Chapter
4

GROUP VA AND VIA ELEMENTS

GROUP VA ELEMENTS

Introduction:

The group VA of periodic table consists of nitrogen, phosphorus, arsenic, antimony and bismuth. Electronic configuration of group VA elements is given below in the table:

Table – Electronic configuration of group VA

Name	Symbol	At. Number	Electronic configuration
Nitrogen	N	7	$1s^2, 2s^2, 2p^3$
Phosphorus	P	15	$1s^2, 2s^2, 2p^6, 3s^2, 3p^3$
Arsenic	As	33	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^3$
Antimony	Sb	51	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^3$
Bismuth	Bi	83	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^3$

GENERAL CHARACTERISTICS OF GROUP VA ELEMENTS

(1) Metallic Characters:

Nitrogen and phosphorus are typical non-metals. These two elements are poor conductors of heat and electricity and form acidic oxides like P_2O_3, P_2O_5, NO_2, NO etc. The compounds of nitrogen and phosphorus are mostly covalent in nature. Arsenic and antimony are metalloids and bismuth is a good metal. The metallic characters increases downward in group.

(2) Formation of Anions:

Nitrogen and phosphorus have greater trend to attract the electrons and can form N^{-3} and P^{-3} anions. This trend decreases in antimony and bismuth.

(3) Bond Nature:

Nitrogen and phosphorus usually form covalent bond while this trend decreases in a group and antimony and bismuth form ionic bond.

(4) Oxidation State:

Oxidation state of group VA element is +3 and +5, however nitrogen exists in –3, +1, +2, +3, +4 and +5.

Table – Physical properties of group VA

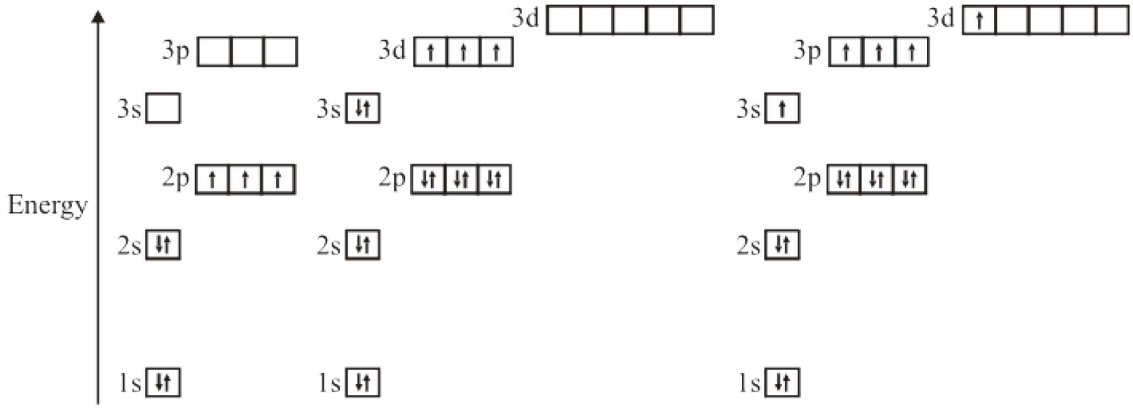
Property	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Physical appearance	Colourless gas	Yellow, red or black solid	Metallic solid	Metallic solid	Metallic solid
Melting point °C	–210	44 red	815	630	271
Boiling point °C	–196	281 red	613	1635	1560
Electronegativity	3.0	2.0	2.0	1.9	1.9
Principal oxidation states	+1, +2, +3, +4, +5, –3	+3, +5	+3, +5	+3, +5	+3, +5
Ionization energy kJ mol^{-1}	1402	1012	950	830	700

PECULIAR BEHAVIOUR OF NITROGEN FROM OTHER FAMILY MEMBERS

(1) Nitrogen is a gas while all other members of this family are solid.

(2) Nitrogen have no allotropes while phosphorus, antimony, bismuth have allotropes.

(3) Nitrogen does not use its d-orbital for bond formation. Phosphorus and other members of the group can make use of d-orbital in their bonding. This is because the energy of these orbital is not much greater than those of the other valence shell orbital. For example, phosphorus can make use of its 3s, 3p and the empty 3d orbital, during bonding with other elements.



Electronic structure of nitrogen and phosphorus

In phosphorus one of the 3s electrons can be promoted to a vacant 3d orbital giving 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) Nitrogen form multiple bond with nitrogen atom or the atoms of other elements while other members do not form multiple bonds (double or triple bonds).

(5) Nitrogen exists in nature in diatomic form N_2 while phosphorus occurs in nature as P_4.

Reason for Difference:

Nitrogen differs from the other members of the family due to the following:

(1) It has small size.

(2) High electronegativity.

(3) Stable as free element.

(4) Unavailability of d-orbital for electron promotion.

NITROGEN AND ITS COMPOUNDS

Occurrence of Nitrogen:

(1) Nitrogen occurs free in the atmosphere as diatomic molecule, N_2. (About 78% by volume of the atmosphere is nitrogen).

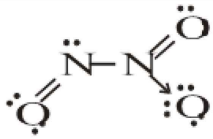
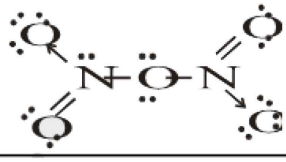
(2) Nitrogen also occurs in plants, animals in the form of proteins, amino acids and urea.

(3) Inorganic compounds of nitrogen are not common. However nitrogen is present in the following mineral; $NaNO_3$ (Chile salt peter), KNO_3 (salt peter).

OXIDES OF NITROGEN

Nitrogen forms several oxides with oxygen. Name, formula and oxidation state of nitrogen oxides are given below in the table.

Table – Oxides of nitrogen

Name	Formula	Oxidation state of N	Structure
(1) Dinitrogen oxide (Nitrous oxide or laughing gas)	N_2O	+1	
(2) Nitrogen oxide (Nitric oxide)	NO	+2	
(3) Dinitrogen trioxide (nitrogen anhydride)	N_2O_3	+3	
(4) Nitrogen oxide (nitrogen per oxide)	NO_2	+4	
(5) Dintrogen pentoxide (Nitrogen anhydride)	N_2O_5	+5	

DINTROGEN OXIDE (N_2O) OR LAUGHING GAS OR NITROUS OXIDE

Preparation:

(1) Dinitrogen oxide can be prepared by the reaction of dilute HNO_3 on metallic zinc.

$$4Zn_{(s)} + 10HNO_{3(dil)} \longrightarrow 4Zn(NO_3)_{2(aq)} + N_2O_{(g)} + 5H_2O_{(l)}$$

(2) Dinitrogen oxide can also be prepared by heating ammonium nitrate NH_4NO_3 at about 200°C.

$$NH_4NO_{3(s)} \xrightarrow{200°C} N_2O_{(g)} + 2H_2O_{(l)}$$

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

PROPERTIES OF DINITROGEN OXIDE

(1) Dinitrogen oxide is a colourless gas with a faint, pleasant smell and a sweetish taste.

(2) It is fairly soluble in cold water.

(3) Its mixture with a little oxygen, if inhaled for a sufficiently long time, produces hysterical laughter, hence it is also known as "laughing gas". It is also used as an anaesthetic.

(4) It is heavier than air.

(5) It boils at –89.5°C.

(6) It is neutral to litmus.

Chemicals 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.

$$S_{(s)} + 2N_2O_{(g)} \longrightarrow SO_{2(g)} + 2N_{2(g)}$$

$$P_{4(s)} + 10N_2O_{(g)} \longrightarrow P_4O_{10(s)} + 10N_{2(g)}$$

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

$$Cu(s) + N_2O_{(g)} \longrightarrow CuO_{(s)} + N_{2(g)}$$

NITROGEN OXIDE (NO) (NITRIC OXIDE)

Preparation:

(1) Nitric oxide can be prepared by the action of dil. HNO_3 on copper.

$$3Cu_{(s)} + 8HNO_{3(dil.)} \longrightarrow 3Cu(NO_3)_2 + 2NO_{(g)} + 4H_2O_{(l)}$$

(2) It can also be prepared by passing air through an electric arc at high temperature.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

PROPERTIES OF NITROGEN OXIDE

(1) Nitrogen oxide is a colourless gas.

(2) Heavier than air.

(3) Sparingly soluble in water.

(4) It is neutral to litmus.

(5) It is paramagnetic in nature.

Chemical Reaction:

(1) Nitrogen oxide reacts with oxygen to forms reddish brown nitrogen dioxide.

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

(2) NO gas decomposes into N_2 and O_2 at about 1000°C.

$$2NO_{(g)} \xrightarrow{1000°C} N_{2(g)} + O_{2(g)}$$

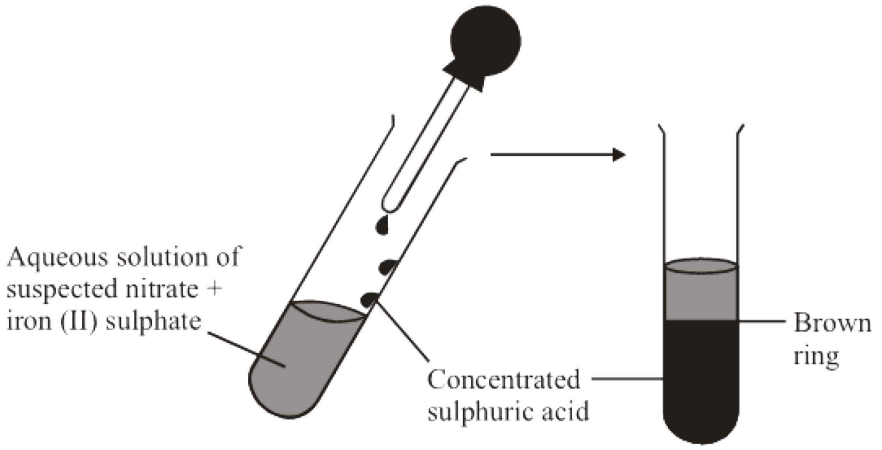
(3) NO gas forms nitrosyl chloride and nitrosyl bromide with chlorine and bromine respectively in the presence of charcoal.

$$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$$

$$2NO_{(g)} + Br_{2(l)} \longrightarrow 2NOBr_{(g)}$$

(4) It forms a brown coloured addition compound with $FeSO_4$. This test is used to confirm the presence of nitrates (Ring Test). The nitrate salt is dissolved in water and some fresh $FeSO_4$ solution is added to it. Concentrated sulphuric acid is slowly run down along the side of the test tube so that two layers are formed. It nitrate is present, it forms a brown ring of $FeSO_4.NO$ complex.

$$FeSO_{4(aq)} + NO_{(g)} \longrightarrow FeSO_4.NO_{(aq)}$$



The brown ring text for nitrates

(5) **NO as Oxidizing Agent:** When NO reacts with reducing agents, it is reduced to nitrous oxide or nitrogen. Oxidation state of nitrogen changes from +2 to +1.

$$H_2S_{(g)} + 2NO_{(g)} \longrightarrow H_2O_{(g)} + N_2O_{(g)} + S_{(s)}$$

$$H_2SO_{3(aq)} + 2NO_{(g)} \longrightarrow H_2SO_{4(aq)} + N_2O_{(g)}$$

(6) **NO as Reducing Agent:** Oxidizing agents can oxidize NO to NO_2 or HNO_3. Oxidation state of nitrogen changes from +2 to +4 or +5.

$$2HNO_{3(aq)} + NO_{(g)} \longrightarrow H_2O_{(l)} + 3NO_{2(g)}$$

$$3I_{2(g)} + 4H_2O_{(l)} + 2NO_{(g)} \longrightarrow 6HI_{(aq)} + 2HNO_{3(aq)}$$

$$3KMnO_{4(aq)} + 6H_2SO_{4(aq)} + 5NO_{(g)} \longrightarrow$$

$$3KHSO_{4(aq)} + 3MnSO_{4(aq)} + 5HNO_{3(aq)} + 2H_2O_{(l)}$$

NITROGEN DIOXIDE NO_2 (NITROGEN PERIOXIDE)

Preparation:

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

$$2Pb(NO_3)_{2(s)} \longrightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

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

$$Cu_{(s)} + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

PROPERTIES OF NITROGEN DIOXIDE

(1) Nitrogen dioxide is a reddish brown gas.

