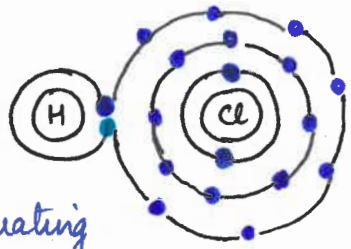
STUDY OF COMPOUNDS : HYDROGEN CHLORIDE

- MOLECULAR FORMULA : HCl
  MOLECULAR MASS : 36.5
  BOND : COVALENT



OR H—Cl

HISTORICAL BACKGROUND : Glauber : Prepared by heating common salt with conc. H_2SO_4
Lavoisier : Named it Muriatic acid
Davy : Named it Hydrochloric acid

PREPARATION OF HYDROGEN CHLORIDE GAS :

- **BY SYNTHESIS (DIRECT COMBINATION)**

$$H_2(g) + Cl_2(g) \xrightarrow{\text{Diffused sunlight}} 2HCl(g)$$

REACTION IN DIRECT SUNLIGHT IS EXPLOSIVE BUT NOT IN DARK

ACTIVATED CARBON ABSORBS HYDROGEN WHICH INCREASES REACTIVITY ALLOWING Rx TO OCCUR IN DARK.

- **BY HEATING METALLIC CHLORIDE WITH CONC. SULPHURIC ACID :**

Metal chloride + conc H_2SO_4 ⟶ Salt + Hydrogen chloride

- **LABORATORY PREPARATION OF HYDROGEN GAS**

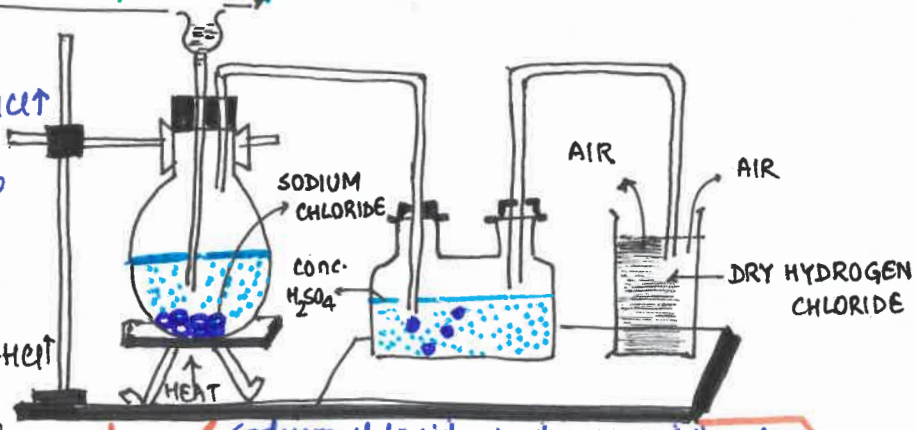
REACTION INVOLVED :

$$NaCl + H_2SO_4 \xrightarrow{<200^\circ C} NaHSO_4 + HCl\uparrow$$

- The reaction can occur upto the stage of formation of Na_2SO_4 on heating above 200°C

- $NaHSO_4 + NaCl \xrightarrow{\text{above } 200^\circ C} Na_2SO_4 + HCl\uparrow$

$$2NaCl + H_2SO_4 \xrightarrow[\text{(conc)}]{\text{above } 200^\circ C} Na_2SO_4 + 2HCl$$



Sodium chloride is cheap and therefore it is preferred for the prep. of HCl

conc. HNO_3 is not used during the prep. of HCl because it is volatile and may volatalize out along with HCl

- **PURIFICATION OF HCl gas**

- Dried by using conc H_2SO_4
- other drying agents like : P_2O_5, CaO cannot be used as they react with HCl

$$2P_2O_5 + 3HCl \longrightarrow POCl_3 + 3HPO_3$$

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

- **COLLECTION OF HCl**

- HCl is collected by downward delivery (upward displacement of air) as it is 1.28 times heavier than air.
- It is not collected over water, since it is highly soluble in water.

IDENTIFICATION

- HCl gas on exposure to air, gives white fumes due to the formation of HCl acid on ~~also~~ dissolving in atmospheric water vapour.

TEST: Bring a rod dipped in NH_4OH near the mouth of the test tube, dense white fumes of NH_4Cl will be produced.

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

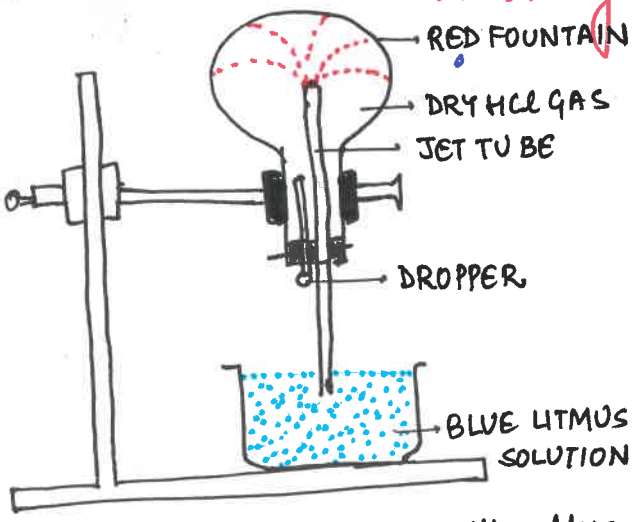
PHYSICAL PROPERTIES OF HYDROGEN CHLORIDE GAS

- COLOUR: colourless gas
- SMELL: Pungent choking smell
- TASTE: sour (acidic) in taste
- PHYSIOLOGICAL NATURE: It is corrosive in nature. It irritates nose, throat and lungs
- DENSITY: V.D of HCl is 18.25
- M.PT: $-113^\circ C$
- B.PT: $-83^\circ C$
- LIQUEFACTION & SOLIDIFICATION: Liquefaction occurs at high pressure and low temperature
- SOLUBILITY: Highly soluble in H_2O. HCl being a polar covalent compound is soluble in organic non-polar solvents such as acetone and toluene.

- EXPERIMENT: To show that HCl gas is heavier than air

This experiment also proves that HCl gas is neither combustible nor a supporter of combustion.

EXPERIMENT : To show that HCl gas is highly soluble



As the water goes in the flask from the dropper, HCl gas present in the flask dissolves due to its high solubility, thereby lowering the pressure inside. The outside pressure being higher pushes the blue litmus solution inside, through the jet tube.

- The blue litmus solution turns red due to the acidic nature of HCl gas.

CHEMICAL PROPERTIES OF HYDROGEN CHLORIDE GAS

COMBUSTIBILITY Gas is neither combustible nor a supporter of combustion. It does not burn, rather it extinguishes a burning splint.

THERMAL DISSOCIATION On heating above 500°C, it dissociates into hydrogen and chlorine

$$2HCl \xrightarrow{> 500^\circ C} H_2 + Cl_2$$

REACTION WITH METALS

$$Metal + HCl(g) \longrightarrow MCl_2 + H_2\uparrow$$

REACTION WITH AMMONIA: It combines with NH_3 to form dense white fumes of ammonium chloride

$$NH_3 + HCl \longrightarrow NH_4Cl(s)$$

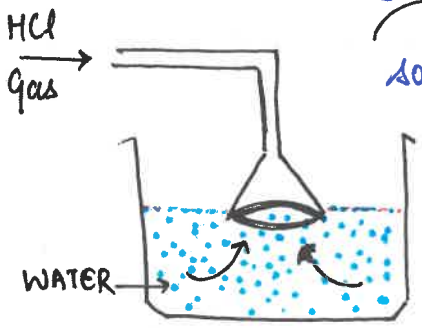
HYDROCHLORIC ACID: Dissolution of HCl gas in water yields HCl acid. It is a polar covalent compound

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

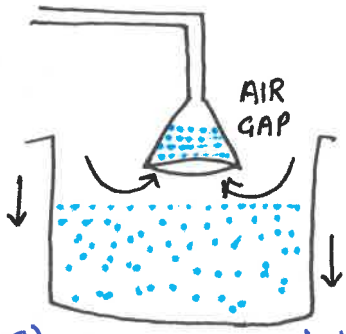
- Dry HCl gas and liquefied HCl do not produce H^+ ions. Hence, they do not conduct electricity and they do not turn blue litmus paper red. It shows non-acidic character and covalent nature of HCl gas.

