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).

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

Reagents:

Sodium sulphite and sulphuric acid

Conditions:

i. Dilute acid
ii. Room temperature

Experimental set up

The Drawing here is what we already have and in case you don’t have it, please contact me

Procedure:

Sodium sulphite is placed in a flat bottomed flask because it is a solid. The flask is fitted with a thistle and a delivery tube. Dilute sulphuric acid is added to sodium sulphite in the flask through a thistle funnel because it is a liquid. Effervescence (many bubbles) of occurs as sulphur dioxide gas is evolved.

\[ Na₂SO₃ (s) + H₂SO₄ → Na₂SO₄(aq) + SO₂(g) + H₂O(l) \]

The gas is passed through a wash bottle containing concentrated sulphuric acid to dry it because sulphurdioxide gas is acidic and cannot react with sulphuric acid.
The gas is finally collected by downward delivery (upward displacement of air) because the gas denser than air.

**Note:**

Sodium hydrogen sulphite can be used instead of sodium sulphite under the same conditions.

\[2 \text{NaHSO}_3(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + \text{SO}_2(g) + 2\text{H}_2\text{O}(l)\]

Dilute hydrochloric acid can be used instead of dilute sulphuric acid.

\[\text{Na}_2\text{SO}_3(s) + 2\text{HCl}(aq) \rightarrow 2\text{NaCl}(aq) + \text{SO}_2(g) + \text{H}_2\text{O}(l)\]

Or \[\text{NaHSO}_3(s) + \text{HCl}(aq) \rightarrow \text{NaCl}(aq) + \text{SO}_2(g) + \text{H}_2\text{O}(l)\]

**Preparation by the action of concentrated sulphuric acid on copper metal**

**Reagents:**

Copper and sulphuric acid

**Conditions:**

i. Concentrated acid

ii. Heat

**Experimental set up**

Some of us already have the Drawing Here But in case you don't it, this Drawing resembles the one in first case except that Dilute sulphuric acid is replaced with Concentrated sulphuric acid and Sodium sulphite with copper turnings.

Also, flat bottomed flask is replaced with round bottomed flask and heat is applied

**Procedure:**

Copper turnings are placed in a rounded bottomed flask because they are solids. The flask is fitted with a thistle funnel and delivery tube. Concentrated sulphuric acid is added to copper turnings through the thistle funnel because it is a liquid. The mixture is heated and effervescence of sulphur dioxide occurs.

\[\text{Cu}(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{CuSO}_4(aq) + \text{SO}_2(g) + \text{H}_2\text{O}(l)\]
The gas is passed through a wash bottle containing concentrated sulphuric acid to dry it because sulphur dioxide gas is acidic and cannot react with sulphuric acid.

The gas is finally collected by downward delivery (upward displacement of air) because the gas denser than air.

Note: The gas is not collected over water as it is very soluble in water.

Physical properties of sulphur dioxide

1. It is a poisonous gas
2. It is a colourless gas with a characteristic pungent smell
3. It is denser than air
4. It liquefies at -10°C 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

\[ H_2O(l) + SO_2 \rightleftharpoons H_2SO_3(aq) \]

Chemical properties of sulphur dioxide

1. Reaction with water

Sulphur dioxide readily reacts with water forming sulphurous acid.

\[ SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq) \]

The acid is responsible for the formation of acid rain hence sulphur dioxide is an atmospheric pollutant.

2. Sulphur dioxide as a reducing agent.

In the presence of water, sulphur dioxide is a powerful reducing agent. It reacts with water to form sulphurous acid which acts as a reducing agent.

a) When sulphur dioxide is bubbled through a solution of iron (III) salt, the iron (III) salt reduces to iron (II) salt. e.g. Sulphur dioxide reduces iron (III) sulphate to iron (II) sulphate and the sulphur dioxide is oxidized to sulphuric acid.

Observation

A brown solution turns green
Equation
\[ Fe_2(SO_4)_3(aq) + 5SO_2(g) + 2H_2O(l) \rightarrow 2FeSO_4(aq) + 2H_2SO_4(aq) \]
Or simply; \( Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq) \)

b) Bleaching action of sulphur dioxide gas.

When a blue or red flower or any other coloured substance is added to moist sulphur dioxide gas, the colour slowly gets bleached by reduction.

Sulphur dioxide is a bleaching gas and when it dissolves in water, it forms sulphurous acid.
\[ SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \]

The acid is a bleaching agent which removes colour by taking up oxygen from the colouring matter of the flower or any other coloured substances and forms sulphuric acid. The removal of oxygen from the coloured substance (dye) turns it into a colourless compound.

