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P-BLOCK ELEMENT

GROUP 13 ELEMENTS: THE BORON FAMILY :

Boron is a typical non-metal, aluminium is a metal but gallium, indium and thallium are almost exclusively metallic in character.

OCCURANCE

Boron: Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3),

borax, $Na_2B_4O_7 \cdot 10H_2O$, and kernite, $Na_2B_4O_7 \cdot 4H_2O$.

There are two isotopic forms of boron ^{10}B (19%) and ^{11}B (81%).

ALUMINIUM :

Aluminium is the most abundant metal.

Third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%).

Bauxite, $Al_2O_3 . 2H_2O$ and cryolite, Na_3AlF_6 are the important minerals of aluminium.

ELECTRONIC CONFIGURATION :

The outer electronic configuration of these elements is ns^2np^1.

ATOMIC RADII :

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, a deviation can be seen.

Atomic and Ionic radii order

$B < Ga < Al < In < T\ell$

Ionization Enthalpy

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group.

Ionization Enthalpies order

$B > T\ell > Ga > Al > In$

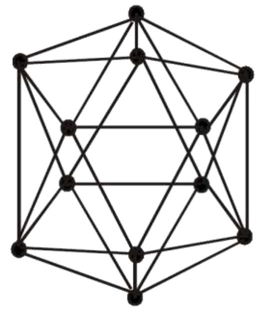
Electronegativity

$B > Tl > In > Ga > Al$

Physical Properties

(i) Boron is non-metallic in nature.

- It is extremely hard and black coloured solid.
- Boron exists in many allotropic forms. All the allotropes have basic building B_{12} icosahedral units made up of polyhedron having 20 faces and 12 corners. For example one is the simplest form : α - rhombohedral boron.



But Al , In & Tℓ all have close packed metal structure.

(ii) Rest of the members are soft metals with low melting point and high electrical conductivity.

(iii) Gallium with unusually low melting point (303K), could exist in liquid state during summer.

(iv) Density of the elements increases down the group from boron to thallium.

Melting and Boiling points order

M.P. B > Al > Tl > In > Ga

B.P. B > Al > Ga > In > Tl

Electropositive Character

$\underbrace{B <}_{\text{Non metal}} \underbrace{Al < Ga < In < Tl}_{\text{metals}}$

Chemical Properties

Oxidation state and trends in chemical reactivity

(i) Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds.

(ii) The relative stability of +1 oxidation state progressively increases for heavier elements: Al < Ga < In < Tl. In thallium +1 oxidation state is predominant whereas the +3 oxidation state is highly oxidizing in character.

(iii) The compounds in +1 oxidation state, as expected from energy considerations, are more ionic than those in +3 oxidation state.

Preparation of Boron :

(i) Preparation of B2O3 from Borax or Colemanite

$Na_2B_4O_7 + HCl/H_2SO_4 \longrightarrow NaX + H_2B_4O_7$

$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3 \xrightarrow{\Delta} B_2O_3 + H_2O$

(ii) Reduction of B_2O_3

$B_2O_3 + Na/K/Mg/Al \longrightarrow B + Na_2O/K_2O/MgO/Al_2O_3$

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Chemical Properties :

(i) Burning in air : $4B + 3O_2 \longrightarrow 2B_2O_3$

$4Al + 3O_2 \longrightarrow 2Al_2O_3$

(ii) Reaction with water

$B + H_2O$ (Cold & hot) $\longrightarrow$ no reaction

$2B + 3H_2O \longrightarrow B_2O_3 + H_2$

$(Al + \underset{\text{(red hot)}}{3H_2O} \longrightarrow Al(OH)_3 + \frac{3}{2} H_2)$

(iii) $B + HCl \longrightarrow$ no reaction

$B + H_2SO_4$ (dil) $\longrightarrow$ no reaction

$2B + 3H_2SO_4$ (conc.) $\longrightarrow 2H_3BO_3 + 3SO_2$

$(2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O)$

$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$

[$Al + HNO_3(80\%) \longrightarrow Al_2O_3$ (passive layer) and does not react further.]

(vi) Ga, In, $T\ell$ dissolve in dilute acids liberating H_2 Ga is amphoteric like Al and it dissolves in aq.

NaOH liberating H2 and forming gallates.

$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$

$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$

(v) $2B + N_2 \longrightarrow 2BN$ $(2Al + N_2 \longrightarrow 2AlN)$

$4B + C \longrightarrow B_4C$ $(4Al + 3C \longrightarrow Al_4C_3)$

(vi) $3Mg + 2B \longrightarrow Mg_3B_2$

SOME IMPORTANT COMPOUNDS OF BORON

Some useful compounds of boron are borax, orthoboric acid and diborane. We will briefly study their chemistry.

Preparation of Borax :

Borax

$2CaO.3B_2O_3 + 2Na_2CO_3 \longrightarrow 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$

$\downarrow$ Filtered –$CaCO_3$(as residue)

$NaBO_2 + Na_2B_4O_7.10H_2O \xleftarrow[\text{and allowed to crystallise out and fillered}]{\text{Concentrated}} \underbrace{Na_2B_4O_7 + NaBO_2}_{\text{In solution}}$

$\downarrow$ CO_2 passed and crystallize out again [$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$]

$Na_2B_4O_7 . 10H_2O \downarrow$

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Properties :

(i) It is a white crystalline solid of formula $Na_2B_4O_7.10H_2O$. In fact it contains the tetranuclear units $[B_4O_5(OH)_4]^{2-}$ and correct formula; therefore, is $Na_2[B_4O_5(OH)_4].8H_2O$.

(ii) Borax dissolves in water to give an alkaline solution.

$$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$$

Orthoboric acid

(iii) On heating, borax first loses water molecules and swells up. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

Orthoboric acid :

Preparation :

(i) It can be prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$$

(ii) It is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.)

Property :

(i) Orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch.

(ii) It is sparingly soluble in water but highly soluble in hot water.

(iii) H_3BO_3 is soluble in water and behaves as weak monobasic acid. It does not donate protons like most the acids, but rather it accepts OH^- . It is therefore is Lewis acid $(B(OH)_3)$

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$$

or

$$H_3BO_3$$

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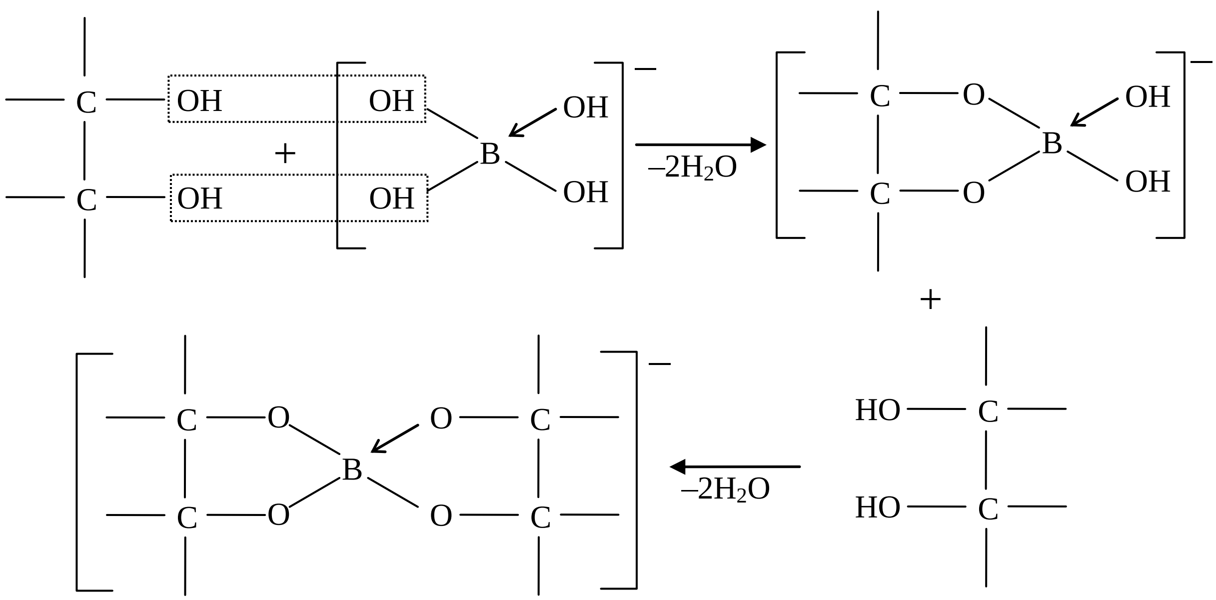
Since $B(OH)_3$ only partially reacts with water to form H_3O^+ and $[B(OH)_4]^-$ it behaves as a weak acid. Thus it cannot be titrated satisfactorily with NaOH as a sharp end point is not obtained. If certain polyhydroxy compounds such as glycerol, mannitol or sugar are added to the titration mixture then $B(OH)_3$ behaves as a strong monobasic acid. and hence can now be titrated with NaOH and end point is diluted using phenolphthalein as indicator.

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

$$NaBO_2 + 2H_2O$$

The added compound must be a as diol to enhance the acidic proprieties in this way the cis-diol forms very stable complexes with $[B(OH)_4]^-$ formed in forward direction above, thus effectively removing it from solution. Hence reaction proceeds in forward direction (Le-Chatelier principle.)



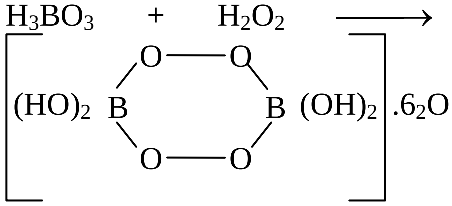
On heating, orthoboric acid above 370K forms metaboric acid, HBO_2 which on further heating yields boric oxide, B_2O_3.

- ***Heating of boric acid :***

$$H_3BO_3 \xrightarrow{100^\circ C} HBO_2 \xrightarrow{140^\circ C} H_2B_4O_7 \xrightarrow[\text{red hot}]{\Delta} B_2O_3$$

Metaboric acid — tetraboric acid — Glassy mass

$$H_3BO_3 + H_2O_2 \longrightarrow (H_2O) + (HO)_2\ B{-}O{-}O{-}H \xrightarrow{NaOH}$$



Sodium peroxy borate used in washing powder as brightner

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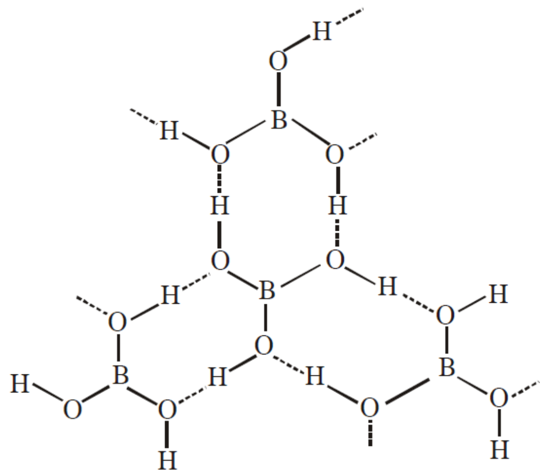
STRUCTRE

It has a layer structure in which planar BO_3 units are joined by hydrogen bonds as shown in figure.



Structure of boric acid; the dotted lines represent hydrogen bonds.

Uses of boric acid :
(i) Boric acid is used in manufacturing of optical glasses
(ii) With borax, it is used in the preparation of a buffer solution.

Diborane, B_2H_6

The simplest boron hydride known, is diborane.

Preparation :

(i) It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

$3LiAlH_4 + 4BF_3 \longrightarrow 3LiF + 3AlF_3 + 2B_2H_6$

or $LiBH_4$ or $3(BF_3)$

(ii) **Laboratory** method : For the preparation of diborane involves the oxidation of sodium borohydride with iodine.

$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$

(iii) **Industrial scale :** By the reaction of BF_3 with sodium hydride.

$2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$

Properties :

(i) Diborane is a colourless, highly toxic gas with a b.p. of 180 K.

(ii) Diborane catches fire spontaneously upon exposure to air.

(iii) It burns in oxygen releasing an enormous amount of energy.

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$; $\Delta_cH^\ominus = -1976$ kJ mol^{-1}

Most of the higher boranes are also spontaneously flammable in air.

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(iv) Boranes are readily hydrolysed by water to give boric acid.

$B_2H_6(g) + 6H_2O(\ell)$ (Cold is enough) $\rightarrow 2B(OH)_3(aq) + 6H_2(g)$

$$B_2H_6 + HCl\ (dry) \xrightarrow[AlCl_3]{anh.} B_2H_5Cl + H_2$$

(v) Diborane undergoes cleavage reactions with Lewis bases(L) to give borane adducts, $BH_3.L$

$B_2H_6 + 2NMe_3 \rightarrow 2BH_3.NMe_3$

$B_2H_6 + 2CO \rightarrow 2BH_3.CO$

Reaction of ammonia with diborane gives initially $B_2H_6.2NH_3$ which is formulated as $[BH_2(NH_3)_2]^+ [BH_4]^-$; further heating gives borazine, $B_3N_3H_6$ known as "inorganic benzene" in view of its ring structure with alternate BH and NH groups.

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

(VI) Metal hydrido borates : Boron also forms a series of hydridoborates; the most important one is the tetrahedral $[BH_4]^-$ ion. Tetrahydridoborates of several metals are known. Lithium and sodium tetrahydridoborates, also known as borohydrides, are prepared by the reaction of metal hydrides with B_2H_6 in diethyl ether.

2MH + B_2H_6 ® 2 M+ [BH4]– (M = Li or Na)

Both LiBH4 and NaBH4 are used as reducing agents in organic synthesis. They are useful starting materials for preparing other metal borohydrides.

- ***Al_2O_3 preparation :***

(i) $2Al(OH)_3 \xrightarrow{300°C} Al_2O_3 + 3H_2O$

(ii) $Al_2(SO_4)_3 \xrightarrow{\Delta} Al_2O_3 + 3SO_3$

(iii) $(NH_4)_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O \xrightarrow{\Delta} Al_2O_3 + 2NH_3 + 4SO_3 + 25H_2O$

Uses:

(i) In making refractory brick

(ii) as abrasive

(iii) To make high alumina cement

- ***$AlCl_3$ preparation :***

(i) $2Al + 6HCl\ (vap.) \longrightarrow 2AlCl_3 + 3H_2$

(over heated) dry

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(ii) $Al_2O_3 + 3C + 3Cl_2 \xrightarrow[1000°C]{\Delta} 2AlCl_3\ (vap.) + 3CO$

$\downarrow$ Cooled

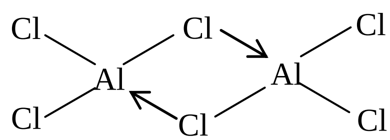
Solid anh. $AlCl_3$

Properties :

(i) Its anhydrous form is deliquescent and fumes in air.

(ii) It sublimes at 180°C.

(iii) It is covalent and exists in the form of dimer even if in non polar solvents e.g. alcohol, ether, benzene, where it is soluble in fair extent.



Uses:

(i) Friedel-Craft reaction

(ii) Dyeing, drug. & perfumes etc.

- **Alumns :** M_2SO_4, $M'_2(SO_4)_3 \cdot 24\ H_2O$

Props:

Swelling characteristics

where $M = Na^+, K^+, Rb^+, Cs^+, As^+, Tl^+, NH_4^+$

$M' = Al^{+3}, Cr^{+3}, Fe^{+3}, Mn^{+3}, Co^{+3}$

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Potash alum

$(NH_4)2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ Ammonium alum

$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ Chrome alum

$(NH_4)2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ Ferric alum

Preparation:

$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

$Al_2(SO_4)_3 + K_2SO_4 + aq.\ sol^n \longrightarrow$ crystallise

Uses:

(i) Act as coagulant

(ii) Purification of water

(iii) Tanning of leather

(iv) Mordant in dying

(v) Antiseptic

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USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS

Boron :

(i) Boron being extremely hard refractory solid of high melting point, low density and very low electrical conductivity, finds many applications.

(ii) Boron fibres are used in making bullet-proof vest and light composite material for aircraft.

(iii) The boron-10 (^{10}B) isotope has high ability to absorb neutrons and, therefore, metal borides are used in nuclear industry as protective shields and control rods.

(iv) The main industrial application of borax and boric acid is in the manufacture of heat resistant glasses(e.g., Pyrex), glass-wool and fibreglass.

(v) Borax is also used as a flux for soldering metals, for heat, scratch and stain resistant glazed coating to earthenwares and as constituent of medicinal soaps.

(vi) An aqueous solution of orthoboric acid is generally used as a mild antiseptic.

Aluminium :

(i) Aluminium is a bright silvery-white metal, with high tensile strength.

(ii) It has a high electrical and thermal conductivity.

(iii) On a weight-to-weight basis, the electrical conductivity of aluminium is twice that of copper.

(iv) Aluminium is used extensively in industry and every day life.

(v) It forms alloys with Cu, Mn, Mg, Si and Zn.

(vi) Aluminium and its alloys can be given shapes of pipe, tubes, rods, wires, plates or foils and, therefore, find uses in packing, utensil making, construction, aeroplane and transportation industry.

(vii) The use of aluminium and its compounds for domestic purposes is now reduced considerably because of their toxic nature.

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GROUP 14 ELEMENTS

The carbon family

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

Occurrence of element

(i) **Carbon :** Carbon is the seventeenth most abundant element by mass in the earth's crust. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C. In addition to these, third isotope, ^{14}C is also present. It is a radioactive isotope with halflife 5770 years and used for radiocarbon dating.

(ii) **Silicon :** Silicon is the second (27.7 % by mass) most abundant element on the earth's crust.

(iii) **Germanium :** Germanium exists only in traces.

(iv) **Tin :** Tin occurs mainly as cassiterite, SnO_2

(v) **Lead :** Lead as galena, PbS.

Note : Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Electronic Configuration

The valence shell electronic configuration of these elements is ns_2np_2.

- **Covalent Radius**

  Covalent radii : C < Si < Ge < Sn < Pb

- **Ionization Enthalpy**

  C > Si > Ge > Pb > Sn (IE_1 values)

- **Melting and Boiling Points**

  M.P. : C > Si > Ge > Pb > Sn

  B.P. : Si > Ge > Sn > Pb

- **Electronegativity**

  C > Si = Ge = Sn = Pb

  Due to small size, the elements of this group are slightly more electronegative than group 13 elements.

  The electronegativity values for elements from Si to Pb are almost the same.

- **Physical Properties**

  All group 14 members are solids. Carbon and silicon are non-metals, germanium is a metalloid, whereas tin and lead are soft metals with low melting points.

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Chemical Properties

Oxidation states and trends in chemical reactivity

(i) The group 14 elements have four electrons in outermost shell.

(ii) The common oxidation states exhibited by these elements are +4 and +2. Carbon also exhibits negative oxidation states.

(iii) In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of ns2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group.

(iv) Carbon and silicon mostly show +4 oxidation state.

(v) Germanium forms stable compounds in +4 state and only few compounds in +2 state.

(vi) Tin forms compounds in both oxidation states (Sn in +2 state is a reducing agent).

(vii) Lead compounds in +2 state are stable and in +4 state are strong oxidising agents.

Reactivity towards oxygen

There are mainly two types of oxides, *i.e.*, monoxide and dioxide of formula MO and MO2 respectively. SiO only exists at high temperature.

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

Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.

Reactivity towards water

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

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

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

Reactivity towards halogen

(i) These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl, Br, I). Except carbon, all other members react directly with halogen under suitable condition to make halides.

(ii) Most of the MX_4 are covalent in nature. The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature.

(iii) PbI_4 does not exist.

(iv) Heavier members Ge to Pb are able to make halides of formula MX_2.

(v) Stability of dihalides increases down the group. Considering the thermal and chemical stability, GeX_4 is more stable than GeX_2, whereas PbX_2 is more than PbX_4.

(vi) Except CCl_4, other tetrachlorides are easily hydrolysed by water.

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Catenation Property

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is because C—C bonds are very strong. The order of catenation is C > > Si > Ge ≈ Sn. Lead does not show catenation.

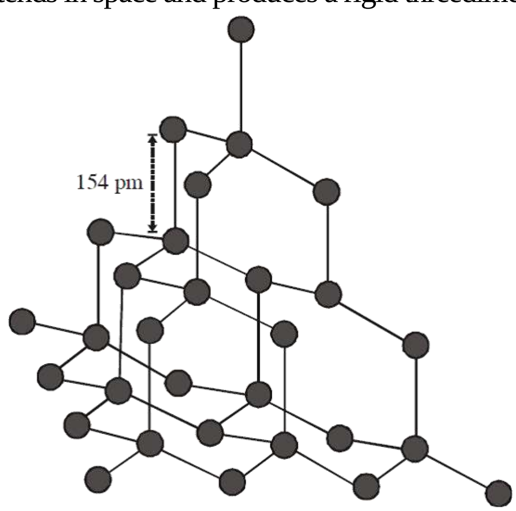
Bond	Bond enthalpy/kJ mol^{-1}
C – C	348
Si – Si	297
Ge – Ge	260
Sn – Sn	240

Due to property of catenation and $p_\pi - p_\pi$ bond formation, carbon is able to show allotropic forms.

ALLOTROPES OF CARBON

Diamond

(i) It has a crystalline lattice.
(ii) In diamond each carbon atom undergoes sp^3 hybridisation.
(iii) The C–C bond length is 154 pm.
(iv) The structure extends in space and produces a rigid threedimensional network of carbon atoms.



The structure of diamond

It is very difficult to break extended covalent bonding and, therefore, diamond is a hardest substance on the earth.

Use : It is used as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.

Graphite

(i) Graphite has layered structure figure.
(ii) Layers are held by van der Waals forces.

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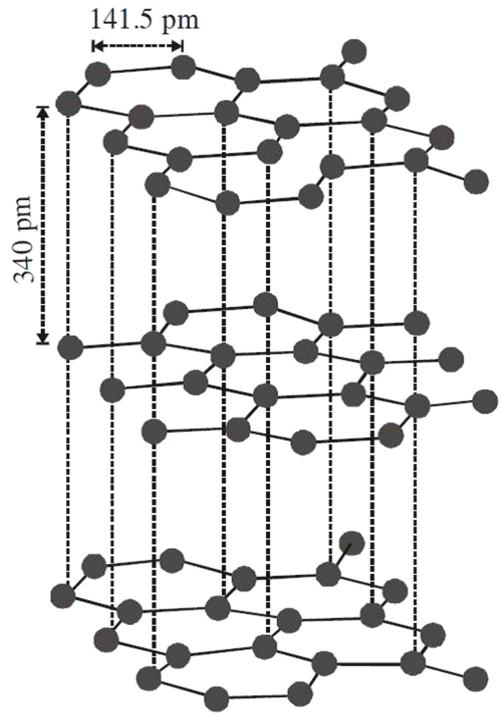
(iii) Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm.

(iv) Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and makes three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a p bond. The electrons are delocalized over the whole sheet. Electrons are mobile and, therefore, graphite conducts electricity along the sheet.



The Structure of Graphite

(v) Graphite cleaves easily between the layers and, therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

Fullerenes

(i) Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourised C^n small molecules consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene**.

(ii) It contains twenty six- membered rings and twelve five membered rings.

(iii) All the carbon atoms are equal and they undergo sp^2 hybridisation.

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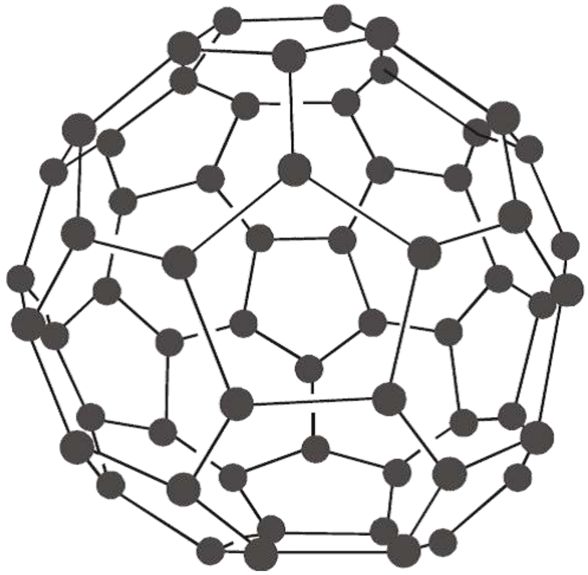
(iv) This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called *bucky balls* in short.



The structure of C_{60}, Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football).

Note: It is very important to know that graphite is thermodynamically most stable allotrope of carbon.

Note: Other forms of elemental carbon like carbon black, coke, and charcoal are all impure forms of graphite or fullerenes.
Carbon black is obtained by burning hydrocarbons in a limited supply of air.
Charcoal and coke are obtained by heating wood or coal respectively at high temperatures in the absence of air.

Uses of Carbon

(i) Used in products such as tennis rackets, fishing rods, aircrafts and canoes.

(ii) Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis.

(iii) Crucibles made from graphite are inert to dilute acids and alkalies.

(iv) Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in airconditioning system to control odour.

(v) Carbon black is used as black pigment in black ink and as filler in automobile tyres.

(vi) Coke is used as a fuel and largely as a reducing agent in metallurgy.

(vii) Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg).

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SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

Types of Carbide

(i) Ionic and salt like:

Classification on basis of no. of carbon atoms present in hydrocarbon found on their hydrolysis
$\begin{cases} \text{(a) } C_1 \text{ unit} \\ \text{(b) } C_2 \text{ unit} \\ \text{(c) } C_3 \text{ unit} \end{cases}$

C_1 unit: Al_4C_3, Be_2C

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

C_2 unit: CaC_2, BaC_2

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH\equiv CH$$

C_3 unit: Mg_2C_3

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH_3\text{–}C\equiv CH \text{ : Propyne}$$

(ii) Covalent carbide : SiC & B4C

(iii) Interstitial carbide :

(Transition element or inner transitional elements forms this kind of carbide)

Interstitial carbide formation doesn't affect the metalic lusture and electrical conductivity.($\because$ no chemical bond is present, no change in property)

SiC (Carborandum)

Preparation

$$SiO_2 + 2C(\text{coke}) \xrightarrow[2500^\circ C]{2000 \text{ to}} Si + 2CO\uparrow$$

$$Si + C \xrightarrow[2500^\circ C]{2000 \text{ to}} SiC$$

Note :

(i) SiC has diamond like or wurtzite structure

(ii) SiC is often dark purple, black or dark green due to traces Fe and other impurities but pure sample are pale yellow to colourless

Properties

(i) It is very hard and is used in cutting tools and abrassive powder(polishing material)

(ii) It is very much inert

(iii) It is not being affected by any acid except H_3PO_4

Carbon Monoxide

Prepration :

(i) Direct oxidation of C in limited supply of oxygen or air yields carbon monoxide.

$$2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

(ii) On small scale pure CO is prepared by dehydration of formic acid with concentrated H_2SO_4 at 373 K

$$HCOOH \xrightarrow[\text{conc.}H_2SO_4]{373 \text{ K}} H_2O + CO$$

(iii) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as water gas or synthesis gas.

$$C(s) + H_2O(g) \xrightarrow{473\text{–}1273K} CO(g) + H_2(g)$$

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When air is used instead of steam, a mixture of CO and N_2 is produced, which is called producer gas.

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

Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

(iv) By heating potassium ferrocyanide with conc. H_2SO_4 : When potassium ferrocyanide in powdered state is heated with concentrated H_2SO_4, CO is evolved. Dilute H_2SO_4 should never be used because it shall evolve highly poisonous gas HCN.

$$K_4[Fe(CN)_6] + 3H_2SO_4 \rightarrow 2K_2SO_4 + FeSO_4 + 6HCN$$

$$6HCN + 12H_2O \rightarrow \underset{\text{Formic acid}}{6HCOOH} + 6NH_3$$

$$6NH_3 + 3H_2SO_4 \rightarrow 3(NH_4)2SO_4$$

$$6HCOOH \xrightarrow{H_2SO_4} 6CO + 6H_2O$$

$$K_4[Fe(CN)_6] + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 6CO + 3(NH_4)_2SO_4$$

Properties :

(i) Carbon monoxide is a colourless, odourless and almost water insoluble gas.