LABORATORY METHOD OF PREPARATION OF HYDROCHLORIC ACID

- It is prepared by dissolving HCl gas in water. The gas is passed into H_2O until no more gas is absorbed. The product is concentrated and contains about 36% of HCl by mass.



(I) Since HCl gas is highly soluble in water, water rises up in the funnel, back suction occurs and in turn, the level outside the funnel falls creating an air gap b/w the rim of the funnel.



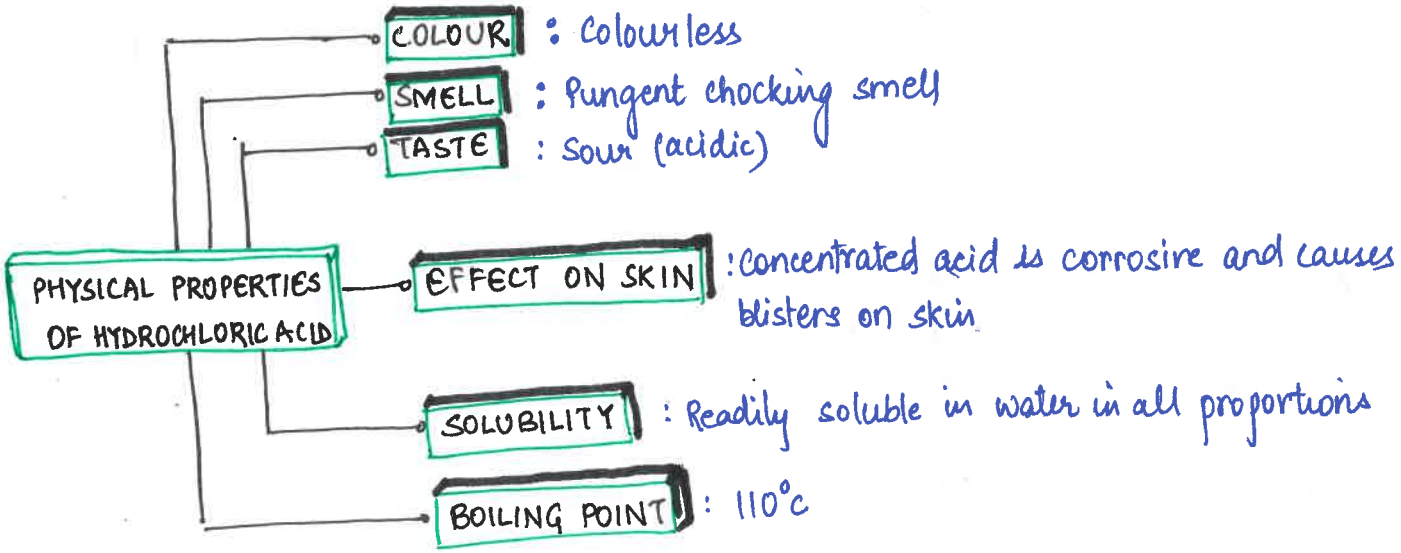
(II) The pressure inside and outside becomes equal and the water which have risie falls, gradually saturating the water in the beaker.

- The mechanism by which back suction is avoided or minimised: THE FUNNEL ARRANGEMENT.

(a) prevents or minimizes the back suction of water

(b) provides a large surface area for absorption of HCl gas.

- A constant boiling mixture or azeotrope is a solution which boils without any change in its composition. HCl acids forms constant boiling mixture at 110°C.



CHEMICAL PROPERTIES OF HYDROCHLORIC ACID

NATURE : Aq. solution is strongly acidic.

Action on litmus : Moist litmus : Blue → Red
Methyl orange : Orange → Pink
Phenolpthalein : Colourless → colourless

ACTION ON METALS

Metal + Hydrochloric acid → Metallic chloride + Hydrogen

ACTION ON OXIDES AND HYDROXIDES

Metallic oxide or metallic hydroxide + Hydrochloric acid → Metallic chloride + water

WITH SALTS OF WEAKER ACIDS It decomposes salts of weaker acids ie: carbonates, hydrogen carbonates, sulphites and sulphides

- carbonates / hydrogen carbonates + Hydrochloric acid (dilute) → Metal chloride + water + $CO_2 \uparrow$
- Sulphites / hydrogen sulphites + Hydrochloric acid (dilute) → Metal chloride + water + $SO_2 \uparrow$
- Metallic sulphide + Hydrochloric acid (dilute) → Metal chloride + $H_2S \uparrow$
- Thiosulphate ($Na_2S_2O_3$) + Hydrochloric acid (dilute) → metal chloride + $SO_2 \uparrow$ + $S \downarrow$ + H_2O

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2 + S \downarrow$$

PRECIPITATION REACTION Dilute HCl does not normally react with nitrates.

- Lead nitrate : $Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 \downarrow + 2HNO_3$
- $Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 \downarrow + 2HNO_3$

$$AgNO_3 + HCl \longrightarrow AgCl \downarrow + HNO_3$$

white ppt*

* White ppt of AgCl is insoluble in HNO_3 but soluble in NH_4OH soln, forms a complex salt c/a diammine silver (I) chloride $[Ag(NH_3)_2]^+Cl^-$

$$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]^+Cl^- + 2H_2O$$

$$\downarrow + HNO_3$$

$$2AgCl \downarrow \text{ white ppt} \xrightarrow{\text{on exposure to sunlight}} Ag + Cl_2$$

CONCENTRATED HYDROCHLORIC ACID :

- Conc. HCl can be readily oxidised to chlorine by strong oxidising agents such as MnO_2, PbO_2 and Pb_3O_4

Oxidising agent + Hydrochloric acid $\longrightarrow$ Metallic chloride + H_2O + Cl_2

- $MnO_2 + \underset{\text{conc.}}{4HCl} \xrightarrow{\Delta} MnCl_2 + 2H_2O + Cl_2\uparrow$
- $PbO_2 + \underset{\text{conc.}}{4HCl} \xrightarrow{\Delta} PbCl_2 + 2H_2O + Cl_2\uparrow$
- $Pb_3O_4 + \underset{\text{conc.}}{8HCl} \xrightarrow{\Delta} 3PbCl_2 + 4H_2O + Cl_2\uparrow$
- $CaOCl_2 + \underset{\text{dil}}{2HCl} \xrightarrow{\Delta} CaCl_2 + H_2O + Cl_2\uparrow$ (Bleaching powder)

USES OF HYDROCHLORIC ACID

GENERAL USES
- As a laboratory reagent and for the preparation of aquaregia.

MEDICINS
- Dilute HCl is prescribed to patients with decreased activity of their gastric juices.

INDUSTRIAL USES
- In the manufacture of chlorine and chlorides, dyes, drugs, glucose from starch.
- For purifying bone black, because HCl dissolves the calcium phosphate present in bones.
- To pickle steel as HCl dissolves the oxides.
- To remove rust from iron sheets.
- For cleaning metal surfaces before painting, electroplating, galvanisation.
- In extraction of glue from bones.

TESTS FOR HYDROGEN CHLORIDE GAS AND HYDROCHLORIC ACID.

1. HCl possesses a characteristic irritating smell.

2. $NH_3 + HCl \longrightarrow NH_4Cl$: HCl gives thick white fumes of NH_4Cl, when a glass rod dipped in ammonia soln is held near the vapours of the acid.

3. $AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$

White ppt → Insoluble in nitric acid but soluble in NH_4OH

4. $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

Greenish yellow gas → The gas liberated turns moist starch iodide paper blue-black.

