

11

Sulphuric Acid

SYLLABUS

Sulphuric Acid : Its behaviour as an acid when dilute. As an oxidizing agent when concentrated – oxidation of carbon and sulphur; as a dehydrating agent – dehydration of sugar and copper (II) sulphate crystals; its non-volatile nature.

Manufacture by Contact process (reference only). Detail of the process to be avoided.

Its behaviour as an acid when dilute – reaction with metal, metal oxide, metal hydroxide, metal carbonate, metal bicarbonate, metal sulphite, metal sulphide.

Concentrated sulphuric acid as an oxidizing agent – the oxidation of carbon and sulphur.

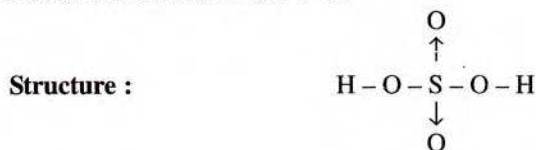
Concentrated sulphuric acid as a dehydrating agent – (a) the dehydration of sugar (b) Copper (II) sulphate crystals.

Non-volatile nature of sulphuric acid – reaction with sodium or potassium chloride and sodium or potassium nitrate.

SULPHURIC ACID

Molecular formula : H_2SO_4

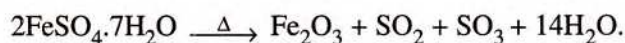
Relative molecular mass : 98



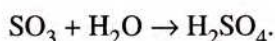
11.1 INTRODUCTION

Sulphuric acid is rightly called the 'King of Chemicals' because there is no other manufactured compound which is used by such a large number of key industries. It has been known for a long time.

In the later Middle Ages, it was obtained as an oily viscous liquid by heating crystals of green vitriol, and was, therefore, known by the name of **oil of vitriol**.



The sulphur trioxide evolved gets dissolved in water forming sulphuric acid.



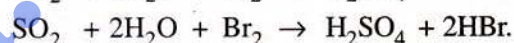
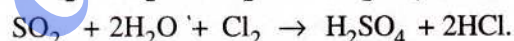
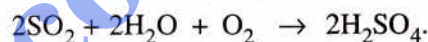
11.2 OCCURRENCE

In the **free state**, it is found in certain mineral springs and is formed by the action of water on certain sulphides.

In the **combined state**, as **Barytes** BaSO_4 , **Gypsum** $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and **Kieserite** $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, etc.

11.3 PREPARATION OF SULPHURIC ACID

- (1) By **oxidation of an aqueous solution of sulphur dioxide** with oxygen, chlorine or bromine.

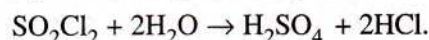


The colour of Cl_2 and Br_2 fades.

- (2) **Sulphur with conc. nitric acid**



- (3) By dissolving sulphuryl chloride in water



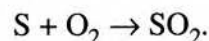
11.4 MANUFACTURE OF SULPHURIC ACID (CONTACT PROCESS)

The various steps in the Contact process are as follows :

- (1) **Production of sulphur dioxide** : Sulphur dioxide is produced by roasting metallic sulphides in air
- $$4\text{FeS}_2 \text{ (Iron pyrites)} + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$$

OR

by burning Louisiana sulphur (99.5% pure) in purified air.



- (2) **Purification of gases** : The mixture of sulphur dioxide and air contains various impurities which must be removed, otherwise the catalyst loses its efficiency.

