SULPHUR AND ITS COMPOUNDS

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Introduction

Sulphur is in period 3 and group VI of the periodic table. It has atomic number number 16 and electronic configuration 2.8.6.

Occurrence

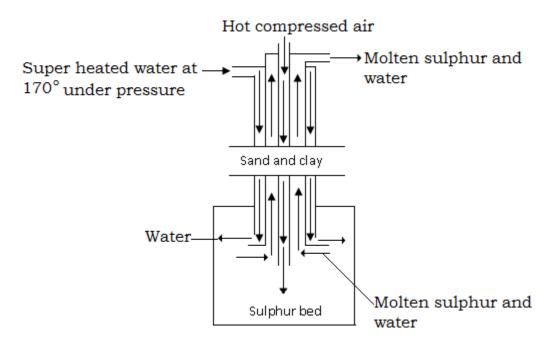
It occurs in both Free State and combined state. In free state, it occurs in underground deposits and it is widely distributed in volcanic regions. In combined states it occurs as sulphates, sulphides (mainly hydrogen sulphide) and sulphite. It also occurs in crude oil.

Extraction of sulpur

1. By frasch process

Sulphur is found deep below the ground (160-200) metres, this makes mining it impossible. It is extracted by a method invented by a man called Frasch and the method is Frasch process. Sulphur is extracted from the underground deposits by this method basing on its low melting point.

The Frasch process



Procedure

- 1. Drill the Frasch pump consisting of three concentric pipes down the sulphur deposit.
- 2. Super heated water (steam) at about 170°C is then forced down the outer most tube to melt the sulphur.
- 3. A jet of hot compressed air is then pumped down through the inner most tube. This hot compressed air pumps the molten sulphur out through the middle tube to the surface where the sulphur is cooled and solidified. The sulphur obtained is about 99.5% pure and can be used directly.

2. From natural gas and petroleum

Natural gas obtained during the distillation of petroleum contains hydrogen sulphide. The hydrogen sulphide can be removed by dissolving it in a suitable solvent. The gas is removed from the solvent and one third (1/3) of the hydrogen sulphide obtained is

burnt in oxygen to form sulphurdioxide.

$$2H_2S(g) + 3O_2(g)$$
 \longrightarrow $2H_2O(1) + 2SO_2(g)$

The sulphurdioxide reacts with the two third (2/3) of the hydrogen sulphide left to form sulphur.

$$SO_2(g) + H_2S(g) \longrightarrow S(s) + H_2O(l)$$

The water is evaporated to leave sulphur solids.

Physical properties of sulphur

- 1. It is a yellow solid at room temperature
- 2. It is a typical non metal
- 3. It is insoluble in water but soluble in some organic solvents e.g. methyl benzene and carbon disulphide

Allotropes of sulphur

Sulphur has two major crystalline forms .i.e. allotropes namely

1. Rhombic sulphur (alpha sulphur, α-sulphur)

Rhombic is an octahedral crystal; its bright yellow in color; its melting point is 114°C; it has a density of 2.8g/cm³ and it is stable at a temperature below 96°C.

Formation of rhombic sulphur

Shake some powdered sulphur with carbon disulphide for some time in a test tube. (Take care to extinguish all flames from the vicinity).

Filter the content of the test tube into a dry beaker through a dry filter paper and funnel over the mouth of the beaker; fasten a filter paper over the mouth of the beaker and pierce a few pin holes in it, and set the beaker aside.

The carbon disulphide will slowly evaporate depositing crystals of rhombic sulphur which because of the slow evaporation will be large enough for their shape to be seen.

NB The formation of the crystal takes place at room temperature.

2. Monoclinic sulphur (Beta sulphur, β -sulphur)

It is a needle shaped crystal (prismatic); it is pale yellow in color (almost transparent); it has a melting point of 119°C; it has a density of 1.98 g/cm³; it is stable above 96°C, below 96°C it reverts to rhombic sulphur.

Formation of monoclinic sulphur

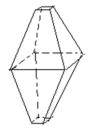
Place powdered sulphur in a very large crucible. Heat it and stir gradually while adding some sulphur until the crucible is full of molten sulphur. Use a small flame for heating otherwise the sulphur will burn.

Allow the sulphur to cool. After some time, a solid crust begins to form on the surface.

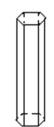
When the crust has formed make two holes (at wide separation) using a glass rod on it and pour out the molten sulphur from inside which has not crystallized.

Remove the crust and observe needle shaped crystals of monoclinic sulphur formed beneath the crust and through out the inner surface of the crucible.

Structure







Transition temperature is a temperature at which rhombic sulphur changes to monoclinic sulphur and vice versa. At a temperature below 96°C, rhombic sulphur exists and as the temperature goes above 96°C, the rhombic sulphur changes to monoclinic form. The transition temperature is there fore 96°C.

To show that both rhombic and monoclinic sulphur are allotropes of sulphur When the same mass of either rhombic or monoclinic sulphur is burnt in oxygen, the same mass of sulphur dioxide is obtained in each case and nothing else.