(2) It has a pungent smell.

(3) It dissolves readily in water to form a blue acidic solution.

(4) It is poisonous.

(5) It turns blue litmus red.

(6) It is used as rocket fuel.

Chemical 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.

$$N_2O_{4(l)} \overset{140^\circ C}{\rightleftharpoons} 2NO_{2(g)} \overset{620^\circ C}{\rightleftharpoons} 2NO_{(g)} + O_{2(g)}$$

Pale yellow — Reddish brown — Colourless

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

$$2NO_{2(g)} \longrightarrow 2NO_{(g)} + O_{2(g)}$$

$$2P_{(s)} + 5NO_{2(g)} \longrightarrow P_2O_{5(s)} + 5NO_{(g)}$$

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

$$2NO_{2(g)} + 2H_2O_{(l)} \longrightarrow HNO_{3(aq)} + HNO_{2(aq)}$$

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

$$4NO_{2(g)} + 2H_2O_{(l)} + O_2 \longrightarrow 4HNO_{3(aq)}$$

(4) A mixture of nitrate and nitrite is formed when NO_2 is passed through strong alkalis. It is disproportionation reaction in which nitrogen is reduced as well as oxidised.

$$2NaOH_{(aq)} + 2NO_{2(g)} \longrightarrow NaNO_{3(aq)} + NaNO_{2(aq)} + H_2O_{(l)}$$

$$2KOH_{(aq)} + 2NO_{2(g)} \longrightarrow KNO_{3(aq)} + KNO_{2(aq)} + H_2O_{(l)}$$

(5) **Oxidizing Agent:** It oxidizes H_2S to sulphur, ferrous sulphate to ferric sulphate and KI to I_2. Charge of S changes from −2 to 0. Charge of Fe^{2+} changes to Fe^{3+} and charge of iodine changes from −1 to 0.

$$H_2S_{(g)} + NO_{2(g)} \longrightarrow H_2O_{(l)} + S_{(s)} + NO_{(g)}$$

$$2FeSO_{4(aq)} + H_2SO_{4(aq)} + NO_{2(g)} \longrightarrow Fe_2(SO_4)_{3(aq)} + H_2O_{(l)} + NO_{(g)}$$

$$2KI_{(aq)} + 2NO_{2(g)} \longrightarrow 2KNO_{2(aq)} + I_{2(s)}$$

OXYACIDS OF NITROGEN

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

NITROUS ACID (HNO_2)

Preparation:

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

$$N_2O_{3(g)} + H_2O_{(l)} \longrightarrow 2HNO_{2(aq)}$$

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

$$Ba(NO_2)_{2(aq)} + H_2SO_{4(aq)} \longrightarrow BaSO_{4(aq)} + 2HNO_{2(aq)}$$

PROPERTIES OF NITROUS ACID

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

Chemical Reactions:

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

$$3HNO_{2(aq)} \longrightarrow HNO_{3(aq)} + 2NO_{(g)} + H_2O_{(g)}$$

(2) **Oxidizing Agent:** It acts as an oxidizing agent and oxidizes HI, SO_2 and $SnCl_2$ into I_2, H_2SO_4 and $SnCl_4$ respectively: Oxidation state of iodine, tin and sulphur increases.

$$2HNO_{2(aq)} + 2HI_{(aq)} \longrightarrow 2H_2O_{(l)} + 2NO_{(g)} + I_{2(s)}$$

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

$$SO_{2(g)} + H_2O_{(l)} + [O]_{(g)} \longrightarrow H_2SO_{4(aq)}$$

$$SnCl_{2(aq)} + 2HCl_{(aq)} + 2HNO_{2(aq)} \longrightarrow SnCl_{4(aq)} + 2NO_{(g)} + 2H_2O_{(l)}$$

(3) **Reducing Agent:** Nitrous acid decolorizes acidified $KMnO_4$ and bromine water. It readily gets oxidized to nitric acid, so it also behaves as a reducing agent. Oxidation state of manganese changes from +7 to +2 and nitrogen +3 to +5.

$$2KMnO_{4(aq)} + 3H_2SO_{4(aq)} + 5HNO_{2(aq)} \longrightarrow$$

$$K_2SO_{4(aq)} + 2MnSO_{4(aq)} + 3H_2O_{(l)} + 5HNO_{3(aq)}$$

$$HNO_{2(aq)} + Br_{2(aq)} + H_2O_{(l)} \longrightarrow HNO_{3(aq)} + 2HBr_{(aq)}$$

(4) As an acid it reacts with alkalis producing salts.

$$NaOH_{(aq)} + HNO_{2(aq)} \longrightarrow NaNO_{2(aq)} + H_2O_{(l)}$$

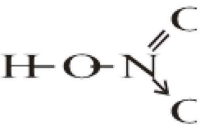
(5) It also reacts with organic compounds containing NH_2 group and produces nitrogen.

$$2HNO_{2(aq)} + CO(NH_2)_{2(aq)} \longrightarrow 2N_{2(g)} + CO_{2(g)} + 3H_2O_{(l)}$$

Urea

$$HNO_{2(aq)} + C_6H_5NH_{2(l)} \longrightarrow C_6H_5OH_{(l)} + N_{2(g)} + H_2O_{(l)}$$

Aminobenzene Phenol

	
Structure of HNO_2	**Structure of HNO_3**

NITRIC ACID (HNO_3) (AQUA FORTIS)

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

$$KNO_{3(s)} + H_2SO_{4(conc.)} \longrightarrow KHSO_{4(aq)} + HNO_{3(aq)}$$

MANUFACTURE OF NITRIC ACID

Birkland Eyde Process:

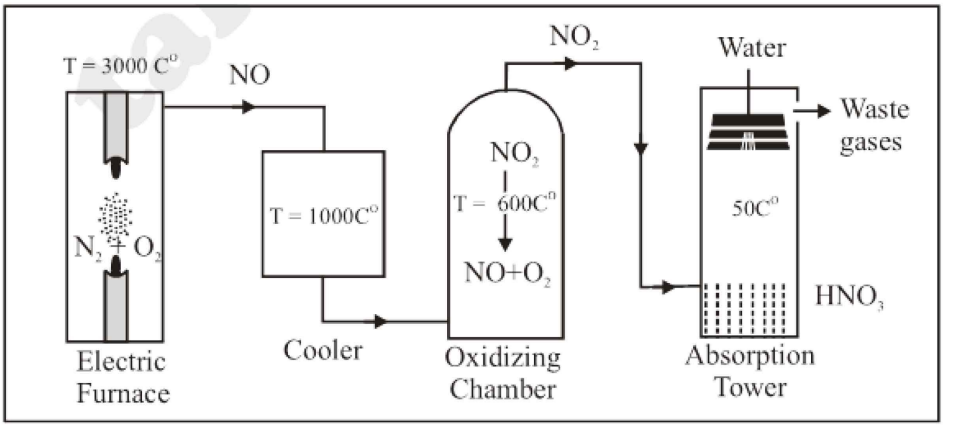
This process consists of the following steps:

(1) Formation of Nitric Acid:

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

$$N_{2(g)} + O_{2(g)} \xrightarrow{3000°C} 2NO_{(g)}$$

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



Manufacture of nitric acid from air

(2) At 600°C NO combines with O_2 to form NO_2.

$$2NO_{(g)} + O_{2(g)} \xrightarrow{600°C} 2NO_{2(g)}$$

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

$$2NO_{2(g)} + H_2O_{(l)} \longrightarrow HNO_{3(aq)} + HNO_2$$

(4) Nitrous acid is oxidized to nitric acid and nitric oxide which is reoxidized to NO_2.

$$3HNO_{2(g)} \longrightarrow HNO_{3(aq)} + 2NO_{(g)} + H_2O_{(l)}$$

PROPERTIES OF NITRIC ACID

(1) Concentrated nitric acid is a colourless volatile liquid which fumes strongly in air.

(2) It has a pungent smell.

(3) Its specific gravity at 15°C is 1.53.

(4) Its B.P = 86°C.

(5) Its specific gravity is 1.538.

Reaction of HNO_3:

(1) Decomposition:

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

$$4HNO_{3(aq)} \longrightarrow 2H_2O_{(l)} + 4NO_{2(g)} + O_{2(g)}$$

(2) Acidic Behaviour:

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.

$$2HNO_{3(aq)} + CaO_{(aq)} \longrightarrow H_2O_{(l)} + Ca(NO_3)_{2(aq)}$$

$$HNO_{3(aq)} + NaOH_{(aq)} \longrightarrow H_2O_{(l)} + NaNO_{3(aq)}$$

$$2HNO_{3(aq)} + Na_2CO_{3(aq)} \longrightarrow 2NaNO_{3(aq)} + CO_{2(aq)} + H_2O_{(l)}$$

(3) Oxidizing Agent:

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

$$2HNO_{3(aq)} \longrightarrow H_2O_{(l)} + 2NO_{2(g)} + [O]_{(g)}$$

(i) Reactions with Non-metals:

It oxidizes non-metals to their corresponding oxides.

$$C_{(s)} + 4HNO_{3(aq)} \longrightarrow CO_{2(g)} + 4NO_{2(g)} + 2H_2O_{(l)}$$

$$S_{(s)} + 6HNO_{3(aq)} \longrightarrow H_2SO_{4(aq)} + 6NO_{2(g)} + 2H_2O_{(l)}$$

$$P_{(s)} + 5HNO_{3(aq)} \longrightarrow H_3PO_{4(aq)} + 5NO_{2(g)} + H_2O_{(l)}$$

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

(ii) Reaction with Metalloids:

Metalloids like arsenic and antimony can be oxidized to their corresponding acids. When reacts with concentrated nitric acid.

