CHAPTER 19

CARBON AND SILICON

(The Elements of Group IV)

The elements of Group IV are divided into two sub-groups as discussed in connection with the periodic classifications. Carbon and silicon are the two non-metals in Group IV and along with the metals germanium, tin and lead they are placed in Group IVA. The Group IVB are metals—titanium, zirconium and hafnium to which sometimes thorium is included. But Th is now generally placed in the Actinide series of elements. Thus the Group IV elements may be divided into A and B sub-groups as,

Group IV A	*Group IV B*
C — Carbon	
Si — Silicon	Ti — Titanium
Ge — Germanium	Zr — Zirconium
Sn — Tin	Hf — Hafnium
Pb — Lead	

The Group IV elements lie in the middle positions between alkali metals and halogens since each one has 4 valence electrons, i. e., 4 more electrons than the preceding inert gas and 4 fewer electrons than the succeeding inert gas. The carbon group may be regarded as a transition group linking metals and non-metals due to their symmetrical placements in the Periodic Table. But if we remember the relative electronegativity of the carbon group elements (IVA) and knowing that elements having similar power of attracting electrons to themselves lie on the "diagonal lines," the difference in chemical behaviour of the group as a whole can be understood. The diagonal relationships between B and Si have been discussed in the previous chapter.

Electronic Structure

The electronic structures of Group IVA elements are given in Table 19.1

Table 19.1. Electronic structure of Group IVA elements.

At. No.	*Elements*	*Electron configuration*	*Valence electrons*
6	C	He core, $2s^2\ 2p^2$	$2s^22p^2$
14	Si	Ne core, $3s^2\ 3p^2$	$3s^23p^2$
32	Ge	Ar core, $3d^{10}\ 4s^24p^2$	$4s^24p^2$
50	Sn	Kr core, $4d^{10}\ 5s^25p^2$	$5s^25p^2$
82	Pb	Xe core, $4f^{14}5d^{10}6s^26p^2$	$6s^26p^2$

Thus the outermost orbitals of each element from C to Pb contain s^2p^2 electrons. But the members of Group IVB elements— Ti, Zr and Hf have quite different electron arrangements as given in Table 19.2.

Table 19.2. Electronic structures of Group IVB elements.

At. No.	*Elements*	*Electron configuration*	*Valence electrons*
22	Ti	Ar core, $3d^2\ 4s^2$	$3d^2\ 4s^2$
40	Zr	Kr core, $4d^2\ 5s^2$	$4d^2\ 5s^2$
72	Hf	Xe core, $4f^{14}\ 5d^2\ 6s^2$	$5d^2\ 6s^2$

Thus the outermost orbitals in the titanium group of elements have s^2 electrons and the previous orbitals have the configurations $s^2p^6d^2$. In effect, the d level contains 2 electrons giving the valence shell electrons as d^2s^2. These arrangements are quite different from the carbon group elements and hence the chemistry is widely different, although the valence electrons remain 4 in both the groups but are of different types.

Before discussing the trends within the series and the gradation of the properties of sub-group IVA, a list of physical properties are given. This gives an idea regarding the comparative chemistry with respect to the treatment of the actual data.

The Physical Properties

Some of the important physical properties are given in Table 19.3 (a & b).

Table 19.3(a). Physical properties of Group IVA elements.

Properties	*C*	*Si*	*Ge*	*Sn*	*Pb*
Atomic No.	6	14	32	50	82
Atomic wt.	12.00	28.06	72.6	118.7	207.2
Outer electron orbitals	$2s^2\,2p^2$	$3s^2\,3p^2$	$4s^2\,4p^2$	$5s^2\,5p^2$	$6s^2\,6p^2$
Atomic radius (Å)	0.77	1.17	1.22	1.40	1.75
Ionic radius, M^{+4} (Å)	0.15	0.41	0.53	0.71	0.84
Ionization potential (ev) (M^+)	11.26	8.15	8.13	7.32	7.42
Density g/cm^3	3.50 2.25	2.33	5.36	7.31	11.34
Melting point °C	3600	1414	959	232	328
Boiling point °C	4830	2355	2700	2362	1755
Oxidation potential (v)	—	Si/Si^{+2} + 1.2	—	Sn/Sn^{+2} + 0.14	Pb/Pb^{+2} +0.12
Electronegativity	2.50	1.80	2.00	1.70	1.60

Table 19.3(b). Physical properties of Group IVB elements.

Properties	*Ti*	*Zr*	*Hf*
Atomic No.	22	40	72
Atomic wt.	47.90	91.20	178.60
Outer electron orbitals	$3d^2 4s^2$	$4d^2 5s^2$	$5d^2 6s^2$
Atomic radius (Å)	1.46	1.57	1.57
Ionic radius, M^{+4} (Å)	0.68	0.80	0.79
Ionization potential (ev) (M^+)	0.68	0.80	—
Density g/cm^3	4.50	6.40	11.40
Melting point °C	1800	1700	1700
Boiling point °C	3000	2900	3200
Oxidation potential (v)	Ti/Ti^{+4} + 1.0	Zr/Zr^{+4} +1.53	Hf/Hf^{+4} +1.70
Electronegativity	1.32	1.22	1.23

Group properties of IVA elements (Carbon Group) : The common properties are :-

(1) Except carbon and silicon, all other members are metals. The two representative elements, C and Si, predominate our environment since our animal and vegetable domains are made up primarily of compounds containing C—C bonds whereas the earth's crust and the minerals consist primarily of compounds containing Si—O bonds.

(2) Elementary Si, Ge and Sn have structures analogous to diamond (C) having crystal coordination number 4. The atom-to-atom bonds are covalent tetrahedral as in diamond. Pb is more metallic and has a cubic structure. The transition from purely covalent to metallic bonding is reflected in the sharp decrease in the m. p. from 3600°C for C to about 300°C for Pb. This decrease is attributed to the decrease in electrostatic attraction with the increase in size.

(3) The +4 oxidation states formed due to the removal of s^2p^2 electrons appear to be a characteristic property of this group. The +4 state is normally reflected in MO_2 but it is rather difficult to achieve an ionic state of +4. Even the ions Sn^{+4} and Pb^{+4} are not so common. But Sn^{+2} and Pb^{+2} are quite stable ions. As the atomic number increases from C to Pb having the outermost electrons s^2p^2, the two s electrons gradually become "inert pair" because of the stable state of $d^{10}s^2$ and do not take part in chemical bonding. Carbon and silicon do not have the inert s^2 pair of electrons. The decrease in the oxidation potentials of the system M^{+2} to M^{+4} also points to the same feature that among higher member the +4 state is rather difficult to achieve :

$Ge^{+2} \rightarrow GeO_2$ — 0.3 volt

$SnCl_4^{-2} \rightarrow SnCl_6^{-2}$— − 0.1 volt

$Pb^{+2} \rightarrow PbO_2$ — − 1.5 volts

(4) Allotropic modifications are more prominent in the cases of C and Sn.

(5) Carbon is a unique element because of the remarkable property of combining with itself to form chains and rings (a process known as "catenation"). Silicon is also a unique element in so far as the formation of Si—O bonds is concerned. Pb is another unique member because it is the end product of the disintegration of many natural radio-elements.

(6) Si does not conduct electricity at normal temperature but at higher temperature its conductivity increases. This property is quite unlike metallic behaviour. Silicon is, therefore, called a semiconductor.

(7) Germanium is a scarce element and a semiconductor.

Comparison of Carbon Group (IVA) and Titanium Group (IVB)

(1) Elements of carbon group are non-transition elements whereas those of titanium group are transition elements with incomplete d level and show variable oxidation states in most of the compounds. The valence shell of carbon group contains s^2p^2 electron whereas the titanium group contains d^2s^2 electrons.

(2) The titanium group elements are tough metals and have very high melting and boiling points. Carbon group elements present a different picture, the melting point ranging from about 3600°C to about 300°C

(3) The oxides of carbon group elements are acidic although the acidic nature decreases from C to Pb. But the oxides of titanium group appear to be amphoteric. These characteristics are connected with the ionic sizes of the various atoms in the group.

Comparison of Carbon and Silicon : Because of the peculiar characteristics of C and Si, comparison of the chemistry of these two elements are made according to the points mentioned below :—

(1) Carbon and silicon are both elements of sub-group IVA and have s^2p^2 electrons in the outermost orbitals which govern their chemical behaviour almost in similar fashion. The difference arises due to the differences in atomic and ionic sizes which are important factors for the chemical properties.

C—$1s^2\,2s^2\,2p^2$ Si—$1s^2\,2s^2\,2p^6\,3s^2\,3p^2$

In Si the 3d orbitals are available for placement of electrons if needed.

(2) Carbon is abundantly found in nature both in the animal and vegetable kingdoms and also in carbonate minerals as well as in the free state as coal. Silicon is most abundant in silicate minerals and as silica and rocks. Thus C—C bonds give rise to a vast number of compounds whilst Si—O bonds produce a large number of silicate structures.

(3) The common oxides of C and Si are CO_2 and SiO_2 and although one is a gas and the other a tough solid both have acid properties producing H_2CO_3 and H_2SiO_3. The difference in properties is because CO_2 occur as isolated molecule whereas SiO_2 has polymeric molecule having 3-dimensional structure.

(4) C and Si form hydrides, halides and other similar compounds. Thus,

$$CCl_4 \quad SiCl_4 \quad CH_4 \quad SiH_4 \quad C_2H_6 \quad Si_2H_6$$

The properties of these compounds differ and the silicon compounds are easily hydrolysed because Si has tendency to form Si—O bonds. Hydrogen compounds of C are stable due to complete saturation of electron orbitals of C forming tetrahedral bonds.

(5) Carbon compounds exhibit the phenomenon of isomerism while it is not so pronounced in silicon compounds and, as a matter of fact, in all other elements this is a rare phenomenon.

(6) C has maximum covalency of 4 whereas in the case of Si it can expand to 6. This is because of the availability of **d** orbitals in the case of Si.

(7) In general, compounds of C are quite stable but most silicon compounds, except silicates and polymers, are unstable and are decomposed readily. Thus H_2CO_3 is stable in acids whereas H_2SiO_3 is decomposed to SiO_2.

Comparison of Silicon and Tin : Silicon has some resemblance with tin. In brief, the following points may be noted :—

(1) Both Si and Sn have s^2p^2 electron arrangement but the two $\mathbf{s}^2$ electrons in Sn also act as *inert pair* giving Sn^{+2} and also Sn^{+4}, whereas Si is only tetravalent.

Si (14) — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Sn (50)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$

(2) Si is non-metal whereas Sn is metallic.

(3) Both $SiCl_4$ and $SnCl_4$ are fuming liquids and are hydrolysed in water giving H_2SiO_3 and H_2SnO_3.

(4) Si-halides and Sn-halides have low melting and boiling points.

(5) SiH_4 and SnH_4 are formed easily and are gases.

(6) SiF_4 and SnF_4 give double flourides with alkali fluorides. Thus Na_2SiF_6 and Na_2SnF_6.

(7) Silicates and stannates are stable compounds. Meta-silicates and meta-stannates are more stable.

(8) Common salts of silicon, such as nitrates, sulphates etc. are not formed; but Sn gives such compounds.

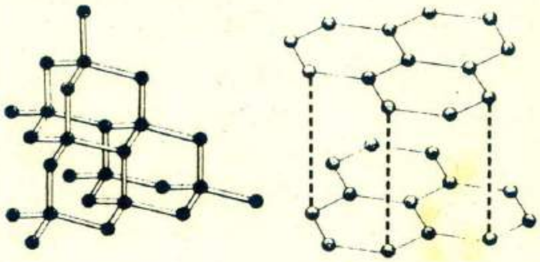
(9) Sn gives more stable compounds of +2 states as $SnCl_2$ but Si does not.

Inorganic Chemistry of Carbon

The bondings system in the atom of carbon has already been discussed earlier. The four equivalent bonds of carbon are homopolar in nature involving sp^3 hybrid orbitals and give rise to the enormous numbers of compounds, which are the basis of organic chemistry. Some compounds, such as oxides, carbides, cyanides, carbonyls etc. are, however, included in inorganic chemistry as a matter of custom.

Occurrence of carbon : (1) Carbon occurs free in nature in the form of diamond and graphite. (2) In the combined state it is found in natural gas, petroleum, coal, plants, animals and some minerals, such as limestone etc. (3) C is also found in air as CO_2. (4) In water it occurs as dissolved H_2CO_3, soluble carbonates and bicarbonates.

Graphite and Diamond : These are the two allotropic modifications of C and are giant molecules. Diamond contains the carbon atoms linked together in tetrahedral positions so that each carbon, in turn, is surrounded by four other carbon atoms (coordination No. 4) in a three-dimensional pattern. In effect, in diamond crystal each carbon uses sp^3 hybrid orbitals like that of CH_4 to produce a three-dimensional lattice. In graphite the polymer consists of sheets of carbon atoms, each sheet separated from the other by a distance of about 3.4Å. The carbon atoms in the graphite may be regarded as fused systems of benzene rings, each carbon atom being surrounded by 3 other carbon atoms using sp^2 hybrid orbitals. In this system each C is bonded to the other two by single covalent bond and to third by double bond which is of the resonating type. Thus carbon atoms are bonded in the graphite structure in the form of layers of hexagons. The illustration in Fig. 19—1 explains the two structures involving sp^3 and sp^2 bonding systems in diamond and graphite respectively.



Diamond

Graphite

Crystal structure of diamond. Black spheres represent carbon held together by tetrahedral arrangement.

Crystal structure of graphite. The layers of carbon held by weak valence bond (*van der Waal's* forces).

Fig. 19—1. Atomic arrangement of carbon in diamond and graphite.

Properties of Diamond and Graphite

Diamond is brittle but the hardest substance known. It is a good conductor of heat but not of electricity because of the electron saturated bonds. Diamond is transformed to graphite by heating at 1000°C. It is extremely inert to all chemicals at the ordinary conditions. Because the C—C bonds in diamond are very strong and extend throughout the crystal in three-dimensions, it is hard and has a high melting point of about 3600°C.

Graphite, also known as *Plumbago*, is a soft, grey solid having metallic lustre and slippery to touch. Graphite is a good conductor of electricity and is used as electrodes. The softness and electrical conductivity of graphite is in accordance with the structure. The layers in graphite are held together by van der Waals' forces and hence the slippery touch and softness of graphite. The graphite sheets in which C uses sp^2 bonding leaves one p orbital free to contribute to the mobile π electrons which is responsible for high electrical conductivity.

Graphite compounds are formed by the introduction of atoms or molecules between the layers of graphite structure. Such substances as $FeCl_3$, F_2, H_2SO_4, K etc. have been introduced in between the layers giving rise to inclusion compounds or *clathrates*. The ill-defined graphitic acid, $C_{11}H_4O_5$, is formed when graphite is boiled with conc. HNO_3.

Charcoal, coke, carbon black and soot are amorphous or microcrystalline forms of carbon and are all of great industrial applications.

Diamond mostly comes from mines but quite recently synthetic diamond has been made by subjecting carbon under great pressure and high temperatures. Graphite is also mined but large quantities of graphite are made from amorphous carbon mixed with a little sand and Fe_2N_3 as catalyst and heating at about 3500°C in an electric furnace for a day or two. The carbon vapour condenses to produce graphite. This can also be made from petroleum, coke or anthracite coal as the starting material :

$$3C + SiO_2 = 2CO + SiC$$

SiC first formed is decomposed to give Si and C and silicon is volatilized away at that temperature leaving the graphite in the solid form :

$$SiC = Si + C$$

Graphite electrodes are mostly used in industrial electrolysis and also for making pencils. Large quantities of carbon are consumed in the manufacture of printing inks and hardening of automobile tyres. "Lamp black" which is actually used in tyres is made by the controlled combustion of methane in insufficient supply of oxygen to have the reaction :

$$CH_4 + O_2 = 2H_2O + C$$

Large quantities of carbon are also used for the extraction of metals.

Oxides of carbon

Carbon dioxide, CO_2 : This is the normal oxide of carbon and is obtained by various methods.

(1) By burning any form of carbon in excess of O_2 :

$$C + O_2 = CO_2 + 199 \text{ Kcal}$$

(2) By burning any compound of carbon in excess of O_2 :

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$$

(3) By strong heating of carbonate minerals, such as limestone, CO_2 is produced :

$$CaCO_3 = CaO + CO_2$$

(4) In the laboratory CO_2 is prepared by the action of dilute HCl on $CaCO_3$:

$$CaCO_3 + 2HCl = CO_2 + CaCl_2 + H_2O$$

(5) Fermentation process or decay of organic matter produces CO_2. Thus fermentation of glucose gives :

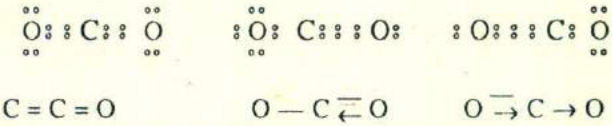
$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$$

(6) Commercially CO_2 is produced by burning coke in excess of air. The impure CO_2 containing N_2 and O_2 is passed under pressure through a cold dilute sodium carbonate solution which dissolves CO_2 but not N_2 and O_2. Pure CO_2 is obtained from the solution by just releasing the pressure :

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Properties of CO_2 : It is a colourless, odourless gas and acidic in nature. It is appreciably absorbed in water and is readily liquefied. It freezes to a snow-like solid which sublimes without melting. This is the reason that solid CO_2 is known as "dry ice" and is a good refrigerant free from liquid. Freezing mixture of dry ice and an organic liquid, such as acetone, ether etc. produces very low temperature (– 77°C).

The electronic structure of CO_2 indicates that it is a linear molecule having the structures which show resonance :



$$\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\,:C::\,\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \qquad :\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:\;C:::\,:O: \qquad :O:::\,:C:\,\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:$$

$$C = C = O \qquad O - C \overset{\rightharpoonup}{\leftarrow} O \qquad O \overset{-}{\rightarrow} C \rightarrow O$$

Due to resonance the bonds between C and O are strong and the molecule is quite stable towards heat. Burning Mg reduces CO_2 to pure C :

$$CO_2 + 2Mg = 2MgO + C$$

CO_2 is taken up by plants in presence of chlorophyll and sunlight synthesizing starch and other substances.

CO_2 dissolves in water to give H_2CO_3 which is a weak acid and most of its metallic salts are insoluble in water, particularly the heavy metals and alkaline earth carbonates. For this reason, these carbonates are found as minerals in nature. H_2CO_3 dissociates in water in two ways as a diprotic acid :

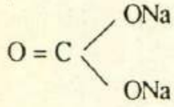
$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{-2}$$

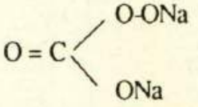
Metal carbonates

CO_2 dissolves in alkali solutions forming alkali carbonates, e. g., Na_2CO_3 and $NaHCO_3$. Bicarbonates of heavy metals or alkaline earth metals are readily soluble in water. The structure of carbonate has been discussed in the chapter on alkali metals. The low basicities of CO_3^{-2} and HCO_3^- do not permit formation of carbonates of those metals which are decidedly acidic. In other words, H_2CO_3 is not sufficiently acidic to form true carbonates with metal ions which are acidic. Thus Al^{+3}, Cr^{+3} and Fe^{+3} do not form true carbonates but give basic carbonates instead.

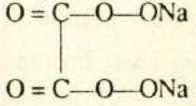
CO_2 when passed into a cold solution of Na_2O_2, the monopercarbonate, Na_2CO_4, is obtained. Dipercarbonate is made by electrolysis of cold saturated solution of, say, K_2CO_3. The relationships between the carbonates and percarbonates are shown below :



Sodium carbonate.



Sodium monopercarbonate



Sodium dipercarbonate
(peroxalate)

Uses of CO_2 : (1) Manufacture of washing soda, $Na_2CO_3.10H_2O$ and baking soda, $NaHCO_3$, by Solvay process. (2) White lead, $2PbCO_3$, $Pb(OH)_2$, used as a pigment, (3) Soft drinks, (4) Fire extinguishers, (5) Dry ice used as refrigerant, (6) manufacture of urea.

Carbon monoxide, CO : Carbon monoxide is also a very familiar oxide of carbon and is of great technical importance. It is produced by various methods.

(1) By heating oxalic acid :

$$H_2C_2O_4 = H_2O + CO_2 + CO$$

CO_2 is absorbed in alkali solutions.

(2) By heating heavy metal oxides with carbon :

$$ZnO + C = Zn + CO$$

(3) By heating a carbonate with a metal :

$$MgCO_3 + Zn = ZnO + MgO + CO$$

(4) By passing CO_2 over C or Zn in the heated condition :

$$CO_2 + C = 2CO$$

$$CO_2 + Zn = ZnO + CO$$

(5) By reacting natural gas with steam in presence of a catalyst (NiO) :

$$CH_4 + H_2O \xrightarrow{NiO} CO + CO_2 + H_2$$

Properties and structure of CO : Carbon monoxide is a colourless, odourless gas, only slightly soluble in water. The structure of CO has been a puzzle and the best Lewis structure can be given by the following formulations representing resonances between the two forms :

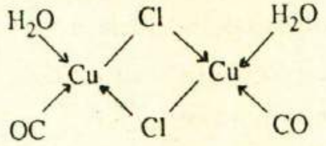
Unlike CO_2, carbon monoxide is an active compound. CO burns in air to give CO_2 and heat energy. It reduces many metallic oxides to metals. Thus,

$$CuO + CO = Cu + CO_2$$

CO is, therefore, an important reducing agent in metallurgical operations. CO reacts with alkalies to produce formate :

$$CO + 2(OH^-) \rightleftharpoons H_2O + HCO_2^-$$

It combines with chlorine in presence of sunlight to give $COCl_2$ (carbonyl chloride, also known as phosgene). Phosgene is a poisonous gas. Another interesting property of CO is that it combines with many metals to form "metallic carbonyls". Thus Ni forms $Ni(CO)_4$, Fe gives $Fe(CO)_5$ and Co produces $Co_2(CO)_8$. Both from industrial and structural points of view, the metallic carbonyls are very important and interesting compounds. CO is dissolved in cuprous chloride solution giving the compound :



Physiological action of CO : It is a highly toxic gas and combines with the hemoglobin of the blood to form a very stable compound destroying the ability of the blood to carry oxygen. CO inhalation causes paralysis of the respiratory organs. This danger of CO is particularly great in the exhaust gases of motor cars.

CO is not adsorbed by active charcoal but a mixture of CuO, MnO_2, Co_2O_3 and Ag_2O, known as *hopcalite*, oxidizes CO to CO_2 and is used in gas masks.

A filter paper moistened with $PdCl_2$ solution is turned pink, green or black due to the liberation of Pd in presence of CO. This is used as a test of CO.

Producer gas : When coke is heated in a limited supply of air, a mixture of CO and N_2 in the ratio of 1 to 3 by volume is formed. The product is known as *Producer gas*. It is used as a cheap fuel for many industrial works :

$$2C + 2O_2 = 2CO_2 + 54 \text{ Kcal}$$

$$CO_2 + C = 2CO - 39 \text{ Kcal}$$

Due to cooling down of the reaction for the second conversion, the temperature of the reaction is kept at 1100°C to effect the complete reduction of CO_2 to CO.

Water gas : When steam is passed over red-hot coke, a mixture of CO and H_2 is formed. This mixture is known as *Water gas* :

$$C + H_2O = H_2 + CO - 29 \text{ Kcal}$$

A high temperature (above 1000°C) is required to start the reaction. Since the reaction is endothermic the temperature soon falls below 1000°C when CO_2 begins to be produced :

$$C + 2H_2O = 2H_2 + CO_2 - 19 \text{ Kcal}$$

The final condition of equilibrium is represented by the reaction :

$$CO_2 + H_2 \rightleftharpoons H_2O + CO - 10 \text{ Kcal}$$

Thus at low temperatures, considerable amount of CO_2 is formed which lowers the calorific value of water gas. Hence devices have been developed to pass steam and air alternately over the bed of red-hot carbon to produce the mixture of $CO + H_2$ in the maximum proportions. When the steam is passed over the red-hot coke, it is called the "run period" or "cold blow"; but due to fall of temperature the passing of steam is stopped and hot air is blown to raise the temperature above 1000°C. This period is known as the "hot blow".

Water gas, known also as blue water gas, has a high calorific value. It is used as a fuel in industry and as a source of hydrogen and industrial alcohol (methyl alcohol) etc.

Carburetted water gas : When water gas is enriched with gaseous hydrocarbons obtained by cracking petroleum, the mixture is known as *carburetted water gas*. This contains mainly H_2, CO, saturated hydrocarbons and some CO_2 and N_2. This is also used as a fuel.

Semi-water gas : When a mixture of air and steam in the right proportions is passed over a bed of red-hot carbon the following reactions take place :

$$2C + 2O_2 = 2CO_2 + 54 \text{ Kcal}$$

$$C + H_2O = CO + H_2 - 29 \text{ Kcal}$$

Heat evolved by the combustion of carbon with oxygen present in air maintains the temperature of water gas reaction. The resulting gaseous mixture containing mainly CO, H_2 and CO_2, N_2 and some methane is called *Semi-water gas.*

Coal Gas

Coal gas is manufactured from coal by heating it in a closed vessel (retorts) in absence of air. The retorts are heated by producer gas (CO and air) to a temperature of about 1300°C. The operation of the coal gas producing plant is continuous and highly technical.

Purification of coal gas : The coal gas produced after carbonization of coal contains a number of impurities. They are mainly NH_3, H_2S, CS_2, HCN, besides naphthalene and tar. The tar condenses first in water condenser and also ammonia is separated as ammonical liquor.

The coal gas now enters the scrubber from the bottom. The scrubber is packed with coke and a fine spray of water slowly trickles downwards. Thereby all the residual NH_3, CO_2 and some H_2S and HCN are removed. The remaining gaseous impurities, such as CS_2, H_2S, and HCN are removed by passing through purifiers containing lime and iron hydroxide. The complicated reaction takes place and may be represented by some of the equations given below. H_2S must always be removed since it produces undesirable products and lowers the calorific value of the coal gas :

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca(OH)_2 + 2H_2S \longrightarrow Ca(HS)_2 + 2H_2$$

$$Ca(HS)_2 + CS_2 \longrightarrow \underset{\text{(Calcium thiocarbonate)}}{CaCS_3} + H_2S$$

$$2Fe(OH)_3 + 3H_2S \longrightarrow Fe_2S_3 + 6H_2O$$

$$Fe_2S_3 + HCN \longrightarrow Fe_4[Fe(CN)_6]_3$$

$$NH_3 + HCN \longrightarrow NH_4CN + H_2S \longrightarrow NH_4CNS$$

Coal gas is a mixture of gases containing the following :

$$CH_4\text{—}30\%,\ C_2H_4\text{—}4\%,\ C_2H_2\text{—}1\%$$

$$H_2\text{—}50\%,\ CO\text{—}10\%,\ N_2\text{—}5\%$$

Uses of coal gas : (1) Gaseous fuel. (ii) For providing inert atmosphere. (iii) For providing reducing atmosphere in metallurgy. (iv) Smelting.

Coke is used as a fuel and reducing agent in metallurgy.

Coal tar is used for extracting a vast number of organic substances.

Carbon disulphide, CS_2 **:** Carbon is oxidized by elementary sulphur to CS_2 at the temperature of electric arc in absence of air. High temperature is required because of the endothermic reaction :

$$C + 2S = CS_2 - 19 \text{ Kcal}$$

CS_2 is also produced commercially by burning methane in sulphur vapour at about 700°C in presence of silica gel or activated Al_2O_3.

The CS_2 obtained in the vapour state is condensed to liquid and purified by shaking the liquid with Hg and distilling over P_2O_5. CS_2 is a colourless liquid with a characteristic smell and boils at 46°C.

It is poisonous and a highly inflammable liquid. It ignites in air forming SO_2 and CO_2. It explodes in air or NO :

$$2CS_2 + 5O_2 = 2CO + 4SO_2$$

$$2CO + O_2 = 2CO_2$$

Thiocarbonates are formed when CS_2 reacts with Na_2S or with NaOH :

$$CS_2 + Na_2S = Na_2CS_3$$

$$3CS_2 + 6NaOH = Na_2CO_3 + 2Na_2CS_3 + 3H_2O$$

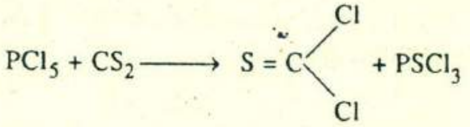
Similarly,

$$3CS_2 + 6NH_4OH\ (conc) = 2(NH_4)_2CS_3 + (NH_4)_2CO_3 + 3H_2O$$

Thiocarbonic acid, H_2CS_3 : This is obtained when sodium or ammonium thiocarbonate, $(NH_4)_2CS_3$, is added to excess of conc. HCl. This is a bright red liquid :

$$(NH_4)_2CS_3 + 2HCl = H_2CS_3 + 2NH_4Cl$$

Thiocarbonyl chloride is formed when CS_2 reacts with PCl_5 :



$$PCl_5 + CS_2 \longrightarrow S=CCl_2 + PSCl_3$$

CS_2 is a good solvent for oils, fats, sulphur, phosphorus, iodine, rubber etc. It is used in making rayon, cellophane and CCl_4. When Cl_2 is passed into CS_2 containing iodine or $SbCl_5$ (catalyst), CCl_4 is obtained. The process is used for the manufacture of CCl_4 :

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$$

Metal Carbides : Carbon combines with many metals to produce carbides. These are produced either by the direct reaction of metals with carbon or by heating the oxide of the metal with carbon at high temperatures. Some of these carbides have very high melting points, such as, TaC—4400°C. Thus,

$$2Li + 2C \rightarrow Li_2C_2$$

$$4Al + 3C \rightarrow Al_4C_3$$

$$BaO + 3C \rightarrow BaC_2 + CO$$

Most of the metal carbides with water give C_2H_2 by hydrolysis of C_2^{-2} ion :

$$Na_2C_2 + 2H_2O \rightarrow NaOH + C_2H_2$$

Only Al_4C_3 and Be_2C give CH_4 on hydrolysis with H_2O :

$$Be_2C + H_2O \rightarrow Be(OH)_2 + CH_4$$

Calcium carbide, CaC_2, is an important commercial product. CaC_2 is manufactured by heating CaO and coke in an electric arc furnace :

$$CaO + 3C = CaC_2 + CO$$

CaC_2 is an ionic compound containing Ca^{+2} and C_2^{-2} ions. It is hydrolysed in water readily giving acetylene, C_2H_2, which is the starting material of a very large number of products :

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

CaC_2 is also used to make calcium cyanamide, $CaCN_2$.

Calcium cyanamide, $CaCN_2$: When nitrogen (air) is passed over CaC_2 mixed with some $CaCl_2$ at a temperature of about 1100°C, N_2 is taken up by CaC_2 forming $CaCN_2$ and liberating C :

$$CaC_2 + N_2 = CaCN_2 + C$$

The mixture $CaCN_2$ and C is known as Nitrolime and is used as a fertilizer and for production of NH_3 by the hydrolysis of $CaCN_2$:

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Cyanogen, C_2N_2 : This colourless gas is obtained by various methods : (1) Cyanides of Ag, Au and Hg give C_2N_2 :

$$2AgCN \rightarrow 2Ag + C_2N_2$$

(2) When $Hg(CN)_2$ is heated with $HgCl_2$. Thus,

$$Hg(CN)_2 + HgCl_2 \rightarrow C_2N_2 + Hg_2Cl_2$$

(3) When $CuSO_4$ solution is treated with KCN, C_2N_2 is evolved. The method is analogous to the liberation of I_2 from KI when it is added to $CuSO_4$ solution :

$$2CuSO_4 + 4KCN = 2K_2SO_4 + 2CuCN + C_2N_2$$

Cyanogen is a poisonous gas, burns with blue flame and it is hydrolysed by water :

$$C_2N_2 + H_2O = HOCN + HCN$$

With KOH it gives KCN and KCNO :

$$C_2N_2 + 2KOH = KCN + KCNO + H_2O$$

In acid aqueous solution C_2N_2 gives oxamide :

$$C_2N_2 + H_2O \longrightarrow (CONH_2)_2$$

C_2N_2 on reduction with hydrogen gives $NH_2—CH_2—CH_2—NH_2$ (ethylene diamine). Hence, C_2N_2 has a linear structure.

$$N \equiv C—C \equiv N$$

or

⁚N⁚ ⁚ ⁚ C ⁚ C⁚ ⁚⁚N⁚

Hydrogen cyanide, HCN : This poisonous, almond smelling gas is formed when a cyanide is heated with an acid :

$$NaCN + HCl = NaCl + HCN$$

HCN in water solution gives a weak acid, hydrocyanic acid. The alkali metal salts of this weak acid in aqueous solution are alkaline by hydrolysis :

$$HCN + H_2O \rightarrow H_3O^+ + CN^-$$
$$CN^- + H_2O \rightarrow HCN + OH^-$$

HCN is a poisonous substance, 0.05 g. is sufficient to kill a man because it easily combines with iron in the blood and enzymes, CN^- ion has all the properties of halide ions and hence C_2N_2 is sometimes referred to as *pseudohalogen*. HCN has the following structure :

$$H—C \equiv N$$

Cyanates, CNO^- : When C_2N_2 is passed through alkali solutions, it gives cyanates and cyanides, just as chlorine gives hypochloride and chloride :

$$C_2N_2 + 2NaOH = NaCNO + NaCN + H_2O$$

KCNO is formed when KCN is heated with PbO or MnO_2 :

$$KCN + PbO = KCNO + Pb$$

HCNO is unstable and is decomposed by water to NH_3 and CO_2 :

$$\begin{array}{c} NaCNO + HCl = HCNO + NaCl \\ \big\downarrow {\scriptstyle +H_2O} \\ NH_3 + CO_2 \end{array}$$

Concentrated solution of NH_4Cl gives NH_4CNO with KCNO :

$$KCNO + NH_4Cl = NH_4CNO + KCl$$

NH_4CNO, on heating, gives urea, $NH_2—CO—NH_2$.

Thiocyanates, CNS^- : These are obtained when a cyanide is melted with S. Thus,

$$KCN + S = KCNS$$

When $(NH_4)_2S$ is treated with HCN, ammonium thiocyanate is obtained :

$$(NH_4)_2S + HCN \rightarrow NH_4CNS + NH_4SH$$

Free HCNS is obtained by treating $Ba(CNS)_2$ with dil. H_2SO_4 :

$$Ba(CNS)_2 + H_2SO_4 = BaSO_4 + 2HCNS$$

With ferric salt solutions thiocyanates give the blood-red colour which is a familiar test for Fe^{+3} ion :

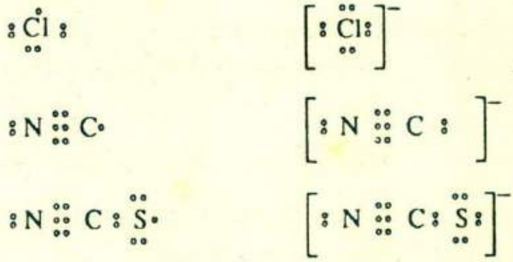
$$3NH_4CNS + FeCl_3 = Fe(CNS)_3 + 3NH_4Cl$$

It will be interesting to note that CO_2, cyanate CNO^- and cyanamide CN_2^{-2}, are isoelectronic and have similar structures :

$$O = C = O \qquad [O = C = N]^- \qquad [N = C = N]^{-2}$$

The ions are easily hydrolysed to give CO_2 and NH_4^+ ion.

The relationship between the structures of Cl^-, CN^- and CNS^- ions may be illustrated as follows :



SILICON

Organic substances containing C—C bonds are dominant in animal and vegetable worlds. Substances containing Si—O—Si bonds are of great importance in the mineral world. The earth's crust is primarily made of clay and silicate minerals which have Si—O—Si bonds arranged in chains, layers and network having SiO_4 tetrahedron as the unit of structure.

Occurrence : Silicon is never found in the free state. SiO_2 and various compounds known as silicates constitute about 86% of the earth's crust. Silicon is about 26%. Silicon is, therefore, next to oxygen in abundance. Silica, SiO_2, occurs in many forms, such as sand, sandstone, quartz, agate, flint etc. The various silicate minerals have been described in their proper places.

Preparation of Silicon : Silicon has been prepared both in the crystalline and amorphous forms. Both the forms appear to have the same atomic arrangement in the crystals and have somewhat diamond-like structures. Each silicon is covalently bonded to four adjacent silicon atoms at the corners of regular tetrahedron and this is extended in three dimensional network giving a giant molecule. Silicon is, therefore, hard and brittle.

Silicon is obtained when $SiCl_4$ is reduced by sodium :

$$SiCl_4 + 4Na = Si + 4NaCl$$

By the action of magnesium on SiO_2 at high temperature, amorphous silicon is obtained :

$$SiO_2 + 2Mg = Si + 2MgO$$

In this reaction some magnesium silicide is also formed :

$$SiO_2 + 4Mg = Mg_2Si + 2MgO$$

The Mg_2Si and MgO are dissolved in HCl giving amorphous brown powder of silicon. Crystalline silicon is obtained by heating K_2SiF_6 with Al in iron tubes :

$$3K_2SiF_6 + 4Al = 6KF + 4AlF_3 + 3Si$$

K_2SiF_6 when heated with Zn and the product dissolved in HCl, needle-shaped crystalline adamantine silicon is obtained :

$$K_2SiF_6 + 2Zn = 2KF + 2ZnF_2 + Si$$

Uses of Si : (1) For making acid resisting steels. (2) Making ferrosilicon, a strong reducing agent. (3) Pure silicon is used as transistors and microchips in electronics.

Some Important Compounds of Silicon

Silicon hydrides : Silicon forms a series of hydrides as in the case of carbon but only in limited number. Some of these are SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{12} and Si_6H_{14}. The chemical properties of these silicon hydrides are quite different from those of the hydrocarbons.

SiH_4, silane or silicomethane, is prepared when Mg_2Si reacts with dil. HCl :

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$

SiH_4 is also obtained when $SiCl_4$ is reduced with $LiAlH_4$ in ether solution :

$$SiCl_4 + LiAlH_4 = SiH_4 + LiCl + AlCl_3$$

Si_2H_6, disilane (silicoethane) is obtained by treating lithium silicide with HCl :

$$Li_6Si_2 + 6HCl = 6LiCl + Si_2H_6$$

SiH_4 is a colourless gas and Si_2H_6 is a colourless liquid. All the silanes are spontaneously inflammable in air forming SiO_2 and water :

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O$$

Silanes are easily hydrolysed forming SiO_2 and H_2. Alkali solutions give the alkali silicates, M_2SiO_3 and H_2 and all silanes are very sensitive to the reactions with alkalies.

The reactivity of silanes as compared to the hydrocarbons is the weakness of Si—H and Si—Si bonds. H_2O or O_2 is easily accommodated by Si atom because of the expansion of the coordination number due to the availability of d orbitals in Si atom.

Silicon compounds having the corresponding formula of carbon compounds are also known, such as, silicochloroform, $SiHCl_3$, obtained by stepwise halogenation of silane by HCl in presence of $AlCl_3$ as a catalyst :

$$SiH_4 + HCl \xrightarrow{AlCl_3} SiH_3Cl + H_2$$

$$SiH_3Cl + HCl \longrightarrow SiH_2Cl_2 + H_2$$

$$SiH_2Cl_2 + HCl \longrightarrow SiHCl_3 + H_2$$

$$SiHCl_3 + HCl \longrightarrow SiCl_4 + H_2$$

Silicon halides : Silicon gives tetrahalides, SiX_4, and also some mixed halides, such as $SiCl_2F_2$.

Silicon tetrachloride : $SiCl_4$ can be prepared by direct chlorination of silicon at high temperature or by direct chlorination of a mixture of SiO_2 and carbon :

$$Si + 2Cl_2 = SiCl_4$$

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

$SiCl_4$ is a colourless liquid, boiling point 58°C. This produces dense fumes in moist air due to the formation of finely divided silicic acid in moist air :

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl$$

During war the smoke screen is produced by liberating NH_3 and $SiCl_4$ at the same time. The density of the smoke is increased due to the formation of solid NH_4Cl.

