

23 The formation of the oxide ion $O^{2-}(g)$, from oxygen atom requires first an exothermic and then an endothermic step as shown below, **➞ CBSE-AIPMT 2015**

$$O(g) + e^- \longrightarrow O^-(g);\ \Delta_f H^\circ = -141\ \text{kJmol}^{-1}$$

$$O^-(g) + e^- \longrightarrow O^{2-}(g);\ \Delta_f H^\circ = +780\ \text{kJ mol}^{-1}$$

Thus, process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that

(a) electron repulsion outweighs the stability gained by achieving noble gas configuration
(b) O^- ion has comparatively smaller size than oxygen atom
(c) Oxygen is more electronegative

(d) addition of electron in oxygen result in large size of the ion

24 Which of the following salt would give SO_2 with hot and dil. H_2SO_4 and also decolourises Br_2 water?

(a) Na_2SO_3 (b) $NaHSO_4$ (c) Na_2SO_4 (d) Na_2S

25 Sulphur trioxide can be obtained by which of the following reaction? **➞ CBSE-AIPMT 2012**

(a) $CaSO_4 + C \xrightarrow{\Delta}$ (b) $Fe_2(SO_4)_3 \xrightarrow{\Delta}$

(c) $S + H_2SO_4 \xrightarrow{\Delta}$ (d) $H_2SO_4 + PCl_5 \xrightarrow{\Delta}$

26 Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reaction does not show oxidising behaviour? **➞ NEET 2016, Phase II**

(a) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(b) $3S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

(c) $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

(d) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

27 Which of the following are peroxoacids of sulphur?

(a) H_2SO_5 and $H_2S_2O_8$ (b) H_2SO_5 and $H_2S_2O_7$

(c) $H_2S_2O_7$ and $H_2S_2O_8$ (d) $H_2S_2O_6$ and $H_2S_2O_7$

28 Acidity of diprotic acids in aqueous solutions increases in the order **➞ CBSE-AIPMT 2014**

(a) $H_2S < H_2Se < H_2Te$ (b) $H_2Se < H_2S < H_2Te$

(c) $H_2Te < H_2S < H_2Se$ (d) $H_2Se < H_2Te < H_2S$

29 In which pair of ions both the species contain $S—S$ bond? **➞ NEET 2017**

(a) $S_2O_7^{2-}$, $S_2O_3^{2-}$ (b) $S_4O_6^{2-}$, $S_2O_3^{2-}$

(c) $S_2O_7^{2-}$, $S_2O_8^{2-}$ (d) $S_4O_6^{2-}$, $S_2O_7^{2-}$

30 The correct order of acidic strength is

(a) $CO_2 > N_2O_5 > SO_3$ (b) $Cl_2O_7 > SO_2 > P_4O_{10}$

(c) $Na_2O > MgO > Al_2O_3$ (d) $K_2 > CaO > MgO$

31 Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules? **➞ NEET 2016, Phase I**

(a) $Cl_2 > Br_2 > F_2 > I_2$ (b) $Br_2 > I_2 > F_2 > Cl_2$

(c) $F_2 > Cl_2 > Br_2 > I_2$ (d) $I_2 > Br_2 > Cl_2 > F_2$

32 Which of the following statements is not true for halogens? **➞ NEET 2018**

(a) All but fluorine show positive oxidation states

(b) All are oxidising agents

(c) All form monobasic oxyacids

(d) Chlorine has the highest electron-gain enthalpy

33 Among the following which is the strongest oxidising agent?

(a) F_2 (b) Br_2 (c) I_2 (d) Cl_2

34 Bromine water reacts with SO_2 to form

(a) HBr and S (b) H_2O and HBr

(c) S and H_2O (d) H_2SO_4 and HBr

35 What is the oxidising agent in chlorine water?

(a) HCl (b) $HClO_2$

(c) HOCl (d) None of these

36 When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from **➞ CBSE-AIPMT 2012**

(a) zero to +1 and zero to –5

(b) zero to –1 and zero to +5

(c) zero to –1 and zero to +3

(d) zero to +1 and zero to –3

37 Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.