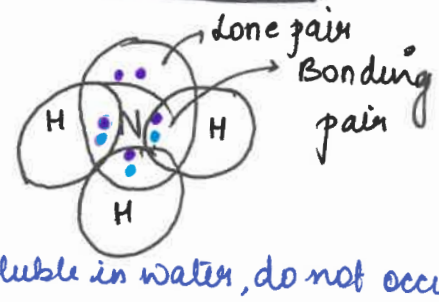
—x—

STUDY OF COMPOUNDS : (B) AMMONIA

MOLECULAR FORMULA : NH_3

RELATIVE MOLECULAR MASS : 17

BONDING : covalent



- NH_3 and ammonium compounds being highly soluble in water, do not occur as minerals.
- The bacterial decomposition of urea yields ammonia which gives a pungent odour.

$$CO(NH_2)_2 + 2H_2O \longrightarrow 2NH_3 + H_2O + CO_2\uparrow$$

FORMS OF NH_3

GASEOUS AMMONIA
- dry ammonia gas

LIQUID AMMONIA
dry ammonia
↓ high pressure
liquid ammonia

LIQUOR AMMONIA FORTIS
- saturated solution of ammonia in H_2O
- 880 ammonia
- stored in tightly stoppered bottles in cool place.

LABORATORY BENCH REAGENT
- Dilute solution of liquor ammonia is used as a laboratory reagent.

I PREPARATION OF AMMONIA GAS

- GENERAL METHODS OF PREPARATION :

$$\text{Ammonium salt} + \text{Alkali} \xrightarrow{\Delta} \text{salt} + \text{water} + \text{Ammonia}$$

(slaked lime / caustic soda / caustic potash)

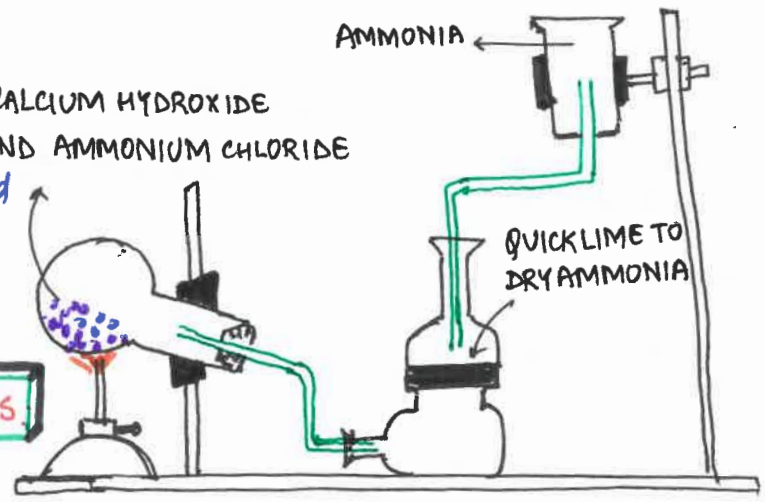
- $2NH_4Cl(s) + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2H_2O + 2NH_3\uparrow$
- $(NH_4)_2SO_4 + Ca(OH)_2 \xrightarrow{\Delta} CaSO_4 + 2H_2O + 2NH_3\uparrow$
- $(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} Na_2SO_4 + 2H_2O + 2NH_3\uparrow$ (caustic soda)
- $(NH_4)_2SO_4 + 2KOH \xrightarrow{\Delta} K_2SO_4 + 2H_2O + 2NH_3\uparrow$ (caustic potash)

LABORATORY PREPARATION OF AMMONIA GAS:

FROM AMMONIUM CHLORIDE

$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3\uparrow$

CALCIUM HYDROXIDE AND AMMONIUM CHLORIDE



- In order to get dry NH_3, the gas is passed through a drying tower containing lumps of quicklime (CaO)

UNSUITABILITY OF OTHER DRYING AGENTS

- Other drying agents like conc. H_2SO_4, P_2O_5, anh. $CaCl_2$ are not used as ammonia being basic reacts with them.
  - $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
  - $6NH_3 + P_2O_5 + 3H_2O \longrightarrow 2(NH_4)_3PO_4$ ammonium phosphate
  - $CaCl_2 + 4NH_3 \longrightarrow CaCl_2.4NH_3$ (addition compound)

PTR:

1. Higher ratio by wt. of alkali is used as it may counteract the loss by sublimation of NH_4Cl.
2. $Ca(OH)_2$ is used as it is cheap and not deliquescent like other alkalies.
3. Though all ammonium salts on heating with alkalis give NH_3 Except: NH_4NO_3 and NH_4NO_2

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

COLLECTION

NH_3 gas is collected in inverted gas jars by the downward displacement of air because it is:

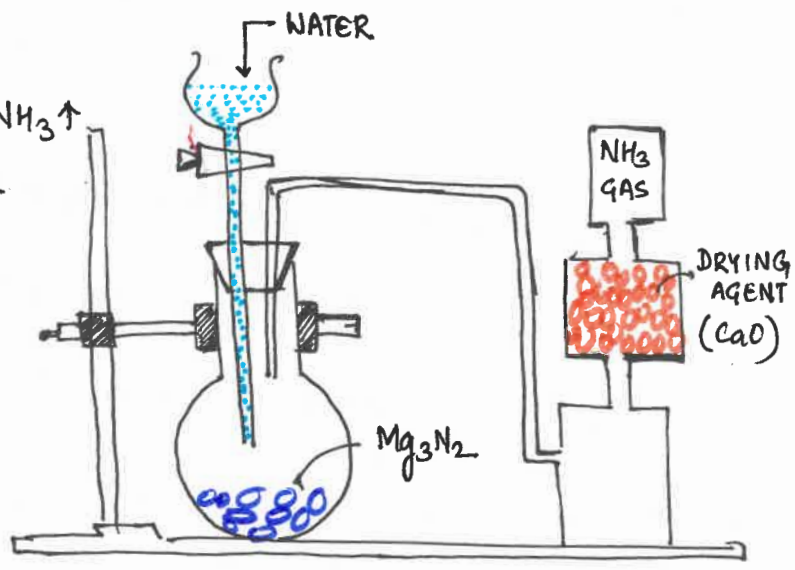
(i) Lighter than air (V.D of NH_3 8.5, VD of air 14.4)

