
CHAPTER



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 .

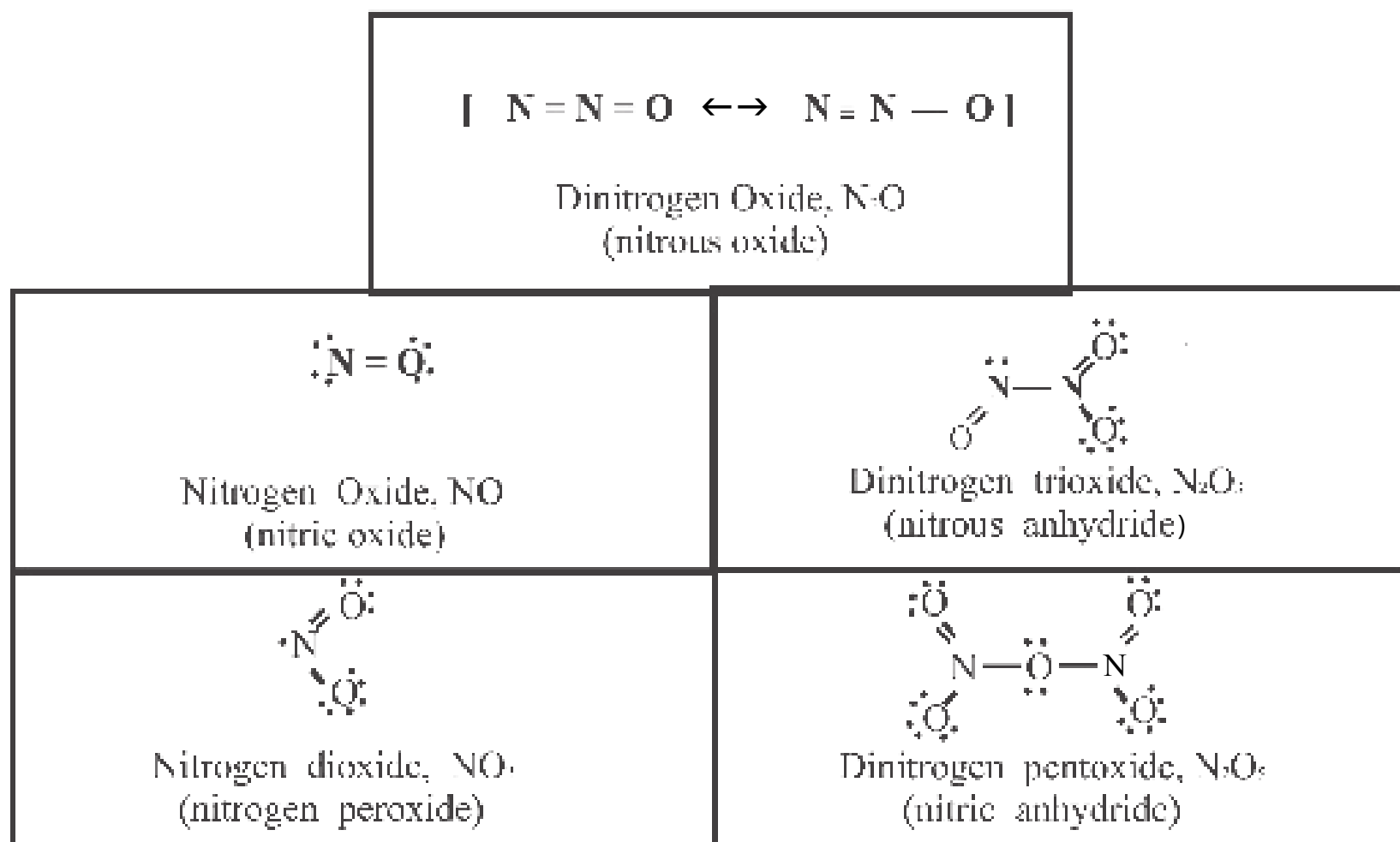


Fig. 4.1 Oxides of Nitrogen

1. Dinitrogen Oxide (N₂O)

Preparation

1. Dinitrogen oxide can be prepared by the action of dil. HNO_3 on metallic zinc.



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



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 of burning substances, such as sulphur, phosphorus, etc. are taken in the cylinder containing this gas.