Question

What are the differences between monoclinic and rhombic sulphur

Other forms of sulphur

• Amorphous sulphur

This is a non crystalline form of sulphur which is insoluble in carbon disulphide(CS₂). It is formed as an almost insoluble powder if a saturated solution of hydrogen sulphide is oxidized by leaving it to stand in open air for some times i.e.

$$2H_2S(aq) + O_2(g)$$
 $\longrightarrow 2S(s) + 2H_2O(l)$ (Amorhous sulphur)

•Plastic sulphur

If sulphur at its boiling point is poured into cold water, a dark-sticky (elastic) solid called plastic sulphur is formed. Plastic sulphur is elastic because it contains zig-zag (entangled) chains of S₈ molecules.

N.B Plastic sulphur is unstable and slowly hardens to form yellow rhombic sulphur. Plastic sulphur is not a separate allotrope of sulphur since it is not crystalline in nature.

Action of heat on sulphur

Sulpur under goes a series of changes when it is heated. Both rhombic and monoclinic sulphur consist of S_8 molecules with different arrangements. It is this differences in arrangement of sulphur atoms that is responsible for the different observations made when sulphur is heated.

- 1. If yellow powdered sulphur is heated in the absence of air just above the melting point (about 115°C), it melts into a clear amber (pale yellow) mobile liquid. This liquid is mobile because the sulphur-8 (S₈) molecule rings can flow over one another with ease.
- 2. On further heating (to about 160°C), the yellow liquid becomes darker and very viscous. This is because the S₈ rings are broken and form long chains of sulphur 8 (S₈) atoms. The liquid is viscous because the long chains entangle with one another and thus do not flow readily over each other. Above 160°C the darker viscous sulphur liquid becomes mobile and reddish brown in color.
- 3. Near its boiling point (444°C), the liquid now becomes lighter in color, thin and more mobile (less viscous). This is because the long entangled chains break down forming chains of S_1 and S_2 atoms which can flow more readily.
- 4. The sulphur eventually boils at 444°C and forms a light brown sulphur vapor.

Other properties of sulphur

- 1. It is a reactive element and it combines directly with other elements (metals and non metals)
- a) If a piece of burning sulphur is lowered into a gas jar of oxygen, it continues to burn even more brightly with a blue flame forming whites fumes with a choking

smell. The white fumes with a choking smell are a mixture of white sulphur trioxide and colorless sulphur dioxide gases.

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

 $2S(s) + 3O_2(g) \longrightarrow 2SO_3(g)$

b) If mixture of iron dust (iron fillings) and powdered sulphur is heated in a hard glass test tube, the two elements combine vigorously and a spontaneous red glow spreads through the mixture since the reaction is exothermic. A dark grey (black) hard mass of iron(II)sulphide is formed.

$$Fe(s) + S(s) \longrightarrow FeS(s) + heat$$

Almost all sulphides are black.

c) Zinc reacts more vigorously with sulphur if the mixture is heated forming zinc sulphide.

$$Zn(s) + S(s)$$
 \longrightarrow $ZnS(s)$

d) Hot copper foil (wire) also glows in sulphur vapor forming copper(I) sulphide.

$$2Cu(s) + S(g) \longrightarrow Cu_2S(s)$$

e) Carbon combines directly with sulphur to form a liquid, carbon disulphide. Very high temperatures are required for this reaction to occur.

$$C(s) + 2S(s) \longrightarrow CS_2(1)$$

- f) Reaction with acids
 - Dilute acids have no effects on sulphur. However,
 - a) Hot concentrated sulphuric acid oxidizes sulphur to sulphur dioxide and the sulphuric acid its self is also reduced to sulphur dioxide.

$$S(s) + 2H_2SO_4(aq) \longrightarrow 3SO_2(g) + 2H_2O(l)$$

b) Hot concentrated nitric acid oxidises sulphur to sulphuric acid and brown fumes of nitrogen dioxide is given off.

$$6HNO_3(aq) + S(s) \longrightarrow 6NO_2(s) + H_2SO_4(aq) + 2H_2O(1)$$

Uses of sulphur

- 1. It is used in the making of matches, gun powder and fire works.
- 2. Used in the vulcanization (hardening) of rubber
- 3. Used in the manufacture of sulphuric acid in the contact process.
- 4. Used as a fungicide and in medicine, ointments and drugs used for the treatment of skin diseases. e.g. Sulphonamide.
- 5. Used in the production of calcium hydrogen sulphite, Ca(HSO₃)₂ that acts as a bleaching agent in the wood pulp in manufacture of paper.
- 6. Sulphur is used in the manufacture of various compounds like carbon disulphide (CS_2) and sodium thiosulphide $Na_2S_2O_3$ used in photography.
- 7. Fruit trees are sprayed with sulphur products like carbon disulphide (CS₂) to kill insects and fungi which cause diseases.