$$As_{(g)} + 5HNO_{3(aq)} \longrightarrow H_3AsO_{4(aq)} + 5NO_{2(g)} + H_2O_{(l)}$$

$$Sb_{(g)} + 5HNO_{3(aq)} \longrightarrow H_3SbO_{4(aq)} + 5NO_{2(g)} + H_2O_{(l)}$$

Antimonic acid

(iii) Reaction with Metals:

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

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

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

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

$$Mg_{(s)} + 2HNO_{3(dil.)} \longrightarrow Mg(NO_3)_2 + H_{2(g)}$$

$$Mn_{(s)} + 2HNO_{3(dil.)} \longrightarrow Mn(NO_3)_{2(aq)} + H_{2(g)}$$

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

$$3Cu_{(s)} + 8HNO_{3(dil.)} \longrightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

$$Cu_{(s)} + 4HNO_{3(conc.)} \longrightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

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

$$6Hg_{(l)} + 8HNO_{3(dil.)} \longrightarrow 3Hg_2(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

With concentrated acid it gives mercuric nitrate and NO_2.

$$Hg_{(l)} + 4HNO_{3(conc.)} \longrightarrow Hg(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$$

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

$$3Ag_{(s)} + 4HNO_{3(aq)} \longrightarrow 3AgNO_{3(aq)} + NO_{(g)} + 2H_2O_{(l)}$$

(h) Dilute nitric acid gives ammonium nitrate, when it reacts with tin. With concentrated acid meta stannic acid H_2SnO_3 is produced.

$$4Sn_{(s)} + 10HNO_{3(dil.)} \longrightarrow 4Sn(NO_3)_2 + NH_4NO_{3(aq)} + 3H_2O_{(l)}$$

$$Sn_{(s)} + 4HNO_{3(conc.)} \longrightarrow H_2SnO_{3(aq)} + 4NO_{2(g)} + H_2O_{(l)}$$

(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.

$$4Zn_{(s)} + 10HNO_{3(v.dil.)} \longrightarrow 4Zn(NO_3)_{2(aq)} + NH_4NO_{3(aq)} + 3H_2O_{(l)}$$

$$4Zn_{(s)} + 10HNO_{3(dil.)} \longrightarrow 4Zn(NO_3)_{2(aq)} + N_2O_{(g)} + 5H_2O_{(l)}$$

$$Zn + 4HNO_{3(conc.)} \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

(iv) Reducing agents like $FeSO_4$, H_2S and HI are converted to $Fe_2(SO_4)_3$, S and I_2 respectively, when they react with conc. HNO_3.

$$6FeSO_{4(aq)} + 3H_2SO_{4(aq)} + 2HNO_{3(conc.)} \longrightarrow 3Fe_2(SO_4)_{3(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

$$2HNO_{3(conc.)} + 3H_2S_{(g)} \longrightarrow 4H_2O_{(l)} + 2NO_{(g)} + 3S_{(s)}$$

$$6HI_{(aq)} + 2HNO_{3(conc.)} \longrightarrow 4H_2O_{(l)} + 2NO_{(g)} + 3I_{2(s)}$$

(v) 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.

$$HNO_{3(conc.)} + 3HCl_{(conc.)} \longrightarrow NOCl_{(aq)} + Cl_{2(g)} + 2H_2O_{(l)}$$

NOCl formed, is decomposed giving NO and Cl_2.

$$2NOCl \longrightarrow 2NO_{(g)} + Cl_{2(g)}$$

This liberated chlorine gas which converts noble metals such as gold and platinum into their chlorides and result in dissolution.

$$2Au + 3Cl_2 \longrightarrow 2AuCl_3$$

It dissolves Pt to form soluble chloride.

$$3Pt + 4HNO_3 + 12HCl \longrightarrow 3PtCl_4 + 4NO + 8H_2O$$

(vi) One or more hydrogen of hydrocarbons are replaced by nitro group ($-NO_2$) when they react with conc. HNO_3 in the presence of conc. H_2SO_4.

$$C_6H_{6(l)} + HONO_{2(conc.)} \xrightarrow{\text{Conc. } H_2SO_4} C_6H_5NO_{2(l)} + H_2O_{(l)}$$

Nitrobenzene

$$CH_{4(g)} + HONO_{2(conc.)} \xrightarrow{\text{Conc. } H_2SO_4} CH_3NO_{2(l)} + H_2O_{(l)}$$

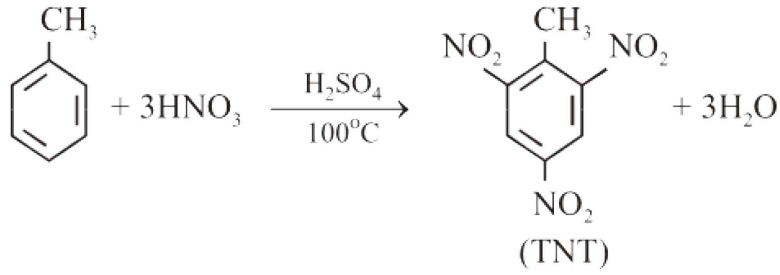
Nitromethane

(7) Nitric acid reacts with glycerin, tolune and phenol to prepare materials used as explosives like nitroglycerin, trinitrotolune (TNT) and picric acid respectively. Trinitroglycerine is also called "Nobel Oil".

(i)
$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3HNO_3 \longrightarrow \begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array} + 3H_2O$$

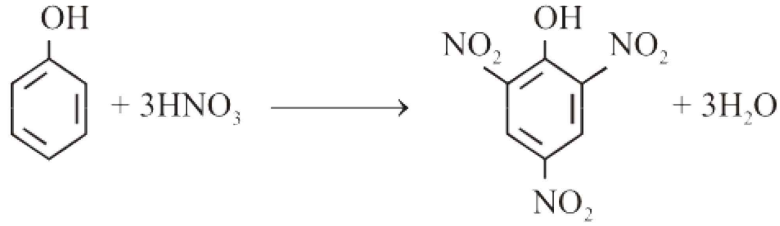
(Trinitroglycerine)

(ii)

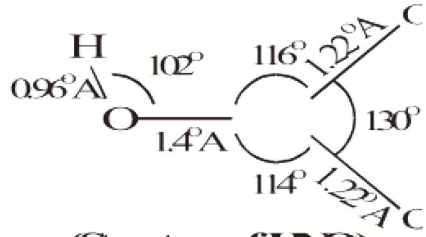


(TNT)

(iii)



(Picric acid)



(Structure of HNO_3)

Uses of Nitric Acid:

(1) It is a laboratory reagent and good oxidizing agent.

(2) It is used for the manufacture of nitrogen fertilizers.

(3) It is used for the manufacture of many explosives like trinitro glycerin (used in dynamite), Trinitro toluene (TNT) etc.

(4) It is used to prepare organic dyes and varnishes artificial silk.

PHOSPHOROUS AND ITS COMPOUNDS

Occurrence of Phosphorus:

(1) 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 $Ca_5F(PO_4)_3$ or $CaF_2.3Ca_3(PO_4)_2$.

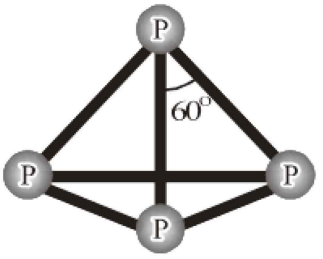
(2) As a constituent of plant and animal tissues, it is essential for their normal growth. It occurs especially in seeds, the yolk of eggs, the nerves, brain and bone marrows, usually in the from of lecithins. Lecithins are important constituents of cell memberane, particularly in the brain. Lecithins are examples of phospholipids.

(3) In the form of calcium phosphate, it is essential constituent of bone. Bone ash which contains 80% calcium phosphate.

ALLOTROPES OF PHOSPHORUS

"The existence of an element into different forms due to their different arrangements are called allotropes." Allotropes have same chemical properties but different physical properties. Phosphorus exists in six different allotropic forms but three are more common.

(1) White Phosphorus:



P_4 molecule

(i) White phosphorus consists of individual tetrahedral P_4 molecules.

(ii) It is a waxy solid that melts at 44°C and boils at 280°C.

(iii) In P-P-P bond angle is 60° which is less than normal bond angle.

(iv) Due to smaller angle, it has strain and **very reactive**.

(v) It is soluble in benzene and carbon tetrachloride.

(vi) When P_4 molecules are heated above 700°C, it dissociates to form P_2 molecules. White phosphorus is toxic and when contacts with skin, produces painful slow healing burns.

(vii) It is more reactive.

(viii) It is more poisonous.

(2) Red Phosphorus:

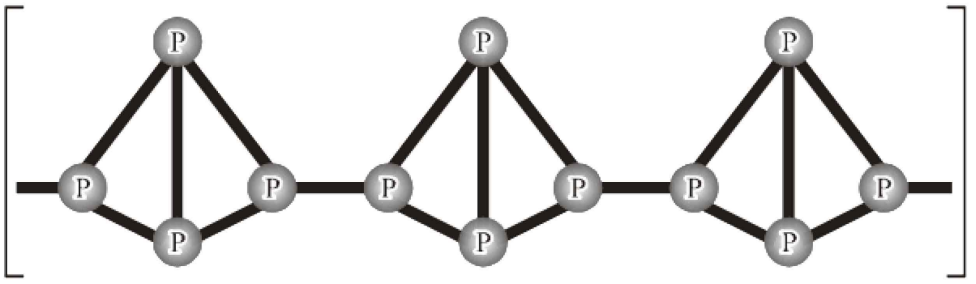
(i) Red phosphorus is less reactive.

(ii) It is less poisonous than white phosphorus.

(iii) It is prepared by heating white phosphorus in the presence of little iodine or sulphur as catalyst upto 250°C in vacuum.

(iv) It is formed by joining the P_4 molecules at their corners to form a **macromolecule**.

(v) Red phosphorus is used to make incendiary devices (bombs, fireworks, flares etc.) Red phosphorus when mixed with sand is used as the rubbing surface of the match box.



Red phosphorus

(3) Black Phosphorus:

(i) Black phosphorus is the **least reactive** form of phosphorus.

(ii) It consists of layers of phosphorus atoms. Within each layer phosphorus atoms are covalently bonded to each other but attraction between the layers is weak like graphite.

(iii) It has flaky appearance due to layers.

(iv) Black phosphorus is prepared by heating red phosphorus at high temperature and pressure.

HALIDES OF PHOSPHORUS

Phosphorus Trihalide, PCl_3:

Preparation:

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

$$2P_{(s)} + 3Cl_{2(g)} \longrightarrow 2PCl_{3(l)}$$

(2) It may also be prepared by the action of phosphorus with thionyl chloride ($SOCl_2$).

$$2P_{(g)} + 4SOCl_{2(l)} \longrightarrow 2PCl_{3(l)} + 2SO_{2(s)} + S_2Cl_{2(s)}$$

PROPERTIES OF PHOSPHORUS TRICHLORIDE

(1) It is a colourless fuming liquid which boils at 76°C and freezes at –112°C.

(2) It is soluble on organic solvents.

(3) Its density is 1.57 g cm^{-3}.