Ion:	ClO_4^-	IO_4^-	BrO_4^-
Reduction Potential E°/V	$E^\circ = 1.19$ V	$E^\circ = 1.65$ V	$E^\circ = 1.74$ V

(a) $ClO_4^- > IO_4^- > BrO_4^-$ (b) $IO_4^- > BrO_4^- > ClO_4^-$

(c) $BrO_4^- > IO_4^- > ClO_4^-$ (d) $BrO_4^- > ClO_4^- > IO_4^-$

38 Which one of the following oxides is expected to exhibit paramagnetic behaviour?

(a) CO_2 (b) SO_2 (c) ClO_2 (d) SiO_2

39 Which of the following statements given below is incorrect? **➞ CBSE-AIPMT 2015**

(a) Cl_2O_7 is an anhydride of perchloric acid

(b) O_3 molecule is bent

(c) ONF is isoelectronic with NO_2

(d) OF_2 is an oxide of fluorine

40 In the manufacture of bromine from sea water, the mother liquor containing bromides is treated with

(a) I_2 (b) Cl_2 (c) CO_2 (d) SO_2

41 AlF_3 is soluble in HF only in presence of KF. It is due to the formation of **➞ NEET 2016, Phase II**

(a) $K_3[AlF_3H_3]$ (b) $K_3[AlF_6]$ (c) AlH_3 (d) $K[AlF_3H]$

42 Which of the following statement is not true?

(a) HF is stronger acid than HCl

(b) Among halide ions, iodide is the most powerful reducing agent

(c) Fluorine is the only halogen that does not show a variable oxidation state

(d) HOCl is a stronger acid than HOBr

43 Which of the following attacks glass?

(a) HCl (b) HF

(c) HI (d) HBr

44 The type of hybrid orbitals used by iodine atom in hypoiodous acid molecule are

(a) sp^3 (b) sp^2

(c) sp (d) sp^3d

45 Which one of the following is present as an active powder for bleaching action? **➞ CBSE-AIPMT 2011**

(a) $Ca(OCl)_2$ (b) CaO_2Cl

(c) $CaCl_2$ (d) $CaOCl_2$

46 Which one of the following is a pseudo halide?

(a) I_3^- (b) IF^-
(c) $I C$ (d) CN^-

47 Match the interhalogen compounds of Column I with the geometry in Column II and assign the correct code.

→ NEET 2017

Column I	Column II
A. XX'	(i) T- shape
B. XX'_3	(ii) Pentagonal bipyramidal
C. XX'_5	(iii) Linear
D. XX'_7	(iv) Square-pyramidal
	(v) Tetrahedral

Code

	A	B	C	D		A	B	C	D
(a)	(iii)	(iv)	(i)	(ii)	(b)	(iii)	(i)	(iv)	(ii)
(c)	(v)	(iv)	(iii)	(ii)	(d)	(iv)	(iii)	(ii)	(i)

48 Which is the strongest acid in the following? **→ NEET 2013**

(a) $HClO_3$ (b) $HClO_4$ (c) H_2SO_3 (d) H_2SO_4

49 Which of the following dissolves in water but does not give any oxyacid solution?

(a) SO_2 (b) OF_2 (c) SCl_4 (d) SO_3

50 Which of the following is not a peroxy acid?

(a) Perphosphoric acid (b) Pernitric acid
(c) Perdisulphuric acid (d) Perchloric acid

51 Among the following, the correct order of acidity is

→ NEET 2016, Phase I

(a) $HClO < HClO_2 < HClO_3 < HClO_4$
(b) $HClO_2 < HClO < HClO_3 < HClO_4$
(c) $HClO_4 < HClO_2 < HClO < HClO_3$
(d) $HClO_3 < HClO_4 < HClO_2 < HClO$

52 The variation of the boiling point of the hydrogen halides is in the order HF > HI > HBr > HCl. What explains the higher boiling point of hydrogen fluoride?

→ CBSE-AIPMT 2015

(a) The electronegativity of fluorine is much higher than for other elements in the group
(b) There is strong hydrogen bonding between HF molecules
(c) The bond energy of HF molecules is greater than in other hydrogen halides
(d) The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule

53 Which of the following pairs of compounds is isoelectronic and isostructural? **→ NEET 2017**

(a) $BeCl_2, XeF_2$ (b) TeI_2, XeF_2
(c) IBr_2^-, XeF_2 (d) IF_3, XeF_2

54 The correct geometry and hybridisation for XeF_4 are

→ NEET 2016, Phase II

(a) octahedral, sp^3d^2 (b) trigonal bipyramidal, sp^3d
(c) planar triangle, sp^3d^3 (d) square planar, sp^3d^2

55 XeF_2 is isostructural with **→ NEET 2013**

(a) TeF_2 (b) ICl_2^-
(c) $SbCl_3$ (d) $BaCl_2$

56 Match the compounds given in column I with the hybridisation and shape given in column II and mark the correct option. **→ NEET 2016, Phase I**

Column I	Column II
A. XeF_6	1. Distorted octahedral
B. XeO_3	2. Square planar
C. $XeOF_4$	3. Pyramidal
D. XeF_4	4. Square pyramidal

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	4	3	(b)	4	3	1	2
(c)	4	1	2	3	(d)	1	3	4	2

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Which forms $p\pi-p\pi$ multiple bonds with itself and with C and O?