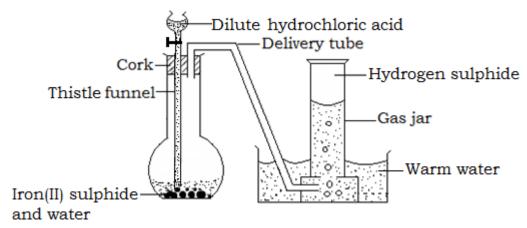
COMPOUNDS OF SULPHUR

Hydrogen sulphide (H₂S)

Laboratory preparation

It can be prepared in a laboratory by the action of dilute hydrochloric acid or dilute sulphuric acid on iron(II) suphide. The preparation must be done in a fume cupboard as hydrogen sulphide gas is very poisonous.

Set up of apparatus



As the acid reaches the iron (II)sulphide, effervescence begins and the hydrogen sulphide is collected over warm water since in is soluble in cold water. If it is required dry, the gas is passed over anhydrous calcium chloride and then collected by downward delivery method.

Equation

FeS(s) + 2HCl(aq)
$$\longrightarrow$$
 H₂S(g) + FeCl₂(aq)

Dilute sulphuric acid may also be used

$$FeS(s) + H_2SO_4(aq) \longrightarrow H_2S(g) + FeSO_4(aq)$$

NB

1. Concentrated sulphuric acid is never used to dry the hydrogen sulphide as it reacts with the gas.

$$(3H_2S(g) + H_2SO_4(aq) \longrightarrow S(s) + 4H_2O(l))$$

2. The hydrogen sulphide prepared in this case contains some impurities especially hydrogen chloride gas and hydrogen.

Physical properties

- i) It has a strong repulsive characteristic of a rotten egg smell
- ii) It is a colorless gas
- iii) It is very poisonous but not as dangerous as carbon monoxide
- iv) It is slightly denser than air that is why it is collected by downward delivery
- v) It can be liquefied under high pressure
- vi) It dissolves in cold water forming a fairly weak acidic solution

$$H_2S(s) + (aq) \longrightarrow H_2S(aq)$$

The weak acid formed dissociates forming ions $H_2S(aq) \longrightarrow 2H^+$ (aq) + S^2 -(aq)

Test for hydrogen sulphide

- a) Hydrogen sulphide can easily be detected by its strong repulsive smell of rotten eggs.
- b) When hydrogen sulphide is passed through a solution of Lead(II)nitrate or Lead(II)ethanoate, a black precipitate of lead(II)sulphide is observed.

i.e.
$$Pb^{2+}(aq) + S^{2-}(aq) \longrightarrow PbS(s)$$

$$Pb(NO_3)_2(aq) + H_2S(g)$$
 \longrightarrow $PbS(s) + 2HNO_3(aq)$

$$(CH_3COO)_2Pb(aq) + H_2S(g) \longrightarrow PbS(s) + 2CH_3COOH(aq)$$

Chemical properties of hydrogen sulphide

1. Hydrogen sulphide burns in excess air (oxygen) with a pale blue flame forming suphur dioxide and water vapor.

$$2H_2S(g) + 3O_2(g) \longrightarrow 2SO_2(g) + 2H_2O(g)$$

However, in limited supply of air, a yellow deposit of sulphur is formed.

$$2H_2S(g) + O_2(g) \longrightarrow 2S(s) + 2H_2O(g)$$

- 2. Hydrogen sulphide is a powerful reducing agent and it gives up its hydrogen to many compounds which are therefore reduced and hydrogen sulphide itself is oxidized to sulphur. For example
- a) When sulphur dioxide is bubbled through a solution of hydrogen sulphide, a yellow deposit of sulphur appears and water is formed.

$$2H_2S(aq) + SO_2(g) \longrightarrow 3S(s) + 2H_2O(1)$$

b) Hydrogen sulphide reacts with halogens to form hydrogen halides and yellow deposits of sulphur e.g. when hydrogen sulphide is mixed with chlorine gas, a pale yellow deposit of sulphur and white fumes of hydrogen chloride gas are produced.

$$H_2S(g) + Cl_2(g) \longrightarrow S(s) + 2HCl(g)$$

When hydrogen sulphide is bubbled through bromine water, the reddish brown bromine water is decolorized and pale yellow precipitate of sulphur appears.

$$H_2S(g) + Br_2(1) \longrightarrow S(s) + 2HBr(aq)$$

c) When hydrogen sulphide is bubbled through a solution of iron(III)chloride, the solution changes from pale yellow to pale green. This is because hydrogen sulphide reduces iron(III)chloride (the pale yellow solution) to iron(II)chloride (a pale green solution). The hydrogen sulphide itself is oxidized to sulphur which appears as a yellow deposit. Hydrogen chloride gas is also formed which dissolves to form hydrochloric acid.

$$2\text{FeCl}_3(\text{ag}) + \text{H}_2\text{S(ag)} \longrightarrow 2\text{FeCl}_2(\text{ag}) + \text{S(s)} + 2\text{HCl(ag)}$$

d) When hydrogen sulphide is bubbled through a solution of acidified potassium manganate(VII), the solution changes color from purple to colorless and a yellow deposit of sulphur is also formed. This is because, hydrogen sulphide reduces manganate(VII) ions (purple in color) to manganese(II) ions(colorless) and the hydrogen sulphide itself is oxidized to sulphur.