Chemical Reactions:

(1) It combines with chlorine to form phosphorus pentachloride.

$$PCl_{3(l)} + Cl_{2(g)} \longrightarrow PCl_{5(s)}$$

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

$$2PCl_{3(l)} + O_{2(g)} \longrightarrow 2POCl_{3(s)}$$

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

$$PCl_{3(l)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 3HCl_{(aq)}$$

(4) It reacts with alcohols forming the respective chloro derivatives and H_3PO_3.

$$3CH_3OH_{(l)} + PCl_{3(l)} \longrightarrow \underset{\text{Methyl chloride}}{3CH_3Cl_{(l)}} + H_3PO_{3(l)}$$

$$3CH_3COOH_{(l)} + PCl_{3(l)} \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl_{(l)}} + H_3PO_{3(l)}$$

PHOSPHORUS PENTACHLORIDE PCl_5

Preparation:

(1) By passing dry chlorine through phosphorus trichloride at temperature of about 0°C, phosphorus pentachloride is formed.

$$PCl_3 + Cl_2 \xrightarrow{0°C} PCl_5$$

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

$$2P_{(l)} + 5Cl_{2(g)} \longrightarrow 2PCl_{5(s)}$$

PROPERTIES OF PHOSPHORUS PENTACHLORIDE

(1) It is a yellowish white crystalline solid which sublimes at about 100°C.

(2) It gives fumes in moist air with an irritation smell.

(3) Its M.P = 148°C and B.P = 165°C.

Chemical Reactions:

(1) It decomposes on heating producing PCl_3 and chlorine.

$$PCl_{5(s)} \xrightarrow{300°C} PCl_{3(l)} + Cl_{2(g)}$$

(2) It gets decomposed by water forming phosphorus oxychloride which further reacts with water to produce ortho phosphoric acid.

$$PCl_{5(s)} + H_2O_{(l)} \longrightarrow POCl_{3(l)} + 2HCl_{(aq)}$$

$$POCl_{3(l)} + 3H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + 3HCl_{(aq)}$$

$$PCl_{5(s)} + 4H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + 5HCl_{(aq)}$$

(3) It reacts metals to from their metal chlorides.

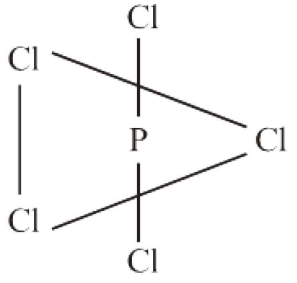
$$Zn_{(s)} + PCl_{5(s)} \longrightarrow ZnCl_{2(s)} + PCl_{3(l)}$$

(4) It reacts with alcohols giving corresponding alkyl chlorides, $POCl_3$ and HCl. With carboxylic acids, it gives acid chlorides.

$$C_2H_5OH_{(l)} + PCl_{5(s)} \longrightarrow \underset{\text{Phosphorus}}{C_2H_5Cl_{(l)}} + \underset{\text{Oxytrichloride}}{POCl_{3(l)}} + 3HCl_{(l)}$$

$$CH_3COOH_{(s)} + PCl_{5(s)} \longrightarrow \underset{\text{Acetylchloride}}{CH_3COCl_{(l)}} + POCl_{3(l)} + HCl_{(l)}$$

Structure of PCl_5:



Trigonal bipyramidal structure of PCl_5 having dsp^3 hybridization

OXIDES OF PHOSPHORUS

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.

$$P_{4(s)} + 3O_{2(g)} \longrightarrow 2P_2O_{3(s)}$$

PROPERTIES OF PHOSPHORUS TRIOXIDE

(1) It is a white waxy solid with garlic like odour.

(2) It melts at 22.8°C and boils at 173°C.

(3) It is highly poisonous in nature.

Chemical Reactions:

(1) When heated in the presence of air it is converted into phosphorus pentoxide.

$$P_2O_{3(s)} + O_{2(g)} \longrightarrow P_2O_{5(s)}$$

(2) It reacts with cold water to give phosphorus acid but reacting with hot water it forms phosphine and phosphoric acid.

$$P_2O_{3(s)} + 3H_2O_{(l)} \xrightarrow[\text{(Cold)}]{} 3H_3PO_{3(s)}$$

$$2P_2O_{3(s)} + 6H_2O_{(l)} \xrightarrow[\text{(Hot)}]{} 3H_3PO_{4(aq)} + PH_{3(g)}$$

PHOSPHORUS PENTOXIDE

Preparation:

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

$$P_{4(s)} + 5O_{2(g)} \longrightarrow 2P_2O_{5(s)}$$

PROPERTIES OF PHOSPHORUS PENTOXIDE

(1) It is a white hygroscopic powder having a faint, garlic like odour due to the presence of traces of P_2O_3.

(2) It sublimes at 360°C.

(3) It is volatile solid.

Chemical Reactions:

(1) With cold water phosphorus pentoxide forms meta phosphoric acid.

$$P_2O_{5(s)} + H_2O_{(l)} \longrightarrow 2HPO_{3(aq)}$$

With hot water, it forms ortho phosphoric acid.

$$P_2O_{5(s)} + 3H_2O_{(l)} \longrightarrow 2H_3PO_{4(aq)}$$

(2) **Dehydrating Agent:** It is a powerful dehydrating agent on reacting 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.

$$2HNO_{3(aq)} + P_2O_{5(s)} \longrightarrow N_2O_{5(g)} + 2HPO_{3(aq)}$$

$$H_2SO_{4(aq)} + P_2O_{5(s)} \longrightarrow SO_{3(g)} + 2HPO_{3(aq)}$$

$$2CH_3COOH_{(aq)} + P_2O_{5(s)} \longrightarrow (CH_3CO)_2O_{(l)} + 2HPO_{3(aq)}$$

$$C_2H_5OH_{(l)} + P_2O_{5(s)} \longrightarrow C_2H_{4(g)} + 2HPO_{3(aq)}$$

OXYACIDS OF PHOSPHORUS

Phosphorus Acid (H_3PO_3):

Preparation:

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

$$P_2O_{3(s)} + 3H_2O_{(l)} \longrightarrow 2H_3PO_{3(aq)}$$

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

$$PCl_{3(l)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 3HCl_{(aq)}$$

PROPERTIES OF PHOSPHOROUS ACID

(1) It is a white crystalline deliquescent solid.

(2) It melts at 73.6°C.

(3) It is highly soluble in water.

Chemical Reactions:

(1) It decomposes into phosphine and orthophosphoric acid on heating.

$$4H_3PO_{3(s)} \xrightarrow{200°C} 3H_3PO_{4(s)} + PH_{3(g)}$$

(2) **Reducing Agent:** It is a powerful reducing agent and reduces $CuSO_4$, $AgNO_3$, etc. to the metallic state.

$$H_3PO_{3(s)} + CuSO_{4(aq)} + H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + H_2SO_{4(aq)} + Cu_{(s)}$$

$$H_3PO_{3(s)} + 2AgNO_{3(aq)} + 2NH_4OH_{(aq)} \longrightarrow H_3PO_{4(aq)} + 2NH_4NO_{3(aq)} + H_2O_{(l)} + 2Ag_{(s)}$$

(3) It reacts with oxygen to form orthophosphoric acid.

$$2H_3PO_{3(s)} + O_{2(g)} \longrightarrow 2H_3PO_{4(s)}$$

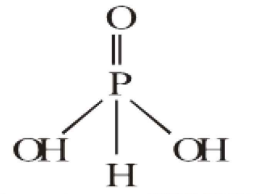
(4) Nascent hydrogen produced by Zn/HCl reduces H_3PO_3 to phosphine.

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$

$$H_3PO_{3(s)} + 6[H]_{(g)} \longrightarrow PH_{3(g)} + 3H_2O_{(l)}$$

Structure of H_3PO_3:

H_3PO_3 is dibasic acid. It has two OH-groups which are ionizable. It releases two H-atoms in the form of protons.



(Structure of H_3PO_3)

ORTHOPHOSPHHORIC ACID (H_3PO_4) OR PHOSPHORIC ACID

Preparation:

(1) It is prepare by dissolving phosphorus pentoxide is hot water.

$$P_2O_{5(s)} + 3H_2O_{(l)} \longrightarrow 2H_3PO_{4(aq)}$$

(Hot)

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

$$P_{(s)} + 5HNO_{3(conc.)} \longrightarrow H_3PO_{4(aq)} + 5NO_{2(g)} + H_2O_{(l)}$$

(3) Hydrolysis of phosphorus pentachloride also gives orthophosphoric acid.

$$PCl_{5(l)} + 4H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + 5HCl_{(aq)}$$

(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.

$$Ca_3(PO_4)_{2(s)} + 3SiO_{2(s)} \longrightarrow 3CaSiO_{3(s)} + P_2O_{5(s)}$$

$$P_2O_{5(s)} + 3H_2O_{(l)} \xrightarrow{\text{(Hot)}} 2H_3PO_{4(aq)}$$

PROPERTIES OF ORTHOPHOSPHORIC ACID

(1) It is a colourless, deliquescent crystalline solid which melts at 41°C.

(2) It is soluble in water. (Deliquescent is the substance which absorbs so much moisture that it changes to liquid).

(3) Its density is 1.87 g cm^{-3}.

Chemical Reactions:

(1) It is a weak tri basic acid. It reacts with NaOH to give three series of salts.

(i) $H_3PO_{4(aq)} + NaOH_{(aq)} \longrightarrow NaH_2PO_{4(aq)} + H_2O_{(l)}$

(ii) $NaH_2PO_{4(aq)} + NaOH_{(aq)} \longrightarrow Na_2HPO_{4(aq)} + H_2O_{(l)}$

(iii) $Na_2HPO_{4(aq)} + NaOH_{(aq)} \longrightarrow Na_3PO_{4(aq)} + H_2O_{(l)}$

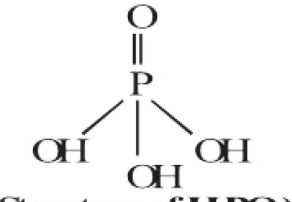
(2) On heating loses water and converted into pyro and meta phosphoric acid.

$$2H_3PO_4 \xrightarrow[-H_2O]{240^\circ C} H_4P_2O_7 \xrightarrow[-H_2O]{316^\circ C} 2HPO_3$$

Orthophosphoric acid	Pyrophosphoric acid	Metaphosphoric acid

Structure of H_3PO_4:

It is tribasic acid. It has three OH-groups which are ionizable. Its structure is



(Structure of H_3PO_4)

GROUP VIA ELEMENTS

Introduction:

The members of group VIA are oxygen, sulphur, selenium, tellurium and polonium. This group is also called "**chalcogen group**" or "ore forming group". Majority of the ores are in the form of oxides or sulphides of carbonates. The electronic configuration of group VIA elements are given in the table.

Table – Electronic configuration of group VA

Name	Symbol	A. Number	Electronic configuration
Oxygen	O	8	$1s^2, 2s^2, 2p^4$
Sulphur	S	16	$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
Selenium	Se	34	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^4$
Tellurium	Te	52	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^4$
Polonium	Po	84	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^4$

GENERAL CHARACTERISTICS OF GROUP VIA

(1) All the elements of group VIA are non-metals except Po which is a radioactive metal.

