CHAPTER

4

GROUP VA AND GROUP VIA ELEMENTS

Animation 4.1 : Nitrogen-Cycle
Source and Credit: Organic

IN THIS CHAPTER YOU WILL LEARN

1. The names, electronic configuration and general characteristics of group VA and VIA elements.
2. The preparation and properties of oxides and oxyacids of nitrogen, phosphorus and halides of phosphorus.
3. Comparison of properties of oxygen and sulphur.
4. The manufacture, properties and uses of sulphuric acid.

GROUP VA ELEMENTS

4.1 INTRODUCTION

The elements of group VA of the periodic table comprises nitrogen, phosphorus, arsenic, antimony and bismuth.

Table . 4.1 Electronic Configurations and Physical Properties of Group VA Elements

Properties	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Electronic configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]4d^{10} 5s^2 5p^3$	$[Xe]5d^{10} 6s^2 6p^3$
Physical appearance	Colourless gas	Black solid	Metallic solid	Metallic solid	Metallic solid
Ionization energy (kJ/mol)	1402	1012	950	830	700
Electron affinity (kJ/mol)	-7	-71.7	-77	-101	-110
Electronegativity	3.0	2.1	2.0	1.9	1.9
Atomic radius(pm)	70	110	121	141	157
Ionic radius of 3- ion (pm)	171	212	222	245	---
Melting points (°C)	-210	44	817	631	271
Boiling points (°C)	-196	280	613	1750	1560
Density (g/cm^3)	0.00125	1.83	5.73	6.68	9.80
Principal oxidation states	+3, +5	+3, +5	+3, +5	+3, +5	+3,+5

4.1.1 General Characteristics

Nitrogen and phosphorus of group VA show the typical properties of non-metals. For example, they are poor conductors of heat and electricity and give acidic oxides. Their compounds are predominantly covalent. Arsenic and antimony are metalloids. However bismuth at the bottom of the group shows definite metallic properties. The metallic character increases going down the group. Nitrogen has the greatest tendency to attract the electrons, antimony and bismuth have the least. The trend down the group also shifts from covalent bonding to ionic bonding. Phosphorus, arsenic and antimony have allotropes.

Allotropes of phosphorus i.e. red and white phosphorus are more important.

Phosphorus and other members of the group can make use of d orbitals in their bonding. This is because the energy of these orbitals is not much greater than those of the other valence shell orbitals. For example, phosphorus can make use of its 3s, 3p and the empty 3d orbitals during bonding with other elements.
In phosphorus one of the 3s electrons can be promoted to a vacant 3d orbital giving 5 unpaired electrons in the valence shell. Phosphorus can thus make three or five covalent bonds. Indeed three and five are the common valencies of the group VA elements.

4.2 NITROGEN AND ITS COMPOUNDS

4.2.1 Occurrence

Nitrogen is present in free state in air as a major constituent (78% by volume). It is an inactive gas in comparison with oxygen which is the next major constituent of air. Inorganic compounds of nitrogen are not commonly found as minerals.

In combined state nitrogen is found in all living matter including, animals and plants in the form of proteins, urea and amino acids.

Animation 4.2 : Nitrogen-Axides-Analyser
Source and Credit: Qld

4.2.2 Oxides of Nitrogen

Nitrogen forms several oxides with oxygen. Common oxides of nitrogen are N_2O, NO and NO_2. It also forms N_2O_3 and N_2O_5.

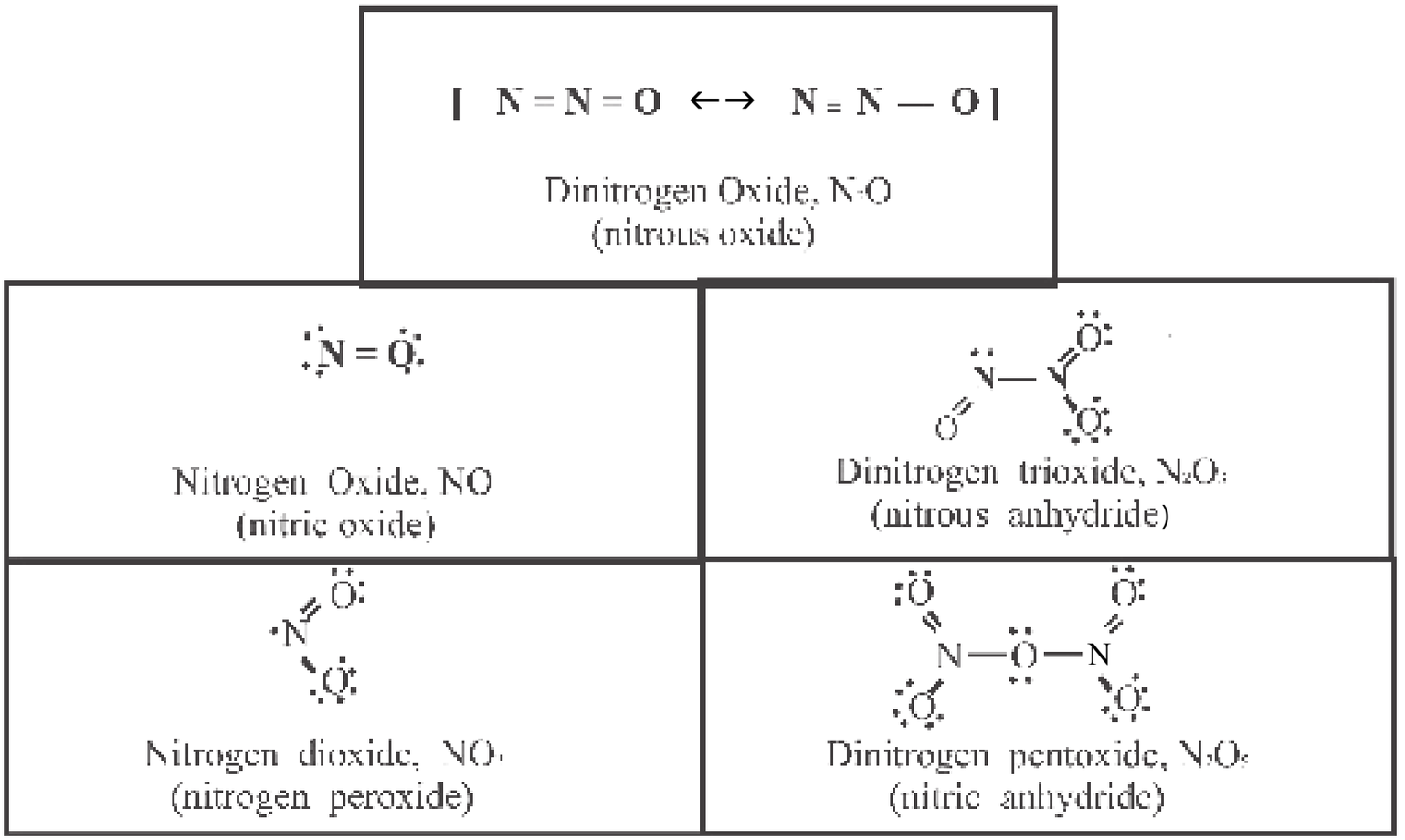


Fig. 4.1 Oxides of Nitrogen

1. Dinitrogen Oxide (N_2O)

Preparation

1.Dinitrogen oxide can be prepared by the action of dil, HNO, on metallic zinc.

$$4Zn(s)+10HNO_2(dil.)\rightarrow 4Zn(NO_3)_2(aq)+N_2O(g)+5H_2O(l)$$

2. It is usually prepared by heating ammonium nitrate to about 200°C .

$$NH_4NO_3(s)\rightarrow N_2O(g)+2H_2O(l)$$

To avoid the danger of explosion, ammonium nitrate can be replaced by a mixture of sodium nitrate and ammonium sulphate.