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



2. Nitrogen Oxide (NO)

Preparation

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



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



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.



2. It decomposes into N_2 and O_2 at about $1000^\circ C$ and supports combustion.



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



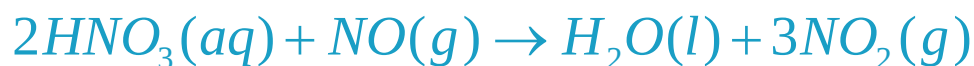
4. It forms a brown coloured addition compound with $FeSO_4$. This test is used to confirm the presence of nitrates (Ring Test).



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



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



3. Nitrogen Dioxide (NO_2)

Preparation

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



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



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 tetroxide (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 .



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



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



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



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





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



4.2.3 Oxyacids of Nitrogen

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



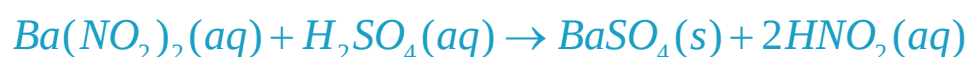
1. Nitrous Acid (HNO_2)

Preparation

1. It can be prepared by dissolving dinitrogen trioxide in water at $0^\circ C$.



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



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.



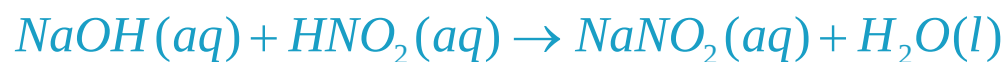
2. It acts as an oxidizing agent and oxidizes HI, SO_2 and SnCl_2 into I_2 , H_2SO_4 and SnCl_4 , respectively.



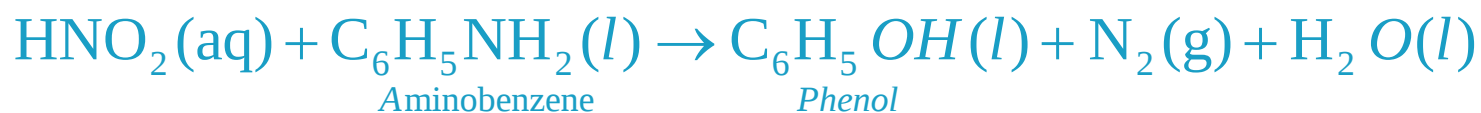
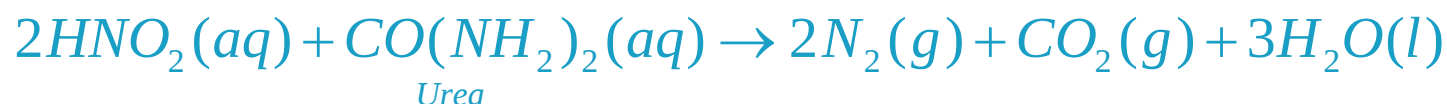
3. Nitrous acid decolourizes acidified KMnO_4 and bromine water. It readily gets oxidized to nitric acid, so it also behaves as a reducing agent.



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



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



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.



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).



