

***S4B CHEMISTRY NOTES ON 'SULPHUR' TO BE COPIED INTO
THE STUDENT'S NOTE BOOK.***

(A CONTINUATION FROM WHERE WE STOPPED)

3. Allotropes of Sulphur

Just like carbon, sulphur also exhibits allotropy. The allotropes of sulphur include the following:

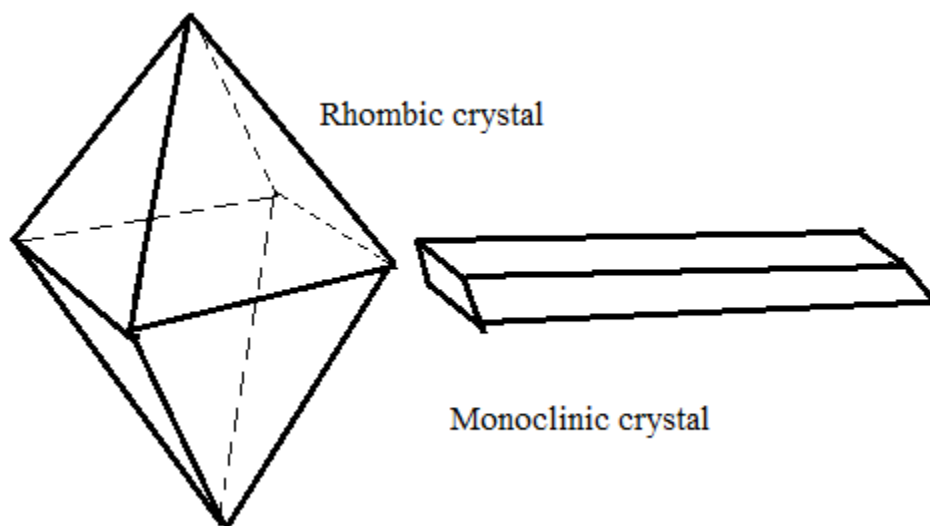
- (i) Rhombic sulphur(also known as Alpha sulphur)
- (ii) Monoclinic sulphur(also known as Beta sulphur)
- (iii) Amorphous sulphur

Of the above allotropes, the crystalline ones include Rhombic and Monoclinic sulphur.

Differences Between Rhombic and Monoclinic Sulphur:

Rhombic Sulphur	Monoclinic Sulphur
Its crystals are octahedral	Its crystals are needle-shaped.
Is stable below 96°C	Is stable above 96°C
Is bright yellow	Is pale yellow
Has a density of 2.06gcm ⁻³	Has a density of 1.98gcm ⁻³
Has a melting point of 113°C	Has a melting point of 120°C

Diagrammatic Representation of Rhombic and Monoclinic sulphur Crystals:



Laboratory Preparation of Rhombic and Monoclinic Sulphur :

(a) Rhombic sulphur:

Some powdered sulphur is added to carbon disulphide (or methylbenzene) in a test tube and the mixture shaken- to dissolve the sulphur.

The resulting mixture is filtered into a dry beaker, using a dry filter paper and a dry filter funnel.

The mouth of the beaker is tightly covered with filter paper and a few pinholes pierced through the paper.

The beaker is then put aside in a fume cupboard. The volatile solvent (carbon disulphide or methyl benzene) slowly evaporates leaving behind bright yellow octahedral crystals of rhombic sulphur.

(b) Monoclinic sulphur:

Powdered sulphur is placed in a large evaporating dish. The sulphur is heated (using a small flame-since a large flame could easily make the sulphur to burn) to melt while gradually stirring and adding more sulphur until the dish is almost filled with molten sulphur.

The molten sulphur is allowed to cool until a thin solid crust forms over the entire surface.

Using a glass rod, two holes are pierced in the crust, at widely separated points. The liquid sulphur underneath the crust is rapidly poured out through one of the holes.(The second hole lets in air).

Using a knife, the crust is cut through all round the dish, near the brim and then lifted out. Pale yellow needle-like crystals (of monoclinic sulphur) are observed both underneath the crust and inside the evaporating dish.

Proof that both Rhombic and Monoclinic Sulphur are Allotropes of Sulphur:

Proof 1:

A given mass of monoclinic sulphur slowly changes at room temperature to the same mass of rhombic sulphur.

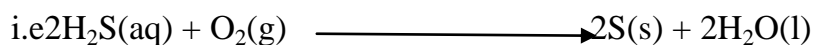
Proof 2:

When a given mass of either forms of sulphur is burnt in air, the same mass of sulphur dioxide (a gas that turns acidified potassium dichromate solution from orange to green) is formed and nothing else.

