7

p-BLOCK (GROUP 15,16,17 & 18)

NITROGEN FAMILY

ELECTRONIC CONFIGURATION

The general outer electronic configuration of elements of VA group is ns^2np^3.Hence these elements belong to p-block.

Elements	Configuration
Nitrogen $[N_7]$	$[He]\ 2s^2 2p^3$
Phosphorus $[P_{15}]$	$[Ne]\ 3s^2\ 3p^2$
Arsenic $[As_{33}]$	$[Ar]\ 3d^{10}\ 4s^2\ 4p^3$
Antimony $[Sb_{51}]$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^3$
Bismuth $[Bi_{83}]$	$[Xe]\ 4f^{14} 5d^{10} 6s^2 6p^3$

PHYSICAL PROPERTIES

1. **Atomic and ionic radii :** Covalent radius :
   $N < P < As < Sb < Bi$
2. **Ionization enthalpies :** $N > P > As > Sb > Bi$ (IE_1 values)
3. **Electronegativity :** $N > P > As > Sb = Bi$
4. **Catenation :**

* The group 15 elements show catenation property but to much smaller extent than carbon. For example hydrazine H_2NNH_2) has two N atoms bonded together HN_3 has three N atoms. $HN_3 : H-\ddot{N}=\overset{+}{N}=\ddot{N}:^{\ominus}$

* Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms. P_2H_4 has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in compression to carbon is their low dissocation enthalpies.

5. **Valency and oxidation number :**
   (a) Gen. configuration : $ns^2\ np^3$
   Valency = 3 ; O.S. = –3, +3, +5 ; P show O.S. = –3, +3
   (b) P has two sleeping valency.
   (c) Slepping valency : These electron of valency shell which does not take part in bonding.
   (d) P in excited state show + 5 O.S.
   So hybridisation = sp^3d
   Shape = Trigonal by pyramidal.
   (e) P, As, Sb show 3 & 5 both O.S.
   N only 3, absence of d-orbital.
   Bi only 3, because of inert pair effect.
6. **Allotropic forms :** Except N and Bi all other elements of this group show allotropy.
   Phosphorous : White, Black and Red
   Arsenic : Yellow or Grey
   Antimoney : Yellow or Silver grey
   Arsenic (As):It is the most poisonous element of V^{th} group.

NOTE

* N and P are non metals.
* As and Sb are metalloids. Bi is of -course metal.
* Nitrogen constitutes about 78% by volume of the atmosphere (essential constituent of fertilizers, explosives and proteins)
* Phosphorus occurs in bones, phosphate rocks. It is used as fertilizers.
* As, Sb, Bi occur mostly as sulphides.
* Bi is the end product of (4n + 1) radioactive series.
* Elements of this group are called pnicogens.

CHEMICAL PROPERTIES

Hydrides : MH_3 type of hydride is formed :

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Ammonia	Phosphine	Arsine	Stibine	Bismuthine

* Hydrides are formed by the action of water of dilute acids on compounds:Mg_3N_2, Ca_3P_2, Zn_3As_2, Mg_3Sb_2 and Mg_3Bi_2.
* All hydrides are coloured gases.
* NH_3 is highly soluble other hydrides are less soluble.
* Poisonous nature increases from NH_3 to BiH_3
Ammonia -- Bismuthine

$$\xrightarrow{\text{Basic character decreases}}$$

$$\xrightarrow{\text{Thermal stability decreases}}$$

$$\xrightarrow{\text{Reducing nature increases}}$$

$$\xrightarrow{\text{Dipole moment decreases}}$$

$$\xrightarrow{\text{Bond angle decreases}}$$

Oxides :

Elements of VA group form oxides of the type M_2O_3, M_2O_4 and M_2O_5.

Moving from :

$$L \xrightarrow{\text{acidic nature of oxide decreases}} R$$

Moving from

$$T \xrightarrow{\text{acidic nature of oxide increases}} B$$

Formation of Hydrites :

(a) $PH_3 + HI \rightarrow PH_4I$
Phosphene
Phosphene is a weak base as compared to NH_3 and rest all have amphoteric nature.

(b) NH_3 will have high boiling point due to H-bond.

(c) Tendency of H-bonding and B.P.
$NH_3 > PH_3 < AsH_3 < SbH_3 < BiH_3$

(d) NH_3 cannot acts as a reducing agent and BiH_3 is strongest reducing agent.

(e) **Oxidation state :**

Hydrazine	NH_2-NH_2 or N_2H_4	$\Rightarrow -2$
Hyzrazoic acid	N_3H	$\Rightarrow -1/3$
	NH_2-OH	$\Rightarrow -1$

(f) H_2O_2 also a better propellent than N_2H_4

H_2O_2 provides nascent O which is more reactive than O_2.

Halides : Trihalides MX_3 and penta halides MX_5

Nitrogen does not form pentahalides due to absence of d-orbital.

Trihalide (MX_3) : All trihalides are stable except NCl_3, NBr_3 and NI_3.

The reason assigned to unstable nature of NCl_3, NBr_3, NI_3 is (i) Low polarity of N–X bond (ii) Large difference in the size of nitrogen and halogen atom.

NOTE

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

$SbCl_3+3H_2O \rightarrow SbOCl$ (Stibynl chloride) $+ 2HCl$

$BiCl_3+H_2O \rightarrow BiOCl$ (Bismithyl chloride) $+ 2HCl$

Lewis base order : $NF_3 < NCl_3 < NBr_3 < NI_3$.

Penta - Halides (MX_5) :

- PCl_5, $AsCl_5$ and $SbCl_5$ are well known
- Bi does not form penta halide due to inert pair effect.
- The hybridized state of the central atom in liquid and gaseous state is sp^3d showing trigonal bipyramidal geometry.
- X-ray analysis have shown that PCl_5 and PBr_5 exist as ionic compounds $[PCl_4]^+[PCl_6]^-$ and $[PBr_4]^+Br^-$.
- PCl_5 undergoes thermal decomposition and also hydrolysed by water.

  $PCl_5 \rightleftharpoons PCl_3+Cl_2$

  $PCl_5+H_2O \rightarrow POCl_3+2HCl$

  $POCl_3+3H_2O \rightarrow H_3PO_4+3HCl$
- PCl_5 acts as an effective chlorinating agent.

ANOMALOUS BEHAVIOUR OF NITROGEN

The anomalous behaviour of nitrogen is due to :

- Small size
- High E.N. and high I.E.
- Non availability of vacant d-orbital
- Tendency to form multiple bond.

Nitrogen differs from other elements of its own group

- Nitrogen is a gas while other elements are solids
- Nitrogen is diatomic, while other elements are tetratomic $[P_4, As_4, Sb_4]$
- Nitrogen can form N_3^- ion (due to small size & high E.N.)
- Nitrogen is chemically inert under ordinary condition due to high dissociation energy of N≡N bond.
- Nitrogen shows oxidation state from –3 to +5
- Hydride of nitrogen i.e. ammonia is stable and forms H-bonding.

NITROGEN

- Nitrogen was discovered by Daniel Rutherford.
- It occurs in the atmosphere to the extent of 78% by volume.
- Nitrogen occurs in the combined form in various compounds KNO_3. $NaNO_3$, NH_4Cl, $(NH_4)_2SO_4$ etc.

Preparation :

(a) **From ammonia and its compounds**

(i) $3CuO+2NH_3 \xrightarrow{\Delta} N_2+3Cu+3H_2O$

(ii) $CaOCl_2+2NH_3 \rightarrow 3CaCl_2+3H_2O+N_2$
(bleaching powder)

(iii) $2NH_3+3Cl_2 \rightarrow 6HCl+N_2$

(iv) **Laboratory method :**

(1) $NH_4NO_2(aq) \xrightarrow{\Delta} N_2(g)+2H_2O\,(1)$

(2) $(NH_4)_2Cr_2O_7 \rightarrow N_2+2H_2O+Cr_2O_3$

(b) **From air :** Nitrogen is prepared commercially from air by liquefaction and fractional distillation .

Properties : Physical

- It is colourless, tasteless and odourless gas
- It is highly soluble in water
- Its m.p. is 63.2 K and b.p. is 77.2 K
- It is absorbed by charcoal

Chemical : Few reactions of N_2 are

(i) Li, Mg, Ca, Al form nitrides

$3Ca+N_2 \xrightarrow{\Delta} Ca_3N_2$

(ii) $N_2+O_2 \rightleftharpoons 2NO$ (electric arc)

This reaction forms the basis for the manufacture of HNO_3 by Birk land and Eyde process.

(iii) $\underset{\text{calcium carbide}}{CaC_2}+N_2 \xrightarrow{1273K} \underset{\text{calcium cyanamide}}{CaCN_2}+C$

Since $CaCN_2$ gives ammonia when reacts with water. Therefore $[CaCN_2+C]$ called nitrolium and it is used as fertilizer.

Uses :

- Used for the manufacture of NH_3, HNO_3, $CaCN_2$ etc.
- To provide inert atmosphere N_2 gas is used in metallurgical processes.
- It is used in filling electric bulbs.

OXIDES OF NITROGEN

(1) **Nitrous oxides $[N_2O]$**, O.S. (+1), laughing gas, colourless.

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

Structure : Resonance

$$:N\equiv \overset{+}{N}-\ddot{\underset{..}{O}}: \leftrightarrow :\underset{..}{\ddot{N}}=\overset{+}{N}=\ddot{O}:$$

Special features : Oxide is neutral

It acts as an anaesthetic agent.

(2) **Nitric Oxide [NO],** O.S. (+2) colourless gas.

Preparation :

$4NH_3+5O_2 \xrightarrow{1100K,\ Pt} 4NO+6H_2O$

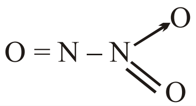
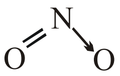
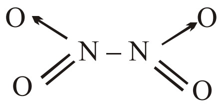
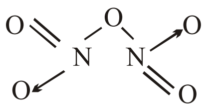
(3) **Dinitrogen trioxide (N_2O_3),** O.S. (+3), blue liquid (<253K)
Preparation :

$$NO(g) + NO_2(g) \xrightarrow{<253K} N_2O_3(g)$$

(4) **Nitrogen dioxide (NO_2),** O.S. (+4) brown gas.

(5) **Dinitrogen pentoxide (N_2O_5),** O.S. (+5), colourless gas

Table : Oxides of Nitrogen

Oxide, Oxidation state	**Structure**	**Physical appearance and chemical nature**	**Preparation**
Nitrous oxide (N_2O) +1	$N \equiv N \rightarrow O$	Colourless gas,neutral Anasthetic gas for dental surgery	By heating ammonium nitrate upto 240°C $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$, It is Collected over hot water
Nitric oxide (NO) +2	$N = O$	Colourless gas, neutral Paramagnetic in gaseous state but diamagnetic in liquid and solid states	(a) By the action of cold dil. HNO_3 on copper turnings (Laboratory method) $3Cu + 8\text{ dil. }HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$ (b) By the action of H_2SO_4 on a mixture of $FeSO_4$ and $NaNO_2$ $2NaNO_2 + 3H_2SO_4 + 2FeSO_4$ $\rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$ (c) By catalytic oxidation of ammonia. $4NH_3 + 5O_2 \xrightarrow[850^0 C]{Pt} 4NO + 6H_2O$
Dinitrogen trioxide (N_2O_3) +3		Blue solid,acidic	$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$ $2Cu + 6HNO_3 \rightarrow 2Cu(NO_3)_2 + N_2O_3 + 3H_2O$
Nitrogen dioxide (NO_2) +4		Brown gas, acidic	(a) By heating nitrates of heavy metals, e.g., lead nitrate. $2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + 2O$ (b)By heating copper turnings with conc. HNO_3. $Cu + 4\ HNO_3\ (conc.)$ $\rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$
Dinitrogen tetraoxide (N_2O_4) +4		Colourless/Solid liquid, acidic	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$
Dinitrogen pentoxide (N_2O_5) +5		Colourless Solid, acidic	By dehydrating HNO_3 with phosphorus pentoxide $4HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4HPO_3$

OXY-ACIDS OF NITROGEN

Nitrous acid [HNO_2]

Preparation :

$N_2O_3 + H_2O \rightarrow 2HNO_2$

$NaNO_2 + HCl \rightarrow NaCl + HNO_2$

Properties :

It is a weak acid and does not exist in free liquid state. In aqueous solution it is unstable and changes to HNO_3.

$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

It acts both as an oxidizing as well as reducing agent.

Oxidizing properties :

$2HNO_2 \rightarrow 2NO + H_2O + [O]$

$H_2S + [O] \rightarrow H_2O + S$

$2KI + H_2S + [O] \rightarrow 2KOH + I_2$

$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$

Reducing properties :

$HNO_2 + [O] \rightarrow HNO_3$

$Br_2 + H_2O + HNO_2 \rightarrow HNO_3 + 2HBr$

$H_2O_2 + HNO_2 \rightarrow HNO_3 + H_2O$

$KMnO_4 \xrightarrow{HNO_2} MnSO_4$

Organic reactions : Urea $\xrightarrow{HNO_2}$ N_2

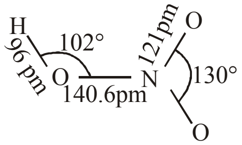
Ethyl amine $\xrightarrow{HNO_2}$ ethyl alcohol

Aniline $\xrightarrow{HNO_2}$ diazonium chloride

Nitric acid (HNO_3)

Structure of nitric acid :

It exists as planar structure.



Preparation :

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

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

Commercial method : 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.

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

(from air)

Nitric oxide thus formed combines with oxygen giving NO_2.

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

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

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

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 of nitric acid :

Nitric acid is a colourless fuming liquid and has a pungent smell. It is yellowish in colour when impure due to the presence of NO_2 dissolved in it. It is miscible in water and forms a constant boiling mixture with water. It is a highly corrosive liquid. The aqueous solution of nitric acid is stable and shows the properties of a strong acid.

$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

When treated with metals, nitric acid does not liberate hydrogen because in comparison to hydrogen ion, nitrate ion is a strong oxidising agent. Most of the reactions of nitric acid are oxidising in which nitrogen undergoes a change from oxidising state +5 to lower states. The reduced products of nitric acid depend on the nature of the reducing agent and concentration of the acid.

(a) Acidic Nature : Nitric acid is a strong acid, and therefore, ionized almost completely in solution.

$HNO_3 \longrightarrow H^+ + NO_3^-$

It reacts with basic oxides, hydroxides and carbonates to give corresponding nitrates.

$ZnO + 2HNO_3 \longrightarrow Zn(NO_3)_2 + H_2O$

$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$

$K_2CO_3 + 2HNO_3 \longrightarrow 2KNO_3 + H_2O + CO_2$

(b) Nitration : With aromatic organic compounds, concentrated HNO_3 reacts in presence of conc. H_2SO_4 giving nitro-compounds. Nitro-groups replace the hydrogen atoms of the ring. This process is known as nitration. $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$

(c) Oxidising properties. On heating nitric acid decomposes to give oxygen. Hence it is a powerful oxidising agent. It oxidises non-metals like, carbon, sulphur, phosphorus and iodine to their highest oxidation states.

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

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

$P_4 + 10HNO_3 + H_2O \longrightarrow 4H_3PO_4 + 5NO + 5NO_2$

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

(d) Action on metalloids : Nitric acid reacts with metalloids like arsenic and antimony to give arsenic acid, H_3AsO_4 and antimonic acid, H_3SbO_4.

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

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

(e) Action on metal : Nitric acid reacts with almost all metals except gold, platinum, rhodium, irridium and tantalum, The products of the reaction of acid on metals depend on the following factors :

(i) Concentration of acid,

(ii) Temperature of reaction and (iii) Nature of metal.

(A) Copper.

(i) With cold and dilute acid it gives NO.

$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(ii) With hot and concentrated acid gives NO_2.

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(B) Tin.

(i) With cold and dilute acid gives NH_4NO_3.

$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

(ii) With hot and concentrated acid gives metastannic acid.

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

(C) Iron.

(i) With cold and dilute acid gives NH_4NO_3.

$4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$

(ii) With hot and dilute acid gives nitric oxide.

$$Fe + 4HNO_3 \longrightarrow Fe(NO_3)_3 + NO + 2H_2O$$

(iii) Highly concentrated or fuming acid does not dissolve iron but renders it passive. Same is true for chromium. Probably a thin film of the oxide is formed on the surface of the metal, which protects the metal from being corroded.

(D) Magnesium and Manganese : With very dilute and cold acid, they give hydrogen gas.

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$
$$Mn + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2$$

Aqua-regia : When one part of concentrated nitric acid is mixed with three parts of concentrated HCl, aqua-regia is formed. Aqua-regia dissolves gold, platinum etc. due to the action of nascent chlorine.

$$HNO_3 + 3HCl \longrightarrow NOCl + 2Cl + 2H_2O$$
$$Au + 3Cl \longrightarrow AuCl_3 \; ; \quad Pt + 4Cl \longrightarrow PtCl_4$$

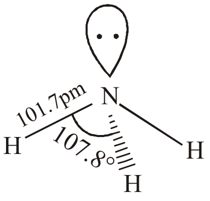
Uses :

(i) Purification of gold silver and platinum.
(ii) In the manufacture of sulphuric acid, fertilizers and nitrates.
(iii) In the manufacture of explosives like T.N.T. (2,4,6-trinitrotoluene), nitroglycerine, dynamite, gun cotton, picric acid etc.
(iv) In cleaning the metal surface in electroplating and in making batteries.
(v) In the manufacture of artificial silk.
(vi) As a reagent in laboratories.
(vii) As an oxidiser in rocket fuels.
(viii) In the pickling of stainless steel.

AMMONIA [NH_3]

Structure of Ammonia :

The N atom in NH_3 is sp^3-hybridized containing a lone pair of electrons due to which the H – N – H bond angle is 107.5°. As a result NH_3 molecule is pyramidal.



Preparation :

Laboratory method :

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_4 + 2H_2O$$
$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

The gas is collected by downward displacement of air. The gas is dried by CaO [P_2O_5, H_2SO_4 and $CaCl_2$ react with ammonia]

Manufactures :

Haber Process : $N_2 + 3H_2 \xrightarrow[450°C,\,250atm]{Fe,\ Mo} 2NH_3$

Cyanamide process :

$$CaC_2 + N_2 \xrightarrow{1000°C} CaCN_2 + C$$
$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

Serpeck's process :

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$
$$AlN + 3H_2O \rightarrow Al\,(OH)_3 + NH_3$$

Properties :

Physical

* Lighter than air
* Easily liquefied by cooling or compression
* Highly soluble in water. The solution is alkaline
* Forms H–bonding with water.
* Turns litmus to blue [$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$]

Chemical reactions : Few of the chemical reaction are :

[i] $NH_3 + HCl \rightarrow NH_4Cl$
[ii] $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
[iii] $2NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2$
[iv] $CaCl_2 + 8NH_3 \rightarrow CaCl_2.8NH_3$
[v] With Cl_2
  [a] $8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$
  [b] $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$
[vi] Complex formation :
  $Ag^+ \xrightarrow{2NH_3} [Ag(NH_3)_2]^+$,
  $Cu^{+2} \xrightarrow{4NH_3} [Cu(NH_3)_4]^{2+}$
[vii] $2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$
[viii] $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
[ix] $K_2HgI_4 + NH_3 + 3KOH \rightarrow NH_3 - HgO.HgI\downarrow + 7KI + 2H_2O$
(red brown ppt.)
[x] $FeCl_3 + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3\downarrow + 3NH_4Cl$
(brown ppt.)

Uses :

* Due to lone pair of electrons it acts as a lewis base.
* Preparation of fertilizers.
* In making artificial silk.
* As a laboratory reagent.
* In refrigeration.
* In making HNO_3, $(NH_4)_2CO_3$, Na_2CO_3 etc.

PHOSPHORUS

Occurrence : Five important minerals of phosphorus are :

* Phosphorite $Ca_3(PO_4)_2$
* Fluoropatite $3Ca_3(PO_4)_2.CaF_2$
* Hydroxyapatite $3Ca_3(PO_4)_2.Ca(OH)_2$.
* Chloroapatite $3Ca_3(PO_4)_2.CaCl_2$

It is mainly present in bones and teeth which constituent about 58% calcium phosphate and also in animal cells (DNA).

Isolation : It is isolated by heating $Ca_3(PO_4)_2$ with coke and silica in an electric furnace.

$$2Ca_3(PO_4)_2 + 6SiO_2 \xrightarrow{1770\ K} 6CaSiO_3 + P_4O_{10}$$
$$P_4O_{10} + 10C \rightarrow P_4 + 10CO$$

Allotropes of phoshorus : Phosphorus exists in the following five different allotropic forms.

White phosphorus : It is a translucent white waxy solid.

(i) White (yellow) phosphorus is extremely reactive.

(ii) Below 800°C, its vapor density corresponds to the formula P_4.
Above 1700°C, it exists as P_2.

(iii) Due to is low ignition temperature (~30°C), it undergoes oxidation in the presence of air which slowly raises its temperature and after a few moments it catches fire spontaneously. Due to this reason, it is stored under water.

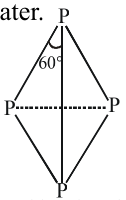


Fig. White phosphorus

Red Phosphorus:

(i) Red phosphorus is stable allotrope at room temperature.

(ii)Red phosphorus is formed by heating white phosphorus in the absence of air at about 250°C.

(iii) It is not poisonous. It is safe to handle because it does not burn spontaneously at room temperature

(iv) It has iron-grey lusture.

(v) It is insoluble in carbon disulphide as well as in water.

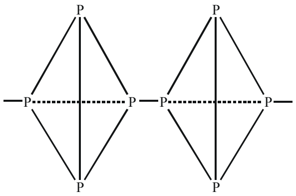


Fig. Red phosphorus

(vi) Red phosphorus is much less reactive than white phosphorus.

(vii) It does not glow in the dark.

Black phosphorus :

(i) It has two forms α-black phosphorus and β-black phosphorus.

(ii) α-Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K. It can be sublimed in air and has opaque monoclinic or rhombohedral crystals. It does not oxidise in air.

(iii) β-Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure. It does not burn in air upto 673 K.

(iv) Like graphite it is a fairly good conductor of electricity.

PHOSPHINE, PH_3

Phosphine, PH_3 is the most stable hydride of phosphorus. It is intermediate in thermal stability between ammonia and arsine.

Preparation :

1. Hydrolysis of metal phosphides such as Ca_3P_2 :
$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$

2. Pyrolysis of phosphorous acid at 480 - 485 K :
$4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4$

3. Alkaline hydrolysis of phosphonium iodide :
$PH_4I + KOH \rightarrow PH_3 + KI + H_2O$

4. Alkaline hydrolysis of white phosphorus :
$P_4 + 3KOH + 3H_2O \rightarrow PH_3 + 3KH_2PO_2$
(Industrial process)

Properties :

* Phosphine is a colourless, extremely poisonous gas having rotten fish smell.

* As the P-H bond is not polar enough to form P-H----P or P-H----O bonds, unlike ammonia, phosphine is not associated in the liquid state and is much less soluble in water.

* In contrast to the basic nature of solutions of ammonia in water, aqueous solutions of phosphine are neutral, which is due to the much weaker tendency of PH_3 to protonate in water. However, it does react with HI to form phosphonium iodide: $PH_3 + HI \rightarrow PH_4I$

* Pure phosphine ignites in air at about 435 K, but when contaminated with traces of P_2H_4 it is spontaneously inflammable: $PH_3 + 2O_2 \rightarrow H_3PO_4$

Uses:

(i) The spontaneous combustion of phosphine is technically used in Holme's signals.

(ii) Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

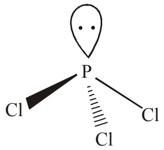
(iii) It is used in smoke screens.

PHOSPHORUS HALIDES

Phosphorus forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

Phosphorus trichloride :

Structure : It has a pyramidal shape as shown, in which phosphorus is sp^3 hybridised.



Preparation : It is obtained by passing dry chlorine over heated white phosphorus.
$P_4 + 6Cl_2 \rightarrow 4PCl_3$

It is also obtained by the action of thionyl chloride with white phosphorus. $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

Properties :

* It is a colourless oily liquid

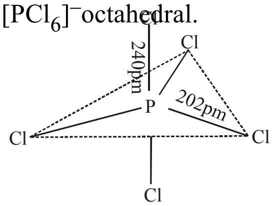
* Hydrolyses in the presence of moisture.
$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

* It reacts with organic compounds containing – OH group such as
$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$
$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$

* It reacts with Cl_2 to form PCl_5 which is more stable.
$PCl_3 + Cl_2 \rightarrow PCl_5$

Phosphorus pentachloride :

Structure : In gaseous and liquid phases, it has a trigonal bipyramidal. The three equatorial P–Cl bonds are equivalent, while the two axial bonds are longer than equatorial bonds. This is due to the fact that the axial bond pairs suffer more repulsion as compared to equatorial bond pairs. In the solid state it exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in whichthe cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$octahedral.



Preparation :

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

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

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

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

Properties :

* PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to phosphoric acid. $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

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

* When heated, it sublimes but decomposes on stronger heating. $PCl_5 \xrightarrow{Heat} PCl_3 + Cl_2$
* It reacts with organic compounds containing –OH group converting them to chloro derivatives.

$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$
$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

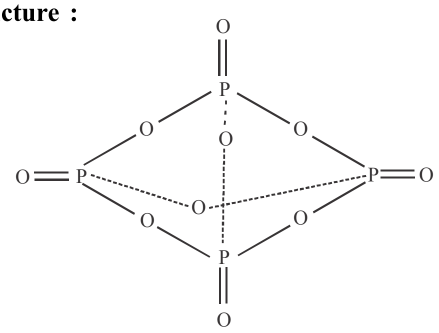
* Finely divided metals on heating with PCl_5 give corresponding chlorides.

$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$
$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$

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

PHOSPHORUS PENTOXIDE $[P_4O_{10}]$

Structure :



It is formed by burning phosphorus in excess of air :

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

Note : Since it is collected as snowy powder hence it is called.

Flower of phosphorus.

Dissolution in cold water :

$P_4O_{10} + 2H_2O\ (cold) \rightarrow 4HPO_3$ metaphosphoric acid

Dissolution in hot water :

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ orthosphosphoric acid

NOTE

* Because of its great affinity for water, it acts as a dehydrating agent.

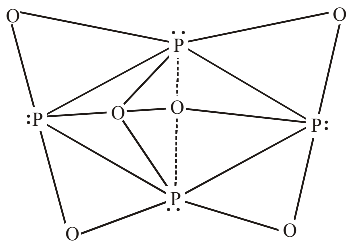
$2HNO_3 + P_4O_{10} \rightarrow 2N_2O_5 + 4\ HPO_3$
$2H_2SO_4 + P_4O_{10} \rightarrow 2SO_3 + 4\ HPO_3$

* Final product on reaction wth water is as follows :

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

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

Phosphorus trioxide: $[P_4O_6]$:



$P_4O_6 + 6H_2O\ (Cold) \rightarrow 4H_3PO_3$
$P_4O_6 + 6H_2O\ (Hot) \rightarrow PH_3 + 3H_3PO_4$

Preparation: Prepared by burning white phosphorus in limited supply of air $P_4 + 3O_2 \rightarrow P_4O_6$

Properties:

* On heating in air, it forms phosphorus (V) oxide

$P_4O_6 + 2O_2 \rightarrow P_4O_{10}$

* Reacts with water as follows :

$P_4O_6 + 2H_2O\ (cold) \rightarrow 4H_3PO_3$ (Phosphorus acid)
$P_4O_6 + 6H_2O\ (hot) \rightarrow 3H_3PO_4 + PH_3$

* It burns in chlorine forming oxy - chlorides.

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

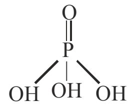
OXY-ACIDS OF PHOSPHORUS

There are two series of oxyacids of phosphorus.

* Phosphorus acid series.
* Phosphoric acid series.

Three prefixes meta, pyro and hypo is used while naming the oxy acids of phosphorus.

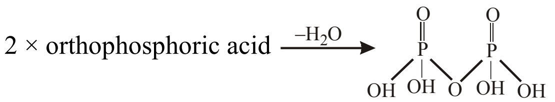
* Meta is used for acid obtained by loss of H_2O molecule from one acid molecule.



[orthophosporic acid]

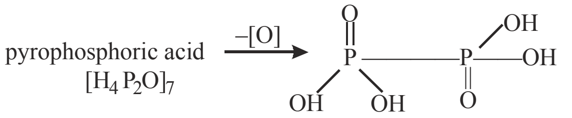
$\xrightarrow{H_2O}$ HPO_3 [metaphosphoric acid]

* Pyro is used for acid obtained by loss of H_2O molecule form two acid molecules



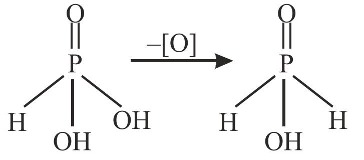
[pyro phosphoric acid]

* Hypo is used for the acid having lower oxygen content than the parent acid.