(ii) It is a powerful reducing agent and reduces almost all metal oxides other than those of the alkali and alkaline earth metals, aluminium and a few transition metals. This property of CO is used in the extraction of many metals from their oxides ores.

$$Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$$

$$ZnO(s) + CO(g) \xrightarrow{\Delta} Zn(s) + CO_2(g)$$

DETECTION

(a) burns with blue flame

(b) CO is passed through $PdCl_2$ solution giving rise to black ppt.

$$CO + PdCl_2 + H_2O \longrightarrow CO_2\uparrow + \underset{\text{Black metallic deposition}}{Pd\downarrow} + 2HCl$$

ESTIMATION

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

$$I_2 + S_2\ O32- \longrightarrow 2I^- + S_4\ O_6^{2-}$$

ABSORBERS

(a) Cu_2Cl_2 : $Cu_2Cl_2 + 2CO + 4H_2O \longrightarrow [CuCl(CO)(H_2O)_2]$

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- **Bonding in CO mole**
  In CO molecule, there are one sigma and two p bonds between carbon and oxygen. Because of the presence of a lone pair on carbon, CO molecule acts as a donor and reacts with certain metals when heated to form **metal carbonyls**.

- **Poisonous nature of CO**
  The highly poisonous nature of CO arises because of its ability to form a **complex with haemoglobin**, which is about 300 times more stable than the oxygen-haemoglobin complex. This prevents haemoglobin in the red blood corpuscles from carrying oxygen round the body and ultimately resulting in death.

Carbon Dioxide

Prepration :

(i) It is prepared by complete combustion of carbon and carbon containing fuels in excess of air.

$$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$$

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

(ii) **Laboratory** by the action of dilute HCl on calcium carbonate.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2\ (g) + H_2O(\ell)$$

(iii) Commercial scale by heating limestone.

Properties :

(i) It is a colourless and odourless gas.

(ii) Its low solubility in water makes it of immense biochemical and geo-chemical importance.

(iii) With water, it forms carbonic acid, H_2CO_3 which is a weak dibasic acid and dissociates in two steps:

$$H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-\ (aq) + H_3O^+(aq)$$

$$HCO_3^-\ (aq) + H2O(\ell) \rightleftharpoons CO_3^{2-}\ (aq) + H_3O^+(aq)$$

H_2CO_3/ HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42. Being acidic in nature, it combines with alkalies to form metal carbonates.

Use of CO_2

Carbon dioxide, which is normally present to the extent of ~ 0.03 % by volume in the atmosphere, is removed from it by the process known as **photosynthesis**. It is the process by which green plants convert atmospheric CO2 into carbohydrates such as glucose.

$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorp 1}]{hv} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

By this process plants make food for themselves as well as for animals and human beings.

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Harmful effect of CO_2

It is not poisonous.

CO_2 lead to increase in **green house effect**.

(i) Carbon dioxide can be obtained as a solid in the form of **dry ice** by allowing the liquified CO_2 to expand rapidly and dry ice is used as a refrigerant for ice-cream and frozen food.

(ii) Gaseous CO_2 is extensively used to carbonate soft drinks.

(iii) A substantial amount of CO_2 is used to manufacture urea.

The resonance structures are shown below:

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

Resonating structures of carbon dioxide

Note : Carbongene has 95% O_2 and 5% CO_2 and is used as an antidote for posining of CO.

Teflon —$(CF_2 - CF_2)_n$—

$$CHCl_3 + HF \xrightarrow[\text{SbFCl}_4 \text{ catalyst}]{\text{heated with}} CF_2HCl \xrightarrow[\text{again } -HCl]{\text{heated}} CF_2{=}CF_2 \xrightarrow[\text{high temp. and press}]{\text{Polymerisation at}} \text{—}(CF_2 - CF_2)_n\text{—}$$

Purpose

Temperature with standing capacity upto 500–550°C (1st organic compound withstand this kind of high temperature)

SILICON (Si)

Occurrence

Silicon is the second most abundant (27.2%) element.

Silica is found in the free state in sand, flint and quartz and in the combined state as silicates like

(i) Feldspar – $K_2O.\ Al_2O_3.\ 6SiO_2$

(ii) Kaolinite – $Al_2O_3.\ 2SiO_2.\ 2H_2O$

(iii) Asbestos – $CaO.\ 3MgO.\ 4SiO_2$

Preparation

(i) From silica (sand): Elemental silicon is obtained by the reduction of silica (SiO_2) with high purity coke in an electric furnace.

$$SiO_2(s) + 2C(s) \xrightarrow{\text{high temperature}} Si(s) + 2CO(g)$$

(ii) From silicon tetrachloride ($SiCl_4$) or silicon chloroform ($SiHCl_3$) : Silicon of very high purity required for making semiconductors is obtained by reduction of highly purified silicon tetrachloride or silicon chloroform with dihydrogen followed by purification by zone refining.

$$SiCl_4(\ell) + 2H_2(g) \longrightarrow Si(s) + 4HCl(g)$$

$$SiHCl_3(s) + H_2(g) \longrightarrow Si(s) + 3HCl\ (g)$$

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Physical Properties :

(i) Elemental silicon is very hard having diamond like structure.

(ii) It has shining luster with a melting point of 1793 K and boiling point of about 3550 K.

(iii) Silicon exists in three isotopes, i.e. ${}^{28}_{14}Si$, ${}^{29}_{14}Si$ and ${}^{30}_{14}Si$ but ${}^{28}_{14}Si$ is the most common isotope.

Chemical Properties :

(i) **Action of air :** Silicon reacts with oxygen of air at 1173 K to form silicon dioxide and with nitrogen of air at 1673 K to form silicon nitride,.

$$Si(s) + O_2(g) \xrightarrow{1173K} \underset{\text{Silicon dioxide}}{SiO_2(s)}$$

$$3Si(s) + 2N_2(g) \xrightarrow{1673K} \underset{\text{Silicon nitride}}{Si_3N_4(s)}$$

(ii) ***Action of steam :*** It is slowly attacked by steam when heated to redness liberating dihydrogen gas.

$$Si(s) + 2H_2O(g) \xrightarrow{\text{redness}} SiO_2(s) + 2H_2(g)$$

(iii) Reaction with halogens: It burns spontaneously in fluorine gas at room temperature to form silicon tetrafluoride (SiF_4).

$$Si(s) + 2F_2(g) \xrightarrow{\text{Room Temperature}} SiF_4(l)$$

However, with other halogens, it combines at high temperatures forming tetrahalides.

(iv) Reaction with carbon : Silicon combines with carbon at 2500 °C forming silicon carbide (SiC) known as carborundum.

$$Si(s) + C(s) \xrightarrow{2500°C} SiC(s)$$

Carborundum is an extremely hard substance next only to diamond. It is mainly used as an abrasive and as a refractory material.

Uses :

It is used in the preparation of alloys such as silicon-bronze, magnesium silicon bronze and ferrosilicon.

Compounds of Silicon :

Silane :

$Si_nH_{2n+2} \rightarrow SiH_4$ & Si_2H_6

Only these two are found

Higher molecules are not formed. $\because$ Si can't show catanetion property

$$\text{Hot Mg} + \text{Si–vap} \longrightarrow Mg_2Si \xrightarrow{\text{dil } H_2SO_4} MgSO_4 + SiH_4 + Si_2H_6 + ...$$

Silicones

It is organo silicon polymer

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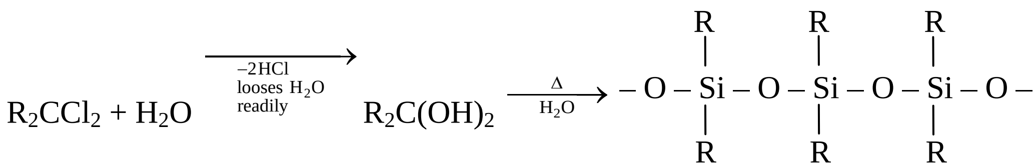
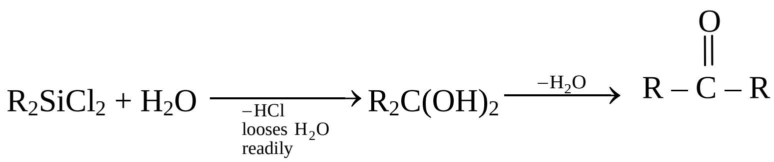
TYPES OF SILICONES

(i) Linear silicones

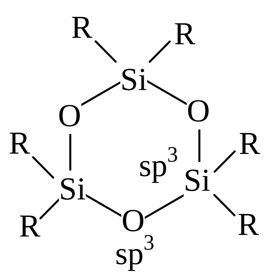


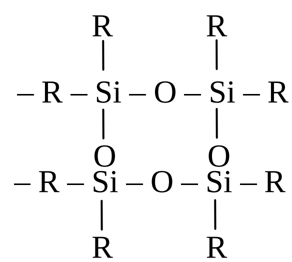
Linear silicone



(ii) Cyclic silicones

Silicones may have the cyclic structure also having 3, 4, 5 and 6 nos. of silicon atoms within the ring. Alcohol analogue of silicon is known as silanol





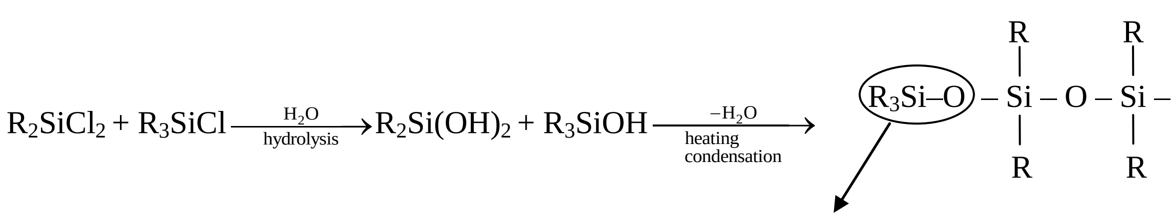
cyclic silicone not planar

(iii) Dimer silicones

$$R_3SiCl \xrightarrow{H_2O} R_3SiOH \xrightarrow[\Delta]{-H_2O} R_3Si\text{-}O\text{-}SiR_3$$

Silanol

Note :



This end of the chain can't be extended hence R_3 SiCl is called as chain stopping unit

* Using R_3SiCl in a certain proportion we can control the chain length of the polymer

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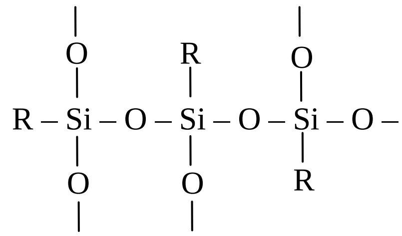
(iv) Crossed linked silicones

$RSiCl_3 + H_2O \longrightarrow R\text{–}Si(OH)_3 \xrightarrow{\Delta}$



cross linked silicone
3 dimensional network

It provides the crosslinking among the chain making the polymer more hard and hence controling the proportion of RSiCl3 we can control the hardness of polymer.

Uses

(1) It can be used as electrical insulator (due to inertness of Si–O–Si bonds)

(2) It is used as water repellant (Q surface is covered) eg. car polish, shoe polish, massonary works in buildings

(3) It is used as antifoaming agent in sewage disposal, beer making and in cooking oil used to prepare potato chips.

(4) As a lubricant in the gear boxes.

SILICA (SiO_2)

Occurrence :

Silica or silicon dioxide occurs in nature in the free state as sand, quartz and flint and in the combined state as silicates like, Feldspar : $K_2O.Al_2O_3.6SiO_2$, Kaolinite : $Al_2O_3.\ 2SiO_2.\ 2H_2O$ etc.

Properties :

(i) Pure silica is colourless, but sand is usually coloured yellow or brown due to the presence of ferric oxide as an impurity.

(ii) Silicon dioxide is insoluble in water and all acids except hydrofluoric acid.

$$SiO_2(s) + 4HF(\ell) \longrightarrow SiF_4(\ell) + 2H_2O(\ell)$$

(iii) It also combines with metallic oxides at high temperature giving silicates e.g.

$$SiO_2(s) + CaO(s) \xrightarrow{\Delta} CaSiO_3(s)$$

(iv) When silica is heated strongly with metallic salts, silicates are formed and the volatile oxides are driven off as vapours.

$$SiO_2(s) + Na_2CO_3(s) \xrightarrow{\text{high temp.}} Na_2SiO_3(s) + CO_2(g)$$

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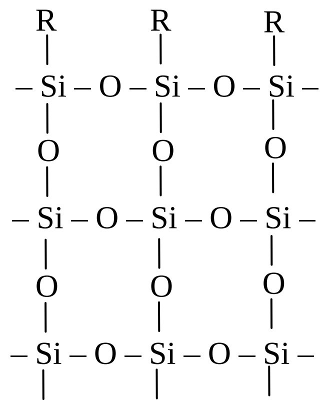
$$SiO_2(s) + Na_2SO_4(s) \xrightarrow{\text{high temp.}} Na_2SiO_3(s) + SO_3(g)$$

$$3SiO_2(s) + Ca_3(PO_4)_2(s) \xrightarrow{\text{high temp.}} 3CaSiO_3(s) + P_2O_5(g)$$

The first two examples quoted here are important in glass making.

Structures of Silica :

Silica has a three-dimensional network structure. In silica, silicon is sp^3-hybridized and is thus linked to four oxygen atoms and each oxygen atom is linked to two silicon atoms forming a three-dimensional giant molecule as shown in figure.



Uses :

(i) Sand is used in large quantities to make mortar and cement.

(ii) Being transparent to ultraviolet light, large crystal of quartz are used for making lenses for optical instruments and for controlling the frequency of radio-transmitters.

(iii) Powdered quartz is used for making silica bricks.

(iv) Silica gel ($SiO_2.xH_2O$) is used as a desiccant (for absorbing moisture) and as an adsorbent inchromatography.

Silicates

A large number of silicates minerals exist in nature. Some of the examples are feldspar, zeolites, mica and asbestos. Two important man-made silicates are glass and cement.

Zeolites

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

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TIN & ITS COMPOUND

(i) $Sn \xrightarrow[+O_2]{1500^\circ C} SnO_2$ [Burns with a bright flame]

$Sn \xrightarrow{Cl_2\Delta} SnCl_4$

$Sn \xrightarrow{S,\Delta}$

(ii) $Sn + 2H_2O \xrightarrow{\text{room temp.}}$ No

$Sn + 2H_2O \xrightarrow{\text{At high temp.}} SnO_2 + 2H_2$

(iii)

$Sn \xrightarrow{\text{dil.HCl}}$ reaction is very slow

$Sn \xrightarrow{\text{hot.conc.HCl}}$ $Sn + 2HCl \longrightarrow SnCl_2 + H_2\uparrow$

{Due to nonoxidising nature}

$Sn \xrightarrow{\text{dil.}H_2SO_4}$ dissolve Sn Slowly forming $SnSO_4 + H_2$

$Sn \xrightarrow{\text{hot conc. }H_2SO_4}$ $Sn + 4H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$

$Sn \xrightarrow{\text{cold dil. }HNO_3}$ $4Sn + 4H_2SO_4 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

$Sn \xrightarrow{\text{hot conc. }HNO_3}$ $5Sn + 20HNO_3 \longrightarrow H_2(NO_3)_2 + NH_4NO_3 + 3H_2O$

Metastannic acid $\xrightarrow{\Delta} SnO_2$

(iv) $Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$.

KOH[In absence of air Na_2SnO_2 forms and in contact with air it readity converts into Na_2SnO_3]

Oxides: $\xrightarrow{+\frac{1}{2}O_2} SnO_2\text{(White)} \xrightarrow[\text{heated}]{\text{strongly}} Sn +$

SnO{grey}

$SnC_2O_4 \xrightarrow[\text{out of contact of air}]{\Delta} SnO\text{(grey)} + CO + CO_2 \longleftarrow H_2Sn_5O_{11}.4H_2O$

$SnC_2O_4 \xrightarrow[\text{out of contact of air}]{\Delta} SnCl_2 \xrightarrow{KOH} Sn(OH)_2 \xrightarrow{\Delta\text{(in absence of air)}} SnO\text{(grey)}$

& SnO_2(white)

Both are amphoteric in nature :

$SnO + H_2SO_4 \longrightarrow SnSO_4 + H_2O$

$SnO + 2HCl \longrightarrow SnCl_2 + H_2O$

$SnO + 2NaOH \text{ or } KOH \xrightarrow{\text{cold}} Na_2SnO_2 \text{ or } K_2SnO_2 + H_2O$

But conc. hot alkali behaves differently.

$2SnO + 2KOH \text{ or } NaOH \longrightarrow K_2SnO_3 \text{ or } Na_2SnO_3 + Sn + H_2O$

$Bi(OH)_3 + [Sn(OH)_4]^{2-} \longrightarrow Bi\downarrow + [Sn(OH)_6]^{2-}$

(black)

$SnO_2 + 2H_2SO_4 \xrightarrow{\Delta} Sn(SO_4)_2 + 2H_2O$

(**Soluble only** in hot conc. H_2SO_4)

$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

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$SnCl_2$ & $SnCl_4$:

(1) $Sn + 2HCl \text{ (hot conc.)} \longrightarrow SnCl_2 + H_2\uparrow$

$SnCl_2.2H_2O \xrightarrow{\Delta} Sn(OH)Cl + HCl + H_2O\uparrow \Rightarrow$ Hence anh. $SnCl_2$ cannot be obtained.

$\downarrow$

$SnO + HCl$

$\{SnCl_4 + 4H_2O \longrightarrow Sn(OH)_4 + 4HCl\uparrow$ fumescomes out$\}$

(2) A piece of Sn is always added to preserve a solution of $SnCl_2$. Explain.

$6SnCl_2 + 2H_2O + O_2 \longrightarrow 2SnCl_4 + 4Sn(OH)Cl\downarrow$ (white ppt)

$SnCl_4 + Sn \longrightarrow 2SnCl_2$

$SnCl_4 + 4H_2O \longrightarrow Sn(OH)4\downarrow$ (white ppt.) + 4HCl

(3) $SnCl_2 + HCl \longrightarrow HSnCl_3 \xrightarrow{HCl} H_2SnCl_4$

$SnCl_4 + 2HCl \longrightarrow H_2SnCl_6$(Hexachloro stannic (IV) acid)

$SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2\, SnCl_6$ (colourless crystalline compound known as "pink salt")

(4) Reducing Properties of $SnCl_2$:

$Sn^{+2} + 2Fe^{+3} \longrightarrow 2Fe^{+2} + Sn^{+4}$

$2Cu^{+2} + Sn^{+2} \longrightarrow 2Cu^{+} + Sn^{+4}$

$Hg^{+2} + Sn^{+2} \longrightarrow Hg\downarrow + Sn^{+4}$

$PhNO_2 + SnCl_2 / HCl \longrightarrow PhNH_2 + Sn^{+4}$

$K_2Cr_2O_7 + SnCl_2 + HCl \longrightarrow Cr^{+3} + Sn^{+4} + KCl + H_2O$

(5) Readily combines with I2 Þ SnCl2I2 Þ This reaction is used to estimate tin.

Formation of $SnCl_4$:

(i) $Sn + Cl_2 \text{ (Excess)} \longrightarrow SnCl_4$

(molten) (dry)

(ii) $2HgCl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_4$

(iii) $Sn + \text{Aq. regia} \longrightarrow SnCl_4 + NO + H_2O$

$SnCl_4.\,5H_2O$ is known as butter of tin $\Rightarrow$ used as mordant.

$(NH_4)_2\, SnCl_6$ is known as 'pink salt' $\Rightarrow$ used in calico printing.

Distinction of Sn^{+2} / Sn^{+4} :

(i) H_2S (ii) Hg^{+2} (iii) $Fe^{+3} + K_3[Fe(CN)_6] \xrightarrow{Sn^{+2}}$ Blue ppt.

COMPOUNDS OF LEAD

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Oxides of lead :

(i) PbO (ii) Pb_3O_4 (Red)

(iii) Pb_2O_3(reddish yellow) (Sesquioxide)

(iv) PbO_2 (dark brown)

(1)

$$PbO \longrightarrow \text{Yellow(Massicot)} \xrightarrow[\text{and powdered}]{\text{fused, cooled}} \text{Litharge}$$

$$PbO \longrightarrow \text{Reddish yellow(litharge)}$$

Laboratory Prep^n. :

$$Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

$$\left.\begin{array}{l} PbO_2 \xrightarrow{\text{above } 600^\circ C} \\ Pb_3O_4 \longrightarrow \\ Pb_2O_3 \longrightarrow \end{array}\right\} \begin{array}{l} \text{PbO, hot oxide} \\ \text{easily reduced to Pb by} \\ H_2 \text{ or C.} \end{array}$$

$$PbO \xrightarrow{H_2} Pb + H_2O$$

$$PbO \xrightarrow{C} Pb + CO$$

Preparation of Pb_2O_3 :

$$\underset{\substack{\text{hot sol}^n \\ \text{of it in NaOH}}}{2PbO} + \underset{\substack{\text{Limited} \\ \text{amount}}}{NaOCl} \longrightarrow Pb_2O_3 + NaCl$$

$$Pb_2O_3 + 2HNO_3 \longrightarrow PbO_2 \downarrow + Pb(NO_3)_2 + H_2O$$

This reaction suggests that Pb_2O_3 contains PbO_2.

(2) **Pb_3O_4**: $6PbO + O_2 \underset{500^\circ C}{\overset{350^\circ C}{\rightleftharpoons}} 2Pb_3O_4$ {In the same way, prove that its formula is 2PbO. PbO_2}

$$Pb_3O_4 + 4HNO_3 \text{ (cold.conc) or (hot dil.)} \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

But $2Pb_3O_4 + 6H_2SO_4 \xrightarrow{\Delta} 6PbSO_4 + 6H_2O + O_2$

(3) **PbO_2** : Insoluble in water :

HNO_3, But reacts with HCl and H_2SO_4(hot conc.) but does not react with HNO_3 and soluble in hot NaOH / KOH.

(i) $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

(ii) $Pb(OAc)_2 + Ca(OCl)Cl + H_2O \longrightarrow PbO_2[\text{Brown(dark)}] + CaCl_2 + 2CH_3CO_2H$

$\downarrow$

Excess bleaching powder
is being removed by stirring with
HNO_3

Reaction :

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$$

$$2PbO_2 + 2H_2SO_4 \xrightarrow{\Delta} 2PbSO_4 + 2H_2O + O_2$$

$$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$$

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$PbCl_2 + Cl_2 + 2H_2O$

$2PbO_2 + 2H_2SO_4 \xrightarrow{\Delta} 2PbSO_4 + 2H_2O + O_2$

$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$

INORGANIC CHEMSITRY

PbO_2 : Powerful oxidising agent :

(i) $PbO_2 + SO_2 \longrightarrow PbSO_4$ [spontaneously]

(ii) $PbO_2 + 2HNO_3 + (COOH)_2 \longrightarrow Pb(NO_3)_2 + 2CO_2 + 2H_2O$

(iii) $2Mn(NO_3)_2 + 5PbO_2 + 2H_2SO_4 \longrightarrow 3Pb(NO_3)_2 + 2PbSO_4\downarrow + 2HMnO_4 + 2H_2O$

$PbCl_4$: Exists as $H_2[PbCl_6]$

$PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$

{ice cold conc. saturated with Cl2}

$PbCl_4 + 2HCl \longrightarrow H_2PbCl_6$

TetraEthyl lead :

$4Na–Pb$(alloy 10%–Na.) + $4C_2H_5Cl$(vap.) $\longrightarrow 3Pb + Pb(Et)_4 + 4NaCl$

It is antiknocking agent.

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NITROGEN FAMILY
GROUP-15 ELEMENTS (N, P, As, Sb, Bi)

Occurrence :

Nitrogen : Molecular nitrogen comprises 78% by volume of the atmosphere. It occurs as sodium nitrate, $NaNO_3$ (called Chile saltpetre) and potassium nitrate (Indian saltpetre).

Phosphorus :

(i) It is eleventh most abundant element in earth's crust occurs in minerals of the apatite family, $Ca_9(PO_4)_6.CaX_2$ (X = F, Cl or OH) (e.g., fluorapatite $Ca_9(PO_4)_6.CaF_2$) and also found as chlorapatite $Ca_9(PO_4)_6.CaCl_2$) .

(ii) Arsenic , antimony and bismuth are found mainly as sulphide minerals.

Electronic Configuration :

The valence shell electronic configuration of these elements is ns^2np^3.

Atomic and Ionic Radii :

Covalent radius : N < P < As < Sb < Bi

Ionisation Enthalpy :

N > P > As > Sb > Bi (IE1 values)

Electronegativity :

$$\underset{(1.9)}{\mathrm{N > P > As > Sb}} = \underset{(1.9)}{\mathrm{Bi}}$$

Metallic Character

N < P	As <	Sb < Bi
None metal	Metalloid	Metals

Physical Properties :

(i) All the elements of this group are polyatomic. Dinitrogen is a diatomic gas while all others are solids.

(ii) Metallic character increases down the group.

(iii) The boiling points, in general, increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth.

(iv) Except nitrogen all the elements show allotropy.

P → exists in three allotropic form as white, red and black

As, Sb → exist as yellow and grey

Bi → exist as α, β, γ, δ allotropic form

Catenation

* The group 15 elements also show catenation property but to much smaller extent than carbon. For example hydrazine (H2NNH2) has two N atoms bonded together HN3 has three N atoms.

HN_3 $\qquad H-\ddot{N}=\overset{+}{N}=\ddot{N}:^{\ominus}$

* Among group 15 elements P has the maximum tendency for catenation forming cyclic as well as open chain compounds consisting of many phosphorous atoms.

P_2H_4 has two P atoms bonded together the lesser tendency of elements of group 15 to show catenation in compression to carbon is their low dissociation enthalpies.

C – C	353.3 kJ /mole
N – N	160.8 kJ / mole
P – P	201.6 kJ / mole
As – As	147.4 kJ / mole

Chemical Properties :

Oxidation states and trends in chemical reactivity

(i) The common oxidation states of these elements are –3, +3 and +5.

(ii) The tendency to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character. Bismuth hardly forms any compound in –3 oxidation state.

(iii) The stability of +5 oxidation state decreases down the group. The only well characterised Bi(V) compound is BiF_5.

(iv) The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.

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

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

(i) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

(vii) Similarly, in case of phosphorus nearly all intermediate oxidation states disproportionate into +5 and –3 both in alkali and acid.

(ii) $4H_3PO_3 \xrightarrow{\text{Heal}} 3H_3PO_4 + PH_3$

(viii) +3 oxidation state in case of arsenic, antimony and bismuth becomes increasingly stable with respect to disproportionation.

(ix) Nitrogen is restricted to a maximum covalency of 4 since only four (one s and three p) orbitals are available for bonding.

(x) The heavier elements have vacant d orbitals in the outermost shell which can be used for bonding 6 (covalency) and hence, expand their covalency as in PF_6^-.

Anomalous properties of nitrogen

(i) Nitrogen has unique ability to form $p_\pi - p_\pi$ multiple bonds with itself and with other elements having small size and high electronegativity (e.g., C, O).

(ii) Heavier elements of this group do not form pp-pp bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping.

(iii) Nitrogen exists as a diatomic molecule with a triple bond (one s and two p) between the two atoms.

N_2 bond enthalpy (941.4 kJ mol^{-1}) is very high.

(iv) Phosphorus, arsenic and antimony form single bonds as P–P, As–As and Sb–Sb while bismuth forms metallic bonds in elemental state.

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(i) Reactivity towards hydrogen:

$NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

(ii) Reactivity towards oxygen: All these elements form two types of oxides: E_2O_3 and E_2O_5.

Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth predominantly basic.

(iii) Reactivity towards halogens: These elements react to form two series of halides: EX_3 and EX_5. In case of nitrogen, only NF3 is known to be stable. Trihalides except BiF_3 are predominantly covalent in nature.

