# Study of Compounds — Ammonia

# SYLLABUS

(i) Ammonia : Its laboratory preparation from ammonium chloride and collection; ammonia from nitrides like  $Mg_3N_2$  and AlN and ammonium salts Manufacture by Haber's Process; density and solubility of ammonia (fountain experiment); aqueous solution of ammonia; its reactions with hydrogen chloride and with hot copper (II) oxide and chlorine; the burning of ammonia in oxygen; uses of ammonia.

Laboratory preparation from ammonium chloride and collection (the preparation can be studied in terms of setting of the apparatus and diagram, procedure, observation, collection and identification).

Manufacture of ammonia on a large scale – reference should be made to Haber Process for the manufacture of ammonia; Ammonia from nitrides like  $Mg_3N_2$  and AlN and ammonium salts; the reactions can be studied in terms of reactant, product, condition, equation.

Density and solubility of ammonia (fountain experiment); the property can be learnt in terms of setting of the apparatus, procedure and observation and inference.

Aqueous solution of ammonia – reaction with sulphuric acid, nitric acid, hydrochloric acid and solutions of iron (III) chloride, iron (II) sulphate. lead nitrate, zinc nitrate and copper sulphate.

Its reaction with : hydrogen chloride, hot copper (II) oxide, with chlorine in excess and ammonia in excess, burning of ammonia in oxygen; all these reactions may be studied in terms of reactants; products, condition, equation and observation; reference should be made to preparation of nitrogen from air and from ammonium nitrite.

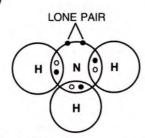
Uses of ammonia – manufacture of fertilizers, explosives, nitric acid, refrigerants gas (Chlorofluro carbon – and its suitable alternatives which are non-ozone depleting), cleansing agents, source of hydrogen.

(ii) The catalytic oxidation of ammonia, as the source of nitric acid (refer to Ostwald process) : simple diagram for a catalytic oxidation of ammonia in the laboratory (with conditions and reactions only).
 Self-explanatory

## Molecular formula : NH<sub>3</sub>

#### Relative molecular mass: 17





Lewis diagram or dot diagram

Covalent bonding in ammonia

### 9.1 OCCURRENCE

**Free state :** Ammonia is present in small amounts in air and in traces in natural water.

**Combined state :** In nature, ammonia occurs in *combined form* in many compounds such as ammonium chloride (Hindi : *Nausadar*), ammonium sulphate, etc. Ammonia and ammonium compounds being highly soluble in water, do not occur as minerals.

*Note*: The pungent smell which one encounters near a *decaying heap* of organic matter or a toilet is due to ammonia.

It is produced due to bacterial decomposition of urea (NH<sub>2</sub>CONH<sub>2</sub>), present in the urine.

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

#### Forms of ammonia

Ammonia is used commonly in the following forms :

- (i) Gaseous ammonia (dry ammonia gas)
- Liquid ammonia. When dry ammonia is liquefied by applying high pressure it is called liquid ammonia.

# (iii) Liquor ammonia fortis is a saturated solution position, mouth downwards as shown in Fig. 9.1.

- Liquor ammonia fortis is a saturated solution of ammonia in water. It is called 880 ammonia. It has a relative density of 0.880. It is stored in tightly stoppered bottles in a cold place.
- (iv) *Laboratory bench reagent* : Dilute solution of liquor ammonia is used as a laboratory reagent.

# 9.2 PREPARATION OF AMMONIA GAS

## 9.2.1 General methods of preparation

Ammonia gas can be prepared by warming an ammonium salt with caustic alkali, such as slaked lime or caustic soda or caustic potash.

Ammonium salt +	Alkali $\xrightarrow{\Delta}$	Salt +	Water + Ammonia
$2NH_4Cl(s) +$	$\begin{array}{c} \text{Ca(OH)}_{2}(s) \xrightarrow{\Delta} \\ \text{Slaked lime} \end{array}$	CaCl <sub>2</sub> (s) +	2H <sub>2</sub> O + 2NH <sub>3</sub> ↑
$(NH_4)_2SO_4 +$	$Ca(OH)_2 \xrightarrow{\Delta}$	CaSO <sub>4</sub> +	$2H_2O + 2NH_3\uparrow$
$(NH_4)_2SO_4 +$	$\begin{array}{ccc} 2NaOH & \stackrel{\Delta}{\rightarrow} \\ Caustic \ soda \end{array}$	$Na_2SO_4 +$	$2H_2O + 2NH_3\uparrow$
$(NH_4)_2SO_4 +$	$\begin{array}{c} \text{Caustic soua} \\ 2\text{KOH} \xrightarrow{\Delta} \\ \text{Caustic potash} \end{array}$	K <sub>2</sub> SO <sub>4</sub> +	2H <sub>2</sub> O + 2NH <sub>3</sub> ↑