$SiCl_4$ is readily attacked by H_2O, but CCl_4 is not.

Silicon tetrafluoride, SiF_4, is made by spontaneous burning of silicon in fluorine or by the action of HF on SiO_2 or a silicate :

$$Si + 2F_2 = SiF_4$$

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

$$CaSiO_2 + 6HF = CaF_2 + SiF_4 + 3H_2O$$

SiF_4 is a gas and is hydrolysed in water forming hydrofluorosilicic acid as well as orthosilicic acid :

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6$$

Fluorosilicic acid is also obtained by the action of HF on sand :

$$SiO_2 + 6HF = H_2SiF_6 + 2H_2O$$

Fluorosilicic acid is a stronger acid than sulphuric acid and it is a fuming liquid. On evaporation it breaks up to produce HF and SiF_4 :

$$H_2SiF_6 = 2HF + SiF_4$$

Hydrolysis of SiX_4 or the group IV metal halides, MX_4, in general proceeds in two manners :—

(1) Simple hydrolysis gives HX and $M(OH)_4$ or MO_2 :

$$SiF_4 + 4H_2O = Si(OH)_4 + 4HF$$

This occurs if the ratio of covalent radii $\frac{rM}{rX}$ is small (1.2).

(M = metal, X = halogen)

(2) When the ratio of covalent radii, $\frac{rM}{rX}$, is larger than 1.2, then the hydrolysis becomes complex forming complex ion, such as $[MX_n(H_2O)_{6-n}]^{4-n}$ and ultimately forming H_3O^+ ion and their conjugate bases. The acidity of the solution is increased. Some of the complex ions are SiF_6^{-2}, $SnBr_2(H_2O)_4^{+2}$.

Silicic acids and silica gel : When a strong mineral acid is added to a solution of an alkali metal silicate, this results in the formation of orthosilicic acid :

$$Na_4SiO_4 + 4HCl = H_4SiO_4 + 4NaCl$$

H_4SiO_4 remains in a colloidal solution but after some time it is precipitated out as a gelatinous mass. A mixture of sodium silicate and ammonium chloride also gives the colloidal solution or a gelatinous precipitate. The gelatinous mass is separated from other ions by dialysis.

Orthosilicic acid on stepwise dehydration by heating gives metasilicic acid, H_2SiO_3, disilicic acid, $H_6Si_2O_7$, and "trisilicic acid". On complete dehydration, SiO_2 is formed.

Silica gel is obtained by the dehydration of silicic acid to form silica containing a very small percentage of moisture. The silica gel has open and porous structure with large surface area and is used for absorption of gases and moisture and as a catalyst in chemical reaction.

Silicon carbide, SiC (Carborundum) : This is obtained on a large scale by heating a mixture of sand and coke in an electric furnace at a temperature of about 2000°C :

$$SiO_2 + 3C \;=\; SiC + 2CO$$

Carborundum is a blue black iridescent crystal as hard as diamond and exists in three different crystalline forms having C and Si at alternate positions in the crystal network so that each atom is surrounded tetrahedrally by four others. This accounts for the inactivity, hardness and thermal stability of SiC. It is used as abrasive for polishing, grinding and cutting.

SiC is attacked by fused alkali to give Na_2SiO_4 and Na_2CO_3.

Silicon dioxide, SiO_2 : Silica occurs in nature as sand and quartz. There are three well-defined crystalline forms of silica :

$$\alpha\ \text{quartz} \overset{573^\circ C}{\rightleftharpoons} \beta\ \text{quartz} \overset{870^\circ C}{\rightleftharpoons} \text{tridymite} \overset{1500^\circ C}{\rightleftharpoons} \text{crystobalite}$$

Crystobalite has a diamond structure having linear Si—O—Si bonds but in quartz and tridymite Si—O—Si bonds are non-linear.

A section of symmetrical arrangement of atoms is β-quartz is shown in Fig. 19—2 showing the plane of the hexagonal pattern.

SiO_2 is hard, refractory, brittle and colourless solid. CO_2 is a gas at ordinary temperature having separate molecules and even in dry ice CO_2 molecules have

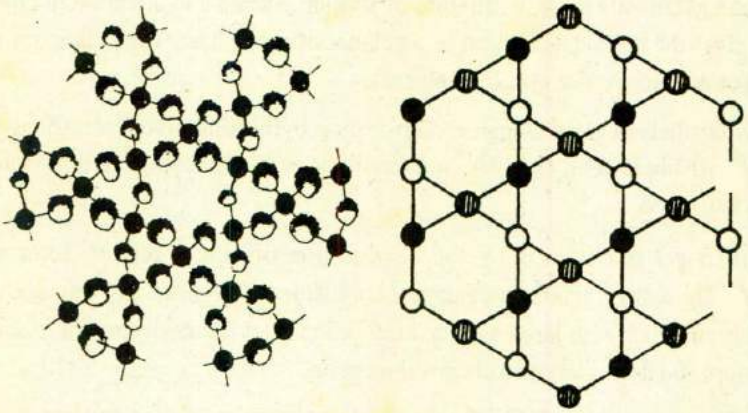


Fig. 19—2. Projection of silicon atom in β-quartz. The silicon atoms lie in three different planes shown by the black circles, shaded circles and empty circles giving a hexagonal pattern.

little intermolecular attractions. Each C in dry ice (CO_2) is linked to two O atoms by double bonds, whereas in SiO_2 each Si is attached to four O atoms by single bonds in tetrahedral forms which are again linked together in three dimensional pattern by sharing oxygen atoms at the corners between two tetrahedra forming a giant molecule having Si—O—Si non-linear bonds. The overall ratio of Si to O is 1: 2 as in SiO_2.

By melting quartz at 1600°C, silica glass is produced which is transparent to visible and ultraviolet light and is used in optical instruments.

SiO_2 is an stable compound and is reduced by only very reactive metal. It is not attacked by acid except by HF.

Ferrosilicon, FeSi : When silicate iron ore is reduced in electric furnace, ferrosilicon is formed. It is used in steel industry to make acid-resistant steel, e. g., "duriron" and steel of high magnetic properties. Silicon also acts as de-oxidizing agent in steel.

Hydrogenite : A mixture of ferrosilicon and solid NaOH liberates H_2 gas with water and is known as hydrogenite.

Water glass, Na_2SiO_3 : When silica is fused with Na_2CO_3 or NaOH, sodium silicate, Na_2SiO_3, is formed :

$$2NaOH + SiO_2 = Na_2SiO_3 + H_2O$$
$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

The product is a glassy mass soluble in water giving a thick viscous liquid which is called "water glass". It is a commercial product and actually does not conform to the simple formula of Na_2SiO_3 but contains excess SiO_2 in the form of $Na_6Si_3O_9$, $Na_4Si_3O_8$ etc. Water glass is used in making soap, washing compounds, fire proofing, adhesive and for egg preservation. Na_2SiO_3 on hydrolysis gives alkaline reaction because NaOH formed is a stronger base :

$$Na_2SiO_3 + 2H_2O = H_2SiO_3 + 2NaOH$$

Glass : Glass is a complex mixture of silicates and is actually a supercooled liquid. It is transparent, brittle and has no orderly arrangements of atoms as in crystals but has random distributions of the atoms. It does not melt on heating at a particular temperature but gradually becomes soft. Colour of the glasses are due to the presence of foreign metal either present in the raw material or deliberately added.

Raw materials for glasses : These vary from type to type and the following are the important raw materials used :—

(a) *Silica, SiO_2 :* Small quantity of Al_2O_3 does not produce any harmful effect but Fe_2O_3 colours the glass and is generally removed.

(b) *Boric oxide, B_2O_3:* This is added in the form of H_3BO_3 or borax only in borosilicate glasses which have low co-efficient of expansion.

(c) P_2O_5 or As_2O_3 is added when opalescent glasses are to be produced.

(d) Li_2O, K_2CO_3, CaO, Na_2CO_3, $BaCO_3$, MgO, PbO_4, ZnO and $CaCO_3$ are used as basic oxides to produce the glasses. These different basic oxides produce different types of glasses, such as,

(i) Soft glass contains Na and Ca silicate.

(ii) Hard glass contains K and Ca silicate and fuses at high temperature.

(iii) Flint glass contains K and Pb silicate for optical instruments.

(iv) Bottle glass is a soda-lime glass without removal of ferrous silicate.

(v) *Jena glass:* Zn and Ba-borosilicate glass.

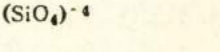
(vi) *Pyrex glass :* Barium borosilicate glass having low co-efficient of expansion.

(e) *Colouring matter for glass:* Certain metallic oxides are added to glass for the purpose of colouring the glass. For instance, ferrous iron gives green colour whereas ferric iron imparts, yellow colour. Cobalt oxide gives intense blue colour, carbon gives amber colour and so on.

The chemical reactions between the ingradients are of very complex nature and no definite compounds are formed. Soft glass consists of sodium-calcium silicates. Glasses manufactured by any of the above ingradients are subjected to annealing, i.e., the process of slow cooling in order to avoid sudden cracking down to pieces.

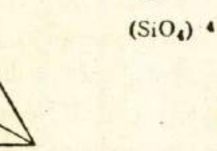
Natural silicates : These are silicate minerals occurring in nature and are of varied chemical compositions and structures. However, a systematic study of the silicate minerals have been made and it has been found that all of them have the same basic structures of SiO_4 tetrahedron joined together in various manners. Each Si atom is at the centre of a tetrahedron with 4 oxygen atoms at the corners. These minerals have been classified on the basis of the linking of Si-O tetrahedra. Thus :-

1. Single SiO_4 tetrahedron has an independent group in the crystal lattice. Thus olivine, Mg_2SiO_4, and zircon, $ZrSiO_4$, have individual SiO_4 tetrahedra bound together by Mg^{+2} or Zr^{+4} ions :



$(SiO_4)^{-4}$

Or

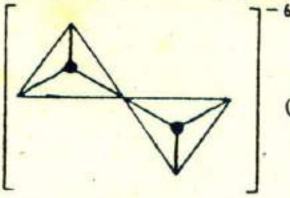


$(SiO_4)^{4}$

Or more simply as,

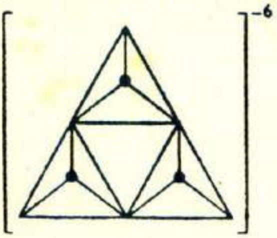
$(SiO_4)^{-4}$ tetrahedron. The black circle indicates Si atom at the centre. 4 oxygen atoms are situated at the 4 corners of the tetrahedron.

2. Two SiO_4 tetrahedra may share one corner forming Si_2O_7 group. Thus in hemimorphite, $Zn_4(OH)_2Si_2O_7$, and $Sc_2Si_2O_7$, we have,

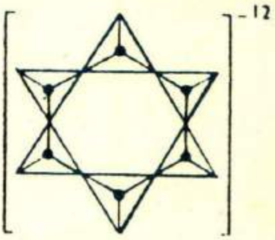


$(Si_2O_7)^{-6}$ anion

3. Three or six SiO_4 tetrahedra may share corners and form a closed ring as in $Ca_3Si_3O_9$ and benitoite, $BaTiSi_3O_9$, and beryl, $Be_3Al_2Si_6O_{18}$ respectively :

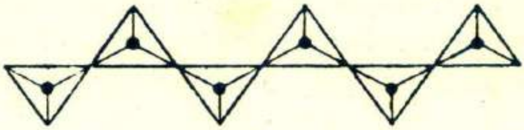


$(Si_3O_9)^{-6}$



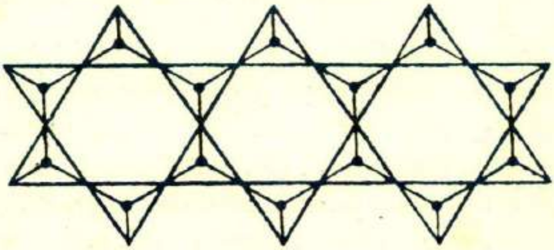
$(Si_6O_{18})^{-12}$

4. Linking of endless chain of SiO_4 tetrahedra by sharing two O atoms as in diopside, $CaMg(SiO_3)_2$, and pyroxenes, $[MgSiO_3]n$:



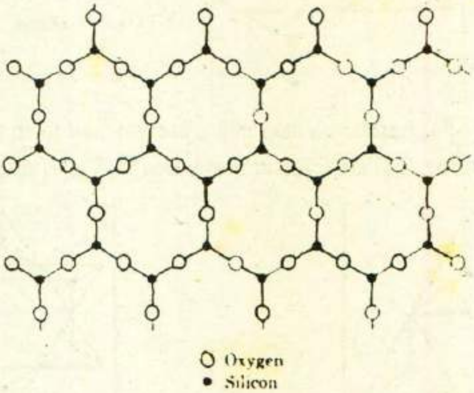
$(SiO_3)_n^{-2n}$ anion

5. Linking of SiO_4 tetrahedra to give double Si—O chains as in the fibrous asbestos and tremolite, $Ca_2Mg_4(Si_4O_{11})_2 . Mg(OH)_2$:



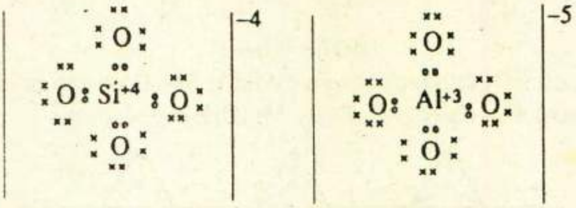
$(Si_4O_{11})_n^{-6n}$ anion

6. Linking of SiO_4 tetrahedra giving extended double chain to form sheets as in the case of talc, $Mg_3Si_4O_{10}(OH)_2$, and mica, $KAl_2AlSi_3O_{10}(OHF)_2$:



$(Si_2O_5)_n^{-2n}$ anion

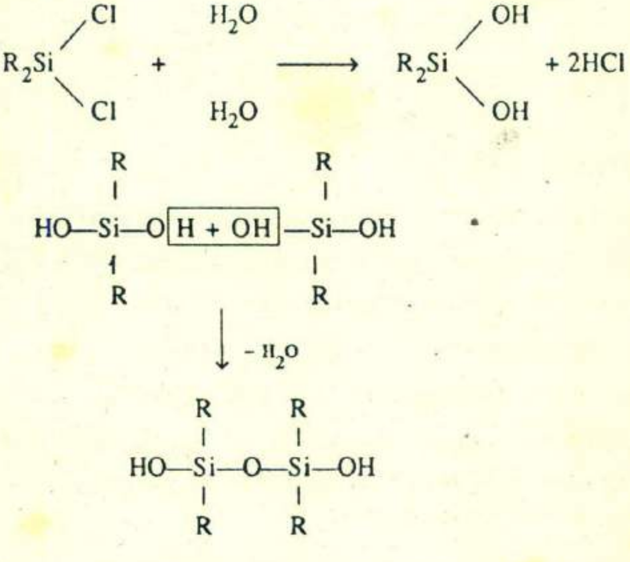
7. Linking of SiO_4 tetrahedra giving three dimensional Si—O network in which some Si^{+4} has been replaced by Al^{+3}. The excess negative charge is neutralized by introduction of a positive ion throughout the network as in feldspar, $KAl(Si_3O_8)$ or zeolites, $Na_2Al_2Si_3O_{10}.H_2O$. Aluminium ion, Al^{+3} replaces Si^{+4} because of the similar size of the two ions (about 0.50 Å).



Zeolite, therefore, contains Na^{+2} or K^+ ion in order to balance the electrical charges and the structure is such that Na^+ or K^+ ions can be dislodged by Ca^{+2} ion because of similar size without changing the basic structure of the silicate. This phenomenon in natural silicates is known as *isomorphous displacement*. Zeolite, therefore, functions as a base exchanger and is used in water purification, although now-a-days synthetic base exchangers are being extensively used.

Silicones : The production of organosilicon polymers has been a recent development in the field of silicon chemistry. The organosilicon polymers are generally known as *Silicones* and have been of great industrial use. They are stable towards heat and chemical reagents and repel water. Depending upon polymerization complexity, the silicones may be in the form of oily liquids, greases, rubber-like substances or resins. They find their use as lubricating oils, electrical insulators, water proofing etc. Silicones lubricating oils are employed where great variations of temperature do not permit the use of ordinary lubricants. Water repellent films are coated on paper, silk, glass, fabrics. etc. by simply exposing the materials to the vapour of trimethyl chlorosilane, $(CH_3)_3SiCl$. The thin film consists of $(CH_3)_2Si{-}O$ groups which repels water.

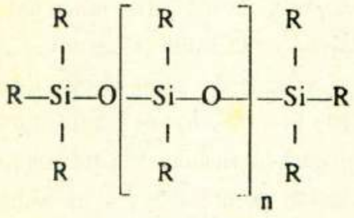
Some of the polymeric forms of the silicone polymers are made from organochlorosilanes of the types R_2SiCl_2 by hydrolysis. R may be CH_3, C_2H_5, C_6H_5 or other radicals. The hydrolysis is followed by polymerization (condensation reaction) through the elimination of H_2O from two adjacent OH groups of $R_2Si(OH)_2$:



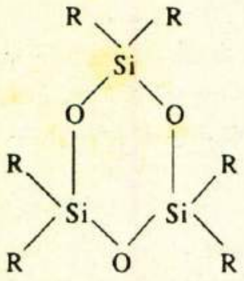
$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCl$$

$$HO{-}SiR_2{-}O\boxed{H + OH}{-}SiR_2{-}OH \xrightarrow{-H_2O} HO{-}SiR_2{-}O{-}SiR_2{-}OH$$

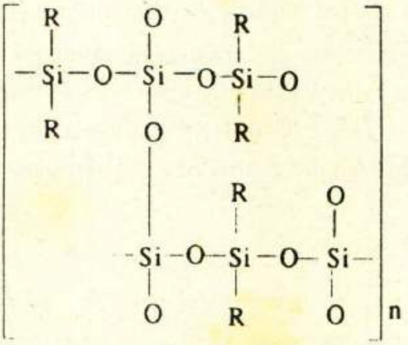
There are linear, cyclic and cross-linked types of silicone polymers as shown below :



linear silicone



cyclic silicone



cross-linked silicone

GERMANIUM

Mendeleef predicted the existence of this element and named it EKA-silicon.

Germanium is rare and occurs in argysodite, Ag_4SeS_4, and in some sulphide ores. It also occurs in coal ash along with other metals.

GeO_2 when reduced with C or H_2 gives the metal Ge.

Also the reaction, $GeBr_4 + 4Na \rightarrow Ge + 4NaBr$ gives Ge.

Ge metal retains its lustre in air like Sn. It is not affected by HCl, H_2SO_4 (dil.), but dissolve in HNO_3 and in dil. NaOH only slightly. Fused alkalies dissolve it completely forming Na_2GeO_3.

Germanium does not form allotropes and occurs only in diamond structure but it is opaque and gray in colour.

Ge forms both Ge^{+2} and Ge^{+4} compounds. Ge^{+2} is easily oxidized to Ge^{+4} or reduced to Ge. GeO and GeO_2 are amphoteric. $GeCl_4$ resembles $SiCl_4$ and Ge forms hydrides GeH_4, Ge_2H_6, Ge_3H_8 and other organometallic compounds.

When Ge is alloyed with other elements, it has the unique property of allowing an electric current to pass in only one direction. The rectifying capacity of metallic Ge crystals has been used in radar and as transistors for amplifying small currents of electricity as a substitute for vacuum tubes or thermionic valves. Germanium belongs to the semiconductor group of elements. It shows increased electrical conductivity at higher temperatures.

TIN

Sn has the electronic configuration :

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$$

This aspect of the electron arrangement is reflected in the properties of Sn and its compounds, particularly with regard to the oxidation states of Sn. Since $4d^{10}\ 5s^2$ electron arrangement represents stable configuration, the outermost $5s^2$ electrons in Sn do not normally show much activity and hence are known as *inert pair* of electrons. Thus Sn^{+2} state is more stable than Sn^{+4}.

Sources of Tin

(1) Cassiterite (Tinstone)—SnO_2.

(2) Various pyrites of Fe, Cu and Zn contain small quantity of Sn.

Metallurgy

1. Concentration of ore is generally done by washing the tinstone in a stream of water. Tinstone fragments being heavier are left at the bottom.

2. The tinstone is then roasted to remove arsenic and sulphur as volatile oxides. The volatile As_2O_3, is actually collected. The oxides of other metals are also formed during roasting.

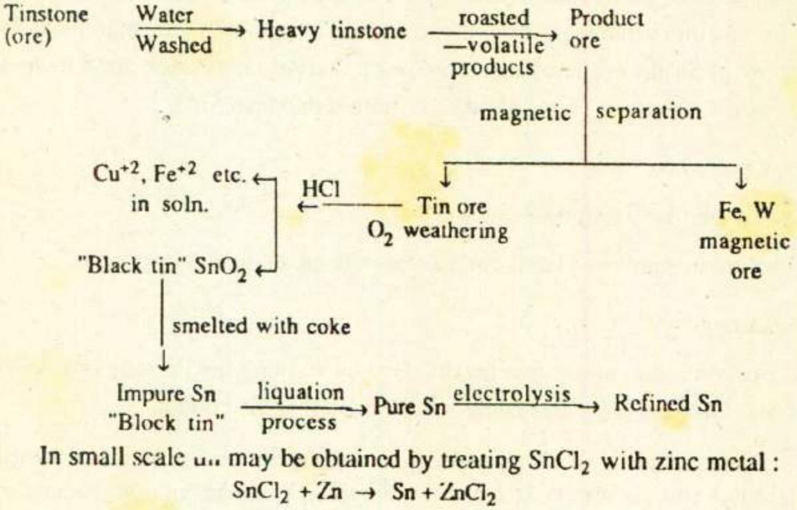
3. Roasted tinstone contains iron and manganese tungstate because $FeWO_4$ occurs in cassiterite. These are separated from tinstone by magnetic separation because both Fe and Mn tungstate are magnetic in nature. Travelling belt with

electromagnetic roller separates the magnetic and non-magnetic parts into two heaps.

4. The roasted tinstone is then treated with hydrochloric acid to dissolve out CuO and Fe_2O_3. Alternately, the roasted tinstone is allowed to stand in a heap in moist condition and then leached with water to dissolve out $CuSO_4$ and $FeSO_4$ formed. The concentrated tinoxide is known as *black tin.*

5. The purified SnO_2 is mixed with coke and smelted in a reverberatory furnace with a little lime as flux to form $CaSiO_3$ with SiO_2. The molten tin which collects on the bottom of the furnace is drawn off and cast into blocks known as *block tin,*

6. The refining of the crude tin is done by *liquation process.* The tin blocks are remelted and allowed to flow away from the higher melting impurities. This may further be purified by electrolysis. As usual, the impure tin is made the anode while the pure tin is cathode and the bath consists of H_2SiF_6 and H_2SO_4.



In small scale u.. may be obtained by treating $SnCl_2$ with zinc metal :

$$SnCl_2 + Zn \rightarrow Sn + ZnCl_2$$

Properties of Tin

Physical properties : Tin exists in three solid allotropic forms : (a) Gray tin having cubic structure; (b) White tin which is malleable and having tetragonal structure ; (c) Brittle tin having rhombic structure. The three forms are interconvertable :

$$\text{Gray tin} \overset{13^\circ\text{C}}{\rightleftharpoons} \text{White tin} \overset{170^\circ\text{C}}{\rightleftharpoons} \text{Brittle tin}$$

Malleable tin is silvery white and when a rod of it is bent or hit with a hammer, it produces a sound described as *tin cry* due to the fact that the crystals slip over one another. Zn and Cd behave similarly. White tin at low temperature (in cold countries where temperature falls below 0°C) automatically changes to gray tin which is a white powder. The change progresses slowly originating from a spot of the tin articles and spreads over the entire area as happens in the case of infection in a plant or animal body. For this reason, it is known as *tin disease* or *tin pest*.

Chemical properties : The chemical properties have been described in the general properties of group IV elements. Sn is a stable metal and is converted to SnO_2 only on heating to above 1500°C. Tin dissolves in HCl giving $SnCl_2$ and evolving H_2. Conc. H_2SO_4 gives $Sn(SO_4)_2$ but dil. H_2SO_4 gives $SnSO_4$:

$$Sn + H_2SO_4 = SnSO_4 + H_2$$

$$Sn + 4H_2SO_4 = Sn(SO_4)_2 + 2SO_2 + 4H_2O$$

It is also dissolved in dil. HNO_3 forming $Sn(NO_3)_2$ and NH_4NO_3, whereas Sn is converted to SnO_2 in hot conc. HNO_3 :

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

$$Sn + 4HNO_3 = \underset{\underset{SnO_2 + H_2O}{\downarrow}}{H_2SnO_3} + 4NO_2 + H_2.$$

Alkali dissolves tin giving alkali metal stannate :

$$Sn + 2NaOH + H_2O = Na_2SnO_3 + 2H_2$$

Halogens directly combine with Sn to give SnX_4. Thus,

$$Sn + 2Cl_2 = SnCl_4$$

Uses of tin : (i) Tin is used in the production of tin plates which are actually iron plates coated with tin. This is widely used for making tin cans and other household utensils. The older method of tinning iron plates is to clean the surface with H_2SO_4 and then running the sheet through molten tin, known as the *hot dip* method. Now-a-days the tinning is done electrolytically.

(ii) Tin is used to make stills for distilled water.

(iii) Tin foils are used for wrapping food, but now it has been replaced by Al-foils or cellophane.

Alloys of tin : (i) Solder : Sn —50%, Pb—50% are used for soldering purpose.

(ii) Bronze : Copper and tin alloy.

(iii) Type metal : Pb—60%, Sb—30%, Sn—10%.

(iv) White metal : Sn—82 %, Sb—12%, Cu—6%.

Some Compounds of Tin

Stannous oxide, SnO : This is obtained by special method :

(a) When $SnCl_2$ is treated with Na_2CO_3 in the hot condition;

(b) heating tin oxalate in the absence of air :

$$SnCl_2 + Na_2CO_3 = SnO + CO_2 + 2NaCl$$

$$SnC_2O_4 = SnO + CO_2 + CO$$

Sn, on strong heating in air, gives SnO_2 which is yellow when hot, white when cold and is used in making opaque glass and enamels.

Stannous hydroxide, $Sn(OH)_2$: It is produced in the form of white gelatinous precipitate when Sn^{+2} compounds in solution are treated with alkali solutions :

$$SnCl_2 + 2NaOH = Sn(OH)_2 + 2NaCl$$

$Sn(OH)_2$ is dissolved in excess of NaOH to give stannite and on boiling precipitates SnO :

$$Sn(OH)_2 + NaOH = NaSn(OH)_3$$

Sodium stannite solution has great reducing properties and is used to test for Bi^{+3} when $Bi(OH)_3$ is reduced to black metallic Bi :

$$2\,Bi(OH)_3 + 3\,NaSn(OH)_3 + 3\,NaOH = 2Bi + 3Na_2Sn(OH)_6$$

Stannic acids and stannates : On adding alkali to a solution of Sn^{+4} such as $SnCl_4$, a white gelatinous mass is produced. It may be expected to have a composition of $Sn(OH)_4$, but neither the acid nor salts derived from it have been made. These have indefinite compositions and may have polymer structure.

Ortho stannic acid is formulated as $H_2[Sn(OH)_6]$ and gives the Na-salt, $Na_2[Sn(OH)_6]$. The ortho acid readily loses H_2O forming meta stannic acid or a α-stannic acid, $SnO(OH)_2$ or H_2SnO_3. This is formed when NH_4OH is added to $SnCl_4$:

$$\begin{tikzcd} SnCl_4 + 4NH_4OH = & Sn(OH)_4 + NH_4Cl \arrow[d, "-H_2O"] \\ SnO_2 & SnO(OH)_2 \arrow[l, dashed, "-H_2O"'] \end{tikzcd}$$

α - or meta stannic acid forms salts with alkali, giving Na_2SnO_3 which are soluble in acids.

β - stannic acid is obtained when Sn reacts with conc. HNO_3 in the hot condition and is said to have the probable composition $H_2Sn_5O_{11}.4H_2O$ because the sodium salt has been formulated as $Na_2Sn_5O_{11}.4H_2O$. Sodium stannate or meta stannate is Na_2SnO_3 and is made by fusing SnO_2 in NaOH :

$$SnO_2 + 2NaOH = Na_2SnO_3 + H_2O$$

Sodium stannate is used in calico printing.

Tin halides, SnX_4 and SnX_2 :

SnF_2 : $Sn(OH)_2 + 2HF = SnF_2 + 2H_2O$

SnF_4 : $SnCl_4 + 4HF = SnF_4 + 4HCl$

SnF_2 is a white crystalline substance whereas SnF_4 is a hygroscopic solid. It forms double compounds with NH_3. On adding HF to K_2SnO_3, potassium fluoro-stannate, K_2SnF_6 is obtained.

$SnCl_2$: It is obtained commercially as $SnCl_2.2H_2O$ by the reaction of Sn or SnO_2 with HCl. Anhydrous $SnCl_2$ is obtained by the action of HCl gas on heated Sn or by heating Sn and $HgCl_2$ together:

$$Sn + 2HCl\ (g) \rightarrow SnCl_2 + H_2$$

$$Sn + HgCl_2 \ = \ SnCl_2 + Hg$$

$SnCl_2$ is soluble in water, ether, alcohol. $SnCl_2$ is hydrolysed in water on standing forming basic Sn(OH)Cl :

$$SnCl_2 + H_2O \ = \ Sn(OH)Cl + HCl$$

$SnCl_2$ is a reducing agent because it is easily oxidized to Sn^{+4} state. A few reducing reactions of analytical use are :

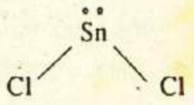
(a) $$\begin{tikzcd} 2HgCl_2 + SnCl_2 \ = \ Hg_2Cl_2 + SnCl_4 \arrow[d, "+SnCl_2"] \\ 2Hg + SnCl_4 \end{tikzcd}$$

(b) $FeCl_3 + SnCl_2 \rightarrow SnCl_4 + FeCl_2$

(c) $SnCl_2 + I_2 + 2HCl \ = \ SnCl_4 + 2HI$

$SnCl_2 . 2H_2O$ is used in industry also as mordant in dyeing, weighting of silk, and tin-coated metal articles, such as pins and paper clips.

The structure of $SnCl_2$ is represented as,



$SnCl_4$: It is obtained by the following reactions :-

(a) $Sn + \text{excess } Cl_2 \rightarrow SnCl_4$

(b) $Sn + \text{excess } HgCl_2 \xrightarrow{\text{distilled}} SnCl_4 + 2Hg$

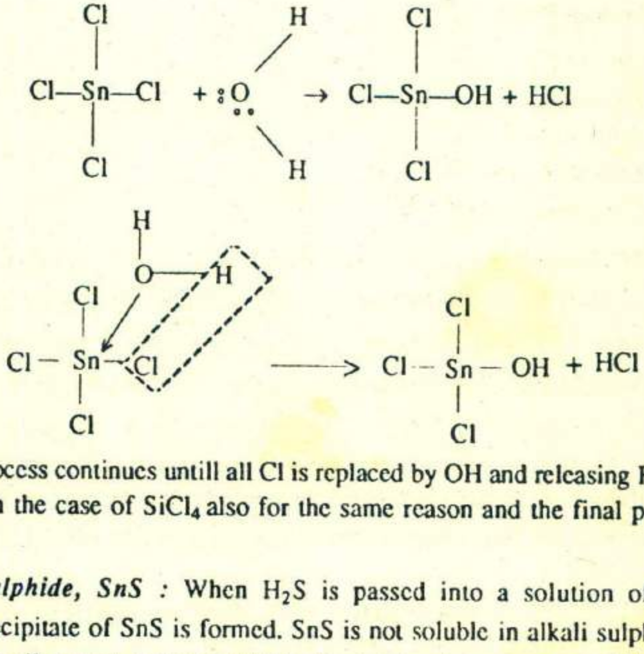
$SnCl_4$ is a colourless fuming liquid, soluble in organic solvents as in CCl_4 and non-conductor of electricity. Thus, it is a typical covalent compound. $SnBr_2$ and $SnBr_4$ are obtained in analogous manner. But when Sn and I_2 are heated together SnI_4 is formed with evolution of much heat and light. SnI_4 are red crystals soluble in organic solvents.

SnX_4 have tetrahedral structure.

It is to be noted that except carbon compounds, e.g., CCl_4, the tetrahalides of group IV elements are hydrolysed in water :

$$MX_4 + 2H_2O = MO_2 + 4HX$$

Thus, in covalent $SnCl_4$, since Sn is less electronegative than Cl, it carries a partial positive charge which attracts the OH ions of H_2O. Similar reaction occurs with $SiCl_4$:



The process continues untill all Cl is replaced by OH and releasing HCl. This happens in the case of $SiCl_4$ also for the same reason and the final product is $Si(OH)_4$.

Tin sulphide, SnS : When H_2S is passed into a solution of $SnCl_2$, yellow precipitate of SnS is formed. SnS is not soluble in alkali sulphides but soluble in yellow ammonium sulphide (containing large amount of S) forming thiostannate :

$$SnS + (NH_4)_2S = SnS_2 + 2NH_4^+$$

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

Stannic sulphide, SnS_2 : This is also known as *Mosaic Gold* and is used as a pigment in gilding. This is made by the action of H_2S on Sn^{+4}-salts :

$$SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

It is also obtained by heating a mixture of Sn, NH_4Cl and S together :

$$Sn + 4NH_4Cl = (NH_4)_2SnCl_4 + H_2 + 2NH_3$$

$$2(NH_2)_2SnCl_4 + 2S = SnS_2 + 2NH_4Cl + (NH_4)_2SnCl_6$$

This is an old method, and mosaic gold is used for imparting the look of gold on such articles as made of wood.

LEAD

In lead also we come across the outermost s^2p^2 electrons after d^{10} and Pb^{+2} is more stable than Pb^{+4}.

Sources of lead :

Galena—PbS
Anglesite—$PbSO_4$
Lanarkite—$PbO.PbSO_4$
Cerussite—$PbCO_3$

The most important mineral source of Pb is galena, PbS, and it is sometimes mixed with other sulphides, such as those of Cu, Zn, Sb and Ag.

Metallurgy : PbS is easily converted to PbO by heat and PbO is easily changed to Pb by reduction with carbon or scrap iron or simply by air.

1. Air Reduction Process : The concentrated ore is roasted in reverberatory furnace under controlled supply of air. Some of the PbS is converted to $PbSO_4$ and PbO which now react with the excess of PbS and thereby reduced to metallic Pb. The molten lead is drawn off and further purified :

$$2PbS + 3O_2 = 2PbO + 2SO_2$$

$$PbS + 2O_2 = PbSO_4$$

$$2PbO + PbS = 3Pb + SO_2$$

$$PbSO_4 + PbS = 2Pb + 2SO_2$$

2. Carbon Reduction Process : The crushed and concentrated galena is converted to PbO by roasting with a slow blast of air. For this purpose PbS is mixed with lime, CaO, in order to prevent the oxidation of PbS to $PbSO_4$ and $PbSiO_4$. Even if $PbSiO_3$ is formed, it reacts with CaO to give PbO :

$$PbSiO_3 + CaO = CaSiO_3 + PbO$$

The sintered ore is then charged in blast furnace with coke and lime. PbO is thus converted to Pb. The molten lead sinks at the bottom of the furnace and the slag floats on the top of the molten lead and is drawn off from different outlets :

$$PbO + C = Pb + CO$$

$$PbO + CO = Pb + CO_2$$

The lead obtained by the above methods contains Cu, Sb, As, Bi, Au, Ag etc. as impurities. The purification of lead is done by various processes.

(a) Softening of Pb : The crude lead is melted in a shallow reverberatory furnace and stirred with a current of air. The oxides of Sb, Bi, As are formed and rise to the surface and the molten lead is drained off for further refining.

(b): Desilverisation of lead : Gold and silver are extracted from lead by : (i) *Parke's process or* (ii) *Pattinson's process.*

(i) Parke's process is based on the extraction of silver from Pb by means of Zn. In the molten state Ag goes with the Zn layer and Pb is desilverised to a great extent.

(ii) Pattinson's process is based on the fact that Pb-Ag alloy (containing 2% Ag) has lower melting point than Pb. The portion of lead which solidifies first is rich in silver.

(c) Betts' electrolytic process for pure lead : This method gives relatively purer variety of Pb and the desilverized lead is subjected to this method. Thin sheets of pure lead are the cathodes and plates of impure lead are made the anodes. The electrolyte is a solution containing lead hexafluorosilicate, $PbSiF_6$ and 10% hexafluorosilicic acid, H_2SiF_6. The pure lead deposits on the cathodes which grow in bulk.

Uses of lead : The uses of lead depend mainly on the ease with which it is worked, its low melting point and resistance to corrosion. Some of the uses of lead are :

(1) Plumbing articles, but now replaced by galvanized iron materials.

(2) Manufacture for lead accumulators.

(3) Covering for electric cables.

(4) Lead chambers in H_2SO_4 plants.

(5) Making lead shots and bullets.

(6) Manufacture of white lead and other pigments.

(7) Making alloys, such as solder, type metal, pewter etc.

Alloys : (1) Type metal : Pb—82%, Sb—15% and Sn—3%.

(2) Solder : Pb—50%, Sn—50%.

(3) Pewter : Pb—20%, Sn—80%.

Compounds of Lead

The common oxidation state of Pb is +2. The +4 oxidation state is seldom formed because the two s^2 electrons in Pb remain associated with the core as a stable electron pair. Because of the high oxidation potential of Pb^{+4}, i. e., $Pb^{+2} \rightarrow PbO_2$, −1.5 volts, Pb^{+2} is the characteristic oxidation state.

Oxides of lead, PbO, Pb_3O_4 and PbO_2 : PbO is known as *litharge*. This is obtained by heating Pb or PbS in air, in the form of yellow-orange powder. This oxide is soluble in acids and alkalies forming Pb^{+2} or $HPbO_2^-$ ions respectively. It is used in the manufacture of lead glass and enamels. A mixture of PbO and glycerine is used as a cement since it sets to a solid lead glyceride. PbO is used in making NaOH also :

$$5PbO + 2NaCl + H_2O \rightleftharpoons PbCl_2.4PbO + 2NaOH$$

Red lead : Pb_3O_4 or *red lead* is made by careful heating of PbO in air at temperatures between 400—500°C. It is decomposed to PbO on strong heating :

$$6PbO + O_2 \rightleftharpoons 2Pb_3O_4$$

When Pb_3O_4 is treated with HNO_3, 2/3 of it dissolves as $Pb(NO_3)_2$ and 1/3 remains as PbO_2 :

$$Pb_3O_4 + 4HNO_3 = PbO_2 + Pb(NO_3)_2 + 2H_2O$$

For this reason, Pb_3O_4 is considered as a plumbate of Pb having 2PbO. PbO_2 or $PbPb_2O_4$ composition having Pb^{+2} as cation and Pb^{+4} in the anion PbO_4^{-4}.

Pb_3O_4 (red lead) is used as paints, making storage batteries, ceramic products and lint glass. Paint of red lead acts as a rust inhibitor for iron and woodwork.

Pb_2O_3, which is a yellow solid, is also formulated as $Pb(PbO_3)$. This is also made from PbO when heated in air.

PbO_2, lead dioxide or lead peroxide is obtained as a dark chocolate-brown powder by various methods. These methods are :

(1) $Pb_3O_4 + 4HNO_3$ (conc.) $= PbO_2 + 2Pb(NO_3)_2 + 2H_2O$.

(2) Oxidation of PbO with alkaline Cl_2 :

$$PbO + NaClO = PbO_2 + NaCl$$

(3) Anodic oxidation of solutions of Pb^{+2} salts :

$$Pb^{+2} + 2H_2O = PbO_2 + 4H^+ + 2e$$

(4) Fusion of PbO with $KClO_3$ and KNO_3.

