

CHAPTER 7-B

Study of Compounds – Ammonia

SYLLABUS - SCOPE OF SYLLABUS - in and after MARCH 2022 - 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 [III] 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

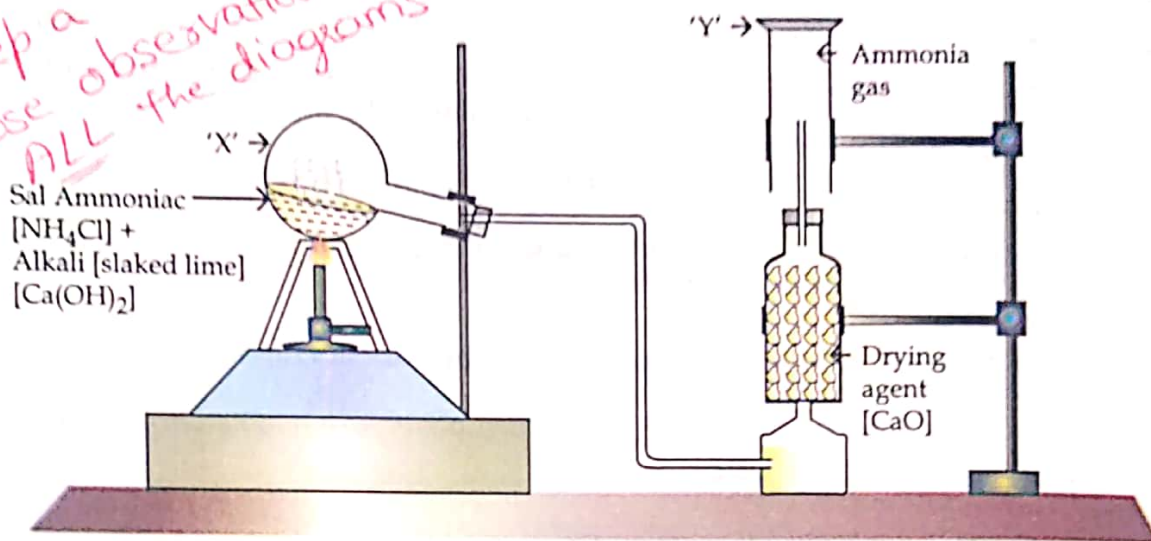
[obtained by destructive distillation of coal] are two important - sources of ammonia.

B. PREPARATION – of Ammonia

1. LABORATORY METHOD - From ammonium salts

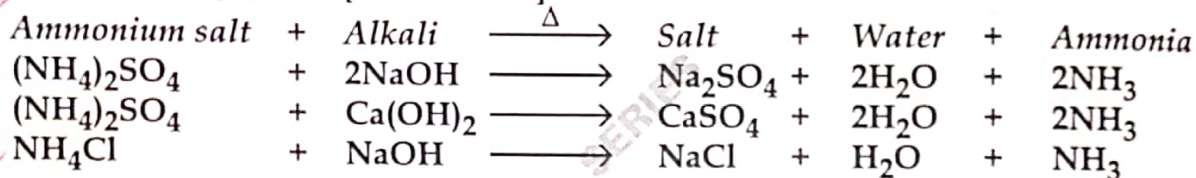
Heating – a mixture of an – ammonium salt [NH_4Cl] with – an alkali [$\text{Ca}(\text{OH})_2$].

Keep a close observation of ALL the diagrams



Laboratory preparation of ammonia - from ammonium chloride

REACTION - EQUATION [CONDITIONS]



Laboratory Preparation



Above reactions of – ammonium salts with alkalis distinguish them from other salts e.g. sodium sulphate 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 alkalis e.g. NaOH or $\text{Ca}(\text{OH})_2$]

REACTANTS : Ammonium chloride [NH_4Cl] and calcium hydroxide [slaked lime] [$\text{Ca}(\text{OH})_2$] – in round bottom flask [X].

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

PROCEDURE : The reactants i.e. 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	$(\text{NH}_4)_2\text{SO}_4$ [ammonium sulphate]
6NH_3	+ $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$ \rightarrow	$2(\text{NH}_4)_3\text{PO}_4$ [ammonium phosphate]
8NH_3	+ CaCl_2 [fused] \rightarrow	$\text{CaCl}_2 \cdot 8\text{NH}_3$ [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.

X [V.D. of ammonia = 8.5, V.D. of air = 14.4].

