DAY TWENTY TWO

p-Block Elements

(Group-13 to Group-18)

Learning & Revision for the Day

- Periodicity in Properties of ***p***-Block Elements
- Group-13 Elements : Boron Family
- Group-14 Elements : Carbon Family
- Group-15 Elements : Nitrogen Family
- Group-16 Elements : Oxygen Family
- Group-17 Elements : Halogens Family
- Group-18 Elements : Noble Gases

In *p*-block elements, the last electron enters in the outermost *p*-orbital. There are six groups of *p*-block elements in the periodic table, numbering from 13 to 18. Their valence shell electronic configuration is ns^2np^{1-6} (except for He). Effective nuclear charge from first to third period decreases and from fourth period and onwards increases, due to poor shielding effect. Therefore, ns^2 electrons bound closely to the nucleus. Therefore, the oxidation state two unit less than the group oxidation state becomes progressively more stable in each group. This is also known as **inert pair effect**.

Periodicity in Properties of *p*-Block Elements

- Non-metals and metalloids exist only in the *p*-block of the periodic table. On moving down a group metallic character increases and non-metallic character decreases. Between metals and non-metals a few metalloids are also present.
- Second period elements have a tendency to form **$p\pi$- $p\pi$ multiple bond** (double or triple bond) due to their smaller atomic size and high bond energy.
  e.g. $C \equiv C, C = C, N \equiv N, O = O, O = C = O$ etc.
- Elements of second period do not expand their **covalency** due to non-availability of *d*-orbitals. Therefore, halides of such elements do not hydrolysed easily.
  e.g. BCl_3, CCl_4 (halides) etc.
- While elements of third period and onwards only form single bond and can expand their covalency due to the presence of vacant *d*-orbitals.
  e.g. P_4, S_8, $[AlF_6]^{3-}$ ion etc.
- Non-metal oxides are acidic or neutral and metal oxides are basic in nature. Generally, metalloid oxides are amphoteric. In a period, from left to right acidic character increases and down a group, basic character increases. Generally, oxides with higher oxidation state are more acidic in nature.

Properties of Hydrides

1. **Basic character** of *p*-block hydrides decreases on moving down a group and **acidic character** increases. Generally, left to right in a period, acidic character increases. e.g.

$$NH_3 > PH_3 > AsH_3$$

(down the group basic character decreases)

$$NH_3 > H_2O > HF$$

(left to right basic character decreases)

2. **Thermal stability** of hydrides on moving down a group decreases due to increase in bond length.

   Thermal stability of the hydrides decreases down the group due to which their tendency to act as reducing agent increases down the group.

3. **Bond angle** of hydrides on moving down a group, decreases due to increase in the size of central atom. Charge density and repulsion interaction also decreases on moving down a group, e.g.

$$\underset{\text{Bond angle}}{H_2O > H_2S > H_2Se}$$

   If central atoms belong to the same period and have the same hybridisation, then as the number of lone pair increases, bond angle decreases. e.g.

$$\underset{\text{Bond angle}}{CH_4 > \ddot{N}H_3 > H_2\ddot{\underset{\cdot\cdot}{O}}}$$

4. **Boiling point** of hydrides increases on moving down a group because van der Waals' forces increases with increase in molecular mass except HF, H_2O, NH_3 etc. HF, NH_3 and H_2O have intermolecular hydrogen bonding as a result of this they have high boiling point.

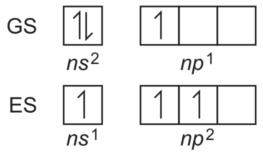
   Unique behaviour of the first element in each group It is due to the (i) small size (ii) high electronegativity and (iii) non-availability of *d*-orbitals in the valence shell of first element in each group.

Group-13 Elements : Boron Family

Boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl) are the members of group-13. Boron is a non-metal while rest of the members are metals.

Important Properties

1. Electronic Configuration (ns^2, np^1)



2. Oxidation State (+3, +1)

Stability of +3 oxidation state decreases down the group and that of +1 oxidation state increases down the group due to inert pair effect.

Fourth period and onwards, effective nuclear charge increases due to poor shielding effect, therefore the radius of gallium (135 pm) is less than that of aluminium (143 pm) and on moving down the group inert pair effect increases.

3. Hydrides

Boron hydrides exist in dimeric or polymeric form. The simplest boron hydride is diborane, B_2H_6. Aluminium forms only one colourless, solid polymeric hydride $(AlH_3)_n$ known as alane.

Hydrides of Ga and In are not very much stable. B, Al and Ga form complex anionic hydrides, e.g. $NaBH_4$, $LiAlH_4$ and $LiGaH_4$. All are strong reducing agents.

4. Halides

Halides have incomplete octet, therefore, have a high tendency to accept electrons and behave as Lewis acid.

$$BI_3 > BBr_3 > BCl_3 > BF_3 \quad \text{(Acidic character)}$$

BF_3 is a colourless gas, BCl_3 is a colourless fuming liquid while BI_3 is a white fusible solid. Due to backbonding and resonance, the B—F bond of BF_3 gets a bond order of 1.33.

5. Oxides

On moving down the group, their basic character increases. e.g. B_2O_3 is weakly acidic, Al_2O_3 is amphoteric and other oxides are basic in nature.

Preparation, Properties and Uses of Boron

- The important minerals of boron are borax ($Na_2B_4O_7 \cdot 10H_2O$), orthoboric acid (H_3BO_3) and kernite ($Na_2B_4O_7 \cdot 4H_2O$).
- **Preparation** Now a days, boron is obtained by electrolysis of a fused mixture containing boric anhydride, magnesium oxide and magnesium fluoride at 1100°C.

$$2MgO \longrightarrow 2Mg + O_2$$

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

  Crystalline boron is obtained by the reduction of B_2O_3 with aluminium powder.

$$B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$$

  Amorphous boron of low purity is called **Moissan boron**. It is black in colour.

- **Physical Properties** Boron exists in two allotropic forms, e.g. amorphous and crystalline. Crystalline boron is chemically inert while amorphous boron is chemically active. It is a bad conductor of heat and electricity.

- **Chemical Properties** Amorphous boron on heating with air at 700°C forms a mixture of oxide and nitride.

  $$4B + 3O_2 \longrightarrow 2B_2O_3,\ 2B + N_2 \longrightarrow 2BN$$

  Boron is attacked by oxidising acids like conc. H_2SO_4 and HNO_3.

  $$B + 3HNO_3 \xrightarrow{H_2SO_4} H_3BO_3 + 3NO_2$$

  It dissolves in fused alkalies and liberates hydrogen.

  $$2B + 6NaOH \longrightarrow 2Na_3\,BO_3 + 3H_2$$

  It reacts with strong electropositive metals at high temperature and forms boride such as Mg_3B_2.

  $$3Mg + B_2 \longrightarrow Mg_3B_2$$

  It is a powerful reducing agent.

  $$3CO_2 + 4B \longrightarrow 2B_2O_3 + 3C$$
  $$3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$$

- **Uses** It is used as control rods in atomic reactors and as a deoxidiser.

Preparation, Properties and Uses of Aluminium

The important ores of aluminium are bauxite $AlO_x(OH)_{3-2x}$ (where, $0 < x < 1$) and kaolinite $[Al_2(OH)_4Si_2O_5]$.

- **Preparation** Bauxite contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities. Leaching of bauxite ore is carried out with conc. NaOH solution. Aluminium is obtained by the electrolysis of Al_2O_3 mixed with Na_3AlF_6 or CaF_2 (Hall-Haroult process). Overall reaction is as follows:

  $$2Al_2O_3 \longrightarrow 4Al + 3O_2$$

- **Physical Properties** It is bluish white lustrous metal and loses its lustre due to the formation of protective oxide film Al_2O_3. It is light, malleable, ductile, good conductor of electricity and heat.
- **Chemical Properties** It burns in oxygen producing brilliant light.

  $$4Al + 3O_2 \longrightarrow 2Al_2O_3;\ \Delta H = -\text{ve}$$

  This reaction is used in thermite process for the reduction of oxides of Cr, Mn, Fe etc.

  It decomposes boiling water evolving hydrogen.

  $$2Al + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2\uparrow$$

  It is rendered passive by nitric acid due to the formation of thin oxide film. It reacts with non-metals and displaces less reactive metals such as copper, zinc and lead from their salt solutions.

- **Uses** It is used for making household utensils, frames, bodies of aircraft automobiles etc. It is used in making paints, as a mordant in dyeing and calico printing.

  Ammonal (mixture of Al powder and ammonium nitrate) is used as explosive. Magnalium, duralumin and alnico are important alloys of aluminium.

Some Important Compounds

Some important compounds of group-13 elements or boron family are given below:

1. Diborane (B_2H_6)

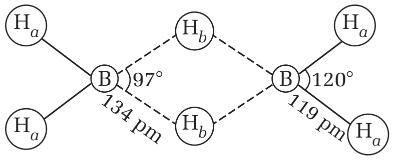
- It is a colourless, highly toxic gas with a boiling point of 180 K. Diborane catches fire spontaneously upon exposure to air.

  $$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

- With ammonia, diborane gives borazine.

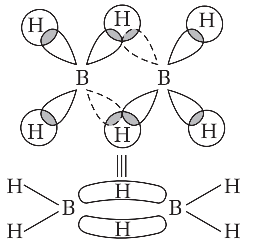
  $$3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \xrightarrow{\text{Heat}} \underset{\text{Borazine}}{2B_3N_3H_6} + 12H_2$$

- Borazine ($B_3N_3H_6$) is known as **"inorganic benzene"** in view of its ring structure with alternative BH and NH groups.
- However, at high temperature, inorganic graphite $(BN)_x$ is obtained instead of borazine.



Structure of diborane

- Terminal hydrogens (H_a) in diborane are bonded by $2c-2e$ (two centred two electrons) bonding and bridge hydrogens (H_b) are bonded by $3c-2e$ (three centred held by two electrons) bonding. This type of bonding is also known as **banana bonding.** Orbital structure of B_2H_6 is



Banana bond

- Due to banana bonding, B_2H_6 complete its electron deficiency and obtain ethane like structure and hybridisation of B_2H_6 becomes sp^3.

  $$2M\,H + B_2H_6 \longrightarrow 2\,M^+[BH_4]^- \qquad (M = \text{Li or Na})$$

  It is used as a catalyst in polymerisation process, for welding torch, as reducing agent in organic reactions etc.