Note:

Amorphous sulphur is non-crystalline and almost white. It is produced by chemical action between materials in solution.

e.g It can be produced by saturating distilled water with hydrogen sulphide and then leaving the solution exposed to air, for a day or two. The almost white amorphous sulphur is slowly precipitated.

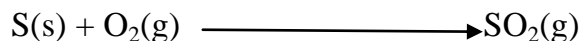


4. Chemical Properties of Sulphur:

(a) Combustion:

Sulphur burns in air with a blue flame evolving a gas with an irritating smell (sulphur dioxide) and giving off misty fumes as well.

The main product of the reaction is sulphur dioxide, formed according to the equation:



The misty fumes are due to traces of sulphur trioxide, that are also formed.

(b) Reaction With Metals:

Sulphur chemically combines with most metals, on heating the mixture, forming the respective metal sulphide.



Black

NB:

The above reaction is employed during the laboratory preparation of Iron(II) sulphide, by direct synthesis. During this reaction, the grey / yellow mixture of iron filings and sulphur glows red , before forming a black solid [of Iron(II) sulphide].

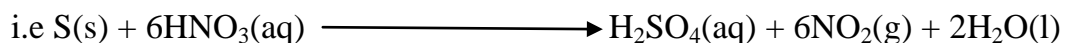
(b) Reaction With Sulphuric acid:

Sulphur is oxidized by hot, concentrated sulphuric acid to sulphurdioxide , water being formed as well.



(c) Reaction With Nitric acid:

Sulphur is oxidized by hot, concentrated nitric acid to sulphuric acid, nitrogen dioxide and water being the other products of the reaction.

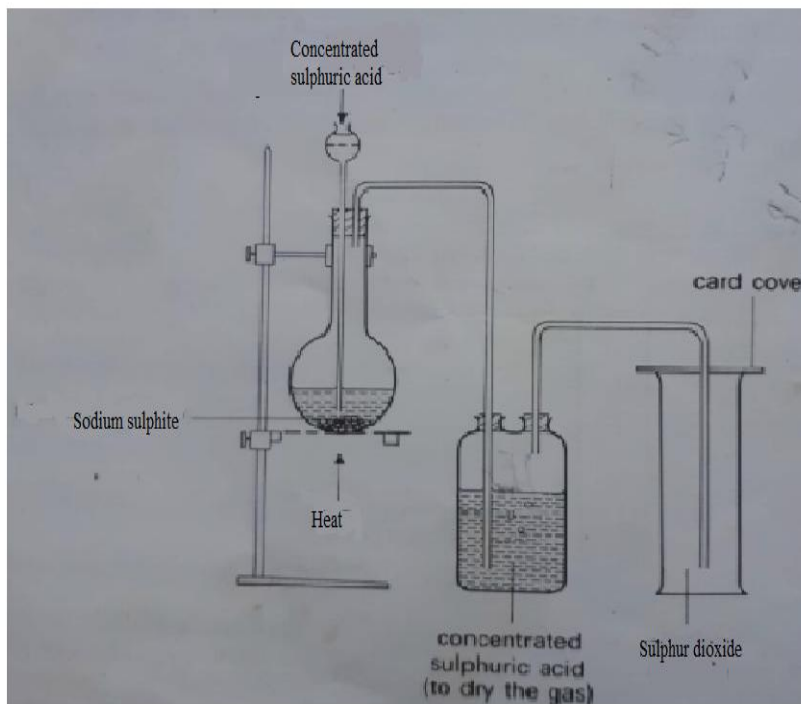


5.Uses of sulphur:

- Used in the manufacture of firewax , match sticks and gunpowder.
- Used as a fungicide.
- Used in the vulcanization of rubber.
- Used in the manufacture of drugs.

SULPHUR DIOXIDE

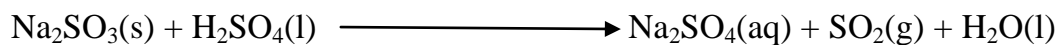
1. Laboratory Preparation



Procedure:

Sodium sulphite crystals are placed in a clamped round-bottomed flask and concentrated sulphuric acid (or hydrochloric acid) is put in a thistle funnel.

