

# CHAPTER 7-B

## Study of Compounds – Ammonia

**SYLLABUS - SCOPE OF SYLLABUS - in and after MARCH 2021 - AMMONIA**

AMMONIA - ITS LABORATORY PREPARATION - FROM AMMONIUM CHLORIDE & COLLECTION;  
AMMONIA - FROM NITRIDES LIKE  $Mg_3N_2$  & AlN & AMMONIUM SALTS.  
MANUFACTURE - BY HABER'S PROCESS -  
DENSITY & SOLUBILITY - OF AMMONIA [FOUNTAIN EXPERIMENT];  
AQUEOUS SOLUTION - OF AMMONIA;  
ITS REACTIONS WITH HYDROGEN CHLORIDE & WITH HOT COPPER [II] OXIDE & CHLORINE;  
THE BURNING OF - AMMONIA IN OXYGEN;  
USES - OF AMMONIA.

- **Laboratory preparation from - ammonium chloride & collection**  
[the preparation to be studied in terms of -  
Setting of the apparatus and diagram, procedure, observation, collection & identification].
  - **Ammonia from - nitrides like -**  
 $Mg_3N_2$  & AlN using warm water.
  - **Ammonia from - ammonium salts - Using alkalies.**  
The reactions to be studied in terms of - reactants, products, conditions & equations.
  - **Manufacture - by Haber's Process.**
  - **Density & solubility of ammonia [fountain experiment].**
  - **The burning of ammonia - in oxygen.**
  - **The catalytic oxidation of ammonia [with conditions & reaction].**
  - **Ammonia - Its reactions with - hydrogen chloride & with hot copper [II] oxide & chlorine**  
[both chlorine in excess & ammonia in excess].
- All these reactions may be studied in terms of - reactants, products, conditions, equations & observations.
- **Aqueous solution of ammonia** - reaction with sulphuric acid, nitric acid, hydrochloric acid & solutions of iron [III] chloride, iron [II] sulphate, lead nitrate, zinc nitrate & copper sulphate.
  - **Uses of ammonia** - manufacture of fertilizers, explosives, nitric acid, refrigerant gas  
[Chlorofluorocarbon - & its suitable alternatives which are non-ozone depleting] & cleansing agents.

## Ammonia

### A. INTRODUCTION

1. **DISCOVERY** - Ammonia was initially called 'alkaline air'
  - In 1774 - Joseph Priestley first prepared ammonia by heating slaked lime with 'sal ammoniac'. He called the gas as 'alkaline air' since it was found to be basic.
  - In 1785 - Claude Berthelot studied the chemical composition of the gas.
  - In 1800 - Davy further established its basic composition & proved ammonia to be a compound formed from the elements nitrogen and hydrogen.

2. **OCCURRENCE** - Ammonia occurs in the free & chemically combined state

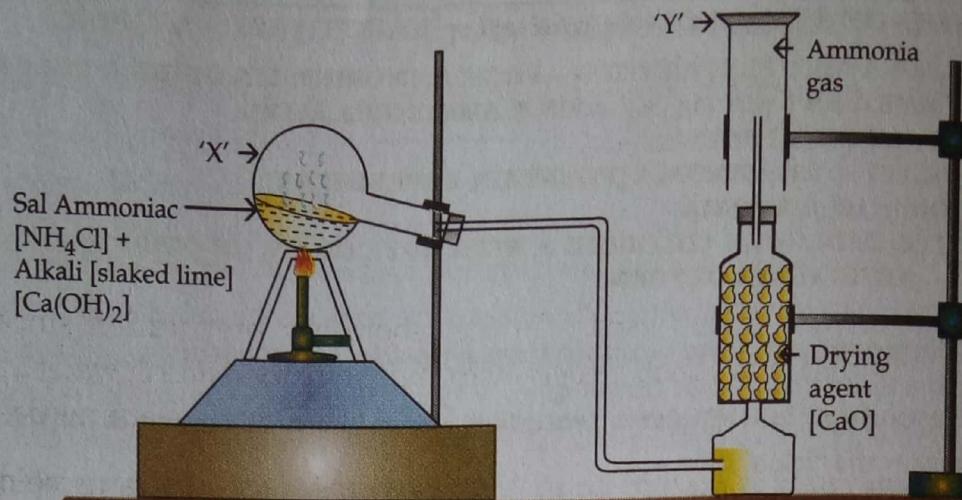
*In the free state* - Small quantities of ammonia occur in the atmospheric air & natural water. Ammonia is also produced when nitrogenous matter decays in the absence of air. Putrefying bacteria on organic matter in the soil and the ammonifying bacteria on nitrogenous organic matter e.g. urine, bring about the decomposition.

*In the combined state* - Ammonium salts & ammoniacal liquor [obtained by destructive distillation of coal] are two important - sources of ammonia.

## B. PREPARATION – of Ammonia

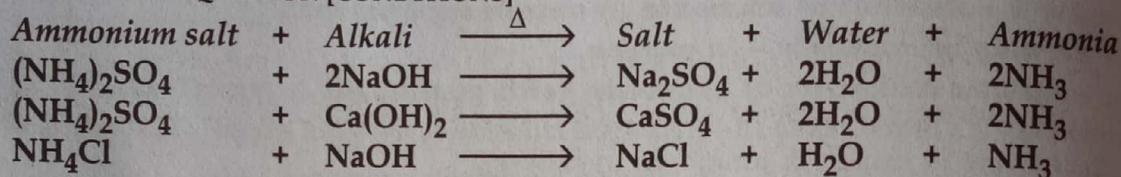
### 1. LABORATORY METHOD - From ammonium salts

Heating – a mixture of an – ammonium salt  $[NH_4Cl]$  with – an alkali  $[Ca(OH)_2]$ .

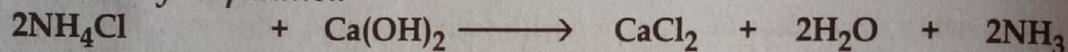


Laboratory preparation of ammonia - from ammonium chloride

#### REACTION - EQUATION [CONDITIONS]



#### Laboratory Preparation



Above reactions of ammonium salts with alkalis distinguish them from other salts since – salts other than ammonium salts will not react with alkalis on heating to liberate – ammonia. [The above ammonium salts are white solids, soluble in water & liberate pungent smelling ammonia gas on heating with alkalies e.g. NaOH or  $Ca(OH)_2$ ]

**REACTANTS** : Ammonium chloride  $[NH_4Cl]$  and calcium hydroxide [slaked lime]  $[Ca(OH)_2]$  - in round bottom flask [X].

**PRODUCTS** : Calcium chloride  $[CaCl_2]$ , water  $[H_2O]$  and ammonia  $[NH_3]$ .

**PROCEDURE** : The reactants ie. ammonium chloride & calcium hydroxide - are ground together and *heated slowly* in a round bottom flask - with its neck sloping downwards.

