UNIT 13

Some p-Block Elements

SYLLABUS

Boron—occurrence, isolation, physical and chemical properties, borax, boric acid, boron hydrides, halides (elementary idea of boranes, diborane, borates). Uses of boron and its compounds.

Carbon—terrestrial abundance and distribution, allotropes (graphite, diamond, elementary idea of fullerenes). Atomic and physical properties, chemical properties, oxides, carbides, halides, sulphides, uses of carbon.

Nitrogen—terrestial abundance and distribution, dinitrogen—isolation, atomic and physical properties, chemical reactivity, fixation of nitrogen—industrial and biological.

Ammonia—industrial preparation, Haber's process only, important properties and reactions.

Oxides of nitrogen—preparation, structure (skeletal only), $p\pi - p\pi$ bonding. Nitric acid—industrial production (Ostwald process). Uses of nitrogen and its compounds.

Oxygen—terrestrial abundance and distribution. Dioxygen—atomic and physical properties. chemical reactivity. Oxides—acidic, basic and amphoteric.

Ozone—preparation, structure and some oxidising properties

13.1. General Introduction

What are p-Block elements ? Elements in which the last electron enters any of the three *p*-orbitals of their respective outermost shells are called *p*-block elements. Since a *p*-subshell has three degenerate (same energy) *p*-orbitals, each of which can accommodate two electrons, therefore, in all, there are six groups of *p*-block elements, *i.e.*, groups 13, 14, 15, 16, 17 and 18 (excluding helium). The atoms of elements of these groups receive their last electrons in $2p$, $3p$, $4p$, $5p$ and $6p$-orbitals.

General chemical behaviour. The elements in the periodic table have been divided into four groups, *i.e.*, *s*-, *p*-, *d*- and *f*-. Out of these four blocks of elements, *p*-block is the only one, of course with few exceptions, which contain non-metallic elements. These elements display diverse chemistry depending on the group to which they belong.

In general,

(*i*) Non-metals have higher ionization enthalpies and higher electronegativities than those of metals. Therefore, in contrast to metals which readily form cations, non-metals readily form anions.

(*ii*) The compounds formed by the union of metals with non-metals are generally ionic because of large differences in their electronegativities. Obviously, compounds resulting from the union of non-metals generally tend to be molecular in nature.

Difference in chemical behaviour of first element of each group. It is interesting to note that first member of each of the groups 13-17 of the *p*-block elements differs in many respects from other members of their respective groups. These differences are quite striking in groups 13-16. But, the elements of group 17, *i.e.*, halogens show much more similarity in their chemical behaviour than the elements of any other group. The main reasons for the different chemical behaviour of the first member of a particular group of elements in the *p*-block compared to other members of the same group are presumably its small size, high electronegativity and absence of *d*-orbitals. For example,

(*i*) First member of each group has only four valence orbitals (one 2*s*- and there 2*p*-orbitals) available for bonding and hence at the maximum can accommodate four pairs or 8 electrons. In other words, these elements cannot expand their valence shell and hence seldom form-compounds in which the coordination number exceeds four.

(*ii*) Because of smaller size and higher electronegativity, first member of each group shows greater ability to form $p\pi - p\pi$ multiple bonds either with itself (*e.g.*, $C = C$, $C \equiv C$, $N \equiv N$) or with other members of the second row of elements (*e.g.*, $C = O$, $C = N$, $C \equiv N$, $N = O$) as compared to the subsequent members of the same group. In other words, elements of third and subsequent rows of the periodic table do not exhibit any strong tendency for this type of multiple π-bonding.

In this unit, we shall study the chemistry of *boron, carbon, nitrogen* and *oxygen*, the first members of groups 13 – 16. Among these, carbon forms the basis of all forms of life on this planet since all, *biomolecules* (*i.e.*, molecules of life) are essentially made up of carbon, nitrogen and oxygen.

13.2. Boron

Boron is the first member of group 13 of the perodic table. It is the only non-metal of this group. Therefore, the chemistry of boron is quite different from rest of the members of this group. The electronic configuration of boron (Z = 5) is $1s^2\,2s^2\,2p_x^1$ and thus has three valence electrons. Because of its small size (80 pm) and high ionization energy, (IE_1 = 800 kJ mol^{-1}, IE_2 = 2427 kJ mol^{-1} and IE_3 = 3658 kJ mol^{-1}) it cannot lose all its three valence electrons to form B^{3+} ions. Instead, because of its small size, high ionization enthalpy and high electronegativity, boron can form three covalent bonds by sharing its three valence electrons. In this respect, boron resembles carbon and silicon of group 14 and differs from other members of its own group, *i.e.*, group 13.

Since boron forms three covalent bonds, therefore, in the compounds of boron, the central boron atom has only a sextet of electrons and thus needs two more electrons to complete its octet. Consequently, boron compounds, especially the hydrides, are usually referred to as *electron-deficient compounds*. Further, because of their electron-deficient nature, boron compounds readily accept electrons from other molecules capable of donating a pair of electrons. Boron compounds, thus behave as *Lewis acids*. For example, BF_3 combines with Lewis base NH_3 to form

$$H_3N : \longrightarrow BF_3.$$

13.2.1. Occurrence of Boron

Boron occurs in two isotopic forms, ${}^{10}_{5}B$ (19%) and ${}^{11}_{5}B$ (81%). Its abundance in the earth's crust is very low (0·0001% by mass). Boron mainly occurs as borates and orthoboric acid. Some important minerals of boron are :

(*i*) ***Orthoboric acid***, H_3BO_3

(*ii*) ***Borax***, $Na_2[B_4O_5(OH)_4]\,.\,8H_2O$

or $Na_2B_4O_7\,.\,10H_2O$

(*iii*) ***Kernite***, $Na_2[B_4O_5(OH)_4]$

or $Na_2B_4O_7\,.\,2H_2O$

(*iv*) ***Colemanite***, $Ca_2[B_3O_4(OH)_3]_2\,.\,2H_2O$

or $Ca_2B_6O_{11}.5H_2O$

Boron in form of borates is chiefly found in California (U.S.A.) and Turkey. In India, boron occurs as borax in Puga Valley of Ladakh region of Kashmir and Sambhar Lake in Rajasthan.

13.2.2. Isolation of Boron

Elemental boron is obtained by any one of the following methods :

(*i*) ***By reduction of boric oxide with highly electropositive metals like potassium and magnesium in absence of air.***

$$B_2O_3\,(s) + 6K(s) \xrightarrow{\text{Heat}} 2B(s) + 3K_2O(s)$$

$$B_2O_3(s) + 3Mg(s) \xrightarrow{\text{Heat}} 2B(s) + 3MgO(s)$$

The product thus obtained is boiled with hydrochloric acid and filtered when K_2O or MgO dissolves leaving behind elemental boron. The powdered boron thus obtained is thoroughly washed with water to free it from hydrochloric acid and is finally dried.

(*ii*) ***By reduction of volatile boron halides with dihydrogen at high temperature (1270 K)*** **on a heated tantalum filament**

$$2BCl_3(g) + 3H_2(g) \xrightarrow{1270\ K} 2B(s) + 6HCl(g)$$

$$2BBr_3(g) + 3H_2(g) \xrightarrow{1270\ K} 2B(s) + 6HBr(g)$$

Boron of high purity (~ 99·9%) can be prepared by this method.

(iii) By electrolytic reduction of fused borates or other compounds such as KBF_4 (potassium tetrafluoroborate) in molten KCl/KF at 1073 K.

(iv) By thermal decomposition of boron tri-iodide over red hot tungsten filament **(van Arkel method)**

$$2BI_3(g) \xrightarrow[1173\ K]{W} 2B(s) + 3I_2(g)$$

(v) By thermal decomposition of boron hydrides

$$\underset{\text{Diborane}}{B_2H_6(g)} \xrightarrow{1173\ K} 2B(s) + 3H_2(g)$$

13.2.3. Physical Properties of Boron

(*i*) Boron is an extremely hard solid with melting point greater than 2450 K. Its boiling point is 2825 K.

(*ii*) Elemental boron exists in several different allotropic* forms. At least four allotropes of boron may be obtained under different conditions. However, transition between different forms is an extremely slow process. All the four allotropic forms contain B_{12} icosahedral units (Fig. 13.1) with boron atoms at all the 12 corners. The different allotropic forms differ from one another in the way the icosahedra are bonded together.**

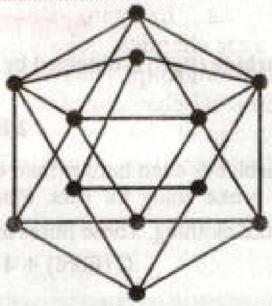

FIGURE 13.1. All allotropic forms of boron consist of B_{12} isocahedral units having 12 corners and twenty faces. Each corner is represented by a thickened circle.

(*iii*) Being a non-metal, boron has low electrical conductivity which, however, increases with rise in temperature.

13.2.4. Chemical Properties of Boron

Chemical inertness. The chemical reactivity of boron depends markedly on the state of subdivision and temperature. At ordinary temperatures, it is *relatively chemically inert.* However, at **higher temperatures, it reacts with all non-metals except hydrogen and noble gases, all metals except heavier metals like Ag, Au, Cd, Hg, Sn, Pb,** Sb and Bi. Some important reactions of boron are described below :

(i) Action of air. Amorphous boron burns in air at 973 K forming boron trioxide (B_2O_3) and boron nitride (BN).

$$4B(s) + 3O_2(g) \xrightarrow{973\ K} 2B_2O_3(s)$$

$$2B(s) + N_2(g) \xrightarrow{973\ K} 2BN(s)$$

ADD TO YOUR KNOWLEDGE

1. **Boron nitride (BN)** can also be prepared by heating boron in a current of ammonia.

$$2B + 2NH_3 \xrightarrow{\Delta} 2BN + 3H_2$$

It is a white crystalline powder with a m.p. of 3273 K. The structure of BN is similar to that of graphite with the only difference that the π-electrons in graphite are completely delocalized over all the carbon atoms of the lattice but the π-electrons in BN are only *partially delocalized* over boron atoms leading to *unequal B—N bond lengths.* Recently, a crystalline form of boron nitride called **borazon** has been synthesized by application of high temperature and pressure. This form is *even harder than diamond and is used as an abrasive.*

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*The phenomenon of existence of an element in two or more forms which have different physical properties but identical chemical properties is called **allotropy** and the different forms are called **allotropes.**

**Polyhedron with 20 faces.

ADD TO YOUR KNOWLEDGE CONTD.

2. **Boron carbide (B_4C)** is obtained by reducing B_2O_3 with carbon at 1873 K.

$$2\,B_2O_3 + 7\,C \xrightarrow{1873\text{ K}} B_4C + 6\,CO$$

Boron carbide is even harder than diamond and is increasingly being used as an abrasive for polishing. It is used for brake lining for cars. Fibres of B_4C have an enormous tensile strength and are used to make bullet-proof clothing. These fibres are made as follows :

$$C\,(\text{fibre}) + 4\,BCl_3 + 6\,H_2 \longrightarrow B_4C\,(\text{fibre}) + 12\,HCl$$

(ii) Action of non-metals. Boron combines with O_2 and N_2 when heated in air giving boron trioxide and boron nitride respectively as shown above.

It also combines with halogens at high temperatures to yield covalent trihalides.

$$2B(s) + 3F_2(g) \xrightarrow{\text{Heat}} 2BF_3(g)$$

$$2B(s) + 3Cl_2(g) \xrightarrow{\text{Heat}} 2BCl_3(g)$$

$$2B(s) + 3Br_2(l) \xrightarrow{\text{Heat}} 2BBr_3(g)$$

$$2B(s) + 3I_2(s) \xrightarrow{\text{Heat}} 2\,BI_3(g)$$

Boron trifluoride (BF_3) can also be prepared indirectly by heating boron trioxide with calcium fluoride and conc. H_2SO_4.

$$B_2O_3(s) + 3\,CaF_2(s) + 3H_2SO_4(l) \xrightarrow{\text{Heat}} 2\,BF_3(g) + 3\,CaSO_4(s) + 3H_2O(l)$$

All the trihalides of boron are *electron-deficient compounds* and act as *Lewis acids*. For example,

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \longrightarrow F_3B \leftarrow NH_3$$

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:\underset{..}{\ddot{F}}:^-} \longrightarrow \underset{\text{Tetrafluoroborate ion}}{BF_4^-}$$

The relative acid strength of boron trihalides follows the order :

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

(iii) Action of acids. Boron does not react with non-oxidising acids such as hydrochloric acid. However, it is attacked at high temperatures by strong oxidising acids such as a mixture of hot conc. H_2SO_4 and HNO_3 (2 : 1) forming boric acid (H_3BO_3)

$$B(s) + 3HNO_3(aq) \xrightarrow{\text{Heat}} \underset{\text{Boric acid}}{H_3BO_3\,(aq)} + 3NO_2(g)$$

$$2B(s) + 3H_2SO_4(aq) \xrightarrow{\text{Heat}} 2\,H_3BO_3(aq) + 3SO_2(g)$$

(iv) Action of alkalies. Boron resists the action of alkalies (NaOH or KOH) upto 773 K but above this temperature, it reacts forming borates and liberating dihydrogen gas.

$$2B(s) + 6KOH(s) \xrightarrow{>773\text{ K}} \underset{\text{Pot. borate}}{2K_3BO_3(s)} + 3H_2(g)$$

It also dissolves in fused $Na_2CO_3/NaNO_3$ mixture at 1123 K

$$2\,B\,(s) + 3\,Na_2CO_3\,(s) + 3\,NaNO_3\,(s) \longrightarrow 2\,Na_3BO_3\,(s) + 3\,NaNO_2\,(s) + 3\,CO_2\,(g)$$

(v) Action of metals. Boron combines with many metals except group 1 and heavy metals (*e.g.* Ag, Au, Cd, Hg, Sn, Pb, Sb, Bi) to form their corresponding borides which are generally very hard and high melting solids.

$$3Mg(s) + 2B(s) \xrightarrow{\text{Heat}} \underset{\text{Mag. boride}}{Mg_3B_2(s)}$$

$$B(s) + Cr(s) \xrightarrow{\text{Heat}} \underset{\text{Chromium boride}}{CrB(s)}$$

(vi) Action of water. Boron is inert towards water. It is not even attacked by steam.

(vii) Reducing character. Boron is a powerful reducing agent and thus reduces CO_2 to C and SiO_2 to Si.

$$4B\,(s) + 3CO_2\,(g) \xrightarrow{\text{Heat}} 2B_2O_3\,(s) + 3C\,(s)$$

$$4B\,(s) + 3SiO_2\,(s) \xrightarrow{\text{Heat}} 2B_2O_3\,(s) + 3Si\,(s)$$

13.2.5. Uses of Boron

(*i*) Metal borides are used in atomic reactors as protective shields and control rods because of the high ability of B–10 ($^{10}_{5}B$) isotope to absorb neutrons. This special property of ^{10}B isotope to absorb neutrons is also of current interest in the possible use of boron compounds in *cancer chemotherapy.*

(*ii*) Boron fibres are used in making light, composite materials for aircrafts.

(*iii*) It is used as a semi-conductor for making electronic devices.

(*iv*) It is used in steel industry for increasing the hardness of steel. Boron has virtually replaced expensive metals like Mo, Cr and W in the manufacture of special steels.

(*v*) Boron compounds are becoming increasingly important as rocket fuels because of their high energy/weight ratio.

(*vi*) Boron is an essential element in plant metabolism.

(*vii*) Boron carbide fibres are very hard but light and hence are used for making bullet-proof vests.

13.3. Compounds of Boron

13.3.1. Borax, $Na_2[B_4O_5(OH)_4]\,.\,8H_2O$ or $Na_2B_4O_7\,.\,10H_2O$

Borax or sodium tetraborate decahydrate is the most important compound of boron. It occurs naturally as *tincal* (Suhaga) in dried up lakes of Notheren India, Tibet, Ceylon and California (U.S.A.).

Preparation (i) From tincal. Tincal obtained from dried up lakes contains about 50% borax. It is boiled with water and filtered to remove insoluble impurities of clay, sand etc. The filtrate is concentrated when crystals of borax separate out.

(ii) From colemanite. The mineral colemanite, ($Ca_2B_6O_{11}$) is finely powdered and is boiled with sodium carbonate solution.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7} + \underset{\text{Sod. metaborate}}{2NaBO_2} + 2CaCO_3\downarrow$$

The precipitate of calcium carbonate thus formed is removed by filtration. The filtrate is concentrated and cooled when crystals of borax separate out. Sodium metaborate present in the mother liquor can be converted into borax by passing a current of carbon dioxide throught it.

$$\underset{\text{Sod. metaborate}}{4NaBO_2} + CO_2 \longrightarrow \underset{\text{Sod. tetraborate}}{Na_2B_4O_7} + Na_2CO_3$$

3. From boric acid. Borax can also be prepared in small amounts by neutralising boric acid with sodium carbonate.

$$4\,H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

On cooling, crystals of borax, *i.e.*, $Na_2B_4O_7.10H_2O$ separate out.

Properties. (*i*) It is a white crystalline solid, less soluble in cold water but more soluble in hot water.

(*ii*) The aqueous solution of borax is *alkaline* due to hydrolysis. Borax is, therefore, used as a water softner and cleaning agent.

$$Na_2B_4O_7 + 2\,H_2O \longrightarrow \underset{\textit{(Strong alkali)}}{2\,NaOH} + \underset{\textit{(Weak acid)}}{H_2B_4O_7}$$

$$\underset{\text{Tetraboric acid}}{H_2B_4O_7} + 5\,H_2O \longrightarrow \underset{\text{Boric acid}}{4\,H_3BO_3}$$

(*iii*) **Action of heat – Borax bead test.** On heating, borax loses its water of crystallisation and swells up to form a puffy mass. On further heating, it melts into a clear liquid which solidifies to a *transparent glass like bead which consists of sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3).*

$$Na_2B_4O_7\,.\,10H_2O \xrightarrow{\text{Heat}} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\text{Heat}} \underbrace{\underset{\text{Sod. metaborate}}{2\,NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}}_{\text{Transparent glassy bead}}$$

The glassy bead is commonly known as *borax bead* and is employed in qualitative analysis for the detection of certain coloured basic radicals such as Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} etc. Whenever a coloured salt containing these cations is heated with borax bead on a platinum wire, the salt decomposes to form the corresponding metal oxide which then combines with B_2O_3 present in the glassy bead to form coloured metaborates. This test is called **borax bead test.** Thus,

$$CoSO_4 \xrightarrow{\text{Heat}} CoO + SO_3$$

$$\underset{\text{Cobalt oxide}}{CoO} + B_2O_3 \xrightarrow{\text{Heat}} \underset{\text{Cobalt metaborate(\textit{blue})}}{Co(BO_2)_2}$$

$$\underset{\text{Nickel oxide}}{NiO} + B_2O_3 \xrightarrow{\text{Heat}} \underset{\text{Nickel metaborate(\textit{brown})}}{Ni(BO_2)_2}$$

$$\underset{\text{Chromium trioxide}}{Cr_2O_3} + 3\,B_2O_3 \xrightarrow{\text{Heat}} \underset{\text{Chromium metaborate(\textit{green})}}{2\,Cr(BO_2)_3}$$

$$\underset{\text{Manganese oxide}}{MnO} + B_2O_3 \xrightarrow{\text{Heat}} \underset{\text{Manganese metaborate (\textit{pink violet})}}{Mn(BO_2)_2}$$

$$\underset{\text{Cupric oxide}}{CuO} + B_2O_3 \longrightarrow \underset{\text{Cupric metaborate(\textit{dark blue})}}{Cu(BO_2)_2}$$

Certain metaborates are reduced to the free metal by the carbon present in the reducing flame of the burner. For example,

$$2Cu(BO_2)_2 + C \longrightarrow \underset{\text{Cuprous metaborate(\textit{colourless})}}{2CuBO_2} + B_2O_3 + CO$$

$$2CuBO_2 + C \longrightarrow \underset{\text{Metal(\textit{red})}}{Cu} + B_2O_3 + CO$$

(*iv*) **Action with sodium hydroxide.** On adding a calculated quantity of sodium hydroxide to borax, sodium metaborate is formed.

$$Na_2B_4O_7 + 2NaOH \longrightarrow 4NaBO_2 + H_2O$$

(*v*) **Action with sulphuric acid.** On adding a calculated quantity of concentrated sulphuric acid to a hot concentrated solution of borax, boric acid is produced.

$$Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$$

$$H_2B_4O_7 + 5H_2O \longrightarrow 4H_3BO_3.$$

(*vi*) **Action with ethyl alcohol and sulphuric acid.** On heating borax with ethyl alcohol and concentrated sulphuric acid, vapours of triethylborate are produced. When ignited these vapours burn with a *green edged flame*.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

$$H_3BO_3 + \underset{\text{Ethyl alcohol}}{3C_2H_5OH} \longrightarrow \underset{\text{Triethylborate}}{B(OC_2H_5)_3} + 3H_2O$$

This reaction is used as a test for borate ion in qualitative analysis.

Uses of Borax. Borax is used

(*i*) in the manufacture of enamels and glazes for earthen wares *i.e.*, tiles, pottery etc. The glazed surface is resistant to heat, stains and scratches.

(*ii*) as a flux in soldering.

(*iii*) in the preparation of medicinal soaps due to its antiseptic properties

(*iv*) in the manufacture of heat resistant (*i.e.* very low coefficient of thermal expansion) borosilicate glass (pyrex).

(*v*) to make peroxoborate [*i.e.*, $Na_2[(OH)_2B(O-O)_2B(OH)_2].6\,H_2O$] – an important cleansing and bleaching agent present in washing powders. They also act as *brightners* since they absorb UV light and emit visible light.

(*vi*) as a stiffening agent for candle wicks

(*vii*) to produce a good finish in laundary

(*viii*) in the laboratory for borax bead test.

(*ix*) in softening of water.

Structure of Borax and other borates. Boron forms strong bonds with oxygen. This is supported by the fact that boron invariably occurs in nature as borates. In borates, the basic structural unit may have one or more boron atoms linked together by intervening oxygen atoms in form of chains or rings. Borax itself contains the tetranuclear units, *i.e.*, $[B_4O_5(OH)_4]^{2-}$ as shown in Fig. 13.2. Therefore, its correct formula is $Na_2[B_4O_5(OH)_4]\,.\,8H_2O$.

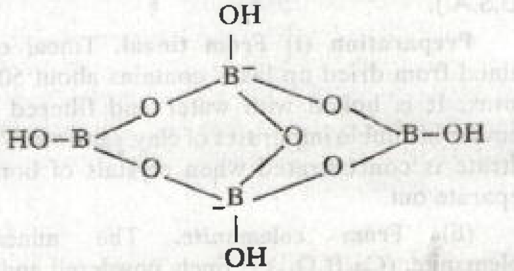


FIGURE 13.2. Structure of $[B_4O_5(OH)_4]^{2-}$ ion.

13.3.2. Orthoboric acid (Boric acid), H_3BO_3 or $B(OH)_3$

Boric acid is the trivial name of *orthoboric acid*.

Preparation (i) From borax. Boric acid is obtained by treating a hot concentrated solution of borax with hydrochloric acid or sulphuric acid. The resulting solution on concentration and cooling gives crystals of boric acid.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$$

(ii) By hydrolysis of boron compounds. Boric acid can also be prepared by the hydrolysis of boron compounds such as halides, hydrides and nitrides.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

(iii) From colemanite. Boric acid is obtained by passing sulphur dioxide through the solution of the mineral colemanite in boiling water. The resulting solution on concentration and cooling gives crystals of boric acid while calcium bisulphite being highly soluble in water remains in the mother liquor.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 4SO_2 + 11H_2O \longrightarrow \underset{\text{Cal. bisulphite}}{2Ca(HSO_3)_2} + \underset{\text{Boric acid}}{6H_3BO_3}$$

Properties. (*i*) It is a white crystalline solid with a soft soapy touch.

(*ii*) It is sparingly soluble in cold water but fairly soluble in hot water.

(iii) **Acidic nature.** Boric acid behaves as a weak ($K_a = 1 \times 10^{-9}$) monobasic acid. It does not act as a *proton-donor, i.e., protonic acid* but behaves a *Lewis acid i.e.*, it accepts a pair of electrons from OH^- ion.

$$H-OH + B(OH)_3 \longrightarrow [B(OH)_4]^- + H^+$$

(iv) Action of heat. Boric acid, on heating, loses water in three different stages at different temperatures ultimately giving boron trioxide.

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{370\text{ K}} \underset{\text{Metaboric acid}}{HBO_2} + H_2O$$

$$\underset{\text{Metaboric acid}}{4\,HBO_2} \xrightarrow[-H_2O]{410\text{ K}} \underset{\text{Tetraboric acid}}{H_2B_4O_7} \xrightarrow{\text{Red heat}} \underset{\text{Boron trioxide}}{2B_2O_3} + H_2O$$

(v) Reaction with ethyl alcohol. Orthoboric acid reacts with ethyl alcohol in presence of conc. H_2SO_4 to form *triethylborate*.

$$\underset{\text{Orthoboric acid}}{B(OH)_3} + \underset{\text{Ethyl alcohol}}{3C_2H_5OH} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Triethylborate}}{B(OC_2H_5)_3} + 3H_2O$$

The vapours of triethylborate when ignited burn with a *green- edged flame*. This forms the basis for detecting borates and boric acid in qualitative analysis.

Uses. Boric acid is used :

(*i*) in the manufacture of heat resistant borosilicate glass.

(*ii*) as a preservative for milk and food stuffs

(*iii*) in the manufacture of enamels and glazes in pottery.

(*iv*) The aqueous solution of boric acid is used as a mild antiseptic especially as eye wash under the **boric lotion.**

Structure of Boric acid. The ground state outer electronic configuration of boron is $2s^2\,2p_x^1$. In the excited state, one of the 2*s*-electrons gets promoted to the vacant $2p_y$-orbital. The three half-filled atomic orbitals ($2s$, $2p_x$ and $2p_y$) thus obtained undergo sp^2-hybridization to give three sp^2-hybridized orbitals. Each one of these three sp^2-orbitals overlaps with 2*p*-orbitals of O^- forming three $B-O^-$ bonds.

Therefore, BO_3^{3-} (borate) ion has trigonal planar structure as shown in Fig. 13.3.

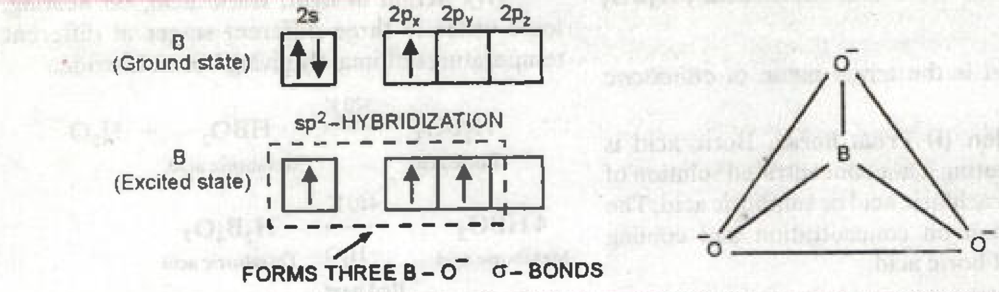


FIGURE 13.3. Trigonal planar structure of BO_3^{3-} unit.

In boric acid, planar BO_3^{3-} units are joined by hydrogen bonds to give a *layer structure* as shown in Fig. 13.4.

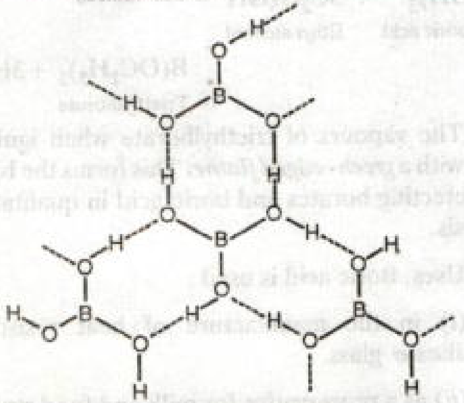


FIGURE 13.4. Structure of boric acid (dotted lines represent hydrogen bonds).

13.3.3. Boron Hydrides

The binary compounds of boron with hydrogen are called *boron hydrides*. Actually boron does not combine directly with hydrogen but a number of hydrides of boron are known. *These hydrides of boron are collectively called* **boranes** *on analogy with alkanes*. These hydrides can be divided into the following two series :

(*i*) B_nH_{n+4} (called *nido-* boranes) such as B_2H_6 (*diborane*), B_5H_9 (*pentaborane-9*), B_6H_{10} (*hexaborane-10*), B_8H_{12} (*octaborane-12*), $B_{10}H_{14}$ (*decaborane*) etc.

(*ii*) B_nH_{n+6} (called *arachno*-boranes) such as B_4H_{10} (*tetraborane*), B_5H_{11} (*pentaborane-11*), B_6H_{12} (*hexaborane-12*), B_8H_{14} (*octaborane-14*), B_9H_{15} (*nonaborane or enneaborane*). etc.

Note. It may be noted that wherever two or more boranes with the same number of B-atoms but different number of H-atoms are known (for example, pentaboranes, hexaboranes, octaboranes etc.), a figure depicting the total of hydrogen atoms in the molecule is included in the name so as to distinguish them from one another.

Preparation of Diborane. It may be prepared by the following methods :

(*i*) *By reduction of boron trifluoride etherate with lithium aluminium hydride* ($LiAlH_4$) *in diethyl ether.*

$$\underset{\text{Boron trifluoride etherate}}{4\,BF_3.\,Et_2O} + 3\,LiAlH_4 \xrightarrow[\text{ether}]{\text{Diethyl}} 2\,B_2H_6 + 3\,LiF + 3\,AlF_3 + 4\,Et_2O$$

(*ii*) **Laboratory method of preparation.** Diborane is prepared in the laboratory by the oxidation of sodium borohydride ($NaBH_4$) with iodine in diglyme ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$) as solvent

$$2\,NaBH_4 + I_2 \xrightarrow{\text{Diglyme}} B_2H_6 + 2\,NaI + H_2$$

(*iii*) **Industrial preparation.** On the industrial scale, diborane is obtained by the reduction of BF_3 with sodium hydride.

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

Preparation of higher boranes. Higher boranes (B_4H_{10}, B_5H_{11}, B_6H_{12} and $B_{10}H_{14}$) are obtained when B_2H_6 is heated at 373-523 K.

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

(*ii*) **Stability.** Diborane is stable only at low temperatures. However, when diborane is heated in a sealed tube, between 373–523K, a complex reaction occurs and various higher boranes are formed.

$$B_2H_6 \xrightarrow[\textit{Sealed tube}]{373-523\text{ K}} B_4H_{10}, C_5H_1, B_6H_{12} \text{ etc.}$$

By careful control of temperature, pressure and reaction time, different individual boranes can be obtained. For example,

$$2B_2H_6 \xrightarrow[200\text{ atm}, 5\,hr]{353-363\text{ K}} B_4H_{10} + H_2$$

(*iii*) **Combustibility.** It catches fire spontaneously upon exposure to air. It burns in oxygen evolving an enormous amount of heat.

$$B_2H_6 + 3\,O_2 \longrightarrow B_2O_3 + 3\,H_2O\,; \qquad \Delta_cH° = -\,1976\text{ kJ mol}^{-1}$$

Like diborane, higher boranes also spontaneously burn in air.

(*iv*) **Hydrolysis.** Boranes are readily hydrolysed by water to form boric acid.

$$B_2H_6\,(g) + 6\,H_2O\,(l) \longrightarrow 2\,H_3BO_3\,(aq) + 6\,H_2\,(g)$$

With methanol, trimethylborate is formed

$$B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$$

(*v*) **Reaction with Lewis bases – Cleavage reaction.** Diborane on treatment with Lewis bases first undergoes cleavage to form borane which then reacts with Lewis bases to form adducts.

$$B_2H_6 + 2\,NMe_3 \longrightarrow 2\,BH_3\,.\,NMe_3$$

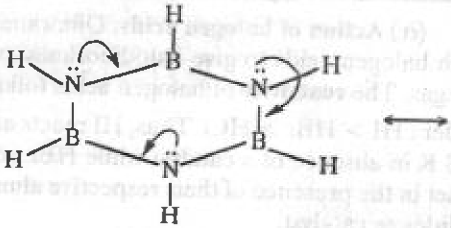
$$B_2H_6 + 2\,CO \longrightarrow 2\,BH_3\,.\,CO$$

(*vi*) **Reaction with ammonia.** Diborane combines with ammonia to form an addition product, $B_2H_6\,.\,2\,NH_3$ formulated as $[BH_2\,(NH_3)_2]^+\,[BH_4]^-$, which when heated to 473 K decomposes to give a volatile compound called borazine (or borazole).

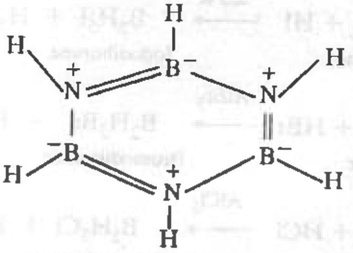
$$3\,B_2H_6 + 6\,NH_3 \xrightarrow{\text{Low temp.}} 3\,[BH_2\,(NH_3)_2]^+[BH_4]^-$$

$$\xrightarrow{473\text{ K}} \underset{\text{Borazine}}{2\,B_3N_3H_6} + 12\,H_2$$

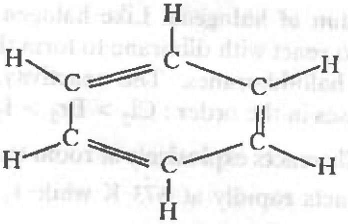
Borazine is isoelectronic and isosteric with benzene and its structure is similar to that of benzene except that in benzene the π-electrons are *completely delocalized* but in borazine, they are only *partially delocalized*



Borazine



Borazine



Benzene

Because of its similarity with benzene, borazine is also called **inorganic benzene.**

(*vii*) **Formation of complex borohydrides.** Several metal hydrides react with diborane to form *tetrahydridoborates* commonly known as **borohydrides.** All these contain the tetrahedral $[BH_4]^-$ ion. For example,

$$\underset{\text{Sod. hydride}}{2NaH} + B_2H_6 \xrightarrow[\text{ether}]{\text{Diethyl}} \underset{\text{Sod. borohydride}}{2Na^+[BH_4]^-}$$

$$\underset{\text{Lithium hydride}}{2LiH} + B_2H_6 \xrightarrow[\text{ether}]{\text{Diethyl}} \underset{\text{Lithium borohydride}}{2Li^+[BH_4]^-}$$

Both sodium borohydride and lithium borohydride are used as reducing agents in organic synthesis. They also serve as starting material for many other borohydrides.

(*viii*) **Reaction with alkalies.** Diborane dissolves in strong alkalies (NaOH or KOH) to produce metaborates and dihydrogen gas.