$$2KMnO_4(aq) + 6H_2SO_4(aq) + 5H_2S(g) \longrightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 5S(s) + 8H_2O(l)$$

e) When hydrogen sulphide is bubbled through a solution of acidified potassium dichromate(VI) the solution changes from orange to green as a result of reduction of the dichromate(VI) ions to chromium(III) ions.

$$2K_2Cr_2O_7(aq) + 8H_2SO_4(aq) + 3H_2S(g) \longrightarrow 2Cr_2(SO_4)_3(aq) + 2K_2SO_4(aq) + 5S(s) + 7H_2O(l)$$

f) Hydrogen sulphide reduces concentrated sulphuric acid according to the following

reaction

$$3H_2S(g) + H_2SO_4(aq) \longrightarrow 3S(s) + 4H_2O(l)$$

g) When hydrogen sulphide is bubbled through concentrated nitric acid, brown fumes of nitrogen dioxide together with a pale yellow precipitate of sulphur are observed.

$$H_2S(g) + 2HNO_3(aq) \longrightarrow 2NO_2(g) + S(s) + 2H_2O(l)$$

3. Hydrogen sulphide gas precipitates insoluble sulphides e.g. it precipitates black copper(II)sulphide from blue copper(II)sulphate solution.

$$CuSO_4(aq) + H_2S(g) \longrightarrow CuS(s) + H_2SO_4(aq)$$

OXIDES OF SULPHUR

There are two principle oxides of sulphur namely sulphur dioxide and sulphur trioxide.

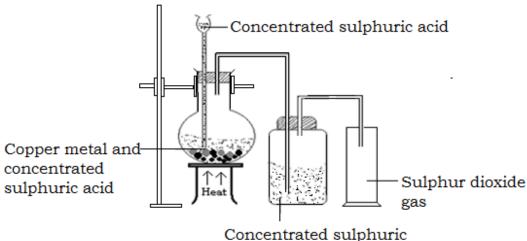
Sulphur dioxide (Sulphur (IV) Oxide), SO2

Laboratory preparation

Sulphur dioxide in the laboratory can be prepared in two ways

- a) Action of concentrated sulphuric acid on copper metal
- b) By action of dilute sulphuric acid or hydrochloric acid on any sulphite salt e.g sodium sulphite(Na₂SO₃).

Preparation by the action of concentrated H_2SO_4 on copper metal Setup



acid to dry the gas

Place copper metal in the flask and arrange the apparatus as shown above. Gently heat the mixture until when it is hot. Effervescence occurs as sulphur dioxide is evolved.

Equation

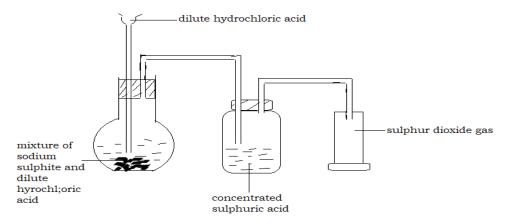
$$Cu(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + SO_2(g) + H_2O(l)$$

The gas is passed through a wash bottle containing concentrated sulphuric acid to dry the gas and it is the collected by downward delivery since it is denser than air. The gas is not collected over water as it is very soluble in water.

Laboratory preparation of sulphur dioxide from sodium sulphite and dilute sulphuric or hydrochloric acid

The procedure and the arrangement of apparatus remains as shown above but no heating is required for the reaction. However, if the reaction slows down, the flask may be heated gently.

Set up



Equation Na₂SO₃(s) + 2HCl(aq)
$$\longrightarrow$$
 SO₂(g) + 2NaCl(aq) +H₂O(l)

Sodium hydrogen sulphite can also be used under the same conditions. $NaHSO_3(s) + HCl(aq) \longrightarrow SO_2(g) + 2NaCl(aq) + H_2O(l)$

Physical properties of sulphur dioxide

- 1. It is a poisonous gas
- 2. It is a colorless gas with a characteristic pungent smell
- 3. It is denser than air
- 4. It can easily be liquefied under pressure
- 5. It is an acidic gas i.e. it turns moist blue litmus paper red
- 6. It is very soluble in water forming sulphurous acid

Chemical properties of sulphurdioxide

1. Reaction with alkalis

Sulphur dioxide is neutralized by alkalis

i) When the alkali is in excess sulphites are formed.

$$2$$
NaOH_(aq) + SO_{2(g)} \longrightarrow Na₂SO_{3(aq)} + H₂O_(l)

ii) When the sulphur dioxide is in excess, hydrogen sulphites are formed and water is not a product in this case.