**OBSERVATION** : The ammonia gas obtained in flask [X] passes through a - delivery tube into a drying tower & is collected in an inverted gas jar.

**DRYING AGENT** : Quicklime  $[CaO]$  in the - drying tower.

**PRECAUTIONS** : The reactants should be in finely powdered form to - initiate maximum surface area and the slaked lime used should be - in a higher ratio. The round bottom flask [X] is kept in an - inclined position.  $NH_4NO_3$  is not used as a reactant - since it is explosive & decomposes.

**COLLECTION** : Ammonia gas is collected by – the downward displacement of air. It is lighter than air.

It is highly soluble in water, hence not collected over water.

**IDENTIFICATION:** A glass rod dipped in conc. HCl acid is brought near the mouth of the jar [Y]. If the jar is full - dense white fumes of ammonium chloride are formed.

### 1. REACTANTS

Dry ammonium chloride & slaked lime are thoroughly mixed & heated gently in the laboratory preparation of ammonia.

- A higher ratio by weight of the alkali used - may counteract the loss by sublimation of ammonium chloride on heating in the solid state.
- Calcium hydroxide is used - since it is - cheap and unlike other caustic alkalis is not deliquescent.
- Ammonium nitrate is not used - in the laboratory preparation since it is - explosive in nature & may itself decompose forming nitrous oxide & water vapour. All ammonium salts in general heated with alkalis liberate - ammonia.
- Round bottom flask is kept in an inclined position - The reactants being solid are ground thoroughly to provide maximum surface area for reaction and - heated in a round bottom flask kept in a inclined position so that the - water vapour formed may not trickle back and crack the hot flask [X].

### 2. DRYING – Of the gas

The ammonia gas is passed through a - drying tower before collection of the gas.

- The drying agent used - for drying ammonia gas is quicklime  $[CaO]$ .  
Reason - quicklime being basic in nature does not react with - basic ammonia gas.
- The drying agents not used - are conc.  $H_2SO_4$ ,  $P_2O_5$  and fused  $CaCl_2$  since - they react chemically with ammonia.

| AMMONIA | DRYING AGENT        | PRODUCT   |
|---------|---------------------|---|
| $2NH_3$ | + $H_2SO_4$ [conc.] | $\rightarrow$ $(NH_4)_2SO_4$ [ammonium sulphate]      |
| $6NH_3$ | + $P_2O_5 + 3H_2O$  | $\rightarrow$ $2(NH_4)_3PO_4$ [ammonium phosphate]    |
| $8NH_3$ | + $CaCl_2$ [fused]  | $\rightarrow$ $CaCl_2 \cdot 8NH_3$ [addition product] |

### 3. COLLECTION – Of the gas

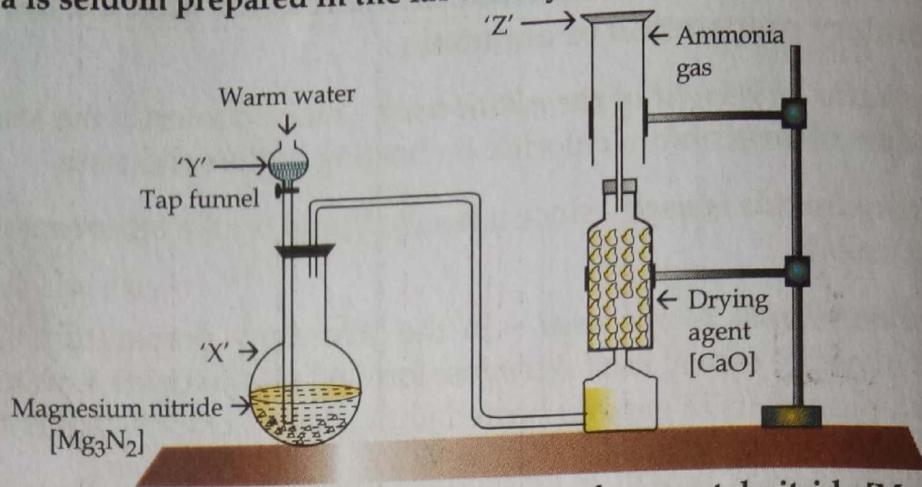
Dry ammonia gas is collected by - the downward displacement of air

- Ammonia gas is collected by the downward displacement of air - since it is lighter than air.  
[V.D. of ammonia = 8.5, V.D. of air = 14.4].
- Ammonia gas is not collected over water - since it is highly soluble in water.  
[1 vol. of water dissolves about 702 vols. at  $20^\circ C$  and 1 atmos. pressure].

## PREPARATION – of Ammonia [Contd.]

### 2. LABORATORY METHOD - From metal nitrides

Ammonia is seldom prepared in the laboratory from – metal nitrides & warm water.



Laboratory preparation of ammonia - from metal nitride  $[Mg_3N_2]$

| FORMATION - Of metal nitrides - | Burning metal | Nitrogen | $\rightarrow$ | Metal nitride         |
|---------------------------------|---------------|----------|---------------|-----------------------|
|                                 | 3Mg           | +        | $N_2$         | $\rightarrow Mg_3N_2$ |
|                                 | 3Ca           | +        | $N_2$         | $\rightarrow Ca_3N_2$ |
|                                 | 2Al           | +        | $N_2$         | $\rightarrow 2AlN$    |

**FORMATION - Of Ammonia from Metal nitrides - by reaction with warm water**  
Metal nitrides react with warm water to liberate ammonia.

|                     | Metal nitride + | Water [warm] $\rightarrow$ | Metal hydroxide +       | Ammonia       |
|---------------------|-----------------|----------------------------|-------------------------|---------------|
| • Magnesium nitride | $Mg_3N_2$       | + $6H_2O$                  | $\rightarrow 3Mg(OH)_2$ | + $2NH_3$ [g] |
| • Calcium nitride   | $Ca_3N_2$       | + $6H_2O$                  | $\rightarrow 3Ca(OH)_2$ | + $2NH_3$ [g] |
| • Aluminium nitride | AlN             | + $3H_2O$                  | $\rightarrow Al(OH)_3$  | + $NH_3$ [g]  |