(iv) Reactivity towards metals: All these elements react with metals to form their binary compounds exhibiting –3 oxidation state, such as, $Ca3N_2$ (calcium nitride) Ca_3P_2 (calcium phosphide), Na_3As (sodium arsenide), Zn_3Sb_2 (zinc antimonide) and Mg_3Bi_2 (magnesium bismuthide).

DINITROGEN

Preparation :

(a) Commercial preparation :

Dinitrogen is produced commerciallyby the liquefaction and fractional distillation of air. Liquid dinitrogen (b.p. 77.2 K) distils out first leaving behind liquid oxygen (b.p. 90 K).

(b) Laboratory preparation :

(i) Dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

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

Small amounts of NO and HNO_3 are also formed in this reaction; these impurities can be removed by passing the gas through aqueous sulphuric acid containing potassium dichromate.

(ii) Dinitrogen can also be obtained by the thermal decomposition of ammonium dichromate.

$$(NH_4)2Cr_2O_7 \xrightarrow{\text{Heat}} N_2 + 4H_2O + Cr_2O_3$$

Note : Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

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

$$2NaN_3 \xrightarrow{300^\circ C} 2Na + 3N_2$$

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(c) Other preparation

$2NH_3 + 3NaOCl \longrightarrow N_2 + 3NaCl + 3H_2O$

$2NH_3 + 3Ca(OCl)_2 \longrightarrow 2N_2 + 3CaCl_2 + 6H_2O$

$8NH_3 + 3Br_2 \longrightarrow N_2 + 6NH_4Br$

$2NO + 2Cu \longrightarrow 2CuO + N_2$

(red, overheated) (Black)

Cl_2 passed into liquor NH_3

$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$

$6NH_3 + 6HCl \longrightarrow 6NH_4Cl$

$3Cl_2 + 8NH_3 \longrightarrow N_2 + 6NH_4Cl$

In this method conc. of NH3 should not be lowered down beyond a particular limit.

$3Cl_2 + NH_3 \longrightarrow NCl_3 + 3HCl$

$\downarrow$

(Trimendously explosive)

Physical properties :

(i) Dinitrogen is a colourless, odourless, tasteless and non-toxic gas.

(ii) Nitrogen atom has two stable isotopes: ^{14}N and ^{15}N.

(iii) It has a very low solubility in water (23.2 cm^3 per litre of water at 273 K and 1 bar pressure)

(iv) Dinotrogen has low freezing and boiling points.

Chemical properties

Reaction with metal : At higher temperatures, it directly combines with some metals to form predominantly ionic nitrides and with non-metals, covalent nitrides. A few typical reactions are:

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

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

Reaction with metal : It combines with hydrogen at about 773 K in the presence of a catalyst (Haber's Process) to form ammonia:

$$N_2(g) + 3H_2(g) \xrightleftharpoons{773k} 2NH_3(g)$$

Dinitrogen combines with dioxygen only at very high temperature (at about 2000 K) to form nitric oxide, NO.

$$NO_2 + (g) \xrightleftharpoons{\text{Heat}} 2NO(g)$$

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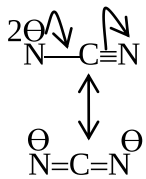
Absorption on calcium carbride

N_2 can be absorbed by calcium carbride at the temperature around 1000°C.

$$CaC_2 + N_2 \xrightarrow{1100^\circ C} \underbrace{CaNCN + C}_{\text{nitrolim}}$$

It is a very good fertiliser.

Cyanamide ion 

$$(Ca(NCN) + C) + 3H_2O \longrightarrow CaCO_3 + 2NH_3 + C$$

Slowly decomposes

$NH_2–CO–NH_2$

(Intermidiate fomed)

Qus. **Why dinitrogen is inert at room temperature ?**

Ans. Dinitrogen is inert at room temperature because of the high bond enthalpy of $N \equiv N$ bond. Reactivity, however, increases rapidly with rise in temperature.

TYPES OF NITRIDE

Salt like or ionic : Li_3N, Na_3N, K_3N (?), Ca_3N_2, Mg_3N_2, Be_3N_2

Covalent : AlN, BN, Si_3N_4, Ge_3N_4, Sn_3N_4

Interstitial : $\underbrace{\text{M = Sc, Ti, Zr, Hf, la}}_{\text{HCP of FCC}}$

AMMONIA

Preparation :

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

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

(ii) Small scale preparation By the decomposition of ammonium salts when treated with caustic soda or calcium hydroxide.

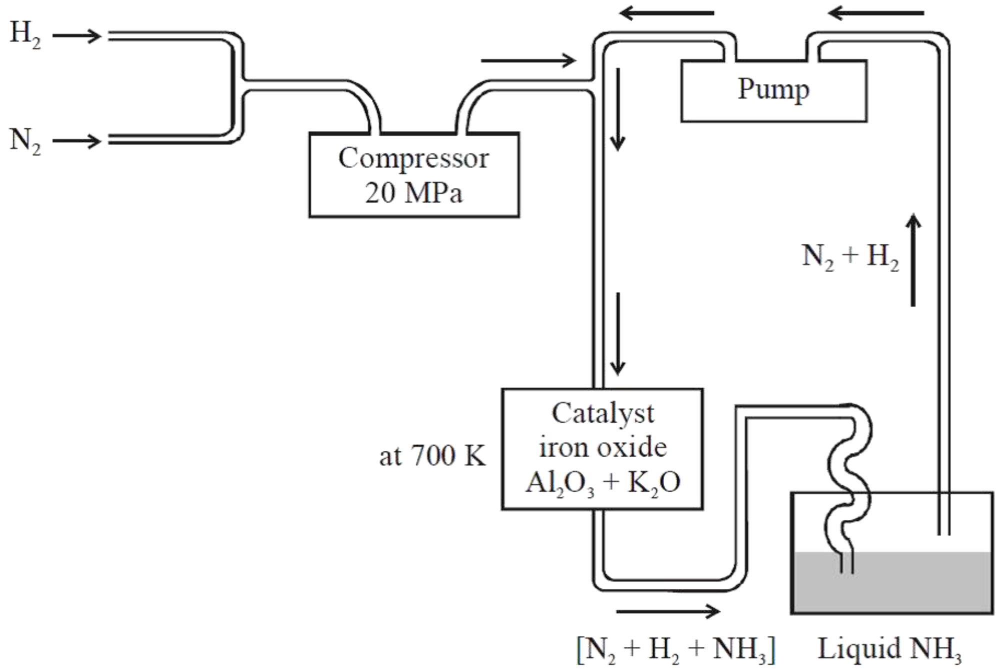
$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + 2H_2O + CaCl_2$$

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

(iii) Large scale manufacturing (Haber's Process)

‡ ˆ $N2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $D_f\ H^{\Theta} = -46.1\ kJ\ mol^{-1}$

- * According to Le Chatelier's principle, high pressure and low temperature would favour the formation of ammonia.
- * The optimum conditions for the production of ammonia are a pressure of 200×10^5 Pa (about 200 atm), a temperature of ~ 700 K.
- * Use of a catalyst such as iron oxide with small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium.
- * The flow chart for the production of ammonia is shown in figure. Earlier, iron was used as a catalyst with molybdenum as a promoter.



Flow chart for the manufacture of ammonia

Other prepration :

(i) Nitrate or nitrite reduction : $NO_3^- / NO_2^- + Zn \text{ or } Al + NaOH \longrightarrow NH_3 + [Zn(OH)_4]^{2-}$ or $[Al(OH)_4]^-$

(ii) Metal nitride hydrolysis : $N^{3-} + 3H_2O \longrightarrow NH_3 \uparrow + 3OH^-$

Properties :

(i) Ammonia is a colourless gas with a pungent odour.
(ii) Its freezing and boiling points are 198.4 and 239.7 K respectively.
(iii) In the solid and liquid states, it is associated through hydrogen bonds.
(iv) Ammonia gas is highly soluble in water.

Basic character :

Its aqueous solution is weakly basic due to the formation of OH^- ions.

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

It forms ammonium salts with acids, e.g., NH_4Cl, $(NH_4)_2SO_4$, etc.

As a weak base, it precipitates the hydroxides (hydrated oxides in case of some metals) of many metals from their salt solutions.

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For example,

$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$
(White ppt)

$FeCl_3(aq) + NH_4OH(aq) \longrightarrow Fe_2O_3.xH_2O(s) + NH_4Cl(aq)$
(brown ppt)

Note - 1: **Other reactions**

CH_3COOH is strong acid in liq. NH_3 while in water is weak acid.

$AcOH \rightleftharpoons Ac\bar{O} + H^+$

$4NH_3 + H^+ \longrightarrow NH_4^+$

$H_2O + H^+ \longrightarrow H_3O^+$

Basisity order $NH_3 > H_2O$

more solvation of H^+ in NH_3.

Note - 2 : **Hydrolysis and Ammonolysis occurs is a same way.**

$SiCl_4 + 4H_2O \longrightarrow 4HCl + Si(OH)_4 \xrightarrow{\Delta} SiO_2 + 2H_2O$

$SiCl_4 + 8NH_3 \longrightarrow 4NH_4Cl + Si(NH_2)_4 \xrightarrow{\Delta} Si_3N_4 + NH_3\uparrow$

Rate of hydrolysis and Ammonolysis will be affected by the presence of HCl vapour & NH_4Cl vapour respectively.

Uses :

(i) Ammonia is used to produce various nitrogenous fertilisers.

(ii) In the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid.

(iii) Liquid ammonia is also used as a refrigerant.

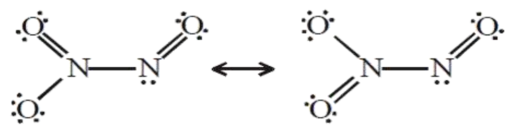
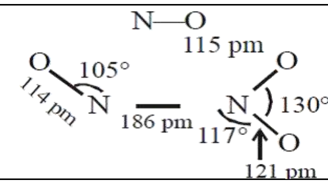
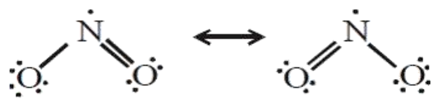
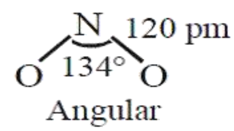
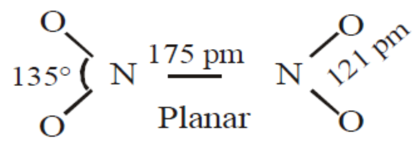
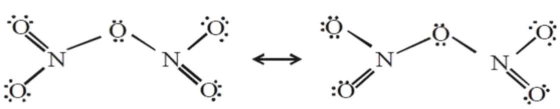
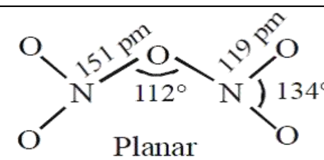
OXIDES OF NITROGEN

Nitrogen forms a number of oxides in different oxidation states. The names, formulas, preparation and physical appearance of these oxides are given in Table.

Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common Methods of Preparation	Physical Appearance and Chemical nature
Dinitrogen oxide [Nitrogen oxide]	N_2O	+1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	Colourless gas, neutral
Nitrogen monoxide [Nitrogen (II) oxide]	NO	+2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	Colourless gas, neutral
Dinitrogen trioxide [Nitrogen (III) oxide]	N_2O_3	+3	$2NO + N_2O_4 \xrightarrow{250K} 2N_2O_3$	Blue solid, acidic Blue liquid (–30ºC)
Nitrogen dioxide [Nitrogen (IV) oxide]	NO_2	+4	$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2 + 2PbO + O_2$	Brown gas. Acidic
Nitrogen tetroxide [Nitrogen (IV) oxide]	N_2O_4	+4	$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$	Colourless solid / liquid, acidic
Nitrogen pentaoxide [Nitrogen (V) oxide]	N_2O_5	+5	$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$	Colourless solid, acidic

Structure of Oxides of Nitrogen

Formula	Resonance structures	Bond Parameters
N_2O	$\ddot{N}=N=\ddot{O} \leftrightarrow :N\equiv N-\ddot{O}:$	N—N—O 113 pm 119 pm Linear
NO	$:N=\ddot{O} \leftrightarrow :\dot{N}=\ddot{O}:$	
N_2O_3		
NO_2		
N_2O_4		
N_2O_5		

Preparations:

1. N_2O

(i) $NH_4NO_3 \longrightarrow N_2O + H_2O$

(ii) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + N_2O + H_2O$
(dil.& cold)

2. NO

(i) $Cu + HNO_3\ (1:1) \longrightarrow Cu(NO_3)_2 + NO + H_2O$
hot

(ii) $KNO_3 + FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + K_2SO_4 + NO + H_2O$

$FeSO_4 + NO \longrightarrow FeSO_4\,.\,NO \xrightarrow{\Delta} FeSO_4 + NO\uparrow$

(iii) Oswald process–Restricted oxidation of NH_3.
Industrial process.

$4NH_3 + 5O_2 \xrightarrow[750^\circ C,\ Pt\text{-}Cat]{6\ atm} 4NO + 6H_2O$

3. N_2O_3

(i) $HNO_3 + As_2O_3 \longrightarrow H_3AsO_4 + N_2O_3$

(ii) $Cu + HNO_3(6M) \longrightarrow Cu(NO_3)_2 + \underbrace{NO + NO_2}_{\text{Cool}(-30^\circ C)\ \downarrow\ \text{Blue liq}\ (N_2O_3)}$

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4. NO_2

(i) $M(NO_3)_2 \xrightarrow{\Delta} MO + 2NO_2 + \frac{1}{2}O_2$

M = Pb, Cu, Ba, Ca

(ii) (Cu, Pb, Ag) + $HNO_3 \longrightarrow$ M-nitrate + NO_2 + H_2O

(hot & conc.)

5. N_2O_5

(i) $2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$

(ii) $4AgNO_3 + 2Cl_2$(dry gas) $\longrightarrow 4AgCl + 2N_2O_5 + O_2$

Properties:

(I) Decoposition Behaviour

(i) $N_2O \xrightarrow{500°C–900°C} 2N_2 + O_2$

(ii) $2NO \xrightarrow{800°C} 2N_2 + O_2$

(iii) $N_2O_3 \xrightarrow{\text{Room temp.}} NO_2 + NO$

(Blue liq.) at (–30°C)

(iv) $2NO_2 \xrightarrow{620°C} 2NO + O_2$

$N_2O_4 \xrightarrow{11°C} 2NO_2$

(white solid) Brown gas

at(–11°C)

(v) $N_2O_5 \xrightarrow{30°C} N_2O_5 \xrightarrow{40°C} 2NO_2 + \frac{1}{2}O_2$

Colourless Solid yellow liq.

(II) Reaction with H2O & NaOH

		H_2O	NaOH
(i)	N_2O :	Fairly soluble in water and produces neutral solution	-------
(ii)	NO :	Sparingly soluble in water and produces neutral soln.	-------
(iii)	N_2O_3 :	$2HNO_2$ Hence it is known as $NaNO_2$ anhydride of HNO_2	$NaNO_2$
(iv)	NO_2:	$HNO_2 + HNO_3$ called as mixed anhydride	$NaNO_2 + NaNO_3$
(v)	N_2O_5:	$2HNO_3$ called as anhydride of HNO_3	$NaNO_3$

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Other properties:

$$N_2O : 2N_2O \longrightarrow 2N_2 + O_2 \left\{ \begin{array}{l} \text{Mixture contains} \\ \text{33\% } O_2 \text{ compared} \\ \text{To 20\% in air} \end{array} \right.$$

Hence it is better supporter for combustion

$S + N_2O \longrightarrow SO_2 + N_2$

$P + N_2O \longrightarrow P_2O_5 + N_2$

$Mg + N_2O \longrightarrow MgO + N_2$

$Na + N_2O \longrightarrow Na_2O + N_2$

$Cu + N_2O \longrightarrow CuO + N_2$

$H_2 + N_2O \longrightarrow H_2O + N_2$

NOTE: -

(i) It burns : $NO + \frac{1}{2}O_2 \longrightarrow NO_2$

(ii) It supports combustion also for molten sulphur and hot phosphorous.

$S + 2NO \longrightarrow SO_2 + N_2$

$2P + 5NO \longrightarrow P_2O_5 + \frac{5}{2}N_2$

(iii) It is being absorbed by $FeSO_4$ solution.

(iv) It is having reducing property.

$KMnO_4 + NO + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + HNO_3 + H_2O$

(v) NO shows oxidising property also.

$SO_2 + 2NO + H_2O \longrightarrow H_2SO_4 + N_2O$

$H_2S + 2NO \longrightarrow H_2O + S\downarrow + N_2O$

$3SnCl_2 + 2NO + 6HCl \longrightarrow 3SnCl_4 + 2NH_2OH$

(Used for NH_2OH preparation)

(vi) NO combines with X_2 (X_2= $Cl_2Br_2F_2$) to produce NO X

$2NO + X_2 \longrightarrow 2NOX$

N_2O_3 : No more properties.

(1) It is having oxidising property.

$S + NO_2 \longrightarrow SO_2 + NO$

$P + NO_2 \longrightarrow P_2O_5 + NO$

$C + NO_2 \longrightarrow CO_2 + NO$

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

$H_2S + NO_2 \longrightarrow H_2O + S\downarrow + NO$

$CO + NO_2 \longrightarrow CO_2 + NO$

NO not formed : $2KI + 2NO_2 \longrightarrow I_2 + 2KNO_2$

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(2) Reducing property of NO_2.

$KMnO_4 + NO_2 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + HNO_3 + H_2O$

$$O_3^0 + 2\overset{+4}{N}O \rightarrow \underbrace{O_2^0}_{} + N_2\overset{+5}{O_5}$$

not the reduction product of O_3

N_2O_5 :

$I_2 + 5N_2O_5 \longrightarrow I_2O_5 + 10NO_2$

I_2O_5 is used for the estimation of CO

$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$

$N_2O_5 + NaCl \longrightarrow NaNO_3 + NO_2Cl$

This likes proves that N2O5 is consisting of ion pair of NO_2^+ & NO_3^-

OXOACIDS OF NITROGEN

$H_2N_2O_2$ (hyponitrous acid), HNO_2 (nitrous acid) and HNO_3 (nitric acid). Amongst them HNO_3 is the most important.

NITROUS ACID (HNO_2)

Preparation

(a) M-nitrite $\xrightarrow[\text{HCl or } H_2SO_4]{\text{dil.acid}}$ HNO_2

(b) $N_2O_3 + H_2O \longrightarrow 2HNO_2$

Properties

(a) **Oxidising property :** Because of its easy oxidation to liberate nascent oxygen, it acts as a strong oxidant $2HNO_2 \longrightarrow H_2O + 2NO + (O)$

$2KI + 2HNO_2 + 2HCl \longrightarrow 2KCl + 2H_2O + 2NO + I_2$

$SnCl_2 + 2HNO_2 + 2HCl \longrightarrow SnCl_4 + 2NO + 2H_2O$

$SO_2 + 2HNO_2 \longrightarrow H_2SO_4 + 2NO$

$H_2S + 2HNO_2 \longrightarrow 2H_2O + S\downarrow + 2NO$

$2FeSO_4 + 2HNO_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$

(b) Reducing property : Nitrous acid also acts as a reducing agent as it can be oxidised into nitric acid.

$HNO_2 + (O) \longrightarrow HNO_3$

$2KMnO_4 + 5HNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$

$K_2Cr_2O_7 + 3HNO_2 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3HNO_3 + 4H_2O$

$H_2O_2 + HNO_2 \longrightarrow H_2O + HNO_3$

$HNO_2 + C_2H_5NH_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

$HNO_2 + C_6H_5\text{-}NH_2 \cdot HCl \xrightarrow{<5^\circ C} C_6H_5N{=}NCl + 2H_2O$

Benzene diazonium chloride

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NITRIC ACID

It was named aqua fortis (means strong water) by alchemists.

Preparation :

Laboratory Method : By heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$KNO_3 / NaNO_3 + H_2SO_4 \rightarrow KHSO_4 / NaHSO_4 + HNO_3$$

Large scale preparation (Ostwald's process) :

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

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

(ii) Nitric oxide thus formed combines with oxygen giving NO_2.

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

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

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

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

Birkel and Eyde Process or arc process

step 1 $N_2 + O_2 \xrightarrow[Electric\ Arc]{3000^oC} -\ heat$

step 2 $NO + O_2 \longrightarrow NO_2$

step 3 $NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

step 4 $HNO_2 \longrightarrow HNO_3 + NO + H_2O$

Properties

Physical properties

(i) It is a colourless liquid (f.p. 231.4 K and b.p. 355.6 K).

(ii) Nitric acid usually acquires yellow or brown colour due to its decomposition by sunlight into NO_2.

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

The yellow or brown colour of the acid can be removed by warming it to 60-80oC and bubbling dry air through it.

Chemical properties

Acidic character in aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

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

Oxidising nature: Nitric acid acts as a strong oxidising agent as it decomposes to give nascent oxygen easily.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$

or

$$2HNO_3 \longrightarrow H_2O + 2NO + 3O$$

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(i) ***Oxidation of non-metals :*** The nascent oxygen oxidises various non-metals to their corresponding oxyacids of highest oxidation state.

(1) Sulphur is oxidised to sulphuric acid

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

conc.and hot

(2) Carbon is oxidised to carbonic acid

$C + 4HNO_3 \rightarrow H_2CO_3 + 4NO_2 + 2H_2O$

(3) Phosphorus is oxidised to orthophosphoric acid.

$2P + 10HNO_3 \rightarrow 2H_3PO_4 + 10NO_2 + 2H_2O$

conc. and hot

(4) Iodine is oxidised to iodic acid

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

conc. and hot

(ii) ***Oxidation of metalloids***

Metalloids like non-metals also form oxyacids of highest oxidation state.

(1) Arsenic is oxidised to arsenic acid

$2As + 10HNO_3 \rightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O$

or $As + 5HNO_3 \rightarrow H_3AsO_4 + 5NO_2 + H_2O$

conc. and hot

(2) Antimony is oxidised to antimonic acid

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

conc. and hot

(3) Tin is oxidised to meta-stannic acid.

$Sn + 2HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$

(iii) ***Oxidation of Compounds:***

(1) Sulphur dioxide is oxidised to sulphuric acid

$SO_2 + 2HNO_3 \rightarrow H_2SO_4 + 2NO_2$

(2) Hydrogen sulphiode is oxidised to sulphur

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

(3) Ferrous sulphate is oxidised to ferric sulphate in presence of H_2SO_4

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

(4) Iodine is liberated from KI.

$6KI + 8HNO_3 \rightarrow 6KNO_3 + 2NO + 3I_2 + 4H_2O$

(5) HBr, HI are oxidised to Br_2 and I_2, respectively.

$2HBr + 2HNO_3 \rightarrow Br_2 + 2NO_2 + 2H_2O$

Similarly, $2HI + 2HNO_3 \rightarrow I_2 + 2NO_2 + 2H_2O$

(6) Ferrous sulphide is oxidised to ferric sulphate

$FeS + HNO_3 \rightarrow Fe_2(SO_4)_3 + 8NO_2 + 4H_2O$

(7) Stannous chloride is oxidised to stannic chloride is presence of HCl.

$2HNO_3 + 14H \rightarrow \underset{\text{Hydroxylamine}}{NH_2OH} + NH_3 + 5H_2O$

$NH_3 + HNO_3 \rightarrow NH_4NO_3$

$7SnCl_2 + 14HCl + 3HNO_3 \rightarrow 7SnCl_4 + NH_2OH + NH_4NO_3 + 5H_2O$

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(ii) ***Reaction with metal*** concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum.
Au & Pt dissolve in aqua regia a mixture of 25% conc. HNO3 & 75% conc. HCl.

Ex. $3Cu + 8\ HNO_3(dilute) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

$Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$4Zn + 10HNO_3(dilute) \rightarrow 4\ Zn(NO_3)_2 + 5H_2O + N_2O$

$Zn + 4HNO_3(conc.) \rightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$

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

Action on Proteins :

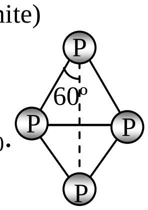
Nitric acid attacks proteins forming a yellow nitro compound called xanthoprotein. It, therefore, stains skin and renders wool yellow. This property is utilized for the test of proteins.

ALLOTROPIC FORMS OF PHOSPHORUS

Phosphorus is found in many allotropic forms, the important ones being white, red and black. White phosphorus dissolves in boiling NaOH solution in an inert atmosphere giving PH3.

$$P + 3NaOH + 3H_2O \longrightarrow PH + \underset{\text{(Sodium hypophosphite)}}{3NaH_2PO_2}$$

It readily catches fire in air to give dense white fumes of P_4O_{10}.

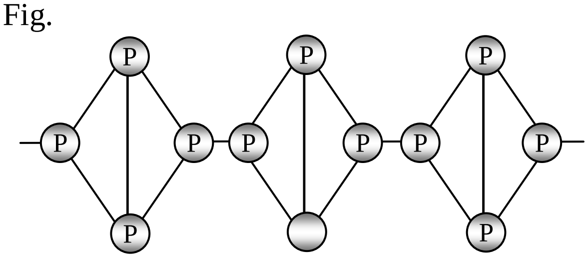


White Phosphorus

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

It consists of discrete tetrahedral P4 molecule as shown in Fig.

Red phosphorus : It is polymeric, consisting of chains of P_4 tetrahedra linked together in the manner as shown in Fig.



Red Phosphorus

Black phosphorus :

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

(ii) α-Black phosphorus is formed when red phosphorus is heated in a sealed tube at 803K.

(iii) It can be sublimed in air and has opaque monoclinic or rhombohedral crystals.

(iv) It does not oxidise in air. β-Black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.

(v) It does not burn in air upto 673 K.

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Comparison between White and Red Phosphorus		
Property	**White phosphorus**	**Red phosphorus**
Physical state	Soft waxy solid.	Brittle powder.
Colour	White when pure. Attains yellow colour On standing.	Red.
Odour	Garlic	Odourless.
Solubility in water	Insoluble.	Insoluble.
Solubility in CS_2	Soluble	Insoluble.
Physiological action	Poisonous.	Non-poisonous.
Chemical activity	Very active.	Less active.
Stability	Unstable.	Stable
Phosphorescence	Glows in dark	Does not glow in dark.
Molecular formula	P_4	Complex polymer.

Prepration of white 'P'

(i) $\underbrace{\text{Bone ash or Apatite rock}}_{\text{Both have same formula}}$ $\left\{ Ca_3(PO_4)_2 + 3SiO_2 \xrightarrow{1200^\circ C} 3CaSiO_3 + P_2O_5 \right.$

$$\underset{\text{(Coke)}}{2P_2O_5 + 10C} \xrightarrow{1500^\circ C} \underset{\text{White 'P'}}{P_4} + 10CO\uparrow$$

(ii) $Ca_3(PO_4)_2 + 3H_2SO_4 \text{ (conc.)} \longrightarrow 3CaSO_4 + 2H_3PO_4$

$H_3PO_4 \xrightarrow[-H_2O]{320^\circ C} HPO_3$

meta phosphoric acid

$12C + 4HPO_3 \xrightarrow{1000^\circ C} 2H_2\uparrow + 12CO\uparrow + P_4$

Coke white 'P'

Reactions of 'P'

$P + H_2SO_4 \text{ (hot \& conc.)} \longrightarrow H_3PO_4 + SO_2 + H_2O$

$P + KIO_3 + H_2SO_4 \longrightarrow H_3PO_4 + I_2 + K_2SO_4$

Reaction with hot metal —

$3Na + P \longrightarrow Na_3P$

$3Mg + 2P \longrightarrow Mg_3P_2$

$3Ca + 2P \longrightarrow Ca_3P_2$

$2Cu + 2P \longrightarrow Cu_3P_2$

$Al + P \longrightarrow AlP$

$Ca_3P_2 + H_2O \longrightarrow M(OH)_n + PH_3$

or Mg_3P_2

or AlP

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PHOSPHINE

Preparation

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

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

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

(ii) Laboratory prepration it is prepared by heating white phosphorus with concentrated NaOH solution in an inert atmosphere of CO_2.