# 9.2.2 Laboratory preparation

### (1) From ammonium chloride

**Reactants :** Ammonium chloride  $(NH_4Cl)$  and calcium hydroxide  $[Ca(OH)_2]$  in the ratio of 2 : 3 by weight.

 $2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O + 2NH_3$ .

#### **Reaction**:

CALCIUM HYDROXIDE AND AMMONIUM CHLORIDE QUICKLIME TO DRY AMMONIA

Fig. 9.1 Lab. preparation of dry ammonia

**Procedure :** Reactants are finely grinded and taken in a round-bottom flask fitted in a slanting

position, mouth downwards as shown in Fig. 9.1. On heating the mixture, ammonia gas is evolved.

**Precautions :** The flask is tilted in such a way that the water formed in the reaction does not trickle back into the heated flask and thus break it.

Drying of ammonia gas : In order to get dry ammonia, the gas is passed through a drying tower containing lumps of *quicklime* (CaO).

Unsuitability of other drying agents : Other drying agents like conc. sulphuric acid, phosphorous pentoxide and anhydrous calcium chloride are not used, as ammonia being basic, reacts with them.

 $2NH_{3} + H_{2}SO_{4} \rightarrow (NH_{4})_{2}SO_{4}$   $6NH_{3} + P_{2}O_{5} + 3H_{2}O \rightarrow 2 (NH_{4})_{3}PO_{4}$ ammonium phosphate  $CaCl_{2} + 4NH_{3} \rightarrow CaCl_{2}.4NH_{3}$ (addition compound)

#### **Collection :**

Ammonia 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; that of *air*, 14.4),
- (ii) highly soluble in water and therefore, it cannot be collected over water.
- **Note :** 1. The reactants  $NH_4Cl$  and  $Ca(OH)_2$  are taken in the ratio of 2 : 3 by weight, higher ratio by weight of the alkali may counteract the loss by sublimation of  $NH_4Cl$ .
  - 2. Calcium hydroxide is used, as it is cheap and not deliquescent like other alkalies.
  - 3. Though all ammonium salts, on heating with alkalies give  $NH_3$ , yet  $NH_4NO_3$  (*explosive in nature*) and  $NH_4NO_2$  on warming with alkalies do not produce ammonia because they decompose on heating.

 $\begin{array}{ccc} \mathrm{NH}_4\mathrm{NO}_3 & \stackrel{\Delta}{\longrightarrow} & \mathrm{N}_2\mathrm{O} + 2\mathrm{H}_2\mathrm{O} \\ \mathrm{NH}_4\mathrm{NO}_2 & \stackrel{\Delta}{\longrightarrow} & \mathrm{N}_2 + 2\mathrm{H}_2\mathrm{O} \end{array}$ 

# (2) From metal nitrides

Ammonia can also be obtained by the action

of warm water on nitrides of metals like magnesium or Aluminium. (This method is costly)

**Reaction :** 

$$Mg_{3}N_{2} + 6H_{2}O \rightarrow 3Mg(OH)_{2} + 2NH_{3}\uparrow$$
  
or  
$$AlN + 3H_{2}O \rightarrow Al(OH)_{3} + NH_{3}\uparrow$$

**Procedure :** Magnesium nitride or Aluminium nitride is kept in a round bottomed flask fitted with a thistle funnel and a delivery tube, as shown in Fig 9.2. Warm water is added very slowly.

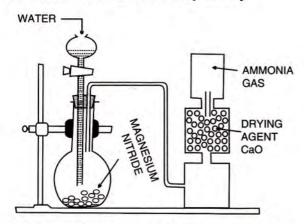


Fig. 9.2 Preparation of ammonia from magnesium nitride

Ammonia gas is liberated and magnesium hydroxide or aluminium hydroxide is also formed, but it remains in the flask and the liberated ammonia gas escapes through the delivery tube.