(ii) highly soluble in H_2O and therefore cannot be collected over water

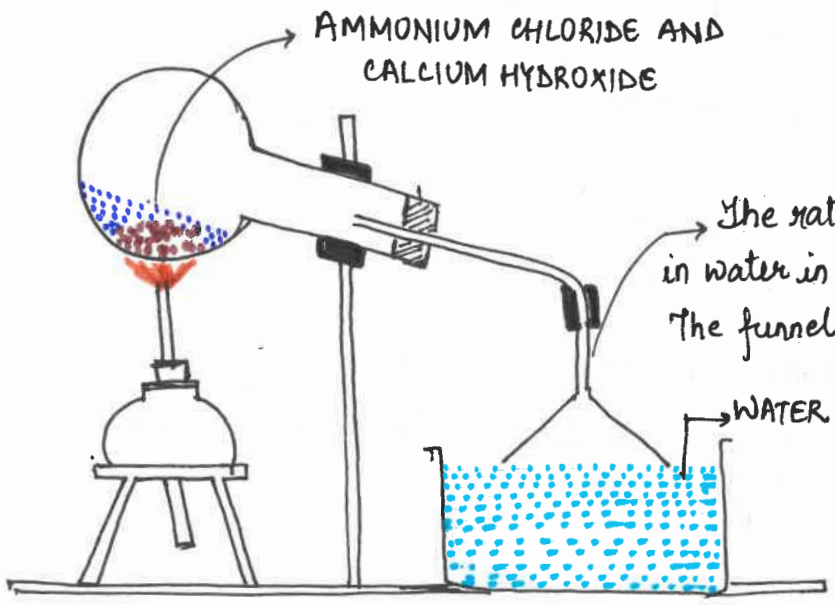
II FROM METAL NITRIDES

- $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3\uparrow$

$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3\uparrow$

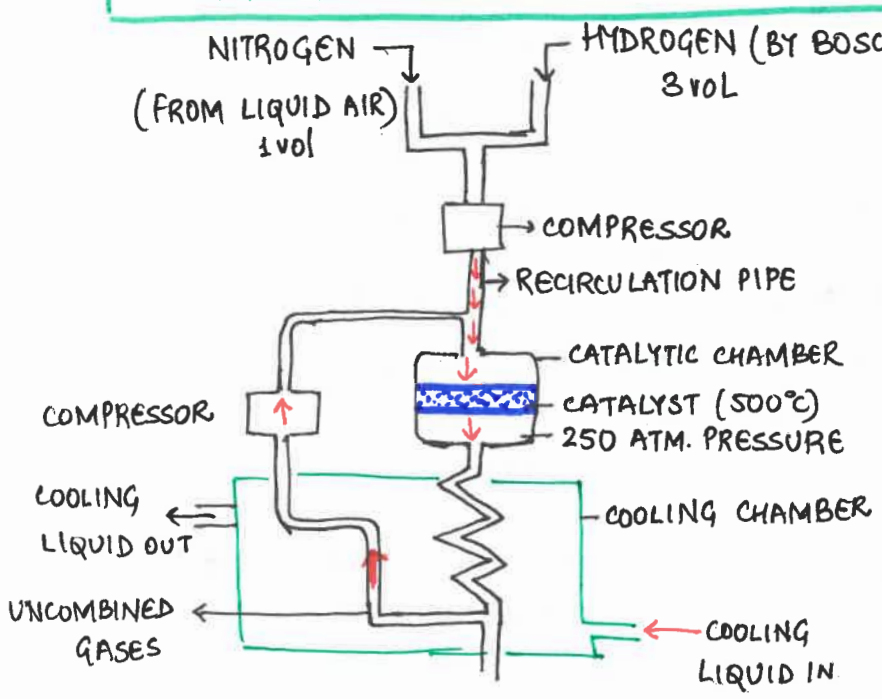


PREPARATION OF AQUEOUS AMMONIA



The rate of dissolution of ammonia in water is very high which leads to back suction. The funnel provides a larger surface area for the dissolution of ammonia in H_2O.

• MANUFACTURE OF AMMONIA (HABER'S PROCESS)



• REACTANTS :

$N_2 : H_2$

1 : 3 (By volume)

$N_2 + 3H_2 \rightleftharpoons 2NH_3 + heat$

Reaction is reversible, exothermic and proceeds with decrease in volume

TEMPERATURE	:	450-500°C (opt. temp)
PRESSURE	:	Above 200 atm
CATALYST	:	Finely divided Iron
PROMOTER	:	Traces of Mo or Al_2O_3

• NH_3 is separated from the unreacted N_2 and H_2 by :

(i) Liquefaction

(ii) Absorbing in water.

FAVOURABLE CONDITIONS:

1) The reaction is exothermic, hence low temp. will favour the synthesis

2) High pressure favours the formation of NH_3

3) The speed of the reaction can be increased by using a catalyst, which is finely divided iron. A promoter Molybdenum or Al_2O_3 is used to ↑ the efficiency of catalyst.

PHYSICAL PROPERTIES OF AMMONIA

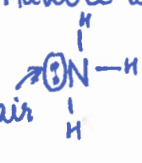
- COLOUR → colourless
- ODOUR → strong pungent choking smell
- TASTE → slightly bitter (alkaline) taste
- PHYSIOLOGICAL ACTION → Non-poisonous
- DENSITY → Vapour density = 8.5
- NATURE → Alkaline Nature
- LIQUEFACTION → Easily liquefied at 10°C by compressing it at 6 atm. pressure
- BOILING POINT → −33.5°C
- FREEZING POINT → −77.7°C
- SOLUBILITY → Highly soluble in water

• To demonstrate the high solubility of NH_3 gas in water: FOUNTAIN EXPERIMENT

CHEMICAL PROPERTIES OF AMMONIA

- THERMAL DISSOCIATION: $2NH_3 \rightleftharpoons N_2 + 3H_2$ (at high temp)
- BASIC PROPERTIES: Dry NH_3 → covalent molecule, neutral in liquefied form
  Aq. solution: weak base, basic nature is due to the presence of lone pair.

  $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (weak base)

  Lone pair: 
- BURNING OF NH_3 IN OXYGEN → Ammonia is not a supporter of combustion.
  It burns in oxygen with greenish yellow flame
- CATALYTIC OXIDATION OF AMMONIA

  $4NH_3 + 5O_2 \xrightarrow{Pt,\ 800°C} 6H_2O + 4NO\uparrow + Heat$

  $2NO + O_2 \longrightarrow 2NO_2$ (Reddish brown gas)
- AMMONIA AS A REDUCING AGENT
  - (i) REDUCTION OF METALLIC OXIDES:

    $2NH_3 + 3CuO \longrightarrow 3Cu + 3H_2O + N_2\uparrow$

    Black solid → Reddish brown solid
  - (ii) REDUCTION OF Cl_2 to HCl
    - (a) When NH_3 is in excess

      $8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$ (excess)
    - (b) When Cl_2 is in excess:

      $NH_3 + 3Cl_2 \longrightarrow 3HCl + NCl_3$ (yellow liq)

REACTION WITH ACIDS:

Ammonia gas + Acid ⟶ Ammonia salt

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

$NH_3(g) + HNO_3 \longrightarrow NH_4NO_3$

$2NH_3(g) + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

AQUEOUS SOLUTION OF NH_3:

$NH_3 + H_2O \longrightarrow NH_4OH$

$Aq.NH_3$ + Acid ⟶ Ammonium salt + Water

$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

REACTION OF AQ. SOLUTION OF AMMONIA WITH SOLUBLE METAL SALTS

Metallic salt solution + NH_4OH ⟶ Ammonium salt + Metallic hydroxide (ppt)

- $FeSO_4 + 2NH_4OH \longrightarrow (NH_4)_2SO_4 + Fe(OH)_2\downarrow$ (Insoluble in excess of NH_4OH)
  (dirty green)
- $FeCl_3 + 3NH_4OH \longrightarrow 3NH_4Cl + Fe(OH)_3\downarrow$ (Insoluble in excess of NH_4OH)
  (Reddish brown)
- $Pb(NO_3)_2 + 2NH_4OH \longrightarrow 2NH_4NO_3 + Pb(OH)_2\downarrow$ (— " —)
  White
- $Zn(NO_3)_2 + 2NH_4OH \longrightarrow 2NH_4NO_3 + Zn(OH)_2\downarrow$ (soluble in excess of NH_4OH)
  white gelatinous
- $CuSO_4 + 2NH_4OH \longrightarrow (NH_4)_2SO_4 + Cu(OH)_2\downarrow$ (soluble in excess of NH_4OH)
  Pale blue

• Ammonium hydroxide is used in qualitative analysis for identifying cations.

TEST FOR AMMONIA GAS AND AMMONIUM ION

1. It has a sharp characteristic odour
2. It turns: (i) moist red litmus blue
   (ii) moist turmeric brown
   (iii) phenolpthalein solution pink.
3. It gives dense white fumes with conc. HCl
   $NH_3 + HCl \longrightarrow NH_4Cl$
4. $NH_3(g) + CuSO_4 \longrightarrow$ deep blue ppt $\xrightarrow[\text{in excess}]{NH_3(g)}$ deep blue solution
5. Ammonium salts gives brown colour ppt with Nessler's solution (K_2HgI_4)

- USES OF AMMONIA

1. Liquid NH_3 → used as a refrigerant in ice plants.

   Anhydrous NH_3 → It is a clear, colourless liquid under pressure. It evaporates rapidly and produces cooling effect. This makes ammonia a good refrigerant.

2. Ammonia is environmentally compatible. It does not deplete O_3 layer and does not contribute towards the global warming

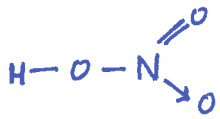
3. Ammonia being lighter than air goes up in the atmosphere not affecting the life too much on earth.