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

Pure PH_3 is non inflammable but becomes inflammable owingto the presence of P_2H_4 or P_4 vapours. To purify it from the impurities, it is absorbed in HI to form phosphonium iodide (PH_4I) which on treating with KOH gives off phosphine.

Other preparation

$$\left.\begin{array}{l} \underset{(PH_3 + HI)}{PH_4I} + KOH \longrightarrow KI + PH_3 + H_2O \\ 2AlP + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + PH_3\uparrow \end{array}\right\} \text{Purest } PH_3$$

$4PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$

$2H_3PO_2 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$

Phyiscal Properties :

(i) It is a colourless gas with rotten fish smell and is highly poisonous.

(ii) It explodes in contact with traces of oxidising agents like HNO_3, Cl_2 and Br_2 vapours.

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

Chemical Properties :

(i) It absorbed in copper sulphate or mercuric chloride solution, the corresponding phosphides are obtained.

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

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

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

$PH_3 + HBr \rightarrow PH_4Br$

(ii) $PH_3 + O_2 \xrightarrow{150^\circ} P_2O_5 + H_2O$

(iii) $PH_3 + 3Cl_2 \longrightarrow PCl_3 + 3HCl$

(iv) $PH_3 + 4N_2O \xrightarrow[\text{sparking}]{\text{electrical}} H_3PO_4 + 4N_2$

(v) $PH_3 + 6AgNO_3 \longrightarrow \underset{\text{yellow ppt.}}{[Ag_3P \bullet 3AgNO_3\downarrow]} + H_3NO_3$

$Ag_3P \bullet 3AgNO_3 + 3H_2O \longrightarrow \underset{\text{Black ppt.}}{6Ag\downarrow} + 3HNO_3 + H3PO3$

(vi) $PH_3 + 4HCHO \quad + \quad HCl \longrightarrow [P(CH_2OH)_4]^{+}Cl^{-}$

white/colourless solid
which is used for making
fire-proof cotton fabrics

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Note :

Like NH_3, PH_3 also can form addition product.

$CaCl_2 \cdot 8NH_3$ $Cu_2Cl_2 \cdot 2PH_3$, $AlCl_3 \cdot 2PH_3$, $SnCl_4 \cdot 2PH_3$

PH_3 can be absorbed by $Ca(OCl)Cl$.

$PH_3 + 3Ca(OCl)Cl + 3H_2O \longrightarrow PCl_3 + 3HCl + 3Ca(OH)_2$

$2NH_3 + 3Ca(OCl)Cl \longrightarrow N_2 + 3CaCl_2 + 3H_2O$

Uses :

(i) The spontaneous combustion of phosphine is technically used in Holme's signals. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

(ii) It is also used in smoke screens.

PHOSPHORUS HALIDES

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

PHOSPHORUS TRICHLORIDE

Preparation

(i) By passing dry chlorine over heated white phosphorus.

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

(ii) By the action of thionyl chloride with white phosphorus.

$P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

Properties

(i) It is a colourless oily liquid

(ii) Hydrolyses in the presence of moisture.

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

(iii) It reacts with organic compounds containing –OH group such as CH3COOH, C2H5OH.

$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$

$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$

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PHOSPHORUS PENTACHLORIDE

Preparation

(i) By the reaction of white phosphorus with excess of dry chlorine.

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

(ii) By the action of SO_2Cl_2 on phosphorus.

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

Properties :

(i) PCl_5 is a yellowish white powder

(ii) It hydroslysis in moist air to $POCl_3$ and finally gets converted to phosphoric acid.

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

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

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

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

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

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

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

(v) Finely divided metals on heating with PCl5 give corresponding chlorides.

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

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

Uses :

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

OXIDES OF PHOSPHORUS

It forms three important oxides which exist in dimeric forms.

PHOSPHORUS TRIOXIDE (P_4O_6)

Preparation

Phosphorus trioxides is formed when phosphorus is burnt in a limited supply of air.

$$P_4 + 3O_2 \text{ (limited)} \longrightarrow P_4O_6$$

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Properties

(a) **Heating in air :** On heating in air, it forms phosphorus pentoxide.

$$P4O_6 + 2O_2 \longrightarrow P_4O_{10}$$

Phosphorus (V) oxide

(b) **Action of water :** It dissolves in cold water to give phosphorus acid.

$$P_4O_6 + 6H_2O \text{ (cold)} \longrightarrow 4H_3PO_3$$

Phosphorus(V)acid

It is, therefore, considered as anhydride of phosphorus acid.

Note: With hot water, it gives phosphoric acid and inflammable phosphine.

PHOSPHORUS (V) OXIDE (P_4O_{10})

Preparation : It is prepared by heating white phosphorus in excess of air.

$$P_4 + 5O_2 \text{ (excess)} \xrightarrow{\Delta} P_4O_{10}$$

Properties

(a) It is snowy white solid.

(b) **Action with water :** It readily dissolves in cold water forming metaphosphoric acid.

$$P_4O_{10} + 2H_2O \text{ (Cold)} \longrightarrow 4HPO_3$$

Metaphosphoric acid.

With hot water it gives phosphoric acid.

$$P_4O_{10} + 6H_2O \text{ (Hot)} \longrightarrow 4H_3PO_4$$

Phosphoric acid

(c) **Dehydrating nature :** Phosphorus pentoxide has strong affinity for water and, therefore, acts as a powerful dehydrating agent. It extracts water from many inorganic and organic compounds.

(d) P_4O_{10} is a very strong dehydrating agent and extracts water from many compounds including sulphuric acid and nitric acid.

$$2HClO_4 \xrightarrow[-H_2O]{P_4O_{10}} Cl_2O7$$

Chlorine (VII) oxide

$$2CH_3CONH_2 \xrightarrow[-H_2O]{P_4O_{10}} CH_3CN$$

Acetamide Methyl cyanide

Structure

(a) Its structure is similar to that of P_4O_6.

(b) In addition, each phosphorus atom forms a double bond with oxygen atom.

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OXOACIDS OF PHOSPHORUS :

The important oxoacids of phosphorus with their formulae, methods of preparation and the presence of some characteristic bonds in their structures are given in a table.

Oxoacids of Phosphorus

Name	**Formula**	**Oxidation State of Phosphorus**	**Characteristic Bonds and their number**	**Preparation**
Hypophosphorus (Phosphinic)	H_3PO_2	+ 1	One P – OH Two P – H One P = O	White P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+ 3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P – OH Two P = O One P – OH	Red P_4 + alkali
Orthophosphoric	H_3PO_4	+ 5	Three P – OH One P = P	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+ 5	Four P – OH Two P = H One P – O – P	Heat phosphoric acid
Metaphosphoric	$(HPO_3)_n$	+ 5	Three P – OH Three P = O Three P – O – P	Phosphorous acid + Br_2, heat in a sealed tube

Heating Effect :

$H_3PO_2 \xrightarrow{140^\circ C} PH_3 + H_3PO_4$

$H_3PO_4 \xrightarrow[200^\circ C]{\text{gentle heat}} H_4P_2O_7 \xrightarrow[320^\circ C]{\text{strong heat}} (HPO_3)_n$

orthophosphoric acid   Pyrophosphoric acid   metaphosphoric acid

Graham salt

Graham's salt is the best known of these long chain polyphosphates, and is formed by quenching molten $NaPO_3$. Graham's salt is soluble in water. These solutions give precipitates with metal ions such as Pb^{2+} and Ag^+ but not with Ca^{2+} and Mg^{2+}. Graham's salt is sold commercially under the trade name Calgon. In industry it is incorrectly called sodium hexametaphosphate crystallizing. It is widely used for softening water.

$NaH_2PO_4 \xrightarrow{> 240^\circ C} (NaPO_3)_3 \xrightarrow{625^\circ C} NaPO_3\text{(liquid melt)} \xrightarrow[\text{cooling}]{\text{rapid}} (NaPO_3)_n$

Sodium trimetaphosphate   (Graham's salt) (glass)

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OXYGEN FAMILY
GROUP 16 ELEMENTS (O, S, Se, Te, Po)

This is sometimes known as group of chalcogens.

- **Occurrence**
  Oxygen is the most abundant of all the elements on earth crust. Oxygen forms about 46.6% by mass of earth's crust. Dry air contains 20.946% oxygen by volume.
- **Electronic Configuration**
  ns^2np^4 is the general valence shell electronic configuration.
- **Atomic and Ionic Radii :** Covalent radius : O < S < Se < Te
- **Ionisation Enthalpy :** O > S > Se > Te > Po (IE1 values)
- **Electron Gain Enthalpy :** S > Se > Te > Po > O
- **Electronegativity** : O > S > Se > Te
- **Metallic Character :** O < S < Se < Te < Po
- **Melting and Boiling points:** M.P. : Te > Po > Se > S > O
  B.P. : Te > Po > Se > S > O

Elemental State

Oxygen exist as diatomic molecular gas in this case there is pπ – pπ overlap thus two O atoms form double bond O = O. The intermolecular forces in O_2 are weak VB forces. ∴ O_2 exist as gas . On the other bond, other elements of family do not form stable pπ – pπ bonds and do not exist as M2 molecules. Other atoms are linked by single bonds and form poly atomic complex molecules for eg.

S – S8, Se – Se8

Catenation

In this group only S has a strong tendency for catenation oxygen has this tendency to a limited extent.

H_2O_2 H – O – O – H (Poly oxides)
H_2S_2 H – S – S – H (Polysulphides or polysulphones)
H_2S_3 H – S – S – S – H
H_2S_4 H – S – S – S – S – H

- **Physical Properties**

(i) Oxygen and sulphur are non-metals, selenium and tellurium metalloids, whereas polonium is a metal.

(ii) Polonium is radioactive and is short lived (Half-life 13.8 days).

(iii) All these elements exhibit allotropy.

Amongst tetrafluorides, SF_4 is a gas, SeF_4 a liquid and TeF_4 a solid. These fluorides have sp_3d hybridisation and thus, have trigonal bipyramidal structures in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry. All elements except selenium form dichlorides and dibromides. These dihalides are formed by *sp^3* hybridisation and thus, have tetrahedral structure. The well known monohalides are dimeric in nature. Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below : $2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$

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DIOXYGEN

(a) Laboratory method

(i) By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_3 \xrightarrow[MnO_2]{Heat} 2KCl + 3O$$

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$2Ag_2O(s) \rightarrow 4Ag(s) + O_2(g)$; $2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$

$2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$; $2PbO_2(s) \rightarrow 2PbO(s) + O_2(g)$

(iii) Hydrogen peroxide is readily decomposed into water and dioxygen by catalysts such as finely divided metals and manganese dioxide.

$2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$

(b) Large scale preparation : It can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen at the anode.

(c) Industrially method : Dioxygen is obtained from air by first removing carbon dioxide and water vapour and then, the remaining gases are liquefied and fractionally distilled to give dinitrogen and dioxygen.

Properties

(i) Dioxygen is a colourless and odourless gas.

(ii) Its solubility in water is to the extent of 3.08 cm^3 in 100 cm^3 water at 293 K which is just sufficient for the vital support of marine and aquatic life.

(iii) It liquefies at 90 K and freezes at 55 K.

(iv) Oxygen atom has three stable isotopes: ^{16}O, ^{17}O and ^{18}O. Molecular oxygen, O_2 is unique in being paramagnetic inspite of having even number of electrons.

(v) Dioxygen directly reacts with nearly all metals and non-metals except some metals (e.g., Au, Pt) and some noble gases. Some of the reactions of dioxygen with metals, non-metals and other compounds are as follows :

$2Ca + O_2 \rightarrow 2CaO$

$4Al + 3O_2 \rightarrow 2Al_2O_3$

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

$C + O_2 \rightarrow CO_2$

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Some compounds are catalytically oxidised. For example,

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

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

Uses:

(i) It's importance in normal respiration and combustion processes, oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.

(ii) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.

(iii) The combustion of fuels, e.g., hydrazines in liquid oxygen, provides tremendous thrust in rockets.

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SIMPLE OXIDES

A binary compound of oxygen with another element is called oxide. In many cases one element forms two or more oxides. The oxides vary widely in their nature and properties. Oxides can be simple (e.g., MgO, Al_2O_3) or mixed (Pb_3O_4, Fe_3O_4).

Types of simple oxide :

Acidic oxide : An oxide that combines with water to give an acid is termed acidic oxide (e.g., SO_2, Cl_2O_7, CO_2, N_2O_5).

$$SO_2 + H_2O \rightarrow H_2SO_3$$

As a general rule, only non-metal oxides are acidic but oxides of some metals in high oxidation state also have acidic character (e.g., Mn_2O_7, CrO_3, V_2O_5).

Basic oxide : The oxides which give a base with water are known as basic oxides (e.g., Na_2O, CaO, BaO). In general, metallic oxides are basic. For example, CaO combines with water to give $Ca(OH)_2$, a base.

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

Amphoteric oxide : Some metallic oxides exhibit a dual behaviour. They show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides.

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

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

Neutral oxide: There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N_2O.

OZONE

Ozone is an allotropic form of oxygen.

Threats to ozone layer

(i) Experiments have shown that nitrogen oxides (particularly nitric oxide) combine very rapidly with ozone and there is, thus, the possibility that nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes might be slowly depleting the concentration of the ozone layer in the upper atmosphere.

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

(ii) Another threat to this ozone layer is probably posed by the use of freons which are used in aerosol sprays and as refrigerants.

Preparation

When a slow dry stream of oxygen is passed through a silent electrical discharge, conversion of oxygen to ozone (10%) occurs. The product is known as ozonised oxygen.

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

Since the formation of ozone from oxygen is an endothermic process, it is necessary to use a silent electrical discharge in its preparation to prevent its decomposition. If concentration of ozone greater than 10 percent is required, a battery of ozonisers can be used, and pure ozone (b.p. 385 K) can be condensed in a vessel surrounded by liquid oxygen.

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Note:

$$\left.\begin{array}{l} 2F_2 + 2H_2O \longrightarrow 4HF + O_2 \\ F_2 + 3H_2O \longrightarrow 6HF + O_3 \end{array}\right] \text{Ozonised} \left]\begin{array}{l}\text{Is separated by passing into spiral tube cooled by liq.} \\ \text{Oxygen air. Ozone condenses at } -112.4^\circ C. \\ [\text{b.p. of } O_2 -183^\circ C \text{ ; b.p. of liq. Air is } -190^\circ C] \end{array}\right.$$

Properties

(i) Pure ozone is a pale blue gas, dark blue liquid and violet-black solid.

(ii) It is diamagnetic gas.

(iii) Ozone has a characteristic fishy smell and in small concentrations it is harmless.

Toxic effect :

(a) Toxic enough (more toxic than KCN). It's intense blue colour is due to the absorption of red light.

(b) However, if the concentration rises above about 100 parts per million, breathing becomes uncomfortable resulting in headache and nausea.

Oxidizing properties

It is one of best oxidising agent, in acid solution, its standard, reduction potential value is 2.07 V.

$$O_3 + 2H^+ + 2e \longrightarrow O_2 + H_2O \qquad E^\circ = +2.07\ V$$

It is next to F_2. [above 2.07 V, only F_2, F_2O are there]

It is not really surprising, therefore, high concentrations of ozone can be dangerously explosive. Due to the ease with which it liberates atoms of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. For example, it oxidises lead sulphide to lead sulphate and iodide ions to iodine.

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

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

(i) Metal Sulphides to Sulphates.

$MS + 4O_3 \longrightarrow MSO_4 + 4O_2$ [M = Pb, Cu, Zn, Cd]

(ii) $2HX + O_3 \longrightarrow X_2 + H_2O + O_2$ [X = Cl, Br, I]

(iii) $NaNO_2 + O_3 \longrightarrow NaNO_3 + O_2$

$Na_2SO_3 + O_3 \longrightarrow Na_2SO_4 + O_2$

$Na_2AsO_3 + O_3 \longrightarrow Na_2AsO_4 + O_2$

(iv) Moist S, P, As + $O_3 \Rightarrow$

$S + H_2O + 3O_3 \longrightarrow H_2SO_4 + 3O_2$

$2P + 3H_2O + 5O_3 \longrightarrow 2H_3PO_4 + 5O_2$

$2As + 3H_2O + 5O_3 \longrightarrow 2H_3AsO_4 + 5O_2$

(v) Moist $I_2 \longrightarrow HIO_3$ whereas dry iodine $\longrightarrow I_4O_9$ (yellow)

$I_2 + 5O_3 + H_2O \longrightarrow 2HIO_3 + 5O_2$

$2I_2 + 9O_3 \longrightarrow I_4O_9 + 9O_2$

(vi) $2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$

$2K_4[Fe(CN)_6] + O_3 + H_2O \longrightarrow 2K_3[Fe(CN)_6] + 2KOH + O_2$

$2FeSO_4 + O_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + O_2 + H_2O$

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(vii) **(a)** $2KI \text{ (acidified)} + O_3 + 2HCl \longrightarrow I_2 + 2KCl + H_2O + O_2$

(b) $2KI \text{ (neutral)} + O_3 + H_2O \longrightarrow \underbrace{I_2 + 2KOH}_{KI + KOI} + O_2$

$2KI + KOI + 2HCl \longrightarrow 2KCl + I_2 + H_2O$

O_3 is estimated by this reaction

$I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I$

alk. $\left\{\begin{array}{l} KI + 3O_3 \longrightarrow KIO_3 + 3O_2 \\ KI + 4O_3 \longrightarrow KIO_4 + 4O_2 \end{array}\right\}$

(viii) Hg loses its fluidity (tailing of Hg)

$2Hg + O_3 \longrightarrow Hg_2O + O_2$

similarly $2Ag + O_3 \longrightarrow \underset{\text{Brown}}{Ag_2O} + O_2$

(ix) $BaO_2 + O_3 \rightarrow BaO + 2O_2$

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$Na_2O_2 + O_3 + H_2O \longrightarrow 2NaOH + 2O_2$

(x) $2KOH + 5O_3 \longrightarrow 2KO_3 + 5O_2 + H_2O$

In all above reaction O_3 gives up O_2 but some reactions are there which consumes all O-atom.

(i) $3SO_2 + O_3 \longrightarrow 3SO_3$

(ii) $3SnCl_2 + 6HCl + O_3 \longrightarrow 3SnCl_4 + 3H_2O$

Uses :

(i) Sterilising water

(ii) Detection of position of the double bond in the unsaturated compound.

(iii) It is used as a germicide, disinfectant and for sterilising water.

(iv) It is also used for bleaching oils, ivory, flour, starch, etc.

(v) It acts as an oxidising agent in the manufacture of potassium permanganate.

Qus. Ozone is thermodynamically unstable with respect to oxygen. Explain ?

Sol. Because its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive). These two effects reinforce each other, resulting in large negative Gibbs energy change (ΔG) for its conversion into oxygen.

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HYDROGEN PEROXIDE (H_2O_2)

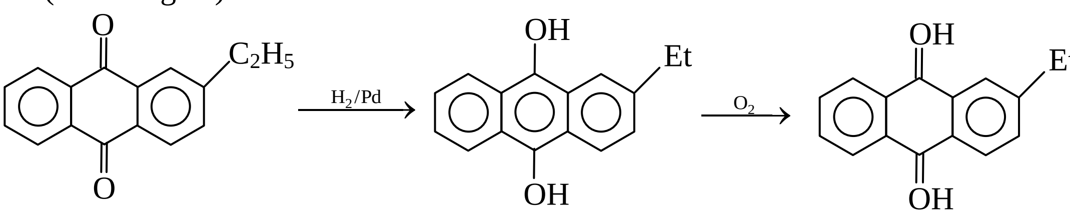
Method of preparation:

(i) $Na_2O_2 + H_2O$ (ice cold water) $\longrightarrow 2NaOH + H_2O_2$

(ii) $BaO_2 + H_2So_4 \longrightarrow BaSO_4 + H_2O_2$

Instead of H_2SO_4, H_3PO_4 is added now-a-days because H_2SO_4 catalyses the decomposition of H_2O_2 whereas H_3PO_4 favours to restore it.

$3BaO_2 + 2H_3PO_4 \rightarrow Ba_3(PO_4)_2 + 3H_2O_2$ and $Ba_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3BaSO_4 + 2H_3PO_4$ (reused again)

(iii) 

$+ H_2O_2$

Properties:

(i) Colourless, odourless liquid (b.p.152°)

(ii) Acidic nature : $H_2O_2 + 2NaOH \longrightarrow Na_2O_2 + H_2O$

$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + CO_2 + H_2O$

(iii) It is oxidant as well as reductant.

$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$ [reaction in acidic medium]

$H_2O_2 + 2e \rightarrow 2OH^-$ [rxn^n in alkali medium]

Oxidising Properties:

(i) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$ (Used in washing of oil painting)

(ii) $NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$

$Na_2SO_3 + H_2O_2 \longrightarrow Na_2SO_4 + H_2O$

$2KI + H_2O_2 \longrightarrow 2KOH + I_2$

$H_2S + H_2O_2 \longrightarrow S\downarrow + 2H_2O$

$H_2SO_4 + 2FeSO_4 + H_2O_2 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$

$2K_4[Fe(CN)_6] + H_2O_2 + H_2SO_4 \longrightarrow 2K_3[Fe(CN)_6] + K_2SO_4 + 2H_2O$

Reducing properties:

(a) $Ag_2O + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

(b) $O_3 + H_2O_2 \longrightarrow H_2O + 2O_2$

(c) $MnO_2 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + O_2$

(d) $PbO_2 + H_2O_2 \rightarrow PbO + H_2O + O_2$

(e) $Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

$PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$

$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$

$Pb_3O_4 + H_2O_2 + 6HNO_3 \longrightarrow 3Pb(NO_3)_2 + 4H_2O + O_2$

(f) $X_2 + H_2O_2 \longrightarrow 2HX + O_2$ [X = Cl, Br]

(g) $2[Fe(CN)_6]^{3-} + 2OH^- + H_2O_2 \longrightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$

(h) $NaOCl + H_2O_2 \longrightarrow NaCl + H_2O + O_2$

(i) $NaIO_4 + H_2O_2 \longrightarrow NaIO_3 + H_2O + O_2$

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Uses : (i) As a rocket propellant:

$NH_2.NH_2 + 2H_2O_2 \longrightarrow N_2 + 4H_2O$ [highly exothermic and large increase in volume]

(ii) In detection of Cr^{+3}, Ti^{+4} etc.

$Ti(SO_4)_2 + H_2O_2 + 2H_2O \longrightarrow \underset{\text{Yellow or orange Pertitanic acid}}{H_2TiO_4} + 2H_2SO_4$

ALLOTROPIC FORMS OF SULPHUR

$$\alpha - \text{sulphur} \underset{<369K}{\overset{>369K}{\rightleftharpoons}} \beta - \text{sulphur}$$

At 369 K both the forms are stable. This temperature is called transition temperature.

Rhombic sulphur (α-sulphur)

(i) This allotrope is yellow in colour, m.p. 385.8 K and specific gravity 2.06.

(ii) Rhombic sulphur crystals are formed on evaporating the solution of roll sulphur in CS_2.

(iii) It is insoluble in water but dissolves to some extent in benzene, alcohol and ether.

(iv) It is readily soluble in CS_2.

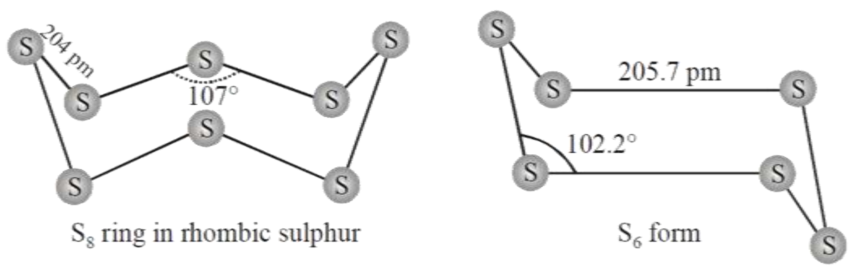
Monoclinic sulphur (β-sulphur)

(i) Its m.p. is 393 K and specific gravity 1.98.

(ii) It is soluble in CS_2.

Structure of α and β sulphur

Both rhombic and monoclinic sulphur have S_8 molecules. These S_8 molecules are packed to give different crystal structures. The S_8 ring in both the forms is puckered and has a crown shape.



S_8 ring in rhombic sulphur　　S_6 form

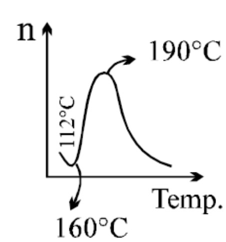
Several other modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesized in the last two decades. In cyclo-S_6, the ring adopts the chair form. At elevated temperatures (~1000 K), S_2 is the dominant species and is paramagnetic like O_2.

Note:Viscosity of 'S' with temperature :

m.p. of 'S' $\longrightarrow$ 112.8°C.

> 112.8°C to 160°C ⇒ slow decreases due to S_8 rings slip and roll over one another easily.

> 160°C, increases sharply due to breaking of S_8 rings into chains and polymerses into large size chain.



Amorphous forms are

(i) Plastic sulphur　　(ii) Milk of sulphur　　(iii) Colloidal sulphur

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SULPHUR DIOXIDE

Preparation

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

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

laboratory method by treating a sulphite with dilute sulphuric acid.

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

other preparation :

$$Cu + 2H_2SO_4\ (conc.) \longrightarrow CuSO_4 + 2H_2O + SO_2$$
$$Hg + H_2SO_4 \longrightarrow HgSO_4 + H_2O + SO_2$$
$$2Ag + H_2SO_4 \longrightarrow Ag_2SO_4 + H_2O + SO_2$$
$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$
$$(Charcoal)C + 2H2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$
$$NaHSO_3 + H_2SO_4 \longrightarrow NaHSO_4 + H_2O + SO_2$$

Industrial method, by-product of the roasting of sulphide ores.

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

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

Properties

(i) Sulphur dioxide is a colourless gas with pungent smell.

(ii) It is highly soluble in water.

(iii) It liquefies at room temperature under a pressure of two atmospheres and boils at 263 K.

(iv) Acdic character sulphur dioxide, when passed through water, forms a solution of sulphurous acid.

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

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

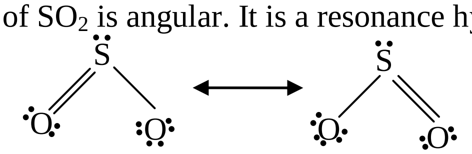
$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$
$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$
$$SO_2(g) + Cl_2 \xrightarrow[\text{of charcoal}]{\text{in presence}} SO_2Cl_2(\ell)$$
$$SO_2\ (g) + O_2\ (g) \xrightarrow{V_2O_5} 2SO_3\ (g)$$

Reducing properties

When moist, sulphur dioxide behaves as a reducing agent.

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$
$$5SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

Bonding in SO_2 : The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:



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Uses:

(i) It is used refining petroleum and sugar

(ii) It is used in bleaching wool and silk

(iii) It is used as an anti-chlor, disinfectant and preservative. Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (industrial chemicals) are manufactured from sulphur dioxide. Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

HYDROGEN SULPHIDE (H_2S) SULPHURATED HYDROGEN

Preparation

By the action of dil. HCl or $H_2\ SO_4$ on iron pyrites.

$$FeS + H_2\ SO_4 \longrightarrow FeSO_4 + H_2S\uparrow$$

Properties

It is a colourless gas having an offensive smell of rotten eggs.

(a) It burn in air with blue flame

$$2H_2S + O_2 \longrightarrow 2H_2O + S$$

If the air supply is in excess

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2$$

(b) It is a mild acid.

$$H_2S \longrightarrow H^+ + SH^-$$

$$SH^- \longrightarrow H^+ + S^{-2}$$

(c) It act as a reducing agent. It reduces halogen into corresponding hydroacid.

$$H_2S + X_2 \longrightarrow 2HX + S$$

Tests of H_2S

(a) Unpleasant odour resembling that of rotten eggs.