$$Na_2SO_{3(aq)}+H_2O_{(l)}+SO_{2(g)} \longrightarrow 2 NaHSO_{3(aq)}$$

2. As a reducing agent

In the presence of water, sulphur dioxide behaves as a reducing agent

a) When sulphur dioxide is bubbled through acidified potassium dichromate(VI) solution, the solution changes from orange to green. This is because, sulphur dioxide reduces chromium (VI) ions to chromium (III) ions.

$$K_2Cr_2O_7(aq) + H_2SO_4(aq) + 3SO_2(g) \longrightarrow Cr_2(SO_4)_3(aq) + K_2SO_4(aq) + H_2O(1)$$

NB This is a characteristic test for sulphurdioxide

b) Sulphur dioxide also reduces acidified potassium Manganate(VII) to manganese (II) sulphate. The color changes from purple to colorless and the sulphur dioxide is itself oxidized to sulphuric acid.

$$2KMnO_{4(aq)} + 2H_2O_{(l)} + 5SO_{2(g)} \longrightarrow 2MnSO_{4(aq)} + 2H_2SO_{4(aq)} + K_2SO_{4(s)}$$

This is also used as a test for sulphur dioxide.

c) When sulphur dioxide is bubbled through a solution of iron(III)suphate, the color changes from yellow to pale green. This is because the sulphur dioxide reduces iron (III) sulphate to iron (II) sulphate and the sulphur dioxide is oxidized to sulphuric acid.

$$Fe_2(SO_4)_3(aq) + 5SO_2(g) + 2H_2O(1) \longrightarrow 2FeSO_4(aq) + 2H_2SO_4(aq)$$

d) Sulphur dioxide reduces concentrated nitric acid to form brown fumes of nitrogen dioxide and itself is oxidized to sulphuric acid.

$$SO_2(g) + 2HNO_3(aq) \longrightarrow 2NO_2(g) + H_2SO_4(aq)$$

e) Colored solutions of halogen are made colorless when sulphur dioxide is bubbled through them. This is because sulphur dioxide reduces the halogens to hydrogen halides. For example

When sulphur dioxide is bubbled through chlorine water (yellowish green liquid), a mixture of hydrochloric acid and sulphuric acid are obtained which appear colorless.

$$H_2O(1) + SO_2(g) + Cl_2(g) \longrightarrow 2HCl(aq) + H_2SO_4(aq)$$

Bromine water (a reddish brown liquid) is turned colorless as bromine is reduced to hydrobromic acid by sulphur dioxide.

$$H_2O(1) + SO_2(g) + Br_2(g) \longrightarrow 2HBr(aq) + H_2SO_4(aq)$$

3. As an oxidizing agent

Sulphur dioxide acts as an oxidizing agent when it reacts with reducing agents more powerful than itself. Consider the reactions below

a) When sulphurdioxide is bubbled through a solution of hydrogen sulphide, a yellow precipitate is observed. This is because sulphur dioxide oxidizes hydrogen sulphide to yellow sulphur and sulphur dioxide is itself reduced to sulphur.

$$SO_2(g) + 2H_2S(aq) \longrightarrow 3S(s) + 2H_2O(l)$$

b) When a piece of magnesium ribbon is lowered into a gas jar of sulphur dioxide, it continuous to burn with a bright flame to form white solids (magnesium oxide) and a yellow solid(sulphur). This is because sulphur dioxide oxidizes magnesium to magnesium oxide and itself is reduced to sulphur.

$$2Mg(s) + SO_2(g)$$
 $\longrightarrow 2MgO(s) + S(s)$

4. As a bleaching agent

Sulphur dioxide bleaches wet flowers like roses and hibiscus and any other wet material by reduction. It does this by removing oxygen from the colored material.

Dye +
$$SO_2(g)$$
 +2 $H_2O(l)$ Dye + H_2 + $H_2SO_4(aq)$

Complex which appears colourless

The original color of the bleached material may be restored after prolong exposure to air due to aerial oxidation. This explains why old news papers appear yellow after some

times.

5. Reaction with oxygen

Under normal conditions, sulphur dioxide does not react with oxygen. However when a mixture of dry and pure sulphur dioxide and oxygen is passed over heated platinum catalyst (or vanadium(V)oxide), sulphur trioxide gas is formed.

$$2SO_2(g) O_2(g) \rightleftharpoons 2SO_3(g)$$

6. As an acid anhydride

Sulphur dioxide is an acid anhydride, reacting with water to form sulphurous acid.

$$SO_2(g) + H_2O(1) \longrightarrow H_2SO_3(aq)$$

Sulphurous acid is a dibasic acid and reacts with sodium hydroxide solution to form two salts of sodium, the acid salt; sodium hydrogen sulphite (NaHSO₃) and the normal salt; sodium sulphite (Na₂SO₃)

$$NaOH(aq) + H_2SO_3(aq) \longrightarrow NaHSO_3(aq) + H_2O(l)$$

 $2NaOH(aq) + H_2SO_3(aq) \longrightarrow Na_2SO_3(aq) + 2H_2O(l)$

Uses of sulphur dioxide

- 1. It is used in the manufacture of sulphuric acid by contact process.
- 2. It is a poisonous gas and it is used in fumigation to kill germs in clothes and houses.
- 3. It is used for preservation of food staff and fruits during transportation and storage, as it prevents fermentation.
- 4. It is used as a bleaching agent e.g it is used to make calcium hydrogen sulphite (Ca(HSO₃)₂) that makes wood pulp white in paper manufacture, used to bleach silk, straw e.t.c.