The tap of the funnel is opened to release the acid onto the sodium sulphite. The mixture is heated and there is effervescence of a colourless gas (sulphurdioxide), produced according to the equation:

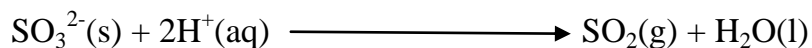


OR (aq)

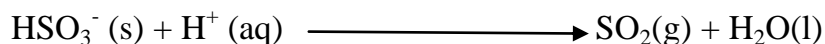
The gas is bubbled through concentrated sulphuric acid (to dry the gas) and then collected by downward delivery, since it is denser than air.

NB:

(i) The ionic equation for the reaction is:



(ii) The gas can also be prepared using sodiumhydrogensulphite , instead of sodium sulphite. In this case, the corresponding ionic equation is:



2. Physical Properties of Sulphur dioxide:

It is a colourless gas with an irritating smell (of burning sulphur).

It is denser than air.

It is readily soluble in water.

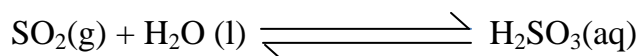
It turns moist blue litmus paper red.

It is fairly poisonous.

3. Chemical Properties of Sulphur dioxide:

(a) Reaction With Water:

Sulphur dioxide gas readily dissolves in and reacts with water forming sulphurous acid.

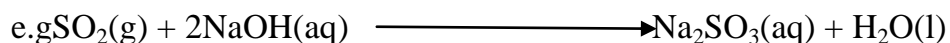


This explains why it turns moist blue litmus paper red.

(b) Reaction With Alkalis:

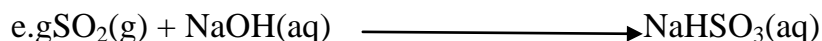
Sulphur dioxide gas reacts with an alkali (soluble metal hydroxide) forming either a sulphite (a normal salt) or a hydrogensulphite(an acid salt) depending on the conditions.

If the alkali is in excess(i.e.sulphur dioxide is limited), a sulphiteis formed.



Sodium sulphite(a normal salt)

If sulphur dioxide is in excess (i.e alkali is limited), a hydrogensulphite is formed.



Sodium hydrogensulphite(an acid salt)

(c) As a Reducing Agent:

Sulphur dioxide is a reducing agent;

(i) It turns acidified potassium dichromate solution from orange to green.

In this reaction, the orange dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$ are reduced to the green chromium(III) ions, Cr^{3+} .

NB:

This reaction is the basis for the confirmatory test of sulphur dioxide; a gas is proved to be sulphur dioxide if it turns acidified potassium dichromate solution from orange to green.

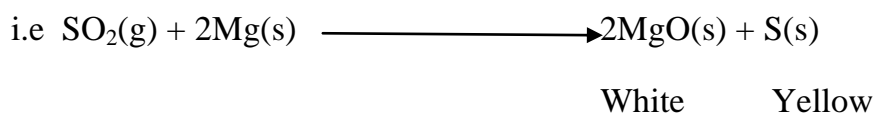
(ii) It turns acidified potassium permanganate solution from purple to colourless.

In this reaction, the purple permanganate ions, MnO_4^- are reduced to the colourless manganese(II) ions, Mn^{2+} .

(d) As an Oxidizing Agent:

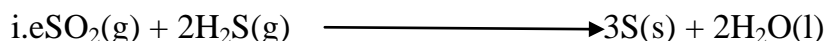
Sulphur dioxide can behave as an oxidizing agent in some limited reactions;

(i) It oxidizes burning magnesium to magnesium oxide while the gas itself gets reduced to sulphur.

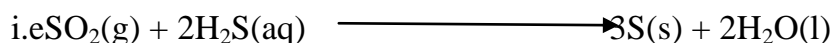


This explains why magnesium burns in sulphur dioxide gas forming a white powder (magnesium oxide) containing some yellow particles (sulphur)

(ii) It oxidizes hydrogen sulphide gas to sulphur (i.e oxidation by removal of hydrogen)



This explains why a yellow precipitate is formed when sulphur dioxide gas is bubbled through aqueous hydrogen sulphide solution.

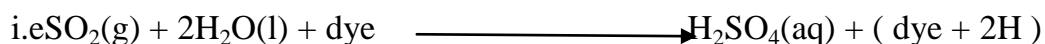


Yellow

(e) As a Bleaching Agent:

Sulphur dioxide is a bleaching agent; it bleaches certain substances e.g wet petals of flowers.