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

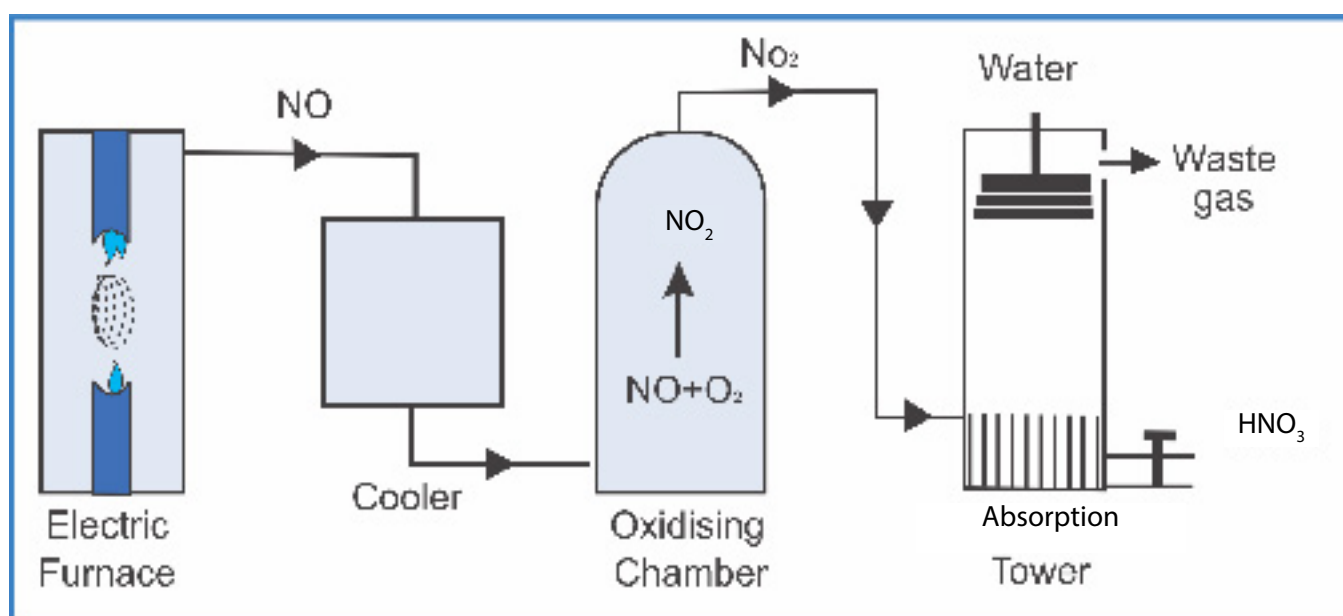


Fig 4.2 Manufacture of nitric acid from air

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



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



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



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.



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.





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



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



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



(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.



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



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



With concentrated acid, it gives mercuric nitrate and NO_2



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



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



- (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 .



4. Reducing agents like FeSO_4 , H_2S and HI are converted to $\text{Fe}_2(\text{SO}_4)_3$, S and I_2 respectively, when they react with conc. HNO_3



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.



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

NOCl formed is decomposed giving NO and Cl_2



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



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 $\text{Ca}_3(\text{PO}_4)_2$ and apatite $\text{Ca}_5\text{F}(\text{PO}_4)_3$. 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 .

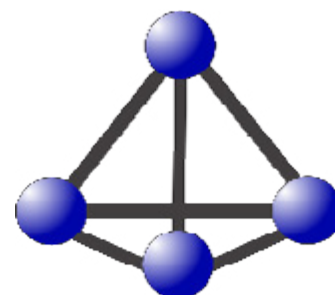


Fig.4.3 White phosphorus

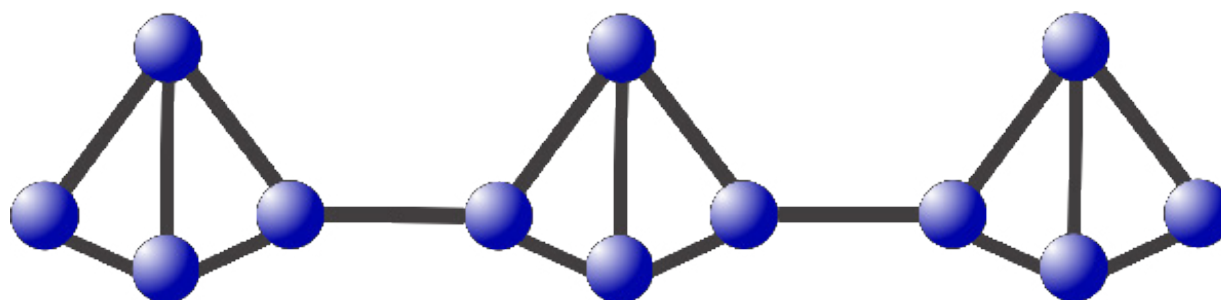


Fig. 4.4 Red phosphorus

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 phosphorus 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.