Sulphites (SO₃²⁻)

These are salts derived from sulphurous acid.

Test for sulphite

Procedure

To a solution of substance containing sulphite, add 3 drops of barium nitrate solution followed by excess nitric acid. (or add barium chloride solution followed by excess hydrochloric acid)

Observation

White precipitates immediately appear which dissolve with effervescence on adding dilute nitric acid.

$$Ba^{2+}(aq) + SO_4^{2-}aq) \longrightarrow BaSO_3(s)$$

On addition of nitric acid

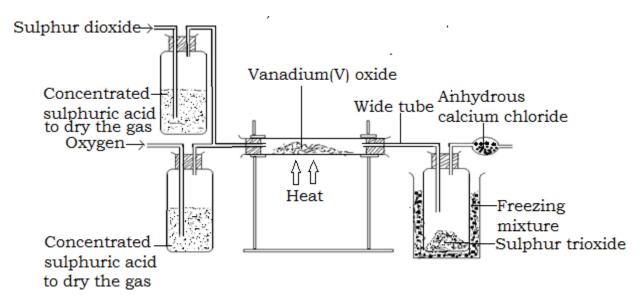
$$BaSO_3(s) + HNO_3(aq)$$
 \longrightarrow $Ba(NO_3)_2(aq) + SO_2(g) + H_2O(l)$

Sulphur trioxide (SO₃)

Laboratory preparation

It can be prepared in the laboratory by passing a dry mixture of oxygen and sulphur dioxide over a heated platinum catalyst or (Platinized asbestos) at a temperature of 450-500°C.

Set up of apparatus



Equation for the reaction

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

The sulphur trioxide is seen as dense white fumes and may be solidified in a freezing mixture of ice and a little sodium chloride. The sulphur trioxide container is protected from atmospheric moisture by calcium chloride tube.

Properties of sulphur trioxide

1. It has very high affinity for water and combines with it violently forming sulphuric acid.

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

This reaction is highly exothermic i.e. it gives out a lot of heat and it is because of this that sulphur trioxide is kept in air tight containers.

2. Sulphur trioxide combines with concentrated sulphuric acid to form fuming sulphuric acid called oleum.

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

Sulphuric acid (H₂SO₄)

Large scale (Industrial) manufactureof sulphuric acid by contact process

In the manufacture of sulphuric acid by contact process, sulphur dioxide and oxygen are the starting materials.

The sulphur dioxide is oxidized to sulphur trioxide which is then absorbed by concentrated sulphuric acid forming oleum (fuming sulphuric acid) to which water is added to form the sulphuric acid.

This process can be divided into the following essential stages;

a) Preparation of sulpur dioxide

Sulpur dioxide can be obtained from the following source;

i) Burning sulpur in air. This is cheap and produces sulphur dioxide in large quantities

ii) Roasting sulphide ores in air
$$4FeS_{2(s)} + 11O_{2(g)} \longrightarrow 8SO_{2(g)} + 2Fe_2O_{3(s)}$$
 (Iron pyrite) $2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2SO_{2(g)} + 2ZnO_{(s)}$ (Zinc blende)

Other sources of sulphur dioxide include; burning of hydrogen sulphide from crude oil in air; flue gas desulphurization in power stations e.t.c.

Oxygen is obtained from fractional distillation of liquid air.

b) Purification of the gases

The sulphur dioxide and the oxygen are purified and dried (i.e. cleared off any dust particles and other impurities which can poison the catalyst especially if it is platinum.

c) Preparation of sulphur trioxide

The purified gases are passed over a finely divided vanadium (V) oxide, (V_2O_5) catalyst at a temperature of 450-500 C and a pressure of 2-3 atmospheres, sulphur trioxide is formed. Vanadium (V) oxide is commonly used because it is cheaper and not easily poisoned by impurities.

$$2SO_{2 (g)} + O_{2 (g)} \qquad \frac{\text{Catalyst (V}_{2}O_{5})}{\text{Temp 450-500 °C}} \quad 2SO_{3 (g)}$$

$$\text{Pressure, 2-3 atm}$$

The catalyst Vanadium (V) oxide is so effective that 95% conversion of sulphur dioxide to sulphur trioxide is achieved at 450-500 C and 2 atmospheres. The reaction is exothermic and there fore produces heat enough to maintain the temperature of the catalyst.

d) Conversion of sulphur trioxide to sulphuric acid

Sulphur trioxide, SO_3 must not be allowed to come in contact with water as the reaction is intensely exothermic that it vaporizes the sulphuric acid formed (i.e. produces a lot of mist consisting of dry droplets of H_2SO_4).