Observation

The dye turns from its colour to a colourless compound

Equation
\[ H_2SO_3(aq) + (dye + O) \rightarrow H_2SO_4(aq) + Colourless \, compound \]

Or
\[ SO_2(g) + H_2O(l) + (dye + O) \rightarrow H_2SO_4(aq) + Colourless \, compound \]

Note: Atmospheric oxygen may slowly oxidise the bleached substance back to the original of the substance. This explains why newspapers gradually yellow after some times.

c) Sulphur dioxide reduces concentrated nitric acid to form reddish-brown fumes of nitrogen dioxide and the mixture becomes warm. Sulphur dioxide gas is oxidized to sulphuric acid.
\[ SO_2(g) + 2HNO_3(aq) \rightarrow 2NO_2(g) + H_2SO_4(aq) \]

d) When sulphur dioxide is bubbled through coloured solutions of halogen, the solutions turn colourless. This is because sulphur dioxide reduces the halogens to hydrogen halides.
For example; When sulphur dioxide is bubbled through chlorine water (greenish-yellow liquid), a mixture of hydrochloric acid and sulphuric acid is obtained which appear colourless.

\[ H_2O(l) + SO_2(g) + Cl_2(aq) \rightarrow 2HCl(aq) + H_2SO_4(aq) \]

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

\[ H_2O(l) + SO_2(g) + Br_2(aq) \rightarrow 2HBr(aq) + H_2SO_4(aq) \]

Also, Iodine solution (dark-brown solution) is turned colourless as iodine is reduced to hydroiodic acid by sulphur dioxide.

\[ H_2O(l) + SO_2(g) + I_2(aq) \rightarrow 2HI(aq) + H_2SO_4(aq) \]

d) 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.

\[ K_2Cr_2O_7(aq) + H_2SO_4(aq) + 3SO_2(g) \rightarrow Cr_2(SO_4)_3(aq) + K_2SO_4(aq) + H_2O(l) \]

e) When sulphur dioxide is bubbled through acidified potassium manganate(VII) solution, the solution changes from purple to colourless. This is because sulphur dioxide reduces manganate (VII) ions to manganese (II) ions. The sulphur dioxide is itself oxidized to sulphuric acid.

\[ 2MnO_4^-(aq) + 2H_2O(aq) + 5SO_2(g) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 4H^+(aq) \]

**NB:** The reactions (d) and (e) are characteristic chemical tests for sulphur dioxide.

3. Sulphur dioxide as an oxidizing agent.

Sulphur dioxide acts as an oxidizing agent when it reacts with reducing agents more powerful than itself. For example;

a) Reaction with hydrogen sulphide.

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

\[ SO_2(g) + H_2S(aq) \rightarrow 3S(s) + 2H_2O(l) \]

b) Reaction with burning magnesium.
When a piece of magnesium ribbon is lowered into a gas jar of sulphur dioxide, it continues to burn with a bright white flame forming white powder of magnesium oxide and a yellow solid of sulphur. This is because sulphur dioxide oxidizes magnesium to magnesium oxide and itself is reduced to sulphur.

\[ 2Mg(s) + SO_2(g) \rightarrow 2MgO(s) + S(s) \]

**Question**: When burning magnesium is lowered into a jar of sulphur dioxide, it continues to burn with a bright white flame forming a white solid and yellow solid. Explain the observation.

*Burning magnesium produces sufficient heat that breaks the covalent bonds between sulphur and oxygen in sulphur dioxide gas thus setting the oxygen free which supports continuous burning of magnesium with a bright white flame forming a white solid of magnesium oxide and a yellow solid of sulphur.*

\[ 2Mg(s) + SO_2(g) \rightarrow 2MgO(s) + S(s) \]

4. **Reaction with oxygen**

Dry and pure sulphur dioxide react with oxygen in presence of vanadium (V) oxide or platinum catalyst at a temperature of 450°C-500°C and pressure of 200 atmospheres, sulphur trioxide is formed.

\[ 2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g) \]

5. **Reaction with alkalis**. Sulphur dioxide is neutralized by alkalis

i) When the alkali is in excess sulphite are formed.
\[ 2NaOH(aq) + SO_2(g) \rightarrow Na_2SO_3(aq) + H_2O(l) \]

ii) When the sulphur dioxide is in excess, hydrogen sulphites are formed and water is not a product in this case.
\[ NaOH(aq) + SO_2(g) \rightarrow NaHSO_3(aq) \]

**Question:**

*Excess sulphur dioxide gas was bubbled through sodium hydroxide solution that contained blue litmus paper.*

a) State what was observed.

