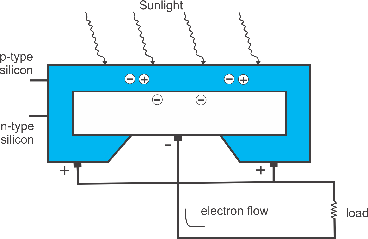
##### 3.6 SEMICONDUCTORS

A semiconductor is a substance that has different resistances to the passages of an electric current under different circumstances. Semiconductors include the elements germanium, selenium and silicon, and the compounds lead sulphide, silicon carbide, cadmium sulphide, lead telluride, gallium arsenide and indium antimonide.

Semiconductors conduct electricity better than insulators, but not as well as good conductors like metals. This gives them their name, which means “half conductors. ” How well they conduct electricity depends upon their temperature. When a metal is heated, its resistance increases, when a semiconductor is heated its resistance decreases.

Semiconductors are also sensitive to light. The greater the intensity of the light that shines on them, the better they conduct electricity. The effects that light and heat energy have on semiconductors make them extremely useful. They are used in photoelectric cells and in solar batteries.

The electrons of semiconductors do not carry electric current as readily as the electrons of good electric conductors like metals. However, when the atoms of the material absorb heat or light, the electrons become less tightly bound to their atoms. They can now conduct electricity.

Another special property of semiconductors is the way they behave when they are joined to another material, which may be a metal or a different semiconductor. The junction between the different materials forms a boundary. It allows electricity to pass more properly and is used in transistors. Transistors are much smaller and less complicated than old fashioned electronic tubes. They are used in radio, television, computers and calculators.

##### 3.7 USES OF LEAD COMPOUNDS IN PAINTS

Varoius oxides of lead, basic lead carbonate and lead chromate are commonly used as pigments in paints.

1. Lead Suboxide, Pb2O

It is black powder, obtained on heating plumbous oxalate in the absence of air.

###### 2PbC O2 4(s) →∆ Pb O2 (s) + 3CO2(g) + CO(g)

Pb2O is decomposed by heat into Pb and PbO.

Other than pigment, it is also used in the manufacture of lead storage batteries.

1. Lead Monoxide (Litharge, Massicot) PbO

Litharge varies in colour from pale yellow to reddish yellow, possibly owing to the existence of two forms, a rhombic (yellow) and a tetragonal (red). It is slightly soluble in water. It is usually used in preparing flint glass and paints. If litharge is boiled with water and olive oil, lead oleate which is a sticky adhesive mass is formed and glycerin passes into solution. Litharge is used in preparing oils and varnishes and in the manufacturing of flint glass.

1. Triplumbic Tetraoxide, (red lead, minium), Pb3O4

When lead is heated in air at about 340°C, it absorbs oxygen and forms a bright scarlet crystalline powder of read lead or minium.

#### 3Pb(s) + 2O2(g) → Pb O3 4(g)

Triplumbic tetraoxide

It decomposes at 470°C

#### 2Pb O3 4(s) → 6PbO(s) + O2

Red lead is used for a variety of purposes. Its principal uses are in the manufacture of storage batteries, as a pigment in paints applied to steel and iron to retard corrosion, and as an ingredient in the manufacture of flint glass, matches and ceramic glazes.

4. Lead Dioxide, PbO2

When red lead is treated with concentrated nitric acid , it is decomposed into lead nitrate and lead dioxide.

##### Pb O3 4(s) + 4HNO3(aq) → 2Pb(NO )3 2(s) + PbO2(s) + 2H O2

Lead dioxide is a reddish brown powder. It is not very soluble in water, but it does dissolve in alkaline water to yield soluble plumbates.

It is not affected by dilute acids.

1. White Lead

Basic lead carbonate 2PbCO3.Pb(OH)2 is an amorphous white pigment. It mixes readily with linseed oil and has a good covering power. If improperly prepared, it becomes crystalline and its covering power is reduced. White lead is not suitable for use as a good pigment since it is darkened by the hydrogen sulphide which is frequently present in the atmosphere.

1. Lead Chromate (PbCrO4)

It is used as a pigment under the name of chrome yellow. Orange or red basic lead chromates are formed when lead chromate is boiled with dilute alkali hydroxide and are used as pigments. The stable yellow modification of lead chromate is monoclinic. Mixture of lead chromate with lead sulphate or barium sulphate are also used as yellow pigments.

Key Points

1. Boron occurs in traces and has been found to be important for the growth of many plants.
2. Borax (Na2B3O7-10H2O), colemanite (Ca2B6O11.5H2O), orthoboric acid (H3BO3) are the common minerals of boron.
3. Aluminium, after oxygen and silicon, is the third most abundant element in the earth’s crust. Feldspar (K2O.Al2O3.6SiO2), corundum (Al2O3), bauxite (Al2O3.2H2O) and cryolite (Na3AlF6) are the common minerals of aluminium.
4. The pair of outermost electrons that does not readily take part in chemical combination is termed as inert pair.
5. When heated, borax fuses, loses water of crystallization and swells up into a white porous mass. It is employed in borax bead test for identification of coloured salts.
6. When a hot concentrated solution of borax is treated with a calculated quantity of conc. H2SO4, on cooling crystals of boric acid are produced. 7. When aluminium is burnt in oxygen a brilliant light is produced.
7. The electronic configuration of group IVA elements show that they have four electrons in their valence shells, two electrons of which are in s-orbital and the remaining two are in p-orbitals.
8. Feldspar, potash mica and zircon are the famous minerals of silicon.
9. Silica has a net work structure in which every silicon atom is bonded tetrahedrally to four oxygen atoms and every oxygen atom is bond ed to two silicon atoms.
10. Sodium silicate, aluminium silicate, talc and asbestos are commercially important compounds of silicon and oxygen called silicates.
11. Methyl silicones can be used as lubricants and for water proofing.
12. Semiconductors conduct electricity better than insulators. They are also light sensitive.
13. Oxides of lead are used as pigments.

|  |  |  |
| --- | --- | --- |
|  | EXERCISE |  |

Q.1. Fill in the blanks.

i ) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ acid has the chemical formula HBO2. ii) Aluminium normally occurs as\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ minerals found in the rocks of outer portion of the earth. iii) Aluminium gives \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_gas with hot concentrated H2SO4. iv) Boron forms------------------------------------------- bond in its compounds. v) The chemical formula of white lead is \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ . vi) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ is the only element with less than four electrons in the outer most shell that is not a metal.

vii) In the Group IIIA of the periodic table,\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ is a semimetal. viii) Borax that occurs as a natural deposit, is called\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_.