Properties of Dinitrogen Oxide

Dinitrogen oxide is a colourless gas with a faint, pleasant smell and a sweetish taste. It is fairly soluble in cold water. Its mixture with a little oxygen, if inhaled for a sufficiently long time, produces hysterical laughter, hence it is also known as "laughing gas".

Reactions

1. It is not combustible but resembles oxygen in rekindling a glowing splinter. Similarly, it supports combustion if burning substances, such as sulphur, phosphorus, etc. are taken in the cylinder containing this gas.

$$S(s)+2N_2O(g)\rightarrow SO_2(g)+2N_2(g)$$

$$P_4(s)+10N_2O(g)\rightarrow P_4O_{10}(s)+10N_2(g)$$

2. When N_2O is passed over red hot copper, it is reduced to nitrogen.

$$Cu(s) + N_2O(g) \rightarrow CuO(s) + N_2(g)$$

2. Nitrogen Oxide (NO)

Preparation

1. Nitrogen oxide can be prepared by the action of dil HNO_3 on copper.

$$3Cu(s) + 8HNO_3(dil.) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

2. It can also be prepared by passing air through an electric arc.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Properties of Nitrogen Oxide

Nitrogen oxide is a colourless gas heavier than air and sparingly soluble in water.

Reactions

1. With oxygen, it forms reddish brown nitrogen dioxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

2. It decomposes into N_2 and O_2 at about 1000°C and supports combustion.

$$2NO(g) \rightarrow N_2(g) + O_2(g)$$

3. It forms nitrosyl chloride and nitrosyl bromide with chlorine and bromine, respectively in the presence of charcoal.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

4. It forms a brown coloured addition compound with $FeSO_4$.This test is used to confirm the presence of nitrates (Ring Test).

$$FeSO_4(aq) + \mathrm{NO(g)} \rightarrow \mathrm{FeSO_4 \cdot NO(aq)}$$

5. With reducing agents, it is reduced to nitrous oxide or nitrogen.

$$H_2S(g) + 2NO(g) \rightarrow H_2O(g) + N_2O(g) + S(s)$$

$$H_2SO_3(aq) + 2NO(g) \rightarrow H_2SO_4(aq) + N_2O(g)$$

6. Oxidizing agents can oxidize NO to NO_2 or HNO_3.

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

$$6KMnO_4(aq) + 12H_2SO_4(aq) + 10NO(g) \longrightarrow 6KHSO_4(aq) + 6MnSO_4(aq) + 10HNO_3(aq) + 4H_2O(l)$$

3. Nitrogen Dioxide (NO_2)

Preparation

1. It can be prepared in small quantities by heating lead nitrate.

$$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$$

2. It can also be prepared by reacting conc. HNO_3 with copper.

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

Animation 4.3 : Nitrogen-Cycle
Source and Credit: Organic

Properties of Nitrogen Dioxide

Nitrogen dioxide is a reddish brown gas with a pungent smell. It dissolves readily in water to form a blue acidic solution.

Reactions

1. On cooling, NO_2 is converted into a yellow liquid which can be frozen to a colourless solid dinitrogen tetraoxide (N_2O_4). If this solid is heated to 140°C, the mixture contains NO_2 and N_2O_4 but above 140°C NO_2 is converted to NO and O_2 molecules which are colourless. This decomposition is complete at 620°C.

$$NO_2(g) \rightarrow NO_2(l) \rightarrow \underset{\substack{Pale\\Yellow}}{N_2O_4(l)} \xrightarrow{140^\circ C} \underset{\substack{Reddish\\brown}}{2NO_2(g)} \xrightarrow{620^\circ C} \underset{Colourless}{2NO(g) + O_2(g)}$$

2.Elements like phosphorus, potassium and carbon continue burning in NO_2 as it yields O_2 on decomposition.

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

$$2P(s) + 5NO_2(g) \rightarrow P_2O_5(s) + 5NO(g)$$

3.In the absence of air, it dissolves in water to form nitric and nitrous acids

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

However in the presence of air or oxygen, nitric acid is the final product.

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

4.A mixture of nitrate and nitrite is formed when NO_2 is passed through strong alkalies.

$$2NaOH(aq) + 2NO_2(g) \rightarrow NaNO_3(aq) + NaNO_2(aq) + H_2O(l)$$

$$2KOH(aq) + 2NO_2(g) \rightarrow KNO_3(aq) + KNO_2(aq) + H_2O(l)$$

5. It is a strong oxidizing agent and oxidizes H_2S to sulphur, ferrous sulphate to ferric sulphate and KI to I_2.

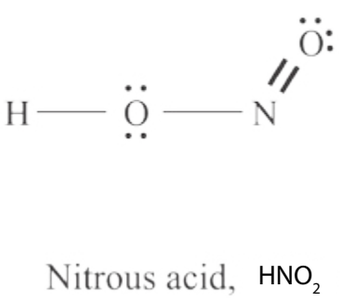
$$H_2S(g) + NO_2(g) \rightarrow H_2O(l) + S(s) + NO(g)$$

$$2FeSO_4(aq) + H_2SO_4(aq) + NO_2(g) \rightarrow Fe_2(SO_4)_3(aq) + H_2O(l) + NO(g)$$

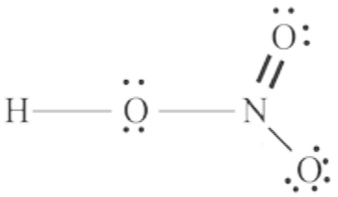
$$2KI(aq) + 2NO_2(g) \rightarrow 2KNO_2(aq) + I_2(s)$$

4.2.3 Oxyacids of Nitrogen

There are two important oxyacids of nitrogen, nitrous acid and nitric acid.



Nitrous acid, HNO_2



Nitric acid, HNO_3

1. Nitrous Acid (HNO_2)

Preparation

1. It can be prepared by dissolving dinitrogen trioxide in water at 0°C.

$$N_2O_3(g) + H_2O(l) \rightarrow 2HNO_2(aq)$$

2. Pure nitrous acid solution can be prepared by reaction between ice cold barium nitrite solution and ice cold dilute sulphuric acid.

$$Ba(NO_2)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HNO_2(aq)$$

Properties of Nitrous Acid

It is only known in the form of its salts and is stable to some extent in a dilute solution.

Reactions

1. It begins to decompose almost as soon as it is formed even at ordinary temperature.

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

2. It acts as an oxidizing agent and oxidizes HI, SO_2 and $SnCl_2$into I_2,H_2SO_4 and $SnCl_4$, respectively.

$$2HNO_2(\text{aq}) + 2\,\text{HI(aq)} \rightarrow 2\,\text{H}_2\,O(l) + 2NO(g) + I_2(s)$$

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

$$SO_2(g) + H_2O(l) + [O](g) \rightarrow H_2SO_4(aq)$$

$$SnCl_2(aq) + 2HCl(aq) + 2HNO_2(\text{aq}) \rightarrow SnCl_4(aq) + 2NO(g) + 2H_2O(l)$$

3. Nitrous acid decolourizes acidified $KMnO_4$ and bromine water. It readily gets oxidized to nitric acid, so it also behaves as a reducing agent.

$$2KMnO_4(aq) + 3H_2SO_4(aq) + 5HNO_2(aq) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 3H_2O(l) + 5\,\text{HNO}_3(\text{aq})$$

$$HNO_2(aq) + Br_2(aq) + H_2O(\text{l}) \rightarrow \text{HNO}_3(\text{aq}) + 2\,\text{HBr(aq)}$$