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



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



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



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



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



2. Phosphorus Pentachloride (PCl_5)

Preparation

1. By passing dry chlorine through phosphorus trichloride.



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



Properties of Phosphorus 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.



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



3. It converts metals into their chlorides.



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.



Properties of Phosphorus Trioxide

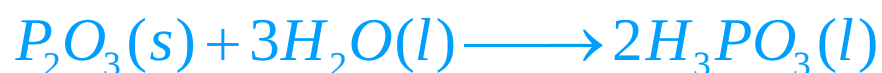
It is a white waxy solid with garlic like odour. It melts at 22.8°C and boils at 173°C. It is highly poisonous in nature.

Reactions

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



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



With hot water, it forms phosphine and phosphoric acid.



Phosphorus Pentoxide, P_2O_5 or P_4O_{10}

Preparation

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



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

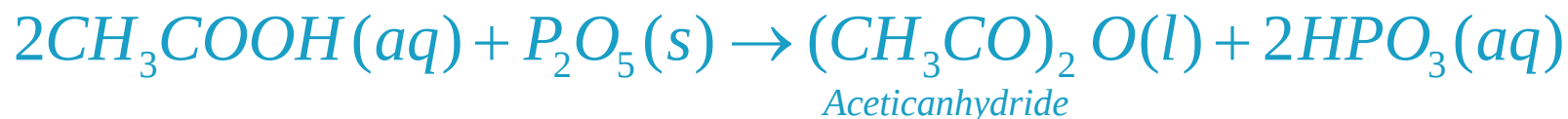
1. With cold water phosphorus pentoxide forms metaphosphoric acid.



With hot water, it forms orthophosphoric acid



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.



4.3.5 Oxyacids of Phosphorus

1. Phosphorus Acid (H_3PO_3)

Preparation

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



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



Properties of Phosphorus Acid

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

Reactions

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



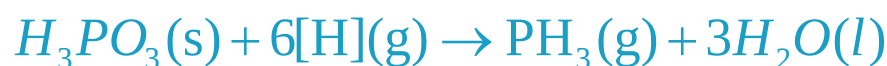
2. It is a powerful reducing agent and reduces $CuSO_4$, $AgNO_3$, etc. to the metallic state.



3. It reacts with oxygen to form orthophosphoric acid.



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



2. Orthophosphoric Acid (H_3PO_4)

Preparation

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



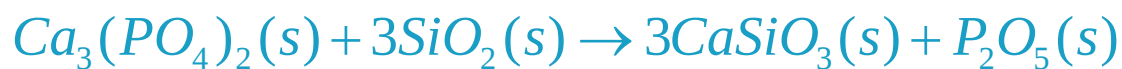
2. It is also obtained by heating red phosphorus with concentrated HNO_3 .



3. Hydrolysis of phosphorus pentachloride also gives orthophosphoric acid.



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.



Properties of Orthophosphoric Acid

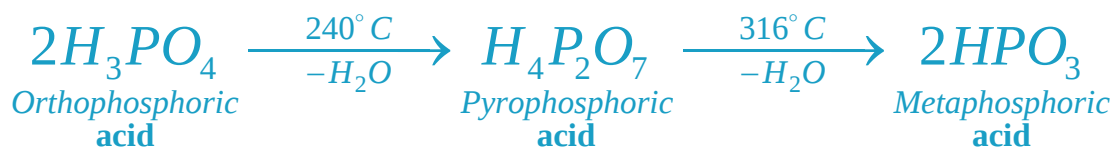
It is a colourless, deliquescent crystalline solid which melts at 41°C. It is soluble in water.

Reactions

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



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



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 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. 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-orbital 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

Similarities:

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.