1. Cryolite is an important mineral of aluminium and its formula is\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
2. A \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_is a substance that has different resistances to the passage of an electric current under different circumstances. Q.2. Indicate True Or False
3. Boron always uses all the three of its valence eletrons for bonding purposes.
4. Diaspore is an ore of carbon.
5. Emerald is an ore of aluminium that has the chemical formula AlO3.2SiO2.

2H2O. iv) An aqueous solution of borax is feebly acidic in nature.

v) In case of borax bead test, of cupric oxide, the beads are coloured blue in the reducing flame. vi) Boric acid can be titrated with sodium hydroxide. vii) Carbon and silicon are the only non-metals in Group IVA. viii) PbO is commonly known as litharge.

ix) Basic lead carbonate is a reddish brown pigment. x) Aluminium oxide (Al2Q3) is also called bauxite.

Q. 4. What is the action of an aqueous solution of borax on litmus?

Q. 5. Give equations to represent the following reactions.

1. Borax is heated with CoO
2. Al2O3 is heated with NaOH solution

Q. 6. Why is aluminium not found as a free element? Explain the chemistry of borax bead test.

Q. 7. How does orthoboric acid react with:

(a) Sodium hydroxide (b) Ethyl alcohol

Q. 8. How will you convert boric acid into borax and vice versa?

Q. 9. Why are liquid silicones preferred over ordinary organic lubricants?

Q. 10. Explain:

1. CO2 is non-polar in nature.
2. CO2 is acidic in character.

Q. 11. Why is CO2 a gas at room temperature while SiO2 is a solid?

Q. 12. Give the names and the formulas of different acids of boron.

Q. 13. What is the importance of oxides of lead in paints?

Q. 14. Give the names, electronic configurations occurrence of Group-IIIA elements of the periodic table.

Q. 15. Discuss the peculiar behaviour of boron with respect to the other members of Group- IIIA elements. Q. 16. (a) What is borax?

1. Describe its commercial preparation.
2. Outline the principal uses of borax.
3. How does borax serve as a water softening agent?Q. 17. (a) What is boric acid?
4. How is boric acid prepared in laboratory?
5. Give properties and uses of boric acid.

Q. 18.(a) Give the names alongwith the formulas of three important ores of aluminium.

(b) How and under what conditions does aluminium react with the following:

i) Oxygen ii) Hydrogen iii) Halogens iv) Acids v) Alkalies

Q. 19. Give the names, electronic configurations and occurrence of Group-IVA elements of the periodic table.

Q. 20. Discuss the peculiar behaviour of carbon with respect to the other members of Group-IVA of the periodic table. Q.21 (a) What are silicones?

1. Give a brief summary of the principal properties of silicones.
2. Outline the uses pf silicones.
3. What are silicates?
4. Describe the important uses of silicates.

CHAPTER

# GROUP VA AND GROUP VIA ELEMENTS

4

Animation 4.1 : Nitrogen-Cycle

Source and Credit: [Organic](http://organicsoiltechnology.com/nitrogen-cycling-down.html)

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  Electronic configuration Physical appearance  Ionization energy (kJ/mol)  Electron affinity (kJ/mol)  Electronegativity  Atomic radius(pm)  Ionic radius of 3- ion (pm)  Melting points (°C)  Boiling points (°C)  Density (g/cm3)  Principal oxidation states | 7  [He]2s22p3  Colourless gas  1402  -7  3.0  70 171  -210  -196  0.00125  +3, +5 | 15  [Ne]3s23p3 Black solid  1012  -71.7  2.1  110  212  44 280  1.83  +3, +5 | 33  [Ar]3d104s24p3  Metallic solid  950  -77  2.0  121  222  817  613  5.73  +3, +5 | 51  [Kr]4d105s25p3  Metallic solid  830  -101  1.9  141  245  631  1750  6.68  +3, +5 | 83  [Xe]5d106s26p3  Metallic solid  700  -110  1.9  157  ---  271  1560  9.80  +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.

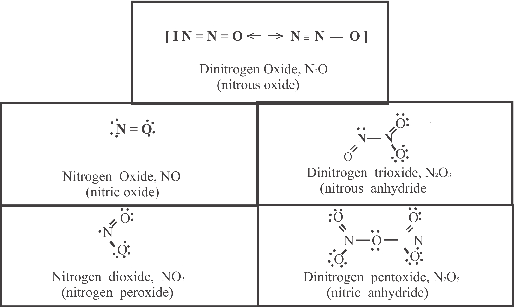
Phosphorus and other members of the group can make use of d orbitals in their bonding. This is because the energy of these orbitals is not much greater than those of the other valence shell orbitals. For example, phosphorus can make use of its 3s, 3p and the empty 3d orbitals during bonding with other 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](https://www.qld.gov.au/environment/pollution/monitoring/air-pollution/nitrogen-oxides/) Source and Credit: [Qld](https://www.qld.gov.au/) | | | | |

4.2.2 Oxides of Nitrogen

Nitrogen forms several oxides with oxygen. Common oxides of nitrogen are N2O, NO and NO2. It also forms N2O3 and N2O5.