2. Borax ($Na_2B_4O_7 \cdot 10H_2O$)

[Sodium Tetra Borate Decahydrate]

- It is the most important compound of boron. It is white crystalline solid.
- Borax dissolves in water to give an alkaline solution.

  $$Na_2B_4O_7 + 7H_2O \longrightarrow 2NaOH + \underset{\substack{\text{Orthoboric acid}\\ \text{(Weak acid)}}}{4H_3BO_3}$$

- On heating, it loses their water of crystallisation and swells up. On further heating, it melts into a liquid which then solidifies to form a glassy mass like bead.

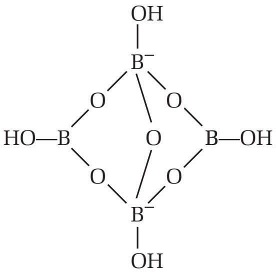
$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} \underset{\substack{\text{Swell up} \\ \text{(Sodium metaborate)}}}{Na_2B_4O_7}$$

$$\xrightarrow{\Delta} \underbrace{2NaBO_2 + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{Glassy mass}}$$

- With acids, it gives orthoboric acid, a weak acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B(OH)_3 \text{ or } \underset{\text{Orthoboric acid}}{H_3BO_3}$$

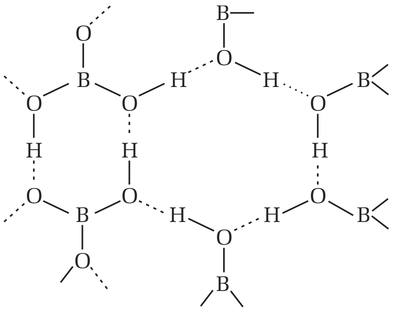
- Borax contains the tetrahedral units, i.e. $[B_4O_5(OH)_4]^{2-}$.



Structure of $[B_4O_5(OH)_4]^{2-}$ ion

3. Boric Acid (H_3BO_3)

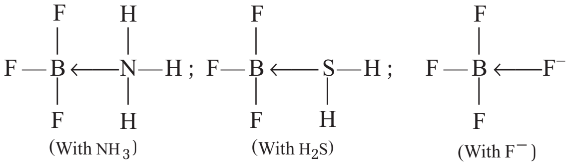
- Boric acid is soft white crystalline solid, soapy to touch and less soluble in cold water.
- Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a **Lewis acid**.
- On heating it above 370 K, it forms metaboric acid, HBO_2 which on heating yield B_2O_3.
- $H_3BO_3 \xrightarrow{\text{Heat}} \underset{\substack{\text{Metaboric} \\ \text{acid}}}{HBO_2} \xrightarrow{\text{Heat}} \underset{\substack{\text{Boron} \\ \text{trioxide}}}{B_2O_3}$
- **Structure of boric acid** shows that it has a layer structure in which planar BO_3 units are joined by H-bonds.



- It is used as an antiseptic, eye wash, as food preservative, in glass industry and in pottery.

4. Boron Trifluoride

- BF_3 is a colourless pungent gas (melting point is –127.1°C and boiling point is – 99.9°C) which strongly fumes in moist air and possesses a pungent smell. It is exceedingly soluble in water that's why it is collected over Hg.
- BF_3 being an electron deficient compound can accept a lone pair of electrons, thus behaves as Lewis acid, e.g. with NH_3, H_2S and F^-, it can form complexes as shown below:



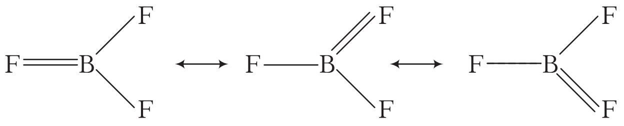
(With NH_3) (With H_2S) (With F^-)

Due to its electron accepting tendency, it is used as a catalyst in a number of organic reactions.

- BF_3 combines with water forming two hydrates, i.e. $BF_3 \cdot H_2O$ (melting point 10.18°C) and $BF_3 \cdot 2H_2O$ (melting point 6.36°C). It gets hydrolysed in aqueous solutions yielding boric acid and hydrofluoroboric acid.

$$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HBF_4$$

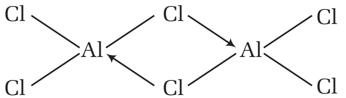
The bond length in BF_3 are 1.30 Å and are shorter than the sum of the covalent radii (B = 0.80Å and F = 0.72Å). The bond energy of BF_3 is very high (646 kJ mol^{-1}) and is higher than for any single bond. Based on modern explanation, the double bond is delocalised.



- Various resonating structures of BF_3 molecules involving $p\pi - p\pi$ back bonding.
- It is used as building block for production of other boron compounds.

5. Aluminium Chloride ($AlCl_3$)

- Anhydrous aluminium chloride is a white deliquescent solid which fumes in air. Its vapour density corresponds to the formula Al_2Cl_6.
- It is covalent and soluble in organic solvents.



Structure of $AlCl_3$

- Due to the formation of HCl, anhydrous aluminium chloride fumes in moist air.

$$Al_2Cl_6(\text{anhy.}) + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$

$$Al_2Cl_6 + 12\,H_2O \longrightarrow \underset{\substack{\text{Hydrated aluminium} \\ \text{chloride (ionic)}}}{2AlCl_3 \cdot 6H_2O}$$

- With ammonia, it gives addition product.

$$Al_2Cl_6\,\text{(anhy.)} + 12\,NH_3 \longrightarrow \underset{\text{Addition product}}{2[AlCl_3 \cdot 6NH_3]}$$

- With NaOH, sodium meta-aluminate is obtained.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 \downarrow + 3NaCl$$

$$Al(OH)_3 + NaOH \longrightarrow \underset{\text{Sodium meta-aluminate}}{NaAlO_2} + 2\,H_2O$$

- Anhydrous $AlCl_3$ is used.
  - (a) As a reagent in Friedel-Crafts reaction.
  - (b) In manufacture of drugs, dyes, perfumes.
  - (c) In cracking of high boiling fractions of petroleum to form gasoline.

6. Alums

- These are double sulphates having composition $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24\,H_2O$ (M = monovalent basic radicals such as Na^+, K^+ etc., and M' = trivalent basic radicals such as Al^{3+}, Cr^{3+} etc.)

  Potash alums; $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$

  Sodium alums; $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$

  Ferric alums; $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24\,H_2O$
- Alums are isomorphous solids and soluble in hot water. Their aqueous solutions are acidic due to hydrolysis.
- On heating, alum swells up leaving behind a porous mass, called burnt alum.

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O \xrightarrow{200^\circ C} K_2SO_4 \cdot Al_2(SO_4)_3 + 24\,H_2O$$

$$K_2SO_4 \cdot Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} K_2SO_4 + Al_2O_3 + 3SO_3$$

- It is used to purify water, stop bleeding from cuts, as an antiseptic, in leather tanning and as a mordant in dyeing and calico printing.

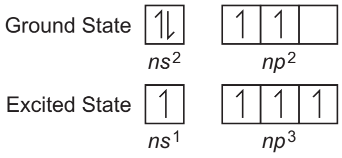
Group-14 Elements : Carbon Family

Carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb) are the members of group-14. Carbon is the seventeenth most abundant element by mass in the earth's crust. C is non-metal, Si, Ge are metalloids and Sn, Pb are metals.

Important Properties

Some of the important properties of group-14 elements or carbon family elements are given below:

1. Electronic Configuration (ns^2np^2)



2. Catenation

The tendency for catenation is maximum in carbon and it decreases down the group due to steady decrease in M—M bond strength.

$$C >> Si > Ge \approx Sn >> Pb$$

3. Allotropy

- All the members of group 14 elements (except Pb) show allotropy.
- Carbon exhibits many allotropic forms both crystalline as well as amorphous. Diamond, graphite and fullerene are crystalline forms while coal, charcoal and lamp black are amorphous forms.
- **Diamond** is the purest, hardest form of carbon with high refractive index and density. In it each carbon atom (sp^3hybridised) is tetrahedrally surrounded by four other carbon atoms. It is three dimensional polymer has very high density and very high refractive index. It does not conduct electricity as it has no free electrons. It is used in cutting, grinding and drilling instruments and in making jewellery.
- **Graphite** has two dimensional structure. sp^2 hybridised carbon atom forms three covalent bonds with three other carbon atoms in the same plane and the 4th electron of each carbon remains free and is responsible for electrical conductivity of graphite. The planar hexagonal rings get fused together to form sheets of one atom thickness. These sheets are held together by weak van der Waals' forces.
- **Fullerenes** are the only pure form of carbon. C_{60} molecule contains 12 five membered rings and 20 six-membered rings. The five membered rings are connected to six membered rings while six membered rings are connected to both five and six membered rings. These are used in microscopic ball bearings, light weight batteries, in synthesis of new plastics and new drugs.

4. Oxidation States

The common oxidation states are +4 and +2. Carbon also exhibits negative oxidation states, i.e. −4. Down the group, stability of +4 oxidation state decreases and of +2 oxidation state increases due to inert pair effect.

5. Oxides

CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature.

- (i) Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.
- (ii) Monomeric form of CO_2 is stable due to non-availability of d-orbitals. Carbon has tendency to form a multiple bond ($O{=}C{=}O$) but SiO_2 exists in three dimensional polymeric form and has high melting point and is solid at room temperature.

6. Reactivity Towards Water

Carbon, silicon and germanium are not affected by water. Tin (Sn) decomposes with steam to form dioxide and dihydrogen gas.

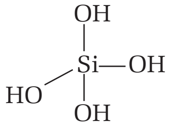
$$Sn + 2H_2O \xrightarrow{Heat} SnO_2 + 2H_2$$

Lead remains unaffected by water, probably because of a protective oxide film formation.

7. Halides

GeX_4 is more stable than GeX_2, whereas PbX_2 is more stable than PbX_4 and $SnCl_2$ is more stable than $SnCl_4$. $SnCl_4$ is liquid at room temperature due to covalent character and $SnCl_2$ is solid at room temperature.

(i) Except CCl_4, other halides are easily hydrolysed due to availability of vacant d-orbitals.

e.g. $SiCl_4 + 4H_2O \longrightarrow$  or $H_4SiO_4 + 4HCl$

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 \text{ or } H_4SiO_4 + 4HCl$$

Silicic acid

(ii) Si has vacant d-orbitals, so can expand its covalency and form higher halides $[SiF_6]^{2-}$ but not $[SiCl_6]^{2-}$ because larger size of chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.