- Both have polyatomic molecules. Oxygen has diatomic O_2 , while sulphur has S_2 and S_8 molecules.
- Both combine with metals in the form of O^{-2} and S^{-2} with oxidation state -2.
- Both combine with non-metals and form covalent compounds, e.g, H_2O and H_2S , CO_2 and CS_2 , etc.
- Both are typical non-metals.
- 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 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 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 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 Knietzsch 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 .

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 $400\text{-}500^\circ\text{C}$. SO_3 formed is absorbed in concentrated H_2SO_4 and "Oleum" ($\text{H}_2\text{S}_2\text{O}_7$) 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 .



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 $400-500^\circ\text{C}$ are passed through vertical iron columns packed with the catalyst V_2O_5 . Here SO_2 is oxidized to SO_3 .



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), $\text{H}_2\text{S}_2\text{O}_7$. It can be diluted with water to get any required concentration of sulphuric acid.



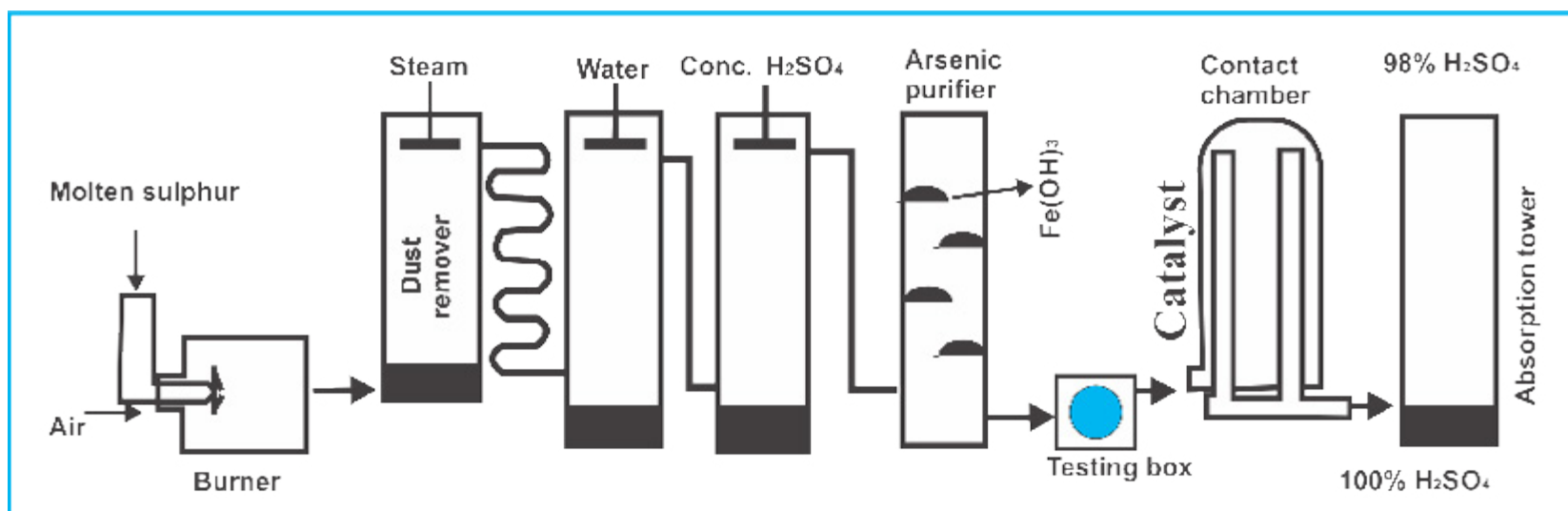


Fig.4.5 Contact Process

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. H₂SO₄ 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 SO₃ and H₂O.



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



3. Reaction as an Acid

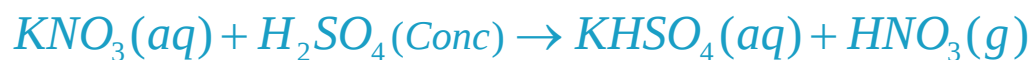
(i) Reactions with alkalies



(ii) Reactions with carbonates and hydrogen carbonates.