(5) Action of bleaching powder on lead acetate gives PbO_2 :

$$Pb(CH_3COO)_2 + Ca(OH)_2 = Pb(OH)_2 + (CH_2COO)_2Ca$$

$$Pb(OH)_2 + CaOCl_2 = PbO_2 + CaCl_2 + H_2O$$

PbO_2 is a powerful oxidizing agent since Pb^{+4} tends to revert to stable +2 state by gaining 2 electrons. PbO_2 readily loses oxygen and is converted to PbO on heating or even in light. With concentrated HCl it liberates Cl_2, but with cold HCl it gives solution of $PbCl_4$:

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$

$$PbO_2 + 4HCl = PbCl_4 + 2H_2O$$

It dissolves in concentrated alkalies to form lumbates. PbO_2 is the principal constituent of the anode of the charged lead storage batteries.

The structure or PbO_2 is, $O = Pb = O$

Lead halides, PbX_2 and PbX_4 : $PbCl_2$ is formed from Pb and Cl_2 or by dissolving PbO in HCl or by adding Cl^- ion to a solution of Pb^{+2} salts. PbF_2 is prepared in the same manner :

$$Pb(NO_3)_2 + 2NaCl = PbCl_2 + 2NaNO_3$$

$PbCl_2$ is soluble in hot water but reappears on cooling.

H_2PbCl_4 is formed when $PbCl_2$ is treated with conc. HCl.

$PbCl_4$ is not a stable compound and is formed when PbO_2 reacts with cold HCl.

$PbBr_2$ and PbI_2 are obtained by double decomposition of a soluble Pb^{+2} salt and soluble KBr or KI respectively. PbI_2 forms beautiful golden spangles soluble in hot but insoluble in the cold condition.

Lead sulphate, $PbSO_4$: It is formed as an insoluble white precipitate on adding a soluble sulphate or dil. H_2SO_4 to a lead salt solution :

$$Pb(NO_3)_2 + Na_2SO_4 + PbSO_4 + 2NaNO_3$$

$PbSO_4$ is soluble in ammonium acetate or alkali solutions :

$$PbSO_4 + 2NH_4COOCH_3 \rightleftharpoons Pb(CH_3COO)_2 + (NH_4)_2SO_4$$

With hot conc H_2SO_4 it gives a solution of $H_2Pb(SO_4)_2$ from which $PbSO_4$ is precipitated out on dilution.

Lead nitrate, $Pb(NO_3)_2$: It is formed when Pb or PbO is dissolved in HNO_3. It is soluble in water to give a stable solution only in presence of a little HNO_3, otherwise hydrolysed to give $Pb(OH)NO_3$:

$$Pb(NO_3)_2 + H_2O \rightleftharpoons Pb(OH)NO_3 + HNO_3$$

$Pb(NO_3)_2$ is decomposed on heating as other nitrates of heavy metals :

$$Pb(NO_3)_2 \rightarrow 2PbO + 4NO + 3O_2$$

Lead acetate, $Pb(OOCCH_3)_2$: It is one of the few soluble salts of lead and was known as sugar of lead since it has sweet taste. It is obtained by dissolving $PbCO_3$ or PbO in acetic acid. In presence of excess PbO, basic lead acetate is obtained:

$$PbO + 2CH_3COOH \rightarrow Pb(OOCCH_3)_2 + H_2O$$

Lead chromate, $PbCrO_4$: It is insoluble in water and is obtained by double decomposition reactions :

$$2Pb(CH_3COO)_2 + K_2Cr_2O_7 \rightarrow 2PbCrO_4 + 2KCH_3COO + CH_3COOH$$

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3$$

It is known as "chrome yellow" and is used as a pigment. When the yellow $PbCrO_4$ is boiled with alkali, a basic Pb chromate, $Pb(OH)_2.PbCrO_4$, is obtained which is orange coloured and is used as a pigment.

$$2PbCrO_4 + 2NaOH = Pb(OH)_2.PbCrO_4 + Na_2CrO_4$$

Lead tetraethyl, $Pb(C_2H_5)_4$: It is a covalent compound and liquid at ordinary temperatures. It is used as petrol additive for producing "antinock" gasoline. It is obtained by the reaction of ethyl chloride with a Na—Pb alloy :

$$4C_2H_5Cl + Na_4Pb = Pb(C_2H_5)_4 + 4NaCl$$

Lead carbonate, $PbCO_3$: The normal carbonate is obtained by the action of $NaHCO_3$ upon $PbCl_2$ or $PbSO_4$:

$$PbCl_2 + NaHCO_3 = PbCO_3 + NaCl + HCl$$

"White lead" or the basic lead carbonate : The basic Pb carbonate has the composition $Pb(OH)_2.2PbCO_3$. This is formed when alkali carbonates are added to solutions of Pb-salts. Until a few years ago the manufacture of white lead was an important chemical industry because of its commercial importance as the paint pigment. It has a good covering power but with time the white paint turns black because of its conversion to PbS due to the action of H_2S which may be present in some places like industrial areas. The large scale development of the titanium dioxide, TiO_2, as a white pigment has almost completely replaced "white lead" industry because TiO_2 is free from the darkening effects. However, a short description of the manufacture of white lead is of interest from the point of view of chemistry.

White lead is manufactured by the action of air, CO_2 and CH_3COOH vapour on metallic Pb. Various technical procedures are adopted to bring about the reactions such as the Dutch Chamber Process in which the bars of Pb are exposed to the action of CH_3COOH vapour and CO_2 in a suitable chamber. In the Carter Process the corrosion of Pb is carried out in wooden cylinders where molten lead is atomised with superheated steam and a spray of CH_3COOH and a stream of CO_2 are introduced. The essential reactions are :

$$2Pb + O_2 + 2CH_2COOH = 2Pb(OH)COOCH_3$$

$$6Pb(OH)COOCH_3 + 2CO_2 = Pb(OH)_2.2PbCO_3 + 3Pb(COOCH_3)_2 + 2H_2O$$

$Pb(COOCH_3)_2$ is used up in the process and CH_3COOH is regenerated which again reacts with more lead. The process is continuous and white lead is removed from the stacks.

Titanium, Zirconium and Hafnium: These group IVB elements are classed as transition metals. Outermost electron groups are :

$Ti—3d^24s^2$ $Zr—4d^25s^2$ $Hf—5d^26s^2$

They are ordinarily tetravalent (+4 state), but also show oxidation states of +2 and +3. These metals are difficult to isolate. Titanium is found as *rutile*, TiO_2, and *ilmenite*, $FeTiO_3$.

Ti is very difficult to obtain in the pure form because of its high melting point (1800°C).

In order to get titanium, its ore is first converted into $TiCl_4$ by the reaction :

$$2TiO_2 + 3C + 4Cl_2 \xrightarrow{700°—1000°C} 2TiCl_4 + 2CO + CO_2$$

$TiCl_4$ is first purified and then metallic titanium is obtained by the reaction with active metals, such as Na, K, Ca, Mg etc. (Kroll process).

$$TiCl_4 + 2Mg \longrightarrow Ti \text{ (spongy)} + 2MgCl_2$$

The spongy titanium is converted to metallic titanium by treatment with dilute sulphuric acid or by the reaction with iodine to form TiI_4 which is decomposed by heating to 800°C in vacuum depositing pure titanium (Van Arkel Process). Iodine in the vapour state is used over and over again :

$$TiI_4 \longrightarrow Ti + 2I_2$$

Uses of Ti : Special properties of Ti has been used to make special alloys, such as in jet motors and high speed aircraft. Ferrotitanium has been used in special steels of great strength. TiO_2 is largely used as pigment in paint industry and is made from ilmenite, $FeTiO_3$, by reaction with HCl and subliming $FeCl_3$:

$$2FeTiO_3 + 4HCl + Cl_2 = 2FeCl_3 + 2TiO_2 + 2H_2O$$

$TiCl_4$ is liquid and is made by passing Cl_2 gas on TiO_2 mixed with C in the heated condition :

$$TiO_2 + C + 2Cl_2 = TiCl_4 + CO_2$$

$TiCl_4$ is used to produce smoke screen. $TiCl_2$ and $TiCl_3$ are good reducing agents.

Zirconium and hafnium occur together in nature. The chief ore is *zircon*, $ZrSiO_4$. All minerals of Zr contain about 5% Hf. The chemical properties of Zr and Hf are almost similar due to the effect of lanthanide contraction giving almost same ionic sizes of both.

ZrO_2 is also known as "Zirconia' and HfO_2 as 'Hafnia'. They are refractory materials and have very high melting points. The metals are obtained by heating K_2ZrF_6 or K_2HfF_6 with metals, such as Na, K or Al.

$ZrCl_4$ is hydrolysed to the extent of $ZrOCl_2$ whereas $TiCl_4$ is hydrolysed to the hydrated oxide TiO_2.

QUESTIONS AND PROBLEMS

1. Describe how coal gas is manufactured. What are its main constituents and how does it differ from producer gas and water gas? Give reasons why hydrogen sulphide is always removed from coal gas and explain the chemical reactions involved in its removal.
2. Describe preparation, properties and uses of lead chromate and basic lead chromate.
3. Write short notes on the preparation and uses of the following fuel gases :—
   (a) Producer gas, (b) Water gas and semi-water gas, (c) Coal gas.
4. Describe the preparation, properties and uses of —
   (a) Calcium cyanamide.
   (b) Calcium carbide.
   (c) Water glass.
   (d) Water gas.
5. Describe the preparation, properties and uses of—(a) Sodium cyanide, (b) Water gas, (c) Carbon disulphide.
6. Describe the preparation and uses of :— (a) Water gas, (b) White lead.

7. How would you prepare lead chromate from lead monoxide and chromium oxide?
8. Compare the chemistry of carbon and silicon and some of their important compounds. Mention salient points only.
9. How tin is extracted from tinstone and how the metal is purified? Discuss the action of :—(a) HCl, (b) HNO_3 and (c) NaOH on tin.
10. Write brief description of the preparation and uses of :— (a) Water gas, (b) Producer gas.
11. How are carborundum and water glass prepared ?
12. Describe the preparation, properties and uses of lead.
13. Compare the nature of the bonds in $PbCl_2$ and $PbCl_4$.
14. Show by suitable equations that $Pb(OH)_2$ is amphoteric.
15. Discuss the properties of group IVA elements in relation to their electronic structures. Explain why tin and lead do not form stable +4 oxidation states.
16. Explain :—
    (a) The inert pair of electrons.
    (b) Hydrolysis of silicon and tin tetrachlorides.
    (c) Tin disease.
    (d) Desilverisation of lead.
17. Discuss the principles involved in the extraction of lead from galena by air roasting process and the reduction process.
18. Compare the chemistry of group IV elements with particular reference to C, Si, Ge, Sn and Pb.
19. What is the theoretical basis of charcoal reduction test in the qualitative chemical analysis?
20. 'Properties of boron and silicon are similar in many respects. Discuss.
21. In Periodic group IVA carbon is a nonmetal, silicon and germanium are metalloids, tin and lead are metals. Explain why this is so.
22. Can you design construction of coinage and fuselage of pure tin? If not, why?
23. Zinc and tin are both used as protective coating for steel. What is the mechanism by which protection occurs in each case.
24. What are the structural formulae of stannic acid and stannous acid?
25. Write the equation showing production of hydrogen by the action of strong alkali solution on tin.
26. Describe Parke's process for the desilverization of lead. For what specific reasons Betts' process is employed.

27. Could you suggest replacing the lead plates in a storage battery by other metals ?
28. What are the uses of titanium metal and TiO_2 ?
29. Point out the commercial use of $TiCl_4$.
30. Zirconium and hafnium have very close resemblance of chemical properties. Discuss.

CHAPTER 20

NITROGEN AND PHOSPHORUS

(The elements of Group V)

The elements of group V are sub-divided into group VA and VB as follows:—

Group VA	*Group VB*
N — Nitrogen	
P — Phosphorus	V — Vanadium
As — Arsenic	Nb — Niobium
Sb — Antimony	Ta — Tantalum
Bi — Bismuth	

In group VA non-metallic character is more pronounced as compared to those of group IVA. The metallic character increases at the bottom of group VA, particularly Sb and Bi are considered to be metallic elements.

The electronic structures of group VA elements are given in Table 20.1.

Table 20.1. Electronic structures of group VA elements.

At. No.	*Elements*	*Electronic structures*	*Valence electrons*
7	N	He core, $2s^22p^3$	$2s^22p^3$
15	P	Ne core, $3s^23p^3$	$3s^23p^3$
33	As	Ar core, $3d^{10}4s^24p^3$	$4s^24p^3$
51	Sb	Kr core, $4d^{10}5s^25p^3$	$5s^25p^3$
83	Bi	Xe core, $4f^{14}5d^{10}6s^2\,6p^3$	$6s^26p^3$

Thus the 5 electrons in the outermost energy levels are s^2p^3 electrons in each case. The group VB elements V, Nb, and Ta are transition metals and have the electronic configurations in which **d** electron levels have the following configurations :—

V (23) — Ar core, ... $3d^34s^2$

Nb(41) — Kr core, ... $4d^45s^1$

Ta (73) — Xe core, ... $5d^36s^2$

Physical Properties

The physical properties of the group VA elements, N, P, As, Sb and Bi and also VB elements, are given in Table 20.2 (a) and (b) respectively.

Table 20.2 (a). Physical properties of group VA elements.

Properties	*N*	*P*	*As*	*Sb*	*Bi*
Atomic No.	7	15	33	51	83
Atomic Wt.	14.01	30.98	74.91	121.76	209.00
Outer electron configuration	$2s^22p^3$	$3s^23p^3$	$4s^24p^3$	$5s^25p^3$	$6s^26p^3$
Covalent radius (Å)	0.74	1.10	1.25	1.44	1.45
Ionic radius M^{+5}	0.11	0.34	0.47	0.62	0.74
Ionization energy (ev)	14.50	11.00	10.00	8.60	8.00
Melting point (°C)	−210	44 (white)	817	630 (sublimes)	271
Boiling point (°C)	−196	280	633	1640	1560
Electronegativity	3.07	2.10	2.00	1.80	1.70
Oxidation states	−3 to +5	−3. 0. 1,3,4,5,	0, 3, 5,	0, 3, 5	0, 3, 5
Oxidation potential (v)	N^{+3}/N^{+5} −0.94	P^{+3}/P^{+5} +0.49	As/As^{+3} −0.25	Sb/Sb^{+3} −0.21	Bi/Bi^{+3} −0.32

Thus we see from the Table 20.2 (a) that transition from non-metallic properties is very much pronounced. N and P are primarily non-metals whereas Sb and Bi show metallic behaviour. Arsenic exists in several forms and sublimes before it boils. N_2 molecule is one of the most stable molecules and requires more than 225 kcal to break into atoms. P is less stable.

As mentioned before V, Nb and Ta are transition elements and have metallic properties of heavy elements [Table 20.2 (b)].

Table 20.2 (b). Physical properties of group VB elements.

Properties	*V*	*Nb*	*Ta*
Atomic No.	23	41	73
Atomic Wt.	50.95	92.91	180.88
Outer electron configuration	$3d^34s^2$	$4d^45s^1$	$5d^3\,6s^2$
Covalent radius (Å)	1.31	1.41	1.43
Ionic radius M^{+5}	0.59	0.70	0.71
Ionization energy (ev)	6.70	6.50	6.10
Melting point (°C)	1710	2450	2850
Boiling point (°C)	3000	3300	4100
Electronegativity	1.45	1.23	1.33
Oxidation states	+2, +3 +4, +5	+3, +4 +5	+3, +4 +5
Oxidation Potential (v)	V/V^{+2} 1.5	Nb/Nb^{+5} 0.62	Ta/Ta^{+5} 0.71

Chemical Properties of N, P, As, Sb and Bi

The outermost electronic configurations of N, P, As, Sb and Bi all have s^2p^3 electrons making the total number of valence electrons equal to 5. The oxidation states of these elements show that N forms compounds having oxidation states −3, −2, −1, 0, +1, +2, +3, +4 and +5. Phosphorus has oxidation states −3, 0, +1, +3, +4, +5. But As, Sb, Bi are known to give oxidation states of 0, +3 and +5 only. In +3 compounds the two unshared electrons are s electrons or as hybrid of s and p orbitals.

The electronegativity values from N to Bi indicate that the elements tend to form covalent compounds with non-metals. In the covalent compounds of N, a total number of electrons around the N nucleus is never greater than 8 since only s and p orbitals are available for sharing of electrons. Thus the electron structure of N atom may be represented by :

$$1s^22s^2\,2p_x^12p_y^1\,2p_z^1$$

using three bonds. The other elements of this group may form bonds by utilising their **d** orbitals. Thus N forms NH_3 and NCl_3, but P in addition to PH_3 and PCl_3, can also form PCl_5 and PF_5. In aqueous solutions, P, As, Sb tend to form 4 bonds rather than 3 even in their trivalent derivatives.

Thus in chemical properties, these five elements show regular gradation of properties which are characteristics of group relationships. Some of the points of similarities and gradations in properties may be cited as follows :—

(1) N being most electronegative, forms more stable nitrides with metals having probably ionic bond. Phosphides and arsenides are formed but are not very stable. No such compounds are formed by Sb and Bi which give alloys.

(2) The stability of the hydrides, MH_3, decreases markedly, NH_3 is a stable compound, PH_3 unstable and AsH_3 very unstable. SbH_3 and BiH_3 have fleeting existence. The basic properties also decrease from NH_3 to PH_3 to AsH_3. NH_3 is most basic but PH_3 is less so, whereas AsH_3 does not combine with acids at all.

(3) Numerous oxides are formed by N and P and others but the acidic character decreases from N to Bi. Thus,

N_2O_3		
P_2O_3		
N_2O_5	As_2O_3	Bi_2O_3
P_2O_5	Sb_2O_3	
Distinctly acidic	Amphoteric	Distinctly basic

As_2O_5 and Sb_2O_5 are unstable. Bi_2O_5 has not been isolated, but sodium bismuthate, $NaBiO_3$, having Bi^{+5} is a well-known oxidizing agent.

(4) N and P and all the others of this group give trichlorides and oxychlorides. But they are hydrolysed in different manners indicating the change from non-metallic state. Thus,

$$NCl_3 + 3H_2O = NH_3 + 3HOCl$$

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3$$

$$AsCl_3 + H_2O = \text{Not hydrolysed}$$

$$SbCl_3 + H_2O = SbOCl + 2HCl$$

$$BiCl_3 + H_2O = BiOCl + 2HCl$$

Sb and Bi may have normal salts in concentrated solution of the acids, such as $BiCl_3$ in conc HCl or $Sb_2(SO_4)_3$ in conc H_2SO_4. But in water they form oxysalts which come out as precipitates. BiF_3 and BiI_3 are insoluble in cold water and are inert.

(5) Normal compounds containing SO_4^{-2}, NO_3^{-1}, CO_3^{-2} are not formed by N, P, As and even by Sb. Such salts of Bi are known.

The behaviour of the gradation of properties from N to Bi indicates that the transition from non-metal to metal takes place gradually. N and P are definitely non-metal. As and Sb may be classed as metalloidic while Bi is distinctly metallic in character. It is to be noted that +3 state of N. P and As exists as oxyacids in aqueous media. The more basic Sb^{+3} and Bi^{+3} exist as positive ions giving BiOCl and SbOCl. The metallic character of Bi may be attributed to the greater distance of the valence electrons from the nucleus which has much less attraction for p^3 electrons in bismuth making the $6s^2$ electrons quite inert. The chemistry of nitrogen and phosphorus are now described separately. After one has grasped the family behaviour as outlined above, the descriptive chemistry of the elements will be easier to remember.

NITROGEN

Nitrogen is one of the most useful elements. Along with phosphorus it is an essential element for plant and animal life.

Sources of nitrogen : (1) Air—78% by volume.

(2) Chile salpetre, $NaNO_3$, and salt petre, KNO_3.

(3) Soil contains NH_4-salts and nitrates.

(4) Animal and vegetable materials as in proteins and plants.

Preparation of nitrogen : (1) Nitrogen is most conveniently isolated from the air in which it is present to the extent of about 78% by volume. Various methods have been adopted to separate nitrogen from air. For example.

(a) When air is passed through KOH to absorb CO_2 and H_2O and and then through heated copper for removing oxygen as CuO, nitrogen is obtained. In a small scale oxygen may be removed by burning phosphorus.

(b) On industrial scale nitrogen is obtained by fractional distillation of liquid air.

Nitrogen isolated from air by either method may contain small quantities of oxygen and inert gases of which argon is the main constituent.

(2) Pure nitrogen is obtained by heating a solution of ammonium nitrite, NH_4NO_2, which decomposes to give N_2 :

$$NH_4NO_2 = N_2 + 2H_2O$$

In practice, a mixture of $NaNO_2$ with NH_4Cl is heated gently to start the reaction: NH_4NO_2 is normally difficult to store because it is unstable :

$$NH_4Cl + NaNO_2 = NaCl + 2H_2O + N_2$$

(3) Nitrogen is also obtained by the oxidation of NH_3. Various methods have been adopted for the reaction :—

(a) NH_3 passed over heated CuO gives N_2 :

$$2NH_3 + 3CuO = 3H_2O + N_2 + 3Cu$$

(b) $8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl$

(c) $2NH_3 + 3CaOCl_2 = 3CaCl_2 + 3H_2O + N_2$

(4) Ammonium dichromate, $(NH_4)_2Cr_2O_7$, when heated, N_2 is evolved vigorously (volcano experiment) :

$$(NH_4)_2Cr_2)_7 = Cr_2O_3 + 4H_2O + N_2$$

(5) When sodium azide, NaN_3, is heated very pure nitrogen is obtained :

$$2NaN_3 = 2Na + 3N_2$$

(6) Urea on heating with a nitrite in presence of H_2SO_4 gives N_2 :

$$NH_2CONH_2 + 2HNO_2 = CO_2 + 3H_2O + 2N_2$$

Properties of nitrogen : Nitrogen exists as a diatomic gas, N_2 at ordinary temperature. The gas is colourless and only slightly soluble in water. It does not support combustion or respiration but it is not poisonous. The lack of reactivity in nitrogen molecule, N_2, may be attributed to the triple bond which is the most stable diatomic molecule :

$$:N:::N: \quad \text{or} \quad N \equiv N$$

N_2 colecule contains one σ bond and two π bonds between N atoms and thereby rotation between N atoms is impossible. In order to dissociate N_2

molecule into atoms, 225 Kcals/mole are required. Thus the lack of chemical reactivity of N_2 and easy decomposition of many nitrogen compounds to give N_2 can be explained.

The triple bond is nitrogen is different from other triple bonds and does not show tendency to undergo addition reactions. for instance, acetylene, $HC \equiv CH$, organic nitriles, $RC \equiv N$, and some nitroso compounds, $(N \equiv O^+)$, have triple bonds but show great reactivity and undergo addition and displacement reactions. N_2 reacts only at high temperature by fist becoming active due to elevation of bonding electrons to higher energy levels followed bý triple bond breaking into $N = N$ and then N—N and finally N in atomic condition.

Nitrogen is a very electronegative element and assumes every oxidation state from –3 to +5 as shown in the following compounds :—

Compounds	*Oxidation states*
NH_3, NH_4^+	–3
N_2H_4 (Hydrazine)	–2
NH_2OH (Hydroxylamine)	–1
N_2 (element)	0
N_2O (Nitrous oxide)	+1
NO (Nitric oxide)	+2
N_2O_3 (Nitrogen trioxide) HNO_2 (Nitrous acid)	+3
NO_2 (Nitrogen peroxide) N_2O_4 (Nitrogen tetroxide)	+4
N_2O_5 (Nitrogen pentoxide) HNO_3(Nitric acid)	+5

Reactions of Nitrogen

1. N_2 reacts with H_2 at about 600°C in presence of catalyst (Fe and Mo) and under pressure to give NH_3 (Haber process) :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 23.8 \text{ Kcals}$$

2. N_2 reacts with O_2 under the influence of electric spark. This happens also at the time of lightning flashes in the atmosphere and NO is formed which combines with more O_2 to give NO_2 :

$$N_2 + O_2 \rightleftharpoons 2\,NO_2 - 43.2 \text{ Kcals}$$

$$NO + O_2 \rightarrow NO_2 \rightarrow N_2O_4$$

3. N_2 reacts with CaC_2 at high temperatures to give $CaCN_2$:

$$CaC_2 + N_2 = CaCN_2 + C$$

4. Some metals, such as Li, Ca, Mg, Ti etc. react with N_2 at high temperature to give nitrides containing N^{-3} ions :

$$N_2 + 3Mg = Mg_3N_2$$

$$N_2 + 2Al = 2AlN$$

$$N_2 + 6Li = 2Li_3N$$

5. Al_2O_3 reacts with N_2 in presence of C at high temperature to give AlN ;

$$N_2 + Al_2O_3 + 3C = 2AlN + 3CO$$

6. N_2 reacts with a mixture of Na_2CO_3 and C on heating to give NaCN :

$$N_2 + 4C + Na_2CO_3 = 2NaCN + 3CO$$

7. N_2 does not combine with halogens by direct reactions because of high heat of formation.

Uses of Elementary Nitrogen

(1) Large quantities of N_2 are used in "fixing" atmospheric nitrogen, such as making NH_3 which in turn are used to manufacture fertilizers, nitric acid and other nitrogen compounds.

(2) Nitrogen is used to provide an inert atmosphere in certain chemical processes.

(3) High temperature mercury thermometers are filled with N_2 to measure temperature upto 500°C.

(4) For preservation of food in tin cans which are filled with N_2.

Atomic nitrogen : When a stream of nitrogen is passed under very low pressure through a tube and subjected to high tension discharge, it produces a glow of yellow colour. This has been attributed due to the production of atomic nitrogen in the active form but there are some doubt about its atomic nature although experiments prove that it is more reactive than ordinary nitrogen.

The nitrogen cycle : Atmospheric nitrogen is the source of all nitrogen containing substances. Nitrogen is also an essential constituent of all plants and animals. Plants obtain their nitrogen through their roots mainly in the form of ammonium and nitrate compounds. Legumens, such as peas, get the nitrogen from air by means of nitrogen fixing bacteria found in the nodules on their roots. These nitrosifying and nitrifying bacteria convert atmospheric nitrogen into nitrites and nitrates which are assimilated by plants in the form of proteins. Quite a large quantity of nitrogen is converted to NO by the photochemical and electrical phenomena in the atmosphere. NO takes up more O_2 from air to become NO_2 forming HNO_2 and HNO_3 with water. These acids are washed down to the soil by rain water and react with oxides to form nitrites and nitrates in the soil. Soil bacteria also oxidize the nitrites to nitrates. Also some bacteria change ammonia into nitrites while denitrifying bacteria decompose nitrites and nitrates to free N_2 which goes to the air.

Animal get the nitrogen in the form of proteins by feeding on plants and other animals. When these animals and plants are dead, the decay products of both return nitrogen to the soil in the form of nitrates and ammonia and then the free nitrogen goes back to the atmosphere. Thus a complex cycle of N_2 from air through the soil to the plants and animals and then to the air maintains the nitrogen balance in nature.

Fixation of Atmospheric Nitrogen

Fixation of atmospheric nitrogen involves the combination of nitrogen of the air with some other elements to form subsequently useful compounds. The various processes used for the fixation of atmospheric nitrogen are :—

1. The Haber Process for NH_3 :

$$N_2 + 3H_2 \xrightarrow[\text{200 atmos}]{600°C} NH_3$$

2. The Arc Process for NO :

$$N_2 + O_2 \xrightarrow[\text{electric arc}]{2000°C} 2NO$$

3. The Cyanamide Process for $CaCN_2$:

$$CaC_2 + N_2 \xrightarrow{1000^\circ C} CaCN_2^-$$

4. The metallic Nitride Process forming AlN :

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$

5. By the nitrifying bacteria in the soil nitrogen is fixed.

These processes have been described in their respective places in this book. The primary products, such as NH_3, NO, $CaCN_2$, AlN are generally converted to other useful nitrogen compounds or are used as such where possible. The processes mainly aim at the production of fertilizers.

Compounds of Nitrogen

Ammonia

This is the most important hydride of nitrogen having formula NH_3. Other hydrides of nitrogen are N_2H_4 (hydrazine) and hydrazoic acid or azoimide, HN_3.

NH_3 is present in small quantities in air due to the decay action of nitrogenous organic matters.

Preparation and production of NH_3 : In the laboratory ammonia gas is usually prepared by heating an ammonium salt with calcium hydroxide or lime. Any alkali evolves NH_3 from ammonium salts but CaO is preferred because of its cheapness and drying action :

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$$

Metal nitrides may also be decomposed by reaction with H_2O to produce NH_3 by hydrolysis :

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$

Production of NH_3

(1) From coal : During the destructive distillation of coal, ammonia gas comes off with the coal gas along with many other volatile products. It is dissolved in water and the resulting solution when treated with lime gives off

pure ammonia which is either absorbed in water to produce liquor ammonia or else absorbed in H_2SO_4 to form $(NH_4)_2SO_4$ and is used as a fertilizer.

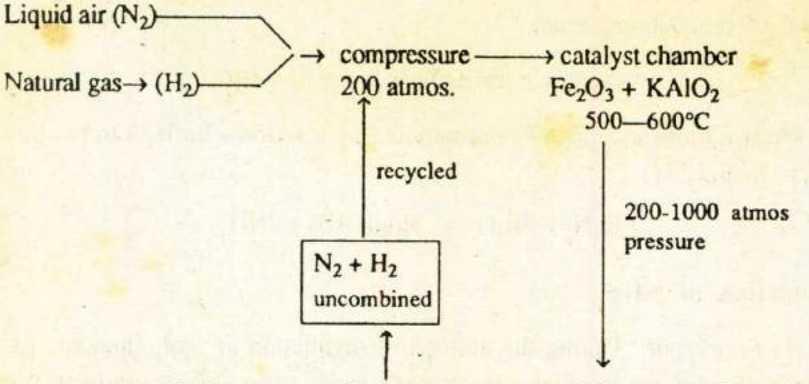
(2) *The Haber Process* "

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 23.8 \text{ Kcal}$$

The above reaction between N_2 and H_2 developed by Haber is an exothermic and reversible reaction and the equilibrium constant K is given by the expression $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$ Decrease in volume and evolution of heat occur. Hence low temperature and high pressure give greater yield of ammonia. But the reactivity of N_2 with H_2 at low temperatures is so low that no NH_3 is produced. Even at high pressure the yield is very small. Haber solved the difficulties by means of using heterogeneous catalyst. Of the many catalysts, such as—(a) finely divided Fe mixed with Mo, (b) Fe_2O_3 mixed with SiO_2; (c) Ni and sodamide etc., the more efficient catalyst has been a mixture of Fe_2O_3 and potassium aluminate. Temperature of 500°C and pressure from 200 atmospheres to 1000 atmospheres have been used to get the maximum yield.

N_2 from liquid air and H_2 from water gas or natural gas are the main sources of the gases.

NH_3 is removed by liquefaction and the residual or uncombined H_2 and N_2 are recycled through the reaction chamber. The flow sheet of the process may be represented simply as :



Flow sheet of synthetic manufacture of ammonia.

(3) *The Cyanamide Process* : CaO on heating with C in an electric furnace gives CaC_2 and when N_2 is passed over crushed CaC_2 mixed with some $CaCl_2$ at 1100°C, $CaCN_2$ is formed.

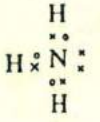
$CaCN_2$ on hydrolysis with steam under pressure in an autoclave gives NH_3:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

NH_3 evolved is absorbed in water or is converted to other ammonium compounds, such as $(NH_4)_2SO_4$ or urea.

Physical properties : (1) It is colourless gas with characteristic irritating odour. (2) It is lighter than air. (3) It is easily liquefied. The liquid boils at −33.35°C and turns to white crystalline solid on cooling. (4) The heat of vaporisation of liquid NH_3 is very high except water, and hence used as a refrigerant. (5) NH_3 is soluble in water, ether and alcohol. NH_3 is completely removed from the aqueous solution on boiling.

Chemical properties : (1) The weakly basic character of ammonia is very familiar and most of the chemical properties of NH_3 can be explained from its structure. The Lewis structure is :

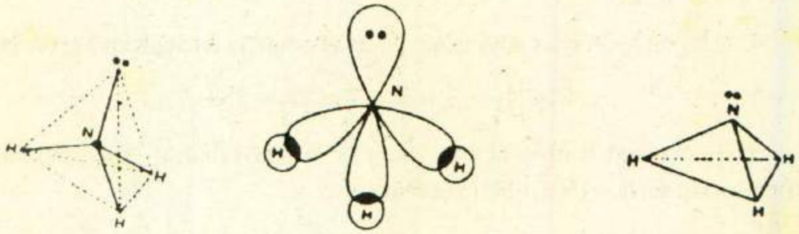


But the structure of NH_3 has been proved to be tetrahedral using sp^3 hybrid orbitals by N in NH_3 as given in Fig. 20—1 with the lone pair at one corner of the tetrahedraon.

The pair of electrons $2s^2$ have acquired bonding characteristic due to its merging with the **p** orbitals and forming sp^3 hybrid orbitals :

$$\text{N—} \qquad 1s^2 \; \underset{sp^3}{\boxed{2s^2\,2p_x^1\,2p_y^1\,2p_z^1}}$$

The lone pair situated at one corner of the tetrahedron occupies large volume of electron cloud and repels the N—H bonds which accounts for the large angle between H—N—H of about 107°. If NH_3 is formed by pairing of electrons in the simple $2p_x^1 2p_y^1 2p_z^1$ orbitals of N with one electron from each of the three

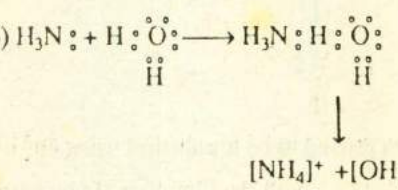


(a) (b) (c)

Fig. 20—1. Shape of NH_3 molecule. In effect, the shape of NH_3 will be pyramidal because of the lone pair occupying one corner of the tetrahedron. (a) Tetrahedral model, (b) Overlap of **s** orbitals of 3 hydrogen with sp^3 orbitals of N, (c) Effective pyramidal model.

H atoms, the angle between each H—N—H should have been 90° since p_x, p_y and p_z are at right angles to each other. Hence the bonding lone pair NH_3 is responsible for its chemical properties. Thus,

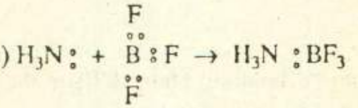
(a) $H_3N : + H^+ \longrightarrow [NH_4]^+$

(b) 

$$H_3N : + H : \underset{H}{\overset{\circ\circ}{O}} : \longrightarrow H_3N : H : \underset{H}{\overset{\circ\circ}{O}} :$$

$$\downarrow$$

$$[NH_4]^+ + [OH]^-$$

(c) 

$$H_3N : + \overset{F}{\underset{F}{B}} : F \rightarrow H_3N : BF_3$$

(d) Hydrogen bonding in NH_3 molecules and in its aqueous solution.

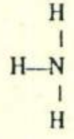
(2) For the same reason H_3N : forms a large number of complexes with metal ions :

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$Cu^{+2} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{+2}$$

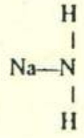
$$Cr^{+3} + 6NH_3 \rightleftharpoons [Cr(NH_3)_6]^{+3}$$

(3) NH_3 also shows weakly acidic properties since the three H may be replaced by metals :



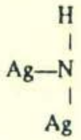
$H-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}$

ammonia



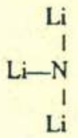
$Na-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}$

sodium amide



$Ag-\overset{\displaystyle H}{\underset{\displaystyle Ag}{N}}$

silver imide



$Li-\overset{\displaystyle Li}{\underset{\displaystyle Li}{N}}$

lithium nitride

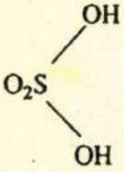
The compounds are formed when the metals are heated in NH_3 gas. But these compounds are readily hydrolysed in H_2O since H_2O is a stronger acid than NH_3 :

$$NaNH_2 + 2H_2O = NaOH + NH_4OH$$

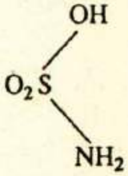
(4) Comparison of H_2O and NH_3 systems : There is analogy in the amides $H—NH_2$ and water $H—OH$ systems. It means that NH_2^- and OH^- may be interchanged in many compounds and similarly $=NH$ group is analogous to $=O$ group. The analogy of H_2O and NH_3 systems are given by the following examples :

	Properties	*H_2O system*	*NH_3 system*
1.	Ionization	$H^+ + OH^-$ or $H_3O^+ + OH^-$	$H^+ + NH_2^-$ $NH_4^+ + NH_2^-$(liq.)
2.	Base	KOH	KNH_2
3,	Acid	HCl $H_3O^+Cl^-$	$NH_4^+Cl^-$
4.	Solvolysis	$Mg(OH)Cl$ (hydrolysis)	$Hg(NH_2)Cl$ (ammonolysis)
5.	Solvates	$CaCl_2.2H_2O$	$CaCl_2.2NH_3$
6.	Neutralization	$KOH + H_3O^+ Cl^-$ $= KCl+2H_2O$	KNH_2+NH_4Cl $= KCl+2NH_3$
7.	Hydrogen bond	Strong H—OH bond	Weak H—NH bond

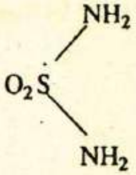
Thus the replacement of – OH by $-NH_2$ gives the following products in acids :—



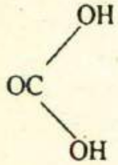
sulphuric acid



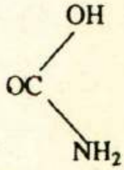
sulphamic acid



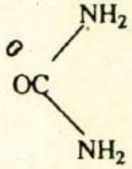
sulphamide



carbonic acid

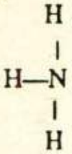


carbamic acid



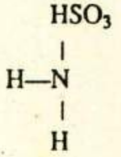
carbamide (urea)

Similarly,



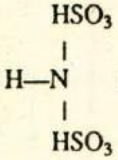
NH_3

ammonia



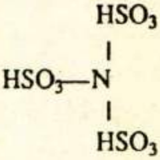
HSO_3-NH_2

amidosulphonic acid



$HN(HSO_3)_2$

imidosulphonic acid



$N(HSO_3)_3$

nitrilosulphonic acid

(5) Other properties of ammonia may be given by the following equations:—

(a) $2NH_3 + 3CuO \xrightarrow{\text{heat}} N_2 + 3Cu + 3H_2O$

(b) $2NH_3 + 3Mg \xrightarrow{\text{heat}} Mg_3N_2 + 3H_2$

(c) $4NH_3 + 3\,O_2 \xrightarrow{\text{burns}} 2N_2 + 6H_2O$

(d) $4NH_3 + 5\,O_2 \xrightarrow[\text{Pt catalyst}]{700°C} 4NO + 6H_2O$

(e) $8NH_3 + 3Cl \xrightarrow{\qquad\qquad} 6NH_4Cl + N_2$

Liquid ammonia : Liquid ammonia is an associated solvent like water. But HNH bond in NH_3 is weaker than HOH bond in H_2O. The property of NH_3 as an associated solvent is less pronounced than H_2O. But liquid NH_3 possesses the ability to dissolve many alkali and alkaline earth metals. The free metals can be recovered by evaporation of ammonia. The alkali metals dissolve in liquid NH_3 giving blue solution without the evolution of H_2. The blue colour is due to ammoniated electron.

$$K + \text{Liq } NH_3 \rightarrow K + e^-(NH_3)$$

But H_2O gives H_2 :

$$Na + H_2O \rightarrow NaOH + H_2$$

This is due to the reduction :

$$2H_3O^+ + 2e \rightarrow 2H_2O + H_2$$

Dilute solutions of Na and other metals in liquid ammonia are blue in colour and concentrated solutions have bronze colour. They conduct electricity like metals. It is believed that free electrons are present in the solution as solvated products :

$$Na = Na^+ + e^-$$

$$Na^+ + xNH_3 \rightleftharpoons Na(NH_3)_x^+$$

$$e^- + yNH_3 \rightleftharpoons e^-(NH_3)_y$$

Evaporation of a solution of metal in liquid ammonia gives the original metal. In presence of catalyst liquid ammonia solution of alkali metal gives H_2 because of the reaction.

$$2K + 2NH_3 \rightarrow 2KNH_2 + H_2$$

Ammonium Salts

General properties : All ammonium salts containing univalent NH_4^+ radical behave like alkali metals salts. NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, i.e., salts of strong acids, closely resemble alkali metal salts. The size of NH_4^+ 1.48 Å is almost the same as that of Cs^+ ion and a little larger than K^+ ion (1.33 Å). All ammonium salts are very soluble in water except the following :—

$$NH_4ClO_4 \qquad (NH_4)_3[Co(NO_2)_6] \qquad (NH_4)_2PtCl_6$$

NH_4- salts of strong acids are slightly hydrolysed in water but those of weak acids, such as carbonate, acetate, cyanides etc., are very much hydrolysed :

$$NH_4CN + H_2O \rightleftharpoons NH_4OH + HCN$$

When NH_4- salts of non-oxidizing acids are heated they decompose to give NH_3 and acids in gaseous states :

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

$$NH_4HCO_3 \rightleftharpoons NH_3 + \begin{array}{c} H_2CO_3 \\ \downarrow\uparrow \\ CO_2 + H_2O \end{array}$$

But NH_4- salts of oxidizing acids give N_2 or N_2O

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$$

$$NH_4NO_3 = N_2O + 2H_2O$$

Some of the important ammonium salts are described here.