Some Important Compounds

Some of the important compounds of group 14 elements or carbon family elements are given below:

1. Oxides of Carbon

Two important oxides of carbon are carbon monoxide (CO) and carbon dioxide CO_2.

Carbon monoxide can be prepared by the following reactions:

$$C(s) + H_2O(g) \xrightarrow{473\text{ K-}1273\text{ K}} \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$$

$$2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273\text{ K}} \underbrace{2CO(g) + 4N_2(g)}_{\text{Producer gas}}$$

Water gas and producer gas are very important industrial fuels.

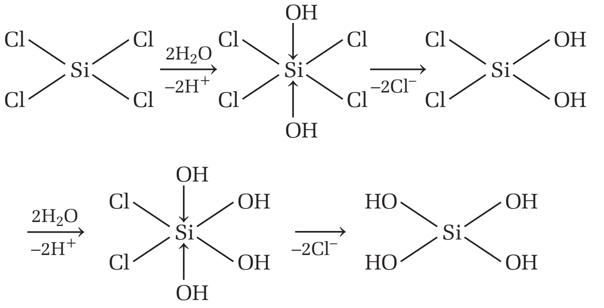
- Carbon dioxide can be prepared by complete combustion of carbon and carbon containing fuels in excess of air.
- Carbon dioxide can be obtained as a solid in the form of dry ice by allowing the liquiefied CO_2 to expand rapidly. Dry ice is used as a refrigerant for ice-cream and frozen food.

2. Silicon Tetrachloride ($SiCl_4$)

- It is tetrahedral and essentially covalent. It is readily hydrolysed by water. It fumes in moist air liberating hydrogen chloride.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

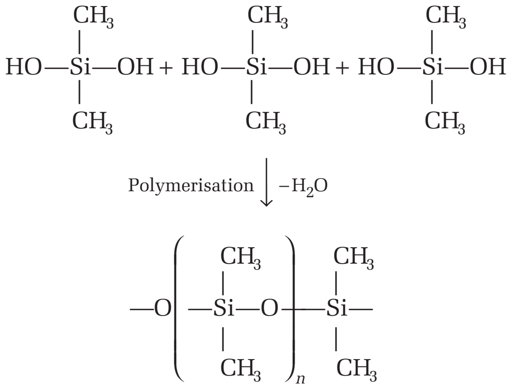
- The hydrolysis of $SiCl_4$ occurs due to coordination of OH with empty $3d$-orbitals in Si-atom of $SiCl_4$ molecule.



3. Silicones

- These are synthetic organosilicon compounds which has repeated unit of R_2SiO.
- These are prepared from alkyl halides.

$$2CH_3Cl + Si \xrightarrow[570\text{ K}]{\text{Cu powder}} (CH_3)_2SiCl_2 \xrightarrow[-2HCl]{+2H_2O} (CH_3)_2Si(OH)_2$$



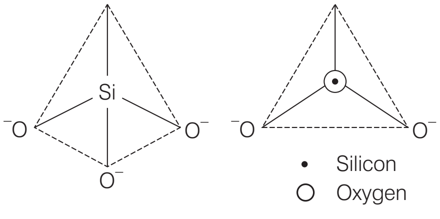
Silicone

Highly cross-linked silicone polymer is obtained by the hydrolysis of $RSiCl_3$.

- They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible, they are also used in surgical and cosmetic plants.

4. Silicates

- A large number of silicate minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. The basic structural unit of silicates is SiO_4^{4-}.



- The SiO_4^{4-} unit is neutralised by positively charged metal ions, if all the four corners are shared with other tetrahedral units.

Generally, the silicates have complex structures but they mainly differ in

(a) Number of oxygen atoms shared between SiO_4^{4-} tetrahedra.

(b) Geometric arrangement of tetrahedra.

(c) The number, type and arrangement of metallic cations.

Different type of silicates are as follows:

(i) **Orthosilicates** Simple silicates containing SiO_4^{4-} tetrahedra.

(ii) **Pyrosilicate** Two tetrahedral units share one O-atom to obtain $Si_2O_7^{6-}$ anion.

(iii) **Cyclic silicates** Two tetrahedral units share two oxygen atoms and form $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ anion.

(iv) **Chain silicates** Share two oxygen atoms, $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ are obtained.

(v) **Sheet silicates** Involve sharing of three O-atoms per tetrahedron to form $(Si_2O_5^{2-})_n$.

(vi) **Three dimensional silicates** All the four corners (O-atoms) of SiO_4^{4-} tetrahedra are shared with other.

(iv) Two important man-made silicates are glass and cement.

5. Zeolites

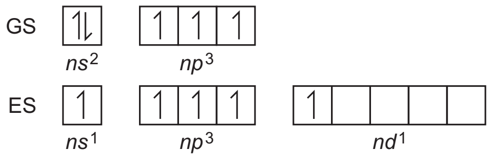
- If aluminium atoms replace few silicon atoms in three dimensional network of silicon dioxide, the obtained overall structure is known as alumino silicate and acquires a negative charge. Cations such as Na^+, K^+ or Ca^{2+} balance the negative charge. Their examples include feldspar and zeolites.
- Zeolites are used as a catalyst in petrochemical industries for cracking of hydrocarbons. ZSM-5 (a type of zeolite) is used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of hard water.

Group-15 Elements : Nitrogen Family

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

Important Properties

Electronic Configuration (ns^2np^3)



In case of nitrogen, ground state and excited state will be same due to the absence of *d*-orbitals.

Oxidation State

The common **oxidation states** of these elements are −3, +3 and +5. The tendency to exhibit −3 oxidation state decreases down the group due to increase in size and metallic character. The stability of + 5 oxidation state decreases down the group and that of +3 oxidation state increases down the group due to inert pair effect. Nitrogen with oxygen exhibits +1, +2, +4 oxidation states. Oxidation states from +1 to +4 tend to disproportionates in acid solution.

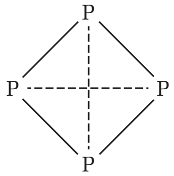
e.g. $$3H\overset{+3}{N}O_2 \longrightarrow H\overset{+5}{N}O_3 + H_2O + 2\overset{+2}{N}O$$

Physical Appearance

Only nitrogen has a tendency to form $p\pi$-$p\pi$ multiple bond ($N \equiv N$) due to the absence of *d*-orbitals.

Chemical Reactivity

N_2 has high bond dissociation energy, therefore reactivity of free N_2 is very less. Phosphorus has tendency to form a single bond due to the presence of *d*-orbitals and thus, exists in polyatomic form (P_4).



(White phosphorus)

P_4 has cyclic structure, therefore it is highly reactive and can expand its covalency as in PF_6^-.

Preparation, Properties and Uses of Dinitrogen

Preparation

- Dinitrogen is produced commercially by liquefaction and fractional distillation of air. Other methods of preparation are as follows:

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

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

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

Properties

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

$$6Li + N_2 \xrightarrow{\text{Heat}} 2Li_3N,\ 3Mg + N_2 \xrightarrow{\text{Heat}} Mg_3N_2$$

- It reacts with dioxygen only at high temperature to form nitric oxide.

$$N_2(g) + O_2(g) \xrightarrow{2000\,K} 2NO(g)$$

Uses

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

Preparation, Allotropic forms and Uses of Phosphorus

Preparation

1. **Retort process**

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

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

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

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

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

Allotropic Forms

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

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

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

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

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

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

It acts as strong reducing agent.

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

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

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

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

$$P + 3Na \longrightarrow Na_3P$$

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

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

$$\text{White P} \xrightarrow[\text{high pressure}]{200^\circ C} \text{black phosphorus}$$

It may occur in orthorhombic, rhombohedral and cubic form.

Uses

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

Some Important Compounds

Some of the important compounds of group 15 or nitrogen family elements are given below:

1. Ammonia (NH_3)

Preparation

- It is prepared by following methods.

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

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

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

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

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

Catalyst iron oxide with small amounts of K_2O and Al_2O_3 is used to increase the rate of attainment of equilibrium.

Properties

- Ammonia is covalent N-atom in NH_3 is sp^3-hybridised. Due to the presence of lone pair of electrons, it acquires pyramidal shape.
- NH_3 is basic in nature, has tendency to form hydrogen bond, therefore soluble in water and form NH_4OH or $NH_3(aq)$.
- Due to basic nature NH_3 is a good complexing agent and reducing agent. e.g.

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

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

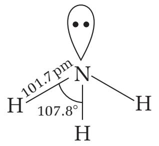
$$\underset{\text{Blue}}{Cu^{2+}(aq)} + 4\,NH_3(aq) \rightleftharpoons \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}(aq)}$$

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

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

Structure

NH_3 is a covalent molecule in which nitrogen possess sp^3-hybridisation. But due to the presence of one lone pair it acquires pyramidal structure. The bond angle is 107° due to *lp-bp* repulsion.



Uses

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

2. Nitric Acid (HNO_3)

Preparation

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

- **Laboratory preparation**

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

- **Ostwald process**

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

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

$$4\,NO_2(g) + O_2(g) + 2\,H_2O(l) \longrightarrow 4\,HNO_3(aq)$$

Properties

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

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

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

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

- It acts as a strong oxidising agent.
- Various reactions given by conc. HNO_3 that shows chemical properties of it are as follows:
- Non-metals such as C, S, P and I_2 are oxidised to carbonic acid, sulphuric acid, orthophosphoric acid and iodic acid respectively. e.g.

$$C + 4HNO_3 \longrightarrow H_2CO_3 + 4NO_2 + H_2O$$
$$S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

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

$$Sb + 5HNO_3 \longrightarrow H_3SbO_4 + 5NO_2 + H_2O$$
$$As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$$
$$Sn + 4\,HNO_3 \longrightarrow H_2SnO_3 + 4\,NO_2 + H_2O$$

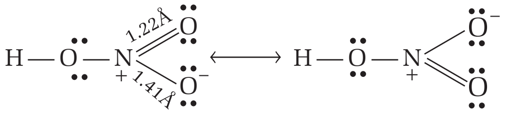
- **Brown ring test for nitrates**

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

- NO is absorbed by $FeSO_4$ and a dark brown ring of nitroso-ferrous sulphate is formed (ring test for nitrates).
- $C_{12}H_{22}O_{11} + 36HNO_3 \longrightarrow \underset{\text{Oxalic acid}}{6(COOH)_2} + 36NO_2 + 23H_2O$
- Metals like iron, cobalt, nickel, chromium, aluminium become passive in conc. HNO_3 due to the formation of a thin protective film of oxide on the surface of the metal.