4. As an acid it reacts with alkalies producing salts.

$$NaOH(aq) + HNO_2(aq) \rightarrow NaNO_2(aq) + H_2O(l)$$

5. It also reacts with organic compounds containing NH_2 group and produces nitrogen.

$$2HNO_2(aq) + \underset{Urea}{CO(NH_2)_2(aq)} \rightarrow 2N_2(g) + CO_2(g) + 3H_2O(l)$$

$$HNO_2(aq) + \underset{Aminobenzene}{C_6H_5NH_2(l)} \rightarrow \underset{Phenol}{C_6H_5OH(l)} + N_2(g) + H_2O(l)$$

Animation 4.4 : Nitric oxide binding
Source and Credit: ESRF

2. Nitric Acid (HNO_3)

Preparation

In the laboratory, nitric acid is prepared by heating potassium nitrate crystals with concentrated sulphuric acid.

$$KNO_3(s) + H_2SO_4(conc.) \rightarrow KHSO_4(aq) + HNO_3(aq)$$

Manufacture of Nitric Acid Birkeland and Eyde's process

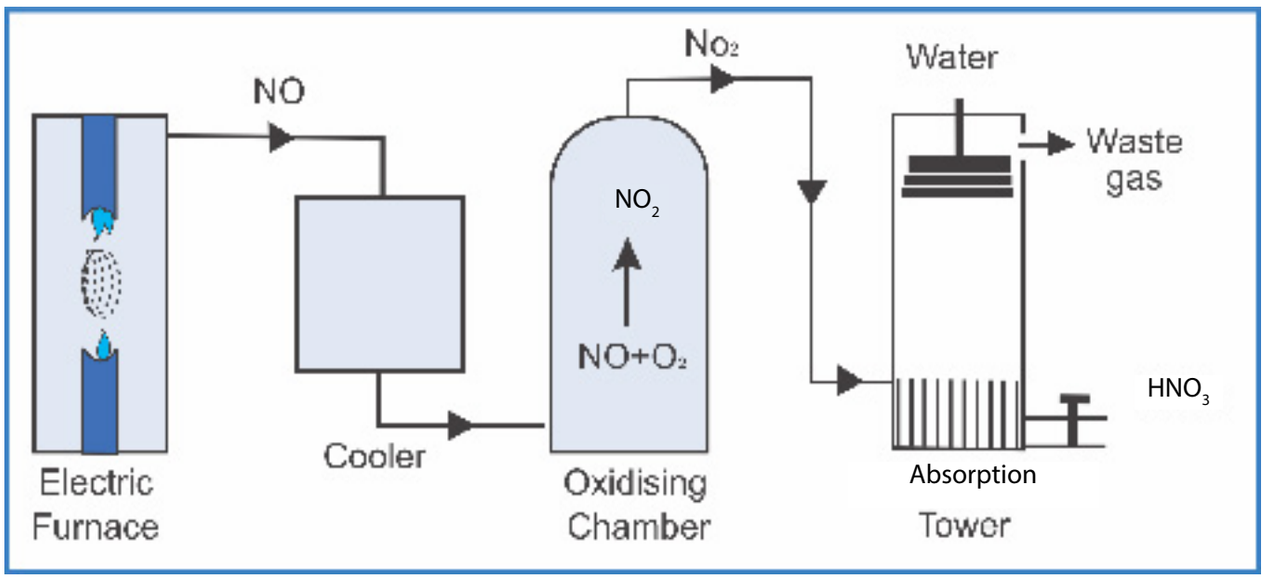
This process consists of the following steps:

(i) Formation of nitric oxide

Atmospheric nitrogen and oxygen are combined to give nitric oxide in an electric arc (3000°C).

$$N_2(g) + O_2(g) \xrightarrow{3000^\circ C} 2NO(g)$$

NO formed is cooled quickly to 1000°C at which it does not decompose.



Fiq 4.2 Manufacture of nitric acid form air

(ii) At 600°C,NO combines with O_2 to form NO_2

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(iii) Nitrogen dioxide is absorbed in water to give dilute HNO_3 along with nitrous acid.

$$2\,NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

(iv) Nitrous acid is oxidized to nitric acid and nitric oxide which is re-oxidized to NO_2.

$$3\,HNO_2(g) \rightarrow HNO_3(aq) + 2\,NO(g) + H_2O(l)$$

Properties of Nitric Acid

Concentrated nitric acid is a colourless volatile liquid which fumes strongly in air . It has a pungent smell. Its specific gravity at 15°C is 1.53.

Reactions

1. Nitric acid is decomposed in the presence of light even at ordinary temperature.

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

2. It is a very strong acid. It exhibits all the usual general properties of acids in all reactions where its oxidizing properties are not shown. It reacts in normal way with basic oxides, hydroxides and carbonates forming respective salts.

$$2\,HNO_3(aq) + CaO(s) \rightarrow H_2\,O(l) + Ca(NO_3)_2(aq)$$

$$HNO_3(aq) + NaOH(aq) \rightarrow H_2O(l) + NaNO_3(aq)$$

$$2\,HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2\,NaNO_3(aq) + H_2\,O(l) + CO_2(g)$$

3. It acts as a strong oxidizing agent due to the ease with which it is decomposed.

$$2HNO_3(aq) \rightarrow H_2O(l) + 2NO_2(g) + [O](g)$$

(i) It oxidizes non-metals to their corresponding oxides.

$$C(s) + 4\,HNO_3(conc.) \rightarrow CO_2(g) + 4\,NO_2(g) + 2\,H_2O(l)$$

$$S(s) + 6HNO_3(conc.) \rightarrow 2H_2O(l) + 6NO_2(g) + H_2SO_4(aq)$$

$$5\,HNO_3(conc.) + P(s) \rightarrow H_3PO_4(aq) + H_2\,O(l) + 5\,NO_2(g)$$

(ii) Metalloids like arsenic and antimony can be oxidized to their corresponding acids.

$$As(g) + 5\,HNO_3(conc.) \rightarrow H_3AsO_4(aq) + 5NO_2(g) + H_2O(l)$$

$$Sb(g) \rightarrow 5HNO_3(conc.) \rightarrow H_3SbO_4(aq) + 5NO_2(g) + H_2O(l)$$

Animation 4.5 : Nitric oxide binding
Source and Credit: ESRF

(iii) Nitric acid behaves differently with different metals.

(a) Gold, platinum, iridium and titanium do not react.

(b) Iron, cobalt, nickel, chromium, aluminium are rendered passive by acid due to the formation of a film of their oxides over them .

(c) Tungsten and uranium are changed into their oxides.

(d) Magnesium, calcium and manganese give hydrogen with dilute nitric acid.

$$Mg(s) + 2HNO_3(dil) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$$

$$Mn(s) + 2HNO_3(dil) \rightarrow Mn(NO_3)_2(aq) + H_2(g)$$

(e) Copper and lead give nitric oxide with dilute acid and nitrogen dioxide with concentrated acid.

$$3Cu(s) + 8HNO_3(dil) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

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

(f) Mercury gives mercurous nitrate and nitric oxide with dilute nitric acid.

$$6Hg(l) + 8HNO_3(dil) \rightarrow 3Hg_2(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

With concentrated acid, it gives mercuric nitrate and NO_2

$$Hg(l) + 4HNO_3(conc) \rightarrow Hg(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

(g) Silver reacts with nitric acid to give silver nitrate and nitric oxide

$$3Ag(s) + 4HNO_3(aq) \rightarrow 3AgNO_3(aq) + NO(g) + 2H_2O(l)$$

(h) Dilute nitric acid gives ammonium nitrate, when it reacts with tin. With concentrated acid meta-stannic acid is produced.

$$4Sn(s)+10HNO_3(dil.)\rightarrow 4Sn(NO_3)_2(aq)+NH_4NO_3(aq)+3H_2O(l)$$

$$\mathrm{Sn(s)}+4HNO_3(conc.)\rightarrow H_2SnO_3(aq)+4NO_2(g)+H_2O(l)$$

(i) Zinc gives different products depending upon the concentration of acid and temperature. Very dilute nitric acid gives NH_4NO_3. Moderately dilute nitric acid gives nitrous oxide while concentrated nitric acid gives NO_2.