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow \underset{\text{Pot. metaborate}}{2KBO_2} + 6H_2$$

(*ix*) **Action of halogen acids.** Diborane reacts with halogen acids to give halodiboranes evolving H_2 gas. The reactivity of halogen acids follows the order : HI > HBr > HCl. Thus, HI reacts at about 323 K in absence of a catalyst while HBr and HCl react in the presence of their respective aluminium halides as catalyst.

$$\underset{\text{Diborane}}{B_2H_6} + HI \xrightarrow{323\ K} \underset{\text{Iododiborane}}{B_2H_5I} + H_2$$

$$\underset{\text{Diborane}}{B_2H_6} + HBr \xrightarrow{AlBr_3} \underset{\text{Bromodiborane}}{B_2H_5Br} + H_2$$

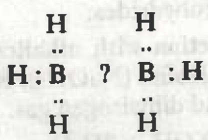
$$\underset{\text{Diborane}}{B_2H_6} + HCl \xrightarrow{AlCl_3} \underset{\text{Chlorodiborane}}{B_2H_5Cl} + H_2$$

(*x*) **Action of halogens.** Like halogen acids, halogens also react with diborane to form the corresponding halodiboranes. The reactivity, however, decreases in the order : $Cl_2 > Br_2 > I_2$.

Thus Cl_2 reacts explosively at room temperature, Br_2 reacts rapidly at 373 K while I_2 reacts slowly at still higher temperatures.

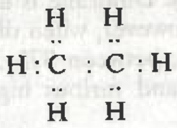
$$B_2H_6 + Cl_2 \xrightarrow[\text{Explosive}]{298\ K} \underset{\text{Chlorodiborane}}{B_2H_5Cl} + HCl$$

Structure of diborane (B_2H_6). The structure of diborane is very interesting. In diborane, each boron atom has three valence electrons for sharing. If we asume that each boron forms three covalent bonds with three hydrogen atoms, then there are no electrons left with boron atom for sharing with other boron atom. Therefore, the two boron atoms cannot be linked. This suggests that unlike ethane which has a C – C bond, diborane does not have a B – B bond. In other words, the structure of diborane is not similar to that of ethane as shown below :



$$\begin{matrix} & H & & H & \\ & \cdot\cdot & & \cdot\cdot & \\ H: & B & ? & B & :H \\ & \cdot\cdot & & & \\ & H & & H & \end{matrix}$$

No electrons for B – B bond formation



$$\begin{matrix} & H & H & \\ & \cdot\cdot & \cdot\cdot & \\ H: & C & :C & :H \\ & \cdot\cdot & \cdot\cdot & \\ & H & H & \end{matrix}$$

X-Diffraction studies have shown that the structure of diborane is as shown in Fig. 13.5.

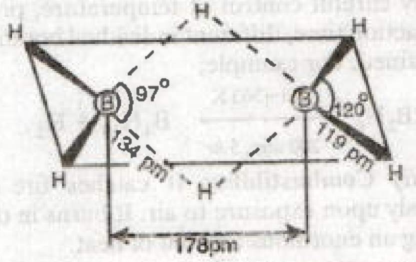


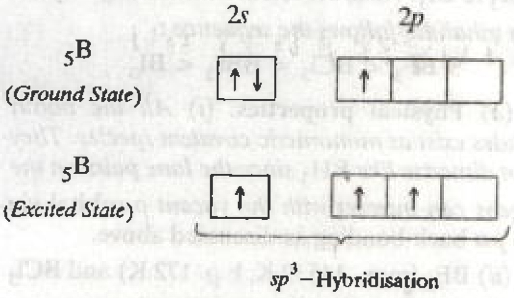
FIGURE 13.5. Structure of a diborane molecule.

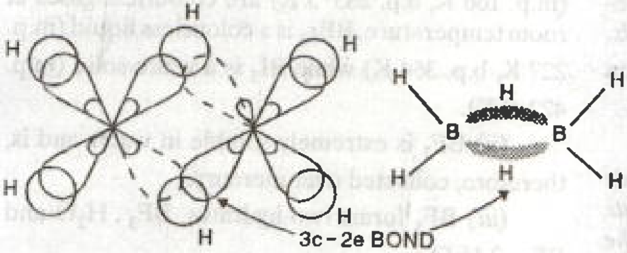
In this structure, there are two types of *hydrogen atoms*. The four hydrogen atoms (two on the left and two on the right shown by thick lines) are called *terminal hydrogens*. These four terminal hydrogens and the two boron atoms lie in the same plane while the remaining two hydrogen atoms – one lying above and one below this plane form bridges and hence are called **bridge hydrogens.** Thus, there are two types of bonds in B_2H_6 molecules.

(*i*) *The four terminal B – H bonds are normal covalent bonds and hence are quite strong.* Each bond is formed by sharing a pair of electrons between B and H atoms and hence are also called **two centre electron pair bonds** or **two centre two-electron bond (2c – 2e).**

(*ii*) The two bridge bonds *i.e.* B......H......B are quite different from normal covalent bonds. Each bridge hydrogen is bonded to two boron atoms by a pair of electrons. In other words, these are **three-centre electron pair bonds** or **three centre two electron bonds (3c – 2e)** *and hence are quite weak. Because of their resemblence to a banana, these three centre electron pair bonds are also called* **banana bonds.**

Explanation of Structure of Diborane on the basis of Hybridisation. The electronic configuration of boron atom in the excited state is $1s^2\, 2s^1\, 2p_x^1\, 2p_y^1\, 2p_z^0$. It undergoes sp^3 hybridisation. The two half-filled hybrid orbitals of each boron atom overlap with the half filled orbitals of hydrogen atoms forming normal covalent bonds whereas the third half-filled hybrid orbital of one boron atom and the vacant hybrid orbital of the second boron atom (shown by dotted lines) overlap simultaneously with the half-filled orbital of H-atom. Thus the electron cloud contains only two electrons but spreads over three atoms (two B atoms and one H-atom). That is why this bond is called **three centre electron pair bond.** Because of the shape of the electron cloud formed, it is also called **banana bond.**





Molecules like B_2H_6 which do not have sufficient number of electrons to form normal covalent bonds (two centre-electron pair bonds) are called **electron deficient molecules.**

The structures of boranes were studied in detail by *William Lipsocomb* who was awarded the 1976 Nobel Prize in Chemistry.

13.4. Boron Halides

Due to small size and high electronegativity boron forms covalent trihalides of the general forms, BX_3 (where X = F, Cl, Br or I)

The covalent character of these trihalides is supported by the following facts

(*i*) *They do not conduct electricity in the liquid state.*

(*ii*) *Their boiling points are much lower than those of the halides of alkali and alkaline earth metals which are distinctly ionic.*

Preparation. (*a*) BF_3 is prepared by either of the following three methods

(*i*) By heating a mixture of boron oxide or borax with calcium fluoride and conc. H_2SO_4

$$\underset{\text{Boron oxide}}{B_2O_3} + 3\,CaF_2 + 3\,H_2SO_4\,(conc.) \xrightarrow{\Delta} 2\,BF_3 + 3\,CaSO_4 + 3\,H_2O$$

$$\underset{\text{Borax}}{Na_2B_4O_7} + 6\,CaF_2 + 8\,H_2SO_4\,(conc.) \xrightarrow{\Delta} 4\,BF_3 + 2\,NaHSO_4 + 6\,CaSO_4 + 7\,H_2O$$

In the above reactions, HF may be used instead of CaF_2 *i.e.*

$$\underset{\text{Boron oxide}}{B_2O_3} + 6HF + 3H_2SO_4 \xrightarrow{\Delta} 2BF_3 + 3H_2SO_4.H_2O$$

$$\underset{\text{Borax}}{Na_2B_4O_7} + 12HF + 2H_2SO_4 \xrightarrow{\Delta} 2NaHSO_4 + 4BF_3 + 7H_2O$$

(*ii*) *By heating a mixture of boron oxide and ammonium tetrafluoroborate*

$$(iii)\ B_2O_3 + 6\,NH_4BF_4 \xrightarrow{\Delta} 8\,BF_3 + 6\,NH_3 + 3\,H_2O$$

Pure BF_3 can, however, be prepared in the laboratory by thermal decomposition of benzenediazonium tetrafluoroborate.

$$C_6H_5N_2BF_4 \xrightarrow{\Delta} C_6H_5F + N_2 + BF_3$$

(*b*) BCl_3 and BBr_3 are obtained by passing Cl_2 or Br_2 on a heated mixture of boron trioxide and powdered charcoal.

$$B_2O_3 + 3\,C + 3\,Cl_2 \xrightarrow{773\,K} 2\,BCl_3 + 3\,CO$$

$$B_2O_3 + 3\,C + 3\,Br_2 \xrightarrow{773\,K} 2\,BBr_3 + 3\,CO$$

BCl_3 can also be prepared by heating boron trioxide with phosphorus pentachloride in a sealed tube.

$$B_2O_3 + 3\,PCl_5 \xrightarrow{\Delta} 2\,BCl_3 + 3\,POCl_3$$

(*c*) BI_3 can be prepared by reduction of BCl_3 with HI

$$BCl_3 + 3\,HI \longrightarrow BI_3 + 3\,HCl$$

Structure. The trihalide of boron are planar molecules (Fig. 13.6) in which the central boron atom is sp^2- hybridized. It has an unhybridized p-orbital which is empty and is perpendicular to the plane of three σ B – X bonds. Since the boron atom has only six electrons in its outer shell, therefore, all the boron trihalides are *electron-deficient* compounds.

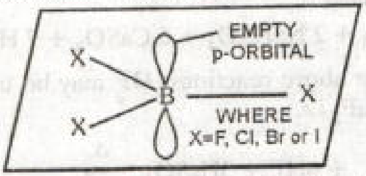


FIGURE 13.6. Structure of boron trihalides.

Relative acid strength of boron trihalides. The boron atom in all the boron trihalides has only six electrons in its valence shell and hence needs two more electrons to complete its octet. Therefore, all the boron trihalides behave as *Lewis acids.*

The relative strength of the various boron trihalides increases in the order :

$$BF_3 < BCl_3 < BBr_3 < BI_3.$$

This order can be easily explained *on the basis of the tendency of the halogen atom to back donate its lone pair of electrons to the empty p-orbital of the boron atom through $p\pi - p\pi$- bonding* (Fig. 13.7).

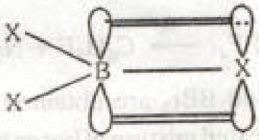


FIGURE 13.7. $p\pi$–$p\pi$-Back bonding in boron trihalides.

Since the size of the vacant $2p$-orbital of B and the $2p$-orbital of F containing a lone pair of electrons are almost identical, therefore, the lone pair of electrons on F is donated towards the B atom. Further, due to back donation by three F-atoms, BF_3 can be represented as a resonance hybrid of the following three structures (Fig. 13.8).

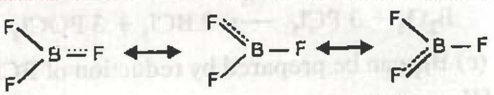


FIGURE 13.8. Resonance structures of BF_3 molecule involving back bonding.

As a result of $p\pi$-$p\pi$ back donation and resonance, the electron deficiency of B decreases and thus BF_3 is the weakest Lewis acid. As the size of the halogen atom increases from Cl to Br to I, the extent of overlap between $2p$ orbital of B and a bigger p-orbital of halogen ($3p$ in Cl, $4p$ in Br and $5p$ in I) decreases and consequently the electron-deficiency of B increases and thus the Lewis acid character increases accordingly from BF_3 to BCl_3 to BBr_3 to BI_3. *Thus, the relative acid strength of the boron trihalides follows the sequence* :

$$BF_3 < BCl_3 < BBr_3 < BI_3.$$

(*a*) **Physical properties.** (*i*) *All the boron trihalides exist as monomeric covalent species. They do not dimerize like* BH_3 *since the lone pairs on the halogens can interact with the vacant p*-orbital via $p\pi - p\pi$ back-bonding as discussed above.

(*ii*) BF_3 (m.p. 145·9 K, b.p. 172 K) and BCl_3 (m.p. 166 K, b.p. 285·5 K) are colourless gases at room temperature. BBr_3 is a colourless liquid (m.p. 227 K, b.p. 364 K) while BI_3 is a white solid (m.p. 422·9 K).

(*ii*) BF_3 is extremely soluble in water and is, therefore, collected over mercury.

(*iii*) BF_3 forms two hydrates, $BF_3 . H_2O$ and $BF_3 . 2\,H_2O$.

(*b*) **Chemical properties.** (*i*) *Hydrolysis.* All the boron trihalides are hydrolysed by water.

BF_3 is hydrolysed slowly and incompletely to form fluoboric acid. This is because HF first formed reacts with H_3BO_3.

$$BF_3 + 3\,H_2O \longrightarrow H_3BO_3 + 3\,HF] \times 4$$

$$4\,HF + H_3BO_3 \longrightarrow HBF_4 + 3\,H_2O] \times 3$$

$$4\,BF_3 + 3\,H_2O \longrightarrow H_3BO_3 + \underset{\text{Fluoboric acid}}{3\,HBF_4}$$

The other trihalides are hydrolysed completely to give boric acid and the corresponding halogen acid

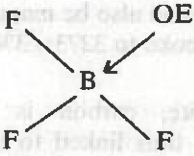
$$BX_3 + 3\,H_2O \longrightarrow H_3BO_3 + 3\,HX \; (X = Cl, Br \text{ or } I)$$

Due to formation of hydrogen halides as a result of hydrolysis, *boron trihalides fume in air.*

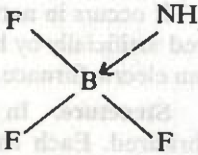
(*ii*) **Complex formation.** Boron halides being strong *Lewis acids* react with bases such as ammonia, amines, ethers, sulphides or phosphides to form adducts or complexes which have tetrahedral

$$BX_3 + NR_3 \longrightarrow X_3B \longleftarrow NR_3$$

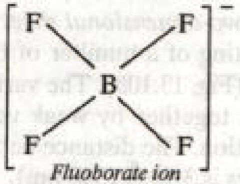
structures. Some of these complexes of BF_3 are shown below :



Boron trifluoride etherate



Boron trifluoride – ammonia complex



Fluoborate ion or Tetrafluoroborate ion

(*iii*) Reaction with Grignard reagents and organolithium reagents. Boron halides react with Grignard reagents and other organolithium reagents to form trialkyl or triarylboranes.

$$BF_3 + 3C_2H_5MgBr \longrightarrow \underset{\text{Triethylborane}}{B(C_2H_5)_3} + 3MgBrF$$

Uses. (*i*) Due to greater resistance of BF_3 to hydrolysis as compared to BCl_3, BBr_3 and BI_3, ***BF_3 is extensively used as catalyst in Friedel-Crafts alkylation and acylation reactions.***

$$C_6H_6 + CH_3CH_2F \xrightarrow{BF_3} \underset{\text{Ethylbenzene}}{C_6H_5-CH_2CH_3} + HF$$

$$C_6H_6 + CH_3CH_2OH \xrightarrow{BF_3} C_6H_5CH_2CH_3 + H_2O$$

(*ii*) BF_3 is also used as a catalyst in esterification and polymerization reactions used to prepare polyisobutylene and butadiene-styrene polymers.

$$RCOOH + R'OH \xrightarrow{BF_3} RCOOR' + H_2O$$

(*iii*) BCl_3 is used in production of elemental boron by its reduction with Mg.

13.5. Carbon

Carbon is the seventeenth most abundant element by weight found in the earth's crust. Nevertheless, it forms more compounds than any other element except hydrogen.

Naturally occurring carbon has two stable isotopes : ^{12}C (98·9%) and ^{13}C (1·1%) in addition to traces of radioactive ^{14}C isotope with a half life of 5770 years. It is used in **radiocarbon dating** to determine the age of archaeological samples of organic origin *i.e.*, fallen trees, dead animals etc. The ^{12}C isotope is assigned a mass number of 12·00000 units and is used as an international unit for atomic mass instruments.

13.5.1. Terrestrial Abundance and Distribution

Carbon is widely distributed in nature both in the free and in the combined state. In the free state, it occurs as diamond, graphite and coal. In the combined state, it occurs as carbonates in many minerals such as *dolomite* ($CaCO_3.MgCO_3$) *malachite* ($CuCO_3.Cu(OH)_2$), *siderite* ($FeCO_3$), *calamine* ($ZnCO_3$) etc. In air, carbon is present as carbon dioxide in small (0.03%) quantities.

All living systems are made up of carbon compounds such as fats, carbohydrates, proteins, vitamins, hormones, nucleic acids etc. Similarly, fossil fuels such as petroleum, lignite, coal etc. which are obtained from living matter are all carbon compounds. In nut shell, life as we live today would have been impossible without carbon compounds.

In this unit we shall highlight some of the important aspects of the chemistry of carbon and its compounds.

13.5.2. Allotropic forms of Carbon

The phenomenon of existence of an element in two or more forms which have different physical properties but identical chemical properties is called allotropy and the different forms are called allotropes.

For example, carbon exists in two allotropic forms : –

I. Crystalline, and II. Amorphous

I. Crystalline allotropic forms of carbon. Three allotropes of carbon having well defined crystal structures are : –

1. Diamond, 2. Graphite and 3. Fullerenes.

Due to different structures, they have different properties.

1. Diamond

It occurs in nature. It can also be prepared artificially but because of the high cost and poor quality, diamonds are seldom made artificially.

Structure. In diamond, carbon is sp^3-hybridized. Each carbon is tetrahedrally linked to four neighbouring carbon atoms through four strong $C-C, sp^3 - sp^3, \sigma$-bonds. This network extends in three dimensions (Fig. 13.9) and is very rigid.

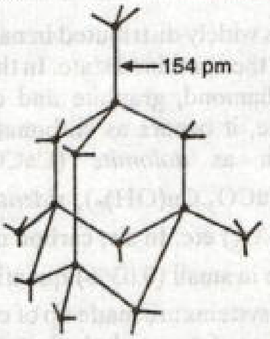


FIGURE 13.9. Structure of diamond.

Properties. (i) Purity. *Diamond is the purest form of carbon.*

(ii) Bond length. Because of sp^3-hybridization, C – C bond lengths in diamond are 1.54 Å (154 pm).

(iii) Hardness. *Since diamond exists as a three-dimensional network solid, it is the hardest substance known with high density and melting point.*

(iv) Conductivity. *Since all the electrons are firmly held in C – C, σ-bonds,* there are no free electrons in a diamond crystal. Therefore, diamond is a bad conductor of electricity.

(v) Transparency. *Because of its high refractive index (2.5), diamond can reflect and refract light. It is, therefore, a transparent substance.*

Uses. (*i*) Because of its hardness, diamond is used for cutting glass, making borers for rock drilling and for making abrasives.

(*ii*) When diamond is cut and polished, brilliant light is refracted from its surfaces. That is why, diamond is used for making precious gems and jewellery.

(*iii*) It is used for grinding and polishing of hard materials.

(*iv*) Diamond is also used for making dies for drawing thin wires from metals.

2. Graphite

It occurs in nature and can also be manufactured artificially by heating coke to 3273 – 3300 K in an elecric furnace.

Structure. In graphite, carbon is sp^2-hybridized. Each carbon is thus linked to three other carbon atoms forming hexagonal rings as shown in Fig. 13.10*a*. Thus, unlike diamond, graphite has a *two-dimensional sheet like (layered) structure* consisting of a number of benzene rings fused together (Fig. 13.10*b*). The various sheets or layers are held together by weak *van der Waals'* forces of attraction. The distance between any two successive layers is 3.40 Å (340 pm).

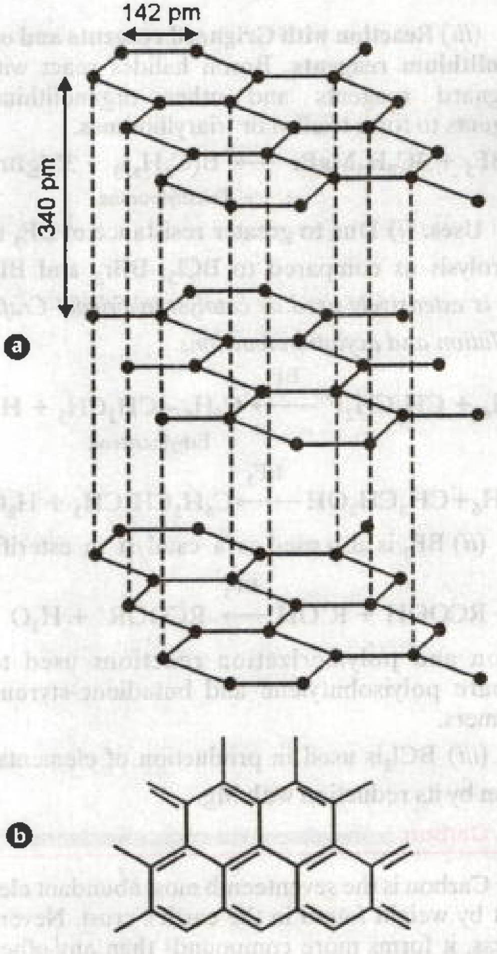


FIGURE 13.10. Structure of graphite.

Properties. (i) Purity. *Like diamond, graphite is also the purest form of carbon.*

(ii) Bond length. *Because of sp^2-hybridization the C – C bond-lengths in graphite are 1.42 Å (142 pm).*

(iii) Softness. *Since any two successive layers are held together by weak forces of attraction, one layer can slip over the other. This makes graphite soft and a good lubricating agent.*

(iv) Conductivity. *Since only three electrons of each carbon are used in making hexagonal rings in graphite, fourth valence electron of each carbon is free to move. This makes graphite a good conductor of heat and electricity.*

(v) Opaqueness. *Unlike diamond, graphite is a black substance and possesses a metallic lustre.*

Uses. (*i*) It is used as a *reducing agent* in steel manufacturing.

(*ii*) It is also used in high-strength composite materials.

(*iii*) Graphite is used for making electrodes for dry cells.

(*iv*) Graphite marks paper black and is, therefore, called *black lead*. Mixed with desired quantities of wax or clay, graphite is used for making cores of lead pencils.

(*v*) It is used in the manufacture of crucibles which can withstand high temperature.

(*vi*) Graphite is also used as a moderator for fast moving neutrons in atomic reactors.

(*vii*) It is used as a *solid lubricant* for heavy machinery.

3. Fullerenes

Discovery. Before 1985, only two crystalline allotropes of carbon called diamond and graphite were known. But in 1985, a third crystalline allotrope of carbon called **fullerenes** was discovered collectively by three scientists namely *R.E. Smalley and R.F. Curl* of Rice University, Houston, Texas (U.S.A.) and *H.W. Kroto* of the University of Sussex, Brighton (U.K.). For this discovery, these scientists shared the 1996 Nobel prize in chemistry.

Preparation and separation. *Fullerenes constitute a new family of carbon allotropes consisting of large spheroidal molecules of composition* (where $n \geq 30$) C_{2n}. These were first prepared by evaporation of graphite using a powerful laser. However, a more practical method for production of fullerenes in macroscopic quantities, involves heating of graphite in an electric arc in an inert gas such as helium or argon when a sooty material is formed by the condensation of C_n small molecules. The sooty material so formed mainly consists of C_{60} fullerene with smaller quantity of C_{70} and traces of other fullerenes consisting of even number of carbon atoms upto 350 or above. The C_{60} and C_{70} fullerenes can be readily separated from the fullerene soot by extraction with benzene or toluene followed by chromatography over alumina.

The complete process of formation and separation of C_{60} and C_{70} fullerenes from graphite may be sketched as follows :

$$\text{Graphite} \xrightarrow[\text{He or Ar}]{\text{Electric arc}} \text{Vapourised carbon}$$

$$\xrightarrow{\text{Condensation}} \underset{(C_{60} + \text{little } C_{70})}{\text{Fullerene soot}}$$

$$\xrightarrow[\text{over } Al_2O_3]{\text{Chromatography}} \underset{\text{Fullerene}}{C_{60}} + \underset{\text{Fullerene}}{C_{70}}$$

It is interesting to note that unlike graphite or diamond, the fullerenes dissolve in organic solvents. A solution of C_{60} in toluene is purple whereas that of C_{70} is orange red. In fact, *fullerenes are the only pure form of carbon because they do not have dangling edge or surface bonds which attract other atoms as is the case of graphite or diamond.*

Structure. Of all the fullerenes, C_{60} allotrope is most stable. It looks like a soccer ball and is sometimes called as **bulky ball.** *It contains 20 six membered rings and 12 five membered rings.* Six-membered rings are fused both to other six-membered rings and five-membered rings, but the five-membered rings are connected only to six-membered rings (Fig. 13.11).

This molecule has spherical shape having 60 vertices with a carbon atom at each vertex. Noting the similarity of this molecule to the geodesic domes (having hexagonal and pentagonal patterns) designed and built by the American architect, Robert Buckminster Fuller, it was named as **buckminster fullerrene** or simply **fullerene.**

Because all the carbon atoms are equivalent, the strain caused by the distortion of the bonds from coplanarity is equally distributed among all the carbon atoms. Consequently the molecule is quite stable.

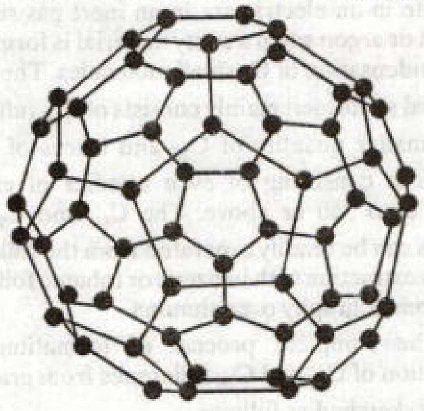


FIGURE 13.11. Buckminster fullerene (C_{60}). Note that all carbons are equivalent and that no five-membered rings are adjacent to one another.

It contains both single and double bonds with C – C distances of 145·3 and 138·3 pm respectively.

C_{70} fullerene, on the other hand, resembles a rugby ball. *It consists of 12 five-membered rings and 25 six- membered rings*. As in C_{60} fullerene, the pentagons are isolated from each other.

Properties. (*i*) Fullerenes being covalent are soluble in organic solvents.

(*ii*) They can be reduced electrochemically and react with group 1 alkali metals, forming solids such as K_3C_{60}. This compound behaves as a superconductor below 18 K which means that it carries electric current with zero resistance.

(*iii*) It reacts with OsO_4 which adds across one of the double bonds in the cage.

(*iv*) It also forms platinum complexes.

Uses. At present, fullerenes do not have any practical uses. However, it is projected that fullerenes may find many nanotechnological applications.

II. Amorphous allotropic forms of carbon

The important amphorphous allotropic forms of carbon are :

1. Coke 2. Charcoal 3. Carbon black. These are all impure forms of graphite or fullerenes.

1. Coke. It is a greyish black hard solid and is obtained by destructive distillation* (strong heating in absence of air).

2. Charcoal. It is obtained in the following four forms, *i.e.*,

(i) Wood charcoal. It is obtained by strong heating of wood in a limited supply of air.

(ii) Animal charcoal. It is also known as *bone black* and is obtained by destructive distillation of bones. It consists of approximately 10% carbon rest being calcium phosphate.

(iii) Sugar charcoal. It is the purest form of amorphous carbon and is obtained by the action of conc. H_2SO_4 on sucrose or cane sugar.

$$C_{12}H_{22}O_{11}\,(s) \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Sugar charcoal}}{12\,C\,(s)} + 11\,H_2O\,(l)$$

(iv) Activated charcoal. All forms of charcoal are highly porous substances and can adsorb many times their own volume of gases. Their adsorption capacity can be further increased by heating charcoal at 1273 K in a current of super heated steam. This treatment removes the impurities such as residual hydrocarbons, oxygen etc. sticking on the surface and thus blocking the capillary pores. Charcoal thus prepared is called **activated charcoal.**

(v) Carbon black or lamp black. It is an almost pure form of amorphous carbon containing 98 – 99% carbon. It is obtained when hydrocarbons such as natural gas and other substances rich in carbon such as kerosene oil, petroleum, turpentine oil, acetylene etc. are burnt in a limited supply of air. The soot obtained is made to stick on wet blankets hung in a chamber. After drying, the soot is removed from the blankets. The soot thus collected is called the *lamp black* or *carbon black.*

$$CH_4 + O_2 \xrightarrow[\text{Limited supply of air}]{\Delta} \underset{\text{Carbon black}}{C} + 2\,H_2O$$

All the allotropic forms of carbon, whether crystalline or amorphous, burn in excess of oxygen at different temperatures to form carbon dioxide. This shows that all the above forms are allotropes of carbon.

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*When coal is subjected to destructive distillation for the manufacture of oil gas, coke is left as residue in the retort. At the same time, a thick deposit is obtained on the roof and sides of the retort. It is called as gas carbon.

ADD TO YOUR KNOWLEDGE

1. Of all the crystalline allotropic forms of carbon, graphite is thermodynamically the most stable allotrope. Its standard enthalpy of formation ($\Delta_f H°$) is assigned a value of zero. The standard enthalpy of formation ($\Delta_f H°$) of diamond and C_{60} fullerene are 1·98 and 38·1 kJ mol^{-1} respectively.

2. **Graphite is thermodynamically more stable than diamond since its free energy of formation is 1·9 kJ mol^{-1} lower at room temperature and atmospheric pressure. Although the conversion of diamond into graphite is thermodynamically favourable, yet is normally does not occur because of high energy of activation for the process.**
   If the energy of activation is made available, the conversion of diamond into graphite can occur.
   The reverse process, *i.e.*, conversion of graphite into diamond is thermodynamically not possible but can be done only under forcing conditions. Thus, graphite can be converted into diamond at 1873 K under a pressure of 50,000—60,000 atmospheres.

3. **Diamond** has the highest thermal conductivity of any known substance (about five times that of Cu) although it is a bad conductor of electricity. It is because of its high thermal conductivity, diamond tipped tools do not over heat and hence are extensively used for drilling and cutting purposes.

4. **Kohinoor diamond.** The value of diamnond is expressed in terms of its weight and purity. The weight of diamond is expressed in terms of carats (1 carat = 200 mg). The famous **Kohinoor** diamond which decorates the crown of England's queen at present weighs 108·93 carats. However, when it was taken from India to England, it weighed 181 carats. To restore its brilliance and lustre, 43% of its original weight was shed.

5. **Carbon nanotubes.** A nanotube is a structure which looks as though it were formed by rolling a sheet of graphite like carbon (a flat network of fused benzene rings resembling chicken wire) into the shape of a cylindrical tube and capping each end with half of a buckyball (or fullerene like hemispheres). These are also produced by electric arc evaporation of graphite.
   The discovery of carbon nanotubes has triggered worldwide interest in studying the physical properties of carbon nanotubes and their potential applications in catalysis, nanotechnology and electronics.
   Nanotubes are very tough-about 100 times as strong as steel. Besides their potential as strengtheners for new composite materials, some nanotubes have been shown to act as electrical conductors or semiconductors depending upon their precise size. They are also being used as tips for analysis of DNA and proteins by atomic force microscopy (AFM) or as molecular size test tubes or capsules for drug delivery.

13.5.3. Atomic and Physical Properties.

(*i*) Carbon exists in various allotropic forms of which *diamond, graphite* and *fullerene* are crystalline while *coal, wood, charcoal, animal* charcoal ; *lamp black, coke and gas carbon are amorphous.* The X-ray analysis has revealed that so called amorphous carbons also have extremely fine crystals. Therefore, these allotropes are called *microcrystalline carbons.*

Some atomic and physical properties of carbon are listed in Table 13.1.

TABLE 13.1. Atomic and Physical Properties of Carbon

Density (*g* cm^{-3}) at 293 K	Melting point (K)	Covalent radius (*pm*)	Electronegativity	Ionization Enthalpy			
				I	II	III	IV
3·51	4373	77	2·5	1086	2352	4620	6220

13.5.4. Chemical Properties

(*i*) **Catenation.** Carbon is the first member of group 14 elements. Its ground state electronic configuration is $1s^2\ 2s^2\ 2p^2$ or [He] $2s^2\ 2p^2$. Carbon is a typical non-metal. It forms a vast majority of covalent compounds by using all its four valence electrons. A remarkable property of carbon is *its ability to link with one another to form covalent bonds to form long or branched chains and rings of different sizes.* This property is called **catenation.** It depends upon the strength of element- element- bond. Since the bond energy of C–C bond is very large (355 kJ mol^{-1}), carbon forms long straight and branched C–C chains or rings of different sizes and shapes. However, as we move down the group, the element-element bond energies decrease rapidly, *viz.*, C–C (355 kJ mol^{-1}), Si–Si (222 kJ mol^{-1}), Ge–Ge (167 kJ mol^{-1} and Sn–Sn (155 kJ mol^{-}1), therefore, the tendency for catenation decreases in the order :
C > Si > Ge > Sn.

(*ii*) **Multiple bonding.** *Due to its small size and higher electronegativity, carbon has a strong tendency to form $p\pi - p\pi$ multiple bonds either with itself ($C = C$, $C \equiv C$) or with other atoms of similar size such as oxygen ($C = O$) and nitrogen ($C = N$, $C \equiv N$).*

In view of these two properties, carbon forms several millions of compounds both naturally occurring and man made.

Some important chemical properties of three important forms of carbon are described below :

(*a*) **Charcoal.** (*i*) Of all the allotropic forms, *charcoal* is the most reactive. It readily burns in air to form CO_2. It reduces conc. H_2SO_4 and conc. HNO_3 to SO_2 and NO_2 respectively.

(*ii*) It combines with many metals to form the corresponding carbides, *e.g.*, CaC_2, Al_4C_3 etc.

(*iii*) When heated with sulphur, it forms carbon disulphide (CS_2).

(*i*) **Diamond.** Chemically, diamond is most resistant towards most of the chemical reagents. It burns in air at 1173 K to form CO_2.

(*ii*) It is slowly oxidised by a mixture of $K_2Cr_2O_7$ + conc. H_2SO_4 at 473 K to give CO_2.

(*iii*) It is stable in vacuum upto 1773 K but changes into graphite at 2073 K and more rapidly at 2273 K.

(*c*) **Graphite.** (*i*) Graphite, like diamond, is not attacked by dilute acids. It is slowly oxidised by chromic acid (H_2CrO_4 *i.e.*, $K_2Cr_2O_7$ + conc. H_2SO_4) to CO_2.

(*ii*) It is oxidised by conc. HNO_3 to give *graphitic acid*, $C_{11}H_4O_5$ which is an insoluble yellowish green substance.

(*iii*) With alkaline $KMnO_4$, it is oxidised to oxalic acid and *mellitic acid*, $C_6(COOH)_6$.

13.6. Oxides of Carbon

Carbon forms many oxides. Two of these oxides, *viz. carbon monoxide* (CO) and *carbon dioxide* (CO_2) are extremely stable and important. The three less stable oxides are : *carbon suboxide* (C_3O_2), C_5O_2 and $C_{12}O_9$. Others which are even less stable include graphite oxides, C_2O and C_2O_3.

1. Carbon monoxide

Preparation. (*i*) It is formed by incomplete combustion of carbon and carbon containing fuels.

$$2C + O_2 \longrightarrow 2CO$$

This type of incomplete combustion occurs during burning of petrol or diesel in automobiles and, therefore, CO is always present in automobile exhausts. It is also present in volcanic gases and gases coming out of furnaces.

(*ii*) Carbon monoxide can also be prepared by reduction of oxides of heavy metals with carbon.

$$ZnO + C \longrightarrow Zn + CO$$

and $$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

(*iii*) In the laboratory, *pure* carbon monoxide is obtained by dehydration of formic acid with conc. H_2SO_4 at 373 K.