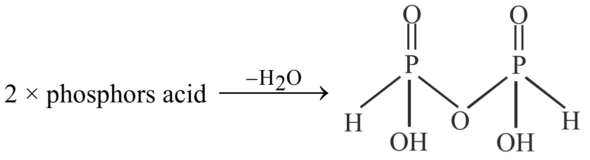


Hypophosphoric acid

Similarly :

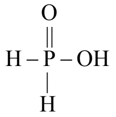
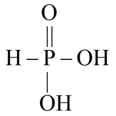
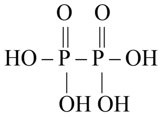
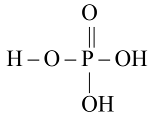
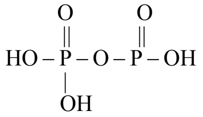
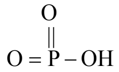


[phosphorus acid] [hyposphorus acid]



(pyrophosphorus acid)

Table : Oxy-acids of phosphorus

Name	Structure	Oxidation state (P)	Basicity
Hypophosphorus acid (H_3PO_2)	 $H-\overset{\overset{O}{\|}}{\underset{\underset{H}{\|}}{P}}-OH$	+1	1
Phosphorus acid (H_3PO_3)	 $H-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\|}}{P}}-OH$	+3	2
Hypophosphoric acid $(H_4P_2O_6)$	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\|}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\|}}{P}}-OH$	+4	4
Orthophosphoric acid (H_3PO_4)	 $H-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\|}}{P}}-OH$	+5	3
Pyrophosphoric acid $(H_4P_2O_7)$	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{OH}{\|}}{P}}-O-\overset{\overset{O}{\|}}{P}-OH$	+5	4
Metaphosphoric acid (HPO_3)	 $O=\overset{\overset{O}{\|}}{P}-OH$	+5	1

NOTE

* Thermally most stable oxide of nitrogen is : NO

* Nature of oxides on moving from P to Bi P_2O_6 (acidic), As_4O_6 & Sb_4O_6 (amphoteric) Bi_2O_3 (basic)

TRY IT YOURSELF-1

Q.1 A compound A on reaction with conc. H_2SO_4 gives compound B. B is also prepared by reaction of H_2O with C. C is also prepared by decomposition of B by sunlight. B is not attacked by noble metals like Au and Pt. Identify compound A, B and C and write the reactions involved.

Q.2 Melting point of hydrides of nitrogen family follows the order

(A) $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

(B) $PH_3 < NH_3 < AsH_3 < SbH_3 < BiH_3$

(C) $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

(D) $PH_3 < AsH_3 < SbH_3 < BiH_3 < NH_3$

Q.3 Which of the following halides of group 15 is not hydrolysed?

(A) NF_3 (B) NI_3

(C) PF_3 (D) Both (A) and (C)

Q.4 Orthophosphorus acid on heating gives –

(A) Hypophosphorus acid (B) Orthophosphoric acid

(C) Phosphen gase (D) Both (B) and (C)

Q.5 Choose the reactions which would liberate nitrogen gas?

(A) $Ca(OCl)Cl + NH_3 \xrightarrow[\text{medium}]{\text{aqueous}} ?$

(B) $NH_3 + PbO \xrightarrow{\Delta} ?$

(C) $NH_3 \text{ (excess)} + Cl_2 \xrightarrow{\Delta} ?$

(D) $NH_4Cl + NaNO_2 \xrightarrow{\Delta} ?$

Q.6 Which of the following is correct?

(A) H_3PO_3 is dibasic and reducing.

(B) H_3PO_3 is dibasic and non-reducing.

(C) H_3PO_4 is tribasic and reducing.

(D) H_3PO_3 is tribasic and non-reducing.

Q.7 The bond angle is maximum in

(A) NH_3 (B) PH_3

(C) AsH_3 (D) SbH_3

Q.8 The covalency of nitrogen in N_2O_5 is –

(A) 2 (B) 5

(C) 4 (D) 6

Q.9 Which of the following oxoacids of P is the best reducing agent ?

(A) Hypophosphorus acid (B) Phosphoric acid

(C) Orthophosphorus acid (D) Metaphosphorus acid

Q.10 Pick out out incorrect statement -

(A) Orthophosphorus acid can be obtained by reacting P_4O_6 with H_2O.

(B) Orthophosphoric acid can be obtained by reacting P_4O_{10} with H_2O.

(C) Pyrophosphoric acid can be obtained by heating orthophosphourus acid.

(D) Metaphosphoric acid is obtained by the dehydration of orthophosphoric acid at 316°C.

ANSWERS

(1) A-$NaNO_3$, B-HNO_3, C-NO_2 **(2)** (D)
(3) (D) **(4)** (D) **(5)** (ABCD)
(6) (A) **(7)** (A) **(8)** (C)
(9) (A) **(10)** (C)

OXYGEN FAMILY

ELECTRONIC CONFIGURATION

The general outer electronic configuration of VI A group is ns^2np^4. Hence these elements belong to p–block

Element	Configuration
Oxygen [O_8]	[He] $2s^22p^4$
Sulphur [S_{16}]	[Ne] $3s^23p^4$
Selenium [Se_{34}]	[Ar] $3d^{10}4s^24p^4$
Tellurium [Te_{52}]	[Kr] $4d^{10}5s^25p^4$
Polonium [Po_{84}]	[Xe] $4f^{14}\,5d^{10}\,6s^26p^4$

PHYSICAL PROPERTIES

1. **Atomic radii and Ionic radii :**
   Covalent radius : $O < S < Se < Te$
2. **Ionization enthalpies :** $O > S > Se > Te > Po$ (IE_1 values)
3. **Melting and boiling points :**
   M. P. : $Te > Po > Se > S > O$
   B.P. : $Te > Po > Se > S > O$
4. **Electronegativity :** $O > S > Se > Te$
5. **Metallic character :** $O < S < Se < Te < Po$
6. **Allotropy :** All element exhibit allotropy for e.g.
   Oxygen – O_2 and O_3
   Liquid O_2 - pale base
   Solid O_2 – blue
   Sulphur – The main allotropic forms are –
   (i) Rhombic sulphur (α-sulphur) :
   This allotropes is yellow in colour (m.p. 385.8 K)
   It is insoluble in water but readily soluble in CS_2.
   (ii) Monoclinic (β-sulphur) : It is soluble in CS_2.

   $$S(\alpha)\underset{<95.5^\circ C}{\overset{>95.5^\circ C}{\rightleftharpoons}}S(\beta)$$

   (iii) Plastic sulphur (δ-sulphur) : It is insoluble in CS_2.
7. **Catenation :** In this group only S has a strong tendency for catenation oxygen has this tendency to a limited extent.
   H_2O_2 $H-O-O-H$ (Poly oxides)
   H_2S_2 $H-S-S-H$ (Polysulphides or polysulphones)
   H_2S_3 $H-S-S-S-H$
   H_2S_4 $H-S-S-S-S-H$

NOTE

* O, S, Se, Te element are collectively called chalcogens (ore forming). Most of the metal ores are oxides or sulphides.
* O, S, Se are non metals, Te is metalloid and Po is metal.
* O resembles N and F. It forms strong pπ–pπ bond. It also forms H–bond like N and F.
* Oxygen, the most abundant element (21% is present in atmosphere, constitute 46.6% of earth's crust).
* Sulphur constitute about 0.05% of earth's crust.
* S, Se, Te can make use of d–orbital and show a covalency of six and can exhibit an octahedral geometry.
* Polonium, the most metallic element is radioactive.

HYDRIDES OF GROUP 16 ELEMENTS

* Form hydrides of the formula H_2X [H_2O, H_2S, H_2Se, H_2Te and H_2Po]
* Bond angle of hydrides decreases from H_2O to H_2Po
* The volatility of hydrides increases from H_2O to H_2S then decrease. High b.p. of H_2O is due to the presence of intermolecular H–bonding.
* The acidic strength increases from H_2O to H_2Te. This is due to increase of size of the anion in the group.
* The thermal stability of hydrides increases in the order :

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po.$$

* The covalent character of hydrides increases in going from O to Po.
* H_2S, H_2Se, H_2Te and H_2Po burn in atmosphere of oxygen with blue flame forming dioxides.
e.g., $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$.
* Except H_2O all hydrides of this group are reductant. This is due to weakening of M–H bond the bond length increase with increases of size of M–atom.
* Except H_2O (liquid), all hydrides are gases at room temperature.

OXIDATION STATES

* Since all the elements of this group have ns^2p^4 configuration in their outermost orbit, they can attain noble gas configuration viz. ns^2p^6 either by gaining or by sharing two electrons. Thus these elements show both positive and negative oxidation states.
* Stability of -2 oxidation state decreases down the group.
* Polonium hardly shows –2 oxidation state.
* Since electronegativity of oxygen is very high, it shows only negative oxidation state as –2 except in the case of OF_2 where its oxidation state is +2.
* Other elements of the group exhibit +2, +4, +6 oxidation states but + 4 and + 6 are more common.
* Sulphur, selenium and tellurium usually show + 4 oxidation state in their compounds with oxygen and + 6 with fluorine.
* The stability of + 6 oxidation state decreases down the group and stability of + 4 oxidation state increase (inert pair effect).
* Bonding in +4 and +6 oxidation states are primarily covalent.

ANOMALOUS BEHAVIOUR OF OXYGEN

The anomalous behaviour of oxygen is due to :
(a) Small size (b) High electronegativity and
(c) absence of d–orbitals.

Point of difference are :

1. Oxygen is a gas while other elements are solids at ordinary temperature.
2. Oxygen is diatomic molecule while others are polyatomic (S, Se etc. are octaatomic)

3. Compounds of oxygen are more ionic than those of other elements.
4. Oxygen forms strong hydrogen bonds whereas other elements of this group from no H–bonding.
5. Oxygen is paramagnetic (molecular orbital theory) while other elements are diamagnetic.
6. Oxygen generally shows O.S. of –2, while other members exhibit o.s. of +2, +4, +6 in addition to –2.

OXYGEN [PRIESTLY AND SCHEELE]

* Oxygen constitutes 21% by volume of the atmosphere (23% by mass)
* It's abundance in earth's crust is 46%.
* It is present to the extent of 89% by weight in water.

Preparations :

1. **On heating suitable compounds such as oxides, Nb(NO_3)$_2$, $CaOCl_2$, $KMnO_4$ etc.**

$$2HgO \xrightarrow{\Delta} 2Hg + O_2, 2BaO_2 \xrightarrow{\Delta} 2BaO + O_2,$$

$$2Ag_2O \xrightarrow{\Delta} 4Ag + O_2,$$

$$3MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2, 2PbO_2 \xrightarrow{\Delta} 2PbO + O_2,$$

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + O_2 + 4NO_2,$$

$$2CaOCl_2 \xrightarrow{\Delta} 2CaCl_2 + O_2,$$

$$2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2,$$

$$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2 \text{ (Lab. method)}$$

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

2. **Reaction of water or acid with certain suitable compounds:**

$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$
$4KMnO_4 + 6H_2SO_4 \rightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2$
$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$
$2MnO_2 + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2$

Manufacture : Oxygen is obtained on commercial scale by following methods.
(a) By Brin's process.
(b) From liquid air by fractional distillation (Claude's process)
(c) By electrolysis of acidic or alkaline water.

Electrolysis of acidic and alkaline water :

$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$
At cathode : $2H^+ + 2e \rightleftharpoons H_2$
At anode : $2H_2O + 2SO_4^{2-} \rightarrow 4H^+ + 2SO_4^{2-} + O_2 + 4e$
$NaOH \rightarrow Na^+ + OH^-$
At cathode: $2Na^+ + 2H_2O + 2e \rightarrow 2Na^+ + 2OH^- + H_2$
At anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e$

Properties :

(a) Physical characteristic :

* It is colourless, odourless and tasteless gas.
* Slightly heavier than air.
* Slightly soluble in water.
* Boiling point is – 183ºC and Freezing point is –219ºC.
* Liquid oxygen is pale blue in colour.
* Paramagnetic (on the basis of molecular orbital theory). ${}_8O^{16} : {}_8O^{17} : {}_8O^{18} :: 10,000 : 1:8$

(b) Chemical characteristics : Important chemical properties of oxygen are given below :

Reactions of Na, Ca, Al, Fe are :
$4Na + O_2 \rightarrow 2Na_2O ; 2Ca + O_2 \rightarrow 2CaO$
$4Al + 3O_2 \rightarrow 2Al_2O_3 ; 3Fe + 2O_2 \rightarrow Fe_3O_4$

Reactions of C, P_4, S and H_2 :
$C + O_2 \rightarrow CO_2 ; P_4 + 5O_2 \rightarrow 2P_2O_5$
$S + O_2 \rightarrow SO_2 ; 2SO_2 + O_2 \xrightarrow{Pt} 2SO_3$
$2H_2 + O_2 \rightarrow 2H_2O$

Reactions of NH_3 and HCl :
$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$
$4HCl + O_2 \xrightarrow{Cu_2Cl_2} 2H_2O + 2Cl_2$

Reactions of organic compounds :
$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$
$C_2H_2 + 2.5O_2 \rightarrow 2CO_2 + H_2O$
$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$
$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

Uses of oxygen :

* It is used in artificial respiration (O_2 + He).
* For the combustion process.
* Liquid oxygen is used as a fuel in the rockets.
* For oxyacetylene (3300ºC) and oxyhydrogen (2800ºC) flames, employed in cutting and welding purposes.
* As an oxidant in several reactions.
* In the preparation of several important oxides.

SIMPLE OXIDES

* A binary compound of oxygen with another element is called oxide.
* Oxides can be simple (e.g., MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4).
* Simple oxides can be classified on the basis of their acidic, basic or amphoteric character.

Classification of oxides :

1. **Acidic oxides :** $H_2O + CO_2 \rightarrow H_2CO_3$
e.g. CO_2, B_2O_3, SiO_2, N_2O_3, NO_2, N_2O_5, P_4O_6.
Note : Mixed anhydrides → Those oxides which form two oxy axids.
e.g. $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$
$P_4O_8 + 6H_2O \rightarrow 2H_3PO_3 + 2H_3PO_4$
$SiO_2 + 2NaOH \rightarrow \underset{\text{salt}}{Na_2SiO_3} + \underset{\text{water}}{H_2O}$

2. **Basic oxides :**
Oxide + H_2O → alkali ; e.g. $Na_2O + H_2O \rightarrow 2NaOH$
Oxide + acid → salt + H_2O
e.g. $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$
Oxide + Acidic oxide → salt; e.g. $PbO + SO_3 \rightarrow PbSO_4$.

3. **Neutral Oxide:** Oxide + Acid → No reaction
Oxide + Base → No reaction
e.g. CO, H_2O, N_2O, NO etc.

4. **Amphoteric oxides :** React with acid & base both to form salts.e.g. ZnO, Al_2O_3, BeO, Sb_2O_3, Cr_2O_3, PbO, PbO_2 etc.

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$
$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$
$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$
$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$
$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$$
$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$$
$$Cr_2O_3 + 2NaOH \rightarrow Na_2Cr_2O_7 + H_2O$$
$$Cr_2O_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2O$$

5. **Compound or mixed oxides :** Oxides which behaves as mixture of two simple oxides. e.g. Pb_3O_4 $(2PbO + PbO_2)$
Fe_3O_4 $(FeO + Fe_2O_3)$; Mn_3O_4 $(2MnO + MnO_2)$

6. **Peroxides :** Oxides + dil acids → H_2O_2
e.g. $Na_2O_2 + H_2SO_4\,(dil) \rightarrow Na_2SO_4 + H_2O_2$
$BaO_2 + H_2SO_4\,(dil) \rightarrow BaSO_4 + H_2O_2$

7. **Dioxides :** Like peroxides, these also contain excess of oxygen but do not form H_2O_2 with dilute acids. They evolve chlorine with conc. HCl and oxygen with conc. H_2SO_4.
e.g. → PbO_2, MnO_2
$MnO_2 + 4HCl\ conc. \rightarrow MnCl_2 + Cl_2 + 2H_2O$
$2MnO_2 + 2H_2SO_4\,(conc.) \rightarrow 2MnSO_4 + O_2 + 2H_2O$

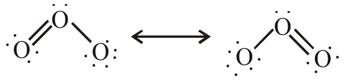
8. **Suboxides :** The oxides which contain less oxygen than expected from the normal valency of the elements are termed sub-oxides. e.g. Carbon suboxide - C_3O_2
Lead suboxide - Pb_3O ; Nitrous oxides - N_2O

9. **Superoxides :** These oxides contain O_2^- ion.
e.g. KO_2, RbO_2, CsO_2.
These react with water to give hydrogen peroxide and oxygen. $2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$

OZONE

Ozone is an allotropic form of oxygen. It is too reactive to remain for long in the atmosphere at sea level. At a height of about 20 kilometres, it is formed from atmospheric oxygen in the presence of sunlight. This ozone layer protects the earth's surface from an excessive concentration of ultraviolet (UV) radiations.

Structure of ozone : The two oxygen-oxygen bond lengths in the ozone molecule are identical (128 pm) and the molecule is angular as expected with a bond angle of about 117°. It is a resonance hybrid of two main forms:



Properties :

* In high concentrations ozone is perceptibly blue. In the liquid condition, it is dark blue in colour.

* The liquid ozone (B.pt.–112.4°) is paramagnetic.

* It is not much miscible with liquid oxygen.

* Even in fair concentration (20 parts per million), ozone is poisonous.

* Ozone is heavier than air and slightly soluble in water but more soluble in turpentine oil.

* Ozone acts as a powerful oxidising agent.

* It is better oxidising agent as compared to H_2O_2.
$H_2O_2 + O_3 \rightarrow H_2O + 2O_2$
$BaO_2 + O_3 \rightarrow BaO + 2O_2$

* Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive).

* When ozone reacts with an excess of potassium iodide solution buffered with a borate buffer (pH 9.2), iodine is liberated which can be titrated against a standard solution of sodium thiosulphate. This is a quantitative method for estimating O_3 gas.

Test of Ozone : In presence of O_3, mercury loses its meniscus and starts sticking to glass. This is known as tailing of mercury. It does not release iodine from KI in presence of $FeSO_4$. In this way it is different from H_2O_2.

Preparation :

* Ozone is obtained when silent electric discharge is passed through pure, cold and dry dioxygen in a specially designed apparatus called the ozoniser. During this reaction, conversion of O_2 to ozone is 10% and the product is called ozonised oxygen.

$$3O_2 \xrightleftharpoons{\text{Silent electric discharge}} 2O_3\,(g)$$
$$\Delta H^\ominus\,(298\,K) = +142\ kJ\ mol^{-1}$$

Since the formation of ozone from oxygen is endothermic therefore, it is necessary to use a silent electric discharge in its preparation.

* Ozone is produced when carbon monoxide or hydrogen flame impinges on liquid oxygen. It is also produced in acetylene flames, or when a platinum wire is electrically heated under liquid oxygen.

Uses of ozones :

(i) As a germicide and disinfectant, it is used in sterilising water and improving the atmosphere in crowded places like underground tunnels, tube railways and mines.

(ii) It is used for bleaching oil, ivory, starch, wax and delicate fabrics.

(iii) It is used in the production of synthetic camphor and artificial silk.

(iv) It is also used in the manufacture of potassium permanganate.

SULPHUR

Constitute about 0.1% earth's crust.

Extraction :

(a) Main source of sulphur are : Sicily and Louisiana the processes employed are called :
Sicilian process and Louisiana (or Frasch) process :

(b) Sulphur from alkali wastes, spent oxides of coal gas and iron pyrites :

Alkali wastes : Contain CaS.

$$CaS + H_2O + CO_2 \rightarrow CaCO_3\downarrow + H_2S\uparrow$$
$$2H_2S + O_2 \rightarrow 2H_2O + S\downarrow$$

Spent oxides of coal gas : Contain Fe_2S_3

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S\downarrow$$

Iron pyrites :

$$3FeS_2 \xrightarrow{\text{distillation}} Fe_3S_4 + 2S\downarrow$$
$$3FeS_2 \xrightarrow{\Delta} Fe_3S_4 + 3O_2 + 3S\downarrow$$
$$FeS + CO_2 \xrightarrow{\Delta} FeO + CO + S\downarrow$$

Flowers of sulphur : In the purification process, vapours of boiling sulphur (444ºC) are condensed on the cold walls of the vessel as a light yellow powder called flowers of sulphur.

Chemical characteristics :

Reactions with H_2, Cl_2, C, As the Fe :

$$H_2 + S \rightarrow H_2S,\ Cl_2 + 2S \rightarrow S_2Cl_2$$
$$C + 2S \rightarrow CS_2,\ 2As + 3S \rightarrow As_2S_3\ ;\ Fe + S \rightarrow FeS$$

Reaction with conc.. HNO_3, conc. H_2SO_4 and NaOH

$$S + HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$$
$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$
$$4S + 6NaOH \rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$$

Reactions with K_2S : $K_2S + 4S \rightarrow K_2S_5$

Allotropic forms :

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

Rhombic sulphur :

* This is also designated as α-sulphur.
* This is the most stable variety of sulphur. All other varieties of sulphur eventually revert to rhombic form on standing.
* Rhombic sulphur is prepared by dissolving powdered sulphur in carbon disulphide at room temperature. The mixture is then filtered.
  The filtrate is then kept in a small beaker covered with a filter paper. The carbon disulphide will slowly evaporate away leaving behind large octahedral crystals of rhombic sulphur (or α-sulphur).
* It exists as rhombic octahedral crystals.
* Its density is 2.06 g/mL.
* It melts at 112.8°C
* When slowly heated to 96°C, it changes into monoclinic or β-sulphur. However, when cooled below 96°C, it returns back to rhombic form.
* It is insoluble in water but dissolves to some extent in benzene, alcohol and ether. It is readily soluble in CS_2.

Monoclinic sulphur (β-sulphur) :

* Its m.p. is 393 K and specific gravity 1.98.
* It is soluble in CS_2.
* It 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 369K both the forms are stable. This temperature is called transition temperature.

Structure of rhombic and monoclinic sulphur:

* Both 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 fig. (a).
* 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 dimensions are as shown in Fig. (b). At elevated temperatures (~1000 K), S_2 is the dominant species and is paramagnetic like O_2.

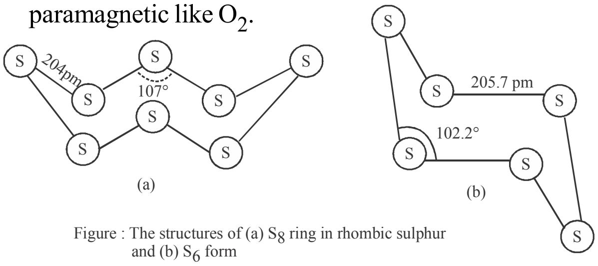


Figure : The structures of (a) S_8 ring in rhombic sulphur and (b) S_6 form

Uses of sulphur :

* In the manufacturer of SO_2, H_2SO_4, CS_2, matches, gun powder.
* Used for destroying bacteria, fungi, insects, etc.
* Used for Vulcanizing rubber and in the manufacture of sulphur dyes.
* Used in medicines.

Milk of Sulphur :

$$\text{Powdered S} + Ca(OH)_2 \text{ suspension} \rightarrow \text{Solution} \xrightarrow{\text{Acidified}} \text{Milk of S}$$

$$12\,S + 3Ca(OH)_2 \rightarrow 2CaS_5 + CaS_2O_3 + 3H_2O$$
$$2CaS_5 + CaS_2O_3 + 6\,HCl \rightarrow 3CaCl_2 + 12S + 3H_2O$$

Colloidal sulphur :

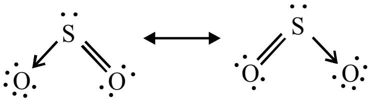
$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 + S\downarrow$$
$$2H_2S + SO_2 \rightarrow S\downarrow + 2H_2O$$

OXIDES OF SULPHUR

Name	**Formula**	**Nature**
Sulphur suboxide	S_2O	Colourless gas
Sulphur monoxide	SO	Colourless gas
Sulphur sesquioxide	S_2O_3	Green crystalline solid
Sulphur dioxide	SO_2	Colourless gas
Sulphur trioxide	SO_3	Volatile liquid
Sulphur heptoxide	S_2O_7	Liquid
Sulphur tetroxide	SO_4	White solid.

SULPHUR DIOXIDE SO_2

Structure : Sulphur dioxide forms discrete molecules even in solid state. Electronically sulphur dioxide is known to be a resonating hybrid of the following two structures. The S – O distance is 1.43Å and O – S – O angle is 119.5°.



Methods of preparation :

Laboratory methods :

$S + 2H_2SO_4 \rightarrow H_2O + 3SO_2\uparrow$
$Cu + 2H_2SO_4\,(conc.) \rightarrow CuSO_4 + 2H_2O + S_2\uparrow$
$2Ag + 2H_2SO_4\,(conc.) \rightarrow Ag_2SO_4 + 2H_2O + SO_2\uparrow$
$Na_2SO_3 + 2HCl\,(dil.) \rightarrow 2NaCl + H_2O + SO_2\uparrow$
$NaHSO_4 + HCl\,(dil.) \rightarrow NaCl + H_2O + SO_2\uparrow$

Industrial method : $S + O_2 \rightarrow SO_2\uparrow$
$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2\uparrow$
$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2\uparrow$
$2CaSO_4 + C \rightarrow 2CaO + 2SO_2\uparrow + CO_2$

Chemical characteristics :

Aqueous solutions of SO_2 acts as a reducing agent :

$H_2O + SO_2 \rightarrow H_2SO_3$;
$H_2SO_3 + H_2O \rightarrow H_2SO_4 + [H]$ (nascent hydrogen)
$2KMnO_4 + 5SO_2 + 2H_2O$
$\rightarrow K_2SO_4 + 2MnSO_4$ (colourless) $+ 2H_2SO_4$
$K_2Cr_2O_7 + 3SO_2 + H_2SO_4$
$\rightarrow K_2SO_4 + Cr_2(SO_4)_3$ (green) $+ H_2O$

Acts as an oxidising agent :

$Mg + SO_2 \rightarrow 2MgO + MgS$
$4K + \rightarrow 3SO_2 \rightarrow K_2SO_3 + K_2SO_4$
$2SnCl_2 + SO_2 + 4HCl \rightarrow SnCl_4 + 2H_2O + S$
$2Hg_2Cl_2 + SO_2 + 4HCl \rightarrow 4HgCl_2 + 2H_2O + S$

Acts as bleaching agent (due to reducing nature)

$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$
Coloured matter + H → Colourless matter

Acidic nature (SO_2) is an acidic oxide)

$SO_2 + H_2O \rightarrow H_2SO_3$; $BaO + SO_2 \rightarrow BaSO_3$

Addition reaction :

$SO_2 + Cl_2 \rightarrow SO_2Cl_2$ (Sulphurly chloride)
$PbO_2 + SO_2 \rightarrow PbSO_4$

Thermal decomposition : $3SO_2 \xrightarrow{1200°C} 2SO_3 + S$

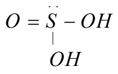
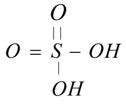
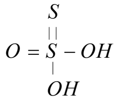
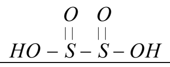
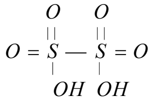
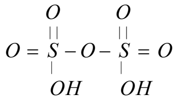
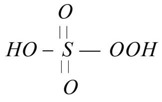
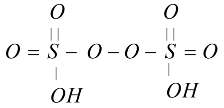
Reaction with burning Mg : $3Mg + SO_2 \rightarrow 2MgO + MgS$

Uses of SO_2

* Used in the manufacture of H_2SO_4, paper (from wood pulp)
* Used as disinfectant, antechoir, bleaching agent.
* As a refrigerant (liquid SO_2)
* Used in refining petroleum and sugar.

OXOACIDS OF SULPHUR

Sulphur forms a number of oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$ (x = 2 to 5), H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts.

Formula	Name	Important properties	Structural formula
H_2SO_3 (+4)	Sulphurous acid	Free acid does not exist diprotic, strong reducing agent	 $O = \underset{\underset{OH}{\vert}}{\overset{..}{S}} - OH$
H_2SO_4 (+6) (Oil of vitriol)	Sulphuric acid	Stable diprotic, dehydrating agent	 $O = \underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{S}} - OH$
$H_2S_2O_3$ (–2 and +6)	Thiosulphuric acid	Free acid does not exist but its salts e.g. $Na_2S_2O_3$ All quite stable reducing agent	 $O = \underset{\underset{OH}{\vert}}{\overset{\overset{S}{\Vert}}{S}} - OH$
$H_2S_2O_4$ (+3)	Dithionous acid		 $HO - \overset{\overset{O}{\Vert}}{S} - \overset{\overset{O}{\Vert}}{S} - OH$
$H_2S_2O_6$ (+5)	Dithionic acid	Free acid is moderately stable but its salts are quite stable.	 $O = \underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{S}} — \underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{S}} = O$
$H_2S_2O_7$ (+6) (Oleum)	Disulphuric acid (Pyrosulphuric acid)	Strong oxidising agent	 $O = \underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{S}} - O - \underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{S}} = O$
H_2SO_5 (+6) (Caro's acid)	Peroxomonosulphuric acid (Its salts known as persulphates)	Stable crystalline solid, powerfull oxidising agent	 $HO - \underset{\underset{O}{\Vert}}{\overset{\overset{O}{\Vert}}{S}} — OOH$
$H_2S_2O_8$ (+6) (Marshals acid)	Peroxodisulphuric acid (its salts are known as disulphates)	Strong oxidising agent.	 $O = \underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{S}} - O - O - \underset{\underset{OH}{\vert}}{\overset{\overset{O}{\Vert}}{S}} = O$

SULPHURIC ACID [H_2SO_4] :

- It is a king of chemicals.
- It is also known as oil of vitriol.
- The three step process for the preparation of H_2SO_4 is described as : $S \rightarrow SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$

Manufacture :

[a] Lead chamber process [b] Contact process

(a) **Lead chamber process :** Here oxidation of SO_2 is affected catalytically by means of oxides of nitrogen in the presence of water.

$2SO_2 + O_2(air) + 2H_2O + [NO]\ (catalyst) \rightarrow 2H_2SO_4 + [NO]$

Mechanism may be described as :

$2NO + O_2 \rightarrow 2NO_2$

$NO_2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$

The unreacted gases (NO, NO_2, O_2 and N_2) are absorbed in H_2SO_4 and nitrosyl sulphuric acid. The product on decomposition gives H_2SO_4.