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

2 Maximum number of covalent bonds formed by N and P respectively are

(a) 3, 5 (b) 3, 6 (c) 4, 5 (d) 4, 6

3 Which of the following is/are paramagnetic?
NO_2, NO, N_2O_4, N_2O_2, N_2O_5

(a) Only NO_2 (b) NO_2, NO
(c) NO, NO_2, N_2O_5 (d) All are paramagnetic

4 In P_4 (tetrahedral)

(a) each P is joined to four P
(b) each P is joined to three P
(c) each P is joined to two P
(d) P_4 does not exist

5 Which is/are correct statements about P_4O_6 and P_4O_{10}?

(a) Both form oxyacids H_3PO_3 and H_3PO_4 respectively
(b) In P_4O_6 each P is joined to three O and in P_4O_{10} each P is joined to four O atoms
(c) Both (a) and (b)
(d) None of the above

6 Phosgene can be obtained when
(a) white phosphorus reacts with alkali
(b) calcium phosphide reacts with water
(c) chloroform reacts with air
(d) bone comes in contact with water

7 Which are acid salts?
(a) NaH_2PO_2, Na_2HPO_3 (b) Na_2HPO_3, Na_2HPO_4
(c) $NaHCO_3, Na_2HPO_4$ (d) All of these

8 Which of the following bonds has the least energy?
(a) Se—Se (b) Te—Te (c) S—S (d) O—O

9 Estimation of ozone can be made quantitatively by
(a) decomposition into O_2 and absorption of O_2 into pyrogallol
(b) volumetric method using KI and titration of the liberated iodine using hypo solution
(c) oxidative ozonolysis method
(d) all methods given above

10 Which has maximum pK_a value?
(a) H_2O (b) H_2S
(c) H_2Se (d) H_2Te

11 In the presence of H_2O, SO_2 acts as
(a) an oxidising agent
(b) a reducing agent
(c) a hydrolysing agent
(d) a redox reagent

12 SO_2 behaves as a reducing agent when
(a) passed over hot CuO
(b) mixed with moist H_2S
(c) passed through acidified $KMnO_4$ solution
(d) passed through $FeSO_4$ solution

13 When an article is bleached by SO_2 it loses its colour. The colour can be restored by
(a) exposure to air (b) heating
(c) dilution (d) None of these

14 Oxalic acid on heating with conc. H_2SO_4 produce
(a) H_2O and CO_2 (b) CO, CO_2 and H_2O
(c) CO_2 and H_2S (d) CO and CO_2

15 The compound which has no reaction with $KMnO_4$ is
(a) perdisulphuric acid
(b) sulphurous acid
(c) hydrogen sulphide
(d) hydrogen peroxide

16 Which of the underlined atoms in oxyacids have *sp*^{3} hybridised atoms?
(a) $H\underline{Cl}O_4, H_2\underline{S}O_4, H\underline{N}O_2$ (b) $H_2\underline{S}O_4, H_3\underline{P}O_4, H\underline{N}O_3$
(c) $H\underline{Cl}O_4, H_2\underline{S}O_4, H_2\underline{S}O_5$ (d) $H\underline{Cl}O_4, H\underline{N}O_3, H\underline{Cl}O_3$

17 The mixture of concentrated HCl and HNO_3 made in 3 : 1 ratio contains
(a) ClO_2 (b) NOCl (c) NCl_3 (d) N_2O_4

18 Which reaction is not feasible?
(a) $2KI + Br_2 \longrightarrow 2KBr + I_2$
(b) $2KBr + I_2 \longrightarrow 2KI + Br_2$
(c) $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$
(d) $2H_2O + 2F_2 \longrightarrow 4HF + O_2$

19 Oxidation state of Xenon in XeO_2F_2
(a) + 2 (b) − 2 (c) 0 (d) + 6

ANSWERS

SESSION 1	**1** (d)	**2** (b)	**3** (a)	**4** (d)	**5** (a)	**6** (c)	**7** (c)	**8** (a)	**9** (c)	**10** (c)
	11 (b)	**12** (c)	**13** (d)	**14** (d)	**15** (a)	**16** (d)	**17** (c)	**18** (c)	**19** (a)	**20** (c)
	21 (a)	**22** (b)	**23** (a)	**24** (a)	**25** (b)	**26** (d)	**27** (a)	**28** (a)	**29** (b)	**30** (b)
	31 (a)	**32** (a)	**33** (a)	**34** (d)	**35** (c)	**36** (b)	**37** (c)	**38** (c)	**39** (d)	**40** (b)
	41 (b)	**42** (a)	**43** (b)	**44** (a)	**45** (a)	**46** (d)	**47** (b)	**48** (b)	**49** (b)	**50** (d)
	51 (a)	**52** (b)	**53** (c)	**54** (a)	**55** (b)	**56** (d)				
SESSION 2	**1** (d)	**2** (a)	**3** (b)	**4** (b)	**5** (c)	**6** (c)	**7** (c)	**8** (b)	**9** (b)	**10** (a)
	11 (b)	**12** (c)	**13** (a)	**14** (b)	**15** (a)	**16** (c)	**17** (b)	**18** (b)	**19** (d)	