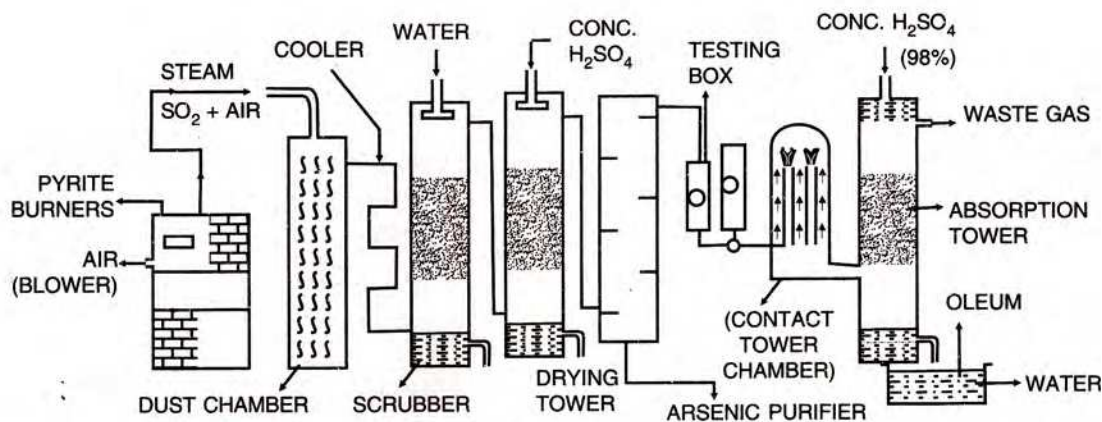
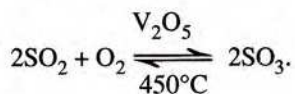


Fig. 11.1. Contact process for the manufacture of H_2SO_4 acid

Parts of the Plant	Function
Blower	For passage of purified air or oxygen.
Sulphur or iron pyrite burners	For production of sulphur dioxide by burning sulphur or iron pyrites.
Dusting chamber	For removal of dust particles by downward blow of steam.
Cooling pipes	For cooling the gases by passage through isolated pipes.
Scrubbing tower	For further removal of impurities and dust particles by downward spray of water.
Drying tower	For drying moist gases by downward spray of conc. H_2SO_4 .
Arsenic purifier	For removing arsenic oxide by passage over ferric hydroxide.
Testing box	For testing the purity of the gases by passage of light through a darkened box.
Contact tower	For catalytic oxidation of SO_2 to SO_3 by passage of sulphur dioxide and oxygen through iron tower packed with vanadium pentoxide catalyst initially heated to $450^\circ C$.
Absorption tower	For absorption of sulphur trioxide vapours by descending stream of conc. H_2SO_4 [98%].
Dilution tank	For dilution of oleum by flow of required amount of water.

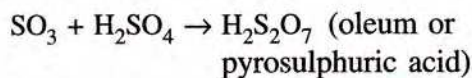
The mixture is passed through a purifier called **electric precipitator**, consisting of a chamber with wires at high electric potential. The electric charge attracts solid particles which are removed. The mixture is then led to a **water scrubber** where it is completely freed from dust particles. It is then dried by a spray of concentrated sulphuric acid in another chamber. It then goes into the **arsenic purifier** where every trace of arsenic oxide is removed (Fig. 11.1).

(3) **Catalytic oxidation of sulphur dioxide.** The clean dried gaseous mixture of sulphur dioxide and air is passed through **contact tower** loosely packed with vanadium pentoxide or platinum on perforated shelves. The catalyst is placed in vertical iron pipes inside a cylindrical iron tower called the **converter**. Here, the preheated mixture of sulphur dioxide and air (oxygen) on passing through catalyst pipes forms sulphur trioxide.

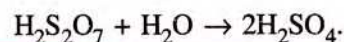


Since the reaction is highly exothermic, the catalyst is heated only in the beginning to about $450^\circ C$. This temperature is maintained by the heat evolved during the reaction.

(4) **Absorption of sulphur trioxide in sulphuric acid.** The gas is cooled in a heat exchanger and is then absorbed in **absorption tower** in concentrated sulphuric acid (98%).



(5) **Dilution of oleum to obtain sulphuric acid.** It is diluted in **dilution tank** by adding calculated amount of water to obtain sulphuric acid of the desired strength.



Since sulphur trioxide does not dissolve in water satisfactorily and it gives a lot of heat and forms misty droplets of sulphuric acid, it is not directly absorbed by water.