The ammonia gas formed is collected by holding the jar with its **mouth downwards** over the delivery tube.

The gas can be dried by passing it through **quicklime packed** in a drying tower.

#### 9.3 PREPARATION OF AQUEOUS AMMONIA

An aqueous solution of ammonia is prepared by dissolving ammonia in water. The rate of dissolution of ammonia in water is very high, therefore, **back suction**<sup>\*</sup> of water is possible. To avoid this, a funnel is attached to the outer end of the delivery tube with rubber tubing (the process is similar to the method used to change HCl gas into hydrochloric acid).

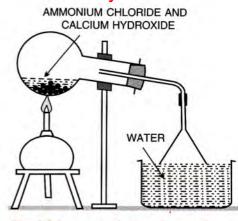
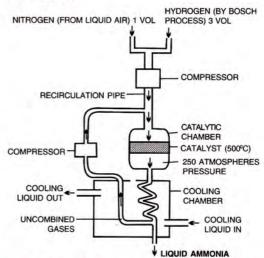


Fig. 9.3 Aqueous solution of ammonia

**Procedure :** Water is taken in a container and only a small portion of the mouth of the funnel is dipped in water.

As ammonia dissolves in water at a higher rate than its production in the flask, the pressure in the funnel above water level decreases for a moment, and water rushes into the funnel. As a result, the rim of the funnel loses its contact with water. Since, ammonia produced pushes the water down, the funnel comes in contact with water again. In this way, ammonia dissolves in water without back suction of water.

### 9.4 MANUFACTURE OF AMMONIA (HABER'S PROCESS)



#### Fig. 9.4. Manufacture of ammonia by Haber's process

**Reactants :** Nitrogen and hydrogen in the ratio of 1 : 3 by volume.

#### Sources of reactants :

**Nitrogen gas** is obtained by fractional distillation of liquid air.

<sup>\*</sup> The funnel provides a larger surface area for dissolution of ammonia in water and prevents back suction of water into the hot flask.

**Hydrogen gas** is obtained from water gas (Bosch process) or from natural gas.

#### **Reaction :**

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

The reaction is reversible, exothermic and proceeds with a decrease in volume.

#### Favourable conditions :

Temperature : Optimum temperature is 450-500 °C.

Pressure : Above 200 atm.

Catalyst : Finely divided iron\*.

**Promoter** : Traces of molybdenum or Al<sub>2</sub>O<sub>3</sub>.

**Rate of conversion :** About 15% of the reacting gases get converted to ammonia.

#### Recovery of ammonia :

Ammonia is separated from the unreacted nitrogen and hydrogen by :

- 1. Liquefaction Ammonia has a much higher boiling point as compared to  $N_2$  and  $H_2$  so it condenses easily.
- 2. Absorbing in water because  $NH_3$  is highly soluble in water, while  $N_2$  and  $H_2$  are very slightly soluble.

**Process :** Nitrogen and hydrogen are dried, purified and then mixed in the ratio of 1 : 3 respectively, at a relatively high pressure. This mixture is passed in an electrically heated catalytic chamber containing finely divided iron with aluminium oxide or a little amount of molybdenum at a temperature of 500°C. Mixture of ammonia formed along with residual nitrogen and hydrogen exchanges their heat with the incoming unreacted nitrogen and hydrogen mixture.

The hot mixture of the outgoing gases contains nearly 15% ammonia. The mixture is passed through the cooling pipes (condenser).

Ammonia **liquefies** first, whereas nitrogen and hydrogen do not liquefy easily.

The unchanged nitrogen and hydrogen are recirculated through the plant to get more ammonia. By re-circulating in this way, an eventual yield of 98% can be achieved. The ammonia produced is stored as liquid under pressure.

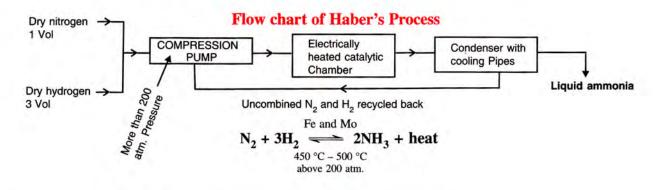
Note :

- (i) The reaction is exothermic, hence low temperature will favour the synthesis. However, at low temperature, the reaction proceeds slowly. In practice, the optimum temperature has been found to be in the range of 450°C to 500°C.
- (*ii*) Four volumes of reactants produce two volumes of product, hence *high pressure* favours the formation of ammonia.