)



N

Fig. 4.1 Oxides of Nitrogen

1. Dinitrogen Oxide (N2O)

Preparation

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

4*Zn s*( )+10*HNO dil*2( .) → 4*Zn NO*( 3 2) (*aq*)+ *N O g*2 ( )+5H O2 ( )*l*

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

## NH NO (s)4 3 → N O(g)+2H O(l)2 2

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

Properties of Dinitrogen Oxide

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

Reactions

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

*S s*( )+2*N O g*2 ( ) →*SO g*2( )+2*N g*2( ) *P*4(s) 10N O+ 2 ( )*g* →*PO s*4 10( ) 10+ *N g*2( )

1. When N2O is passed over red hot copper, it is reduced to nitrogen.

### *Cu s*( )+*N O g*2 ( )→*CuO s*( )+*N g*2( )

2. Nitrogen Oxide (NO)

Preparation

1. Nitrogen oxide can be prepared by the action of dil HNO3 on copper.

### 3*Cu s*( )+8*HNO dil*3( .) → 3*Cu NO*( 3 2) (*aq*)+ 2*NO g*( )+ 4*H O l*2 ( )

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

*N g O g*2 ( )+ 2 ( )2*NO g*( )

Properties of Nitrogen Oxide

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

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

2*NO g O g*( )+ 2( )→2*NO g*2( )

1. It decomposes into N2 and O2 at about 1000°C and supports combustion.

### 2*NO g*( )→*N g O g*2( )+ 2( )

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

2*NO g*( )+*Cl g*2( ) → 2*NOCl g*( )

1. It forms a brown coloured addition compound with FeSO4.This test is used to confirm the presence of nitrates (Ring Test).

*FeSO aq*4( )+ NO(g) → FeSO .NO(aq)4

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

### *H S g*2 ( ) 2+ *NO g*( )→*H O g N O g S*2 ( )+ 2 ( )+ (s)

*H SO aq*2 3( ) 2+ *NO g*( )→*H SO aq N O g*2 4( )+ 2 ( )

6. Oxidizing agents can oxidize NO to NO2 or HNO3.

#### 2*HNO aq*3( )+ *NO g*( )→ *H O l*2 ( ) 3+ *NO g*2( )

6*KMnO aq*4( ) 12+ *H SO aq*2 4( ) 10+ *NO g*( ) →6*KHSO aq*4( )+6*MnSO aq*4( ) 10+ *HNO aq*3( )+4*H O l*2 ( )

3. Nitrogen Dioxide (NO2)

Preparation

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

2*Pb NO*( 3 2) ( )*s* →2*PbO s*( ) 4+ *NO g*2( )+*O g*2( )

1. It can also be prepared by reacting conc. HNO3 with copper.

#### *Cu s*( )+ 4*HNO conc*3( .) →*Cu NO*( 3 2) (*aq*)+ 2*H O l*2 ( )+ 2*NO g*2( )

Animation 4.3 :  [Nitrogen-Cycle](http://organicsoiltechnology.com/wp-content/uploads/Nitrogen-Cycle-Diagram-original-animated.gif) Source and Credit: [Organic](http://organicsoiltechnology.com/nitrogen-cycling-down.html)

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, NO2 is converted into a yellow liquid which can be frozen to a colourless solid dinitrogen tetraoxide (N2O4). If this solid is heated to 140°C, the mixture contains NO2 and N2O4 but above 140°C NO2 is converted to NO and O2 molecules which are colourless. This decomposition is complete at 620°C.

*NO g*2( )→ *NO l*2( )→ *N O lPale*2 4( )140*C* 2Re*NO gddish*2( )620*C Colourless*2*NO g*( )+*O g*2( )

*Yellow brown*

2.Elements like phosphorus, potassium and carbon continue burning in NO2 as it yields O2 on decomposition.

2*NO g*2( )→2*NO g O g*( )+ 2( )

2 ( )*P s* +5*NO g*2( ) → *PO s*2 5( )+5*NO g*( )

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

2*NO g*2( )+ *H O l*2 ( )→ *HNO aq*3( )+ *HNO aq*2( )

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

##### 4*NO g*2( )+ 2*H O l*2 ( )+*O g*2( ) → 4*HNO aq*3( )

4.A mixture of nitrate and nitrite is formed when NO2 is passed through strong alkalies.

2*NaOH aq*( ) 2+ *NO g*2( )→ *NaNO aq*3( )+ *NaNO aq*2( )+ *H O l*2 ( )

##### 2*KOH aq*( )+ 2*NO g*2( ) → *KNO aq*3( )+ *KNO aq*2( )+ *H O l*2 ( )

5. It is a strong oxidizing agent and oxidizes H2S to sulphur, ferrous sulphate to ferric sulphate and KI to I2.

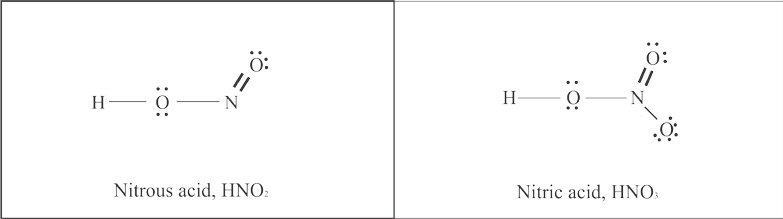
*H S g*2 ( )+ *NO g*2( ) → *H O l*2 ( )+ *S s*( )+ *NO g*( )

2*FeSO*4(aq)+ H SO (aq)2 4 + NO (g)2 → Fe (SO ) (aq)2 4 3 + H2 *O l*( )+ *NO g*( )

##### 2*KI aq*( ) 2+ *NO g*2( )→2*KNO aq*2( )+ *I s*2( )

4.2.3 Oxyacids of Nitrogen

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



HNO

2

HNO

3

1. Nitrous Acid (HNO2)

Preparation

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

###### *N O g*2 3( )+ *H O l*2 ( )→2*HNO aq*2( )

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 SO aq*2 4( )→*BaSO s*4( ) 2+ *HNO aq*2( )

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.