Structure

- Nitrogen present in nitric acid is sp^2-hybridised and has a trigonal planar geometry. Structure of HNO_3 can be represented as



Uses

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

Oxides of Nitrogen

- $N_2O(g)$ is neutral, colourless gas, with *sp*-hybridisation and linear geometry (it is also called laughing gas).

$$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + H_2O$$

- $NO(g)$ is colourless, neutral gas. $NO(g)$ also contains odd number of electrons (paramagnetic) but in solid or liquid state NO exists in dimeric form and have paired electrons (diamagnetic). It is very reactive and harmful to health.

$$2\,NaNO_2 + 2\,FeSO_4 + 3\,H_2SO_4 \longrightarrow$$
$$Fe_2(SO_4)_3 + 2\,NaHSO_4 + 2\,H_2O + 2\,NO$$

- N_2O_3 is blue solid. It is acidic and planar with sp^2 hybridisation.

$$2\,NO + N_2O_4 \xrightarrow{\text{250 K}} 2\,N_2O_3$$

- $NO_2(g)$ is brown, acidic gas with angular shape and sp^2 hybridisation. NO_2 contains odd number of valence electrons (paramagnetic). On dimerisation, it gets converted to stable N_2O_4 molecule with even number of electrons (diamagnetic).

$$2Pb(NO_3)_2 \xrightarrow{\text{673 K}} 4NO_2 + 2PbO + O_2$$

- N_2O_4 is colourless solid/liquid. It is acidic with planar geometry and sp^2 hybridisation. Its covalency is four (total number of bonds with central atom).

$$2\,NO_2 \xrightleftharpoons[\text{Heat}]{\text{Cool}} N_2O_4$$

- N_2O_5 is colourless, acidic solid with planar shape and sp^2-hybridisation and four covalency.

$$4HNO_3 + P_4O_{10} \longrightarrow 4HNO_3 + 2N_2O_5$$

Oxides of Phosphorus

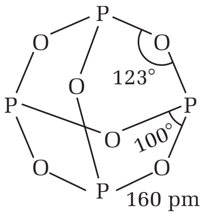
Phosphorus trioxide and phosphorus pentoxide are the two oxides of phosphorus. Oxides of phosphorus exist in dimeric forms.

1. Phosphorus trioxide (P_4O_6)

It is prepared from white phosphorus.

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

- It is a poisonous waxy solid with garlic odour.
- $4P_4O_6 \xrightarrow{\text{Heat}} \underset{\text{Phosphorus tetroxide}}{3P_4O_8} + 4P$
- $P_4O_6 + 4Cl_2 \longrightarrow \underset{\text{Phosphorus oxychloride}}{2POCl_3} + \underset{\text{Metaphosphorus oxychloride}}{2PO_2Cl}$
- $P_4O_6 + 6H_2O(\text{hot}) \longrightarrow 3H_3PO_4 + PH_3$



Structure of P_4O_6

2. Phosphorus Pentoxide (P_4O_{10})

It is obtained by burning of white phosphorus in free supply of air.

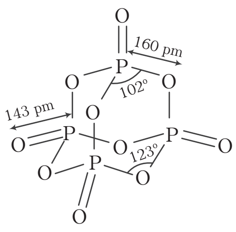
$$P_4 + 5O_2 \xrightarrow[\text{free supply of air}]{\text{Burning}} P_4O_{10}$$

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

$$P_4O_{10} \xrightarrow{2H_2O} \underset{\text{Metaphosphoric acid}}{4HPO_3} \xrightarrow{2H_2O} 2H_4P_2O_7$$

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

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



Structure of P_4O_{10}

3. Phosphine (PH_3)

Preparation

It is prepared by following methods:

(a) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
(b) $Ca_3P_2 + 6HCl \longrightarrow 3CaCl_2 + 2PH_3$
(c) $P_4 + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2$
(d) $PH_4I + KOH \longrightarrow KI + H_2O + PH_3$

Properties

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

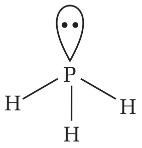
$$3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$$

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

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

Structure

Phosphine is a covalent molecule having pyramidal structure like ammonia. The bond angle H — P — H is 93°. It can be represented as



Structure of phosphine

Uses

It is used for making smoke screens, metallic phosphides, holme signals due to spontaneous combustion of PH_3.

4. Phosphorus Halides (PCl_3 and PCl_5)

Preparation

Following methods are used to prepare phosphorus halides.

(a) $P_4 + 6Cl_2 \longrightarrow 4PCl_3$
(b) $P_4 + 10Cl_2 \longrightarrow 4PCl_5$
(c) $P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
(d) $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

Properties

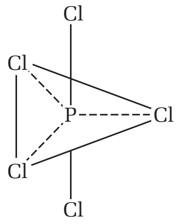
- PCl_5 is a yellowish white powder and in moist air it gets hydrolysed to $POCl_3$ and finally gets converted to phosphoric acid.

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

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

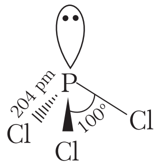
Structure

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



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

- In solid state, PCl_5 exists as an ionic solid, $[PCl_4]^+[PCl_6]^-$ in which, the cation, $[PCl_4]^+$ is tetrahedral and the anion $[PCl_6]^-$ is octahedral.
- **Structure of PCl_3** is similar to ammonia. P-atom is sp^3-hybridised.



Structure of PCl_3

Uses

- PCl_3 is used in the manufacture of $POCl_3$ and in preparation of organic compounds.
- PCl_5 is used as a chlorinating agent in organic chemistry.

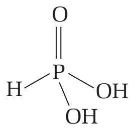
Oxoacids of Phosphorus and Nitrogen

- $H_2N_2O_2$ (hyponitrous acid); HNO_2 (nitrous acid) and HNO_3 (nitric acid) are the oxoacids of nitrogen. Out of these HNO_3 is the most important. HNO_2 (conc.) is strong oxidising agent. e.g.

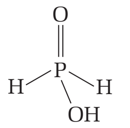
$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$P_4 + 20HNO_3 \text{ (conc.)} \longrightarrow 4H_3PO_3 + 20NO_2 + 4H_2O$$

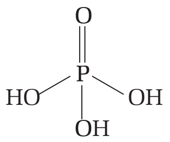
- The structure of oxoacids of phosphorus are given below :



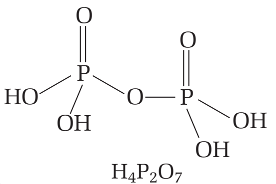
H_3PO_3
(Orthophosphorus acid)
sp^3, diprotic



H_3PO_2
(Hypophosphorus acid)
monoprotic, sp^3



H_3PO_4
(Orthophosphoric acid)
triprotic, sp^3



$H_4P_2O_7$
(Pyrophosphoric acid)
sp^3

Pyrophosphorus acid = $H_4P_2O_5$

Hypophosphoric acid = $H_4P_2O_6$

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

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

- The acids which contain P—H bond, have strong reducing properties, thus hypophosphorus acid is a good reducing agent as it contains two P—H bonds. e.g.
$4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow 4Ag + 4HNO_3 + H_3PO_4$

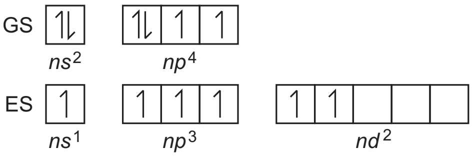
Group-16 Elements : Oxygen Family

Group 16 elements are sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). This is sometimes known as group of **chalcogens** (due to ore forming nature). Oxygen is the most abundant of all the elements on earth. Oxygen and sulphur are non-metals, selenium and tellurium are metalloids and polonium is radioactive metal.

Important Properties

The group-16 elements exihibit the properties may be given as:

Electronic Configuration (ns^2np^4)



Oxidation States

Oxidation states exhibited by 16th group elements are −2, +2, +4, +6 but +4 and +6 are more common. On moving down the group, stability of +6 oxidation state decreases and that of +4 oxidation state increases due to inert pair effect. The oxidation state of O is −1 and $-\frac{1}{2}$ in peroxides and superoxides respectively. In case of OF_2, O_2F_2, oxidation states of oxygen are +2, +1 respectively.

Physical Appearance

Oxygen has a tendency to form **$p\pi$-$p\pi$ multiple bond** (O═O) due to the absence of *d*-orbitals and high bond dissociation enthalpy. Sulphur has tendency to form single bond due to the presence of *d*-orbitals and exist in polyatomic (S_8) form.

Allotropy

Oxygen exists in two molecular allotropic forms; the diatomic molecule, O_2 (most stable) and the triatomic molecule, O_3 (ozone comparatively less stable). Sulphur forms numerous allotropes, out of which the yellow rhombic (α-sulphur) and monoclinic (β-sulphur) forms are the most important.

$$\text{Rhombic sulphur} \xrightarrow{\text{369 K above}} \text{Monoclinic sulphur}$$

At elevated temperatures (1000 K), S_2 is the dominant species and is paramagnetic like O_2.

Hydrides

Down the group acidic character increases from H_2O to H_2Se. All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

Oxides

All these elements (except O_2) form MO_2 type **oxides**. SO_2 is gas while SeO_2 is solid. Reducing property of dioxide decreases from SO_2 to TeO_2. SO_2 is reducing while TeO_2 is an oxidising agent.

Halides

The stability of the **halides** decreases in the order

$$F^- > Cl^- > Br^- > I^-.$$

Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature. SF_6 is exceptionally stable for steric reasons. SF_4 is a gas, SeF_4 is a liquid and TeF_4 is a solid. These fluorides have sp^3d hybridisation and *see-saw* geometry. The well known mono halides are dimeric in nature. e.g. $S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2$ and Se_2Br_2. These dimeric halides undergo disproportionation as given below:

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

Some Important Compounds

Some of the important compounds considered under group 16 are given below:

1. Dioxygen

Preparation

- **Laboratory method**

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

- It is manufactured from liquid air. Air is liquefied by making use of Joule Thomson effect. Liquid air is a mixture of liquid nitrogen and liquid oxygen. The difference in their boiling points is about 12.8°C, hence they are easily separated by fractional evaporation.
- **By electrolysis of water** (acidified water)

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

At cathode $2H^+ + 2e^- \longrightarrow H_2$

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

Properties

- Colourless, odourless, tasteless gas which is slightly soluble in water. Liquid oxygen exhibits paramagnetism.
- It is non-inflammable but a supporter of combustion.
- $O{=}O$, bond dissociation energy is high, therefore it reacts with metals or non-metals after external heating to start the reaction.