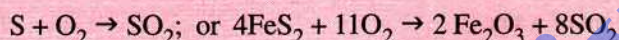
Favourable conditions for the conversion of SO₂ to SO₃ (contact process)

- (i) **Exothermic reactions are favoured at low temperature** : The temperature should be as low as possible. The yield has been found to be maximum at about 410-450°C.
- (ii) **High pressure** : High pressure favours the reaction because the product formed has less volume than reactant. But the acid-resistant towers which are able to withstand high pressure are difficult to build. Hence the pressure of 1 - 2 atmosphere is used.
- (iii) **Excess of oxygen** : This increases the production of sulphur trioxide.
- (iv) **A suitable catalyst** : Platinum is more efficient as a catalyst than vanadium pentoxide (V₂O₅), but platinum is more expensive and also it easily gets poisoned by impurities like arsenic (III) oxide.

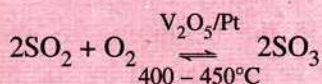
Vanadium pentoxide is used as a catalyst.

SUMMARY OF CONTACT PROCESS

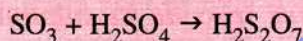
Formation of Sulphur dioxide :



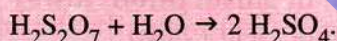
Conversion of purified SO₂ to SO₃ :



Conversion of sulphur trioxide into oleum :



Dilution of oleum :



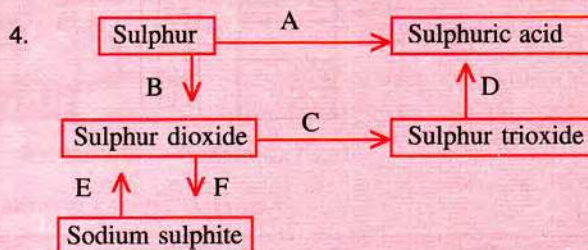
Intext Questions

1. Comment, sulphuric acid is referred to as :
(a) King of chemicals, (b) Oil of vitriol.
2. Sulphuric acid is manufactured by Contact process.
(a) Give two balanced equations to obtain SO₂ in this process,
(b) Give the conditions for the oxidation of SO₂,
(c) Why H₂SO₄ is not obtained by directly reacting SO₃ with water ?
(d) Name the chemical used to dissolve SO₃ and also

name the product formed. Give all the main reactions of this process.

(e) Name a gas that can be oxidized to sulphur.

3. Why the impurity of arsenic oxide must be removed before passing the mixture of SO₂ and air through the catalytic chamber ?



- (a) Name the catalyst which helps in the conversion of sulphur dioxide to sulphur trioxide in step C.
- (b) In the Contact process for the manufacture of sulphuric acid, sulphur trioxide is not converted to sulphuric acid by reacting it with water. Instead a two-steps procedure is used. Write the equations for the two steps involved in D.
- (c) What type of substance will liberate sulphur dioxide from sodium sulphite in step E ?
- (d) Write the equation for the reaction by which sulphur dioxide is converted to sodium sulphite in step F.

11.5 PROPERTIES OF SULPHURIC ACID

11.5.1 Physical properties

1. Colour	Colourless.
2. Odour	Odourless.
3. Taste	Slightly sour in taste.
4. Nature	Dense, oily, hygroscopic liquid. It absorbs moisture, so H ₂ SO ₄ should always be kept stoppered.
5. Density	Pure acid : 1.85 g/cc.
6. Boiling point	338°C.
7. Melting point	Pure sulphuric acid freezes to colourless crystals at 10.4°C.
8. Solubility	Soluble in water in all proportions.
9. Conductivity	Pure acid : Almost a non-conductor of electricity. Dilute acid : Good conductor of electricity.
10. Constant boiling mixture	It forms a constant boiling mixture at 338°C containing 98.5% of the acid.
11. Physiological nature	Concentrated acid is highly corrosive in nature and chars the skin black.

11.5.2 Chemical properties

Pure (100% H_2SO_4) hydrogen sulphate is not an acid as it does not ionise.

Sulphuric acid when dissolved in water form hydronium ion and so shows acidic properties.



It ionises in two stages and thus it is a **dibasic acid**. The chemical properties of sulphuric acid depend on whether the acid is dilute or concentrated.

Dilution of H_2SO_4 : Water is never poured on acid to dilute it as large amount of heat is evolved which changes poured water to steam. The steam so formed causes spurting of acid which can cause burn injuries, so dilution is done by pouring acid on a given amount of water in a controlled manner by continuous stirring, else acid being heavier will settle down. The evolved heat is dissipated in the water itself and hence the spurting of the acid is minimized.