(iii) Reactions with salts



(iv) Reaction with metals

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





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

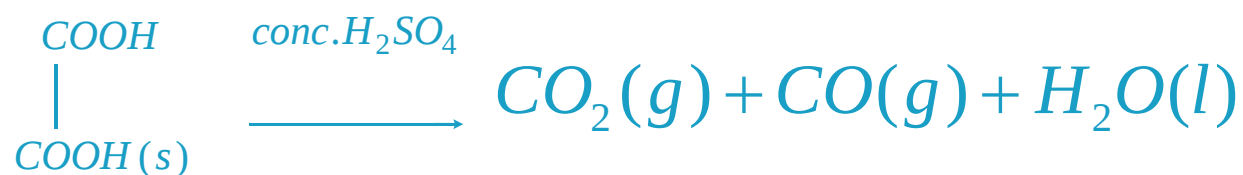
(c) With certain metals hot concentrated sulphuric acid gives metal sulphates, water and SO_2 .



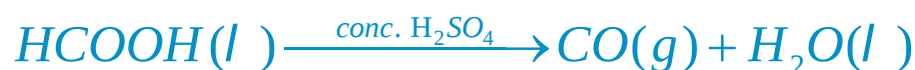
4. Reactions as a Dehydrating Agent

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

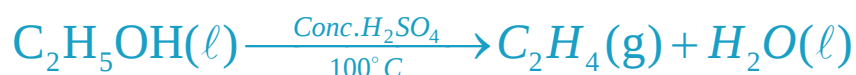
(i) With oxalic acid it forms CO_2 and CO.



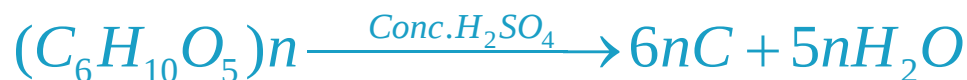
(ii) With formic acid, CO is formed.



(iii) With ethyl alcohol it forms ethylene.



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



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.



(ii) H_2S is oxidized to S.



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



6. Reactions with Gases.

(i) It absorbs SO_3 and forms oleum

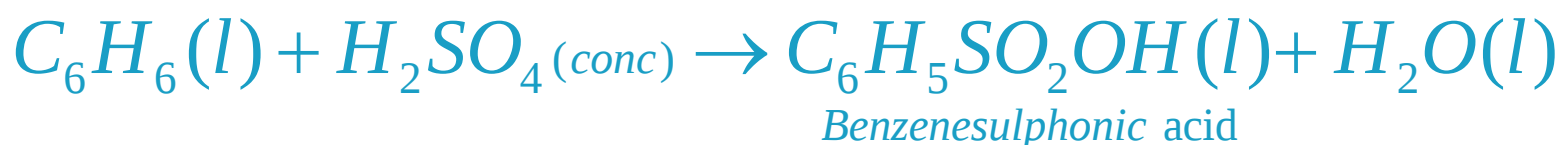


(ii) It reacts with ammonia forming ammonium sulphate.



7. Reaction with Benzene

Benzene sulphonic acid is produced when H_2SO_4 reacts with benzene.



8. Precipitation Reactions

White precipitates are produced when H_2SO_4 reacts with solutions of BaCl_2 , $\text{Pb}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$.



9. Reactions with Oxidizing Agents

It reacts with oxidizing agents like KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ to liberate oxygen which may oxidize other compounds.



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 and P_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. Phosphoric 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 group VIA. 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_5 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 phosphorus 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 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.
- 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 species 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 Birkeland 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?

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.

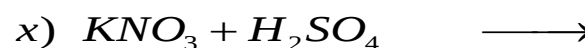
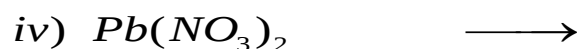
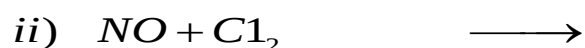
ii) NO_2 is a strong oxidizing agent. Prove the truth of this statement giving examples.

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:



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.