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

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

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

Uses

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

2. Ozone

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

Preparation

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

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

Properties

- It is pale blue gas with pungent odour. It is diamagnetic and poisonous.
- Ozone is unstable; $2O_3 \xrightarrow{\text{Heat}} 3O_2$
- It acts as a powerful oxidising agent. It liberates iodine from neutral KI solution and the liberated I_2 turns starch paper blue.

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

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

- Alkaline KI is oxidised to potassium iodate and periodate.

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

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

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

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

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

Uses

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

Allotropic forms of Sulphur

It exists in several allotropic forms. These are as follows:

1. **Rhombic sulphur** (α-sulphur) is common crystalline form of sulphur, yellow in colour, melting point 114.5°C and specific gravity 2.06. Its crystals are prepared by evaporating sulphur solution in CS_2. It is insoluble in water but readily soluble in CS_2.
2. **Monoclinic sulphur** (β-sulphur) is stable above 95.6°C. Its crystals are amber yellow in colour, melting point 119°C, specific gravity 1.98. It is insoluble in CS_2. It is prepared by melting rhombic sulphur in a dish followed by cooling till crust is formed.

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

   At 95.6°C both the forms are stable. This temperature is called **transition temperature.** S_8 rings in both the forms is puckered and has a crown shape.
3. **Plastic sulphur** is obtained by pouring boiling sulphur into cold water. It is amber brown in colour, specific gravity 1.95 and insoluble in CS_2.
4. **Milk of sulphur** is obtained by boiling milk of lime with sulphur and decomposing the products formed with HCl. It is used in medicines.
5. **Colloidal sulphur** is prepared by passing H_2S through a solution of an oxidising agent such as nitric acid etc.

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

Colloidal sulphur changes into ordinary form on heating.

Sulphuric Acid (H_2SO_4)

Preparation

It is manufactured by contact process which involves three steps :

(i) Burning of sulphur ores in air to generate SO_2.

(ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5).

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

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

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

Properties

- Concentrated sulphuric acid is a strong dehydrating agent.

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

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

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

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

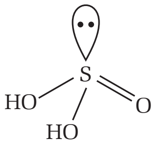
Uses

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

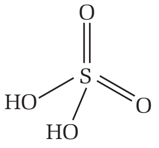
NOTE H_2SO_3 acts as bleaching agent but it is temporary and the bleached material regains its colour due to oxidation.

Oxoacids of Sulphur

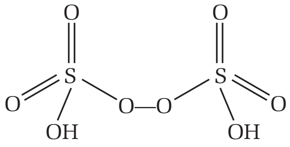
The structures of oxoacids of sulphur are as follows:



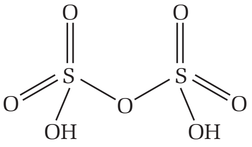
Sulphurous acid
(H_2SO_3)



Sulphuric acid
(H_2SO_4)



Peroxodisulphuric acid
($H_2S_2O_8$)



Pyrosulphuric acid (oleum)
($H_2S_2O_7$)

Group-17 Elements :

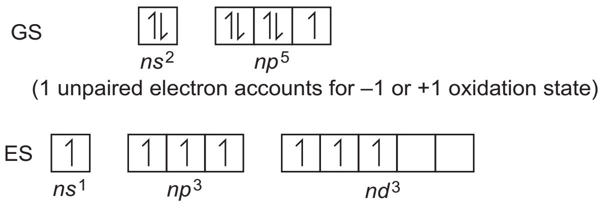
Halogens Family

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

Important Properties

Electronic Configuration

All elements of group have seven electron in their outermost shell $ns^2\ np^2$.



Oxidation State

Ground state and excited state in fluorine will be same due to absence of *d*-orbitals and oxidation state of fluorine is always –1.

Chemical Reactivity

All the halogens are highly reactive. Halogens are strong oxidising agent and their oxidising power decreases down the group.

$$F_2 > O_2 > Cl_2 > Br_2 > I_2$$

Oxidising power decreases

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

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

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

(where, $X = \text{Cl or Br}$)

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

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

- The order of bond dissociation enthalpy is $Cl—F > Cl_2 > Br_2 > F_2 > I_2$.
- Here, fluorine shows anomalous behaviour because of its very small size and high electronegativity. F_2 has less bond enthalpy than Cl_2 and Br_2 and absence of *d*-orbitals in valence shell.
- Hydrogen halides dissolve in water to form hydrohalic acids. The acidic strength of these acids varies as $HF < FCl < HBr < HI$.
- HF is a liquid while rest of hydrogen halides are gases. It reacts with glass, so it is stored in waxed glass bottles. This property of HF to act on glass is utilised in etching of glass.

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

(i) Chlorine forms a number of oxides such as, Cl_2O, Cl_2O_3, Cl_2O_5, Cl_2O_7, ClO_2. ClO_2 is used as a bleaching agent for paper pulp, textiles and in water treatment.

(ii) Br_2O, BrO_2, BrO_3 are the least stable bromine oxides and exist only at low temperatures. They are very powerful oxidising agents.

(iii) The iodine oxides, i.e. I_2O_4, I_2O_5, I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and is used in the estimation of carbon monoxide.

Some Important Compounds

Some of the important compounds of group 17 elements.

1. Chlorine (Cl_2)

Preparation

It can be prepared by the following methods:

(a) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ (Lab method)

(b) $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacon's process)

Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution). Chlorine is liberated at anode (electrolytic process). It is also obtained as a by product in many chemical industries.

Properties

- It is a greenish yellow gas with pungent and suffocating odour. It is soluble in water.
- $8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$
- $NH_3 + \underset{\text{Excess}}{3Cl_2} \longrightarrow \underset{\text{Explosive}}{NCl_3} + 3HCl$
- $\underset{\text{Cold and dil.}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$
- $\underset{\text{Hot and conc.}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$
- With dry slaked lime, it gives bleaching powder.
  $Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$

Uses

- For bleaching woodpulp, bleaching cotton and textiles.
- In extraction of gold and platinum.
- In manufacture of dyes, drugs and organic compounds.

2. Hydrogen Chloride (HCl)

Preparation

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

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

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

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

Properties

It is a colourless and pungent smelling gas. Its aqueous solution is called hydrochloric acid.

When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, *aqua-regia* is formed which is used for dissolving noble metals, e.g. gold, platinum.

Uses

- In manufacture of chlorine, NH_4Cl and glucose.
- For extracting glue from bones.
- In medicine and as laboratory agent.

Oxoacids of Halogens

Higher oxoacids of fluorine such as HFO_2, HFO_3 do not exist because fluorine is most electronegative and has absence of *d*-orbitals. +3 oxidation state of bromine and iodine is unstable due to inert pair effect, therefore $HBrO_2$ and HIO_2 do not exist.

Decreasing order of acidic nature

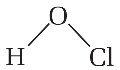
$$\underset{\text{(Hypofluorous acid)}}{HOF} > \underset{\text{(Hypochlorous acid)}}{HOCl} > \underset{\text{(Hypobromous acid)}}{HOBr} > \underset{\text{(Hypoiodous acid)}}{HOI}$$

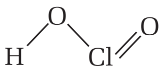
$$\longrightarrow \underset{\text{(Chloric acid)}}{HOClO_2} > \underset{\text{(Bromic acid)}}{HOBrO_2} > \underset{\text{(Iodic acid)}}{HOIO_2}$$

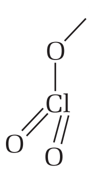
$$\longrightarrow HOClO_3 > HOClO_2 > HOClO > HOCl$$

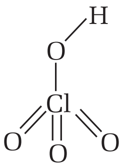
$$\longrightarrow HClO_4 > HBrO_4 > HIO_4$$

Structures of various oxoacids of chlorine are as follows:


Hypochlorous acid


Chlorous acid


Chloric acid


Perchloric acid

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

Interhalogen Compounds

- When two different halogens react with each other, interhalogen compounds are formed. These compounds are covalent and diamagnetic in nature.
- They are volatile solids or liquids except ClF which is a gas at 298 K. Interhalogen compounds are more reactive than halogens (except fluorine).

Some Properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure
XX'	CIF	Colourless gas	Linear
	BrF	Pale brown gas	Linear
	IF (very unstable)	Detected spectroscopically	Linear
	BrCl (Pure solid is known at r.t.)	Ruby red solid (α-form)	Linear
	ICl	Brown red solid (β-form)	Linear
	IBr	Black solid	Linear
XX'_3	ClF_3	Colourless gas	Bent T-shaped
	BrF_3	Yellow green liquid	Bent T-shaped
	IF_3	Yellow power	Bent T-shaped
	ICl_3(dimerises as Cl-bridged dimer,I_2Cl_6)	Orange solid	Bent T-shaped
XX'_5	IF_5	Colourless gas but solid below 77K	Square pyramidal
	BrF_5	Colourless liquid	Square pyramidal
	ClF_5	Colourless liquid	Square pyramidal
XX'_7	IF_7	Colourless gas	Pentagonal bipyramidal

Group-18 Elements : Noble Gases

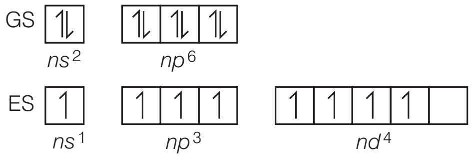
- Elements of group 18 are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) (radioactive).
- All of these are gases and chemically unreactive. Down the group their ionisation enthalpy decreases, therefore Xe reacts with oxygen and fluorine and forms different compounds. Xenon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

Occurrence

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

Important Properties

- **Electronic configuration** is (ns^2np^6) (except helium).



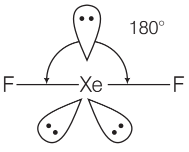
Chemical Reactivity

- $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$
- $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$
- $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$
- Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.
- XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K. They are powerful fluorinating agents.
- XeF_6 is extremely reactive. It cannot be stored in glass or quartz vessels as it readily reacts with SiO_2 present in glass.