4. NH_3 soln is used as an important laboratory reagent in qualitative analysis as it gives characteristic coloured metallic hydroxide precipitates.

5. Aq. NH_3 emulsifies or dissolves fats, grease etc.

6. Ammonia is used in the manufacture of nitrogenous fertilizers, explosives, other ammonium salts such as $(NH_4)_2CO_3$, NH_4Cl, nylon and rayon.

STUDY OF COMPOUNDS : (C) NITRIC ACID

- MOLECULAR FORMULA : HNO_3
- REL. MOLECULAR MASS : 63 u
- STRUCTURE : 
- OCCURENCE : (i) FREE STATE : Nitric acid is found in rain water, where it occurs in traces after lightning
  (ii) COMBINED STATE : Chile saltpetre ($NaNO_3$)
  Nitre (KNO_3)
  Calcium nitrate [$Ca(NO_3)_2$]

FORMATION OF NITRIC ACID IN ATMOSPHERE

1) $N_2 + O_2 \xrightleftharpoons{3000^\circ C} 2NO$ .... during lightning discharge

2) $2NO + O_2 \rightleftharpoons 2NO_2$ .... oxidation of nitric oxide

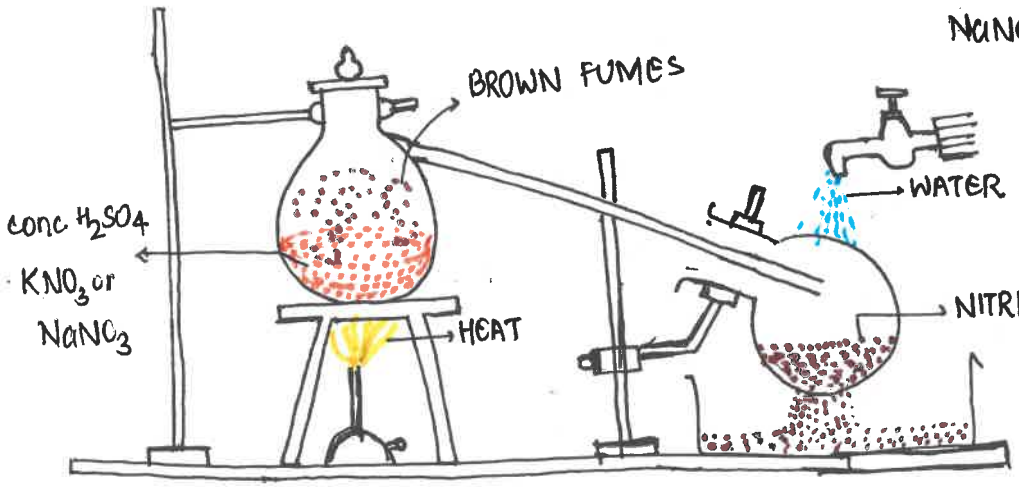
3) $4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$ .... Nitrogen dioxide dissolves in atmospheric moisture or rainwater in the presence of oxygen of the air and forms nitric acid in the free state

- The conversion of the free atm. nitrogen into useful nitrogeneous compounds in the soil is known as fixation of atmospheric nitrogen.

LABORATORY PREPARATION OF NITRIC ACID

$KNO_3 + H_2SO_4$ (conc) $\xrightarrow{< 200^\circ C} KHSO_4 + HNO_3$

$NaNO_3 + H_2SO_4$ conc $\xrightarrow{< 200^\circ C} NaHSO_4 + HNO_3$



The vapours of Nitric acid are condensed to a light yellow liquid by chilling.

- Pure acid is colourless but the acid obtained in lab is slightly yellow. The yellow colour is due to the dissolution of reddish brown coloured NO_2 gas in the acid.

REMOVAL OF YELLOW COLOUR FROM ACID:

(i) If dry air or CO_2 is bubbled through yellow acid, acid turns colourless bcoz it removes NO_2 from warm acid which is further oxidised to HNO_3.

(ii) $NO_2 + H_2O \longrightarrow$ colourless
(excess)

PTR: (i) In lab method all glass apparatus is used because HNO_3 vapours attack rubber and cork.

(ii) conc. HCl is not used in place of conc. H_2SO_4 because HCl is volatile and hence HNO_3 vapours will carry HCl vapours

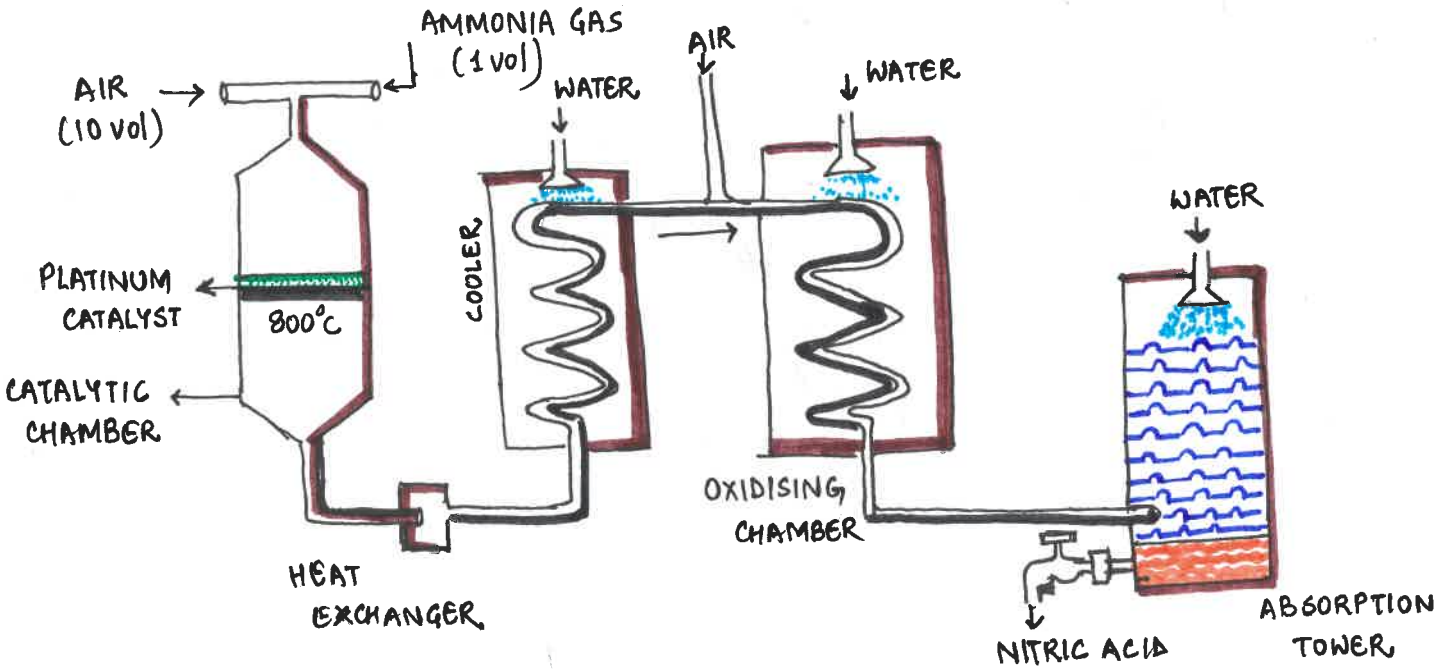
(iii) The temperature of the reaction should not exceed 200°C: Na_2SO_4 formed at higher temperature forms a hard crust which sticks to the wall of the retort and is difficult to remove.