*The blue litmus paper turned red*

b) Write an equation for the reaction that took place
\[ NaOH(aq) + SO_2(g) \rightarrow NaHSO_3(aq) \]

c) Explain your observation in a) above.

The sodium hydrogen sulphite formed is acidic salt which turns blue litmus red.

**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 stuff 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 \((Ca(HSO_3)_2)\) that makes wood pulp white in paper manufacture, used to bleach silk, straw, sponges.

**Questions:**

1. Sodium sulphite reacts with sulphuric acid to liberate gas Q

   a) Name the gas Q

   b) Write an equation for the reaction

   c) Name one reagent that can be used to identify gas Q

   d) Write an equation to show how Q reacts with a wet dye.

2. a) Describe with a well-labelled diagram how a dry sample of sulphur dioxide can be prepared in the laboratory.

   b) Write an equation for the reaction that takes place in (a)

   c) Describe a test that can be carried out to confirm the presence of sulphur dioxide.

   d) Excess sulphur dioxide was bubbled through a solution of sodium hydroxide. Write equation(s) for the reaction(s) that took place.

**SULPHITES** \((SO_3^{2-})\)

These are salts derived from sulphurous acid.
Test for sulphite

Procedure

To a solution of substance containing sulphite, 3 drops of barium nitrate solution are added 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.

\[ Ba^{2+}(aq) + SO_3^{2-}(aq) \rightarrow BaSO_3(s) \]

On addition of nitric acid

\[ BaSO_3(s) + 2HNO_3(aq) \rightarrow Ba(NO_3)_2(aq) + SO_2(g) + H_2O(l) \]

SULPHURIC ACID \((H_2SO_4)\)

Sulphuric acid is a mineral acid manufactured industrially by contact process.

It is a strong dibasic acid i.e. it dissolves in water and ionizes completely as below;

\[ H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) \]

A dibasic acid is one that produces two hydrogen ions per mole when dissolved in water.

MANUFACTURE OF SULPHURIC ACID BY CONTACT PROCESS.

Raw materials:

i. Sulphur
ii. Excess oxygen (excess air)

The manufacture of sulphuric acid by contact process involves four stages;

i. Production of sulphur dioxide
ii. Purification of gases
iii. Conversion of sulphur dioxide to sulphur trioxide
iv. Conversion of sulphur trioxide to sulphuric acid
Explanation/Description of Contact process.

Sulphur dioxide is produced by burning sulphur in excess air (excess oxygen from fractional distillation of air).

\[ S(s) + O_2(g) \rightarrow SO_2(g) \]

Sulphur dioxide and oxygen gases are cleaned and dried to remove any impurities such as arsenic compounds or dust that would poison the catalyst (i.e. make the catalyst ineffective).

Sulphur dioxide is then reacted with oxygen in presence of finely divided Vanadium (V) oxide catalyst at a temperature of 450°C-500°C under pressure of 200 atmospheres to form sulphur trioxide.

\[ 2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \]

Sulphur trioxide gas formed is then dissolved in concentrated sulphuric acid forming a fuming liquid called Oleum.

\[ H_2SO_4(l) + SO_3(g) \rightarrow H_2SO_7(l) \]

The oleum is then diluted by dissolving it in a correct amount of water to give ordinary concentrated sulphuric acid which is about 98% acid and 2% water.

\[ H_2SO_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l) \]

Note:

1) Platinum catalyst can be used instead of Vanadium (V) oxide catalyst but vanadium (V) oxide is preferred to Platinum because it is cheaper and cannot easily be poisoned like Platinum.

2) Sulphur trioxide is not dissolved in water directly because the reaction is too exothermic and the heat produced from the reaction vapourises the acid forming only tiny droplets of the acid leading to a spray of sulphuric acid which is dangerous to the workers in the factory.
SUMMARY OF THE CONTACT PROCESS

SULPHUR BURNER-
$S$ reacts with $O_2$ to form $SO_2$

CLEANERS AND DRIERS-
removes impurities and moisture from the gases

Sulphur

Air
(excess $O_2$)

98% Sulphuric acid

DILUTION CHAMBER-
the oleum is diluted with water to form concentrated sulphuric acid

ABSORPTION CHAMBER - Conc.
$H_2SO_4$ absorbs $SO_3$
forming oleum

Note: In the above process, the following conditions favour high/maximum yield of sulphur trioxide:

✓ Presence of a catalyst. The catalyst must be finely divided to increase the surface area for the reaction.
✓ Low temperature (450-500°C) as the forward reaction is exothermic (releases heat),
✓ High pressure as the forward reaction proceeds with a decrease in volume.
✓ High concentration of oxygen or sulphur dioxide.