$2H_2SO_4 + NO + NO_2 \rightarrow 2NO^{+}H\,SO_4^{-} + H_2O$

$2NOHS_4 + H_2O \rightarrow 2H_2SO_4 + NO\uparrow + NO_2\uparrow$

(b) **Contact process :** It involves the oxidation of SO_2 by air in presence of a catalyst

$$2SO_2 + O_2 \xrightarrow[\text{Pt or } V_2O_5]{Fe_2O_3 \text{ or}} 2SO_3$$

SO_3 is dissolved in 98% sulphuric acid resulting in the formation of oleum.

$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$ (oleum)

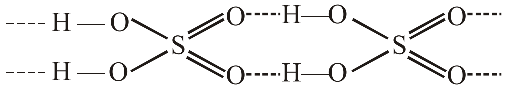
On dilution, H_2SO_4 of required concentration can be obtained.

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

PROPERTIES

Physical characteristics :

- H_2SO_4 is colourless, only liquid.
- Freezing point and boiling point are 10.5ºC and 340ºC respectively. Forms constant boiling mixture (at 370ºC) containing 98.33% of the acid.
- Density is 1.84 gm cm^{-3}.
- Forms hydrate with the evolution of heat :
  $H_2SO_4.H_2O$ [monohydrate], $H_2SO_4.2H_2O$ [dihydrate], $H_2SO_4.3H_2O$ [tri hydrate]
- Conductor of heat and electricity
- High b.p. and viscosity of H_2SO_4 is due to H–bonding.



Chemical characteristics :

Acid character (dibasic acid)

$H_2SO_4 \rightarrow H^+ + HSO_4^-$, $HSO_4^- \rightarrow H^+ + SO_4^{2-}$

Forms two type of salts :

$NaOH + H_2\,SO_4 \rightarrow NaH\,SO_4 + H_2O$

$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$

Dehydrating agent [due to high affinity for water]

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

$$HCOOH \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$$

$$3C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4} C_2H_4 + (C_2H_5)_2O$$

Acts as an oxidizing agent

$C + 2H_2SO_4 \rightarrow CO_2\uparrow + 2SO_2\uparrow + 2H_2O$

$2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2\uparrow + Br_2$

$H_2S + H_2SO_4 \rightarrow 2H_2O + SO_2\uparrow + S$

Displaces more volatile acids :

$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$

$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$

$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$

$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4$

Reaction with metals : Zn, Mg, Fe gives hydrogen :

$Zn + H_2SO_4(dil) \rightarrow ZnSO_4 + H_2$

Cu gives SO_2.

$Cu + 2H_2SO_4\ (conc.) \rightarrow CuSO_4 + 2H_2O + SO_2$

Formation of insoluble sulphates :

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$

$Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4\downarrow + 2HNO_3$

Reaction with PCl_5 and $KClO_3$:

$PCl_5 + H_2SO_4 \rightarrow ClSO_2OH + POCl_3 + HCl$

$3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + HClO_3 + 2ClO_2 + H_2O$

Uses of H_2SO_4 :

- Used as a laboratory reagent.
- Used in the manufacture of acids (HNO_3, HCl, H_3PO_4), dyes, drugs, disinfectants,alum, ferrous sulfate for ink etc.
- Used as a dehydrating and oxidizing agents.
- Used in the textile, paper and dyeing industries.
- Used in leather industry for tanning.
- Used in the refining of petroleum.
- Used in the manufacture of explosives such as nitroglycerine gun coating, TNT, picric acid acid.
- Used in lead storage batteries.
- Used for cleansing metals before electroplating, enameling, galvanizing etc.

Sulphurous acid (H_2SO_3):

Preparation: It is formed when SO_2 is dissolved in water

$SO_2 + H_2O \rightarrow H_2SO_3$

Properties:

- It acts as reducing agent and its chemical properties are similar to those of solution e.g.
  $2FeCl_3 + (SO_2 + H_2O) + H_2O \rightarrow 2FeCl_2 + H_2SO_4 + 2HCl$
- It reacts with iron, forming ferrous sulphite and ferrous thiosulphate.
  $2Fe + 2H_2SO_3 \rightarrow FeSO_3 + FeS_2O_3 + 3H_2O$

Reactions:

It is strong diprotic acid

$H_2SO_3 \rightarrow H^+ + HSO_3^-$

$HSO_3^- \rightarrow H^+ + SO_3^{2-}$

$NaHSO_3 + HCl \rightarrow NaCl + H_2O + SO_2$

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

As reducing agent

$SO_3^{-} + I_2 + H_2O \rightarrow H_2SO_4 + 2I^{-}$

$2FeCl_3 + H_2SO_3^{-} + H_2O \rightarrow 2FeCl_2 + H_2SO_4 + 2HCl$

$MnO_4^{-} + 5SO_3^{2-} + 6H^{+} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^{+} \rightarrow 3SO_4^{2-} + 2Cr^{3+} + 4\,H_2O$

$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$):

If one of the oxygen atoms in the sulphate ion is replaced by sulphur, the resulting ion ($S_2O_3^{2-}$) is as known as thiosulphate.

Preparation:

* Sodium thiosulphate is prepared by boiling aq. solution of metal sulphites with elemental sulphur.

$$Na_2SO_3 + (1/8)\,S_8 \xrightarrow[373\,K]{H_2O} Na_2S_2O_3$$

Hydrated sodium thiosulphate $Na_2S_2O_3.5H_2O$ is known as HYPO

* Spring's reaction may be used for the preparation of sodium thiosulphate. It consists in treating a mixture of sodium sulphide and sodium sulphite with calculated quantity of iodine. $Na_2S + Na_2SO_3 + I_2 \rightarrow Na_2S_2O_3 + 2NaI$

Properties :

Reaction with dilute acids : It reacts with dilute acids to liberate sulphur dioxide gas along with precipitate of sulphur. $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + S\downarrow + SO_2$

Reaction with $BaCl_2$

It gives white ppt. of barium thiosulphate.

$S_2O_3^{2-} + Ba^{2+} \rightarrow \underset{\text{white}}{BaS_2O_3}\downarrow$

Reaction with Silver Nitrate Solution

Gives white ppt. which quickly changes to yellow, brown and finally black due to the formation of silver sulphide.

$S_2O_3^{2-} + 2Ag^{+} \rightarrow \underset{\text{white ppt}}{Ag_2S_2O_3}\downarrow$

$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$

With conc. solution of sodium thiosulphate, silver nitrate gives no ppt.

* It reacts with silver salts to form sodium argento thiosulphate complex

$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag\,(S_2O_3)_2]$

Sodium argento thiosulphate complex

* Thiosulphate ($S_2O_3^{2-}$) ion is oxidized by iodine I_2 to tetrathionate ($S_4O_6^{2-}$) ion

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI.$

HYDROGEN SULPHIDE

* It is colourless gas having foul smell of rotten eggs.

* H_2S has angular (bent) structrue figure like that of water.

* Prepared by the action of dil. HCl or H_2SO_4 on iron sulphide

$FeS + 2HCl\,(dil)\,) \rightarrow FeCl_2 + H_2S\uparrow$

Properties: !t is a colourless, poisonous gas having the smell of rotten eggs.

As reducing agent

Action on halogens : $H_2S + Cl_2 \rightarrow 2HCl + S\downarrow$

Action on $FeCl_3$: $2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S\downarrow$

Reaction with acidified $KMnO_4$

$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + S\downarrow$

Reaction with acidified $K_2Cr_2O_7$

$K_2Cr_2O_7 + 4\,H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + S\downarrow$

TRY IT YOURSELF-2

Q.1 Find out the oxidation state of sulphur in thiosulphuric acid and its basicity

Q.2 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 $H_2S_2O_7$

Q.3 Which of the following is not a reducing oxide?
(A) SO_2 (B) SeO_2
(C) TeO (D) SO_3

Q.4 Pick out the incorrect statement.
(A) central oxygen in O_3 is sp^2 hybridised.
(B) the two O – O bonds in O_3 are equal
(C) with BaO_2, O_3 reacts to produce H_2O_2
(D) O_3 causes tailing of mercury

Q.5 Which of the following compounds does not exist
(A) SF_6 (B) S_2Cl_2
(C) SCl_2 (D) $SeBr_2$

Q.6 S_8 ring of both rhombic sulphur and monoclinic sulphur has crown shaped structure. The S – S – S bond angle in S_8 ring is –
(A) 109°28' (B) 107°
(C) 104° (D) 120°

Q.7 Maximum covalency of sulphur is –
(A) 2 (B) 4
(C) 6 (D) –2

Q.8 Number of S = O bonds in pyrosulphuric acid are
(A) Two (B) Four
(C) Five (D) Six

Q.9 The correct order of acidity of hydrides of oxygen family
(A) $H_2O > H_2S > H_2Se > H_2Te$
(B) $H_2O < H_2S < H_2Se < H_2Te$
(C) $H_2S > H_2O > H_2Se > H_2Te$
(D) $H_2S < H_2O < H_2Se < H_2Te$

Q.10 Identify the correct sequence of increasing number of π-bonds in structures of the following molecules
(I) $H_2S_2O_6$ (II) H_2SO_3 (III) $H_2S_2O_5$
(A) I, II, III (B) II, III, I
(C) II, I, III (D) I, III, II

ANSWERS

(1) Oxidation state = +6 & –2 ; Basicity = 2
(2) (A) **(3)** (D) **(4)** (C)
(5) (D) **(6)** (B) **(7)** (C)
(8) (B) **(9)** (B) **(10)** (B)

HALOGEN FAMILY

ELECTRONIC CONFIGURATION

The general outer electronic configuration of elements of VII group is ns^2np^5. Hence these elements belong to p–block.

Element	Configuration
Fluorine $[F_9]$	$[He]\ 2s^22p^5$
Chlorine $[Cl_{17}]$	$[Ne]\ 3s^23p^5$
Bromine $[Br_{35}]$	$[Ar]\ 3d^{10}4s^24p^5$
Iodine $[I_{53}]$	$[Kr]\ 4d^{10}5s^25p^5$
Astatine $[At_{85}]$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^26p^5$

* First four member F, Cl, Br and I are called halogens as their salts are present in sea water.

* At is radioactive, artificially prepared and unstable.

* Strong tendency to accept one electron to acquire stable inert gas configuration. Hence exhibit nonmetallic behaviour.

* High electronegativity makes them very reactive and here they are not available in free state.

* Except At, the members are found in combined state in suitable quantities in nature.

GENERAL PHYSICAL PROPERTIES

(i) Physical state :

F	Cl	Br	I
Gas	Gas	Fuming liquid	Volatile solid

(ii) Colour : Halogens are coloured

F	Cl	Br	I
Pale yellow	Greenish yellow	Reddish brown	Deep violet

The molecules absorb visible region of light for excitation of outer electrons to higher energy levels.

Fluorine – [Absorbs violet light] → Appears pale yellow

Iodine – [Absorbs yellow light] → Appears violet

(iii) Atomic Radii, Ionic Radii, Boiling point and Melting point, Density: All these character increases down the group.

(iv) Ionisation potential and Electronegativity : Down the group atomic size increases so IP & EN decreases down the group.

(v) Electron Affinity (E.A.) : Cl > F > Br > I. Generally down the group electron affinity decreases but the electron affinity of Cl is more than F because due to the small size and high electron density of F the incoming electron is not easily enters as comparison Cl because it's size not as small as size of F and not large as Br and I.

(vi) Valency and Oxidation state :

(a) ns^2np^5 (b) Valency = 1

If Halogens combines with more E.N. elements then O.S. = + 1.

(vii) Bond energy : F – F bond dissociation energy is less than that of Cl – Cl and Br – Br. It is due to larger inter electronic (electron - electron) repulsion between the non bonding electrons in the 2p orbitals of fluorine atom then these in the 3p orbitals of chlorine atoms.

F – F	Cl – Cl	Br – Br	I – I
38 kcal/mol	57 kcal/mol	45.5 kcal/mol	35.6 kcal/mol

$Cl_2 > Br_2 > F_2 > I_2$

(viii) Oxidising Power :

The electron affinity, or tendency to gain electrons reaches a maximum at chlorine. Oxidation may be regarded as the removal of electron so that an oxidising agent gains electrons. Thus the halogens act as oxidizing agents.

The strength of an oxidising agent (i.e. oxidation potential) depends upon several energy terms and represented by following diagram.

$$X_2 \xrightarrow{(\Delta H)\text{ disso.}} 2X \xrightarrow[(\Delta H)_{eg.}]{+2e^-} 2X^- \xrightarrow{(\Delta H)\text{ hydra.}} \text{hydrated ion}$$

ΔH (reduction potential) = ΔH (dissociation energy) + ΔH (electron gain enthalpy) + ΔH (hydration energy)

Reduction potential for

$F_2 : -186.5\ ;\ Cl_2 : -147.4\ ;\ Br_2 : -136.4\ ;\ I_2 : -122.4$

Thus oxidising powers decrease on descending in group VII. Fluorine is so strong oxidising agent that H oxidizes water to oxygen. The oxidation of H_2O by Cl_2 is thermodynamically possible but since the energy of activation is high this reaction does not occur.

$$F_2 + H_2O \rightarrow 2H^+ + 2F^- + \tfrac{1}{2}O_2$$

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

Iodine is even weaker oxidising agent and the free energy change indicate that energy would have to be supplied to make it oxidise water.

CHEMICAL CHARACTERISTICS

Halogens are most reactive due to :

(i) Low bond dissociation energy.

(ii) High electron affinities

In halogen F_2 is the most reactive I_2 is least reactive

Reaction with water :

$$F_2 \xrightarrow{+H_2O} O_2, O_3$$

$$(Cl_2 \text{ or } Br_2)\ X_2 \xrightarrow[\text{sun light}]{+H_2O} HX, HXO$$

$$I_2 \xrightarrow{+H_2O} \text{no reaction}$$

Reaction with metals and nonmetals :

* F_2 combines with metals to give fluorides.

* Cl_2, combines with large number of metals. The reaction is slow.

* Br_2 and F_2 do not react with noble and less active metals.

Examples : CuF_2, NaF, KI, NaCl, NaBr, $MgCl_2$

* X_2 combines with nonmetals like S, P, As etc.

Reaction with hydrocarbons :

* F_2 decomposes hydrocarbons

$$CH_4 + 2F_2 \rightarrow C + 4HF$$

Cl_2 and Br_2 gives substitution reaction.

$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl, CH_2Cl_2, CHCl_3, CCl_4$$

* I_2 has practically no action on hydrocarbons.

Halogen displacement reaction :

* Fluorine replaces (Cl, Br, I)
* Chlorine replaces (Br, I)

$2NaX + F_2 \rightarrow 2NaF + X_2$ [X = Cl, Br, I]

$2NaX + Cl_2$

$2NaCl + X_2$ [X = Br, I]

$2NaX + Br_2 \rightarrow 2NaBr + X_2$ [X = I]

Reaction with alkalines :

Cl_2, Br_2 and I_2 behave similarly when treated with alkali (It is a disproportionation reaction)

Cold and dilute alkali :

$$X_2 + 2NaOH \rightarrow NaX + \underset{\text{Sodium hypohalite}}{NaXO} + H_2O$$

Hot and concentrated alkali :

$$2X_2 + 6NaOH \rightarrow 5NaX + \underset{\text{Sodium halate}}{NaXO} + H_2O$$

F_2 behaves differently with alkalies :

$F_2 + 2NaOH\ (dil) \rightarrow 2NaF + OF_2 + H_2O$

$2F_2 + 4NaOH \rightarrow 4NaF + O_2 + 2H_2O$

Reaction with hydrogen :

$$H_2 + F_2 \xrightarrow{\text{dark}} 2HF$$
$$H_2 + Cl_2 \xrightarrow{\text{diffused sunlight}} 2HCl$$
$$H_2 + Br_2 \xrightarrow{\Delta} 2HBr$$
$$H_2 + I_2 \rightleftharpoons 2HI\ (\text{catalyst})$$

Table : Comparison of chlorine, Bromine and Iodine

S.N.	Property	Chlorine	Bromine	Iodine
1	Physical State	Gas	Liquid	Solid
2	Colour of Vapour	Greenish Yellow	Dark Red	Violet
3	Action of H_2O	Decomposes into HCl & O_2	Decomposes slowly in presence of light	No action
4	Oxidising Action	Strong	Good	Weak
5	Bleaching Action	Moist Cl_2 is a Good Bleaching agent	Moist Br_2 is a good bleaching agent	No Bleaching
6	Action of Halides	Displaces Br_2 & I_2	Displaces I_2	No Action
7	Combination with H_2	Explosive in Light Slow in Dark	Only on heating	Heating + Catalyst

OXY-ACIDS OF HALOGENS

* F forms only one oxy acid HOF (hypfluorous acid)
* Cl, Br and I form four series of acids.

Acid–character :

* The acid – character of the oxy acids of same halogen increases with the increase in the oxidation number of the halogen. **Example :** HOCl > HOBr > HOI
  $HClO_3 > HBrO_3 > HIO_3$
  $HClO_4 > HBrO_4 > HIO_4$

Oxidising power : Oxidizing power of the oxy acids of same halogen decreases with the increase of O.S. of halogen.

Example : $HOCl > HClO_2 > HClO_3 > HClO_4$

The order of oxidizing power of parhelic acid (or their salts) follows the order : $ClO_4 < BrO_4^- < IO_4^-$

Thermal stability : Thermal stability of oxyacid of chlorine follows the order : $HOCl < HClO_2 < HClO_3 < HClO_4$

Stability of conjugate bases :

ClO^-, ClO_2^-, ClO_3^-, ClO_4^- are the conjugate bases of the acids HClO, $HClO_2$, $HClO_3$ and $HClO_4$.

Conjugate bases [$HX + H_2O \rightleftharpoons H_3O^+ + A^-$]

The stability of conjugate bases of oxy acids increases with the increase in the number of oxygen atoms in the anion thus : $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$

ANOMALOUS BEHAVIOUR OF FLUORINE

Anomalous behaviour of Fluorine is due to :

– Small size, – high electronegativity

– Non – availability of d–orbital, –low dissociation energy

– Highest positive reduction potential.

Main points of differences are :

* Fluorine shows only –1 oxidation state.
* Fluorine exhibits one as its covalency.
* Fluorine forms inter and intramolecular H–bonding.
* HF is weak acid as compared to HCl, HBr and HI.
* Fluorine forms two series of salts [$NaHF_2$ and Na_2F_2]
* AgF is soluble in water while AgCl, AgBr and AgI are insoluble.
* Fluorine does not forms oxy acids while oxy acids of other halogens are well known ($HClO_3$, HBrO, HiO_4 etc.]
* Fluorine is most reactive amongst halogens (due to low F–F energy).
* Fluorine forms SF_6 whereas no other halogens forms SX_6.
* CaF_2 is insoluble in water whereas $CaCl_2$, $CaBr_2$ and CaI_2 are soluble.
* Fluorides are more stable than other halides UF_6 is more stable than UCl_6. NF_3 is stable while NCl_3 is unstable and explosive. SF_6 is stable SCl_6 is unstable.
* Fluorine directly combines with carbon whereas other halogens do not.
* F^- has more complex forming tendency as compared to other halides ions. $[(AlF_6]^{3-}$, $[FeF_6]^{3-}]$
* Fluorine does not form poly halide ion like I_3^-, Br_3^- etc.

FLUORINE

Occurrence : Fluorine is very reactive and hence it does not occur in free state. In combined state it occurs as :

* Fluorspar [CaF_2] * Cryolite [Na_3AlF_6]
* Fluorapatite [$CaF_2 . 3Ca_3 (PO_4)_2$]

Fluorine occurs in small quantities in plant, teeth, bones, sea water etc.

Reaction of F_2 are :

Directly combines with metals and non metals

$2Na + F_2 \rightarrow 2NaF_2$ $\quad$ $2B + 3F_2 \rightarrow 2BF_3$

$Mg + F_2 \rightarrow MgF_2$ $\quad$ $C + 2F_2 \rightarrow CF_4$

$2Ag + F_2 \rightarrow 2AgF$ $\quad$ $P_4 + 10F_2 \rightarrow 4PF_5$

Reaction with H_2, O_2 :

$H_2 + F_2 \rightarrow H_2F_2$ (expoldes even in dark)
$O_2 + F_2 \rightarrow O_2F_2$ (explodes in presence of silent electric discharge)

Reaction with HCl, H_2S and NH_3 :

$2HCl + F_2 \rightarrow 2HF + Cl_2$
$H_2S + 4F_2 \rightarrow 2HF + SF_6$
$2NH_3 + 3F_2 \rightarrow 6HF + N_2$

Reaction with NaOH :

$2F_2 + 2NaOH\ (dil) \rightarrow 2NaF + OF_2 + H_2O$
$2F_2 + NaOH\ (conc.) \rightarrow 4NaF + O_2 + 2H_2O$

Reaction with halides :

$2NaX + F_2 \rightarrow 2NaF + X_2$
$[X = Cl^-, Br^-, I^-]$ $[X_2 = Cl_2, Br_2, I_2]$

* Reacts with water to give O_2 and O_3
* Reacts with other halogens to form inter halogen compounds [ClF, ClF_3, IF_3, IF_7 etc.]
* Reacts with CH_4 explosively to give CH_3, F, CH_2F_2, CHF_3 and CF_4.

Uses :

1. Fluorides are used as insecticides (CaF_2 is added to tooth paste).
2. Sodium and antimony fluorides are used as mordants in dyeing industry.
3. Freons (poly chloro fluoro alkanes) are used in refrigeration and air conditioning.
4. Br_2 and HF are used as catalyst in petroleum industry.
5. CuF_2 is used in ceramic industry.
6. Teflon (C_2F_4) is polymer used as insulting material in cables.
7. For the separation of U^{235} from natural uranium, UF_6 is used.
8. Na_3AlF_6 and CaF_2 are used for the extraction of aluminium.
9. Sodium fluoro acetate is used as rat poison.

CHLORINE

Occurrence : It is widely distributed in the form of chlorides. NaCl is the most important chloride occurs in sea water, lakes and in rocks.

Chloride mineral are :

* Rock salt [NaCl] . Sylvine (KCl)
* Carnallite [$KCl.MgCl_2.6H_2O$]
* Horn silver [AgCl]

Preparation :

1. By the oxidation of HCl by MnO_2, $K_2Cr_2O_7$, PbO_2, $KMnO_4$, $CaOCl_2$, NaClO etc.

$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$ (Lab. method)
$NaClO + 2HCl \rightarrow NaCl + H_2O + Cl_2$
$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$
$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 3CrCl_3 + 7H_2O + 3Cl_2$

2. **Commercial methods :**

(a) **[Decon's process]** Air oxidation of hydrochloric acid in presence of copper (II) chloride catalyst.

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

(b) **By the electrolysis of aqueous NaCl solution :**

At anode ---------------------- Cl_2 is liberated
At cathode ---------------------- H_2 is liberated
(Caster – Kellner and Nelson cell)

Properties : Physical characteristics :

* Cl_2 is greenish yellow gas.
* Cl_2 is poisonous having a suffocating odour.
* Cl_2 is soluble in water and carbon disulphide.
* Cl_2 is 2.5 times heavier than air.

Chemical characteristics :

Reaction with metals and nonmetals.

$2Na + Cl_2 \rightarrow 2NaCl$; $2P + 5Cl_2 \rightarrow 2PCl_5$
$Ca + Cl_2 \rightarrow CaCl_2$; $2S + Cl_2 \rightarrow S_2Cl_2$

Reaction with SO_2, CO and NO

$SO_2 + Cl_2 \rightarrow SO_2Cl_2$ (sulphuryl chloride)
$CO + Cl_2 \rightarrow COCl_2$; $2NO + Cl_2 \rightarrow 2NOCl$

Reaction with NH_3 :

$8NH_3\ (excess) + 3Cl_2 \rightarrow 6NH_4Cl + N_2$
$NH_3 + 3Cl_2\ (excess) \rightarrow NCl_3 + 3HCl$

Reaction with NaOH and $Ca(OH)_2$:

$Cl_2 + 2NaOH\ (cold\ dil.) \rightarrow 2NaClO + H_2O$
$3Cl_2 + 6NaOH\ (hot\ \&\ conc.) \rightarrow 5NaCl + NaClO_3 + 3H_2O$
$Cl_2 + Ca(OH)_2 \rightarrow CaOCl_2 + H_2O$

Reaction of F_2, Br_2, and I_2 : The compounds obtained are:
ClF, BrCl and ICl_3

Reaction with organic compounds :

$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$
$C_2H_4 + Cl_2 \rightarrow ClCH_2 - CH_2Cl$

Oxidizing and bleaching action of Cl_2 :

[Cl_2 on reaction with water liberates nascent oxygen. Hence it is a powerful oxidant.]

$Cl_2 + H_2O \rightarrow 2HCl + [O]$
(Permanent) Coloured substance + [O]
→ Colourless substance other reactions :

$SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$
$Na_2SO_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl$
$Na_2SO_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl + S$

Liberation of Br_2 and I_2 from KBr and KI

$2KBr + Cl_2 \rightarrow 2KCl + Br_2$
$2KI + Cl_2 \rightarrow 2KCl + I_2$

Uses of chlorine :

1. Used in the manufacture of bleaching powder, hydrochloric acid, hypochlorites, chlorates, $CHCl_3$, CCl_4, DDT, Phosgene, mustard gas etc.
2. Used in the purification of drinking water.
3. Used in extraction of Au and Pt.

4. Used as a bleaching agent for cotton fabrics, paper and rayon.
5. Used as a germicide and disinfectant.
6. Used as an oxidant.

BROMINE

Occurrence : Bromine occurs in the combined state as bromides of Na, K and Mg. It was discovered by Ballard (1826). If is present in :

Carnalite : Mother liquor of carnallite contains bromo carnallite KBr $MgBr_2 . 6H_2O$.

Sea water and mineral springs : Contain NaBr, $MgBr_2$

Bromargyrite : AgBr

Preparation :

Laboratory method :

Reactants : KBr, MnO_2 and conc. H_2SO_4.

$2KBr + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + Br_2 + 2H_2O$

Liberation of Br_2 Using Cl_2 gas :

Reactants : (KBr, Cl_2) or ($MgBr_2$, Cl_2)

$2KBr + Cl_2 \rightarrow 2KCl + Br_2; MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$

Commercial method :

(a) **From carnallite [$KCl . MgCl_2 . 6H_2O$]**
Mother liquor left after the separation of crystals of KCl and $MgCl_2$ contains 0.25% $MgBr_2$ (bittern). This on treating with Cl_2 gas Br_2 is liberated.

(b) **From sea water :** Sea water contains 0.006% (by weight) of bromine as $MgBr_2$. Here also Br_2 can be obtained by passing chlorine gas.

Properties : Physical characteristics

* It is dark–red, poisonous liquid gives brown–red fumes.
* Boiling point is 59.5ºC, Freezing point is –7.2ºC.
* Sparingly soluble in water and is soluble in CCl_4, CS_2, $CHCl_3$ etc.

Chemical characteristics :

Due to liberation of oxygen it can act as an oxidant and bleaching agent.

e.g. $SO_2 + Br_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$
$H_2S + Br_2 \rightarrow 2HBr + S$

Reaction with NH_3 :

With cold and dil. NaOH :

$2NaOH + Br_2 \rightarrow NaBr + NaBrO + H_2O$

With hot and conc. NaOH :

$6NaOH + Br_2 \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

Uses of bromine :

1. Used in the form of AgBr as coating on photographic plates, films etc.
2. Used in the manufacture of KBr, NaBr (used as a sedative in medicine).
3. Used to prepare 1, 2 dibromoethane which is employed with TEL as an antiknock compound in gasoline.
4. Used as an oxidant in organic synthesis.

IODINE

Occurrences : Chief sources of iodine are :

(i) Sea Weeds : Contain 0.5% of iodine in the form of iodies.
(ii) Caliche or crude chile saltpetre : Contains 0.2% of sodium iodate.

Preparation :

Laboratory method :

Reactants : KI, MnO_2 and conc. H_2SO_4,

$2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$

Liberation of I_2 using Cl_2 gas :

Reactants : KI and Cl_2 ; $2KI + Cl_2 \rightarrow 2KCl + I_2$

Commercial methods :

From sea weeds : Dry weeds are carefully burnt in shallow pits. The residue called kelp is treated with conc. H_2SO_4 and MnO_2

$2NaI + MnO_2 + 3H_2SO_4 \rightarrow 2NHSO_4 + MnSO_4 + I_2$

From caliche or crude chile salt peter : It contains 0.2% sodium iodate ($NaIO_3$). After removal of $NaNO_3$ from caliche, the mother liquor contains $NaIO_3$. It is treated with calculated quantity of sodium bisulphate to obtain iodine.

$2NIO_3 + 5NaHSO_3 \rightarrow 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2$

Properties : Physical characteristics :

* Iodine is a dark violet shining solid.
* Sublimes below its melting point (114ºC) giving violet vapours.
* Iodine is sparingly soluble in water. In presence of KI, the solubility of iodine increases due to the formation of tri iodide ion $I^- + I_2 \rightleftharpoons I_3^-$.
* Iodine is soluble in organic solvents such as $CHCl_3$, CCl_4, CS_2 etc.
* Its vapours are pungent and poisonous to inhale.
* At high temperature the equilibrium is maintained between molecular and atomic form $I_2 \xrightleftharpoons{1700°C} I + I$.

Chemical characteristics : Less reactive as compared to Cl_2 and Br_2.

Reaction with H_2 and non–metals :

$H_2 + I_2 \xrightarrow[pt]{\Delta} 2HI;\ 2K + I_2 \rightarrow 2KI ; 2P + 3I_2 \rightarrow 2PI_3$

Reaction with NaOH : Iodine with cold and dil. NaOH gives sodium hypo iodite (NaOI). With concentrated NaOH iodide (NaI) and idodate ($NaIO_3$) are formed.