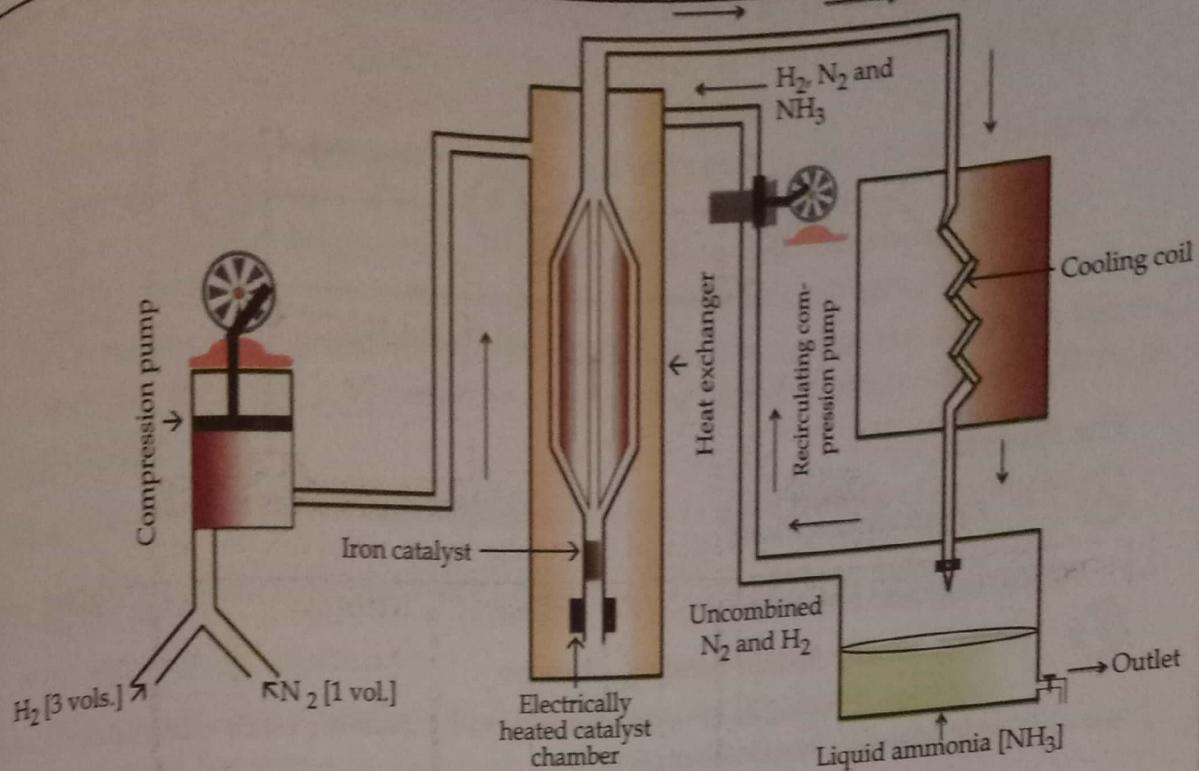
Burning metals eg. Mg, Ca & Al when burnt in nitrogen gas, form the respective **metal nitrides** i.e. magnesium nitride, calcium nitride & aluminium nitride as the products.

When warm water is added to the products formed i.e. the respective metal nitrides – the **metal nitrides undergo hydrolysis** – & are decomposed by warm water to give **pungent ammonia gas**. The corresponding **insoluble metal hydroxide** is precipitated out.

- |                |   |
|----------------|---|
| REACTANTS      | : Metal nitride [e.g. $Mg_3N_2$ ] and warm water [ $H_2O$ ]   |
| PROCEDURE      | : The reactant ie. magnesium nitride is placed in the dry flask [X] and warm water is allowed to trickle down the – tap funnel [Y].                         |
| OBSERVATION    | : The ammonia gas obtained in flask [X] passes through a delivery tube into a drying tower and is collected in an – inverted gas jar.                       |
| DRYING AGENT   | : Quicklime [ $CaO$ ] in the – drying tower.  |
| PRECAUTION     | : The lower end of the thistle funnel should dip – below the warm water in the flask [X]. <i>Since nitrides are expensive, the method is seldom used.</i>   |
| COLLECTION     | : Ammonia gas is collected by the – downward displacement of air. It is lighter than air.<br>It is highly soluble in water, hence not collected over water. |
| IDENTIFICATION | : A glass rod dipped in conc. HCl acid is brought near the mouth of the jar [Z]. If the jar is full, dense white fumes of ammonium chloride are formed.     |

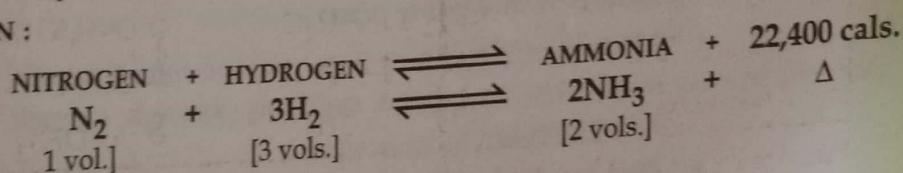
# MANUFACTURE - of Ammonia [Contd.]

## MANUFACTURE OF AMMONIA - Haber's Process



Manufacture of Ammonia - Haber's Process

Nitrogen reacts with hydrogen under specific conditions liberating - Ammonia  
REACTION - EQUATION :



**REACTANTS** : Nitrogen [N₂] and hydrogen [H₂] in the ratio 1:3 by volume.  
**PRODUCT** : Ammonia [NH₃] - 2 volumes.

**CONDITIONS** :

**Reaction** : Reversible  
Exothermic  
Proceeds with a - decrease in volume.

*Low temperatures and high pressures - favour the forward reaction.*

**Temperature** : 450-500°C [Optimum temperature]

**Pressure** : 200 to 900 atmospheres [Optimum pressure]

**Catalyst** : Finely divided iron [Fe]

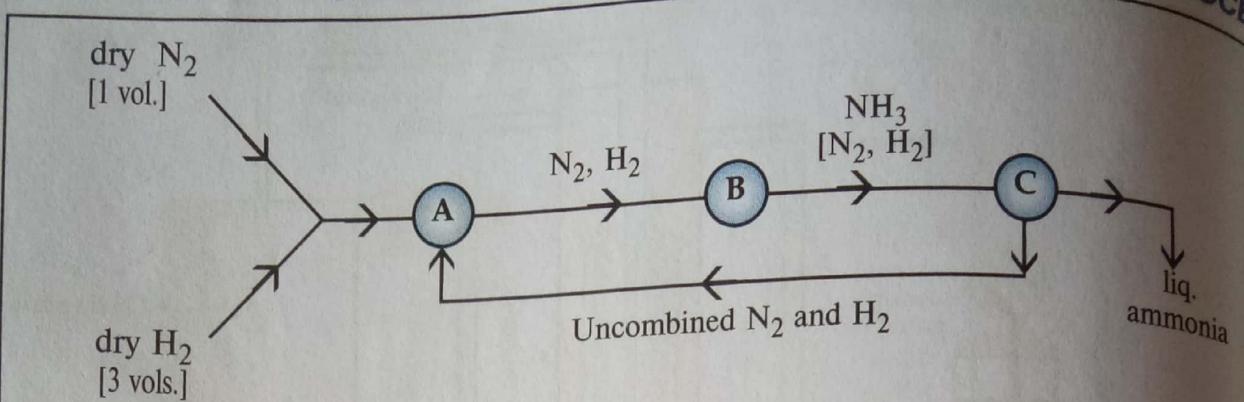
**Promotor** : Molybdenum [Mo]

[Catalyst - iron [III] oxide [Fe₂O₃] may also be used containing -  
promoters - about 1% K₂O and 3% Al₂O₃]

**PRECAUTION** : Impurities like CO, CO₂ and H₂S may poison the catalyst -  
hence the nitrogen-hydrogen reactant mixture must be free from them.