PROPERTIES OF SULPHURIC ACID

Physical properties

✓ It is a colourless and odourless oily liquid
✓ Has a high affinity for water (hygroscopic) and that is why it is used as a drying agent.
✓ It has a density of 1.84 g cm$^{-3}$
✓ It decomposes at its boiling point which is 338°C forming sulphur trioxide.

$$H_2SO_4(l) \rightarrow H_2O(l) + SO_3(g)$$
Chemical properties

1. Sulphuric acid as an acid

Sulphuric acid reacts as a strong mineral acid (dibasic acid) when it is dilute. Examples include:

a) Reaction with metals

Dilute sulphuric acid reacts with metals that are more reactive than hydrogen in the reactivity series to produce a metal sulphate and hydrogen gas. E.g. Sodium, Magnesium, Calcium, Aluminium, Zinc.

\[ Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g) \]
\[ 2Al(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g) \]
\[ Zn(s) + 3H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g) \]

b) Reaction with bases and alkalis

Dilute sulphuric acid reacts with alkalis and bases to form a metal sulphate and water only. E.g.

\[ 2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) \]
\[ 2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l) \]
\[ Na_2O(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) \]

c) Reaction with metal carbonates and metal hydrogen carbonates

Dilute sulphuric acid reacts with metal carbonates and metal hydrogen carbonates to form a metal sulphate, carbon dioxide and water. E.g.

\[ Na_2CO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l) \]
\[ ZnCO_3(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + CO_2(g) + H_2O(l) \]

Observation for the above reactions:

A white powder dissolves with effervescence of a colourless forming a colourless solution.

\[ CuCO_3(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + CO_2(g) + H_2O(l) \]

Observation:

The green powder dissolves with effervescence of a colourless gas forming blue solution.
\[2\text{NaHCO}_3(\text{s}) + H_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{CO}_2(\text{g}) + H_2\text{O}(\text{l})\]

**Note:**

- The observation for the hydrogen carbonates is the same as that for carbonates.
- The reaction between calcium carbonate and calcium hydrogen carbonate with dilute sulphuric acid proceeds for a short time and then stops. This is because the reaction forms an insoluble calcium sulphate which forms a coating on the remaining calcium carbonate or calcium hydrogen carbonate hence stopping further reaction.

2. **Sulphuric acid as an oxidizing agent.**

When **hot and concentrated**, sulphuric acid is a powerful oxidizing agent. It oxidizes metals to their sulphates and non-metals to their oxides and is itself reduced.

a) **Reaction with copper.**

Hot concentrated sulphuric acid oxidizes copper metal to copper (II) sulphate and itself reduced to sulphur dioxide and water.

**Equation:**

\[\text{Cu(s)} + 2\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{CuSO}_4(\text{aq}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})\]

**Observation:**

The brown solid dissolves with effervescence of a colourless gas forming a blue solution.

Other metals that are oxidised by hot concentrated sulphuric acid include; copper, zinc, silver and aluminium which are oxidised to the corresponding metal sulphates.

**Equations:**

\[\text{Zn(s)} + 2\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})\]
\[2\text{Ag(s)} + 2\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{Ag}_2\text{SO}_4(\text{aq}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})\]
\[2\text{Al(s)} + 6\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{Al}_2(\text{SO}_4)_3(\text{aq}) + 3\text{SO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})\]

b) **Reaction with non-metals**

Hot concentrated sulphuric acid slowly oxidizes carbon to carbon dioxide and sulphur to sulphur dioxide and itself is reduced to sulphur dioxide and water.
**Equations:**

\[ C(s) + 2H_2SO_4(l) \rightarrow CO_2(g) + SO_2(g) + 2H_2O(g) \]

\[ S(g) + 2H_2SO_4(aq) \rightarrow 3SO_2(g) + 2H_2O(l) \]

It also oxidizes hydrogen sulphide to yellow deposits of sulphur and itself is reduced to sulphur dioxide and water.

\[ H_2S(g) + H_2SO_4(l) \rightarrow S(s) + SO_2(g) + 2H_2O(l) \]

3. Sulphuric acid as a dehydrating agent.

When **concentrated**, sulphuric acid is a very strong dehydrating agent. This is because concentrated sulphuric acid has strong affinity for water.