Reaction with sodium thisulphate :

$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$ (Sodium tetrahionate)

Reactions showing oxidising properties (It is a weak oxidant)

$Na_3AsO_3 + H_2O + I_2 \rightarrow Na_3AsO_4 + 2HI$
$H_2S + I_2 \rightarrow 2HI + S$
$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$

Reaction showing basic character : It shows basic properties and forms I^+ and I^{3+} ions.

Formation of ICl, ICN, INO_2 etc. shows the presence of I^+

$$ICl \rightleftharpoons I^+ + Cl^- \qquad ICN \rightleftharpoons I^+ + CN^-$$

Formation of $I(CH_3COO)_3$ and IPO_4 etc show the presence of I^{3+}.

Reaction with $KClO_3$ and $KBrO_3$:

$$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$$
$$2KBrO_3 + I_2 \rightarrow 2KIO_3 + Br_2$$

Iodine does not liberated Cl_2 and Br_2 from the corresponding chloride and bromide respectively.

Reaction with strong oxidants :

$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$
$$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$$
$$I_2 + H_2O + 5O_3 \rightarrow 2HIO_3 + 5O_2$$

Reaction with starch : Iodine turns starch solution blue.

Uses of iodine :

1. Used in the preparation of iodoform, iodides, dyes etc.
2. Used as a laboratory reagent.
3. Used in making medicines such as iodex, tincture iodine.
4. Solution of I_2 in KI is used in the treatment of goitre.
5. Used in making photosensitive papers, films etc.

INTERHALOGEN COMPOUNDS

* When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX', XX'_3, XX'_5 and XX'_7 where X is halogen of larger size and X' of smaller size and X is more electropositive than X'.

* Iodine (VII) fluoride formula is IF_7.

Reason : As the ratio between radii of X and X' increases, the number of atoms per molecule also increases. Thus, iodine (VII) fluoride should have maximum number of atoms as the ratio of radii between I and F should be maximum. That is why its formula is IF_7 (having maximum number of atoms).

Preparation : The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds. The product formed depends upon some specific conditions,

$$\text{e.g., } Cl_2 + F_2 \xrightarrow{473K} 2ClF\ ;\ I_2 + \underset{\text{excess}}{3Cl_2} \longrightarrow 2ICl_3\ ;$$

$$Cl_2 + \underset{\text{excess}}{3F_2} \xrightarrow{573K} 2ClF_3\ ;\ \underset{\text{(diluted with water)}}{Br_2 + 3F_2 \longrightarrow 2BrF_3}$$

$$\underset{\text{(equimolar)}}{I_2 + Cl_2} \longrightarrow 2ICl\ ;\ Br_2 + \underset{\text{excess}}{5F_2} \longrightarrow 2BrF_5$$

Properties :

Some Properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure
XX'_1	ClF	colourless gas	–
	BrF	pale brown gas	–
	IF^a	detected spectroscopically	–
	$BrCl^b$	gas	
	ICl	ruby red solid (α-form) brown red solid (β-form)	– –
	IBr	black solid	–
XX'_3	ClF_3	colourless gas	Bent T-shaped
	BrF_3	yellow green liquid	Bent T-shaped
	IF_3	yellow powder	Bent T-shaped
	$ICl_3{}^c$	orange solid	Bent T-shaped
XX'_5	IF_5	colourless gas but solid below	Square pyramidal
	BrF_5	colourless liquid	Square pyramidal
	ClF_5	colourless gas	Square pyramidal
XX'_7	IF_7	colourless gas	Pentagonal bipyramidal

* These are all covalent molecules and are diamagnetic in nature.

* They are volatile solids or liquids except CIF which is a gas at 298 K.

* Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.

* Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because X – X' bond in interhalogens is weaker than X – X bond in halogens except F – F bond. All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX'), halite (when XX'_3), halate (when XX'_5) and perhalate (when XX'_7) anion derived from the larger halogen. $XX + H_2O \rightarrow HX' + HOX$

* Their molecular structures are very interesting which can be explained on the basis of VSEPR theory. The XX_3 compounds have the bent T shape, XX_5 compounds square pyramidal & IF_7 has pentagonal bipyramidal structures.

Uses:

* These compounds can be used as non aqueous solvents.

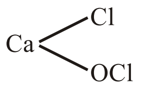
* Interhalogen compounds are very useful fluorinating agents.

* ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of ^{235}U. $U(s) + 3ClF_3(\ell) \rightarrow UF_6(g) + 3ClF(g)$

BLEACHING POWDER [$CaCOCl_2$] :

* It is a mixed salt called calcium chloro hypochlorite.

* Proton of HCl and HOCl are cumulatively replaced by calcium [$2H^+$ by one Ca^{2+}]



* In fact, bleaching power is a mixture of calcium hypochlorite $Ca(OCl)_2\,4H_2O$ and basic calcium chloride $CaCl_2.Ca(OH)_2\,H_2O$.

Manufacture : There are two plants used in the manufacture of bleaching powder. Hasenclever's plant and Backmann's Plant (Modern process)

Basic reaction : When slaked lime [$Ca(OH)_2$ is treated with chlorine at 40°C results in the formation of bleaching powder.

$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$
$CaCl_2 + Ca(OH)_2 + H_2O \rightarrow CaCl_2.Ca(OH)_2.H_2O$
$2Cl_2 + 3Ca(OH)_2 \rightarrow Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O + H_2$
Bleaching powder is : $[Ca(OCl)_2 + CaCl_2.Ca(OH)_2.H_2O]$

Properties :

Physical characteristics :

- Bleaching powder is a pale yellow in colour having a strong odour of chlorine.
- Soluble in water but clear solution cannot be obtained due to the presence of $Ca(OH)_2$.
- It is ionises as : $CaOCl_2 \rightarrow Ca^{2+} + Cl^- + OCl^-$

Chemical characteristics :

Oxidizing and bleaching action :

It loses its oxygen when treated with dilute acid.
$2CaOCl_2 + H_2SO_4 \rightarrow CaCl_2 + CaSO_4 + 2HClO$
$HClO \rightarrow HCl + [O]$ nascent oxygen
The oxidizing and bleaching action of bleaching powder is due to the formation of nascent oxygen.

Oxidizing action :

$CaOCl_2 + 2KI + 2HCl \rightarrow CaCl_2 + 2KCl + H_2O + I_2$
$Na_3AsO_3 + CaOCl_2 \rightarrow CaCl_2 + Na_3AsO_4$
$CaOCl_2 + H_2S \rightarrow CaCl_2 + H_2O + S$
$3CaOCl_2 + 2NH_3 \rightarrow 3CaCl_2 + 3H_2O + N_2$

Bleaching action :

Coloured matter + [O] → Colourless matter
Reaction with ethylalcohol and acetone :

$$C_2H_5OH \text{ or } CH_3COCH_3 \xrightarrow{CaOCl_2.H_2O} CHCl_3$$

Reaction with dilute acids or acids or CO_2 (available chlorine) :

The chlorine obtained from a sample of bleaching powder by treatment with excess of dilute acids or CO_2 is called available chlorine :

$CaOCl_2 + 2HCl \rightarrow CaCl_2 + H_2O + Cl_2$
$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$
$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$

Reaction in presence of $CoCl_2$

$$2CaOCl_2 \longrightarrow 2CaCl_2 + O_2$$

Uses of bleaching powder :

1. Used in the sterilization of drinking water (disinfectant and germicide)
2. Used as bleaching agent for cotton, linen and wood pulp.
3. Used for the commercial preparation of chloroform.
4. Used as an oxidizing agent in industry.

TRY IT YOURSELF-3

Q.1 Write the decreasing order of bond angle of Br_2O, Cl_2O and F_2O.

Q.2 Which of the following reactions will give bleaching powder
(A) $CaCl_2 + H_2O$
(B) $CaO + HCl$
(C) $Ca(OH)_2 + Cl_2$
(D) $ClO_2 + Ca(OH)_2$

Q.3 The oxidation states shown by halogen are –1, +1, +3, +5 and +7. Oxidation state(s) shown by all the halogen is
(A) –1 and +3
(B) –1, +1 and +3
(C) only –1
(D) only +3

Q.4 The stability order of oxides of chlorine
(I) Cl_2O (II) Cl_2O_3 (III) Cl_2O_5 (IV) Cl_2O_7
(A) I < II < III < IV
(B) I > II > III > IV
(C) I > III > II > IV
(D) IV > I > II > III

Q.5 When chlorine water is added to an aqueous solution of sodium iodide in the presence of chloroform, a violet colouration is obtained. On adding more of chlorine water and vigorous shaking, the violet colour disappears. This shows the conversion of ...... .into .....
(A) I_2, HIO_3
(B) I_2, HI
(C) HI, HIO_3
(D) I_2, HIO

Q.6 Aqua regia, which is used for dissolving noble metals like gold and platinum etc. is
(A) 1 : 3 mixture of conc. HCl and conc. HNO_3
(B) 3 : 1 mixture of conc. HCl and conc. HNO_3
(C) 1 : 1 mixture of conc. HCl and conc. HNO_3
(D) 3 : 1 mixture of conc. HCl and conc. HNO_3

Q.7 The number of peroxide linkages in perchloric acid is
(A) zero
(B) one
(C) two
(D) four

Q.8 Affinity for hydrogen decreases in the group from fluorine to iodine. Which of the halogen acids should have highest bond dissociation enthalpy?
(A) HF
(B) HCl
(C) HBr
(D) HI

Q.9 Which of the following options are not in accordance with the property mentioned against them?
(A) $F_2 > Cl_2 > Br_2 > I_2$ Oxidising power.
(B) MI > MBr > MCl > MF Ionic character of metal halide.
(C) $F_2 > Cl_2 > Br_2 > I_2$ Bond dissociation enthalpy.
(D) HI< HBr < HCl < HF Hydrogen-halogen bond strength.

Q.10 Which of the following statements are correct?
(A) Among halogens, radius ratio between iodine and fluorine is maximum.
(B) Leaving F—F bond, all halogens have weaker X—X bond than X—X' bond in interhalogens.
(C) Among interhalogen compounds maximum number of atoms are present in iodine fluoride.
(D) Interhalogen compounds are more reactive than halogen compounds.

ANSWERS

(1) $Br_2O > Cl_2O > F_2O$ **(2)** (C) **(3)** (C)
(4) (A) **(5)** (A) **(6)** (B)
(7) (A) **(8)** (A) **(9)** (BC)
(10) (ACD)

NOBLE GASES

PRELUDE

- Zero group of group–18 contains six gaseous elements He, Ne, Ar, Kr, Xe and Rn.
- First five elements are present in small quantities in atmosphere and as such called rare gas.
- Radon is obtained by the dins integration of radium and is radioactive.
- Due to stable outer configuration of s^2p^6 (octet) these gases exhibit inert character and are called inert gases.
- Under specific conditions, these gases can form compounds [XeF_2, XeF_4 etc.]. These gases are referred as noble gases,

Electronic configuration of noble gases :

Element	Electronic Configuration
Helium [He_2]	$1s^2$
Neon [Ne_{10}]	[He] $2s^2\ 2p^6$
Argon [Ar_{18}]	[Ne] $3s^2\ 3p^6$
Krypton [Kr_{36}]	[Ar] $3d^{10}\ 4s^2\ 4p^6$
Xenon [Xe_{54}]	[Kr] $3d^{10}\ 5s^2\ 5p^6$
Radon [Rn_{86}]	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

- These element occupy position between most electronegative (halogens) and the most electropositive (alkali metals) elements. Thus zero group elements are neither electro-positive nor electronegative in nature.
- Helium has stable s^2 (duplex) configuration. Because of duplex and octet configuration they show zero valency.

PHYSICAL PROPERTIES

- All the noble gases are monoatomic.
- They are colourless, odourless and tasteless.
- They are sparingly soluble in water.
- They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.
- Helium has the lowest boiling point (4.2 K) of any known substance. It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

CHEMICAL PROPERTIES

Trends in chemical reactivity of group 18 elements :

- Noble gases are not reactive. This non-reactivity of noble gases may be due to the following reasons.
  (a) Completely filled outermost shell, ($ns^2\ np^6$), and the next available electronic shell is of much higher enthalpy.
  (b) High ionisation enthalpies of the noble gases.
  (c) Nearly zero electron gain enthalpy.

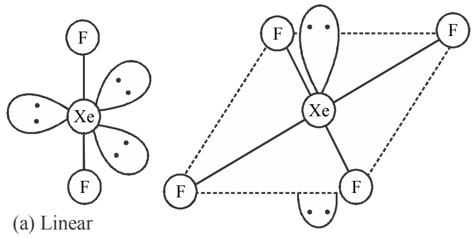
However, one would expect at least the heavier noble gases to show more reactivity as a result of electron loss. Radon, thus, is expected to react with greater ease. But very little is known about radon because of its short half-life.

- Xenon forms the largest number of compounds.
- Krypton tends to form compounds but with great difficulty. Krypton is known to form KrF_2 only.
- Xenon forms some compounds with fluorine and oxygen.

Xenon-Fluorine compounds :

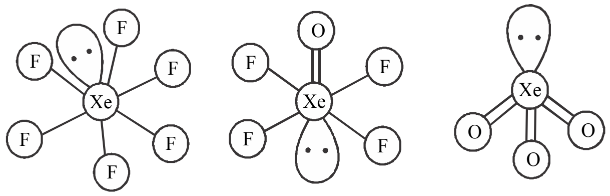
- Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6.
- They are colourless crystalline solids and sublime readily at 298 K.
- They are powerful fluorinating agents.
- They are readily hydrolysed even by traces of water.
- The structure of the three xenon fluorides can be deduced from VSEPR. XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and would, thus, have a distorted octahedral structure as found experimentally in the gas phase.

Structure :



(a) Linear

(b) Square planar



(c) Distorted octahedral (d) Square pyramidal (e) Pyramidal

Figure : The structures of (a) XeF_2 (b) XeF_4 (c) XeF_6 (d) $XeOF_4$ (e) XeO_3

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

Xenon-oxygen compounds :

- Hydrolysis of XeF_4 and XeF_6 with water gives XeO_3.
- Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.
- XeO_3 is a colourless explosive solid and has a pyramidal molecular structure.
- $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.

DISCOVERY OF NOBLE GASES

Ramsay and Rayleigh [1894] [Argon] :

It was found that the density of atmospheric nitrogen was 0.5% higher than that obtained by chemical methods. They isolated this gas from air by passing over heated copper to remove oxygen and then nitrogen by passing over heated magnesium.

$2Cu + O_2 \rightarrow 2CuO$; $3Mg + N_2 \rightarrow Mg_3N_2$

The vapour density and atomic weight of the gas was found to be 20 & 40 respectively. The gas was named Argon.

Ramsay & travers [1898] (Helium, Neon, Krypton & Xenon) : They carried out fractional distillation fo liquid argon under reduced pressure. From the first fraction they isolated Helium and Neon. By further fractional distillation they had isolated Krypton and Xenon.

Dorn [1900] (Radon)

Radon is a dis integration product of radium.

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

ISOLATION

There are two methods employed to isolate noble gases commercially.

Fractional distillation of liquid air :

Since the noble gases have the boiling points quite far apart. Hence fractional distillation is easily employed.

Claude's apparatus : This is used for the manufacture of liquid O_2 and N_2 where noble gases are obtained as by – products.

First fraction : [He, N_2] : The mixture of gases is passed through a spiral cooled in liquid nitrogen. In this process most of the nitrogen condenses while He and Ne passes out. This mixture is cooled in a rectifying column (low temperature containing liquid H_2) where neon solidifies. Helium still remains in the gaseous state escapes out.

Note : N_2 is removed from He by CaC_2

$CaC_2 + N_2 \rightarrow CaCN_2 + C$

Second fraction : [Ar, O_2]

Mixture of Ar and O_2 is passed through spiral tube cooled by liquid nitrogen. In this process most of the oxygen is liquefied and argon with a little bit of oxygen escapes out.

Note : O_2 is removed from Ar by heated Cu

$2Cu + O_2 \rightarrow 2Cu$

Third fraction [Kr, Xe]

This fraction is evaporated whereby the residual liquid becomes richer in Kr and Xe. The separation of Kr and Xe is then becomes easier as they have wide difference in their boiling points.

USES OF NOBLE GASES

Helium :

1. Used in balloons and airships as it is light and non-inflammable.
2. Used in creating inert atmosphere in metallurgy and welding metals.
3. Used in filling tungsten lamps required for signaling.
4. A mixture of He and O_2 is used for respiration by divers in deep sea. Since He is much less soluble in the blood than nitrogen at high pressure.
5. Used for filling vacuum tubes and radio tubes.
6. Used for producing low temperature (–269ºC)

Neon :

1. Neon lamps are used in green houses as it is effective in the growth of chlorophyll.
2. Neon lamps ar used in botanical gardens.
3. Neon lights are visible in fog and mist and there fore neon lights are used for making signals in night for pilots.
4. Neon is also used in discharge tubes required for decorative and advertising purpose.

Argon :

1. Used for creating inert atmosphere for welding.
2. Ar plus He mixture is used for signal electrical device.
3. Ar plus Ne are used in filling fluorescent tubes, radio–valves etc.
4. Used in bulbs to enhance the life of filament.

Krypton and Xenon : Used in filling up bulbs containing incandescent filaments.

Radon : **1.** Used in radio therapy of cancer.
2. Used to check the defects in steel sheets.

TRY IT YOURSELF-4

Q.1 Write the decreasing order of heat of vaporisation and solubility of noble gases in water.

Q.2 Noble gases can be separated by-
(A) Passing them through some solution
(B) Electrolysis of their compounds
(C) Adsorption and desorption on coconut charcol
(D) None

Q.3 The lowest boiling point of any known substance
(A) H_2 (B) He
(C) O_3 (D) Xe

Q.4 Which of the noble gases does not form clathrates?
(A) He (B) Br_2
(C) Ar (D) Xe

Q.5 XeF_2 is hydrolysed to give –
(A) $XeOF_4$ (B) $XeOF_3$
(C) Xe (D) XeO_2F_2

Q.6 In the preparation of compounds of Xe, Bartlett had taken $O_2^+ Pt F_6^-$ as a base compound. This is because
(A) both O_2 and Xe have same size.
(B) both O_2 and Xe have same electron gain enthalpy.
(C) both O_2 and Xe have almost same ionisation enthalpy.
(D) both Xe and O_2 are gases.

Q.7 Which of the following statements are true?
(A) Only type of interactions between particles of noble gases are due to weak dispersion forces.
(B) Ionisation enthalpy of molecular oxygen is very close to that of xenon.
(C) Hydrolysis of XeF_6 is a redox reaction.
(D) Xenon fluorides are not reactive.

ANSWERS

(1) Heat of vapourisation, Xe > Kr > Ar > Ne > He.
Solubility of noble gases, Xe > Kr > Ar > Ne > He.

(2) (C) **(3)** (B) **(4)** (A)
(5) (C) **(6)** (C) **(7)** (AB)

USEFUL TIPS

IMPORTANT ORDERS

* The order of stability : $Cl_2O < ClO_2 < Cl_2O_6 < Cl_2O_7$.
* The oxidising power of oxides follows the order
  $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$.
* Stability: $NF_3 > NCl_3 > NBr_3$
* Boiling point: $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$
* Melting point: $PH_3 < AsH_3 < SbH_3 < NH_3$
* Thermal stability : $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$
* Reducing character: $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$
* Ease of hydrolysis of hexahalides : $SF_6 > SeF_6 > TeF_6$
* Stability of dioxides : $SO_2 > TeO_2 > SeO_2 > PoO_2$
* Thermal stability: $H_2O > H_2S > H_2Se > H_2Te$
* Bond energy of halogens : $Cl_2 > Br_2 > F_2 > I_2$
* Bond length in X_2 molecule : $F_2 < Cl_2 < Br_2 < I_2$
* Solubility of halogen in water : $F_2 > Cl_2 > Br_2 > I_2$
* Oxidising power : $F_2 > Cl_2 > Br_2 > I_2$
* Enthalpy of hydration of X^- ion : $F^- > Cl^- > Br^- > I^-$
* Reducing character of X^- ion : $I^- > Br^- > Cl^- > F^-$
* The order of reactivity : $F_2 > Cl_2 > Br_2 > I_2$
* Boiling points : $HF > HI > HBr > HCl$
* Melting points : $HI > HF > HBr > HCl$
* Bond lengths : $HI > HBr > HCl > HF$
* Bond dissociation enthalpy : $HF > HCl > HBr > HI$
* Acidic strength : $HI > HBr > HCl > HF$
* Thermal stability : $HF > HCl > HBr > HI$
* Reducing power : $HI > HBr > HCl > HF$
* Conjugate base strength of halogen acids
  $I^- < Br^- < Cl^- < F^-$
* Dipole moment of hydrogen halides
  $HF > HCl > HBr > HI$
* Oxidising power of oxides of chlorine
  $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$
* Acidic character of oxyacids of chlorine
  $HClO < HClO_2 < HClO_3 < HClO_4$
* Oxidising power of oxyacids of chlorine
  $HClO > HClO_2 > HClO_3 > HClO_4$
* Thermal stability of oxyacids of chlorine
  $HClO < HClO_2 < HClO_3 < HClO_4$
* Stability of anions of oxyacids of chlorine
  $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$

ADDITIONAL EXAMPLES

Example 1 :

Nitrogen behaves almost as –

(A) Halogens
(B) Alkali metals
(C) Transition elements
(D) Inert elements

Sol. **(D).** Nitrogen has exactly half-filled p-orbitals in outermost shell thus, it is fairly stable and not so reactive.

Example 2 :

At high temperature nitrogen combines directly with –

(A) Na
(B) Zn
(C) Al
(D) Fe

Sol. **(C).** $Al + N \longrightarrow AlN$ (Aluminium nitride)

Example 3 :

A greenish yellow gas reacts with an alkali hydroxide to form a halate which can be used in fireworks and safety matches. The gas and the halate are –

(A) $Br_2, KBrO_3$
(B) $Cl_2, KClO_3$
(C) $I_2, NaIO_3$
(D) I_2, KIO_3

Sol. **(B).** The halate used in fireworks and safety matches is $KClO_3$. Thus, the gas is Cl_2.

$$3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O$$

greenish yellow gas

Example 4 :

In P_4O_6 and P_4O_{10}, the number of oxygen atoms bonded to each phosphorus atoms are respectively –

(A) 3 and 3
(B) 4 and 4
(C) 3 and 4
(D) 4 and 3

Sol. **(C).** In P_4O_6, each phosphorus is linked to three oxygen atoms; whereas in P_4O_{10} each phosphorus atom is linked to four oxygen atoms.

Example 5 :

Which of the following is the strongest oxidant –

(A) F_2
(B) Cl_2
(C) Br_2
(D) I_2

Sol. **(A).** F_2 is strongest oxidant, because (i) F_2 has exceptionally low dissociation energy of F – F bond, (ii) F^- has high energy of hydration due to small size of the F^- ion.

Example 6 :

Which of the following is a false statement –

(A) Halogen are strong oxidizing agent
(B) Halogens show only (–1) oxidation state
(C) HF molecules from intermolecular H-bonds
(D) Fluorine is highly reactive.

Sol. **(B).** Fluorine, being most electronegative element, always show the oxidation state of –1. Other halogens can show higher positive oxidation states in addition to negative oxidation of –1.

Example 7 :

Which of the following halides is most acidic ?

(A) PCl_3 (B) $SbCl_3$

(C) $BiCl_3$ (D) CCl_4

Sol. **(A).** In CCl_4, carbon atom does not have d-orbitals to accommodate a line pair of electrons and hence is not a lewis acid. In PCl_3, $SbCl_3$, $BiCl_3$ centre atom has empty d-orbitals but electronegativity of P is maximum, hence PCl_3 is strongest acid.

Example 8 :

Nitrogen forms N_2 but phosphorus do not forms P_2, but it exists as P_4 the reason for this is –

(A) Triple bond is present between phosphorus atoms

(B) $p\pi$-$p\pi$ bonding is weak

(C) $p\pi$-$p\pi$ bonding is strong

(D) Multiple bond is formed easily.

Sol. **(B).** Due to bigger size orbital of P cannot overlap to form strong π-bond.

Example 9 :

The wrong statement about ammonia is –

(A) NH_3 is oxidised with oxygen at 700°C in the presence of platinum.

(B) NH_3 gives black precipitate with calomel.

(C) NH_3 can be dried by P_2O_5, H_2SO_4 and $CaCl_2$.

(D) NH_3 gives white fumes with HCl

Sol. **(C).** NH_3 reacts with P_2O_5, H_2SO_4 and $CaCl_2$ and being basic form $(NH_4)_3PO_4$ & $(NH_4)_2SO_4$.

Example 10 :

The solubility of noble gases in water increases with the increase in –

(A) Ionization potential of noble gases

(B) Thermal conductivity of noble gases

(C) Polarizability of noble gases

(D) Electron affinity of noble gases

Sol. **(C).** The solubility of noble gases increases with increase in mol wt. due to increase in polarizability. How ever, these are sparingly soluble.

QUESTION BANK

CHAPTER 7 : p-BLOCK (GROUP 15,16,17 & 18)

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

PART 1 : GROUP 15 ELEMENTS

Q.1 Which of the following elements of group 15 does not show allotropy –
(A) N (B) Bi
(C) P (D) As

Q.2 Which one of the following hydrides is least stable
(A) AsH_3 (B) SbH_3
(C) NH_3 (D) PH_3

Q.3 The boiling points of the following hydrides follow the order of
(A) $NH_3 > AsH_3 > PH_3 > SbH_3$
(B) $SbH_3 > AsH_3 > PH_3 > NH_3$
(C) $SbH_3 > NH_3 > AsH_3 > PH_3$
(D) $NH_3 > PH_3 > AsH_3 > SbH_3$

Q.4 Choose the correct statement
(A) PH_3 has lower boiling point than NH_3
(B) Nitrogen and phosphorus are non-metals.
(C) Arsenic and antimony are metalloids.
(D) All of these

Q.5 Ionic radii of As^{3+}, Sb^{3+}, , Bi^{3+} follow the order
(A) $As^{3+} > Sb^{3+} > Bi^{3+}$ (B) $Sb^{3+} > Bi^{3+} > As^{3+}$
(C) $Bi^{3+} > As^{3+} > Sb^{3+}$ (D) $Bi^{3+} > Sb^{3+} > As^{3+}$

Q.6 The oxidation state of nitrogen is highest in
(A) N_3H (B) NH_3
(C) NH_2OH (D) N_2H_4

Q.7 Consider the following statements,
I. All the elements of group 15 are polyatomic.
II. Dinitrogen is a diatomic gas while all others are solids.
III. Metallic character decreases down the group.
Which of the above statements are true?
Choose the correct option.
(A) I and II (B) I and III
(C) II and III (D) I, II and III

Q.8 Maximum covalency of nitrogen is –
(A) 3 (B) 5
(C) 4 (D) 6

Q.9 Nitrogen can form only one chloride with chlorine which is NCl_3 whereas P can form PCl_3 and PCl_5. This is –
(A) due to absence of d-orbitals in nitrogen.
(B) due to difference in size of N and P.
(C) due to higher reactivity of P towards Cl than N.
(D) due to presence of multiple bonding in nitrogen.

Q.10 Chilesaltpetre is the common name of
(A) $AgNO_3$ (B) $NaNO_3$
(C) $NaSO_4$ (D) AgCl

Q.11 I. Covalency of N is restricted to four.
II. N cannot form $d\pi$–$p\pi$ bond as the heavier element can.
III. P and As cannot form $d\pi$ – $d\pi$ bond with transition elements when their compounds like $P(C_2H_5)_3$ and as $(C_6H_5)_3$ act as ligands.
Which of the above statements are true?
Choose the correct option
(A) I and II (B) II and III
(C) I and III (D) All of these

Q.12 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

Q.13 Covalent and ionic radii of group 15 elements
(A) increase down the group upto P and then decrease.
(B) increase down the group.
(C) decrease upto P and then increase down the group.
(D) decrease down the group.

PART 2 : DINITROGEN

Q.14 Ammonium dichromate on heating gives –
(A) Chromium oxide and ammonia
(B) Chromic acid and nitrogen
(C) Chromium oxide and nitrogen
(D) Chromic acid and ammonia

Q.15 Nitrogen combines with metals to form
(A) Nitrites (B) Nitrates
(C) Nitrosyl chloride (D) Nitrides

Q.16 Dinitrogen
(A) is a colourless, odourless, tasteless and non–toxic gas.
(B) has a very low solubility in water.
(C) is rather inert at room temperature.
(D) All of these

Q.17 What causes nitrogen to be chemically inert ?
(A) High electronegativity of nitrogen
(B) Absence of bond polarity
(C) Short internuclear distance
(D) High bond energy

Q.18 The reason behind the low reactivity of nitrogen is
(A) stable configuration
(B) small atomic radius
(C) high dissociation energy
(D) high electronegativity

PART 3 : AMMONIA

Q.19 Liquid ammonia is used for refrigeration because–
(A) It has a high dipole moment
(B) It has a high heat of vapourisation
(C) It is basic
(D) It is a stable compound

Q.20 In the Haber's process, metallic oxides catalyse reaction between gaseous nitrogen and hydrogen to yield ammonia whose volume (STP) relative to the total volume of the reactants taken (STP) would be
(A) One-fourth (B) One-half
(C) Same (D) Three-fourth

Q.21 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
$\Delta_f H^{\Theta} = -46.1 \text{ kJ mol}^{-1}$
The above reaction of manufacturing NH_3 is of
(A) Mond's process (B) Hall–Heroult process
(C) van Arkel method (D) Haber's process

Q.22 Which of the following catalysis is commonly employed in the manufacture of ammonia by the Haber's process ?
(A) Finely divided platinum together with a nickel promoter.
(B) Finely divided nickel together with a platinum promoter.
(C) Finely divided iron together with a molybdenum promoter.
(D) Finely divided palladium together with a zinc promoter.