(b) It turns lead acetate into paper black

$$(CH_3COO)_2\ Pb + H_2\ S \longrightarrow \underset{\text{Black}}{PbS\downarrow} + 2CH_3\ COOH$$

Uses

(a) It is mainly employed in salt analysis for the detection of cation.

(b) Reducing agent for H_2SO_4, $KMnO_4$, $K_2Cr_2O_7$, O_3, H_2O_2, $FeCl_3$

Note: Drying agent for this gas : fused $CaCl_2$, Al_2O_3 (dehydrated) P_2O_5 etc.

But not H_2SO_4, because

$$H_2SO_4 + H_2S \longrightarrow 2H_2O + SO_2 + S$$

SULPHURIC ACID

Industrial Manufacturing (Contact process)

Steps involved :

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

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

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

$$2SO_2\ (g) + O_2\ (g) \xrightarrow{V_2O_5} 2SO_3\ (g)\ \Delta_r H^\Theta = -196.6\ kJ\ mol^1$$

The reaction is exothermic, reversible and the forward reaction leads to a decrease in volume.

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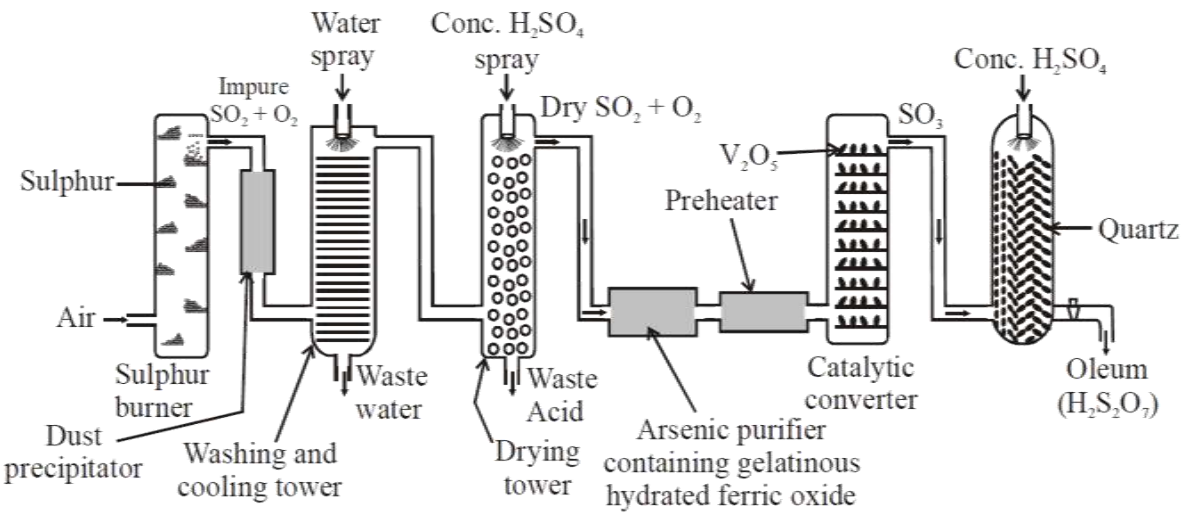
(iii) The SO_3 gas from the catalytic converter is absorbed in concentrated H_2SO_4 to produce oleum. Dilution of oleum with water gives H_2SO_4 of the desired concentration.

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



Flow diagram for the manufacture of sulphuric acid

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

P_2O_5 is stronger dehydrating agent than H_2SO_4 : $H_2SO_4 + P_2O_5 \longrightarrow 2HPO_3 + SO_3$

Properties

(i) Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 298 K.

(ii) The acid freezes at 283 K and boils at 611 K.

(iii) It dissolves in water.

Chemical properties

The chemical reactions of sulphuric acid are as a result of the following characteristics:

(1) Acidic character :

In aqueous solution, sulphuric acid ionises in two steps.

$$H_2SO_4(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HSO_4^-(aq):\ K_{a_1} = \text{Very large } (K_{a1} > 10)$$

$$HSO_4^-(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq);\ K_{a_2} = 1.2 \times 10^{-2}$$

(2) Dehydrating Propert :

Concentrated sulphuric acid is a strong dehydrating agent.

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

$$C_6H_{12}O_6 \xrightarrow[-6H_2O]{H_2SO_4} 6C$$

$$(COOH)_2 \xrightarrow[-H_2O]{H_2SO_4} CO + CO_2$$

$$HCO_2H \xrightarrow[-H_2O]{} CO$$

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(3) Oxidizing Nature :

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

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

$HBr / HI + H_2SO_4\ (conc.) \rightarrow Br_2/I_2 + SO_2 + H_2O$

$3S + 2H_2SO_4(conc.) \rightarrow 3SO_2 + 2H_2O$

$C + 2H_2SO_4(conc.) \rightarrow CO_2 + 2SO_2 + 2H_2O$

$2P + 5H_2SO_4\ (conc.) \rightarrow H_3PO_4 + 5SO_2$

H_2SO_4 & SO_3 :

$$\overbrace{SO_2 + Cl_2}^{\text{Both gas}} \longrightarrow SO_2Cl_2$$

$$H_2SO_4 + 2PCl_5 \longrightarrow \underset{\text{good chlorinating agent}}{\underset{\downarrow}{SO_2Cl_2}} + 2POCl_3 + 2HCl$$

Uses:

(i) petroleum refining
(ii) manufacture of pigments, paints and dyestuff intermediates
(iii) detergent industry
(iv) metallurgical applications (e.g., cleansing metals before enameling, electroplating and galvanising
(v) storage batteries
(vi) in the manufacture of nitrocellulose products and
(vii) as a laboratory reagent.

SODIUM THIOSULPHATE

Prep^n.:

(i) $Na_2SO_3\ sol^n. + S\ (powder) \xrightarrow{\text{boiling}} Na_2S_2O_3 \xrightarrow{\text{eavporation}}$ monoclinic crystal

(ii) $\underset{\text{Salt cake}}{Na_2SO_4} + \underset{\text{Coke}}{4C} \xrightarrow{\text{roasting}} Na_2S\ +$

$\downarrow$ SO_2 passed into it

$Na_2S_2O_3\ [3SO_2 + 2Na_2S \longrightarrow 2Na_2S_2O_3 + S]$

(iii) $6NaOH + 4S \longrightarrow Na_2S_2O_3 + 2Na_2S + 3H_2O$

$3Ca(OH)_2 + 12\ S \longrightarrow CaS_2O_3 + 2CaS_5 + 3H_2O$

(iv) $Na_2SO_3 + Na_2S + I_2 \longrightarrow Na_2S_2O_3 + 2NaI$

Props: (i) $4Na_2S_2O_3 \xrightarrow{\Delta} Na_2S_5 + 3Na_2SO_4$

(ii) $Na_2S_2O_3 + 2H^+ \longrightarrow H_2S_2O_3 \xrightarrow{\Delta} H_2O + SO_2 + S\downarrow$ (White turbidity)

Reaction: (i) $Na_2S_2O_3 + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

$+ Cl - water \longrightarrow SO_4^{2-} + S + 2HCl$

$+ Br2 - water \longrightarrow SO_4^{2-} + S + 2HBr$

$+ 4OI^- + 2OH^- \longrightarrow 2SO_4^{2-} + 4I^- + H_2O$

$+ 4Cl_2 + 5H_2O \longrightarrow Na_2SO_4 + 8HCl + H_2SO_4$

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HALOGEN FAMILY
GROUP 17 ELEMENTS (F, Cl, Br, I, At)

Electronic Configuration

The electronic configuration of outermost shell 17th group element is (ns^2np^5).

- Atomic and ionic radii : F < Cl < Br < I
- Ionisation Enthalpy : F > Cl > Br > I
- Electron Gain Enthalpy: Cl > F > Br > I
- Electronegativity : F > Cl > Br > I

Physical Properties

(i) Their melting and boiling points steadily increase with atomic number.

(ii) All halogens are coloured. For example, F_2 has yellow gas, Cl_2 greenish yellow gas, Br_2 red liquid and I_2 violet coloured solid.

(iii) Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water but are soluble in various organic solvents such as chloroform, carbon tetrachloride, carbon disulphide and hydrocarbons to give coloured solutions.

(iv) Bond energy order ; $Cl_2 > Br_2 > F_2 > I_2$

Chemical Properties

Oxidation states :

(i) All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also as explained below:

	ns	ns	n*d*	
Halogen atom In ground state (other than fluorine)	↑↓	↑↓ ↑↓ ↑		1 unpaired electron accounts For – 1 or + 1 oxidation states
First excited state	↑↓	↑↓ ↑ ↑	↑	3 unpaired electron accounts For + 3 oxidation states
Second excited state	↑↓	↑ ↑ ↑	↑ ↑	5 unpaired electron accounts For + 5 oxidation states
Third excited state	↑	↑ ↑ ↑	↑ ↑ ↑	7 unpaired electron accounts For + 7 oxidation states

(ii) The higher oxidation states of chlorine, bromine and iodine are realised mainly when the halogens are in combination with the small and highly electronegative fluorine and oxygen atoms. e.g., in interhalogens, oxides and oxoacids.

(iii) The oxidation states of +4 and +6 occur in the oxides and oxoacids of chlorine and bromine.

(iv) The fluorine atom has no d orbitals in its valence shell and therefore cannot expand its octet. Being the most electronegative, it exhibits only –1 oxidation state.

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Chemical reactivity

(i) All the halogens are highly reactive.

(ii) They react with metals and non-metals to form halides and the reactivity of the halogens decreases down the group. i.e. the order is $F_2 > Cl_2 > Br_2 > I_2$

(iii) The ready acceptance of an electron is the reason for the strong oxidising nature of halogens. F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or even in the solid phase.

In general, a halogen oxidises halide ions of higher atomic number.

$F_2 + 2X^- \rightarrow 2F^- + X_2$ (X = Cl, Br or I)

$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2$ (X = Br or I)

$Br_2 + 2I^- \rightarrow 2Br^- + I_2$

(1) Reactivity towards water

$2F_2(g) + H_2O(l) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$

$X_2(g) + H2O(l) \rightarrow HX(aq) + HOX(aq)$

(where X = Cl or Br)

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

(2) Reactivity towards hydrogen : They all react with hydrogen to give hydrogen halides but affinity for hydrogen decreases from fluorine to iodine.

(i) The acidic strength order : HF < HCl < HBr < HI

(ii) The stability order of these halides : H–F > H–Cl > H–Br > H–I.

(3) Reactivity towards oxygen :

(i) Halogens form many oxides with oxygen but most of them are unstable. Fluorine forms two oxides OF_2 and O_2F_2. However, only OF_2 is thermally stable at 298 K. These oxides are essentially oxygen fluorides because of the higher electronegativity of fluorine than oxygen. Both are strong fluorinating agents. $O2F_2$ oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

(ii) Chlorine, bromine and iodine form oxides in which the oxidation states of these halogens range from +1 to +7.

(iii) A combination of kinetic and thermodynamic factors lead to the generally decreasing order of stability of oxides formed by halogens, I > Cl > Br.

(iv) The higher oxides of halogens tend to be more stable than the lower ones.

(v) Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode. ClO_2 is used as a bleaching agent for paper pulp and textiles and in water treatment.

(vi) The bromine oxides, Br_2O, BrO_2 , BrO_3 are the least stable halogen oxides (middle row anomally) and exist only at low temperatures. They are very powerful oxidising agents.

(vii) The iodine oxides, 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.

(4) Reactivity towards metals : Halogens react with metals to form metal halides.

$Mg(s) + Br_2(l) \rightarrow MgBr_2(s)$

The ionic character of the halides decreases in the order MF > MCl > MBr > MI where M is monovalent metal.

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FLUORINE

Method of Prep^n :

Moissan process : [By electrolysis of KHF_2 (which is obtained from CaF_2)]

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

$$HF + KF \longrightarrow KHF_2$$

$$KHF_2 \xrightarrow{\text{Electrolysis}} H_2(\text{at cathode}) + F_2(\text{at anode})$$

{KF decreases the m.p.of the mix. depending upon the composition.}

CHLORINE

Preparation

(i) By electrolysis of aq. NaCl :

$$2NaCl + 2H_2O \longrightarrow 2NaOH + \underbrace{H_2}_{\text{at cathode}} + \underbrace{Cl_2}_{\text{(anode)}}$$

$$\underset{\text{(Molten)}}{2NaCl} \xrightarrow{\text{Electrolysis}} \underset{\text{(cathode)}}{2Na} + \underset{\text{(anode)}}{Cl_2}$$

(ii) By heating manganese dioxide with concentrated hydrochloric acid.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

However, a mixture of common salt and concentrated H_2SO_4 is used in place of HCl.

$$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

(iii) By the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

❑ **MANUFACTURE OF CHLORINE**

(i) **Deacon's process :** By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

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

(ii) **Electrolytic process :** Chlorine is obtained by the electrolysis of brine (concentrated NaCl solution).

Chlorine is liberated at anode. It is also obtained as a by–product in many chemical industries.

Properties

(i) It is a greenish yellow gas with pungent and suffocating odour.

(ii) It is soluble in water. Chlorine reacts with a number of metals and non-metals to form chlorides.

$$2Al + 3Cl_2 \rightarrow 2AlCl_3 \; ; \; P_4 + 6Cl_2 \rightarrow 4PCl_3$$

$$2Na + Cl_2 \rightarrow 2NaCl \; ; \; S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3 \; ;$$

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Reaction with hydrogen

It has great affinity for hydrogen. It reacts with compounds containing hydrogen to form HCl.

$H_2 + Cl_2 \rightarrow 2HCl$

$H_2S + Cl_2 \rightarrow 2HCl + S$

$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$

Reaction with amonia

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine,
nitrogen trichloride (explosive) is formed.

$\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \rightarrow 6NH_4Cl + N_2$; $\quad NH_3 + \underset{\text{(excess)}}{3Cl_2} \rightarrow NCl_3 + 3HCl$

Reaction with alkalies

$2NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O$
(cold and dilute)

$6\ NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$
(hot and conc.)

$5X^- + XO_3^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$

[X = Cl, Br, I]

Reaction with slaked lime

With dry slaked lime it gives bleaching powder.

$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(OCl_2) + CaCl_2 + 2H_2O$

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

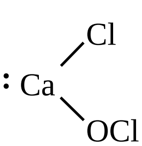
Note : Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

It is a powerful bleaching agent; bleaching action is due to oxidation.

$Cl_2 + H_2O \rightarrow 2HCl + O$

Coloured substance + O $\rightarrow$ Colourless substance

Uses: It is used (i) for bleaching woodpulp (required for the manufacture of paper and rayon), bleaching cotton and textiles, (ii) in the extraction of gold and platinum (iii) in the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc. (iv) in sterilising drinking water and (v) preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Bleaching Powder : 

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Prep^n .: $Cl_2(g) + \underset{\text{Slaked lime}}{Ca(OH)_2} \xrightarrow{40°C} Ca(OCl)Cl + H_2O$

(a) On long standing it undergoes

(i) auto oxiation $6Ca(OCl)Cl \longrightarrow Ca(ClO_3)_2 + 5CaCl_2$

(ii) $2Ca(OCl)Cl \xrightarrow[\text{Cat.}]{CoCl_2} 2CaCl_2 + O_2$

(iii) $Ca(OCl)Cl + H2O \longrightarrow Ca(OH)_2 + Cl_2$

Oxidising Prop.:

$CaOCl_2 + H_2S \longrightarrow S + CaCl_2 + H_2O$
$CaOCl_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + CaCl_2 + H_2O$
$CaOCl_2 + KNO_2 \longrightarrow CaCl_2 + KNO_3$
$3CaOCl_2 + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$
$CaOCl_2 + 2KI + 2HCl \longrightarrow CaCl_2 + 2KCl + H_2O + I_2$
$CaOCl_2 + 2KI + 2AcOH \longrightarrow CaCl_2 + 2KOAc + H_2O + I_2$
$CaOCl_2 + Na_3AsO_3 \longrightarrow Na_3AsO_4 + CaCl_2$

Reaction with acid:

$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$; $Ca(OCl)Cl + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$
$Ca(OCl)Cl + CO2 \longrightarrow CaCO_3 + Cl_2$

Note: ClO_2 does not dimerise because odd e' undergoes delocalisation (in its own vaccant 3d-orbital)
Cl_2O_4 ($Cl.ClO_4$) is not the dimer of ClO_2. Actually it is Cl-perchlorate.

HYDROGEN CHLORIDE

Preparation

Laboratory method : it is prepared by heating sodium chloride with concentrated sulphuric acid.

$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$
$NaHSO_4 + NaCl \xrightarrow{823K} Na_2SO_4 + HCl$

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

Properties

(i) It is a colourless and pungent smelling gas.

(ii) It is easily liquefied to a colourless liquid (b.p.189 K) and freezes to a white crystalline solid
(f.p. 159 K).

(iii) It is extremely soluble in water

(iv) **Acidic character :** It ionises as follows
$HCl(g) + H_2O(l) \rightarrow H_3O^+ (aq) + Cl^-(aq)\ K_a = 10^7$

Its aqueous solution is called hydrochloric acid. High value of dissociation constant (Ka) indicates that it is a strong acid in water. It reacts with NH_3 and gives white fumes of NH_4Cl.

$NH_3 + HCl \rightarrow NH_4Cl$

Note : Aqua regia

When three parts of concentrated HCl and one part of concentrated HNO3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$Au + 4H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2H_2O$
$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \rightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$

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Reaction with salts

Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogencarbonates, sulphites, etc.

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

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

Uses:
(i) It is used in the manufacture of chlorine, NH_4Cl and glucose (from corn starch)
(ii) It is used for extracting glue from bones and purifying bone black
(iii) It is used in medicine and as a laboratory reagent.
(iv) It bleaches vegetable or organic matter in the presence of moisture. Bleaching effect of chlorine is permanent.

INTERHALOGEN COMPOUNDS

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as XX′ , XX_3', XX_5' and XX_7' where X is halogen of larger size and X′ of smaller size and X is more electropositive than X′.

Preparation

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

$\underset{\text{(equal volume)}}{Cl_2 + F_2} \xrightarrow{473K} 2CIF$; $\qquad I_2 + 3Cl_2 \longrightarrow 2ICl_3$

$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{573K} 2CIF_3$; $\qquad \underset{\text{(diluted with water)}}{Br_2 + 3F_2} \longrightarrow 2BrF_3$

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

Properties

(i) These are all covalent molecules and are diamagnetic in nature.
(ii) They are volatile solids or liquids at 298 K except ClF which is a gas.
(iii) Their physical properties are intermediate between those of constituent halogens except that their m.p. and b.p. are a little higher than expected.
(iv) Their chemical reactions can be compared with the individual halogens. In general, interhalogen compounds are more reactive than halogens (except fluorine). This is because
X–X′ bond in interhalogens is weaker than X–X bond in halogens except F–F bond.
(v) All these undergo hydrolysis giving halide ion derived from the smaller halogen and a hypohalite (when XX′), halite (when XX'_3), halate (when XX'_5) and perhalate (when XX'_7) anion derived from the larger halogen.

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

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PSEUDO HALOGEN

There are univalent ion consisting of two or more atoms of which at least one is N, that have properties similar to those of the halide ions. E.g.

(i) Na-salts are soluble in water but Ag-salts are insoluble in water.

(ii) H-compounds are acids like HX.

(iii) Some anions can be oxidised to give molecules X_2.

Anions :	**Acids**	**Dimer**
CN^-	HCN	$(CN)_2$
SCN^-	HSCN(thiocyanic acid)	$(SCN)_2$
$SeCN^-$		$(SeCN)_2$
OCN^-	HOCN	(cyanic acid)
NCN^{2-}(Bivalent)	H_2NCN (cyanamide)	
ONC^-	HONC (Fulminic acid)	
N_3^-	HN_3 (Hydrazoic acid)	

$CN^{\ominus}$ shows maximum similarities with Cl^-, Br^-, I^-

(i) forms HCN (ii) forms$(CN)_2$ (iii) AgCN, $Pb(CN)_2$, are insoluble

(iv) Interpseudo halogen compounds ClCN, BrCN, ICN can be formed

(v) AgCN is insoluble in H_2O but soluble in NH_3

(vi) forms large no.of complex.e.g. $[Cu(CN)_4]^{3-}$ & $[CuCl_4]^{-3}$
$[Co(CN)_6]^{-3}$ & $[CoCl_6]^{-3}$

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NOBLE GASES FAMILY
GROUP 18 ELEMENTS (He, Ne, Ar, Kr, Xe, Rn)

Occurrence

(i) All the noble gases except radon occur in the atmosphere.
Relative abundance : Ar is highest (Ne, Kr, He, Rn)

(ii) Their atmospheric abundance in dry air is ~ 1% by volume of which argon is the major constituent.

(iii) Helium and sometimes neon are found in minerals of radioactive origin e.g., pitchblende, monazite, cleveite.

(iv) The main commercial source of helium is natural gas.

(v) Xenon and radon are the rarest elements of the group.

(vi) Radon is obtained as a decay product of ^{226}Ra.

$$^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}He$$

(vii) He liquid can exist in two forms. I-form when changes to II-form at λ-point temperature many physical properties change abruptly.

e.g.

(i) Sp. heat <u>changes</u> by a factor of 10

(ii) Thermal conductivity increases by 10^6 and it becomes 800 times faster than Cu

(iii) It shows zero resistance

(iv) It can flow up the sides of the vessel

❑ **Electronic Configuration**

General electronic configuration of 18 group element is ns^2np^6 except helium which has $1s^2$.

❑ **Ionisation Enthalpy**

He > Ne > Ar > Kr > Xe > Rn (I.E. order)

❑ **Atomic Radii**

He < Ne < Ar < Kr < Xe < Rn (atomic radius order)

❑ **Electron Gain Enthalpy**

They have large positive values of electron gain enthalpy due to stable electronic configurations, and there for have no tendency to accept the electron

❑ **Melting point and boiling point**

He < Ne < Ar < Kr < Xe < Rn (Melting point order)

↓

(–269°C)

B.P. order : He < Ne < Ar < Kr < Xe < Rn (Boiling point order)

❑ **Density order :**

He < Ne < Ar < Kr < Xe < Rn (Density order)

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Physical properties :

(i) All the noble gases are monoatomic.

(ii) They are colourless, odourless and tasteless.

(iii) They are sparingly soluble in water.

(iv) They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces.

(v) Helium has the lowest boiling point (4.2 K) of any known substance.

(vi) It has an unusual property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

❑ **Chemical Properties**

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

Note : The reactivity of noble gases has been investigated occasionally, In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First, he prepared a red compound which is formulated as $O_2^+ PtF_6^-$. He, then realised that the first ionisation enthalpy of molecular oxygen (1175 $kJmol^{-1}$) was almost identical with that of xenon (1170 $kJ\ mol^{-1}$). He made efforts to prepare same type of compound with Xe and was successful in preparing another red colour compound $Xe^+PtF_6^-$ by mixing PtF_6 and xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised. The compounds of krypton are fewer. Only the difluoride (KrF_2) has been studied in detail. Compounds of radon have not been isolated but only identified (e.g., RnF_2) by radiotracer technique. No true compounds of Ar, Ne or He are yet known.

FLUORINEDES OF XENON

Preparation

$$\underset{(\text{xenon in excess})}{Xe(g) + F_2(g)} \xrightarrow{673K, 1bar} XeF_2(s)$$

$$\underset{(1:5\ \text{ratio})}{Xe(g) + 2F_2(g)} \xrightarrow{873K, 7bar} XeF_4(s)$$

$$\underset{(1:20\ \text{ratio})}{Xe(g) + 3F_2(g)} \xrightarrow{573K, 60-70bar} XeF_6(s)$$

$$XeF_4 + O_2F_2 \xrightarrow{143K} XeF_6 + O_2$$

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Physical properties

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids and sublime readily at 298 K.

Chemical properties

(i) **Hydrolysis :**

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

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

$XeF_6 + 3H_2O \rightarrow XeO_3 + 6\,HF$

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

$XeF_6 + 2H_2O \rightarrow XeO_2F\rightarrow + 4HF$

Note : **Hydrolysis in alkaline medium**

$2XeF_2 + 4OH^- \longrightarrow 2Xe + 4F^- + 2H_2O + O_2$

$XeF_6 + 7OH^- \longrightarrow \underset{\text{Xenate ion}}{HXeO_4^-} + 3H_2O + 6F^-$

$2HXeO_4^- + 2OH^- \longrightarrow XeO_6^{4-} \downarrow + Xe + 2H_2O + O_2$

(ii) As fluorinating agents : They are powerful fluorinating agents.

$2SF_4 + XeF4 \longrightarrow 2SF_6 + Xe$

$Pt + XeF_4 \longrightarrow PtF_4 + Xe$

(iii) As fluoride donar

$XeF_2 + MF_5 \longrightarrow [XeF]^+ [MF_6]^-$ (M = As, Sb, P)

$XeF_6 + BF_3 \longrightarrow [XeF_5]^+ [BF_4^-]$

$XeF_6 + HF \longrightarrow [XeF_5]^+ [HF_2]^-$

(iv) As Fluoride acceptor

$XeF_6 + MF \longrightarrow M^+ [XeF_7]^-$ (M = Na, K, Rb, Cs)

$2Cs^+[XeF_7]^- \xrightarrow[50°C]{\Delta} XeF_6 + Cs_2[XeF_8]$

$XeF_4 + MF \longrightarrow M^+ + XeF_5^-$

(alkali metals fluoride)

(v) Reaction with SiO_2

SiO_2 also converts XeF_6 into $XeOF_4$

$2XeF_6 + SiO_2 \longrightarrow SiF_4\uparrow + \underset{\text{violet}}{2XeOF_4}$

Similarly, $XeO_3 + XeOF_4 \longrightarrow 2XeO_2F_2$ | $XeO_3 + 2XeF_6 \longrightarrow 3XeOF_4$

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(vi) Oxdizing properties

H_2 reduces Xe – fluorides to Xe

$XeF_2 + H_2 \longrightarrow Xe + 2HF$ and so on

Xe – fluorides oxidise Cl^- to Cl_2 and I^- to I_2

$XeF_2 + 2HCl \longrightarrow 2HF + Xe + Cl_2$

$XeF_4 + 4KI \longrightarrow 4KF + Xe + 2I_2$

Uses of helium :

(i) He a non-inflammable and light gas. Hence, it is used in filling balloons for meteorological observations.

(ii) It is also used in gas-cooled nuclear reactors.

(iii) It is used in cryoscopy to obtain the very low temperature required for superconductor and laser

(b.p. 4.2 K) finds use as cryogenic agent for carrying out various experiments at low temperatures.

(iv) It is used to produce and sustain powerful superconducting magnets which form an essential part of modern NMR spectrometers and Magnetic Resonance Imaging (MRI) systems for clinical diagnosis.

(v) It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood. He is used in preference to N_2 to dil. O_2 in the gas cylinders used by divers. This is because N_2 is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of N_2 in the blood. This causes the painful condition called bends. He is slightly soluble so the risk of bends is reduced.

USES OF NEON :

(i) Ne is used in discharge tubes and fluorescent bulbs for advertisement display purposes.

(ii) Neon bulbs are used in botanical gardens and in green houses.

USES OF ARGON :

(i) Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys) and for filling electric bulbs.

(ii) It is also used in the laboratory for handling substances that are air-sensitive.

USES OF XENON AND KRYPTON :

There are no significant uses of Xenon and Krypton. They are used in light bulbs designed for special purposes.

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SOLVED EXAMPLE

1. Though nitrogen exhibits +5 oxidation state, it does not form pentahalide. Give reason.

Sol. Nitrogen with n = 2, has s and p orbitals only. It does not have d orbitals to expand its covalency beyond four. That is why it does not form pentahalide.

2. PH_3 has lower boiling point than NH_3. Why?

Sol. Unlike NH_3, PH_3 molecules are not associated through hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3.