Hints and Explanations

SESSION 1

1 (a) Electronegativity decreases down the grop due to increase in size of the elements.
(b) Acidic nature of pentaoxides decreases down the group due to inert pair effect.
(c) As elements down the group becomes less electronegative so their stability in-3 oxidation state decreases.
(d) Reducing character of hydrides increases down the group because bond dissociation energy decreases down the group.

2 Stability of $+5$ oxidation state decreases and $+3$ oxidation state increases from top to bottom due to inert pair effect. Meanwhile compound having $+5$ oxidation state of Bi is BiF_5. It is due to smaller size and high electronegativity of fluorine.

3 The thermal stability of the hydrides of nitrogen family or group 15 elements decreases on moving downwards in the group. Therefore, NH_3 is the most stable and BiH_3 is the least stable.

The stability of the hydrides of group 15 elements decreases in the order

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

4 (I) The reducing property of the hydrides of VA group increase from NH_3 to BiH_3

$$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$$

(II) The tendency to donate lone pair or basic strength decrease from NH_3 to BiH_3

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

(III) Thermal stability of VA group hydrides decreases from NH_3 to BiH_3

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

(IV) Bond angle of VA group hydrides decreases from NH_3 to BiH_3

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

5 $$NH_3 + \underset{\text{Excess}}{2Cl_2} \longrightarrow \underset{\text{Explosive}}{NCl_3} + 3HCl$$

6 $$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

$$Zn(ClO_3)_2 \xrightarrow{\Delta} ZnCl_2 + 3O_2$$

$$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$$

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

7 NCl_5 is not known because of the absence of *d*-orbitals in nitrogen.

8 NCl_3 is highly reactive and unstable. Hence, it is explosive.

9 (A) $$Mg + 2HNO_3(\text{dil.}) \longrightarrow \underset{\text{Magnesium nitrate}}{Mg(NO_3)_2} + H_2$$

(B) $$4Zn + 10HNO_3(\text{dil.}) \longrightarrow \underset{\text{Zinc nitrate}}{4Zn(NO_3)_2} + \underset{\text{Nitrous oxide}}{N_2O} + 5H_2O$$

(C) $$4Sn + 10HNO_3(\text{dil.}) \longrightarrow \underset{\text{Stanous nitrate}}{4Sn(NO_3)_2} + \underset{\text{Ammonium nitrate}}{NH_4NO_3} + 3H_2O$$

(D) $$3Pb + 8HNO_3\ (\text{dil.}) \longrightarrow \underset{\text{Lead nitrate}}{3Pb(NO_3)_2} + 2NO + 4H_2O$$

10 Let the oxidation state of nitrogen in each of the given N compounds be *x*.

Oxidation no. of oxygen $= -2$,

Oxidation no. of Cl $= -1$

Oxidation no. of H $= +1$.

(i) $HNO_3 : +1 + x + 3(-2) = 0$

$x = +5$

$\therefore$ Oxidation state of N in HNO_3 is $+5$.

(ii) $NO : x + 1(-2) = 0$

$x = +2$

$\therefore$ Oxidation state of N in NO is $+2$

(iii) $NH_4Cl : x + 4(+1) + 1(-1) = 0$

$x = -3$

$\therefore$ Oxidation state on N in NH_4Cl is -3.

(iv) N_2: $x = 0$ [$\because N_2$ is present in element state]

$\therefore$ Oxidation state of N in N_2 is 0.

Thus, the correct decreasing order of oxidation states of given N compounds will be

$$H\overset{+5}{N}O_3 > \overset{+2}{N}O > \overset{0}{N_2} > \overset{-3}{N}H_4Cl$$

Note: The order is correct, as (-3) is a lower number than zero and $(+)$ ve values.

11 The main constituents of air are nitrogen (78%) and oxygen (21%). Only N_2 reacts with three moles of H_2 in the presence of a catalyst to give NH_3 (ammonia) which is a gas having basic nature. On oxidation NH_3 gives NO_2 which is a part of acid rain. So the compounds *A* to *D* are as:

$A = NH_4NO_2$; $B = N_2$; $C = NH_3$;
$D = HNO_3$

12

Species	Hybridisation	Bond angle
NO_2	*sp*	less than 120°
NO_2^-	sp^2	115.4°
NO_2^+	*sp* (linear)	180°
NO_3^-	sp^2	120°

So, NO_2^+ has maximum bond angle.