Q.23 It is recommended that ammonia bottle should be opened after cooling in ice for some time because –
(A) it has high vapour pressure.
(B) it comes out with brisk effervescence.
(C) it is a corrosive fluid.
(D) it vaporises at room temperature.

Q.24 Ammonia molecule is a Lewis base due to –
(A) the presence of a lone pair of electrons on the N-atom of NH_3.
(B) the absence of a lone pair of electron on the N-atom of NH_3.
(C) Either (A) or (B)
(D) None of the above

PART 4 : OXIDES OF NITROGEN

Q.25 Ammonium nitrate decomposes on heating into –
(A) Ammonia and nitric acid
(B) Nitrous oxide and water
(C) Nitrogen, hydrogen and ozone
(D) Nitric oxide, nitrogen dioxide and hydrogen

Q.26 Nitrogen dioxide cannot be obtained by heating
(A) KNO_3 (B) $Pb(NO_3)_2$
(C) $Cu(NO_3)_2$ (D) $AgNO_3$

Q.27 Nitrous oxide
(A) Is a mixed oxide.
(B) Is an acidic oxide.
(C) Is highly soluble in hot water.
(D) Supports the combustion of sulphur.

Q.28 The correct order for the decreasing acidic strength of oxides of nitrogen is
(A) $N_2O_5 > N_2O_3 > N_2O_4 > NO > N_2O$
(B) $NO > N_2O > N_2O_3 > N_2O_4 > N_2O_5$
(C) $N_2O > NO > N_2O_3 > N_2O_4 > N_2O_5$
(D) $N_2O_5 > N_2O_4 > N_2O_3 > NO > N_2O$

Q.29 Which one of the following nitrogen oxides is an anhydride of nitric acid ?
(A) N_2O_5 (B) N_2O_4
(C) N_2O_3 (D) N_2O

Q.30 Following compounds have planar structure except any one. Find that odd one
$N_2O_3, NO_2, N_2O_4, N_2O_5$
(A) N_2O_3 (B) N_2O_4
(C) N_2O_5 (D) NO_2

Q.31 Which oxide of nitrogen is obtained on heating ammonium nitrate at 250°C?
(A) Nitric oxide (B) Nitrous oxide
(C) Nitrogen dioxide (D) Dinitrogen tetraoxide.

PART 5 : NITRIC ACID

Q.32 Nitrogen dioxide
(A) Dissolves in water forming nitric acid.
(B) Does not dissolve in water.
(C) Dissolves in water to form nitrous acid and gives off oxygen.
(D) Dissolves in water to form a mixture of nitrous and nitric acids.

Q.33 Nitric oxide is prepared by the action of HNO_3 on–
(A) Fe (B) Cu
(C) Zn (D) Sn

Q.34 Nitric acid converts iodine into
(A) Iodic acid (B) Hydroiodic acid
(C) Iodine nitrate (D) Iodine pentaoxide

Q.35 Brown ring test for nitrates depends on
I. the ability of Fe^{2+} to reduce nitrates to nitric oxide.
II. it reacts with Fe^{2+} to form a brown coloured complex.
Which of the above statement(s) regarding brown test for nitrates is/are true? Choose the correct option.
(A) Only I (B) Only II
(C) Both I and II (D) Neither I nor II

Q.36 When zinc reacts with very dilute nitric acid, one of the products obtained is
(A) NO (B) NH_4NO_3
(C) NO_2 (D) H_2

Q.37 In the laboratory, HNO_3 is prepared as
(A) $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$
(B) $3NaNO_3 + 2H_2SO_4 \rightarrow NaHSO_4 + HNO_3$
(C) $NaNO_3 + H_2SO_4 \rightarrow 2NaHSO_4 + 3HNO_3$
(D) None of the above

Q.38 The oxide of nitrogen obtained as a product of the following reaction is
$Zn + 4HNO_3(\text{conc.}) \rightarrow Zn(NO_3)_2 + 2H_2O + ...$
(A) NO (B) N_2O
(C) NO_2 (D) N_2O_3

Q.39 The oxidising property of nitric acid is due to
(A) Its concentration
(B) The positive valency of N
(C) Its dilution
(D) Presence of N_2 in its highest oxidation state

PART 6 : PHOSPHORUS ALLOTRIPIC FORMS

Q.40 Each of the following is true for white and red phosphorus except that they
(A) Are both soluble in CS_2.
(B) Can be oxidised by heating in air.
(C) Consist of the same kind of atoms.
(D) Can be converted into one another.

Q.41 Red phosphorus is chemically unreactive because
(A) It does not contain P–P bonds.
(B) It does not contain tetrahedral P_4 molecules.
(C) It does not catch fire in air even upto 400ºC.
(D) It has a polymeric structure.

Q.42 Phosphorus is produced by heating in a furnace
(A) bone ash, silica and coke.
(B) bone ash, silica and lime.
(C) bone ash, coke and limestone.
(D) bone ash, coke and sodium chloride.

Q.43 Atomicity of phosphorus is –
(A) one (B) two
(C) three (D) four

Q.44 The structure of white phosphorus is
(A) square planar (B) pyramidal
(C) tetrahedral (D) trigonal planar.

Q.45 Red P is less reactive, less volatile and less soluble in non-polar solvent than white/yellow P because
(A) it has high molecular energy.
(B) it has low molecular energy.
(C) it forms condensation products.
(D) it possesses highly polymerised structures.

PART 7 : PHOSPHINE

Q.46 Phosphine is generally prepared in the laboratory
(A) By heating phosphorus in a current of hydrogen.
(B) By heating white phosphorus with aqueous solution of caustic potash.
(C) By decomposition of P_2H_4 at 110°C.
(D) By heating red phosphorus with an aqueous solution of caustic soda.

Q.47 Phosphine is
I. colourless gas II. rotten fish smell
III. highly poisonous
The correct option is
(A) I and II (B) II and III
(C) I and III (D) I, II and III

Q.48 Phosphine is not obtained, when
(A) Red P is heated with NaOH
(B) White P is heated with NaOH
(C) Ca_3P_2 reacts with water
(D) Phosphorus trioxide is boiled with water

Q.49 The laboratory method of preparation phosphine is–
(A) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$
(B) $Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$
(C) $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$
(D) None of the above

PART 8 : PHOSPHORUS HALLIDES

Q.50 Dehydrated phosphorus trichloride in water gives
(A) HPO_3 (B) H_3PO_4
(C) H_3PO_2 (D) H_3PO_3

Q.51 In the structure of PCl_5, the P–Cl_{axial} bonds are longer than P–$Cl_{equatorial}$ bond because
(A) Axial bond pairs suffer more repulsion
(B) Equatorial bond pairs suffer more repulsion
(C) Axial bond pairs suffer less repulsion
(D) Unequal bond lengths are more stable

Q.52 PCl_5 is a ____ white powder.
(A) brownish (B) bluish
(C) yellowish (D) greenish

Q.53 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.

Q.54 Arrange the following in decreasing Lewis acid strength: PF_3, PCl_3, PBr_3, PI_3.
(A) $PI_3 > PBr_3 > PCl_3 > PF_3$
(B) $PF_3 > PCl_3 > PBr_3 > PI_3$
(C) $PCl_3 > PBr_3 > PI_3 > PF_3$
(D) $PBr_3 > PI_3 > PF_3 > PCl_3$

Q.55 In gaseous and liquid phases, the structure of PCl_5 is–
(A) trigonal pyramidal (B) tetrahedral
(C) trigonal bipyramidal (D) trigonal

Q.56 PCl_3 on hydrolysis gives
(A) H_3PO_3 (B) HPO_3
(C) H_3PO_4 (D) $POCl_3$

Q.57 Which of the following statements is not correct about the structureof PCl_5 ?
(A) PCl_5 has a trigonal bipyramidal structure.
(B) Three equatorial P–Cl bonds are equivalent.
(C) The two axial bonds are different and longer than equatorial bonds.
(D) Equatorial bond pairs suffer more repulsion than that of the axial bond pairs.

PART 9 : OXOACIDS OF PHOSPHORUS

Q.58 Phosphorous acid on heating gives the following products: $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$
The above reaction is an example of
(A) oxidation (B) thermal decomposition
(C) disproportionation (D) reduction

Q.59 Metaphosphoric acid has the formula
(A) H_3PO_4 (B) HPO_3
(C) H_2PO_3 (D) H_3PO_2

Q.60 How many P–O–P bonds appear in cyclic metaphosphoric acid?
(A) Four (B) Three
(C) Two (D) One

Q.61 Hypophosphorus acid H_3PO_2 is –
(A) Tribasic acid (B) Dibasic acid
(C) Monobasic acid (D) Not acidic at all

Q.62 The acid which forms two series of salts is
(A) H_3PO_4 (B) H_3PO_3
(C) H_3PO_5 (D) H_3PO_2

Q.63 Which of the following is a tetrabasic acid?
(A) Hypophosphorous acid (B) Metaphosphoric acid
(C) Pyrophosphoric acid (D) Orthophosphoric acid

Q.64 Strong reducing behaviour of H_3PO_2 is due to
(A) Low oxidation state of phosphorus.
(B) Presence of two –OH groups and one P–H bond
(C) Presence of one –OH group and two P–H bonds.
(D) High electron gain enthalpy of phosphorus

PART 10 : GROUP 16 ELEMENTS

Q.65 Covalency of oxygen cannot exceed 2 unlike sulphur which can show +4 or +6 because
(A) oxygen atom does not have d-orbitals.
(B) oxygen atom has two unpaired electrons in its valence shell.
(C) oxygen can form a double bond with another oxygen atom.
(D) electrons of oxygen atom cannot be promoted to d-orbitals due to its small size.

Q.66 The stability of the halides of group 16 elements decreases in the order
(A) $Br^- > I^- > Cl^- > F^-$ (B) $F^- > I^- > Cl^- > Br^-$
(C) $F^- > Cl^- > Br^- > I^-$ (D) $I^- > Cl^- > Br^- > F^-$

Q.67 The physical properties of group 16 elements are
I. polonium is a metal and is radioactive.
II. all these elements exhibit allotropy.
III. with increase in atomic number, the melting and boiling point increases down the group.
The option with correct set of properties is
(A) I and II (B) II and III
(C) I and III (D) I, II and III

Q.68 Arrange the following elements in the correct order of increasing ionic radii. Se, Te, P, O, S
(A) O < S < Se < Te < Po (B) Po < Te < Se < S < O
(C) S < O < Se < Te < Po (D) S < O < Po < Se < Te

Q.69 The incorrect trend regarding group 16 hydrides (H_2E) is –
(A) Down the group, the H–E–H bond angle increases
(B) The acidic character of hydrides increases down the group.
(C) Except water, all hydrides possess reducing properties
(D) Thermal stability of hydrides decreases down the group.

Q.70 Dioxygen is a gas but sulphur is a solid because
(A) Oxygen atom has the tendency to form multiple $p\pi - p\pi$ bonds.
(B) S – S bond is not as stable as S = S bond.
(C) O – O chains are less stable than S – S chains.
(D) Oxygen is paramagnetic while sulphur is diamagnetic.

Q.71 Electron affinity of sulphur is
(A) More than O and Se
(B) More than O but less than Se
(C) Less than O but more than Se
(D) Equal to O and Se

Q.72 Group 16 elements have lower value of first ionisation enthalpy as compared to group 15 elements because –
(A) half filled p-orbitals in group 15 elements are more stable.
(B) group 16 elements have smaller size than group 15 elements.
(C) group 16 elements contain double bond while group 15 elements have triple bond.
(D) group 16 elements have more number of electrons in p-orbitals.

Q.73 Hexahalides of group 16 elements
I. are gaseous in nature.
II. have octahedral geometry.
III. SF_6 is exceptionally stable for steric reasons.
Which of the above mentioned statement(s) is/are correct?
(A) I and II (B) II and III
(C) Only III (D) I, II and III

PART 11 : DIOXYGEN

Q.74 Which of the following does not react with oxygen directly?
(A) Zn (B) Ti
(C) Pt (D) Fe

Q.75 On heating $KClO_3$ we get
(A) $KClO_2 + O_2$ (B) $KCl + O_2$
(C) $KCl + O_3$ (D) $KCl + O_2 + O_3$

Q.76 Solid oxygen has a pale blue colour which is attributed to –
(A) Electronic transitions from the singlet ground state to the triplet excited state.
(B) Electronic transitions from antibonding π-molecular orbitals to bonding $\sigma 2p_z$ M.O.'s.
(C) Electronic transitions from the triplet ground state to anti bonding $\sigma 2p_z$ molecular orbital.
(D) Electronic transitions from the triplet ground state to the excited singlet state.

Q.77 Oxygen shows anomalous behaviour from other members of its family because
I. oxygen shows maximum valency of two.
II. among chalcogens, oxygen is of the smallest size.
III. oxygen exhibits allotropy.
IV. oxygen has no vacant d-orbital.
The correct option explaining the reasons is
(A) I, II and III (B) I, II and IV
(C) I, III and IV (D) All of these

Q.78 Hydrogen peroxide is readily decomposed into water and dioxygen by catalyst(s)
(A) manganese dioxide
(B) finely divided metals
(C) Both (A) and (B)
(D) None of these

Q.79 Oxygen molecule is
(A) Diamagnetic with no-unpaired electron
(B) Diamagnetic with two unpaired electrons
(C) Paramagnetic with two unpaired electrons
(D) Paramagnetic with no unpaired electron

PART 12 : SIMPLE OXIDES

Q.80 Which of the following is not correctly matched?
(A) Acidic oxides – P_2O_5, NO_2, Cl_2O_7
(B) Basic oxides – Na_2O, CaO, MgO
(C) Neutral oxides – CO_2, CO, BeO
(D) Amphoteric oxides – ZnO, SnO, Al_2O_3

Q.81 Which of the following oxide is amphoteric in nature?
(A) Cl_2O_7 (B) Na_2O
(C) N_2O (D) Al_2O_3

PART 13 : OZONE

Q.82 Which of the following is incorrect ?
(A) O_2 is weaker oxidant than O_3
(B) O_2 has larger bond length than O_3
(C) Both O_2 and O_3 are paramagnetic
(D) O_2 is linear and O_3 is angular in shape.

Q.83 Incorrect statement with respect to ozone
(A) Ozone is formed in the upper atmosphere by a photochemical reaction involving dioxygen.
(B) Ozone is more reactive involving dioxygen.
(C) Ozone is diamagnetic whereas dioxygen is paramagnetic.
(D) Ozone protects the earth's inhabitants by absorbing gamma radiation.

Q.84 Ozone (O_3) is
(A) an allotropic form of oxygen.
(B) too reactive to remain for long in the atmosphere at sea level.
(C) formed from atmospheric oxygen in the presence of sunlight at a height of about 20km.
(D) All the above statements are correct.

Q.85 Which of the properties is not correct for ozone?
(A) It oxidizes lead sulphide
(B) It oxidizes potassium iodide
(C) It oxidizes mercury
(D) It cannot act as a bleaching agent

Q.86 What is the product formed when ozone reacts with mercury ?
(A) HgO (B) Hg_2O_2
(C) Hg_2O (D) HgO_2

Q.87 Which of the following is the wrong statement?
(A) Ozone is paramagnetic gas.
(B) ONCl and ONO^- are not isoelectronic.
(C) O_3 molecule is bent.
(D) Ozone is violet–black in solid state.

PART 14 : SULPHUR ALLOTROPIC FORMS

Q.88 Crystalline form of sulphur stable at room temperature is
(A) Rhombic sulphur (B) Monoclinic sulphur
(C) Plastic sulphur (D) Prismatic sulphur

Q.89 I. Melting point of rhombic sulphur is higher than that of monoclinic sulphur.
II. Specific gravity of rhombic sulphur is lower than that of rhombic sulphur.
The incorrect statement(s) is/are
(A) Only I (B) Only II
(C) Both I and II (D) Neither I nor II

Q.90 I. Sulphur forms only two types of allotropes.
II. Rhombic and monoclinic sulphur are the types of allotropic sulphur.
Which of the above statement(s) is/are true?
Choose the correct option.
(A) Only I (B) Only II
(C) Both I and II (D) Neither I nor II

Q.91 Sulphur molecule is –
(A) diatomic (B) triatomic
(C) tetratomic (D) octa–atomic.

PART 15 : SULPHUR DIOXIDE

Q.92 Which of the following after burning at room temperature gives gaseous oxide
(A) H (B) Na
(C) S (D) He

Q.93 Which of the following statements is not correct for SO_2 gas?
(A) It acts as bleaching agent in moist conditions.
(B) Its dilute solution is used as disinfectant.
(C) Its molecules have linear geometry.
(D) Acidified $KMnO_4$ is decolourised when SO_2 is passed through it.

Q.94 Bleaching action of SO_2 is due to its
(A) Oxidizing property (B) Acidic property
(C) Reducing property (D) Basic property

Q.95 Why is sulphur dioxide considered as an air pollutant?
(A) It increases the temperature of the atmosphere.
(B) It is used as insecticide which causes pollution.
(C) It causes acid rain due to formation of sulphuric acid on combining with O_2 and H_2O.
(D) It is a strong oxidising agent hence oxidises the other components of air.

Q.96 The molecule of SO_2 is –
(A) planar (B) pyramidal
(C) angular (D) None of these

PART 16 : OXOACIDS OF SULPHUR

Q.97 Oleum is :
(A) Peroxodisulphuric acid (B) Pyrosulphuric acid
(C) Sulphuric acid (D) Sulphurous acid

Q.98 The oxyacid of sulphur that contains a lone pair of electrons on sulphur is
(A) sulphurous acid (B) sulphuric acid
(C) peroxodisulphuric acid (D) pyrosulphuric acid

PART 17 : SULPHURIC ACID

Q.99 The most efficient agent for the absorption of SO_3 is –
(A) 80% H_2SO_4 (B) 98% H_2SO_4
(C) 50% H_2SO_4 (D) 20% H_2SO_4

Q.100 The final acid obtained during the manufacture of H_2SO_4 by contact process is
(A) H_2SO_4 (conc.) (B) H_2SO_4 (dil.)
(C) H_2SO_4 (D) $H_2S_2O_7$

Q.101 The catalyst used in the manufacture of H_2SO_4 by contact process is
(A) Al_2O_3 (B) Cr_2O_3
(C) V_2O_5 (D) MnO_2

Q.102 Properties of sulphuric acid are
I. a coloured, dense, oily liquid with a specific gravity of 1.84 at 298 K.
II. freezing point is 283 K.
III. boiling point is 611 K
IV. it dissolves in water with the evolution of a large quantity of heat.
The correct set of properties is
(A) I, II and III (B) II, III and IV
(C) I, III and IV (D) I, II and IV

Q.103 Make the incorrect statement
(A) The chemical reactions of H_2SO_4 are as a result of its ability to act as an oxidising agent
(B) Dilution of oleum with water gives H_2SO_4
(C) The key step in the manufacture of H_2SO_4, is the catalytic reduction of SO_2
(D) H_2SO_4, because of its low volatility can be used to manufacture more volatile acids from their corresponding salts.

Q.104 Which is incorrect about H_2SO_4 ?
(A) Reducing agent (B) Dehydrating agent
(C) Sulphonating agent (D) Highly viscous

Q.105 The acid used in lead storage cells is
(A) Phosphoric acid (B) Nitric acid
(C) Sulphuric acid (D) Hydrochloric acid

Q.106 The characteristics of H_2SO_4 responsible for the chemical reactions of H_2SO_4 are
(A) low volatility
(B) strong acidic character as well as affinity for water.
(C) ability to act as an oxidising agent.
(D) All of the above

Q.107 Dissolution of sulphuric acid in water is
(A) an endothermic process (B) an exothermic process
(C) a dehydrating process (D) a displacement process.

PART 18 : GROUP 17 ELEMENTS

Q.108 Which is the correct arrangement of the compounds based on their bond strength?
(A) HF > HCl > HBr > HI (B) HI > HBr > HCl > HF
(C) HCl > HF > HBr > HI (D) HF > HBr > HCl > HI

Q.109 Following are the statements related to group-17 elements
I. Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution.
II. The deposits of dried up seas contain carnallite, $KCl . MgCl_2 . 6H_2O$
III. Certain forms of marine life contain iodine in their system.
Which of the above statements are correct?
(A) I and II (B) II and III
(C) I and III (D) I, II and III

Q.110 With increase in molecular weight the boiling point of halogens increase, it happens because –
(A) van derWaals' forces increase with increase in number of electrons per mole.
(B) bond strength increases due to increase in electronegativity.
(C) with the increase in size, molecules undergo association leading to higher stability.
(D) None of the above

Q.111 Which of the following halogen does not exhibit positive oxidation state in its compounds ?
(A) Cl (B) Br
(C) I (D) F

Q.112 Consider the following statements.
I. Due to maximum effective nuclear charge, the halogens have the smallest atomic radii in their respective periods.
II. These have low ionisation enthalpy.
III. Halogens have maximum negative electron gain enthalpy in the corresponding periods.
IV. Fluorine is the most electronegative element in the Periodic Table.
The correct statements are
(A) I, II, III, IV (B) I, II, III
(C) I, III, IV (D) II, III, IV

Q.113 The correct order of increasing electron affinity of halogens is
(A) I < Br < Cl (B) Br < I < Cl
(C) Cl < Br < I (D) I < Cl < Br

Q.114 Mark the correct statements about halogens.
(A) Electron affinity of halogens is in the order F > Cl > Br > I
(B) HF is the strongest hydrohalic acid.
(C) F_2 has lower bond dissociation energy than Cl_2.
(D) All halogens show variable oxidation states.

Q.115 I. Fluorine forms two oxides OF_2 and O_2F_2.
II. OF_2 is thermodynamically stable at 298 K.
III. O_2F_2 oxidises plutonium to PuF_6.
The correct set of statements is
(A) I and II (B) II and III
(C) I and III (D) I, II and III

PART 19 : CHLORINE

Q.116 Which of the following facts is/are true about chlorine?
(A) It is a greenish yellow gas.
(B) It has pungent and suffocating odour.
(C) It is about 2–5 times heavier than odour.
(D) All of the above.

Q.117 Chlorine acts as a bleaching agent only in the presence of
(A) Dry air (B) Moisture
(C) Sunlight (D) None of these

Q.118 If chlorine is passed through a solution of hydrogen sulphide in water, the solution turns turbid due to the formation of –
(A) free chlorine (B) free sulphur
(C) nascent oxygen (D) nascent hydrogen.

Q.119 Chlorine is used in
(A) the extraction of gold and platinum.
(B) bleaching wood pulp.
(C) sterilising drinking water.
(D) All of the above

Q.120 Which of the following is used to prepare Cl_2 gas at room temperature from concentrated HCl?
(A) MnO_2 (B) H_2S
(C) $KMnO_4$ (D) Cr_2O_3

Q.121 Composition of bleaching powder is
(A) $Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O$
(B) $CaCl_2 \cdot CaOCl_2 \cdot Ca(OH)_2 \cdot 2H_2O$
(C) $Ca(OCl_2) \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 4H_2O$
(D) None of the above

PART 20 : HYDROGEN CHLORIDE

Q.122 Which of the following reactions show the reducing property of hydrochloric acid?
(A) $ZnCO_3 + 2HCl \rightarrow ZnCl_2 + H_2O + CO_2$
(B) $Mg + 2HCl \rightarrow MgCl_2 + H_2$
(C) $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$
(D) $NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

Q.123 HCl gas can be dried by passing through
(A) conc. H_2SO_4 (B) dil. H_2SO_4
(C) conc. HNO_3 (D) dil. HNO_3

PART 21 : OXOACIDS OF HALOGENS

Q.124 Fluorine forms only one oxoacid due to
(A) high electronegativity
(B) small size
(C) low electronegativity and large size
(D) Both (A) and (B)

Q.125 Which of the following increasing order is not correct as mentioned in the property with it?
(A) Thermal stability : $HClO < HClO_2 < HClO_3 < HClO_4$
(B) Oxidising power : $HClO_4 < HClO_3 < HClO_2 < HClO$
(C) Reducing nature : $F^- < Cl^- < Br^- < I^-$
(D) Oxidation number of iodine : $HIO_4 < ICl < I_2 < HI$

PART 22 : INTERHALOGEN COMPOUNDS

Q.126 Which of the following is not the characteristic of interhalogen compounds ?
(A) They are more reactive than halogens.
(B) They are quite unstable but none of them is explosive.
(C) They are covalent in nature.
(D) They have low boiling points and are highly volatile.

Q.127 Interhalogen compounds are
(A) covalent molecules
(B) diamagnetic in nature
(C) volatile solids/liquids at 298 K except ClF
(D) All of the above

Q.128 Interhalogen compounds are more reactive than the individual halogens because
(A) they are prepared by direct combination of halogens.
(B) X – X' bond is weaker than X – X or X' – X' bonds.
(C) they are thermally more stable than halogens
(D) there is a large difference in their electronegativity.

Q.129 Interhalogen compounds can be used as
I. non-aqueous solvents II. fluorinating agents
The correct use(s) is/are
(A) Only I (B) Only II
(C) I and II (D) Neither I nor II

PART 23 : GROUP 18 ELEMENTS

Q.130 Which one of the following noble gases is not found in the atmosphere
(A) Rn (B) Kr
(C) Ne (D) Ar

Q.131 Helium was discovered by
(A) Crooks (B) Rutherford
(C) Frankland and Lockyer (D) Dorn

Q.132 The inert gases are
(A) Polyatomic (B) Triatomic
(C) Diatomic (D) Monoatomic

Q.133 The noble gas which forms maximum number of compounds is
(A) Ar (B) He
(C) Xe (D) Ne

Q.134 Nuclear fusion produces
(A) Argon (B) Deuterium
(C) Helium (D) Krypton

Q.135 Which one of the following configuration represents a noble gas
(A) $1s^2, 2s^22p^6, 3s^2$ (B) $1s^2, 2s^22p^6, 3s^1$
(C) $1s^2, 2s^22p^6$ (D) $1s^2, 2s^22p^6, 3s^23p^6$

Q.136 Noble gases can be separated by –
(A) Passing them through some solution
(B) Electrolysis of their compounds
(C) Adsorption and desorption on coconut charcoal
(D) None of these

Q.137 I. $XeOF_4$ has square pyramidal structure.
II. XeF_2 has linear structure.
Which of the above mentioned statement{s} is/are true? Choose the correct option.
(A) Only I (B) Only II
(C) Both I and II (D) Neither I nor II

Q.138 Group 18 consists of ____ elements.
(A) six (B) seven
(C) five (D) eight

Q.139 Which of the following is not a use of noble gases?
(A) Argon is widely used for filling incandescent electric bulbs.
(B) Neon is used in safety devices for protecting electrical instruments.
(C) Radon is used in radiotherapy of cancer.
(D) Helium is filled in tubes of cycles and scooters tyres.

Q.140 Helium is added to oxygen used by deep sea divers because –
(A) it is less soluble in blood than nitrogen under high pressure.
(B) it is lighter than nitrogen.
(C) it is readily miscible with oxygen.
(D) it is less poisonous than nitrogen.

Q.141 Which compound is prepared by the following reaction:

$$Xe + F_2 \xrightarrow[673\text{ K}]{Ni}$$

(2 : 1 volume ratio)

(A) XeF_4 (B) XeF_2

(C) XeF_6 (D) None of these

Q.142 Compound with the geometry square pyramidal and sp^3d^2 hybridisation is

(A) $XeOF_2$ (B) $XeOF_4$

(C) XeO_4 (D) XeO_2F_2

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

Q.1 A salt of sulphurous acid is called –

(A) Sulphate (B) Sulphurate

(C) Sulphite (D) Sulphide

Q.2 Chlorine can remove –

(A) Br from NaBr solution (B) F from NaF solution

(C) Cl from NaCl solution (D) F from CaF_2 solution

Q.3 When chlorine is passed over dry slaked lime at room temperature, the main reaction product is

(A) $Ca(ClO_2)_2$ (B) $CaCl_2$

(C) $CaOCl_2$ (D) $Ca(OCl_2)_2$

Q.4 HI cannot be prepared by the action of conc. H_2SO_4 on KI

(A) HI is stronger than H_2SO_4

(B) HI is more volatile than H_2SO_4

(C) H_2SO_4 is an oxidising agent

(D) H_2SO_4 forms complex

Q.5 White enamel of our teeth is

(A) $Ca_3(PO_4)_2$ (B) CaF_2

(C) $CaCl_2$ (D) $CaBr_2$

Q.6 Which of the following reaction is not feasible

(A) $2KI + Br_2 \rightarrow 2KBr + I_2$

(B) $2H_2O + 2F_2 \rightarrow 2HF + O_2$

(C) $2KBr + I_2 \rightarrow 2KI + Br_2$

(D) $2KBr + Cl_2 \rightarrow 2KCl + Br_2$

Q.7 Which of the following is not known

(A) NCl_5 (B) NI_3

(C) $SbCl_3$ (D) NCl_3

Q.8 Which of the following oxide of nitrogen is the anhydride of HNO_3

(A) NO (B) N_2O_3

(C) N_3O_4 (D) N_2O_5

Q.9 If phosphoric acid is allowed to react with sufficient quantity of NaOH, the product obtained is

(A) $NaHPO_3$ (B) Na_2HPO_4

(C) NaH_2PO_4 (D) Na_3PO_4

Q.10 Electrolysis temperature is maximum for

(A) AsH_3 (B) NH_3

(C) PH_3 (D) SbH_3

Q.11 Which of the following is kept in water?