The optimum pressure is found to be 200 to 900 atm. Practically, a pressure of about 250 atm. is used.

(iii) Catalyst and promoter : The speed of the reaction can be improved by using a catalyst, which is finely divided iron, obtained by the reduction of iron oxide.

A promoter **molybdenum** or  $Al_2O_3$  is used to increase the efficiency of the catalyst.



\* Finely divided catalyst has more surface area, this increases the efficiency of the catalyst.

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

**Note**: The purification of nitrogen and hydrogen is necessary as impurities like *carbon* dioxide, carbon monoxide and traces of sulphur compounds ( $H_2S$ ) poisons the catalyst. The removal of these **catalytic poisons** from nitrogen and hydrogen is very essential.

## Intext Questions

- (a) State the type of bonding present in ammonia, show by a diagram.
  - (b) What is the formula of liquid ammonia ? Account for the basic nature of this compound.
- (a) Write a balanced chemical equation for the lab preparation of ammonia.
  - (b) How is ammonia dried and collected in the laboratory?
  - (c) Ammonia cannot be collected over water. Give reason.
  - (d) Explain with a diagram the preparation of aqueous ammonia.
- Name a drying agent for ammonia. Why are other drying agents such as, P<sub>2</sub>O<sub>5</sub> and CaCl<sub>2</sub> are not used ?
- A substance 'A' was heated with slaked lime and a gas 'B' with a pungent smell was obtained. Name the substances A and B and give a balanced equation.
- 5. Ammonia is manufactured by Haber Process.
  - (a) Under what conditions do the reactants combine to form ammonia ? Give a balanced equation for the reaction.
  - (b) In what ratio by volume, are the above gases used ?
  - (c) State one possible source of each reactant used in Haber Process.
  - (d) State whether the formation of ammonia is promoted by the use of high pressure or low pressure?
  - (e) Mention two possible ways by which ammonia produced is removed from unchanged gases.
  - (f) What is the function of :
    - (i) finely divided iron,
    - (ii) molybdenum in the above process ?
  - (g) What is the percentage formation of ammonia ?
  - (h) How can this percentage formation be increased ?
- 6. Give reasons :
  - (a) Ammonium compounds do not occur as minerals.

- (b) Ammonium nitrate is not used in the preparation of ammonia.
- (c) Conc H<sub>2</sub>SO<sub>4</sub> is a good drying agent, yet it is not used to dry NH<sub>3</sub>.
- 7. (a) Complete the table.

Name of process	Inputs	Equations	Output
		and the second	Ammonia

(b) State the following conditions required in above process

- (i) Temperature (ii) Pressure (iii) Catalyst
- Choose the correct word or phrase from the brackets to complete the following sentences and write balanced equations for the same.
- 9. Correct the following :
  - (a) A reddish brown precipitate is obtained when ammonium hydroxide is added to ferrous sulphate.
  - (b) Liquid ammonia is a solution of NH<sub>3</sub>.
  - (c) Finely divided platinum is used in Haber Process.
  - (d) Conc. H<sub>2</sub>SO<sub>4</sub> is a drying agent for NH<sub>3</sub>.
  - (e) Ammonium salts, on heating, decompose to give ammonia.
- 10. Give reasons for the following :
  - (a) Liquid ammonia is used as a refrigerant in ice plants.
  - (b) Aqueous solution of ammonia is used for removing grease stains from woollen clothes.
  - (c) Aqueous solution of ammonia gives a pungent smell.
  - (d) Aqueous solution of ammonia conducts electricity.

#### 9.5 PHYSICAL PROPERTIES OF AMMONIA

- **1. Colour** : Colourless.
- 2. Odour : Strong, pungent choking smell.
- **3. Taste** : Slightly bitter (alkaline) taste.
- 4. Physiological : Non-poisonous.

action If inhaled, affects the respiratory system and brings tears to eyes. It is a powerful heart stimulant and may cause death when inhaled in large quantities. -

- **5. Density** : Vapour density = 8.5 [Lighter than air]
- 6. Nature : Alkaline nature

- 7. Liquefaction : Easily liquefied at 10°C by compressing it at 6 atm. pressure.
- 8. Boiling point : Liquid ammonia boils at -33.5°C.
- 9. Freezing point : Solid NH<sub>3</sub> melts at -77.7°C.
- **10. Solubility** : *Highly soluble in water,* 1 vol. of water dissolves about 702 vols. of ammonia at 20°C and 1 atm. pressure.