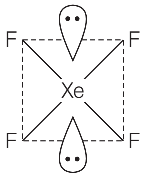
Summary of Stable Compounds of Xe

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

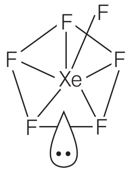
- **Molecular Structures of Xenon Compounds**



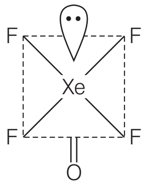
XeF_2
(Xe atom in 1st excited state)



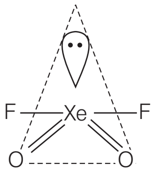
XeF_4
(Xe atom in 2nd excited state)



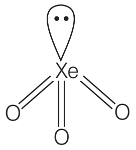
XeF_6
(Xe atom in 3rd excited state)



$XeOF_4$
(Xe in 3rd excited state)



XeO_2F_2
(Xe in 1st excited state)



XeO_3
(Xe in 1st excited state)

Uses

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

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Boric acid is called acid because its molecule

(a) contains replaceable H^+ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule

2 Heating of an aqueous solution of aluminium chloride to dryness will give

(a) $Al(OH)Cl_2$ (b) Al_2O_3 (c) Al_2Cl_6 (d) $AlCl_3$

3 Boron cannot form which one of the following anions?

➜ AIEEE 2011

(a) BF_6^{3-} (b) BH_4^-
(c) $B(OH)_4^-$ (d) BO_2^-

4 Mark the oxide which is amphoteric in character.

(a) CO_2 (b) SiO_2 (c) SnO_2 (d) CaO

5 Graphite is a soft, solid lubricant, extremely difficult to melt. The reason for this anomalous behaviour is that graphite

(a) is an allotropic form of diamond
(b) has molecules of variable molecular masses like polymers
(c) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds
(d) is a non-crystalline substance

6 Carborundum is obtained when silica is heated at high temperature with

(a) carbon (b) carbon monoxide
(c) carbon dioxide (d) calcium carbonate

7 Among the following substituted silanes the one which will give rise to cross linked silicon polymer on hydrolysis, is

(a) R_3SiCl (b) R_4Si
(c) $RSiCl_3$ (d) R_2SiCl_2

8 Name of the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared is

(a) pyrosilicate (b) sheet silicate
(c) linear chain silicate (d) three dimensional silicate

9 In curing cement plasters water is sprinkled from time to time. This helps in

(a) keeping it cool
(b) developing interlocking needle like crystals of hydrated silicates
(c) hydrating sand and gravel mixed with cement
(d) converting sand into silicic acid

10 The catenation tendency of C, Si and Ge is in the order $Ge < Si < C$. The bond energies (in kJ mol^{-1}) of C—C, Si—Si and Ge—Ge bonds are respectively

➜ JEE Main (Online) 2013

(a) 348, 297, 260 (b) 297, 348, 260
(c) 348, 260, 297 (d) 260, 297, 348

11 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

12 Nitrogen shows different oxidation states in the range

(a) 0 to +5 (b) –3 to +5
(c) –5 to +3 (d) –3 to+3

13 A hydride of nitrogen which is acidic is

(a) NH_3 (b) N_2H_4
(c) N_2H_2 (d) N_3H

14 The compound that does not produce nitrogen gas by the thermal decomposition is ➜ JEE Main 2018

(a) $Ba(N_3)_2$ (b) $(NH_4)_2Cr_2O_7$
(c) NH_4NO_2 (d) $(NH_4)_2SO_4$

15 Extra pure N_2 can be obtained by heating

(a) NH_3 with CuO (b) NH_4NO_3
(c) $(NH_4)_2Cr_2O_7$ (d) $Ba(N_3)_2$

16 The number of σ bonds in P_4O_{10} is

(a) 6 (b) 16
(c) 20 (d) 7

17 PH_3, the hydride of phosphorus is

(a) metallic (b) ionic
(c) non-metallic (d) covalent

18 When concentrated HNO_3 is heated with P_2O_5 it forms

(a) N_2O (b) NO
(c) NO_2 (d) N_2O_5

19 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}.

(a) 1 (b) 2
(c) 3 (d) 4

20 When conc. H_2SO_4 is heated with P_2O_5, the acid is converted to

(a) sulphur trioxide
(b) sulphur dioxide
(c) sulphur
(d) a mixture of sulphur dioxide and sulphur trioxide

21 The pair in which phosphorus atoms have a formal oxidation state of +3 is ➜ JEE Main 2016

(a) pyrophosphorus and hypophosphoric acids
(b) orthophosphorus and hypophophoric acids
(c) pyrophosphorus and pyrophosphoric acids
(d) orthophosphorus and pyrophosphorus acids

22 White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a

(a) dimerisation reaction (b) disproportionation reaction
(c) condensation reaction (d) precipitation reaction

23 The molecule having smallest bond angle is ➜ AIEEE 2012

(a) NCl_3 (b) $AsCl_3$ (c) $SbCl_3$ (d) PCl_3

24 Which of the following statements is incorrect? ➜ AIEEE 2011

(a) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the periodic table
(b) Nitrogen cannot form $d\pi$-$p\pi$ bond
(c) Single N—N bond is weaker than the single P—P bond
(d) N_2O_4 has two resonance structures

25 Which one of the following compounds has the smallest bond angle in its molecule?

(a) OH_2 (b) SH_2 (c) NH_3 (d) SO_2

26 The number of S—S bonds in sulphur trioxide trimer (S_3O_9) is

(a) three (b) two (c) one (d) zero

27 Which of the following are peroxoacids of sulphur?

(a) H_2SO_5 and $H_2S_2O_8$ (b) H_2SO_5 and $H_2S_2O_7$
(c) $H_2S_2O_7$ and $H_2S_2O_8$ (d) $H_2S_2O_6$ and $H_2S_2O_7$

28 Which of the following is the wrong statement?

(a) O_3 molecule is linear ➜ JEE Main (Online) 2013
(b) Ozone is violet black in solid state
(c) Ozone is diamagnetic gas
(d) ONCl and ONO^- are not isoelectronic

29 Which of the following statements regarding sulphur is incorrect? ➜ AIEEE 2011

(a) S_2 molecule is paramagnetic
(b) The vapour at 200°C consists mostly of S_8 rings
(c) At 600°C, the gas mainly consists of S_2 molecules
(d) The oxidation state of sulphur is never less than +4 in its compounds

30 Which among the following is the most reactive?

(a) Cl_2 (b) Br_2 ➜ JEE Main 2015
(c) I_2 (d) ICl

31 The correct order of the thermal stability of hydrogen halides (H—X) is

(a) HI > HCl > HF > HBr (b) HCl < HF > HBr < HI
(c) HF > HCl > HBr > HI (d) HI > HBr > HCl > HF

32 Among the following oxoacids, the correct decreasing order of acid strength is ➜ JEE Main 2014

(a) $HOCl > HClO_2 > HClO_3 > HClO_4$
(b) $HClO_4 > HOCl > HClO_2 > HClO_3$
(c) $HClO_4 > HClO_3 > HClO_2 > HOCl$
(d) $HClO_2 > HClO_4 > HClO_3 > HOCl$

33 The solubility order of alkali metal fluoride in water is

➜ JEE Main (Online) 2013

(a) LiF < RbF < KF < NaF (b) RbF < KF < NaF < LiF
(c) LiF > NaF > KF > RbF (d) LiF < NaF < KF < RbF

34 Which one has the highest boiling point? ➜ JEE Main 2015

(a) He (b) Ne (c) Kr (d) Xe

35 Argon is used in arc welding because of its

(a) low reactivity with metal
(b) ability to lower the melting point of metal
(c) flammability
(d) high calorific value

36 The structure of XeO_3 is

(a) linear (b) planar
(c) pyramidal (d) T-shaped

37 XeF_4 and XeF_6 are expected to be

(a) oxidising (b) reducing
(c) unreactive (d) strongly basic

38 Which of the following acids possesses oxidising, reducing and complex forming properties?

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

39 Match the species given in Column I with properties given in Column II.

	Column I		Column II
A.	Diborane	1.	Used as a flux for soldering metals
B.	Gallium	2.	Crystalline form of silica
C.	Borax	3.	Banana bonds
D.	Aluminosilicate	4.	Low melting, high boiling,useful for measuring high temperatures
E.	Quartz	5.	Used as catalyst in petrochemical industries

Codes

	A	B	C	D	E
(a)	3	4	1	5	2
(b)	4	3	1	5	2
(c)	4	3	5	2	1
(d)	1	2	5	4	3

Directions (Q. Nos. 40-42) *Each of these questions contains two statements : Statement* I *and Statement* II. *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c), (d) given below:*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I
(c) Statement I is true; Statement II is false
(d) Both the Statement I and II are false

40 **Statement I** Boron always forms covalent bond.

Statement II The small size of B^{3+} favours formation of covalent bond.

41 **Statement I** In water, orthoboric acid behaves as a weak monobasic acid.

Statement II In water, orthoboric acid acts as a proton donor.

42 **Statement I** Between $SiCl_4$ and CCl_4, only $SiCl_4$ reacts with water.

Statement II $SiCl_4$ is ionic and CCl_4 is covalent.

Direction (Q. Nos. 43 and 44) *In the following questions, Assertion (A) followed by Reason (R) is given. Choose the correct answer out of the following choices.*

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct and Reason is incorrect
(d) Both Assertion and Reason are incorrect

43 **Assertion** (A) Silicones are water repelling in nature.

Reason (R) Silicones are organosilicon polymers, which have (—R_2SiO—) as repeating unit.

44 **Assertion** (A) Nitrogen and oxygen are the main components in the atmosphere but these do not react to form oxides of nitrogen.

Reason (R) The reaction between nitrogen and oxygen requires high temperature.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 Identify the incorrect statement among the following.