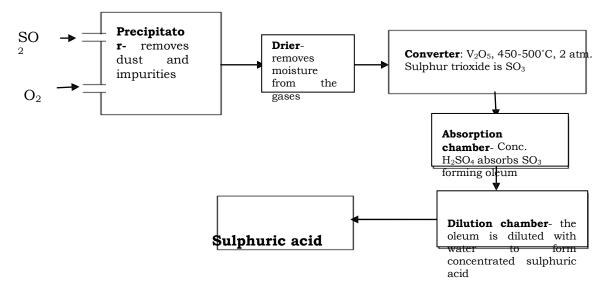
To prevent this happening, the sulphur trioxide, SO₃ is absorbed in concentrated sulphuric acid, H₂SO₄ to form an oily liquid called an Oleum

$$H_2SO_4(aq) + SO_3(aq) \longrightarrow H_2S_2O_7(l)$$

The oleum produced is carefully diluted to give 95-98% pure concentrated sulphuric acid.

$$H_2S_2O_7(1) + H_2O(1) \longrightarrow 2H_2SO_4(aq)$$

Summary of the contact process



In the above process, the following conditions favor high yield of sulphur trioxide:

- Presence of a catalyst. The catalyst must be finely divided to increase the surface area for the reaction.
- Low temperature as the reaction is exothermic (releases heat),
- Slightly high pressure above the atmospheric pressure as the reaction is
- Accompanied by a decrease in volume.
- High concentration of oxygen or sulphur dioxide.

Properties of sulphuric acid

a) Physical properties

- 1. Concentrated Sulphuric acid is a dense, colorless and oily liquid.
- 2. Concentrated sulphuric acid has very high affinity for water and a lot of heat is produced when the acid is diluted.
- 3. Concentrated sulphuric acid is hygroscopic. I.e. gradually absorbs moisture from the air and therefore when left exposed to air, in a beaker, the total volume gradually increases due to absorption of water. This is why it is used as a drying agent for many of the gases.

b) Chemical properties

1. Sulphuric acid as an acid

It is the dilute sulphuric acid that reacts as a typical acid.

i. Dilute sulphuric acid ionizes to form hydrogen ions

$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

ii. Sulphuric acid liberates hydrogen gas from reactive metals e.g. Na, Mg.

$$Na(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2(g)$$

iii. It reacts with bases to form salt and water only. Since it is a dibasic acid, it produces two types of salts, the normal salt (sulphate) when alkali is in excess and the acidic salt (hydrogen sulphate) when the acid is in excess.

$$H_2SO_4(aq) + NaOH(aq)$$
 \longrightarrow $NaHSO_4(aq) + 2H_2O(l)$ $H_2SO_4(aq) + 2NaOH(aq)$ \longrightarrow $Na_2SO_4(aq) + 2H_2O(l)$

- iv. It reacts with carbonates and hydrogen carbonates to liberate carbondioxide gas $Na_2CO_3(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$ $Ca(HCO_3)_2(aq) + H_2SO_4(aq) \longrightarrow CaSO_4(aq) + H_2O(l) CO_2(g)$
- **NB**. With calcium carbonate and lead (II) carbonate, there is little effervescence and the reaction stops soon because the sulphates formed are insoluble and form a coating around the carbonate preventing any further attack by sulphuric acid on the carbonate.

2. As an oxidizing agent

Hot concentrated sulphuric acid is a powerful oxidizing agent and in all reactions, it is itself reduced to sulphur dioxide. Metals are oxidized to sulphates and non metals to their oxides. Example include:

a) Hot concentrated sulphuric acid oxidizes copper to copper (II) sulphate and the sulphuric acid itself is reduced to sulphur dioxide.

$$2H_2SO_4(1) + Cu(s) \longrightarrow CuSO_4(aq) +SO_2(g) +2H_2O(1)$$

b) When charcoal is heated with concentrated sulphuric acid, the charcoal is oxidized to carbon dioxide and the sulphuric acid is reduced to sulphur dioxide.

$$2H_2SO_4(1) + C(s) \longrightarrow CO_2(aq) + 2SO_2(g) + 2H_2O(1)$$

c) Hot concentrated sulphuric acid oxidizes sulphur to sulphur dioxide and the sulphuric acid itself is reduced to sulphur dioxide also.

$$2H_2SO_4(1) + S(s) \longrightarrow 3SO_2(g) + 2H_2O(1)$$

d) When a sample of hydrogen sulphide gas is bubbled through concentrated sulphuric acid, the hydrogen sulphide is oxidized to sulphur and the sulphuric acid is reduced to sulphur dioxide.

$$H_2S + H_2SO_4(1) \longrightarrow S(s) + SO_2(g) + 2H_2O(1)$$

3. As a dehydrating agent

Concentrated sulphuric acid is a very strong dehydrating agent i.e. it removes the elements of water from many compounds. Examples

a) When concentrated sulphuric acid is added to blue copper (II) sulphate crystals, the copper(II) sulphate crystals gradually become white as their water of crystallization is lost.

$$CuSO_4.5H_2O(s)$$
 Concentrated H_2SO_4 \rightarrow $CuSO_4(s) + 5H_2O(g)$

b) When cold concentrated sulphuric acid is added to sugar crystals in an evaporating dish, the sugar crystals turn progressively from white, to yellow then to brown and finally to black. A spongy black mass of charcoal rises almost filling up the dish, water vapor is given off and the dish becomes very hot as the reaction is exothermic (generates energy).

$$C_{12}H_{22}O_{11}(s)$$
 Concentrated H_2SO_4 \longrightarrow $12C(s) + $11H_2O(g)$ + Heat$

In this reaction ,the concentrated acid removes the elements of water from sugar leaving a black mass of carbon.