The reaction between concentrated sulphuric acid and water is highly exothermic, thus concentrated sulphuric acid is diluted by adding the acid to water but not water to acid.

a) **Reaction with hydrated copper (II) sulphate** \((CuSO_4 \cdot 5H_2O)\)

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

\[ CuSO_4 \cdot 5H_2O(s) \xrightarrow{conc. H_2SO_4} CuSO_4(s) + 5H_2O(g) \]

b) **Reaction with sugar** \((C_{12}H_{22}O_{11})\)

When cold concentrated sulphuric acid is added to sugar crystals, the white/brown crystals turn black, swell up forming a black porous mass of carbon. A lot of heat and steam are given off.

\[ C_{12}H_{22}O_{11}(s) \xrightarrow{conc. H_2SO_4} 12C(s) + 11H_2O(g) + Heat \]

c) **Reaction with ethanol** \((C_2H_5OH)\)

Excess concentrated sulphuric acid dehydrates ethanol at a temperature of 170°C forming ethene gas.

\[ C_2H_5OH(l) \xrightarrow{conc. H_2SO_4, 170^\circ C} C_2H_4(g) + H_2O(g) \]

d) **Reaction with Oxalic acid/ ethanedioic** \((H_2C_2O_4)\)

Concentrated sulphuric acid dehydrates oxalic acid when heated to form carbon monoxide gas, carbon dioxide gas and water.
\[
H_2C_2O_4(aq) \xrightarrow{\text{Conc. } H_2SO_4, \text{ heat}} CO_2 (g) + CO(g) + H_2O(g)
\]

**Question:** Concentrated sulphuric acid was added to crystals of oxalic acid and the mixture was heated.

a) State what was observed

b) State gaseous product(s) was/were passed over heated lead (II) oxide.
   i) State what was observed
   ii) Write an equation for the reaction that took place in (b).

**Solution:**

a) The crystals dissolved with effervescence/bubbles of a colourless gas

b) Carbon monoxide and carbon dioxide
   i) The reddish-brown solid turns grey
   ii) \( \text{PbO}(s) + CO(g) \rightarrow \text{Pb}(s) + CO_2(g) \)

e) Reaction with paper/cloth

Concentrated sulphuric acid dehydrates paper or cloth to a black solid. The products of this reaction are carbon and water. The reaction is faster when the material is wet than it is dry.

4. Sulphuric acid as a drying agent.

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

Gases such as carbon dioxide, sulphur dioxide etc are dried by bubbling them through concentrated sulphuric acid. For basic gases like ammonia, another drying agent is used.

**Uses of sulphuric acid**

✓ Used in the manufacture of fertilizers like ammonium sulphate.
✓ Making of paints and pigments
✓ Manufacture of detergents such as Omo, Nomi etc
✓ Production of other chemicals such as metallic sulphates, hydrochloric acid, hydrofluoric acid and plastics.
✓ It is used in car batteries and accumulators as an electrolyte
✓ Extraction of metals and metal manufacturing including pickling to clean metallic surfaces.
✓ It is used as a drying agent.
With nitric acid, it is used to make dyes and explosives.

**SULPHATES**

**Sulphates** are compounds formed when the ionisable hydrogen ions in sulphuric acid are replaced by metallic ion or ammonium ion. e.g. ZnSO₄, Al₂(SO₄)₃, (NH₄)₂SO₄ e.t.c.

**Properties of sulphates**

1. **Solubility.**
   All sulphates are soluble in water except Barium sulphate (BaSO₄), lead (II) sulphate (PbSO₄), and calcium sulphate (CaSO₄) which is sparingly soluble in water.

2. **Effect of heat on sulphates.**
   Most sulphates are stable and when heated gently do not decompose. However, on strong heating some decompose to form sulphur trioxide and metal oxides.

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   Their sulphates do not decompose on heating because they are stable

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   Their sulphates decompose oh heating to form metal oxides and sulphur trioxide gas except Iron (II) sulphate. e.g

   ZnSO₄(s) → ZnO(s) + SO₃(g)
   CuSO₄(s) → CuO(s) + SO₃(g)

**Question:** State what is observed when lead (II) sulphate is heated strongly until no further change.

**Solution:** The white solid decomposes with evolution of white fumes forming a reddish-brown solid that turns yellow on cooling.

**Note:** Iron (II) sulphate decomposes on heating to form Iron (III) oxide which is brown, sulphur dioxide gas and sulphur trioxide gas

2FeSO₄(s) → Fe₂O₃(s) + SO₂(g) + SO₃(g)
Effect of heat on hydrated sulphates.