(1) *Ammonium sulphate,* $(NH_4)_2SO_4$: The ammonical liquor obtained from the manufacture of coal gas is decomposed by lime and the liberated ammonia and steam is passed through dil H_2SO_4 to give $(NH_4)_2SO_4$. The synthetic ammonia is also absorbed in H_2SO_4 to produce $(NH_4)_2SO_4$.

This is also obtained when NH_3 gas and CO_2 are passed through powdered gypsum, $CaSO_4$, suspended in water :

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = (NH_4)_2SO_4 + CaCO_3$$

$(NH_4)_2SO_4$ is largely used as a fertilizer and for making other NH_4- salts. It is rapid action fertilizer and supplies N_2 to the plants at a rapid rate.

(2) *Ammonium nitrate,* NH_4NO_3: This is prepared by passing NH_3 gas in HNO_3 and also by double decomposition between $NaNO_3$ and $(NH_4)_2SO_4$:

$$2NaNO_3 + (NH_4)_2SO_4 = 2NH_4NO_3 + Na_2SO_4$$

NH_4NO_3 is used in explosives. NH_4NO_3 with Al powder known as *Ammonal* and NH_4NO_3 mixed with T.N.T. known as *Amatol* are high explosives.

(3) *Ammonium chloride,* NH_4Cl : This is much used in the laboratory as a reagent. This is obtained when $(NH_4)_2SO_4$ is boiled with NaCl solution and also by absorbing NH_3 gas in HCl.

NH_4Cl dissociates on heating to $NH_3 + HCl$:

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

It is for this reason that NH_4Cl is used as a flux in soldering because it cleans the oxide-coated surface of the metal :

$$CuO + 2NH_4Cl = CuCl_2 + 2NH_3 + H_2O$$

It is also used in dry, cells.

(4) ***Ammonium phosphate,* $(NH_4)_3PO_4$** : The normal $(NH_4)_3PO_4$ is actually formed from $(NH_4)_2HPO_4$ when the aqueous solution of $(NH_4)_2HPO_4$ is saturated with NH_3 gas. On evaporating H_3PO_4 which has been saturated with NH_3 gas, the compound which crystallises out, is $(NH_4)_2HPO_4$. The controlled neutralization of H_3PO_4 with NH_3 produces $NH_4H_2PO_4$. DAP which is diammonium-phosphate $(NH_4)_2HPO_4$ is used as fertilizer.

Ammonium phosphate is used as fertilizer and for fire-proofing of timber.

Microcosmic salt is $NaNH_4HPO_4.H_2O$. When Na_2HPO_4 and $(NH_4)_2HPO_4$ in the ratio of $\frac{5}{2}$ are mixed in aqueous solution and crystallised, the crystals consist of $NaNH_4HPO_4.H_2O$. The sparingly soluble microcosmic salt is also formed when Na_2HPO_4 and NH_4Cl are mixed together in molar proportions in aqueous solution and crystallized.

Microcosmic salt is used for identification of metals and also silica in qualitative analysis as in the case of borax bead test. The microcosmic salt forms colourless bead on a platinum wire and becomes coloured with a trace of metal oxide due to the formation of coloured metal phosphate. Silica gives the familiar skeleton-like mass with this salt in a similar manner.

(5) Ammonium carbonate, $(NH_4)_2CO_3$: When NH_4Cl or $(NH_4)_2SO_4$ is heated with $CaCO_3$ the product is $(NH_4)_2CO_3$. This is extensively hydrolysed in water and even in the solid state it smells of NH_3. Some ammonium carbamate is also formed during the reaction :

$$(NH_4)_2CO_3 \rightleftharpoons NH_2COONH_4 + H_2O$$

(6) ***Ammonium sulphide,* $(NH_4)_2S$** : When H_2S is passed in aqueous NH_3 the first product is NH_4HS, but at lower temperature and excess of NH_3

the normal salt $(NH_4)_2S$ is formed. It is also extensively hydrolysed and easily decomposed in the solid state to NH_3 and H_2S.

Yellow ammonium sulphide is obtained when H_2S is passed in NH_4OH to which fine powder of sulphur has been suspended. The yellow ammonium sulphide has a yellow colour and contains a polymer having —S—S—S— chain. This composition is generally expressed as $(NH_4)_2Sx$. This is used in qualitative analysis because it dissolves sulphides of As, Sb, Sn forming thiosalts from which the sulphides are precipitated by adding dilute acids.

Ammonium amalgam : When ammonium salts are electrolysed with a Hg cathode, the metallic mercury is supposed to contain free NH_4^+ ion which is stabilized in Hg by incorporating an extra electron. It is difficult to arrive at any conclusive picture about the free NH_4^+ ion in Hg except as an alloy, i.e., NH_4—Hg.

Hydrazine. N_2H_4

Hydrazine is another hydride of nitrogen. This is obtained by the following methods :—

1. On oxidizing NH_3 by NaOCl in presence of alkali and gelatine or glue which prevent side reactions :

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

$$NH_3 + NH_2Cl + NaOH \rightarrow N_2H_4 + NaCl + H_2O$$

Chloramine, NH_2Cl, is an intermediate compound. N_2H_4 remains in the solution and is crystallised as hydrazine sulphate, $N_2H_4.H_2SO_4$, or chloride, $N_2H_4.HCl$, by adding respective acids. When these crystals are distilled with KOH under reduced pressure, $N_2H_4.H_2O$ is obtained as distillate.

2. By reducing nitric oxide with Na—Hg in presence of saturated solution of K_2SO_3 :

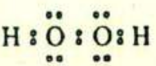
$$2NO + 8H = N_2H_4.H_2O + H_2O$$

$$N_2H_4.H_2O + BaO = N_2H_4 + Ba(OH)_2$$

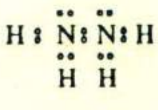
$$N_2H_4.HCl + CH_3ONa = N_2H_4 + CH_3OH + NaCl$$

Hydrazine is a fuming liquid, boiling point being 114°C. Anhydrous N_2H_4 is thermally stable but highly reactive. The free base is not obtained by the action of alkali on acid salts, such as $N_2H_4.HCl$ but the reaction always gives $N_2H_4.H_2O$:

N_2H_4 may be regarded as the analogous of H_2O_2 with which it is isoelectronic. Hydrazine may thus be regarded as a difunctional amine, $NH_2.NH_2$:



$$H:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{O}}:H$$



$$H:\underset{H}{\underset{\cdot\cdot}{\ddot{N}}}:\underset{H}{\underset{\cdot\cdot}{\ddot{N}}}:H$$

Properties of N_2H_4 : (1) On heating, N_2H_4 is decomposed into ammonia and N_2 :

$$N_2H_4 = N_2 + 4NH_3$$

(2) It burns in air and reacts vigorously with halogens :

$$N_2H_4 + O_2 = N_2 + 2H_2O$$

$$\begin{array}{rcl} N_2H_4 + 2Cl_2 & = & ClHN{-}NHCl + 2Cl^- \\ & & \downarrow \\ & & N_2 + 2HCl \end{array}$$

(3) Aqueous N_2H_4 is weakly basic :

$$N_2H_4 + H_3O^+ = \underset{\text{Hydrazinium ion}}{N_2H_5^+ + H_2O}$$

$$N_2H_4 + HCl = N_2H_5^+ + Cl^-$$

$$Zn^{+2} + 4N_2H_4 = Zn(N_2H_4)_4^{+2}$$

$$CH_3Br + N_2H_4 = \underset{\text{Nucleophilic displacement on carbon}}{CH_3NHNH_2 + HBr}$$

N_2H_4 is a reducing agent. "One electron" oxidizing agent, such as Fe^{+3} and Ce^{+4}, Cu^{+1} or halogens yield N_2. In basic solution, the yield of N_2 is quantitative. The quantitative reaction with iodine can be used to determine hydrazine :

N_2H_4 thus behaves as a good reducing agent and a base.

$N_2H_4 + 2I_2 = N_2 + 4HI$

The reaction of N_2H_4 with H_2O_2 (both liquids) gives N_2 and steam (both gases) with high liberation of energy accompanied by tremendous increase in volume and the mixed liquids have been used as rocket fuels:

$$N_2H_4 + 2H_2O_2 = N_2 + 2H_2O$$

Hydrazoic acid, HN_3, and Azides

Hydrazoic acid or azoimide, HN_3, contains 98% N_2 and is explosive in the pure state. It can be studied in aqueous solutions. HN_3 can be prepared as follows:—

(1) The sodium salt, sodium azide, NaN_3, can be prepared by nucleophilic attack on N_2O with sodamide :

$$NaNH_2 + N_2O = NaN_3 + H_2O$$

(2) By the action of HNO_2 on $N_2H_4.HCl$:

$$N_2H_4.HCl + NaNO_2 = N_2H_4.HNO_2 + NaCl$$

$$N_2H_4.HNO_2 \rightarrow HN_3 + 2H_2O$$

(3) By the action of NCl_3 on N_2H_4 :

$$N_2H_4 + NCl_3 = HN_3 + 3HCl$$

Properties of hydrazoic acid : It is a colourless smelling liquid and detonates violently on shock. It is a weak acid and reacts with both oxidizing and reducing agents :

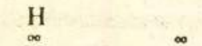
$$HN_3 + 4H_2 = 3NH_3$$

$$2HN_3 + O = 3N_2 + H_2O$$

Azides : Metals, like Zn, Fe, Al, Mg, Hg and Pb react with HN_3 giving azides. With Mg, H_2 is also liberated but other metals give NH_3 and other nitrogen compounds :

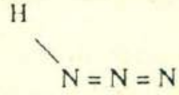
The azides are unstable compounds and some of them are used as explosives. $Pb(N_3)_2$ (lead azide) is used as a detonator for military explosives.

The linear structure of HN_3 and also the azide ion N_3^- has been proved :



$$:\overset{\overset{H}{\infty}}{N}:\,:N:\,:\overset{\infty}{N}:$$

The three atoms of N in the azide ions also lie in the same straight line. H is not is the same line and the formula can be written as,

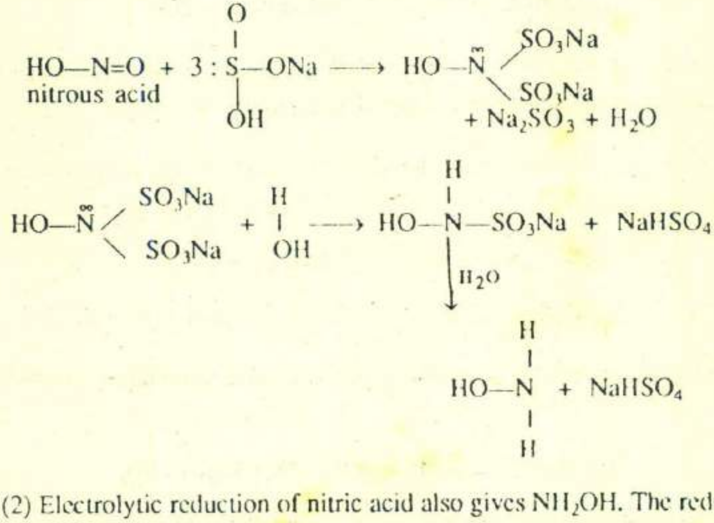


$$\overset{H}{\diagdown}N = N = N$$

Hydroxylamine, NH_2OH

Hydroxylamine, NH_2OH, may also be regarded as a nitrogen analogue of H_2O_2 or a derivative of ammonia. It is prepared by the following methods :—

(1) Hydroxylamine is prepared by the reduction of HNO_2 with H_2SO_3. It is an example of reduction-reaction that proceeds in shifts of two electrons by formation and breakage of covalent bonds. In actual practice, $NaNO_2$ is reduced by SO_2 in presence of Na_2CO_3 at low temperature. Sodium salt of hydroxylamine sulphonic acid is first formed which on hydrolysis gives NH_2OH:



$$\underset{\text{nitrous acid}}{HO{-}N{=}O} + 3 : \overset{O}{\underset{OH}{S}}{-}ONa \longrightarrow HO{-}\ddot{N}\begin{matrix} \diagup SO_3Na \\ \diagdown SO_3Na \end{matrix} + Na_2SO_3 + H_2O$$

$$HO{-}\ddot{N}\begin{matrix} \diagup SO_3Na \\ \diagdown SO_3Na \end{matrix} + \overset{H}{\underset{OH}{|}} \longrightarrow HO{-}\overset{H}{N}{-}SO_3Na + NaHSO_4$$

$$\xrightarrow{H_2O} HO{-}\overset{H}{\underset{H}{N}} + NaHSO_4$$

(2) Electrolytic reduction of nitric acid also gives NH_2OH. The reduction of HNO_3 occurs at the cathode. HNO_2 is first formed which is reduced to NH_2OH :

$$HNO_3 + 2H = HNO_2 + H_2O$$

$$HNO_2 + 4H = NH_2OH + H_2O$$

(3) When NO is reduced with Sn + conc HCl :

$$NO + 3H = NH_2OH$$

(4) Ethyl nitrate on reduction with Sn + HCl :

$$C_2H_5NO_3 + 6H = NH_2OH + H_2O + C_2H_5OH$$

NH_2OH prepared by the above methods is an aqueous solution. Anhydrous NH_2OH can be prepared by the following processes :—

(1) By the reaction of hydroxylamine hydrochloride with sodium methoxide in alcoholic solution :

$$NH_2OH.HCl + CH_3ONa = NH_2OH + NaCl + CH_3OH$$

NH_2OH is somewhat soluble in alcohol and is separated from insoluble NaCl. Methyl alcohol is removed by distillation under reduced pressure.

(2) Hydroxylamine phosphates on heating gives NH_2OH :

$$(NH_2OH)_3.H_3PO_4 \longrightarrow 3NH_2OH + H_3PO_4$$

Properties of NH_2OH : (1) It is needle-like white solid, melting point 33°C. It is soluble in water and in ether. It is thermally unstable.

(2) It is an active reducing agent and reacts violently with halogens and other powerful oxidizing agents :

$$2NH_2OH + 2Cl_2 = N_2O + H_2O + 4HCl$$

$$2NH_2OH + 4FeCl_3 = 4FeCl_2 + N_2O + H_2O + 4HCl$$

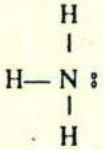
(3) NH_2OH also acts as an oxidizing agent in alkaline medium evolving NH_3 :

$$NH_2OH + 2Fe(OH)_2 + H_2O = 2Fe(OH)_3 + NH_3$$

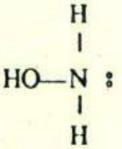
(4) Like hydrazine, NH_2OH forms salts with HCl and H_2SO_4 and are available in these forms :

$$NH_2OH.HCl \qquad NH_2OH.H_2SO_4$$

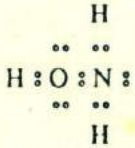
These compounds are examples of addition compounds. NH_2OH may be considered as a derivative of NH_3 in which one H has been replaced by OH :



$$\begin{array}{c} H \\ | \\ H\text{—}N: \\ | \\ H \end{array}$$



$$\begin{array}{c} H \\ | \\ HO\text{—}N: \\ | \\ H \end{array}$$



$$\begin{array}{c} H \\ \cdot\cdot\ \cdot\cdot \\ H:O:N: \\ \cdot\cdot\ \cdot\cdot \\ H \end{array}$$

Nitrogen halides : There are no direct reactions between N_2 and halogens. Only NF_3 and NCl_3 are known. NBr_3 or NI_3 are doubtful compounds. But $NH_3(NX_3)$ type of compounds are formed with Br_2 and I_2(X=Br or I).

NF_3 is obtained by the reaction of NH_3 and F_2 :

$$NH_3 + F_2 \longrightarrow NH_2F + HF$$

$$NH_2F + F_2 \longrightarrow NHF_2 + HF$$

$$NH_2F + F_2 \longrightarrow NF_3 + HF$$

Electrolysis : $NH_4HF_2 + 12F = 2NF_3 + 10HF$

NF_3 is a colourless poisonous gas and a very stable molecule. It reacts with steam :

$$2NF_3 + 3H_2O = 6HF + NO_2 + NO$$

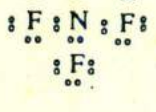
NCl_3 is a highly explosive compound. It is obtained by the reaction of Cl_2 with NH_4Cl or NH_3 and also by the action of HOCl on NH_3 :

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl$$

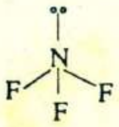
$$NH_3 + 3HOCl = NCl_3 + 3H_2O$$

NCl_3 is an oily liquid and explodes violently even on exposure to light.

The stability in the case of NF_3 has been attributed to the partial ionic bonding between N and F although NCl_3 and NF_3 both are shown to have covalent bond using the tetrahedral sp^3 bonds of nitrogen :



Lewis structure



Tetrahedral structure

In effect, NCl_3 and NF_3 have pyramidal shapes. The energy released on breaking the NCl_3 bond is tremendous :

$$2NCl_3 \ = \ N_2 + 3Cl_2 + 111 \text{ Kcal}$$

Oxides of Nitrogen

Nitrogen froms oxides having oxidation state from +1 to + 6. Some of the important oxides are given in Table 20.3 indicating their formula, name, structures and reactivities. The structures given do not represent the actual distributions of electrons but give only the total number of electrons involved in the formation of the molecules. Molecules having unpaired electrons must, as a rule, show the resonance structure due to the shifts of the electrons from the paired to unpaired state.

Nitrous oxide, N_2O : (i) When ammonium nitrate, NH_4NO_3, is gently heated, nitrous oxide, N_2O, is formed :

$$NH_4NO_3 \ = \ N_2O + 2H_2O$$

This is oxidation-reduction reaction in which N of NH_4^+ is oxidized by N in the NO_3^- ion. The heating of NH_4NO_3 must be gentle, otherwise explosion may occur.

(ii) N_2O is also obtained from NH_2OH being oxidized with $NaNO_3$, $CuSO_4$, $FeCl_3$ etc :

$$NH_2OH + HNO_2 \ = \ N_2O + 2H_2O$$

(iii) N_2O is also formed when Zn reacts with dil HNO_3 :

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

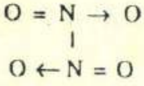
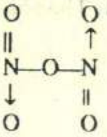
N_2O is a colourless gas with pleasant taste and odour and when inhaled it produces hysterical laughter. Hence its name is *laughing gas*. N_2O is isoelectronic with CO_2 with which it forms mixed crystals. N_2O does not react with H_2O or alkalies. However, hyponitrous acid, $H_2N_2O_2$, gives N_2O on dehydration.

N_2O is not very reactive but has the tendency to release N_2 and O_2, which gives it reactivity when heated. N_2O then reacts with S and P in the heated condition :

$$S + 2N_2O \ = \ SO_2 + 2N_2$$

N_2O is oxidized to NO by strong oxidizing agents, such as $KMnO_4$.

Table 20·3. Oxides of Nitrogen.

Formula	*Structures*	*Oxn. states of N*	*Name*	*Colour*	*Reactivity*
N_2O	$N\equiv N\rightarrow O$	+1	Nitrous oxide	Colourless gas	Uureactive
NO	$\left\{\begin{array}{l}\overset{\circ}{N}=O\\ \\ N=\overset{\circ}{O}\end{array}\right.$ or	+2	Nitric oxide	Colourless gas	Reactive
N_2O_3	$O=N-O-N=O$	+3	di-Nitrogen trioxide	Blue solid	Dissociated as gas
NO_2	$O\leftarrow N\rightarrow O$	+4	Nitrogen peroxide	Brown gas	Reactive
N_2O_4	 $\begin{array}{c}O=N\rightarrow O\\ \vert\\ O\leftarrow N=O\end{array}$	+4	Nitrogen tetroxide	Colourless gas	Dissociated as gas & liquid
N_2O_5	 $\begin{array}{ccc}O & & O\\ \Vert & & \uparrow\\ N & -O- & N\\ \downarrow & & \Vert\\ O & & O\end{array}$	+5	Nitrogen pentoxide	Colourless solid	Ionic
NO_3 or N_2O_6	—	+6	—	Colourless solid	Unstable

N_2O has all the atoms in a line and possesses resonance structure :

$$:\ddot{N}::N::\underset{\cdot\cdot}{\ddot{O}}\longleftrightarrow\ :N:::N:\underset{\cdot\cdot}{\ddot{O}}:$$

N_2O does not decompose at room temperature but dissociates into N_2 and O_2 when heated at above 560°C.

Nitric oxide, NO : There are various ways of preparing NO :—

(i) Heating Cu turnings with conc HNO_3 :

$$3\,Cu + 8NHO_2 = 2NO + 3\,Cu(NO_3)_2 + 4H_2O$$

(ii) Pure NO is obtained by heating $FeSO_4$ with KNO_3 and H_2SO_4 :

$$2KNO_3 + 6FeSO4 + 4H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + 2NO + 4H_2O$$

(iii) By the reaction of $NaNO_2$ and KI in presence of H_2SO_4, pure NO is obtained :

$$2NaNO_2 + 3H_2SO_4 + 2KI = 2NaHSO_4 + K_2SO_4 + 2NO + 2H_2O + I_2$$

(iv) N_2 and O_2 combine in the arc process in presence of platinum. NH_3 may also be oxidized to NO :

$$N_2 + O_2 = 2NO \qquad 2NH_3 + 5\,O_2 = 4NO + 6H_2O$$

NO is a colourless gas but rapidly takes up O_2 from the air to form NO_2 which is brown-red. The reaction is reversible at room temperature.

$$2NO + O_2 \rightleftharpoons 2NO_2 \text{ or } N_2O_4$$

NO is readily absorbed in $FeSO_4$ solution forming intensely brown solution, $FeSO_4.NO$ or $[Fe(NO)]^{+2}$ ions actually $[Fe\,(NO)(H_2O)_5]^{+2}$ with is used in NO_3^- test.

NO acts both as a reducing agent and an oxidizing agent. Thus NO oxidize H_2SO_3 to H_2SO_4 :

NO is oxidized by $KMnO_4$ solution to HNO_3.

NO is an odd molecule and has an unpaired electron :

$$:\overset{\infty}{N}::\overset{\circ}{O}: \qquad\qquad :\overset{\circ}{N}::\overset{\infty}{O}:$$

NO easily forms nitrosonium or nitrosyl ion (NO^+) by losing the odd electron as in the case of NO^+Cl^- (nitrosyl chloride), NO^+HSO_4- (nitrosonium bisulphate), $NO^+\,ClO_4-$ (nitrosyl perchlorate).

Odd molecules are defined as molecules containing odd number of electrons in their outer electron level, such as NO (5+6=11) and NO_2 (5+12=17). The odd unpaired electron is not confined to a specific orbital of nitrogen or oxygen atom in NO but it is said to be "delocalized". The unpaired electron is present in an orbital which is combined to both N and O.

Dinitrogen trioxide, N_2O_3 : When a mixture of one part of NO and one part of NO_2 is cooled, it becomes a blue liquid at -21°C and freezes to a blue solid. On warming the equilibrium gas mixture is again formed :

$$N_2O_3 \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} NO + NO_2$$

It is also obtained by the action of HNO_3 on As_2O_3 :

$$As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3$$

When N_2O_3 gas is passed into aqueous KOH, the product is KNO_2 :

$$N_2O_3 + 2KOH = 2KNO_2 + H_2O$$

The structure is ambiguous containing both ONONO and N—N bonds. N_2O_3 is an acidic oxide being the anhydride of HNO_2.

Nitrogen peroxide, NO_2: NO_2, and Nitrogen tetroxide, N_2O_4 : NO_2 is prepared by heating $Pb(NO_3)_2$:

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

When Cu reacts with very concentrated HNO_3 in the heated condition, NO_2 is evolved :

NO_2 is commercially formed when NO is exposed to air as the deep brown coloured gas :

$$2NO + O_2 = 2NO_2$$

At ordinary temperature NO_2 is in equilibrium with its dimer, N_2O_4, but at the higher temperature N_2O_4 is dissociated into NO_2 :

$$2NO_2 \rightleftharpoons N_2O_4$$

N_2O_4 is a colourless gas. In the solid state and at low temperature N_2O_4 predominates since it is colourless. At higher temperature the colour becomes intense brown because of predominance of NO_2 :

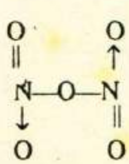
NO_2 is absorbed in alkalis to form both nitrites and nitrates :

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

NO_2 is an acidic oxide.

NO_2 also contains an odd number of electron. The resonance forms are :

N_2O_5 is represented as



OXYACIDS OF NITROGEN

Nitrogen forms a series of oxyacid. The most important of these are the following :—

1. Nitric Acide, HNO_3.
2. Nitrous Acid, HNO_2.
3. Hyponitrous Acid, HNO or $H_2N_2O_2$.

Nitric acid, HNO_3

Nitric acid is one of the most important chemicals for industrial use. It has been manufactured from $NaNO_3$ or KNO_3 since the days of alchemists. Now-a-days other methods for the manufacture of HNO_3 have been developed. Generally, the following methods are used for large-scale production of HNO_3.

(i) **From nitrates** : HNO_3 was produced commercially by heating a mixture of $NaNO_3$ and conc H_2SO_4. The charge of $NaNO_3$ and H_2SO_4 is taken in cast iron retorts and heated to about 200°C when HNO_3 is distilled off :

$$NaNO_3 + H_2SO_4 \rightleftharpoons NaHSO_4 + HNO_3$$

At ordinary temperature the reaction is reversible and an equilibrium is established. But HNO_3 boils at 83°C and H_2SO_4 boils at 338°C and the solid $NaNO_3$ are not volatile, the HNO_3 formed is readily distilled. The distillate is passed through water-cooled silica tubes to condense the conc HNO_3 first. Fumes of HNO_3 escaping condensation is scrubbed with cold water and collected as dilute HNO_3. The yellow colour of HNO_3 is due to dissolved NO_2 and is removed by distillation in vacuum.

(ii) From air (Arc process) : Air (which contains mainly N_2 and O_2) is subjected to high tension electric discharge or passed through an arc at temperature of above 3000°C. N_2 and O_2 combine to give NO.

$$N_2 + O_2 \rightleftharpoons 2NO - 43.2 \text{ Kcal}$$

The endothermic reaction gives only about 5% conversion at 3000°C. On cooling NO combines with more O_2 to form NO_2 :

$$2NO + O_2 = 2 NO_2$$

The brown fumes of NO_2 is washed with water on counter current principle, i.e., the gases and vapours going upward and water trickling downward in quartz vessel :

$$\begin{aligned} 2NO_2 + H_2O &= HNO_3 + HNO_2 \\ NO + NO_2 + H_2O &= 2 HNO_2 \\ 3HNO_2 &= HNO_3 + 2NO + H_2O \end{aligned}$$

The escaping gases may contain some NO and NO_2 and are absorbed in alkali solutions to produce $NaNO_2$:

$$NO + NO_2 + Na_2CO_3 = 2NaNO_2 + CO_2$$

This is one of the processes for the fixation of atmospheric nitrogen. The high cost of electricity and low yield of HNO_3 has led to the discontinuation of the process.

It has been estimated that in nature about 40 million tons of nitrogen is fixed annually as a result of electric discharge during lightning and other photochemical phenomena.

(iii) From ammonia (Ostwald's Process) : This process consists of the oxididation of ammonia to NO and NO to NO_2 which with water gives HNO_3. Ammonia mixed with 10 times its volume of air and heated to 600°C is passed through a converter containing platinum gauze which acts as a catalyst. NH_3 is oxidized to NO :

$$4NH_3 + 5\,O_2 \;=\; 4NO + 6H_2O + 215 \text{ Kcal}$$

The exothermic reaction proceeds without supply of heat except the initial heating. About 90% of NH_3 is converted to NO. Additional air is admitted to cool the mixture and oxidize NO to NO_2 :

$$2\,NO + O_2 \;=\; 2NO_2 + 27.8 \text{ Kcal}$$

The mixed gases containing NO, NO_2, unreacted N_2 and O_2 etc. are passed in an absorption tower on counter current principle where HNO_3 is formed :

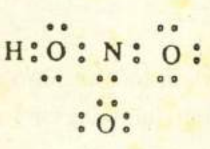
$$3NO_2 + H_2O \;=\; 2\,HNO_3 + NO$$

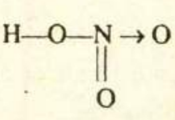
NO is returned to absorption tower with more air.

Pure HNO_3 is made by distillation of the product under reduced pressure and passing ozone to the distillate. Distillation of an aqueous solution of HNO_3 leads to a constant boiling mixture when the concentration of HNO_3 is 68.4% at 122°C. Pure HNO_3 is obtained from this mixture by distillation in presence of H_2SO_4.

Fuming HNO_3 is a red liquid and is made by bubbling NO_2 gas into concentrated HNO_3. Fuming HNO_3 reacts more vigorously with many substances.

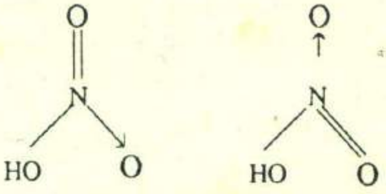
Properties of HNO_3: It is a fuming liquid, miscible with water and has a high vapour pressure. Concentrated acid gives off NO_2 by light and heat. Nitric acid has the following electronic formula :—



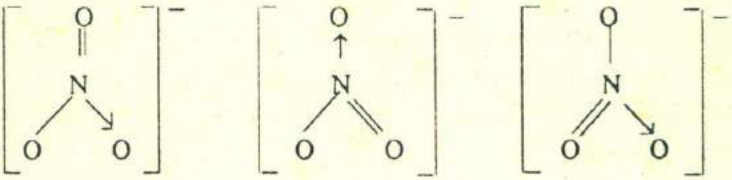


$$H—O—\underset{\underset{O}{\|}}{N} \rightarrow O$$

In fact, NO_3 group of HNO_3 has a triangular arrangement and has a resonating structure :



The NO_3^- ion, therefore, has three different contributing structures :



The unstable nature of HNO_3 is shown by its decomposition to NO_2 and O_2 when heated :

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

Nitric acid exhibits three types of properties : (a) Acid properties, (b) Oxidizing agent, (c) Nitrating agent.

(a) HNO_3 as an acid : This is illustrated by the following equations : When nitric acid reacts with bases, such as metal oxides, hydroxides and carbonates to produce metal nitrates and water. In dilute solution HNO_3 is completely dissociated into H^+ ions and NO_3^- ions. Hence HNO_3 in dilute solutions behaves as an acid. Thus,

$$CuO + 2\,HNO_3 = Cu(NO_3)_2 + H_2O$$

$$Mg(OH)_2 + 2\,HNO_3 = Mg(NO_3)_2 + 2H_2O$$

$$CaCO_3 + 2\,HNO_3 = Ca(NO_3)_2 + H_2O + CO_2$$

With Mg and some sulphides in dilute solution, it evolves H_2 or H_2S as the case may be :

$$Mg + 2\,HNO_3 = Mg(NO_3)_2 + H_2$$

$$MnS + 2\,HNO_3 = Mn(NO_3)_2 + H_2S$$

(b) HNO_3 as an oxidizing agent : Nitric acid is a powerful oxidizing agent. The reduction products of HNO_3 are N_2 or one or more of the nitrogen compounds, such as N_2O, NO, NO_2, NH_3. This depends upon three factors : (i) Acid concentration ; (ii) nature of the reducing agents ; (iii) temperature of the reactions.

The oxidizing actions of HNO_3 may be classified according to the nature of reducing agent as follows :—

(a) Action of HNO_3 on metals : In dilute solution with possibly Mg only, HNO_3 behaves as an acid liberating H_2. But with other metals the oxidizing actions predominate. Au and Pt do not react with HNO_3 under any condition. Although the reduction products may be a mixture of nitrogen compounds, but for the sake of simplicity the following points may be remembered for writing the equations :

HNO_3 in extremely dilute solutions gives NH_3. (Change of oxidation number of N from +5 to −3).

HNO_3 in very dilute solutions gives N_2O (Change of oxidation number of N from +5 to +1).

HNO_3 in dilute solution gives NO (Change of oxidation number of N from +5 to +2).

HNO_3 in concentrated solution and hot condition gives NO_2 (Change of oxidation number of N from +5 to +4).

HNO_3 vapour passed over red-hot metal gives N_2 (Change of oxidation number of N from +5 to 0).

(i) Zn, Fe and Sn with extremely dilute HNO_3 in the cold give NH_3 which combines with excess HNO_3 to form NH_4NO_3 :

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_4NO_3$$

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

(ii) Zn reacts with very dilute HNO_3 in the cold to give N_2O :

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(iii) In the ordinary conditions the dilute HNO_3 always produces NO. This is the most common reaction product of HNO_3 with metals in dilute conditions (moderately) and also whenever HNO_3 acts with any substance in aqueous solutions :

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

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

With Hg, NO is formed. Dilute HNO_3 gives $Hg_2(NO_3)_2$ but conc HNO_3 gives $Hg(NO_3)_2$.

(iv) In concentrated and hot condition most metals react with HNO_3 to give NO_2 :

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

$$Fe + 6\,HNO_3 = Fe(NO_3)_2 + 3NO + 3H_2O$$

(v) When HNO_3 in the vapour form is passed over heated Cu nitrogen gas is evolved :

$$5Cu + 10\,HNO_3 \rightarrow 5Cu(NO_3)_2 + 6H_2O + N_2$$

$Cu(NO_3)_2$ formed may also be decomposed to CuO and NO_2.

Passive condition :

Some of the metals in concentrated HNO_3 are rendered *Passive* and no action takes place with Fe, Cr, Ni, Co and even Al. This happens particularly when the metals are pure and HNO_3 is also pure. Impurities in metals and in HNO_3 produce vigorous reactions possibly due to the electron transfer by setting up miniature galvanic cells.

(b) Action of HNO_3 on non-metals : Non-metals, such as S, C, I_2, etc. are oxidized by concentrated HNO_3 in the hot condition evolving NO_2 and the oxyacids or oxides of the non-metals :

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

$$S + 4HNO_3 = H_2SO_4 + 6NO_2 + 2H_2O$$

$$P + 5HNO_3 = H_3PO_4 + 10NO_2 + H_2O$$

$$I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O$$

(c) Action of HNO_3 on compounds in solutions : In aqueous solutions HNO_3 is always converted to NO :

$$3H_2S + 2HNO_3 = 3S + 2NO + 4H_2O$$

$$3Fe^{+2} + HNO_3 + 3H^+ = 3Fe^{+3} + NO + 2H_2O$$

But compounds when heated with concentrated HNO_3 give NO_2 :

$$SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$$

$$PbS + HNO_3 \rightarrow Pb(NO_3)_2 + PbSO_4 + NO_2$$

$$CuS + 8HNO_3 = CuSO_4 + 8NO_2 + 4H_2O$$

There are some metals like Au and Pt and also compounds, such as HgS, which are not oxidized by HNO_3 at all. Such substances can be oxidized by means of a mixture of HNO_3 and HCl in volume ratio of 1 : 3. The mixture is known as *Aqua Regia.* HNO_3 oxidizes HCl to form Cl_2 and NOCl (nitrosyl chloride). The formation of chlorocmplexes of the metal facilitates the reactions :

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$$

$$\begin{tikzcd} HgS \arrow[r, leftrightharpoons] & Hg^{+2} \arrow[d, "4Cl^-"] & + & S^{-2} \arrow[d, "2HNO_3"] \\ & HgCl_4^{-2} & & S + NO_2 + H_2O \end{tikzcd}$$

(d) Nitration reactions of HNO_3 : These reactions generally take place with organic compounds. Thus, nitration of glycerine is carried out with HNO_3 mixed with H_2SO_4 to absorb the H_2O formed :

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O$$

The reaction of HNO_3 with H_2SO_4 produces NO_2^+ cations which reacts with organic molecules by an atom or group of atoms originally present. Thus, TNT is formed by nitrating toluene in presence of H_2SO_4 :

$$CH_3C_6H_5 + 3HNO_3 = CH_3C_6H_2(NO_2)_3 + 2H_2O$$

Uses of HNO_3 : (1) It is used as an active oxidizing agent. (2) Manufacture of explosives, T. N. T., dyes, plastics, drugs etc. (3) Nitrates are used as fertilizers.

Nitrous acid, HNO_2

HNO_2 is obtained in solution only. Pure HNO_2 has not been isolated because it is unstable. Even in solution it decomposes to form HNO_3 and NO :

$$3HNO_2 = HNO_3 + 2\,NO + H_2O$$

It is obtained by dissolving N_2O_3 in water at ice-cold temperature :

$$N_2O_3 + H_2O = 2\,HNO_2$$

HNO_2 is formed when $Ba(NO_2)_2$ is treated with H_2SO_4 :

HNO_2 is a weak acid in solution. It acts as an *oxidizing agent* towards strong reducing agents and also as a *reducing agent* in presence of active oxidizing agents. HNO_2 itself cannot be isolated from solution since it decomposes easily.

$NaNO_2$ or KNO_2 in H_2SO_4 has the same action as HNO_2 solution. Hence, whenever HNO_2 is required it is used in the form of $NaNO_2$.

HNO_2 is oxidized by $KMnO_4$ or H_2O_2 or halogens :

$$2KMnO_4 + 3H_2SO_4 + 5NaNO_2 = K_2SO_4 + 2MnSO_4 + 2H_2O + 5NaNO_3$$

$$H_2O_2 + NaNO_2 = NaNO_3 + H_2O$$

$$Br_2 + NaNO_2 + H_2O = NaNO_3 + 2HBr$$

HNO_2 oxidizes KI to I_2 in presence of acid :

$$2KI + 2HNO_2 + H_2SO_4 = I_2 + 2NO + 2H_2O + K_2SO_4$$

$SnCl_2$ is oxidized to $SnCl_4$:

$$SnCl_2 + 2NaNO_2 + 4HCl = SnCl_4 + 2H_2O + 2NO + 2NaCl$$

$$H_2S + 2NaNO_2 + H_2SO_4 = S + 2NO + Na_2SO_4 + 2H_2O$$

Sodium nitrite, $NaNO_2$, is produced from $NaNO_3$ by heating with Pb or coke :

$$NaNO_3 + Pb \rightarrow NaNO_2 + PbO$$

$$NaNO_3 + C \rightarrow NaNO_2 + CO$$

HNO_2 has the structure :

$$\mathrm{H:\underset{\cdot\cdot}{\ddot{O}}:\ddot{N}::\underset{\cdot\cdot}{\ddot{O}}} \quad \text{or} \quad \mathrm{HO-\ddot{N}=O}$$

The presence of unshared pair on the nitrogen imparts basic and reducing properties to HNO_2. The N = O double bond gives the acid and oxidizing properties. $-NO_2$ ion is also a coordinating agent and coordinates as — ONO in some cases as in $Na_2Co(NO_2)_6$.