(2) Atomic radii, density, melting and boiling points generally increase with increase in atomic number, down the group.

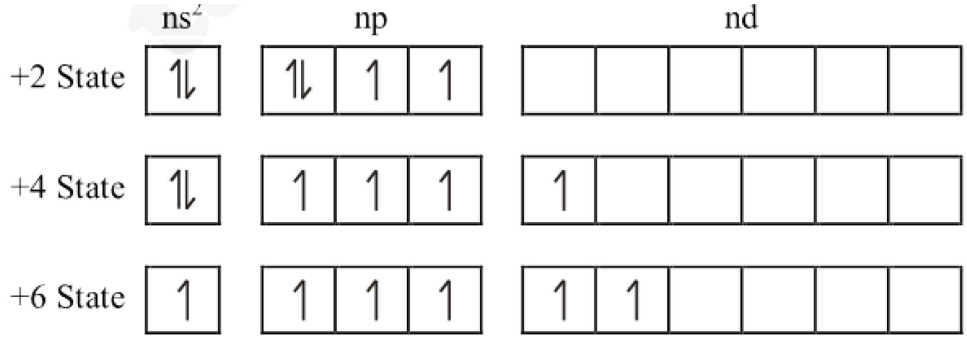
(3) Ionization energies of the group VIA members are very high which shows their reluctance to lose electrons. Oxygen is the most electronegative element after fluorine.

(4) 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).

(5) They also show the property of catenation. This property decreases down the group.

(6) All the elements are polymeric in nature (they form poly-atomic molecules). They attain the electronic configuration of the nearest noble gas by gaining 2 electrons forming O^{-2}, S^{-2}, Se^{-2} etc.

(7) Except oxygen, the other members of the group VIA show a covalency of +2, +4 and +6, for example, SCl_2, SCl_4, SCl_6, +4 oxidation state is shown when 1 electron from p-orbital is promoted to the next vacant d-orbital, while +6 oxidation state is shown when the next vacant d-orbital, while +6 oxidation state is shown when another electron from s-orbital also promoted to the next vacant d-orbital.



Oxidation states of group VIA elements

Table – Physical properties of group VIA elements

Physical properties	O	S	Se	Te	Po
At. number	8	16	34	52	84
Density g/cm^3	1.27	2.06	4.8	6.24	9.5
M. point (°C)	–219	112	220	452.5	254
B. point (°C)	–183	444.6	685	1390	962
At. radii (pm)	74	104	114	137	152
Electronegativity	3.44	2.58	2.55	2.10	2.0
Ionization energy (kJ/mol)	1314	1000	941	869	818
Electron affinity (kJ/mol)	141.1	200.42	197	190	180
Ionic radius 2 – ion (pm)	140	184	198	221	----

OCCURRENCE OF OXYGEN

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.

OCCURRENCE OF SULPHUR (BRIMSTONE)

Brimstone:

(1) Sulphur is also widely distributed in nature both as free and in combined forms. Many important metallic ores of sulphides are, e.g.,

Sulphide ores:

(i)	Galena	(PbS)	(ii)	Zinc blende	(ZnS)
(iii)	Cinnabar	(HgS)	(iv)	Copper pyrite	(Cu_2S, Fe_2S_3)
(v)	Iron pyrite	(FeS_2)	(vi)	Stibnite	(Sb_2S_3)
		(Fool's gold)			(Valentine)

Sulphates ores:

(i)	Gypsum	($CaSO_4.2H_2O$)	(ii)	Heavy spar	($BaSO_4$)
(iii)	Glauber salt	($Na_2SO_4.10H_2O$)			

(2) Sulphur also occurs in organic compounds in animals and vegetables like onions, garlic, mustard, hair, many oils, eggs, proteins etc. It also occurs as a constituent of coal and petroleum.

COMPARISON OF OXYGEN AND SULPHUR

Similarities:

(1) Both oxygen and sulphur have same outer electronic configuration of ns^2, np^4.

(2) Both oxygen and sulphur are usually divalent, O^{2-}, S^{2-}.

(3) Both oxygen and sulphur exhibit allotropic forms. Allotropes of oxygen are O_3 and O_2 while allotropes of sulphur are, rhombic, monoclinic and plastic sulphur.

(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.

Dissimilarities:

	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 insoluble 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. $3S + 2H_2O \longrightarrow 2H_2S + SO_2$
(7)	It does not react with acids.	It is readily oxidized by conc. sulphuric acid or nitric acid. $S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$ $S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$

(8)	It does not react with acids.	It reacts with alkali solution and forms sulphides and thiosulphate. $4S + 6NaOH \longrightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O$
(9)	It shows oxidation states of –2, +2, –1, –1/2.	It shows oxidation states of –2, +2, +4 and +6.

SULPHURIC ACID H_2SO_4

Sulphuric acid was first prepared by a Muslim scientist Jabir Bin Hyyan in 8th century. In Europe, in 14th and 15th 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 river water and spring water.

Sulphuric acid is also called **"king of chemicals"** and its consumption is scale for industrial development of a country.

MANUFACTURE OF SULPHURIC ACID

Sulphuric acid is being manufactured commonly by contact process.

CONTACT PROCESS

This method was developed by Knietsch in Germany.

Following process are involved during the manufacturing of sulphuric acid by contact process.

(a) Pyrite Burner (Production of SO_2):

In pyrite burner, sulphur or iron pyrite (FeS_2) is roasted in excess of air and SO_2 is formed.

$$S + O_2 \longrightarrow SO_2$$

or $$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

(b) Purification of Sulphur Dioxide:

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 Chamber:*

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 tricking 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 Chamber:

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

$$2SO_{2(g)} + O_{2(g)} \underset{400\text{-}500^\circ C}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_{3(g)} \qquad \Delta H = -269.3 \text{ kJ/mol}$$

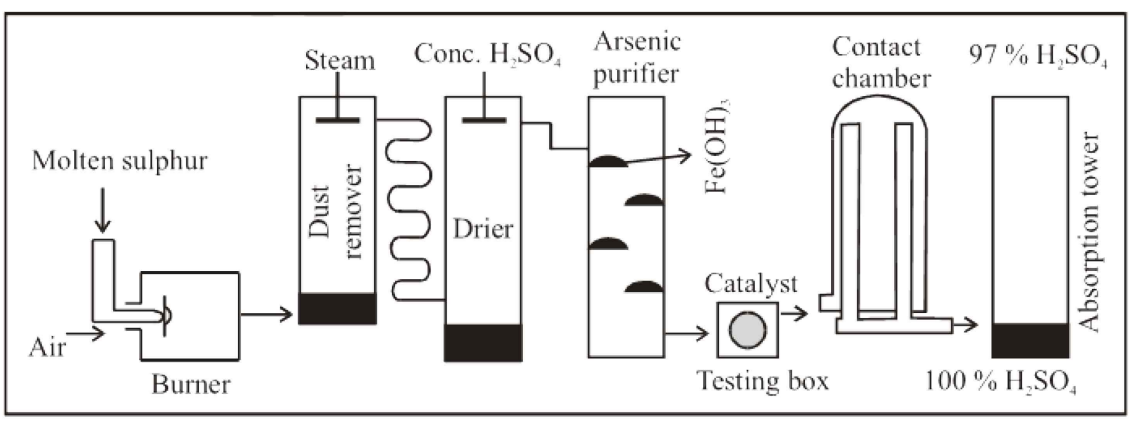
The reaction is highly exothermic so no heating is required when the reaction is started.

(d) Absorption Unit:

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

$$H_2SO_{4(aq)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(l)}$$

$$H_2S_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2H_2SO_{4(aq)}$$



Contact process

PHYSICAL PROPERTIES OF SULPHURIC ACID

(1) Pure sulphuric acid is a colourless oily liquid without any 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 non-conductor 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.

CHEMICAL PROPERTIES OF SULPHURIC ACID

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

$$H_2SO_4 \xrightarrow{\text{Strong heat}} SO_3 + H_2O$$

(2) It is dibasic acid. In an aqueous solution, it ionizes to give hydronium ions, hydrogen sulphate ions and sulphate ions.

$$H_2SO_{4(aq)} + H_2O_{(l)} \longrightarrow HSO^-_{4(aq)} + H_3O^+_{(aq)}$$

$$H_2SO_{4(aq)} + 2H_2O_{(l)} \longrightarrow SO^{2-}_{4(aq)} + 2H_3O^+_{(aq)}$$

(3) Reactions as an acid:

(*i*) It reacts with alkalis to form salt and water:

$$H_2SO_{4(aq)} + NaOH_{(aq)} \longrightarrow NaHSO_{4(aq)} + H_2O_{(l)}$$

$$NaHSO_{4(aq)} + NaOH_{(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(l)}$$

(*ii*) Reactions with carbonates and hydrogen carbonates:

$$Na_2CO_{3(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + CO_{2(g)} + 2H_2O_{(l)}$$

$$2NaHCO_{3(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + CO_{2(g)} + 2H_2O_{(l)}$$

(*iii*) Reactions with some salts:

$$2NaCl_{(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + 2HCl_{(g)}$$

$$2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_{3(aq)}$$

(*iv*) Reaction with metals:

The nature of the products of the reaction with metals depends upon:

(a) The nature of metals.

(b) The concentration of acid.

(c) The temperature.

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

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$$

$$Sn + H_2SO_4 \longrightarrow SnSO_4 + H_2$$

(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 metals sulphates and SO_2.

$$Cu_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CuSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$$

$$2Ag_{(s)} + 2H_2SO_{4(aq)} \longrightarrow Ag_2SO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$$

$$Hg_{(l)} + 2H_2SO_{4(aq)} \longrightarrow HgSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$$

(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.

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\text{Conc. } H_2SO_4} CO_{2(g)} + CO_{(g)} + H_2O_{(l)}$$

(ii) With formic acid, CO is formed.

$$HCOOH_{(aq)} \xrightarrow{\text{Conc. } H_2SO_4} CO_{(g)} + H_2O_{(l)}$$

(iii) With ethyl alcohol it forms ethylene or ethene.

$$C_2H_5OH \xrightarrow[180^\circ C]{\text{Conc. } H_2SO_4} C_2H_{4(g)} + H_2O_{(l)}$$

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

$$C_6H_{12}O \xrightarrow{\text{Conc. } H_2SO_4} 6C + 6H_2O$$

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

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

(5) H_2SO_4 acts as a strong oxidizing agent:

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

$$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(l)}$$

$$S_{(s)} + 2H_2SO_{4(aq)} \longrightarrow 3SO_{2(g)} + 2H_2O_{(l)}$$

(ii) H_2S is oxidized to S.

$$H_2S_{(g)} + H_2SO_{4(aq)} \longrightarrow S_{(s)} + SO_{2(g)} + 2H_2O_{(l)}$$

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

$$2HBr_{(aq)} + H_2SO_{4(aq)} \longrightarrow Br_{2(g)} + SO_{2(g)} + 2H_2O_{(l)}$$

$$2HI_{(aq)} + H_2SO_{4(aq)} \longrightarrow I_{2(g)} + SO_{2(g)} + 2H_2O_{(l)}$$

(6) Reaction with some gases:

(i) It absorbs SO_3 and forms oleum (Fuming sulphuric acid or Pyro sulphuric acid).

$$H_2SO_{4(aq)} + SO_{3(g)} \longrightarrow H_2S_2O_{7(l)}$$

(ii) It reacts with ammonia forming ammonium sulphate.

$$2NH_{3(g)} + H_2SO_{4(aq)} \longrightarrow (NH_4)_2SO_{4(aq)}$$

(7) Reaction with benzene (sulphonating agent):

Benzene sulphonic acid is produced when H_2SO_4 reacts with benzene.

$$C_6H_{6(l)} + H_2SO_{4(aq)} \longrightarrow C_6H_5SO_2OH_{(l)} + H_2O_{(l)}$$

(8) Precipitation reactions:

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

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HCl$$

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4\downarrow + 2HNO_3$$

$$Sr(NO_3)_2 + H_2SO_4 \longrightarrow SrSO_4 + 2HNO_3$$

(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.