Hydrated iron (II) sulphate and hydrated copper (II) sulphate decompose on heating to give off water of crystallisation and anhydrous sulphates. On further heating, the anhydrous sulphates also decompose. i.e.

(i) **Hydrated Iron (II) sulphate**

**Observation:**

The green crystals decompose to a white powder/solid and a white condensate. The white powder/solid turns reddish-brown on further heating with evolution of white fumes.

**Equations:**

\[ \text{FeSO}_4 \cdot 7\text{H}_2\text{O}(s) \xrightarrow{\Delta} \text{FeSO}_4(s) + 7\text{H}_2\text{O}(l) \]

\[ 2\text{FeSO}_4(s) \xrightarrow{\Delta} \text{Fe}_2\text{O}_3(s) + SO_2(g) + SO_3(g) \]

(ii) **Hydrated copper (II) sulphate**

**Observation:**

The blue crystals decompose to a white powder/solid and a white condensate. The white powder/solid turns black on further heating with evolution of white fumes.

**Equation:**

\[ \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \xrightarrow{\Delta} \text{CuSO}_4(s) + 5\text{H}_2\text{O}(l) \]

\[ \text{CuSO}_4(s) \xrightarrow{\Delta} \text{CuO}(s) + SO_3(g) \]

**Overall:**

\[ \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \xrightarrow{\Delta} \text{CuO}(s) + SO_3(g) + 5\text{H}_2\text{O}(l) \]

**Note:** Ammonium sulphate decomposes to sulphuric acid and ammonia gas.

\[ (\text{NH}_4)_2\text{SO}_4(s) \xrightarrow{\Delta} 2\text{NH}_3(g) + SO_3(g) + \text{H}_2\text{O}(l) \]
TEST OF SULPHURIC ACID AND SOLUBLE SULPHATES.

1. **Reagent**: Dilute nitric acid and barium nitrate solution (or dilute hydrochloric acid and barium chloride)
   
   **Procedure**: To an aqueous solution of the suspected sulphate or sulphuric acid, add dilute nitric acid and barium nitrate solution (dilute hydrochloric acid and barium chloride can also be used).
   
   **Observation**: A white precipitate.
   
   **Equation**: \( \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{BaSO}_4(s) \)

   **Note**: Dilute nitric acid or dilute hydrochloric acid is used to prevent the precipitation of carbonates or sulphites. i.e.

   \( \text{Ba}^{2+}(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{BaCO}_3(s) \)

   \( \text{Ba}^{2+}(aq) + \text{SO}_3^{2-}(aq) \rightarrow \text{BaSO}_3(s) \)

2. **Reagent**: Dilute nitric acid and lead (II) nitrate solution.
   
   **Procedure**: To an aqueous solution of the suspected sulphate or sulphuric acid, add dilute nitric acid and lead (II) nitrate solution and then warm.
   
   **Observation**: A white precipitate insoluble on warming.
   
   **Equation**: \( \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{PbSO}_4(s) \)

   **Note**: The purpose of warming is to dissolve any insoluble lead (II) chloride.

**Question**: Study the following tests and observations. Give the anions that are likely to be present in the solutions A, B, C, D, E, F and G.

a) Barium nitrate solution was added to solution A. A white precipitate was formed.

b) Barium nitrate solution was added to solution B followed by dilute nitric acid. A white precipitate was formed and it dissolved in the acid with effervescence of a colourless gas.

c) Dilute hydrochloric acid was added to solution C followed by barium chloride solution. A white precipitate was observed.

d) Lead (II) nitrate was added to solution D. A white precipitate was formed.

e) Dilute nitric acid was added to solution E followed by lead (II) nitrate solution. A white precipitate was formed.

f) Dilute nitric acid was added to F followed by lead (II) nitrate solution and the mixture warmed. A white precipitate was formed and dissolved on warming to form a colourless solution. With G, a white precipitate insoluble on warming was formed.
Name the reagents that can be used to distinguish pairs of ions. In each case state what is observed when each member of the pair is separately treated with the reagent you have named.

a) $SO_3^{2-}$ and $SO_4^{2-}$
b) $CO_3^{2-}$ and $SO_4^{2-}$
c) $Cl^-$ and $SO_4^{2-}$

**HYDROGEN SULPHIDE GAS ($H_2S$)**

**Laboratory preparation of hydrogen sulphide gas**

The gas is normally prepared in a laboratory by reacting dilute hydrochloric acid.