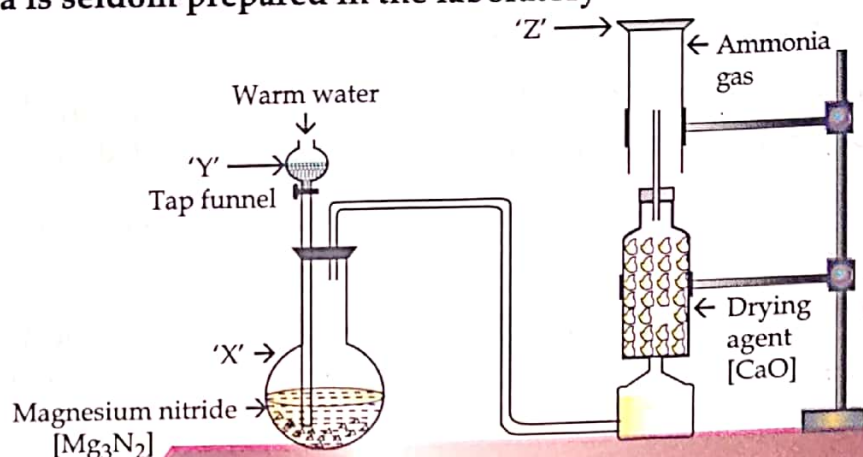
- Ammonia gas is not collected over water – since it is highly soluble in water.

X [1 vol. of water dissolves about 702 vols. at 20°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	→	Metal nitride
	3Mg	+ N_2	→	Mg_3N_2
	3Ca	+ N_2	→	Ca_3N_2
	2Al	+ N_2	→	$2AlN$

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

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

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.

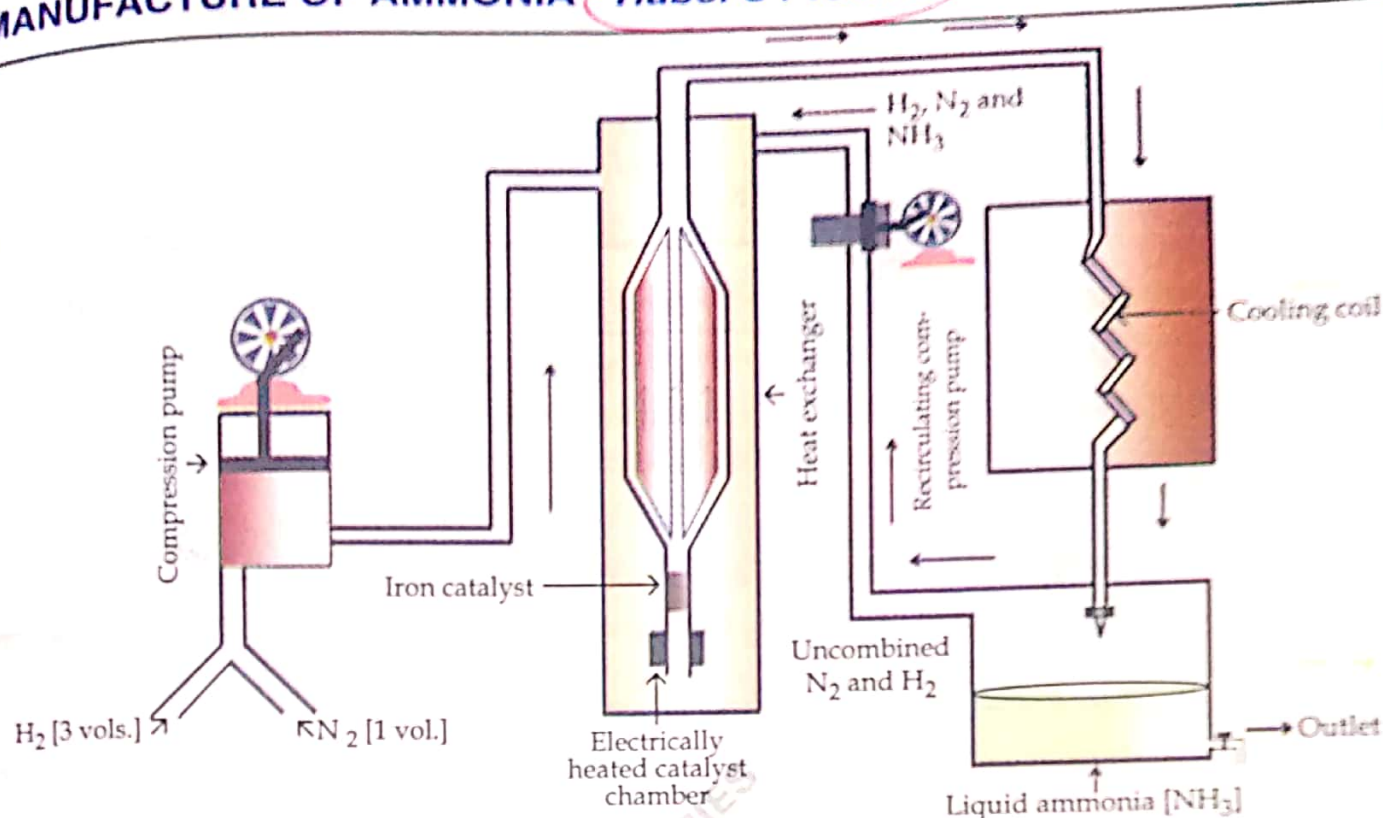
PRECAUTION : The lower end of the thistle funnel should dip - below the warm water in the flask [X]. Since nitrides are expensive, the method is seldom used.