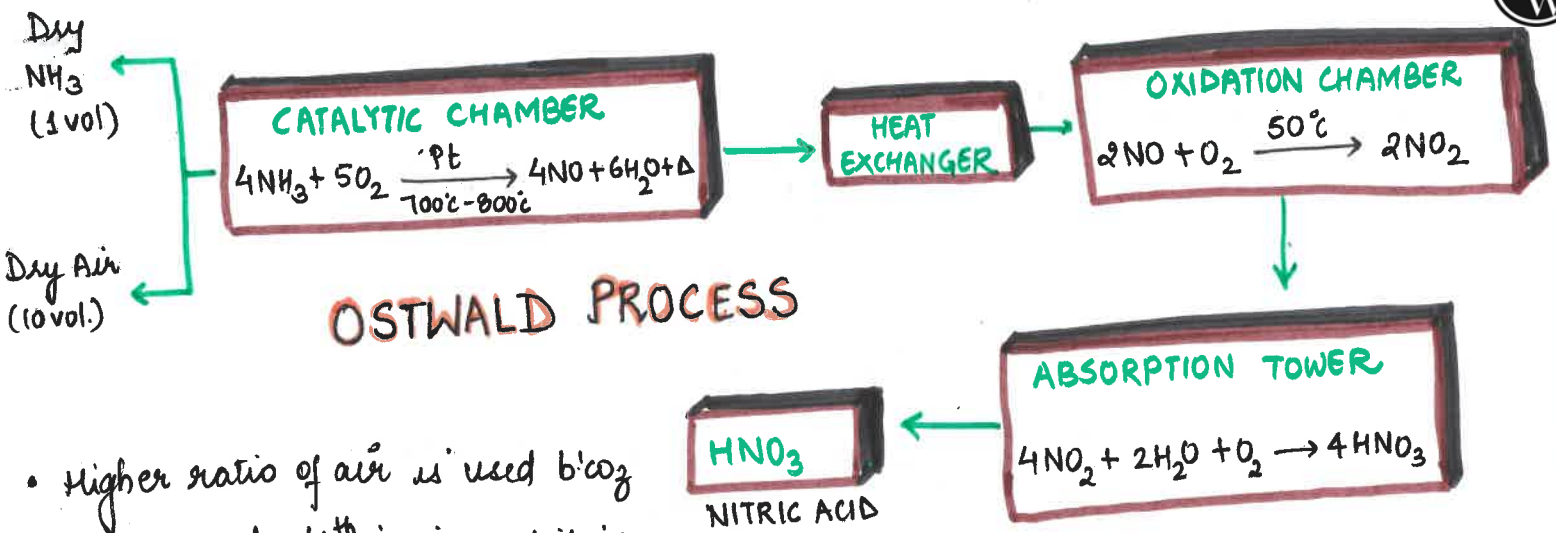
$$NaNO_3 + NaHSO_4 \xrightarrow{>200^\circ C} Na_2SO_4 + HNO_3$$

$$2NaNO_3 + H_2SO_4 \xrightarrow{>200^\circ C} Na_2SO_4 + 2HNO_3$$

- Higher temp may lead to → damage of glass apparatus
  → decomposition of HNO_3
  – wastage of fuel.

MANUFACTURE OF NITRIC ACID "OSTWALD PROCESS"





OSTWALD PROCESS

- Higher ratio of air is used b'coz oxygen is only $1/5^{th}$ in air and it is required in all three chambers
- Acid obtained at the bottom of the tower is conc. above 50%

Further Distillation → 68% HNO_3 → distillation → 98% Fuming HNO_3 → strong cooling → 100% Pure HNO_3

PROPERTIES OF NITRIC ACID

- **COLOUR**: Fuming HNO_3 : 98% : colourless; 68% HNO_3 : Yellow in colour
- **ODOUR**: suffocating smell
- **TASTE**: Acidic (sour taste)
- **NATURE**: Hygroscopic and fumes in air.
- **DENSITY**: 1.54 g/cm³ (98%)
- **BOILING POINT AND MELTING POINT**: B.pt : 86°C Melt : −42°C
- **SOLUBILITY**: soluble in water in all proportions
- **PHYSIOLOGICAL ACTION**: corrosive action on skin and causes painful blisters. It stains the skin yellow due to the presence of xanthoproteic acid.

CHEMICAL PROPERTIES OF NITRIC ACID

STABILITY
: Pure HNO_3 is unstable to heat or sunlight.

$$4HNO_3 \xrightarrow[\text{sunlight}]{\Delta} 4NO_2 + 2H_2O + O_2$$

--- The nitric acid stored in a bottle turns yellow. The colour is due to the dissolved NO_2 in HNO_3. To avoid the decomposition HNO_3 is stored in coloured bottles

ACIDIC PROPERTIES
Strong monobasic acid $HNO_3 \rightleftharpoons H^+ + NO_3^-$

Litmus test: Blue → Red

Phenolpthalein: colourless, methyl orange pink.

- Reaction with alkalis:

  Base + HNO_3 (dil) → salt + water

- Reaction with carbonates and bicarbonates:

  carbonate / bicarbonate + HNO_3 → salt + water + CO_2

- Reaction with metallic sulphites and bisulphites:

  Metallic sulphite + HNO_3 (dil) → Metallic nitrate + H_2O + SO_2 (g)

OXIDISING PROPERTIES
HNO_3: Powerful oxidising agent

$$2HNO_3 (conc) \longrightarrow 2NO_2 + H_2O + [O]$$

$$2HNO_3 (dil) \longrightarrow 2NO + H_2O + 3[O]$$

(i) Action on non-metals
Nonmetal + Acid (conc) → oxidised product + water + NO_2

$$C + 4HNO_3 (conc) \longrightarrow CO_2 + H_2O + NO_2$$

(ii) Action on metals:
(a) cold and dilute HNO_3:

Metal + HNO_3 (cold and dilute) → oxidised product + water + 2NO

Metals like Iron, Copper, cobalt, aluminium, Nickel show passivity when treated with pure conc. HNO_3

(b) conc. HNO_3 or hot dilute HNO_3:

Metal + HNO_3 (conc / Hot dilute) → oxidised product + H_2O + $2NO_2$

(c) very dilute (1% HNO_3) {only Mg and Mn}

$$Mg + 2HNO_3 (v\text{-dilute}) \longrightarrow Mg(NO_3)_2 + H_2$$

REACTION AS AQUA REGIA

Conc. HNO_3 : conc. HCl .... aqua regia / Royal water

1 : 3

$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2[Cl]$

Nitrosyl chloride

- $Pt + 4[Cl] \longrightarrow PtCl_4$ (soluble) ; $Au + 3[Cl] \longrightarrow AuCl_3$ (soluble)

Platinum (IV) chloride — Gold (III) chloride

USES OF NITRIC ACID

1) To etch designs on Copper and brassware
- Acts as a solvent for a large number of metals

2) To purify gold

3) It acts as a rocket fuel oxidant

4) In the preparation of fertilizers
- $Ca(NO_3)_2$
- NH_4NO_3
- $NH_4NO_3 + CaCO_3$
- $CaO.Ca(NO_3)_2$

5) In the preparation of aqua regia which dissolves noble metals

6) In the manufacture of explosives like T.N.T

7) In the manufacture of synthetic fibers like artificial silk, nylon.

8) In the manufacture of imp. compounds like nitrates of potassium, silver etc.