13 $$\underset{\text{Lead nitrate}}{2Pb(NO_3)_2} \xrightarrow[673\ \text{K}]{\Delta} 2PbO + \underset{\text{Brown}[A]}{4NO_2(g)} + O_2$$

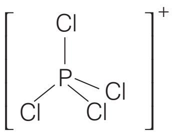
$$2NO_2(g) \xrightarrow[\text{heating}]{\text{Cooling}} \underset{\text{Colourless }[B]}{N_2O_4(g)}$$

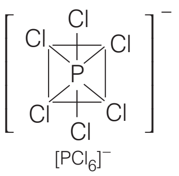
$$2NO + N_2O_4 \xrightarrow{250\ \text{K}} \underset{\text{Blue }[C]}{2N_2O_3(s)}$$

14 The ignition temperature of black phosphorus is highest among all allotropes because it is thermodynamically more stable than other allotropes of phosphorus.

15 In Holme's signal of the ship, mixture of CaC_2 and Ca_3P_2 is used.

16 Solid PCl_5 shows ionic lattices. It has tetrahedral cations $[PCl_4]^+$ and octahedral anions $[PCl_6]^-$.

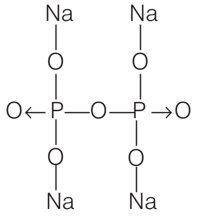

$[PCl_4]^+$


$[PCl_6]^-$

17 Na_2O is a basic oxide and reacts with water to give NaOH, so that its pH is higher than both SiO_2 and P_4O_{10}. Both SiO_2 and P_4O_{10} are acidic oxides but SiO_2 is insoluble while P_4O_{10} reacts with water to give H_3PO_4. Thus, for P_4O_{10}, pH when mixed with water is lower than that of SiO_2.

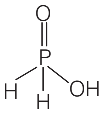
18 Sodium pyrophosphate is represented by $Na_4P_2O_7$. It is sodium salt of pyrophosphoric acid ($H_4P_2O_7$), which may be considered to be made up by two molecules of orthophosphoric acid (H_3PO_4), eliminating one molecule of H_2O.

$$2H_3PO_4 \xrightarrow{H_2O} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7}$$

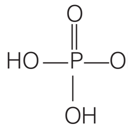


Sodium Pyrophosphate

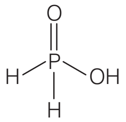
19 The oxy acid of phosphorus which contain P—H bond, acts as a reducing agent or reductant.



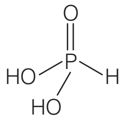
In H_3PO_2 one —OH group and two P—H bonds are present.

20  $HO—\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}—OH$ ionises in three steps because three —OH groups are present.

21 Phosphinic acid

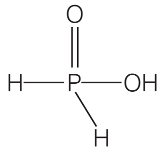


Phosphonic acid



Due to the presence of one replaceable proton in phosphinic acid, it is monoprotic acid and due to presence of two replaceable proton in phosphonic acid, it is diprotic acid.

22 Hypophosphorus acid, H_3PO_2, has the following structure



As it contains only one replaceable H-atom. Hence, it is monoprotic acid (that is attached with O, not with P directly) so it is a monoprotic acid. All other given statements are true.

23 Since, electron repulsion predominate over the stability gained by achieving noble gas configuration. Hence, formation of O^{2-} in gas phase is unfavourable.

24 Na_2SO_3 reacts with hot and dil. H_2SO_4 to give SO_2 gas which decolourise bromine water.

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + H_2O$$

$$Br_2 + H_2O \longrightarrow 2HBr + [O]$$

$$SO_2 + [O] \longrightarrow SO_3$$

Decolourisation of bromine water.