$$4Zn(s)+10HNO_3(v.\mathrm{dil.})\rightarrow 4Z\,\mathrm{n(NO_3)_2}(aq)+NH_4NO_3(aq)+3H_2O(l)$$

$$4Zn(s)+10HNO_3(dil.)\rightarrow 4Zn(NO_3)_2(aq)+N_2O(g)+5H_2O(l)$$

$$Zn(s)+4HNO_3(conc.)\rightarrow Zn(NO_3)_2(aq)+2\,\mathrm{NO_2}+2H_2O(l)$$

4 .Reducing agents like $FeSO_4$, H_2S and HI are converted to F $e_2(SO_4)_3$, S and I_2 respectively, when they react with conc. HNO_3

$$6FeSO_4(aq)+3H_2SO_4(aq)+2HNO_3(conc.)\rightarrow 3Fe_2(SO_4)_3(aq)+2NO(g)+4H_2O(l)$$

$$2HNO_3(aq)+3H_2S(g)\rightarrow 4H_2O(l)+2NO(g)+3S(s)$$

$$6HI(aq)+2HNO_3(conc.)\rightarrow 4H_2O(l)+2NO(g)+3I_2(s)$$

5 Aqua Regia

When one volume of concentrated HNO_3 is mixed with 3 volumes of concentrated HCl, aqua regia is formed.It is employed to dissolve gold and platinum.

$$HNO_3(conc.) + 3\,HCl(conc.) \rightarrow NOCl(aq) + Cl_2(g) + 2H_2O(l)$$

Animation 4.6 : Gold Coin Dissolving in Acid
Source and Credit: Makeagif

NOCl formed is decomposed giving NO and Cl_2

$$NOCl \rightarrow NO(g) + [Cl](g)$$

This liberated chlorine gas converts noble metals such as gold and platinum into their water soluble chlorides.

$$Au(s) + 3[Cl](aq) \rightarrow 2\,AuCl_3(aq)$$

6. Nitric acid reacts with glycerine, toluene and phenol to prepare materials used as explosives like nitroglycerine, trinitrotoluene (TNT) and picric acid, respectively.

Uses

It is used

1. as a laboratory reagent.
2. in the manufacture of nitrogen fertilizers.
3. in the manufacture of explosives.
4. for making varnishes and organic dyes.

4.3 PHOSPHORUS AND ITS COMPOUNDS

4.3.1 Occurrence

Phosphorus is the second member of group VA. Its name comes from Greek word meaning "Light bearing". Unlike, nitrogen it does not occur in free state in nature. Most of the phosphorus is found in deposits of phosphate rock, i.e.impure $Ca_3(PO_4)_2$ and apatite $Ca_5F(PO_4)_3$. As a constituent of plant and animal tissues, it is essential for their normal growth. It occurs especially in seeds, the yolk of eggs, the nerves, brain and bone marrows, usually in the form of lecithins. In the form of calcium phosphate, it is an essential constituent of bones. Bone ash (80% calcium phosphate) is an important source of phosphorus.

4.3.2 Allotropes of Phosphorus

Phosphorus can exist in at least six different solid allotropic forms, of which we will mention only three.

White phosphorus is a very reactive, poisonous, volatile, waxy, yellowish white substance, which is soluble in benzene and carbon disulphide. It exists in the form of tetraatomic molecules (P_4) which have a tetrahedral structure, Fig. 4.3. It boils at 280°C to P_4 vapours which dissociate above 700°C to form P_2 molecules.

Red phosphorus is much less reactive and less poisonous than white phosphorus. It is prepared by heating white phosphorus in the presence of a little iodine or sulphur as a catalyst upto 250°C in vacuum. The tetra-atomic molecules of red phosphorus combine to form macromolecules, Fig. 4.4 .

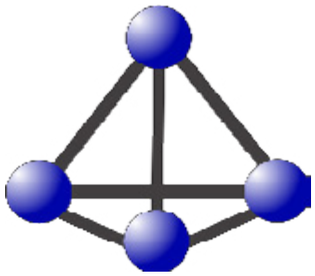


Fig.4.3 White phosphorus

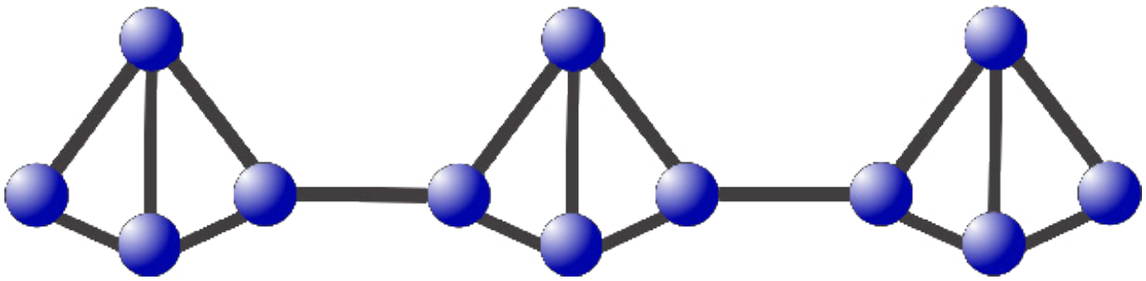


Fig. 4.4 Red phosphorus

Black phosphorus is the third form which is most stable under ordinary conditions. Black phosphorus is prepared by heating red phosphorus to high temperature and pressure.

4.3.3 Halides of Phosphorus

1. Phosphorus Trichloride (PCl_3)

Preparation

1. It is usually prepared by melting white phosporus in a retort in an inert atmosphere of CO_2 and current of dried chlorine is passed over it. The vapours of PCl_3 are collected in a flask kept in an ice-bath.

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l)$$

2. It may also be prepared by the action of phosphorus with thionyl chloride.

$$2P(g) + 4SOCl_2(l) \rightarrow 2PCl_3(l) + 2SO_2(g) + S_2Cl_2(s)$$

Properties of Phosphorus Trichloride

It is a colourless fuming liquid which boils at 76°C and freezes at-112°C.

Reactions

1. It combines with chlorine to form phosphorus pentachloride

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$

2. It combines with atmospheric oxygen slowly to form phosphorus oxychloride.

$$2PCl_3(l) + O_2(g) \rightarrow 2POCl_3(s)$$

3. It is soluble in organic solvents, but readily reacts with water to form phosphorus acid.

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$$

4. It reacts with alcohols and carboxylic acidsforming the respective chloro derivatives and H_3PO_3.

$$3CH_3OH(l) + PCl_3(l) \rightarrow 3CH_3Cl(l) + H_3PO_3(l)$$

$$3CH_3COOH(l) + PCl_3(l) \longrightarrow 3CH_3COCl(l) + H_3PO_3(l)$$

2. Phosphorus Pentachloride (PCl_5)

Preparation

1. By passing dry chlorine through phosphorus trichloride.

$$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$$

2. It may also be prepared by passing dry chlorine in a well cooled solution of phosphorus in carbon disulphide

$$2P(l) + 5Cl_2(g) \rightarrow 2PCl_5(s)$$

Properties of Phophorus Pentachloride

1. It is a yellowish white crystalline solid which sublimes at about 100°C. It gives fumes in moist air with an irritating smell.