$NaNO_2$ is used in industry for the manufacture of dyes. Thus, when cooled aniline is treated with HNO_2 it gives the diazonium base which on coupling with other molecules, such as phenol, gives bright coloured dyes:

$$C_6H_5NH_2 + HNO_2 \rightarrow C_6H_5N = NOH + H_2O$$

Hyponitrous acid, $H_2N_2O_2$

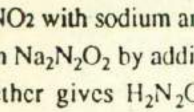
The salts of hyponitrous acid are generally made by reducing $NaNO_3$ or $NaNO_2$ with sodium amalgam (Na—Hg) giving $Na_2N_2O_2$.Ag-salt is precipitated from $Na_2N_2O_2$ by adding $AgNO_3$. Silver hyponitrite when reacted with HCl gas in ether gives $H_2N_2O_2$ in the ether solution. On evaporation the solution $H_2N_2O_2$ is obtained :

$$2\,NaNO_2 + 8H \xrightarrow{Na\text{-}Hg} Na_2N_2O_2 + 4H_2O$$

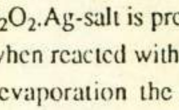
$$Na_2N_2O_2 + 2AgNO_3 \longrightarrow Ag_2N_2O_2 + 2NaNO_3$$

$$Ag_2N_2O_2 + 2HCl \xrightarrow{ether} 2AgCl + H_2N_2O_2$$

$K_2N_2O_2$ is also obtained by electrolysing KNO_2 solution. H_2 is evolved at the cathode which reduces KNO_2 to $K_2N_2O_2$. $H_2N_2O_2$ is a white crystalline solid having the formula :



or



All hyponitrites have also got the same structure :

$$NaO — N = N—ONa$$

$H_2N_2O_2$ gives a Pb-salt with Pb acetate and Ag-salt with $AgNO_3$. The Ag-salt, $Ag_2N_2O_2$, is soluble in acid but not in ammonia. $Na_2N_2O_2$ and also

$NaHN_2O_2$ are formed. The ethyl derivatives have also been prepared having the composition $(C_2H_5)_2N_2O_2$. The formula $H_2N_2O_2$ is supported from the vapour density measurements. The presence of azo group, —N = NO, is supported from the decomposition of $C_2H_5ON = NOC_2O_5$ which gives N_2 :

$$C_2H_5O{-}N = N{-}OC_2H_5 \rightarrow C_2H_5OH + CH_3CHO + N_2$$

PHOSPHORUS

Phosphorus is the second element of the nitrogen group. Although in many respects the chemistry of P resembles that of nitrogen as mentioned earlier and shows the gradation in properties, there are some marked contrasts as well.

Comparison between N and P

1. N2 occurs in nature in the free state, P never occurs in the free state. In fact, phosphorus is the only element of the group V which does not occur in the free state.

2. The electronic structures of N and P are :

$N{-}1s^22s^22p^3$

$P{-}1s^22s^22p^63s^23p^3$

3. N_2 is an active gas whereas P is highly reactive in its white modification. The strength of $P \equiv P$ bond is much less than $N \equiv N$ bond.

4. N_2 is diatomic ; P is tetra-atomic (P_4) at ordinary condition.

5. Nitrogen combines with O2 only at the high temperature in electric arc. Phosphorus burns in air on exposure liberating energy.

6. HNO_3 and HNO_2 are strong oxidizing agents whereas H_3PO_4 and H_3PO_3 are very weak oxidizing agents.

7. PH_3 is a greater reducing agent than NH_3.

8. Nitrogen forms double and triple bonds but such bonds in phosphorus are not common.

9. In aqueous solution N can exist as NH_4^+, NO_3^- and NO_2^- ions. Whereas P can exist as HPO_3^{-2}, PO_4^{-3} and such other ions.

10. Trivalent P is a greater reducing agent than trivalent N or trivalent As. This is a departure from the general gradation of properties in the Periodic Table.

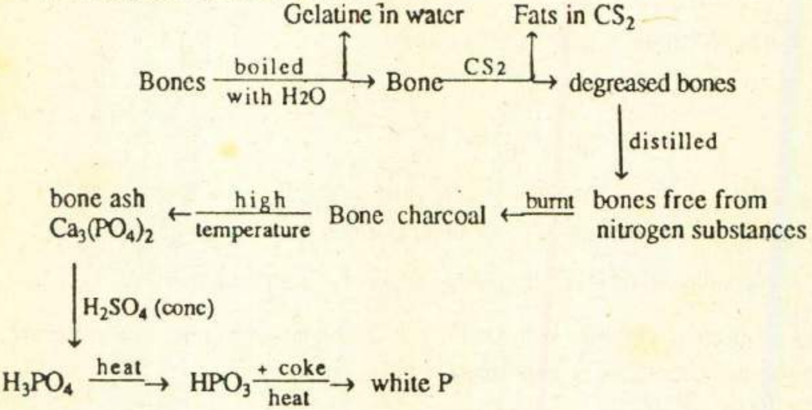
Occurrence of P : Because it is very reactive with O_2, phosphorus does not occur free in nature. It occurs as :

Phosphorite—$Ca_3(PO_4)_2$
Fluorapatite—$Ca_{10}F_2(PO_4)_6$ or $3Ca_3(PO_4)_2.4CaF_2$
Chlorapatite—$Ca_{10}Cl_2(PO_4)_6$ or $3Ca_3(PO_4)_2.CaCl_2$

Phosphorus is essential to plants and animals ; bones, teeth and even muscle tissues contain P. Foods, such as eggs, beans, milk etc. provide P. Plants take up P from soil as soluble phosphates.

Preparation of phosphorus : White phosphorus is obtained from bone ash or a mineral phosphate. The flow sheet of the preparation is given below.

(a) Phosphorus from bone ash :



(b) Phosphorus from phosphate rock : Phosphorus is commercially obtained from phosphate rocks, $Ca_3(PO_4)_2$, by reduction with carbon in presence of silica (SiO_2) in an electric furnace heated by two stout carbon electrodes to temperatures of about 1500°C :

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 10CO + P_4$$

The phosphorus is distilled off and condensed to the solid state or may be burnt into P_2O_5, i.e., P_4O_{10}, for the production of other compounds of P. The slag of $CaSiO_3$ along with CaF_2 or ferrophosphorus (formed from impurities in the ore or from apatite ore) is drawn off from the bottom of the furnace in the molten state. At the temperature of about 1150°C, P_2O_5 is formed which is converted to P_4 at about 1500°C :

$$Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$$

$$2P_2O_5 + 10\,C = P_4 + 10\,CO$$

The crude P is purified by melting under water and adding an oxidizing agent, such as $Na_2Cr_2O_7$, in presence of some acid and filtered through canvas bags. The pure P is cast into sticks and stored under water.

Properties of P : (1) The well-known white phosphorus is a wax-like thing, having low melting point of 44°C and it boils at 280°. It is volatile and readily soluble in CS_2.

(2) It is spontaneously inflammable in air and is poisonous. It is, therefore. stored and worked under water in which it is insoluble.

(3) The solid as well as the vapour consists of discrete molecule consisting of P_4 tetrahedra, each P shares a pair of electrons with each of the three other P Each P has one lone pair of electrons as shown in Fig. 20—2.

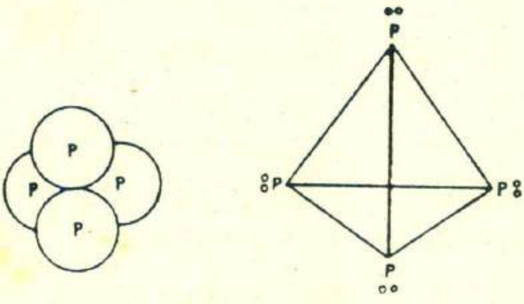


Fig. 20—2. P_4 molecule.

(4) Phosphorus gives green glow in the dark, the phenomenon is known as *phosphorescence.*

(5) In the vapour state at very high temperature P consists of P_2 molecules similar to N_2 i.e. (: P : : : P :).

(6) White P is converted to red P, another allotropic from, by heating to 230—400°C in iron retorts in absence of air. The change is catalysed by a trace of iodine :

$$P\,(\text{white}) \rightleftharpoons P\,(\text{red}) + 4\ \text{Kcal}$$

White P changes to red P slowly on exposure to light. Red phosphorus consists of aggregates and, because heat is liberated during the change from white P to red P, the heat of combustion of red P is less than that of white P. It does not inflame in air at ordinary temperature and is insoluble in CS_2. It is much less reactive and not poisonous. Its melting point is 593°C. A black variety of P is also formed which is electrically conductive having lamellar structure like graphite.

Reactions of Phosphorus

(a) Reaction with oxygen : P has ignition temperature of only 35—45°C and hence it burns spontaneously due to the initial slow reaction of P with atmospheric oxygen at room temperature. Depending upon the supply of oxygen. P_4O_{10} and P_4O_6 may be formed :

$$P_4 + 5O_2 \longrightarrow P_4O_{10}\ (\text{ample supply of } O_2)$$

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

(b) Reactions with H_2 : P does not react with H_2 in the elementary state. hydrides of P are obtained by reaction with alkali.

(c) Reaction with halogens : P reacts directly with all halogens forming PX_3. The reactions with F_2 is very vigorous :

$$P_4 + 6F_2 \rightarrow 4PF_3\ (\text{colourless gas})$$

$$P_4 + 6Cl_2 \rightarrow 4PCl_3\ (\text{colourless liquid}))$$

$$P_4 + 6Br_2 \rightarrow 4PBr_3\ (\text{colourless liquid}))$$

$$P_4 + 6I_2 \rightarrow 4PI_3\ (\text{orange solid})$$

(d) Reactions with metals : Alkali and alkaline earth metals react with P on heating forming phosphides like nitrides, e. g., Na_3P, Ca_3P_2 etc.

(e) Reactions with HNO_3 : P is oxidized to H_3PO_4 by conc HNO_3 :

$$P + 5HNO_3 = H_3PO_4 + 5NO_2 + H_2O$$

(f) Reaction with alkali : P reacts with NaOH to give PH_3 :

$$4P + 2H_2O + 3NaOH = PH_3 + 3NaH_2PO_2$$

(g) Reactions with S : With S it combines on heating to form P_4S_3, P_4S_7 and P_4S_{10} depending on the ratios of the components used and the reaction conditions.

Red phosphorus : By heating white P alone or in light or in presence of a catalyst, such as iodine, it produces the allotropic modification of phosphorus.

Properties of red P : (1) Red P is non-poisonous. (2) It is insoluble in CS_2. (3) Chemically it is less reactive than white phosphorus.

Uses of Phosphorus

Phosphorus is used in,

(1) Manufacture of matches.

(2) Production of acids of phosphorus and their salts for fertilizers.

(3) Special alloys, such as phosphor bronze.

(4) In incendiary bombs and explosives.

Match Industry : Formerly white phosphorus was used in the manufacture of matches, but workers in the factory suffered from *Phossy jaw* or necrosis of the bones. It has now been replaced by phosphorus sulphide, P_4S_3, and also in safety match by antimony trisulphide, Sb_2S_3.

Three types of matches have been developed : (1) Lucifer matches, (2) safety friction matches and (3) safety matches.

Lucifer matches and friction matches consists of P_4S_3 at the tip of the match-head together with $KClO_3$, sulphur, sand and binding material (glue). The stick is impregnated with ammonium phosphate and paraffin. These matches can be lighted by striking anywhere on a rough surface.

The heads of the safety matches contain no phosphorus but Sb_2S_3 mixed with an oxidizing agent, such as $K_2Cr_2O_7$ or red lead and fixed with glue. The surface on the side of the box consists of red phosphorus and powdered glass mixed with glue. The head of the safety match can be lighted only on rubbing against this special surface on the side of the match box. It is not ignited by friction anywhere else. The glass powder or sand is added to reduce sensitivity of the matches and to provide friction.

The match sticks are given initial coat of sulphur or paraffin to help combustion. Impregnation in borax or ammonium phosphate solution prevents the flame from glowing after it has been extinguished.

The match industry is now a highly mechanized process. The splints are produced in machines from logs of wood and also the flat thin sheets of wood which are made into boxes. The process of match industry is highly automatic. From the start to the finish the packing is done by automation.

Compounds of Phosphorus

1. Hydrides of phosphorus : P forms a series of hydrides, the most important of which is *phosphine*, PH_3. Others are P_2H_4, $P_{12}H_6$, P_5H_2,P_9H_2. Phosphine is a gas, P_2H_4 is liquid and all others are solid.

PH_3 is prepared by heating white phosphorus in a concentrated solution of NaOH. Phosphine prepared in this way is spontaneously inflammable forming a fog of phosphoric acid when bubbled through water. The fog rise in the air in the form of smoke rings :

$$P_4 + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3$$

It has been found that pure PH_3 is not inflammable, but prepared by the above method, it contains some P_2H_4 which ignites with PH_3.

PH_3 is also formed by the reactions :

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

$$AlP + 5H_2O \xrightarrow{acid} Al(OH)_3 + PH_3$$

The reaction of O_2 (air) on PH_3 is given by the equation :

$$PH_3 + 2\,O_2 = H_3PO_4$$

Non-inflammable PH_3 is obtained when P is heated with alcoholic solution of KOH or when Ca_3P_2 is reacted with HCl.

PH_3 is a much weaker base than NH_3 because it shows less tendency to donate a pair of electrons to a H^+ ion. PH_3 is decomposed on heating to P_4 and H_2. PH_3 combines with HCl, HBr or HI to form *phosphonium compounds*, PH_4Cl, PH_4Br and PH_4I. In aqueous solutions PH_4^+, ions are unstable, easily hydrolysed and give off PH_3. PH_4^+ ion is essentially a strong acid :

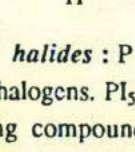
$$PH_4I + H_2O = PH_3 + HI + H_2O$$

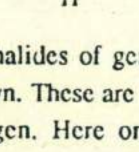
PH_4I is best obtained by the reaction of white P with iodine in CS_2 solution to which water is added while heating :

$$9P + 5I + 16H_2O = 5PH_4I + 4H_3PO_4$$

Like NH_3, phosphine forms coordination compounds, e. g. $Cl_3B{:}PH_3$.

PH_3 has the same structure as NH_3 using sp^3 bonds of P in the tetrahedral positions with a lone pair of electrons at one corner. But P—H bonds are much larger than N—H and also H—P—H angle is smaller than H—N—H angle :





Phosphorus halides : P forms the halides of general formula PX_3 and PX_5 with all the halogens. PI_5 is not known. These are much more stable than the corresponding compounds of nitrogen. Here only PCl_3 and PCl_5 are described.

Phosphorus trichloride, PCl_3, is prepared by passing dry Cl_2 over molten phosphorus :

$$P_4 + 6Cl_2 = 4PCl_3$$

It can also be prepared by the action of thionyl chloride on P :

$$2P + 4SOCl_2 = PCl_3 + 2SO_2 + S_2Cl_2$$

PCl_3 is a colourless liquid and is completely hydrolysed by water to give H_3PO_3 and HCl, and even in moist air:

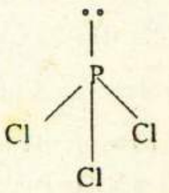
$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

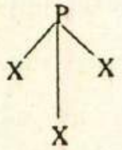
Generally, the phosphorus trihalides are rapidly attacked by water:

$$PX_3 + 3H_2O \rightarrow H_3PO_3 + 3\,HX$$

These reaction are used for the preparation of HBr and HI.

PCl_3 has the pyramidal structure given below in which P uses the sp^3 orbitals to form the bonds with 3Cl :





The bonds may also be described as due to the sp^3 bonds of P as in PH_3 and NH_3. PCl_3 can replace CO in $Ni(CO)_4$ forming $Ni(PCl_3)_4$ showing the coordinating action of PCl_3.

Phosphorus pentachloride, PCl_5, is prepared by oxidizing PCl_3 with excess of Cl_2 :

$$PCl_3 + Cl_2 = PCl_5$$

Sulphuryl chloride also gives PCl_5 with P or PCl_3 :

$$P_4 + 10SO_2Cl_2 = 4PCl_5 + 10SO_2$$

$$PCl_3 + SO_2Cl_2 = PCl_5 + SO_2$$

PCl_5 is a straw-coloured solid and dissociates reversibly and sublimes :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

PCl_5 is hydrolysed as :

$$PCl_5 + H_2O = POCl_3 + 2HCl$$

Excess H_2O gives :

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

In the vapour and liquid state PCl_5 has a trigonal bipyramidal structure as given in Fig. 20—3.

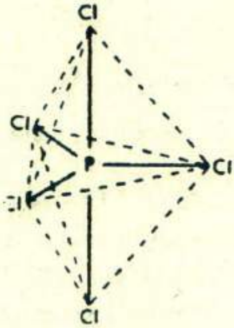


Fig. 20—3. PCl_5 molecule.

The reason why PCl_5 is formed and not NCl_5 is that N atom having the electronic structure $1s^2\ 2s^2\ 2p^3$ has no stable **d** orbitals available to form 5. bonds by using $3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^1$ or $3s^1\ 3p^3\ 3d^1$ (sp^3d) hybrid bonding orbitals.

In the solid state PCl_5 consists of an ionic structure $[PCl_4]^+[PCl_6]^-$. The cation $[PCl_4]^+$ has the tetrahedral structure and the anion $[PCl_6]^-$ has octahedral structure.

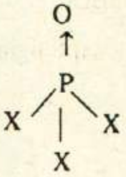
Phosphorus oxyhalides, POX_3, are readily obtained by the action of PCl_5 on P_2O_5, i.e., P_4O_{10}:

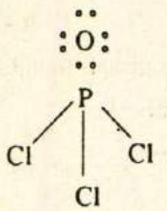
$$6PX_5 + P_4O_{10} = 10POX_3$$

Partial hydrolysis of PCl_5 gives $POCl_3$ as mentioned before.POX_3 is completely hydrolysed in water :

$$POX_3 + 3H_2O = H_3PO_4 + 3HX$$

The structure is tetrahedral as shown below :





Oxides of Phosphorus

P forms several oxides of which P_4O_6, P_8O_{16} and P_4O_{10} are well-defined.

The combustion of P in air generally produces a mixture of P_4O_6 and P_4O_{10}.

Phosphorus(III)oxides, P_4O_6 : This compound is often called phosphorus trioxide. It is a white crystalline solid having melting point of 22.5°C. On heating, it is decomposed to red P and P_8O_{16}. P_4O_6 is made by burning white P in a limited supply of air. With cold water P_4O_6 gives H_3PO_3 but with hot water it gives H_3PO_4 and PH_3 :

$$P_4 + 3O_2 \rightarrow P_4O_6$$

$$P_4 + 6H_2O \rightarrow 4H_3PO_3$$

$$4H_3PO_3 \xrightarrow{\text{heat}} 3H_3PO_4 + PH_3$$

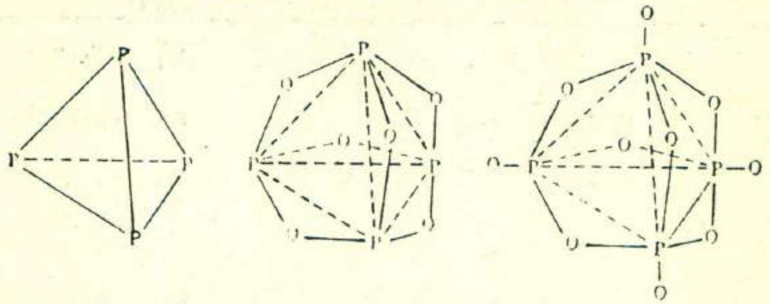
Phosphorus(V)oxide, P_4O_{10} : It is commonly called phosphorus pentoxide and is represented as P_2O_5. It is obtained by burning P in excess of air or oxygen. It is a white flocculent powder and melts at 800°C. It is quite stable. With water it forms H_3PO_4 and also HPO_3 (in limited amount of water) :

$$P_4O_{10} + 2H_2O = 4HPO_3$$

$$P_4O_{10} + 6H_2O = 4H_3PO_4$$

P_4O_{10} is used as an efficient drying agent and also for removing water from many hydroxy compounds.

The structure of P_4O_6 and P_4O_{10} are related to P_4 molecules. P_4 tetrahedra has six P—P bonds. In P_4O_6, each of P—P bonds is changed to P—O—P bridge. If an extra O atom is attached to each P in P_4O_6, it gives P_4O_{10}. Sketches of these structural changes are shown in Fig. 20—4.



P_4 P_4O_6 P_4O_{10}

Fig. 20—4. Structures of P_4O_6 and P_4O_{10} in relation to P_4

Oxyacids of Phosphorus

Phosphorus froms a number of oxyacids and these can be classified in two groups :

1. Oxyacids of phosphorus (V).
2. Oxyacids of phosphorus (III).

1. The oxyacids of P(V) : The well-known oxyacids of +5 state of P are :

H_3PO_4 — Orthophosphoric acid.

$H_4P_2O_7$ — Pyrophosphoric acid.

$(HPO_3)n$ —Metraphosphoric acid.

The structural formula and the number of OH groups in the acids (basicity of the acids) of P(V) acids are given in Table 20.4.

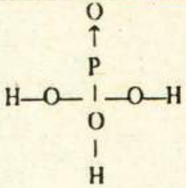
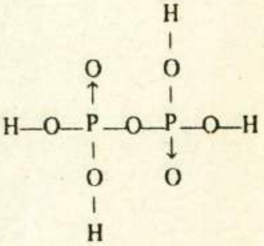
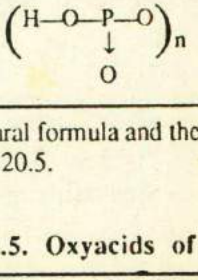
2. The oxyacids of P(III) : The oxyacids of P in +3 oxidation states are :

H_3PO_3—Orthophosphorous acid.

$H_4P_2O_5$—Pyrophosphorous acid.

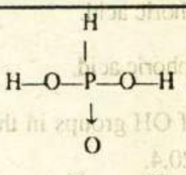
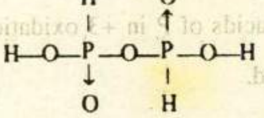
$(HPO_2)_n$—Metaphosphorous acid.

Table 20.4. Oxyacids of P(V)(P^{+5}).

Formula	*Structural formula*	*No. of OH groups*	*Ionization constants at 20°C*
H_3PO_4 Ortho–		3	$K_1 = 7.5\times10^{-3}$ $K_2 = 6{\cdot}2\times10^{-8}$ $K_3 = 1\times10^{-13}$
$H_4P_2O_7$ Pyro–		4	$K_1 = 1.4\times10^{-1}$ $K_2 = 1{\cdot}1\times10^{-2}$ $K_3 = 2{\cdot}1\times10^{-7}$ $K_4 = 4{\cdot}0\times10^{-10}$
$(HPO_3)_n$ Meta—		n n = 6 or more	—

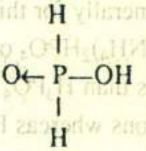
The structural formula and the number of OH groups in acids of P (III) are given in Table 20.5.

Table 20.5. Oxyacids of phosphorus(III) (P^{+3}).

Formula	*Structural formula*	*No. of OH groups*	*Ionization constants in aq. soln. at 20°C*
H_3PO_3 Ortho-		2	$K_1 = 2\times10^{-2}$ $K_2 = 2\times10^{-7}$
$H_4P_2O_5$		2	—
$(HPO_2)_n$	(H—O—P=O)n	n n = 6 or more	—

Besides the above two groups of oxyacids of phosphorus we can also include the following :

H_3PO_2—Hypophosphorous acid.



$$O \leftarrow \overset{H}{\underset{H}{P}} - OH$$

H_3PO_5—Permonophosphoric acid

$H_4P_2O_8$—Perdiphosphoric Acid.

Orthophosphoric acid, H_3PO_4 : This is also known as phosphoric acid and is obtained by various processes.

1. When P_4O_{10} is fully dissolved in water H_3PO_4 is produced :
2. PCl_5 on complete hydrolysis gives H_3PO_4 :

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

3. Oxidation of P with HNO_3 :

$$P_4 + 20\ HNO_3 = 4H_3PO_4 + 4H_2O + 20\ NO_2$$

4. H_3PO_4 is manufactured from $Ca_3(PO_4)_2$ by heating with H_2SO_4 :

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

Properties : H_3PO_4 has three replaceable H atoms because each H is covalently bonded to O atom which is in turn bonded to P. The ionization constants K_1, K_2, K_3 of H_3PO_4 indicate that there is only one strong H^+ ion, the other two have decreased acid or ionization character:

$$\begin{tikzcd}
H_3PO_4 \arrow[r, shift left, "K_1"] & H^+ \arrow[l, shift left] + H_2PO_4^- \arrow[d, shift left, "K_2"] \\
 & H^+ + HPO_4^{-2} \arrow[u, shift left] \arrow[d, shift left, "K_3"] \\
 & H^+ + PO_4^{-3} \arrow[u, shift left]
\end{tikzcd}$$

Since PO_4^{-3} concentrations in H_3PO_4 solutions are exceedingly small phosphates containing PO_4^{-3} ion are normally not precipitated from H_3PO_4 solutions. Generally for this purpose, compounds containing $H_2PO_4^-$ or HPO_4^{-2} ions such as $(NH_4)_2HPO_4$ or NaH_2PO_4 are used. Moreover, H_2SO_4 and HNO_3 are stronger acids than H_3PO_4 because H_2SO_4 and HNO_3 are fully dissociated into ions in solutions whereas H_3PO_4 is not.

H_3PO_4 thus forms three series of salts containing $H_2PO_4^-$, HPO_4^{-2} and PO_4^{-3} ions which are known as primary, secondary and tertiary phosphates. It is evident that in dilute solutions the soluble phosphates give acidic, less acidic and basic reactions depending on the anionic species. Thus NaH_2PO_4 gives acidic reaction. Na_2HPO_4 slightly basic but Na_3PO_4 gives alkaline solutions :

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{-2} + H_3O^+$$

$$HPO_4^{-2} + H_2O \rightleftharpoons PO_4^{-3} + H_3O^+$$

$$PO_4^{-3} + H_2O \rightleftharpoons HPO_4^{-2} + OH^-$$

In concentrated solution and at high temperatures the reactions of H_3PO_4 become complicated by means of condensation reaction. The PO_4 groups having the tetrahedral structure are linked together by sharing oxygen atoms forming in the long run polyphosphate. This phenomenon of polymerisation is particularly important when phosphates are heated to higher temperatures.

It is to be noted that when the ortho-phosphates, particularly the primary and the secondary phosphates are heated, the products obtained may be meta-, pyro- or poly-phosphates :

$$2H_3PO_4 \xrightarrow[\text{heat}]{\text{low}} H_4P_2O_7 \xrightarrow{200°C} 2HPO_3 + H_2O$$

$$2Na_2HPO_4 \xrightarrow{\text{heat}} Na_4P_2O_7 + H_2O$$

Calcium superphosphate : Calcium forms three salts with phosphates, $Ca(H_2PO_4)_2$, $CaHPO_4$ and $Ca_3(PO_4)_2$. The hydrogen phosphates are soluble to some extent and are used as fertilizers for plants. This compound, $Ca(H_2PO_4)_2$, is prepared commercially by treating $Ca_3(PO_4)_2$ with H_2SO_4 :

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = Ca(H_2PO_4)_2 + 2CaSO_4.2H_2O$$

The mixture of $Ca(H_2PO_4)_2$ and $CaSO_4.2H_2O$ is called *super-phosphate of lime or calcium superphosphate. TSP or Triple superphosphate of lime* is a product containing higher percentage of phosphate. This is manufactured by treating pulverized calcium phosphate, $Ca_3(PO_4)_2$, with H_3PO_4 :

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2$$

Large quantities of superphosphates are produced for use as fertilizers under the controlled conditions of concentration of H_3PO_4, quantity of water, proper mixing and formation of the granular products. *MSP* (monosuperphosphate) is also produced.

Pyrophosphoric acid, $H_4P_2O_7$: This is prepared by heating H_3PO_4 to 250°C :

$$2H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O$$

The reaction of H_3PO_4 and HPO_3 at 100°C also gives $H_4P_2O_7$:

$$H_3PO_4 + HPO_3 = H_4P_2O_7$$

Pyrophosphoric acid is a white solid which melts at 61°C. It is gradually hydrolysed to ortho acid in water. The normal pyrophosphates are prepared by heating dihydrogen phosphate :

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$

$$2CaHPO_4 = Ca_2P_2O_7 + H_2O$$

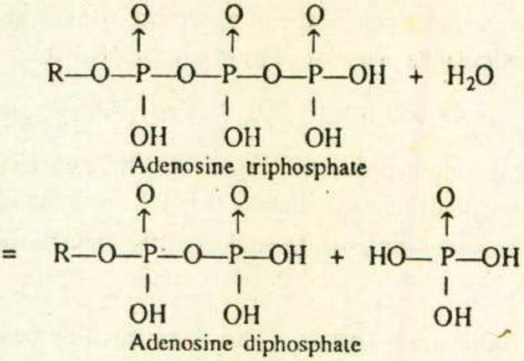
The well-known case of $MgNH_4PO_4$ or $ZnNH_4PO_4$ formerly used in quantitative analysis by ignition to $Mg_2P_2O_7$ or $Zn_2P_2O_7$ depends on the reaction :

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$$

Triphosphoric acid, $H_5P_3O_{10}$, is formed by elimination of two molecules of H_2O from three molecules of H_3PO_4.

Polyphosphate linkages have great biochemical importance. The energetic hydrolysis of a complex organic ployphosphate known as adenosine triphosphate in muscle tissues provides 10 Kcal of energy per mole of adenosine triphosphate.

Representing the complex organic part of the molecules as R—, the following equation may be written for the reaction :



$$R-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH + H_2O$$

Adenosine triphosphate

$$= R-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH + HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH$$

Adenosine diphosphate

Metaphosphoric acid, $(HPO_3)_n$: This is also obtained by a number of methods as given by the equations :

(a) $P_4O_{10} + 2H_2O = 4HPO_3$

(b) $H_3PO_4 \xrightarrow[400°C]{-H_2O} HPO_3 + H_2O$

(c) $Pb(PO_3)_2 + H_2S = PbS + 2HPO_3$

Metaphosphoric acid forms transparent glassy product, called *glacial phosphoric acid*. The P—O—P linkages in $(HPO_3)_n$ form rings and chains. HPO_3 molecules polymerise to give $(HPO_3)_n$. The acid is slowly hydrolysed to give H_3PO_4. The salts of HPO_3, i.e., metaphosphates are obtained by heating dihydrogen phosphate, e.g., NaH_2PO_4 :

$$nNaH_2PO_4 = (NaPO_3)_n + nH_2O$$

If the product is heated to 700°C and then rapidly cooled a glassy *Polymetaphosphate* is obtained. This is generally known as *Graham's salt* and has ben given the formula $(NaPO_3)_6$ or *Sodium hexametaphophate*. This is not the correct composition but it is rather more complex and contains a number of different polyphosphate ions. This is also obtained by heating microcosmic salt, $NaHNH_4PO_4.4H_2O$. If the heated product is cooled slowly it gives $(NaPO_3)_3$.

Sodium hexametaphophate is soluble in water and forms soluble complexes with Ca^{+2} even when Ca is present as $CaCO_3$, CaC_2O_4, $CaSO_4$ etc. This is, therefore, used for removing scales from the boilers and softening of hard water and as detergents. The detergent action is due to (i) complexation of Ca ion and softening of water : (ii) formation of highly charged ions which attract particles of dirt. The resultant dirt particles repel one another and are rinsed off with water.

The distinctive tests for ortho-, meta- and pyro-phosphoric acids or their salts in solutions are given below :

	Reagent	*Ortho-* H_3PO_4	*Meta-* HPO_3	*Pyro-* $H_4P_2O_7$
1.	$AgNO_3$	Orange-yellow ppt.	White ppt.	White ppt.
2.	Albumin	No change	Coagulated	No change
3.	Ammonium molybdate	Yellow ppt.	×	×

In order to test for PO_4^{-3} ions all phosphorus compounds must be converted to the PO_4^{-3} form by oxidation with HNO_3. It is H_3PO_4 which gives the yellow precipitate of ammonium phospho-molybdate with ammonium molybdate. This is a sensitive test for phosphorus :

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21\ HNO_3 \rightarrow (NH_4)_3PO_4.12MoO_3 + 21\ NH_4NO_3 + 12H_2O$$

$$\text{or } (NH_4)_3\,[PMo_{12}O_{40}]$$

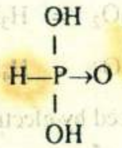
Phosphorous acid, H_3PO_3 : This can be made by hydrolysing P_4O_6, PCl_3, PBr_3 or PI_3 :

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

H_3PO_3 is a white crystalline substance, deliquescent and highly soluble in water with a garlic odour. It melts at 70°C. Its decomposition at 200°C is an example of auto-oxidation-reduction reaction giving PH_3 and H_3PO_4 :

$$4H_3PO_3 = PH_3 + 3H_3PO_4$$

H_3PO_3 has only two ionizable H indicating one H to be covalently bonded with P :



$$\begin{array}{c} OH \\ | \\ H-P\rightarrow O \\ | \\ OH \end{array}$$

H_3PO_3 and its salts phosphites are active reducing agents because these are easily oxidized to H_3PO_4 and phosphates respectively. Thus it reduces silver salts to Ag, mercury salts to mercurous salts and SO_2 to sulphur.

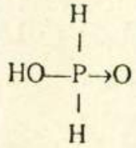
Two series of salts are obtained having the compositions, as in NaH_2PO_3 and Na_2HPO_3. When NaH_2PO_3 is heated Na-salt of pyrophosphorous acid is formed. Metaphophites are also polymers like metaphosphates.

Hypophosphorous acid, H_3PO_2 : The solution which is left after the preparation of PH_3 by the reaction of white P and NaOH, contains NaH_2PO_2. H_3PO_2 may be obtained by the following reactions in which NaOH is replaced by $Ba(OH)_2$ for the preparation of PH_3 :

$$3Ba(OH)_2 + 2P_4 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3$$

Barium hypophosphite on treatment with H_2SO_4 gives free H_3PO_2 :

The filtrate on evaporation gives a syrupy liquid. It is a mono-basic acid having only one ionizable H^+ ion. The other two H are covalently linked to P :



$$\begin{array}{c} H \\ | \\ HO\!-\!P\!\rightarrow\!O \\ | \\ H \end{array}$$

H_3PO_2 gives only one series of salts known as hypophosphites.

These are soluble in water and alcohol and possess reducing properties because P^{+1} is readily changed to P^{+3} state :

$$H_3PO_2 + Cl_2 + H_2O = H_3PO_3 + 2HCl$$

$$H_3PO_2 + Fe^{+3} + 3H_2O = H_3PO_3 + 2Fe^{+2} + 2H_2O$$

Perphosphoric acid : H_3PO_5 is obtained on adding H_2O_2 to P_4O_{10} at low temperature. $H_4P_2O_7$ on treatment with H_2O_2 gives $H_4P_2O_8$:

$$H_3PO_4 + H_2O_2 = H_3PO_5 + H_2O$$

$$H_4P_2O_7 + H_2O_2 = H_4P_2O_8 + H_2O$$

The salts of these acids are produced by electrolytic methods.

Some Compounds of As, Sb and Bi

The compounds of N, P, As, Sb and Bi differ in their stability in some cases and there is some departure from the regular gradation of properties as well. For instance, PCl_5 is more stable than $AsCl_5$. Some of the compounds of As, Sb and Bi in their different oxidation states are given in Table 20.6 These give some idea as regards the stability of the various oxidation states of the elements.

Table 20.6. Compounds of As, Sb and Bi.

Oxidation states	*As*	*Sb*	*Bi*
–3	AsH_3	SbH_3	BiH_3
+3	As_4O_6	Sb_4O_6	Bi_4O_6
	As_4S_6	Sb_2S_3	Bi_2S_3
	H_3AsO_3	H_3SbO_3	—
	$NaAsO_2$	$NaSbO_2$	—
	$AsCl_3$	$SbCl_3$	$BiCl_3$
+5	As_4O_{10}	Sb_4O_{10}	—
	H_3AsO_4	H_3SbO_4	$HBiO_3$
	Na_3AsO_4	Na_3SbO_4	$NaBiO_3$
	—	$SbCl_5$	—

As, Sb and Bi form a large number of organo-compounds in conformity with the properties of N and P which are essential for organic substances as mentioned before.

Potassium antimonyl tartrate, $KSbOC_4H_4O_6$, is formed when potassium hydrogen tartrate and Sb_2O_3 are heated together. The product is known as *tartar emetic*. The compound contains SbO^+ ion. It is used as a medicine.

Potassium pyroantimonate, $K[Sb(OH)_6]$, $0.5H_2O$ or $K_2H_2Sb_2O_7$, $5H_2O$: This is soluble in water and is used as a reagent for Na^+ ion. The Na-salt of pyroantimonate, $Na[Sb(OH)_6]$ is insoluble in water and hence on addition of potassium pyroantimonate solution, in the hot condition, the sodium compound is formed as a white precipitate.

Sodium bismuthate, $NaBiO_3$: It is brown powder and the composition is uncertain. However, it is an oxidizing agent used in analytical chemistry and the composition is $NaBiO_3$.,It **is** particularly used for the determination of manganese in steel. Mn^{+2} in HNO_3 is oxidized to MnO_4^- by $NaBiO_3$:

$$2Mn^{+2} + 5\,NaBiO_3 + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{+3} + 5\,Na^+ + 7H_2O$$

Antimony and Bismuth oxyhalides SbOX and BiOX: When excess of water is added to a solution containing Sb or Bi in, say HCl, SbOCl and BiOCl are precipitated out from their respective solutions. SbOCl is white crystalline substance. It is very slowly hydrolysed by water. It is insoluble in alcohol and ether but soluble in CS_2, C_6H_6 and $CHCl_3$ indicating covalent antimonyl chloride, SbOCl. Other halides and nitrate and sulphate of antimony behave similarly :

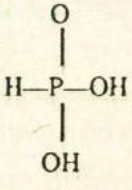
$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$

BiOCl is more stable than SbOCl and is not hydrolysed by water or alkali.

Water in large quantity is, therefore, used as a reagent for Sb or Bi, the presence of which is indicated by the formation of white precipitate.

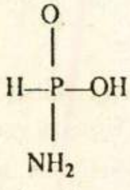
N-P compounds

A number of compounds have been reported which contain N—P bond together :



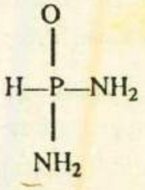
$$\mathrm{H{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{|}}{P}}{-}OH}$$

Phosphorous acid



$$\mathrm{H{-}\underset{\underset{NH_2}{|}}{\overset{\overset{O}{|}}{P}}{-}OH}$$

Amidophosphorous acid

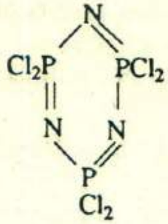


$$\mathrm{H{-}\underset{\underset{NH_2}{|}}{\overset{\overset{O}{|}}{P}}{-}NH_2}$$

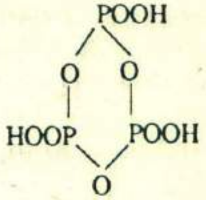
Diamido phosphorous acid

Cyclic Compounds of P : A series of phosphonitrilic halides (phosphazines) having the general formula $(PNX_2)n$ have ben prepared. These are polymers and the most important is the trimer, $P_3N_3Cl_6$, having benzene-like ring. In fact, this resembles the trimetaphosphate :

These are rubber-like substances (inorganic rubbers) but they are hydrolysed in water to give Cl^-, NH_4^+ and H_3PO_4.