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

(10) Reaction with $KMnO_4$:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(O)$$

(11) Reaction with $K_2Cr_2O_7$:

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

USES OF SULPHURIC ACID

(1) Sulphuric acid is largely used for the manufacture of fertilizers like ammonium sulphate $(NH_4)_2SO_4$ and calcium super phosphate $Ca(H_2PO_4)_2$.

(2) In the refining of petroleum, sulphuric acid is used to remove nitrogen and sulphur.

(3) Sulphuric acid is used for the manufacture of HCl, H_3PO_3, HNO_3 and many sulphates like $PbSO_4$, $BaSO_4$ etc.

(4) Sulphuric acid is used as dehydrating agent in many industries.

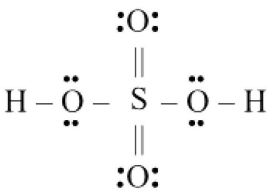
(5) It is used as electrolyte in lead storage batteries.

(6) It is used for the manufacture of many chemicals like dyes, drugs, plastics, disinfectants, paints, explosives and synthetic fibers.

(7) It used in the laboratory as an acid, oxidizing agent and dehydrating agent.

(8) It is used in textile industry, metallurgies of iron and steal, leather industry and in paper industry.

Structure of H_2SO_4:



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_4 at 15°C is ————.

(vii) H_2 is produced by reacting H_2SO_4 with metals, like ————.

(viii) The elements of group VA 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.

ANSWERS

(i)	arsenic, antimony	**(ii)**	nitric oxide	**(iii)**	catenation
(iv)	allotropy	**(v)**	red and grey	**(vi)**	1.834
(vii)	zinc, magnesium, tin etc.	**(viii)**	+5	**(ix)**	VIA
(x)	paramagnetic	**(xi)**	dehydrating agent	**(xii)**	solid
(xiii)	aqua regia	**(xiv)**	+2, +4 and +6	**(xv)**	nitrogen

Q.2 Indicate True or False:

(i) The metallic character in group 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 group 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.

ANSWERS

(i)	True	**(ii)**	True	**(iii)**	False	**(iv)**	True	**(v)**	True
(vi)	False	**(vii)**	False	**(viii)**	True	**(ix)**	True	**(x)**	True

Q.3 Multiple choice questions. 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 elements, 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

(viii) Which catalyst is used in contact process:

(a) Fe_2O_3 **(b)** V_2O_5

(c) SO_3 **(d)** Ag_2O

(ix) Which of the following specie has the maximum number of unpaired electrons:

(a) O_2 **(b)** O_2^{+1}

(c) O_2^{-2} **(d)** O_2^{+2}

ANSWERS

(i)	(a)	**(ii)**	(b)	**(iii)**	(c)	**(iv)**	(c)	**(v)**	(b)
(vi)	(a)	**(vii)**	(c)	**(viii)**	(b)	**(ix)**	(a)		

Q.4 (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 VI-A other than oxygen show more than two oxidation states?

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

(v) Write the equation for the reaction between conc. H_2SO_4 and copper and explain the type of reaction.

Ans.

(i)

- Nitrogen is a gas.
- It is a poor conductor of heat and electricity.
- Nitrogen form acidic oxides.
- Its compounds are predominantly covalent.
- Nitrogen has the greatest tendency to attract the electrons.

All these properties are not shown by other elements of V-A group. Therefore these properties make nitrogen different from rest of its group members.

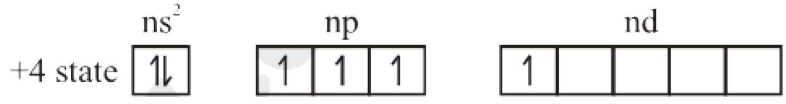
(ii) See text book for details.

(iii) Except oxygen, the other members of group VI-A show the valences of +2, +4 or +6 e.g.,

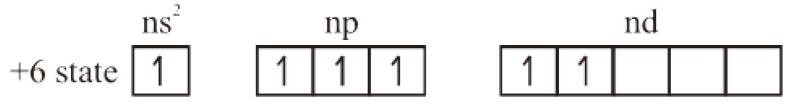
- +2 oxidation state is shown due to unpaired electrons in the p-orbital.



- +4 oxidation state is shown when 1 electron from p-orbital is promoted to the next vacant d-orbital.



- +6 oxidation state is shown when another electron from s-orbital is also promoted to the next vacant d-orbital.



(iv) See text book for details.

(v) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(Cupric sulphate)

It is a redox reaction. Cu acts as reducing agent and H_2SO_4 acts as an oxidizing agent.

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 along with chemical equations.

(c) What is meant by fuming nitric acid?

Ans.

(a) Descriptive questions. See text for details.

(b) Magnesium and manganese react with HNO_3 and evolve hydrogen gas:

$$Mn + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2$$

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

(c) Concentrated HNO_3 is a colourless volatile liquid and it fumes strongly in air and evolve NO_2 gas. Therefore mixture of $HNO_3 + NO_2$ is called as 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.

Ans.

(a) (i) As an acid:

$$H_2SO_{4(aq)} + NaOH_{(aq)} \longrightarrow NaHSO_{4(aq)} + H_2O_{(1)}$$

$$NaHSO_{4(aq)} + NaOH_{(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(1)}$$

(ii) As on oxidizing agent:

$$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(g)}$$

$$H_2S_{(g)} + H_2SO_{4(aq)} \longrightarrow S_{(s)} + SO_{2(g)} + 2H_2O_{(g)}$$

(iii) As dehydration agent:

$$HCOOH_{(aq)} \xrightarrow{\text{Conc. } H_2SO_4} CO_{(g)} + H_2O_{(l)}$$

$$C_2H_5OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} C_2H_4 + H_2O$$

(b) (i) Solid catalysts V_2O_5 is used and there is no chance of nitrogen oxide impurities.

(ii) In this process 100% H_2SO_4 is produced.

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 along with chemical equations.

Ans.

(a) Descriptive question. See text book for details.

(b) In the process of the formation of H_2SO_4, SO_3 is dissolved in H_2SO_4 to form oleum ($H_2S_2O_7$) which is dilluted to get pure H_2SO_4.

If SO_3 is dissolved in water, the reaction will be highly exothermic and metallic fog is formed which impures the product (H_2SO_4).

(c) See text book for details.

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

Ans. Descriptive question. See text book for details.

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

Ans. Consult text book for answer.

Q.10 Answer the following questions:

(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_5.

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

Ans. For answer see text book.

Q.11 Complete and balance the following chemical equations:

Ans. **(i)** $2P + 5NO_2 \longrightarrow P_2O_5 + 5NO$

(ii) $2NO + Cl_2 \longrightarrow 2NOCl$

(iii) $H_2S + 2NO \longrightarrow H_2O + N_2O + S$

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

(v) $2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$

(vi) $2HNO_2 + 2HI \longrightarrow 2H_2O + 2NO + I_2$

(vii) $HNO_2 + NH_3 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(viii) $2HNO_2 + CO(NH_2)_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$

(ix) $2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_3$

Q.12 Describe the methods of preparation of phosphours pentoxide and explain its reaction.

Ans. Descriptive question. See text book for details.

Q.13 Discuss the trends in physical properties of group VI-A elements.

Ans. Descriptive question. See text book for details.

DO YOU KNOW?

(1) N_2O (nitrous oxide) is called laughing gas.

(2) N_2O is colourless gas while NO_2 is reddish brown in colour.

(3) HNO_2 is oxidising agent as well as reducing agent.

(4) $H_2S_2O_7$ (olum) is called fuming sulphuric acid.

(5) ($HNO_3 + NO_2$) is called fuming nitric acid.

(6) H_2SO_4 is called "king of chemicals".

(7) Bone ash contains 80% $Ca_3(PO_4)_2$.

(8) PCl_3 is white crystalline solid.

(9) P_2O_3 reacts with cold water to form H_3PO_3.

$$P_2O_3 + 3H_2O \xrightarrow[\text{(Cold)}]{} 2H_3PO_3$$

(10) P_2O_3 reacts with hot water to form H_3PO_4 and PH_3.

$$2P_2O_3 + 6H_2O \longrightarrow 3H_3PO_4 + PH_3$$

(11) H_3PO_3 is white deliquescent solid.

(12) Phosphorous is Greek word which means "Light bearing".

(13) Lecithins are important constituents of cell membranes particularly in brain.

(14) H_3PO_4 is colourless, deliquescent solid which melts at 41°C.

(15) HNO_3 is also called aqua-fortis.

(16) Glycerine trinitrate is also called "Nobel oil".

(17) Brimstone is another name of sulphur.

(18) Iron pyrites (FeS_2) is called "Fool's gold".

(19) Stibinite (Sb_2S_3) is called "Valentine".

(20) Contact process was developed by Knietsch is Germany.