Reactions

1. It decomposes on heating producing PCl_3 and chlorine.

$$PC1_5(s) \rightarrow PC1_3(l) + C1_2(g)$$

2. It gets decomposed by water forming phosphorus oxychloride which further reacts with water to produce orthophosphoric acid.

$$PC1_5(s) + H_2O(l) \rightarrow POC1_3(l) + 2HC1(aq)$$

$$POC1_3(l) + 3H_2O(l) \rightarrow H_3PO_4(aq) + 3HC1(aq)$$

$$PC1_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HC1(aq)$$

3. It converts metals into their chlorides.

$$Zn(s) + PC1_5(s) \rightarrow ZnC1_2(s) + PC1_3(l)$$

4.3.4 Oxides of Phosphorus

1. Phosphorus Trioxide, P_2O_3 (P_4O_6)

Preparation

1. P_2O_3 can be prepared by burning white phosphorus in a limited supply of air.

$$P_4(s) + 3O_2(g) \rightarrow 2P_2O_3(s)$$

Properties of Phoshorus Trioxide

It is a white waxy solid with garlic like odour. It melts at 22.8°C and boils at 173°C. It is highly poisonous in nature.

Reactions

1. When heated in the presence of air or oxygen, it is converted into phosphorus pentoxide.

$$P_2O_3(s) + O_2(g) \rightarrow P_2O_5(s)$$

2. It reacts with cold water to give phosphorus acid.

$$P_2O_3(s) + 3H_2O(l) \longrightarrow 2H_3PO_3(l)$$

With hot water, it forms phosphine and phosphoric acid.

$$2P_2O_3(s) + 6H_2O(l) \rightarrow 3H_3PO_4(aq) + PH_3(g)$$

Phosphorus Pentoxide, P_2O_5 or P_4O_{10}

Preparation

1. It is prepared by burning phosphorus in excess of dry air.

$$P_4(s) + 5O_2(g) \rightarrow 2P_2O_5(s)$$

Properties of Phosphorus Pentoxide

It is a white hygroscopic powder having a faint, garlic like odour due to the presence of traces of P_2O_3. It sublimes at 360°C.

Reactions

1. With cold water phosphorus pentoxide forms metaphosphoric acid.

$$P_2O_5(s) + H_2O(l) \rightarrow 2HPO_3(aq)$$

With hot water, it forms orthophosphoric acid

$$P_2O_5(s) + 3H_2O(l) \rightarrow 2H_3PO_4(aq)$$

2. It is a powerful dehydrating agent, thus, with HNO_3, H_2SO_4, CH_3COOH and C_2H_5OH, it gives N_2O_5, SO_3, $(CH_3CO)_2O$ and C_2H_4 ,respectively.

$$2HNO_3(aq) + P_2O_5(s) \rightarrow N_2O_5(g) + 2HPO_3(aq)$$

$$H_2SO_4(aq) + P_2O_5(s) \rightarrow SO_3(g) + 2HPO_3(aq)$$

$$2CH_3COOH(aq) + P_2O_5(s) \rightarrow \underset{Aceticanhydride}{(CH_3CO)_2O(l)} + 2HPO_3(aq)$$

$$C_2H_5OH(l) + P_2O_5(s) \rightarrow C_2H_4(g) + 2HPO_3(aq)$$

4.3.5 Oxyacids of Phosphorus

1. Phosphorus Acid (H_3PO_3)

Preparation

1. It is prepared by dissolving phosphorus trioxide in cold water.

$$P_2O_3(s) + 3H_2O(l) \rightarrow 2H_3PO_3(aq)$$

2. It is also obtained by the hydrolysis of phosphorus trichloride.

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$$

Properties of Phosphorus Acid

It is a white crystalline solid, which melts at 73.6°C.

Reactions

1. It decomposes into phosphine and orthophophoric acid on heating.

$$4H_3PO_3(s) \rightarrow 3H_3PO_4(l) + PH_3(g)$$

2. It is a powerful reducing agent and reduces $CuSO_4$, $AgNO_3$, etc. to the metallic state.

$$H_3PO_3(s) + CuSO_4(aq) + H_2O(l) \rightarrow H_3PO_4(aq) + H_2SO_4(aq) + Cu(s)$$

$$H_3PO_3(s) + 2AgNO_3(aq) + 2NH_4OH(aq) \rightarrow H_3PO_4(aq) + 2NH_4NO_3(aq) + H_2O(l) + 2Ag(s)$$

3. It reacts with oxygen to form orthophosphoric acid.

$$2H_3PO_3(s) + O_2(g) \rightarrow 2H_3PO_4(s)$$

4. Nascent hydrogen produced by Zn/HCl reduces H_3PO_3 to phosphine

$$H_3PO_3(s) + 6[H](g) \rightarrow PH_3(g) + 3H_2O(l)$$

2. Orthophosphoric Acid (H_3PO_4)

Preparation

1. It is prepared by dissolving phosphorus pentoxide in hot water.

$$P_2O_5(s) + 3H_2O(l) \rightarrow 2H_3PO_4(aq)$$

2. It is also obtained by heating red phosphorus with concentrated HNO_3.

$$P(s) + 5HNO_3(conc.) \rightarrow H_3PO_4(aq) + 5NO_2(g) + H_2O(l)$$

3. Hydrolysis of phosphorus pentachloride also gives orthophosphoric acid.

$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$$

4. On large scale, it can be prepared by heating a mixture of phosphorite (bone ash) and sand in an electric furnace. The phosphorus pentoxide formed is treated with hot water to obtain phosphoric acid.

$$Ca_3(PO_4)_2(s) + 3SiO_2(s) \rightarrow 3CaSiO_3(s) + P_2O_5(s)$$

$$P_2O_5(s) + 3H_2O(l) \rightarrow 2H_3PO_4(aq)$$

Properties of Orthophosphoric Acid

It is a colourless, deliquescent crystalline solid which melts at 41°C. It is soluble in water.

Reactions

1. It is a weak tribasic acid. It reacts with NaOH to give three series of salts.

i. $H_3PO_4(aq) + NaOH(aq) \rightarrow NaH_2PO_4(aq) + H_2O(l)$

ii. $NaH_2PO_4(aq) + NaOH(aq) \rightarrow Na_2HPO_4(aq) + H_2O(l)$

iii. $Na_2HPO_4(aq) + NaOH(\text{aq}) \rightarrow \text{Na}_3\text{PO}_4(\text{aq}) + H_2O(l)$

2. On heating, it loses water and converted into pyro and metaphosphoric acid.

$$\underset{\substack{\textit{Orthophosphoric}\\ \textbf{acid}}}{2H_3PO_4} \xrightarrow[-H_2O]{240^\circ C} \underset{\substack{\textit{Pyrophosphoric}\\ \textbf{acid}}}{H_4P_2O_7} \xrightarrow[-H_2O]{316^\circ C} \underset{\substack{\textit{Metaphosphoric}\\ \textbf{acid}}}{2HPO_3}$$

GROUP VIA ELEMENTS

4.4 Group VIA Elements

The group VIA of the periodic table consists of oxygen, sulphur, selenium, tellurium and polonium. These elements are called chalcogens from the Greek for "copper giver", because they are often found in copper ores. The electronic configuration and physical properties of group VIA elements are shown in Table 4.2

Table . 4.2 Electronic Configuration and Physical Properties of Group VIA Elements

Physical Properties	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Electronic configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]4s^2 4p^4$	$[Kr]5s^2 5p^4$	$[Xe]6s^2 6p^4$
Ionization energy (kJ/mol)	1314	1000	941	869	813
Electron affinity (kJ/mol)	-141.1	-200.42	-195	-183	-180
Electronegativity	3.5	2.5	2.4	2.1	2.0
Atomic radius(pm)	66	104	117	137	152
Ionic radius 2-ion (pm)	140	184	198	221	-----
Melting points (°C)	-218	113	217	450	254
Boiling points (°C)	-183	444.6	684	990	962
Density (g/cm^3)	0.00143	2.06	4.8	6.25	9.4

4.4.1 General Characteristics

All the elements of group VIA are non-metals except Po which is a radioactive metal. Atomic radii, density, melting and boiling points generally increase with increase in atomic number down the group. Ionization energies of the group members are very high which shows their reluctance to lose electrons. Oxygen is the most electronegative element after fluorine. All these elements show the property of allotropy.