##### 3*HNO aq*2( )→*HNO aq*3( ) 2+ *NO g H O g*( )+ 2 ( )

2. It acts as an oxidizing agent and oxidizes HI, SO2 and SnCl2into I2,H2SO4 and SnCl4, respectively.

2*HNO*2(aq) 2HI(aq+ )→2H2 *O l*( ) 2+ *NO g*( )+ *I*2( )*s*

2*HNO*2 →*H O NO O*2 + 2 +[ ]

##### *SO g*2( )+ *H O l*2 ( ) [ ]( )+ *O g* → *H SO aq*2 4( )

*SnCl aq*2( ) 2+ *HCl aq*( ) 2+ *HNO*2(aq)→ *SnCl aq*4( ) 2+ *NO g*( ) 2+ *H O l*2 ( )

1. Nitrous acid decolourizes acidified KMnO4 and bromine water. It readily gets oxidized to nitric acid, so it also behaves as a reducing agent.

2*KMnO aq*4( ) 3+ *H SO aq*2 4( ) 5+ *HNO aq*2( )→ *K SO aq*2 4( ) 2+ *MnSO aq*4( ) 3+ *H O l*2 ( ) 5+ HNO (aq3 )

*HNO aq*2( )+*Br aq*2( )+*H O*2 (l) → HNO (aq)3 +2HBr(aq)

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

*NaOH aq*( )+ *HNO aq*2 ( )→ *NaNO aq*2 ( )+ *H O l*2 ( )

1. It also reacts with organic compounds containing NH2 group and produces nitrogen.

2*HNO aq*2( )+*CO NH*( 2 2) (*aq*)→2*N*2( )*g* +*CO g*2( ) 3+ *H O l*2 ( )

*Urea*

#### HNO (aq) C H NH ( )2 + 6 5 2 *l* →C H6 5 *OH l*( )+N (g) H2 + 2 *O l*( )

*A*minobenzene *Phenol*

Animation 4.4 [: Nitric oxide binding](http://www.esrf.eu/Apache_files/Spotlight/spotlight154-fig2-anim.gif) Source and Credit: [ESRF](http://www.esrf.eu/news/spotlight/spotlight154/index_html)

2. Nitric Acid (HNO3)

Preparation

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

*KNO s*3( )+*H SO conc*2 4( .) →*KHSO aq*4( )+*HNO aq*3( )

Manufacture of Nitric Acid Birkeland and Eyde's process

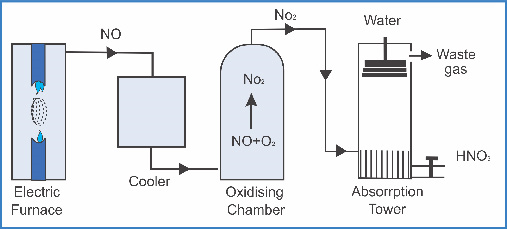
This process consists of the following steps:

1. Formation of nitric oxide

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

N (g)2 +O (g)2 →3000*C* 2*NO g*( )

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



Fiq 4.2 Manufacture of nitric acid form air

Absorption

NO

2

HNO

3

1. At 600oC,NO combines with O2 to form NO2

2*NO g O g*( )+ 2( )→2*NO g*2( )

1. Nitrogen dioxide is absorbed in water to give dilute HNO3 along with nitrous acid.

#### 2NO (g2 )+ *H O l*2 ( ) → *HNO aq*3( )+ *HNO aq*2( )

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

NO2 .

3HNO (g2 )→HNO (aq) 2NO(g)3 + + *H O l*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.

#### 4HNO (aq3 )→2*H O l*2 ( ) 4+ *NO g*2( )+*O g*2( )

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.

#### 2HNO (aq) CaO(s3 + )→H2 *O l*( )+*Ca NO*( 3 2) (*aq*) HNO (aq)3 + NaOH(aq) → H O( )2 *l* + *NaNO aq*3( )

2HNO (aq3 )+ Na CO (aq)2 3 → 2NaNO (aq3 )+ H2 *O l*( )+*CO*2(g)

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

##### 2*HNO aq*3( )→ *H O l*2 ( ) 2+ *NO g*2( ) [ ]( )+ *O g*

1. It oxidizes non-metals to their corresponding oxides.

C(s)+ 4HNO3(*conc*.) → CO (g)2 + 4NO (g2 )+ 2H O2 ( )*l*

*S s*( )+6*HNO conc*3( .) → 2*H O l*2 ( )+6*NO g*2( )+ *H SO*2 4(aq)

5HNO3(*conc*.)+ P(s) → H PO (aq)3 4 + H2 *O l*( )+5NO (g2 )

1. Metalloids like arsenic and antimony can be oxidized to their corresponding acids.

As(g)+5HNO3(*conc*.) → *H AsO aq*3 4( )+5*NO g*2( )+ *H O l*2 ( )

*Sb g*( ) → 5*HNO conc*3( .) → *H SbO aq*3 4( )+5*NO g*2( )+ *H O l*2 ( )

Animation 4.5 : Nitric oxide binding Source and Credit: ESRF

1. Nitric acid behaves differently with different metals.
   1. Gold, platinum, iridium and titanium do not react.
   2. Iron, cobalt, nickel, chromium, aluminium are rendered passive by acid due to the formation of a film of their oxides over them .
   3. Tungsten and uranium are changed into their oxides.
   4. Magnesium, calcium and manganese give hydrogen with dilute nitric acid.

*Mg s*( )+ 2*HNO dil*3( ) → *Mg NO*( 3 2) (*aq*)+ H ( )2 *g*

*Mn s*( )+ 2*HNO dil*3( ) → *Mn NO*( 3 2) (*aq*)+ *H*2( )*g*

* 1. Copper and lead give nitric oxide with dilute acid and nitrogen dioxide with concentrated acid.