25 (a) $CaSO_4 + C \xrightarrow{\Delta} CaO + SO_2 + CO$

(b) $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$

(c) $S + 2H_2SO_4 \xrightarrow{\Delta} 3SO_2 + 2H_2O$

(d) $H_2SO_4 + PCl_5 \xrightarrow{\Delta} \underset{\text{Chlorosulphonic acid}}{SO_3 \cdot HCl} + POCl_3 + HCl$

26 An oxidising agent is a species, which oxidises the other species and itself gets reduced.

(i) $\overset{0}{Cu} + 2H_2SO_4 \longrightarrow \overset{+2}{Cu}SO_4 + SO_2 + 2H_2O$

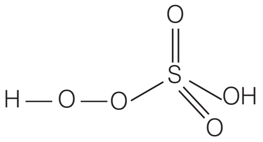
(ii) $3\overset{0}{S} + 2H_2SO_4 \longrightarrow 3\overset{+4}{S}O_2 + 2H_2O$

(iii) $\overset{0}{C} + H_2SO_4 \longrightarrow \overset{+4}{C}O_2 + 2SO_2 + 2H_2O$

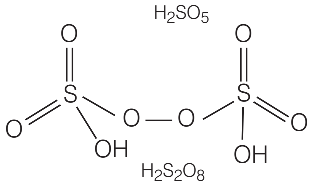
(iv) $\overset{+2}{Ca}\overset{-1}{F}_2 + H_2SO_4 \longrightarrow \overset{+2}{Ca}SO_4 + 2H\overset{-1}{F}$

In reaction (iv), oxidation number of elements remains unchanged. Thus, in this reaction, H_2SO_4 does not act as an oxidising agent.

27 Peroxoacids of sulphur must contain one —O—O— bonds as shown below:



H_2SO_5



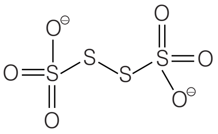
$H_2S_2O_8$

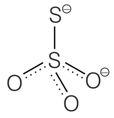
28 Acidic strength of hydrides increases as the size of central atom increases which weakens the *M*—H bond. Since, the size increases from S to Te thus acidic strength follows the order

$H_2S < H_2Se < H_2Te$

$$\text{Acidic nature} \propto \frac{1}{\text{Bond dissociation enthalpy}}$$

29 $S_4O_6^{2-}$ and $S_2O_3^{2-}$ have S—S bond





1

($S_4O_6^{2-}$)
(tetrathionate)

Thiosulphate ion
($S_2O_3^{2-}$)

30 Acidic nature of halide ∝ non-metallic nature of element. Non-metallic nature in decreasing order Cl > S > P.

31 As the size increases, bond dissociation enthalpy becomes lower. Also, as the size of atoms get smaller, ion pairs on the two atoms get close enough together to experience repulsion. In case of F_2, this repulsion is bigger and bond becomes weaker.

Hence, the correct order is $Cl_2 > Br_2 > F_2 > I_2$.

32 Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have *d*-orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states. Thus, option (a) is incorrect.

Note : Fluorine can form on oxyacid. HOF in which oxidation state fo F is +1 But HOF is highly unstable compound.

(b) All halogens are strong oxidising agents as they have strong tendency to accept an electron. Thus, option (b) is correct.

(c) All halogens form monobasic oxyacids. Thus, option (c) is also correct.

(d) Electron gain enthalpy of halogens become less negative down the group. However, the negative electron gain enthalpy of fluorine is less than chlorine due to small size of fluorine atom

Thus, option (d) is also correct.

33 (a) Fluorine is the most electronegative element because electronegativity decreases on moving down the group. Hence, it gets reduced readily into F^- ion and is the strongest oxidising agent.

Note : The electron gain enthalpy of fluorine is less negative than that of chlorine inspite of that fluorine is the strongest oxidising agent. This is due to its low bond dissociation energy and high heat of hydration as compared to those of chlorine.

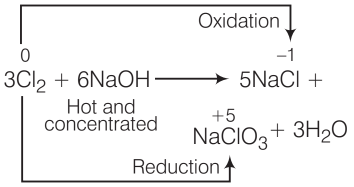
34 When bromine water reacts with SO_2, it oxidises it to sulphuric acid and it self gets reduced to HBr.

$$\underbrace{Br_2 + 2H_2O}_{\text{Bromine water}} + SO_2 \longrightarrow 2HBr + H_2SO_4$$

35 Chlorine acts as oxidising and bleaching agent in the presence of moisture. Chlorine reacts with water forming HCl and HClO. HClO further decomposes to give nascent oxygen which is responsible for oxidising and bleaching properties of chlorine. Thus, in chlorine water, oxidising agent is HOCl.

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$
$$HClO \longrightarrow HCl + O$$
$$\overline{Cl_2 + H_2O \longrightarrow 2HCl + O}$$

36 When chlorine gas reacts with hot and concentrated NaOH solution, it disproportionates into chloride (Cl^-) and chlorate (ClO_3^-) ions.

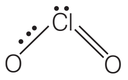


$$3\overset{0}{Cl_2} + 6NaOH \xrightarrow[\text{Hot and concentrated}]{} 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$

37 Oxidising power of species is directly proportional to reduction potentials. Therefore, order of oxidising power of given ions is as follows:

Ion	$BrO_4^- > IO_4^- > ClO_4^-$
$E°(V)$	1.74 1.65 1.19

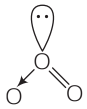
38 ClO_2 shows paramagnetic behaviour due to the presence of unpaired electron in its structure.