A similar action is the explanation of a very marked corrosive action of the acid on flesh and cloth made of cotton. Cotton is largely cellulose whose simplest formula is $(C_6H_{10}O_5)n$.

c) Concentrated sulphuric acid dehydrates oxalic acid on heating to form a mixture of carbon monoxide, carbon dioxide and water.

$$H_2C_2O_4(s)$$
 Concentrated H_2SO_4 $CO(g) + CO_2(g) + H_2O(l)$

d) Excess concentrated sulphuric acid dehydrates ethanol at a temperature of 170 C forming ethene.

$$C_2H_5OH(l)$$
 Concentrated H_2SO_4 ,170°C $C_2H_4(g) + H_2O(l)$

When concentrated sulphuric acid removes elements of water from a compound with the formation of a new compound, it is described as a dehydrating agent.

4. As a drying agent

When concentrated sulphuric acid removes water from a mixture, it acts as a drying agent.

Concentrated sulphuric acid reacts exothermically with water. When a solution is made, it is essential to pour the acid into water, stirring to disperse the heat evolved. It is dangerous to add water to concentrated sulphuric acid as small pockets of water are likely to boil.

Gases are dried by bubbling them through concentrated sulphuric acid. For basic gases like ammonia, another drying agent is used.

Uses of sulphuric acid

- 1. Used in the manufacture of fertilizers like ammonium sulphate.
- 2. Making of paints and pigments
- 3. Manufacture of detergents and soap
- 4. Production of other chemicals such as metallic sulphates, hydrochloric acid, hydrofluoric acid and plastics.
- 5. Extraction of metals and metal manufacturing including pickling to clean metallic surfaces.
- 6. Extraction of alkenes in petroleum refinery.
- 7. With nitric acid, it is used to make dyes and explosives.

Sulphates

These salts are derived from sulphuric acid.

All sulphates are soluble in water except barium sulphate, lead(II) sulphate and calcium sulphate is slightly soluble in water.

Action of heat on sulphates

Most of the sulphates are resistant to heat, but if they are hydrated, they lose their water of crystallization and become powdery upon slight heating. E.g.

$$Na_2SO_4.10H_2O(s)$$
 \rightarrow $Na_2SO_4(s) + 10H_2O(l)$

However, iron (II) sulphate, copper (II) sulphate, ammonium sulphate and sulphates of other metals lower than copper in the reactivity series are decomposed upon strong heating. For example

i. When a green hydrated solid of iron (II) sulphate is heated gently, it loses its water

of crystallization which condenses on the cooler part of the test tube forming dirty yellow anhydrous solids of iron (II) sulphate.

$$FeSO_4.7H_2O(s)$$
 \longrightarrow $FeSO_4(s) + 7H_2O(l)$

On further heating, the anhydrous dirty yellow solids decompose giving off sulphur dioxide (which turn orange potassium dichromate green) in addition to white fumes of sulphur trioxide and leave a brown solid of iron (III) oxide.

$$2FeSO_4(s)$$
 \longrightarrow $Fe_2O_3(s) + SO_3(g) + SO_2(g)$

Overall equation:
$$2\text{FeSO}_4.7\text{H}_2\text{O(s)}$$
 \longrightarrow $\text{Fe}_2\text{O}_3(\text{s}) + 14\text{H}_2\text{O(l)} + \text{SO}_3(\text{g}) + \text{SO}_2(\text{g})$

ii. When a blue copper(II)sulphate crystal is heated, it loses its water of crystallization forming white anhydrous powder of copper(II)sulphate.

$$CuSO_4.5H_2O(s)$$
 — $CuSO_4(s) + 5H_2O(1)$

On strong heating, the white anhydrous white solid decomposes into white fumes of sulphur trioxide and a black solid residue (copper(II)oxide).

$$CuSO_4(s)$$
 — $CuO(s) + SO_3(g)$

Chemical test for sulphates

To the solution of the suspected sulphate in water, add barium chloride and dilute hydrochloric acid (barium nitrate solution and dilute nitric acid can also be used.) a white precipitate which is insoluble in excess acid indicates the presence of a sulphate.

$$BaCl_2$$
 (aq) + Na_2SO_4 (aq) \longrightarrow $BaSO_4$ (s) + $2NaCl$ (aq)

White precipitate (Insoluble barium