**Experimental set up**

![Experimental setup diagram]

**Procedure**

Solid iron (II) sulphide is placed in a flat bottomed flask fitted with a delivery tube and the apparatus is arranged as shown above.

Dilute hydrochloric acid is carefully added through the thistle/dropping funnel because it is a liquid. Effervescence of a colourless gas occurs and hydrogen sulphide gas is produced according to the equation.

$$FeS(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2S(g)$$

The gas is then collected over warm water because it is less soluble in warm/hot water.
Note:

- If the gas is required dry, it is passed through a U-tube containing phosphorous pentaoxide ($P_2O_5$) or silicon (IV) oxide ($SiO_2$) and is then collected by downward delivery since it is denser than air.
- Concentrated sulphuric acid and anhydrous calcium chloride should not be used to dry the gas because they react with hydrogen sulphide.
  
  $$H_2S(g) + H_2SO_4(l) \rightarrow S(s) + SO_2(g) + 2H_2O(l)$$
  
  $$CaCl_2(s) + H_2S(g) \rightarrow CaS(s) + 2HCl(g)$$
- Hydrogen sulphide gas can also be prepared by using dilute sulphuric acid with iron (II) sulphide and the reaction also occurs at room temperature.
  
  $$FeS(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2S(g)$$
- Hydrogen sulphide gas must be prepared in a fume cupboard because it is very poisonous.

**PROPERTIES OF HYDROGEN SULPHIDE GAS**

**Physical properties**

- It is a colourless gas.
- It has a strong repulsive characteristic smell of a rotten egg.
- It is very poisonous.
- It is slightly denser than air.
- It can be liquefied under high pressure.
- It is fairly soluble in water forming a weak acidic solution. (i.e. it turns wet blue litmus paper red)

**Chemical properties**

1. Hydrogen sulphide as a reducing agent.

i) Reaction with concentrated nitric acid.

Hydrogen sulphide gas reduces concentrated nitric acid to nitrogen dioxide gas and itself oxidised to sulphur.

**Equation:**

$$H_2S(g) + 2HNO_3(aq) \rightarrow S(s) + 2NO_2(g)$$

**Observation:**

A colourless gas dissolves with effervescence of reddish brown fumes or gas forming yellow deposits in a colourless.
ii) Reaction with concentrated sulphuric acid.

Hydrogen sulphide gas reduces concentrated sulphuric acid to sulphur dioxide gas and itself is oxidised to yellow deposits of sulphur.

Equation:

\[ H_2S(g) + H_2SO_4(l) \rightarrow S(s) + SO_2(g) + 2H_2O(l) \]

Observation:

A colourless gas dissolves with effervescence or bubbles of a colourless gas forming yellow deposits in a colourless liquid.

iii) Reaction with iron (III)chloride solution.

Iron (III)chloride solution is reduced by hydrogen sulphide gas to iron (II) chloride solution and the gas is oxidised to yellow deposits of sulphur.

Equation:

\[ H_2S(g) + 2FeCl_3(aq) \rightarrow S(s) + 2FeCl_2(aq) + 2HCl(aq) \]

Ionic equation:

\[ H_2S(g) + 2Fe^{3+}(aq) \rightarrow S(s) + 2Fe^{2+}(aq) + 2H^+(aq) \]

Observation:

The brown solution turns green with formation of yellow deposits.

iv) Reaction with acidified potassium manganate (VII) solution.

Hydrogen sulphide gas reduces acidified potassium manganate (VII) solution to manganese (II) ions.

Equation:

\[ 2MnO_4^-(aq) + 6H^+(aq) + 5H_2S(g) \rightarrow 2Mn^{2+}(aq) + 5S(s) + 8H_2O(l) \]

Observation:

The purple solution turns colourless with formation of yellow deposits.

v) Reaction with acidified potassium dichromate solution.

Hydrogen sulphide reduces acidified potassium dichromate solution to chromium (III) ions and itself is oxidised to sulphur.

Equation:
\[ Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3H_2S(g) \rightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O(l) \]

**Observation:**

The orange solution turns green and yellow deposits are formed

**vi) Reaction with hydrogen peroxide.**

Hydrogen sulphide reduces hydrogen peroxide to water and itself is oxidised to sulphur.

**Equation:**

\[ H_2S(g) + H_2O_2(l) \rightarrow S(s) + 2H_2O(l) \]

**Observation:**

Yellow deposits are formed

**vii) Reaction with sulphur dioxide gas.**

Hydrogen sulphide gas is a stronger reducing agent than sulphur dioxide gas. It reduces sulphur dioxide gas to sulphur.