## MANUFACTURE – of Ammonia [Contd.]

### FLOW CHART – FOR MANUFACTURE OF AMMONIA - HABER'S PROCESS



#### The Process

**(A) = Compression Pump**

- Mixture of  $N_2$  and  $H_2$  in the ratio 1:3 is compressed to 200-900 atmos. press.

**(B) = Electrically heated catalytic chamber**

- The nitrogen, hydrogen compressed mixture is passed over heated catalyst having a heat exchanger.
- Mixture of  $NH_3$  formed along with residual nitrogen and hydrogen exchange their heat with the incoming unreacted nitrogen and hydrogen mixture.

**(C) = Condenser with cooling pipes**

- Mixture of  $NH_3$  along with residual nitrogen and hydrogen under pressure is allowed to expand suddenly through a small nozzle into a region of low pressure.
- This results in fall in temperature, thereby liquefying the ammonia which is collected at the base.
- The unreacted nitrogen and hydrogen is recycled through the catalytic chamber.

#### 1. REACTANTS

In the production of ammonia [Haber's process] the reactants nitrogen and hydrogen in the ratio 1:3 by volume are first passed into the catalytic chamber.

- The reactant nitrogen gas* – is obtained by *fractional distillation of liquid air*.  
*The reactant hydrogen* – is obtained from *water gas* [Bosch process].
- A higher ratio of hydrogen* – or an increase in concentration of the reactants favours the forward reaction to give optimum yield of ammonia.
- The reactants should be free from impurities* – pure and dry since – impurities tend to poison the catalyst and reduce its effectiveness.

## 2. TEMPERATURE

An optimum temperature of  $450\text{-}500^{\circ}\text{C}$  is used in the Haber's process.

- If a reaction is exothermic - it is favoured [ie. higher % yield of ammonia] - by lowering the temperature. [Le Chatelier's principle]
- However if the temperature is low - the speed of the reaction is slow & - the yield of ammonia is low.

Hence, an optimum temperature of  $450\text{-}500^{\circ}\text{C}$  is used in the above process.

[Above this temperature the ammonia may decompose to give nitrogen and hydrogen].

- External heating is therefore not required - after the reactants are initially heated, since the reaction is - exothermic the evolved heat further maintains the temperature.

## 3. PRESSURE

An optimum pressure of 200-900 atmospheres is used during the process.

- If a reaction proceeds with decrease in volume - i.e. [1 vol. of  $\text{N}_2 + 3$  vols. of  $\text{H}_2 \rightarrow 2$  vols. of  $\text{NH}_3$ ] then the forward reaction is favoured - by increasing the pressure.
- However if the pressure is too high - the production plant may not - withstand the pressure. Hence an optimum pressure of 200-900 atmos. is used.

## 4. CATALYST

A catalyst is required to accelerate the reaction at optimum temperature

- The catalyst used is finely divided iron - it is mixed with small amounts of the promotor - molybdenum which enhances - the efficiency of the catalyst.
- The catalyst only accelerates the reaction - and does not form a part of the reaction, hence it - does not affect the percentage yield of ammonia.

## 5. THE PRODUCT - AMMONIA

The ammonia is separated and recovered from the uncombined - nitrogen & hydrogen by techniques based on the physical properties of ammonia

| TECHNIQUE             | PHYSICAL PROPERTY OF AMMONIA INVOLVED  |
|-----------------------|--|
| • Liquefaction        | <p>Ammonia is - easily liquefiable</p> <ul style="list-style-type: none"> <li>It condenses to a liquid at around <math>-33^{\circ}\text{C}</math> at 8 atmos. press.</li> <li><math>\text{N}_2</math> and <math>\text{H}_2</math> are - difficult to liquefy.</li> </ul> <p>They condense at temperatures around <math>-196^{\circ}\text{C}</math> and <math>-253^{\circ}\text{C}</math> respectively and at comparatively higher pressures.</p> |
| • Dissolving in water | <p>Ammonia is - highly soluble in water</p> <ul style="list-style-type: none"> <li>1 vol. of water dissolves about 702 vols. of <math>\text{NH}_3</math> at <math>20^{\circ}\text{C}</math> and 1 atmos. pressure.</li> <li><math>\text{N}_2</math> and <math>\text{H}_2</math> are - almost insoluble in water.</li> </ul>  |

Hence liquefaction & dissolution in water - are two techniques used for separating ammonia from the uncombined nitrogen and hydrogen reactant mixture during - Haber's process.

## C. PROPERTIES – Of Ammonia

### 1. PHYSICAL PROPERTIES – Of Ammonia

- ✓ 1. Colour, odour, taste
- ✓ 2. Physiological nature
- ✓ 3. Density
- ✓ 4. Solubility
  
- ✓ 5. Liquefaction
- ✓ 6. Boiling point
- ✗ 7. Freezing point

Colourless; Strong, pungent smell; Slight alkaline taste.  
Non-poisonous. If inhaled affects the respiratory system. It is fatal in large doses.

*Lighter than air [V.D. of ammonia = 8.5 (V.D. of air = 14)]*  
*Highly soluble in water [1 vol. of water dissolves about 702 vols. at 20°C and 1 atmos. pressure]*

#### Fountain experiment

The *high solubility* of ammonia in water is demonstrated by the fountain experiment.

Easily liquefied at low temperatures.

Liquid ammonia boils at  $-33.5^{\circ}\text{C}$

Solid  $\text{NH}_3$  melts at  $-77.7^{\circ}\text{C}$

#### FOUNTAIN EXPERIMENT - To demonstrate – the high solubility of $\text{NH}_3$ gas in water

##### Experiment :

The high solubility of ammonia gas in water – can be demonstrated by the fountain experiment.

##### Apparatus :

- Dry round bottom flask filled with ammonia gas.
- Mouth of the flask has a rubber stopper with two holes for a] Jet tube, b] Dropper containing water.
- Red litmus solution is placed in the trough below.

##### Procedure :

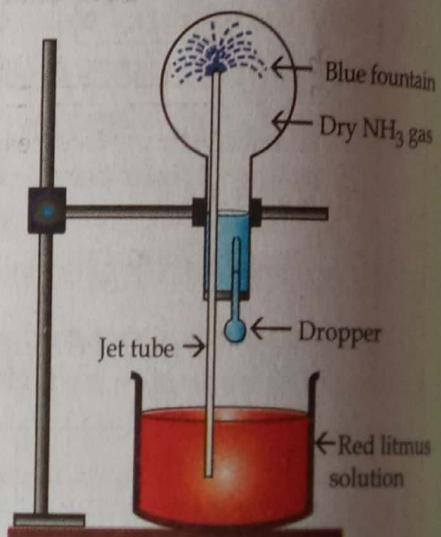
- The dropper containing water is squeezed – and the water enters the flask.