CHAPTER 4

GROUP VA AND GROUP VIA ELEMENTS

MULTIPLE CHOICE QUESTIONS

1. In group V-A element the most electronegative element is:

(a) Sb **(b)** N

(c) P **(d)** As

2. Which one the following elements occur free in nature:

(a) Sb **(b)** As

(c) N **(d)** P

3. Which one of the following compounds is not known:

(a) $SbCl_3$ **(b)** NCl_3

(c) NI_3 **(d)** NCl_5

4. Which is a laughing gas:

(a) N_2O_5 **(b)** N_2O

(c) NO **(d)** N_2O_4

5. Oxidation of NO in air produces:

(a) N_2O **(b)** N_2O_4

(c) N_2O_3 **(d)** N_2O_5

6. Yellow colour of Nitiric Acid is due to the presence of:

(a) NO_2 **(b)** NO

(c) N_2O **(d)** N_2O_4

7. Gold dissolve in Aqua regia to give:

(a) $AuCl_2$ **(b)** AuCl

(c) $AuCl_3$ **(d)** None

8. When red phosphorous is heated with HNO_3 it forms:

(a) H_3PO_4 **(b)** HPO_2

(c) H_2PO_3 **(d)** H_3PO_3

9. Which of the following is used at the tips of match stick:

(a) $K_2Cr_2O_7$ + S + White P **(b)** $K_2Cr_2O_7$ + K + S

(c) S and K **(d)** Sb_2S_3

10. What is the number of electrons present in the valence shell of P in PCl_3:

(a) 4 **(b)** 6

(c) 8 **(d)** 2

11. Phosphorous shows oxidation state (+3) in which of the following:

(a) $H_4P_2O_7$ **(b)** PO_4^{-3}

(c) H_3PO_3 **(d)** H_3PO_4

12. Which element is the most abundant in the earth's crust:

(a) Fe **(b)** O

(c) Si **(d)** C

13. Which catalyst is used in contact process:

(a) Fe_2O_3 **(b)** V_2O_5

(c) SO_3 **(d)** Ag_2O

14. The brown gas formed when metal reduces HNO_3 is:

(a) N_2O_5 **(b)** N_2O_3

(c) NO_2 **(d)** NO

15. Which of the following specie has the maximum number of unpaired electrons:

(a) O_2^{-1} **(b)** O_2^{+2}

(c) O_2^{-2} **(d)** O_2

16. The contact process for the manufacturing of H_2SO_4 was developed by:

(a) Jabir-Bin-Hayan **(b)** Knietsch

(c) Al-Khwarzmi **(d)** Mendleeve

17. In which compound of nitrogen, the oxidation state of N is (+1):

(a) N_2O **(b)** NO

(c) NO_2 **(d)** N_2O_4

18. $FeSO_4$ forms brown ring with:

(a) N_2O_4 **(b)** NO

(c) NO_2 **(d)** None of these

19. "Lead" in lead pencil is:

(a) Bone black **(b)** Graphite and clay

(c) Lead oxide **(d)** Lead peroxide

20. Formula of Gibbsite is:

(a) Al_2O_3 **(b)** $Al_2O_3 . H_2O$

(c) $Al_2O_3 . 2H_2O$ **(d)** $Al_2O_3 . 3H_2O$

answers

1.	(b)	**2.**	(c)	**3.**	(d)	**4.**	(b)	**5.**	(b)
6.	(a)	**7.**	(c)	**8.**	(a)	**9.**	(a)	**10.**	(c)
11.	(c)	**12.**	(b)	**13.**	(b)	**14.**	(c)	**15.**	(d)
16.	(b)	**17.**	(a)	**18.**	(b)	**19.**	(b)	**20.**	(d)

SOLVED 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_4 at 15°C is ————.

(vii) H_2 is produced by reacting H_2SO_4 with metals, like ————.

(viii) The elements of group VA 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.

answers

(i)	arsenic, antimony	**(ii)**	nitric oxide	**(iii)**	catenation
(iv)	allotropy	**(v)**	red and grey	**(vi)**	1.834
(vii)	zinc, magnesium, tin etc.	**(viii)**	+5	**(ix)**	VIA
(x)	paramagnetic	**(xi)**	dehydrating agent	**(xii)**	solid

(xiii)	aqua regia	**(xiv)**	+2, +4 and +6	**(xv)**	nitrogen

Q.2 Indicate True or False:

(i) The metallic character in group 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 group 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.

answers

(i)	True	**(ii)**	True	**(iii)**	False	**(iv)**	True	**(v)**	True
(vi)	False	**(vii)**	False	**(viii)**	True	**(ix)**	True	**(x)**	True

Q.3 Multiple choice questions. 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 elements, 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

(viii) Which catalyst is used in contact process:

(a) Fe_2O_3 **(b)** V_2O_5

(c) SO_3 **(d)** Ag_2O

(ix) Which of the following specie has the maximum number of unpaired electrons:

(a) O_2 **(b)** O_2^{+1}

(c) O_2^{-2} **(d)** O_2^{+2}

answers

(i)	(a)	**(ii)**	(b)	**(iii)**	(c)	**(iv)**	(c)	**(v)**	(b)
(vi)	(a)	**(vii)**	(c)	**(viii)**	(b)	**(ix)**	(a)		

Q.4 (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 VI-A other than oxygen show more than two oxidation states?

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

(v) Write the equation for the reaction between conc. H_2SO_4 and copper and explain the type of reaction.

Ans.

(i) (i) Nitrogen is a gas while other members are solids.

(ii) Nitrogen has no allotropes while P, Sb, Bi has allotropes.

✷ Nitrogen does not use its d-orbital for bond formation.

✷ Nitrogen forms multiple bond with nitrogen atom (N ≡ N) and with the atoms of other elements.

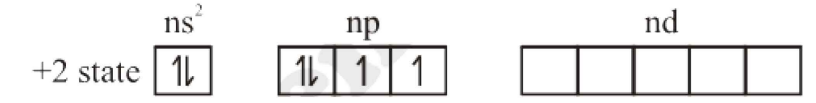
✷ Nitrogen exists in diatomic form (N_2) while phosphorous occurs as P_4.

All these properties are not shown by other elements of V-A group. Therefore these properties make nitrogen different from rest of its group members.

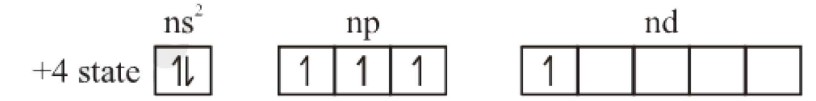
(ii) See text book for details.

(iii) Except oxygen, the other members of group VI-A show the valences of +2, +4 or +6 e.g.,

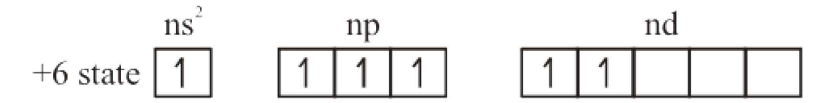
✷ +2 oxidation state is shown due to unpaired electrons in the p-orbital.



✷ +4 oxidation state is shown when 1 electron from p-orbital is promoted to the next vacant d-orbital.



✷ +6 oxidation state is shown when another electron from s-orbital is also promoted to the next vacant d-orbital.



(iv) See text book for details.

(v) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

(Cupric sulphate)

It is a redox reaction. Cu acts as reducing agent and H_2SO_4 acts as an oxidizing agent.

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 along with chemical equations.

(c) What is meant by fuming nitric acid?

Ans.

(a) Descriptive questions. See text for details.

(b) Magnesium and manganese react with HNO_3 and evolve hydrogen gas:

$$Mn + 2HNO_3 \longrightarrow Mn(NO_3)_2 + H_2$$

$$Mg + 2HNO_3 \longrightarrow Mg(NO_3)_2 + H_2$$

(c) Concentrated HNO_3 is a colourless volatile liquid and it fumes strongly in air and evolve NO_2 gas. Therefore mixture of $HNO_3 + NO_2$ is called as 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.

Ans.

(a) (i) As an acid:

$$H_2SO_{4(aq)} + NaOH_{(aq)} \longrightarrow NaHSO_{4(aq)} + H_2O_{(1)}$$

$$NaHSO_{4(aq)} + NaOH_{(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(1)}$$

(ii) As on oxidizing agent:

$$C_{(s)} + 2H_2SO_{4(aq)} \longrightarrow CO_{2(g)} + 2SO_{2(g)} + 2H_2O_{(g)}$$

$$H_2S_{(g)} + H_2SO_{4(aq)} \longrightarrow S_{(s)} + SO_{2(g)} + 2H_2O_{(g)}$$

(iii) As dehydration agent:

$$HCOOH_{(aq)} \xrightarrow{\text{Conc. } H_2SO_4} CO_{(g)} + H_2O_{(l)}$$

$$C_2H_5OH \xrightarrow[100°C]{\text{Conc. } H_2SO_4} C_2H_4 + H_2O$$

(b) (i) Solid catalysts V_2O_5 is used and there is no chance of nitrogen oxide impurities.

(ii) In this process 100% H_2SO_4 is produced.

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 along with chemical equations.

Ans.

(a) Descriptive question. See text book for details.

(b) In the process of the formation of H_2SO_4, SO_3 is dissolved in H_2SO_4 to form oleum ($H_2S_2O_7$) which is diluted to get pure H_2SO_4.

While if SO_3 is dissolved in water, the reaction will be highly exothermic and metallic fog is formed which impures the product (H_2SO_4).

(c) See text book for details.

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

Ans. Descriptive question. See text book for details.

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

Ans. Consult text book for answer.

Q.10 Answer the following questions:

(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_5.

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

Ans.

(i) **Ring Test:** This test is used to confirm NO_3^{-1}. The nitrate is dissolved in H_2O and freshly prepared $FeSO_4$ is added in it. Conc. H_2SO_4 is added along the walls of the test tube. Brown ppts. of $FeSO_4$. NO are formed.

$$FeSO_4 + NO \longrightarrow FeSO_4 . NO$$

(ii) NO_2 is Strong Oxidizing Agent:

$$2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2$$

$$H_2S_{(g)} + NO_{2(g)} \longrightarrow S_{(s)} + NO_{(g)} + H_2O_{(l)}$$

$$2FeSO_4 + H_2SO_4 + NO_2 \longrightarrow Fe_2(SO_4)_3 + NO + H_2O$$

(iii) Reactions of HNO_3 on As, Sb:

$$As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$$

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

(iv) Preparation of PCl_5:

(i) By passing Cl_2 through PCl_3 at 0°C:

$$PCl_3 + Cl_2 \xrightarrow{0°C} PCl_5$$

(ii) By passing Cl_2 in cold solution of phosphorous in CS_2:

$$2P_{(l)} + 5Cl_{2(g)} \longrightarrow 2PCl_{5(s)}$$

(v) P_2O_5 is Dehydrating Agent:

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

$$2HNO_3 + P_2O_5 \longrightarrow N_2O_5 + 2HPO_3$$

$$C_2H_5OH + P_2O_5 \longrightarrow CH_2 = CH_2 + 2HPO_3$$

$$2CH_3 - \overset{\overset{O}{\|}}{C} - OH + P_2O_5 \longrightarrow CH_3 - \overset{\overset{O}{\|}}{C} - O - \overset{\overset{O}{\|}}{C} - CH_3 + 2HPO_3$$

Q.11 Complete and balance the following chemical equations:

Ans. **(i)** $2P + 5NO_2 \longrightarrow P_2O_5 + 5NO$

(ii) $2NO + Cl_2 \longrightarrow 2NOCl$

(iii) $H_2S + 2NO \longrightarrow H_2O + N_2O + S$

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

(v) $2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$

(vi) $2HNO_2 + 2HI \longrightarrow 2H_2O + 2NO + I_2$

(vii) $HNO_2 + NH_3 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O$

(viii) $2HNO_2 + CO(NH_2)_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$

(ix) $2KNO_3 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_3$

Q.12 Describe the methods of preparation of phosphours pentoxide and explain its reaction.

Ans. Descriptive question. See text book for details.

Q.13 Discuss the trends in physical properties of group VI-A elements.