(A) White phosphorous (B) Sodium

(C) Potassium (D) Calcium

Q.12 Pure nitrogen can be prepared from

(A) NH_4OH (B) Ca_3N_2

(C) NH_4NO_2 (D) $Ba(NO_3)_2$

Q.13 Sulphur molecule is converted into sulphur ion, when it

(A) Gains two electrons (B) Loses two electrons

(C) Gains two protons (D) Shares two electrons

Q.14 Which compound acts as an oxidising as well as reducing agent

(A) SO_2 (B) MnO_2

(C) Al_2O_3 (D) CrO_3

Q.15 Which of the following is acidic

(A) SO_3 (B) N_2O

(C) BeO (D) HgO

Q.16 Fluorine reacts with water to give

(A) HF and O_2 (B) HF and OF_2

(C) HF and O_3 (D) HF, O_2 and O_3

Q.17 In the manufacture of bromine from sea water, the mother liquor containing bromides is treated with

(A) CO_2 (B) Cl_2

(C) I_2 (D) SO_2

Q.18 Hydrogen bonding does not play any role in boiling of

(A) NH_3 (B) H_2O

(C) HI (D) C_2H_5OH

Q.19 Aqueous solutions of hydrogen sulphide and sulphur dioxide when mixed together, yield

(A) Sulphur and water

(B) Sulphur trioxide and water

(C) Hydrogen peroxide and sulphur

(D) Hydrogen and sulphurous acid

Q.20 H_2S react with O_2 to form

(A) $H_2O + S$ (B) $H_2O + SO_2$

(C) $H_2O + SO_3$ (D) $H_2SO_4 + S$

Q.21 Bromine is liberated when an aqueous solution of potassium bromide is treated with

(A) Cl_2 (B) I_2

(C) Dilute H_2SO_4 (D) SO_2

Q.22 When Cl_2 gas is passed through hot and conc. solution of KOH, following compound is formed

(A) KCl (B) $KClO_3$

(C) $KClO_2$ (D) $KClO_4$

Q.23 In KI solution, I_2 readily dissolves and forms

(A) I^- (B) KI_2

(C) KI_2^- (D) KI_3

Q.24 Which one of the following elements does not form stable diatomic molecules –

(A) Iodine (B) Phosphorus

(C) Nitrogen (D) Oxygen

Q.25 Maximum covalency of sulphur is –

(A) 2 (B) 4

(C) 6 (D) –2

Q.26 Which of the following is soluble in water –

(A) AgF (B) AgCl

(C) AgBr (D) AgI

Q.27 Which one is most stable to heat –
(A) HClO (B) $HClO_2$
(B) $HClO_3$ (D) $HClO_4$

Q.28 The weakest Cl – O bond found in –
(A) ClO_4^- (B) ClO_2^-
(C) ClO^- (D) ClO_3^-

Q.29 Which one of the following noble gases is most abundant in atmosphere
(A) He (B) Ne
(C) Ar (D) Xe

Q.30 The boiling point and melting point of inert gases are –
(A) Low (B) High
(C) Very high (D) Very low

Q.31 The ease of liquefaction of noble gases increases in the order
(A) He < Ne < Ar < Kr < Xe (B) Xe < Kr < Ne < Ar < He
(C) Kr < Xe < He < Ne < Ar (B) Ar < Kr < Xe < Ne < He

Q.32 Chlorine water on standing loses its yellow colour due to
(A) Formation of HCl and HOCl
(B) Formation of HCl and $HClO_4$
(C) Evaporation of water
(D) All of these

Q.33 Conc. H_2SO_4 displaces hydrogen chloride from chlorides because
(A) It is stronger acid
(B) Sulphates are less soluble than chlorides
(C) Sulphates are more soluble than chlorides
(D) HCl is a gas while H_2SO_4 is a liquid

Q.34 Which of the following formula represents the fuming sulphuric acid (oleum) ?
(A) $H_2S_2O_4$ (B) H_2SO_5
(C) $H_2S_2O_7$ (D) $H_2S_2O_8$

Q.35 If HNO_3 changes into N_2O, the oxidation number is changed by
(A) 2 (B) 6
(C) 0 (D) 4

Q.36 In nitrogen family, the H–M–H bond angle in the hydrides gradually becomes closer to 90° on going from N to Sb. This shows that gradually
(A) The basic strength of the hydrides increases.
(B) Almost pure p-orbitals are used for M–H bonds.
(C) The bond energies of M–H bonds increase.
(D) The bond pairs of electrons become nearer to the central atom.

Q.37 What is the hybridization state of the central atom in the conjugate base of NH_4^+ ion ?
(A) sp (B) sp^3
(C) sp^2 (D) dsp^2

Q.38 How is H_2S prepared in laboratory ?
(A) $FeSO_4 + H_2SO_4$
(B) FeS + dil. H_2SO_4
(C) FeS + conc. H_2SO_4
(D) Elementary H_2 + elementary S

Q.39 Nitric acid on standing develops brownish colour which may be attributed to the presence of
(A) NO_2^+ ions (B) NO_3^- ions
(C) NO_2 (D) HNO_2

Q.40 Bromine water reacts with SO_2 to form
(A) H_2O and HBr (B) H_2SO_4 + HBr
(C) HBr and S (D) S and H_2O

Q.41 Iron sulphide is heated in air to form A, an oxide of sulphur. A is dissolved in water to give an acid. The basicity of this acid is ..
(A) 2 (B) 3
(C) 1 (D) Zero

Q.42 One mole of calcium phosphide on reaction with excess water gives
(A) One mole of phosphine
(B) Two moles of phosphoric acid
(C) Two moles of phosphine
(D) One mole of phosphorus pentoxide

Q.43 Which of the following is obtained when N_2 reacts with calcium carbide ?
(A) Calcium cyanate (B) Calcium acetate
(C) Calcium cyanamide (D) Calcium carbonate

Q.44 What are the products obtained when ammonia is reacted with excess chlorine ?
(A) N_2 and NCl_3 (B) N_2 and HCl
(C) N_2 and NH_4Cl (D) NCl_3 and HCl

Q.45 Which of the following has $p\pi - d\pi$ bonding ?
(A) NO_3^- (B) SO_3^{2-}
(C) BO_3^{3-} (D) CO_3^{2-}

Q.46 In the given reaction for the preparation of XeF_4, what is the ratio of Xe and F_2 used ?

$$Xe_{(g)} + 2F_2(g) \xrightarrow{873K,\ 7bar} XeF_{4(s)}$$

(A) 1 : 2 (B) 1 : 5
(C) 1 : 10 (D) 1 : 20

Q.47 Which of the following is used to remove plutonium from spent nuclear fuel ?
(A) OF_2 (B) O_2F_2
(C) OF_3 (D) O_2F_3

Q.48 When conc. H_2SO_4 comes in contact with sugar, it becomes black due to
(A) Hydrolysis (B) Hydration
(C) Decolourisation (D) Dehydration

Q.49 Among noble gases (from He to Xe) only xenon reacts with fluorine to form stable xenon fluorides because xenon
(A) Has the largest size
(B) Has the lowest ionization enthalpy
(C) Has the highest heat of vapourization
(D) Is the most readily available noble gas

Q.50 When I_2 is passed through KCl, KF, KBr solutions
(A) Cl_2 and Br_2 are evolved (B) Cl_2 is evolved
(C) Cl_2, Br_2, F_2 are evolved (D) None of these

Q.51 Which one of the following reactions of xenon compounds is not feasible ?
(A) $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$
(B) $3XeF_4 + 6H_2O \rightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$
(C) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
(D) $XeF_6 + RbF \longrightarrow Rb[XeF_7]$

Q.52 Which of the following is not correct ?

(A) Hydrolysis of NCl_3 gives NH_3 and HOCl
(B) NH_3 is less stable than PH_3
(C) NH_3 is a weak reducing agent compared to PH_3
(D) Nitric oxide in solid state exhibits diamagnetism.

Q.53 Each of the following is true for white and red phosphorus except that they

(A) are both soluble in CS_2.
(B) can be oxidized by heating in air.
(C) consist of the same kind of atoms.
(D) can be converted into one another.

Q.54 In XeF_2, XeF_4 and XeF_6 the number of lone pairs on Xe is respectively

(A) 2, 3, 1 (B) 1, 2, 3
(C) 4, 1, 2 (D) 3, 2, 1

Q.55 Nitrogen forms N_2 but phosphorus is converted into P_4 from P_2. The reason for this is

(A) Triple bond is present between phosphorus atoms
(B) P – P bonding is weak
(C) P – P bonding is strong
(D) Multiple bond is formed easily.

Q.56 $2SO_2 + O_2 \xrightarrow{I} 2SO_3$

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

Here, I and II are

(A) I–$CuCl_2$, II - V_2O_5 (B) I – V_2O_5, II–$CuCl_2$
(C) I-V_2O_5, II–MnO_2 (D) I – MnO_2, II – $CuCl_2$

Q.57 Dry SO_2 does not bleach dry flowers because

(A) nascent hydrogen responsible for bleaching is produced only in presence of moisture.
(B) water is the actual reducing agent responsible for bleaching.
(C) water is stronger acid than SO_2.
(D) the OH^- ions produced by water cause bleaching.

Q.58 White phosphorus when boiled with strong solutions of caustic soda produces :

(A) Sodium phosphide (B) Sodium phosphate
(C) Phosphine (D) Red phosphorus

Q.59 Ionisation enthalpy of group 15 elements –

I. decreases down the group due to the gradual increase in atomic size.
II. it is higher than that of group 14 elements in the corresponding periods.
III. the order of successive ionisation enthalpies is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$

Which of these statements is/are true? Choose the correct option.

(A) I and II (B) II and III
(C) I and III (D) I, II and III

Q.60 Which oxide of the chlorine is used as a bleaching agent for paper pulp and textiles and in water treatment?

(A) Cl_2O (B) ClO_2
(C) Cl_2O_6 (D) Cl_2O_7

Q.61 The behaviour of sulphur while reacting with water and alkalies is similar to that of

(A) CO (B) O_2
(C) O_3 (D) CO_2

Q.62 Which species is basic and reducing?

(A) SO_3^{2-} (B) SO_4^{2-}
(C) $S_2O_4^{2-}$ (D) HSO_4^-

Q.63 Which of the following statements is not correct?

(A) All the oxides of halogens are powerful oxidants.
(B) The compounds of oxygen and fluorine are not called oxides but fluorides.
(C) Oxygen fluorides form oxoacids.
(D) In oxyhalides, bonds are mainly covalent due to small difference in electro negativity of oxygen and halogens.

Q.64 Nitrogen forms stable N_2 molecule but phosphorus is converted to P_4 from P_2 because

(A) $p\pi - p\pi$ bonding is strong in phosphorus.
(B) $p\pi - p\pi$ bonding is weak in phosphorus.
(C) triple bond is present in phosphorus.
(D) single P–P bond is weaker than N –N bond.

Q.65 I. N_2O is a linear molecule.

II. Its resonating structure is

$$\underset{..}{\ddot{N}} = N = \underset{..}{\ddot{O}} \leftrightarrow :N \equiv N - \underset{..}{\ddot{O}}:$$

III. Bond length of N – N and N – O is 113pm and 119 pm respectively in N_2O

The correct statement{s) is/are

(A) Only I (B) Only II
(C) Only III (D) All of these

Q.66 An element (X) forms compounds of the formula XCl_3, X_2O_5 and Ca_3X_2 but does not form XCl_5. Which of the following is the element X ?

(A) B (B) Al
(C) N (D) P

Q.67 Which of the following is not correctly matched?

(A) PCl_5 – sp^3d hybridisation
(B) PCl_3 – sp^3 hybridisation
(C) PCl_5 (solid) – $[PtCl_4]^+ [PtCl_6]^-$
(D) H_3PO_3 – tribasic

EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

NOTE : The answer to each question is a NUMERICAL VALUE.

Q.1 Among the following, the number of compounds that can react with PCl_5 to give $POCl_3$ is O_2, CO_2, SO_2, H_2O, H_2SO_4, P_4O_{10}.

Q.2 Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is

$$XeF_6 \xrightarrow[\text{Hydrolysis}]{\text{Complete}} P + \text{Other product} \xrightarrow{OH^-/H_2O} Q$$

$$\xrightarrow[\text{in } OH^-/H_2O]{\text{Slow disproportionation}} \text{Products}$$

Q.3 Consider the following list of reagents :
Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3, and $Na_2S_2O_3$.
The total number of reagents that can oxidise aqueous iodide to iodine is –

Q.4 The number of P – O – P bonds in cyclic metaphosphoric acid is –

Q.5 The number of S – S bonds in sulphur trioxide trimer (S_3O_9) is –

Q.6 The volume of 2M NaOH required to convert 12 grams of NaH_2PO_4 [$M = 120 \text{gm mo}^{-1}$] into Na_3PO_4 is

EXERCISE - 4 [PREVIOUS YEARS JEE MAIN QUESTIONS]

Q.1 The correct no. of lone pairs on the central atom of compounds XeF_2, XeF_4 & XeF_6 are respectively-
(A) 3, 2, 1 (B) 4, 3, 2 **[AIEEE-2002]**
(C) 1, 3, 4 (D) 1, 2, 3

Q.2 The no. of σ bonds in the compound P_4O_{10} is -
(A) 1 (B) 4 **[AIEEE-2002]**
(C) 3 (D) 16

Q.3 The number of hydrogen atoms (s) attached to phosphorus atom in hypophosphorous acid is –
(A) two (B) zero **[AIEEE-2005]**
(C) three (D) one

Q.4 What products are expected from the disproportionation reaction of hypochlorous acid – **[AIEEE- 2006]**
(A) $HClO_2$ and $HClO_4$ (B) HCl and Cl_2O
(C) HCl and $HClO_3$ (D) $HClO_3$ and Cl_2O

Q.5 Which one of the following statements regarding helium is incorrect - **[AIEEE-2007]**
(A) It is used to produce and sustain powerful superconducting magnets.
(B) It is used as a cryogenic agent for carrying out experiments at low tempeatures.
(C) It is used to fill gas balloons instead of hydrogen because it it lighter then hydrogen and non-inflammable
(D) It is used in gas-cooled nuclear reactors.

Q.6 Which one of the following reactions of Xenon compounds is not feasible ? **[AIEEE-2009]**
(A) $3\,XeF_4 + 6\,H_2O \rightarrow 2\,Xe + XeO_3 + 12\,HF + 1.5\,O_2$
(B) $2\,XeF_2 + 2H_2O \rightarrow 2\,Xe + 4\,HF + O_2$
(C) $XeF_6 + RbF \rightarrow Rb\,[XeF_7]$
(D) $XeO_3 + 6\,HF \rightarrow XeF_6 + 3\,H_2O$

Q.7 In which of the following arrangements, the sequence is not strictly according to the property written against it ? **[AIEEE-2009]**
(A) $HF < HCl < HBr < HI$: increasing acid strength
(B) $NH_3 < PH_3 < AsH_3 < SbH_3$: increasing basic strength
(C) $B < C < O < N$: increasing first ionization enthalpy
(D) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power

Q.8 Which of the following statement is wrong ?
(A) The stability of hydrides increase from NH_3 to BiH_3 in group 15 of the periodic table. **[AIEEE-2011]**
(B) Nitrogen cannot form dπ-pπ bond.
(C) Single N–N bond is weaker than the single P– P bond.
(D) N_2O_4 has two resonance structure

Q.9 Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides? **[AIEEE-2011]**
(A) $Al_2O_3 < MgO < Na_2O < K_2O$
(B) $MgO < K_2O < Al_2O_3 < Na_2O$
(C) $Na_2O < K_2O < MgO < Al_2O_3$
(D) $K_2O < Na_2O < Al_2O_3 < MgO$

Q.10 Which of the following statements regarding sulphur is incorrect ? **[AIEEE-2011]**
(A) S_2 molecule is paramagnetic.
(B) The vapour at 200ºC consists mostly of S_8 rings.
(C) At 600ºC the gas mainly consists of S_2 molecules.
(D) The oxidation state of sulphur is never less than +4 in its compounds.

Q.11 The molecule having smallest bond angle is –
(A) NCl_3 (B) $AsCl_3$ **[AIEEE-2012]**
(C) $SbCl_3$ (D) PCl_3

Q.12 Which of the following is the wrong statement ?
(A) ONCl and ONO^- are not isoelectronic.
(B) O_3 molecule is bent **[JEE MAIN 2013]**
(C) Ozone is violet-black in solid state
(D) Ozone is diamagnetic gas.

Q.13 Which one of the following properties is not shown by NO? **[JEE MAIN 2014]**
(A) It combines with oxygen to form nitrogen dioxide.
(B) It's bond order is 2.5.
(C) It is diamagnetic in gaseous state.
(D) It is a neutral oxide

Q.14 Among the following oxoacids, the correct decreasing order of acid strength is: **[JEE MAIN 2014]**
(A) $HClO_4 > HClO_3 > HClO_2 > HOCl$
(B) $HClO_2 > HClO_4 > HClO_3 > HOCl$
(C) $HOCl > HClO_2 > HClO_3 > HClO_4$
(D) $HClO_4 > HOCl > HClO_2 > HClO_3$

Q.15 **Assertion :** N_2 & O_2 are the main components in the atm but these do not react to form oxides of nitrogen.
Reason : The reaction between nitrogen and oxygen requires high temperature. **[JEE MAIN 2015]**
(A) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.
(B) The assertion is incorrect, but the reason is correct.
(C) Both the assertion and reason are incorrect.
(D) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.

Q.16 Which among the following is the most reactive?
(A) Br_2 (B) I_2 **[JEE MAIN 2015]**
(C) ICl (D) Cl_2

Q.17 Which one has the highest boiling point?
(A) Ne (B) Kr **[JEE MAIN 2015]**
(C) Xe (D) He

Q.18 The pair in which phosphorous atoms have a formal oxidation state of +3 is : **[JEE MAIN 2016]**
(A) Pyrophosphorous and hypophosphoric acids
(B) Orthophosphorous and hypophosphoric acids
(C) Pyrophosphorous and pyrophosphoric acids
(D) Orthophosphorous and pyrophosphorous acids

Q.19 The reaction of zinc with dilute and concentrated nitric acid, respectively, produces: **[JEE MAIN 2016]**
(A) NO_2 and NO (B) NO and N_2O
(C) NO_2 and N_2O (D) N_2O and NO_2

Q.20 The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are: **[JEE MAIN 2017]**

(A) Cl^- and ClO_2^- (B) ClO^- and ClO_3^-

(C) ClO_2^- and ClO_3^- (D) Cl^- and ClO^-

Q.21 Which reactions is an example of a redox reaction? **[JEE MAIN 2017]**

(A) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

(B) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

(C) $XeF_2 + PF_5 \rightarrow [XeF]^+ PF_6^-$

(D) $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

Q.22 The compound that does not produce nitrogen gas by the thermal decomposition is : **[JEE MAIN 2018]**

(A) NH_4NO_2 (B) $(NH_4)_2SO_4$

(C) $Ba(N_3)_2$ (D) $(NH_4)_2Cr_2O_7$

Q.23 Good reducing nature of H_3PO_2 attributed to the presence of: **[JEE MAIN 2019 (Jan)]**

(A) One P-OH bond (B) One P-H bond

(C) Two P-H bonds (D) Two P-OH bonds

Q.24 The correct order of the oxidation states of nitrogen in NO, N_2O, NO_2 and N_2O_3 is : **[JEE MAIN 2019 (APRIL)]**

(A) $NO_2 < N_2O_3 < NO < N_2O$

(B) $NO_2 < NO < N_2O_3 < N_2O$

(C) $N_2O < N_2O_3 < NO < NO_2$

(D) $N_2O < NO < N_2O_3 < NO_2$

Q.25 HF has highest boiling point among hydrogen halides, because it has : **[JEE MAIN 2019 (APRIL)]**

(A) lowest dissociation enthalpy.

(B) strongest van der Waals' interactions.

(C) strongest hydrogen bonding.

(D) lowest ionic character.

Q.26 The oxoacid of sulphur that does not contain bond between sulphur atoms is : **[JEE MAIN 2019 (APRIL)]**

(A) $H_2S_4O_6$ (B) $H_2S_2O_7$

(C) $H_2S_2O_3$ (D) $H_2S_2O_4$

Q.27 The number of pentagons in C_{60} and trigons (triangles) in white phosphorus, respectively, are: **[JEE MAIN 2019 (APRIL)]**

(A) 12 and 3 (B) 20 and 4

(C) 12 and 4 (D) 20 and 3

Q.28 The electron gain enthalpy (in kJ/mol) of fluorine, chlorine, bromine and iodine, respectively are : **[JEE MAIN 2020 (JAN)]**

(A) –296, – 325, – 333, – 349

(B) –333, – 349, – 325, –296

(C) –349, – 333, – 325, – 296

(D) –325, – 333, – 349, – 296

Q.29 Chlorine reacts with hot and concentrated NaOH and produces compounds (X) and (Y). Compound (X) gives white precipitate with silver nitrate solution. The average bond order between Cl and O atoms in (Y) is ______. **[JEE MAIN 2020 (JAN)]**

Q.30 $\underset{\text{Hot \& conc.}}{NaOH} + Cl_2 \rightarrow A + \text{other products}$

$\underset{\text{Cold \& dil.}}{Ca(OH)_2} + Cl_2 \rightarrow B + \text{other products}$

A and B are respectively **[JEE MAIN 2020 (JAN)]**

(A) $NaClO_3$, $Ca(OCl)_2$ (B) $NaClO_3$, $Ca(ClO_3)_2$

(C) NaCl, $Ca(ClO_3)_2$ (D) NaClO, $Ca(ClO_3)_2$

Q.31 Number of S–O bond in $S_2O_8^{2-}$ and number of S–S bond in Rhombic sulphur are respectively: **[JEE MAIN 2020 (JAN)]**

(A) 8, 8 (B) 6, 8

(C) 2, 4 (D) 4, 2

Q.32 A metal A on heating in nitrogen gas gives compound B. B on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a dark blue-violet coloured solution. a and b respectively, are : **[JEE MAIN 2020 (JAN)]**

(A) Mg and Mg_3N_2 (B) Na and $NaNO_3$

(C) Mg and $Mg(NO_3)_2$ (D) Na and Na_3N

Q.33 White Phosphorus on reaction with concentrated NaOH solution in an inert atmosphere of CO_2 gives phosphine and compound (X). (X) on acidification with HCl gives compound (Y). The basicity of compound (Y) is : **[JEE MAIN 2020 (JAN)]**

(A) 1 (B) 2

(C) 3 (D) 4

Q.34 The acidic, basic and amphoteric oxides, respectively, are : **[JEE MAIN 2020 (JAN)]**

(A) MgO, Cl_2O, Al_2O_3 (B) Cl_2O, CaO, P_4O_{10}

(C) Na_2O, SO_3, Al_2O_3 (D) N_2O_3, Li_2O, Al_2O_3

EXERCISE - 5 [PREVIOUS YEARS AIPMT / NEET QUESTIONS]

Q.1 Among the following molecules
(i) XeO_3 (ii) $XeOF_4$ (iii) XeF_6 **[AIPMT 2005]**
those having same number of lone pairs on Xe are –
(A) (i) and (ii) only
(B) (i) and (iii) only
(C) (ii) and (iii) only
(D) (i), (ii) and (iii)

Q.2 The correct order of acid strength is – **[AIPMT 2005]**
(A) $HClO_4 < HClO_3 < HClO_2 < HClO$
(B) $HClO < HClO_2 < HClO_3 < HClO_4$
(C) $HClO_4 < HClO < HClO_2 < HClO_3$
(D) $HClO_2 < HClO_3 < HClO_4 < HClO$

Q.3 Which of the following is the most basic oxide –
(A) Sb_2O_3
(B) Bi_2O_3 **[AIPMT 2006]**
(C) SeO_2
(D) Al_2O_3

Q.4 Which one of the following orders is not in in accordance with the property stated against is **[AIPMT 2006]**
(A) Acidic property in water : $HI > HBr > HCl > HF$
(B) Electronegativity : $F_2 > Cl_2 > Br_2 > I_2$
(C) Bond dissociation energy : $F_2 > Cl_2 > Br_2 > I_2$
(D) Oxidising power : $F_2 > Cl_2 > Br_2 > I_2$

Q.5 The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5D) is larger than that NF_3 (0.2 D). This is because **[AIPMT 2006]**
(A) In NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite directions.
(B) In NH_3 as well as NF_3 the atomic dipole and bond dipole are in opposite directions
(C) In NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3 these are in same direction.
(D) In NH_3 as well as in NF_3 the atomic dipole and bond dipole are in the same direction.

Q.6 In which of the following molecules all the bonds are not equal:- **[AIPMT 2006]**
(A) ClF_3
(B) BF_3
(C) AlF_3
(D) NF_3

Q.7 Which one of the following orders correctly represents the increasing acid strengths of the given acids – **[AIPMT 2007]**
(A) $HOClO < HOCl < HOClO_3 < HOClO_2$
(B) $HOClO_2 < HOClO_3 < HOClO < HOCl$
(C) $HOClO_3 < HOClO_2 < HOClO < HOCl$
(D) $HOCl < HOClO < HOClO_2 < HOClO_3$

Q.8 The angular shape of ozone molecule (O_3) consists of: **[AIPMT 2008]**
(A) 2 sigma and 1 pi bonds
(B) 1 sigma and 2 pi bonds
(C) 2 sigma and 2 pi bonds
(D) 1 sigma and 1 pi bonds

Q.9 Among the following which is the strongest oxidising agent? **[AIPMT 2009]**
(A) Br_2
(B) I_2
(C) Cl_2
(D) F_2

Q.10 The tendency of BF_3, BCl_3 and BBr_3 to behave as Lewis acid decreases in the sequence : **[AIPMT [PRE] 2010]**
(A) $BCl_3 > BF_3 > BBr_3$
(B) $BBr_3 > BCl_3 > BF_3$
(C) $BBr_3 > BF_3 > BCl_3$
(D) $BF_3 > BCl_3 > BBr_3$

Q.11 Oxidation states of P in $H_4P_2O_5$, $H_4P_2O_6$, $H_4P_2O_7$ are respectively **[AIPMT [PRE] 2010]**
(A) +3, +5, +4
(B) +5, +3, +4
(C) +5, +4, +3
(D) +3, +4, +5

Q.12 The correct order of increasing bond angles in the following species are : **[AIPMT [PRE] 2010]**
(A) $Cl_2O < ClO_2 < ClO_2^-$
(B) $ClO_2 < Cl_2O < ClO_2^-$
(C) $Cl_2O < ClO_2^- < ClO_2$
(D) $ClO_2^- < Cl_2O < ClO_2$

Q.13 How many bridging oxygen atoms are present in P_4O_{10}? **[AIPMT [MAIN] 2010]**
(A) 6
(B) 4
(C) 2
(D) 5

Q.14 Which one of the following is present as an active ingredient in bleaching powder for bleaching action? **[AIPMT [PRE] 2011]**
(A) $CaCl_2$
(B) $CaOCl_2$
(C) $Ca(OCl)_2$
(D) CaO_2Cl

Q.15 Sulphur trioxide can be obtained by which of the following reaction : **[AIPMT [PRE] 2012]**
(A) $CaSO_4 + C \xrightarrow{\Delta}$
(B) $Fe_2(SO_4)_3 \xrightarrow{\Delta}$
(C) $S + H_2SO_4 \xrightarrow{\Delta}$
(D) $H_2SO_4 + PCl_5 \xrightarrow{\Delta}$

Q.16 Which of the following statements is not valid for oxoacids of phosphorus ? **[AIPMT [PRE] 2012]**
(A) Orthophosphoric acid is used in the manufacture of triple superphosphate.
(B) Hypophosphorous acid is a diprotic acid.
(C) All oxoacids contain tetrahedral four coordinated phosphorus.
(D) All oxoacids contain atleast one P = O unit and one P–OH group.

Q.17 In which of the following arrangements the given sequence is not strictly according to the property indicated against it ? **[AIPMT [MAINS] 2012]**
(A) Increasing acidic strength : $HF < HCl < HBr < HI$
(B) Increasing pK_a values : $H_2O < H_2S < H_2Se < H_2Te$
(C) Increasing acidic character: $NH_3 < PH_3 < AsH_3 < SbH_3$
(D) Increasing oxidising power : $CO_2 < SiO_2 < SnO_2 < PbO_2$

Q.18 Which of the following statements about the interstitial compounds is incorrect ? **[NEET 2013]**
(A) They have higher melting points than the pure metal.
(B) They retain metallic conductivity.
(C) They are chemically reactive.
(D) They are much harder than the pure metal.

Q.19 Which is the strongest acid in the following **[NEET 2013]**
(A) H_2SO_3
(B) H_2SO_4
(C) $HClO_3$
(D) $HClO_4$

Q.20 Acidity of diprotic acids in aqueous solutions increases in the order **[AIPMT 2014]**
(A) $H_2S < H_2Se < H_2Te$
(B) $H_2Se < H_2S < H_2Te$
(C) $H_2Te < H_2S < H_2Se$
(D) $H_2Se < H_2Te < H_2S$

Q.21 Nitrogen dioxide and sulphur dioxide have some properties in common. Which property is shown by one of these compounds, but not by the other?
(A) is a reducing agent. **[AIPMT 2015]**
(B) is soluble in water.
(C) is used as a food-preservative.
(D) form 'acid-rain'.

Q.22 Strong reducing behaviour of H_3PO_2 is due to :
(A) High oxidation state of phosphorus. **[RE-AIPMT 2015]**
(B) Presence of two – OH groups and one P – H bond.
(C) Presence of one – OH group and two P – H bonds.
(D) High electron gain enthalpy of phosphorus.

Q.23 Which of the statements given below is incorrect?
(A) ONF is isoelectronic with O_2N^- **[RE-AIPMT 2015]**
(B) OF_2 is an oxide of fluorine.
(C) Cl_2O_7 is an anhydride of perchloric acid.
(D) O_3 molecule is bent

Q.24 The variation of the boiling points of the hydrogen halides is in the order HF > HI > HBr > HCl. What explains the higher boiling point of hydrogen fluoride?
(A) The bond energy of HF molecules is greater than in other hydrogen halides. **[RE-AIPMT 2015]**
(B) The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule.
(C) The electronegativity of fluorine is much higher than for other elements in the group.
(D) There is strong hydrogen bonding between HF molecules.