##### Observation :

- Ammonia gas present in the flask dissolves in water due to its *high solubility*, thereby creating a *partial vacuum* in the flask.
- The outside pressure being higher pushes the red litmus solution up the jet tube which emerges out at the end of the tube as a – *blue fountain*.

##### Inference :

- Ammonia gas is – *highly soluble in water* and *basic in nature*.  
[Since dry ammonia gas was present in the round bottom flask, the red litmus solution kept in the trough below, emerges out as a blue fountain since ammonia is – *basic*. On the other hand if dry  $\text{HCl}$  gas was used in the flask instead of ammonia, the blue litmus solution kept in the trough below, emerges out as a red fountain since  $\text{HCl}$  is – *acidic*].



Fountain Experiment

## PROPERTIES – Of Ammonia [Contd.]

### CHEMICAL PROPERTIES – Of Ammonia

#### 1. AMMONIA GAS - Combustibility

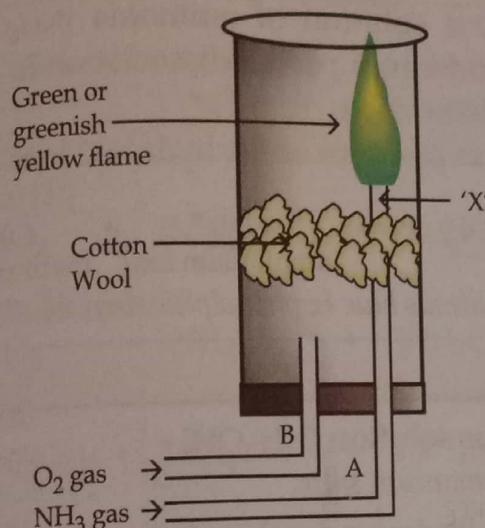
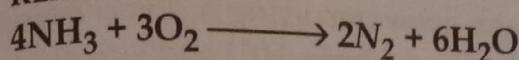
Ammonia is – neither combustible nor a supporter of combustion

*Reaction with oxygen*

Ammonia burns in an atmosphere of oxygen and undergoes catalytic oxidation.

##### BURNING OF AMMONIA IN OXYGEN

###### REACTION



Ammonia burns in excess oxygen

###### PROCEDURE :

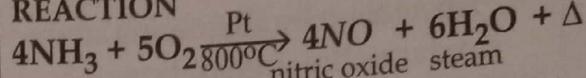
- Pass dry ammonia gas through tube A & – ignite the gas at the nozzle end [X]
- Pass oxygen gas through tube-B & – reignite the ammonia gas at the nozzle end [X].

###### OBSERVATIONS :

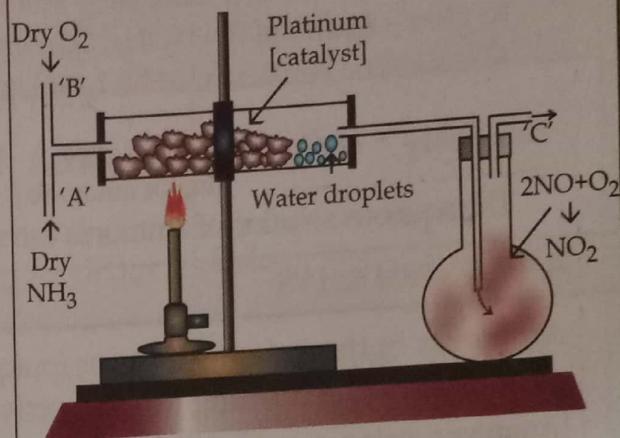
- Dry ammonia gas passed through the ignition tube A & – ignited, alone does not burn.
- After passage of oxygen, ammonia burns in an atmosphere of excess oxygen with a – green or greenish yellow flame forming – nitrogen & water.

##### CATALYTIC OXIDATION OF AMMONIA

###### REACTION



[Starting reaction for – Ostwald's process – manufacture of – nitric acid]



Catalytic oxidation of ammonia

###### PROCEDURE :

- Pass dry ammonia gas & oxygen gas through inlets [A & B] – respectively in the ratio 1:2
- The ammonia-oxygen mixture passes over heated platinum placed in the – combustion tube which in the heated state emits a reddish glow.

###### OBSERVATIONS :

- The colourless *nitric oxide* formed, on oxidation gives reddish brown – *nitrogen dioxide* in the flask 'C'.  

$$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$$
- The platinum [catalyst] continues to glow even after the heating is discontinued since the catalytic oxidation of ammonia is an – exothermic reaction.

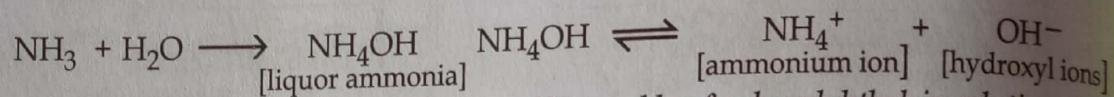
## PROPERTIES – Of Ammonia [Contd.]

### CHEMICAL PROPERTIES – Of Ammonia [contd.]

#### 2. AMMONIA GAS – Basic Nature

An aqueous solution of ammonia is basic in nature.

- Perfectly dry ammonia gas or ammonia in the liquefied form is – neutral to dry litmus. [ammonia is a very weak base, the basicity due to the lone pair of electrons on the nitrogen atom in ammonia].
- **Liquor ammonia** : An aqueous solution of ammonia in water is called liquor ammonia or liquor ammonia fortis [saturated soln. - specific gravity 0.88].  
*Preparation:* By dissolving ammonia gas in water using a funnel arrangement similar to the preparation of hydrochloric acid from HCl gas.
- **Basic nature of ammonia:** The aqueous solution of ammonia  $[\text{NH}_4\text{OH}]$  is alkaline and acts as a weak base, since it undergoes partial dissociation in aq. soln to give – hydroxyl ions  $[\text{OH}^{1-}]$  in low concentration.  
The alkaline behaviour of  $\text{NH}_4\text{OH}$  is due to presence of the hydroxyl ions  $[\text{OH}^{1-}]$ .



The aqueous solution of ammonia turns *red litmus blue & phenolphthalein solution pink*.

#### AMMONIUM SALTS

Ammonia in the gaseous form or in aqueous solution  $[\text{NH}_4\text{OH}]$  – neutralises acids forming the respective *ammonium salts*.

[Ammonia being a weak base accepts protons [hydrogen ions] to form ammonium ions,  $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$  [aq.]. It therefore reacts with acids to form ammonium salts.]