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow[373\text{ K}]{H_2SO_4} \underset{\text{Carbon monoxide}}{CO} + H_2O$$

Carbon monoxide can also be prepared in the laboratory by the action of conc. H_2SO_4 on potassium ferrocyanide.

$$K_4[Fe(CN)_6] + 3\,H_2SO_4 \longrightarrow$$
$$2\,K_2SO_4 + FeSO_4 + 6\,HCN$$
$$HCN + 2\,H_2O \longrightarrow HCOOH + NH_3] \times 6$$
$$HCOOH \longrightarrow H_2O + CO\,] \times 6$$
$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4] \times 3$$

$$\underset{\text{Pot. ferrocyanide}}{K_4[Fe(CN)_6]} + 6H_2SO_4 + 6H_2O \longrightarrow$$
$$2K_2SO_4 + FeSO_4 + 3\,(NH_4)_2SO_4 + 6CO$$

Commercial preparation. (*i*) It is commercially produced by passing steam over red hot coke. This reaction also produces hydrogen.

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

A mixture of CO and H_2 is called **water gas** or **synthesis gas.**

(*ii*) When air is used instead of steam, a mixture of CO and N_2 are prdouced. This mixture is called **producer gas.**

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

CO present in water gas or producer gas can further undergo combustion forming CO_2 with evolution of heat.

$$2\,\mathrm{CO}\,(g) + \mathrm{O_2}\,(g) \longrightarrow 2\,\mathrm{CO_2}\,(g)\,; \qquad \Delta_r H^\circ = -\,566\ \mathrm{kJ\ mol^{-1}}$$

Thus, water gas and producer gas are two industrially important fuel gases.

Structure. In CO molecule, both C and O atoms are *sp*- hybridized. One *sp*-hybrid orbital each of C and O overlap to form a C – O, σ-bond while the other *sp*-orbital on each atom contains the lone pair of electrons. The two unhybridized *p*-orbitals of C and O form two *pπ – pπ* bonds. Thus, *CO is a linear molecule.*

$$\underset{\text{in } sp \text{ hybrid orbital}}{\text{lone pair}} \longrightarrow :\mathrm{C}\equiv\overset{+}{\mathrm{O}}: \longleftarrow \underset{sp\text{-hybrid oribital.}}{\text{lone pair in}}$$

Due to the presence of a lone pair of electrons on the carbon atom, CO acts a *Lewis base or a ligand* and can form a coordinate bond with metals ($\mathrm{M} \longleftarrow \mathrm{C}\equiv\overset{+}{\mathrm{O}}$) to form metal carbonyls.

The electron dot structure for CO may be represented either by formula I or Ia.

$$\underset{\mathbf{I}}{:\mathrm{C}::\ddot{\mathrm{O}}:} \quad \text{or} \quad \underset{\mathbf{Ia}}{:\mathrm{C}=\ddot{\mathrm{O}}:}$$

In these structures, C has 6 while O has 8 electrons in the valence shell. To complete the octet around C, O donates a pair of electrons as shown in structure (IIa or IIb or IIc).

$$\underset{\mathbf{IIa}}{{}^{-}\!:\mathrm{C}:::\overset{+}{\mathrm{O}}:} \quad \text{or} \quad \underset{\mathbf{IIb}}{{}^{-}\!:\mathrm{C}\equiv\overset{+}{\mathrm{O}}:} \quad \text{or} \quad \underset{\mathbf{IIc}}{:\mathrm{C}\overset{\leftarrow}{\equiv}\mathrm{O}:}$$

However, CO is best represented as a resonance hybrid of the following two structures.

$$:\mathrm{C}=\ddot{\mathrm{O}}: \longleftrightarrow {}^{-}\!:\mathrm{C}\equiv\overset{+}{\mathrm{O}}:$$

The presence of a triple bond between C and O is supported by the following evidences :

(*i*) The carbon-oxygen bond length is just 113 pm which corresponds to a carbon-oxygen triple bond.

(*ii*) The dipole momentof CO is very low due to back donation of a pair of electrons from the more electronegative O to the less electronegative C-atom.

Properties. Some physical properties of CO are given in Table 13.2.

(*i*) It is a *neutral oxide.*

(*ii*) It is a colourless and odourless gas which is only slightly soluble in water.

(*iii*) **Poisonous nature.** Carbon monoxide is highly poisonous (toxic) in nature. Its toxic nature is due to its ability to form a stable complex with the haemoglobin present in the red blood cells to form *carboxyhaemoglobin* as discussed below :

$$\text{Haemoglobin} + \mathrm{CO} \longrightarrow \text{Carboxyhaemoglobin}$$

In the lungs, haemoglobin combines with molecular oxygen loosely and reversibly to form *oxyhaemoglobin.*

$$\text{Haemoglobin} + \mathrm{O_2} \rightleftharpoons \text{Oxyhaemoglobin}$$

Oxyhaemoglobin thus formed in the lungs then travels to all parts of the body through blood stream and delivers O_2 to the various tissues of the body. However, CO combines with haemoglobin irreversiby (*i.e.* forms stronger bonds than O_2). Therefore, if CO is present, it will form stable complex with haemoglobin (*i.e.* carboxyhaemoglobin) which destroys the oxygen carrying capacity of haemoglobin. As a result, haemoglobin does not take up oxygen easily thereby causing suffocation and ultimately death.

(iv) **Reducing properties.** Since CO can be easily oxidised to CO_2, it acts a as *powerful reducing agent.* As such it reduces many metal oxides to their respective metals.

$$\mathrm{ZnO} + \mathrm{CO} \longrightarrow \mathrm{Zn} + \mathrm{CO_2}$$

$$\mathrm{CuO} + \mathrm{CO} \longrightarrow \mathrm{Cu} + \mathrm{CO_2}$$

$$Fe_2O_3 + 3CO \xrightarrow{1273\ K} 2Fe + 3CO_2$$

It also reduces $PdCl_2$ to Pd and I_2O_5 to I_2.

$$PdCl_2 + CO + H_2O \longrightarrow Pd + CO_2 + 2\,HCl$$

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

(v) Formation of metal carbonyls. It combines with many transition metals such as iron, cobalt, nickel etc. forming metal carbonyls. For example,

$$Ni + 4CO \xrightarrow{330-350\ K} \underset{\text{Nickel carbonyl}}{Ni(CO)_4}$$

$$Fe + 5CO \xrightarrow{473\ K,\ 100\ atm.\ pressure} \underset{\text{Iron carbonyl}}{Fe(CO)_5}$$

Nickel carbonyl is volatile. When heated to 440 – 450 K, it decomposes to form pure nickel.

$$Ni(CO)_4 \xrightarrow{450-470\ K} Ni + 4CO$$

Therefore, nickel carbonyl is used for purification of nickel by *Mond's process*.

(vi) Formation of phosgene. It readily combines with Cl_2 in presence of sunlight to give carbonyl chloride or **phosgene** which is an extremely poisonous gas.

$$CO\,(g) + Cl_2\,(g) \xrightarrow{h\nu} \underset{\textit{Phosgene}}{COCl_2\,(g)}$$

(vii) Absorption. Carbon monoxide is readily absorbed by a solution of CuCl in conc. HCl or NH_3 due to the formation of soluble complexes. For example,

$$CuCl + NH_3 + CO \longrightarrow \underset{\textit{(Soluble complex)}}{[Cu(CO)NH_3]^+\,Cl^-}$$

$$CuCl + HCl + CO \longrightarrow \underset{\textit{(Soluble complex)}}{H^+[Cu(CO)Cl_2]^-}$$

Uses. (*i*) it is an important constituent of two industrial fuels *i.e., water gas* and *producer gas*.

(*ii*) It is used in *Mond's process* for purification of nickel via its nickel carbonyl.

(*iii*) It is used in the manufacture of methyl alcohol, acetic acid, synthetic petrol, sodium formate etc.

(*iv*) In the metallurgy of iron as a reducing agent.

(*v*) Iron carbonyl is used in the manufacture of magnetic tapes for videoes and tape recorders.

2. Carbon dioxide

Preparation. (*i*) It is prepared by burning carbon, fossil fuels and other organic compounds in excess of air or oxygen.

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$$

$$C_5H_{12}\,(g) + 8\,O_2\,(g) \longrightarrow 5\,CO_2\,(g) + 6\,H_2O\,(g)$$

(*ii*) *In the laboratory,* it is prepared by the action of acids on carbonates.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

(*iii*) *Commercially,* CO_2 is produced as a by-product during manufacture of ammonia. The hydrogen needed for the purpose is obtained by passing steam over heated CO or CH_4.

$$CO\,(g) + H_2O\,(g) \xrightarrow{\Delta} CO_2\,(g) + H_2\,(g)$$

$$CH_4\,(g) + 2\,H_2O\,(g) \xrightarrow{\Delta} CO_2\,(g) + 4\,H_2\,(g)$$

It is also formed during manufacture of lime or ethyl alcohol by fermentation of glucose or fructose.

$$\underset{\text{Limestone}}{CaCO_3} \xrightarrow{1600\ K} \underset{\text{Lime}}{CaO} + CO_2$$

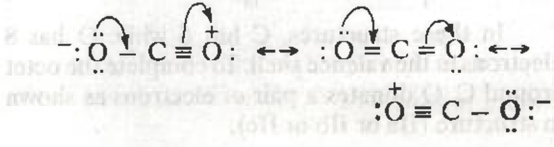
$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2\,C_2H_5OH} + 2CO_2$$

Structure. In CO_2 molecule, C is *sp*-hybridized, it forms two σ-bonds with two oxygen atoms and two *pπ–pπ* multiple bonds. As a result, CO_2 is a *linear, monomeric covalent compound.*

The electron dot structure for CO_2 may be represented by either formula I or Ia

$$\underset{\text{I}}{:\ddot{O}::C::\ddot{O}:} \quad \text{or} \quad \underset{\text{Ia}}{:\ddot{O}=C=\ddot{O}:}$$

This structure predicts that both the carbon-oxygen bond lengths in CO_2 should be equal and should have a typical bond length of 122 pm. However, experimentally, it has been found that carbon-oxygen bond length in CO_2 is only 115 pm. This can be explained, if CO_2 is considered to be a resonance hybrid of the following structures :



Due to resonance, carbon oxygen bond length acquires some triple bond character and hence the bond length decreases from 122 pm to 115 pm.

Properties. The physical properties of CO_2 are quite different from those of CO. Some important physical properties of CO and CO_2 are given in table 13.2.

TABLE 13.2. Physical properties of CO and CO_2

PROPERTY	CO	CO_2
Melting point (K)	68	216·4 at 5·2 atm.
Boiling point (K)	81·5	194·5 (*Sublimes*)
Density (gL^{-1}) at 273 K	1·250	1·977
C—O bond length (pm)	112	115
Heat of formation *i.e.* H_f ($kJ\ mol^{-1}$)	—110·5	—393·5

(i) It is a colourless and odourless gas about 1·5 times heavier than air.

(ii) Unlike CO, CO_2 is not poisonous. However, it does not support life in animals and human beings. However, it can cause soffocation and eventually death due to lack of oxygen.

(iii) Non-combustible nature. Ordinarily CO_2 is neither combustible nor a supporter of combustion. However, certain active metals such as Na, K, Mg etc. continue burning in it.

$$2Mg + CO_2 \longrightarrow 2MgO + C$$

(iv) Solubility. It is slightly soluble in water. Its solubility in water, however, increases with increase in pressure. Soda water and other *aerated soft drinks* are, in fact, solutions of carbon dioxide in water (containing sugar, some flavouring and colouring agents) under pressure.

(v) Acidic nature. When CO_2 dissolves in water, only some of the molecules react with water to form carbonic acid (H_2CO_3) while most of the dissolved CO_2 remains loosely hydrated. Carbonic acid is a *weak dibasic acid.* It forms two series of salts, *i.e.*, the hydrogen carbonates and carbonates derived from the anions HCO_3^- and CO_3^{2-}. Thus, *CO_2 is the anhydride of carbonic acid.*

$$CO_2\,(g) + H_2O\,(l) \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3\,(aq)}$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$$

$$HCO_3^-\,(aq) \rightleftharpoons H^+\,(aq) + CO_3^{2-}\,(aq)$$

Thus, a solution of CO_2 in water is actually an equilibrium mixture of CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}. These equilibria are very important in H_2CO_3/HCO_3^- buffer system which helps to maintain the pH of the human blood between 7·26 – 7·42. Furthermore, the rate at which CO_2 comes in equilibrium with H_2CO_3 is slow and this is also important in the physiology of CO_2.

(vi) Reaction with lime water. When CO_2 is passed through lime water, it turns lime water milky due to the formation of *insoluble calcium carbonate.*

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{(\textit{Insoluble})}{CaCO_3} + H_2O$$

However, if CO_2 is passed for a longer period, the turbidity disappears due to the formation of *soluble calcium bicarbonate.*

$$CaCO_3 + H_2O + CO_2 \longrightarrow \underset{(\textit{Soluble})}{Ca(HCO_3)_2}$$

$$\text{or}\quad Ca(OH)_2 + 2CO_2 \longrightarrow Ca(HCO_3)_2$$

(vii) Photosynthesis. Carbon dioxide is absorbed by plants. In presence of *chlorophyll* (the green colouring pigment of the leaves) and sunlight, the absorbed CO_2 combines with H_2O to form glucose and starch (carbohydrates) which are used as food by the plants. This process is called *photosynthesis*.

$$6CO_2 + 6H_2O \xrightarrow[\text{sunlight}]{\text{Chlorophyll}} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

(viii) Action of ammonia. When CO_2 is reacted with liquid ammonia at 453 – 473 K under a pressure of 220 atmospheres, it first forms ammonium carbamate which subsequently decomposes to give urea.

$$2\,NH_3 + CO_2 \xrightarrow[220\text{ atm.}]{453-473\text{ K}} \underset{\text{Amm. carbamate}}{[NH_2COONH_4]} \longrightarrow \underset{\text{Urea}}{NH_2CONH_2} + H_2O$$

Uses. Carbon dioxide is used :

(*i*) in the preparation of aerated waters.

(*ii*) as a *fire extinguisher* because it is a non-supporter of combustion.

(*iii*) in the manufacture of washing soda by *Solvay ammonia process*.

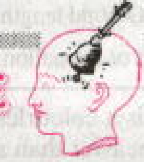
(*iv*) Solid carbon dioxide is used as a refrigerant under the commercial name *dri kold* (see under dry ice).

(*v*) Supercritical CO_2* is used as a solvent to extract organic compounds from their natural sources such as caffeine from coffee beans and perfumes from flowers.

(*vi*) for *artificial respiration* (for victims of CO poisoning) as a mixture of 95% O_2 and 5% CO_2 under the name *carbogen*

(*vi*) for purification of sugar in sugar industry.

ADD TO YOUR KNOWLEDGE



1. The suboxide, $C_{12}O_9$ is also somewhat stable. It is a white solid and is an anhydride of mellitic acid, $C_6(COOH)_6$.
2. Nickel carbonyl, $Ni(CO)_4$ has tetrahedral while iron carbonyl, $Fe(CO)_5$ has trigonal bipyramid geometry.

13.6.1. Dry ice

Dry ice is the name given to solid carbon dioxide. It is also called cardice. It is obtained when CO_2 is cooled under pressure (50 – 60 atm.). When solid carbon dioxide is allowed to evaporate in *air under one atmospheric pressure*, it changes directly into the gaseous state without liquefying. As a result, unlike ordinary ice it does not wet the surface on which it melts. Therefore, it is called *dry ice*.

Dry ice is used for making *cold baths* in the laboratory by mixing it with volatile organic solvents. For example, a temperature of 196 K (–77°C) is obtained by using a mixture of dry ice and acetone and a temperature of 165 K (–108°C) is obtained by using a mixture of dry ice and ether. It is also used as a coolant for preserving perishable articles in food industry. Dry ice is also used for curing local burns and in hospitals for surgical operation of sores.

13.6.2. Carbonates and bicarbonates

Being an acidic oxide, CO_2 readily reacts with alkalies forming carbonates and bicarbonates

$$NaOH + CO_2 \longrightarrow NaHCO_3$$
$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$
$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Carbonates and bicarbonates of many metals are known but the bicarbonates of ony alkali metals exist in the solid state.

In aqueous solutions, both carbonates and bicarbonates undergo hydrolysis producing OH^- ions.

$$HCO_3^- + H_2O \longrightarrow OH^- + H_2CO_3$$
$$CO_3^{2-} + H_2O \longrightarrow OH^- + HCO_3^-$$

Thus, aqueous solutions of both bicarbonates and carbonates are basic in nature.

Importance. **Many carbonates such as $Na_2CO_3.10H_2O$ (*washing soda*), K_2CO_3, $CaCO_3$, $NaHCO_3$ (*baking soda*) are widely used in industry and for domestic purposes. Further, it is interesting to mention here that bicarbonates of calcium and magnesium are responsible for temporary hardness of water.**

Structure. **The central carbon atom of H_2CO_3, HCO_3^- and CO_3^{2-} ion is sp^2-hybridized. It forms three σ-bonds with three oxygen atoms. The unhybridized *p*-orbital on the carbon atom is delocalized over the *p*-orbitals of the three oxygen atoms to form π-bonds (for details refer to unit 6).**

---

*A gas can be liquefied by applying pressure if it is below its critical temperature. For CO_2, the critical pressure and temperture are $73 \times 1{\cdot}013 \times 10^5$ Pa (approx. 72·9 atm) and 304 K respectively. A substance above its critical pressure is called *super critical fluid.* Although at this pressure, CO_2 is a gas, yet it is very dense and hence can behave as a solvent.

13.7. Carbides

Compounds of carbon with elements of lower or about equal electronegativity are called carbides.

Some important examples are CaC_2, Al_4C_3, Be_2C, SiC etc. These are further classified according to the type of bonding involved in them.

1. Ionic or salt like carbides. These are the compounds of carbon with strongly electropositive elements such as Mg, Ca, Al etc. Salt-like carbides are further classified according to the type of hydrocarbon they give on hydrolysis as shown below :

(*i*) **Methanides.** The carbides which give methane on hydrolysis are called methanides. For example, beryllium carbide (Be_2C) and aluminium carbide (Al_4C_3).

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

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

These carbides contain C^{4-} ions.

(*ii*) **Acetylides.** The carbides which on hydrolysis give acetylene are called acetylides. For example, magnesium carbide (MgC_2), calcium carbide (CaC_2), barium carbide (BaC_2) etc.

$$MgC_2 + 2H_2O \longrightarrow Mg(OH)_2 + HC \equiv CH$$

These carbides contain C_2^{2-} or $(C \equiv C)^{2-}$ ions.

Some other carbides having similar structures are Cu_2C_2, Ag_2C_2 etc. However, these carbides on hydrolysis do not give acetylene and hence are not regarded as true carbides.

(*iii*) **Allylides.** The carbides which on hydrolysis give allylene or propyne are called allylides. For example, magnesium carbide (Mg_2C_3).

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + \underset{\text{Allylene or propyne}}{CH_3C \equiv CH}$$

These carbides contain C_3^{4-} ions.

2. Covalent carbides. These are the compounds of carbon with elements having electronegativity slightly less than that of carbon, *i.e.*, silicon and boron. For example, SiC, B_4C, B_4C_3 etc.

3. Interstitial carbides. These are the compounds of carbon with transition elements. *e.g.* TiC, WC, ZrC, VC, V_3C, V_4C_3, Fe_3C (cementite) etc.

In these compounds, the carbon atoms occupy interstitial voids in the close packed lattice of metal atoms. Carbides of this type are extremely hard and electrically conducting.

Preparation. Carbides are usually prepared by heating the element or its oxide with carbon at a very high temperature. For example,

(*i*) Silicon carbide is prepared by heating either silicon or silica with carbon.

$$\underset{\text{Silicon}}{Si} + C \xrightarrow{2500\ K} \underset{\text{Silicon carbide}}{SiC}$$

$$\underset{\text{Silica}}{SiO_2} + 3C \xrightarrow{2273\ K} \underset{\text{Silicon carbide}}{SiC} + 2CO$$

(*ii*) Calcium carbide is prepared by heating CaO with carbon at 2273 K

$$\underset{\text{Lime}}{CaO} + 3C \xrightarrow{2273\ K} \underset{\text{Calcium carbide}}{CaC_2} + CO$$

(*iii*) Aluminium carbide is prepared by heating Al and C in an electric furnace

$$4Al + 3C \xrightarrow{\text{Electric furnace}} \underset{\text{Aluminium carbide}}{Al_4C_3}$$

(*iv*) Beryllium carbide is prepared by heating BeO with carbon at 2200-2300 K.

$$2\,BeO + 3C \xrightarrow{2200-2300\ K} \underset{\text{Beryllium carbide}}{Be_2C} + 2\,CO$$

However, BeC_2 is prepared by heating Be with ethyne

(*v*) Magnesium carbide (MgC_2) is obtained by heating magnesium oxide with carbon.

$$MgO + 3C \xrightarrow{2273\ K} MgC_2 + CO$$

MgC_2, however, changes to Mg_2C_3 on heating.

Uses. Carbides find extensive applications in industry.

(*i*) Calcium carbide is the chief source for acetylene gas.

$$\underset{\text{Cal. carbide}}{CaC_2} + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{CH \equiv CH}$$

Acetylene is the raw meterial for a number of industrially important compounds such as vinyl plastics, ethyl alcohol, acetic acid etc. It is also employed in *oxy-acetylene flame* for welding purposes.

(*ii*) Silicon carbide (SiC) is very hard and is used as an abrasive under the name *carborundum*.

(*iii*) Tungsten carbide (WC) is also very hard. It is used for polishing, drilling and cutting tools.

(*i*) B_4C (boron carbide) which is even harder than silicon carbide is now increasingly being used as an abrasive. It is also used as a shield for radioactive radiations and for making bullet-proof vests (*i.e.*, clothing).

13.8. Halides of Carbon

Carbon combines with halogens to form both simple and mixed halides. All the four simple halides of carbon, *i.e.*, CF_4, CCl_4, CBr_4 and CI_4 are known. The stability of these tetrahalides decreases as the size of the halogen increases, *i.e.* $CF_4 > CCl_4 > CBr_4 > CI_4$. This is due to the reason that the bond energies of the carbon-halogen bonds decrease in order ; $C-F > C-Cl > C-Br > C-I$. Amongst the mixed halides, $CFCl_3$, CF_2Cl_2, CCl_3Br etc. are quite common.

Preparation. (*i*) Tetrafluoromethane or carbon tetrafluoride (CF_4) is prepared as follows :

$$CO_2 + SF_4 \longrightarrow CF_4 + SO_2$$

$$SiC + 2\,F_2 \longrightarrow CF_4 + SiF_4$$

$$\underset{\text{Freon}}{CF_2Cl_2} + F_2 \longrightarrow CF_4 + Cl_2$$

(*ii*) Carbon tetrachloride is prepared by the action of Cl_2 on CS_2 in presence of ferric chloride as a catalyst.

$$CS_2 + 3\,Cl_2 \xrightarrow{FeCl_3,\ 303\ K} CCl_4 + S_2Cl_2$$

$$CS_2 + 2\,S_2Cl_2 \xrightarrow{FeCl_3,\ 333\ K} CCl_4 + 6\,S$$

(*iii*) Freon (CCl_2F_2) is prepared as follows :

$$CCl_4 + 2\,HF \xrightarrow{SbCl_5} CCl_2F_2 + 2\,HCl$$

$$3\,CCl_4 + 2\,SbF_3 \xrightarrow{SbCl_5} CCl_2F_2 + 2\,SbCl_3$$

Properties. (*i*) *All the tetrahalides are covalent compounds having tetrahedral shapes.*

(*ii*) *They are chemically inert, non-flammable compounds.*

(*iii*) *They are not hydrolysed by water under normal conditions since carbon cannot expand its coordination number beyond four because of the absence of d-orbitals.*

However, if sufficient energy is provided by using superheated steam then CCl_4 is hydrolysed to form a poisonous gas called phosgene or carbonyl chloride

$$CCl_4 + H_2O \xrightarrow[\text{steam}]{\text{superheated}} \underset{\text{Phosgene}}{COCl_2} + 2\,HCl$$

Uses. (*i*) Carbon tetrachloride is a common solvent. It is also used as a fire extinguisher under the name *pyrene*. Carbon tetrachloride is also used in medicines as anti hook-worm in intestines.

(*ii*) Mixed halides of flourine and chlorine are especially important as coolants or refrigerants *because of being easily liquefiable gases having low b.p.'s and low specific heats*. For example, CF_2Cl_2 (dichlorodifluoromethane) is widely used as a refrigerant under the name ***freon***.

13.9. Sulphides of Carbon

Carbon forms three sulphides, *i.e.*, CS, (carbon monosulphide), CS_2 (Carbon disulphide) and C_3S_2 (carbon subsulphide) corresponding to three oxides, *i.e.*, CO, CO_2 and C_3O_2. CS is produced when CS_2 is subjected to sunlight. It is also produced when CS_2 is subjected to high frequency electric charge. CS is unlike CO, and is a highly reactive radical even at the temperature of liquid air.

However, when electric arc is passed through CS_2, it gives C_3S_2. Its structure is

$$S = C = C = C = S.$$

It is a *red liquid.* Like C_3O_2, it also polymerises slowly.

Of these three sulphides, carbon disulphide (CS_2) is the most important and is discussed below :

Preparation. (*i*) It is prepared directly by heating sulphur and coke in iron retorts at 1023-1273 K.

$$C + 2\,S \xrightarrow{1023-1273\ K} CS_2$$

(*ii*) Now a days, it is produced mainly by gas phase reaction between natural gas and sulphur in presence of Al_2O_3 or silica gas as catalyst.

$$CH_4 + 4\,S \xrightarrow[Al_2O_3\text{ or Silica gel}]{873\ K} CS_2 + 2\,H_2O$$

Structure. CS_2 is a linear molecule, $S=C=S$ like CO_2 in which carbon is *sp*- hybridized.

Physical Properties : (*i*) Pure carbon disulphide is a colourless, volatile liquid b.p. 319·2 K.

(*ii*) It freezes at 161·4 K.

(*iii*) It is inflammable. It has a low flash point (303 K) and it ignites spontaneously at 373 K.

(*iv*) Its vapours are toxic affecting brain and central nervous system.

Chemical Properties. (*i*) Highly inflammable. CS_2 is highly inflammable and burns in air to give CO_2 and SO_2.

$$CS_2 + 3\,O_2 \longrightarrow CO_2 + 2\,SO_2$$

Sunlight changes CS_2 to CS. That is why CS_2 is stored is dark coloured bottles.

(*ii*) Reaction with metal sulphides. It combines with metal sulphides to give thiocarbonates.

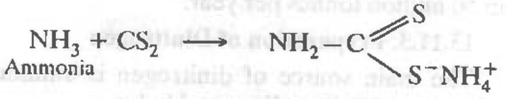
$$MS + CS_2 \longrightarrow MCS_3$$

where M is a divalent metal.

(*iii*) **Reaction with NaOH.** It reacts with NaOH to give a mixture of Na_2CO_3 and Na_2CS_3 (sodium trithiocarbonate or simply sodium thiocarbonate)

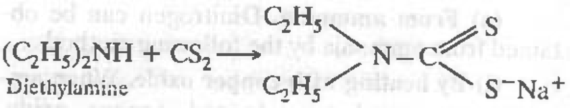
$$3\,CS_2 + 6\,NaOH \longrightarrow Na_2CO_3 + 2\,Na_2CS_3 + 3\,H_2O$$

(*iv*) **Reaction with ammonia and amines.** It reacts with ammonia, primary and secondary amines to form dithiocarbamates.



$$\underset{\text{Ammonia}}{NH_3} + CS_2 \longrightarrow NH_2-C\begin{cases}{=}S\\ S^-NH_4^+\end{cases}$$

Amm. dithiocarbamate



$$\underset{\text{Diethylamine}}{(C_2H_5)_2NH} + CS_2 \longrightarrow \begin{matrix}C_2H_5\\ \\ C_2H_5\end{matrix}\!\!>N-C\begin{cases}{=}S\\ S^-Na^+\end{cases}$$

Sod. salt of N, N–diethyldithiocarbamate

(*v*) **Reaction with water.** CS_2 reacts with water to give thiocarbon dioxide (COS) and H_2S at 473 K and CO_2 and H_2S at higher temperatures.

$$CS_2 + H_2O \xrightarrow{473\text{ K}} \underset{\text{Thiocarbon dioxide}}{COS} + H_2S$$

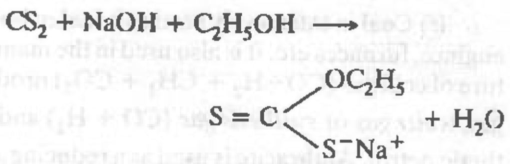
$$COS + H_2O \xrightarrow{>473\text{ K}} CO_2 + H_2S$$

MgO, SO_2 and HSO_2Cl (chlorosulphonic acid) all react in a similar manner to form COS.

$$MgO + CS_2 \longrightarrow COS + MgS$$

$$COS + MgO \longrightarrow CO_2 + MgS$$

(*vi*) **Reaction with ethanol and cellulose.** CS_2 reacts with ethanol in presence of alkalies to give xanthates.



$$CS_2 + NaOH + C_2H_5OH \longrightarrow S=C\begin{cases}OC_2H_5\\ S^-Na^+\end{cases} + H_2O$$

Sod. xanthate
(*Sod. ethyldithiocarbonate*)

If in the above reaction, ethanol is replaced by cellulose, celulose xanthate is formed which dissolves in aqueous alkali to form a viscous solution called **viscose.** When viscose is acidified, cellulose is regenerated either in form of fibres called **viscose rayon** (artificial silk) or as a thin film called **cellophane.**

(*vii*) **Reaction with chlorine.** CS_2 reacts with Cl_2 in presence of ferric chloride or aluminium chloride as catalyst to form carbon tetrachloride.

$$CS_2 + 3\,Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

$$CS_2 + S_2Cl_2 \longrightarrow CCl_4 + 6\,S$$

(*viii*) **Reaction with sulphur trioxide.** CS_2 combines with SO_3 to form thiocarbon dioxide (or carbonyl sulphide)

$$CS_2 + 3SO_3 \longrightarrow \underset{\text{Thiocarbon dioxide}}{COS} + 4SO_2$$

(*ix*) **Action with phosphorus pentachloride.** CS_2 reacts with PCl_5 to form thiocarbonyl chloride.

$$CS_2 + PCl_5 \longrightarrow \underset{\text{Thiocarbonyl chloride}}{CSCl_2} + \underset{\text{Thiophosphonyl chloride}}{PSCl_3}$$

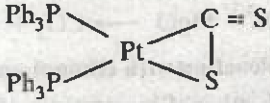
(*x*) **Action with nitric oxide.** It forms an explosive mixtue with nitric oxide.

$$2CS_2 + 10NO \longrightarrow 2CO + 4SO_2 + 5N_2\,.$$

(*xi*) **Formation of complexes.** CS_2 is an efficient complexing agent, and forms complexes more readily than CO_2. It acts as a *bidendate ligand* with one C atom and one S atom bonded to the metal, and CS_2 molecule is bent. For example,

$Pt(PPh_3)_2Cl_2 + CS_2 \longrightarrow$

Bis (triphenylphosphine)
Pt (II) chloride



$+ 2Cl^-$

13.10. Uses of Carbon

(*i*) Coal is extensively used as a fuel in boilers, engines, furnaces etc. It is also used in the manufacture of coal gas ($CO+H_2 + CH_4 + CO_2$) producer gas, *water gas* or *synthesis gas* ($CO + H_2$) and synthetic petrol. Anthracite is used as a reducing agent in metallurgical processes and for the manufacture of graphite.

(*ii*) **Coke** is used as a fuel and as a reducing agent in metallurgical operations.

(*iii*) **Charcoal.** *Activated charcoal* is used as an excellent absorbent in gas masks and for removing offensive odour from the air used in air-conditioning processes. It is also used as a decolourising agent in sugar industry, in refining of oils, fats and other chemicals and gases by adsorption and also as a catalyst. It has also been used in the treatment of drinking water after chlorination to adsorb excess of chlorine. Sugar charcoal is used to colour wine and whisties.

(*iv*) **Lamp black.** It is used for making black inks, paints and shoe-polishes, black pigments etc. It is widely used as a **filler** for rubber tyres to make them hard and strong.

(*v*) **Gas carbon** is a good conductor of electricity. It is used for making electrodes.

(*vi*) For uses of diamond and graphite refer to **sec.** 13.5.2.

13.11. Dinitrogen

Nitrogen was discovered by *Daniel Rutherford in 1772*. Nitrogen is the first element of group 15 of the periodic table and has the electronic configuration, $1s^2\ 2s^2\ 2p^3$. It has five electrons in the valence shell. Nevertheless, it forms a maximum of four covalent bonds (*e.g.* NH_4^+) because of the absence of *d*-orbitals in the valence shell. Like hydrogen and oxygen, nitrogen also exists in its elemental form as a diatomic molecule (N_2). Therefore, it is also called *dinitrogen*. It is a typical non-metal with a high electronegativity (3·0) next only to fluorine (4·0) and oxygen (3·5). Nitrogen forms a variety of compounds in all oxidation states ranging from -3 to $+5$. The common oxidation states are -3 (*e.g.*, NH_3, Mg_3N_2), $+3$ (*e.g.* $NaNO_2$) and $+5$(*e.g.* N_2O_5, HNO_3).

13.11.1. Terrestrial Abundance and Distribution

Dinitrogen occurs both in the free state as well as in the combined state.

(a) In the free state. Dinitrogen occurs in the atmosphere to an extent of 79% by volume. It is also present in *volcanic gases* and gases evolved by the burning of coal.

(b) In combined state. Nitrogen is present in many compounds such as potassium nitrate (*Indian salt petre or simply nitre*), sodium nitrate (*chile salt petre*) and many ammonium salts (*e.g.* NH_4Cl, $(NH_4)_2SO_4$ etc.). Nitrogen is an important constituent of proteins in plants and animals. Its total abundance in earth including the atmosphere is 0·01% by weight.

13.11.2. Isolation from air – Commercial preparation of dinitrogen.

Dinitrogen is prepared commercially from air by liquefaction and fractional distillation. When liquid air is allowed to distil, dinitrogen having lower boiling point (77 K) distils over first leaving behind liquid dioxygen (b.p. 90 K). The dinitrogen obtained from air contains traces of dioxygen and some of the noble gases as impurities. World wide production of dinitrogen from liquid air is more than 50 million tonnes per year.

13.11.3. Preparation of Dinitrogen

The main source of dinitrogen is ammonia and its compounds as discussed below :

(a) From ammonia. Dinitrogen can be obtained from ammonia by the following methods :

(i) By heating with copper oxide. When ammonia is passed over heated copper oxide, dinitrogen is obtained.

$$3CuO + 2NH_3 \xrightarrow{\text{Heat}} N_2 + 3Cu + 3H_2O$$

(ii) By action on bleaching powder.

$$\underset{\text{Bleaching powder}}{3CaOCl_2} + 2NH_3 \longrightarrow 3CaCl_2 + 3H_2O + N_2$$

(iii) By action on chlorine. Ammonia reacts vigorously with chlorine evolving dinitrogen.

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

(b) From ammonium compounds. Dinitrogen is obtained from ammonium compounds as follows:

(i) By heating ammonium nitrite – Laboratory method of preparation. In the laboratory, dinitrogen is obtained by heating ammonium nitrite. Since ammonium nitrite is an unstable compound, an aqueous solution containing an equivalent amount of ammonium chloride and sodium nitrite is heated gently in a round-bottomed flask (Fig. 13.12). Ammonium nitrite is first formed by double decomposition which subsequently decomposes to form dinitrogen.