Phosphazine



Trimetaphophoric acid

The Vanadium Group Metals

The properties of these transition metals are listed in Table 20·2(b) page 496 and comparisons of some of their compounds throw some light on their chemistry. Because these metals are transition metals, they have variable oxidation states due to five valence electrons. Oxidation states of +5 is the characteristic of V, Nb and Ta. For Nb and Ta it is the only important oxidation state as in Nb_2O_5 and Ta_2O_5. The difference of electron arrangements in $Nb(4d^45s^1)$ and $Ta(5d^36s^2)$ does not affect their chemical behaviour. The respective sizes of their ions are almost similar which make their chemical behaviour almost identical like those of Hf and Zr. Vanadium show variable oxidation states.

Vanadium group metals are hard and have very high melting points. They show passivity towards acids, particularly Ta. The compounds of V, Nb and Ta are all obtained from their respective oxides V_2O_5, Nb_2O_5, Ta_2O_5.

QUESTIONS AND PROBLEMS

1. Give the preparation, properties and uses of oxides and oxyacids of phosphorus.
2. Give a comparative study of the chemistry of nitrogen and phosphorus and that of their compounds.
3. Starting with phosphorus how will you obtain phosphoric acid ?
   How is phosphate detected in a solution ?
4. Describe the preparation, properties and structure of :—(a) Nitrous oxide and (b) phosphorus pentoxide.

5. Describe the methods for the synthesis of ammonia explaining clearly the physico-chemical principles on which it is based. Explain what happens when a solution of ammonia is added to —(a) silver chloride, (b) a solution of $HgCl_2$, (c) an alkaline solution of KI.
6. Write an account of the oxyacids of phosphorus. Discuss their properties and constitution.
7. Write a note on the natural and artificial fixation of nitrogen.
8. Describe the various methods used for the industrial preparation of nitric acid.
9. Give an account of the chemistry of match industry.
10. How is nitric acid prepared industrially ? What is the action of nitric acid on copper, tin and zinc ?
11. How is orthophosphoric acid prepared from—(i) bone ash, (ii) phosphorus ? How is orthophosphoric acid converted into other phosphoric acids.
12. Write a note on the match industry.
13. Write an eassay on the fixation of atmospheric nitrogen.
14. Write notes on—(i) Chloride of phosphorus. (ii) Nitrogen tetroxide.
15. How would you prepare orthophosphoric acid from phosphate rock?
16. Write a brief note on action of ammonia on salts of mercury and silver?
17. Name the inorganic compounds containing nitrogen and phosphorus used as fertilizers. Discuss in detail the manufacture of any two of them.
18. Write a detailed account on the oxide of nitrogen with special reference to their preparation, properties and structure.
19. Discuss the uses of—(i) microcosmic salt, (ii) sodium cobaltinitrite, (iii) stannous chloride, (iv) Nessler's reagent in analytical chemistry.
20. Describe the preparation and properties of the following :—(i) nitrosyl chloride, (ii) nitrososulphuric acid, (iii) dinitrogen trioxide.
21. Write an analytical scheme for the detection and separation of arsenic, antimony and tin in a mixture. Give important chemical equations.
22. Compare the chemistry of nitrogen and phosphorus, including their oxides and oxyacids.
23. Compare the chemistry of nitrogen and phosphorus.
24. Write a note on oxides and oxyacids of phosphorus.
25. "Nitrogen is an inactive gas". Discuss.
26. Discuss the bonding systems and the shapes of NH_3 and PCl_5.
27. Which of the oxides of nitrogen are designated as odd molecules. Write their structures.

28. Ammonia is a Lewis base. What happens when it reacts with H_3O^+ ion in HCl solution ?
29. Ammonia and hydrazine have some similar properties. Discuss.
30. Why white phosphorus is stored under water ?
31. Why PCl_5 is formed but no NCl_5 occur ?
32. Phosphine is less stable and less basic then ammonia. Explain.
33. What is TSP ? How it is made ? For what purpose TSP is used ?
34. The formula for nitric acid is HNO_3 whereas that of phosphoric acid is H_3PO_4. Why ?

CHAPTER 21

OXYGEN, SULPHUR AND CHROMIUM

(The Elements of Group VI)

The elements of group VI are sub-divided into two sub-groups—VIA and VIB.

Group VIA	*Group VIB*
O — Oxygen	
S — Sulphur	
Se — Selenium	Cr — Chromium
Te — Tellurium	Mo — Molybdenum
Po — Polonium	W — Tungsten

THE OXYGEN OR SULPHUR FAMILY

(The Chalcogens)

The elements of group VIA consisting of O, S, Se, Te and Po are sometimes called chalcogens (which means chalk-formers) as is the nomenclature in the case of halogens (meaning salt-formers): Oxygen, the first member of group VIA, differs from the rest of the elements and hence the name *Sulphur Family* is more appropriate. In this book, we shall mainly deal with some aspects of chemistry of oxygen and sulphur and that of chromium from sub-group VIB. The general chemistry and their relationships with each other is restricted to some salient features. The element polonium is radioactive element.

Table 21.1. Electronic structures of Sulphur Family.

At. No.	*Elements*	*Electronic structure*	*Valence electrons*
8	O	He core, $2s^2 2p^4$	$2s^2\ 2p^4$
16	S	Ne core, $3s^2 3p^4$	$3s^2\ 3p^4$
34	Se	Ar core, $3d^{10} 4s^2 4p^4$	$4s^2\ 4p^4$
52	Te	Kr core, $4d^{10} 5s^2 5p^4$	$5s^2\ 5p^4$
84	Po	Xe core, $4f^{14} 5d^{10} 6s^2 6p^4$	$6s^2\ 6p^4$

The electronic structures of the group VIA are given in Table 21.1

The six electrons in the outermost energy levels are $\mathbf{s^2p^4}$ electrons in each of the elements. The group VIB elements are transition metals and will be discussed at the end of this chapter separately.

Before discussing the chemistry of the elements on the basis of $\mathbf{s^2p^4}$ electrons, a list of physical properties are given in Table 21.2

Table 21.2. Physical properties of the Sulphur Family.

Physical properties	*O*	*S*	*Se*	*Te*
Atomic No.	8	16	34	52
Atomic weight	16.00	32.006	78.96	127.61
Physical state	colourless gas	yellow solid	red or grey solid	silvery solid
Outer electron orbitals	$2s^22p_x^2$ $2p_y^12p_z^1$	$3s^23p_x^2$ $3p_y^13p_z^1$	$4s^24p_x^2$ $4p_y^14p_z^1$	$5s^25p_x^2$ $5p_y^15p_z^1$
Atomic or covalent radius (Å)	1.32	1.74	1.91	2.03
Ionic radius X^{-2} ion (Å)	0.47	1.06	1.16	1.44
Ionization energy (ev)	13.60	10.40	9.80	9.00
Melting point (°C)	−219	119	220	450
Boiling point (°C)	−183	415	688	1390
Electronegativity	3.50	2.50	2.40	2.10
Oxidation potential X^{-2}/X (v)	−1.23	+0.51	+0.77	+0.91
Oxidation states	+2, 0, −2, −1	−2, 0, +2, +4, +6	−2, 0, +4, +6	−2, 0, +2 +6

Comparison of Oxygen with Sulphur Group : Oxygen differs from the rest of the Sulphur Family in many respects. for instance :

(1) Oxygen is a colourless gas, others are all solids with S as non-metal, and the metallic character increase with the increasing atomic number.

(2) The six valence electrons in these elements consist of $\mathbf{s^2p^4}$ arrangement.

(3) Oxygen occurs abundantly in nature in the free state and both in the inorganic and organic materials.

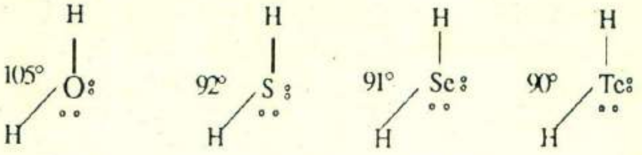
(4) Oxygen adopts generally the negative oxidation state of –2 much more readily as compared to other elements. The 6 electrons in the outermost level take up 2 electrons to form X^{-2} ion in this group. But this tendency decreases in the order $O > S > Se > Te > Po$. Oxygen in –2 state is present in all combined materials. The tendency to form negative oxidation states is less in other elements of this group. Hence O_2 is the strongest oxidizing agent and Te the weakest. Oxygen does not lose 6 electrons to assume +6 state which is quite common for S, Se and Te.

(5) Oxygen having small atomic volume and high ionization potential as compared to the other elements of the group is characterised with the difference in physical constants which result in special properties of oxygen.

(6) Oxygen is more electronegative than any other element except fluorine. This is one reason for the special properties of oxygen in its compounds. For instance, all the elements of this group form hydrides of the general formula XH_2, i.e., OH_2, SH_2, SeH_2, TeH_2 and also PoH_2. But the heats of formation of H_2O (59 Kcal/mole) is much higher than any of the compounds H_2S, H_2Se, H_2Te. Water is a highly stable associated and neutral liquid. H_2S, H_2Se and H_2Te are gases having acidic properties and unpleasant odour and these are easily decomposed because of their reducing properties. The strength of acid behaviour and reducing power increases in the order :

$$H_2O < H_2S < H_2Se < H_2Te < H_2Po$$

But the thermal stability decreases from H_2O to H_2Po in the hydracid series. All these have similar structure of their molecules but due to the difference in the electronegativities of O,S, Se, Te, Po with that of H, and the increase in their ionic radii, the bond lengths and bond angles are not the same. H_2O shows hydrogen bonding due to much greater difference in the electronegativity values of O and H as compared to those between S and H and others. H_2S and H_2Te do not have the property of hydrogen bonding.



These factors give rise to difference in the properties of these compounds as given in Table 21.3.

Table 21.3. Properties of H_2O, H_2S H_2Se and H_2Te.

Hydride	*Melting point (°C)*	*Boiling point (°C)*	*Heat of formation Kcal/mole*	*Acid strength Ka_1*	*Remark*
H_2O	0	100	68	10^{-14}	Associated liquid (neutral)
H_2S	−86	−61	5	3×10^{-7}	weakly acidic
H_2Se	−60	−41	−19	2×10^{-4}	acidic
H_2Te	−51	−2	−34	10^{-2}	strongly acidic

(7) The double bond in O_2 is stronger than S—S or Te—Te bond. Hence oxygen can exist as separate molecular species as O_2. This is not the case with S, Se and Te although these may occur in nature in the free state but in the form of atomic aggregates and as the atomic number increases, these assume more pronounced metallic character with much higher melting and boiling points. Oxygen forms two double bonds whereas, S, Se and Te usually form two single bonds. Thus S forms S_8 ring in which each S has two single bonds. The three atoms of oxygen in O_3 is highly unstable.

(8) O_2 molecule has been found to have magnetic properties, which in the case of other members is not so pronounced.

(9) A marked characteristic of this group is the existence of a number of allotropic forms. In this property oxygen also shows likeness to other elements of this group.

(10) Photoelectric behaviour of Se is much more pronounced than Te and for this reason Se is on great demand for photo-electric tubes. Other elements of this group do not show this property.

Thus it can be inferred that oxygen as a member of the group VIA elements differs markedly in physical and chemical behaviours from S, Se and Te. The latter three elements have similar chemical properties with the usual gradations that is expected on account of the electronic configuration.

OXYGEN

Sources of oxygen : Oxygen is the most plentiful element in the earth's atmosphere, sea-water and the earth's crust. It is an essential element for all forms of life. Without oxygen no life can exist since it is required to convert the food materials to CO_2 and H_2O.

Preparation of oxygen :

1. By heating an unstable oxide :

$$2\,HgO \xrightarrow{\text{heat}} 2Hg + O_2$$

2. From peroxide : In metal peroxides and H_2O_2 oxygen has the unusual oxidation number of -1 and hence these are unstable compounds and decompose to evolve oxygen in zero oxidation state and also in -2 oxidation state. Thus :

$$2\,H_2O_2 \xrightarrow{\text{heated}} 2\,H_2O + O_2$$

$$(BaO + O_2 \xrightarrow[500°C]{\text{heated}} BaO_2)$$

$$BaO_2 \xrightarrow[700°C]{\text{heated}} BaO + O_2 \text{ (Brin's Process)}$$

Some reactions undergo swift decomposition when heated or in presence of other substances, e.g.,

$$2Na_2O_2 + 2H_2O \xrightarrow{\text{heat}} 4NaOH + O_2$$

3. From oxygen-rich compounds :

$$2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$$

$$KClO_3 \xrightarrow[(MnO_2\text{ catalyst})]{\text{heat}} 2\,KCl + 3O_2$$

4. Electrolytic method : Water, containing a little acid or alkali when subject to electrolysis, evolves O_2 and H_2 at the anode and cathode respectively due to the following reactions :—

$$2H_2O + 2e \rightarrow 2H_2 + O_2$$

$$4(OH)^- \rightarrow 2H_2O + O_2 + 4e$$

5. From liquid air : Large quantities of oxygen are produced by the fractional evaporation of liquid air. Since the boiling point of liquid nitrogen is −196°C compared to −183°C for oxygen, nitrogen is volatilized away first by distillation of the liquid air leaving the residue of almost pure liquid oxygen (Claude's Process).

Properties of oxygen : The physical properties of oxygen have been shown in Table 21.2 and a list of chemical properties which are common is given below .

(1) Oxygen is an active element and combines with all the other elements either directly or by some other methods (exception—inert gases). The process of combination of oxygen with an element or compound is called oxidation because oxygen normally changes from zero valent state to O^{-2} state by accepting electrons. Some typical examples are given by the following equations :—

(a) With metals :

$$2Na + O_2 = Na_2O_2 \text{ (ordinary condition)}$$

$$2Mg + O_2 = 2MgO \text{ (heat)}$$

$$3Fe + 2O_2 = Fe_3O_4 \text{ (heat)}$$

(b) With non-metals :

$$2H_2 + O_2 = 2H_2O \text{ (burning)}$$

$$C + O_2 = CO_2 \text{ (burning)}$$

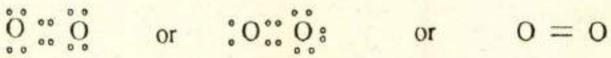
$$S + O_2 = SO_2 \text{ (burning)}$$

(c) With compounds :

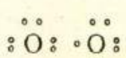
$$\begin{aligned} 2H_2S + 3O_2 &= 2H_2O + 2SO_2 \text{ (burning)} \\ CS_2 + 3O_2 &= CO_2 + 2SO_2 \text{ (burning)} \\ 2ZnS + 3O_2 &= 2ZnO + 2SO_2 \text{ (burning)} \\ 2CO + O_2 &= 2CO_2 \quad \text{ (burning)} \\ P_4O_6 + 2O_2 &= P_4O_{10} \end{aligned}$$

The Structure of Oxygen Molecule

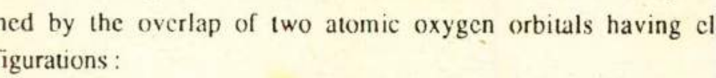
The structure of O_2 molecule has been represented as formed by sharing two pairs of electrons between the two O atoms in which all the electrons are paired :



But O_2 molecule has magnetic properties. It is attracted by a magnetic filed and calculations show that O_2 molecule has two single (unpaired) electrons. Therefore, the modified Lewis structure of O_2 molecule may be written as,



with one electron on each atom of oxygen. Pauling considered that O_2 is an odd molecule with three electron bonds as,



Each Lewis structure contain 12 electrons between the two oxygen atoms in O_2 molecule.

But from the point of view of molecular orbital method the O_2 molecule is formed by the overlap of two atomic oxygen orbitals having electronic configurations :

$$1s^2\, 2s^2\, 2p_x{}^2\, 2p_y{}^1\, 2p_z{}^1$$

Neglecting the non-bonding electrons of $1s^2$ and $2s^2$ and considering the overlap of **p** orbitals of one oxygen atom with **p** orbitals of another oxygen atom, we find that there are 6 molecular orbitals by the LCAO of 2 oxygen atoms, each having 3 atomic 2**p** orbitals. Out of six molecular orbitals three will be bonding orbitals and three anti-bonding orbitals. When we distribute the 8 electrons of **p** orbitals from each O atom i.e. $(2p^4 + 2p^4)$ each of the molecular orbitals accommodate 2 electrons. Therefore, 6 electrons can be placed in the 3 bonding molecular orbitals leaving a balance of 2 electrons. Since the energy of the two anti-bonding orbitals are the same, the remaining two electrons are accommodated singly (unaired) in each of the two anti-bonding orbitals with parallel spins to have the maximum stability. Thus, these two unpaired electrons in the two anti-bonding molecular orbitals confer the magnetic properties to the O_2 molecule. This feature is diagrammatically shown in Fig. 21—1 showing the combination of three **p** orbitals of each oxygen atom.

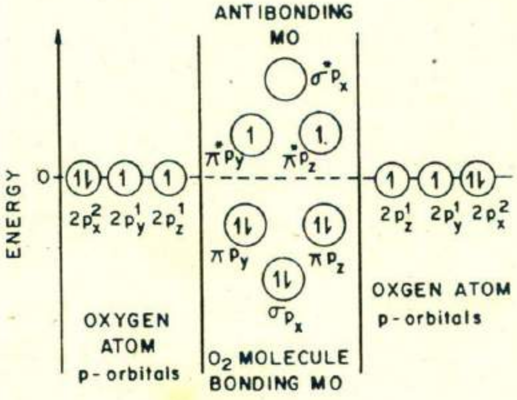


Fig. 21—1. Unpaired electrons in oxygen molecule in π^*p_y and π^*p_z orbitals.

Atomic Oxygen

At the ordinary conditions O_2 is slow to react possibly because the breaking of the O—O bond is rather difficult. In order to separate O_2 molecule into O atoms, 118 Kcal/mole of energy is required :

$$O_2 + 118 \text{ Kcal} = O + O$$

Hence O—O bond is rather strong. But at the elevated temperature O_2 is very reactive. At the ordinary temperature O_2 reacts with some substances without bond breaking. Thus, Na_2O_2 and BaO_2 are formed in which O—O bonds remain unbroken.

The oxygen molecule can be broken up into atoms by ultraviolet radiation or by electron discharge. The atomic oxygen so produced is very reactive and releases more energy when reacting. The reactivity of atomic oxygen is indicated in its oxidation potential O/O^{-2}. This is greater than that of ozone or oxygen fluoride, OF_2, and is about the same as that of F_2 (−2.85V).

Uses of oxygen : (1) Metabolic process of respiration. (2) O_2-enriched air to patients with serious ailment. (3) In combination of fuels. (4) Metallurgical operations. (5) Cutting and welding metals with oxyhydrogen or oxyacetylene flames. (6) Oxygen masks for high altitudes. (7) Heavier isotopes of oxygen O^{18} are particularly used in tracer experiments for determining the structures of compounds.

OZONE

Ozone (O_3) is an allotropic form of O_2. Higher regions of atomosphere contain molecules of O_3. Generally referred to as the ozone layer.

Preparation : Ozone can be prepared in a number of ways. The main principle of the formation of ozone is to subject O_2 to an electric discharge. It is probable that atomic oxygen first formed combines with O_2 to give O_3.

There are various forms of apparatus used for the preparation and industrial production of ozone. These are known as *Ozonizers* which consist mainly of two electrically charged plates between which dry oxygen is passed. The gaseous products formed decrease in volume and possesses a pungent odour with a pale blue colour.

The formation of ozone from oxygen is an endothermic reaction and energy may be provided by means of electronic discharge. But other forms of energy may produce slight amount of ozone. Thus heat, ultraviolet light, slow oxidation of phosphorus, a jet of burning hydrogen during thunderstorm also form little ozone. Also, when F_2 reacts with water at low temperature, O_3 is formed :

$$3H_2O + 3F_2 = 6HF + O_3$$

Properties of Ozone

Physical properties : It is a pale blue gas with a pungent odour. The gas itself is colourless but it absorbs light strongly in the ultraviolet region and for this reason upper atmosphere appears to be blue. O_3 thus acts as a shield by absorbing the deadly ultraviolet light for the earth's living beings. It is an allotropic form of oxygen. Due to high concentrations of industrial gases there is nowadays depletion of ozone layer of the atmosphere. This has been a case of great concern world-wide.

Chemical properties : O_3 is an unstable molecule because it is formed by endothermic reaction and hence it tends to lose energy by decomposition :

$$2O_3 = 3O_2 + 69 \text{ Kcal}$$

Ozone is, therefore, one of the most powerful oxidizing agents known. Only F_2, F_2O and atomic O stand above O_3 in oxidizing power.

The following oxidation reactions may be cited as examples of oxidizing nature of O_3 :

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2$$

$$2HCl + O_3 = H_2O + Cl_2 + O_2$$

$$PbS + 4O_3 = PbSO_4 + 4O_2$$

$$N_2O_4 + O_3 = N_2O_5 + O_2$$

$$3SO_2 + O_3 = 3SO_3$$

$$3SnCl_2 + O_3 + 6HCl = 3SnCl_4 + 3H_2O$$

$$H_2O_2 + O_3 = H_2O + 2O_2$$

$$Ag + O_3 = AgO + O_2$$

$$Hg + O_3 = HgO + O_2$$

$$I_2 + 5O_3 + H_2O = 2HIO_3 + 5O_2$$

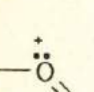
Unsaturated organic molecules form explosive compounds called ozonides, O_3 combines at the double bond. C_2H_4 gives ethylene ozonide :

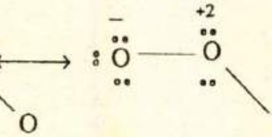
ethylene ozonide

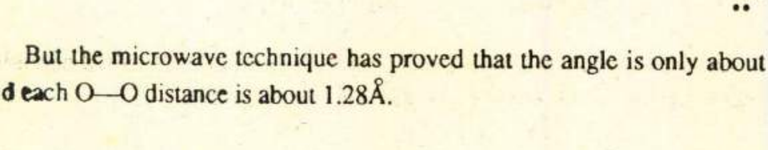
Recently ozonates, KO_3, CsO_3, have also been prepared. Distinctions between O_3, O_2 and H_2O_2 are given below :—

Reagent	O_2	O_3	H_2O_2
Hg	No reaction	HgO	×
$KMnO_4$ soln.	×	×	Mn^{+2} formed
H_2CrO_4	×	×	Cr^{+3} formed
Rubber	×	Brittle	No immediate action

Structure of O_3 : Previously O_3 was considered to be formed by the combination of three oxygen atoms so that each oxygen atom shared a pair of electrons with two others giving a triangular structure. But ozone is paramagnetic and the angle between three oxygen has been fond to be 127°. Therefore, the true structure must have two unpaired electrons in O_3 as in O_2 :







But the microwave technique has proved that the angle is only about 127° and each O—O distance is about 1.28Å.

SULPHUR

Sources of Sulphur

(1) Sulphur has been known from ancient time since it occurs free in nature in the solid state, particularly in volcanic regions of the earth. Volcanic gases also contain H_2S. and SO_2 which come in contact on the surface leading to their interaction and sulphur is precipitated which melts but solidifies when the volcanoes become extinct.

(2) Free sulphur also occurs in mines in the U.S.A and Mexico under the earth's surface about 700—900 feet below.

(3) In combined state sulphur is widely distributed in various compounds. The important ores of sulphur are :—

Iron pyrites	—	FeS_2
Copper pyrites	—	Cu_2S, FeS_2
Galena	—	PbS
Orpiment	—	As_2S_3
Cinnabar	—	HgS
Gypsum	—	$CaSO_4.2H_2O$

It may be noted here that the sulphide ores, such as PbS, HgS, Cu_2S, FeS_2 etc., contain small quantities of selenium and tellurium in the form of $PbSe$, $HgSe$ and also in the free state in sulphur. Tellurium also occurs free along with Cu, Ag, Au and also as silver and gold tellurides (sylvanite,Ag_2Te, Au_3Te_3).

Extraction of Sulphur

Depending upon the source, various methods are being used for the extraction of elementary sulphur.

1. Frasch Process: This process is employed for underground sulphur in Lousiana, U. S. A. A drill-hole is made through which four concentric pipes are passed upto the sulphur-bearing bed. Superheated steam under pressure is forced down the next to the outermost of the four pipes. The hot steam melts the sulphur. The compressed air is forced through the innermost pipe. The molten sulphur mixed with steam and air forms light emulsion which readily flows up through the third pipe. The outermost pipe serves as an outlet for superheated steam. The emulsified sulphur is conveyed to large settling tanks where it solidifies upon cooling. Frasch method gives very pure sulphur, almost 99.9% pure, and no further purification is required.

2. The Sicilian Method : In Sicily sulphur is found mixed with quartz and gypsum. The method of extraction of crude sulphur from this source consists in heating the lumps of the ore in a heap in closed chambers. Sulphur melts and runs off at the base.

Refining of sulphur is done by boiling sulphur in closed iron retorts and sulpur vapour is condensed in a large chamber in the form of fine particles known as *flowers of sulphur*. This melts at higher temperature and the molten sulphur is rolled into mould to give *roll sulphur* or *brimstone*.

3. From coal gas : Coal gas contains H_2S which is removed by passing the gas over heated Fe_2O_3 when FeS and Fe_2S_3 are formed. The mixture of FeS and Fe_2S_3 is known as *spent oxide*. When the spent oxide is exposed to the weathering conditions of air and water vapour, elementary sulphur is deposited :

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$$

$$2Fe_2S_3 + 3O_2 + 2H_2O = 2F_2O_3 + 6S$$

4. From CaS : Sulphur is also recovered from CaS which is formed during the manufacture of Na_2CO_3 by Le Blanc Process. This is done by liberating H_2S from CaS in water suspension by means of CO_2. H_2S mixed with air passed over heated Fe_2O_3 gives elementary sulphur :

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$

$$2H_2S + O_2 = 2S + 2H_2O$$

5. By bacterial action : Certain bacteria have the remarkable property of converting sulphates to elementary sulphur. Calcium sulphates have been converted to free sulphur by the artificially prepared strains of bacteria.

.*6. From roasting of sulphides* : It is to be noted that the sulphide ores are not used for extraction of sulphur. These are roasted for the extraction of metals and SO_2 formed is mainly used for the manufacture of H_2SO_4. But sometimes it becomes necessary to reduce SO_2 to S by passing the gases through coke heated at 1100°C when the reaction $SO_2 + C = CO_2 + S$ produces S. Also on roasting the sulphide ores contaminated with selenium, both SO_2 and SeO_2 are formed. But SeO_2 is reduced by SO_2 giving fine powder of free selenium in the flue gas from which it is precipitated by electrical cottrell precipitator :

$$SeO_2 + 2SO_2 = 2SO_3 + Se$$

Selenium is also recovered from the metal oxide formed, and from the anode mud obtained during the electrolytic refining of copper.

Properties of Sulphur

Physical properties : The electronic configurations and other physical constants have been listed in Table 21.2. An interesting feature is the well-marked property of sulphur in having several allotropic forms as is the case with O, Se and also to some extent in Te.

Allotropic forms of sulphur : Sulphur exists in a variety of forms—in the solid, liquid and gaseous states.

Solid sulphur : Several crystalline forms of sulphur are known. At room temperature the solid sulphur has rhombic form and is the stablest form of sulphur composed of S_8 molecules. This is also known as octahedral or *α-sulphur*. Each S atom in S_8 molecule has two single bonds and thus forms an eight-membered ring. The molecule is puckered, i.e., four S atoms lie in one plane and the four S atoms lie in another plane. The structure of S_8 molecule is shown in Fig. 21—2.

On heating rhombic sulphur below 100°C, it is changed to monoclinic form. This also consists of S_8 molecules which are arranged in a different geometric form. This is also known are as *prismatic* or *β-sulphur*. The transition temperature from rhombic to monoclinic form contains more energy and at lower temperature or room temperature it tends to convert itself to the rhombic form.

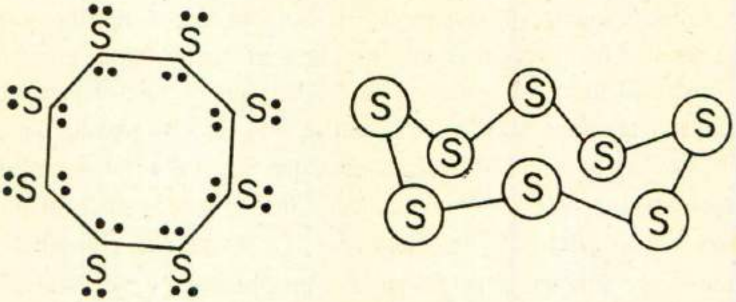


Fig. 21—2. Structure of S_8 molecule in sulphur, (a) Electron arrangement in S_8 molecule ; (b) "Puckered" arrangement of 8 S atoms.

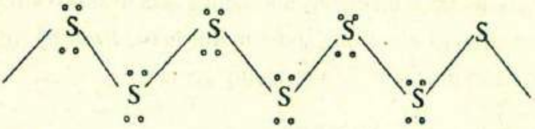
Both rhombic and monoclinic sulphurs are insoluble in water but soluble in CS_2, S_2Cl_2 etc. But the monoclinic form has greater solubility than the rhombic form. Their molecular weights have been determined both in the vapour state and in solutions.

Liquid sulphur : On heating solid sulphur to just above the melting point (119°C), a clear straw-coloured mobile liquid is formed. This also contains S_8 molecules. As the temperature is raised, the S_8 ring of the yellow mobile sulphur is present as long open chains of S atoms known as *λ-sulphur* :

$$-\underset{\circ\circ}{\overset{\circ\circ}{S}}-\underset{\circ\circ}{\overset{\circ\circ}{S}}-\underset{\circ\circ}{\overset{\circ\circ}{S}}-\underset{\circ\circ}{\overset{\circ\circ}{S}}-\underset{\circ\circ}{\overset{\circ\circ}{S}}-\underset{\circ\circ}{\overset{\circ\circ}{S}}-\underset{\circ\circ}{\overset{\circ\circ}{S}}-\underset{\circ\circ}{\overset{\circ\circ}{S}}-$$

On further heating the liquid gradually darkness and becomes very viscous at above 200°C when it gives a thick gum-like mass with darkend colour. The long chains of S atoms become entangled with each other as the temperature is raised above 200°C indicated by the increased viscosity. This darkend form of liquid sulphur is known as *μ-sulphur*.

When the yellow mobile liquid, *λ-sulphur*, is suddenly cooled to room temperature by pouring it into water, a rubber-like material is formed which is known as *plastic sulphur*. The long chains of S atoms become oriented in a zig-zag manner of indefinite lengths which imparts the elastic rubber-like property. The plastic sulphur is insoluble in CS_2. Upon standing, plastic sulphur, like all other forms of sulphur, changes to the rhombic sulphur :



Sulphur vapour : Sulphur boils at 444.6°C and molecular breakdown occurs in the vapour state consisting of S_8, S_6, S_2 molecules both in the cyclic ing form and open chain form. At the boiling point (in equilibrium with the iquid sulphur) the sulphur vapour is red due to the lone electrons on each sulphur atom. At above 1000°C, the rings and chains of sulphur atoms break lown and the vapour consists of S_2 molecules and is of yellow colour. At about 2000°C, S_2 dissociates to give atomic S to some extent.

Some other forms of sulphur : When elementary S is precipitated out from Ca-Thiosulphate or polysulphide by means of HCl, a white amorphous product is obtained which is known as *milk of sulphur* soluble in CS_2 :

$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S$$

Colloidal sulphur is formed when H_2S ans SO_2 react together in aqueous solution or when sodium thiosulphate is decomposed by a solution of H_2SO_4. Sulphur remains in a clear yellow solution and can be coagulated by adding electrolytes, such as alum solution.

It may be noted that several allotropic forms of selenium contains zig-zag chains of selenium atoms in the solid state. Red and black forms of selenium are also known. Tellurium is a brittle silvery white metal and an amorphous form of tellurium also exists.

Chemical properties : Although the elements O, S, Se, Te and Po form one group, the chemistry of O and Po are so different that these are considered separately. But the sulphur family having S, Se and Te have the general gradation of group characteristics and have almost similar chemistry.

Elementary sulphur, although a non-metallic stable solid, is quite reactive. Many metals react with S at ordinary temperature, e.g., Hg on rubbing with sulphur powder forms HgS. Elementary S is both an oxidizing and a reducing agent. S containing $\mathbf{s^2p^4}$ electrons has a tendency to form the stable $\mathbf{s^2p^6}$

arrangement by taking up 2 electrons and hence acts as an oxidizing agent. The oxidation involves loss of electrons and sulphur is oxidized by most non-metals to + 4 or + 6 state and thus acts as a reducing agent.

Oxidizing Properties of Sulphur

(a) Reaction with H_2 : Sulphur reacts directly with H_2 forming H_2S :

$$H_2 + S \rightleftharpoons H_2S$$

The proportions of H_2S formed increase with the increase of temperature

(b) Reaction with non-metals : C at elevated temperature forms CS_2:

$$C + 2S \rightleftharpoons CS_2$$

(c) Reactions with metals : Metals, such as Zn, Al, Fe, on gently heating with S, form metal sulphides :

$$Zn + S = ZnS$$

$$Fe + S = FeS$$

It may be noted that properties of sulphides containing S^{-2} ion are quite different form the corresponding oxides containing O^{-2} ions.

Reducing Properties of Sulphur

When sulphur reacts with non-metals which are more electronegative than sulphur, it assumes the oxidation state of + 4 or + 6.

(a) Reaction with O_2 : Sulphur burns in air (O_2) with a blue flame forming SO_2 and traces of SO_3 (about 3—4%) :

$$S + O_2 = SO_2$$

$$2SO_2 + O_2 = 2SO_3$$

These are very important reactions industrially and will be described in connection with H_2SO_4.

It has been noticed that S, when exposed to moist air, is slowly oxidized to give H_2SO_4 :

$$2S + 2H_2O + 3O_2 = 2H_2SO_4$$

(b) Reaction with halogens : Sulphur forms a large number of halides by direct union with halogens except iodine:

$$\begin{array}{llllll} S + F_2 \rightarrow & S_2F_2 & S + Cl_2 \rightarrow & S_2Cl_2 & S + Br_2 \rightarrow S_2Br_2 \\ & SF_4 & & SCl_2 & \\ & SF_6 & & SCl_4 & \\ & S_2F_{10} & & & \end{array}$$

(c) Reaction with HNO_3 and H_2SO_4 (Concentrated and hot condition):

$$S + 6HNO_3 = H_2SO_4 + 2H_2O + 6NO_2$$

$$S + 2H_2SO_4 = 2H_2O + 3SO_2$$

(d) Reaction with alkali : Both S^{-2} and thiosulphates are formed when S is boiled with alkalies :

$$4S + 6NaOH = Na_2S_2O_3 + 2Na_2S + 3H_2O$$

N.B. Selenium more or less has similar reactions but is a weaker oxidizing and weaker reducing agent than sulphur.

Uses of S, Se and Te

Sulphur : (1) Production of sulphuric acid, one of the basic materials for many industries.

(2) SO_2 from S is used for industrial bleaching purpose.

(3) Production of CS_2, an industrial solvent.

(4) S in vulcanization of rubber.

(5) Gunpowder, explosive and a host of other compounds of sulphur.

Selenium and its compounds are used in :

(1) Electronic industries as an efficient rectifier.

(2) Producing colourless glass which is generally coloured green due to iron silicate.

Some Important Compounds of Sulphur

Hydrogen sulphide, H_2S : It is a quite familiar gas. It is much used in the laboratory for qualitative analysis.

(1) It is generally prepared in Kipps' apparatus by the reaction of FeS with dilute H_2SO_4 or HCl :

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

H_2S prepared by the above method is impure.

(2) Pure H_2S may be obtained by the hydrolysis of sulphides of more electropositive metals, such as Al_2S_3, or by the action of dilute HCl on NaHS :

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$$

$$NaHS + HCl = H_2S + NaCl$$

(3) Recently a convenient and less obnoxious source of H_2S has been found in some sulphur-containing organic compounds, such as methyl thioacetamide (Methyl thiorurea), CH_3CSNH_2. Whenever H_2S is required, a pinch of this substance in water gives H_2S and ammonium acetate by hydrolysis :

$$CH_3CSNH_2 + 2H_2O = CH_3COONH_4 + H_2S$$

The hydrolysis is very rapid in hot solutions.

Properties of H_2S : (1) It is a colourless gas having the smell of rotten eggs. (2) It is highly poisonous. (3) It can be condensed to a colourless liquid at −60°C (and solidifies at −86°C).

Aqueous solution of H_2S : H_2S is moderately soluble in water and the aqueous solution is freely acidic. It ionizes as :

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad Ka_1 = 3 \times 10^{-7} \text{ at } 20°C$$

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{-2} \qquad Ka_2 = 2 \times 10^{-16} \text{ at } 20°C$$

When the aqueous solution is exposed for a long time to the action of air, sulphur is precipitated out due to aerial oxidation of H_2S :

Reducing properties of H_2S : The sulphur in H_2S readily gives up the electrons and becomes oxidized to S, S^{-4} S^{+6} depending upon the conditions and the nature of the other substances which react with it. H_2S burns in air to form SO_2 and when the air is insufficient, only S is formed. In presence of strong oxidizing agents in excess, H_2S may be oxidized to H_2SO_4 :

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

$$2H_2S + O_2 = 2H_2O + 2S$$

$$H_2S + 4Br_2 + 4H_2O = H_2SO_4 + 8HBr$$

In aqueous acid solutions H_2S reduces Fe^{+3} to Fe^{+2}, I_2 to I^-, MnO_4^- to Mn^{+2}, $Cr_2O_7^{-2}$ to Cr^{+3}, HNO_3 to NO. In all these reactions, H_2S is oxidized to free sulphur in aqueous solutions :

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$

$$5H_2S + 2KMnO_4 + 3H_2SO_4 = 5S + 2MnSO_4 + 8H_2O + K_2SO_4$$

Precipitating action of H_2S : The importance of H_2S in analytical chemistry lies in the fact that it precipitates metal sulphides from acidic, neutral and alkaline solutions. These metal sulphides show a wide variation in solubility and thus can be divided into several analytical groups. For instance, CuS, PbS and CdS are insoluble in dilute HCl. Others, such as ZnS, are soluble in dilute HCl but insoluble in NH_4OH solution.

The most important factor which enables the use of H_2S in qualitative analysis is the control of S^{-2} ion concentration in the solution. In an aqueous solution containing a number of metal ions M^{+2} and sulphide ions S^{-2}, a metal sulphide MS will be precipitated only if the product of the concentrations of the S^{-2} ion and M^{+2} ion (raised to their appropriate powers) exceeds the solubility product constant, K*sp* of the metal sulphides. Thus :

If $[M^{+2}] \times [S^{-2}] > K_{sp}$—metal sulphide is precipitated.

$[M^{+2}] \times [S^{-2}] < K_{sp}$—metal sulphide is not precipitated.

The S^{-2} ion concentration can be easily controlled to achieve the above condition. The reactions are based on the equilibrium dissociation of H_2S as :

$$H_2S \rightleftharpoons HS^- + H^+$$

$$HS^- \rightleftharpoons H^+ + S^{-2}$$

and the solubility of metal sulphide as represented by the equilibrium equation :

$$MS\ (\text{solid}) + 2H^+ \rightleftharpoons M^{+2} + H_2S\ (\text{gas})$$

The solubility of a metal sulphide according to the equilibrium equation depends upon the following factors :—

1. *The solubility of the solid in water* : The greater the solubility, the greater the equilibrium displaced towards the right of the equilibrium equation. This also gives greater solubility in acid. CoS ($Ksp = 1 \times 10^{-21}$) is more soluble in water than CuS ($Ksp = 1 \times 10^{-25}$). Ksp of CuS > Ksp of CoS. This is also true for acid solution. In 2N HCl, it is only CuS which is precipitated out but CoS remains in solution.