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 [Z]. If the jar is full, dense white fumes of ammonium chloride are formed.

MANUFACTURE – of Ammonia [Contd.]

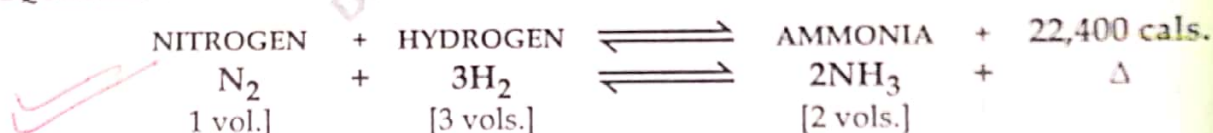
3. MANUFACTURE OF AMMONIA - Haber's Process



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]

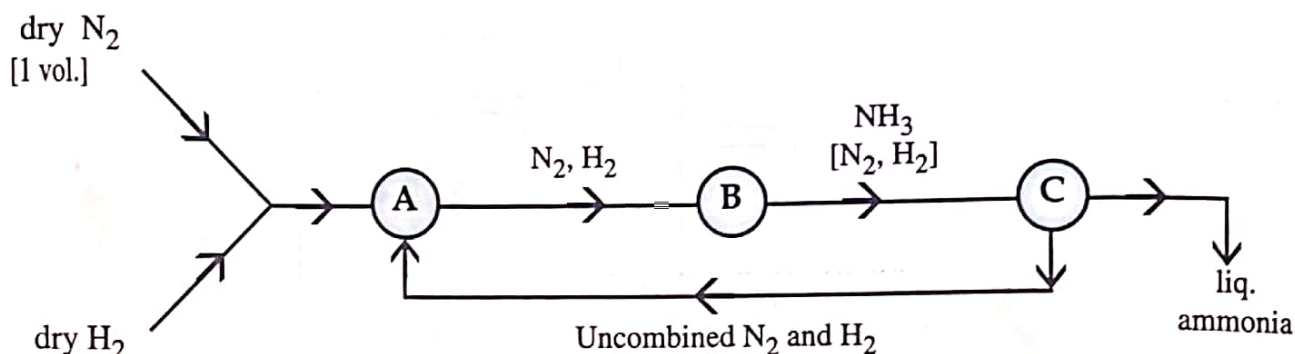
Promotor : Molybdenum [Mo]

[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 N₂ and H₂ 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 NH₃ 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 NH₃ 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.

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page

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* – *like CO₂, CO, H₂S etc* – pure and dry since – *impurities tend to poison the catalyst and reduce its effectiveness.*

2. TEMPERATURE

An optimum temperature of 450-500°C is used in the Haber's process.

through initial electrical heating

- 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 450-500°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 N_2 + 3 vols. of $H_2 \rightarrow$ 2 vols. of 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	Ammonia is – easily liquefiable <ul style="list-style-type: none"> • It condenses to a liquid at around -33°C at 8 atmos. press. • N_2 and H_2 are – difficult to liquefy. They condense at temperatures around –196°C and –253°C respectively and at comparatively higher pressures.
• Dissolving in water	Ammonia is – highly soluble in water <ul style="list-style-type: none"> • 1 vol. of water dissolves about 702 vols. of NH_3 at 20°C and 1 atmos. pressure. • N_2 and H_2 are – almost insoluble in water.

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

Colourless; Strong, pungent smell; Slight alkaline taste

2. Physiological nature

Non-poisonous. If inhaled affects the respiratory system. It is fatal in large doses.

3. Density

Lighter than air [V.D. of ammonia = 8.5 (V.D. of air = 14.4)]

4. Solubility

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.

5. Liquefaction

Easily liquefied at low temperatures.

6. Boiling point

Liquid ammonia boils at -33.5°C

7. Freezing point

Solid NH_3 melts at -77.7°C

FOUNTAIN EXPERIMENT - To demonstrate - the high solubility of 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:

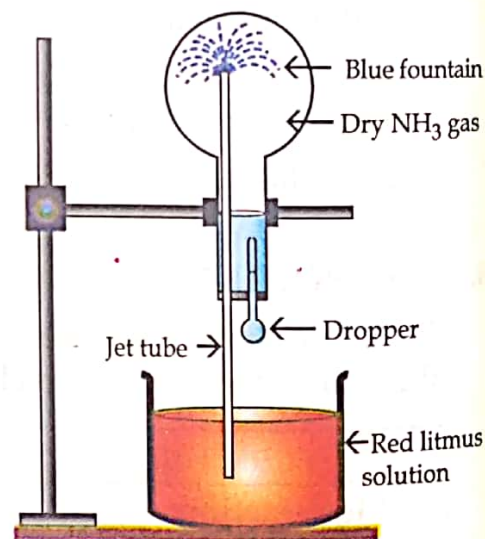
- The dropper containing water is squeezed - and the water enters the flask.

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 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 HCl is - *acidic*.]



Fountain Experiment