(a) Properties of dilute sulphuric acid

Acidic property :

- (1) Dilute sulphuric acid reacts **with metals, which are above** hydrogen in the activity series to form metallic sulphate and hydrogen at ordinary temperature.

Active metal	+	Acid	→	Metal sulphate	+	Hydrogen
Mg	+	H_2SO_4	→	MgSO_4	+	$\text{H}_2 \uparrow$
Zn	+	H_2SO_4	→	ZnSO_4	+	$\text{H}_2 \uparrow$
Fe	+	H_2SO_4	→	FeSO_4	+	$\text{H}_2 \uparrow$

Note : Noble metals like gold and platinum do not react with H_2SO_4 under any condition.

- (2) It **neutralises** bases (oxides and hydroxides) to form salts and water.

Base/Alkali	+	Acid	→	Salt	+	Water
CuO	+	H_2SO_4	→	CuSO_4	+	H_2O
NaOH	+	H_2SO_4	→	NaHSO_4	+	H_2O
2NaOH	+	H_2SO_4	→	Na_2SO_4	+	$2\text{H}_2\text{O}$
FeO	+	H_2SO_4	→	FeSO_4	+	H_2O

- (3) It liberates carbon dioxide from metallic **carbonates** and **bicarbonates**.

Carbonate/ bicarbonate	+	Acid	→	Salt	+	Water	+	Carbon dioxide
Na_2CO_3	+	H_2SO_4	→	Na_2SO_4	+	H_2O	+	$\text{CO}_2 \uparrow$
2NaHCO_3	+	H_2SO_4	→	Na_2SO_4	+	$2\text{H}_2\text{O}$	+	$2\text{CO}_2 \uparrow$
2KHCO_3	+	H_2SO_4	→	K_2SO_4	+	$2\text{H}_2\text{O}$	+	$2\text{CO}_2 \uparrow$

- (4) It evolves hydrogen sulphide from metal **sulphides**.

Metal sulphide	+	Acid	→	Salt	+	Hydrogen sulphide
Na_2S	+	H_2SO_4	→	Na_2SO_4	+	$\text{H}_2\text{S} \uparrow$
FeS	+	H_2SO_4	→	FeSO_4	+	$\text{H}_2\text{S} \uparrow$
ZnS	+	H_2SO_4	→	ZnSO_4	+	$\text{H}_2\text{S} \uparrow$

- (5) It evolves sulphur dioxide from **sulphites** and hydrogen sulphites (bisulphites).

Sulphite / bisulphites	+	Acid	→	Salt	+	Water	+	Sulphur dioxide
Na_2SO_3	+	H_2SO_4	→	Na_2SO_4	+	H_2O	+	$\text{SO}_2 \uparrow$
2NaHSO_3	+	H_2SO_4	→	Na_2SO_4	+	$2\text{H}_2\text{O}$	+	$2\text{SO}_2 \uparrow$

Note : Sulphur dioxide is poisonous and, is therefore, responsible for polluting environment.

It adversely affects the human health and vegetation.

(b) Properties of concentrated sulphuric acid

(1) Non-volatile nature

Concentrated sulphuric acid has a high boiling point (338°C) and so, it is considered to be a non-volatile acid. It is, therefore, used for preparing volatile acids like hydrochloric acid, nitric acid and acetic acid from their salts by double decomposition.

Salt of volatile acid	+	Acid (conc.)	→	Acid salt	+	Volatile acid
NaCl	+	H_2SO_4	→	NaHSO_4	+	HCl
KCl	+	H_2SO_4	→	KHSO_4	+	HCl
NaNO_3	+	H_2SO_4	→	NaHSO_4	+	HNO_3
KNO_3	+	H_2SO_4	→	KHSO_4	+	HNO_3
CH_3COONa Sodium acetate	+	H_2SO_4	→	NaHSO_4	+	CH_3COOH Acetic acid

Difference between dilute and conc. sulphuric acid

Dilute	Concentrated
1. It ionises to great extent so behaves as strong acid.	1. It is a weak acid
2. Strong electrolyte.	2. Weak electrolyte.
3. It cannot act as an oxidising agent.	3. Conc. H_2SO_4 act as an oxidising agent.
4. Dilute sulphuric acid cannot be used as a drying or dehydrating agent.	4. It is used to dry gases like HCl and even dehydrate substances like $CuSO_4 \cdot 5H_2O$

(4) Preparation of insoluble sulphates

Sulphuric acid precipitates the insoluble sulphates of lead, barium and calcium from the solutions of their salts.