### FOUNTAIN EXPERIMENT

To demonstrate the high solubility of ammonia gas in water.

### **Apparatus** :

- 1. A round bottomed flask filled with ammonia gas.
- 2. Mouth of the flask is fitted with a rubber stopper with two holes, one for jet tube and the other for a dropper containing water.
- 3. A trough containing red litmus solution.
- 4. A retort stand is used to fix the round bottomed flask in inverted position as shown in Fig. 9.5.

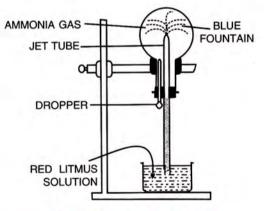


Fig. 9.5. Fountain experiment

## **Procedure :**

- 1. The dropper containing water is squeezed.
- 2. As few drops of water enter the flask, ammonia gas present in the flask gets dissolved in water, due to its high solubility. This creates a partial vacuum in the flask.
- 3. Since, outside pressure is higher, the red litmus solution rushes up through the jet tube and emerges as a blue fountain. [Ammonia gas being basic, changes red litmus solution blue.]

A bottle of liquor ammonia should be opened very carefully, only after cooling it in ice or cold water. There is high pressure inside the bottle of ammonia and on cooling, the pressure drops. This prevents sudden flushing out of the gas.

# 9.6 CHEMICAL PROPERTIES OF AMMONIA

 Thermal dissociation : Ammonia gas dissociates into nitrogen and hydrogen at high temperature or by electric sparks.

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

2. Basic properties : Dry ammonia is a covalent molecule. So, it is neutral even in liquefied form.

Its aqueous solution is a weak base, *the basicity is due to a lone pair of electrons on* its nitrogen atom.

Lone pair 
$$\rightarrow \begin{array}{c} H \\ | \\ N \\ | \\ N \\ H \\ H \end{array}$$

An aqueous solution of ammonia  $[NH_4OH]$  is a weak base. It dissociates partially to give hydroxyl ions.

The alkaline behaviour is due to the hydroxyl ions  $[OH^{-}]$ 

$$NH_3 + H_2O \iff NH_4OH$$
$$NH_4OH \iff NH_4 + OH$$

Action on indicators

	Change in colour				
Indicator	Original	То			
Moist litmus	Red	Blue			
Methyl orange	Orange	Yellow			
Phenolphthalein	Colourless	Pink			

3. **Reaction with acids :** Ammonia being a weak base accepts protons [hydrogen ions] to form ammonium ions.

It reacts with acids to form ammonium salts.

Ammonia gas	Acid	Ammonia salt	
NH <sub>3</sub> (gas) +	HCl (gas) $\rightarrow$	NH <sub>4</sub> Cl (solid) Ammonium chloride	
NH <sub>3</sub> (gas) +	HNO <sub>3</sub> →	NH <sub>4</sub> NO <sub>3</sub> Ammonium nitrate	
2NH <sub>3</sub> (gas) +	$H_2SO_4 \rightarrow$	$(NH_4)_2$ SO <sub>4</sub> Ammonium sulphate	

Ammonium chloride is a good example, where two colourless gases react to form a white solid, directly.

Note : Ammonium nitrate and ammonium chloride both show thermal dissociation reaction.

$$NH_4Cl \Longrightarrow NH_3 + HCl$$
  
 $NH_4NO_3 \Longrightarrow N_2O + 2H_2O$ 

The same salts, which are produced by the action of ammonia on acids, are produced if ammonia is first dissolved in water to form ammonium hydroxide.

Ammonia [aq.]	+	Acid →	Ammonium + salt	Water
NH4OH	+	HCl →	NH <sub>4</sub> Cl +	H <sub>2</sub> O
NH <sub>4</sub> OH	+	$HNO_3 \rightarrow$	NH <sub>4</sub> NO <sub>3</sub> +	H <sub>2</sub> O
2NH <sub>4</sub> OH	+	$H_2SO_4 \rightarrow$	$(NH_4)_2SO_4 +$	2H <sub>2</sub> O

 $NH_3 + H_2O \rightarrow NH_4OH$ 

Reaction with soluble metal salts : Ammonium 4. hydroxide reacts with soluble salts of metals to give insoluble precipitates of their respective metallic hydroxides, (except sodium and potassium).