TESTS FOR NITRIC ACID AND NITRATES:

1) Conc HNO_3 gives brown fumes on heating: $4HNO_3 \xrightarrow{\Delta} 2H_2O + 4NO_2 + O_2$

Brown fumes

2) Nitrates (other than potassium, sodium, ammonium) produce reddish brown fumes

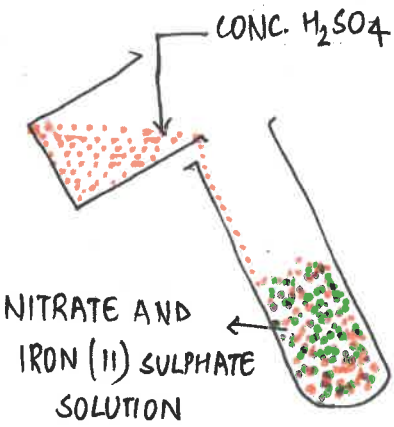
Metallic nitrate $\xrightarrow{\Delta}$ Metallic oxide + $NO_2 + O_2$

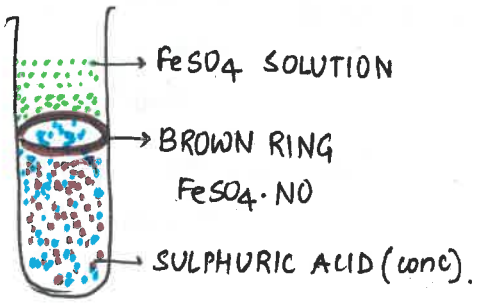
3) On adding copper to HNO_3 or acidified nitrates : Dense reddish brown fumes of NO_2 are evolved

$Cu + 4HNO_3 \xrightarrow{\Delta} Cu(NO_3)_2 + 2H_2O + 2NO_2$

$Cu + 4NaNO_3 + 4H_2SO_4 \xrightarrow{\Delta} 4NaHSO_4 + Cu(NO_3)_2 + 2H_2O + 2NO_2$

BROWN RING TEST





REACTION:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$FeSO_4 + NO \longrightarrow FeSO_4 \cdot NO$$

[Nitroso ferrous sulphate]

"Brown ring"

POINTS TO REMEMBER:

(i) A freshly prepared ferrous sulphate solution is used, because on exposure to the atmosphere it is oxidised to ferric sulphate which will not give ring test

(ii) The brown ring of nitroso ferrous sulphate is formed at the junction of two liquids

(iii) The brown ring decomposes on disturbing the test tube. The heat evolved decomposes the brown ring.

EFFECTS OF HEAT ON NITRATES

I. ALKALI METAL NITRATES: On heating melts into colourless liq. which decompose on heating to give O_2 gas

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2\uparrow$$

$$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2\uparrow$$

* As O_2 is formed glowing splinter bursts into flame

II. ALL OTHER NITRATES (except silver and mercury)

(i) $2Ca(NO_3)_2 \xrightarrow{\Delta} 2CaO + 4NO_2(g) + O_2\uparrow$ (CaO: white)

(ii) $2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$

Yellow when hot
White when cold

III SILVER AND MERCURIC NITRATE:

$$2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$$

$$Hg(NO_3)_2 \xrightarrow{\Delta} Hg + 2NO_2 + O_2$$

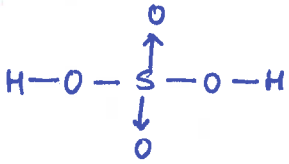
IV $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

STUDY OF COMPOUNDS: SULPHURIC ACID

MOLECULAR FORMULA: H_2SO_4

RELATIVE MOLECULAR MASS: 98

STRUCTURE:



PREPARATION OF SULPHURIC ACID

I. BY OXIDATION OF AN AQUEOUS SOLUTION OF SULPHUR DIOXIDE:

- $2SO_2 + 2H_2O + O_2 \longrightarrow 2H_2SO_4$
- $SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$ .... Greenish yellow colour of chlorine fades
- $SO_2 + 2H_2O + Br_2 \longrightarrow H_2SO_4 + 2HBr$ ..... Reddish brown colour of bromine fades
- $S + 6HNO_3 \longrightarrow H_2SO_4 + 6NO_2 + 2H_2O$

MANUFACTURE OF SULPHURIC ACID : CONTACT PROCESS

STEP I:

PRODUCTION OF SO_2

$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

STEP II

PURIFICATION OF GASES USING ELECTRICAL PRECIPITATOR, WATER SCRUBBER AND ARSENIC PURIFIERS

STEP III

CATALYTIC OXIDATION OF SO_2

$2SO_2 + O_2 \underset{450^\circ C}{\overset{V_2O_5/Pt}{\rightleftharpoons}} 2SO_3 + \text{heat}$

STEP IV

ABSORPTION OF SO_3 IN H_2SO_4

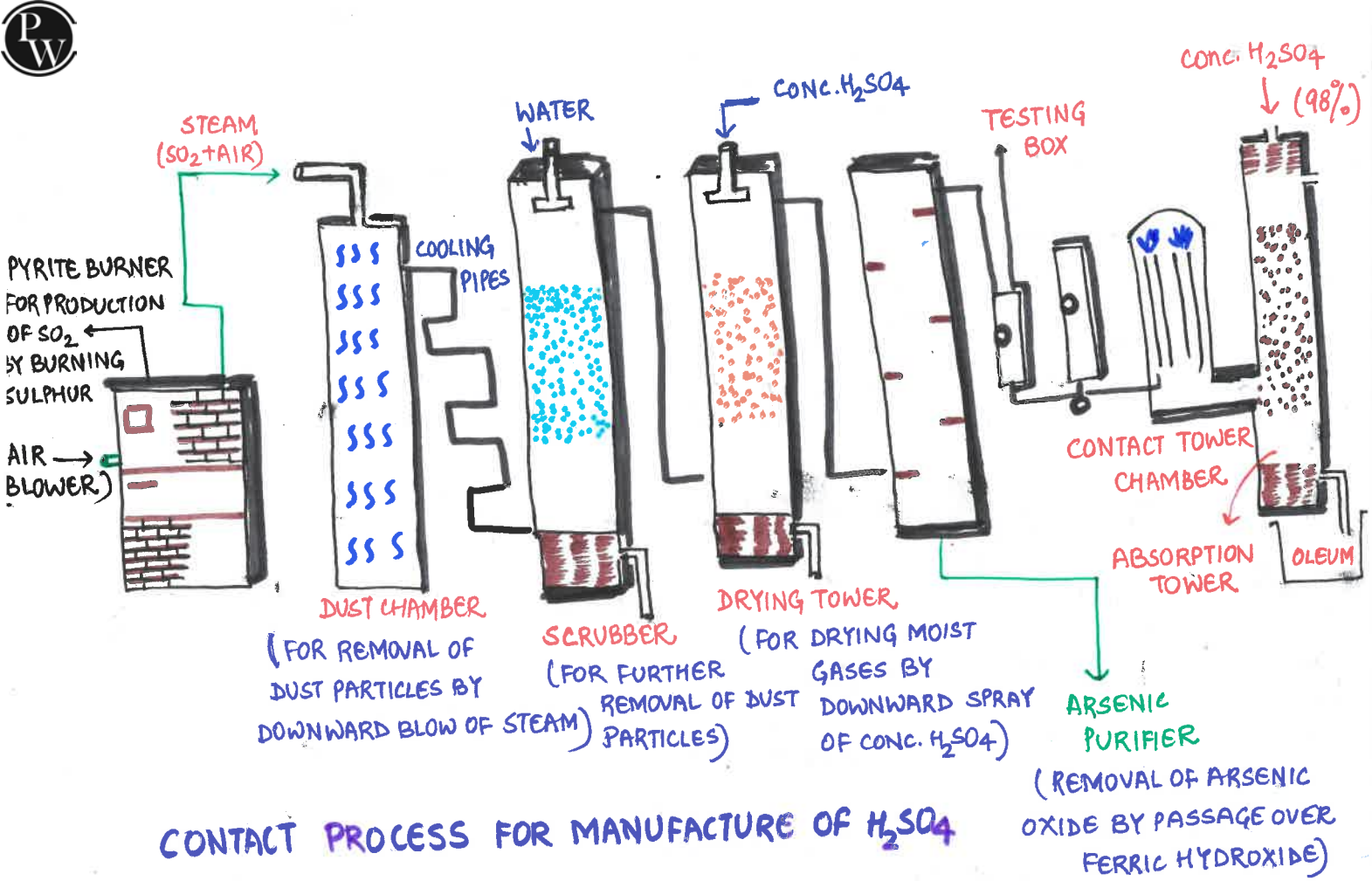
$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

(oleum/pyrosulphuric acid)

STEP V

DILUTION OF OLEUM TO OBTAIN H_2SO_4

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$



CONTACT PROCESS FOR MANUFACTURE OF H_2SO_4

• FAVOURABLE CONDITIONS FOR THE CONVERSION OF SO_2 TO SO_3

CONTACT PROCESS

1. EXOTHERMIC REACTIONS ARE FAVOURED AT LOW TEMPERATURE: The reactions are favoured at low temperature. optimum temperature : 410 - 450°C
2. HIGH PRESSURE: 1 - 2 atm. pressure
3. EXCESS OF OXYGEN: This increases the production of SO_3
4. CATALYST: Platinum is the more efficient as a catalyst than V_2O_5 but it is expensive and also it gets poisoned by impurities like arsenic (III) oxide.
   * V_2O_5 : catalyst.