**Equation:**

\[ 2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l) \]

**Observations:**

Yellow deposits are formed.

**viii) Reaction with bromine water.**

Hydrogen sulphide reduces bromine water to hydrobromic acid and itself is oxidised to sulphur.

**Equation:**

\[ H_2S(g) + Br_2(aq) \rightarrow S(s) + 2HBr(aq) \]

**Observation:**

The reddish-brown solution turns colourless and yellow deposits are formed.

**ix) Reaction with chlorine water.**

Hydrogen sulphide reduces chlorine water to hydrochloric acid and itself is oxidised to sulphur.
Equation:
\[ H_2S(g) + Cl_2(aq) \rightarrow S(s) + 2HCl(aq) \]

Observation:
The greenish-yellow solution turns colourless and yellow deposits are formed.

2. Reaction with oxygen gas.
i) In plentiful supply of oxygen, hydrogen sulphide burns with a blue flame forming sulphur dioxide gas and steam.

Equation:
\[ 2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g) \]

ii) In limited supply of oxygen, hydrogen sulphide burns forming steam and sulphur.

Equation:
\[ 2H_2S(g) + O_2(g) \rightarrow 2S(s) + 2H_2O(g) \]

Observation:
Yellow residue and white fumes are formed.

3. Reaction with water.

Hydrogen sulphide sparingly dissolves in water to form an acidic solution.

Equation:
\[ H_2S(g) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq) \]

It is hydroxonium ions that are responsible for the acidity of hydrogen sulphide gas.

4. Reaction with alkalis.

As a weak acid, hydrogen sulphide in solution reacts with alkalis to form sulphides and water only. e.g.

\[ 2NaOH(aq) + H_2S(aq) \rightarrow Na_2S(aq) + 2H_2O(l) \]

\[ Mg(OH)_2(aq) + H_2S(g) \rightarrow MgS(aq) + 2H_2O(l) \]

Note:
With excess of hydrogen sulphide, an acid salt known as hydrogen sulphide salt is formed. e.g.

\[ Na_2S(aq) + H_2S(aq) \rightarrow 2NaHS(aq) \]

5. Reacting with salts of metals.

Hydrogen sulphide can precipitate insoluble sulphides of copper and lead only by reacting with solutions of their salts. i.e.

\[ CuSO_4(aq) + H_2S(g) \rightarrow CuS(s) + H_2SO_4(aq) \]

**Observation:**

The blue solution turns colourless and dark-brown deposits are formed.

\[ Pb(NO_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2HNO_3(aq) \]

\[ Pb(NO_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2HNO_3(aq) \]

**Observation:**

A black precipitate was formed.

**TEST FOR HYDROGEN SULPHIDE GAS:**

1. Hydrogen sulphide can easily be detected by its **strong repulsive smell of rotten eggs**. (Physical test)

2. a) When hydrogen sulphide is passed through a solution of Lead(II)nitrate, a **black precipitate** of lead (II) sulphide is observed.

**Equation:**

\[ Pb(NO_3)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2HNO_3(aq) \]

b) When hydrogen sulphide is passed through a solution of Lead (II) ethanoate, a **black precipitate** of lead (II) sulphide is observed.

**Equation:**

\[ (CH_3COO)_2Pb(aq) + H2S(g) \rightarrow PbS(s) + 2CH_3COOH(aq) \]
Questions:

1. **UNEBA 2015 P/2 Qn 2.**
   a) A mixture of iron fillings and sulphur was heated strongly. Write the equation for the reaction that took place
   b) Dilute sulphuric acid was added to the product in above
      i) State what was observed
      ii) Write equation for the reaction that took place
   c) One of the substance formed in (b) pollutes air.
      i) Identify the substance.
      ii) Give one reason why the substance pollutes air.

2. a) Explain how sulphur can be extracted by Frasch process. (No diagram is required)
   b) Write an equation to show sulphur can react.
      i) Oxygen
      ii) Charcoal
      iii) Sulphuric acid
   c) Concentrated nitric acid was added to sulphur powder in a porcelain dish and the mixture warmed. State what was observed and write an equation for the reaction that took place.
   d) The mixture in (c) was diluted with some water, filtered and the filtrate was added acidified barium chloride solution.
      i) State what was observed
      ii) Write an ionic equation for the reaction between the filtrate and barium chloride solution.

3. **UNEBA 2014 P/2 Qn 11.**