Q.25 The formation of the oxide ion, O^{2-} (g), from oxygen atom requires first an exothermic and then an endothermic step as shown below :
$O(g) + e^- \rightarrow O^-(g)\ ;\ \Delta_f H^\ominus = -141\ kJ\ mol^{-1}$
$O^-(g) + e^- \rightarrow O^{2-}(g)\ ;\ \Delta_f H^\ominus = +780\ kJ\ mol^{-1}$
Thus process of formation of O^{2-} in gas phase is unfavourable even thought O^{2-} is isoelectronic with neon. It is due to the fact that, **[RE-AIPMT 2015]**
(A) Oxygen is more electronegative
(B) Addition of electron in oxygen results in larger size of the ion.
(C) Electron repulsion outweighs the stability gained by achieving noble gas configuration.
(D) O^- ion has comparatively smaller size than oxygen atom.

Q.26 Among the following, the correct order of acidity is **[NEET 2016 PHASE 1]**
(A) $HClO_3 < HClO_4 < HClO_2 < HClO$
(B) $HClO < HClO_2 < HClO_3 < HClO_4$
(C) $HClO_2 < HClO < HClO_3 < HClO_4$
(D) $HClO_4 < HClO_2 < HClO < HClO_3$

Q.27 When copper is heated with conc. HNO_3, it produces **[NEET 2016 PHASE 1]**
(A) $Cu(NO_3)_2$ and NO_2 (B) $Cu(NO_3)_2$ and NO
(C) $Cu(NO_3)_2$, NO and NO_2 (D) $Cu(NO_3)_2$ and N_2O

Q.28 Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules? **[NEET 2016 PHASE 1]**
(A) $I_2 > Br_2 > Cl_2 > F_2$ (B) $Cl_2 > Br_2 > F_2 > I_2$
(C) $Br_2 > I_2 > F_2 > Cl_2$ (D) $F_2 > Cl_2 > Br_2 > I_2$

Q.29 The product obtained as a result of a reaction of nitrogen with CaC_2 is **[NEET 2016 PHASE 1]**
(A) $CaCN_2$ (B) CaCN
(C) $CaCN_3$ (D) Ca_2CN

Q.30 Match the compounds given in Column-I with the hybridisation and shape given in Column-II and mark the corect option. **[NEET 2016 PHASE 1]**

Column-I	Column-II
(a) XeF_6	(i) Distorted octahedral
(b) XeO_3	(ii) Square planar
(c) $XeOF_4$	(iii) Pyramidal
(d) XeF_4	(iv) Square pyramidal

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

Q.31 Which is the correct statement for the given acids? **[NEET 2016 PHASE 1]**
(A) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid.
(B) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid.
(C) Both are triprotic acids
(D) Both are diprotic acids

Q.32 Which of the following fluoro-compounds is most likely to behave as a Lewis base? **[NEET 2016 PHASE 2]**
(A) BF_3 (B) PF_3
(C) CF_4 (D) SiF_4

Q.33 Hot concentrated sulphuric acid is a moderately strong oxidizing agent. Which of the following reactions does not show oxidizing behaviour? **[NEET 2016 PHASE 2]**
(A) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + + 2H_2O$
(B) $3S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$
(C) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$
(D) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

Q.34 The correct geometry and hybridization for XeF_4 are **[NEET 2016 PHASE 2]**
(A) Octahedral, sp^3d^2 (B) Trigonal bipyramidal, sp^3d
(C) Planar triangle, sp^3d^3 (D) Square planar, sp^3d^2

Q.35 Among the following, which one is a wrong statement?
(A) PH_5 and $BiCl_5$ do not exist **[NEET 2016 PHASE 2]**
(B) $p\pi$-$d\pi$ bonds are present in SO_2
(C) SeF_4 and CH_4 have same shape
(D) I_3^+ has bent geometry.

Q.36 Name the gas that can readily decolourise acidified $KMnO_4$ solution : **[NEET 2017]**
(A) SO_2 (B) NO_2
(C) P_2O_5 (D) CO_2

Q.37 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

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

Q.38 In which pair of ions both the species contain S–S bond? **[NEET 2017]**

(A) $S_4O_6^{2-}$, $S_2O_3^{2-}$
(B) $S_2O_7^{2-}$, $S_2O_8^{2-}$
(C) $S_4O_6^{2-}$, $S_2O_7^{2-}$
(D) $S_2O_7^{2-}$, $S_2O_3^{2-}$

Q.39 Which of the following statements is not true for halogens? **[NEET 2018]**

(A) All but fluorine show positive oxidation states.
(B) All are oxidizing agents.
(C) All form monobasic oxyacids.
(D) Chlorine has the highest electron-gain enthalpy

Q.40 Which oxide of nitrogen is not a common pollutant introduced into the atmosphere both due to natural and human activity? **[NEET 2018]**

(A) N_2O
(B) NO_2
(C) N_2O_5
(D) NO

Q.41 Match the following : **[NEET 2019]**

(a) Pure nitrogen	(i) Chlorine
(b) Haber process	(ii) Sulphuric acid
(c) Contact process	(iii)Ammonia
(d) Deacon's process	(iv) Sodium azide or Barium azide

Which of the following is the correct option?

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

Q.42 Match the Xenon compounds in Column-I with its structure in Column-II and assign the correct code: **[NEET 2019]**

Column-I	**Column-II**
(a) XeF_4	(i) Pyramidal
(b) XeF_6	(ii) Square planar
(c) $XeOF_4$	(iii) Distorted octahedral
(d) XeO_3	(iv) Square pyramidal

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

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	B	C	D	D	A	A	C	A	B	A	B	B	C	D	D	D	C	B	B	D	C	A	A	B
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	A	D	D	A	D	B	D	B	A	C	B	A	C	D	A	D	A	D	C	D	B	D	A	C	D
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
A	A	C	D	B	C	A	D	C	B	B	C	B	C	C	A	C	D	A	A	A	A	A	D	C	B
Q	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
A	D	B	C	C	C	D	C	D	D	D	C	A	A	C	B	D	C	C	C	C	C	B	A	B	D
Q	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125
A	C	B	C	A	C	D	B	A	D	A	D	C	A	C	D	D	B	B	D	C	A	C	A	D	D
Q	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142								
A	D	D	B	C	A	C	D	C	C	C	C	C	A	D	A	B	B								

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	C	A	C	C	B	C	A	D	D	B	A	C	A	A	A	D	B	C	A	A	A	B	D	B	C
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	A	D	C	C	D	A	A	D	C	D	B	B	B	C	B	A	C	C	D	B	B	B	D	B	D
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67								
A	A	B	A	D	B	B	A	C	D	B	D	A	C	B	D	C	D								

EXERCISE - 3

Q	1	2	3	4	5	6
A	4	2	7	3	1	100

EXERCISE - 4

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
A	A	D	A	C	C	D	B	A	A	D	C	None	C	A	D	C	C	D	D	D	B	B	C
Q	24	25	26	27	28	29	30	31	32	33	34												
A	D	C	B	C	B	1.67	A	A	A	A	D												

EXERCISE - 5

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	D	B	B	C	A	A	D	A	D	B	D	D	A	C	B	B	B	C	D	A	C	C	B	D	C
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42								
A	B	A	B	A	A	B	B	D	A	C	A	A	A	A	C	D	B								

p-BLOCK

TRY IT YOURSELF-1

(1) $\underset{A}{NaNO_3} + \underset{(conc.)}{H_2SO_4} \rightarrow \underset{B}{2HNO_3} + NaHSO_4$

$\underset{(C)}{3NO_2} + H_2O \rightarrow \underset{(B)}{2HNO_3} + NO\ (g)$

$\underset{(B)}{4HNO_3} \xrightarrow{Sunlight} \underset{(C)}{4NO_2} + 2H_2O + O_2$

(2) (D)

(3) (D)

(4) (D)

(5) **(ABCD).**

(A) $3Ca(OCl)Cl + NH_3 \xrightarrow[medium]{aqueous} 3CaCl_2 + N_2\uparrow + 3H_2O$

(B) $2NH_3 + 3PbO \xrightarrow{\Delta} 3Pb + N_2 + 3H_2O$

(C) $8NH_3\ (excess) + 3Cl_2 \xrightarrow{\Delta} N_2\uparrow + 6NH_4Cl$

(D) $NH_4Cl + NaNO_2 \xrightarrow{\Delta} NH_4NO_2 + NaCl$

$NH_4NO_2 \rightarrow N_2\uparrow + 2H_2O$

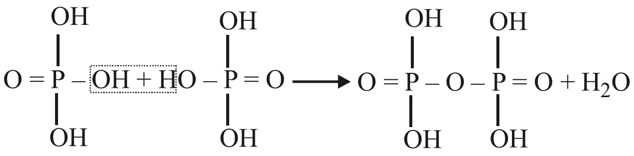
(6) (A)

(7) (A)

(8) (C)

(9) (A)

(10) **(C).**



$$O=\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}-\boxed{OH+H}O-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}=O \longrightarrow O=\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}=O+H_2O$$

TRY IT YOURSELF-2

(1) Oxidation state = +6 & –2 ; Basicity = 2

(2) (A)

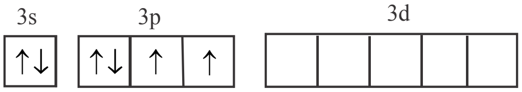
(3) (D)

(4) **(C).** Only (C) is wrong because $BaO_2 + O_3 \rightarrow BaO + 2O_2$. The rest of the alternatives are correct.

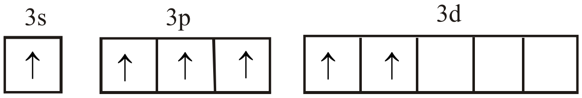
(5) (D)

(6) (B)

(7) **(C).** Sulphur atom in ground state



Sulphur atom in excited state

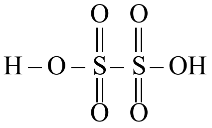


Due to presence of six unpaired electrons, it can form maximum of six bonds, so covalency is six.

(8) (B)

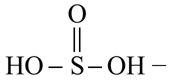
(9) (B)

(10) **(B).** $H_2S_2O_6$,



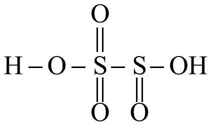
$H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$ – 4π-bonds

H_2SO_3,



$HO-\overset{\overset{O}{\|}}{S}-OH$ – one π-bonds

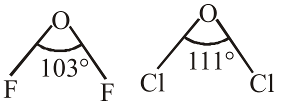
$H_2S_2O_5$,



$H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{S}-OH$ – 3π-bonds

TRY IT YOURSELF-3

(1) $Br_2O > Cl_2O > F_2O$



Angle increases because of steric crowding of the larger halogen atoms.

(2) **(C).** $Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$
(Slaked lime)

(3) (C)

(4) (A)

(5) **(A).** $Cl_2 + 2NaI \rightarrow 2NaCl + I_2$
(Violet colouration in chloroform)

$5Cl_2 + 6H_2O + I_2 \rightarrow 2HIO_3 + 10\,HCl$
colourless

(6) (B) **(7)** (A)

(8) (A) **(9)** (BC)

(10) (ACD)

TRY IT YOURSELF-4

(1) Heat of vapourisation, Xe > Kr > Ar > Ne > He.
Solubility of noble gases, Xe > Kr > Ar > Ne > He.

(2) **(C).** Coconut charcoal possess characteristic property for adsorbing different noble gases at different temperatures.

(3) (B)

(4) **(A).** Due to small size of He it does not form clathrates.

(5) (C)

(6) (C)

(7) (AB)

CHAPTER-7:
p-BLOCK (15, 16, 17 & 18)
EXERCISE-1

(1) **(B).** Bismuth does not show allotropy other elements show allotropy.
Nitrogen → α-nitrogen and β-nitrogen (solid crystalline forms)
Phosphorus → White, Red and Black forms
Arsenic → Yellow and Grey forms
Antimony → Yellow and Grey forms

(2) **(B).** $\xrightarrow{NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3}$
Stability decreases down the group because bond energy decreases down the group.

(3) **(C).** Boiling points of $SbH_3 (254\ K)$, $NH_3 (238\ K)$, $AsH_3 (211 K)$ and $PH_3 (185\ K)$ therefore boiling points are of the order $SbH_3 > NH_3 > AsH_3 > PH_3$.

(4) **(D).** Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.
Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids.

(5) **(D).** Ionic radii increases down the group.

(6) **(A).** O.S.of N in $N_3H = -1/3$
O.S.of N in $NH_3 = -3$
O.S.of N in $NH_2OH = -1$
O.S.of N in $N_2H_4 = -2$

(7) **(A).** Metallic character increases down the group.

(8) **(C).** Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.

(9) **(A).** Due to unavailability of d-orbitals in nitrogen it can form only NCl_3 and not NCl_5.

(10) **(B).** Chilesaltpetre is the common name of sodium nitrate $(NaNO_3)$.

(11) **(A).** P and As can form $d\pi - d\pi$ bond with transition elements when their compounds like $P(C_2H_5)_3$ & $As(C_6H_5)_3$ act as ligands.

(12) **(B).** The stability of +5 oxidation state decreases down the group due to inert pair effect.
The only well characterised Bi(V) compound is BiF_5 as fluorine being most electronegative element is able to unpair ns electrons.

(13) **(B).** Covalent and ionic radii of group 15 elements increase down the group.

(14) **(C).** $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4H_2O$

(15) **(D).** $6Li + N_2 \rightarrow 2Li_3N$ Lithium nitride
$3Mg + N_2 \rightarrow Mg_3N_2$ Magnesium nitride

(16) **(D).** Dinitrogen is a colourless, odourless, tasteless and non–toxic gas. It is less soluble in water and is rather inert at room temperature.

(17) **(D).** Because of high bond energy of N–N bond, N_2 is chemically inert.

(18) **(C).** Nitrogen has low reactivity due to high dissociation energy.

(19) **(B).** Liquid ammonia is used in refrigeration because it has high heat of vaporisation.

(20) **(B).** $\underset{1\text{ vol.}}{N_2} + \underset{3\text{ vol.}}{3H_2} \longrightarrow \underset{2\text{ vol.}}{2NH_3}$
Volume of NH_3 is half to that of total volume of the reactants.

(21) **(D).** Ammonia is commercially manufactured by Haber's process.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
$\Delta_f H^{\ominus} = -46.1\ kJ\ mol^{-1}$

(22) **(C).** Haber's process for manufacturing of ammonia involves finely divided iron as catalyst along with molybdenum promoter.

(23) **(A).** Due to high vapour pressure, the ammonia bottle may burst on opening. So it must be opened after cooling in ice for some time.

(24) **(A).** Ammonia molecule has a lone pair of electrons on the N-atom. Thus it acts as a Lewis base.

(25) **(B).** $\underset{(S)}{NH_4NO_3} \xrightarrow{\Delta} 2H_2O\uparrow + \underset{\substack{\text{Nitrous oxide}\\\text{(Laughing gas)}}}{N_2O\uparrow}$

(26) **(A).** $\underset{(S)}{2KNO_3} \xrightarrow{\Delta} \underset{(S)}{2KNO_2} + O_2$

(27) **(D).** N_2O is itself non-combustible but supports combustion. $S + 2N_2O \rightarrow SO_2 + 2N_2$

(28) **(D).** The correct order for the decreasing acidic strength of oxides of nitrogen is
$N_2O_5 > N_2O_4 > N_2O_3 > NO > N_2O$

(29) **(A).** N_2O_5 is the anhydride of nitric acid as it gives HNO_3 on adding water.
$N_2O_5 + H_2O \longrightarrow 2HNO_3$

(30) **(D).** NO_2 does not have a planar structure. It is angular in shape.

(31) **(B).** $NH_4NO_3 \xrightarrow{250°C} N_2O + 2H_2O$

(32) **(D).** $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$

(33) **(B).** $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

(34) **(A).** $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(35) **(C).** Both the statements are correct.
$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$
$[Fe(H_2O)_6]^{2+} + NO$
$\rightarrow [Fe(H_2O)_5(NO)]^2$ (brown) $+ H_2O$

(36) **(B).** $4Zn + 10HNO_3$(very dil.)
$\rightarrow 4\ Zn(NO_3)_2 + 3H_2O + NH_4NO_3$

(37) **(A).** Laboratory preparation of HNO_3 is
$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

(38) **(C).** $Zn + \underset{\text{(conc.)}}{4\ HNO_3} \rightarrow Zn(NO_3)_2 + 2\ H_2O + 2\ NO_2$

(39) **(D).** HNO_3 has nitrogen in its highest oxidation i.e., +5 state, due to this it reduces itself by oxidising other substances, hence is very strong oxidizing agent.

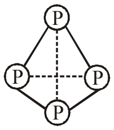
(40) **(A).** Both white and red phosphorus are not soluble in CS_2. Only white P is soluble.

(41) **(D).** In red phosphorus, one of the P_4 bonds is broken, and one additional bond is formed with a neighbouring tetrahedron resulting in a more chain-like structure.

It is formed by heating white phosphorus to 250ºC, it becomes an amorphous network of atoms that reduces strain and gives greater stability thereby renders it unreactive.

(42) **(A).** Phosphorus is produced by heating in a furnace bone ash, silica and coke.

(43) **(D).** Atomicity of phosphorus is 4.



(44) **(C).** Structure of white phosphorus is tetrahedral.

(45) **(D).** Red P is less reactive, less volatile and less soluble in non-polar solvent than white/yellow P because it possesses highly polymerised structures.

(46) **(B).** $\underset{\text{White}}{P_4} + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3} + 3NaH_2PO_2$

(47) **(D).** Phosphine is a colourless gas with a rotten fish smell. It is highly poisonous.

(48) **(A).** Red P does not react with alkali.

(49) **(C).** Laboratory method of preparation of PH_3

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

(50) **(D).** $3H_2O + PCl_3 \rightarrow H_3PO_3 + 3HCl$

(51) **(A).** Axial bonds suffer more repulsion thus are longer than equatorial bonds.

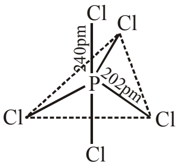
(52) **(C).** PCl_5 is a yellowish white powder.

(53) **(D).** In the solid state it exists as an ionic solid, $[PCl_4]^+$ $[PCl_6]$– in which the cation., $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ is octahedral.

(54) **(B).** Decreasing order of Lewis acid strength is

$PF_3 > PCl_3 > PBr_3 > PI_3$ as Lewis acids have a tendency to accept electrons by the empty d-orbitals of phosphorus and also the electronegativity of halides decreases as F < Cl < Br < I.

(55) **(C).** In gaseous and liquid phases, the structure of PCl_5 is trigonal bipyramidal.



(56) **(A).** $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$.

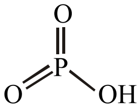
Thus in this reaction, phosphorous acid (H_3PO_3) is produced.

(57) **(D).** The axial bond pairs suffer more repulsion on compared to equatorial bond pairs.

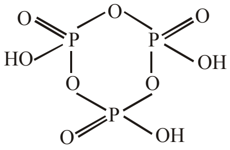
(58) **(C).** $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$

In the reaction, the acid in +3 oxidation state of P tends to disproportionate to higher (+5) and lower (–3) oxidation state in H_3PO_4 and PH_3 respectively.

(59) **(B).** HPO_3, metaphosphoric acid

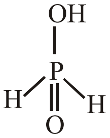


(60) **(B).** Cyclic metaphosphoric acid is $(HPO_3)_3$



Number of P – O – P bonds = 3

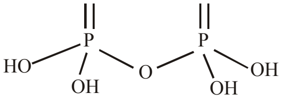
(61) **(C).** Structure of Hypophosphorus acid. As it contains only one replaceable H atom. It is monobasic.



(62) **(B).** H_3PO_3 is dibasic acid thus forms two series of salts NaH_2PO_3 & Na_2HPO_3 respectively.

While H_3PO_4 and H_3PO_5 are tribasic and form three series of salts, H_3PO_2 being monobasic forms only one series of salts.

(63) **(C).** Pyrophosphoric acid ($H_4P_2O_7$) is tetrabasic acid.



(64) **(C).** H_3PO_2 behaves as a stronger reducing agent as it contains two P – H bonds.

(65) **(A).** Oxygen atom does not have d-orbitals in the valence shell. Sulphur can show +4 and +6 oxidation states due to presence of vacant 3d-orbitals to which electrons can be promoted.

(66) **(C).** Elements of group 16 form a large number of halides of the type EX_6, EX_4 and EX_2 where, E is an element of the group and X is a halogen. $F^- > Cl^- > Br^- > I^-$

(67) **(D).** Oxygen and sulphur are non-metals, selenium and tellurium are metalloids, whereas polonium is a radioactive metal. It is short lived (half-life 13.8 days). All these elements exhibit allotropy. The melting and boiling point increases with an increase in atomic number down the group.

(68) **(A).** The correct order of increasing ionic radii is :

O < S < Se < Te < Po

(69) **(A).** As we move down the group from O to Te, the size of the central atom goes on increasing and its electronegativity goes on decreasing. Consequently, the position of bond pairs of electrons shifts more and more away from the central atom in moving from H_2O to H_2Te. For example, the bond pair in O–H bond is closer to oxygen than the bond pair in S–H bond. As a result, the force of repulsion between bonded pairs of electrons in H_2O is more than in H_2S. In general, the force or repulsion between the bonded pairs of electrons decreases as we move from

H_2O to H_2Te and therefore, the bond angle decreases in the same order as :

$$H_2O > H_2S > H_2Se > H_2Te$$

Bond angle 104º5 92.1º 91º 90º

(70) **(A).** Oxygen atom can form multiple pπ– pπ bonds with other oxygen atom on account of small size while S=S is not so stable as compared to –S–S–S– chains. Hence, S exists as S_8 while O exists as O_2.

(71) **(A).** The values of electron affinity decrease down the group 16. But electron affinity of oxygen is unexpectedly lower because of small size of oxygen.

S > Se > Te > Po > O

Electron affinity (kJ/mol) –208.8 –195.5 –190.0 –174 –141.4

(72) **(A).** Due to extra stability of half-filled p-orbitals of group 15 elements, large amount of energy is required to remove electrons as compared to group 16 elements.

(73) **(D).** The stability of the halides decreases in the order $F^- > Cl^- > Br^- > I^-$. Amongst hexahalides, hexafluorides are of octahedral shape, SF_6 is exceptionally stable for steric reasons.

(74) **(C).** Platinum does not react with oxygen directly because it is a noble metal.

(75) **(B).** $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

(76) **(D).** Pale blue colour of solid oxygen is due to the electronic transitions from the triplet ground state ($\pi^*2p_x{}^1\pi^*2p_y{}^1$) to the excited single state ($\pi^*2p_x{}^2$ or $\pi^*2p_y{}^2$).

(77) **(B).** Among chalcogens, oxygen is of the smallest size. It shows maximum valency of two. It has no vacant d-orbital.

(78) **(C).** Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

$$2H_2O_2\,(aq) \xrightarrow{MnO_2} 2H_2O\,(\ell) + O_2\,(g)$$

(79) **(C).** Oxygen molecule is paramagnetic with two unpaired electrons.

(80) **(C).** CO_2 is an acidic oxide, CO is neutral and BeO is an amphoteric oxide.

(81) **(D).** A binary compound of oxygen with another element is called oxide. These oxides can be simple (e.g., MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4).

Simple oxides can be classified on the basis of their acidic, basic or amphoteric character.

An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO_2, Cl_2O_7, CO_2, N_2O_5). Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. Al_2O_3 is such an example. There are some oxides which are neither acidic nor basic. Such oxides are called neutral oxides. Examples CO, NO and N_2O.

(82) **(C).** O_3 is not paramagnetic, it is diamagnetic.

(83) **(D).** Ozone protects the earth's inhabitants by absorbing ultraviolet radiations.

(84) **(D).** Ozone (O_3) is an allotropic form of oxygen. It is too reactive to remain for long in the atmosphere at sea level and it is formed from atmospheric oxygen in the presence of sunlight at a height of about 20km.

(85) **(D).** Ozone acts as good bleaching agent due to its oxidising property.

(86) **(C).** $O_3 + 2Hg \rightarrow Hg_2O + O_2$

(87) **(A).** Ozone is diamagnetic gas.

(88) **(A).** Rhombic sulphur is most stable form at room temperature.

(89) **(C).** Melting point of rhombic sulphur is 385.8K and specific gravity 2.06 while melting point of monoclininic sulphur is 393 K & specific gravity 1.98.

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

(91) **(D).** Sulphur exists as octa-atomic molecule.

(92) **(C).** $S + O2 \rightarrow SO_2$

(93) **(C).** SO_2 is an angular molecule with O–S–O bond angle of 119.5°.

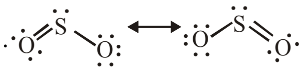
(94) **(C).** Bleaching action of SO_2 is due to its reducing property.

(95) **(C).** After oxidation, it dissolves in rain water to produce acid rain which reacts with limestone of buildings made up of marble resulting in extensive damage.

$$2SO_2(g) + O_2(g) + 2H_2O(\ell) \rightarrow 2H_2SO_4\,(aq)$$

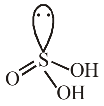
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

(96) **(C).** The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms



(97) **(B).** Oleum : Pyrosulphuric acid.

(98) **(A).** H_2SO_3 has a lone pair ofelectrons.



(99) **(B).** 98% H_2SO_4 is used for absorbing dense fog of acid which is formed by dissolving SO_3 in water. Hence 98% H_2SO_4 is the most efficient agent for the absorption of SO_3.

(100) **(D).** $H_2SO_4 + SO_3 \rightarrow \underset{\text{(oleum)}}{H_2S_2O_7}$

(101) **(C).** V_2O_5 catalyst are used for the manufacture of H_2SO_4 by Contact process,

(102) **(B).** Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298K. The acid freezes at 283 K and boils at 611 K. It dissolves in water with the evolution of a large quantity of heat.

Hence, care must be taken while preparing H_2SO_4. The concentrated acid must be added slowly into water with constant stirring.

(103) (C). The key step in the formation of sulphuric acid is catalytic oxidation of sulphur dioxide to sulphur trioxide with atmospheric oxygen.

(104) (A). H_2SO_4 is strong oxidising agent.

(105) (C). Sulphuric acid is used in lead storage cells.

(106) (D). The characteristics of H_2SO_4 responsible for the chemical reactions of H_2SO_4 are low volatility, strong acidic character as well as affinity for water and its ability to act as an oxidising agent. It is also act as strong dehydrating agent.

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

(107) (B). Sulphuric acid dissolved in water accompanied by the release of a large amount of energy.

(108) (A). Bond strength $\propto \dfrac{1}{\text{Bond length}}$

Bond length : $HI > HBr > HCl > HF$
Bond strength: $HF > HCl > HBr > HI$
As we move down the group from F to I, the atomic size increases thus, the bond length $(H - X)$ increases hence, the bond strength decreases from HF to HI.

(109) (D). Sea water contains chlorides, bromides and iodides of sodium, potassium, magnesium and calcium, but is mainly sodium chloride solution. Fluorine is present mainly as insoluble fluorides (fluorspar CaF_2, cryolite Na_3AlF_6 and fluoroapatite $3Ca_3(PO_4)_2.CaF_2$) and small quantities are present in soil, river water plants and bones and teeth of animals.The deposits of dried up seas contain carnallite, KCl. $MgCl_2 . 6H_2O$ Certain forms of marine life contain iodine in their system ; various seaweeds, for example, contain upto 0.5% of iodine and Chile saltpetre contains upto 0.2% of sodium iodate.

(110) (A). With increase in molecular weight, the boiling point of halogens increases because van derWaals' forces increases with increase in number of electrons per mole.

(111) (D). Fluorine is most electronegative element, thus it will never lose electron to form positive ions.

(112) (C). Due to maximum effective nuclear charge, the halogens have the smallest atomic radii in their respective periods. They have very high ionisation enthalpy, due to their little tendency to lose electrons.

Halogens have maximum negative electron gain enthalpy and fluorine is the most electronegative element in the Periodic Table.

(113) (A). Electron affinity decreases down the group as atomic size increases.

(114) (C). F_2 has lower bond dissociation energy than Cl_2 due to its small size which results in interelectronic repulsion.

(115) (D). Fluorine forms two oxides $-OF_2$ and O_2F_2.
OF_2 is thermodynamically stable at 298 K.
These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

(116) (D). Chlorine is a greenish yellow gas and tt has pungent and suffocating odour. It is about 2–5 times heavier than air.

(117) (B). Chlorine bleaches the articles by oxidation permanently only in presence of moisture due to the formation of HClO which liberates nascent oxygen on decomposition.
$Cl_2 + H_2O \rightarrow HCl + HClO$
$HClO \rightarrow HCl + [O];$
Colouring matter + [O] → Colourless matter

(118) (B). $H_2S + Cl_2 \xrightarrow{\text{water}} 2HCl + S$

Due to formation of free sulphur the solution becomes turbid.

(119) (D). Chlorine is used in
(a) the extraction of gold and platinum.
(b) bleaching wood pulp.
(c) sterilising drinking water.
(d) the preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

(120) (C). $KMnO_4$ oxidises halogen acids to halogen.
$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
$\therefore$ $KMnO_4$ is used to prepare Cl_2 from concentrated HCl.

(121) (A). Composition of bleaching powder is $Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O$.
It is a mixed salt.

(122) (C). HCl is oxidised by strong oxidising agents like manganese dioxide, lead dioxide, potassium permanganate, potassium dichromate, etc. hence as a reducing agent.
$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$

(123) (A). In laboratory, HCl is prepared by heating sodium chloride with conc. H_2SO_4.

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

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

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

(124) (D). Due to high electronegativity and small size, fluorine forms only one oxoacid. HOF known as fluoric (I) acid or hypofluorous acid.

(125) (D). Increasing oxidation number of iodine is in the order : $HI < I_2 < ICl < HIO_4$

(126) (D). Some interhalogens are solids and are not volatile.