(a) Ozone reacts with SO_2 to give SO_3
(b) Silicon reacts with NaOH (*aq*) in the presence of air to give Na_2SiO_3 and H_2O
(c) Cl_2 reacts with excess of NH_3 to give N_2 and NH_4Cl
(d) Br_2 reacts with hot and strong NaOH solution to give NaBr, $NaBrO_4$ and H_2O

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

Ion	ClO_4^-	IO_4^-	BrO_4^-
Reduction potential $E^{\ominus}/V$	$E^{\ominus} = 1.19$ V	$E^{\ominus} = 1.65$ V	$E^{\ominus} = 1.74$ V

(a) $ClO_4^- > IO_4^- > BrO_4^-$ (b) $IO_4^- > BrO_4^- > ClO_4^-$
(c) $BrO_4^- > IO_4^- > ClO_4^-$ (d) None of these

3 Which of the following statements is true?

(a) H_3PO_3 is a stronger acid than H_2SO_3
(b) In aqueous medium, HF is a stronger acid than HCl
(c) $HClO_4$ is weaker acid than $HClO_3$
(d) HNO_3 is a stronger acid than HNO_2

4 Which one of the following reaction of xenon compounds is not feasible?

(a) $XeO_3 + 6HF \longrightarrow XeF_6 + 3H_2O$
(b) $3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$
(c) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
(d) $XeF_6 + RbF \longrightarrow Rb[XeF_7]$

5 Among the following, the correct statement is :

(a) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional
(b) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(c) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(d) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical '*s*' orbital and is less directional

6 The formation of $O_2^+[PtF_6]$ is the basis for the formation of xenon fluorides. This is because

(a) O_2 and Xe have comparable sizes
(b) both O_2 and Xe are gases
(c) O_2 and Xe have comparable I.E.
(d) Both (a) and (c)

7 The hydrides of the first elements in groups 15-17 namely NH_3, H_2O and HF respectively shows abnormally high values for melting and boiling points. This is due to

(a) small size of N, O and F
(b) the ability to form extensive intermolecular H-bonding
(c) the ability to form extensive intramolecular H-bonding
(d) effective forces of interaction

8 An inorganic compound '*X*', made of two most occurring elements in the earth's crust and used in building construction, when reacts with carbon forms a diatomic molecule, which is poisonous in nature. Compound '*X*' may be

(a) SiO_2 (b) Al_2O_3
(c) CaO (d) CO_2

9 Which one of the following reactions does not occur ?

(a) $F_2 + Cl^- \longrightarrow 2F^- + Cl_2$ (b) $Cl_2 + 2F^- \longrightarrow 2Cl^- + F_2$
(c) $Br_2 + 2I^- \longrightarrow 2Br^- + I_2$ (d) $Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$

10 $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4)] + H_2O$

How can this reaction is made to proceed in forward direction?

(a) Addition of *cis* 1, 2-diol (b) Addition of borax
(c) Addition of *trans* 1, 2-diol (d) Addition of Na_2HPO_4

11 An inorganic compound containing ($3c$-$2e^-$) and ($2c$-$2e^-$) bonds when reacts with NH_3, at a certain temperature, gives a compound '*X*' which is isostructural with benzene and when reacts at high temperature forms a substance '*Y*'. The substance '*Y*' is

(a) B_2H_6 (b) $B_3N_3H_6$
(c) inorganic graphite (d) $B_2H_6 \cdot 2NH_3$

12 In which of the following arrangements, the sequence is not strictly according to the property written against it?

(a) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power
(b) HF < HCl < HBr < HI : increasing acid strength
(c) $NH_3 > PH_3 < AsH_3 < SbH_3$: increasing basic strength
(d) B < C < O < N : increasing first ionisation enthalpy

13 The correct order of pseudohalide, polyhalide and interhalogen are

(a) BrI_2^-, OCN^-, IF_5 (b) IF_5, BrI_2^-, OCN^-
(c) OCN^-, IF_5, BrI_2^- (d) OCN^-, BrI_2, IF_5

14 Consider the following statements.

I. NCl_5 does not exist while PCl_5 does
II. Both O_2^+ and NO are paramagnetic
III. Three C — O bonds are not equal in carbonate ion.
IV. Lead prefers to form tetravalent compound.

Which of the above statements are incorrect?

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

15. The molecule BF_3 and NF_3 both are covalent compounds, but BF_3 is non-polar and NF_3 is polar. The reason is that

(a) boron is a metal and nitrogen is a gas in uncombined state
(b) BF_3 bonds have no dipole moment whereas NF_3 bond have dipole moment
(c) atomic size of boron is smaller than that of N_2
(d) BF_3 is symmetrical molecule whereas NF_3 is unsymmetrical

ANSWERS

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

Hints and Explanations

SESSION 1

1 Due to the small size of boron atom and presence of six electrons. Boric acid accepts a pair of electron from OH^-ion of H_2O thereby releasing a proton.

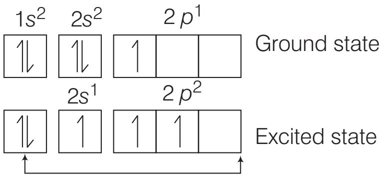
2 Aqueous solution of $AlCl_3$ is acidic due to hydrolysis.

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$$

On strong heating, $Al(OH)_3$ is converted into Al_2O_3.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

3 $_5B$



Fourth lone pair is accomodated in this empty orbital
Maximum covalency = 4

Due to the absence of $2d$-orbital, maximum covalency is four. Thus, BF_6^{3-} is not formed.

BH_4^- ($BH_3 + H^-$); $B(OH)_4^-$ ($B(OH)_3 + OH^-$) and BO_2^- are formed.

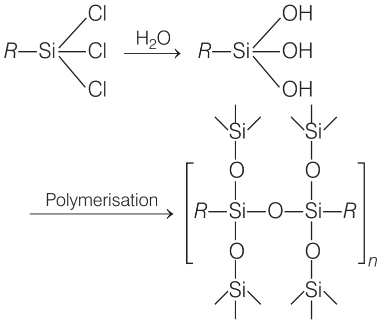
4 SnO_2 is amphoteric. It dissolves in acids as well as in alkalies e.g.

$$SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$$
$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

5 Graphite has carbon atoms arranged in large hexagonal layers with weak van der Waals' interactions between the layers.

6 $$SiO_2 + 3C \xrightarrow[2300\ K]{\text{High temp.}} \underset{\text{Carborundum}}{SiC} + 2CO$$

7 $RSiCl_3$, gives cross-linked silicon polymer on hydrolysis.



8 The structure of silicates has been found with the help of X-ray diffraction techniques. Sheet silicates are formed when three oxygen atoms (bridging O-atoms) of each $(SiO_4)^{4-}$ unit are shared. Hence, the general formula of sheet silicates is $(Si_2O_5)^{2n-}$.

9 The hydration of calcium aluminates and silicates involved in the setting of cement is an exothermic process, hence cement structures have to be cooled during setting by sprinkling water.

10 Higher the catenation tendency, higher is the bond energy.

∴ The bond energies of C—C, Si—Si and Ge—Ge bonds are respectively 348, 297 and 260 kJ mol^{-1}.

11 Due to the presence of one —OH group and two P — H bonds, H_3PO_2 act as reducing agent.

12 Nitrogen shows all the oxidation states ranging from −3 to + 5 in its compounds.

13 N_3H is acidic. It shows following resonating structures.

$$[N\equiv N^+ - N^-]^- \longrightarrow [N^- - N^+ \equiv N]^-$$

14 The thermal decomposition of given compounds is shown below:

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

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$$

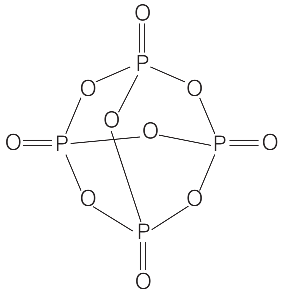
$$BO(N_3)_2 \longrightarrow Ba + 3N_2$$

Thus, only $(NH_4)_2SO_4$ does not gives N_2 on heating while rest of the given compounds give N_2 on their thermal decomposition.

15 $Ba(N_3)_2 \xrightarrow{\text{Heat}} Ba(s) + 3N_2(g)$

Azide salt of barium can be used to obtain purest form of N_2. The decomposition product contain solid Ba as by product along with gaseous nitrogen.

16 The number of σ-bonds in P_4O_{10} is 16. There are also four π-bonds present in P_4O_{10} molecule.



(P_4O_{10} molecule)

17 PH_3 is a covalent hydride.

18 $4HNO_3 + 2P_2O_5 \xrightarrow{\Delta} 2N_2O_5 + 4HPO_3$

19 PCl_5 produces $POCl_3$ with the following reagents.

$$2\,PCl_5 + SO_2 \longrightarrow POCl_3 + SOCl_2$$

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

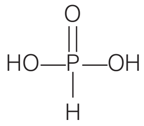
$$2PCl_5 + H_2SO_4 \longrightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$$

$$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$$

20 When conc. H_2SO_4 is heated with P_2O_5, the acid is converted into sulphur trioxide.

$$2H_2SO_4 + 2P_2O_5 \longrightarrow 2SO_3 + 4HPO_3$$

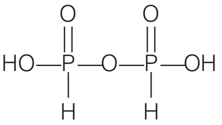
21 Orthophosphorus acid, H_3PO_3



$$HO-\underset{\displaystyle H}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}-OH$$

$H_3\overset{x}{P}O_3 = 3 + x + 3(-2) = 0$ or $x = +3$

Pyrophosphorus acid, $H_4P_2O_5$:



$$HO-\underset{\displaystyle H}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}-O-\underset{\displaystyle H}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}-OH$$

$H_4\overset{x}{P}_2O_5 = 4 + 2x + 5\,(-2) = 0$

$4 + 2x - 10 = 0 \Rightarrow x = +3$

22 White phosphorus on reaction with NaOH gives PH_3 as one of the product in disproportionation reaction.

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

23
N
P
As
Sb
] Group = 15
Valence electrons] = 5

MCl_3 has sp^3 hybridised M-element with one lone pair.

Lone pair and bond pair repulsion decreases bond angle. However, the bond-pairs of electrons are much farther away from the central atom in $SbCl_3$ than they are in NCl_3. Thus, lone pair causes even greater distortion in PCl_3, $AsCl_3$ and $SbCl_3$. Hence, bond angle decreases from NCl_3 (maximum) to $SbCl_3$ (minimum).

24 (a) Thermal stability of the hydrides decrease as we go down the group in periodic table for group 15 (N-family).

$BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

Least stable Most stable

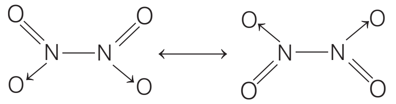
M–H – 255 247 322 391

bond energy (kJ mol^{-1})

(b) Due to the absence of d-orbital, nitrogen cannot from $d\pi$-$p\pi$ bond, thus it is correct.

(c) The N—N bond (BE 160 kJ mol^{-1}) is weaker than P—P bond (BE 209 kJ mol^{-1}) thus, it is correct.