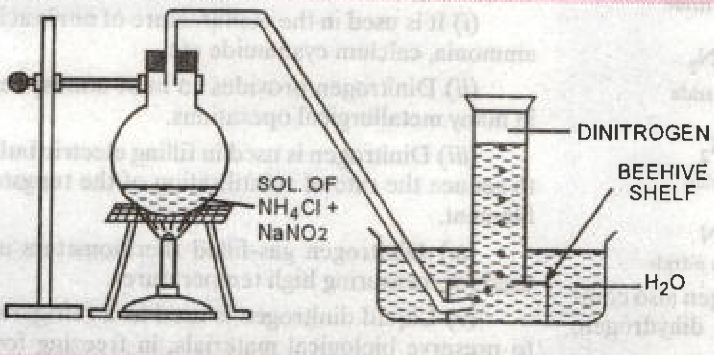


FIGURE 13.12. Laboratory preparation of dinitrogen.

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow NH_4NO_2(aq) + NaCl(aq)$$

$$NH_4NO_2(aq) \xrightarrow{\text{Heat}} N_2(g) + 2H_2O(l)$$

Since dinitrogen is insoluble in water, it is collected by downward displacement of water. During this reaction, small amounts of NO and HNO_3 are also formed. These impurities can be easily removed by passing the gas through aqueous sulphuric acid containing a small amount of potassium dichromate.

(ii) By heating ammonium dichromate. Pure dinitrogen gas can also be prepared in the laboratory by heating ammonium dichromate.

$$(NH_4)_2Cr_2O_7 \longrightarrow \underset{\text{Chromium oxide}}{Cr_2O_3} + N_2 + 4H_2O$$

$(NH_4)_2Cr_2O_7$ may be prepared *in situ* by heating an equimolar mixture of potassium dichromate and ammonium chloride.

(c) From barium azide. Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide.

$$\underset{\text{Barium azide}}{Ba(N_3)_2} \xrightarrow{\Delta} Ba + 3\,N_2$$

13.11.4. Chemical volcano

When a heap of ammonium dichromate is ignited, a spontaneous reaction occurs. The N_2 produced quickly rushes out of the heap splashing green ash of Cr_2O_3 around. This phenomenon is called **chemical volcano.**

13.11.5. Atomic and Physical Properties

(a) Physical properties. (*i*) Dinitrogen is a *colourless, odourless and tasteless gas*. It has two stable isotopes : ^{14}N and ^{15}N.

(*ii*) It is slightly lighter than air ; its vapour density being 14.

(*iii*) Dinitrogen gas is not poisonous (*i.e.* non- toxic) but animals die in its atmosphere for want of dioxygen.

(*iv*) It is very slightly soluble in water (23.2 cm^3 per litre of water at 273 K under one atmosphere or 1 bar pressure).

(*v*) It is adsorbed by charcoal.

Some important physical properties of atomic and molecular nitrogen are given in Table 13.3.

TABLE 13.3. Atomic and Molecular properties of nitrogen

ATOMIC PROPERTIES		MOLECULAR PROPERTIES	
Ionization enthalpy ($kJ\ mol^{-1}$)	1402	Melting point (K)	63·2
Electron gain enthalpy ($kJ\ mol^{-1}$)	7	Boiling point (K)	77·2
Electronegativity (*Pauling scale*)	3·0	Density (*g*/L) at S.T.P.	1·25
Atomic radius (*pm*)	70	Bond length (*pm*)	109·8
Ionic radius (N^{3-}) (*pm*)	171	Bond energy ($kJ\ mol^{-1}$)	946

13.11.6. Chemical Reactivity

Dinitrogen is chemically *inert or unreactive*. In its molecule, the two nitrogen atoms are linked by a triple bond (N≡N) with a bond length of 109·8 pm and bond dissociation energy of 946 kJ mol^{-1}. *The low reactivity of dinitrogen is due to its small size* *and high bond dissociation energy*. However, at high temperatures, dinitrogen reacts with many active metals and non- metals.

Some important chemical properties of dinitrogen are discussed below :

1. Action of litmus. It is *neutral* towards litmus.

2. Action of metals. Dinitrogen in neither combustible nor a supporter of combustion. However, many active metals when heated strongly keep on burning in an atmosphere of dinitrogen forming their respective nitrides.

$$6\,Li + N_2 \xrightarrow{\text{Heat}} \underset{\text{Lithium nitride}}{2Li_3N}$$

$$3Mg + N_2 \xrightarrow{\text{Heat}} \underset{\text{Mag. nitride}}{Mg_3N_2}$$

$$3Ca + N_2 \xrightarrow{\text{Heat}} \underset{\text{Cal. nitride}}{Ca_3N_2}$$

$$2Al + N_2 \xrightarrow{\text{Heat}} \underset{\text{Aluminium nitride}}{2AlN}$$

3. Action of non-metals. Dinitrogen also combines with non- metals such as dihydrogen, dioxygen etc. as discussed below :

(i) Action of dihydrogen. When a mixture of dinitrogen and dihydrogen is heated to about 673 K under a pressure of 200 atmospheres, in presence of iron as catalyst and molybdenum as promoter, ammonia is formed.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\,; \quad \Delta_f H^\circ = -\,92{\cdot}2\text{ kJ mol}^{-1}$$

This reaction forms the basis of *Haber's method* for the manufacture of ammonia.

(ii) Action of dioxygen. Dinitrogen and dioxygen combine to form nitric oxide when the mixture is heated to about 3300 K in an electric arc.

$$N_2 + O_2 \rightleftharpoons \underset{\text{Nitric oxide}}{2NO}\,; \quad \Delta_f H^\circ = +\,135\text{ kJ mol}^{-1}$$

This reaction forms the basis of manufacture of nitric acid by ***Birkland and Eyde process***.

4. Action of alumina. Aluminium nitride is formed.

$$Al_2O_3 + 3C + N_2 \xrightarrow{2073\text{ K}} 2AlN + 3CO$$

5. Action of calcium carbide. Calcium cyanamide is formed.

$$\underset{\text{Cal. carbide}}{CaC_2} + N_2 \xrightarrow{1373\text{ K}} \underset{\text{Cal. cyanamide}}{CaCN_2} + C$$

Calcium cyanamide reacts with water to form ammonia.

$$\underset{\text{Cal. cyanamide}}{CaCN_2} + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Therefore, it is used as a fertilizer under the name *nitrolim* ($CaCN_2$ + C).

13.11.7. Uses of Dinitrogen

In spite of the fact that dinitrogen is an inert gas and does not enter into combination with many elements, yet it finds many applications :

(*i*) It is used in the manufacture of nitric acid, ammonia, calcium cyanamide etc.

(*ii*) Dinitrogen provides an inert atmosphere in many metallurgical operations.

(*iii*) Dinitrogen is used in filling electric bulbs to reduce the rate of volatilisation of the tungsten filament.

(*iv*) Dinitrogen gas-filled thermometers are used for measuring high temperatures.

(*v*) Liquid dinitrogen is used as a refrigerant to preserve biological materials, in freezing food articles and in cryosurgery.

13.12. Fixation of Nitrogen

Nitrogen is vital to life. Although we live in an atmosphere which contains 79% of N_2 by volume yet it cannot be used by plants until it is fixed, *i.e.*, converted into biologically useful forms such as ammonia.

The process of conversion of atmospheric nitrogen into its useful compounds is called fixation of nitrogen. The fixation can be either natural or artificial.

(*i*) **Natural or Biological fixation.** A large amount of atmospheric dinitrogen is brought to the soil by the following two processes

(*a*) During lightining, N_2 and O_2 of the atmosphere combine to form NO which then combines with more O_2 to form NO_2. NO_2 thus formed combines with more O_2 in presence of H_2O to form HNO_3

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

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

$$4\,NO_2 + O_2 + 2\,H_2O \longrightarrow 4\,HNO_3$$

Nitric acid is carried by rain water to the soil where it combines with $CaCO_3$ and $MgCO_3$ present in the soil to form their respective nitrates which serve as fertilizers.

These nitrates are converted into ammonia by **denitrifying bacteria** probably through the following stages.

$$\text{Nitrates} \longrightarrow \text{Nitrites} \longrightarrow NO_2 \longrightarrow N_2 \longrightarrow NH_3$$

Ammonia thus produced is utilized by plants for production of proteins and other nitrogenous compounds required for their growth and other functions.

(*b*) Organisms such as **blue-green algae** and symbiotic bacteria present in the roots of leguminous plants such as beans, peas, clover, alfalfa etc. fix atmospheric nitrogen into compounds which can be easily utilized by plants. This biochemical process is carried out by the enzyme *nitrogenase* whose active sites contain molybdenum and iron atoms.

(ii) Artificial or Industrial fixation. A large amount of atmospheric dinitrogen is fixed in form of NH_3 in industry by Haber's process.

$$N_2 + 3\,H_2 \xrightarrow[\text{Fe catalyst, Mo promoter}]{650-800\text{ K, }200-350\text{ atom}} 2\,NH_3$$

Ammonia thus produced can be converted into number of useful compounds such as nitric acid, urea, hydrazine, ammonium nitrate by chemical methods :

(*i*) Nitric acid (*Ostwald process*)

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

NO thus produced is converted into HNO_3 by the reactions listed above.

(*ii*) Urea

$$2\,NH_3 + CO_2 \xrightarrow[\text{220 atm}]{453-473\text{ K}} \underset{\text{Amm. carbonate}}{[NH_2COONH_4]} \longrightarrow \underset{\text{Urea}}{NH_2CONH_2} + H_2O$$

(*iii*) Amm. nitrate

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

Both urea and NH_4NO_3 are used as fertilizers. A mixture of NH_4NO_3 and fuel oil is used as an explosive in mining operations.

(*iv*) Hydrazine (*Raschig process*)

$$2\,NH_3 + NaOCl \xrightarrow[\text{gelatin}]{\text{Aq. alkali}} N_2H_4 + NaCl + H_2O$$

N_2H_4 is used as a rocket fuel and for removing dissolved O_2 (which causes corrosion) from H_2O used in boilers.

Calcium carbide (CaC_2) can also be used to fix the N_2 of the atmosphere in form of calcium cyanamide which is extensively used as a fertilizer.

$$\underset{\text{Cal. carbide}}{CaC_2} + N_2 \xrightarrow{1373\text{ K}} \underbrace{CaNCN + C}_{\text{Nitrolim}}$$

13.13. Ammonia

It is the most important compound of nitrogen

13.13.1. Preparation of Ammonia*

Ammonia may be prepared by the following methods :

(1) By heating ammonium salts. When the salts of non- volatile acids such as ammonium sulphate, ammonium sodium hydrogen phosphate or ammonium phosphate are heated, ammonia is produced.

$$\underset{\text{Amm. sulphate}}{(NH_4)_2SO_4} \xrightarrow{\Delta} 2NH_3 + H_2SO_4$$

$$\underset{\text{Amm. sod. hydrogen phosphate}}{NH_4NaHPO_4} \xrightarrow{\Delta} NH_3 + \underset{\text{Sod. metaphosphate}}{NaPO_3} + H_2O$$

$$\underset{\text{Amm. phosphate}}{(NH_4)_3PO_4} \xrightarrow{\Delta} 3NH_3 + \underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O$$

(2) By heating ammonium salts with a strong base such as sodium hydroxide, potassium hydroxide or calcium hydroxide either in the solid state or dissolved in water.

$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} Na_2SO_4 + 2H_2O + 2NH_3$$

$$NH_4Cl + KOH \xrightarrow{\Delta} KCl + H_2O + NH_3$$

Laboratory method of preparation. Ammonia is prepared in the laboratory by heating a mixture of slaked lime and ammonium chloride.

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*Not included in the New C.B.S.E. syllabus.

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$$

A mixture of ammonium chloride and slaked lime (1 : 3) is heated in a round bottomed flask. Ammonia thus produced is collected by downward displacement of air since it is lighter than air.

(3) By the action of water on metal nitrides

$$\underset{\text{Mag. nitride}}{Mg_3N_2} + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

$$\underset{\text{Aluminium nitride}}{AlN} + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

Drying of ammonia gas. The moisture present in ammonia may be removed by passing it through a tower packed with *quick lime*, CaO. It cannot be dried by :

(*i*) *Conc.* H_2SO_4 since it reacts with it forming ammonium sulphate.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

(*ii*) *Anhydrous calcium chloride* since it forms a complex having the composition, $CaCl_2.8NH_3$.

(*iii*) *Phosphorus pentoxide* since it reacts to form ammonium phosphate.

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

$$3NH_3 + H_3PO_4 \longrightarrow (NH_4)_3PO_4$$

13.13.2. Manufacture of Ammonia

Haber's Process (synthesis of ammonia). It involves direct combination of dinitrogen and dihydrogen as shown below :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \ ; \quad \Delta_f H^\circ = -92.2 \text{ kJ mol}^{-1}$$

This reaction is reversible, exothermic and occurs with decrease in volume. Therefore, according to *Le Chatelier's principle*, the favourable conditions for the manufacture of ammonia are :

(*i*) **Low temperature.** Since the forward reaction is exothermic, low temperature will favour the formation of ammonia. However, at low temperatures, the rate of the reaction will be slow. The optimum temperature for the reaction has been found to be around 700 K.

(*ii*) **High pressure.** Since the forward reaction occurs with decrease in volume, high pressure will favour the formation of ammonia. The reaction is usually carried out at a pressure of 200×10^5 *Pa* (about 200 atm).

(*iii*) **Catalyst.** The rate of reaction is fairly low around 700 K. It is increased by using finely divided iron as catalyst and molybdenum as promoter (which increases the efficiency of the catalyst). Instead of iron, iron oxide with small amounts of K_2O and Al_2O_3 can also be used.

Details of the process. The plant commonly used for the manufacture of ammonia is shown in Fig. 13.13.

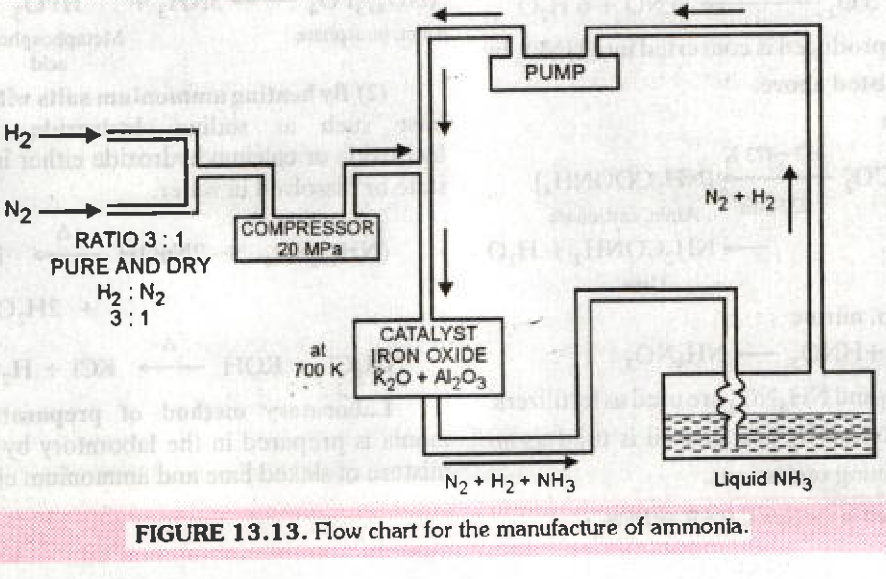


FIGURE 13.13. Flow chart for the manufacture of ammonia.

A mixture of N_2 and H_2 in the ratio 1 : 3 by volume is compressed under a pressure 200×10^5 Pa (about 200 atm). The compressed gases are passed through soda lime tower (not shown in the Fig.) to remove moisture and traces of carbon dioxide.

The compressed gases are then passed into a catalyst chamber where the gases are heated electrically to about 700 K in presence of iron oxide as catalyst alongwith small amounts of K_2O and Al_2O_3 to increase the rate of attainment of equilibrium. The reaction being exothermic ; the heat evolved maintains the desired temperature and further heating is not required.

The gases which leave the catalyst chamber contain NH_3 and unreacted N_2 and H_2. These gases are cooled by passing through condensing pipes where NH_3 gets liquefied and is collected in the receiver. The unreacted gases are pumped back to the compression pump where they are mixed with fresh gaseous mixture and recirculated. The yield of NH_3 is about 8%.

The annual world production of ammonia now exceeds 100 million tonnes.

13.13.3. Properties of Ammonia

I. Physical properties :

1. Ammonia is a *colourless gas* with a characteristic pungent smell called the ammoniacal smell. It causes tears in the eyes.

2. It is lighter than air (density = $0 \cdot 68\ g/cm^3$)

3. It is extremely soluble in water ; one volume of water can dissolve about 1000 volumes of the gas at 273 K.

4. Ammonia can be easily liquefied by cooling under pressure. Liquid ammonia boils at 239·7 K and freezes at 198·4K. In the solid and the liquid states, it undergoes *extensive intermolecular H-bonding* (just as in case of H_2O) which accounts for its high melting and boiling points.

5. When vapourized, liquid ammonia causes intense cooling.

Structure of ammonia. The nitrogen atom in NH_3 is sp^3-hybridised, therefore, NH_3 should have tetrahedral geometry. The three of the four sp^3-orbitals form three N – H σ-bonds while the fourth contains a lone pair of electrons. Since the lone pair-bond pair repulsions are stronger than bond pair-bond pair repulsions, therefore, the H – N – H bond angle decreases from 109° – 28′ to 107·8°. As a result, *NH_3 molecule has* **pyramidal geometry** *with N – H bond length of 101·7 pm and bond angle of 107·5°.* (Fig. 13.14).

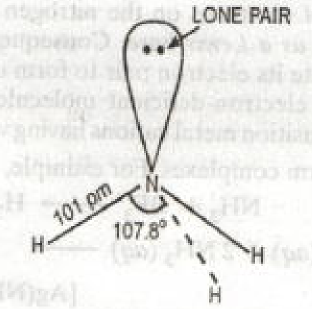


FIGURE 13.14. Structure of ammonia.

(b) Chemical properties :

1. Basic nature. Ammonia is highly soluble in water. Its aqueous solution is weakly basic due to the formation of OH^- ions.

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

Being basic, it turns moist *red litmus blue* and neutralises acids in the dry state as well as in aqueous solutions forming their corresponding salts.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$2NH_4OH + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + 2H_2O$$

2. Reaction with heavy metal salt solutions. Ammonium hydroxide reacts with many metallic salts and precipitates them as hydroxides.

$$FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3 \downarrow} + 3NH_4Cl$$

$$AlCl_3 + 3NH_4OH \longrightarrow \underset{\text{White ppt.}}{Al(OH)_3 \downarrow} + 3NH_4Cl$$

$$CrCl_3 + 3NH_4OH \longrightarrow \underset{\text{Green ppt.}}{Cr(OH)_3 \downarrow} + 3NH_4Cl$$

This property is made use of in precipitating these metals as their hydroxides in the group III of qualitative analysis.

3. Oxidation. (*a*) *It is oxidised to nitrogen when passed over heated copper oxide.*

$$2NH_3 + 3CuO \xrightarrow{\text{Heat}} 3Cu + 3H_2O + N_2$$

(*b*) *When ammonia, mixed with an excess of air, is passed over red hot platinum gauze at 1100 K, it is oxidised to nitric oxide.*

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

This reaction forms the basis for manufacture of nitric acid by *Ostwald's process*.

4. As a Lewis base. Due to the presence of a lone pair of electrons on the nitrogen atom, *ammonia acts as a Lewis base*. Consequently, it can easily donate its electron pair to form co-ordinate bond with electron-deficient molecules (such as BF_3) or transition metal cations having vacant *d*-orbitals to form complexes. For example,

$$NH_3 + BF_3 \longrightarrow H_3N \rightarrow BF_3$$

$$Ag^+ (aq) + 2\,NH_3\,(aq) \longrightarrow [Ag(NH_3)_2]^+\,(aq)$$

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

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

Due to the formation of complex ions, white ppt. of silver chloride dissolves in excess of ammonia to form a complex compound $[Ag(NH_3)_2]Cl$, diamminesilver (I) chloride. Similarly, copper sulphate dissolves in excess of ammonia to form soluble deep blue coloured complex $[Cu(NH_3)_4]SO_4$, tetrammine copper (II) sulphate.

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Diamminesilver (I) chloride}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$CuSO_4 + 4NH_4OH \longrightarrow \underset{\text{Tetramminecopper (II) sulphate (deep blue)}}{[Cu(NH_3)_4]\,SO_4} + 4H_2O$$

These reactions are used as tests for these cations in qualitative analysis.

5. Action of halogens. Halogens react with ammonia as follows :

With excess NH_3 :

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

With excess Cl_2 :

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

With Br_2 :

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

With I_2 :

$$2NH_3 + 3I_2 \longrightarrow \underset{\text{Nitrogen tri–iodide ammoniate (brown ppt.)}}{NH_3.NI_3} + 3HI$$

When $NH_3.NI_3$, in the dry state, is either rubbed or struck against a surface, it explodes with noise liberating vapours of iodine.

$$8\,NH_3.NI_3 \longrightarrow 5N_2 + 9I_2 + 6NH_4I$$

Thus, it is a mild and harmless explosive.

6. Reaction with carbon dioxide. When gaseous CO_2 is reacted with liquid NH_3 at 453 – 473 K under a pressure of 220 atmaspheres, it first forms ammonium carbamate which subsequently decomposes to give urea.

$$2\,NH_3 + CO_2 \xrightarrow[\text{220 atm.}]{\text{453 – 473 K}} \underset{\text{Amm. carbamate}}{[NH_2COONH_4]}$$

$$\longrightarrow \underset{\text{Urea}}{NH_2CONH_2} + H_2O$$

Urea is widely used as a fertilizer since it slowly decomposes in soil to give NH_3 and CO_2.

$$NH_2CONH_2 + H_2O \longrightarrow 2\,NH_3 + CO_2$$

It has a very high nitrogen content (46%)

7. Action of metals. Ammonia when passed over molten sodium or potassium metal at 575 K form corresponding amides with the liberation of dihydrogen.

$$2\,Na + 2\,NH_3 \xrightarrow{\text{575 K}} \underset{\text{Sodamide}}{2\,NaNH_2} + H_2$$

$$2\,K + 2\,NH_3 \xrightarrow{\text{575 K}} \underset{\text{Pot. amide}}{2\,KNH_2} + H_2$$

8. Reaction with Nessler's reagent. With Nessler's reagent (an alkaline solution of K_2HgI_4), ammonia or ammonium slats give a brown precipitate due to the formation of *iodide of Millon's base.*

$$\underset{\text{Nessler's reagent}}{2\,K_2HgI_4} + NH_3 + 3\,KOH \longrightarrow$$

$$\underset{\substack{\text{Iodide of Millon's base} \\ \text{(brown ppt.)}}}{H_2N - Hg - O - Hg - I} + 7\,KI + 2\,H_2O$$

9. Reaction with sodium hypochlorite. When a large excess of aqueous ammonia is treated with sodium hypochlorite in presence of glue or gelatine, it gets oxidised to hydrazine.

$$2\,NH_3 + NaOCl \longrightarrow \underset{\text{Hydrazine}}{NH_2.NH_2} + NaCl + H_2O$$

Actually the reaction proceeds in two steps :

$$(i)\; NH_3 + NaOCl \longrightarrow NaOH + \underset{\text{Chloramine}}{NH_2Cl} \qquad \textit{(Fast reaction)}$$

$$(ii)\; NH_2Cl + 2\,NH_3 \longrightarrow NH_2.NH_2 + NH_4Cl \qquad \textit{(Slow reaction)}$$

Glue or gelatine catalyses the slow reaction and inhibits the secondary reaction, *i.e.,*

$$N_2H_4 + 2\,NH_2Cl \longrightarrow N_2 + 2\,NH_4Cl$$

10. Liquid ammonia as a solvent. Just like water, ammonia also undergoes *self-ionisation* in liquid state.

$$2\,NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$(c.f. \quad 2\,H_2O \rightleftharpoons H_3O^+ + OH^-)$$

Therefore, liquid ammonia is used for dissolving many polar compounds and also for carrying out many reactions in the *non- aqueous medium.*

13.13.4. Uses of Ammonia

Some important uses of ammonia are :

(*i*) In the formation of various nitrogenous fertilizers such as urea, ammonium nitrate, ammonium sulphate, ammonium phosphate, calcium ammonium nitrate (CAN) etc.

(*ii*) In the manufacture of nitric acid by the *Ostwald's process* and in the manufacture of sodium carbonate by the *Solvay's process.*

(*iii*) Liquid ammonia is used as a refrigerant in ice-factories and cold storages.

(*iv*) As a cleansing agent for removing grease etc.

(*v*) As a laboratory reagent.

13.13.5. Tests of Ammonia

(*i*) It turns moist red litmus paper blue and moist turmeric paper brown.

(*ii*) It gives brown precipitate with Nessler's reagent.

(*iii*) With a drop of HCl, it produces dense white fumes of ammonium chloride.

(*iv*) With copper sulphate solution, it gives a deep blue solution.

(*v*) It gives a yellow precipitate with chloroplatinic acid.

$$\underset{\substack{\text{Chloroplatinic}\\\text{acid}}}{H_2PtCl_6} + 2\,NH_3 \longrightarrow \underset{\substack{\text{Amm. chloroplatinate}\\\text{(yellow ppt.)}}}{(NH_4)_2PtCl_6}$$

13.14. Oxides of Nitrogen

Nitrogen forms a number of oxides in which the oxidation state of nitrogen varies from +1 to +5.

Some important characteristics of the oxides of nitrogen are given in Table 13.4.

TABLE 13.4. Oxides of nitrogen

Formula	Name	Oxidation State of N	Properties
1. N_2O	Dinitrogen monoxide or Nitrous oxide	+1	Colourless gas, rather unreactive
2. NO	Nitrogen monoxide or Nitric oxide	+2	Colourless gas, reactive, paramagnetic
3. N_2O_3	Dinitrogen trioxide	+3	Dark blue in the liquid or the solid state, unstable in the gas phase.
4. (*a*) NO_2	Nitrogen dioxide	+4	Brown gas
(*b*) N_2O_4	Dinitrogen tetroxide	+4	Colourless, exists in equilibrium with NO_2 both in the gaseous and liquid state.
5. N_2O_5	Dinitrogen pentoxide		Unstable as gas, in the solid state exists as $[NO_2]^+ [NO_3]^-$

1. Dinitrogen monoxide or Nitrous oxide (N_2O) is prepared by heating ammonium nitrate or by the action of nitrous acid on hydroxylamine.

$$NH_4NO_3 \xrightarrow{\text{Heat}} N_2O + 2H_2O$$

$$NH_2OH + HONO \longrightarrow N_2O + 2H_2O$$

It is also called *laughing gas* because it causes hysterical laughter or euphoria. In small amounts, it also acts as an anaesthetic agent particularly in dentistry. However, its largest use is as a propellant for whipped ice cream because it has no taste and is non-toxic.

It is a neutral oxide and reacts with sodamide to form sodium azide (NaN_3)

$$N_2O + 2\,NaNH_2 \longrightarrow NaN_3 + NH_3 + NaOH$$

N_2O does not burn itself but decomposes on heating to produce O_2 which supports combustion.

$$2N_2O \xrightarrow{873\text{ K}} 2N_2 + O_2$$

$$S + 2N_2O \xrightarrow{\Delta} SO_2 + 2N_2$$

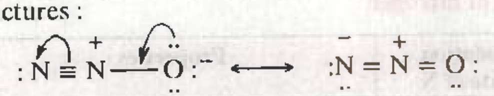
$$Mg + N_2O \xrightarrow{\Delta} MgO + N_2$$

Structure. The simplest electronic structure of N_2O in which both nitrogen and oxygen atoms have complete octets is shown below :

$$:N:::N:\overset{..}{\underset{..}{O}}: \qquad \text{or}$$

$$N \overset{113\text{ pm}}{\equiv} N \overset{119\text{ pm}}{\longrightarrow} O \quad \text{or} \quad :N{\equiv}\overset{+}{N}{-}\ddot{\underset{..}{O}}:^-$$

Thus N_2O is a linear molecule and is expected to have a large dipole moment. However, its dipole moment is very low, *i.e.*, 0·17D, therefore, it is regarded as a resonance hybrid of the following two structures :



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

2. Nitric oxide (NO). Preparation. It is prepared by catalytic oxidation of ammonia at 1100 K in presence of Pt as catalyst.

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

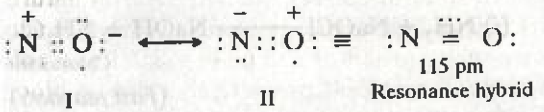
In the laboratory, NO is prepared either by the action of dil. HNO_3 on copper metal or by reduction of HNO_2 by I^- ions.

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

$$2HNO_2 + 2I^- + 2H^+ \longrightarrow 2NO + I_2 + 2H_2O$$

Like N_2O, NO is also a *neutral oxide.*

Structure. Nitric oxide is regarded as a resonance hybrid of the following two structures, I and II



$$\overset{+}{:N}\,\overset{..}{::}\,\overset{..}{\underset{\cdot}{O}}:^- \longleftrightarrow :\overset{-}{\underset{..}{N}}::\overset{+}{\underset{\cdot}{O}}: \equiv :N \overset{...}{=} O:$$

Thus the resonance hybrid contains a double bond as well as a *three electron bond* between nitrogen and oxygen atoms.

Thus, nitric oxide has an odd number of electrons (11 valence electrons) and hence is *paramagnetic* in the gaseous state. But it is diamagnetic in liquid and solid states since in these states it dimerises forming symmetrical dimer,

$$2\,NO \longrightarrow \underset{\text{Symmetrical dimer}}{O=N-N=O}$$

The asymmetrical dimer (Fig. 13.15) has been observed to be formed as a red solid in the presence of HCl or Lewis acids.

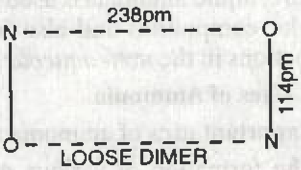


FIGURE 13.15. Structure of nitric oxide in liquid and solid states.

Properties. (*i*) Since odd electron molecules are usually highly reactive, therefore, NO instantly reacts with O_2 to give NO_2 and Cl_2 to give nitrosyl chloride (NOCl)

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO + Cl_2 \longrightarrow 2\,NOCl$$

(*ii*) NO readily forms coordination complexes with transition metals. For example, Fe^{2+} combines with NO to form the complex, $[Fe(H_2O)_5NO]^{2+}$ which is responsible for the colour in the *brown-ring test* for nitrates (refer to page 13/42).

(*iii*) It is thermodynamically unstable and decomposes into its elements at high temperatures (1373 – 1473 K).

$$2NO\,(g) \xrightarrow{1373\,-\,1473\text{K}} N_2\,(g) + O_2\,(g)$$

Therefore, it supports combustion at high temperatures.

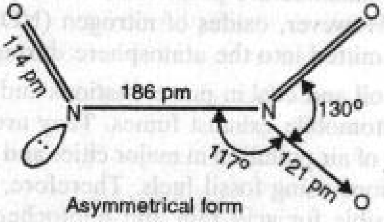
$$Mg + 2NO \xrightarrow{1373-1473\ K} MgO + N_2$$

In spite of its reactive and harmful nature, NO occurs in biological systems in traces. It acts as a neurotransmitter and plays a significant role in controlling blood pressure by relaxing blood vessels. It also provides protection from bacterial infections.

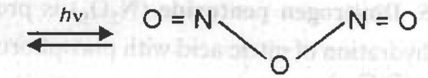
3. Dinitrogen trioxide (N_2O_3) is prepared by cooling an equimolar mixture of nitric oxide and nitrogen dioxide below 253 K

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

Structure. This oxide exists in two different forms which can be interconverted by irradiation with light of appropriate wavelength

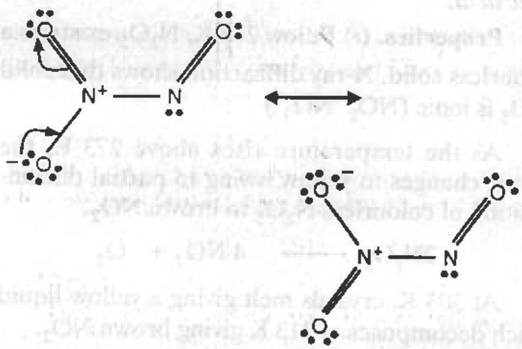


Asymmetrical form



Symmetrical form

The asymmetrical form may also be regarded as a resonance hybrid of the following two canonical structures.



Properties. (*i*) N_2O_3 condenses to a blue coloured liquid below 243 K.

(*ii*) It is an acidic oxide and dissolves in water to form nitrous acid.

$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$

Therefore, it is regarded as an *anhydride of nitrous acid.*

(*iii*) It reacts with alkalies forming corresponding nitrites.

$$2NaOH + N_2O_3 \longrightarrow \underset{\text{Sod. nitrite}}{2NaNO_2} + H_2O$$

(*iv*) It reacts with concentrated acids forming nitrosyl salts.

$$N_2O_3 + \underset{\text{Perchloric acid}}{HClO_4} \longrightarrow \underset{\text{Nitrosyl perchlorate}}{2NO[ClO_4]} + H_2O$$

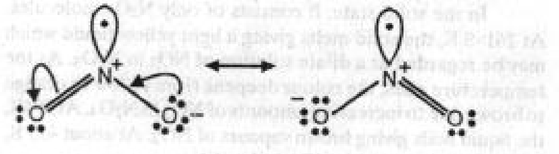
$$N_2O_3 + H_2SO_4 \longrightarrow \underset{\text{Nitrosyl hydrogen sulphate}}{2NO[HSO_4] + H_2O}$$

4. Nitrogen dioxide (NO_2) is prepared either by heating nitrates of heavy metals such as $Pb(NO_3)_2$ or by the action of conc. HNO_3 on copper, silver, lead etc.

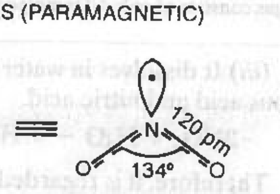
$$2Pb(NO_3)_2 \xrightarrow{\text{Heat}} 2PbO + 4NO_2 + O_2$$

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

Structure. The NO_2 molecule is angular with a bond angle of 134° and N–O bond length of 120 pm.



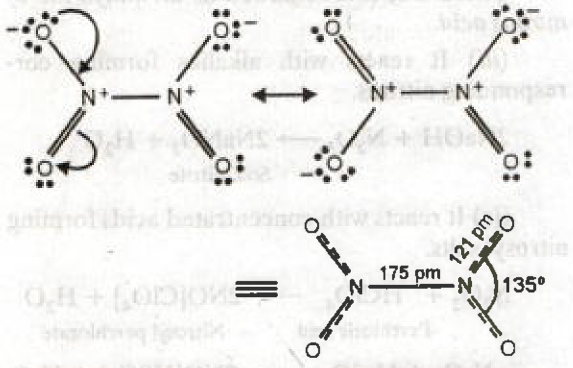
NO_2, BROWN GAS (PARAMAGNETIC)



RESONANCE HYBRID

Because of the presence of an unpaired electron on N atom, NO_2 undergoes dimerization at low temperature to form N_2O_4.