Oxygen has two allotropic forms (O_2 and O_3), sulphur has 3(α, β, γ), Se has two (red and grey) ,Te has two (metallic and non-metallic). They also show the property of catenation. This property decreases down the group. All the elements are polymeric in nature (they form poiy-atomic molecules). They attain the electronic configuration of the nearest noble gas by gaining 2 electrons forming O^{-2}, S^{-2}, Se^{-2}, etc. Except oxygen the other members of the group show a covalency of +2 ,+4, and +6, for example, SCl_2, SCl_4, SCl_6. +2 oxidation state is shown due to 2 unpaired electrons in the p-orbitals. +4 oxidation state is shown when 1 electron from p-orbilal is promoted to the next vacant d-orbital, while + 6 oxidation state is shown when another electron from s-orbital is also promoted to the next vacant d-orbital.

4.4.2 Occurrence

Oxygen is the most widely distributed and common of all the elements, comprising about 50% of the earth's crust. About one-fourth of the atmospheric air by weight consists of free oxygen and water contains nearly 89% of combined oxygen. The calcium carbonate which occurs as chalk, limestone, marble etc, contains 48% oxygen. Silica which is found in flint, quartz, etc, contains more than 53% oxygen by weight.

Sulphur is also widely distributed in nature both as free and in combined forms. Many important metallic ores are sulphides, e.g, galena (PbS), Zinc blende (ZnS), cinnabar (HgS), stibnite (Sb_2S_3), copper pyrite ($Cu_2S.Fe_2S_3$), iron pyrite (FeS_2), etc. Some important sulphates are also found in nature, e.g. gypsum ($CaSO_4$), heavy spar ($BaSO_4$), etc.

Sulphur also occurs in organic compounds present in animals and vegetables. Onions, garlic, mustard, hair, many oils, eggs and proteins consist of compounds containing sulphur in them . It also occurs as a constituent of coal and petroleum .

4.4.3 Comparison of Oxygen and Sulphur

Smililarities:

1. Both oxygen and sulphur have same outer electronic configuration of ns^2p^4.
2. Both oxygen and sulphur are usually divalent.
3. Both oxygen and sulphur exhibit allotropic forms.

4. Both have polyatomic molecules. Oxygen has diatomic O_2, while sulphur has S_2 and S_8 molecules.
5. Both combine with metals in the form of O^{-2} and S^{-2} with oxidation state -2.
6. Both combine with non-metals and form covalent compounds, e.g, H_2O and H_2S, CO_2 and CS_2 ,etc.
7. Both are typical non-metals.
8. Both are found in free and combined states on earth.

Dissmililarities:

Oxygen	Sulphur
1. There are two allotropic forms of Oxygen-O_2 and O_3.	There are 3 allotropic forms of sulphur, rhombic, monoclinic and plastic.
2. It is gas at ordinary temperature.	It is solid at ordinary temperature.
3. Oxygen is sparingly soluble in water.	Sulphur is not soluble in water.
4. Oxygen helps in combustion.	Sulphur is itself combustible.
5. It is paramagnetic in nature.	It is diamagnetic in nature.
6. It does not react with water.	When steam is passed through boiling sulphur a little hydrogen sulphide and sulphur dioxide are formed.
7. It does not react with acids.	It is readily oxidized by conc. sulphuric acid or nitric acid.
8. It does not react with alkalies.	It reacts with alkali solution and forms sulphides and thiosulphate.
9. It shows -2 oxidation state.	It shows oxidation states of -2, +2, +4 and +6.

4.5 SULPHURIC ACID (H_2SO_4)

Sulphuric acid was first prepared by a muslim scientist Jabir bin Hayyan in 8th century. In Europe, in 14^{th} and 15^{th} centuries, its preparation on commercial level was started due to the awareness of its properties and uses. It was called "oil of vitriol".It does not occur as such in nature , however, small quantities of H_2SO_4 are found in the waters of some springs and rivers.

4.5.1 Manufacture of Sulphuric Acid

Sulphuric acid is being manufactured commonly by contact process.

Contact Process

This method was developed by Knietsch in Germany. Basically, it involves the catalytic combination of sulphur and oxygen to form SO_2 which is then dissolved in water to form H_2SO_4.

Animation 4.8 : Sulfuric acid - contact process
Source and Credit: Dynamicscience

Principle

SO_2 obtained by burning sulphur or iron pyrites is oxidized to SO_3 in the presence of V_2O_5 which acts as a catalyst. The best yield of SO_3 can be obtained by using excess of oxygen or air and keeping the temperature between 400-500°C. SO_3 formed is absorbed in concentrated H_2SO_4 and "Oleum" ($H_2S_2O_7$) formed can be converted to sulphuric acid of any strength by mixing adequate quantities of water.

The process is completed in the steps given below.

a. Sulphur Burners

Sulphur or iron pyrites are burnt in excess of air to produce SO_2.

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

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

b. Purifying Unit

SO_2 is purified from impurities like dust and arsenic oxide, to avoid poisoning of the catalyst. Purifying unit consists of the following parts.

(i) Dust remover

Steam is injected to remove dust particles from the gases.

(ii) Cooling Pipes

The gases are passed through lead pipes to cool them to 100°C.

(iii) Scrubbers

The cooled gases are washed by a spray of water, as SO_2 is not soluble in water at high temperature.

(iv) Drying Tower

The moisture of gases is removed by concentrated H_2SO_4 trickling down through the coke filled in this tower.

(v) Arsenic Purifier

Arsenic oxide is then removed by passing the gases through a chamber provided with shelves packed with freshly prepared ferric hydroxide.

(vi) Testing box

In this box a beam of light is introduced which indicates the presence or absence of solid particles. If present the gases are sent back for further purification.

c. Contact Tower

Preheated gases at 400-500°C are passed through vertical iron columms packed with the catalyst V_2O_5. Here SO_2 is oxidized to SO_3.

$$2SO_2(g) + O_2(g) \rightarrow \xrightarrow[V_2O_5]{400-500^\circ C} 2SO_3 \qquad \Delta H = -269.3kJ/mol.$$

The reaction is highly exothermic so no heating is required once the reaction is started.

d. Absorption Unit

The SO_3 obtained from the contact tower is dissolved in 98% H_2SO_4 to form pyrosulphuric acid (oleum), $H_2S_2O_7$. It can be diluted with water to get any required concentration of sulphuric acid.

$$H_2SO_4(aq) + SO_3(g) \rightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$$