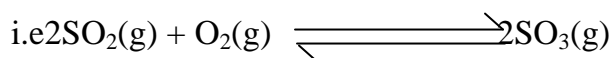
Sulphur dioxide bleaches by reducing the dye(i.e making the dye to gain hydrogen)



coloured colourless

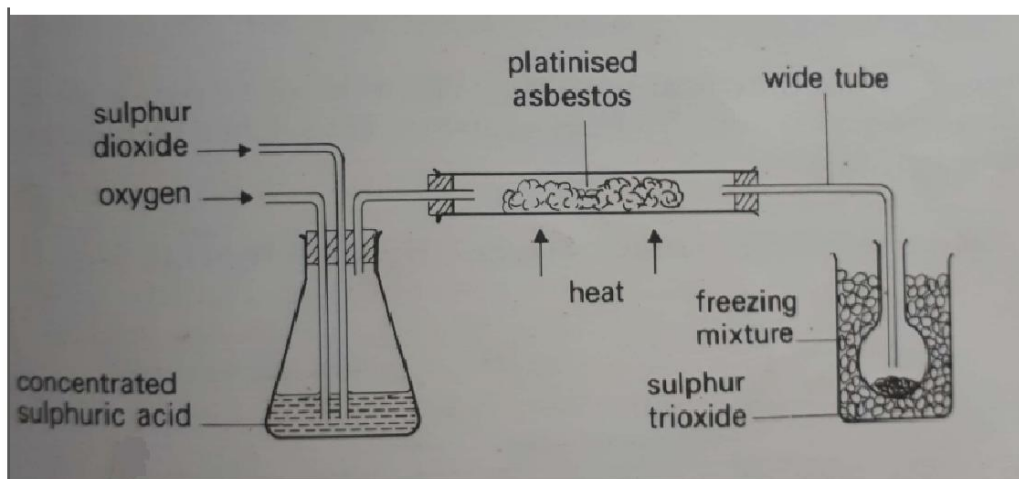
(f) Reaction With Oxygen:

Sulphur dioxide chemically combines with oxygen to form sulphur trioxide [also known as sulphur(VI) oxide]; the reaction taking place in the presence of a catalyst of platinum or vanadium(V) oxide, V_2O_5 (also known as vanadium pentoxide) and at a temperature of 450°C.



Note:

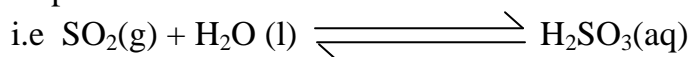
The above reaction is the basis for the laboratory preparation of sulphur trioxide(as illustrated in the diagram below). In the diagram, the catalyst used is platinized asbestos , although vanadium(V) oxide could have also been used.



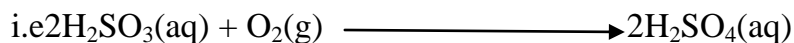
4.Environmental Pollution Effect:

Sulphur dioxide pollutes the atmosphere by leading to the formation of acid rain. Acid rain contains sulphuric acid and is formed as follows:

- When in the atmosphere, sulphur dioxide readily dissolves in rain water forming sulphurous acid.



- The sulphurous acid is oxidized by atmospheric oxygen to sulphuric acid.



Acid rain is not good in that it;

- It is harmful to both plants and animals, via its corrosive effect.
- It dissolves away minerals and stone works of buildings.
- It increases soil acidity.

5. Uses of Sulphur dioxide:

- Used in the manufacture of sulphuric acid, by the Contact process.
- Used in fumigation of houses, clothes and grain due to its poisonous nature-that enables it to kill germs, termites, white ants etc.
- Used as a preservative in foodstuffs and fruit squashes. It does this by preventing oxidation of the liquids.
- Used to manufacture calcium hydrogensulphite- that is in turn used to make wood-pulp white, in the process of manufacture of paper.
- Used to bleach materials that are damaged by chlorine e.g wool, silk etc.

SULPHURIC ACID

1. Industrial Manufacture:

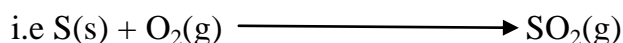
Sulphuric acid is prepared commercially (i.e on large scale) by the Contact process.

The major raw materials for this process include sulphur(or Iron pyrites), air and water.

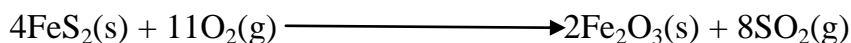
The process involves the following steps:

Step 1:

Sulphur(or iron pyrites) is burnt in air to produce sulphur dioxide.