39 (a) Cl_2O_7 is an anhydride of perchloric acid

$$2HClO_4 \xrightarrow[-H_2O]{\Delta} Cl_2O_7$$

(b) Shape of O_3 molecule is bent.



(c) Number of electrons in ONF = 24

Number of electrons in NO_2 = 24

∴ ONF and NO_2 both are isoelectronic.

(d) OF_2 is a fluoride of oxygen because electronegativity of fluorine is more than that of oxygen.

OF_2 = Oxygen difluoride

40 $MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$

41 (b)Al^{3+} shows maximum coordination number 6, thus it will form AlF_6^{3-}.

AlF_3 forms $K_3[AlF_6]$ when dissolved in HF in the presence of KF as shown below:

$$AlF_3 + 3KF \xrightarrow{HF} K_3[AlF_6]$$

42 HF is a weak acid than HCl due to intermolecular hydrogen bonding.

43 Hydrofluoric acid attacks glass and form greasy fluorosilicates. It is called etching of glass. So, HF is not stored in the glass vessels.

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$
$$Ca_2SiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$$

44 Word 'hypo' reveals that it is in +1 oxidation state, i.e. it is iodous (I) acid or HOI. In HOI, number of hybrid orbitals $= \frac{1}{2}\ [7 + 1 - 0 + 0] = 4$

∴ In it, iodine atom uses sp^3-hybrid orbitals.

45 $Ca(OCl)_2$, calcium hypochlorite is the active ingredient in bleaching powder which releases chlorine.

46 CN^- is pseudo halide ion as it shows properties similar to those of halogens.

47 (b) Two different halogens may react to form interhalogen compounds as

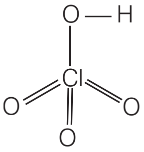
XX′ (ClF, BrF, BrCl, IF, ICl)	Linear
XX'_3 (ClF_3, BrF_3, IF_3, ICl_3)	Bent T-shaped
XX'_5 (ClF_5, $BrCl_5$, IF_5)	Square-pyramidal
XX'_7 (IF_7)	Pentagonal bipyramidal

48 $HClO_4$ is with highest oxidation number and its conjugate base is resonance stabilised, hence it is most acidic.

49 OF_2 dissolves in water but does not give any oxyacid solution. While SO_2, SCl_4 and SO_3 give oxyacid solution in water.

$$SO_2 + H_2O \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_3}$$
$$SCl_4 + 3H_2O \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_3} + 4HCl$$
$$SO_3 + H_2O \longrightarrow \underset{\text{Sulphuric acid}}{H_2SO_4}$$

50 Perchloric acid is not a peroxyacid while perphosphoric acid, pernitric acid and perdisulphuric acid are the examples of peroxyacid.



$HClO_4$

51 (a) As the oxidation state of halogen i.e. —Cl in this case increases, acidity of oxyacid increases.

HClO : Oxidation state of Cl = +1

$HClO_2$: Oxidation state of Cl = + 3

$HClO_3$: Oxidation state of Cl = + 5

$HClO_4$: Oxidation state of Cl = + 7

Therefore, the correct order of acidity would be

$HClO < HClO_2 < HClO_3 < HClO_4$

52 (b) Since, there is a strong hydrogen bonding between HF molecules. Hence, boiling point is highest for HF.

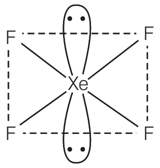
HF > HI > HBr > HI

53 (c) Isoelectronic species have equal number of valence electrons .

Both IBr_2^- and XeF_2 are linear and number of valence electrons present in both the species is same, i.e. they are also isoelectronic.

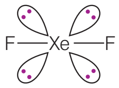
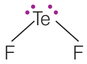
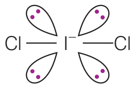
Compounds	**Number of valence electrons**	**Geometry**
$BeCl_2$	2 + 14 = 16	Linear
XeF_2	8 + 14 = 22	Linear
TeI_2	6 + 14 = 20	Bent or V-shape
IBr_2^-	7 + 14 + 1 = 22	Linear
IF_3	7 + 21 = 28	T-shape

54 Geometry is determined by electron pair arrangement whereas shape is determined by arrangement of atoms around the centre atom.



Geometry – octahedral, Hybridisation – sp^3d^2. Thus, option (a) is correct.

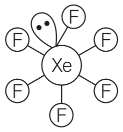
55 Species having the same number of bond pairs and lone pairs are isostructural (have same structure).