3. Write the reaction of thermal decomposition of sodium azide.

Sol. Thermal decomposition of sodium azide gives dinitrogen gas.

$$2NaN_3 \rightarrow 2Na + 3N_2$$

4. Why does NH_3 act as a Lewis base ?

Sol. Nitrogen atom in NH_3 has one lone pair of electrons which is available for donation. Therefore, it acts as a Lewis base.

5. NH_3 can't be dried by H_2SO_4, P_2O_5 and anh.$CaCl_2$

Sol. because : $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\ SO_4$

$H_2O + NH_3 + P_2O_5 \longrightarrow (NH_4)_3\ PO_4$

$CaCl_2 + 8NH_3 \longrightarrow \underset{\text{forms adduct}}{CaCl_2\ .\ 8NH_3}$

Quick lime is used for this purpose

$$\left.\begin{array}{l} CaO + H_2O \longrightarrow Ca(OH)_2\ (\text{base}) \\ \qquad\qquad NH_3\ (\text{base}) \end{array}\right\} \text{Hence no interaction}$$

6. Why does NO_2 dimerise ?

Sol. NO_2 contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerisation, it is converted to stable N_2O_4 molecule with even number of electrons.

7. In what way can it be proved that PH_3 is basic in nature?

Sol. PH_3 reacts with acids like HI to form PH_4I which shows that it is basic in nature.

$$PH_3 + HI \rightarrow PH_4I$$

Due to lone pair on phosphorus atom, PH_3 is acting as a Lewis base in the above reaction.

8. Why does PCl_3 fume in moisture ?

Sol. PCl_3 hydrolyses in the presence of moisture giving fumes of HCl.

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

9. Are all the five bonds in PCl_5 molecule equivalent? Justify your answer.

Sol. PCl_5 has a trigonal bipyramidal structure and the three equitorial P-Cl bonds are equivalent, while the two axial bonds are different and longer than equitorial bonds.

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10. How do you account for the reducing behaviour of H_3PO_2 on the basis of its structure?

Sol. In H_3PO_2, two H atoms are bonded directly to P atom which imparts reducing character to the acid.

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

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

12. H_2S is less acidic than H_2Te. Why?

Sol. Due to the decrease in bond (E–H) dissociation enthalpy down the group, acidic character increases.

13. Which form of sulphur shows paramagnetic behaviour ?

Sol. In vapour state sulphur partly exists as S_2 molecule which has two unpaired electrons in the antibonding π^* orbitals like O_2 and, hence, exhibits paramagnetism.

14. What happens when

(i) Concentrated H_2SO_4 is added to calcium fluoride

(ii) SO_3 is passed through water?

Sol. (i) It forms hydrogen fluoride

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

(ii) It dissolves SO_3 to give H_2SO_4.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

15. Halogens have maximum negative electron gain enthalpy in the respective periods of the periodic table. Why?

Sol. Halogens have the smallest size in their respective periods and therefore high effective nuclear charge.

As a consequence, they readily accept one electron to acquire noble gas electronic configuration.

16. Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

Sol. It is due to

(i) low enthalpy of dissociation of F-F bond

(ii) high hydration enthalpy of F–

17. Fluorine exhibits only –1 oxidation state whereas other halogens exhibit + 1, + 3, + 5 and + 7 oxidation states also. Explain.

Sol. Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have d orbitals and therefore, can expand their octets and show + 1, + 3, + 5 and + 7 oxidation states also.

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18. Write the balanced chemical equation for the reaction of Cl2 with hot and concentrated NaOH. Is this reaction a disproportionation reaction? Justify.

Sol. $3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

Yes, chlorine from zero oxidation state is changed to –1 and +5 oxidation states.

19. CaF_2 used in HF prep^n. must be free from SiO_2. Explain.

Ans. $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + HF$

If SiO_2 present as impurity

$$\left.\begin{array}{l} 4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \\ SiF_4 + 2HF \longrightarrow H_2[SiF_6] \end{array}\right\} \begin{array}{l} \text{Hence presence of one molecule } SiO_2 \\ \text{Consume 6 molecule of HF} \end{array}$$

HF can not be stored in glass vessel due to same reason.

20. When HCl reacts with finely powdered iron, it forms ferrous chloride and not ferric chloride. Why?

Sol. Its reaction with iron produces H_2.

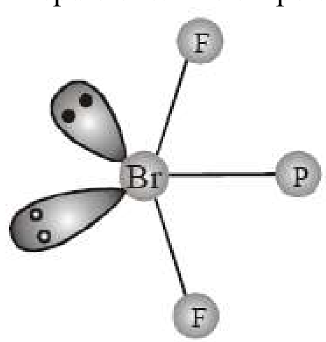
$Fe + 2HCl \rightarrow FeCl_2 + H_2$

Liberation of hydrogen prevents the formation of ferric chloride.

21. Discuss the molecular shape of BrF_3 on the basis of VSEPR theory.

Sol. The central atom Br has seven electrons in the valence shell. Three of these will form electronpair bonds with three fluorine atoms leaving behind four electrons. Thus, there are three bond pairs and two lone pairs. According to VSEPR theory, these will occupy the corners of a trigonal bipyramid.

The two lone pairs will occupy the equatorial positions to minimise lone pair-lone pair and the bond pair-lone pair repulsions which are greater than the bond pair-bond pair repulsions. In addition, the axial fluorine atoms will be bent towards the equitorial fluorine in order to minimize the lone-pair-lone pair repulsions. The shape would be that of a slightly bent 'T'.



22. Why are the elements of Group 18 known as noble gases ?

Sol. The elements present in Group 18 have their valence shell orbitals completely filled and, therefore, react with a few elements only under certain conditions. Therefore, they are now known as noble gases.

23. Noble gases have very low boiling points. Why?

Sol. Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.

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24. Does the hydrolysis of XeF_6 lead to a redox reaction?

Sol. No, the products of hydrolysis are $XeOF_4$ and XeO_2F_2 where the oxidation states of all the elements remain the same as it was in the reacting state.

25. Standard electrode potential values, $E^{\ominus}$ for Al^{3+}/Al is –1.66 V and that of Tl^{3+}/Tl is +1.26 V. Predict about the formation of M^{3+} ion in solution and compare the electropositive character of the two metals.

Sol. Standard electrode potential values for two half cell reactions suggest that aluminium has high tendency to make $Al^{3+}(aq)$ ions, whereas Tl^{3+} is not only unstable in solution but is a powerful oxidizing agent also. Thus Tl^{+} is more stable in solution than Tl^{3+}. Aluminium being able to form +3 ions easily, is more electropositive than thallium.

26. White fumes appear around the bottle of anhydrous aluminium chloride. Give reason.

Sol. Anhydrous aluminium chloride is partially hydrolysed with atmospheric moisture to liberate HCl gas. Moist HCl appears white in colour.

27. Boron is unable to form BF_6^{3-} ion. Explain.

Sol. Due to non-availability of d orbitals, boron is unable to expand its octet. Therefore, the maximum covalence of boron cannot exceed 4.

28. Why is boric acid considered as a weak acid ?

Sol. Because it is not able to release H^{+} ions on its own. It receives OH^{-} ions from water molecule to complete its octet and in turn releases H^{+} ions.

29. Select the member(s) of group 14 that (i) forms the most acidic dioxide, (ii) is commonly found in +2 oxidation state, (iii) used as semiconductor.

Sol. (i) carbon (ii) lead (iii) silicon and germanium

30. $[SiF_6]^{2-}$ is known whereas $[SiCl_6]^{2-}$ not. Give possible reasons.

Sol. The main reasons are :

(i) six large chloride ions cannot be accommodated around Si^{4+} due to limitation of its size.

(ii) interaction between lone pair of chloride ion and Si^{4+} is not very strong.

31. Diamond is covalent, yet it has high melting point. Why ?

Sol. Diamond has a three-dimensional network involving strong C—C bonds, which are very difficult to break and, in turn has high melting point.

32. SiH_4 is more reactive than CH_4. Explain

<u>Reasons</u>

(i) $Si^{\delta+} - H^{\delta-}$ in $C^{\delta-} - H^{\delta+}$

C – more electronegative than H

Si less electronegative than H

So bond polarity is reversed when Nu^{-} attacks, it faces repulsion in C but not in Si

(ii) Silicon is having vacant d orbital which is not in case of carbon

(iii) Silicon is larger in size compared to C. By which the incoming Nu^{-} doesn't face any steric hindrance to attack at Si whereas CH_4 is tightly held from all sides.

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EXERCISE-I

Only one option is correct :

1. PH_3(Phosphine) when passed in aqueous solution of $CuSO_4$ it produce -
(A) Blue precipitate of $Cu(OH)_2$
(B) dark blue solution of $[Cu(PH_3)_4]SO_4$
(C) Black precipitate of Cu_3P_2
(D) Colorless solution of $[Cu(H_2O)_4]^+$

2. $H_3PO_2 \xrightarrow{\Delta} (X) + PH_3$; is
(A) Dehydration reaction
(B) Oxidation reaction
(C) Disproportionation reaction
(D) Dephosphorelation reaction

3. Which of the following species is not a pseudohalide?
(A) CNO^-
(B) $RCOO^-$
(C) OCN^-
(D) N_3^-

4. An orange solid (X) on heating, gives a colourless gas (Y) and a only green residue (Z). Gas (Y) on treatement with Mg, produces a white solid substance ....
(A) Mg_3N_2
(B) MgO
(C) Mg_2O_3
(D) $MgCl_2$

5. Conc. HNO3 is yellow coloured liquid due to
(A) dissolution of NO in conc. HNO3
(B) dissolution of NO2 in conc. HNO3
(C) dissolution of N2O in conc. HNO3
(D) dissolution of N2O3 in conc. HNO3

6. A gas at low temperature does not react with the most of compounds. It is almost inert and is used to create inert atmosphere in bulbs. The combustion of this gas is exceptionally an endothermic reaction. Based on the given information, we can conclude that the gas is
(A) oxygen
(B) nitrogen
(C) carbon mono-oxide
(D) hydrogen

7. When chlorine gas is passed through an aqueous solution of a potassium halide in the presence of chloroform, a voilet colouration is obtained. On passing more of chlorine water, the voilet colour is disappeared and solution becomes colourless. This test confirms the presence of .... in aqueous solution.
(A) chlorine
(B) fluorine
(C) bromine
(D) iodine

8. $H_3PO_2 \xrightarrow{140°C} A \xrightarrow{220°C} B \xrightarrow{320°C}$
Compound (C) is
(A) H_2PO_3
(B) H_3PO_3
(C) $(HPO_3)_n$
(D) $H_4P_2O_7$

9. An explosive compound (A) reacts with water to produce NH4OH and HOCl. Then, the compound (A), is
(A) TNG
(B) NCl_3
(C) PCl_3
(D) HNO_3

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10. An inorganic compound (A) made of two most occuring elements into the earth crust, having a polymeric tetra-headral network structure. With carbon, compound (A) produces a poisonous gas (B) which is the most stable diatomic molecule. Compounds (A) and (B) will be

(A) SiO_2, CO_2 (B) SiO_2, CO (C) SiC,CO (D) SiO_2' N_2

11. A sulphate of a metal (A) on heating evolves two gases (B) and (C) and an oxide (D). Gas (B) turns $K_2Cr_2O_7$ paper green while gas (C) forms a trimer in which there is no S–S bond. Compound (D) with HCI, forms a Lewis acid (E) which exists as a dimer. Compounds (A), (B), (C), (D) and (E) are respectively

(A) $FeSO_4$, SO_2, SO_3, Fe_2O_3, $FeCl_3$ (B) $Al_2(SO_4)_3$, SO_2, SO_3, Al_2O_3, $FeCl_3$

(C) FeS, SO_2, SO_3, $FeSO_4$, $FeCl_3$ (D) FeS, SO_2, SO_3 , $Fe_2(PO_4)_3$, $FeCl_2$

12. A tetra-atomic molecule (A) on reaction with nitrogen(I)oxide, produces two substances (B) and (C). (B) is a dehydrating agent in its monomeric form while substance (C) is a diatomic gas which shows almost inert behaviour. The substances (A) and (B) and (C) respectively will be

(A) P_4, P_4O_{10}, N_2 (B) P_4, N_2O_5, N_2 (C) P_4, P_2O_3, Ar (D) P_4, P_2O_3, H_2

13. First compound of inert gases was prepared by scientist Neil Barthlete in 1962. This compound is

(A) $XePtF_6$ (B) XeO_3 (C) XeF_6 (D) $XeOF_4$

14. Carbongene has X% of CO_2 and is used as an antidote for poisoning of Y . Then, X and Y are

(A) X = 95% and Y = lead poisoning (B) X = 5% and Y = CO poisoning

(C) X = 30% and Y = CO2 poisoning (D) X = 45% and Y = CO poisoning

15. The correct order of acidic strength of oxides of nitrogen is

(A) $NO < NO_2 < N_2O < N_2O_3 < N_2O_5$ (B) $N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$

(C) $NO < N_2O < N_2O_3 < N_2O_5 < N_2O_4$ (D) $NO < N_2O < N_2O_5 < N_2O_3 < N_2O_4$

16. $H_3BO_3 \xrightarrow{T_1} X \xrightarrow{T_2} Y \xrightarrow{\text{red hot}} B_2O_3$

If $T_1 < T_2$ then X and Y respectively are

(A) X = Metaboric acid and Y = Tetraboric acid

\ (B) X = Tetraboric acid and Y = Metaboric acid

(C) X = Borax and Y = Metaboric acid

(D) X = Tetraboric acid and Y = Borax

17. When conc. H_2SO_4 was treated with $K_4[Fe(CN)_6]$, CO gas was evolved. By mistake, somebody used dilute H_2SO_4 instead of conc. H_2SO_4 then the gas evolved was

(A) CO (B) HCN (C) N_2 (D) CO_2

18. An inorganic white crystalline compound (A) has a rock salt structure. (A) on reaction with conc. H_2SO_4 and MnO_2, evolves a pungent smelling, greenish-yellow gas (B). Compound (A) gives white ppt. of (C) with $AgNO_3$ solution. Compounds (A), (B) and (C) will be respectively

(A) NaCl, Cl_2, Agcl (B) NaBr, Br_2, NaBr

(C) NaCl, Cl_2, Ag_2SO_4 (D) Na_zCO_3, CO_2, Ag_2CO_3

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19. RCl $\xrightarrow[Si]{Cu-powder}$ R_2SiCl_2 $\xrightarrow{H_2O}$ $R_2Si(OH)_2$ $\xrightarrow{condensation}$ A

Compound (A) is

(A) a linear silicone (B) a chlorosilane (C) a linear silane (D) a network silane

20. When oxalic acid reacts with cone. H_2SO_4 , two gases produced are of neutral and acidic in nature respectively. Potassium hydroxide absorbs one of the two gases. The product formed during this absorption and the gas which gets absorbed are respectively

(A) K_2CO_3 and CO_2 (B) $KHCO_3$ and CO_2 (C) K_2CO_3 and CO (D) $KHCO_3$ and CO

21. Conc. H_2SO_4 cannot be used to prepare HBr from NaBr because it

(A) reacts slowly with NaBr (B) oxidises HBr

(C) reduces HBr (D) disproportionates HBr

22. Ammonia can be dried by

(A) conc. H_2SO_4 (B) P_4O_{10} (C) CaO (D) anhydrous $CaCl_2$

23. When chlorine reacts with a gas X, an explosive inorganic compound Y is formed. Then X and Y will be

(A) X = O_2 and Y = NCl_3 (B) X = NH_3 and Y=NCl_3

(C) X = O_2 and Y = NH_4Cl (D) X = NH_3 and Y = NH_4Cl

24. $HNO_3 + P_4O_{10} \longrightarrow HPO_3 + A$; the product A is

(A) N_2O (B) N_2O_3 (C) NO_2 (D) N_2O_5

25. Which of the following is the correct order of acidic strength?

(A) $Cl_2O_7 > SO_3 > P_4O_{10}$ (B) $CO_2 > N_2O_5 > SO_3$

(C) $Na_2O > MgO > Al_2O_3$ (D) $K_2O > CaO > MgO$

26. $Ca + C_2 \longrightarrow CaC_2 \xrightarrow{N_2} A$

Compound (A) is used as a/an

(A) fertilizer (B) dehydrating agent (C) oxidising agent (D) reducing agent

27. A gas which exists in three allotropic forms a, b and g is

(A) SO_2 (B) SO_3 (C) CO_2 (D) NH_3

28. A red coloured mixed oxide (X) on treatment with cone. HNO3 gives a compound (Y). (Y) with HCl, produces a chloride compound (Z) which can also be produced by treating (X) with cone. HCl.

Compounds (X) , (Y), and (Z) will be

(A) Mn_3O_4, MnO_2, $MnCl_2$ (B) Pb_3O_4, PbO_2, $PbCl_2$

(C) Fe_3O_4, Fe_2O_3, $FeCl_2$ (D) Fe_3O_4, Fe_2O_3, $FeCl_3$

29. One mole of calcium phosphide on reaction with excess of water gives

(A) one mole of phosphine

(B) two moles of phosphoric acid

(C) two moles of phosphine

(D) one mole of phosphorus penta-oxide

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30. $NaH_2PO_4 \xrightarrow{>240°C} (NaPO_3)_3 \xrightarrow{625°C} NaPO_3$ (liquid melt) $\xrightarrow[\text{cooling}]{\text{rapid}}$ D(glass)

Sodium trimetaphosphate

Compound (D) is known as

(A) Microcosmic salt (B) Graham's salt (C) Reimann's salt (D) Switzer's Salt

31. Three allotropes (A), (B) and (C) of phosphorous in the following change are respectively

$$A \xrightarrow[1200\ \text{atm}]{473\ \text{K}} B$$

$$A \xrightarrow[CO_2 - \text{atm}]{573\ \text{K}} C$$

(A) white, b-black, red
(B) b-black, white, red
(C) red, b-black, white
(D) red, violet, b-black

32. When an inorganic compound reacts with SO_2 in aqueous medium, produces (A). (A) on reaction with Na_2CO_3, gives compound (B) which with sulphur, gives a substance (C) used in photography.

Compound (C) is

(A) Na_2S (B) $Na_2S_2O_7$ (C) Na_2SO_4 (D) $Na_2S_2O_3$

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

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

(A) addition of cis 1,2 diol
(B) addititon of borax
(C) addition of trans 1,2 diol
(D) addition of Na_2HPO_4

34. Which is the compound responsible for the flickering light called **will-o-the-wisp**, some times seen in the Marsh.

(A) PH_3 (B) P_2H_4 (C) H_2S (D) $PH_3 + H_2S$

35. The gun powder is consisting of '______' + sulphur + Charcoal what is the missing substance for gun powder

(A) $LiNO_3$ (B) NH_4NO_2 (C) KNO_3 (D) (A) and (B) mixture

36. An aqueous solution of borax is

(A) Neutral (B) Amphoteric (C) Basic (D) Acidic

37. Boric acid is polymeric due to

(A) Its acidic nature
(B) The presence of hydrogen bonds
(C) Its monobasic nature
(D) Its geometry

38. The type of hybridisation of boron in diborane is

(A) sp (B) sp^2 (C) sp^3 (D) dsp^2

39. Thermodynamically the most stable form of carbon is

(A) Diamond (B) Graphite (C) Fullerenes (D) Coal

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40. Elements of group 14

(A) Exhibit oxidation state of + 4 only (B) Exhibit oxidation state of +2 and +4 only

(C) Form M^{2-} and M^{4+} ions (D) Form M^{2+} and M^{4+} ions

41. $A + Br_2 \rightarrow N_2 + (B)$

$$(B) \xrightarrow{NaOH} (A)$$

if A is a basic gas then identified (A) and (B)

(A) NH_3, NH_4Br (B) NH_3, N_2O (C) NH_3, N_2O_5 (D) None of these

Question No. 50 to 55 (6 questions)

Questions given below consist of two statements each printed as Assertion (A) and Reason (R); while answering these questions you are required to choose any one of the following four responses:

(A) if both (A) and (R) are true and (R) is the correct explanation of (A)

(B) if both (A) and (R) are true but (R) is not correct explanation of (A)

(C) if (A) is true but (R) is false

(D) if (A) is false and (R) is true

42. **Assertion :** Borax bead test is applicable only to coloured salt.

Reason : In borax bead test, coloured salts are decomposed to give coloured metal meta borates.

43. **Assertion :** Aluminium and zinc metal evolve H_2 gas from NaOH solution

Reason : Several non-metals such as P, S, Cl, etc. yield a hydride instead of H_2 gas from NaOH

44. **Assertion :** Conc. H_2SO_4 can not be used to prepare pure HBr from NaBr

Reason : It reacts slowly with NaBr.

45. **Assertion :** Oxygen is more electronegative than sulphur, yet H_2S is acidic, while H_2O is neutral.

Reason : H–S bond is weaker than O–H bond.

46. **Assertion :** Chlorine gas disproportionates in hot & conc. NaOH solution.

Reason : NaCl and NaOCl are formed in the above reaction.

47. **Assertion :** Liquid IF_5 conducts electricity.

Reason : Liquid IF_5 self ionizes as, $2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$

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EXERCISE-II

One or more than one option may be correct :

1. When a compound X reacts with ozone in aqueous medium, a compound Y is produced. Ozone also reacts with Y and produces compound Z. Z acts as an oxidising agent, then X, Y and Z will be

(A) X = HI, Y = I_2 and Z = HIO_3

(B) X = KI, Y = I_2 and Z = HIO_3

(C) X = KI, Y = I_2 and Z = HIO_4

(D) X = HI, Y = I_2 and Z = HIO_4

2. Which of the following statements is/are correct regarding B_2H_6?

(A) banana bonds are longer but stronger than normal B–H bonds

(B) B_2H_6 is also known as 3c–2e compound

(C) the hybrid state of B in B_2H_6 is sp^3 while that of sp^2 in BH_3

(D) it cannot be prepared by reacting BF_3 with $LiBH_3$ in the presence of dry ether

3. Which of the following statements is/are correct regarding inter-halogen compounds of ABx types?

(A) x may be 1,3,5 and 7

(B) A is a more electronegative halogen than B

(C) FBr_3 cannot exit

(D) The interhalogens are generally more reactive than the halogens (except F_2) due to weaker A–X bonds compared to X–X bond.

4. When an inorganic compound (X) having 3e-2e as well as 2e-2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y) iso-structural with benzene. Compound (X) with ammonia at a high temperature, produces a hard substance (Z). Then

(A) (X) is B_2H_6

(B) (Z) is known as inorganic graphite

(C) (Z) having structure similar to graphite

(D) (Z) having structure similar to (X)

5. Boric acid

(A) exists in polymeric form due to inter-molecular hydrogen bonding.

(B) is used in manufacturing of optical glasses.

(C) is a tri-basic acid

(D) with borax, it is used in the preparation of a buffer solution.

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6. The correct statement(s) related to allotropes of carbon is/are

(A) graphite is the thermodynamically most stable allotrope of carbon and having a two dimensional sheet like structure of hexagonal rings of carbon (sp^2)

(B) diamond is the hardest allotrope of carbon and having a three dimensional network structure of $C(sp^3)$

(C) fullerene (C_{60}) is recently discovered non-crystalline allotrope of carbon having a football-like structure.

(D) Vander Waal's force of attraction acts between the layers of graphite 6.14 Å away from each other

7. $Al_2(SO_4)_3 + NH_4OH \longrightarrow X$, then

(A) X is a white coloured compound
(B) X is insoluble in excess of NH_4OH
(C) X is soluble in NaOH
(D) X cannot be used as an antacid

8. The species that undergo(es) disproportionation in an alkaline medium is/are

(A) Cl_2
(B) MnO_4^{2-}
(C) P_4
(D) ClO_4^-

9. Select correct statement(s):

(A) Borax is used as a buffer

(B) 1 M borax solution reacts with equal volumes of 2 M HCl solution

(C) Titration of borax can be made using methyl orange as the indicator

(D) Coloured bead obtained in borax-bead test contains metaborate

10. Which of the following is / are correct for group 14 elements?

(A) The stability of dihalides are in the order CX2 < SiX2 < GeX2 < SnX2 < PbX2

(B) The ability to form pp–pp multiple bonds among themselves increases down the group

(C) The tendency for catenation decreases down the group

(D) They all form oxides with the formula MO2.

11. Zeolite is used in which of the following cases :

(A) Conversion of alcohols into gasoline
(B) Cracking of hydrocarbon
(C) Isomerisation of hydrocarbons
(D) Softning of hard water

12. Which of the following oxides are mixed oxide :

(A) PbO_2
(B) SnO_2
(C) Pb_2O_3
(D) Pb_3O_4

13. Which of the following oxide(s) gives brown ppt on reaction with conc. HNO_3 :

(A) PbO
(B) SnO
(C) Pb_2O_3
(D) Pb_3O_4

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14. Which of the following reaction produces PH_3 :

(A) $Ca_3P_2 + H_2O \rightarrow$ (B) $P_4 + NaOH \rightarrow$ (C) $PH_4I + KOH \rightarrow$ (D) $H_3PO_2 \xrightarrow{\Delta}$

15. Which of the following element of chalcogen group can form MX_2 type of compound where X = Cl and Br :

(A) O (B) S (C) Se (D) Te

16. $Ca_2B_6O_{11} + Na_2CO_3 \xrightarrow{\Delta} [X] + CaCO_3 + NaBO_2$ (Unbalanced equation)

Correct statement for [X]

(A) Structure of anion of crystalline (X) has one boron atom sp^3 hybridised and other three boron atoms sp^2 hybridised

(B) (X) with NaOH(aq.) gives a compound which on reaction with H_2O_2 in alkaline medium yields a compound used as brightner in soaps

(C) Hydrolysis of (X) with HCl or H_2SO_4 yields a compound which on reaction with HF gives fluoroboric acid

(D) [X] on heating with cobalt salt in oxidising flame gives blue coloured bead

17. $(A) + 2C \xrightarrow[2500°C]{2000°C\text{ to}} (B) + 2CO\uparrow$

$(B) + \text{Carbon} \xrightarrow[2500°C]{2000°C\text{ to}} (C)$

If A is an example of 3-d silicate then select the correct statements about (C)

(A) Central atom of C is sp^3 hybridised

(B) (C) is non planar and all atoms are sp^3 hybridised

(C) C has diamond like structure, and it is colourless when impurity is present but yellow solid at room temperature

(D) (C) is silicon carbide (SiC) and it is not being affected by any acid except H_0PO_4

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EXERCISE-III

Paragraph for Question No. 1 & 2

A + alkaline solution $\rightarrow B + C$

$A \xrightarrow{6Cl_2} (D)$

$B \xrightarrow{3Cl_2} (D)$

$(F) \xleftarrow{3H_2O} (D) \xrightarrow{CH_3COOH} E + F$

1. When D react with C_2H_5OH then product will be

(A) C_2H_5Cl, H_3PO_4 (B) $C2H_5Cl$, H_3PO_3

(C) CH_3COCl, H_3PO_3 (D) Only H_3PO_3

2. B can be absorbed by :

(A) Ca(OCl) Cl (B) H_2S (C) Both (D) None

Paragraph for Question No. 3 to 6

$$HCOOH \xrightarrow[\text{Conc.}H_2SO_4]{373K} H_2O + (X)$$

$$C(s) + H_2O \xrightarrow{423\text{–}1273K} (X) + H_2(g)$$

3. Select the correct statement about (X)

(A) (X) is a colourless, odourless and almost water insoluble gas

(B) X is highly poisonous and burns with blue flame

(C) When (X) gas is passed through $PdCl_2$ solution giving rise to balck ppt

(D) All of these

4. Mixture of (X) gas + H_2 is called

(A) Water gas or synthesis gas (B) Producer gas

(C) Methane gas (D) None of these

5. In second reaction when air is used instead of steam a mixed of (X) gas and N2 is produced which is called

(A) Water gas (B) Synthesis gas (C) Producer gas (D) Carbon dioxide gas

6. Select the correct statement about (X)

(A) (X) gas is estimatate by I_2O_5

(C) (X) gas is the purifying agent for Ni

(B) Cu_2Cl_2 is absorber of (X) gas

(D) All of these

Paragraph for Question No. 7 & 8

Read the following write-ups and answer the questions at the end of it.