PROPERTIES OF SULPHURIC ACID

PHYSICAL PROPERTIES OF SULPHURIC ACID

- **COLOUR**: colourless
- **ODOUR**: Odourless
- **TASTE**: slightly sour in taste
- **NATURE**: Dense, oily, hygroscopic liquid. It absorbs moisture, so H_2SO_4 should always be kept stoppered
- **DENSITY**: Pure acid: 1.85 g/cc
- **BOILING POINT**: 338°C
- **MELTING POINT**: 10.4°C
- **SOLUBILITY**: soluble in water in all proportions
- **CONDUCTIVITY**: Pure acid: Almost a non conductor of electricity
  Dilute acid: Good conductor of electricity
- **CONSTANT BOILING MIXTURE**: It forms a constant boiling mixture at 338°C containing 98.5% of the acid
- **PHYSIOLOGICAL NATURE**: concentrated acid is highly corrosive in nature and chars the skin black.

CHEMICAL PROPERTIES :

- H_2SO_4 when dissolved in water form hydronium ion and shows acidic properties

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

} dibasic acid

- It can form two types of salt :

(i) **Acid salt**: $NaCl + H_2SO_4 \xrightarrow{\text{below } 200^\circ C} NaHSO_4 + HCl$
(acid salt)

(ii) **Normal salt**: $2NaCl + H_2SO_4 \xrightarrow{\text{below } 200^\circ C} Na_2SO_4 + 2HCl$
Normal salt

PROPERTIES OF DILUTE H_2SO_4

ACIDIC PROPERTY

- **WITH METALS ABOVE HYDROGEN**
  - Active metal + Acid (dil) → Metal sulphate + Hydrogen
  - $Mg + H_2SO_4(dil) \longrightarrow MgSO_4 + H_2\uparrow$
- **BASES: NEUTRALISATION**
  - Base/Alkali + Acid (dil) → salt + water
  - $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$
- **WITH CARBONATES AND BICARBONATES**
  - carbonate/bicarbonate + Acid → Salt + CO_2 + H_2O
  - $CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + H_2O + CO_2\uparrow$
  - $2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2\uparrow + H_2O$
- **WITH SULPHITES AND BISULPHITES**
  - sulphites/bisulphites + Acid → Salt + H_2O + $SO_2\uparrow$
  - $Na_2SO_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2\uparrow$
- **WITH METAL SULPHIDES**
  - Metal sulphide + Acid → salt + $H_2S\uparrow$
  - $Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S\uparrow$

PROPERTIES OF CONC. SULPHURIC ACID

(1) NON VOLATILE NATURE

Due to its high boiling point. Used for the prep. of volatile acids from their salts by double decomposition

Salt of volatile acid + Acid (conc) → Acid salt + volatile acid

(2) OXIDISING AGENT

Thermal decomposition of H_2SO_4 yields nascent oxygen

$H_2SO_4 \longrightarrow H_2O + SO_2 + [O]$

(i) Non metals: $C + H_2SO_4 \longrightarrow CO_2 + 2SO_2\uparrow + H_2O$

(ii) Metals: $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2\uparrow$

(iii) Inorganic compounds: $2HBr + H_2SO_4 \xrightarrow{(conc)} Br_2 + 2H_2O + SO_2\uparrow$

(3) DEHYDRATING AGENT:

(i) Conc H_2SO_4 removes water of crystallisation from salts

$CuSO_4 \cdot 5H_2O \xrightarrow{conc.\ H_2SO_4} CuSO_4(s) + 5H_2O$

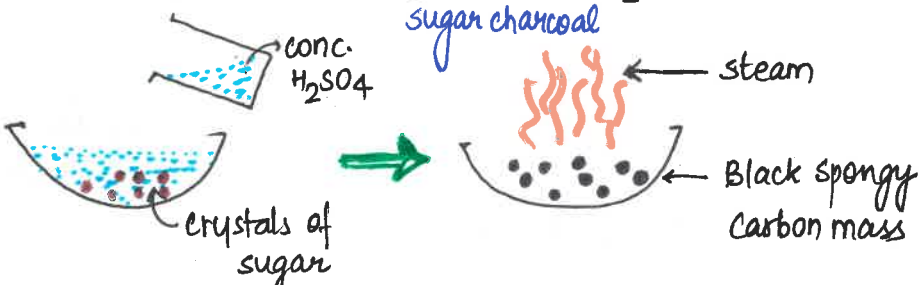
(Blue) → (White)

(ii) All carbohydrates such as glucose, sugar and cellulose react immediately to give a black spongy mass of carbon. The reaction is called 'charring'

$$C_6H_{12}O_6 \xrightarrow{\text{conc. } H_2SO_4} 6C + 6H_2O$$

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$$

sugar charcoal



Organic compounds and organic acids are dehydrated by conc. H_2SO_4:

(i) $HCOOH \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$

(ii) $\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{\text{conc } H_2SO_4} CO_2 + H_2O + CO$

(iii) $C_2H_5OH \xrightarrow[170^\circ C]{\text{conc } H_2SO_4} C_2H_4\uparrow + H_2O$

PREPARATION OF INSOLUBLE SULPHATES

H_2SO_4 precipitates the insoluble sulphates of lead, barium and calcium from the solutions of their salts.

soluble salt + Acid ⟶ Insoluble salt + acid

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4\downarrow + 2HNO_3$$

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HCl$$

TESTS FOR SULPHURIC ACID AND SULPHATES

TEST 1: When barium chloride solution is added to H_2SO_4 or any soluble metal sulphate, white ppt of barium sulphate is formed

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HCl$$

white ppt (Insoluble)

TEST 2: Conc. H_2SO_4 on heating with Cu evolves SO_2. SO_2 turns acidified $K_2Cr_2O_7$ green

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2\uparrow$$

(conc)

$$K_2Cr_2O_7 + H_2SO_4 \xrightarrow{+SO_2} Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

(orange) (Green)

(TEST 3) (3) Conc. H_2SO_4 on heating with NaCl evolves pungent fumes of HCl gas HCl gives dense white fumes of NH_4Cl with a glass rod in NH_4OH

$$NaCl + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HCl\uparrow$$
(conc.)

$$HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$$
(dense white fumes)

USES OF SULPHURIC ACID

- IT IS USED IN THE PREPARATION OF: (a) Halogens (b) Carbon Monoxide (c) Hydrogen (d) Sulphur Dioxide

  conc. H_2SO_4 is used to dry HCl gas.
- METALLURGY
  - EXTRACTION: Its reaction with metallic compounds gives sulphates which on electrolysis give the metal in the pure form.
  - PICKLING METALS: Removes metallic impurities like oxides and carbonates from the surface of metals before galvanising.
- IN LEAD ACCUMULATORS: It undergoes electrolysis in the aqueous state
- OIL REFINING: sulphuric acid is used to remove harmful impurities in purification of oil products.
- INDUSTRIAL USES: IN THE MANUFACTURE OF
  - FERTILIZERS: Ammonium sulphate $[(NH_4)_2SO_4]$, superphosphate of lime $[Ca(H_2PO_4)_2 + CaSO_4]$
  - DYES, DRUGS: Rayon, Nylon
  - EXPLOSIVES: TNT (Tri Nitro Toluene), Picric acid, TriNitroGlycerine
  - ACIDS: HNO_3, HCl, H_3PO_4, CH_3COOH
  - COMPOUNDS: sodium sulphate, Ferrous sulphate