##### 3*Cu s*( ) 8+ *HNO dil*3( )→3*Cu NO*( 3 2) (*aq*) 2+ *NO g*( ) 4+ *H O l*2 ( )

*Cu*(s)+ 4HNO3(*conc*.) →*Cu NO*( 3 2) (*aq*)+ 2*NO g*2( )+ 2*H O l*2 ( )

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

##### 6*Hg l*( ) 8+ HNO3(*dil*)→3*Hg*2 (*NO*3) (2 *aq*) 2+ *NO g*( ) 4+ *H O l*2 ( )

With concentrated acid, it gives mercuric nitrate and NO2

*Hg l*( )+ 4*HNO conc*3( ) → *Hg NO*( 3 2) (*aq*)+ 2*NO g*2( )+ 2*H O l*2 ( )

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

###### 3*Ag s*( ) 4+ *HNO aq*3( )→3*AgNO aq*3( )+ *NO g*( ) 2+ *H O l*2 ( )

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

4*Sn s*( )+10*HNO dil*3( .) → 4*Sn NO*( 3 2) (*aq*)+ *NH NO aq*4 3( )+3*H O l*2 ( ) Sn(s)+ 4*HNO conc*3( .) → *H SnO aq*2 3( )+ 4*NO g*2( )+ *H O l*2 ( )

(i) Zinc gives different products depending upon the concentration of acid and temperature. Very dilute nitric acid gives NH4NO3. Moderately dilute nitric acid gives nitrous oxide while concentrated nitric acid gives NO2.

4*Zn s*( )+10*HNO v*3( .dil.) → 4*Z* n(NO ) (3 2 *aq*)+ *NH NO aq*4 3( )+3*H O l*2 ( )

###### 4*Zn s*( )+10*HNO dil*3( .) → 4*Zn NO*( 3 2) (*aq*)+ *N O g*2 ( )+5*H O l*2 ( )

*Zn s*( )+ 4*HNO conc*3( .) → *Zn NO*( 3 2) (*aq*)+ 2NO2+ 2*H O l*2 ( )

1. .Reducing agents like FeSO4, H2S and HI are converted to F e2(SO4)3, S and I2 respectively, when they react with conc. HNO3

6*FeSO aq*4( )+3*H SO aq*2 4( )+ 2*HNO conc*3( .) → 3*Fe SO*2( 4 3) (*aq*)+ 2*NO g*( )+ 4*H O l*2 ( )

2*HNO aq*3( )+3*H S g*2 ( ) → 4*H O l*2 ( )+ 2*NO g*( )+3 ( )*S s*

6*HI aq*( )+ 2*HNO conc*3( .) → 4*H O l*2 ( )+ 2*NO g*( )+3*I*2( )*s*

1. Aqua Regia

When one volume of concentrated HNO3 is mixed with 3 volumes of concentrated HCl, aqua regia is formed.It is employed to dissolve gold and platinum.

*HNO conc*3( .)+3HC1(conc.) → NOC1(aq)+*C*1 ( )2 *g* + 2*H O l*2 ( )

Animation 4.6 : [Gold Coin Dissolving in Acid](http://makeagif.com/a2QVl_)

Source and Credit:  [Makeagif](http://makeagif.com/)

NOCI formed is decomposed giving NO and Cl2

##### *NOC*1→ *NO g*( )+[ 1]( )*C g*

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

*Au s*( ) 3[ 1](+ *C aq*)→2*AuC aq*1 (3 )

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 Ca3(PO4)2 and apatite Ca5F (PO4)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 (P4) which have a tetrahedral structure, Fig. 4.3. It boils at 280°C to P4 vapours which dissociate above 700°C to form P2 molecules.

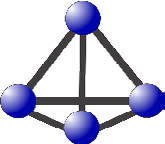
Red phosphorus is much less reactive and less poisonous than white phosphorus. It is prepared by heating white phosphorus in the presence of a little iodine or sulphur as a catalyst upto 250°C in vacuum. The tetra-atomic molecules of red phosphorus combine to form macromolecules, Fig. 4.4 .

Fig.4.3 White phosphorus

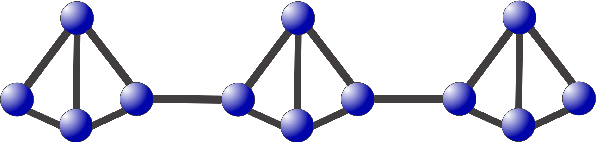


Fig. 4.4 Red phosphorus

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 (PCl3) Preparation

1. It is usually prepared by melting white phosporus in a retort in an inert atmosphere of CO2 and current of dried chlorine is passed over it. The vapours of PCl3 are collected in a flask kept in an ice-bath.

### 2 ( ) 3 1 ( )*P s* + *C* 2 *g* →2*PC*1 ( )3 *l*

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

2 ( ) 4*P g* + *SOC*1 ( )2 *l* →2*PC*1 ( ) 23 *l* + *SO g*2( )+ *S C*2 1 ( )2 *s*

Properties of Phosphorus Trichloride

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

Reactions

1. It combines with chlorine to form phosphorus pentachloride

*PC*1 ( )3 *l* +Cl ( )2 *g* → *PC*1 (5 s)

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

#### 2PC1 ( )3 *l* +*O g*2( )→2*POC*1 (3 s)

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

##### PC1 ( )3 *l* +3*H O l*2 ( ) → *H PO aq*3 3( )+3*HC aq*1( )

4. It reacts with alcohols and carboxylic acidsforming the respective chloro derivatives and H3PO3.

3*CH OH l*3 ( )+ *PC*1 ( )3 *l* → 3*CH C l*3 1( )+ *H PO l*3 3( )

3*CH COOH l*3 ( )+ *PC*1 ( )3 *l* →3*CH COC l*3 1( )+ *H PO l*3 3( )

2. Phosphorus Pentachloride (PC15) Preparation

1. By passing dry chlorine through phosphorus trichloride. *PC*1 ( )3 *l* +*C*1 ( )2 *g* → *PC*1 (5 s)
2. It may also be prepared by passing dry chlorine in a well cooled solution of phosphorus in carbon disulphide