Ans. Descriptive question. See text book for details.

DO YOU KNOW?

1. N_2O (nitrous oxide) is called laughing gas.
2. N_2O colourless gas whole NO_2 is reddish brown in colour.
3. HNO_2 is oxidising agent as well as reducing agent.
4. $H_2S_2O_7$ (oleum) is called fuming sulphuric acid.
5. ($HNO_3 + NO_2$) is called fuming nitric acid.
6. H_2SO_4 is called "king of chemicals".
7. Bone ash contains 80% $Ca_3(PO_4)_2$.
8. PCl_3 is white crystalline solid.
9. P_2O_3 reacts with cold water to form H_3PO_3.

$$P_2O_3 + 3H_2O \xrightarrow[\text{(Cold)}]{} 2H_3PO_3$$

10. P_2O_3 reacts with hot water to form H_3PO_4 and PH_3.

$$2P_2O_3 + 6H_2O \longrightarrow 3H_3PO_4 + PH_3$$

11. H_3PO_3 is white deliquescent solid.
12. Phosphorous is Greek word which means "Light bearing".
13. Lecithins are important constituents of cell membranes particularly in brain.
14. H_3PO_4 is colourless, deliquescent solid which melts at 41°C.
15. HNO_3 is also called aqua-fortis.
16. Glycerine trinitrate is also called "Nobel oil".
17. Sb_2S_3 (stibinite) is also called "Valentine".

SHORT QUESTIONS

Q.1 How nitrogen differ from other elements of its group?

Ans. (i) Nitrogen is gas while other elements of group V-A are solids.

(ii) Nitrogen has no allotropic form while other member have allotropic forms.

(iii) Oxidation states of nitrogen are –3, +1, +2, +3, +4 and +5 in its compound while other elements have –3, +3 and +5 oxidation states.

(iv) Nitrogen does not use its d-orbitals for bond formation while other elements uses their empty d-orbitals for bond formation.

(v) It exists in diatomic state (N_2) while phosphorous exists as P_4.

Q.2 How does aqua regia dissolves gold and platinum?

Ans. Aqua Regia is 3 parts of concentrated HCl and one part of concentrated HNO_3. Metals like gold and platinum can dissolve in aqua regia by the formation of their chlorides.

$$3HCl + HNO_3 \longrightarrow NOCl + Cl_2 + 2H_2O$$

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

This liberated chlorine gas converts noble metals to their chlorides.

$$2Au + 3Cl_2 \longrightarrow 2AuCl_3$$

Over all reaction is as follows:

$$2Au + 3HCl + HNO_3 \longrightarrow AuCl_3 + NO + 2H_2O$$

Q.3 Write down the equation for the reaction between concentrated HNO_3 and copper. Explain what type of reaction it is?

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

It is a redox reaction in which HNO_3 acts as oxidizing agent and Cu acts as reducing agent. Oxidation state of copper changes from zero to +2. Oxidation state of nitrogen changes from +5 to +4 and it is reduced.

Q.4 What is meant by fuming nitric acid and fuming sulphuric acid?

Ans. The mixture of HNO_3 and NO_2 is called fuming nitric acid. The mixture of H_2SO_4 and SO_3 is called fuming sulphuric acid.

Q.5 Why is SO_3 dissolved in H_2SO_4 and not in water in contact process?

Ans. In contact process, SO_3 is dissolved in conc. H_2SO_4 to form oleum.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

A measured quantity of water can be added to liquid oleum to change it into H_2SO_4.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

When SO_3 is directly dissolved in water, the reaction is highly exothermic and metallic fog is formed in the chamber.

Q.6 How ring test is performed for nitrate radical?

Ans. In this test, some drops of freshly prepared $FeSO_4$ are added to metal nitrate solution. Then few drops of concentrated H_2SO_4 are added along the side of test tube. A brown coloured ring is formed at the junction of acid and aqueous solution. This brown ring is chemically $FeSO_4$. NO.

Q.7 Give one reaction of HNO_2 in which it behave as oxidising agent and one reaction in which it behave as reducing agent?

Ans. HNO_2 acts as oxidising agent as well as reducing agent. HNO_2 when reacts with HI and oxidation state of N changes from +4 → +2. HNO_2 acts as oxidising agent.

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

$$2HNO_2 + 2HI \longrightarrow 2H_2O + 2NO + I_2$$

HNO_2 when reacts with aqueous bromine, the oxidation state of nitrogen changes from +4 to +5. In this reaction, HNO_2 acts as reducing agent.

$$HNO_2 + Br_2 + H_2O \longrightarrow HNO_3 + 2HBr$$

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

Q.8 Why white phosphorus is more reactive than red phosphorus?

Ans. White phosphorus consists of individual P_4 molecules. The bond angle of P.P.P. in P_4 molecule is of 60°. Due to smaller angle it has strain and more reactive because bond can be broken down easily. Red phosphorus is less reactive. It is macromolecule formed by the combination of P_4 molecules.

Q.9 P_2O_5 is a good dehydrating agent. Justify this statement by some reactions.

Ans. The substance which is used to remove water from a substance is called dehydrating agent.

$$2HNO_3 + P_2O_5 \longrightarrow N_2O_5 + 2HPO_3$$

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

$$2CH_3COOH + P_2O_5 \longrightarrow (CH_3CO)_2O + 2HPO_3$$

$$C_2H_5OH + P_2O_5 \longrightarrow C_2H_4 + 2HPO_3$$

Q.10 What is effect of heat on H_3PO_3 and H_3PO_4?

Ans. H_3PO_3 on heating changes to orthophosphoric acid and phosphine.

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$

H_3PO_4 on heating changes to pyrophosphoric acid and finally to metaphosphoric acid.

$$2H_3PO_4 \xrightarrow[-H_2O]{240^\circ C} H_4P_2O_7 \xrightarrow[-H_2O]{316^\circ C} 2HPO_3$$

Orthophosphoric acid	Pyrophosphoric acid	Metaphosphoric acid

Q.11 H_3PO_3 acts as reducing as well as oxidising agent. Give one reaction to support this statement.

Ans. H_3PO_3 acts as reducing agent when reacts with aqueous copper sulphate.

$$H_3PO_3 + CuSO_4 + H_2O \longrightarrow H_3PO_4 + H_2SO_4 + Cu$$

H_3PO_3 acts as oxidising agent when reacts with nascent hydrogen.

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$

$$H_3PO_3 + 6[H] \longrightarrow PH_3 + 3H_2O$$

Q.12 H_2SO_4 acts as dehydrating agent. Give three reactions to support this statement.

Ans.

$$C_6H_{12}O_6 \xrightarrow{\text{Conc. } H_2SO_4} 6C + 6H_2O$$

$$C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} C_2H_4 + H_2O$$

$$HCOOH \xrightarrow{\text{Conc. } H_2SO_4} CO + H_2O$$

Q.13 H_2SO_4 acts as oxidising agent. Give some examples?

Ans.

$$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$

$$H_2S + H_2SO_4 \longrightarrow S + SO_2 + 2H_2O$$

Q.14 Sulphuric acid is dibasic acid. Explain it.

Ans. The acid which furnishes two protons when dissolved in water is called dibasic acid. H_2SO_4, H_2S and oxalic acid are examples.

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$$

$$HSO_4^- + H_2O \longrightarrow H_3O^+ + SO_4^{-2}$$

Q.15 What is poisoning of catalyst? How V_2O_5 is prevented from poisoning in contact process?

Ans. The phenomenon in which catalytic activity of a substance is reduced is called poisoning of catalyst. Vanadium pentoxide is poisoned by arsenic. Before going to contact chamber, the gases are passed through arsenic purifier which contains $Fe(OH)_3$ to remove arsenic.

Q.16 Which gases cannot be dried over sulphuric acid?

Ans. H_2SO_4 is good dehydrating agent and can be used to dry many gases. However, H_2S, SO_3 and NH_3 cannot be dried with H_2SO_4 because these gases react with conc. H_2SO_4.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

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

$$H_2SO_4 + H_2S \longrightarrow S + SO_2 + 2H_2O$$

Q.17 Why HNO_3 and H_2SO_4 acts as oxidising agents and never reducing agents? Give reason for it.

Ans. Oxidation of N in HNO_3 is +5 and S in H_2SO_4 is +6. During redox reaction charge of S or N always reduces or decreases and they always acts as oxidising agent. Maximum oxidation state of the element is equal to its group No. Nitrogen belongs to group VA and sulphur belongs to group VIA.

Q.18 Give two chemical reactions in which NO behave as oxidising agent.

Ans. Oxidation state of N in NO is +2. If charge of nitrogen reduces, it is called reduction. In these reactions, NO acts as oxidising agent and H_2S or H_2SO_3 are reducing agents.

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

$$H_2SO_3 + 2NO \longrightarrow H_2SO_4 + N_2O$$

Q.19 Give two chemical reactions of NO, in which it behaves as reducing agent.

Ans. Oxidation state of N in NO is +2. If in a chemical reaction, the oxidation number of nitrogen increases then NO will be a reducing agent.

$$2HNO_3 + NO \longrightarrow H_2O + 3NO_2$$

$$3I_2 + 4H_2O + 2NO \longrightarrow 6HI + 2HNO_3$$

FORMULAS OF ORES OF SULPHUR

(i)	Galena	PbS	
(ii)	Zinc blende	ZnS	
(iii)	Cinnabar	HgS	
(iv)	Stibinite	Sb_2S_3	
(v)	Copper pyrites	Cu_2S, Fe_2S_3	$(CuFeS_2)$
(vi)	Iron pyrites	FeS_2	(Fool's gold)
(vii)	Heavy spar	$BaSO_4$	
(viii)	Gypsum	$CaSO_4 . 2H_2O$	

Q.1 Formula of the ores of phosphorous.

Ans.

Phosphate rock	$Ca_3(PO_4)_2$
Fluor-apatite	$CaF_2 . 3Ca_3(PO_4)_2$
Chlor-apatite	$CaCl_2 . 3Ca_3(PO_4)_2$

Q.2 Complete and balance the following:

Ans.

$$2P + 5NO_2 \longrightarrow P_2O_5 + 5NO$$

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

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

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$NO_2 + H_2SO_4 \longrightarrow H_2SO_4 + NO + [O]$$

Q.3 Action of heat on the following:

Ans. $NH_4NO_3 \xrightarrow{200°C} N_2O + 2H_2O$

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$

$2NO \xrightarrow{1000°C} N_2 + O_2$

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

$4H_3PO_3 \xrightarrow{200°C} 3H_3PO_4 + PH_3$

Q.4 What is the effect of temperature on NO_2?

Ans. There is equilibrium between NO_2 and N_2O_4. When temperature of the gas is increased, then it is in the NO_2 state. At lower temperature it is in the N_2O_4 state.



Q.5 Complete and balance the following.

Ans. $2HNO_2 + 2HI \longrightarrow I_2 + 2NO + 2H_2O$

$HNO_2 + NH_3 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O$

$2HNO_2 + CO(NH_2)_2 \longrightarrow 2N_2 + CO_2 + 3H_2O$

$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$