Silicons are synthetic polymers containing repreated R_2SiO units. Since, the empirical formula is that of a ketone (R_2CO), the name silicone has been given to these materials. Silicones can be made into oils, rubbery elastomers and resins. They find a variety of applications because of their chemical inertness, water repelling nature, heat-resistance and good electrical insulating property.

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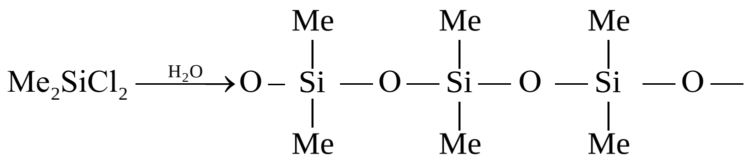
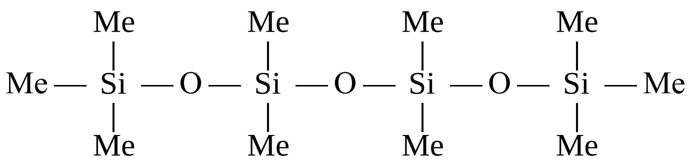
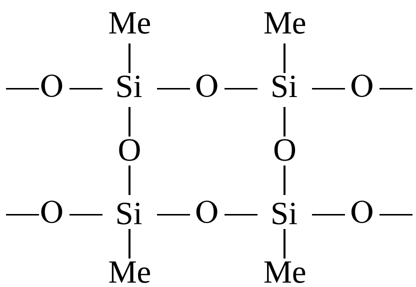
Commercial silicon polymers are usually methyl derivatives and to a lesser extent phenyl derivatives and are synthesised by the hydrolysis of

R_2SiCl_2[R=methyl (Me) or phenyl (ϕ)]



7. If we mix Me_3SiCl with Me_2SiCl_2, we get silicones of the type:

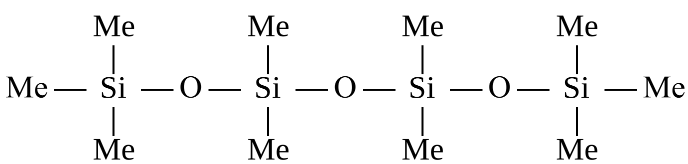
(A) 

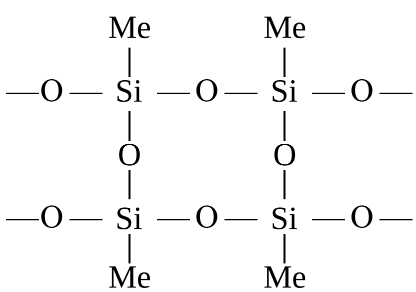
(B) 

(C) both of the above

(D) none of the above

8. If we start with $MeSiCl_3$ as the starting material, silicones formed is:

(A) 

(B) 

(C) Both of the above

(D) None of the above

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Paragraph for Question No. 9 & 10

CO gas is absorbed by aqueous suspension of cuprous chloride forming the complex like $[CuCl(CO)(H_2O)_2]$.

9. Comment on the shape of the above complex.

(A) Tetrahedral (B) TBP (C) Square planar (D) Can not be predicted

10. Choose the correct statement regarding the above molecule

(A) Cl-atom is separated by equal angle from both of the water molecule

(B) Magnetic moment of the above complex is 1.73 B.M.

(C) There are two stereo isomer for the above complex.

(D) Both (A) and (C)

Paragraph for Question No. 11 to 12

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorous.

11. Among the following, the correct statement is

(A) Phosphates have no biological significance in humans

(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust

(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust

(D) Oxidation of nitrates is possible in soil

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

(A) dimerization reaction (B) disproportionation reaction

(C) condensation reaction (D) precipitation reaction

13. Match List-I with List-II

List-I (Chemical reaction)		**List-II (Name of process)**	
(I)	$4NH_3 + 5O_2 \xrightarrow{800°C/Pt} 4NO + 6H_2O$	(a)	Contact process
(II)	$4HCl + O_2 \xrightarrow{230°C/CuCl_2} 2Cl_2 + 2H_2O$	(b)	Ostwald's process
(III)	$2SO_2 + O_2 \xrightarrow{450-500°/V_2O_5} 2SO_3$	(c)	Deacon's process
(IV)	$2N_2 + 3H_2 \xrightarrow{Fe+Mo} 2NH_3$	(d)	Haber's process

(A) I-a, II-b, III-d, IV-c (B) I-b, II-c, III-a, IV-d

(C) I-a, II-d, III-c, IV-b (D) I-a, II-c, III-b, IV-d

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14. **Column-I** **Column-II**

	Column-I		Column-II
(P)	Dry ice	(1)	Used as antidote for CO-poisoning
(Q)	Carbongene	(2)	Used as nonstick coating
(R)	Carborundum	(3)	Used as refrigerant
(S)	Teflon	(4)	Used as abrasive

Code :

	P	Q	R	S
(A)	4	1	3	2
(B)	4	2	1	3
(C)	3	1	4	2
(D)	1	4	3	2

15.

	Column-I Compound		Column-II Correct statement for compounds given
(P)	$SnCl_2$	(1)	Used in printing technology
(Q)	Butter of tin	(2)	Used for gilding purpose (in joining gold pieces)
(R)	Mosaic gold	(3)	Reducing agent
(S)	Pink salt	(4)	Mordant

Code :

	P	Q	R	S
(A)	4	3	2	1
(B)	3	4	2	1
(C)	2	1	3	4
(D)	1	3	4	2

16.

	Column-I (Metal)		Column-II (Correct statements)
(P)	Fe	(1)	Produces NO with 20% HNO_3
(Q)	Cu	(2)	Produces NH_4NO_3 with 6% HNO_3
(R)	Pb	(3)	Produces NO_2 with 70% HNO_3
(S)	Sn	(4)	Produces NH_4NO_3 with 20% HNO_3

Code :

	P	Q	R	S
(A)	2, 1	1	3, 4	2, 3
(B)	2, 3	1, 3	1, 3	2, 3, 4
(C)	1, 3	1, 2	3, 4	2
(D)	1, 4	2, 3	1, 3	1, 4

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17. **Column-I (Reactions)** | **Column-II (Correct statements)**

	Column-I (Reactions)		Column-II (Correct statements)
(P)	$XeF_2 + PF_5 \rightarrow$	(1)	Fluoride of Xe acts as fluoride acceptor
(Q)	$XeF_4 + Pt \rightarrow$	(2)	Fluoride of Xe undergoes disproportion
(R)	$XeF_4 + H_2O \rightarrow$	(3)	Fluoride of Xe acts as fluorinating agent
(S)	$XeF_6 + CsF \rightarrow$	(4)	Fluoride of Xe act as fluoride donor

Code :

	P	Q	R	S		P	Q	R	S
(A)	4	2	3	1	(B)	3	2	1	4
(C)	4	3	2	1	(D)	3	4	2	1

18.

	Column-I (Substances)		Column-II (Can be prepared by)
(P)	O_3	(1)	Acidification of BaO_2 with H_3PO_4
(Q)	Bleaching powder	(2)	Birkeland Eyde process
(R)	H_2O_2	(3)	Dry O_2 is passed through a silent electrical discharge
(S)	HNO_3	(4)	Cl_2 gas is passed through slaked lime

Code :

	P	Q	R	S		P	Q	R	S
(A)	3	4	1	2	(B)	1	3	4	2
(C)	2	1	3	4	(D)	4	1	2	3

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EXERCISE-IV (JEE-MAINS)

1. Which products are expected from the disproportionation of hypochlorous acid: **[AIEEE-2002]**
(1) $HClO_3$ and Cl_2O (2) $HClO_2$ and $HClO$
(3) HCl and Cl_2O (4) HCl and $HClO_3$

2. Identify the incorrect statement among the following : **[AIEEE-2002]**
(1) Ozone reacts with SO_2 to give SO_3
(2) Silicon reacts with NaOH(aq.) in the presence of air to give Na_2SiO_3 and H_2O
(3) Cl_2 reacts with excess of NH_3 to give N_2 and HCl
(4) Br_2 reacts with hot and strong NaOH solution to given NaBr, $NaBrO_4$ and H_2O

3. Aluminium is industrially prepared by: **[AIEEE-2002]**
(1) Fused cryolite (2) Bauxite ore (3) Alunite (4) Borax

4. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be : **[AIEEE-2003]**
(1) Sodium (2) Magnesium (3) Mercury (4) Tin

5. What may be expected when phosphine gas is mixed with chlorine gas: **[AIEEE-2003]**
(1) PCl_5 and HCl are formed and mixture cools down
(2) $PH_3.Cl_2$ is formed with warming up
(3) The mixture only cools down
(4) PCl_3 and HCl are formed and the mixture warms up

6. Graphite is a soft solid lubricant extremely difficult to melt. The reason for this anomalous behaviour is that graphite : **[AIEEE-2003]**
(1) Has molecules of variable molecular masses like polymers
(2) Has carbon atoms arranged in large plated of rings of strongly bonded carbon atoms with weak interplate bonds
(3) Is a non crystalline substance
(4) Is an allotropic form of diamond

7. Concentrated hydrochloric acid when kept in open air sometimes produces a cloud of white fumes. This is due to : **[AIEEE-2003]**
(1) Strong affinity of HCl gas for moisture in air results in forming of droplets of liquid solution which appears like a cloudy smoke
(2) Due to strong affinity for water, conc. HCl pulls moisture of air towards self. The moisture forms droplets of water and hence the cloud
(3) Conc. HCl emits strongly smelling HCl gas all the time
(4) Oxygen in air reacts with emitted HCl gas to form a cloud of Cl_2 gas

8. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives- **[AIEEE-2004]**
(1) $Al^{3+} + 3Cl^-$ (2) $[Al(H_2O)_6]^{3+} + 3Cl^-$
(3) $[Al(OH)_6]^{3-} + 3HCl$ (4) $Al_2O_3 + 6HCl$

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9. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White Metallic tin buttons get converted to grey powder.
This transformation is related to:- **[AIEEE-2004]**
(1) An interaction with water vapour contained in humid air
(2) A change in crystalline structure of tin
(3) A change in the partial pressure of O_2 in air
(4) An interaction with N_2 of air at low temperature

10. Which one of the following statements regarding helium is incorrect **[AIEEE-2004]**
(1) It is used to produce and sustain powerful superconducting magnets
(2) It is used as a cryogenic agent for carrying out experiments at low temperatures
(3) It is used to fill gas balloons instead of hydrogen because it is lighter then hydrogen and noninflammable
(4) It is used in gas-cooled nuclear reactors

11. The number of hydrogen atoms attached to phosphorus atom in hypophosphorous acid is : **[AIEEE-2005]**
(1) Zero (2) Two (3) One (4) Three

12. Heating an aqueous solution of aluminium chloride to dryness will give :- **[AIEEE-2005]**
(1) $AlCl_3$ (2) Al_2Cl_6 (3) Al_2O_3 (4) $Al(OH)Cl_2$

13. Which one of the following is the correct statement **[AIEEE-2005]**
(1) Boric acid is a protonic acid
(2) Beryllium exhibits coordination number of six
(3) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase
(4) B_2H_6, $2NH_3$ is known as "inorganic benzene"

14. In silicon dioxide : **[AIEEE-2005]**
(1) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms
(2) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms
(3) Silicon atom is bonded to two oxygen atoms
(4) There are double bonds between silicon and oxygen atoms

15. Regular use of which of the following fertilizer increases the acidity of soil : **[AIEEE-2007]**
(1) Potassium nitrate (2) Urea
(3) Superphosphate of lime (4) Ammonium sulphate

16. The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence: **[AIEEE-2007]**
(1) $GeX_2 << SiX_2 << SnX_2 << PbX_2$ (2) $SiX_2 << GeX_2 << PbX_2 << SnX_2$
(3) $SiX_2 << GeX_2 << SnX_2 << PbX_2$ (4) $PbX_2 << SnX_2 << GeX_2 << SiX_2$

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17. Among the following substituted silanes the one which will give rise to cross linked silicone polymer on hydrolysis is **[AIEEE-2008]**

(1) R_4Si (2) $RSiCl_3$ (3) R_2SiCl_2 (4) R_3SiCl

18. Which one of the following reactions of Xenon compounds is not feasible ? **[AIEEE-2009]**

(1) $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$

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

(2) $XeF_6 + RbF \rightarrow Rb[XeF_7]$

(4) $3XeF_4 + 6H_2O \rightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$

19. Which of the following statement is wrong ? **[AIEEE-2011]**

(1) Single N–N bond is weaker than the single P–P bond

(2) N_2O_4 has two resonance structures

(3) The stability of hydrides increases from NH_3 to BiH_3 in group 15 of the periodic table

(4) Nitrogen cannot form dp-pp bond

20. Which of the following statements regarding sulphur is incorrect ? **[AIEEE-2011]**

(1) At 600°C the gas mainly consists of S_2 molceules

(2) The oxidation state of sulphur is never less than +4 in its compounds

(3) S_2 molecule is paramagnetic

(4) The vapour at 200°C consists mostly of S_8 rings

21. Boron cannot form which one of the following anions ? **[AIEEE-2011]**

(1) $B(OH)_4^-$ (2) BO_2^- (3) BF_6^{3-} (4) BH_4^-

22. In view of the signs of $\Delta_rG°$ for the following reactions

$PbO_2 + Pb \rightarrow 2\ PbO,\ \Delta_rG° < 0$

$SnO_2 + Sn \rightarrow 2\ SnO,\ \Delta_rG° > 0,$

Which oxidation states are more characteristic for lead and tin ? **[AIEEE-2011]**

(1) For lead + 4, for tin + 2 (2) For lead + 2, for tin + 2

(3) For lead + 4, for tin + 4 (4) For lead + 2, for tin + 4

23. The number of S–S bonds in SO_3, $S_2O_3^{2-}$, $S_2O_6^{2-}$ and $S_2O_8^{2-}$ respectively are :- **[Jee Main(Online)-2012]**

(1) 1, 0, 1, 0 (2) 0, 1, 1, 0 (3) 1, 0, 0, 1 (4) 0, 1, 0, 1

24. Which one of the following depletes ozone layer ? **[Jee Main(Online)-2012]**

(1) NO and freons (2) SO_2 (3) CO (4) CO_2

25. In which of the following arrangements, the sequence is not strictly according to the property written against it ? **[Jee Main(Online)-2012]**

(1) $CO_2 < SiO_2 < SnO_2 < PbO_2$: increasing oxidising power

(2) B < C < O < N : increasing first ionisation enthalpy

(3) $NH_3 < PH_3 < AsH_3 < SbH_3$: increasing basic strength

(4) HF < HCl < HBr < HI : increasing acid strength

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26. The formation of molecular complex $BF_3 – NH_3$ results in a change in hybridisation of boron :-
[JEE(Main) Online–2012]

(1) from sp_3 to sp_3d
(2) from sp_2 to dsp_2
(3) from sp_3 to sp_2
(4) from sp_2 to sp_3

27. 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]

(1) 348, 260, 297
(2) 348, 297, 260
(3) 297, 348, 260
(4) 260, 297, 348

28. The gas evolved on heating CaF_2 and SiO_2 with concentrated H_2SO_4, on hydrolysis gives a white gelatinous precipitate. The precipitate is: **[Jee Main(Online)-2014]**

(1) silica gel
(2) silicic acid
(3) hydrofluosilicic acid
(4) calciumfluorosilicate

29. Which of the following series correctly represents relations between the elements from X to Y?

	$X \rightarrow Y$ **[Jee Main(Online)-2014]**
(1) $_{18}Ar \rightarrow {}_{54}Xe$	Noble character increases
(2) $_{3}Li \rightarrow {}_{19}K$	Ionization enthalpy increases
(3) $_{6}C \rightarrow {}_{32}Ge$	Atomic radii increases
(4) $_{9}F \rightarrow {}_{35}Br$	Electron gain enthalpy with negative sign increases

30. Which of the following statements about the depletion of ozone layer is correct?
[Jee Main(Online)-2014]

(1) The problem of ozone depletion is more serious at poles because ice crystals in the clouds over poles act as catalyst for photochemical reactions involving the decomposition of ozone by $Cl^\bullet$ and $ClO^\bullet$ radicals
(2) The problem of ozone depletion is less serious at poles because NO_2 solidifies and is not available for consuming $ClO^\bullet$ radicals
(3) Oxides of nitrogen also do not react with ozone in stratosphere
(4) Freons, chlorofluorocarbons, are inert chemically, they do not react with ozone in stratosphere

31. Which of the following xenon-OXO compounds may not be obtained by hydrolysis of xenon fluorides ? **[Jee Main(Online)-2014]**

(1) XeO_2F_2
(2) XeO_3
(3) XeO_4
(4) $XeOF_4$

32. Hydrogen peroxide acts both as an oxidising and as a reducing agent depending upon the nature of the reacting species. In which of the following cases H_2O_2 acts as a reducing agent in acid
medium ? **[Jee Main(Online)-2014]**

(1) MnO_4^-
(2) SO_3^{2-}
(3) KI
(4) $Cr2O_7$

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33. Consider the reaction **[Jee Main(Online)-2014]**

$H_2SO_{3(aq)} + Sn^{4+}_{(aq)} + H_2O_{(n)} \rightarrow Sn^{2+}_{(aq)} + HSO^{-}_{4(aq)} + 3H^{+}_{(aq)}$

Which of the following statements is correct?

(1) H_2SO_3 is the reducing agent because it undergoes oxidation

(2) H_2SO_3 is the reducing agent because it undergoes reduction

(3) Sn^{4+} is the reducing agent because it undergoes oxidation

(4) Sn^{4+} is the oxidizing agent because it undergoes oxidation

34. In the following sets of reactants which two sets best exhibit the amphoteric character of $Al_2O_3.\ xH_2O$? **[JEE(Main) Online–2014]**

Set-1 : $Al_2O_3.xH_2O(s)$ and OH^- (aq)

Set-2 : $Al_2O_3.xH_2O(s)$ and H_2O (ℓ)

Set-3 : $Al_2O_3.xH_2O(s)$ and H^+ (aq)

Set-4 : $Al_2O_3.xH_2O(s)$ and NH_3 (aq)

(1) 1 and 2 (2) 2 and 4 (3) 1 and 3 (4) 3 and 4

35. Which of the following compounds has a P-P bond :- [Jee Main(Online)-2015]

(1) $H_4P_2O_5$ (2) $(HPO_3)_3$ (3) $H_4P_2O_7$ (4) $H_4P_2O_6$

36. Chlorine water on standing loses its colour and forms :- **[Jee Main(Online)-2015]**

(1) HCl and $HClO_2$ (2) HCl only

(3) HOCl and $HOCl_2$ (4) HCl and HOCl

37. Which among the following is the most reactive ? **[Jee Main-2015]**

(1) I_2 (2) IC_l (3) Cl_2 (4) Br_2

38. Which one has the highest boiling point ? **[Jee Main-2015]**

(1) Kr (2) Xe (3) He (4) Ne

39. From the following statements regarding H_2O_2, choose the incorrect statement :

[Jee Main-2015]

(1) It has to be stored in plastic or wax lined glass bottles in dark

(2) It has to be kept away from dust

(3) It can act only as an oxidizing agent

(4) It decomposes on exposure to light

40. The reaction of zinc with dilute and concentrated nitric acid, respectively produces :

[JEE (Main) 2016]

(1) NO_2 and N_2O (2) N_2O and NO_2 (3) NO_2 and NO (4) NO and N_2O

41. The non-metal that does not exhibit positive oxidation state is : **[JEE (Main) 2016]**
(1) Oxygen (2) Fluorine (3) Iodine (4) Chlorine

42. Which intermolecular force is most responsible in allowing xenon gas to liquefy? **[JEE (Main) Online 2016]**
(1) Ionic (2) Instantaneous dipole- induced dipole
(3) Dipole – dipole (4) Ion - dipole

43. The following statements concern elements in the periodic table. Which of the following is true ? **[JEE (Main) Online 2016]**
(1) The group 13 elements are all metals.
(2) For group 15 elements, the stability of +5 oxidation state increases down the group.
(3) All the elements in Group 17 are gases.
(4) Elements of group 16 have lower ionization enthalpy values compared to those of group 15 in the corresponding periods.

44. **Assertion :** Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity. **[JEE (Main) Online 2016]**
Reason : Hybridization of carbon in diamond and graphite are sp^3 and sp^2, respectively.
(1) Assertion is incorrect statement, but the reason is correct.
(2)Both assertion and reason are correct, and the reason is the correct explanation for the assertion.
(3) Both assertion and reason are incorrect.
(4) Both assertion and reson are correct, but the reason is not the correct explanation for the assertion.

45. Identify the incorrect statement : **[JEE (Main) Online 2016]**
(1) S_8 ring has a crown shape.
(2) The S–S–S bond angles in the S_8 and S_6 rings are the same
(3) S_2 is paramagnetic like oxygen
(4) Rhombic and monoclinic sulphur have S_8 molecules.

46. The product obtained when chlorine reacts with cold and dilute aqueous NaOH are : **[JEE-Main 2017]**
(1) ClO^- and ClO_3^- (2) ClO_2^- and ClO_3^- (3) Cl^- and ClO^- (4) Cl^- and ClO_2^-

47. In graphite and diamond, the percentage of p-characters of the hybrid orbitals in hybridisation are respectively : **[Main-2018(Online)]**
(1) 33 and 25 (2) 33 and 75 (3) 50 and 75 (4) 67 and 75

48. In the following sets of reactants which two sets best exhibit the amphoteric character of $Al_2O_3.xH_2O$? **[Main-2018(Online)]**
Set-1 : $Al_2O_3.xH_2O(s)$ and OH^- (aq) Set-2 : $Al_2O_3.xH_2O(s)$ and H_2O (ℓ)
Set-3 : $Al_2O_3.xH_2O(s)$ and H^- (aq) Set-4 : $Al_2O_3.xH_2O(s)$ and NH_3 (aq)
(1) 1 and 2 (2) 2 and 4 (3) 1 and 3 (4) 3 and 4

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49. The compound that does not produce nitrogen gas by the thermal decomposition is **[Main-2018(Online)]**

(1) $(NH_4)_2SO_4$ (2) $Ba(N_3)_2$ (3) $(NH_4)_2Cr_2O_7$ (4) NH_4NO_2

50. Good reducing nature of H_3PO_2 is attributed to the presence of : **[Main-2019(Online)]**

(1) Two P–H bonds (2) One P–OH bond (3) One P–H bond (4) Two P–OH bonds

51. Among the following reactions of hydrogen with halogens, the one that requires a catalyst is : **[Main-2019(Online)]**

(1) $H_2 + Br_2 \rightarrow 2HBr$ (2) $H_2 + F_2 \rightarrow 2HF$ (3) $H_2 + I_2 \rightarrow 2HI$ (4) $H_2 + Cl_2 \rightarrow 2HCl$

52. The pair that contains two P–H bonds in each of the oxoacids is: **[Main-2019(Online)]**

(1) $H_4P_2O_5$ and H_3PO_3 (2) $H_4P_2O_5$ and $H_4P_2O_6$
(3) H_3PO_2 and $H_4P_2O_5$ (4) H_3PO_3 and H_3PO_2

53. Iodine reacts with concentrated HNO_3 to yield Y along with other products. The oxidation state of iodine in Y is : **[Main-2019(Online)]**

(1) 5 (2) 1 (3) 3 (4) 7

54. The element that does NOT show catenation is: **[Main-2019(Online)]**

(1) Si (2) Ge (3) Pb (4) Sn

55. Chlorine on reaction with hot and concentrated sodium hydroxide gives : **[Main-2019(Online)]**

(1) ClO_3^- and ClO_2^- (2) Cl^- and ClO_2^- (3) Cl^- and ClO^- (4) Cl^- and ClO_3^-

56. The element that shows greater ability to form $p-{}_{\pi}p_{\pi}$ multiple bond, is : **[Main-2019(Online)]**

(1) Si (2) C (3) Sn (4) Ge

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EXERCISE-V (JEE-ADVANCED)

(IIT JEE ASKED QUESTIONS)

Fill in the blanks

1. The hydrolysis of alkyl substituted chlorosilanes given..... **[1991]**

2. The hydrolysis of trialkychlorosilane R_3 SiCl, yields ...... **[1994]**

3. One recently discovered allotrope of carbon (e.g., C_{60}) is commonly known as .... **[1994]**

True/False

4. Carbon tetrachloride burns in air when lighted to give phosgene. **[1983]**

5. Graphite is a better lubricant on the moon than on the earth. **[1987]**

6. All the Al—Cl bonds in Al_2Cl_6 are equivalent. **[1989]**

7. Diamond is harder than graphite. **[1993]**

8. The basic nature of the hydroxides of group 13 (Gr. IIIB) decreases progressively down the group. **[1993]**

9. The tendency for catenation is much higher for C than for Si. **[1993]**

10. Complete and balance the following chemical equations – **[IIT-1998, 2 M]**

(i) $P_4O_{10} + PCl_5 \longrightarrow$ (ii) $SnCl_4 + C_2H_5Cl + Na \longrightarrow$

11. Work out the following using chemical equations **[IIT- 1998, 2M]**

"Chlorination of calcium hydroxide produces bleaching powder"

12. Hydrogen peroxide acts both as an oxidizing and as a reducing agent in alkaline solution towards certain first row transition metal ion. Illustrate both these properties of H_2O_2 using chemical equations – **[IIT- 1998, 4 M]**

13. In the contact process for industrial manufacture of sulphuric acid, some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of SO_2? **[IIT- 1998,4 M]**

14. Give reasons in one or two sentences for each of the following : **[1985]**

(i) Graphite is used as a solid lubricant,

(ii) Fluorine cannot be prepared from fluorieds by chemical oxidation.

15. Write balanced equations for : **[1990]**

(i) The preparation of crystalline silicon from $SiCl_4$

(ii) The preparation of phosphine from CaO and white phosphorus

(iii) The preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide.

16. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. **[1997]**

Ionisation energy for Al = 5137 kJ mol^{-1}

$\Delta H_{hydration}$ for Al^{3+} = –4665 kJ mol^{-1}

$\Delta H_{hydration}$ for Cl^{-} = –381 kJ mol^{-1}

17. Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. **[1997]**

18. Draw the structure of a cyclic silicate, $(Si_3O_9)^{6-}$ with proper labelling – **[IIT-1998]**

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19. Give reasons for the following in one or two sentences only. **[IIT- 1999]**
"$BeCl_2$ can be easily hydrolysed."

20. Give reason : **[IIT- 2000]**
Why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetra atomic molecule.

21. Give an exapmle of oxidation of one halide by another halogen. Explain the feasibility of the reaction. **[IIT- 2000]**

22. Compounds X on reduction with $LiAlH_4$ gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air Draw the structure of Y. **[IIT- 2001]**

23. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parenthesis (reactions only) **[IIT- 2001]**

(i) Silicon (1)

(ii) Linear silicon containing methyl group only (4)

(iii) Na_2SiO_3 (3)

24. Write the balanced chemical equation for developing photographic films. **[IIT- 2001]**

25. Identify (X) in the following synthetic scheme and write their structures. **[IIT- 2001]**

$$Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow X \text{ (gas) (C denotes } C^{14})$$

26. Write the balanced equations for the reactions of the following compounds with water **[2002]**

(i) Al_4Cl_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_3

27. Write the balanced equations for the reactions of the following compounds with water: **[IIT- 2002]**

(i) Al_4C_3 (ii) CaNCN (iii) BF_3 (iv) NCl_3 (v) XeF_4

28. Identify the following: **[IIT- 2003]**

$$\underset{(aq)}{Na_2CO_3} \xrightarrow{SO_2} A \xrightarrow{Na_2CO_3} B \xrightarrow[\Delta]{\text{elemental S}} C \xrightarrow{I_2} D$$

Also mention the oxidation state of S in all the compounds.