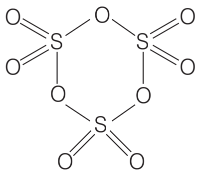
(d) N_2O_4 can form two resonance structures.



Thus, it is correct.

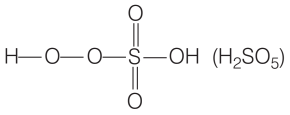
25 Bond angles are OH_2 (104°), H_2S (92°), NH_3 (107°) and SO_2 (119.5°).

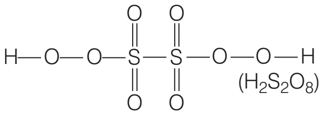
26 S_3O_9 is as



Hence, number of S—S bond = 0.

27





28 O_3 molecule is sp^3-hybridised and has bent shape.

29 (a) S_2 molecule is paramagnetic due to unpaired electrons in MO and is blue-coloured compound, thus true.

(b) The vapour at 200°C consists mostly of S_8 rings, thus correct.

(c) At 600°C, the gas mainly consists of S_2 molecules, thus correct.

(d) Oxidation states of sulphur are:

-2	in	H_2S
0	in	S_8
$+2$	in	$S_2O_3^{2-}$
$+4$	in	SO_2
$+6$	in	SO_3

Thus, incorrect oxidation state can be less than 4.

30 Cl_2,Br_2 and I_2 are homonuclear diatomic molecule in which electronegativity of the combining atoms is same,so they are more stable and less reactive whereas, I and Cl have different electronegativities and bond between them are polarised and hence, reactive. Therefore, interhalogen compounds are more reactive.

Time Saving Technique In this type of question of halogen, only go through the polarity of the molecule. As we know, diatomic molecule does not have polarity but molecules with dissimilar sizes have polarity resulting in more reactivity.

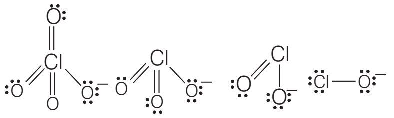
31 As the size of the halogen atom increases from F to I, the bond length of H — *X* increases. This increase in bond length decreases the bond strength and thus the thermal stability. Therefore, the order is

$$HF > HCl > HBr > HI.$$

32 Decreasing order of strength of oxoacids

$$HClO_4 > HClO_3 > HClO_2 > HOCl$$

Reason Negative charge is more delocalised on ClO_4^- due to resonance, hence, ClO_4^- is more stable (and less basic).



Hence, we can say as the number of oxygen atom (s) around Cl-atom increases as oxidation number of Cl-atom increases and thus, the ability of loose the H^+ increases.

33 For a substance to dissolve, the hydration energy must be greater than lattice energy. Due to the small size of Li^+ ion, the hydration energy of LiF is considerably high, but it has low solubility in water because of its higher lattice energy.

On moving down the group lattice energy decreases which results in increased solubility. Thus, the order of solubility for alkali metal fluorides in water is

$$LiF < NaF < KF < RbF.$$

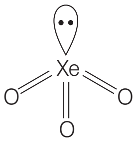
34 As we move down the group of noble gases, molecular mass increases by which dipole produced for a moment and hence London forces increases from He to Xe. Therefore, more amount of energy is required to break these forces, thus boiling point also increases form He to Xe.

35 Argon is used in arc welding to cause the inert atmosphere around, i.e. without interaction with metal.

36 In XeO_3, total electron pairs

$$= 4\,(3bp + 1lp),$$

i.e. sp^3-hybridisation ⇒ pyramidal shape.



37 XeF_4 oxidises potassium iodide.

$$XeF_4 + 4I^- \longrightarrow 2I_2 + 4F^- + Xe$$

XeF_6 oxidises hydrogen like other xenon fluorides.

38 HNO_2 posseses oxidising, reducing and complex forming properties as in it oxidation number of nitrogen is $+3$ (i.e. in between -3 to $+5$).

39 $A \rightarrow 3$, $B \rightarrow 4$, $C \rightarrow 1$, $D \rightarrow 5$, $E \rightarrow 2$

A. BH_3 is unstable froms diborane B_2H_6 by ($3c$ —$2e^-$) electron bond show banana bond.

B. Gallium with low melting point and high boiling points makes it useful to measure high temperatures.

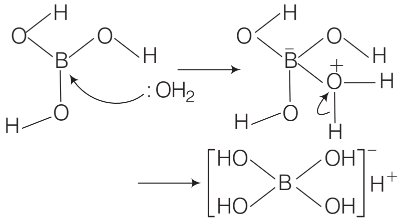
C. Borax is used as a flux for soldering metals for heat,scratch resistant coating in earthernwares.

D. Alumino silicate used as catalyst in petrochemical industries.

E. Quartz is a crystalline form of silica.

40 Boron always form covalent bond because boron requires very high energy to form B^{3+} and again B^{3+} due to its very small size, have high polarising power, thus cause greater polarisation and eventually significant covalent characteristics (Fajan's rule.)

41 In water, orthoboric acid behave as a weak monobasic Lewis acid.



42 Statement I is true but Statement II is false ($SiCl_4$ is also covalent bonded).

43 Silicones are a group of organosilicon polymers which have (R_2SiO) as a repeating unit.

This suggests that silicones are surrounded by non-polar alkyl groups that are water repelling in nature. They have wide applications it is used for water proofing of fabrics.

44 Nitrogen is an inert gas because of the presence of strong bond. That's why although there is 78% N_2 in the atmosphere but nitrogen oxide in not formed under ordinary conditions.

But when temperature is high enough i.e. = 2000 K, it reacts with oxygen to form nitrogen oxide.

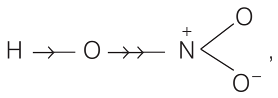
$$N_2 + O_2 \xrightarrow{\approx 2000K} 2NO$$

Thus, Assertion and Reason are true and Reason is the correct explanation of the Assertion.

SESSION 2

1 Br_2 reacts with hot and strong NaOH to give NaBr, $NaBrO_3$ and H_2O.

2 Higher the reduction potential stronger the oxidising agent, i.e. option (c) is correct.

3 

$$H \rightarrow\!\!- O \rightarrow\!\!- N = O$$

Polarity along O—H in HNO_3 is more in comparison to —O—H in HNO_2.

4 XeF_6 has much tendency to hydrolyse. The reverse reaction is more spontaneous.

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

5 NH_3 is better electron donor because the lone pair of electrons occupies sp^3-orbital and is more directional.

6 The first ionisation energy of xenon is quite close to that of oxygen and the molecular diameter of xenon and oxygen are almost identical. Based on the above facts it is suggested that since, oxygen combines with PtF_6, so xenon should also form similar compound with PtF_6.

7 Hydrides like NH_3, H_2O and HF have extensive intermolecular hydrogen bonding due to which they show high melting and boiling point.

8 The two most abundant elements in the earth's crust are Si and oxygen and the compound made by them is SiO_2. This compound is used in building construction.

$$SiO_2 + 2C \longrightarrow Si + \underset{\text{Poisonous}}{2CO}$$

9 With progressive increase in atomic number, the reduction potential of halogens decreases, thus oxidising power also decreases.

Hence, a halogen with lower atomic number will oxidise the halide ion of higher atomic number and therefore, will liberate them from their salt solution. Hence, the reaction,

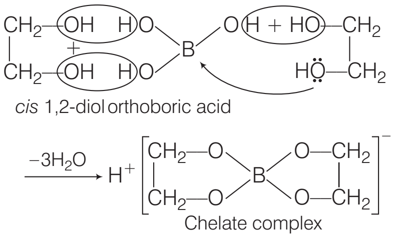
$$Cl_2 + 2F^- \longrightarrow 2Cl^- + F_2$$

is not possible.

10 $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na^+[B(OH)_4]^- + H_2O$

This reaction is reversible reaction because sodium metaborate, $Na^+[B(OH)_4]^-$ formed by the reaction between $B(OH)_3$ and NaOH gets hydrolysed to regenerate $B(OH)_3$ and NaOH.

$$Na^+[B(OH)_4]^- \xrightarrow{\text{Hydrolysis}} NaOH + B(OH)_3$$



If some quantity of polyhydroxy compounds like *cis* 1,2-diol, catechol, glycerol etc., is added to the reaction mixture, then the $B(OH)_3$ combines with such polyhydroxy compounds to give chelated complex compound. Due to complex compound formation, stability increases and due to higher stability of complex, reaction moves in forward direction.

11 B_2H_6 contains ($3c$-$2e^-$) and ($2c$-$2e^-$) bonds.

$$B_2H_6 + 2NH_3 \xrightarrow{\text{Low temp.}} B_2H_6 \cdot 2NH_3 \xrightarrow{200°C} \underset{\substack{\text{'X'} \\ \text{Inorganic benzene}}}{B_3N_3H_6}$$

$$B_2H_6 + NH_3 \xrightarrow{\text{High temp.}} \underset{\substack{\text{'Y'} \\ \text{Inorganic} \\ \text{graphite}}}{(BN)_x}$$

12 The correct increasing basic strength

$$SbH_3 < AsH_3 < PH_3 < NH_3$$

NH_3 is the most basic because of its small size, the electron density of electron pair is concentrated over small region. As the size increases, the electron density gets diffused over a large surface area and hence, the ability to donate the electron pair (basicity) decrease.

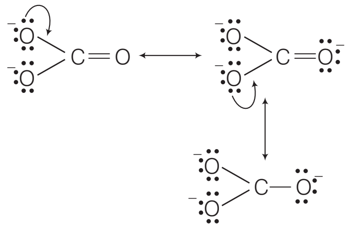
13 Pseudohalide are the combination of more than one electronegative atoms that have one unit negative charge. e.g. OCN^-, CN^-.

Polyhalide ions The complex ions which are formed by reaction of halogens among themselves are called polyhalide ions, e.g. I_3^-, BrI_2^-.

14 I. In nitrogen, *d*-orbitals are absent hence, it does not form NCl_5. Thus, NCl_5 does not exist but PCl_5 does.

II. O_2^+ and NO are isoelectronic and contains one unpaired electron each, thus both are paramagnetic.

III. In carbonate ion CO_3^{2-} all three C—O bonds are identical due to resonance.



IV. Pb^{2+} is more stable than Pb^{4+} due to inert pair effect, hence, prefers to form divalent compounds.

Thus, the incorrect statements are III and IV.

15 BF_3 is symmetrical planar, although it has polar bonds but resultant dipole moment is zero. In NF_3 lone pair cause distortion hence polarity arises.