Species	$lp + bp$	Structure
XeF_2	$4lp + 2bp$	Linear 
TeF_2	$2lp + 2bp$	Angular or V-shape 
ICl_2^-	$4lp + 2bp$	Linear 
$BaCl_2$	$0lp + 2bp$	Cl—Ba—Cl (linear)

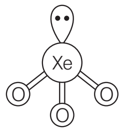
Thus, XeF_2 is isostructural with ICl_2^-.

56 A – 1, B – 3, C – 4, D – 2

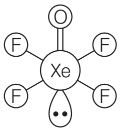
The structures of the xenon compounds are given below:



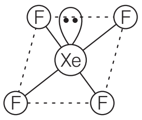
Distorted octahedral XeF_6



Pyramidal XeO_3



Square pyramidal $XeOF_4$



Square planar XeF_4

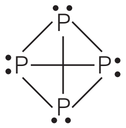
SESSION 2

1 $C \equiv N$, $N \equiv N$, $O \leftarrow N = O$

2 Nitrogen and phosphorus have three electrons in $2p$ and $3p$ subshells respectively and five electrons in its outermost shell, but phosphorus has $3d$ vacant orbitals thus, they can form maximum of 3 and 5 covalent bonds. respectively.

3 NO and NO_2 have unpaired electrons, thus paramagnetic.

4



Each P-atom is sp^3-hybridised.

Thus, p-character is 75%.

5 $P_4O_6 + H_2O \longrightarrow H_3PO_3$ (ON of +3 in both)

$P_4O_{10} + H_2O \longrightarrow H_3PO_4$ (ON of +5 in both)

6 $CHCl_3 + O_2 \longrightarrow \underset{\text{Phosgene}}{COCl_2} + HCl$

7 Acid salts have ionisable H^+ and can further react with base forming next series of salts.

Salts		Normal salts	Acid salts
H_3PO_2	monobasic	NaH_2PO_2	NaH_2PO_3
H_3PO_3	dibasic	Na_2HPO_3	NaH_2PO_4
H_3PO_4	tribasic	Na_3PO_4	Na_2HPO_4
H_2CO_3	dibasic	Na_2CO_3	$NaHCO_3$

8 Bond-energy decreases going down the group

Te—Te < Se—Se < S—S < O—O

9 $KI + H_2O + O_3 \longrightarrow I_2 + KOH + O_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

10 Acidic nature increases down the group means K_a values increases, while pK_a values decreases down the group, thus H_2O has highest pK_a value.

$H_2O < H_2S < H_2Se < H_2Te$

$K_a \xrightarrow{\hspace{6cm}}$ (max.)

$pK_a \xleftarrow{\hspace{6cm}}$
(max.)

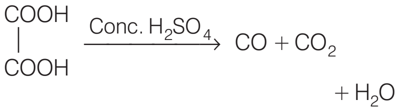
11 $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$

SO_2 acts as reducing agent.

12 $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$

13 $\text{Colour} \underset{\text{air/oxidation}}{\overset{SO_2\text{/reduction}}{\rightleftarrows}} \text{Colourless}$

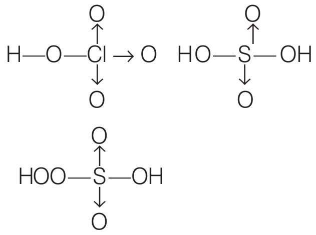
14 H_2SO_4 is dehydrating agent.



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\text{Conc. } H_2SO_4} CO + CO_2 + H_2O$$

15 $H_2S_2O_8$ has maximum oxidation state of sulphur and thus cannot be further oxidised by $KMnO_4$.

16



$$H—O—\underset{\downarrow \atop O}{\overset{O \atop \uparrow}{Cl}} \rightarrow O \quad HO—\underset{\downarrow \atop O}{\overset{O \atop \uparrow}{S}}—OH$$

$$HOO—\underset{\downarrow \atop O}{\overset{O \atop \uparrow}{S}}—OH$$

17 Mixture is called ***aqua regia***.

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

18 Oxidising power of $F_2 > Cl_2 > Br_2 > I_2$

Hence, I_2 can n't oxidise KBr and this reaction (option b) is not feasible.

19 Let oxidation state of Xe in

$XeO_2F_2 = x$

$\because$ Oxidation-no. of oxygen = (–)2

and oxidation-no. of fluorine = (–)1

$\therefore$ Oxidation no. of 'Xe' in XeO_2F_2

$\Rightarrow \quad x + [(-2) \times 2] + [(-1) \times 2]$

$\Rightarrow \quad x - 4 - 2 = 0$

$\therefore \quad x = (+)6$

Hence, oxidation no. of Xe = (+)6.