2 ( ) 5 1 ( )*P l* + *C* 2 *g* →2*PC*1 ( )5 *s*

Properties of Phophorus Pentachloride

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

Reactions

1. It decomposes on heating producing PCl3 and chlorine.

#### *PC*1 ( )5 *s* → *PC*1 ( )3 *l* +*C*1 ( )2 *g*

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

*PC*1 ( )5 *s* + *H O l*2 ( ) → *POC*1 ( )3 *l* + 2*HC aq*1( )

*POC*1 ( )3 *l* +3*H O l*2 ( ) → *H PO aq*3 4( )+3*HC aq*1( )

#### *PC*1 ( )5 *s* + 4*H O l*2 ( ) → *H PO aq*3 4( )+5*HC aq*1( )

3. It converts metals into their chlorides.

##### *Zn s*( )+ *PC*1 ( )5 *s* → *ZnC*1 ( )2 *s* + *PC*1 ( )3 *l*

4.3.4 Oxides of Phosphorus

1. Phosphorus Trioxide, P2O3 (P4O6) Preparation

1. P2O3 can be prepared by burning white phosphorus in a limited supply of air.

*P s*4( ) 3+ *O g*2( )→2*PO s*2 3( )

Properties of Phoshorus Trioxide

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

Reactions

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

*PO s*2 3( )+O2( )*g* →*PO s*2 5( )

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

*PO s*2 3( ) 3+ *H O l*2 ( )→2*H PO l*3 3( )

With hot water, it forms phosphine and phosphoric acid.

2*PO s*2 3( ) 6+ *H O l*2 ( )→3*H PO aq*3 4( )+ *PH*3( )*g*

Phosphorus Pentoxide, P2O5 or P4O10

Preparation

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

*P s*4( ) 5+ *O g*2( )→2*PO s*2 5( )

Properties of Phosphorus Pentoxide

It is a white hygroscopic powder having a faint, garlic like odour due to the presence of traces of P2O3. It sublimes at 360°C.

Reactions

1. With cold water phosphorus pentoxide forms metaphosphoric acid.

*PO s*2 5( )+H2 *O l*( )→2*HPO aq*3( )

With hot water, it forms orthophosphoric acid

#### *PO s*2 5( )+3*H O l*2 ( ) → 2*H PO aq*3 4( )

2. It is a powerful dehydrating agent, thus, with HNO3, H2SO4, CH3COOH and C2H5OH, it gives N2O5, SO3, (CH3CO)2O and C2H4 ,respectively.

##### 2*HNO aq PO*3( )+ 2 5(s)→ N2 *O g*5( ) 2+ *HPO aq*3( )

###### *H SO aq*2 4( )+*PO s*2 5( ) →*SO g*3( )+ 2*HPO aq*3( )

2*CH COOH aq*3 ( )+ *PO s*2 5( )→(*CH CO*3 )2 *O l*( ) 2+ *HPO aq*3( )

*Aceticanhydride*

##### C H OH(l)2 5 +P O (s)2 5 → C H (g)2 4 +2HPO (aq3 )

4.3.5 Oxyacids of Phosphorus

1. Phosphorus Acid (H3PO3)

Preparation

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

*PO s*2 3( ) 3+ *H O l*2 ( )→2*H PO aq*3 3( )

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

*PC*1 ( )3 *l* +3*H O l*2 ( ) → *H PO aq*3 3( )+3*HC aq*1( )

Properties of Phosphorus Acid

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

Reactions

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

4*H PO s*3 3( )→3*H PO l*3 4( )+ *PH*3( )*g*

* 1. It is a powerful reducing agent and reduces CuSO4, AgNO3, etc. to the metallic state.

###### *H PO s*3 3( )+*CuSO aq*4( )+ *H O l*2 ( )→ *H PO aq*3 4( )+ *H SO aq*2 4( )+*Cu s*( )

*H PO s*3 3( ) 2+ *AgNO aq*3( ) 2+ *NH OH aq*4 ( )→ *H PO aq*3 4( ) 2+ *NH NO aq*4 3( )+ *H O l*2 ( ) 2+ *Ag s*( )

1. It reacts with oxygen to form orthophosphoric acid.

2*H PO s*3 3( )+*O g*2( ) → 2*H PO s*3 4( )

1. Nascent hydrogen produced by Zn/HCl reduces H3PO3 to phosphine

*H PO*3 3(s)+6[H](g) → PH (g)3 +3*H O l*2 ( )

2. Orthophosphoric Acid (H3PO4)

Preparation

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

###### *PO s*2 5( ) 3+ *H O l*2 ( )→2*H PO aq*3 4( )

1. It is also obtained by heating red phosphorus with concentrated HNO3.

*P s*( )+5*HNO conc*3( .) → *H PO aq*3 4( )+5*NO g*2( )+ *H O l*2 ( )

1. Hydrolysis of phosphorus pentachloride also gives orthophosphoric acid.

*PC*1 ( ) 45 *s* + *H O l*2 ( )→ *H PO aq*3 4( ) 5+ *HC aq*1( )

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 PO*3( 4 2) ( ) 3*s* + *SiO s*2( )→3*CaSiO s*3( )+ *PO s*2 5( )

#### *PO s*2 5( ) 3+ *H O l*2 ( )→2*H PO aq*3 4( )

Properties of Orthophosphoric Acid

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

Reactions

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

i. *H PO aq*3 4( )+ *NaOH aq*( ) → *NaH PO aq*2 4( )+ *H O l*2 ( ) ii. *NaH PO aq*2 4 ( )+ *NaOH aq*( ) → *Na HPO aq*2 4 ( )+ *H O l*2 ( ) iii. *Na HPO aq*2 4( )+ *NaOH*(aq) → Na PO (aq)3 4 + *H O l*2 ( )