X-ray diffraction on solid N_2O_4 suggests that it is planar. The N–N bond length is abnormally long (175 pm).



N_2O_4, COLOURLESS, DIAMAGNETIC (RESONANCE HYBRID)

Properties. (*i*) NO_2 is a reddish brown poisonous gas. On cooling (294 K), it turns into a liquid and a solid at 261·8 K.

(*ii*) It is an odd electron molecule (23 electrons) and is *paramagnetic* and very reactive. At low temperatures, it dimerises to form N_2O_4 which is colourless and *diamagnetic*.

Thus NO_2 exists in equilibrium with N_2O_4 and the equilibrium is temperature dependent.

$$\underset{(Colourless)}{N_2O_4} \rightleftharpoons \underset{(Reddish\ brown)}{2NO_2}$$

In the solid state, it consists of only N_2O_4 molecules. At 261·8 K, the solid melts giving a light yellow liquid which may be regarded as a dilute solution of NO_2 in N_2O_4. As the temperature rises, the colour deepens from yellow to orange to brown due to increasing amounts of NO_2 in N_2O_4. At 294K, the liquid boils giving brown vapours of NO_2. At about 415 K, the gas consists of only NO_2 molecules.

(*iii*) It dissolves in water forming a mixture of nitrous acid and nitric acid.

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

Therefore, it is regarded as a *mixed anhydride* of HNO_2 and HNO_3.

(*iv*) It reacts with alkalies to form a mixture of nitrites and nitrates.

$$2NO_2 + 2NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

(*v*) The $NO_2 - N_2O_4$ system is a strong oxidising agent. NO_2 reacts with F_2 and Cl_2 forming nitryl flouride and nitryl chloride respectively

$$2NO_2 + F_2 \longrightarrow \underset{\text{Nitryl fluoride}}{2NO_2F}$$

$$2NO_2 + Cl_2 \longrightarrow \underset{\text{Nitryl chloride}}{2NO_2Cl}$$

It also oxidises HCl to Cl_2 and CO to CO_2

$$4HCl + 2NO_2 \longrightarrow 2NOCl + Cl_2 + 2H_2O$$

$$NO_2 + CO \longrightarrow NO + CO_2$$

Uses. Liquid N_2O_4 is used as an oxidiser for rocket fuels in missiles and space vehicles.

Both nitric oxide and nitrogen dioxide are used in the manufacture of nitric acid and nitrate fertilizers. However, oxides of nitrogen (NO and NO_2) are emitted into the atmosphere during the burning of oil and coal in power stations and also through automobile exhaust fumes. They are the main cause of air pollution in major cities and near power stations using fossil fuels. Therefore, they are responsible for acid rain and photochemical smog (for details, refer to unit 18).

5. Dinitrogen pentoxide (N_2O_5) is prepared by dehydration of nitric acid with phosphorus pentoxide (P_4O_{10})

$$4HNO_3 + P_4O_{10} \longrightarrow 2\,N_2O_5 + \underset{\text{Metaphosphoric acid}}{4HPO_3}$$

Thus, N_2O_5 is regarded as an *anhydride of nitric acid.*

Properties. (*i*) Below 273 K, N_2O_5 exists as a colourless solid. X-ray diffraction shows that solid N_2O_5 is ionic ($NO_2^+\ NO_3^-$)

As the temperature rises above 273 K, the colour changes to yellow owing to partial decomposition of colourless N_2O_5 to brown NO_2.

$$2N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

At 303 K, crystals melt giving a yellow liquid which decomposes at 313 K giving brown NO_2.

(*ii*) It acts as a *strong oxidising agent* and oxides I_2 to I_2O_5 and Na to $NaNO_3$

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

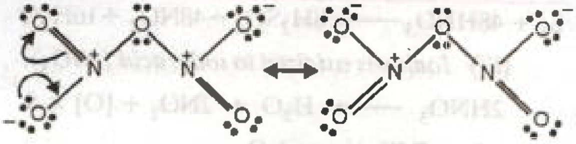
$$Na + N_2O_5 \longrightarrow NaNO_3 + NO_2$$

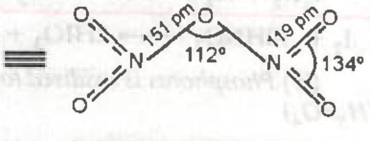
(iii) It also reacts with H_2SO_4 to form nitronium ion and NaCl to form nityl chloride.

$$N_2O_5 + 3H_2SO_4 \longrightarrow 2NO_2^+ + H_3O^+ + 3HSO_4^-$$

$$N_2O_5 + NaCl \longrightarrow NaNO_3 + NO_2Cl$$

Structure. N_2O_5 is considered to be a resonance hybrid of the following two Lewis structures :





RESONANCE HYBRID

13.15. Nitric Acid

Nitric acid (HNO_3) is the most stable and most important oxy-acid of nitrogen. Another important oxy-acid is nitrous acid (HNO_2). It is, however, quite unstable and exists only in very dilute solutions.

13.15.1. Manufacture of Nitric acid

Nitric acid is prepared commercially exclusively by the catalytic oxidation of ammonia (**Ostwald process**). The flow-sheet diagram of the plant employed is given in Fig. 13.16.

The process involves the following steps :

(i) Converter. Ammonia obtained by Haber's process is mixed with dust free air in the ratio 1 : 10 by volume and the mixture is passed through a converter made up of steel and packed with a metal gauze made of pure platinum or 90% platinum and 10% rhodium at a temperature of 1100 K and 9×10^5 *Pa* (9 bar) pressure when ammonia is oxidised to nitric oxide.

$$4NH_3\,(g) + 5O_2\,(g) \xrightarrow[1100\text{ K}]{\text{Pt, Rh}} 4NO\,(g) + 6H_2O\,(g)\ ;$$

$$\Delta H = -90{\cdot}0 \text{ kJ}$$

Since the reaction is exothermic, the heat of the reaction maintains the temperature of the catalyst and further heating is not required. About 90 – 95% NH_3 is oxidised to NO.

(ii) Oxidation chamber. The gases coming out of the catalyst tower are cooled below 420 K when the unreacted oxygen in air reacts with NO to give NO_2.

$$2\,NO\,(g) + O_2\,(g) \xrightarrow{< 420\text{ K}} 2\,NO_2\,(g)$$

(iii) Absorption tower. Nitrogen dioxide from oxidation chamber is introduced at the bottom of an absorption tower packed with acid- proof flint or quartz pieces. Water is sprayed from the top of this tower. Nitrogen dioxide dissolves in water to give nitric acid and NO which is recycled.

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

(iv) Concentration of the acid. Dilute nitric acid collected at the bottom of the absorption tower is concentrated by distillation under reduced pressure to about 68·5% by weight. Further concentration to about 98% is achieved by dehydration with conc. H_2SO_4. *Fuming nitric acid* is obtained by dissolving an excess of NO_2 in conc. HNO_3. It is brown in colour.

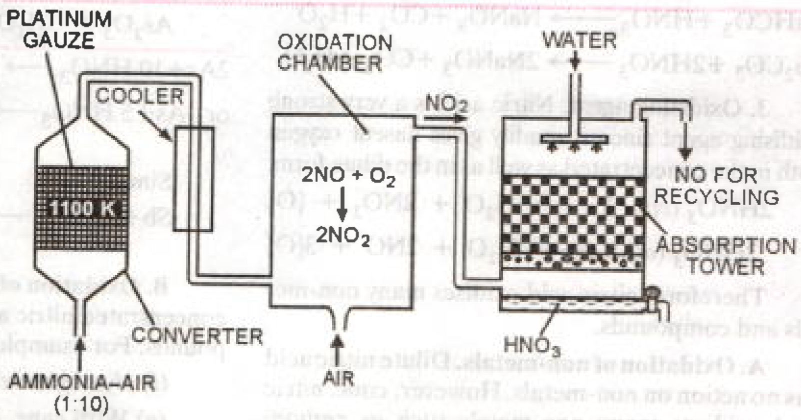


FIGURE 13.16. Manufacture of HNO_3 by Ostwald's process.

Laboratory preparation of nitric acid. Nitric acid is prepared in the laboratory by heating sodium or potassium nitrate with conc. H_2SO_4 at 423 – 473 K in a glass retort.

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

Anhydrous nitric acid is obtained by distillation of conc. HNO_3 with P_4O_{10}

13.15.2. Physical Properties of Nitric acid

1. Pure nitric acid is a colourless *fuming liquid* with pungent odour. However, impure acid is yellow due to the presence of dissolved oxides of nitrogen in it.

2. It forms a constant boiling (393·5 K) mixture *i.e*, azeotrope with water containing about 68.5% of nitric acid.

3. It has a corrosive action on skin and produces painful blisters.

4. It boils at 355.6 K and freezes to a white solid at 231.4 K. Its density at 298 K is $1\cdot504\ g\ cm^{-3}$.

13.15.3. Chemical Properties of Nitric acid*

1. Decomposition. It decomposes on heating giving nitrogen peroxide, oxygen and water.

$$4\ HNO_3\ (aq) \xrightarrow{\text{heat}} 4NO_2\ (g) + O_2\ (g) + 2\ H_2O\ (l)$$

2. Acidic nature. Nitric acid is a strong monobasic acid. In aqueous solution, it ionizes as :

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

Being a monobasic acid, it reacts with metallic oxides, hydroxides, carbonates and bicarbonates giving only one series of salts called *nitrates*.

$$CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$$

$$NaHCO_3 + HNO_3 \longrightarrow NaNO_3 + CO_2 + H_2O$$

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

3. Oxidising agent. Nitric acid is a very strong oxidising agent since it readily gives nasent oxygen both in the concentrated as well as in the dilute form.

$$2HNO_3\ (conc.) \longrightarrow H_2O + 2NO_2 + [O]$$

$$2HNO_3\ (dil.) \longrightarrow H_2O + 2NO + 3[O]$$

Therefore, nitric acid oxidises many non-metals and compounds.

A. Oxidation of non-metals. Dilute nitric acid has no action on non-metals. However, conc. nitric acid oxidises many non-metals *such as carbon, sulphur, iodine* and metalloids like *arsenic, antimony* etc.to their corresponding oxy-acids while nitric acid itself is reduced to nitrogen dioxide. For example,

(*i*) *Carbon is oxidised to carbonic acid* (H_2CO_3).

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + [O] \times 2$$

$$C + 2[O] + H_2O \longrightarrow H_2CO_3$$

$$C + 4HNO_3 \longrightarrow H_2CO_3 + H_2O + 4NO_2\uparrow$$

(*ii*) *Sulphur is oxidised to sulphuric acid* (H_2SO_4).

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + [O] \times 24$$

$$S_8 + 24[O] + 8H_2O \longrightarrow 8H_2SO_4$$

$$S_8 + 48HNO_3 \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

(*iii*) *Iodine is oxidized to iodic acid* (HIO_3).

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + [O] \times 5$$

$$I_2 + 5[O] \longrightarrow I_2O_5$$

$$I_2O_5 + H_2O \longrightarrow 2HIO_3$$

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

(*iv*) *Phosphorus is oxidised to phosphoric acid* (H_3PO_4)

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + [O] \times 10$$

$$P_4 + 10[O] \longrightarrow P_4O_{10}$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

(*v*) *Arsenic is oxidised to arsenic acid* (H_3AsO_4)

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + [O] \times 5$$

$$2As + 5[O] \longrightarrow As_2O_5$$

$$As_2O_5 + 3H_2O \longrightarrow 2H_3AsO_4$$

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

$$\text{or}\quad As + 5\ HNO_3 \longrightarrow \underset{\text{Arsenic acid}}{H_3AsO_4} + H_2O + 5NO_2$$

Similarly,

$$Sb + 5HNO_3 \longrightarrow \underset{\text{Antimonic acid}}{H_3SbO_4} + H_2O + 5NO_2$$

B. Oxidation of compounds. Dilute as well as concentrated nitric acid oxidises a number of compounds. For example,

(*i*) *Hydrogen sulphide is oxidised to sulphur*

(a) With conc. HNO_3 :

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

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

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

(b) With dil. HNO_3 :

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

$$H_2S + [O] \longrightarrow H_2O + S\,] \times 3$$

$$3H_2S + 2HNO_3 \longrightarrow 4H_2O + 2NO + 3S\downarrow$$

(*ii*) *Sulphur dioxide is oxidised to sulphuric acid*

(a) With conc. HNO_3 :

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

$$SO_2 + H_2O + [O] \longrightarrow H_2SO_4$$

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

(b) With dil. HNO_3 :

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

$$SO_2 + H_2O + [O] \longrightarrow H_2SO_4\,] \times 3$$

$$3SO_2 + 2HNO_3 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO$$

(*iii*) *Ferrous sulphate is oxidised to ferric sulphate*

(a) With conc. HNO_3 :

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

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

$$2FeSO_4 + 2HNO_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2H_2O + 2NO_2$$

(b) With dil. HNO_3 :

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

$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$

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

Nitric oxide evolved combines with ferrous sulphate to form a dark brown addition compound, $FeSO_4.NO$, nitroso-ferrous sulphate. This reaction forms the basis of the *ring test* for nitrates.

4. Action on metals. With the exception of gold and platinum (noble metals), nitric acid attacks all metals forming a variety of products. On the basis of reactivity, metals have been divided into three categories :

A. Reaction with metals which are more electropositive than hydrogen (Na, K, Ca, Mg, Al, Mn, Zn, Cr, Cd, Fe, Co, Ni, Sn, Pb, Sb etc). *In this case, nascent hydrogen is liberated which further reduces nitric acid* giving a variety of reduction products such as NO_2, NO, NH_3, NH_4NO_3 and N_2O as shown below :

$$\text{Metal} + HNO_3 \longrightarrow \text{Metal nitrate} + H$$

$$HNO_3 + H \longrightarrow \text{Reduction product} + H_2O$$

$$HNO_3 \xrightarrow[-H_2O]{+H} NO_2 \xrightarrow[-H_2O]{+2H} NO \xrightarrow[-H_2O]{+5H}$$

$$NH_3 \xrightarrow{HNO_3} NH_4NO_3 \xrightarrow[-2H_2O]{\Delta} N_2O$$

The stage to which the reduction actually occurs, however, depends upon the following factors : (*a*) *nature of the metal,* (*b*) *concentration of the acid and* (*c*) *temperature.* For example,

(i) Very dilute nitric acid. *Magnesium and manganese* are the only metals which produce hydrogen with very dilute (1 – 2%) nitric acid.

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

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

(ii) Cold dilute nitric acid. More active metals like magnesium, zinc, tin and iron react with cold dil. HNO_3 to form ammonium nitrate.

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H] \times 4$$

$$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$4Zn + 10\,HNO_3 \longrightarrow 4\,Zn(NO_3)_2 + 3H_2O + \underset{\text{Amm. nitrate}}{NH_4NO_3}$$

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

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

Lead, under similar conditions gives nitric oxide instead of ammonium nitrate.

$$Pb + 2HNO_3 \longrightarrow Pb(NO_3)_2 + 2H] \times 3$$

$$HNO_3 + 3H \longrightarrow NO + 2H_2O\,] \times 2$$

$$3Pb + 8HNO_3 \longrightarrow 3\,Pb(NO_3)_2 + 4H_2O + \underset{\text{Nitric oxide}}{2NO}$$

(iii) With hot dilute nitric acid. With hot dilute nitric acid, ammonium nitrate thus formed undergoes decomposition to form nitrous oxide (N_2O).

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H\,] \times 4$$

$$HNO_3 + 8H \longrightarrow 3H_2O + NH_3$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

$$4\,Zn + 10\,HNO_3 \longrightarrow$$

$$4\,Zn(NO_3)_2 + 5H_2O + \underset{\text{Nitrous oxide}}{N_2O}$$

Similarly, $4Mg + 10\,HNO_3 \longrightarrow$

$$4Mg(NO_3)_2 + 5H_2O + N_2O$$

(iv) With conc. nitric acid. With conc. HNO_3, metals like zinc, magnesium, bismuth, lead etc. form nitrogen dioxide (NO_2).

$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H$$

$$HNO_3 + H \longrightarrow H_2O + NO_2] \times 2$$

$$Zn + 4HNO_3 \longrightarrow$$

$$Zn(NO_3)_2 + 2H_2O + \underset{\text{Nitrogen dioxide}}{2NO_2}$$

Similarly, $Mg + 4HNO_3 \longrightarrow$

$$Mg(NO_3)_2 + 2H_2O + 2NO_2$$

$$Bi + 6HNO_3 \longrightarrow Bi(NO_3)_3 + 3H_2O + 3NO_2$$

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

Exception. Tin, however, reacts with conc. HNO_3 to form meta-stannc acid (H_2SnO_3) and nitrogen dioxide.

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O\,] \times 2$$

$$Sn + 2[O] + H_2O \longrightarrow H_2SnO_3$$

$$Sn + 4HNO_3 \longrightarrow \underset{\text{Meta. stannic acid}}{H_2SnO_3}$$

$$+ 4NO_2 + H_2O$$

Passivity. When dipped in conc. HNO_3, metals like iron, chromium, nickel and aluminium lose their normal activity and become passive. *This passivity of these metals is due to the formation of a thin protective layer of the metal oxide on the surface of the metal which prevents further action.*

For example, in case of iron, a protective layer of ferrosoferric oxide, $FeO.Fe_2O_3$ is formed on the surface of iron

B. Reaction with metals which are less electropositive than hydrogen (Cu, Ag, Hg etc.).

In this case, hydrogen is not liberated. Instead nitric acid oxidises these metals to their respective oxides while it itself is reduced to form either brown fumes of NO_2 or colourless vapours of NO.

$$\text{Metal} + HNO_3 \longrightarrow \text{Metal oxide} + NO_2$$

$$\text{or } NO + H_2O$$

$$\text{Metal oxide} + HNO_3 \longrightarrow \text{Metal nitrate} + H_2O$$

The metal oxide thus formed reacts further with excess of nitric acid to form the corresponding metal nitrate and water. For example,

(i) With conc. HNO_3, nitrogen dioxide (NO_2) is formed.

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

$$Cu + [O] \longrightarrow CuO$$

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

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

Similarly,

$$Ag + 2HNO_3 \longrightarrow AgNO_3 + H_2O + NO_2$$

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

(ii) With dil HNO_3, nitric oxide is evolved.

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

$$Cu + [O] \longrightarrow CuO \qquad] \times 3$$

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O] \times 3$$

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

Similarly,

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + 2H_2O + NO$$

$$6Hg + 8HNO_3 \longrightarrow 3\,Hg_2(NO_3)_2 + 4H_2O + 2NO$$

C. Reaction with noble metals. Noble metals like gold and platinum do not react with conc. HNO_3. However, these metals dissolve in *aqua regia* (3 parts of conc. HCl + 1 part conc. HNO_3) forming their respective chlorides.

HCl first reacts with HNO_3 to produce nascent chlorine which then reacts with noble metals forming their respective chlorides.

$$\underset{\text{Aqua regia}}{3HCl + HNO_3} \longrightarrow \underset{\text{Nitrosyl chloride}}{NOCl} + 2H_2O + \underset{\text{Nascent chlorine}}{2Cl}$$

$$Au + 3Cl \longrightarrow \underset{\text{Auric chloride}}{AuCl_3}$$

$$Pt + 4Cl \longrightarrow \underset{\text{Platinic chloride}}{PtCl_4}$$

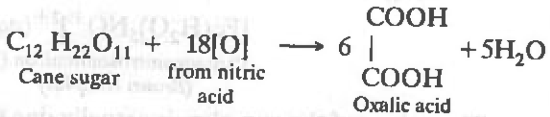
These chlorides subsequently dissolve in excess of HCl forming their corresponding soluble complexes. Thus,

$$\underset{\text{Auric chloride}}{AuCl_3} + HCl \longrightarrow \underset{\text{Aurochloric acid}}{H[AuCl_4]}$$

$$\underset{\text{Platinic chloride}}{PtCl_4} + 2HCl \longrightarrow \underset{\text{Chloroplatinic acid}}{H_2[PtCl_6]}$$

5. Action of organic compounds

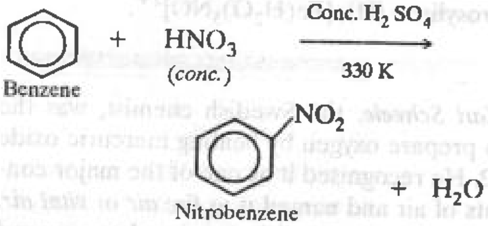
(i) Oxidation. Many organic compounds are oxidised by conc. HNO_3. For example, cane sugar on oxidation gives oxalic acid.

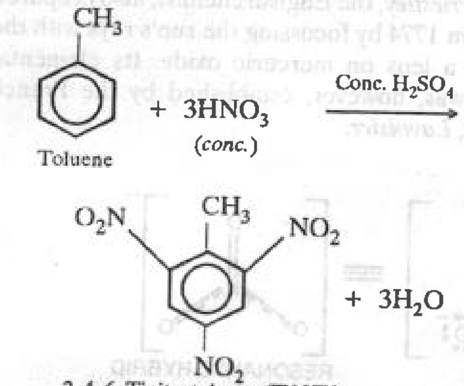


$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{from nitric acid}}{18[O]} \longrightarrow 6\begin{matrix}COOH\\|\\COOH\end{matrix} + 5H_2O$$

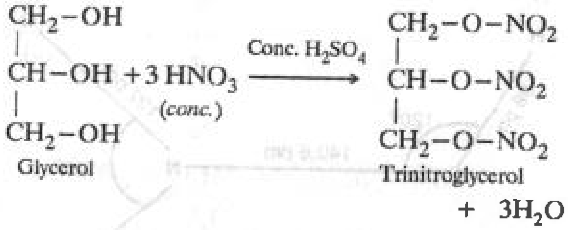
Oxalic acid

(ii) Nitration. A mixture of conc. HNO_3 and conc. H_2SO_4 (*also called nitrating mixture*) is used for introducing one or more $-NO_2$ (nitro) groups into the benzene ring. This process is called **nitration**. For example,





2, 4, 6-Tinitrotoluene (T.N.T.)



$$\underset{\text{Glycerol}}{\begin{matrix}CH_2-OH\\|\\CH-OH\\|\\CH_2-OH\end{matrix}} + \underset{(conc.)}{3HNO_3} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Trinitroglycerol}}{\begin{matrix}CH_2-O-NO_2\\|\\CH-O-NO_2\\|\\CH_2-O-NO_2\end{matrix}} + 3H_2O$$

Similarly phenol reacts with a mixture of conc. HNO_3 + conc. H_2SO_4 to form 2, 4, 6- trinitrophenol (*picric acid*), albeit in low yield.

Both T.N.T. and trinitroglycerol (or trinitroglycerine or simply nitroglycerine) are used as explosives. Dynamite, the well-known explosive which is widely used for shooting oil wells, building roads, dams and tunnels in rocks is a *mixture of glyceryl trinitrate and glyceryl dinitrate absorbed over kieselguhr* (a kind of porous earth).

Nitric acid also reacts with proteins giving a yellow compound called *xanthoprotein*. It is because of this reason that ntiric acid turns the skin as well as wool yellow.

13.15.4. Uses of Nitric acid

The important uses of nitric acid are :

(*i*) In the manufacture of ammonium nitrate and basic calcium nitrate $[CaO.Ca(NO_3)_2]$ which are used as fertilizers.

(*ii*) In the manufacture of explosives such as gun cotton, nitroglycerine, trinitrotoluene (T.N.T.), picric acid etc.

(*iii*) In the preparation of nitro compounds which are used as perfumes, dyes and medicines.

(*iv*) In the manufacture of artificial silk.

(*v*) For purification of gold and silver.

(*vi*) For pickling of *stainless steel and etching of metals*.

(*vii*) As an oxidiser in rocket fuels.

(*viii*) As a reagent in the laboratory.

13.15.5. Structure of Nitric acid

Spectroscopic studies have shown that in the gaseous state, nitric acid has a planar structure as shown in Fig. 13.17.

The above structure of nitric acid is, in fact, a resonance hybrid of the following two structures.

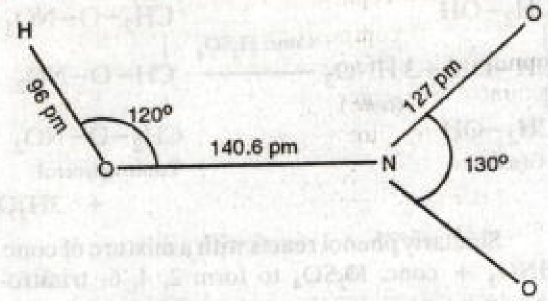
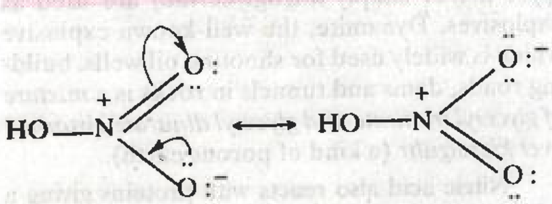


FIGURE 13.17. Structure of nitric acid in the gaseous state.



13.15.6. Structure of Nitrate Ion

Like nitric acid, nitrate ion also has a planar structure. The nitrogen atom is sp^2-hybridized and hence the O – N – O bond angle is 120° as shown in Fig. 13.18.

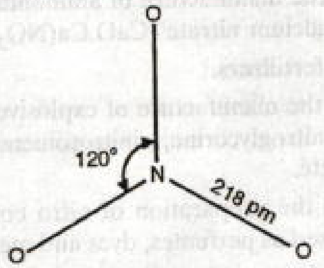


FIGURE 13.18. Structure of nitrate ion.

In fact, nitrate ion (NO_3^-) is a resonance hybrid of three structures (Fig. 13.19) :

As a result of resonance, all the three N – O bond lengths are equal and are 218 pm long.

13.15.7. Ring Test for Nitrate ion

In qualitative analysis, the presence of nitrate ion is detected by *ring test*. In this test, a freshly prepared solution of ferrous sulphate is added to the aqueous solution of a nitrate. Pure conc. H_2SO_4 is then added carefully dropwise along the walls of the test tube. *The appearance of a dark brown ring at the junction of the two layers indicates the presence of a nitrate ion*.

The brown ring is due to the formation of a brown complex between nitric oxide (formed as a result of reduction of the nitrate ion by the Fe^{2+} ions) and Fe^{2+} ions.

$$2\,HNO_2 \longrightarrow H_2O + 2\,NO + O$$

$$NO_3^-(aq) + 3Fe^{2+}(aq) + 4H^+(aq) \longrightarrow \underset{\text{Nitric oxide}}{NO(g)} + 3Fe^{3+}(aq) + 2H_2O(l)$$

$$Fe^{2+}(aq) + NO(g) + 5H_2O(l) \longrightarrow \underset{\substack{\text{Pentaquanitrosoniumiron (I)}\\ \textit{(Brown complex)}}}{[Fe(H_2O)_5NO^+]^{2+}(aq)}$$

The colour of the complex, is actually due to *charge transfer, i.e.,* an electron is transferred from NO to Fe^{2+}. As a result, this complex formally contains iron in the +1 state and NO^+. Consequently the correct name of this complex should be pentaaquanitrosoniumiron (I) and not pentaaquanitrosyliron (II), $[Fe(H_2O)_5NO]^{2+}$.

13.16. Dioxygen

Karl Scheele, the Swedish chemist, was the first to prepare oxygen by heating mercuric oxide in 1772. He recognised it as one of the major constituents of air and named it as *fire air* or *vital air*. *Joseph Priestley*, the English chemist, also prepared oxygen in 1774 by focussing the sun's rays with the help of a lens on mercuric oxide. Its elemental nature was, however, established by the French chemist, *Lavoisier*.

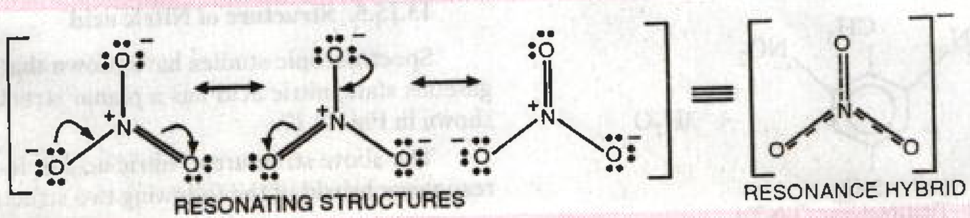


FIGURE 13.19. Resonating structures of NO_3^- ion

The electronic configuration of oxygen in the ground state is $1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$. Oxygen has three naturally occurring isotopes, *i.e.* $^{16}_{8}O$ (99·762%), $^{17}_{8}O$ (0·038%) and $^{18}_{8}O$ (0·200%). Out of these three isotopes, $^{18}_{8}O$ is *radioactive* and hence is widely used in studying the mechanism of organic reactions and in other tracer techniques. Like hydrogen, oxygen also exists in the elemental form as a diatomic molecule (O_2) and is, therefore, referred to as **dioxygen.** An interesting point about dioxygen is that although its molecule contains even number of electrons (16), it has two unpaired electrons and hence is *paramagnetic* in nature.

Oxygen has two allotropes, *i.e.*, dioxygen (O_2) and trioxygen or **ozone** (O_3).

13.16.1. Terrestial Abundance and Distribution

Just as hydrogen is the most abundant element in the cosmos, dioxygen is the most abundant element on the surface of the earth. It occurs both in the free as well as in the combined state. It constitutes about 50% by weight of the earth, bodies of water and atmosphere. In the free state, it is present in air to an extent of 21% by volume and 23·2% by weight. In the combined state, it is present in water to an extent of 88·8% by weight. In the earth's crust, it is present mainly in form of silicates, aluminates, carbonates and oxides of metals. Almost all the dioxygen in the atmosphere is believed to have been produced by *photosynthesis* taking place in green plants in the presence of chlorophyll (*sensitizer*) and sunlight

$$xCO_2 + xH_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} \underset{\text{Carbohydrate}}{(CH_2O)_x} + xO_2(g)$$

13.16.2. Preparation of Dioxygen

1. By decomposition of oxygen-rich compounds. Certain compounds containing large amounts of oxygen such as $KClO_3$, $KMnO_4$, KNO_3 etc. give dioxygen on strong heating.

$$\underset{\text{Pot. permanganate}}{2\,KMnO_4} \xrightarrow{\text{Heat}} \underset{\text{Pot. manganate}}{K_2MnO_4} + MnO_2 + O_2$$

$$\underset{\text{Pot. chlorate}}{2KClO_3} \xrightarrow{\text{Heat}} \underset{\text{Pot. chloride}}{2KCl} + 3O_2$$

$$\underset{\text{Pot. nitrate}}{2KNO_3} \xrightarrow{\text{Heat}} \underset{\text{Pot. nitrite}}{2KNO_2} + O_2$$

$$\underset{\text{Barium peroxide}}{2\,BaO_2} \xrightarrow{\text{Heat}} \underset{\text{Barium oxide}}{2\,BaO} + O_2$$

Laboratory method of preparation (a) Thermal decomposition of potassium chlorate. In the laboratory, dioxygen is produced by heating a mixture of potassium chlorate and manganese dioxide (*catalyst*) in the ratio 4 : 1 in a hard glass test tube at 420 K.

$$2KClO_3(s) \xrightarrow[\text{420 K}]{MnO_2} 2KCl(s) + 3O_2(g)$$

The gas is collected by downward displacement of water as shown in Fig. 13.20.

In the absence of MnO_2, the thermal decomposition of $KClO_3$ occurs slowly at 670-720 K. Therefore, *MnO_2 acts as a catalyst. It not only lowers the temperature of decomposition of $KClO_3$ from 670 – 720 K to 420 K but also accelerates the rate of decomposition.*

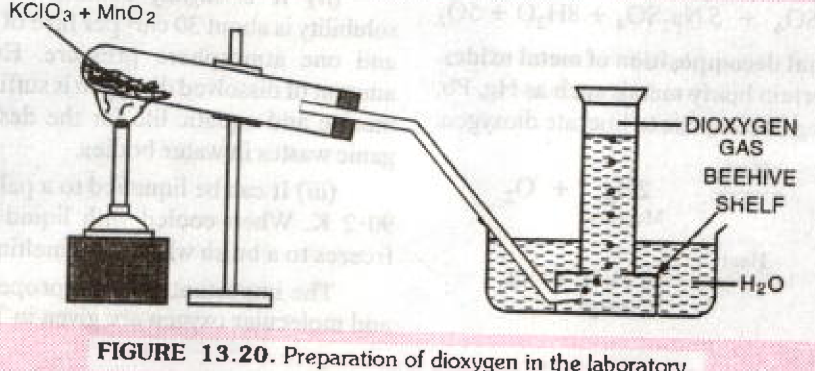


FIGURE 13.20. Preparation of dioxygen in the laboratory.

(b) By the action of water on sodium peroxide. Dioxygen can also be prepared in the laboratory by the action of water on sodium peroxide.

$$2Na_2O_2(s) + 2H_2O(l) \longrightarrow 4\,NaOH(aq) + O_2(g)$$

For this purpose, sodium peroxide is placed in a flat-bottomed flask fitted with a dropping funnel and a delivery tube (Fig. 13.21). Water is dropped in small lots on sodium peroxide. Dioxygen, thus liberated, is collected by downward displacement of water.

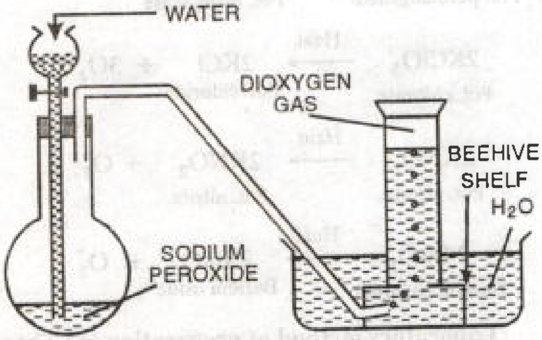


FIGURE 13.21. Preparation of dioxygen from sodium peroxide.

Dioxygen can also be prepared by the action of acidified potassium permanganate on sodium peroxide.

$$2\,KMnO_4 + 3\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,[O]$$

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2\ ] \times 5$$

$$H_2O_2 + [O] \longrightarrow H_2O + O_2\ ] \times 5$$

$$2KMnO_4 + 5Na_2O_2 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5\,Na_2SO_4 + 8H_2O + 5O_2$$

2. By thermal decomposition of metal oxides. The oxides of certain heavy metals such as Hg, Pb, Ag etc. on heating decompose to liberate dioxygen.

$$\underset{\text{Mercuric oxide}}{2\,HgO} \xrightarrow{\text{Heat}} \underset{\text{Mercury}}{2Hg} + O_2$$

$$\underset{\text{Red lead}}{2\,Pb_3O_4} \xrightarrow{\text{Heat}} \underset{\text{Litharge}}{6\,PbO} + O_2$$

$$\underset{\text{Silver oxide}}{2\,Ag_2O} \xrightarrow{\text{Heat}} \underset{\text{Silver}}{4\,Ag} + O_2$$

$$\underset{\text{Manganese dioxide}}{3MnO_2} \xrightarrow{\text{Heat}} \underset{\text{Trimanganic tetroxide}}{Mn_3O_4} + O_2$$

13.16.3. Pure Dioxygen from Barium hydroxide

Pure dioxygen can be prepared by electrolysis of a solution of $Ba(OH)_2$ using nickel or platinum electrodes.