Soluble salt	+ Acid	→	Insoluble salt	+ Acid
$Pb(NO_3)_2$	$+ H_2SO_4$	→	$PbSO_4 \downarrow$	$+ 2HNO_3$
$BaCl_2$	$+ H_2SO_4$	→	$BaSO_4 \downarrow$	$+ 2HCl$

11.6 USES OF SULPHURIC ACID

1. It is used in the preparation of :

(a) Halogens, (b) Carbon monoxide, (c) Carbon dioxide, (d) Hydrogen, (e) Sulphur dioxide.

2. Metallurgy

(i) Extraction

Its reaction with metallic compounds gives sulphates which on electrolysis give the metal in the pure form.

(ii) Pickling metals

Removes metallic impurities like oxides and carbonates from the surface of metals before galvanizing.

3. In lead accumulators

It undergoes electrolysis in the aqueous state.

4. Oil refining

Sulphuric acid is used to remove harmful impurities in purification of oil products, e.g., petrol, kerosene and lubricants.

5. Industrial uses : in the manufacture of :

(i) Fertilizers like

(a) **Ammonium sulphate** $[(NH_4)_2SO_4]$,

(b) **Superphosphate of lime** $[Ca(H_2PO_4)_2 + CaSO_4]$,

(ii) Dyes, drugs

(a) **Artificial fibres :**

[I] Rayon, [II] Nylon.

(b) **Dyes, drugs** [from coal tar derivatives].

(iii) Explosives like

(a) **Tri-nitro toluene** [T.N.T.],

(b) **Picric acid**,

(c) **Tri-nitro glycerine** $[C_3H_5O_3(NO_2)_3]$.

(iv) Acids like

(a) **Nitric acid** $[HNO_3]$,

(b) **Hydrochloric acid** $[HCl]$,

(c) **Phosphoric acid** $[H_3PO_4]$,

(d) **Acetic acid** $[CH_3COOH]$.

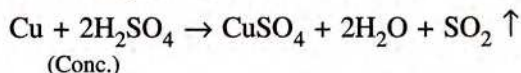
(v) Compounds like

(a) **Sodium sulphate** [glass industry],

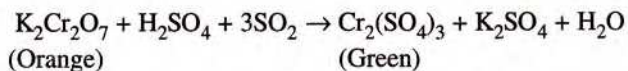
(b) **Ferrous sulphate** [ink industry].

11.7 TESTS FOR SULPHURIC ACID AND SULPHATES

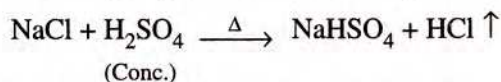
- (1) **Conc. sulphuric acid** on heating with copper evolves sulphur dioxide.



Sulphur dioxide turns *acidified potassium dichromate solution green* (Reducing property of SO_2).

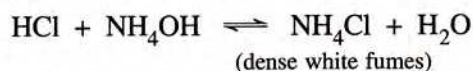


- (2) **Conc. sulphuric acid** on heating with NaCl evolves pungent fumes of HCl gas.

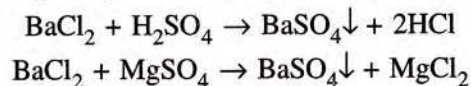


HCl gas gives dense white fumes of ammonium

chloride, with a glass rod dipped in ammonium hydroxide.



- (3) When barium chloride solution is added to sulphuric acid or any soluble metal sulphate, **white precipitate** of barium sulphate is formed.



The **white precipitate of barium sulphate is insoluble in any mineral acid like hydrochloric acid or nitric acid.**

Note : Precipitates of both barium sulphate and barium sulphite are white in colour but barium sulphite precipitate dissolves in mineral acids while barium sulphate precipitate does not.