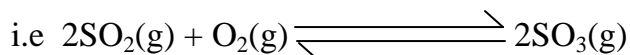


In case of iron pyrites, the equation of reaction is:



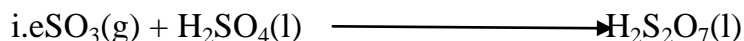
Step 2:

The sulphur dioxide is cleaned, dried and then passed over a catalyst of vanadium(V) oxide(vanadium pentoxide) heated to a temperature of 450°C at a pressure of 1atm in the presence of air. Sulphur dioxide gets oxidized to sulphur trioxide.



Step 3:

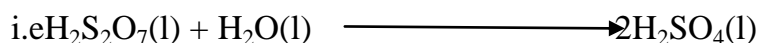
Sulphur trioxide is then dissolved in some concentrated sulphuric acid forming a liquid known as oleum.



oleum

Step 4:

Oleum is then diluted with a calculated amount of water forming concentrated sulphuric acid- of composition 98% acid and 2% water.



Note:

(i) If sulphur trioxide were dissolved in water directly to form sulphuric acid, the violent reaction would cause the sulphuric acid to spray in air-which is dangerous to the workers. This explains why the gas is first dissolved in some concentrated sulphuric acid instead; it dissolves in the acid safely.

(ii) Vanadium pentoxide is preferred to platinum, as catalyst in the Contact process. This is because the former is cheaper and not easily poisoned by impurities unlike the latter.

2.Physical Properties of Sulphuric acid:

- Concentrated sulphuric acid is a colourless, oily liquid.
- Concentrated sulphuric acid is very soluble (miscible) in water, giving off a lot of heat in the process.
- Concentrated sulphuric acid is hygroscopic (i.e absorbs water from the atmosphere)

This can be proved by putting some concentrated sulphuric acid in a beaker and marking the level at which the acid stops on the beaker. The beaker is put aside and left exposed to air for a few days.

Observation:

After this period, the level of acid in the beaker is observed to be above the original level indicated.

Explanation:

The acid absorbed some water from the atmosphere thereby increasing the volume of liquid in the beaker-thus a rise in the level.

3. Chemical Properties of Sulphuric acid:

The chemical properties of sulphuric acid can be divided into the following properties:

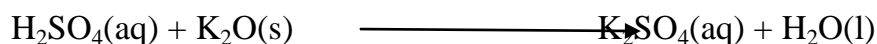
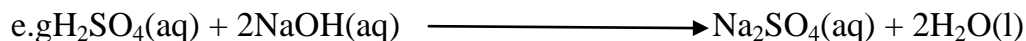
- (i) as an acid (when dilute)
- (ii) as an oxidizing agent (when concentrated)
- (iii) as a dehydrating agent (when concentrated)
- (iv) as an acid- displacement agent (when concentrated)

(a) As an Acid:

Sulphuric acid is a strong, dibasic acid. In dilute aqueous solution, it is completely ionized-releasing many hydrogen ions. These hydrogen ions are responsible for the reactions below, that are characteristic of any other acid.

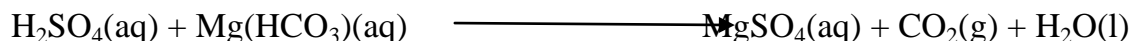
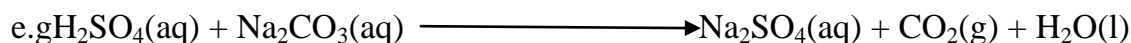
(i) Neutralization of a Base:

Sulphuric acid reacts with a base forming a salt and water only.



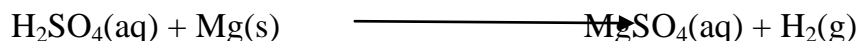
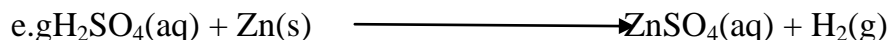
(ii) Reaction With Carbonates and Hydrogencarbonates:

Sulphuric acid reacts with a carbonate or a hydrogencarbonate forming a salt, carbon dioxide and water.



(iii) Reaction With Metals:

Dilute sulphuric acid reacts with highly electropositive metals forming a salt and hydrogen gas.

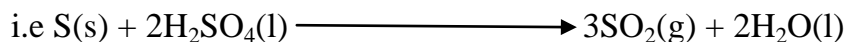


(b) As an Oxidizing Agent:

When concentrated, sulphuric acid can behave as an oxidizing agent.

e.g

(i) Hot, concentrated sulphuric acid oxidizes sulphur to sulphurdioxide, water being the other product.