2. *The concentration of acid* : H^+ occurs in the left of the equation. It is natural that increased concentration of H^+ lead to greater solubility of MS. Decreasing the concentration therefore, precipitate out the more soluble metal sulphide. It is for this reason that CoS and ZnS are precipitated out by H_2S in alkaline solution (decreasing the H^+ ions by adding OH^- ion in the form of NH_4OH).

3. *The strength of the weak acid formed* : The weaker the acid formed the more soluble the salt is in the strong acid. For instance, most heavy metal carbonates are easily soluble in dilute mineral acid because of the formation of H_2CO_3 a weak acid, during the reaction. The reason that some heavy metal sulphides are not soluble in mineral acids is due to the crystal structure.

Thus we can see that by adding H^+ from outside (HCl as usual) the concentration of S^{-2} ion is reduced and under this condition only sulphides of analytical Group II metals, such as CuS, PbS, CdS, Bi_2S_3 etc. precipitated because their Ksp values are very small. ZnS, MnS, NiS etc. are not precipitated under this condition because their Ksp values are very high, These can be precipitated if S^{-2} ion concentration is increased by decreasing H^+ ions (usually by adding NH_4OH or OH^- ions) as in the case of Zn, Mn, Co, Ni etc. metal ions of the analytical group.

Test for H_2S or Sulphides : A paper moistened with lead acetate solution turns black on exposure to H_2S due to the formation of black PbS. In solution S^{-2} ion is detected by sodium nitroprusside which gives violet colour in presence of S^{-2} ion :

$$2Na_2[Fe(CN)_5 NO] + H_2S \rightarrow Na_4 [Fe (CN)_5NOS]_2 + H_2O$$

Uses of H_2S : (1) It is a versatile analytical reagent and is used for classification of metals into different groups in analytical chemistry identification tests and separation procedures. (2) In synthetic work for the preparation of sulphur containing compounds.

Sulphides : Normally the diprotic H_2S forms two series of sulphides (so also H_2Se and H_2Te). Normal sulphides and hydro-sulphides of metals are well-known and have been dealt in appropriate chapters. These sulphides are formed from H_2S in solution or by direct reactions of metal and sulphur.

It has been found that only very slightly soluble sulphides can exist in the presence of water. This is because of the strong tendency of the S^{-2} and HS^- ions to act as proton acceptors. The soluble ionic sulphides BaS, Na_2S, K_2S etc. are readily hydrolysed into HS^- and OH^- and in some cases to H_2S (as in the case of Al_2S_3, Cr_2S_3 etc.

$$S^{-2} + H_2O \rightleftharpoons HS^- + OH^-$$

$$HS^- + H_2O \rightleftharpoons H_2S + OH^-$$

Aqueous solutions of such sulphides are alkaline. As_4S_6 is not hydrolysed because it is insoluble. Sulphides of Al, Cr, Fe cannot be prepared in aqueous media because of hydrolysis.

Some of the coloured sulphides, such as FeS_2, PbS etc., prepared under controlled condition resemble alloys in their properties. They exhibit metallic lustre and conduct electricity in the solid state. This is due to delocalization of some of the electrons in the structure of metal sulphides as is the case in metals and also in graphite. The selenides have similar structures.

Polysulphides :When sulphur is boiled with an alkali solution or a soluble sulphide, polysulphide ions are obtained. The resulting solution is yellow or orange-red in colour. Acidification of the polysulphides gives a mixture of hydrogen polysulphides, H_2Sx, where X = 1, 2, 3, 4, 5, 6. The combination of S with S^{-2} ions may be represented as,

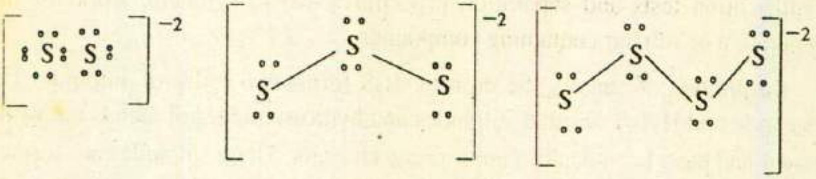
$$S + S^{-2} \rightleftharpoons S_2^{-2}$$

$$2S + S^{-2} \rightleftharpoons S_3^{-2}$$

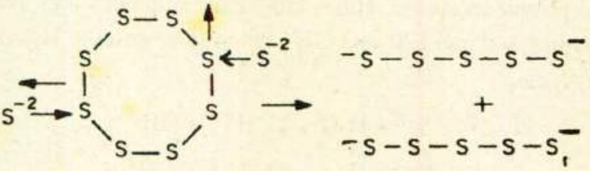
$$3S + S^{-2} \rightleftharpoons S_4^{-2}$$

$$4S + S^{-2} \rightleftharpoons S_5^{-2}$$

H_2S_2 is called hydrogen persulphide as an analogue of H_2O_2.



A mechanism suggesting the breaking open of the S_8 ring in sulphur by S^{-2} ion has been put forward as :



The polysulphide ions, like the peroxide ion, are oxidizing agents. Most of the metal sulphides are oxidized to the thiocomplexes :

$$As_2S_3 + 5S^{-2} \rightleftharpoons 2AsS_4^{-3}$$

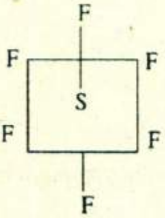
$$Sb_2S_3 + 5S^{-2} \rightleftharpoons 2SbS_4^{-3}$$

$$SnS_2 + S^{-2} \rightleftharpoons SnS_3^{-2}$$

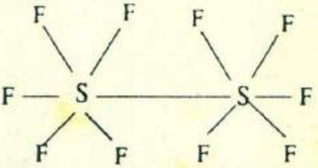
In alkaline solutions in the absence of excess polysulphide ion the polysulphide chain is unstable and breaks down to give elementary S and simple sulphides :

$$2AsS_4^{-3} \rightarrow 5S + As_2S_3$$

Sulphur hexafluoride, SF_6 : This is most remarkable sulphur halide. It is formed when S burn in F_2. Along with SF_6 some lower fluorides of S are also formed. These may be removed by liquefaction and fractional distillation. SF_6 is an inert gaseous substance and is not affected by any reagent, acid, alkali metals etc. It is the most inert sulphur compound known. The larger S atom (as compared to oxygen) has **d** orbitals available which can be used in covalent bond formation. SF_6 is an octahedral molecule with S atom at the centre of the octahedron and the 6F atoms situated at the 6 corners of the octahedron. The inertness is possibly due to *steric hinderance* by which S atom in SF_6 is protected. An stable S_2F_{10} formed in small amount along with SF_6 has been separated from the liquid by fractionation. S_2F_{10} is less inert than SF_6 possibly due to S—S bond.



SF_6



S_2F_{10}

SF_6 finds application as electrical insulator at very high temperature.

SeF_6 and TeF_6 are more reactive than SF_6 and are prepared from the elements.

Sulphur monochloride, S_2Cl_2: This is the most important halide of sulphur and finds application in rubber industry for vulcanization. This is obtained by several processes :—

(a) Chlorination of S in limited amount of Cl_2 :

$$2S + Cl_2 = S_2Cl_2$$

(b) When thionyl chloride, $SOCl_2$, or sulphuryl chloride, SO_2Cl_2, are heated with sulphur :

$$2SOCl_2 + 3S = 2S_2Cl_2 + SO_2$$

$$SO_2Cl_2 + 2S = S_2Cl_2 + SO_2$$

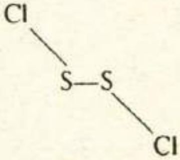
(c) It is obtained as a by-product when CCl_4 is manufactured from CS_2 and Cl_2 :

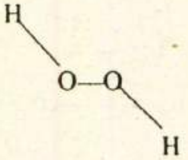
$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$$

S_2Cl_2 is an orange-yellow oily liquid readily hydrolysed by water accompanied by self-oxidation forming elementary S and SO_2 :

$$2S_2Cl_2 + 2H_2O = SO_2 + 2HCl + 2S$$

S_2Cl_2 has the same structure as H_2O_2 :





S_2Cl_2 is a good solvent for S, I_2 and many organic compounds. It reacts with C_2H_4 to give mustard gas :

$$S_2Cl_2 + 2C_2H_4 \rightarrow Cl\text{–}CH_2\text{–}CH_2\text{–}S\text{–}CH_2\text{–}CH_2\text{–}Cl + S$$

Sulphur dichloride, SCl_2 : This is obtained by further chlorination of S_2Cl_2 in the form of a dark coloured liquide :

$$S_2Cl_2 + Cl_2 = 2SCl_2$$

Further chlorination also gives SCl_4.

Sulphur oxychlorides : SO_2Cl_2 and $SOCl_2$ are known as *sulphuryl chloride* and *thionyl chloride* respectively.

Thionyl chloride, $SOCl_2$, is a colourless liquid and prepared readily from PCl_5 and SO_2. It can also be prepared from $COCl_2$ and SO_2 :

$$SO_2 + PCl_5 = SOCl_2 + POCl_3$$

$$COCl_2 + SO_2 = SOCl_2 + CO_2$$

$SOCl_2$ is an important reagent in organic chemistry and is used to convert carboxylic acid to their acid chlorides and SO_2 gas is out :

$$SOCl_2 + R\text{—}COOH = R\text{—}COCl + SO_2 + HCl$$

The structure of $SOCl_2$ is related to H_2SO_3.

Sulphuryl chloride, SO_2Cl_2, is obtained as a liquid by direct combination of SO_2 with liquid Cl_2 in presence of a catalyst (camphor) :

$$SO_2 + Cl_2 = SO_2Cl_2$$

and also from H_2SO_4 and PCl_5 :

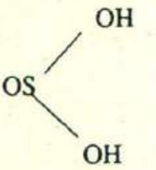
$$H_2SO_4 + 2PCl_5 = SO_2Cl_2 + 2POCl_3 + 2HCl$$

Both SO_2Cl_2 and $SOCl_2$ are hydrolysed in water forming H_2SO_4 and H_2SO_3 respectively :

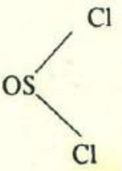
$$SO_2Cl_2 + 2HOH \rightarrow SO_2(OH)_2 + 2HCl$$

$$SOCl_2 + 2HOH \rightarrow SO(OH)_2 + 2HCl$$

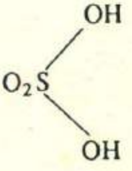
Hence, structurally these are related to H_2SO_4 and H_2SO_3 :



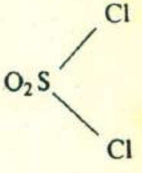
Sulphurous acid



Thionyl chloride



Sulphuric acid



Sulphuryl chloride .

Oxides of sulphur : In the sulphur family, S forms more numerous oxides. These are :

SO — sulphur monoxide

S_2O_3 — sulphur sesqioxide

SO_2 — sulphur dioxide

SO_3 — sulphur trioxide

S_2O_7 — sulphur heptoxide

SO_4 — sulphur tetroxide

Of the above six sulphur oxides, only SO_2 and SO_3 are important. Others are unstable and unimportant.

Sulphur Dioxide, SO_2

This is of considerable technological importance and is obtained by various methods :

(a) By burning sulphur (brimstone) in air :

$$S + O_2 = SO_2$$

(b) By roasting of pyrites and other metal sulphides :

$$4FeS_2 + 11\,O_2 = 2Fe_2O_3 + 8SO_2$$

$$2ZnS + 3\,O_2 = 2ZnO + 2SO_2$$

(c) By reducing H_2SO_4 with metals or non-metals :

$$2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$$

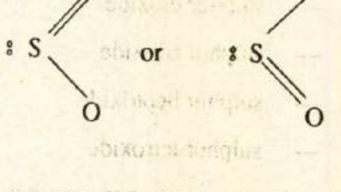
$$2H_2SO_4 + S = 3SO_2 + 2H_2O$$

(d) By the action of dilute acids on sulphits or bisulphites :

$$Na_2SO_3 + 2HCl = SO_2 + 2NaCl + H_2O$$

Properties : It is a colourless gas with choking smell. It readily condenses to liquid SO_2 at −10°C and freezes at −72.7°C.

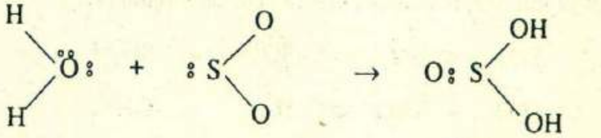
The properties of SO_2 is best understood from the structure of its molecule. SO_2 gas has a large value of dipole moment indicating O—S—O bond to be non-liner. The contributing structures may be written as,



The structure confers on SO_2 four-fold properties : (1) Lewis acid, (2) Lewis base, (3) reducing agent, (4) oxidizing agent.

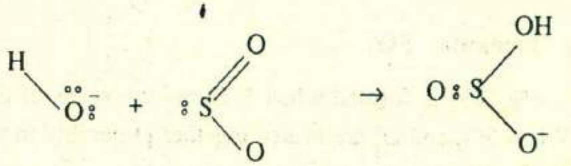
1) As Lewis acid :

(a)



Sulphurous acid

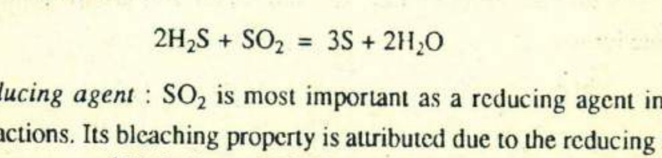
(b)



HSO_3^- ion

(c) $CaO + SO_2 = CaSO_3$

(2) As Lewis base :



(3) Oxidizing agent :

$$2H_2S + SO_2 = 3S + 2H_2O$$

(4) Reducing agent : SO_2 is most important as a reducing agent in most chemical reactions. Its bleaching property is attributed due to the reducing action of SO_2 in presence of H_2O (i.e., of H_2SO_3) as compared to chlorine which bleaches by oxidation. As reducing agent SO_2 liberates I_2 from KIO_3, decolourises $KMnO_4$ and turns $K_2Cr_2O_7$, green.

Uses of SO_2 : (1) Bleaching of paper, silk, wool etc. (2) Preservative for dried fruits. (3) Largely used for the manufacture of H_2SO_4. (4) In petroleum industry for bleaching of kerosene. (5) Liquid SO_2 is used as a refrigerant. (6) Liquid SO_2 as a non-aqueous solvent.

Liquid SO_2 : It conducts electricity and is a good solvent for a number of ionic compounds and is used for carrying out chemical reactions. The auto-oxidation of liquid SO_2 resembles that of H_2O and liquid NH_3:

$$SO_2 + SO_2 \rightleftharpoons SO^{+2} + SO_3^{-2}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

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

Sulphur Trioxide, SO_3

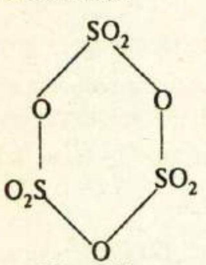
About 3—4% SO_3 is formed when S Burns in excess of air producing mainly SO_2. When SO_2 and O_2 are heated together preferably in presence of a catalyst, such as Pt or V_2O_5 giving SO_3 :

$$2\,SO_2 + O_2 \underset{V_2O_5}{\overset{Pt}{\rightleftharpoons}} 2SO_3 + 45 \text{ Kcal}$$

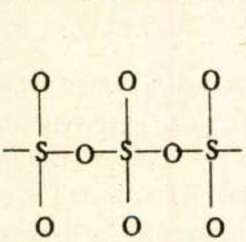
SO_3 is the dehydrated product of H_2SO_4 and can be obtained by gently distilling H_2SO_4 preferably with an excess of P_2O_5 :

Properties : SO_3 gas freezes at 15°C to give transparent ice-like crystals. On exposure to air it gives asbestos-like solid. It is, therefore, liquid at ordinary temperature and boils at 46°C.

The three solid forms of SO_3 consist of (1) trimer $(SO_3)_3$, ice-like, (2) long-chain, SO_3 groups, asbestos-like, (3) long-chain SO_3 groups joined in layers (unstable form) :



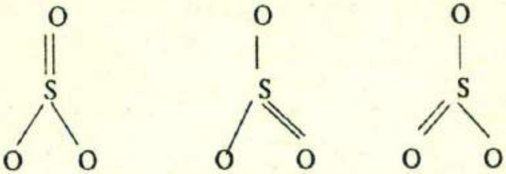
Trimer SO_3



Chain SO_3

Stabilized SO_3 are now being sold commercially under the trade name of *Sulphans.*

In the vapour state SO_3 is a monomer (consisting of only one molecule). In the solid state it has several structural modification as mentioned. Liquid SO_3 mainly consists of three molecules of SO_3 (trimer) joined together in 6-membered ring. In the single molecule the oxygen atoms occupy the three corners of an equilateral triangle with S atom at the centre :

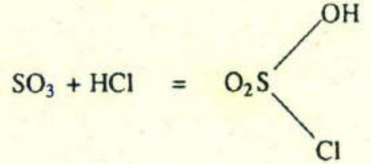


SO_3 is the strongest Lewis acid. It reacts almost vigorously with bases, such as H_2O, amines, ethers, oxides etc. :

$$SO_3 + H_2O = H_2SO_4 + 45\ \text{Kcal}$$

$$SO_3 + BaO = BaSO_4$$

It also reacts with non-basic substances, such as HCl, H_2SO_4 :



$$SO_3 + HCl = O_2S\begin{matrix} \diagup OH \\ \diagdown Cl \end{matrix}$$

(Chlorosulphonic acid)

$$SO_3 + H_2SO_4 = H_2S_2O_7$$ (Pyrosulphuric acid)

The pyrosulphuric acid (disulphuric acid) along with more polymerised forms, $H_2S_3O_{10}$ and $H_2S_4O_{13}$, gives rise to the familiar *fuming sulphuric acid* or *oleum*.

OXYACIDS OF SULPHUR

Oxyacids of sulphur contain S atom in the oxidation states from +2, +3, +4 and +6. A very large number of oxyacids of sulphur is known. On the basis of their nomenclature, some of these may be classified into the following groups:—

(I) Normal oxyacids : These are well-known acids :

H_2SO_3 H_2SO_4

(II) Pyroacids : These are formed from H_2SO_3 or H_2SO_4 generally by condensation reaction :

$$H_2S_2O_5 \qquad H_2S_2O_7$$

(III) Thioacids : These again consist of—

(a) Thionic acids : $H_2S_xO_6$ where $x = 2$ to 6

(b) Thionous or hyposulphurous : $H_2S_2O_4$

(c) Thiosulphuric acid : $H_2S_2O_3$

(IV) Peroxyacids : These contain—O—O— link :

H_2SO_5	$H_2S_2O_8$
Permonosulphuric acid	Perdisulphuric acid

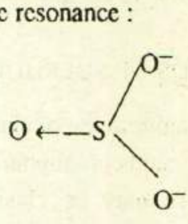
(I) Sulphurous acid, H_2SO_3 : Sulphur dioxide gas dissolves in water to the extent of about 10% by weight at 20°C at the ordinary condition. The solution contains H_2SO_3 :

On cooling a saturated solution of H_2SO_3, crystals have been obtained supposed to contain H_2SO_3 in the hydrated form ($H_2SO_3.6H_2O$).

H_2SO_3 solution is slowly oxidized by oxygen form the air :

$$2H_2SO_3 + O_2 = 2H_2SO_4$$

H_2SO_3 in aqueous solution ionizes to give HSO_3^- and SO_3^{-2} ions ($Ka_1 = 1.3 \times 10^{-2}$, $Ka_2 = 5.6 \times 10^{-8}$). The SO^{-2} ion has a pyramidal structure as the ClO_3^- ion with possible resonance :



Since both HSO_3^- and SO_3^{-2} ions are present, both normal and bisulphite salts are formed from H_2SO_3. This is done by passing appropriate amounts of SO_2 gas into an aqueous solution of the metal carbonates or hydroxides :

$$Ca(OH)_2 + 2SO_2 + H_2O = Ca(HSO_3)_2 + H_2O$$

$$K_2CO_3 + 2SO_2 + 2H_2O = 2KHSO_3 + CO_2 + H_2O$$

$$2NaOH + SO_2 + H_2O = Na_2SO_3 + 2H_2O$$

On heating a bisulphite salt, both water and SO_2 are evolved forming sulphite compound :

$$2NaHSO_3 = Na_2SO_3 + SO_2 + H_2O$$

Further heating of Na_2SO_3 gives rise to an auto-oxidation reduction reaction:

$$4\ Na_2\overset{+4}{S}O_3 = Na_2\overset{-2}{S} + 3Na_2\overset{+6}{S}O_4$$

H_2SO_3 solution is a good reducing agent towards strong oxidizing agents. Thus Cl_2, $KMnO_4$, $K_2Cr_2O_7$ etc. in aqueous solutions oxidize H_2SO_3 to H_2SO_4.

Uses of H_2SO_3 and its salts : (1) Bleaching agent : (2) antiseptic : (3) $Ca(HSO_3)_2$, calcium bisulphite, is extensively used for the manufacture of paper from wood. The chips of wood are digested in $Ca(HSO_3)_2$ solution at 177°C under pressure, as a result the lignin of wood is removed and at the same time the wood pulp is bleached. (4) Na_2SO_3 is used for making other compounds.

Sulphuric Acid

Sulphuric acid is a strong aid generally called "the king of chemicals". Many other chemical industries are based on H_2SO_4 as the basic material. For instance, petroleum refining, fertilizers, paints, drugs, explosives etc. are some of the fields of applications.

The two methods of manufacture of H_2SO_4 are well-known as—(i) Contact Process and (ii) Lead Chamber Process. Both the processes depend upon the oxidation of SO_2 to SO_3.

The Contact Process : Pure sulphur is burnt in air to form SO_2 :

$$S + O_2 = SO_2$$

SO_2 is oxidized by means of air (O_2) in Presence of suitable catalyst (such as Pt, V_2O_5, Fe_2O_3, CuO etc.):

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45 \text{ Kcal}$$

The purity of SO_2 and air is a very important factor. Presence of impurities renders the catalyst ineffective and it is said to be poisoned.

The reversible reaction is exothermic. hence, low temperature favours the formation of SO_3, but the rate of reaction at low temperature is slow. Therefore, in order to increase the rate of reaction the temperature is increased to about 650°C. The temperature is brought down to 450°C while the mixture of SO_2 and air continued to pass. The increased rate of reaction at 650°C and the change of condition to 450°C shift the equilibrium towards the right giving greater yield of SO_3.

Because SO_3 vapour mixed with oxygen does not readily dissolve in water, the SO_3 vapour is passed into a solution of 98% H_2SO_4 in which SO_3 is absorbed smoothly giving pyrosulphuric acid :

$$H_2SO_4 + SO_3 = H_2S_2O_7$$

Water is carefully added to the resulting solution to convert the $H_2S_2O_7$ to H_2SO_4 :

H_2SO_4 made by the Contact Process is quite pure and concentrated.

The Lead Chamber Process : The process derived its name from the fact that the reaction of SO_2 with O_2 in the presence of NO is carried out in large lead-lined chambers. The mode of oxidation of SO_2 to SO_3 is different in this case.

SO_2 may be produced from burning the sulphur or by roasting pyrites or sulphides, such as FeS_2. ZnS etc., SO_2 gas is passed into the lead chamber along with air (O_2), NO, NO_2 and steam. Reactions in the lead chamber are quite complicated but the changes may be represented by the equations :

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$2SO_2 + 3NO_2 + H_2O \rightleftharpoons \underset{\text{Nitrosyl sulphonic acid}}{2NO(HSO_4)} + NO$$

$$2NO(HSO_4) + H_2O \rightleftharpoons 2H_2SO_4 + NO + NO_2$$

The mixture of NO and NO_2 is recirculated and thus functions as oxygen carrier.

The acid from the Chamber Process contains only 60—70% H_2SO_4. A schematic diagram of the manufacture of H_2SO_4 by the Lead Chamber Process is given in Fig. 21—3.

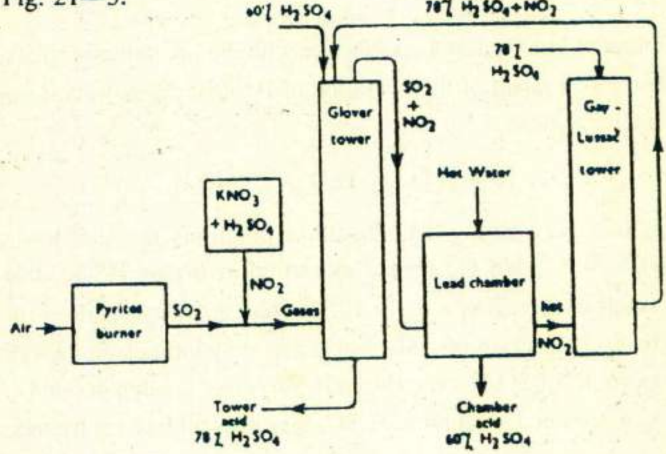


Fig. 21—3. A schematic diagram of the manufacture of H_2SO_4 by the Lead Chamber Process.

Concentration of H_2SO_4 may be increased to 93% by heating in silica or duriron pans (pans made of an alloy of Fe and Si). This may be concentrated by passing hot air from below while the dilute acid is percolated from the top as in the Gaillard Process. Acid made by the Lead Chamber process contains Pb, Fe, As etc.

H_2SO_4 from gypsum : Instead of metal sulphides or sulphur, gypsum, $CaSO_4$, has also been used to produce SO_2. A mixture of $CaSO_4$, SiO_2, clay and coke is heated in a furnace to produce a mixture of gases containing SO_2, N_2 and oxygen known as burner gases :

$$CaSO_4 + 2C = CaS + 2CO_2$$

$$CaSO_4 + CaS + O_2 = 2CaO + 2SO_2$$

$$2CaS + 2CaO + 6SiO_2 + 3O_2 = 6CaSiO_3 + 2SO_2$$

$$2CaS + 2CaO + 2Al_2O_3 + 3O_2 = 6CaO.2Al_2O_3 + 2SO_2$$

This method is specially suitable where gypsum is abundantly available.

Properties of H_2SO_4 : 100% pure H_2SO_4 is an oily liquid having covalent bonds. The acid boils at 317°C at which point it has a composition of 98.54% and is reached from either dilute or more concentrated side by loss of SO_3 or H_2O, as the case may be.

Concentrated H_2SO_4 dissolves in water with the liberation of great quantity of heat mostly as a result of the hydration of H^+ ions through the formation of H_2SO_4 as intermediates :

$$H^+ + H_2O = H_3O^+ + 288\ \text{Kcal}$$

H_2SO_4 is a very strong acid. In dilute solutions the first ionization is complete ($Ka_1 \sim 10^3$) but the second ionization involving HSO_4^- takes place only to a small extent ($Ka_2 = 3.5 \times 10^{-2}$). Thus a strong solution of H_2SO_4 contains greater proportion of HSO_4^{-2} whereas very dilute solutions contains a greater proportions of SO_4^{-2} ions. Hence H_2SO_4 gives bisulphates and sulphates of metals. Concentrated solution of H_2SO_4 dissolves all basic substances giving HSO_4^-:

$$\begin{aligned}
H_2SO_4 + NH_3 &= NH_4^+ + HSO_4^- \\
H_2SO_4 + H_2O &= H_3O^+ + HSO_4^- \\
H_2SO_4 + KOH &= KHSO_4 + H_2O \\
Na_2SO_4 + H_2SO_4 &= 2NaHSO_4
\end{aligned}$$

Thus the acid salts may be prepared by the above reactions. Acid salts are highly ionized in aqueous solutions and can be titrated as acid.

Reactions of H_2SO_4 : It reacts in three ways :—

(1) ***Oxidizing actions of H_2SO_4***: Dilute H_2SO_4 does not react with metals which occur below hydrogen in the E.M.F. series. Metals above hydrogen react to give H_2 with dilute H_2SO_4. for instance, Zn is oxidized to Zn^{+2} state and H^{+2} is reduced to H_2 in the zero oxidation state :

$$\overset{0}{Zn} + H_2SO_4 = \overset{+2}{Zn}SO_4 + H_2$$

In this type of reaction oxidation state of S is not changed. But when hot and concentrated H_2SO_4 is used, a different types of oxidation-reduction reaction takes place is which S is involved in the reaction and no H_2 is evolved. Thus when hot and concentrated H_2SO_4 is used, the following reactions take place :

$$\overset{0}{Cu} + 2H_2\overset{+6}{S}O_4 = \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + 2H_2O$$

$$\overset{0}{C} + 2H_2\overset{+6}{S}O_4 = \overset{+4}{C}O_2 + 2\overset{+4}{S}O_2 + 2H_2O$$

$$2HI + H_2SO_4 = \overset{0}{I_2} + \overset{+4}{S}O_2 + 2H_2O$$

(2) Dehydrating reactions : When H_2SO_4 is added to water a great deal of heat is evolved because of the formation of H_3O^+ ions. H_2SO_4 has great affinity for water and hence its use as an efficient drying agent for gases and liquids which do not react with it chemically. H_2O may also be removed from some organic substances so effectively that only carbon is left, e. g., from sugar and glucose :

$$C_{12}H_{22}O_{11} + 11H_2SO_4 = 12C + 11(H_2SO_4.H_2O)$$

Formic acid, oxalic acid etc. are converted to CO, CO_2 etc. :

$$HCOOH + H_2SO_4 = CO + H_2SO_4.H_2O$$

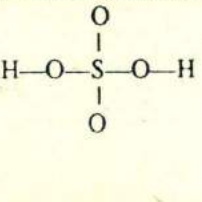
Most organic substances such as cotton, wood etc. are carbonized by concentrated H_2SO_4 for the same reason.

(3) Displacement of compounds due to high boiling point : Volatile acids, such as HCl, HNO_3 etc., are readily displaced by the reaction of their respective salts with concentrated H_2SO_4. H_2SO_4 being non-volatile is left behind if present in excess :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

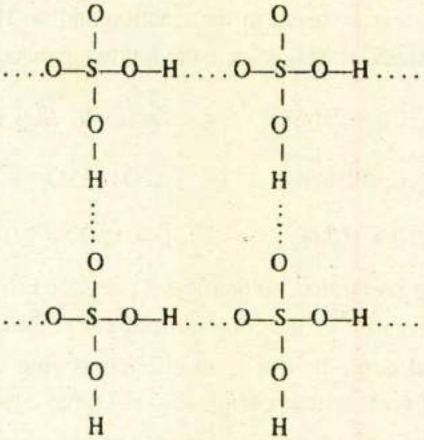
$$KNO_3 + KHSO_4 = KHSO_4 + HNO_3$$

Structure of H_2SO_4 : The S atom in SO_4^{+2} is surrounded tetrahedrally by the four oxygen atoms. The H atoms form hydrogen bonds between these SO_4 tetrahedra in three-dimensional pattern and hence the boiling



$$\begin{array}{c} O \\ | \\ H{-}O{-}S{-}O{-}H \\ | \\ O \end{array}$$

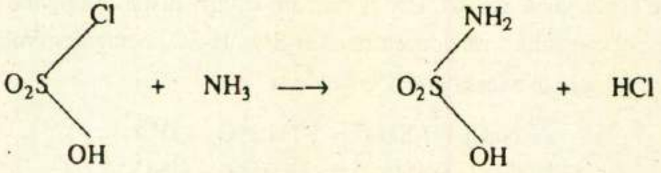
point (or decomposition temperature) of H_2SO_4 is very high. A two-dimensional pattern is given below :



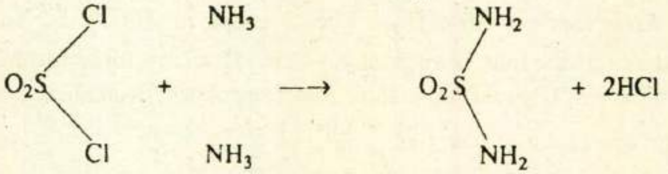
Derivatives of H_2SO_4

(1) Mono-acid chloride and di-acid chloride of H_2SO_4 have already been described. These are also known as chlorosulphonic acid $Cl.SO_2,OH$ and sulphuryl chloride, $ClSO_2.Cl$, respectively.

(2) Chlorosulphonic acid or sulphuryl chloride, on treatment with NH_3, gives the corresponding amides known as *sulphamic* acid and ***Sulphamide*** respectively.



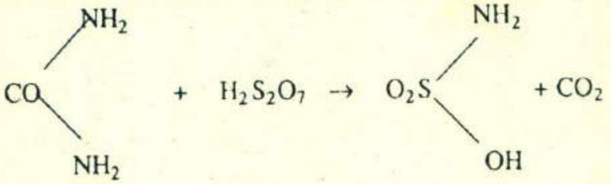
sulphamic acid



sulphamide

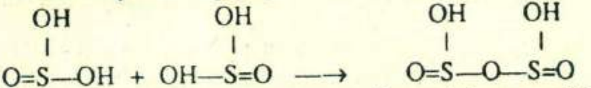
Sulphamic acid HSO_3NH_2 is an stable solid and is used as a primary standard for alkali titrations. ammonium sulphamate, $NH_4SO_2.NH_2$, has been used as a weed-killer and as fire-proofing agent.

Sulphamic acid can also be prepared from urea and fuming H_2SO_4 :



(3) Metal sulphates tend to hold one molecule of water (anion water) by H bond as in the case of $CuSO_4.5H_2O$, i.e., $[Cu(H_2O)_4]^{+2}$ $[SO_4 \cdot H_2O]^{-2}$ All other hydrated sulphates can be represented in the same manner. Large number of double sulphates of many metals (alums) are formed.

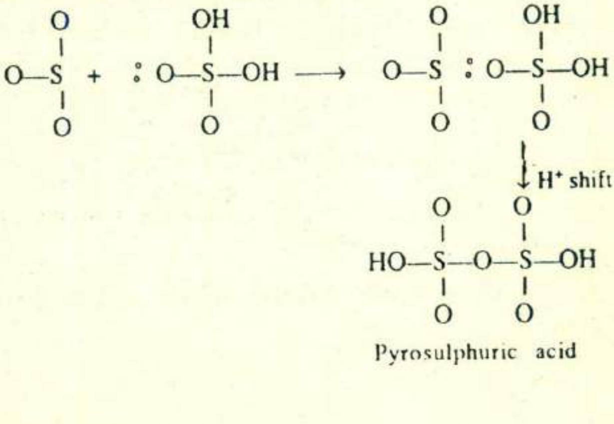
Pyroacids of sulphur : These have been mentioned earlier. Both pyrosulphurous acids and pyrosulphuric acids are known. Pyrosulphurous acid, $H_2S_2O_5$, is formed by heating a bisulphite and by acidification. SO_2 may be absorbed by H_2SO_3 to give $H_2S_2O_5$. The sodium salt is incorrectly known as sodium metabisulphite, $Na_2S_2O_5$:



$$O{=}\overset{\overset{OH}{|}}{S}{-}OH + OH{-}\overset{\overset{OH}{|}}{S}{=}O \longrightarrow O{=}\overset{\overset{OH}{|}}{S}{-}O{-}\overset{\overset{OH}{|}}{S}{=}O$$

Pyrosulphurous acid

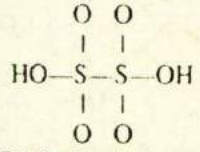
SO_3 is absorbed by concentrated H_2SO_4 to give a number of pyro-acids, $H_2S_2O_7$, $H_2S_3O_{10}$ and $H_2S_4O_{13}$. These are present in oleum. The reaction between SO_3 and H_2SO_4 may be represented as :



Pyrosulphuric acid

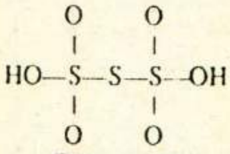
Thioacids of Sulphur

(a) Thionic acids : These consist of the general formula $H_2S_xO_6$ where x can vary from 2 to 6. Obviously, it is the S—S bond which is responsible for the various thionic acids. In fact, these are analogous to the peroxy acids containing O—O chain :



$$\mathrm{HO{-}\overset{O}{\underset{O}{S}}{-}\overset{O}{\underset{O}{S}}{-}OH}$$

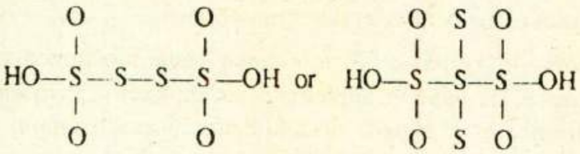
Dithionic acid



$$\mathrm{HO{-}\overset{O}{\underset{O}{S}}{-}S{-}\overset{O}{\underset{O}{S}}{-}OH}$$

Trithionic acid

Tetrathionic acid is formulated in two forms :



$$\mathrm{HO{-}\overset{O}{\underset{O}{S}}{-}S{-}S{-}\overset{O}{\underset{O}{S}}{-}OH \quad or \quad HO{-}\overset{O}{\underset{O}{S}}{-}\overset{S}{\underset{S}{S}}{-}\overset{O}{\underset{O}{S}}{-}OH}$$

The acids have never been isolated, but salts of each acid have been made.

Dithionic acid, $H_2S_2O_6$, is a strong acid and is not oxidized by even $KMnO_4$, Cl_2. $Na_2S_2O_6$ is prepared by the oxidation of SO_2 or Na_2SO_3 either by electrolytic method or MnO_2 :

$$2NaHSO_3 + MnO_2 \rightarrow Na_2S_2O_6 + Mn(OH)_2$$

The other thionates are made by reduction of H_2SO_3 or $NaHSO_3$ by electrolytic process. The tetrathionate, e.g., $Na_2S_4O_6$, is most easily made by the action of I_2 on sodium thiosulphate, $Na_2S_2O_3$, or by the anodic oxidation of $NaHS_2O_3$:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

$$NaHS_2O_3 \xrightarrow[\text{oxidation}]{\text{anodic}} Na_2S_4O_6$$

Salts of thionic acids are water-soluble, unstable and are decomposed by alkali to sulphites and thiosulphates.

(b) Thionous or hyposulphurous acid, $H_2S_2O_4$: The salt $Na_2S_2O_4$ is known as sodium dithionite, sodium hydrosulphite or hypo-sulphite. This is made by reducing Na_2SO_3 or Na_2HSO_3 with zinc in alcohol or by cathodic reduction of HSO_3^- ions :

$$2NaHSO_3 + Zn + SO_2 \ = \ Na_2S_2O_4 + ZnSO_3 + H_2O$$

$$2NaHSO_3 \xrightarrow[\text{reduction}]{\text{cathodic}} Na_2S_2O_4 + \ H_2O$$

$Na_2S_2O_4$ is a powerful reducing agent and is used in industry as a bleach for dyes, such as indigo blue to indigo white. Cu_2H_2 and CuH_2 are formed with $CuSO_4$. Air oxidizes it to $Na_2S_2O_5$.

(c) Thiosulphuric acid, $H_2S_2O_3$

Sodium thiosulphate : Sodium thiosulphate, $Na_2S_2O_3$, is a common reagent in the laboratory and is known as hypo in photography. It is obtained commercially as $Na_2S_2O_3.5H_2O$ by the following methods :—

(i) Boiling Na_2SO_3 solution with sulphur powder, the solution is filtered and crystals of $Na_2S_2O_3$ separated by evaporation :

$$Na_2SO_3 + S \ = \ Na_2S_2O_3$$

(ii) Adding I_2 to a mixture of Na_2S and Na_2SO_3 :

$$Na_2S + Na_2SO_3 + I_2 \ = \ 2NaI + Na_2S_2O_3$$

(iii) $Na_2S_2O_3$ is manufactured from Na_2S, Na_2CO_3 and SO_2 :

$$2Na_2S + Na_2CO_3 + 4SO_2 \ = \ 3Na_2S_2O_3 + CO_2$$

(iv) Also by the reaction of Na_2CO_3 and SO_2 and sulphur :

$$\begin{aligned} Na_2CO_3 + H_2O + 2SO_2 \ &= \ 2NaHSO_3 + CO_2 \\ 2NaHSO_3 + Na_2CO_3 \ &= \ 2Na_2SO_3 + H_2O + CO_2 \\ Na_2SO_3 + S \ &= \ Na_2S_2O_3 \end{aligned}$$

In each case the solution after filtration is evaporated and $Na_2S_2O_3.5H_2O$ is isolated by crystallisation.