13.16.4. Isolation of Dioxygen

The main sources for large scale preparation of dioxygen are (*i*) air and (*ii*) water.

(i) **From liquid air.** The most economical method for commercial preparation of dioxygen involves *liquefaction of air followed by fractional distillation of the liquid air thus obtained.* During this process, dinitrogen (N_2) with lower boiling point (77 K) distils over in the gaseous form leaving behind dioxygen with higher boiling point (90 K) in the liquid state which can be separated.

(ii) **From water.** Dioxygen can also be prepared by the electrolysis of water containing a small amount of a mineral acid or an alkali.

$$2H_2O(l) \xrightarrow{\text{Electrolysis}} 2H_2(g) + O_2(g)$$

Dioxygen is collected at the anode while dihydrogen is liberated at the cathode.

The world's total production of dioxygen is over 100 million tonnes per year.

13.16.5. Atomic and Physical Properties

I. Physical properties (*i*) Dioxygen is a *colourless, odourless* and *tasteless gas*.

(*ii*) It is *slightly soluble in water* and its solubility is about 30 cm³ per litre of water at 298 K and one atmosphere pressure. Even this small amount of dissolved dioxygen is sufficient to sustain marine and aquatic life for the destruction of organic wastes in water bodies.

(*iii*) It can be liquefied to a pale blue liquid at 90·2 K. When cooled with liquid dihydrogen, it freezes to a buish white solid melting at 54·4 K.

The important physical properties of atomic and molecular oxygen are given in Table 13.5.

TABLE 13.5. Atomic and molecular properties of oxygen

ATOMIC PROPERTIES		MOLECULAR PROPERTIES	
Ionisation enthalpy (kJ mol^{-1})	1310	Melting point (K)	54·4
Electron gain enthalpy (kJ mol^{-1})	140	Boiling pint (K)	90·2
Electronegativity	3·50	Density (g/L) at S.T.P.	1·429
Atomic radius (pm)	73	Bond length (pm)	120·7
Ionic radius (O^{2-}) (pm)	140	Bond energy (kJ mol^{-1})	493·4

13.13.6. Chemical Reactivity

The bond dissociation energy of dioxygen is high and hence the reactions of dioxygen require initiation by external heating. However, when the reaction starts, it continues of its own. This is due to the reason that the chemical reactions of dioxygen are *exothermic* and the heat liberated during the reaction is sufficient to carry on the reactions.

Some important chemical properties are discussed below :

1. Action of litmus. Dioxygen is *neutral to litmus*.

2. Supporter of combustion. *Dioxygen is not combustible but is a supporter of combustion*. When a glowing wooden splinter is brought in an atmosphere of dioxygen, it bursts out into a flame.

3. Oxidation. Dioxygen is a powerful oxidising agent and hence can oxidise metals, non-metals and other compounds to their respective oxides.

(a) Reaction with metals. Dioxygen directly combines with most of the metals (except some of the less reactive metals such as gold and platinum) to form their respective oxides. For example,

(*i*) *Active metals like sodium, calcium* etc. react at room temperature forming their respective oxides.

$$4Na\,(s) + O_2\,(g) \longrightarrow 2\,Na_2O\,(s)$$

$$2\,Ca\,(s) + O_2\,(g) \longrightarrow 2\,CaO\,(s)$$

However, sodium also reacts with dioxygen at 575 K to form sodium peroxide.

$$2\,Na\,(s) + O_2\,(g) \xrightarrow{575\text{ K}} Na_2O_2\,(s)$$

(*ii*) *Magnesium* burns in dioxygen to form magnesium oxide.

$$2\,Mg\,(s) + O_2\,(g) \xrightarrow{\text{Heat}} 2\,MgO\,(s)$$

(*iii*) *Aluminium and iron*. When heated in air form their respective oxides.

$$4\,Al\,(s) + 3\,O_2\,(g) \xrightarrow{\text{Heat}} 2\,Al_2O_3\,(s)$$

$$4\,Fe\,(s) + 3\,O_2\,(g) \xrightarrow{\text{Heat}} 2\,Fe_2O_3\,(s)$$

(*iv*) *Less active metals like gold and platinum* do not react with dioxygen.

(b) Reaction with non-metals. Dioxygen combines with many non-metals except noble gases forming their corresponding oxides. For example,

(*i*) *With dihydrogen* :

$$2\,H_2\,(g) + O_2\,(g) \xrightarrow[\text{or Electric discharge}]{1073\text{ K}} \underset{\text{water}}{2\,H_2O\,(g)}$$

(*ii*) *With dinitrogen* :

$$N_2\,(g) + O_2\,(g) \xrightarrow{3300\text{ K}} \underset{\text{Nitric oxide}}{2\,NO\,(g)}$$

(*iii*) *With sulphur* :

$$S\,(s) + O_2\,(g) \xrightarrow{\text{Heat}} \underset{\text{Sulphur dioxide}}{SO_2\,(g)}$$

(*iv*) *With carbon* :

$$2\,C\,(s) + \underset{(limited)}{O_2\,(g)} \xrightarrow{\text{Heat}} \underset{\text{Carbon monoxide}}{2\,CO\,(g)}$$

$$C\,(s) + \underset{(excess)}{O_2\,(g)} \xrightarrow{\text{Heat}} \underset{\text{Carbon dioxide}}{CO_2\,(g)}$$

(*v*) *With phosphorus* :

$$P_4\,(s) + \underset{(excess)}{5\,O_2\,(g)} \xrightarrow{\text{Heat}} \underset{\text{Phosphorus pentoxide}}{P_4O_{10}\,(s)}$$

(c) Reaction with compounds

(*i*) With sulphur dioxide. Dioxygen reacts with sulphur dioxide at 723 K under a pressure of 2 atmospheres and in presence of platinum or vanadium pentoxide as catalyst to form sulphur trioxide

$$2SO_2(g) + O_2(g) \xrightarrow[\text{Pt or } V_2O_5]{723\text{ K, 2 atm}} 2SO_3(g)$$

This reaction forms the basis of *Contact process* for the manufacture of sulphuric acid.

***(ii)* With ammonia.** Dioxygen oxidises ammonia to nitric oxide in presence of platinum gauze as catalyst at 500 K.

$$4NH_3(g) + 5O_2(g) \xrightarrow{500\text{ K, Pt}} 4NO(g) + 6H_2O(g)$$

This reaction forms the basis of *Ostwald process* for the manufacture of nitric acid.

***(iii)* Hydrogen chloride.** Dioxygen oxidises hydrogen chloride to chlorine in presence of cupric chloride as catalyst at 700 K.

$$4\,HCl(g) + O_2(g) \xrightarrow{700\text{ K}\,;\ CuCl_2} 2H_2O(g) + Cl_2(g)$$

This reaction forms the basis of *Decon's process* for the manufacture of chlorine.

***(iv)* With carbon disulphide.** Carbon disulphide burns in dioxygen to form carbon dioxide and sulphur dioxide.

$$CS_2(g) + 3O_2(g) \xrightarrow{\text{Heat}} CO_2(g) + 2SO_2(g)$$

***(v)* With metal sulphides.** Many metal sulphides such as ZnS, HgS etc. react with dioxygen at high temperature to form metal oxides and sulphur dioxide.

$$2ZnS\,(s) + 3O_2\,(g) \xrightarrow{\text{Heat}} 2ZnO\,(s) + 2SO_2\,(g)$$

$$2HgS\,(s) + 3O_2\,(g) \xrightarrow{\text{Heat}} 2HgO\,(s) + 2SO_2\,(g)$$

***(vi)* With hydrocarbons.** Both saturated and unsaturated hydrocarbons burn in excess of air or dioxygen to form carbon dioxide and water.

$$\underset{\text{Methane}}{CH_4\,(g)} + 2O_2\,(g) \longrightarrow CO_2\,(g) + H_2O\,(g)\,; \quad \Delta_cH^\circ = -890\text{ kJ mol}^{-1}$$

$$\underset{\text{Ethylene}}{CH_2 = CH_2\,(g)} + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 2H_2O\,(g)\,; \quad \Delta_cH^\circ = -1411\text{ kJ mol}^{-1}$$

$$2\,\underset{\text{Acetylene}}{CH \equiv CH\,(g)} + 5O_2\,(g) \longrightarrow 4CO_2\,(g) + 2H_2O\,(g)\,; \quad \Delta_cH^\circ = -1300\text{ kJ mol}^{-1}$$

These reactions are called **combustion reactions** and are highly exothermic in nature. That is why hydrocarbons are used as fuels.

4. Action of silent electric discharge. Under the action of silent electric discharge, dry dioxygen gets converted into ozone which is an allotropic form of oxygen.

$$\underset{\text{Dioxygen}}{3O_2} \xrightarrow{\text{Silent electric discharge}} \underset{\text{Ozone}}{2O_3}$$

5. Respiration. When air is inhaled, dioxygen is carried by the haemoglobin of the blood to various tissues of the body where it is used in the slow oxidation of biomolecules such as glucose, fats and oils etc. The energy produced during this oxidation sustains life while CO_2 and H_2O produced are exhaled.

13.16.7. Uses of Dioxygen

(i) Dioxygen is used in *oxy-hydrogen* and *oxy-acetylene* torches which are used for cutting and welding of metals.

(ii) It is used in *metallurgical processes* to remove the impurities of those metals and non-metals which form volatile oxides.

(iii) It is used for *artificial respiration* in hospitals during surgery, by mountaineers and pilots at high altitudes and by divers in deep-water diving.

(iv) Liquid dioxygen is used as a *rocket fuel.*

(v) It is used in the manufacture of a large number of compounds such as phenol, ethylene oxide, sulphur dioxide, sulphuric acid, nitric acid, chlorine etc.

(vi) It is also used in large scale production of TiO_2 and synthesis gas ($CO + H_2$).

13.17. Oxides

Most of the elements in the periodic table, metals as well as non-metals, form binary compounds with oxygen. *These binary compunds of metals and non-metals with oxygen are called* **oxides**. In these oxides, the oxidation state of oxygen is always -2. Some elements (*e.g.*, Li, Mg, Al, Zn etc.) form only one oxide while many others (*e.g.*, Fe, Cu, N, S, P etc.) form more than one oxide. The nature of bonding in these oxides may be either ionic or covalent.

Classification. Oxides are best classified on the basis of their acid-base properties. These are classified into the following four categories : *(i) Basic oxides*, *(ii) Acidic oxides*, *(iii) Amphoteric oxides* and *(iv) Neutral oxides*

(i) Basic oxides. *An oxide is said to be basic if it combines with water to form a base.* Alkali metals, alkaline earth metals (except beryllium) and transition metals generally form basic oxides. For example,

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

$$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(aq)$$

$$Fe_2O_3(s) + 3H_2O(l) \longrightarrow 2Fe(OH)_3(aq)$$

The basic oxides react with acids to form salts and water.

$$Na_2O(s) + 2\,HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l)$$

$$Fe_2O_3(s) + 3\,H_2SO_4(aq) \longrightarrow Fe_2(SO_4)_3(aq) + 3H_2O(l)$$

(ii) Acidic oxides. *An oxide which combines with water to form an acid is called an acidic oxide.* The oxides of non- metals are acidic in nature. For example,

$$CO_2(g) + H_2O(l) \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3(aq)}$$

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4(aq)}$$

$$N_2O_5\,(l) + H_2O\,(l) \longrightarrow 2\,HNO_3\,(aq)$$

$$Cl_2O_7(g) + H_2O(l) \longrightarrow \underset{\text{Perchloric acid}}{2HClO_4(aq)}$$

These acidic oxides react with bases to form salts and water. For example,

$$SO_2(g) + 2NaOH(aq) \longrightarrow Na_2SO_3(aq) + H_2O(l)$$

$$P_4O_{10}(s) + 12\,NaOH(aq) \longrightarrow 4Na_3PO_4(aq) + 6H_2O(l)$$

(iii) Amphoteric oxides. *Oxides which react with both acids and bases are called amphoteric oxides.* These are generally formed by elements that are on the border line between metals and non-metals, *i.e.*, elements (Al, Zn, Sn, Pb etc.) which lie in the centre of the periodic table. For example,

$$\underset{(Basic)}{Al_2O_3(s)} + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O(l)$$

$$\underset{(Acidic)}{Al_2O_3(s)} + 6NaOH(aq) + 3H_2O(l) \longrightarrow \underset{\text{Sod. hexaaquaaluminate}}{2Na_3[Al(OH)_6](aq)}$$

Other examples of amphoteric oxides are : ZnO, PbO, SnO.

(iv) Neutral oxides. *Oxides which neither react with acids nor with bases are called neutral oxides.* For example, H_2O, N_2O, NO, CO etc.

Trends in Acid-base behaviour of oxides in the Periodic table.

(*i*) **On moving from left to right in a given period in the periodic table,** ***the nature of the oxides shows a gradual variation from strongly basic through amphoteric to strongly acidic.*** **For example,**

Na_2O	MgO	Al_2O_3	SiO_2
Strongly basic	Basic	Amphoteric	Weakly acidic

P_4O_{10}	SO_2	Cl_2O_7
Strongly acidic	Strongly acidic	Very strongly acidic

(*ii*) Amongst *s*-block elements, *on moving down a group, the basic character of the oxides increases.* For example

Li_2O	Na_2O	K_2O
Weakly basic	Basic	More strongly basic

Rb_2O, Cs_2O
Very strongly basic

(*iii*) **Among** ***p*****-block elements,** ***on moving down the group, the acidic character of the oxides decreases while the basic character increases.*** For example, in group 13, the acidic character of oxides decreases as :

B_2O_3	Al_2O_3	Ga_2O_3
Acidic	Amphoteric	Weakly basic

In_2O_3	Tl_2O_3
Basic	Strongly basic

(*iv*) Amongst non-metallic oxides, *the acidic character increases as the oxidation state of the non-metal increases.* For example,

$\overset{+1}{N_2O}$	$\overset{+2}{NO}$	$\overset{+3}{N_2O_3}$
Neutral	Neutral	Acidic

$\overset{+4}{N_2O_4}$	$\overset{+5}{N_2O_5}$
Strongly acidic	Very strongly acidic

Mixed Oxides. ***Metal oxides which consist of two simple metal oxides with the metal in different oxidation states are called mixed oxides.*** These mixed oxides show the properties of both the metal oxides simultaneously. For example,

$$\underset{\text{Red lead}}{Pb_3O_4} + 4\,HNO_3 \longrightarrow \underset{\textit{(from lead dioxide)}}{PbO_2} + \underset{\textit{(from led oxide)}}{2\,Pb(NO_3)_2} + 2\,H_2O$$

Thus, red lead is considered to be a mixture of two oxides – lead dioxide (PbO_2) and lead oxide (PbO) and is given the formula, $PbO_2 . 2\,PbO$.

Similarly, magnetic oxide or ferrosoferric oxide (Fe_3O_4) is considered to be a mixture of ferric oxide (Fe_2O_3) and ferrous oxide (FeO) and is given the formula, $Fe_2O_3 . FeO$. Consequently, it gives a mixture of ferric and ferrous salts on treatment with acids,

$$Fe_2O_3 . FeO + 8HCl \longrightarrow 2\,FeCl_3 + FeCl_2 + 4\,H_2O$$

Likewise, trimanganese tetroxide, Mn_3O_4 ($2\,MnO . MnO_2$) is considered to be a mixed oxide of manganous oxide (MnO) and manganese dioxide (MnO_2).

EXAMPLE 13.1. *Classify the following into acidic, basic or amphoteric oxides. Write balanced equations for the reactions of the oxides with water, acids or alkalies.* SO_2, *ZnO, BaO.*

Solution. (*i*) SO_2 is an acidic oxide since its reaction with water produces sulphurous acid.

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

(*ii*) ZnO is an amphoteric oxide since it dissolves in an acid to form Zn^{2+} ions and in an alkali to form $[Zn(OH)_4]^{2+}$ ion.

$$ZnO\,(s) + 2\,H^+\,(aq) \longrightarrow Zn^{2+}\,(aq) + H_2O\,(l)$$

$$ZnO\,(s) + 2\,OH^-\,(aq) + H_2O\,(l) \longrightarrow [Zn(OH)_4]^{2+}\,(aq)$$

(*iii*) BaO is a basic oxide since it reacts with water to form an alkaline solution of $Ba(OH)_2$

$$BaO\,(s) + H_2O\,(l) \rightleftharpoons Ba(OH)_2$$

13.18. Ozone

Elemental oxygen exists in two molecular allotropic forms, *i.e.*, O_2 and O_3. The triatomic molecule, *i.e.*, O_3 is called *trioxygen or ozone*.

Ozone is present in the upper atmosphere (about 20 km from the surface of the earth) where it is formed by the action of ultraviolet (UV) radiations on dioxygen.

$$3O_2(g) \xrightarrow{\text{UV light}} 2O_3(g)$$

Ozone absorbs ultraviolet radiations (220–290 *nm*) and thus protects the earth and its inhabitants from the harmful radiations of the sun. If there were no ozone layer, more ultraviolet radiations will reach the surface of the earth causing much damage to plant and animal life.

Ozone layer in the stratosphere is depleted by (*a*) nitric oxide, (*b*) atomic oxygen and (*c*) reactive hydroxyl radicals which are also present in the atmosphere due to bio-mass burning.

$$(a)\quad O_3\,(g) + NO\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)$$

$$(b)\quad O_3\,(g) + O\,(g) \longrightarrow O_2\,(g) + O_2\,(g)$$

$$(c)\quad O_3\,(g) + HO^{\cdot}\,(g) \longrightarrow O_2\,(g) + HOO^{\cdot}\,(g)\,;$$

$$HOO^{\cdot}\,(g) + O\,(g) \longrightarrow HO^{\cdot}\,(g) + O_2\,(g)$$

Flights of supersonic aeroplanes and nuclear explosions and lightning release NO into the atmosphere.

Ozone layer is also depleted by man-made chlorofluorocarbons (CFC's) which have been used since long as aerosol propellants and as refrigerants (CF_2Cl_2, freon). Chlorofluorocarbons are long lived molecules and diffuse into the stratosphere where they undergo photochemical dissociation to produce chlorine atoms. These chlorine atoms react with ozone thereby decreasing the concentration of ozone at a rate much faster than its formation from O_2.

$$Cl_2CF_2\,(g) \xrightarrow{h\nu} \bullet Cl\,(g) + \bullet CClF_2\,(g)$$

$$\bullet Cl\,(g) + O_3\,(g) \longrightarrow ClO\bullet\,(g) + O_2\,(g)$$

$$ClO\bullet\,(g) + \bullet O\,(g) \longrightarrow \bullet Cl\,(g) + O_2\,(g)$$

Volcanic eruptions also release chlorine atoms into the atmosphere. Due to the hazardous effects of CFC's on the ozone layer, U.S.A. has banned the use of CFC's in spray cans.

Three scientists namely P.J. Crutzen, M.J. Molina and F.S. Rowland received 1995 Nobel Prize in Chemistry for their pioneering work in this area. As a result of their work, there is a world-wide concern about the depletion of the ozone layer in the stratosphere and serious efforts are being made to find alternatives for CFC's and to limit the emissions of oxides of nitrogen $(NO)_x$ into the stratosphere.

13.18.1. Preparation of Ozone (Trioxygen)

Ozone is prepared by passing *silent electric discharge* through pure, cold and dry dioxygen in a specially designed apparatus called the **ozoniser**.

$$3O_2(g) \xrightleftharpoons{\text{Silent electric discharge}} 2O_3(g)\ ;$$
$$\Delta H_{298} = +142 \cdot 7 \text{ kJ mol}^{-1}$$

The reaction is thus endothermic and 142·7 kJ of energy is absorbed when one mole of ozone is formed from dioxygen.

A silent electric discharge (*sparkless electric discharge*) is used since it produces less heat. This prevents the local rise in temperature which may decompose ozone back to dioxygen.

Ozone is prepared in the laboratory by the following two types of ozonizers : (*i*) *Siemen's Ozonizer* and (*ii*) *Brodie's Ozonizer*. The description of Siemen's ozonizer is given in Fig. 13.22.

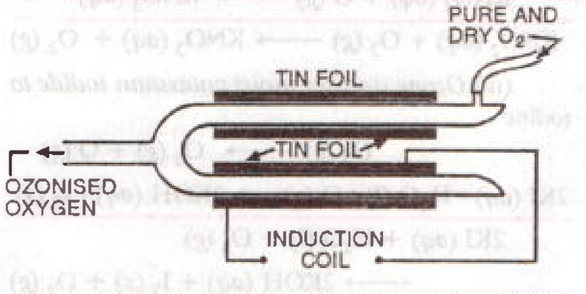


FIGURE 13.22. Seimen's Ozoniser.

It consists of two co-axial glass tubes sealed at one end. The inner surface of the inner tube and the outer surface of the outer tube are covered with tin foils. The inner and outer coatings of tin foil are connected to the terminals of an induction coil. One end of the coaxial tubes has an inlet for pure and dry dioxygen and the other end has an outlet for the ozonised oxygen.

A slow stream of pure, dry and cold dioxygen is passed through the annular space between the concentric tubes and subjected to the silent electric discharge when some of the dioxygen gets converted into ozone. The product which actually comes out of the outlet is a mixture of O_2 and O_3. It is called *ozonised oxygen and contains about 10–15% ozone*.

The yield of ozonised oxygen can be increased by using (*i*) *pure and dry dioxygen, (ii) dry ozoniser (iii) avoiding sparking and (iv) maintaining fairly low temperature (about 273 K)*

Preparation of pure ozone. In order to prepare pure ozone, the ozonised oxygen is cooled with liquid air when ozone (b.p. 161.2 K) condenses in preference to oxygen (b.p. 90.2 K). The liquid ozone thus formed still contains some dissolved dioxygen which can be easily removed by fractional distillation.

13.18.2. Structure of Ozone

The central oxygen atom in ozone is sp^2-hybridized. Thus, it has an angular structure as shown in Fig. 13.23. The O – O – O bond angle is 116·8° and both the oxygen-oxygen bond lengths are equal *i.e.* 127·8 pm. This bond length lies in between O – O single bond length of 148 pm and O = O double bond length of 110 pm.

FIGURE 13.23. Structure of ozone.

In order to explain the oxygen-oxygen bond length in ozone, it is considered to be a resonance hybrid of the following two resonating structures (Fig. 13.24).

Because of resonance, both the oxygen-oxygen bonds have partial double bond character. In other words, both the oxygen-oxygen bonds are equal (127.8 pm) and lie in between those of oxygen-oxygen double bond length of 110 pm and oxygen-oxygen single bond length of 148 pm.

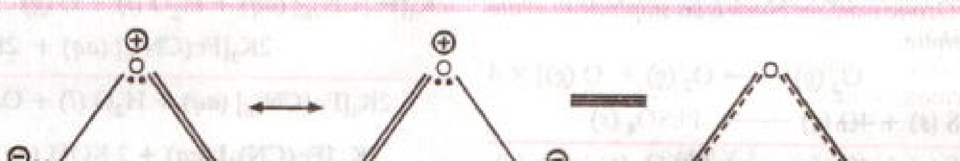


FIGURE 13.24. Resonance structures of ozone.

13.18.3. Properties of Ozone

(a) Physical properties. (*i*) Ozone is a pale blue gas having a strong characteristic smell.

(*ii*) When cooled in liquid air, the ozone present in ozonized oxygen condenses to a deep blue liquid (b.p. 161·2K) and then to a violet-black solid (m.p. 80·6 K).

(*iii*) It is about 1·67 times heavier than air because its vapour density (V.D.) is 24 while that of air is 14·4.

(*iv*) It is slightly soluble in water but readily dissolves in organic solvents such as turpentine oil, cinnamon oil, carbon tetrachloride, glacial acetic acid etc.

(*v*) Ozone is diamagnetic while dioxygen is paramagnetic.

(b) Chemical properties 1. Neutral character. Ozone (trioxygen) is neutral to litmus.

2. Decomposition. Ozone is not a very stable compound. Even at ordinary temperature, it decomposes slowly to give dioxygen. However, when heated to 473 K or in the presence of a catalyst such as manganese dioxide, platinum black or copper oxide, the decomposition takes place very rapidly.

$$\underset{\text{Ozone}}{2O_3\,(g)} \xrightarrow{\text{473 K or catalyst}} \underset{\text{Dioxygen}}{3O_2\,(g)}$$

3. Oxidising agent. *Ozone is a powerful oxidising agent much stronger than dioxygen.* This is due to the reason that ozone has higher energy content than dioxygen and hence decomposes to give dioxygen and atomic oxygen.

$$\underset{\text{Ozone}}{O_3\,(g)} \longrightarrow \underset{\text{Dioxygen}}{O_2\,(g)} + \underset{\text{Atomic oxygen}}{O\,(g)}$$

The atomic oxygen thus liberated brings about the oxidation while molecular oxygen is set free. Some important oxidation reactions of ozone are discussed below :

(a) Oxidation of compounds

(*i*) *Ozone oxidises black lead sulphide to white lead sulphate.*

$$[O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)] \times 4$$
$$PbS\,(s) + 4O\,(g) \longrightarrow PbSO_4\,(s)$$
$$PbS\,(s) + 4O_3\,(g) \longrightarrow PbSO_4\,(s) + 4O_2\,(g)$$

Similarly, ozone oxidises sulphides of Cu, Zn and Cd to their respective sulphates.

$$CuS\,(s) + 4O_3\,(g) \longrightarrow CuSO_4\,(s) + 4O_2\,(g)$$
$$ZnS\,(s) + 4O_3\,(g) \longrightarrow ZnSO_4\,(s) + 4O_2\,(g)$$
$$CdS\,(s) + 4O_3\,(g) \longrightarrow CdSO_4\,(s) + 4O_2\,(g)$$

(*ii*) *Ozone oxidises halogen acids to corresponding halogens*

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$
$$2HCl\,(aq) + O\,(g) \longrightarrow Cl_2\,(g) + H_2O\,(l)$$
$$2HCl\,(aq) + O_3\,(g) \longrightarrow Cl_2\,(g) + H_2O\,(l) + O_2\,(g)$$

Similarly, HBr is oxidised to Br_2 and HI to I_2.

(*iii*) *Ozone oxidises nitrites to nitrates*

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$
$$KNO_2\,(aq) + O\,(g) \longrightarrow KNO_3\,(aq)$$
$$KNO_2\,(aq) + O_3\,(g) \longrightarrow KNO_3\,(aq) + O_2\,(g)$$

(*iv*) *Ozone oxidises moist potassium iodide to iodine*

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$
$$2KI\,(aq) + H_2O\,(l) + O\,(g) \longrightarrow 2KOH\,(aq) + I_2\,(s)$$
$$2KI\,(aq) + H_2O\,(l) + O_3\,(g) \longrightarrow 2KOH\,(aq) + I_2\,(s) + O_2\,(g)$$

This reaction is used for quantitive estimation of ozone.

(*v*) *Ozone oxidises acidified ferrous salts to ferric salts.*

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$
$$2FeSO_4\,(aq) + H_2SO_4\,(aq) + O\,(g) \longrightarrow Fe_2(SO_4)_3\,(aq) + H_2O\,(l)$$
$$2FeSO_4\,(aq) + H_2SO_4\,(aq) + O_3\,(g) \longrightarrow Fe_2(SO_4)_3\,(aq) + H_2O\,(l) + O_2\,(g)$$

(*vi*) *Ozone oxidises potassium ferrocyanide to potassium ferricyanide*

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$
$$2K_4[Fe(CN)_6]\,(aq) + H_2O\,(l) + O\,(g) \longrightarrow 2K_3[Fe(CN)_6]\,(aq) + 2KOH\,(aq)$$
$$2K_4[Fe(CN)_6]\,(aq) + H_2O\,(l) + O_3\,(g) \longrightarrow 2K_3[Fe(CN)_6]\,(aq) + 2\,KOH\,(aq) + O_2\,(g)$$

(*vii*) *Ozone oxidises potassium manganate (green) to potassium permanganate (pink)*

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$

$$2K_2MnO_4\,(aq) + H_2O\,(l) + O\,(g) \longrightarrow 2\,KMnO_4\,(aq) + 2\,KOH\,(aq)$$

$$2K_2MnO_4\,(aq) + H_2O\,(l) + O_3\,(g) \longrightarrow 2KMnO_4\,(aq) + 2KOH\,(aq) + O_2\,(g)$$

(b) Oxidation of non-metals. Ozone oxidises non-metals like iodine, sulphur and phosphorus to their corresponding oxyacids. For example,

(i) Ozone oxidises moist iodine to iodic acid (HIO_3)

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)\,] \times 5$$

$$I_2\,(s) + 5O\,(g) \longrightarrow I_2O_5\,(s)$$

$$I_2O_5\,(s) + H_2O\,(l) \longrightarrow 2HIO_3\,(aq)$$

$$I_2\,(s) + 5O_3\,(g) + H_2O\,(l) \longrightarrow 2HIO_3\,(aq) + 5O_2\,(g)$$

(ii) Ozone oxidises moist sulphur to sulphuric acid (H_2SO_4).

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)] \times 3$$

$$S_8\,(s) + 24O\,(g) \longrightarrow 8\,SO_3\,(g)$$

$$SO_3\,(g) + H_2O\,(l) \longrightarrow H_2SO_4\,(aq)] \times 8$$

$$S_8\,(s) + 24O_3\,(g) + 8H_2O\,(l) \longrightarrow 8H_2SO_4\,(aq) + 24O_2\,(g)$$

(iii) Ozone oxidises moist phosphorus to phosphoric acid (H_3PO_4).

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)] \times 10$$

$$P_4\,(s) + 10\,O\,(g) \longrightarrow P_4O_{10}\,(s)$$

$$P_4O_{10}\,(s) + 6H_2O\,(l) \longrightarrow 4H_3PO_4\,(aq)$$

$$P_4\,(s) + 10O_3\,(g) + 6H_2O\,(l) \longrightarrow 4\,H_3PO_4\,(aq) + 10\,O_2\,(g)$$

(c) Oxidation of metalloids. Like non-metals, ozone also oxidises metalloids like arsenic and antimony to their corresponding oxy acids. For example,

(i) Ozone oxidises moist arsenic to arsenic acid (H_3AsO_4)

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)] \times 5$$

$$2\,As\,(s) + 5O\,(g) \longrightarrow As_2O_5\,(s)$$

$$As_2O_5\,(s) + 3H_2O\,(l) \longrightarrow 2H_3AsO_4\,(aq)$$

$$2As\,(s) + 5O_3\,(g) + 3H_2O\,(l) \longrightarrow 2H_3AsO_4\,(aq) + 5O_2\,(g)$$

(ii) Ozone oxidises moist antimony to antimonic acid (H_3SbO_4)

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)] \times 5$$

$$2Sb\,(s) + 5O\,(g) \longrightarrow Sb_2O_5\,(s)$$

$$Sb_2O_5\,(s) + 3H_2O\,(l) \longrightarrow 2H_3SbO_4\,(aq)$$

$$2Sb\,(s) + 5O_3\,(g) + 3H_2O\,(l) \longrightarrow 2H_3SbO_4\,(aq) + 5O_2\,(g)$$

(d) Oxidation of metals. Ozone also oxidises certain metals like silver, mercury, copper etc. to their corresponding oxides. For example,

(i) Silver is oxidised to silver oxide (Ag_2O)

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$

$$2Ag\,(s) + O\,(g) \longrightarrow Ag_2O\,(s)$$

$$2Ag\,(s) + O_3\,(g) \longrightarrow Ag_2O\,(s) + O_2\,(g)$$

(ii) Mercury is oxidised to mercurous oxide (Hg_2O)

$$O_3\,(g) \longrightarrow O_2\,(g) + O\,(g)$$

$$2Hg\,(l) + O\,(g) \longrightarrow Hg_2O\,(s)$$

$$2Hg\,(l) + O_3\,(g) \longrightarrow Hg_2O\,(s) + O_2\,(g)$$

The mercurous oxide thus formed dissolves in mercury. As a result, mercury loses its meniscus and starts sticking to the glass. *This is called* **tailing of mercury.** The meniscus can, however, be restored by shaking it with water which dissolves mercurous oxide.

(e) Exceptional behaviour. In all the oxidation reactions discussed above, the oxidation is brought about by the atomic oxygen and dioxygen is always evolved. *However, during the oxidation of SO_2 to SO_3 and acidified $SnCl_2$ to $SnCl_4$ the ozone is utilized as a whole and dioxygen is not evolved.* Thus,

$$(i)\quad \underset{\text{Sulphur dioxide}}{3\,SO_2\,(g)} + O_3\,(g) \longrightarrow \underset{\text{Sulphur trioxide}}{3SO_3\,(aq)}$$

$$(ii)\quad \underset{\text{Stannous chloride}}{3\,SnCl_2\,(s)} + 6HCl\,(aq) + O_3\,(g) \longrightarrow \underset{\text{Stannic chloride}}{SnCl_4\,(aq)} + 3H_2O\,(l)$$

(f) Bleaching action. *Because of its oxidising action, ozone acts as a mild bleaching agent and bleaches vegetable colouring matter.*

$$\text{Vegetable colouring matter} + O_3 \longrightarrow \text{Colourless oxidised matter} + O_2$$

As such ozone bleaches indigo, ivory, litmus, delicate fabrics like silk, wool etc.

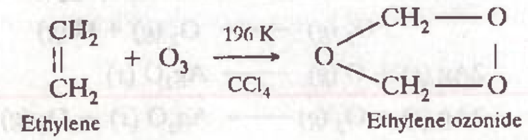
4. Reducing agent. Although ozone is an extremely powerful oxidising agent yet in some reactions, it acts as a weak reducing agent. For example, it reduces peroxides such as hydrogen peroxide, barium peroxide etc. liberating dioxygen.

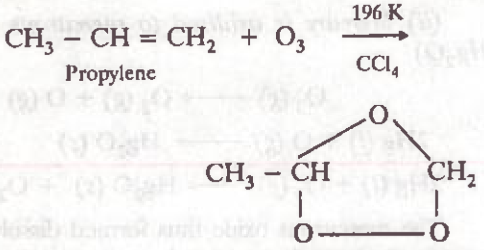
$$H_2O_2\,(aq) + O_3\,(g) \longrightarrow H_2O\,(l) + 2O_2\,(g)$$

$$BaO_2\,(s) + O_3\,(g) \longrightarrow BaO\,(s) + 2O_2\,(g)$$

5. Formation of ozonides – addition reaction

When ozone is bubbed through the solution of an alkene in an inert solvent such as CH_2Cl_2, $CHCl_3$, CCl_4 etc. at 196 K, it adds across the double bond forming an ozonide.





Propylene ozonide

13.18.4. Uses of Ozone (Trioxygen)

(*i*) Because of its oxidising nature, it is used as a disinfectant and as a germicide for sterilizing water.

(*ii*) It is used for bleaching delicate fabrics, oils, starch, ivory etc.

(*iii*) It is used for purifying air in crowded places such as cinema halls, underground railway stations, tunnels, mines, slaughter houses etc.

(*iv*) It is used in industry during the manufacture of artificial silk, synthetic camphor, potassium permanganate etc.

(*v*) It is used as a reagent in Organic Chemistry for carrying out ozonolysis and other oxidation reactions.

13.18.5. Tests of Ozone

(*i*) If turns alcoholic solution of benzidine brown.

(*ii*) In presence of O_3, mercury loses meniscus and starts sticking to glass (*tailing of mercury*)

(*iii*) It turns moist starch-iodide paper blue.