(ii) Concentrated sulphuric acid reacts with copper on heating the mixture, forming sulphur dioxide, copper(II) sulphate and water. In this reaction, copper is oxidized to copper(II) ions (via loss of electrons)



(c) As a Dehydrating Agent:

When concentrated, sulphuric acid can behave as a dehydrating agent.

e.g

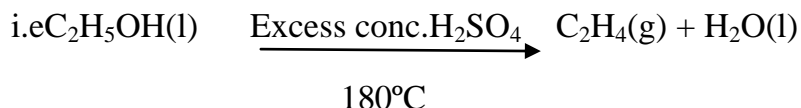
(i) It dehydrates hydrated copper(II) sulphate, making the salt anhydrous. During this reaction, it is observed that the blue crystals turn white.



Blue

White

(ii) At a temperature of 180°C, excess concentrated sulphuric acid dehydrates ethanol forming ethene.

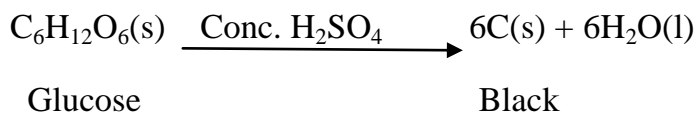


(iii) Concentrated sulphuric acid dehydrates both sucrose (cane sugar) and glucose forming carbon.



Sucrose

Black

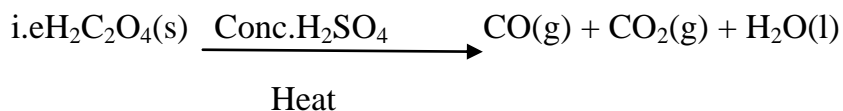


Note:

When concentrated sulphuric acid is added to cane sugar (sucrose) in a beaker, it is observed that the white crystals turn to a black porous solid, which expands and also a misty vapour is evolved.

In the reaction, a lot of heat is produced- which causes the water to vapourise and form steam (the misty vapour observed).

(iv) Concentrated sulphuric acid dehydrates oxalic acid when the mixture is heated, forming carbon monoxide, carbon dioxide and water.

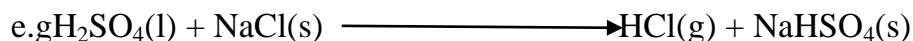


(d) As an Acid-Displacement Agent:

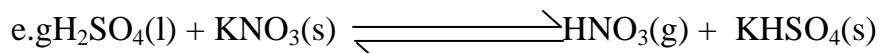
Concentrated sulphuric acid can displace more volatile acids from their salts, in the solid state. This is because concentrated sulphuric acid is largely non-volatile.

e.g

(i) Concentrated sulphuric acid displaces hydrochloric acid (displaced as hydrogen chloride gas) from a solid chloride

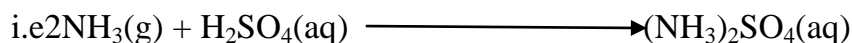


(ii) Concentrated sulphuric acid displaces nitric acid (displaced as nitric acid vapour) from a solid nitrate.



4. Uses of Sulphuric acid:

- Used in the manufacture of fertilizers e.g ammonium sulphate.



- Used in the manufacture of dyes, paints , explosives.

- Used in the manufacture of detergents.
- Used as an electrolyte in car batteries.

SULPHATES

1. Introduction:

A sulphate is a salt of sulphuric acid. It is formed when all the ionizable hydrogen atoms in sulphuric acid are replaced by a metallic ion.

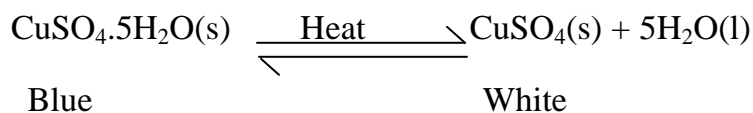
2. Solubility:

All sulphates are soluble in water EXCEPT barium sulphate, lead(II) sulphate and calcium sulphate(sparingly soluble).