#### PREPARATION OF AMMONIUM SALTS – TWO METHODS

| a] | AMMONIA GAS      | ACID [DIL.]               | AMMONIUM SALT                                       |
|----|------------------|---------------------------|---|
|    | • $\text{NH}_3$  | + $\text{HCl}$            | $\text{NH}_4\text{Cl}$<br>[ammonium chloride]       |
|    | • $\text{NH}_3$  | + $\text{HNO}_3$          | $\text{NH}_4\text{NO}_3$<br>[ammonium nitrate]      |
|    | • $2\text{NH}_3$ | + $\text{H}_2\text{SO}_4$ | $(\text{NH}_4)_2\text{SO}_4$<br>[ammonium sulphate] |

| B) | AMMONIA [AQ.]             | ACID [DIL.]               | AMMONIUM SALT                | +                       | WATER |
|----|---------------------------|---------------------------|------------------------------|-------------------------|-------|
|    | • $\text{NH}_4\text{OH}$  | + $\text{HCl}$            | $\text{NH}_4\text{Cl}$       | + $\text{H}_2\text{O}$  |       |
|    | • $\text{NH}_4\text{OH}$  | + $\text{HNO}_3$          | $\text{NH}_4\text{NO}_3$     | + $\text{H}_2\text{O}$  |       |
|    | • $2\text{NH}_4\text{OH}$ | + $\text{H}_2\text{SO}_4$ | $(\text{NH}_4)_2\text{SO}_4$ | + $2\text{H}_2\text{O}$ |       |

NEUTRALIZATION REACTIONS – resulting in formation of ammonium salt & water.

**Ammonium salt:** Ammonium chloride is an ammonium salt which undergoes – thermal dissociation on heating.  $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$ .

## PROPERTIES – Of Ammonia [Contd.]

### CHEMICAL PROPERTIES – Of Ammonia [contd.]

#### AMMONIA GAS – Basic Nature [contd.]

Aqueous solution of ammonia or excess ammonia passed through aqueous salt solutions, precipitates hydroxides of metals from the solution of their salts

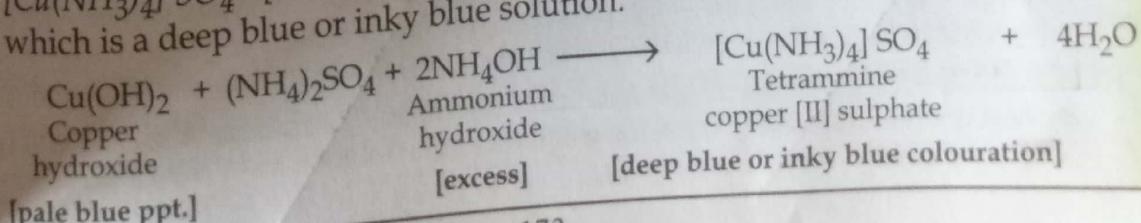
- Ammonium hydroxide reacts with metallic salt solutions – [salts of Na and K excluded] to give - insoluble precipitates of the respective metallic hydroxides.
- The precipitates which are hydroxides of metallic radicals vary in – i] colour ii] solubility in excess  $\text{NH}_4\text{OH}$  – and hence ammonium hydroxide is used in qualitative analysis for identifying positive radicals or cations.

| Metallic salt solution               | Ammonium hydroxide  | Ammonium salt | Metallic hydroxide [ppt.]    | Colour of precipitate | Solubility of precipitate in excess of $\text{NH}_4\text{OH}$ |
|--------------------------------------|---|---------------|------------------------------|-----------------------|---|
| • Iron [II]<br>$\text{FeSO}_4$       | $+ 2\text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{Fe(OH)}_2 \downarrow$   |               | $\text{Fe(OH)}_2 \downarrow$ | Dirty green           | Insoluble   |
| • Iron [III]<br>$\text{FeCl}_3$      | $+ 3\text{NH}_4\text{OH} \rightarrow 3\text{NH}_4\text{Cl} + \text{Fe(OH)}_3 \downarrow$  |               | $\text{Fe(OH)}_3 \downarrow$ | Reddish brown         | Insoluble   |
| • Lead<br>$\text{Pb}(\text{NO}_3)_2$ | $+ 2\text{NH}_4\text{OH} \rightarrow 2\text{NH}_4\text{NO}_3 + \text{Pb(OH)}_2 \downarrow$  |               | $\text{Pb(OH)}_2 \downarrow$ | Chalky white          | Insoluble   |
| • Zinc<br>$\text{ZnSO}_4$            | $+ 2\text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{Zn(OH)}_2 + (\text{NH}_4)_2\text{SO}_4 + 2\text{NH}_4\text{OH} \rightarrow [\text{Zn}(\text{NH}_3)_4]\text{SO}_4 + 4\text{H}_2\text{O}$ |               | $\text{Zn(OH)}_2 \downarrow$ | White gelatinous      | Soluble   |
| • Copper<br>$\text{CuSO}_4$          | $+ 2\text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{Cu(OH)}_2 + (\text{NH}_4)_2\text{SO}_4 + 2\text{NH}_4\text{OH} \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4 + 4\text{H}_2\text{O}$ |               | $\text{Cu(OH)}_2 \downarrow$ | Pale blue             | Soluble   |

[Lead salt solns. & zinc salt solns. can be distinguished using excess ammonium hydroxide soln. – since of the precipitated metallic hydroxides formed, lead hydroxide is insoluble while zinc hydroxide is soluble in - excess ammonium hydroxide soln.]

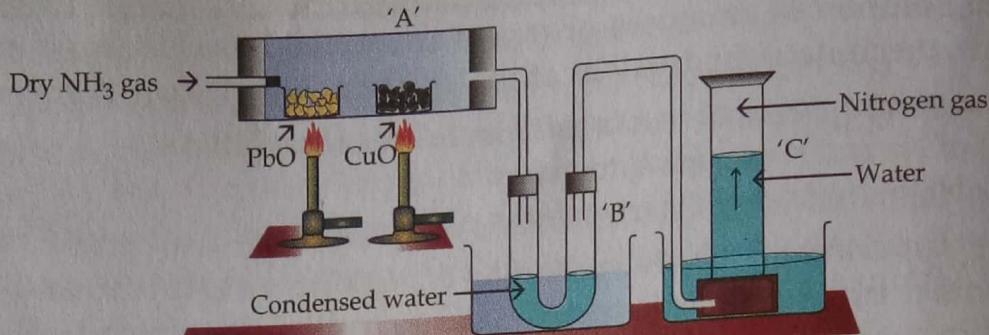
Ammonium hydroxide if first added in a small quantity & then in excess to a solution of copper [II] sulphate, forms a pale blue precipitate of copper hydroxide which dissolves in excess of ammonium hydroxide – forming a soluble complex salt.