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

2*H PO*3 4 →240−*H O*2*C H PO*4 2 7 →316−*H O*2*C* 2*HPO*3

*Orthophosphoric Pyrophosphoric Metaphosphoric* **acid acid 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  Electronic configuration  Ionization energy (kJ/mol)  Electron affinity (kJ/mol)  Electronegativity  Atomic radius(pm)  Ionic radius 2-ion (pm)  Melting points (°C)  Boiling points (°C)  Density (g/cm3) | 8  [He]2s22p4  1314  -141.1  3.5  66 140  -218  -183  0.00143 | 16  [Ne]3s23p4  1000  -200.42  2.5  104  184  113  444.6  2.06 | 34  [Ar]4s24p4  941  -195  2.4  117  198  217  684  4.8 | 52  [Kr]5s25p4  869  -183  2.1  137  221  450  990  6.25 | 84  [Xe]6s26p4  813  -180  2.0  152  -----  254  962  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 (O2 and O3), sulphur has 3(α, β, γ), Se has two (red and grey) ,Te has two (metallic and non-metallic). They also show the property of catenation. This property decreases down the group. All the elements are polymeric in nature ( they form poiy-atomic molecules). They attain the electronic configuration of the nearest noble gas by gaining 2 electrons forming O-2, S-2, Se-2, etc. Except oxygen the other members of the group show a covalency of +2 ,+4, and +6, for example, SCl2, SCl4, SCl6. +2 oxidation state is shown due to 2 unpaired electrons in the p-orbitals. +4 oxidation state is shown when 1 electron from p-orbilal is promoted to the next vacant d-orbital, while + 6 oxidation state is shown when another electron from s-orbital is also promoted to the next vacant d-orbital.

4.4.2 Occurrence

Oxygen is the most widely distributed and common of all the elements, comprising about 50% of the earth’s crust.

About one-fourth of the atmospheric air by weight consists of free oxygen and water contains nearly 89% of combined oxygen. The calcium carbonate which occurs as chalk, limestone, marble etc, contains 48% oxygen. Silica which is found in flint, quartz, etc, contains more than 53% oxygen by weight.

Sulphur is also widely distributed in nature both as free and in combined forms. Many important metallic ores are sulphides, e.g, galena (PbS), Zinc blende (ZnS), cinnabar (HgS), stibnite (Sb2S3), copper pyrite (Cu2S.Fe2S3), iron pyrite (FeS2), etc. Some important sulphates are also found in nature, e.g. gypsum (CaSO4), heavy spar (BaSO4), etc.

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

4.4.3 Comparison of Oxygen and Sulphur Smililarities:

1. Both oxygen and sulphur have same outer electronic configuration of ns2p4.
2. Both oxygen and sulphur are usually divalent.
3. Both oxygen and sulphur exhibit allotropic forms.
4. Both have polyatomic molecules. Oxygen has diatomic O2, while sulphur has S2 and S8 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, H2O and H2S, CO2 and CS2 ,etc.
7. Both are typical non-metals.
8. Both are found in free and combined states on earth.

Dissmililarities:

|  |  |
| --- | --- |
| Oxygen | Sulphur |
| 1. There are two allotropic forms of Oxygen-O2 and O3. | 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 (H2SO4)

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 H2SO4 are found in the waters of some springs and rivers. 4.5.1 Manufacture of Sulphuric Acid

Sulphuric acid is being manufactured commonly by contact process.

Contact Process

This method was developed by Knietsch in Germany. Basically, it involves the catalytic combination of sulphur and oxygen to form SO2 which is then dissolved in water to form H2SO4.

Animation 4.8 :  [Sulfuric acid - contact process](http://www.dynamicscience.com.au/tester/solutions1/chemistry/sulfuricacid.html) Source and Credit: [Dynamicscience](http://www.dynamicscience.com.au/)

Principle

SO2 obtained by burning sulphur or iron pyrites is oxidized to SO3 in the presence of V2O5 which acts as a catalyst. The best yield of SO3 can be obtained by using excess of oxygen or air and keeping the temperature between

400-500°C. SO3 formed is absorbed in concentrated H2SO4 and “Oleum” (H2S2O7) 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 SO2.

*S s*( )+*O g*2( )→*SO g*2( )

### 4*FeS s*2( ) 11 ( )+ *O g*2 →2*Fe O s*2 3( ) 8+ *SO g*2( ) b. Purifying Unit

SO2 is purified from impurities like dust and arsenic oxide, to avoid poisoning of the catalyst. Purifying unit consists of the following parts.

1. Dust remover

Steam is injected to remove dust particles from the gases.

1. Cooling Pipes

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

1. Scrubbers

The cooled gases are washed by a spray of water, as SO2 is not soluble in water at high temperature.

1. Drying Tower

The moisture of gases is removed by concentrated H2SO4 trickling down through the coke filled in this tower.

1. Arsenic Purifier

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

1. Testing box

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

Preheated gases at 400-500°C are passed through vertical iron columms packed with the catalyst V2O5. Here SO2 is oxidized to SO3.

**2SO g O g2**( )+ **2**( ) →→**400 500VO**−**2 5****C 2SO3** ∆ =−*H* 269.3*kJ mol*/ .

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

d. Absorption Unit

The SO3 obtained from the contact tower is dissolved in 98% H2SO4 to form pyrosulphuric acid (oleum), H2S2O7. It can be diluted with water to get any required concentration of sulphuric acid.

*H SO aq*2 4( )+ *SO g*3( )→ *H S O l*2 2 7( )

*H S O l*2 2 7( )+ *H O l*2 ( )→2*H SO aq*2 4( )

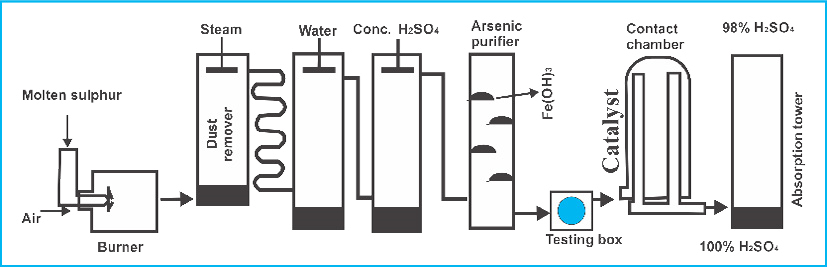


Fig.4.5 Contact Process

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.