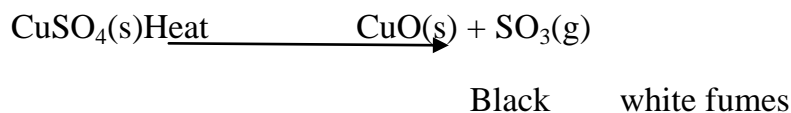
3. Action of Heat:

On gentle heating, hydrated sulphates lose their water of crystallization to become anhydrous.

e.g When hydrated copper(II) sulphate crystals (blue in colour) are gently heated they lose their water of crystallization forming anhydrous copper(II) sulphate (white in colour)



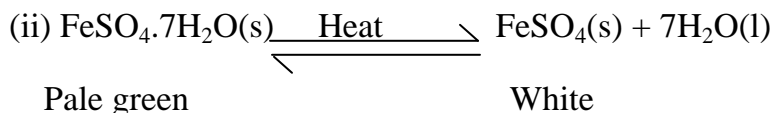
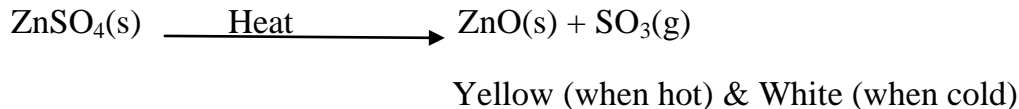
On stronger heating, the anhydrous copper(II) sulphate decomposes forming copper(II) oxide (black solid) and sulphur trioxide (white fumes).



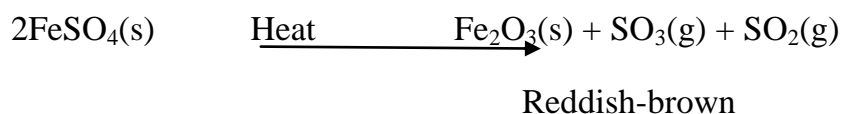
Likewise, the hydrated sulphates below behave in a similar way, first losing their water of crystallization (on gentle heating) and later decomposing on stronger heating, to form an oxide.



Then:



Then:



4. Test For Sulphate Ions:

The presence of sulphate ions in solution can be confirmed using the sets of reagents below:

(a) Barium nitrate solution and dilute nitric acid:

Procedure:

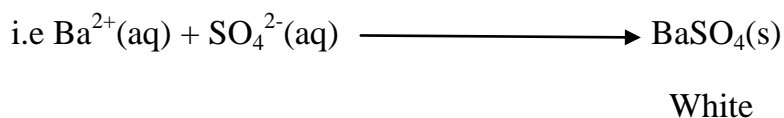
To a sample of the solution in a test tube, a few drops of barium nitrate solution are added followed by addition of a few drops of dilute nitric acid.

Observation:

A white precipitate is formed, insoluble in the acid.

Explanation:

Precipitate is due to formation of the insoluble barium sulphate.



The procedure may be slightly altered by first adding dilute nitric acid, followed by barium nitrate solution.

In this case the observation is stated as 'white precipitate formed' (i.e the observation after adding barium nitrate solution).

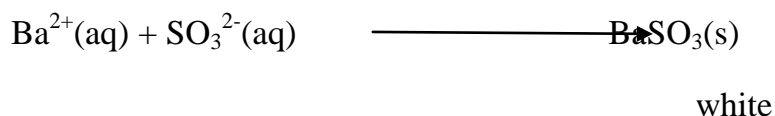
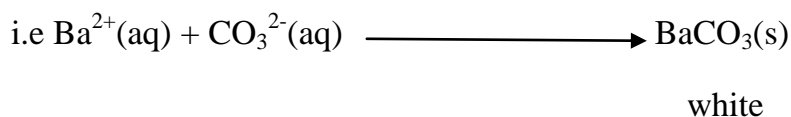
(b) Barium chloride solution and dilute hydrochloric acid:

Procedures, observations and explanation are as in (a) above.

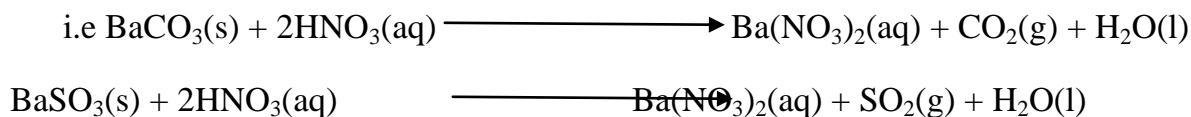
NB:

The purpose of adding acid as well (and not barium nitrate or barium chloride solution alone) is to prove that the precipitate formed is due to barium sulphate and hence confirm presence of sulphate ions in the solution.

In case the solution had contained carbonate ions (CO_3^{2-}) or sulphite ions (SO_3^{2-}), a white precipitate (of barium carbonate or barium sulphite) respectively would be formed on addition of barium nitrate or barium chloride solution.