- The pale blue precipitate of copper hydroxide formed is – soluble in excess of ammonium hydroxide, since a soluble complex  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  - [tetrammine copper [II] sulphate] is formed which is a deep blue or inky blue solution.



### 3. AMMONIA GAS – Reducing action

Ammonia gas is a strong reducing agent and reduces metallic oxides & chlorine.



Reducing action of ammonia on lead [II] oxide and copper [II] oxide

#### a) AMMONIA REDUCES – Heated Metallic Oxides to Metals.

**REACTANTS** : Copper [II] oxide [CuO] or lead [II] oxide [PbO] and ammonia

**PRODUCTS** : Copper or lead as reduced products respectively, water & nitrogen.

**PROCEDURE** : Dry ammonia gas is passed over heated – black copper [II] oxide or buff yellow lead [II] oxide placed in a combustion tube [A].

**OBSERVATION:** • Black copper [II] oxide is reduced to – brown copper.

Buff yellow lead [II] oxide is reduced to – greyish metallic lead.

• The water vapour condenses in U-tube [B] & N<sub>2</sub> collects in gas jar [C].

| Reducing agent   | Metallic oxide [heated]      | Reduced product           | Water                | Nitrogen |
|------------------|------------------------------|---------------------------|----------------------|----------|
| 2NH <sub>3</sub> | + 3CuO<br>[basic oxide]      | → 3Cu + 3H <sub>2</sub> O | + N <sub>2</sub> [g] |          |
| 2NH <sub>3</sub> | + 3PbO<br>[amphoteric oxide] | → 3Pb + 3H <sub>2</sub> O | + N <sub>2</sub> [g] |          |

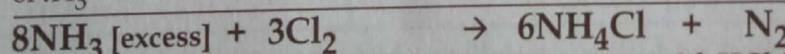
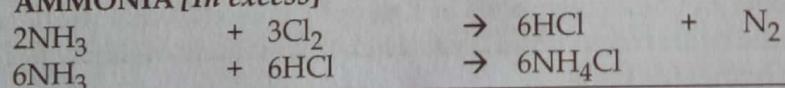
[the above reactions illustrate – the reducing nature of ammonia].

Ammonia is thus oxidised by a metal oxide [CuO, PbO] & by a gas other than oxygen [chlorine]

#### b) AMMONIA REDUCES – Chlorine to Hydrogen Chloride.

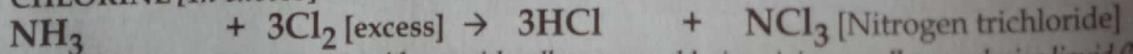
When ammonia and chlorine are mixed, the chlorine is reduced to HCl – which further combines with excess ammonia forming NH<sub>4</sub>Cl.

- AMMONIA [In excess]



Dense white fumes – are thus seen when NH<sub>3</sub> reacts with HCl & also when it reacts with Cl<sub>2</sub>.

- CHLORINE [In excess]



[colourless ammonia gas – reacts with greenish yellow excess chlorine giving a yellow explosive liquid (NCl<sub>3</sub>)]

#### REFERENCE – Preparation of nitrogen from – air

- Air freed from – a] CO<sub>2</sub> – by passage through conc. KOH soln. b] Water vapour – by passage through CaO. c] Oxygen – by passage over heated copper [2Cu + O<sub>2</sub> → 2CuO] now contains unreactive residual N<sub>2</sub> which is collected by – downward displacement of water.

#### REFERENCE – Preparation of nitrogen from unstable – Ammonium nitrite [NH<sub>4</sub>NO<sub>2</sub>]

- By heat on a saturated soln. containing equimolecular weights of – NH<sub>4</sub>Cl & NaNO<sub>2</sub>.  

$$\text{NH}_4\text{Cl} + \text{NaNO}_2 \rightarrow \text{NaCl} + \text{NH}_4\text{NO}_2$$

$$\text{NH}_4\text{NO}_2 \rightarrow 2\text{H}_2\text{O} + \text{N}_2$$

## TESTS – For Ammonia

| TEST  | OBSERVATION   |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
|---|---|---|--------------------------------------|--|--------------------------------------|---|---|-----|------|---------------|--------|--------|-----------------|------------|------|
| A. From its   |   |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| • Odour   | Characteristic irritating and <i>pungent odour</i> – which is easily recognizable.  |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| • Physiological nature  | It causes an irritating, burning sensation in the upper part of the nasal passage and – brings tears to the eyes.   |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| • Action on indicators  | Its solution being – <i>basic [alkaline]</i> in nature turns  |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
|   | <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th rowspan="2" style="text-align: center; width: 30%;">Indicator</th> <th colspan="2" style="text-align: center; border-bottom: 1px solid black;">Colour change</th> </tr> <tr> <th style="text-align: center;">Original</th> <th style="text-align: center;">To</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">Litmus</td> <td style="text-align: center;">Red</td> <td style="text-align: center;">Blue</td> </tr> <tr> <td style="text-align: center;">Methyl orange</td> <td style="text-align: center;">Orange</td> <td style="text-align: center;">Yellow</td> </tr> <tr> <td style="text-align: center;">Phenolphthalein</td> <td style="text-align: center;">Colourless</td> <td style="text-align: center;">Pink</td> </tr> </tbody> </table> | Indicator   | Colour change                        |  | Original                             | To  | Litmus  | Red | Blue | Methyl orange | Orange | Yellow | Phenolphthalein | Colourless | Pink |
| Indicator   | Colour change   |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
|   | Original  | To  |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| Litmus  | Red   | Blue  |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| Methyl orange   | Orange  | Yellow  |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| Phenolphthalein   | Colourless  | Pink  |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| B. A glass rod dipped in conc. HCl acid brought near ammonia gas  | <p>Neutral litmus [purple] turns – blue in alkaline medium.</p> <p>Ammonia – an alkaline gas gives – <i>dense white fumes</i> – of <math>\text{NH}_4\text{Cl}</math> with hydrogen chloride [HCl].</p>  |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
|   | <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center; width: 30%;">Ammonia<br/>[gas]</th> <th style="text-align: center; width: 30%;">Conc. HCl<br/>[on glass rod]</th> <th style="text-align: center; width: 30%;">Ammonium chloride<br/>[Dense white fumes]</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;"><math>\text{NH}_3</math></td> <td style="text-align: center;">+</td> <td style="text-align: center;"><math>\text{HCl} \longrightarrow \text{NH}_4\text{Cl}</math></td> </tr> </tbody> </table>  | Ammonia<br>[gas]                                  | Conc. HCl<br>[on glass rod]          | Ammonium chloride<br>[Dense white fumes] | $\text{NH}_3$                        | +   | $\text{HCl} \longrightarrow \text{NH}_4\text{Cl}$ |     |      |               |        |        |                 |            |      |
| Ammonia<br>[gas]  | Conc. HCl<br>[on glass rod]   | Ammonium chloride<br>[Dense white fumes]          |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| $\text{NH}_3$   | +   | $\text{HCl} \longrightarrow \text{NH}_4\text{Cl}$ |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| C. By passage of ammonia gas through  |   |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| • Copper sulphate soln.   | <p>Pale blue precipitate of copper hydroxide is formed.</p>   |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
|   | <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center; width: 25%;">Copper sulphate<br/>soln.</th> <th style="text-align: center; width: 25%;">Ammonia<br/>[soln.]</th> <th style="text-align: center; width: 25%;">Ammonium sulphate</th> <th style="text-align: center; width: 25%;">Copper hydroxide<br/>[pale blue ppt.]</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;"><math>\text{CuSO}_4 + 2\text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{Cu}(\text{OH})_2 \downarrow</math></td> <td></td> <td></td> <td></td> </tr> </tbody> </table>   | Copper sulphate<br>soln.                          | Ammonia<br>[soln.]                   | Ammonium sulphate                        | Copper hydroxide<br>[pale blue ppt.] | $\text{CuSO}_4 + 2\text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{Cu}(\text{OH})_2 \downarrow$ |   |     |      |               |        |        |                 |            |      |
| Copper sulphate<br>soln.  | Ammonia<br>[soln.]  | Ammonium sulphate                                 | Copper hydroxide<br>[pale blue ppt.] |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| $\text{CuSO}_4 + 2\text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{Cu}(\text{OH})_2 \downarrow$ |   |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
|   | <p>The pale blue precipitate turns into a – <i>deep blue coloured solution</i> on passage of excess ammonia.</p> $\text{Cu}(\text{OH})_2 + (\text{NH}_4)_2\text{SO}_4 + 2\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4 + 4\text{H}_2\text{O}$ <p>This is due to the formation of the soluble complex – tetra amine copper [II] sulphate – <math>[\text{Cu}(\text{NH}_3)_4]\text{SO}_4</math></p>  |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |
| • Nessler's reagent<br>[ $\text{K}_2\text{HgI}_4$ ]<br>[potassium mercuric iodide]                        | <p>Colourless Nessler's reagent turns – <i>pale brown</i>.</p> <p>On passage of excess ammonia – a brown precipitate is obtained.</p>   |   |                                      |  |                                      |   |   |     |      |               |        |        |                 |            |      |