Properties and uses : $Na_2S_2O_3.5H_2O$ (hypo) is a colourless crystalline substance. It is a good reducing agent and is used in the photographic processing known as fixing which dissolves the excess AgBr not reduced to metallic silver by the developer :

$$AgBr + Na_2S_2O_3 = NaAg(S_2O_3) + NaBr$$

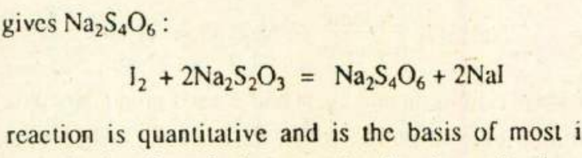
With I_2 it gives $Na_2S_4O_6$:

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

This reaction is quantitative and is the basis of most iodometric and iodimetric methods of analysis, e.g., in the determination of Cu^{+2}. The formation of $S_4O_6^{-2}$ ions occurs only with weak oxidizing agent, such as I_2. Strong oxidizing agent converts the $S_4O_6^{-}$ ions to SO_4^{-2} ions.

$Na_2S_2O_3$ is also used to remove excess chlorine in the bleaching industry. for this reason sodium thiosulphate is also known as *antichlor*.

Structure : $S_2O_3^{-2}$ ion is similar in structure to SO_4^{-2} ion. The mode of preparation from SO_3^{-2} and S itself is indicative of the structure :



This $S_2O_3^{-2}$ ion is, in fact, SO_4^{-2} ion in which one oxygen atom has been replaced by the sulphur atom. In $S_2O_3^{-2}$ ion the central S atom has oxidation number −2. The average oxidation number of S in $S_2O_3^{-2}$ ion is +2. The two S atoms are, therefore, non-equivalent. There is no transfer or exchange of S atoms in $S_2O_3^{-2}$ ion.

When $Na_2S_2O_3$ is treated with a dilute solution of a strong acid, $H_2S_2O_3$ formed in solution is readily decomposed to give elementary S and SO_2 :

$$\begin{array}{r} Na_2S_2O_3 + 2H^+ \rightarrow 2Na^+ + S^- + H_2SO_3 \\ \Updownarrow \\ SO_2 + H_2O \end{array}$$

Peroxysulphuric acids : Two important acids containing —O—O— link are known. These are :

Permonosulphuric acid (Caro's acid)—H_2SO_5

Perdisulphuric acid (Marshall's acid)—$H_2S_2O_8$

$H_2S_2O_8$ is obtained by various methods :—

(a) S_2O_7 formed in small amounts by an electric discharge in a mixture of SO_2 and O_2 dissolves in water to give $H_2S_2O_8$.

(b) Action of cold concentrated H_2SO_4 and concentrated H_2O_2 gives $H_2S_2O_8$:

$$2H_2SO_4 + H_2O_2 = H_2S_2O_8 + 2H_2O$$

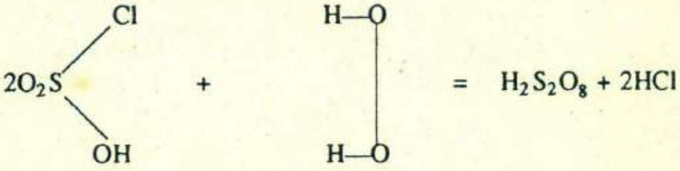
(c) Anodic oxidation of H_2SO_4. (60% solution) gives $H_2S_2O_8$ (see page .....):

$$2HSO_2^- - 2e \rightarrow H_2S_2O_8$$

Concentrated H_2SO_4 is electrolysed in a cell having Pt anode separated from the copper cathode coiled round the outer cylinder.

If concentrated solution of $(NH_4)_2SO_4$ or K_2SO_4 dissolved in concentrated H_2SO_4 is used as the electrolyte, crystals of $(NH_4)_2S_2O_8$ or $K_2S_2O_8$ separate out at the anode compartment.

(d) Pure $H_2S_2O_8$ in the anhydrous state is made by the reaction of chlorosulphonic acid with pure H_2O_2 :



$H_2S_2O_8$ is a very hygroscopic crystalline substance, melts at 65°C and decomposes with loss of oxygen. It is hydrolysed easily giving first H_2SO_5 and then H_2O_2 and is used for the technical production of H_2O_2. The acid and its salts are powerful oxidizing agents. In alkaline solutions Ag, Ni, Co, Pb etc. are converted to their peroxides :

$$2AgNO_3 + K_2S_2O_8 + 2H_2O = 2KHSO_4 + 2HNO_3 = Ag_2O_2$$

$K_2S_2O_8$ oxidizes Fe^{+2} to Fe^{+3}, Cr^{+2} to Cr^{+3} and to CrO_4^{-2} and even I_2 to IO_3^-. But it does not decolourize $KMnO_4$ solutions.

Caro's acid, H_2SO_5 : It is obtained from $K_2S_2O_8$ by the action of H_2SO_4 at low temperature and controlled hydrolysis with ice :

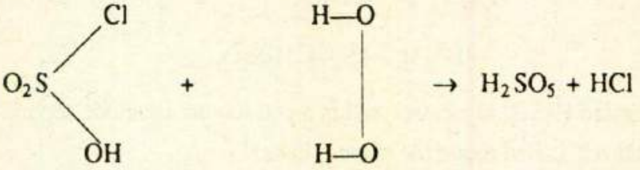
$$K_2S_2O_8 + H_2SO_4 = H_2S_2O_8 + H_2SO_4$$

$$H_2S_2O_8 + H_2O = K_2SO_5 + H_2SO_4$$

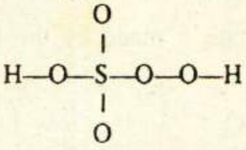
When SO_3 reacts with H_2O_2, Caro's acid is formed :

$$SO_3 + H_2O_2 = K_2SO_5$$

It is also obtained when $ClSO_3H$ is reacted with proper quantity of H_2O_2 :

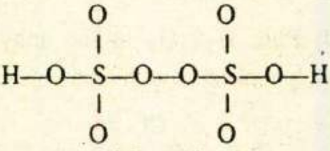


H_2SO_5 is also readily hydrolysed to give H_2O_2 and H_2SO_4. In fact, these acids are derivatives of H_2O_2 containing —O—O— linkages and H atoms replaced by HSO_3 group one by one :



$$\mathrm{H{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}{-}O{-}O{-}H}$$

Caro's acid
(Permonosulphuric acid)



$$\mathrm{H{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}{-}O{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}{-}O{-}H}$$

Marshall's acid
(Perdisulphuric acid)

CHROMIUM, MOLYBDENUM AND TUNGSTEN

(The Elements of Group VIB)

The elements of sb-group VIB, Cr, Mo and W are transition metals. Uranium used to be included in this group, but U now belongs to the Actinide series of elements and hence it is excluded from this group. In the present book the individual chemistry of chromium will only be described.

Although Cr, Mo and W (Wolfram) have some similarities with the elements of group VIA, O, S, Se and Te, the marked difference between sub-group VIA and VIB arises due to the electronic configurations.

Comparison between S and Cr groups :

(a) Similarities : There is no resemblance in the various elements of the group except in certain compounds, such as,

(1) Both the sub-groups exhibit the highest oxidation state of +6 in many compounds, e.g., H_2SO_4, H_2CrO_4 etc.

(2) The compounds, CrO_3, MoO_3 and WO_3 are highly acidic as is SO_3 and with water produce the respective acids.

(3) SO_4^{-2} and SeO_4^{-2} compounds are isomorphous with CrO_4^{-2} and MoO_4^{-2} compounds and show similar behaviour.

(4) H_2CrO_4 and H_2MoO_4 have similar acid behavior as H_2SO_4 and H_2SeO_4.

(5) $BaCrO_4$ is as insoluble as $BaSO_4$. Similarly, $PbSO_4$ and $PbCrO_4$ are insoluble compounds.

(6) CrO_2Cl_2 behave like SO_2Cl_2 in some properties and particularly in easy hydrolysis.

(b) Dissimilarities : The points of dissimilarities can be best understood from the electronic configurations. In the case of Sulphur Family the outer electron levels have the arrangement of s^2p^4, but the arrangements in Cr, Mo and W as,

S (16)—Ne core, $3s^23p^4$

Cr (24)—Ar core, $3d^54s^1$

Mo (42)—Kr core, $4d^55s^1$

W (74)—Xe core, $4f^{14}\ 5d^46s^2$

The outer electron orbitals in the case of Cr, Mo and W consist of $3d^54s^1$, $4d^55s^1$, and $5d^46s^2$ respectively although the total of 6 valence electrons are present in each sub-group. The presence of incomplete **d** orbitals in Cr, Mo and W makes their chemistry very different from those of the S group.

Some of the points of contrasts may be enumerated as follows :—

1. Chromium group elements are transition metals with high density. Sulphur group elements are mostly non-metals, only tellurium shows metallic property.

2. Chromium group metals occur only in the combined state and are extracted from their ores with difficulty. Sulphur group elements occur free in nature and also as compounds.

4. Lower oxides of chromium group elements are basic or amphoteric. Thus CrO is basic and Cr_2O_3 is amphoteric. But lower oxides of sulphur group are acidic. Thus SO_2, SeO_2 are acidic.

5. Chromium group elements show a large number of variable oxidation states than sulphur group and form coloured compounds. $K_2Cr_2O_7$, $KCrO_2$ and K_2CrO_4 are coloured.

6. Chromium group elements do not combine with hydrogen to form volatile hydrides. But H_2S, H_2O, H_2Se are very well-known compounds.

7. Three is a marked tendency for the formation of more complex ployacid compounds in the case of chromium (and particularly Mo). Ammonium phosphomolybdate $(NH_4)_3[PMo_{12}O_{40}]$ is a well-known example.

8. Chromium group elements, because of the unfilled **d** orbitals, form a very large number of complex compounds which is not so well-marked in the sulphur group.

$Cr(NH_3)_6Cl_3$, $Cr(H_2O)_6Cl_3$ etc. are Cr-complexes; but no such compounds are formed with sulphur.

Chromium in some of its properties resembles Mn and Fe which are in group VII and VIII. The metallic property, oxidation states, oxidizing and magnetic properties of some salts of Cr, Fe and Mn appear to be alike because these ar **3d** transition metals.

Group Properties of Cr, Mo and W

(a) Physical properties : Some of the physical properties of Cr, Mo and W are given in Table 21·4.

Table 21.4. Physical properties of Cr, Mo and W.

Element	*Cr*	*Mo*	*W*
At. No	24	42	74
At. Wt.	52.01	95.95	183.92
Outer electron orbitals	$3d^54s^1$	$4d^55s^1$	$5d^46s^2$
Ionization potential (ev)	6.74	7.35	7.98
Atomic radius (Å)	1.25	1.36	1.37
Ionic radius			
Ion M^{+6} (Å)	0.52	0.62	0.68
Melting point (°C)	1575	2620	3370
Boiling point (°C)	2475	4800	5930
Oxidation potential (v)	Cr/Cr^{+2} 0.91	Mo/Mo^{+3} 0.20	W/W^{+2} 0.04
Electronegativity	1.56	1.30	1.40

Table 21.5. Reactions of Cr, Mo and W.

Reaction with	*Cr*	*Mo*	*W*	*Conditions*
Air (O_2)	Cr_2O_3	MoO_3	WO_3	On strong heating
F_2	CrF_3	MoF_6	WF_6	On heating
Cl_2	$CrCl_3$	$MoCl_6$	WCl_6	"
Br_2	$CrBr_3$	$MoBr_4$	WBr_6	"
Acids ($HCl.H_2SO_4$)	Cr^{+2}, Cr^{+3}	No reaction	No reaction	
HNO_3	Cr^{+3} Soln.	MoO_3 ppt.	WO_3 ppt.	Boiling
Alkali	CrO_2^- (Soln.)	No reaction	WO_4^{-2} (soln.)	Boiling
Carbon	Cr_2C_3 interstitial	WC Refractory	MoC Refractory	High temperature
N_2	CrN (hydrolysed)	No action	No action	On strong heating
S	CrS	MoS_2	WS_2	On heating
H_2	No reaction	No action	No action	Adsorption
Important uses	Special steels	Special steels	Filaments	

(b) Chemical properties : The valence electrons of Cr, Mo and W throw some light on the pattern of chemical properties which are exhibited by these transition metals. The reaction of these metals with familiar reagents do not follow any trend but are varied in nature. Instead of describing reactions in details, these are summarised in Table 21.5 for ready reference.

CHROMIUM

Sources of chromium : Chromium does not occur free in nature. The most important sources are :

Chromite, Chrome iron stone—$FeO.Cr_2O_3$ or $FeCr_2O_4$
Crocoite, Lead chromate—$PbCrO_4$
Chrome ochre—Cr_2O_3

Chromite is the only important ore which is profitably utilized for obtaining chromium and all its compounds.

Metallurgy of Chromium

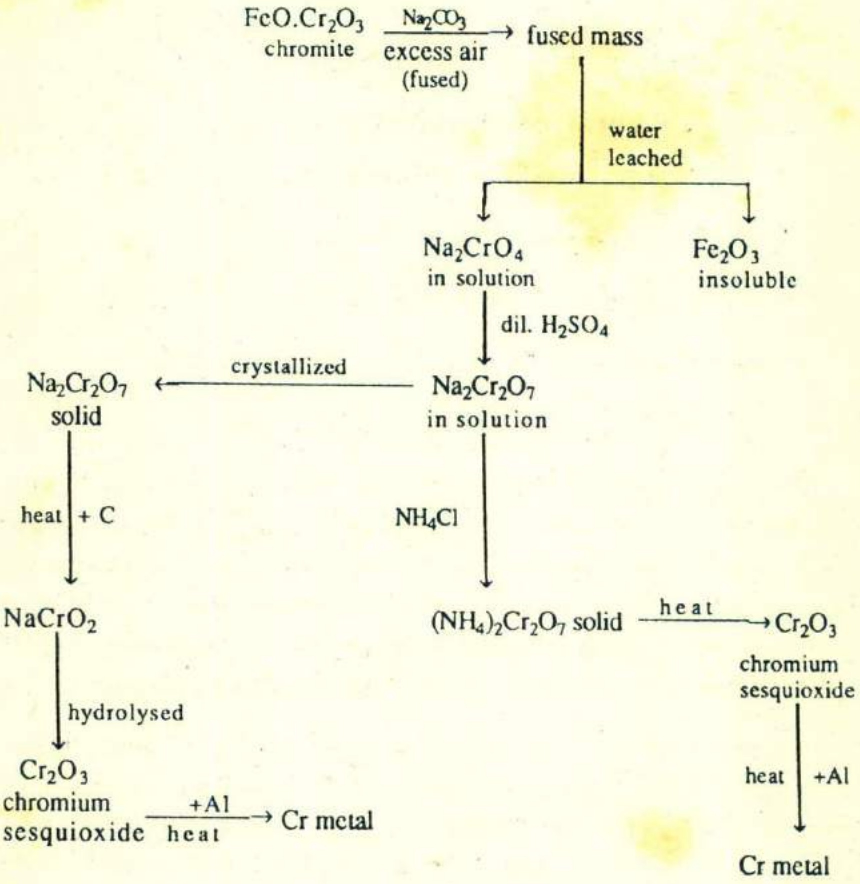
Metallic chromium is normally extracted from chromite or chrome iron ore, $FeO.Cr_2O_3$. The extraction of chromium from chromite depends upon the use for which it is intended.

Ferrochrome : Chromium for steel industry is generally converted to *Ferrochrome*. The crushed chromite ore is freed from the gangue by washing with a current of water. The heavy chromite ore is left behind while the impurities are washed away. The concentrated chromite is then reduced by means of carbon in an electric furnace to give ferrochrome :

Thus Cr_2O_3 can be obtained from $Na_2Cr_2O_7$ by either methods through $NaCrO_2$ or through $(NH_4)_2Cr_2O_7$ as given in the flow sheets on page 601. If K_2CO_3 is used instead of Na_2CO_3, the product formed is $K_2Cr_2O_7$ which can be treated in similar manner to get Cr_2O_3.

Chromium metal is obtained from Cr_2O_3 by aluminothermic process. Cr_2O_3 is mixed with Al powder in a crucible and ignited by means of Mg ribbon and BaO_2 powder. The high thermal energy reduces Cr_2O_3 to Cr :

$$Cr_2O_3 + Al \rightarrow Al_2O_3 + 2Cr + 112\ Kcal$$



The reactions involved in the fusion process of chromite are given by the following equations :—

1. Fusion :

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 = 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

2. Dichromate conversion :

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

3. (a) Reduction :

$$Na_2Cr_2O_7 + 3C = 2NaCrO_2 + 3CO$$

(b) Hydrolysis :

$$2NaCrO_2 + H_2O = 2NaOH + Cr_2O_3$$

4. (a) Ammonium dichromate conversion :

$$Na_2Cr_2O_7 + 2NH_4Cl = (NH_4)_2Cr_2O_7 + 2NaCl$$

(b) Thermal decomposition :

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

5. Extraction of Cr :

$$Cr_2O_3 + Al \rightarrow Al_2O_3 + Cr$$

Properties of Cr : Chromium is a silvery white and hard metal and has high resistance to corrosion. Its lustre is like platinum and remains untarnished. For this reason, chromium is much used in producing chrome-plated copper and iron materials for motor cars and domestic use. In fact, chromium metal is not very much extracted from chromite but converted to either ferrochrome for steel industry and to chromium compounds for chrome-plating and other purposes.

Chrome plating : This is, in fact, a process for the production of chromium metal by the electrolytic reduction of chromium compounds from aqueous solution. For this purpose, solutions of H_2CrO_4 together with $Cr_2(SO_4)_3$ or other salts, such as borate and phosphate, are added to the electrolytic bath. Very small amount of $Cr_2(SO_4)_3$ is needed. The mixed solutions constitute the electrolytic bath. High current density is used. the article to be plated is the cathode and lead (Pb) is the anode.

Chromium is a rather difficult metal to use as a plating element and the coating tends to fall away due to the porosity. For this purpose, the article to be chrome-plated is given a very thin coating of copper or nicked first and then chrome-plated giving the bright platinum-like appearance on polishing which is not stained even in rain water :

$$\begin{aligned} CrO_4^{-2} + 8H_3O^+ + 6e &\rightarrow Cr^{+3} + 12H_2O \\ Cr^{+3} + 3e &\rightarrow Cr\ (\text{metal}) \\ CrO_4^{-2} + 8H_3O^+ + 9e &\rightarrow Cr + 12H_2O \end{aligned}$$

Thus the real plating agent is Cr^{+3} ion. But the actual concentration of Cr^{+3} ion in the plating bath is kept very small because under this condition the formation of hard deposit of chromium metal takes place.

Although chromium metal is more electropositive than iron and reacts with dilute acids to evolve hydrogen, yet it acquires a firmly held thin film of oxide coating which renders it chemically inactive and it is said to be in the passive state. Chromium exhibits greater passivity than any other metal. Passivity is produced by the action of concentrated HNO_3, H_2CrO_4 or exposure of the metal to air.

Uses of Chromium : (i) In making chrome steel, these are very hard and tough and contain various proportions of chromium.

(ii) Stainless steel : Stainless steel : 12—14% Cr, 0.3%C and rest iron, does not rust and is used in making cutlery, turbine blades, valves etc.

(iii) Nichrome (Chromel) : 60% Ni, 15% Cr and 25% Fe, is used as a resistance wire in heaters and in electric furnace since it is not oxidized at high temperature by air.

Some Important Compounds of Chromium

Chromium is a transition metal with $3d^5 4s^1$ valence electrons and chromium compounds can have several oxidation states. The compounds with +2, +3 and +6 oxidation states are the most common. Compounds with +3 state are very stable, those with +6 state are good oxidizing agents and compounds with +2 state are good reducing agents.

Compounds of Cr of +2 oxidation states : Cr (II) compounds : Chromium metal is electropositive and in the finely divided state dissolves in acids evolving H_2 :

$$\begin{aligned} Cr + 2HCl &= CrCl_2 + H_2 \\ Cr + H_2SO_4 &= CrSO_4 + H_2 \end{aligned}$$

Cr(II)halides : These can be obtained by the following methods :—

(1) Cr metal + $Cl_2 \xrightarrow{\text{(ignited)}} CrCl_2$ anhydrous chromous chloride

(2) $CrCl_3 + H_2 \xrightarrow[+HCl]{Zn} CrCl_2 + HCl$

(3) $CrCl_2 + HF \rightarrow CrF_2 + HCl$

(4) $Cr + I_2 = CrI_2$ in preference to CrI_3.

Anhydrous $CrCl_2$ is colourless but its solution in water has the bright blue colour of the hydrated $Cr(H_2O)_6^{+2}$ ion. This is unstable and easily oxidized to the hydrated $Cr(H_2O)_6^{+3}$ by aerial oxidation.

Chromous sulphate, $CrSO_4.7H_2O$, prepared by dissolving the metal in H_2SO_4, is isomorphous with $FeSO_4.7H_2O$ and also forms alum, $K_2SO_4.CrSO_4.6H_2O$.

Chromous acetate, $Cr(CH_3COO)_2$: This is prepared in the form of a red precipitate when a saturated solution of sodium acetate is added to a solution of $CrCl_2$ in presence of H_2 :

$$CrCl_2 + 2CH_3COONa = Cr(CH_3COO)_2 + 2NaCl$$

Chromous acetate is insoluble in water and very stable. In general, acetates are soluble but chromous acetate is an exception.

Chromous hydroxide, $Cr(OH)_2$: This is obtained as a brownish-yellow precipitate when NaOH is added to $CrCl_2$ solution :

$$CrCl_2 + 2NaOH = Cr(OH)_2 + 2NaCl$$

$Cr(OH)_2$ is readily oxidized by air to the green $Cr(OH)_3$, much faster than $Fe(OH)_2$.

Cr^{+2} forms relatively few complexes. Solutions of Cr^{+2} are the strongest reducing positive ions in aqueous media, Cr^{+2} forms stable complexes with NH_3 and CN^- as in

$$[Cr(NH_3)_6]Cl_2 \text{ and } K_4[Cr(CN)_6]$$

Chromium(III)compounds : Compounds of Cr of +3 oxidation states : This is the most stable oxidation state of chromium and a number of intensely coloured hydrated salts of trivalent chromium are well-known. The aqueous solution invariably contains the $Cr(H_2O)_6^{+3}$ ion which is violet but the Cr^{+3} salt solutions are often green due to the exchange of H_2O with anion present in the Cr-compounds.

$$[Cr(H_2O)_6]^{+3}Cl_3 \xrightarrow[heat]{H_2O} [Cr(H_2O)_5Cl]^{+2}Cl_2 + H_2O$$

Cr (III) oxide, Cr_2O_3 : Chromium sesquioxide is the middle member of the series of this oxides of Cr, namely CrO (basic), Cr_2O_3 (amphoteric) and CrO_3 (acidic) having Cr in +2, +3 and +6 oxidation states.

Cr_2O_3 is obtained by various methods :—

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

$$Na_2Cr_2O_7 + S \xrightarrow{heat} Na_2SO_4 + Cr_2O_3$$

$$2NaCrO_2 + H_2O \xrightarrow{boil} Cr_2O_3 + 2NaOH$$

$$Na_2Cr_2O_7 + NH_4Cl \xrightarrow{heat} Cr_2O_3 + N_2 + 4H_2O + 2NaCl$$

Cr_2O_3 may also be obtained by heating $Cr(OH)_3$ precipitate obtained by adding alkali to a Cr^{+3} salt solution :

$$2Cr(OH)_3 \rightarrow Cr_2O_3 + 3H_2O$$

Cr_2O_3 has a beautiful green colour, insoluble and inert and is used as a pigment under the name *Chrome Green*. Cr_2O_3 may be obtained from the mineral chromite already described before.

Chromic hydroxide, $Cr(OH)_3$: When a Cr^{+3} salt solution is treated with alkali hydroxides, carbonate or a solution of sodium or ammonium sulphide, a blue-green precipitate is formed which is $Cr(OH)_3$ but is hydrated to various degrees. The gelatinous precipitate is assumed to have the composition $Cr(OH)_3.(H_2O)_3$. This is amphoteric dissolving both in acid and alkali solutions

$Cr(OH)_3 + 3H^+ \rightarrow Cr^{+3} + 3H_2O$

$Cr(OH)_3 + OH^- \rightarrow Cr(OH)_4^-$ (Chromite ion)

The conversion of $Cr(OH)_3$ precipitate to chromate by alkaline oxidation is a quite familiar process in analysis. $Cr(OH)_3$ is easily converted to CrO_4^{-2} by oxidation with Na_2O_2, NaOH + Br_2, KNO_3 + Na_2CO_3, NaOH + H_2O_2 etc. :

$Cr_2O_3 + 4KOH \xrightarrow{+O} 2K_2CrO_4 + 2H_2O$

Chromic chloride, $CrCl_3$: Anhydrous $CrCl_3$ is obtained by the following reactions :—

$$Cr\ (metal) + Cl_2 \xrightarrow{heat} CrCl_3$$

$$Cr_2O_3 + 3C + 3Cl_2 \xrightarrow{heat} 2CrCl_3 + 3CO$$

$$4Cr_2O_3 + 3S_2Cl_2 + 9Cl_2 \longrightarrow 8CrCl_3 + 6SO_2$$

Violet crystals of pure $CrCl_3$ are insoluble in water but dissolves in presence of a little $CrCl_2$ or $CuCl_2$. The dilute solutions of $CrCl_3$ in water is violet, but the strong solution is green. The crystals of $CrCl_3.6H_2O$ in the solid form is green. In concentrated solution $[Cr(H_2O)_4Cl_2]^+$ is responsible for the green colour whereas in dilute solutions $[Cr(H_2O)_6]^{+3}$ assumes the violet tinge. This is also true of $Cr_2(SO_4)_3$ solutions.

Chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$: This is obtained by adding K_2SO_4 to a solution of $Cr_2(SO_4)_3$ which is prepared by the action H_2SO_4 on freshly precipitated $Cr(OH)_3$ or hydrated Cr_2O_3.

Chrome alum is manufactured directly from $K_2Cr_2O_7$ by reduction with SO_2 in presence of H_2SO_4 :

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4.Cr_2(SO_4)_3 + H_2O$

The deep violet crystals separate on evaporation of the solution. The crystals can be grown to a very large sized octahedron. Chrome alum is isomorphous with other alums. The cold solution is violet but on heating it turns green for the reason stated in the property of $Cr(H_2O)_6^{+3}$ ion.

The formula of chrome alum may also be written as $KCr(SO_4)_2.12H_2O$.

It is the most important of the soluble chromium salts. It is used in the tanning of leather, printing of calico, as a mordant in dyeing industry and in water-proofing of fabrics.

$NH_4Cr(SO_4)_2.12H_2O$ ammonium chrome alum, is obtained by using $(NH_4)_2Cr_2O_7$ as the starting material.

Chromium(VI)compounds : Compounds of Cr of +6 oxidation state : In the +6 oxidation state, chromium is usually combined with oxygen.

Chromium trioxide, CrO_3 : It is obtained by adding concentrated H_2SO_4 to a strong solution of $K_2Cr_2O_7$ in the cold. Scarlet coloured needle-shaped crystals, only slightly soluble in the cold acid, separate out :

$$K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O$$

CrO_3 is the anhydride of chromic acid, H_2CrO_4, and reacts with water in different proportion forming H_2CrO_4, $H_2Cr_2O_7$, $H_2Cr_3O_{10}$ etc. These acids exist only in solutions :

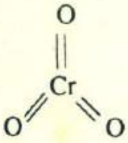
$$CrO_3 + H_2O \rightleftharpoons H_2CrO_4 \rightleftharpoons 2H^+ + CrO_4^{-2}$$

$$2CrO_3 + H_2O \rightleftharpoons H_2Cr_2O_7 \rightleftharpoons 2H^+ + CrO_7^{-2}$$

It is powerful oxidizing agent but does not oxidize CH_3COOH or ether. When heated, it loses oxygen forming the green Cr_2O_3 :

$$4CrO_3 = 2Cr_2O_3 + 3O_2$$

CrO_3 is a covalent compound and melts at 169°C. The structure is given as,



Potassium dichromate, $K_2Cr_2O_7$: It can be directly obtained from chromite ore by fusion with K_2CO_3, and subsequent crystallisation on aqueous extract. When $Na_2Cr_2O_7$ is produced from chromite, the K-salt is precipitated from $Na_2Cr_2O_7$ by adding KCl :

$$Na_2Cr_2O_7 + 2KCl = K_2Cr_2O_7 + 2NaCl$$

Potassium salt is less soluble than the Na-salt. $Na_2Cr_2O_7$, $K_2Cr_2O_7$ and $(NH_4)_2Cr_2O_7$ obtained from chromite are the starting materials for most of the chromium compounds. $K_2Cr_2O_7$ is an oxidizing agent and is used in quantitative chemical analysis of Fe^{+2}, soluble S^{-2}, SO_2 etc. It is also used in dying and chrome tanning. A mixture of $Na_2Cr_2O_7$ and H_2SO_4 is used in chromic acid mixture as a cleaning solution for glasswares in the laboratory. This is because of the strong oxidizing power of $Cr_2O_7^{-2}$ ion and dehydrating action of concentrated H_2SO_4.

Potassium chromate, K_2CrO_4 : Potassium, K_2CrO_4, or sodium chromate, Na_2CrO_4, may be obtained directly from chromite by the reaction :

$$4FeCrO_4 + 8K_2CO_3 + 7O_2 = 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2$$

The yellow K_2CrO_4 is extracted with water and crystallised. It may be obtained by the following reactions also :

$$2Cr(OH)_3 + 10KOH + 3Br_2 = 2K_2CrO_4 + 6\,KBr + 8H_2O$$

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$$

When K_2CrO_4 is added to $BaCl_2$, the yellow $BaCrO_4$ is precipitated out. This is used as a pigment under the name *Lemon Chrome*. $AgNO_3$ gives a brick-red precipitate of Ag_2CrO_4. Pb-acetate forms two types of precipitates. $PbCrO_4$ is yellow and is known as *Chrome Yellow*. When $PbCrO_4$ is digested with alkali, it is converted to basic lead chromate, $PbO.PbCrO_4$, which is known as *Chrome Red*. By mixing varying proportions of $PbCrO_4$ and $PbO.PbCrO_4$, another pigment is obtained which is known as *Chrome Orange*.

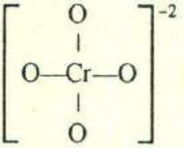
The chromate-dichromate equilibrium : Cr^{+6} generally exist as $Cr_2O_7^{-2}$ ion in aqueous acid solution but in the neutral or alkaline solutions it forms CrO_4^{-2} ion. Thus by adding acid to the yellow CrO_4^{-2} solution, it changes to orange $Cr_2O_7^{-2}$ ion :

$$CrO_4^{-2} + 2H^+ \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

On adding alkali to $Cr_2O_7^{-2}$ ion the orange colour is changed to yellow of CrO_4^{-2}:

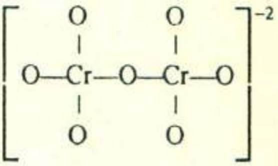
$$Cr_2O_7^{-2} + OH^- \rightleftharpoons 2CrO_4^{-2} + H_2O$$

In strong acid solution, further linking of CrO_4^{-2} to more condensed polychromate occurs. The CrO_4^{-2} has similar structure as SO_4^{-2} and in $Cr_2O_7^{-2}$ the atoms are linked through an oxygen atoms as in pyrosulphate :



$$\left[\mathrm{O{-}\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{Cr}}{-}O}\right]^{-2}$$

and



$$\left[\mathrm{O{-}\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{Cr}}{-}O{-}\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{Cr}}{-}O}\right]^{-2}$$

It is to be noted that when Pb-acetate solution is added to $K_2Cr_2O_7$ solution, the precipitate of $PbCrO_4$ is formed rather than $PbCr_2O_7$ because the solubility product of $PbCrO_4$ is much lower than that of $PbCr_2O_7$. The small amount of CrO_4^{-2} in $Cr_2O_7^{-2}$ solution is precipitated out as $PbCrO_4$ shifting the equilibrium toward CrO_4^{-2} ion.

Chromyl chloride, CrO_2Cl_2 : This is analogous to SO_2Cl_2 and contains Cr in the +6 state. This is formed when a metal chloride, such as NaCl is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4.

The deep red vapour of CrO_2Cl_2, which evolves on heating, condenses to a dark-red liquid at the room temperature :

$$K_2Cr_2O_7 + 6H_2SO_4 + 4\,NaCl = 2CrO_2Cl_2 + 2KHSO_4 + 4NaHSO_4 + 2H_2O$$

The vapour of CrO_2Cl_2 is soluble in water by hydrolysis :

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$$

The aqueous solution gives a precipitate of $PbCrO_4$ with Pb-acetate solution.

Neither bromide nor iodide forms this type of compound and the formation of CrO_2Cl_2 is used as an efficient means to detect the presence of Cl^- either alone or in presence of Br^- and I^- ions.

Peroxychromates : A number of perchromates has been made but the familiar blue ether soluble CrO_5 is obtained by adding H_2O_2 to a solution of $K_2Cr_2O_7$ in presence of H_2SO_4. The peroxychromate gives blue solution extracted by ether. CrO_5 is only a possible composition and $HCrO_5$ has also been proposed for the same substance.

Molybdenum and Tungsten

Molybdenum occurs chiefly as molybdenite, MoS_2. and tungsten as wolframite, $FeWO_4$. Mo and W are obtained from the respective ores by the following processes :

$$MoS_2 \xrightarrow[O_2]{\text{roasting}} MoO_3 \xrightarrow[\text{heat}]{H_2 \text{ or } Al} Mo$$

$$FeWO_4 \xrightarrow{Na_2CO_3} \begin{cases} \rightarrow Fe_2O_3 \text{ insolution} \\ \rightarrow \underset{\text{water soluble}}{Na_2WO_4} \xrightarrow{HCl} WO_3 \xrightarrow[\text{heat}]{C} W \end{cases}$$

The properties of Mo and W are subjected to the dragging effect of lanthanide contraction and the +6 oxidation states are important in both the metals. Both MoO_3 and WO_3 are stable and acidic but less than that of CrO_3. MoO_3 and WO_3 dissolve in alkali to form molybdates and tungstates containing MoO_4^{-2} and WO_4^{-2} ions respectively. The tendency for condensation of molybdate and tungstate ions is far greater than that of chromate and hence ploymolybdates and polytungstates are quite numerous.

Ammonium molybdate, $(NH_4)_2MoO_4$, is formed when MoO_3 is dissolved in NH_4OH and recrystallised. $(NH_4)_2MoO_4$ is the familiar compound used for testing PO_4^{-3} ion. In presence of HNO_3 ammonium mloybdate gives a canary yellow precipitate usually called ammonium phosphomolybdate of the composition $(NH_4)_3PO_4.12MoO_3.H_2O$. Both M and W show variable oxidation states as discussed before, particularly W has +2, +3, +4, +5 and +6 states.

Uses of Mo and W : Molybdenum and tungsten are used to produce special steels and for high speed tools.

QUESTIONS AND PROBLEMS

1. How would you prepare the following compounds ? Give their reactions and tests : (a) Sodium thiosulphate, (b) Sulphonyl chloride.
2. What are persulphuric acids ? How are these prepared ? Describe some important properties of these acids.
3. Write the electronic structure of sulphur chloride.
4. Sketch and explain the flow sheet for the manufacture of sulphuric acid by the Contact Process. Compare the different catalysts used in the process. Also give the advantages of the Contact Process over the Chamber Process.
5. (a) What is chromite ? What are its important uses ?
   (b) Starting with chromite, how would you obtain pure Cr_2O_3.
   (c) Cite some examples of the complex salts of chromium.
6. Describe in detail the various steps involved in the extraction of chromium metal from its ore laying special emphasis on the type of equipments used in the process. Give important uses of this metal.
7. Describe the preparation, properties and uses of the following :—
   (a) Ferrochrome from chromite.
   (b) Sulphur trioxide.
   (c) Sodium thiosulphate.
   (d) Potassium dichromate.
8. Explain the principle underlying the use of hydrogen sulphide in group separation of inorganic qualitative analysis.
9. Compare the chemistry of sulphur and chromium and mention uses of their important compounds.
10. How would you prepare—(a) thionyl chloride from sodium sulphite. (b) lead chrome from lead monoxide (PbO) (c) chromium oxide (Cr_2O_3) from chromite ?
11. Give a brief description of aluminothermic process of chromium.
12. Starting from chrome-iron ore, how would you obtain specimens of the following:—(a) K_2CrO_4 ; (b) CrO_2Cl_2 ; (c) Cr_2O_3 ; (d) $(NH_4)_2Cr_2O_7$ and (e) chrome alum ? Give equations of the reactions involved.
13. Describe the preparation and properties of the following:—(a) chromyl chloride (b) sodium thiosulphate. (c) ferrochrome.
14. Compare the chemistry of the following elements and their compounds :— Oxygen, sulphur, selenium and tellurium. Justify their position in the Periodic Table and give their atomic structure

15. Describe the preparation, properties and structure of the following : (a) Sulphurous acid, (b) perdisulphuric acid.
16. What is stainless steel ?
17. Starting from chromite how will you get ferrochrome and potassium chromate ? Write he structural formula of CrO_3, $[Cr(H_2O)_6]^{+3}$ and K_2CrO_4.
18. "H_2S is a useful reagent in analytical chemistry" Discuss.
19. Draw and compare the structural formula of H_2SO_4, H_2SO_5, $H_2S_2O_3$, $H_2S_2O_7$ and $H_2S_2O_8$. Name each of these compounds and write at least one chemical equation for each for their preparations.
20. An iron sulphide has been found to have the formula FeSx (x > 1 but not a whole number). Comment on the chemical nature of FeSx.
21. Why do the preparations of H_2SeO_4 and H_2SO_4 follow different processes ?
22. Can you visualize the existence of O_4, keeping in view that both O_3 and SO_3 do exist ?
23. Draw the resonance structures of O_2 and O_3. Do they predict that O_3 should be relatively unstable ? Which rule of resonance may be applied in this case ?
24. Explain : SO_2 is both oxidizing and a reducing agents.
25. Explain : Pure H_2SO_4 conducts electricity whereas pure HCl is a non-conductor.
26. Sulphur shows allotropy whereas this property is not well marked in the case of Se and Te. Explain.
27. SF_6 is well-defined compound but SCl_6 is not known.
28. Explain O—O bond energy in O_2 is much higher than S—S bond energy in S_8. Why ?
29. Compare the properties of H_2O and H_2S.
30. H_2S is a better reducing agent then H_2O. Explain.
31. The normal oxidation states of oxygen is −2 whereas S in the same group of Periodic Table exhibits oxidation states −2, +4 and +6. Discuss.
32. Compare the chemistry of oxygen and sulphur.
33. Discuss the structure of SO_2.
34. Compare the structure of S_2Cl_2, O_2F_2 and H_2O_2.
35. Describe briefly the chemistry of oxyacids of sulphur.
36. The structure of SO_3 in gaseous, liquid and solid state are not the same. Draw the structure.
37. What do you understand by the term "depletion of ozone layer of the atmosphere"? How this is happening ? Describe the effect.
38. Disinfection of drinking water may be brought about by. Cl_2 or O_3. Comment which reagent is preferable for the purpose.

39. Certain quantity of dissolved oxygen in water is necessary for life of aquatic animals. What factors are responsible for the lowering of dissolved oxygen in water and to what adverse effect.

40. Aluminium alum is used for water purification but chromium alum is not. Write the formula and explain why chromium alum can not be used for water treatment.

41. Compare the oxidizing character of $K_2Cr_2O_7$, $K_2S_2O_7$ and $K_2S_2O_8$.