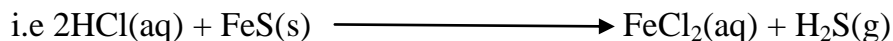
However, in this case (unlike the case of sulphate ions) the precipitate formed is soluble in the acid.



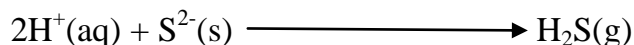
HYDROGEN SULPHIDE

1. Preparation:

Hydrogen sulphide gas can be prepared by adding dilute hydrochloric acid (or sulphuric acid) to Iron(II) sulphide the reaction taking place at room temperature.



The ionic equation is:



2. Physical Properties of Hydrogen sulphide:

- It is a colourless gas with a characteristic repulsive rotten-egg smell.
- It is a highly poisonous gas.
- It is fairly soluble in water forming a weakly acidic solution.
Hence it cannot be collected over cold water; it is instead collected over warm water.
- It is denser than air. Hence it can be collected by downward delivery.

3. Test For Hydrogen sulphide:

Procedure:

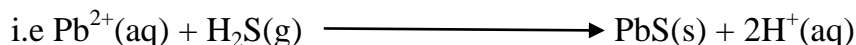
A strip of filter paper is soaked in lead(II) ethanoate solution [also known as lead(II) acetate paper] dropped in a gas jar of the gas.

Observation:

The paper turns black

Explanation:

Precipitate is due to depositing of the insoluble lead(II) sulphide (black in colour) on the paper's surface.



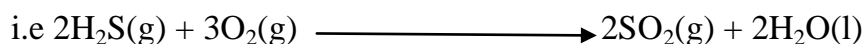
Black

4. Chemical Properties:

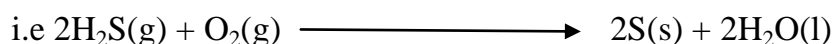
(a) Combustion:

Hydrogen sulphide burns in oxygen (air) with a blue flame forming either sulphur dioxide or sulphur (and water) depending on the amount of oxygen.

If oxygen is in excess, sulphur dioxide is produced.



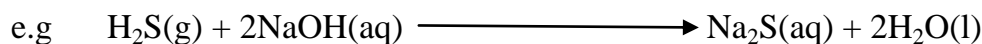
If oxygen is limited, sulphur is formed.



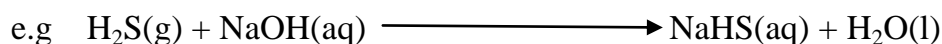
(b) As an acid

Hydrogen sulphide can behave as an acid, in reacting with an alkali to form a salt and water. The salt formed can either be a sulphide (normal salt) or a hydrogensulphide (an acid salt) depending on the relative amount of alkali.

If the alkali is in excess (i.e. hydrogen sulphide is limited) a sulphide is formed.



If hydrogen sulphide is in excess (i.e. alkali is limited) a hydrogensulphide is formed.

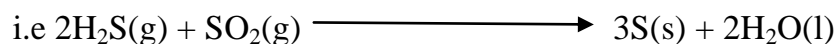


(c) As Reducing Agent:

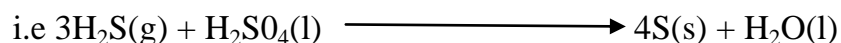
Hydrogen sulphide is a reducing agent.

e.g

(i) It reduces sulphur dioxide gas to sulphur.

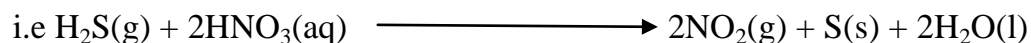


(ii) It reduces concentrated sulphuric acid to sulphur.



This explains why hydrogen sulphide gas cannot be dried using concentrated sulphuric acid.

(iii) It reduces concentrated nitric acid to nitrogen dioxide (a reddish-brown gas), the other product being water.



(iv) Just like sulphur dioxide, it reduces dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$ in acidic medium to chromium(III) ions, Cr^{3+} . Hence, the gas also turns acidified potassium dichromate solution from orange to green; but in this case a yellow precipitate(due to the sulphur formed) is also deposited in the solution.

(v) Just like sulphur dioxide, it reduces permanganate ions, MnO_4^- in acidic medium to manganese(II) ions, Mn^{2+} . Hence, the gas also turns acidified potassium permanganate solution from purple to colourless; but in this case a yellow precipitate(due to the sulphur formed) is also deposited in the solution.

NEXT TOPIC IS 'ENTHALPY CHANGES'-NOTES TO BE SENT EARLY NEXT WEEK.