## E. USES – Of Ammonia

### 1. AMMONIA GAS - Industrial Uses [Manufacture of]

| SYNTHETIC PRODUCTS   | FERTILIZERS  | AMMONIUM COMPOUNDS   |
|--|--|--|
| <ul style="list-style-type: none"> <li>Source of - Hydrogen</li> <li>Source of - Nitric acid [by Ostwald's process]</li> </ul> <p><b>MANUFACTURE OF:</b></p> <ul style="list-style-type: none"> <li>Explosives [Ammonium nitrate]</li> <li>Dyes and Drugs</li> <li>Plastics &amp; Resins</li> <li>Baking soda <math>[NaHCO_3]</math></li> <li>Washing soda <math>[Na_2CO_3 \cdot 10H_2O]</math> [Solvay process]</li> <li>Artificial silk</li> </ul> | <ul style="list-style-type: none"> <li>Urea <math>[NH_2CO.NH_2]</math></li> <li>Ammonium sulphate <math>[(NH_4)_2SO_4]</math></li> <li>Ammonium nitrate <math>[NH_4NO_3]</math></li> <li>Calcium ammonium nitrate</li> <li>Di-ammonium hydrogen phosphate</li> </ul> | <ul style="list-style-type: none"> <li>Ammonium carbonate <math>[(NH_4)_2CO_3]</math></li> <li>Constituent of <i>smelling salt</i> [dissociates evolving pungent ammonia gas - revives a fainted person]</li> <li><i>Application</i> : In baking and dyeing industry</li> <li>Ammonium chloride <math>[NH_4Cl]</math></li> <li>Cleaning metal surfaces [dissociates into <math>NH_3</math> and <math>HCl</math> and the <math>HCl</math> dissolves the - metallic oxide coating.]</li> <li><i>Application</i> : In dry cells, medicine &amp; textile industry</li> <li>Ammonium sulphate <math>[(NH_4)_2SO_4]</math></li> <li>It is an important <i>fertilizer</i></li> <li><i>Application</i> : In manufacture of alum</li> </ul> |

### 2. LIQUOR AMMONIA - Aq. soln. of ammonia gas in water

|                      |   |
|----------------------|---|
| As a cleansing agent | <ul style="list-style-type: none"> <li>Liquor ammonia - emulsifies or dissolves fats, grease etc., hence is used for - removing oil or grease stains from clothes.</li> <li>Liquor ammonia - is also used for cleaning window panes, porcelain articles etc.</li> </ul> |
|----------------------|---|

### 3. LIQUID AMMONIA - Ammonia gas liquefied at low temperature

|                           |  |
|---------------------------|--|
| Refrigerant in ice plants | <ul style="list-style-type: none"> <li>Liquid ammonia - is used as a refrigerant since -           <ul style="list-style-type: none"> <li>i] It is highly volatile &amp; has a high latent heat of evaporation.</li> <li>ii] It easily liquefies under pressure, at low temperatures.</li> </ul> </li> <li>If therefore liquid ammonia is evaporated - a relatively large amount of heat is absorbed from the surroundings and the water is converted to ice.</li> </ul> $NH_3 \text{ [liquid]} \longrightarrow NH_3 \text{ [gas]} - 5.7 \text{ K cals}$ <p>[Heat of evaporation of ammonia is 5.7 K cals at <math>-33^\circ C</math>]</p> |
|---------------------------|--|

#### Chlorofluorocarbons - in refrigeration gas - cause ozone depletion

- Chlorofluorocarbons [CFC ie  $CFCl_3$  - freon] - are chemicals which like liquefied ammonia gas are used in - refrigeration gas. Unlike liq. ammonia, chlorofluorocarbons enter the atmosphere due to their use as coolants in refrigeration & A/C plants & aerosol sprays & cause ozone depletion in the atmosphere. [Ozone layer - is a layer of ozone located in the stratosphere above the earth. Chlorofluorocarbons are decomposed by U.V. rays to give - free Cl radicals.  $CFCl_3 \rightarrow Cl$  atom This Cl atom breaks the ozone layer causing - ozone depletion.  $Cl + O_3 \text{ [ozone]} \rightarrow ClO + O_2$ ] Hence ozone layer which prevents harmful U.V. radiations from reaching the earth - gets depleted.
- Suitable alternatives to chlorofluorocarbons which are non-ozone depleting include - Hydrochlorofluorocarbons [HCFC] which act as a substitute for CFCs. [The hydrochlorofluorocarbons include: HCFC - 123 i.e. 2,2 - dichloro - 1,1,1 trifluoroethane & HCFC - 124 i.e. 2 - chloro - 1,1,1,2 - tetrafluoroethane.