(*iv*) Ozone does not reduce acidified solution of $KMnO_4$ and $K_2Cr_2O_7$.

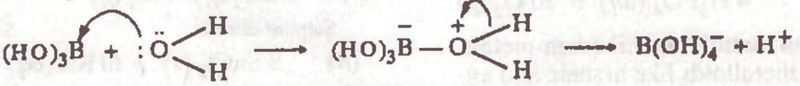
Conceptual Questions

Q. 1. Why does not boron form B^{3+} ions ?

Ans. Boron has three electrons in the valence shell. Because of its small size and high sum of the first three ionization enthalpies (*i.e.*, $IE_1 + IE_2 + IE_3$), boron does not lose all its valence electrons to form B^{3+} ions.

Q. 2. Although boric acid $B(OH)_3$, contains three hydroxyl groups yet it behaves as a monobasic acid. Explain why ?

Ans. Because of the small size of boron atom and presence of only six electrons in its valence shell in $B(OH)_3$, it accepts a lone pair of electrons from the oxygen atom of the H_2O molecule to form a hydrated species.



Hydrated species

The +ve charge on the O-atom, in turn, pulls the σ-electrons of the O—H bond towards itself, thereby facilitating the release of a proton. As a result, *$B(OH)_3$ acts a weak* monobasic *Lewis acid* and thus reacts with NaOH solution to form sodium metaborate.

$$B(OH)_3 + NaOH \longrightarrow Na^+[B(OH)_4] \quad \text{or} \quad \underset{\text{Sod. metaborate}}{Na^+BO_2^-} + 2H_2O$$

Q. 3. Diamond is covalent, yet it has a high melting point. Why ?

Ans. Diamond has three-dimensional net-work structure involving strong C—C bonds. Hence diamond has high melting point inspite of its covalent nature.

Q. 4. **Which oxide of carbon is an anhydride of carbonic acid ?**

Ans. Since carbonic acid decomposes to give CO_2 and H_2O, therefore, CO_2 is regarded as an anhydride of carbonic acid $H_2CO_3 \longrightarrow H_2O + CO_2$

Q. 5. **Carbon monoxide is readily absorbed by ammoniacal cuprous chloride solution but carbon dioxide is not. Explain.**

Ans. Due to the presence of a lone pair of electrons on carbon in CO, it acts as a *Lewis base (or ligand)* and thus forms a soluble complex with ammoniacal cuprous chloride solution.

$$CuCl + NH_3 + CO \longrightarrow \underset{\textbf{Soluble complex}}{[Cu(CO)NH_3]^+Cl^-}$$

On the other hand, CO_2 does not act as a *Lewis base* since it does have a lone pair of electrons on the carbon atom and hence does not dissolve in ammoniacal cuprous chloride solution.

Q. 6. **Silanes are few in number whereas alkanes are large in number. Explain.**

Ans. Carbon has the maximum tendency for catenation due to stronger C—C (355 kJ mol^{-1}) bonds. As a result, it forms a large number of alkanes.

Silicon, on the other hand, due to weaker Si—Si (200 kJ mol^{-1}) bonds has much lesser tendency for catenation and hence forms only a few silanes.

Q. 7. **Classify the following into (*i*) ionic, covalent and interstitial carbides :**
(*i*) SiC (*ii*) VC (*iii*) WC (*iv*) Al_4C_3

Ans. (*i*) covalent, (*ii*) and (*iii*) interstitial and (*iv*) ionic.

Q. 8. **Write balanced equation for the hydrolysis of HCO_3^- and CO_3^{2-} ions.**

Ans. $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

Q. 9. **Give one reaction in which ammonia acts as a reducing agent.**

Ans. When NH_3 is passed over heated cupric oxide, metallic copper is formed

$$3\,CuO + 2\,NH_3 \xrightarrow{\text{Heat}} 3\,Cu + N_2 + 3\,H_2O$$

In this reaction, NH_3 acts a reducing agent and thus reduces CuO to metallic copper, while it itself is oxidised to N_2 gas.

Q. 10. **Conc. HNO_3 turns yellow in sun light. Why ?**

Ans. In presence of sun light, HNO_3 partially decomposes to produce NO_2 which then dissolves in HNO_3 to impart yellow colour to it.

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

Q. 11. **Aluminium containers can be used for storing conc. HNO_3. Explain.**

Ans. In presence of conc. HNO_3, Al becomes *passive, i.e.*, a thin protective layer of its oxide (Al_2O_3) is formed on its surface which prevents the further action between the metal and the acid. Therefore Al containers can be used for storing conc. HNO_3.

Q. 12. **Burning magnesium continues to burn while burning sulphur gets extinguished when dropped into a jar of nitric oxide. Explain.**

Ans. Heat evolved during burning of Mg is quite enough to decompose NO to N_2 and O_2. The O_2 thus produced supports combustion of Mg. In contrast, the heat produced during burning of S is not quite sufficient to decompose NO. As a result, sulphur stops burning.

Q. 13. **Name an ion which is isoelectronic with nitrate ion. What is its shape ?**

Ans. NO_3^- ion is isoelectronic with CO_3^{2-} ion since both contain 32 electrons. Like NO_3^- ion, CO_3^{2-} ion is also planar.

Q. 14. **How will you prepare a sample of ND_3 ?**

Ans. By the action of heavy water on magnesium nitride.

$$2\,Mg_3N_2 + 6\,D_2O \longrightarrow 3\,Mg(OD)_2 + 2\,ND_3 \qquad (N.C.E.R.T.)$$

Very Short Answer Questions CARRYING 1 MARK

Q. 1. What happens when a borax solution is acidified ? Write a balanced equation for the reaction. (*N.C.E.R.T.*)

Ans. Boric acid is formed, $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$

Q. 2. By means of a balanced equation show how $B(OH)_3$ behaves as an acid in water. (*N.C.E.R.T.*)

Ans. $B(OH)_3 + 2\,HOH \longrightarrow [B(OH)_4]\ + H_3O^+$

Q. 3. What happens when boric acid is heated ? (*N.C.E.R.T.*)

Ans. $4H_3BO_3 \xrightarrow[-4H_2O]{370\text{ K}} 4HBO_2 \xrightarrow[-H_2O]{410\text{ K}} H_2B_4O_7 \xrightarrow{\text{Red heat}} 2B_2O_3 + H_2O$

Q. 4. Why do boron halides form addition compounds with amines ? (*N.C.E.R.T.*)

Ans. Boron halides are Lewis acids and hence accept a pair of electrons from amines to form addition compounds.

Q. 5. Write the structure of diborane.

Ans. Refer to Fig. 13.5 on page 13/10.

Q. 6. Why do boron halides behave as Lewis acids ?

Ans. Boron halides behave as Lewis acids since the boron atom in them has only six electrons in the valence shell and needs two more electrons to complete its octet.

Q. 7. What are boranes ?

Ans. Stable covalent boron hydrides like B_2H_6 , B_4H_{10} , B_5H_9 etc. on analogy with alkanes are called boranes.

Q. 8. How is diborane prepared ?

Ans. $BF_3 + 3LiBH_4 \xrightarrow{\text{Dry ether}} 2B_2H_6 + 3LiF$

Q. 9. What is the correct structural formula of borax ($Na_2B_4O_7.10H_2O$)

Ans. $Na_2\,[B_4O_5(OH)_4]\,.\,8H_2O$.

Q. 10. Why does boron not form B^{3+} ions ?

Ans. Because of very high first three ionization energies.

Q. 11. What is dry ice ? Why is it so called ? (*N.C.E.R.T.*)

Ans. Solid CO_2 ; it does not wet the surface when it melts.

Q. 12. What is carborundum ? What is its common use ?

Ans. Silicon carbide (SC). It is used as an abrasive.

Q. 13. What is the chemical name of freon ?

Ans. Dichlorodifluoromethane.

Q. 14. What is catenation ?

Ans. Property of self-linking of atoms to form chains is called catenation.

Q. 15. What is water gas ? How is it prepared ?

Ans. An equimolar mixture of CO with H_2 is called water gas. It is obtained by passing steam over red hot coke.

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

Q. 16. Carbon dioxide is passed through a suspension of limestone in water. Write balanced chemical equation for the above reaction. (*I.I.T. 1991*)

Ans. $CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$

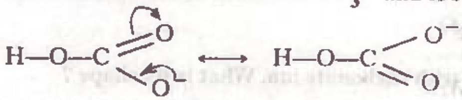
Q. 17. What is the oxidation state of carbon in each of the followign compounds ?

(*a*) CO (*b*) HCN (*c*) H_2CO_3 (*d*) CaC_2. **(N.C.E.R.T.)**

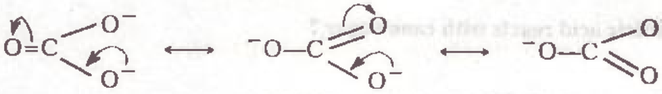
Ans. (*a*) + 2 (*b*) + 2 (*c*) + 4 (*d*) —1.

Q. 18. Write resonance structures of CO_3^{2-} and HCO_3^- ion. **(N.C.E.R.T.)**

Ans.



Resonance structures of HCO_3^- ion.



Resonance structures of CO_3^{2-} ion.

Q. 19. What is the state of hybridization of carbon in

(*a*) CO_3^{2-} (*b*) HCN (*c*) diamond (*d*) graphite. **(N.C.E.R.T.)**

Ans. (*a*) sp^2 (*b*) sp (*c*) sp^3 (*d*) sp^2.

Q. 20. Determine the oxidation number of nitrogen in

(*a*) N_2O (*b*) NO_2 (*c*) HNO_3 (*d*) NH_3. **(N.C.E.R.T.)**

Ans. (*a*) + 1 (*b*) + 4 (*c*) + 5 (*d*) —3.

Q. 21. Write balanced equation for the preparation of elemental boron by reduction of BBr_3 with dihydrogen.

Ans. $2\,BBr_3\,(g) + 3\,H_2\,(g) \longrightarrow 2\,B\,(s) + 6\,HBr\,(g)$

Q. 22. How is dinitrogen prepared in the laboratory ? **(N.C.E.R.T.)**

Ans. By heating a solution of $NH_4Cl + NaNO_2$.

Q. 23. Give examples of compounds in which nitrogen exhibits oxidation states of (*i*) —3, (*ii*) + 3 and (*iii*) + 5. **(N.C.E.R.T.)**

Ans. (*i*) NH_3 (*ii*) NF_3 (*iii*) N_2O_5.

Q. 24. Give one example of a reaction in which dinitrogen acts an oxidising agent.

Ans. $3\,\overset{0}{Mg} + \overset{0}{N_2} \longrightarrow \overset{+2}{Mg_3}\,\overset{-3}{N_2}$.

In this reaction, N_2 oxidises Mg to Mg^{2+} and is itself reduced to N_3^-.

Q. 25. Give one example of industrial fixation of nitrogen.

Ans. $N_2 + 3\,H_2 \xrightarrow[200\text{ atm}]{673\text{ K}} 2\,NH_3$ (Haber's process).

Q. 26. What is Nessler's reagent ? What is its use ?

Ans. An alkaline solution of K_2HgI_4 is called Nessler's reagent. It is used for detection of NH_3 and NH_4^+ salts.

Q. 27. Why does nitrogen fail to form pentahalide ?

Ans. Due to absence of *d*-orbitals in the valence shell and also due to high energy required for promotion of 2 *s*-electron to 3 *s*-orbital.

Q. 28. Explain why reddish brown nitrogen peroxide on cooling undergoes dimerisation to give colourless dinitrogen tetroxide?

Ans. Because of the presence of an unpaired electron on N, NO_2 undergoes dimerization on cooling to form colourless N_2O_4. $2\,NO_2 \longrightarrow O_2N—NO_2$

Q. 29. Name the oxide of nitrogen which is paramagnetic in the gaseous state and diamagnetic in the liquid or the solid state.

Ans. Nitric oxide (NO).

Q. 30. What is laughing gas ? How is it prepared ?

Ans. N_2O. It is prepared by heating NH_4NO_3

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

Q. 31. Name a nitrogen containing ion which is isoelectronic with carbonate ion. What is its shape ?

Ans. NO_3^- is isoelectronic with CO_3^{2-} since both contain 32 electrons. Like CO_3^{2-}, NO_3^- is also planar.

Q. 32. What happens when concentrated nitric acid reacts with cane sugar ?

Ans. Oxalic acid is formed.

$$C_{12}H_{22}O_{11} + 36\,HNO_3 \longrightarrow \underset{\text{oxalic acid}}{6\,(COOH)_2} + 36\,NO_2 + 23\,H_2O$$

Q. 33. Write the formula of the brown complex formed during ring test of nitrates.

Ans. $[Fe(H_2O)_5NO^+]^{2+}$ pentaaquanitrosoniumiron (I).

Q. 34. Name a nitrogen containing ion which is isoelectronic with CO_2 ? What is its shape ?

Ans. Cyanamide ion (CN_2^{2-}) is isoelectronic with CO_2 since both contain 22 electrons. Like CO_2, CN_2^{2-} is also linear.

Q. 35. What happens when iron is dipped in concentrated nitric acid.

Ans. Iron is rendered passive due to the formation of a thin protective layer of ferrosoferric oxide, $FeO \cdot Fe_2O_3$, on its surface which prevents further action.

Q. 36. Give two reactions of ozone in which dioxygen is not liberated ?

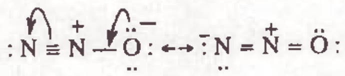
Ans. (*i*) $3\,SO_2 + O_3 \longrightarrow 3\,SO_3$ (*ii*) $3\,SnCl_2 + 6\,HCl + O_3 \longrightarrow 3\,SnCl_4 + 3\,H_2O$

Q. 37. What is tailing of mercury ? How can it be removed ?

Ans. O_3 oxidises Hg to Hg_2O. The Hg_2O thus formed dissolves in mercury. As a result, Hg loses its meniscus and starts sticking to the glass. This is called **tailing of mercury**. The meniscus can, however, be restored by shaking it with H_2O which dissolves Hg_2O.

Q. 38. Write the resonance structures of N_2O that will satisfy the octet rule. *(I.I.T. 1985 ; M.L.N.R. Allahabad 1993)*

Ans.



$$:N \equiv \overset{+}{N} - \ddot{\underset{\cdot\cdot}{O}}:^{-} \longleftrightarrow {}^{-}\!:\underset{\cdot\cdot}{N} = \overset{+}{N} = \ddot{O}:$$

Q. 39. What happens when aqueous ammonia is added dropwise to a solution of copper sulphate until it is in excess ?

Ans. To begin with a bluish white ppt. of $Cu(OH)_2$ is obtained which dissolves in excess of ammonia to form a deep blue solution due to the formation of a deep blue complex, $[Cu(NH_3)_4]\,SO_4$. *(I.I.T. 1987)*

Q. 40. Gold is dissolved in aqua regia. Give equation.

Ans. $Au + 3\,HNO_3 + 4\,HCl \longrightarrow HAuCl_4 + 3\,NO_2 + 3\,H_2O$. *(B.I.T. Ranchi 1996)*

Q. 41. Write the reaction of ozonised oxygen with ethylene.

Ans. Ethylene ozonide is formed. Consult the text for reaction.

Q. 42. What are fullerenes ? How many pentagonal and hexagonal rings are present in C_{60} molecule ?

Ans. Fullerenes constitute a new family of carbon allotropes consisting of large spheroidal molecules of composition C_{2n} (where $n \geq 30$). C_{60} fullerene contains 20 hexagonal and 12 pentagonal rings.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec.13.1. to 13.4.

1. How does boron occur ? How is it extracted ?
2. Describe briefly how elemental boron can be obtained ? (N.C.E.R.T.)
3. Why does boron resemble more with silicon than with aluminium ?
4. Why are boron halides and diborane referred to as electron deficient compounds ? (N.C.E.R.T.)
5. Write balanced equations for the reaction of elemental boron with elemental chlorine, oxygen and nitrogen at high temperatures. (N.C.E.R.T.)
6. Explain the chemistry of borax bead test.
7. Write the structure of diborane and explain the nature of bonding in it. (N.C.E.R.T.)
8. How are boron trihalides prepared ?
9. Discuss the structure of boron trihalides.
10. Why do boron trihalides behave as Lewis acids ? Discuss their relative acid strength.
11. Describe the shapes of BF_3 and BH_4^-. What type of hybridization can we assign to boron in each of these compounds ? (N.C.E.R.T.)
12. List some uses of boron and its compounds.

Sec.13.5.

13. What is allotropy ? Name two elements which exhibit allotropy.
14. Explain the differences in the properties of diamond and graphite on the basis of their structures. (N.C.E.R.T.)
15. Account for the following :
    (*i*) Diamond is hard but graphite is soft.
    (*ii*) Graphite is a good conductor of electricity but diamond is not.
    (*iii*) Diamond is used in jewellery
    (*iv*) Graphite is used as a lubricant but diamond is used as an abrasive.
16. What are fullerenes ? How are they prepared ? Discuss their structure. (N.C.E.R.T.)
17. What is catenation ? How does it explain huge number of carbon compounds.

Sec.13.6. to 13.10.

18. What is dry ice ? Why is it so called ? Give its one use.
19. Account for the toxic nature of carbon monoxide.
20. Write equations for the production of water gas and producer gas from coke.
21. Explain the following : (*i*) Carbon dioxide turns lime water milky. But if it passed for a long time, the solution becomes clear again.
    (*ii*) CCl_4 is resistant to hydrolysis. (*iii*) Freon is used as a refrigerant.
22. Give equations for the following :
    (*i*) Preparation of carbon dioxide (*ii*) Basic properties of sodium carbonate solution
    (*iii*) Formation of acetylene.
23. Why carbonates and bicarbonates of alkali metals behave as weak bases in their aqueous solutions ?
24. What are carbides ? Name the different types of carbides. Give one example of each type.
25. Give equations for the preparation of acetylene from calcium carbide and methane from aluminium carbide.
26. How is carbon disulphide prepared from natural gas ? How is cellulose converted into (*i*) viscose rayon (*ii*) cellophane ?
27. Discuss the structures of CO and CO_2.
28. Write equations for the following :
    (*i*) Carbon disulphide reacts with C_2H_5OH in presence of NaOH.

(*ii*) Carbon disulphide reacts with Cl_2 in presence of ferric chloride as catalyst.

(*iii*) Malonic acid is treated with P_4O_{10}.

29. Write balanced equations for the following reactions.

(*a*) Combustion of C_4H_{10} in a limited supply of oxygen to form carbon monoxide.

[**Hint.** $2\ C_4H_{10}\ (g) + 9\ O_2\ (g) \longrightarrow 4\ CO\ (g) + 10\ H_2O\ (l)$]

(*b*) The reaction of calcium carbide with water to form acetylene.

(*c*) The preparation of calcium cyanamide from calcium carbide and nitrogen.

(*d*) Formation of hydrogen cyanide from methane and ammonia. (*N.C.E.R.T.*)

[**Hint.** $CH_4\ (g) + NH_3\ (g) \xrightarrow[1500\ K]{Pt\ catalyst} HCN\ (g) + 3\ H_2\ (g)$]

30. What is freon ? How is it prepared from CCl_4 ? Write its important uses.

Sec.13.11. to 13.12. **31.** How will you prepare dinitrogen in the laboratory ? Why is dinitrogen somewhat inert in nature ?

32. Discuss one method each for biological and industrial fixation of dinitrogen.

Sec.13.13. **33.** Briefly discuss the manufacture of ammonia by Haber's process. Explain clearly the effect of temperature and pressure on the process.

34. Discuss the conditions required in the Haber process for the manufacture of ammonia. (*N.C.E.R.T.*)

35. Explain

(*i*) Ammonia is a good complexing agent (*ii*) Shape of ammonia molecule.

Sec.13.14. to 13.15. **36.** List the oxides of nitrogen and give oxidation number of nitrogen in each oxide. Give their structures and uses.

37. Illustrate how nitrogen compounds provide good examples of multiple bonding and resonance. (*N.C.E.R.T.*)

38. Write the resonance Lewis structures for N_2O, NO_2 and NO_3^-. (*N.C.E.R.T.*)

39. How is nitric acid manufactured from ammonia ?

40. Write balanced equation(s) for the manufacture of nitric acid by the oxidation of ammonia. (*N.C.E.R.T.*)

41. Give three reactions to show that nitric acid acts as an oxidising agent.

42. What is the action of conc. nitric acid on :

(*a*) acidified ferrous sulphate solution (*b*) phosphorus (*c*) copper?

43. What happens when dilute nitric acid reacts with copper ?

44. What happens when ammonia gas mixed with oxygen is passed over heated platinum catalyst ? What is the utility of this reaction in industry ?

45. What is the structure of nitric acid ?

46. Illustrate how a metal like copper can give different products with nitric acid. Give balanced equations.

47. Describe the uses of ammonia and nitric acid. (*N.C.E.R.T.*)

48. Identify the products of the following reactions. Give balanced equations :

(*i*) $Mg_3N_2 + H_2O \longrightarrow$ (*ii*) $I_2 + HNO_3$ (conc.) $\longrightarrow$ (*iii*) $Cu + HNO_3$ (*conc.*) $\longrightarrow$

(*iv*) $Li + N_2 \longrightarrow$ (*v*) $HNO_3 + P_4O_{10} \longrightarrow$ (*N.C.E.R.T.*)

Sec.13.16. to 13.17. **49.** (*a*) Give one laboratory method for the preparation of dioxygen gas.

(*b*) Why is MnO_2 added to potassium chlorate for getting dioxygen ?

(*c*) What is the action of water on sodium peroxide?

50. How is dioxygen obtained from liquid air ?

51. How does dioxygen react with sulphur dioxide, ammonia, hydrochloric acid and nitric oxide ? State the conditions under which these reactions take place.

52. Give at least four uses of dioxygen.

53. Classify different oxides on the basis of their acid-base character.

54. Classify the following compounds into acidic, basic and amphoteric oxides :
$SrO, SiO_2, Al_2O_3, N_2O_5, SO_2, P_4O_6, Cl_2O_7$
Write balanced equations for the reaction of each of these compounds with water, a base or the acid as the case may be. *(N.C.E.R.T.)*
[**Ans.** Basic : SrO, Amphoteric : Al_2O_3 ; Acidic : $N_2O_5, SO_2, P_4O_6, Cl_2O_7$]

Sec.13.18. 55. How would you convert dioxygen into ozonised oxygen ?

56. What is the shape of ozone molecule ? Write Lewis dot structure(s) for ozone molecule and explain why O—O distances in ozone are equal. *(N.C.E.R.T.)*

57. Give an account of the structure of ozone ? Give reasons for the following. Both O—O bonds in O_3 have same length.

58. How does ozone react with KI and lead sulphide?

59. Give at least two uses of ozone.

60. What is the importance of ozone for plant and animal life on earth ? *(N.C.E.R.T.)*

61. Give two chemical properties of ozone which show that it is a more powerful oxidising agent than oxygen.

Long Answer Questions CARRYING 5 or more MARKS

Sec.13.1. to 13.4. 1. How does boron occur in nature ? How is it extracted from boric oxide and boron halides ? Give its reactions with air, halogens, concentrated nitric acid, concentrated sulphuric acid and fused alkali. Mention a few important uses of boron and its compounds.

2. Give the preparation of borax from the mineral colemanite. Briefly describe its properties and uses.

Sec.13.6. to 13.10. 3. Explain the differences in properties of diamond and graphite based upon their structures.

4. Name two oxides of carbon. Discuss briefly their preparation, properties and uses.

5. What are carbides ? How are they classified ? Discuss one method of preparation, two properties and two uses of each type.

6. Discuss the methods of preparation, properties and uses of halides of carbon.

7. How is carbon disulphide prepared ? Discuss its important properties and uses.

Sec.13.11. to 13.15. 8. How is dinitrogen prepared ? Describe its properties and uses.

9. How is ammonia obtained by Haber's process ? What are the optimum conditions to obtain its maximum yield ? Give balanced chemical equations for its reactions with halogens and oxygen.

10. Describe Ostwald process for the manufacture of nitric acid. Describe its action on metals with the help of balanced chemical equations.

11. Name the various oxides of nitrogen. Give their oxidation states and draw their structures.

Sec.13.16. to 13.17. 12. Discuss briefly the methods of preparation, properties and uses of dioxygen.

13. How are the oxides classified ? Give two examples of each type.

14. How is ozone prepared ? Discuss briefly its oxidising properties. Also comment upon the structure of ozone molecule.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Sodium borohydride, $Na[BH_4]$ is obtained by heating sodium hydride with diborane.

$$2\,NaH + B_2H_6 \xrightarrow{\Delta} 2\,NaBH_4$$

$NaBH_4$ is a mild reducing agent and is extensively used in organic chemistry for the reduction of aldehydes and ketones to the corresponding alcohols and also for the reduction of cyanides ($R—C \equiv N$) to 1° amines ($R—NH_2$).

2. Carbon suboxide

Carbon suboxide (C_3O_2) is prepared by dehydration of malonic acid with P_4O_{10}

$$\underset{\text{Malonic acid}}{HO—CO—CH_2—CO—OH} \xrightarrow[\Delta]{P_4O_{10}} \underset{\text{Carbon suboxide}}{O=C=C=C=O} + 2\,H_2O$$

Properties. (*i*) Carbon suboxide is a linear molecule.

(*ii*) It is a foul smelling gas, b.p. 279 K. At room temperature, the gas polymerises to a yellow solid, and at higher tempertures to red and purple solids.

(*iii*) It reacts with H_2O to form malonic acid, with HCl to form malonyl chloride and with NH_3 to form malonamide.

$$C_3O_2 + H_2O \longrightarrow \underset{\text{Malonic acid}}{CH_2(COOH)_2}$$

$$C_3O_2 + 2\,HCl \longrightarrow \underset{\text{Malonyl chloride}}{CH_2(COCl)_2}$$

$$C_3O_2 + 2\,NH_3 \longrightarrow \underset{\text{Malonamide}}{CH_2(CONH_2)_2}$$

3. Carbon-nitrogen compounds. (i) Calcium cyanamide. One of the most important compounds containing both carbon and nitrogen is calcium cyanamide, $CaCN_2$. It is obtained by the reaction of calcium carbide with nitrogen at 1373 K

$$CaC_2\,(s) + N_2\,(g) \xrightarrow{1373\ K} CaNCN\,(s) + C\,(s)$$

Calcium cyanamide is used as a fertilizer. It is also used for the manufacture of melamine plastic needed for making non- breakable crockery.

(ii) Sodium cyanide. Sodium cyanide is formed when calcium cyanamide is fused with carbon and sodium carbonate.

ADDITIONAL USEFUL INFORMATION contd.

$$CaCN_2 + C + Na_2CO_3 \xrightarrow{Fuse} CaCO_3 + 2\,NaCN$$

Sodium cyanide is used for the extraction of gold and silver from their ores.

(iii) Hydrocyanic acid. HCN is produced when sodium cyanide is treated with strong acids. HCN is a colourless gas and behaves as a weak acid in aqueous solution ($pK_a = 9{\cdot}0$). Industrially, HCN is obtained by action of ammonia on methane at high temperature.

$$CH_4\,(g) + NH_3\,(g) \xrightarrow[1500\ K]{Pt\ catalyst} HCN\,(g) + 3\,H_2\,(g)$$

Cyanides (NaCN, KCN) and HCN are extremely poisonous substances. Their ingestion or inhalation can lead to instant death. HCN is used in the manufacture of methylmethacrylate polymers and adiponitrile which is used for the manufacture of hexamethylenediamine which is the starting material for nylon-66.

(iv) Cyanogen, $(CN)_2$. It is produced by the oxidation of HCN by O_2 in the presence of silver as a catalyst or by the oxidation of CN^- by Cu^{2+}

$$4\,HCN + O_2 \xrightarrow{\Delta} 2\,(CN)_2 + 2\,H_2O$$

$$2\,Cu^{2+} + 4\,CN^- \longrightarrow 2\,CuCN + (CN)_2$$

Like HCN, cyanogen is a colourless poisonous gas. It is a linear molecule. Cyanogen resembles halogens in its properties and hence it is referred to as *pseudohalogen*. For example, in basic medium, like halogens, it undergoes disproportionation to give cyanide and cyanate ions.

$$(CN)_2 + 2\,OH^- \longrightarrow CN^- + OCN^- + H_2O$$

(v) Cyanamide, H_2NCN. Treatment of CaNCN with water gives cyanamide which is a solid with m.p. 318 K.

$$CaNCN + H_2O \longrightarrow CaO + H_2NCN$$

It is used in the preparation of *guanidine* and *thiourea*.

4. Nitrous acid (HNO_2) acts as a strong oxidising agent since it can be easily reduced to oxides of nitrogen. In contrast, nitrous acid (HNO_2) can be either reduced to nitric oxide (NO) or oxidised to nitric acid and hence it acts both as an oxidising as well as a reducing agent.

$$2\,HNO_2 \longrightarrow 2\,NO + H_2O + [O]$$

$$HNO_2 + [O] \longrightarrow HNO_3$$

(a) Oxidising properties. It oxidises H_2S to S, H_2SO_3 to H_2SO_4, $SnCl_2$ in HCl to $SnCl_4$, acidified $FeSO_4$ to $Fe_2(SO_4)_3$ and moist KI to I_2.

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

$$H_2SO_3 + 2\,HNO_2 \longrightarrow H_2SO_4 + H_2O + 2\,NO$$

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

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

$$2\,KI + 2\,HNO_2 \longrightarrow 2\,KOH + I_2 + 2\,NO$$

(b) Reducing properties. It reduces acidified $KMnO_4$, acidified $K_2Cr_2O_7$, halogens to halogen acids and H_2O_2 to H_2O.

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

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

$$Cl_2 + H_2O + HNO_2 \longrightarrow 2\,HCl + HNO_3$$

$$H_2O_2 + HNO_2 \longrightarrow H_2O + HNO_3$$

C.B.S.E.-P.M.T. (MAINS) SPECIAL

Q. 1. Boric acid can be titrated against sodium hydroxide using methyl orange as indicator only in the presence of polyhydroxy compounds like catechol, mannitol etc. Explain.

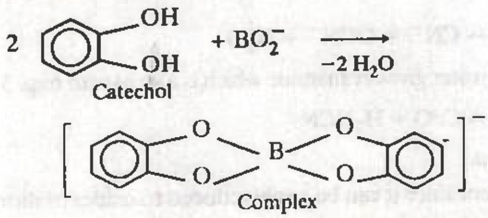
Ans. $B(OH)_3$ reacts with NaOH to form sodium metaborate.

$$B(OH)_3 + NaOH \longrightarrow Na^+BO_2^- + 2H_2O$$

The end point during the titration of H_3BO_3 with NaOH is not sharp since $NaBO_2$ undergoes excessive hydrolysis to give back H_3BO_3 and NaOH

$$NaBO_2 + 2\,H_2O \rightleftharpoons B(OH)_3 + NaOH$$

However, when certain polyhydroxy compounds such as catechol, glycerol, mannitol or sugars are added to the titration solution, the metaborate ion combines with polyhydroxy compound to form a complex.



Due to the formation of this complex, BO_2^- ion does not undergo hydrolysis. As a result, boric acid behaves as a strong monobasic acid and the end point can thus be easily detected.

Q. 2. Commercial nitrogen is passed through copper chips kept in ammonia to remove oxygen. Explain.

Ans. Copper dissolves in ammonia in presence of O_2 to form blue coloured tetrammine copper (II) hydroxide.

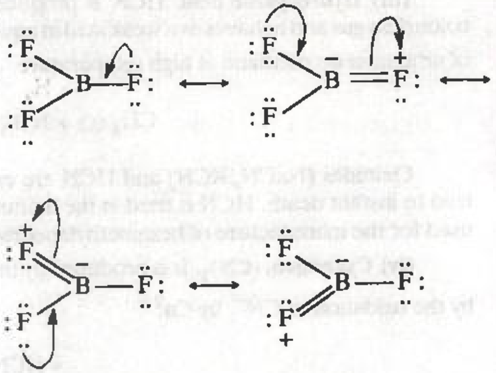
$$2\,Cu + 8\,NH_3 + O_2 + 2H_2O \longrightarrow 2\,[Cu(NH_3)_4]\,(OH)_2$$

As a result, commerical nitrogen is freed from traces of O_2 present in it.

Q. 3. (a) Explain why BF_3 exists whereas BH_3 does not.

(b) Compare the B—F bond length in BF_3 and BF_4^-.

Ans. (*a*) Due to $p\pi - p\pi$ back bonding, the lone pair of electrons of F is denoted to the B-atom. This delocalization reduces the deficiency of electrons on B thereby increasing the stability of BF_3 molecule.



Due to absence of lone pair of electrons on H-atom, this compensation does not occur in BH_3. In other words, electron deficiency of B stays and hence to reduce its electron deficiency, BH_3 dimerises to form B_2H_6.

(*b*) Because of double bond character of B—F bonds in BF_3, it has a shorter B—F bond length than in BF_4^-.

Q. 4. Nitrous oxide supports combustion more vigorously than air. Explain.

Ans. N_2O dicomposes to produce O_2 which is about

$$2\,N_2O \xrightarrow{\text{Heat}} 2\,N_2 + O_2$$

1/3 of the volume of gases produced $(2N_2 + O_2)$ while air contains O_2 which is about 1/5 of its volume. Due to this greater oxygen content, N_2O supports combustion more vigorously than air.

Q. 5. Write the chemical reactions associated with 'brown ring test'. ***(I.I.T. 2000)***

Ans. Refer to page 13/42.

Q. 6. How is boron obtained from borax? Give chemical equations with reaction conditions. Write the structure of B_2H_6 and its reaction with HCl. ***(I.I.T. 2002)***

Ans.

$$\underset{\text{Borax}}{Na_2B_4O_7.10H_2O} + H_2SO_4\,(conc.) \longrightarrow Na_2SO_4 + \underset{\text{Tetraboric acid}}{H_2B_4O_7} + 10\,H_2O$$

$$H_2B_4O_7 + 5\,H_2O \longrightarrow \underset{\text{Boric acid}}{4\,H_3BO_3}$$

$$2\,H_3BO_3 \xrightarrow{\text{Red heat}} \underset{\text{Boric oxide}}{B_2O_3} + 6\,H_2O$$

$$B_2O_3 + 3\,Mg \xrightarrow{\Delta} 2\,B + 3\,MgO$$

For structure of B_2H_6, refer to page 13/10. With dry HCl, B_2H_6 evolves H_2 gas

$$B_2H_6 + HCl\,(dry) \longrightarrow B_2H_5Cl + H_2$$

Q. 7. **(i) Describe with equation what happens when carbon is heated with conc. H_2SO_4?** ***(West Bengal J.E.E. 2003)***

(ii) State how will you separate CO_2 and SO_2 from their mixture?

Ans. (*i*) H_2SO_4 oxidises C to CO_2 and itself is reduced to SO_2

$$C + 2\,H_2SO_4 \longrightarrow \overset{+4}{C}O_2 + 2\,\overset{+4}{S}O_2 + 2\,H_2O$$

(*ii*) Since the O.N. of C in CO_2 is + 4 which is the maximum for C, therefore, it cannot act as a *reducing agent*. In contrast the O.N. of S in SO_2 is also + 4 but its maximum O.N. is + 6, therefore, it can act as a *reducing agent*. This reducing gas can be removed by passing the mixture of these gases through acidified $K_2Cr_2O_7$ solution when orange solution turns green due to reduction of $Cr_2O_7^{2-}$ ion to Cr^{3+} ions while CO_2 passes out unreacted.