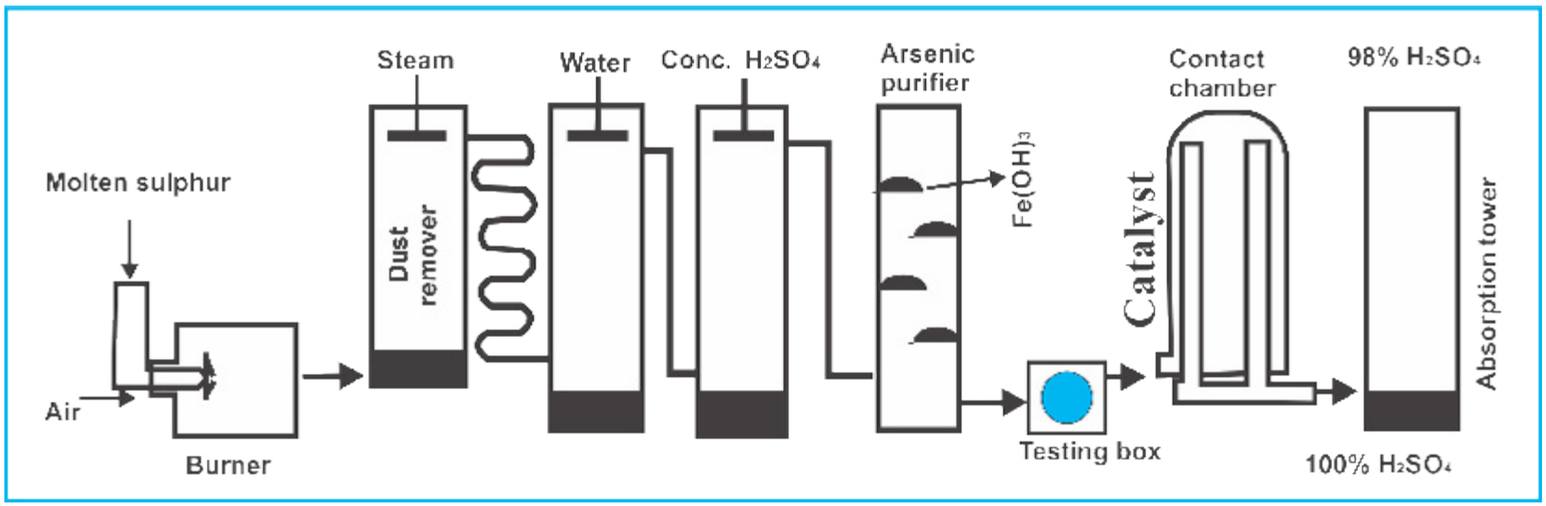


Fig.4.5 Contact Process

4.5.2 Properties

Physical Properties

1. Pure sulphuric acid is a colourless oily liquid without an odour.
2. Its specific gravity is 1.834 at 18°C.
3. It freezes at 10.5°C.
4. Its boiling point is 338°C.
5. It dissolves in water liberating a lot of heat which raises the temperature of the mixture up to 120°C. H_2SO_4 should always be poured in water in a thin stream to avoid any accident.
6. Pure acid is a nonconductor of electricity but the addition of a little water makes it a good conductor.
7. It is extremely corrosive to skin and causes very serious burns to all the tissues.

Reactions

1. It is stable at ordinary temperature but on strong heating it dissociates into SO_3 and H_2O.

$$H_2SO_4 \rightarrow SO_3 + H_2O$$

2.It is a strong acid. In an aqueous solution it completely ionizes to give hydrogen, hydrogen sulphate and sulphate ions. The dissociation take place in two steps.

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(l) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(l)$$

3. Reaction as an Acid

(i) Reactions with alkalies

$$H_2SO_4(aq) + NaOH(aq) \rightarrow NaHSO_4(aq) + H_2O(l)$$

$$NaHSO_4(aq) + NaOH \rightarrow Na_2SO_4(aq) + H_2O(l)$$

(ii) Reactions with carbonates and hydrogen carbonates.

$$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

$$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$$

(iii) Reactions with salts

$$2\,NaCl(s) + H_2SO_4(Conc) \xrightarrow{Strong\ heat} Na_2SO_4(aq) + 2HCl(g)$$

$$KNO_3(aq) + H_2SO_4(Conc) \rightarrow KHSO_4(aq) + HNO_3(g)$$

(iv) Reaction with metals

(a) Cold dilute acid reacts with almost all metals to produce hydrogen gas and sulphate salts.

$$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$$

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

$$Sn(S) + H_2SO_4(aq) \rightarrow SnSO_4(g) + H_2(g)$$

(b) Cold concentrated H_2SO_4 does not react with most of the metals like Cu, Ag, Hg, Pb, Au.

(c) With certain metals hot concentrated sulphuric acid gives metal sulphates, water and SO_2.

$$Cu(s) + 2H_2SO_4(conc) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$

$$2Ag(s) + 2H_2SO_4(conc) \rightarrow Ag_2SO_4(aq) + 2H_2O(l) + SO_2(g)$$

$$Hg(l) + 2H_2SO_4(conc) \rightarrow HgSO_4(aq) + 2H_2O(l) + SO_2(g)$$

4. Reactions as a Dehydrating Agent

H_2SO_4 has a great affinity for water , so it acts as dehydrating agent and eliminates water from different compounds.

(i) With oxalic acid it forms CO_2 and CO.

$$\begin{matrix} COOH \\ | \\ COOH(s) \end{matrix} \xrightarrow{conc.H_2SO_4} CO_2(g) + CO(g) + H_2O(l)$$

(ii) With formic acid, CO is formed.

$$HCOOH(l) \xrightarrow{conc.\ H_2SO_4} CO(g) + H_2O(l)$$

(iii) With ethyl alcohol it forms ethylene.

$$C_2H_5OH(\ell) \xrightarrow[100^\circ C]{Conc.H_2SO_4} C_2H_4(g) + H_2O(\ell)$$

(iv) With wood, paper, sugar and starch it forms carbon and water.

$$C_6H_{12}O_6(s) \xrightarrow{Conc.H_2SO} 6C(s) + 6H_2O(g)$$

$$C_{12}H_{22}O_{11}(s) \xrightarrow{Conc.H_2SO_4} 12C(s) + 11H_2O(g)$$

$$(C_6H_{10}O_5)n \xrightarrow{Conc.H_2SO_4} 6nC + 5nH_2O$$

5. As an Oxidizing Agent

H_2SO_4 acts as a strong oxidizing agent.

(i) It oxidizes C and S giving CO_2 and SO_2 , respectively.

$$C(s) + 2\,H_2SO_4(conc) \rightarrow CO_2(g) + 2\,SO_2(g) + 2\,H_2O(g)$$

$$S(s) + 2\,H_2SO_4(conc) \rightarrow 3\,SO_2(g) + 2\,H_2O(l)$$

(ii) H_2S is oxidized to S .

$$H_2S(g) + H_2SO_4(aq) \rightarrow S(s) + SO_2(g) + 2H_2O(g)$$

(iii) Reactions of H_2SO_4 with HBr and HI produces bromine and iodine respectively.

$$2HBr(aq) + H_2SO_4(aq) \rightarrow Br_2(g) + SO_2(g) + 2H_2O(g)$$

$$2HI(aq) + H_2SO_4(aq) \rightarrow I_2(g) + SO_2(g) + 2\,H_2O(g)$$

6 . Reactions with Gases.

(i) It absorbs SO_3 and forms oleum

$$H_2SO_4(Conc) + SO_3(g) \rightarrow H_2S_2O_7(l)$$

(ii) It reacts with ammonia forming ammonium sulphate.

$$2\,NH_3(g) + H_2\,SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

7. Reaction with Benzene

Benzene sulphonic acid is produced when H_2SO_4 reacts with benzene.

$$C_6H_6(l) + H_2SO_4(conc) \rightarrow \underset{Benzenesulphonic\ acid}{C_6H_5SO_2OH(l)} + H_2O(l)$$

8. Precipitation Reactions

White precipitates are produced when H_2SO_4 reacts with solutions of $BaCl_2$, $Pb(NO_3)_2$ and $Sr(NO_3)_2$.

$$BaCl_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s)\downarrow + 2\,HCl(aq)$$

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

9. Reactions with Oxidizing Agents

It reacts with oxidizing agents like $KMnO_4$ and $K_2Cr_2O_7$ to liberate oxygen which may oxidize other compounds.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$10FeSO_4 + 5H_2SO_4 + 5[O] \rightarrow 5Fe_2(SO_4)_3 + 5H_2O$$

$$2KMnO_{4(aq)} + 8H_2SO_{4(aq)} + 10FeSO_{4(aq)} \rightarrow K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 5Fe_2(SO_4)_{3(aq)} + 8H_2O_{(l)}$$

4.5.3 Uses of Sulphuric Acid

It is used

1. in the manufacture of fertilizers like ammonium sulphate and calcium superphosphate.
2. in refining of petroleum to remove nitrogen and sulphur compounds.
3. in the manufacture of HCl, H_3PO_4, HNO_3 and sulphates.
4. in the manufacture of many chemicals, dyes, drugs, plastics, disinfectants, paints, explosives, synthetic fibers, etc.
5. in electrical batteries and storage cells.
6. as a dehydrating agent for drying gases.
7. as a laboratory reagent.
8. in textile, iron, steel, leather and paper industries.