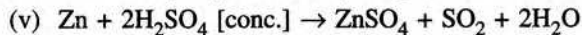
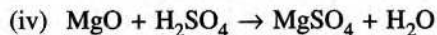
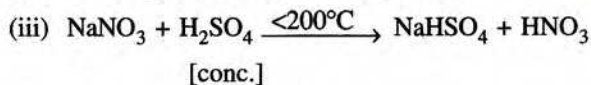
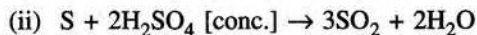
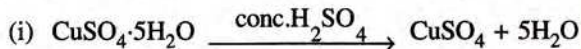
EXERCISE

- Why is water not added to concentrated H_2SO_4 in order to dilute it ?
- Give two balanced reactions of each type to show the following properties of sulphuric acid :
 - Acidic nature,
 - Oxidising agent,
 - Dehydrating nature,
 - Non-volatile nature.
- Give a chemical test to distinguish between :
 - dilute sulphuric acid and dilute hydrochloric acid,
 - dilute sulphuric acid and conc. sulphuric acid.
- Name the products formed when hot and concentrated sulphuric acid reacts with the following :
 - Sulphur,
 - NaOH,
 - Sugar,
 - Carbon,
 - Copper.
- Why is :
 - concentrated sulphuric acid kept in air tight bottles ?
 - H_2SO_4 not a drying agent for H_2S ?
 - sulphuric acid used in the preparation of HCl and HNO_3 ? Give equations in both cases.
- What property of conc. H_2SO_4 is made use of in each of the following cases? Give an equation for the reaction in each case :
 - in the production of HCl gas when it reacts with a chloride,
 - in the preparation of CO from HCOOH ,
 - as a source of hydrogen by diluting it and adding a strip of magnesium,
 - in the preparation of sulphur dioxide by warming a mixture of conc. sulphuric acid and copper-turnings,
 - hydrogen sulphide gas is passed through concentrated sulphuric acid.
- What is the name given to the salts of :
 - sulphurous acid,
 - sulphuric acid ?
- Give reasons for the following :
 - Sulphuric acid forms two types of salts with NaOH,
 - Red brown vapours are produced when concentrated sulphuric acid is added to hydrogen bromide,
 - A piece of wood becomes black when concentrated sulphuric acid is poured on it,
 - Brisk effervescence is seen when oil of vitriol is added to sodium carbonate.
- Copy and complete the following table :

Column 1 Substance reacted with acid	Column 2 Dilute or concentrated acid	Column 3 Gas
		Hydrogen
		Carbon dioxide
		Only chlorine

or D which is responsible for the reactions (i) to (v).
Some role/s may be repeated.

- (1) Dilute acid (2) Dehydrating agent
(3) Non-volatile acid (4) Oxidising agent



- (c) Give balanced equation for the reaction : Zinc sulphide and dilute sulphuric acid.

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- (a) State one appropriate observation for : Conc. H_2SO_4 is added to a crystal of hydrated copper sulphate.
(b) In the given equation – $\text{S} + 2\text{H}_2\text{SO}_4 \rightarrow 3\text{SO}_2 + 2\text{H}_2\text{O}$:
Identify the role played by conc. H_2SO_4 .
(i) Non-volatile acid (ii) Oxidising agent
(iii) Dehydrating agent (iv) None of the above

- (c) Give a balanced equation for : Dehydration of concentrated sulphuric acid with sugar crystals.

- (d) Identify the substance underlined : A dilute mineral acid which forms a white precipitate when treated with barium chloride solution.

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- (a) Write balanced equations for the following : Action of concentrated sulphuric acid on carbon.
(b) Distinguish between the following pairs of compounds using the test given within brackets.
Dilute sulphuric acid and dilute hydrochloric acid [using barium chloride solution].
(c) State the conditions required for the following reactions to take place :
The conversion of sulphur dioxide to sulphur trioxide.
(d) Give one equation each to show the following properties of sulphuric acid :
(i) Dehydrating property
(ii) Acidic nature
(iii) As a non-volatile acid