Why BBr_3 is a stronger Lewis acid as compared to BF_3 though fluorine is more electronegative than chlorine. ***(C.B.S.E. P.M.T. 2004)***

Ans. The B atom in BF_3 and BBr_3 has only six electrons in its valence shell and hence can accept a pair of electrons to complete its octet. Therefore, both BF_3 and BBr_3 act as Lewis acids. But in BF_3, the sizes of empty 2*p*-orbital of B and the 2*p*- orbital of F containing the lone pair of electrons are almost identical and hence effective $p\pi - p\pi$ bonding occurs. As a result, the lone pair of F is donated to B atom and hence the *electron-deficiency of boron decreases*. In contrast in BBr_3, the size of 5*p*-orbital of Br containing the lone pair of electrons is much bigger than the empty 2*p*-orbital of B and hence donation of lone pair of electrons of Br to B does not occur to any significant extent. As a result, the electron- deficiency of B is much higher in BBr_3 than that in BF_3, and hence BBr_3 is a stronger Lewis acid than BF_3

I.I.T. (MAINS) SPECIAL

Q. 8. **An orange solid A on heating gave a green residue B, a colourless gas C and water vapours. The dry gas C on passing over heated Mg gave a white solid D. D on reaction with water gave a gas E which formed dense white fumes with HCl. Identify A to E and give the reactions involved.** ***(I.I.T. 1993)***

Ans. (*i*) Since the gas E formed dense white fumes with *HCl, it may be NH_3.*

(*ii*) Since gas E is produced when a white solid D containing Mg reacts with H_2O, therefore, *D must be magnesium nitride.*

(*iii*) Since white solid D *i.e.* magnesium nitride, is produced when a colourless gas C reacts with Mg, therefore, C *must be N_2*.

(*iv*) Since a colourless gas C *i.e.* N_2 along with a green solid **B** and water vapours are obtained when an orange solid **A** is heated, therefore, **A** *must be ammonium dichromate and* **B** *must be chromic oxide* (Cr_2O_3). All the reactions involved in the question are :

$$\underset{\substack{\text{Amm. dichromate}\\ \text{A}}}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{\substack{\text{Green residue,}\\ \text{B}}}{Cr_2O_3} + \underset{\substack{\text{Colourless}\\ \text{gas, C}}}{N_2} + 2H_2O$$

$$3Mg + N_2 \xrightarrow{\Delta} \underset{\text{Mag. nitride, D}}{Mg_3N_2}$$

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + \underset{\text{Ammonia, E}}{2NH_3}$$

$$NH_3 + HCl \longrightarrow \underset{\text{(Dense white fumes)}}{NH_4Cl}$$

Q. 2. **Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds (A) and (B).** ***(I.I.T. 1996)***

Ans. $$3Ca + N_2 \xrightarrow{\Delta} \underset{\substack{\text{Cal.nitride}\\ \textit{(White powder)}}}{Ca_3N_2}$$

$$Ca_3N_2 + 6H_2O \longrightarrow \underset{\textit{(alkaline solution)}}{3Ca(OH)_2} + \underset{(A)}{2NH_3}$$

$$Ca(OH)_2 + \underset{\textit{(from air)}}{CO_2} \longrightarrow \underset{\substack{\text{(Cal.carbonate)}\\ \text{(B)}}}{CaCO_3 \downarrow} H_2O$$

Q. 3. **A colourless inorganic salt (A) decomposes at about 250° C to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the reactions involved in the above process :** ***(I.I.T. 1996)***

Ans. (*i*) $$\underset{(A)}{NH_4NO_3} \xrightarrow{250°C} \underset{\substack{\text{Nitrous}\\ \text{oxide (B)}}}{N_2O} + \underset{\substack{\text{Neutral}\\ \text{oxide (C)}}}{2H_2O}$$

(*ii*) $$\underset{\text{Nitrous oxide (B)}}{10N_2O} + P_4 \longrightarrow 10N_2 + \underset{\substack{\text{Phosphorus pentoxide}\\ \textit{(dehydrating agent)}}}{P_4O_{10}}$$

Q. 4. **Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes milky on bubbling carbon dioxide Identify A, B, C and D.** ***(I.I.T. 1997)***

Ans. (*i*) Since element A burns in nitrogen to give an ionic compound B, therefore, *B must be a metal nitride.*

(*ii*) Since B (a metal nitride) on treatment with water gives C and D, therefore, C and D must be *metal hydroxide and ammonia.*

(*iii*) Since C becomes milky on bubbling CO_2, therefore, *C must be calcium hydroxide.*

(*iv*) If C is calcium hydroxide, then A must be calcium and B must be calcium nitride (Ca_3N_2)

All the reactions involved in the question can now be explained as follows :

$$\underset{(A)}{3Ca} + N_2 \xrightarrow{\Delta} \underset{\text{Cal.nitride (B)}}{Ca_3N_2}$$

$$\underset{(B)}{Ca_3N_2} + 6H_2O \longrightarrow \underset{(C)}{Ca(OH)_2} + \underset{(D)}{2NH_3}$$

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\textit{D (Milkiness)}}{CaCO_3} + H_2O$$

Q. 5. **Compound 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 equations involved in the formation of Y and its reaction with air. Draw the structure of Y.** ***(I.I.T. 2001)***

Ans. **Step 1.** ***To determine the molecular formula and structure of compound Y.***

(*i*) Since the hydride Y reacts with air forming boron trioxide, *therefore, Y must be an hydride of boron.*

(*ii*) %H = 21·72% (*Given*)

$\therefore$ %B = 100—21·72 = 78·28%

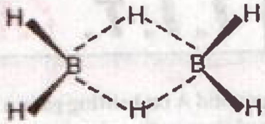
$$\text{Now B : H} = \frac{78 \cdot 28}{11} : \frac{21 \cdot 72}{1} = 7 \cdot 12 : 21 \cdot 72 = 1 : 3$$

$\therefore$ E.F. of Y = BH_3

Since boron forms two types of hydrides, *i.e.*, B_nH_{n+4} (*nidoboranes*) and B_nH_{n+6} (*arachnoboranes*), therefore, Y must be a nidoborane with $n=2$. Thus, M.F. of Y = B_2H_6. If Y is B_2H_6 (dibrone), then its structure must be as follows :

Bridges B......H = 133 pm

Terminal B—H = 119 pm



Step 2. ***To determine the structure of the compound X.***

Since compound Y *i.e.*, B_2H_6 is formed by reduction of compound X with $LiAlH_4$, therefore, X must either BCl_3 or BF_3.

$$\underset{X}{4BF_3} + 3LiAlH_4 \xrightarrow{\text{ether}} \underset{Y}{2B_2H_6} + 3LiAlF_4$$

The equation representing the reaction of Y with O_2 may be written as follows :

$$\underset{\text{Diborane, Y}}{B_2H_6} + 3O_2 \longrightarrow \underset{\text{Boron trioxide}}{2B_2O_3} + 3H_2O$$

Thus X = BF_3 and Y = B_2H_6.

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. An aqueous solution of borax is
   (a) basic (b) acidic
   (c) neutral (d) amphoteric.
2. Orthoboric acid when heated to red heat gives
   (a) metaboric acid (b) tetraboric acid
   (c) boron trioxide (d) borax.
3. Carborundum is
   (a) Boron carbide (b) Silicon carbide
   (c) Aluminium carbide (d) Calcium carbide.
4. Diamond and graphite are
   (a) Homologues (b) Allotropes
   (c) Isomers (d) None of the above.
5. Which of the following is the hardest substance known ?
   (a) Graphite (b) Carborundum
   (c) Diamond (d) Coke.
6. Which of the following is the most commonly used refrigerant ?
   (a) $CFCl_3$ (b) CCl_3Br
   (c) CF_3Cl (d) CF_2Cl_2.
7. Which of the following is the least stable carbon halide ?
   (a) CCl_4 (b) CF_4
   (c) CBr_4 (d) CI_4.
8. Carbon forms a large number of compounds because it has
   (a) Variable valency (b) Low electron affinity
   (c) High ionization energy
   (d) Property of catenation.
9. Tailing of mercury is due to the formation of
   (a) Mercuric oxide (b) Mercurous oxide
   (c) Mercuric chloride (d) Mercurous chloride.
10. The oxide which is amphoteric is
   (a) H_2O (b) CaO
   (c) Al_2O_3 (d) Cl_2O_7.
11. The oxide of nitrogen obtained by dehydration of nitric acid by phosphorus pentoxide is
   (a) N_2O_5 (b) N_2O_3
   (c) N_2O (d) NO.
12. Which of the following metals gives hydrogen with dil. HNO_3 ?
   (a) Mg (b) Zn
   (c) Al (d) Sn.
13. The compound which gives off oxygen on moderate heating is
   (a) cupric oxide (b) mercuric oxide
   (c) zinc oxide (d) aluminium oxide. *(I.I.T. 1986)*
14. The bonds present in N_2O_5 are—
   (a) only ionic (b) covalent and coordinate
   (c) only covalent (d) covalent and ionic. *(I.I.T. 1986)*
15. The brown ring complex compound is formulated as $[Fe(H_2O)_5NO^+]SO_4$. The oxidation state of iron is
   (a) 1 (b) 2
   (c) 3 (d) 4. *(I.I.T. 1987)*
16. Which of the following oxides of nitrogen is a coloured gas ?
   (a) N_2O (b) NO
   (c) N_2O_4 (d) NO_2. *(I.I.T. 1987)*
17. Amongst the trihalides of nitrogen, which one is least basic ?
   (a) NF_3 (b) NCl_3
   (c) NBr_3 (d) NI_3. *(I.I.T. 1987)*
18. The lightning bolts in the atmosphere cause the formation of
   (a) NO (b) NH_3
   (c) NH_4OH (d) NH_2OH. *(I.I.T. 1988)*
19. Concentrated HNO_3 reacts with iodine to give
   (a) HI (b) HOI
   (c) $HOIO_2$ (d) $HOIO_3$. *(I.I.T. 1989)*

ANSWERS

1. a	2. c	3. b	4. b	5. c	6. d	7. d	8. d	9. b	10. c
11. a	12. a	13. b	14. b	15. a	16. d	17. a	18. a	19. c	

20. Boric acid is polymeric due to
(*a*) Its acidic nature
(*b*) The presence of hydrogen bonds
(*c*) Its monobasic nature
(*d*) Its geometry. *(N.C.E.R.T. 1990)*

21. Which will quickly absorb oxygen ?
(*a*) Alkaline solution of pyrogallol
(*b*) Conc. H_2SO_4 (*c*) Lime water
(*d*) Alkaline solution of $CuSO_4$. *(C.B.S.E. Med. 1992)*

22. When ammonia is passed over heated Cu, it is oxidised to
(*a*) N_2 (*b*) NO_2
(*c*) N_2O (*d*) HNO_2 *(Roorkee 1992)*

23. Pure nitrogen can be prepared from
(*a*) NH_4OH (*b*) Ca_3N_2
(*c*) NH_4NO_2 (*d*) $Ba(NO_2)_2$. *(A.F.M.C. 1993)*

24. All the following decompose easily on heating to give oxygen as the only gaseous product except
(*a*) Lead nitrate (*b*) Potassium chlorate
(*c*) Mercuric oxide (*d*) Manganese dioxide. *(D.C.E.E. 1994)*

25. Identify the incorrect statement with respect to ozone
(*a*) Ozone is formed in the upper atmosphere by a photochemical reaction involving dioxygen.
(*b*) Ozone is more reactive than dioxygen
(*c*) Ozone is diamagnetic while dioxygen is paramagnetic
(*d*) Ozone protects the earth's inhabitants by absorbing gamma radiations. *(A.I.I.M.S. 1994)*

26. Which of the following statements about boric acid is false ?
(*a*) It acts as a monobasic acid
(*b*) It is formed by the hydrolysis of boron halides
(*c*) It has planar structure
(*d*) It acts as a tribasic acid. *(C.B.S.E. P.M.T. 1994)*

27. From B_2H_6 all the following can be prepared except
(*a*) H_3BO_3 (*b*) $B_2(CH_3)_4H_2$
(*c*) $B_2(CH_3)_6$ (*d*) $NaBH_4$. *(C.B.S.E. P.M.T. 1994)*

28. When formic acid is treated with conc. H_2SO_4, the gas evolved is :
(*a*) H_2S (*b*) SO_2
(*c*) CO (*d*) CO_2. *(M.L.N.R. Allahabad 1996)*

29. Thermodynamically the most stable form of carbon is
(*a*) Diamond (*b*) Graphite
(*c*) Peat (*d*) Coal *(M.L.N.R., Allahabad 1996)*

30. The metal which reacts with HNO_3 to give five different products depending upon the concentration of the acid is :
(*a*) Cu (*b*) Fe
(*c*) Zn (*d*) Al. *(M.L.N.R. Allahabad 1996)*

31. Which of the following oxides is neutral ?
(*a*) CO (*b*) SnO_2
(*c*) ZnO (*d*) SiO_2. *(I.I.T. 1996)*

32. The test of ozone can be done by
(*a*) Ag (*b*) Hg
(*c*) Au (*d*) None of these. *(A.F.M.C. 1997)*

33. Which one of the following has the highest dipole moment ?
(*a*) NH_3 (*b*) PH_3
(*c*) SbH_3 (*d*) AsH_3 *(C.B.S.E. 1997)*

34. Among the following species, identify the isostructural pairs.
NF_3, NO_3^-, BF_3, H_3O^+, HN_3
(*a*) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$
(*b*) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$
(*c*) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$
(*d*) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$. *(I.I.T. 1996)*

35. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is
(*a*) CrO_3 (*b*) Cr_2O_3
(*c*) Cr (*d*) $CrO(O_2)$ *(I.I.T. 1997)*

ANSWERS

20. *b* **21.** *a* **22.** *a* **23.** *c* **24.** *a* **25.** *d* **26.** *d* **27.** *c* **28.** *c* **29.** *b*
30. *c* **31.** *a* **32.** *b* **33.** *a* **34.** *c* **35.** *b*

36. In graphite, electrons are

(*a*) Localized on every third carbon
(*b*) Present in antibonding orbitals
(*c*) Localized on each carbon atom
(*d*) Spread out between the structure

(C.B.S.E. P.M.T. 1997)

37. Sodium nitrate decomposes above ~ 800°C to give

(*a*) N_2 (*b*) O_2
(*c*) NO_2 (*d*) Na_2O *(I.I.T. 1998)*

38. Which of the following does not show electrical conduction ?

(*a*) Potassium (*b*) Graphite
(*c*) Diamond (*d*) Sodium.

(C.B.S.E. P.M.T. 1999)

39. Percentage of lead in lead pencil is

(*a*) zero (*b*) 20
(*c*) 80 (*d*) 70.

(C.B.S.E. P.M.T. 1999)

40. The correct structure of $Fe(CO)_5$ is

(*a*) Octahedral (*b*) Tetrahedral
(*c*) Square planar (*d*) Trigonal pyramidal.

(C.B.S.E. P.M.T. 2000)

41. The geometry and the type of hybrid orbital present about the central atom in BF_3 is

(*a*) linear, *sp* (*b*) trigonal planar, sp^2
(*c*) tetrahedral, sp^3 (*d*) pyramidal, sp^3

(I.I.T. 1998)

42. The correct order of increasing C—O bond length of CO, CO_3^{2-}, CO_2 is

(*a*) $CO_3^{2-} < CO_2 < CO$ (*b*) $CO_2 < CO_3^{2-} < CO$
(*c*) $CO < CO_3^{2-} < CO_2$ (*d*) $CO < CO_2 < CO_3^{2-}$

(I.I.T. 1999)

43. In compounds of the type ECl_3, where E = B, P, As or Bi, the angle Cl—E—Cl for different E are in the order

(*a*) B > P = As = Bi (*b*) B > P > As > Bi
(*c*) B < P = As = Bi (*d*) B < P < As < Bi

(I.I.T. 1999)

44. On heating ammonium dichromate, the gas evolved is

(*a*) oxygen (*b*) ammonia
(*c*) nitrous oxide (*d*) nitrogen. *(I.I.T. 1999)*

45. O_2 molecule is

(*a*) paramagnetic (*b*) diamagnetic
(*c*) ferromagnetic (*d*) none of these.

(C.P.M.T. 1999)

46. In the Ostwald's process for the manufacture of HNO_3, the catalyst used is

(*a*) Mo (*b*) Fe
(*c*) Ni (*d*) Pt. *(M.P. C.E.E. 1999)*

47. Which is detected by Nessler's reagent ?

(*a*) NH_4^+ (*b*) MnO_4^-
(*c*) PO_4^{3-} (*d*) CrO_4^{2-}.

(M.P. C.E.E. 1999)

48. Conc. HNO_3 is stored in containers made up of

(*a*) Cu (*b*) Zn
(*c*) Al (*d*) Sn.

(Haryana C.E.E.T. 1999)

49. Which of the following leaves no residue on heating ?

(*a*) $Cu(NO_3)_2$ (*b*) $NaNO_3$
(*c*) $Pb(NO_3)_2$ (*d*) NH_4NO_3.

(B.H.U. 1994 ; Haryana C.E.E.T. 2000)

50. The correct O—O bond length (decreasing) in O_2, H_2O_2 and O_3 is

(*a*) $O_2 > H_2O_2 > O_3$ (*b*) $O_3 > O_2 > H_2O_2$
(*c*) $H_2O_2 > O_3 > O_2$ (*d*) $H_2O_2 > O_2 > O_3$.

(D.C.E. 2000)

51. A metal X on heating in nitrogen gas gives Y. Y on treatment with H_2O gives a colourless gas which when passed through $CuSO_4$ solution gives a blue colour. Y is

(*a*) $Mg(NO_3)_2$ (*b*) Mg_3N_2
(*c*) NH_3 (*d*) MgO. *(D.C.E. 2000)*

52. Ammonia can be dried by

(*a*) Conc. H_2SO_4 (*b*) P_4O_{10}
(*c*) CaO (*d*) anhydrous $CaCl_2$

(I.I.T. 2000)

53. The hybridization of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are

(*a*) *sp*, sp^3 and sp^2 respectively
(*b*) *sp*, sp^2 and sp^3 respectively

ANSWERS

36. *d* **37.** *b* **38.** *c* **39.** *a* **40.** *d* **41.** *b* **42.** *a* **43.** *b* **44.** *d* **45.** *a*
46. *d* **47.** *a* **48.** *c* **49.** *d* **50.** *c* **51.** *b* **52.** *c*

(*c*) sp^2, sp and sp^3 respectively

(*d*) sp^2, sp^3 and sp respectively *(I.I.T. 2000)*

54. Among the following the electron-deficient compound is

(*a*) CCl_4 (*b*) PCl_5

(*c*) $BeCl_2$ (*d*) BCl_3

(C.B.S.E. P.M.T. 2000)

55. Which of the following allotropic forms of carbon is isomorphous with crystalline silicon ?

(*a*) Graphite (*b*) Coal

(*c*) Coke (*d*) Diamond

(E.A.M.C.E.T. 2001)

56. The type of hybridization of boron in diborane is

(*a*) *sp*-hybridization (*b*) sp^2-hybridization

(*c*) sp^3-hybridization (*d*) sp^3d^2-hybridization

(C.B.S.E. P.M.T. 1999)

57. What is the product formed when ozone reacts with mercury ?

(*a*) HgO (*b*) Hg_2O_2

(*c*) Hg_2O (*d*) HgO_2

(E.A.M.C.E.T. 2001)

58. When ammonia is passed over heated copper oxide, metallic copper is obtained. The reaction shows that ammonia is

(*a*) Dehydrating agent (*b*) An oxidising agent

(*c*) A reducing agent (*d*) A nitrating agent

(M.P. P.E.T. 2002)

59. In NO_3^- ion, the number of bond pair and lone pair of electrons on nitrogen atom are

(*a*) 2, 2 (*b*) 3, 1

(*c*) 1, 3 (*d*) 4, 0

(C.B.S.E. P.M.T. 2002)

60. A mixture of concentrated HCl and HNO_3 made in 3 : 1 ratio contains

(*a*) ClO_2 (*b*) NOCl

(*c*) NCl_3 (*d*) N_2O_4

(A.I.I.M.S. 2003)

61. Specify the co-ordination geometry around and hydridisation of N and B atoms in a 1 : 1 complex of BF_3 and NH_3

(*a*) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3

(*b*) N : pyramidal, sp^3 ; B : pyramidal, sp^3

(*c*) N : pyramidal, sp^3 ; B : planar, sp^2

(*d*) N : pyramidal, sp^3 ; B : tetrahedral, sp^3

(I.I.T. Test 2002)

62. Which one of the following is an amphoteric oxide ?

(*a*) B_2O_3 (*b*) ZnO

(*c*) Na_2O (*d*) SO_2

(A.I.E.E.E. 2003)

63. Which of the following molecular species has unpaired electron(s) ?

(*a*) N_2 (*b*) F_2

(*c*) O_2^- (*d*) O_2^{2-}

(I.I.T. Test 2002)

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

(*a*) has carbon atoms arranged in large plates of rings of strongly bound carbon atoms with weak interplate bonds

(*b*) is a non-crystalline substance

(*c*) is an allotropic form of carbon

(*d*) has molecules of variable molecular masses like polymers *(A.I.E.E.E. 2003)*

65. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solutions. What is reason for it ?

(*a*) Copper hydroxide is an amphoteric substance

(*b*) In acidic solutions, hydration protects Cu^{2+} ions

(*c*) In acidic solutions, protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available

(*d*) In alkaline solutions, soluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali *(A.I.E.E.E. 2003)*

66. Which of the following is not a protonic acid ?

(*a*) $B(OH)_3$ (*b*) $PO(OH)_3$

(*c*) $SO(OH)_2$ (*d*) $SO_2(OH)_2$

(C.B.S.E. P.M.T. 2003)

67. H_3BO_3 is

(*a*) Monobasic and weak Lewis acid

(*b*) Monobasic and weak Bronsted acid

(*c*) Monobasic and strong Lewis acid

(*d*) Tribasic and weak Bronsted acid *(I.I.T. 2003)*

ANSWERS

53. *b* **54.** *d* **55.** *d* **56.** *c* **57.** *c* **58.** *c* **59.** *d* **60.** *b* **61.** *a* **62.** *b*

63. *c* **64.** *a* **65.** *c* **66.** *a* **67.** *a*

68. Which of the following are isoelectronic and isostructural ?

$NO_3^-, CO_3^-, ClO_3^-, SO_3$

(*a*) NO_3^-, CO_3^{2-} (*b*) SO_3, NO_3^-

(*c*) ClO_3^-, CO_3^{2-} (*d*) CO_3^{2-}, SO_3

(I.I.T. 2003)

69. The element which forms oxides is all oxidation states +I to +V is

(*a*) N (*b*) P

(*c*) As (*d*) Sb *(A.I.I.M.S. 2004)*

70. Which of the following oxides of nitrogen is a solid ?

(*a*) NO_2 (*b*) N_2O

(*c*) N_2O_3 (*d*) N_2O_5

(A.F.M.S. 2004)

71. The ONO angle is maximum in

(*a*) NO_3^- (*b*) NO_2^-

(*c*) NO_2 (*d*) $\overset{+}{N}O_2$

(A.I.I.M.S. 2004)

72. $(NH_4)_2Cr_2O_7$ on heating gives a gas which is also given by

(*a*) Heating NH_4NO_2 (*b*) Heating NH_4NO_3

(*c*) $Mg_3N_2 + H_2O$ (*d*) Na (comp.) + H_2O_2

(I.I.T. 2004)

73. Which of the following imparts green colour to the burner flame ?

(*a*) $B(OMe)_3$ (*b*) NaOMe

(*c*) $Al(OPr)_3$ (*d*) $Sn(OH)_2$

(A.I.I.M.S. 2004)

74. Shape of O_2F_2 is similar to that of

(*a*) C_2F_2 (*b*) H_2O_2

(*c*) H_2F_2 (*d*) C_2H_2

(A.I.I.M.S. 2004)

75. Metal which does not form ammonium nitrate by reaction with dilute nitric acid is

(*a*) Al (*b*) Fe

(*c*) Pb (*d*) Mg

(Karnataka C.E.T. 2004)

76. Among the halogens, the one which is oxidised by nitric acid is

(*a*) fluorine (*b*) iodine

(*c*) chlorine (*d*) bromine

77. Which of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere ?

(*a*) Polyhalogens (*b*) Ferrocene

(*c*) Fullerenes (*d*) Freons

(C.B.S.E. P.M.T. 2004)

78. Ozone (O_3) dissolves in

(*a*) turpentine oil (*b*) acetone

(*c*) both (*a*) and (*b*) (*d*) None of these

(M.G.I.M.S. Wardha 2004)

79. Ozone in stratosphere is depleted by

(*a*) CF_2Cl_2 (*b*) C_7H_{16}

(*c*) $C_6H_6Cl_6$ (*d*) C_6F_6

(A.I.I.M.S. 2004)

HINTS/EXPLANATIONS to Multiple Choice Questions

13. Heavy metal oxides on heating give O_2 gave, *i.e.*

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

17. Due to high electronegativity, F pulls the lone pair of electrons on N towards itself. As a result, it is not available for protonation.

24. $2\,Pb(NO_3)_2 \xrightarrow{\Delta} 2\,PbO + 4\,NO_2 + O_2.$

25. Ozone absorbs UV radiations but not gamma radiations.

27. CH_3 group being big cannot form a bridge between two small sized boron atoms.

29. Graphite is thermodynamically more stable than diamond and its free energy of formation is 1·9 kJ mol^{-1} lower at room temperature and ordinary pressure.

30. Zinc or reaction with HNO_3 under different conditions gives five different products, *i.e.*,

N_2O, NO, NO_2, NH_3 and NH_4NO_3.

31. CO is neutral, SnO_2, ZnO and SiO_2 are amphoteric.

32. Tailing of Hg.

ANSWERS

68. *a* **69.** *a* **70.** *d* **71.** *d* **72.** *a* **73.** *a* **74.** *b* **75.** *d* **76.** *d* **77.** *d*
78. *c* **79.** *a*

33. As we move from $NH_3 \longrightarrow PH_3 \longrightarrow AsH_3 \longrightarrow SbH_3$, electronegativity of the element decreases and hence the metal- hydrogen bond becomes less and less polar, thereby lowering the dipole moment. Thus NH_3 has the highest dipole moment.

34. [NF_3 and H_3O^+] are pyramidal while [NO_3^- and BF_3] are planar.

39. Lead pencils contain graphite mixed with clay or wax but no lead.

42. The bond order in CO_3^{2-} is 1·5, in CO_2 it is 2 while in CO it is 2·5. Therefore, higher the bond order, smaller the C—O bond length, *i.e.* $CO_3^{2-} < CO_2 < CO$.

43. In BCl_3, B is sp^2 hybridized and hence has an angle of 120° while in PCl_3, $AsCl_3$ and $BiCl_3$, the elements P, As and Bi are sp^3-hybridized. Further, as the electronegativity of the element decreases from P to Bi, the bond pairs move away from the central atom and hence the bond angle decreases from P to Bi. Thus, option (*b*) is correct.

48. Al is rendered passive by formation of a thin impervious layer of Al_2O_3 on its surface when brought in contact with conc. HNO_3.

50. Bond distances decreases as bond order increases. Now bond order decreases in the order H_2O_2 (1), O_3 (1·5), O_2 (2), *i.e.*

H_2O_2 (148 pm) > O_3 (127·8 pm) > O_2 (120·7 pm).

51. $3\,Mg + N_2 \xrightarrow{\Delta} Mg_3N_2$;
(X)

$Mg_3N_2 + 6\,H_2O \longrightarrow 3\,Mg(OH)_2 + 2\,NH_3$

$CuSO_4 + 4\,NH_3 \longrightarrow [Cu(NH_3)_4]\,SO_4$ (*blue*)

53. In NO_2^+, *i.e.*, $O = \underset{+}{N} = O$, N is *sp*-hybridized, in NO_3^- it is sp^2-hybridized while in NH_4^+ it is sp^3-hybridized.

55. Each silicon atom in crystalline structure of silicon is tetrahedrally surrounded by four other silicon atoms. This structure is similar to that of diamond.

61. Originally in NH_3, N is pyramidal (sp^3) but in BF_3, B is planar (sp^2). But after the bond formation, *i.e.*, in the complex $H_3N \rightarrow BF_3$, both N and B have four shared pairs of electrons and hence both have tetrahedral (sp^3) geometry, *i.e.*, option (*a*) is correct.

68. No. of electrons in $NO_3^- = 7 + 8 \times 3 + 1 = 32$

No. of electrons in $CO_3^{2-} = 6 + 3 \times 8 + 2 = 32$

Both NO_3^- and CO_3^{2-} have same number of electrons and hence are isostructural (trigonal planar).

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of two statements each, printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

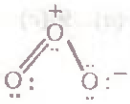
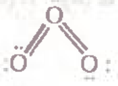
(*a*) If both Assertion and Reason are true and the Reason is a correct explanation of the Assertion.

(*b*) If both Assertion and Reason are true but Reason is not a correct explanation of the Assertion.

(*c*) If Assertion is true but the Reason is false.

(*d*) If both Assertion and Reason are false.

	Assertion	Reason
1.	Although PF_5, PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.	Phosphorus has lower electronegativity than nitrogen. (*I.I.T. 1995*)
2.	The bond angle of PBr_3 is greater than that of PH_3 but the bond angle of NBr_3 is less than that of NH_3.	The size of bromine is less than that of hydrogen. (*A.I.I.M.S. 1997*)
3.	Diamond does not reflect or refract light.	Diamond has low refractive index.
4.	Graphite is a good conductor of heat and electricity.	Graphite has all the electrons firmly held in C—C, σ-bonds.

	Assertion	Reason
5.	Carbon monoxide is highly toxic (poisonous) in nature.	Carbon monoxide forms a stable complex with haemoglobin present in red blood cells.
6.	Carbides containing C_2^{2-} units are called acetylides.	Cu_2C_2 and Ag_2C_2 are not true acetylides because these on hydrolysis do not produce acetylene.
7.	Ammonium nitrite on heating gives NO.	NO is an acidic oxide.
8.	All the N—O bonds in NO_3^- are equal.	NO_3^- is a resonance hybrid of three equivalent resonating structures.
9.	Nitrogen is unreactive at room temperature but becomes reactive at elevated temperatures or in presence of a catalyst.	In nitrogen molecule there is extensive delocalization of electrons. *(A.I.I.M.S. 1996)*
10.	Ozone is a polar molecule although it is homoatomic.	It contains a coordinate bond and has a bent structure.
11.	Nitrous acid (HNO_2) may act as an oxidising as well as a reducing agent.	The oxidation number of nitrogen remains same in all the compounds.
12.	Liquid ammonia is used for refrigeration.	It vapourises quickly. *(A.I.I.M.S. 1997)*
13.	NO_3^- is planar while NH_3 is pyramidal.	N in NO_3^- is sp^2- hybridized but in NH_3 it is sp^3-hybridized. *(A.I.I.M.S. 1997)*
14.	HNO_3 is a stronger acid than HNO_2.	In HNO_3 there are two nitrogen-oxygen bonds while in HNO_2 there is only one. *(I.I.T. 1998)*
15.	The electronic structure of O_3 is 	 structure is not allowed because octet around O cannot be expanded. *(I.I.T. 1998)*
16.	Dinitrogen is chemically unreactive at ordinary temperature and is very stable.	The bond dissociation energy is 946 kJ mol^{-1}. *(A.I.I.M.S. 1998)*
17.	Tailing of mercury occurs on passing O_3 through it.	Due to oxidation of mercury. *(A.I.I.M.S. 1999)*

True/False Statements

Select the true and false statements from the following :

1. All elements give borax bead test.
2. Silicon has diamond like structure.
3. The tendency for catenation is much higher for C than for Si. *(I.I.T. 1993)*
4. A aqueous solution of Na_2CO_3 is acidic to litmus.
5. Carbon dioxide combines with haemoglobin of blood to form carboxyhaemoglobin.
6. Diamond is harder than graphite. *(I.I.T. 1993)*
7. Dinitrogen is almost chemically unreactive because of its high bond dissociation energy.
8. During ring test for nitrate ions, ferrous ions reduce NO_3^- to NO.
9. In copper sulphate pentahydrate, all the water molecules are attached to the Cu^{2+} ion by coordinate covalent bonds.
10. Chlorofluorocarbons deplete the ozone layer in the atmosphere.
11. Oxide ion is considered as hard ion since it cannot be easily polarized.
12. N_2O and NO are neutral oxides of nitrogen.

Fill In The Blanks

1. Of all the boron trihalides, the weakest Lewis acid is ....
2. A compound of fluorine known as .... is widely used in refrigeration and aerosols.
3. The two types of bonds present in B_2H_6 are covalent and .... *(I.I.T. 1994)*
4. Conc. HNO_3 on dehydration with P_4O_{10} gives .... *(Roorkee 1999)*

5. Ozone is .... while .... is paramagnetic.
6. .... is an acidic oxide while SiO_2 is an .... oxide.
7. Aqua regia is a mixture of ....
8. In gaseous state, nitric oxide is .... while in the liquid or solid state it is ....
9. Nitric acid containing .... is called fuming nitric acid.
10. Laughing gas is obtained when .... is heated.
11. The tailing of mercury is due to the formation of ....
12. O_2 is absorbed by .... and O_3 is absorbed by ....
13. The formula of acidic nitrogen hydride is ....

Matching Type Questions

Match items of column I with appropriate atoms of column II.

Column-I	Column-II
1. Dinitrogen tetroxide	(*a*) Fullerene and diamond
2. Ammonia	(*b*) Diamond structure
3. Carborundum	(*c*) Boric acid
4. Colemanite	(*d*) Complexing agent
5. Allotropes	(*e*) Oxidiser in rocket fuels.

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*b*) 2. (*d*) 3. (*d*) 4. (*c*) 5. (*a*) 6. (*a*) 7. (*d*) 8. (*a*) 9. (*c*) 10. (*a*) 11. (*c*) 12. (*b*) 13. (*a*) 14. (*c*) 15. (*a*) 16. (*a*) 17. (*a*).

TRUE/FALSE STATEMENTS

1. False 2. True 3. True 4. False, basic. 5. False, CO combines with haemoglobin of blood to form carboxyhaemoglobin. 6. True 7. True 8. True 9. False, four are bonded to Cu^{2+} ion by coordinate bonds while the fifth one is bonded to SO_4^{2-} ion by H-bond. 10. True 11. True due to small size of oxide ion and large electronegativity (3.5) of oxygen atom, the electron cloud of O^{2-} ion cannot be distored and hence O^{2-} ion is a hard ion. 14. True.

FILL IN THE BLANKS

1. BF_3 2. freon 3. hydrogen bridge or two electrons three centre bonds. 4. N_2O_5 5. diamagnetic, O_2 6. NO_2 or Cl_2O_7 amphoteric 7. HNO_3 + 3 HCl 8. paramagnetic, diamagnetic 9. oxides of nitrogen 10. ammonium nitrate 11. mercurous oxide 12. an alkaline solution of pyrogallol, turpentine oil 13. N_3H (hydrazoic acid).

MATCHING TYPE QUESTIONS

1. (*e*) 2. (*d*) 3. (*b*) 4. (*c*) 5. (*a*).