### *H SO*2 4 →*SO H O*3 + 2

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

*H SO aq*2 4( )+ *H O l*2 ( )→ *H O l*3 +( )+ *HSO*4−(*aq*)

#### *HSO*4−(*aq*)+ *H O l*2 ( )→ *SO*42−(*aq*)+ *H O l*3 +( )

3. Reaction as an Acid

(i) Reactions with alkalies

#### *H SO aq*2 4( )+ *NaOH aq*( ) → *NaHSO aq*4( )+ *H O l*2 ( )

*NaHSO aq*4( )+ *NaOH* → *Na SO aq*2 4( )+ *H O l*2 ( )

1. Reactions with carbonates and hydrogen carbonates.

*Na CO aq*2 3( )+ *H SO aq*2 4( )→ *Na SO aq*2 4 ( )+ *H O l*2 ( )+*CO g*2 ( )

2*NaHCO aq*3( )+ *H SO aq*2 4 ( )→ *Na SO aq*2 4 ( ) 2+ *H O l*2 ( ) 2+ CO (g2 )

1. Reactions with salts

2NaC1(s) H SO+ 2 4 (*Conc*) →*Strong* heat *Na SO aq*2 4 ( ) 2+ *HC g*1( )

##### *KNO aq H SO*3( )+ 2 4(*Conc*) →*KHSO aq HNO g*4( )+ 3( )

(iv) Reaction with metals

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

*Fe*( )*s* +*H SO*2 4(*aq*) →*FeSO*4(*aq*) +*H*2( )*g*

*Zn*( )*s* +*H SO*2 4(*aq*) →*ZnSO*4(*aq*) +*H*2( )*g*

*Mg*( )*s* +*H SO*2 4(*aq*) →*MgSO*4(*aq*) +*H*2( )*g*

*Sn*( )*S* +*H SO*2 4(*aq*) →*SnSO*4( )*g* +*H*2( )*g*

1. Cold concentrated H2SO4 does not react with most of the metals like Cu, Ag, Hg, Pb, Au.
2. With certain metals hot concentrated sulphuric acid gives metal sulphates, water and SO2.

#### *Cu s*( )+ 2*H SO conc*2 4( ) →*CuSO aq*4( )+ 2*H O l*2 ( )+ *SO g*2( )

##### 2*Ag s*( )+ 2*H SO conc*2 4( ) → *Ag SO aq*2 4( )+ 2*H O l*2 ( )+ *SO g*2( ) *Hg l*( )+ 2*H SO conc*2 4( ) → *HgSO aq*4( )+ 2*H O l*2 ( )+ *SO g*2( )

4. Reactions as a Dehydrating Agent

H2SO4 has a great affinity for water , so it acts as dehydrating agent and eliminates water from different compounds.

(i) With oxalic acid it forms CO2 and CO.

*COOH conc H SO*. 2 4

#### | *CO g*2 ( )+*CO g*( )+ *H O l*2 ( )

*COOH s*( )

1. With formic acid, CO is formed.

*HCOOH*( )*l* →*conc*. H2*SO*4 *CO g H O*( )+ 2 ( )*l*

1. With ethyl alcohol it forms ethylene.

C H OH( )2 5 →*Conc H SO*100. *C*2 4 *CH*2 4 (g)+*HO*2 ( )

1. With wood, paper, sugar and starch it forms carbon and water.

*CH O*6 12 6 ( )*s* →*Conc H SO*. 2 6*C*( )*s* +6*HO*2 ( )*g*

*C H O*12 22 11( )*s* →*Conc H SO*. 2 4 12*C*( )*s* +11*HO*2 ( )*g*

##### (*C H O n*6 10 5 ) →*Conc H SO*. 2 4 6*nC nH O*+5 2

5. As an Oxidizing Agent

H2SO4 acts as a strong oxidizing agent.

1. It oxidizes C and S giving CO2 and SO2 , respectively.

*C s*( ) 2+ H SO2 4(*conc*)→CO (g) 2SO (g) 2H O(g)2 + 2 + 2

S(s)+2H SO2 4(*conc*) →3SO (g2 )+2H O(l2 )

1. H2S is oxidized to S .

###### *H S g*2 ( )+*H SO aq*2 4( ) →*S s*( )+*SO g*2( )+ 2*H O g*2 ( )

(iii) Reactions of H2SO4 with HBr and HI produces bromine and iodine respectively.

2*HBr aq*( )+ *H SO aq*2 4( )→ *Br g*2( )+ *SO g*2( ) 2+ *H O g*2 ( )

###### 2*HI aq*( )+*H SO aq*2 4( ) → *I g*2( )+SO (g)2 + 2H O(g2 )

6 . Reactions with Gases.

1. It absorbs SO3 and forms oleum

H SO2 4(*Conc*) +SO (g)3 → H S O (l)2 2 7

1. It reacts with ammonia forming ammonium sulphate.

2NH (g) H3 + [[1]](#footnote-1)*SO aq*4( )→(*NH*4 2) *SO aq*4( )

7. Reaction with Benzene

Benzene sulphonic acid is produced when H2SO4 reacts with benzene.

*C H l*6 6( )+ *H SO*2 4 (*conc*) →*C H SO OH l*6 5 2 ( )+ *H O l*2 ( )

*Benzenesulphonic* acid

8. Precipitation Reactions

White precipitates are produced when H2SO4 reacts with solutions of BaCl2, Pb(NO3)2 and Sr(NO3)2.

BaCl2(aq)+H SO2 4(aq) → BaSO4( )*s* ↓+2HCl(aq)

##### Pb(NO )3 2(aq) +H SO2 4(aq) →PbSO4( )*s* ↓+2HNO3(aq)

1. *KMnO*4(*aq*) +8*H SO*2 4(*aq*) +10*FeSO*4(*aq*) →*K SO*2 4(*aq*) + 2*MnSO*4(*aq*) +5*Fe SO*2( 4 3) (*aq*) +8*H O*2 ( )*l* [↑](#footnote-ref-1)