29. Arrange the following oxides in the increasing order of Bronsted basicity. **[IIT- 2004]**
Cl_2O_7, BaO,SO_3, CO_2, B_2O_3

30. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with : **[1990]**

(A) H^+ ions (B) Ca^{2+} ions (C) SO_4^{2-}ions (D) Mg^{2+} ions

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31. Which of the following halides is least stable and has doubtful existence ? **[1996]**
(A) CCl_4 (B) GeI_4 (C) SnI_4 (D) PbI_4

32. The number of P—O—P bonds in cyclic tetrametaphosphoric acid is – **[IIT-2000]**
(A) Zero (B) Two (C) Three (D) Four

33. The correct order of acidic strength is – **[IIT- 2000]**
(A) $Cl_2O_7 > SO_2 < P_4O_{10}$
(B) $CO_2 > N_2O_5 > SO_3$
(C) $Na_2O > MgO > Al_2O_3$
(D) $K_2O > CaO > MgO$

34. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is – **[IIT- 2000]**
(A) H_2O because of hydrogen bonding
(B) H_2Te because of higher molecular weight
(C) H_2S because of hydrogen bonding
(D) H_2Se because of lower molecular weight.

35. Ammonia can be dried by – **[IIT- 2000]**
(A) Conc. H_2SO_4 (B) P_4O_{10} (C) CaO (D) Anhydrous $CaCl_2$

36. Which of the following are hydrolysed – **[REE 2000]**
(A) NCl_3 (B) BCl_3 (C) CCl_4 (D) $SiCl_4$

37. The set with correct order of acidity is – **[IIT- 2001]**
(A) $HClO < HClO_2 < HClO_3 < HClO_4$
(B) $HClO_4 < HClO_3 < HClO_2 < HClO$
(C) $HClO < HClO_4 < HClO_3 < HClO_2$
(D) $HClO_4 < HClO_2 < HClO_3 < HClO$

38. – The reaction, $3ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$ is an example of – **[IIT- 2001]**
(A) Oxidation reaction
(B) reduction reaction
(C) Disproportionation reaction
(D) Decomposition reaction

39. The number of S–S bonds in sulphur trioxide trimer, (S_3O_9) is – **[IIT- 2001]**
(A) Three (B) Two (C) One (D) Zero

40. **Statement-I :** Between $SiCl_4$ and CCl_4, only SiCl4 reacts with water **[IIT- 2001]**
Because :
Statement-II : $SiCl_4$ is ionic and CCl_4 is covalent
(A) If both assertion and reason are correct and reason is the corect explanation of the assertion
(B) If both assertion and reason are correct, but reason is not the correct explanation of the assertion
(C) If assertion is correct, but reason is incorrect
(D) If assertion is incorrect, but reason is correct.

41. Polyphosphates are used as water softening agents because they – **[IIT- 2002]**
(A) Form soluble complexes with anionic species
(B) Precipitate anionic species
(C) Form soluble complexes with cationic species
(D) Precipitate cationic species

42. Identify the correct order of solubility of Na_2S, CuS, and ZnS in aqueous medium – **[IIT- 2002]**
(A) CuS > ZnS > Na_2S (B) ZnS > Na_2S > CuS
(C) Na_2S > CuS > ZnS (D) Na_2S > ZnS > CuS

43. Identify, the correct order of acidic strength of CO_2, CuO, CaO, H_2O – **[IIT- 2002]**
(A) CaO < CuO < H_2O < CO_2 (B) H_2O < CuO < CaO < CO_2
(C) CaO < H_2O < CuO < CO_2 (D) H_2O < CO_2 < CaO < CuO

44. H_3BO_3 is – **[IIT- 2002, 3]**
(A) Monobasic acid and weak Lewis acid (B) Monobasic and weak Bronsted acid
(C) Monobasic and strong Lewis acid (D) Tribasic and weak Bronsted acid

45. When I^- is oxidised by MnO_4^- in alkaline medium, I^- converts into – **[IIT- 2003]**
(A) IO_3^- (B) I_2 (C) IO_4^- (D) IO^-

46. **[IIT- 2003]**

Column-I (Change)		**Column-II (Given change is done by)**	
(A)	$Bi^{3+} \longrightarrow (BiO)^+$	(p)	Heat
(B)	$[AlO_2]^- \longrightarrow Al(OH)_3$	(q)	Hydrolysis
(C)	$SiO_4^{4-} \longrightarrow Si_2O_7^{6-}$	(r)	Acidification
(D)	$(B_4O_7^{2-}) \longrightarrow [B(OH)_3]$	(s)	Dilution by water

47. $(Me)_2\ SiCl_2$ on hydrolysis will produce – **[IIT- 2003]**
(A) $(Me)_2Si(OH)_2$ (B) $(Me)_2Si = O$
(C) $[—O—(Me)_2\ Si—O—]_n$ (D) $Me_2SiCl(OH)$

48. Which is the most thermodynamically stable allotropic form of phosphorus? **[IIT- 2004]**
(A) Red (B) White (C) Black (D) Yellow

49. When PbO_2 reacts with conc. HNO_3 the gas evolved may be : **[IIT- 2004]**
(A) NO_2 (B) O_2 (C) N_2 (D) N_2O

50. Which of the following is not oxidised by O_3? **[IIT- 2005]**
(A) KI (B) $FeSO_4$ (C) $KMnO_4$ (D) K_2MnO_4

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51. Which blue-liquid is obtained on reacting equimolar amounts of two gases at – 30ºC ? **[IIT- 2005]**
(A) N_2O (B) N_2O_3 (C) N_2O_4 (D) N_2O_5

52. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$ how can this reaction is made to proceed in forward direction ? **[IIT- 2006]**
(A) Addition of cis 1, 2 diol (B) Addition of borax
(C) Addition of trans 1, 2 diol (D) Addition of Na_2HPO_4

53. Among the following, the paramagnetic compound is – **[IIT- 2007]**
(A) Na_2O_2 (B) O_3 (C) N_2O (D) KO_2

54. **Statement-I :** Boron always forms covalent bond **[IIT-2007]**
Because :
Statement-II : The small size of B^{3+} favours formation of covalent bond.
(A) Statement-I is True, Statement-II is Ture, Statement-II is a correct explanation for Statement-I
(B) Statement-I is Ture, Statement-II is Ture, Statement-II is not a correct explanation for Statement-II
(C) Statement-I is Ture, Statement-II is False
(D) Statement-I is False, Statement-II is Ture

55. **Statement-I :** In water, orthoboric acid behaves as a weak monobasic acid. **[IIT-2007]**
Statement-II : In water, orthoboric acid acts as a proton donor.
(A) Statement-I is True, Statement-II is Ture, Statement-II is a correct explanation for Statement-I
(B) Statement-I is Ture, Statement-II is Ture, Statement-II is not a correct explanation for Statement-II
(C) Statement-I is Ture, Statement-II is False
(D) Statement-I is False, Statement-II is Ture

Comprehension # 1 (Q. 56 to 58)

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling point of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions. The direct reaction of xenon with fluorine leads to a series of compounds with oxidation number + 2, + 4 and + 6. XeF_4 reacts violently with water to give XeO_3. The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell. **[IIT- 2007]**

56. 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

57. The structure of XeO_3 is –
(A) Linear (B) Planar (C) Pyramidal (D) T-shaped

58. XeF_4 and XeF_6 are expected to be –
(A) Oxidising agent (B) Reducing agent (C) Unreactive (D) Strongly basic

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Comprehension # 2 (Q.59 to 61)

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorous. **[IIT- 2008]**

59. Among the following, the correct statement is :-
(A) Phosphates have no biological significance in humans
(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust
(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust
(D) Oxidation of nitrates is possible in soil

60. 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.

61. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a :-
(A) dimerization reaction (B) disproportionation reaction
(C) condensation reaction (D) precipitation reaction

62. The reaction of P_4 with X leads selectively to P_4O_6. The X is **[JEE 2009]**
(A) Dry O_2 (B) A mixture of O_2, and N_2
(C) Moist O_2 (D) O_2 in the presence of aqueous NaOH

63. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type ; the oxidation states of phosphorus in phosphine and the other product are respectively **[JEE 2012]**
(A) redox reaction ; -3 and –5 (B) redox reaction ; +3 and +5
(C) disproportionation reaction ; -3 and +1 (D) disproportionation reaction ; -3 and +3

64. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is : **[JEE 2012]**
(A) Cl_2O (B) Cl_2O_7 (C) ClO_2 (D) Cl_2O_6

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65. With respect to graphite and diamond, which of the statement(s) given below is (are) correct ?
(A) Graphite is harder than diamond. **[JEE 2012]**
(B) Graphite has higher electrical conductivity than diamond.
(C) Graphite has higher thermal conductivity than diamond.
(D) Graphite has higher C–C bond order than diamond.

66. Concentrated nitric acid, upon long standing, turns yellow-brown due to the formation of -
(A) NO (B) NO_2 (C) N_2O (D) N_2O_4 **[JEE 2013]**

67. The correct statement(s) about O_3 is(are) **[JEE 2013]**
(A) O–O bond lengths are equal
(B) Thermal decomposition of O_3 is endothermic
(C) O_3 is diamagnetic in nature
(D) O_3 has a bent structure

Comprehension # 3 (Q. 68 and 69)

The reaction of Cl_2 gas with cold dilute and hot concentrated NaOH in water give sodium salt of two (different) oxoacids of chlorine P and Q respectively. The Cl_2 gas reacts with SO_2 gas , in presence of charcoal to give a product R. R reacts with white phosphorous to give a compound S. On hydrolysis, S gives as oxoacid of phosphorous T.

68. R, S and T, respectively are - **[JEE 2013]**
(A) SO_2Cl_2, PCl_5 and H_3PO_4
(B) SO_2Cl_2, PCl_3 and H_3PO_3
(C) $SOCl_2$, PCl_3 and H_3PO_2
(D) SO_2Cl_2, PCl_5 and H_3PO_4

69. P and Q, respectively, are the sodium salts of -
(A) Hypochlorus and chloric acid
(B) Hypochlorus and chlorus acid
(C) Chloric and perchloric acids
(D) Chloric and hypochlorus acids

70. The unbalanced chemical reactions given in List-I show missing reagent or condition (?) which are provided in List-II. Match List-I with List-II and select the correct answer using the code given below the lists :A **[JEE 2013]**

	List-I		**List-II**
(P)	$PbO_2 + H_2SO_4 \xrightarrow{?} PbSO_4 + O_2$ + other product	(1)	NO
(Q)	$Na_2S_2O_3 + H_2O \xrightarrow{?} NaHSO_4$ + other product	(2)	I_2
(R)	$N_2H_4 \xrightarrow{?} \overset{o}{N}_2$ + other product	(3)	Warm
(S)	$XeF_2 \xrightarrow{?} Xe$ + Other product	(4)	Cl_2

Codes :

	P	Q	R	S
(A)	4	2	3	1
(B)	3	2	1	4
(C)	1	4	2	3
(D)	3	4	2	1

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71. Under ambient conditions, the total number of gases released as products in the final step of the reaction scheme shown below is **[JEE Adv. 2014]**

$$XeF_6 \xrightarrow[\text{Hydrolysis}]{\text{Complete}} P + \text{other product}$$

$$P \xrightarrow{OH^- / H_2O} Q$$

$$Q \xrightarrow{\text{slow disproportionation in } OH^-/H_2O} \text{products}$$

(A) 0 (B) 1 (C) 2 (D) 3

72. The product formed in the reaction of $SOCl_2$ with white phosphorous is **[JEE Adv. 2014]**

(A) PCl_3 (B) SO_2Cl_2 (C) SCl_2 (D) $POCl_3$

73. The correct statements(s) for orthoboric acid is / are - **[JEE Adv. 2014]**

(A) It behaves as a weak acid in water due to self ionization

(B) Acidity of its aqueous solution increses upon addition of ethylene glycol

(C) It has a three dimensional structure due to hydrogen bonding.

(D) It is a weak electrolyte in water

74. The correct statement(s) regarding, (i) HClO, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$, is(are)

(A) The number of Cl=O bonds in (ii) and (iii) together is two **[JEE Adv. 2015]**

(B) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three

(C) The hybridization of Cl in (iv) is sp^3

(D) Amongst (i) to (iv), the strongest acid is (i)

75. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The **TRUE,** statement (s) regarding this adsorption is (are) **[JEE Adv. 2015]**

(A) O_2 is physisorbed (B) heat is released

(C) occupancy of π^*_{2p} of O_2 is increased (D) bond length of O_2 is increased

76. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are **[JEE (Adv.) 2015]**

(A) CH_3SiCl_3 and $Si(CH_3)_4$ (B) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$

(C) $(CH_3)_2SiCl_2$ and CH_3SiCl_3 (D) $SiCl_4$ and $(CH_3)_3SiCl$

77. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is - **[JEE (Adv.) 2015]**

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78. The increasing order of atomic radii of the following group 13 elements is : **[JEE Adv. 2016]**

(A) Al < Ga < In < Tl (B) Ga < Al < In < Tl

(C) Al < In < Ga < Tl (D) Al < Ga < Tl < In

79. The crystalline form of borax has **[JEE Adv. 2016]**

(A) Tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit

(B) All boron atoms in the same plane

(C) Equal number of sp^2 and sp^3 hybridized boron atoms

(D) One terminal hydroxide per boron atom

80. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}

(A) can also be prepared by reaction of P_4 and HNO_3 **[JEE Adv. 2016]**

(B) is diamagnetic

(C) contains one N-N bond

(D) reacts with Na metal producing a brown gas

PARAGRAPH Q.81 to 82

Upon heating $KClO_3$ in the presence of catalytic amount of MnO_2, a gas W is formed. Excess amount of W reacts with white phosphorus to give X. The reaction of X with pure HNO_3 gives Y and Z. **[JEE(Advanced) 2017]**

81. W and X are, respectively

(A) O_2 and P_4O_6 (B) O_3 and P_4O_{10} (C) O_3 and P_4O_6 (D) O_2 and P_4O_{10}

82. Y and Z are, respectively

(A) N_2O_4 and HPO_3 (B) N_2O_3 and H_3PO_4 (C) N_2O_5 and HPO_3 (D) N_2O_4 and H_3PO_3

83. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are) **[JEE(Advanced) 2018]**

(A) NH_4NO_3 (B) $(NH_4)_2Cr_2O_7$ (C) $Ba(N_3)_2$ (D) Mg_3N_2

84. A tin chloride Q undergoes the following reactions (not balanced) **[JEE(Advanced) 2019]**

$Q + Cl^- \rightarrow X$

$Q + Me_3N \rightarrow Y$

$Q + CuCl_2 \rightarrow Z + CuCl$

X is a monoanion having pyramidal geometry. Both Y and Z are neutral compounds.

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Choose the correct option(s)

(1) There is a coordinate bond in Y

(2) The central atom in Z has one lone pair of electrons

(3) The central atom in X is sp3 hybridized

(4) The oxidation state of the central atom in Z is +2

85. With reference to aqua regia, choose the correct options(s) **[JEE(Advanced) 2019]**

(1) Reaction of gold with aqua regia produces NO_2 in the absence of air

(2) Reaction of gold with aqua regia produces an anion having Au in +3 oxidation state

(3) Aqua regia is prepared by mixing conc. HCl and conc. HNO_3 in 3 : 1 (v/v) ratio

(4) The yellow colour of aqua regia is due to the presence of NOCl and Cl_2

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ANSWER KEY

EXERCISE-I

1.	C	**2.**	C	**3.**	B	**4 .**	A	**5 .**	B	**6.**	B	**7.**	D
8.	C	**9.**	B	**10.**	B	**11.**	A	**12.**	A	**13.**	A	**14.**	B
15.	B	**16.**	A	**17.**	B	**18.**	A	**19.**	A	**20.**	A	**21.**	B
22.	C	**23.**	B	**24.**	D	**25.**	A	**26.**	A	**27.**	B	**28.**	B
29.	C	**30.**	B	**31.**	A	**32.**	D	**33.**	A	**34.**	B	**35.**	C
36.	C	**37.**	B	**38.**	C	**39.**	B	**40.**	D	**41.**	A	**42.**	A
43.	B	**44.**	C	**45.**	A	**46.**	C	**47.**	A				

EXERCISE-II

1.	A,B	**2.**	A,B,C	**3.**	A,C,D	**4.**	A,B,C	**5.**	A,B,D
6.	A,B	**7.**	A,B,C	**8.**	A,B,C	**9.**	A,B,C,D	**10.**	A, C,
11.	A,B,C,D	**12.**	C,D	**13.**	C,D	**14.**	A,B,C,D	**15.**	A,B,D
16.	B,C,D	**17.**	A,B,C,D						

EXERCISE-III

1.	B	**2.**	A	**3.**	D	**4.**	A	**5.**	C	**6.**	D	**7.**	A
8.	B	**9.**	A	**10.**	A	**11.**	C	**12.**	B	**13.**	B	**14.**	C
15.	B	**16.**	B	**17.**	C	**18.**	A						

EXERCISE-IV(JEE-MAIN)

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

EXERCISE-IV(JEE- ADVANCED)

Fill in the blanks

1. Silicones **2.** $R_3Si(OH)$ **3.** Buckminstre fullerene

True/False

4. F **5.** T **6.** F **7.** T **8.** F **9.** T

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Subjective

10. (i) $P_4O_{10} + 6PCl_3 \longrightarrow 10POCl_3$ (ii) $SnCl_4 + 2C_2H_5Cl + 2Na \longrightarrow Na_2SnCl_6 + C_4H_{10}$

11. $3Ca(OH)_2 + 2Cl_2 \longrightarrow \underbrace{Ca(OCl)_2 + Ca(OH)_2\, CaCl_2 \cdot 2H_2O}_{\text{Bleaching powder is a mixture of } CaOCl_2 \text{ And hydrated basic calcium chloride.}}$

12. When H_2O_2 acts as oxidizing agent, therefore, following reaction takes place:

$$H_2O_2 + 2e^- \longrightarrow 2OH^-$$

while, regarding is action on reducing agent, the following reaction takes place :

$$H_2O_2 + 2OH^- \longrightarrow O_2 + 2H_2O + 2e^-$$

Oxidizing character :

$$2Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

Reducing character:

$$2K_3\,[Fe(CN)_6] + 2KOH + H_2O_2 \longrightarrow 2K_4\,[Fe(CN)_6] + 2H_2O + O_2$$

13. In $SO_3 + H_2O \longrightarrow H_2SO_4$ reaction, H_2SO_4 is obtained in misty form and reaction is explosive (highly exothermic). By adding H_2SO_4 the above reaction is prevented.

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

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The catalyst used is V_2O_5 and K_2O is used as promotor for the oxidation of SO_2 into SO_3.

14. (i) Graphite, hexagonal planes are held by weak van der Waals forces. Since these forces are overcome, one plane slides over the other. This explains the lubricating properties of graphite.

(ii) Fluoride has negative oxidation potential

$$2F^- \longrightarrow F_2 + 2e^-,\ E_{OP} = -2.87 \text{ volts}$$

Hence, fluoride is the poorest reducing agent.

Hence, F_2 can't be prepared by oxidation of HF by even strong oxidising agents such as $KMnO_4$, MnO_2 etc.

15. (i) $$\underset{\text{vapour}}{3SiCl_4} + \underset{\text{molten}}{4Al} \xrightarrow{\Delta} \underset{\text{volatilized}}{4AlCl_3} + 3Si$$

(ii) $$15CaO + 4P_4 \xrightarrow{\Delta} 5Ca_3P_2 + 3P_2O_5\uparrow$$

$$[Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3\uparrow] \times 5$$

$$15CaO + 4P_4 + 30H_2O \rightarrow 15CaO(OH)_2 + 3P_2O_5\uparrow + 10\,PH_3\uparrow$$

(iii) $$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$$

$$\underset{\text{gypsum}}{CaSO_4} + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow (NH_4)_2SO_4$$

$$CaSO_4 + 2NH_3 + CO_2 + H_2O \rightarrow CaCO_3\downarrow + (NH_4)_2SO_4$$

16. Total hydration energy of Al^{3+} and $3Cl^-$ ions of $AlCl_3$

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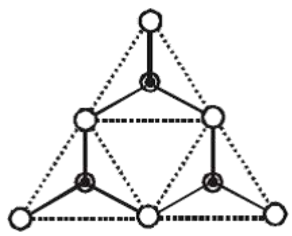
$(\Delta H_{hydration})$
= (Hydration energy of Al^{3+} + 3 × hydration energy of Cl^{-})
= [–4665 + 3(–381)] kJ mol^{-1} = 5808 kJ mol^{-1}
This amount of energy is more than that required for the ionisation of Al into Al^{3+} (Ionisation energy of Al to Al^{3+}). Due to this reason, $AlCl_3$ becomes ionic in aqueous solution. In aqeous solution, it exists in ionic form as below :
$AlCl_3 + 6H_2O \longrightarrow (Al(H_2O)_6^{3+} + 3Cl^{-}$

17. $Al_2S_3 + 6H_2O \rightarrow 2Al(OH)3\downarrow + 3H_2S$
foul odour
Foul odour, on damping of Al2S3 is due to formation of H2S gas.

18. In cyclic $(Si_3O_9)^{6-}$, three tetrahedral of SiO_4 are joined together by sharing of two oxygen atoms per tetrahedral.
Structure of $(Si_3O_9^{6-})$



In it dark circles (·) represent Si and open circles (O) represent oxygen atom or iron.

19. $BeCl_2$ is hydrolysed due to high polarising power and presence of vacant p-orbitals in Be atom.
(Be = $1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$)

20. In nitrogen, d-orbitals are not present, so in it the possiblity of intramolecular multiplicity exists which leads to the completion of octet through π-bond between two nitrogen atoms.
In phosphorus, d-orbitals are present, so in it due to large size of P, the P–P bonds are longer and hence intramolecular multiplicity is ruled out. So, for the completion of octet, it forms the bonds with three other 'P' atoms. Hence due to this reason it shows molecular formula as P_4.

21. $2I^{-}$ (aqueous) + $Cl_2 \longrightarrow I_2 + 2Cl^{-}$ (aqueous)
(i) $2I^{-}$ (aqueous) $\longrightarrow I_2$ (s) + $2e^{-}$
(ii) Cl_2 (g) + $2e^{-} \longrightarrow 2Cl^{-}$ (aq)
Thus, I^{-} is oxidised into I_2 by Cl_2 due to higher oxidised potential of Cl_2 than I_2

22. X : BCl_3
Y : B_2H_6
$4BCl_3 + 3LiAlH_4 \longrightarrow 3AlCl_3 + 3LiCl + 2B_2H_6$
X
$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$ (exothermic)
Y

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23. (i) $3\,SiCl_4 + 4Al \longrightarrow 3Si + 4AlCl_3$ (in one step)

(ii) $SiCl_4 + 2Mg \longrightarrow 2MgCl_2 + Si$

$Si + Cu \longrightarrow Si - Cu$

$2CH_3Cl + Si\text{–}\,Cu \longrightarrow (CH_3)_2\,SiCl_2 + Cu$

$(CH_3)_2SiCl_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl$

$$2(CH_3)_2Si(OH)_2 \xrightarrow[-H_2O]{\Delta} H—O—\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}—O—\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{Si}}}}—OH$$

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

$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O$

$SiO_2 + Na_2CO_3 \xrightarrow[1673K]{\Delta} Na_2SiO_3 + CO_2$

24. Unreacted AgBr is removed by hypo ($Na_2S_2O_3$)

$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

25. $14CO_2$

26. **(i)** $Al_4Cl_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4\uparrow$

(ii) $CaNCN + 3H_2O \longrightarrow CaCO_3\downarrow + 2NH_3$

(iii) $4BF_3 + 3H_2O \longrightarrow \underset{\text{boric acid}}{H_3BO_3} + \underset{\text{fluoboric acid}}{3HBF_4}$

(iv) $NCl_3 + 3H_2O \longrightarrow NH_3 + \underset{\text{hypochlorous acid}}{3HOCl}$

(iv) $2XeF_4 + 3H_2O \longrightarrow Xe + \underset{\text{xenon trioxide}}{XeO_3} + F_2 + 6HCl$

27. (i) $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

(ii) $CaNCN + 3H_2O \longrightarrow CaCO_3 + 2NH_3$

(iii) $BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$

$3HF + 3BF_3 \longrightarrow 3HBF_4$

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

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28. Oxidation state

(A) : $NaHSO_3$ + 4 (B) : Na_2SO_3 + 4 (C) : $Na_2S_2O_3$ + 2 (D) : $Na_2S_4O_6$ + 2.5

29. $Cl_2O_7 < SO_3 < CO_2 < B_2O_3 < BaO$

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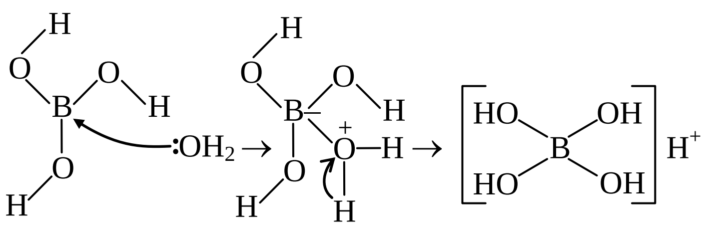
Objective

30. BD **31.** D **32.** D **33.** A **34.** A **35.** C **36.** ABD
37. A **38.** C **39.** D **40.** C **41.** C **42.** D **43.** A
44. A **45.** A
46. (A) $\rightarrow$ Q, S ; (B) $\rightarrow$ R, S ; (C) $\rightarrow$ P ; (D) $\rightarrow$ Q, R
47. C **48.** C **49.** B **50.** C **51.** B **52.** A **53.** D
54. A

Boron always forms covalent bond because boron requires very high energy of form B^{3+} and again B^{3+} due to its very small size having high polarising power thus cause greater polarisation and eventually significant covalent characteristics-Fajans rule.

55. C



Comprehension # 1 **(Q. 56 to 58)**

56. A **57.** C **58.** A

Comprehension # 2 **(Q.59 to 61)**

59. C **60.** C **61.** B **62.** B **63.** C **64.** A **65.** B,D
66. B **67.** A,C,D

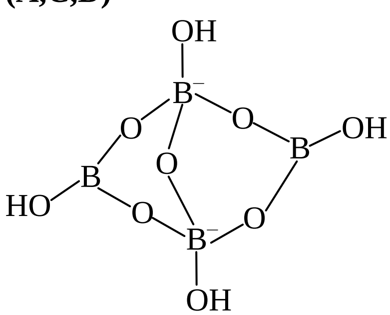
Comprehension # 3 **(Q. 68 and 69)**

68. A **69.** A **70.** D **71.** C **72.** A **73.** B,D **74.** B,C
75. B,C,D **76.** B **77.** 6
78. (B)

Sol. The order of radius of 13^{th} group elements is Ga < Al < In < Tl.
Reason $\Rightarrow$ Due to poor shielding effect of d-orbital, radius of Ga is smallar than Al.

79. **(A,C,D)**

Sol.



(A) Having $[B_4O_5(OH)_4]^{2-}$ tetranuclear (boron) unit
(B) All boron atoms not in same plane
(C) Two boron are sp^2 hybridised and two boron are sp^3 hybridised
(D) One terminal hydroxide per boron atom is present.

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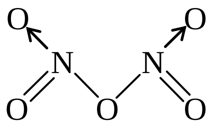
80. **(B,D)**

Sol. $P_4O_{10} + 4HNO_3 \xrightarrow{\text{dehydration } HNO_3} \underset{\text{(required product)}}{4(HPO_3) + 2N_2O_5}$

(A) $P_4 + 20\ HNO_3 \rightarrow 4H_3PO_4 + 20NO_2\uparrow + 4H_2O$

(B) N_2O_5 is diamagnetic in nature

(C) $N_2O_5 \rightarrow$ 

(D) $Na + N_2O_5 \rightarrow NaNO_3 + \underset{\text{(Brown gas)}}{NO_2}\uparrow$

81. **(D)** **82.** **(C)** **83. (B,C)** **84. (1,3)** **85. (2,3,4)**