(127) (D). Interhalogen compounds are covalent molecules and diamagnetic in nature. These are volatile solids or liquids at 298 K except ClF.

(128) **(B).** Since dissimilar halogens are combined in interhalogen compounds hence the bond between them (X - X' bond) is weaker than homoatomic halogen (X – X or X' – X' bonds).

(129) **(C).** Interhalogen compounds can be used as non-aqueous solvents and fluorinating agents.

(130) **(A).** Rn because it is radioactive element obtained by the disintegration of radium

$$_{88}Ra^{206} \rightarrow {}_{86}Rn^{202} + {}_{2}He^{4}$$

(131) **(C).** Helium (In Greek Helios = Sun)
Discovered by Frankland and Lockyer.

(132) **(D).** All the noble gases are monoatomic, colourless and odourless gases. Their monoatomic nature is due to the stable outer configuration $ns^2\ np^6$ of their atoms. As a result, they do not enter into chemical combination even amongst themselves.

(133) **(C).** $XeF_2, XeOF_2.\ XeF_4, XeOF_4.\ XeF_6, XeO_3$.

(134) **(C).** $_1H^2 + {}_1H^2 \rightarrow {}_2He^4$

(135) **(C).** $1s^2\ 2s^2\ 2p^6 \rightarrow$ Neon

(136) **(C).** Coconut charcoal possess characteristic property for adsorbing different noble gases at different temperatures.

(137) **(C).** XeF_2 has linear structure. $XeOF_4$ has square pyramidal structure.

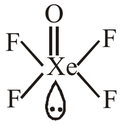
(138) **(A).** Group 18 consists of six elements. He, Ne, Ar, Kr, Xe and Rn. All these are gases and chemically unreactive. These form very few compounds. Hence, these are termed noble gases.

(139) **(D).** Helium is used in filling tubes of aeroplane tyres.

(140) **(A).** Unlike nitrogen, helium is less soluble in blood even under high pressure. Hence a mixture of 80% helium and 20% oxygen is used instead of ordinary air.

(141) **(B).** $Xe + F_2 \xrightarrow[673\ K]{Ni} XeF_2$
(2 : 1)

(142) **(B).**



EXERCISE-2

(1) **(C).** $H_2SO_3 + 2NaOH \rightarrow \underset{\text{Sodium sulphite}}{Na_2SO_3} + 2H_2O$

(2) **(A).** $Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$

(3) **(C).** $\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \rightarrow CaOCl_2 + H_2O$

(4) **(C).** $KI + H_2SO_4 \rightarrow KHSO_4 + HI$
HI is formed but it is further oxidised by conc. H_2SO_4 into I_2.

$$2HI + H_2SO_4 \rightarrow 2H_2O + \underset{\text{Violet vapour}}{I_2} + SO_2$$

(5) **(B).** The enamel of our teeth is the hardest substance in the body made up of CaF_2 and dentine below it made of $Ca_3(PO_4)_2$.

(6) **(C).** Iodine is a less electronegative compare to Bromine hence iodine does not change Br^- to Br_2.

(7) **(A).** NCl_5 is not known because of absence of d-orbitals in nitrogen.

(8) **(D).** $\underset{\text{Nitric acid}}{2HNO_3} \rightarrow N_2O_5 + H_2O$

(9) **(D).** $3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$

(10) **(B).** NH_3 is most thermally stable hydride. Hence, electrolysis temperature is maximum.

(11) **(A).** Phosphorus is kept in water due to it burnt at 30°C.

(12) **(C).** $NH_4NO_2 \rightarrow N_2 + 2H_2O$

(13) **(A).** $\frac{1}{8}S_8 + 2e^- \rightarrow S^{2-}$

(14) **(A).** The minimum and maximum oxidation number of S are –2 and +6 respectively. Since the oxidation number of S in SO_2 is +4, therefore it can be either increased or decreased. Therefore SO_2 behaves both as an oxidising as well as reducing agent.

(15) **(A).** $H_2O + SO_3 \rightarrow H_2SO_4$

(16) **(D).** $2F_2 + 2H_2O \rightarrow 4HF + O_2$

$$3F_2 + 3H_2O \rightarrow 6HF + O_3$$

(17) **(B).** $MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$

(18) **(C).** Hydrogen bonding is absent in HI while it is present in NH_3, H_2O and C_2H_5OH.

(19) **(A).** $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$

(20) **(A).** $2H_2S + O_2 \rightarrow 2H_2O + 2S$

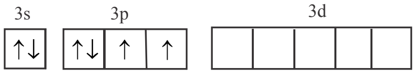
(21) **(A).** $Cl_2 + 2KBr \rightarrow 2KCl + Br_2$
A more electronegative halogen can displaces less electronegative halogen.

(22) **(B).** $6KOH + 3Cl_2 \rightarrow 5KCl + KClO_3 + 3H_2O$.

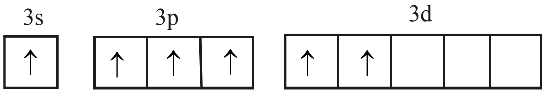
(23) **(D).** $KI + I_2 \rightarrow KI_3$

(24) **(B).** Phosphorus form stable P_4 molecule.

(25) **(C).** Sulphur atom in ground state



Sulphur atom in excited state



Due to presence of six unpaired electrons, it can form maximum of six bonds, so covalency is six.

(26) **(A).** Solubility of fluorides is almost opposite to that of other halides. AgF is soluble in water while other silver halides are insoluble. CaF_2 is insoluble in water while other calcium halides are soluble in water.

(27) **(D).** As the oxidation state of the halogen atom increases, the halogen-oxgyen bond becomes more and more covalent. As a result the thermal stability of the oxo acid increases. Thus, $HClO_4$ is most stable to heat, whereas HClO is least stable to heat.

(28) **(C).** Stability of Cl – O bond increases with the increasing oxidation number of chlorine.

	HClO	$HClO_2$	$HClO_3$	$HClO_4$
Ox. state of chlorine	+1	+3	+5	+7

(29) **(C).** In atmosphere, Ar is 0.934% by volume and 1.285% by mass.

(30) **(D).** Very weak, Vander Waals forces.

(31) **(A).** As size increases, Vander Waals forces also increases.

(32) **(A).** $Cl_2 + H_2O \longrightarrow HCl + HOCl$
yellow colour

(33) **(D).** Gas (HCl, more volatile) can be displaced more easily from the chloride salt solution by H_2SO_4 which is less volatile.

(34) **(C).** $H_2S_2O_7$ represents oleum i.e. fuming sulphuric acid.

(35) **(D).** $\overset{+5}{HNO_3} \longrightarrow \overset{+1}{N_2O}$

Change in oxidation number = +5 – 1 = 4.

(36) **(B).** On moving down the group, electronegativity decreases, consequently bond pair shifts more and more away from the central atom. Hence H–M–H bond angle decreases and becomes closer to 90º in SbH_3 which reveals that almost pure p-orbitals are used for M–H bonding.

(37) **(B).** $NH_4^+ \rightleftharpoons \underset{\text{Conjugate base}}{NH_3} + H^+$

In NH_3, N is sp^3 hybridised.

(38) **(B).** $FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$

(39) **(C).** $4HNO_3 \xrightarrow{\text{Sunlight}} \underset{\text{Brownish colour}}{4NO_2} + 2H_2O + O_2$

(40) **(B).** $SO_2 + Br_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4$

(41) **(A).** $4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2$

$\underset{(A)}{SO_2} + H_2O \rightarrow \underset{(Acid)}{H_2SO_3} \rightleftharpoons 2H^+ + SO_3^{2-}$

Hence basicity of acid H_2SO_3 is two.

(42) **(C).** $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + \underset{\text{Phosphine}}{2PH_3}$

(43) **(C).** $CaC_2 + N_2 \longrightarrow \underset{\text{Calcium cyanamide}}{CaCN_2} + C$

(44) **(D).** $NH_3 + 3Cl_2(\text{excess}) \longrightarrow NCl_3 + 3HCl$

(45) **(B).** SO_3^{2-} involves pπ-dπ bonding.

(46) **(B).** Xenon tetrafluoride (XeF_4) is prepared by heating a mixture of xenon and fluorine in ratio of 1 : 5 in a nickel vessel at 673 K.

(47) **(B).** Dioxygen difluride (O_2F_2) is used to remove plutonium from spent nuclear fuel.

(48) **(D).** H_2SO_4 is a strong dehydrating agent.

(49) **(B).** Only Xe reacts with F_2 because it has the lowest ionization enthalpy (energy).

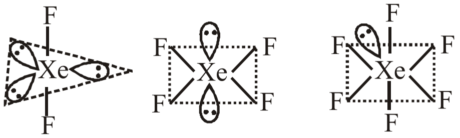
(50) **(D).** I_2 cannot oxidise Cl^-, F^- and Br^- as it is the weakest oxidising agent.

(51) **(A).** The reaction $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$ is not feasible because XeF_6 formed will further produce XeO_3 by getting hydrolysed.

(52) **(B).** NH_3 is more stable than PH_3.

(53) **(A).** White phosphorus is soluble in CS_2 whereas red phosphorus is insoluble in CS_2.

(54) **(D).**



(55) **(B).** pπ-pπ bonding is weak in case of phosphorus because of comparatively larger size it is unable to form multiple bonds. Hence P_2 gets converted to P_4.

(56) **(B).** Some compounds are catalytically oxidised like,

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

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

(57) **(A).** Nascent hydrogen is produced only in presence of moisture and is responsible for bleaching.

$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2\,[H]$

Coloured flower + [H] → Colourless flower

(58) **(C).** $P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_4}$

(59) **(D).** Ionisation enthalpy decreases down the group due to the gradual increase in atomic size. Because of the extra stable half-filled p-orbitals electronic configuration and smaller size, the ionisation enthalpy of group 15 elements is much greater than that of group 14 elements in the corresponding periods. The order of successive ionisation enthalpies is $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3$.

(60) **(B).** ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

(61) **(D).** The behaviour of sulphur while reacting with water and alkalies is similar to that of CO_2.

(62) **(A).** All the given species are basic but only SO_3^{2-} is reducing in nature. It reduces water to hydrogen.

$H_2SO_3 + H_2O \longrightarrow H_2SO_4 + 2H$

(63) **(C).** Oxygen fluorides do not form oxoacids.

(64) **(B).** pπ – pπ bonding in nitrogen is strong hence it can form triple bond with another N. Single N – N bond is weaker than P – P bond due to high interionic repulsion of non-bonding electrons. Hence, $N \equiv N$ is stable and P_2 is not.

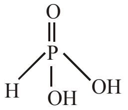
(65) **(D).** N_2O is a linear molecule. Its resonating structure is

$$\ddot{\underset{\cdot\cdot}{N}} = N = \ddot{\underset{\cdot\cdot}{O}} \leftrightarrow :N \equiv \ddot{\underset{\cdot\cdot}{O}}:$$

The bond length of N – N and N – O is 113pm and 119 pm respectively in N_2O

(66) **(C).** Nitrogen can not form NCl_5 because of absence of vacant d-orbitals.

(67) **(D).** H_3PO_3 is a dibasic acid.



EXERCISE-3

(1) **4.** PCl_5 produces $POCl_3$ on reaction with these compounds.

$$PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$$
$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$
$$PCl_5 + H_2SO_4 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$
$$6PCl_5 + P_4O_{10} \longrightarrow 10\ POCl_3$$

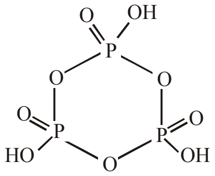
(2) **2.**

$$XeF_6 \xrightarrow[\text{Hydrolysis}]{\text{Complete}} XeO_3 + H_2F_2 \xrightarrow{OH^-/H_2O} HXeO_4^-$$

$$\xrightarrow[\text{in } OH^-/H_2O]{\text{Slow disproportionation}} XeO_6^{-4} + Xe\,(g) + H_2O + O_2\,(g)$$

(3) **7.** $K_2Cr_2O_7 + I^- + H^+ \rightarrow I_2$
$CuSO_4 + I^- \rightarrow I_2$
$H_2O_2 + I^- \rightarrow I_2$
$Cl_2 + I^- \rightarrow I_2$
$O_3 + I^- \rightarrow I_2$
$FeCl_3 + I^- \rightarrow I_2$
$HNO_3 + I^- \rightarrow I_2$

(4) **3.** In cyclic metaphosporic acid is number of P – O – P bonds is three.



(5) **1.** Sulphur trioxide trimer S_3O_9 (all called γ-sulphur trioxide) two sulphur atoms are linked to each other via O atoms, hence there is no S – S bond.

(6) **100.** The reaction is

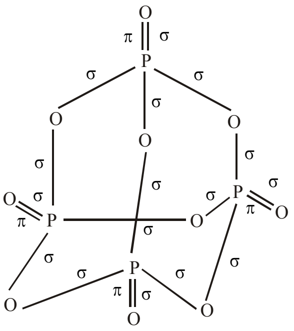
$NaH_2PO_4 + 2NaOH \rightarrow Na_3PO_4 + 2H_2O$ n
120 g 2 x 40 = 80 g
(1 mole) (2 moles)
120g NaH_2PO_4 requires 80 g NaOH
12g NaH_2PO_4 requires 8 g NaOH
80 g NaOH is present in 1 litre i.e. 1000 ml. of 2M NaOH.

8 g NaOH is present in $\frac{1000}{80}$ x 8 = 100 ml of 2 M NaOH.

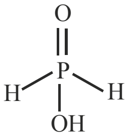
EXERCISE-4

(1) **(A).** $F-\overset{\bullet\bullet}{\underset{\bullet\bullet}{Xe}}-F$, XeF_4, XeF_6
3-ℓp 2-ℓp 1-ℓp

(2) **(D).** In P_4O_{10}, each P atom form four sigma bonds, therefore total number of σ bond = 16



(3) **(A).** In hypophosphorus acid two hydrogen directly attach with phosphorus.



(4) **(C).** $\overset{+1}{HClO} \longrightarrow \overset{+5}{HClO_3} + \overset{-1}{HCl}$

(disproportionation reaction)

(5) **(C).** We know that Helium is heavier correction than Hydrogen.

(6) **(D).** XeF_6 reacts violently with water and gets hydrolysed to give highly explosive XeO_3.
$XeF_6 + 6H_2O \rightarrow XeO_3 + 3H_2O$
Reaction (B) is reverse of this, so it is not feasible.

(7) **(B).** On moving down the group, the basic tendency of hydrides of group 15 decreases.

(8) **(A).** The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. The correct order is

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

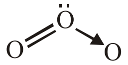
Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
$\Delta_{diss}H^{\ominus}(E-H)$ /kJ mol^{-1}	389	322	297	255	–

(9) **(A).** As metallic character of element attached to oxygen atom increases, the difference between the electronegativity values of element and oxygen increases and thus basic character of oxides increases and vice-versa. Hence the increasing correct order of basic nature is : $Al_2O_3 < MgO < Na_2O < K_2O$.

(10) **(D).** Sulphur exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common.

(11) **(C).** As electronegativity of central atom decreases, bond angle decreases.
(Hybridisation and number of lone pair on cental atom are same in all options)

(12) **None.** (All statement are correct there is no answer).
(1) $ONCl = 8 + 7 + 17 = 32e^-$
$ONO^- = 8 + 7 + 8 + 1 = 24e^-$ (correct)

(2) 

Central atom O is sp^2 hybridised with 1 lone pair, so bent shape (correct).

(3) Ozone is violet-black in solid state.

(4) O_3 has no unpaired electrons, so diamagnetic (correct)

(13) **(C).** NO is paramagnetic in gaseous state due to the presence of unpaired electron in its structure.

(14) **(A).** $HClO < HClO_2 < HClO_3 < HClO_4$

Increasing acid strength due to increase in oxidation state of central atom.

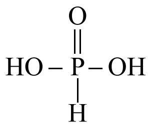
(15) **(D).** $N_2 + O_2 \rightarrow 2NO$

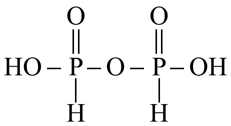
Required temperature for above reaction is around 3000° C which is a quite high temperature. This reaction is observed during thunderstorm.

(16) **(C).** Because of polarity and weak bond interhalogen compounds are more reactive.

(17) **(C).** Down the group strength of van der Waal's force of attraction increases hence Xe have highest boiling point.

(18) **(D).** H_3PO_3 is orthophosphorous acid : $H_4P_2O_5$ is pyrophosphorous acid





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

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

(20) **(D).** $Cl_2 + NaOH\,(cold\ \&\ dil) \rightarrow NaCl + NaClO + H_2O$

(21) **(B).** Any reaction having a substance in its elemental form is a redox reaction.

+4 +1 +6 0

$XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

Xenon undergoes oxidation while oxygen undergoes reduction.

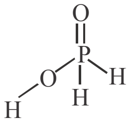
(22) **(B).** $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$(NH_4)_2\,SO_4 \xrightarrow{\Delta} NH_3 + H_2SO_4$

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

$(NH_4)_2\,Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

(23) **(C).** H_3PO_2 is good reducing agent due to presence of two P–H bonds.



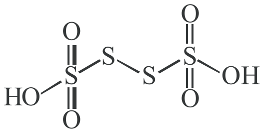
(24) **(D).** Correct order of oxidation state of nitrogen in oxides of nitrogen is following:

+1 +2 +3 +4

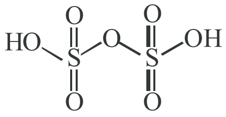
$N_2O < NO < N_2O_3 < NO_2$

(25) **(C).** HF has highest boiling point among hydrogen halides because it has strongest hydrogen bonding.

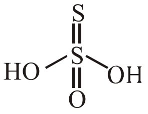
(26) **(B).**



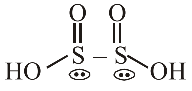
$H_2S_4O_6$



$H_2S_2O_7$



$H_2S_2O_3$



$H_2S_2O_4$

$H_2S_2O_7$ does not contain bond between sulphur atoms.

(27) **(C).** Total no. of pentagons in $C_{60} = 12$

Total no. of trigons (triangles) in white phosphorus $(P_4) = 4$

(28) **(B).** Order of electron gain enthalpy (magnitude) is $Cl > F > Br > I$.

(29) **01.67**

$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

(Hot & conc.) (X) (Y)

$NaCl + AgNO_3 \rightarrow AgCl\,(ppt) + NaNO_3$

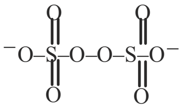
Y is $NaClO_3$

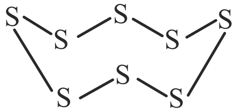
ClO_3^- (bond order) = 5/3 = 1.67

(30) **(A).** $6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

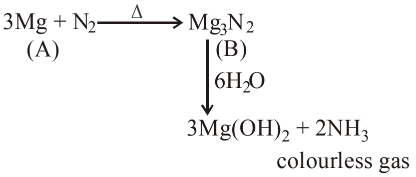
$2Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + H_2O$

(31) **(A).** $S_2O_8^{2-}$

$S_2O_8^{2-}$ 

S_8 

(32) **(A).**



$3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$ (A) (B); $Mg_3N_2 \xrightarrow{6H_2O} 3Mg(OH)_2 + 2NH_3$ colourless gas

$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4$

Deep blue solution

(33) **(A).** $P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2\,PO_2 + PH_3$

(X)

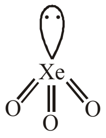
$NaH_2PO_2 + HCl \rightarrow NaCl + H_3PO_2\,(Y)$

Basicity = 1

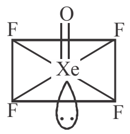
(34) **(D).** A. MgO Basic, Cl_2O Acidic
Al_2O_3 amphoteric
B. Cl_2O Acidic, CaO Basic, P_4O_{10} Acidic
C. Na_2O Basic, SO_3 Acidic,
Al_2O_3 amphoteric
D. N_2O_3 Acidic, Li_2O Basic,
Al_2O_3 amphoteric.

EXERCISE-5

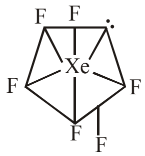
(1) **(D).**



XeO_3



$XeOF_4$



XeF_6

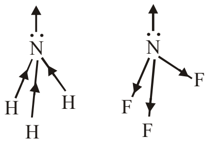
(2) **(B).** As oxidation number of central atom in oxyacid increases strength increases.
The correct order of acidic strength is

$$\overset{+1}{HClO} < \overset{+3}{HClO_2} < \overset{+5}{HClO_3} < \overset{+7}{HClO_4}$$

(3) **(B).** More the oxidation state of the central atom (metal) more is its acidity. Hence SeO_2 (O.S. of Se = +4) is acidic. Further for a given O.S., the basic character of the oxides increases with the increasing size of the central atom. Thus Al_2O_3 and Sb_2O_3 are amphoteric and Bi_2O_3 is basic.

(4) **(C).** Bond dissociation energy of fluorine is less because of its small size and repulsion between electrons of two atoms. So option (C) is wrong order. The correct order is : $Cl_2 > Br_2 > F_2 > I_2$

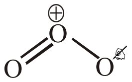
(5) **(A).** In NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite direction so in the former case they are added up whereas in the latter case net result is reduction of dipole moment.



(6) **(A).** In the ClF_3, Cl atom is sp^3d hybridised, having trigonal bipyramidal geometry, in which axial bonds are longer than equatorial bonds.

(7) **(D).** $\overset{+1}{HOCl} < \overset{+3}{HOClO} < \overset{+5}{HOClO_2} < \overset{+7}{HOClO_3}$
As the oxidation number of the central atom increases, strength of acid also increases.

(8) **(A).**

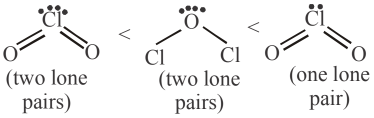


(9) **(D).** Fluorine is the most electronegative element because electronegativity decreases or moving down the group. Hence, it gets reduced readily into F^- ion and is the strongest oxidising agent.

(10) **(B).** As the size of halogen atom increases, the acidic strength of boron halides increases. Thus, BF_3 is the weakest Lewis acid. This is because of the pπ-pπ back bonding between the fully-filled unutilised 3p orbitals of F and vacant 2p orbitals of boron which makes BF_3 less electron deficient. Such back donation is not possible in case of BCl_3 or BBr_3 due to larger energy difference between their orbitals. Thus, these are more electron deficient. Since on moving down the group the energy difference increases, Lewis acid character also increases. Thus, the tendency to behave as Lewis acid follows the order : $BBr_3 > BCl_3 > BF_3$.

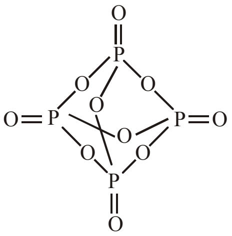
(11) **(D).** Oxidation state of H is + 1 and that of O is –2. Let the oxidation state of P in the given compounds is x.
In $H_4P_2O_5$, $(+1) \times 4 + 2 \times x + (-2) \times 5 = 0$
$4 + 2x - 10 = 0 ; 2x = 6 \therefore x = +3$
In $H_4P_2O_6$, $(+1) \times 4 + 2 \times x + (-2) \times 6 = 0 ;\ x = +4$
In $H_4P_2O_7$, $4 + 2x + 7(-2) = 0 ;\ x = +5$

(12) **(D).** As the number of lone pairs of electrons increases, bond angle decreases due to repulsion between $\ell p - \ell p$. Moreover, as the electronegativity of central atom decreases, bond angle decreases. Hence, the order of bond angle is



(Cl is less electronegative as compared to O).

(13) **(A).** P_4O_{10} has the following structure :

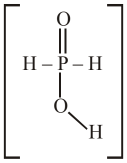


The number of bridging oxygen atoms = 6.

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

(15) **(B).** $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + SO_3$

(16) **(B).** Hypophosphorous acid (H_3PO_2) is a monobasic acid.



(17) **(B).** Acidic strength of hydrides increase with increase in molecular mass.
Thus order of acidic strength :
$HF < HCl < HBr < HI$
$H_2O < H_2S < H_2Se < H_2Te$
$NH_3 < PH_3 < AsH_3 < SbH_3$
Acidic strength increaes, pK_a decreases.
Order of pK_a : $H_2O > H_2S > H_2Se > H_2Te$

(18) **(C).** The interstitial compounds are chemically inert.

(19) **(D).** $\overset{7}{HClO_4}$ with highest oxidation number and its conjugate base is resonance stabilised, hence it is most acidic. Cl is more electronegative than S.

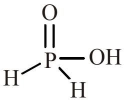
(20) **(A).** Acidic strength of chalcogen hydride increase down the group because bond length increases and dissociation energy decreases.

Acidic strength $\xrightarrow{H_2S < H_2Se < H_2Te}$

Bond length ↑
Bond dissociation energy ↓
Acidic strength ↑

(21) **(C).** SO_2 is used as a food preservatives but NO_2 does not.

(22) **(C).** Strong reducing behaviour of H_3PO_2.
All oxy-acid of phosphorus which contain P– H bond act as reductant.



presence of one – OH group and two P – H bonds.

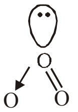
(23) **(B).** (i) No. of electron in ONF = 24
No. of electron in NO_2^- = 24
both are isoelectronic

(ii) OF_2 is a fluoride of oxygen not oxide of fluorine because EN of fluorine is more than oxygen
OF_2 = oxygen difluoride

(iii) Cl_2O_7 is an anhydride of perchloric acid

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

(iv) O_3 molecule is bent shape



(24) **(D).** Due to strong H-bonding in HF molecule, boiling point is highest for HF.
HF > HI > HBr > HI

(25) **(C).** Electron repulsion outweighs the stability gained by achieving noble gas configuration.

(26) **(B).** $$\xrightarrow[\text{Acidic strength}]{\overset{+1}{HClO} < \overset{+3}{HClO_2} < \overset{+5}{HClO_3} < \overset{+7}{HClO_4}}$$

(27) **(A).** $Cu + 4\,HNO_3\,(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

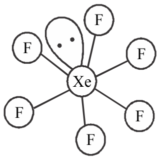
(28) **(B).** Bond dissociation enthalpy

Cl_2 >	Br_2 >	F_2 >	I_2
242.6	192.8	158.8	151.1 (kJ/mole)

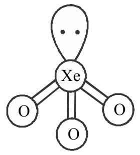
Enthalpy of dissociation decreases as the bond distance increases from F_2 to I_2 due to increase in size of the atom as we move down the group. Due to electron-electron repulsions between the lone pairs in small sized F atoms, the bond dissociation enthalpy of F_2 is, however, smaller than that of Cl_2 and even smaller than that of Br_2.

(29) **(A).** $N_2 + CaC_2 \xrightarrow{\Delta} CaCN_2 + C$

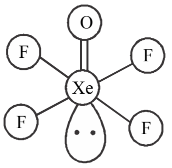
(30) **(A).** XeF_6 : sp^3d^3 - distorted octahedral
XeO_3 : sp^3 - pyramidal
$XeOF_4$: sp^3d^2 - square pyramidal
XeF_4 : sp^3d^2 - square planar



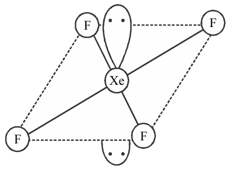
Distorted octahedral



Pyramidal

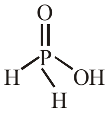


Square pyramidal

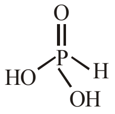


Square planar

(31) **(B).**



(Phosphinic acid)
Monoprotic



(Phosphonic acid)
Diprotic

(32) **(B).** In PF_3, P has a lone pair of electrons.

(33) **(D).** $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$
In this reaction there is no change in oxidation state of any atom.

(34) **(A).** XeF_4, has octahedral geometry where hybridisation of Xe is sp^3d^2.

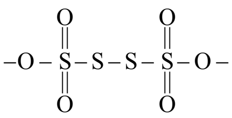
(35) **(C).** Shape of SeF_4 would be see saw whereas that of CH_4 would be tetrahedral.

(36) **(A).** $$\underset{(O.A.)}{\overset{+7}{KMnO_4}} + \underset{(R.A.)}{\overset{+4}{SO_2}} \rightarrow \underset{(Colourless)}{MnSO_4} + H_2SO_4 + K_2SO_4$$

$KMnO_4$ is an oxidising so it can oxidise SO_2 readily. NO_2 is strong oxidising agent, CO_2 is neither oxidising agent nor reducing agent.

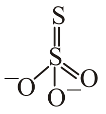
(37) **(A).** XX ' ⇒ Linear
$XX'_3 \Rightarrow$ T-shape sp^3d
$XX'_5 \Rightarrow$ Square pyramidal sp^3d^2
$XX'_7 \Rightarrow$ Pentagonal bipyramidal (sp^3d^3)

(38) **(A).** $S_4O_6^{2-}$:



$$-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-$$

; $S_2O_3^{2-}$:



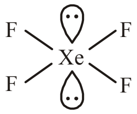
(39) **(A).** Due to high electronegativity and small size, F forms only one oxoacid, HOF known as Fluoric (I) acid. Oxidation number of F is +1 in HOF.

(40) **(C).**

(41) **(D).** (a) Pure nitrogen : Sodium azide or Barium azide
(b) Haber process : Ammonia
(c) Contact process : Sulphuric acid
(d) Deacon's process : Chlorine

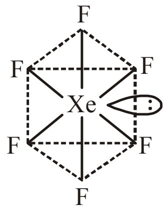
(42) **(B).**

(a) XeF_4 :



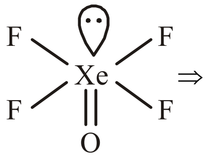
⇒ Square planar

(b) XeF_6 :



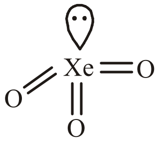
⇒ Distorted octahedral

(c) $XeOF_4$:



⇒ Square pyramidal

(d) XeO_3 :



⇒ Pyramidal