KEY POINTS

1. In group VA the metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids while bismuth is a metal.
2. Phosphorus and other members of VA group can make use of d-orbitals in bonding.
3. Common oxides of nitrogen are N_2O, NO, NO_2,N_2O_3 and N_2O_5.
4. Nitrogen forms two oxyacids, HNO_2 and HNO_3, HNO_2 is an unstable acid and exists only in solution.
5. HNO_3 is not only a strong acid but it also acts as a strong oxidising agent.
6. Aqua regia is a mixture of one volume of concentrated HNO_3 and three volumes of concentrated HCl.
7. Phosphorus exists in six allotropic forms. White phosphorus is very reactive as compared to red phosphorus.
8. Phosphorus forms two types of chlorides PCl_3, PCl_5 and two types of oxides P_2O_3 andP_2O_5
9. Just like nitrogen, phosphorus also gives two types of oxyacids; phosphorus acid (H_3PO_3) and phosphoric acid (H_3PO_4).
10. Posphoric acid is a weak tribasic acid and it gives three series of salts with strong base.

11. Group VIA of the periodic table contains only one metal, polonium, the rest of members are non-metals. All these elements show the property of allotropy and they are polymeric in nature

12. Oxygen and sulphur are the most abundant elements of groupVIA. Oxygen is the most widely distributed of all the elements. Sulphur is widely distributed in nature in both free and combined forms

13. Sulphuric acid is commercially prepared by oxidation of SO_2 in the presence of a catalyst to SO_3 in a process called Contact Process.

14. H_2SO_4 is a very strong acid. It acts as a dehydrating agent as well as an oxidizing agent.

EXERCISE

Q.1 Fill in the blanks.

(i) The elements_____ of group VA are called metalloids.

(ii) In Birkeland and Eyde's process is prepared from atmospheric oxygen and nitrogen.

(iii) The tendency to form long chain of atoms is called _____ .

(iv) All the elements of group VIA show the property of_____ .

(v) Selenium shows two allotropic forms which are called ___ forms.

vi) Specific gravity of H_2SO_s at 18°C is _____ .

vii) H_2 is produced by reacting H_2SO_4 with metals, like_____ .

viii) The elements of group VIA exhibit maximum oxidation state of _____ .

ix) The outermost shell of group_____ elements contain six electrons.

x) Oxygen shows_____behaviour due to the presence of unpaired electrons.

xi) Conc.phosphoric acid acts as a_____.

xii) Nitrogen is a gas while other elements of the same group are _____ .

xiii) Noble metals like gold and platinum are dissolved in _____ .

xiv) Sulphur is different from oxygen because it shows _____ oxidation states.

xv) HNO_3 is used in the manufacture of _____ fertilizers.

Q.2 Indicate True or False.

i) The metallic character in groups VA and VIA elements increases down the group.

ii) The elements of group VA exhibit maximum oxidation state of +5.

iii) Ionization energy of phoshorus is greater than that of nitrogen.

iv) The electronegativity of oxygen is greater than all other elements of groups VA and VIA.

v) V_2O_5 is used as a catalyst for the oxidation of SO_2 to SO_3.

vi) The oxides of nitrogen are basic in nature.

vii) Aqua regia is prepared by mixing 3 parts of conc. HNO_3 with one part of conc. HCl.

viii) TNT is prepared by the reaction of nitric acid with toluene.

ix) P_2O_3 when reacts with cold water gives phosphorus acid and with hot water it gives phosphoric acid.

x) Sulphur occurs in many organic compounds of animal and vegetable origins.

Q.3 Multiple choice question. Encircle the correct answer.

(i) Out of all the elements of group VA, the highest ionization energy is possessed by

(a) N (b) P (c) Sb (d) Bi

ii) Among group VA elem ents, the most electronegative element is

(a) Sb (b) N (c) P (d) As

iii) Oxidation of NO in air produces

(a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5

iv) The brown gas formed, when metal reduces HNO_3 to

(a) N_2O_5 (b) N_2O_3 (c) NO_2 (d) NO

v) Laughing gas is chemically

(a) NO (b) N_2O (c) NO_2 (d) N_2O_4

(vi) Out of all the elements of group VIA, the highest melting and boiling points is shown by the element

(a) Te (b) Se (c) S (d) Pb

vii) SO_3 is not absorbed in water directly to form H_2SO_4 because
(a) the reaction does not go to completion.
(b) the reaction is quite slow.
(c) the reaction is highly exothermic.
(d) SO_3 is insoluble in water.

ix) Which catalyst is used in contact process?
(a) Fe_2O_3 (b)V_2O_5 (c)SO_3 (d)Ag_2O

x) Which of the following specie has the maximum number of unpaired electrons?
(a) O_2 (b) O_2^+ (c) O_2^- (d) O_2^{2}

Q.4 Short questions.

(i) How does nitrogen differ from other elements of its group?

ii) Why does aqua regia dissolve gold and platinum?

iii) Why the elements of group VIA other than oxygen show more than two oxidation states?

iv) Write down a comparison of the properties of oxygen and sulphur.

v) Write down the equation for the reaction between conc. H_2SO_4 and copper and explain what type of reaction is it.

Q.5 (a) Explain the Brikeland and Eyde's process for the manufacture of nitric acid.

(b) Which metals evolve hydrogen upon reaction with nitric acid? Illustrate alongwith chemical equations.

(c) What is meant by fuming nitric acid?

Q.6 (a) Sulphuric acid is said to act as an acid, an oxidizing agent and a dehydrating agent, describe two reactions in each case to illustrate the truth of this statement.

(b) Give the advantages of contact process for the manufacture of sulphuric acid.

Q.7 (a) Describe the chemistry of the industrial preparation of sulphuric acid from sulphur by the contact process.

(b) Why is SO_3 dissolved in H_2SO_4 and not in water?

(c) Explain the action of sulphuric acid on metals alongwith chemical equations.

Q.8 Describe the preparation of NO_2 gas. Also give its reactions.

Q.9 How PCl_3 and PCl_5 can be used for the preparation of other chemical compounds.

Q.10 Answer the following question.

i) Describe "Ring test" for the confirmation of the presence of nitrate ions in solution.

ii) NO_2 is a strong oxidizing agent. Prove the truth of this statement giving examples.

iii) Write down the chemical equations and names of the products formed as a result of the reaction of HNO_3 with arsenic and antimony.

iv) Give the methods of preparation of PCl_3.

v) P_2O_5 is a powerful dehydrating agent. Prove giving example.

Q.11 Complete and balance the following chemical equation:

$i)$ $P+NO \longrightarrow$

$ii)$ $NO + Cl_2 \longrightarrow$

$iii)$ $H_2S + NO \longrightarrow$

$iv)$ $Pb(NO_3)_2 \longrightarrow$

$v)$ $NO_2 + H_2O \longrightarrow$

$vi)$ $NO_2 + H_2SO_4 \longrightarrow$

$vii)$ $HNO_2 + HI \longrightarrow$

$viii)$ $HNO_2 + NH_3 \longrightarrow$

$ix)$ $HNO_2 + CO(NH_2)_2 \longrightarrow$

$x)$ $KNO_3 + H_2SO_4 \longrightarrow$

Q. 12 Describe the methods of preparation of phosphorus pentoxide and explain its reactions.

Q.13 Discuss the trends in physical properties of group VIA elements.