This behaviour is similar to NaOH solution and KOH solution.

The precipitates formed by different metallic hydroxides differ in colour and solubility. Hence, ammonium hydroxide is used in qualitative analysis for identifying cations.

**Reaction with oxygen :** Ammonia is not a 5. supporter of combustion. It extinguishes a burning splint and does not burn in air. It burns in oxygen with yellowish green flame.

**Experiment :** Burning of ammonia in oxygen (Fig. 9.6).

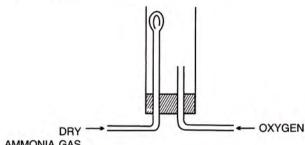




Fig. 9.6 Burning of ammonia in oxygen

**Reaction :**  $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ 

Procedure : A wide glass tube is fitted with a cork carrying two tubes, one of which reaches just near the top and the other remains lower. Ammonia is passed through the longer tube, and oxygen through the shorter tube and a lighted match is applied.

**Observation :** Ammonia burns with a yellowish green flame and produces water vapours and nitrogen. It shows that ammonia contains nitrogen and hydrogen.

The reaction is irreversible and strongly exothermic.

Mixture of ammonia and oxygen is explosive and therefore dangerous.

Metallic salt Ammonium solution hydroxide		Ammonium salt		Metallic hydroxide [ppt.]	Colour of precipitate	Solubility in excess of NH <sub>4</sub> OH		
FeSO <sub>4</sub>	+	2NH <sub>4</sub> OH	<b>→</b>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	+	Fe(OH) <sub>2</sub> ↓	Dirty green	Insoluble
FeCl <sub>3</sub>	+	3NH <sub>4</sub> OH	<b>→</b>	3NH <sub>4</sub> Cl	+	Fe(OH) <sub>3</sub> ↓	Reddish brown	Insoluble
Pb(NO <sub>3</sub> ) <sub>2</sub>	+	2NH <sub>4</sub> OH	→	2NH <sub>4</sub> NO <sub>3</sub>	+	Pb(OH) <sub>2</sub> ↓	White	Insoluble
$Zn(NO_3)_2$	+	2NH <sub>4</sub> OH	<b>→</b>	2NH <sub>4</sub> NO <sub>3</sub>	+	Zn(OH) <sub>2</sub> ↓	White gelatinous	Soluble
CuSO <sub>4</sub>	+	2NH <sub>4</sub> OH		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	+	*Cu(OH) <sub>2</sub> ↓	Pale blue	Soluble

The pale blue precipitate of copper hydroxide dissolves in excess of ammonium hydroxide forming tetraamine copper [II] sulphate, an azure blue (deep blue) soluble complex salt.  $Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2OH = Cu(NH_3)_4 + 2NH_4OH = CU(NH_3)_4 +$ 

# Downloaded from https:// www.studiestoday.com Catalytic oxidation of ammonia

In the presence of platinum at 800°C, ammonia reacts with oxygen to give nitric oxide and water vapour.

Procedure : Pass dry ammonia gas and oxygen gas through inlets over heated platinum placed in the combustion tube, which in the heated state emits a reddish glow.

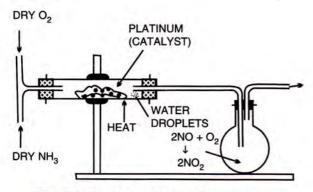


Fig. 9.7 Catalytic oxidation of ammonia

### **Reaction :**

 $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt, 800°C}} 6\text{H}_2\text{O} + 4\text{NO}\uparrow + \text{Heat}$  $2NO + O_2 \longrightarrow 2NO_2$  (brown gas)

#### **Observations:**

(i) Reddish brown vapours of nitrogen dioxide [NO<sub>2</sub>] are seen in the flask due to the oxidation of nitric oxide [NO].

$$2NO + O_2 \rightarrow 2NO_2$$

- (ii) The platinum [catalyst] continues to glow even after the heating is discontinued since the catalytic oxidation of ammonia is an exothermic reaction.
- 6. Reaction with carbon dioxide : Ammonia reacts with carbon dioxide at 150°C and 150 atm. pressure to give urea which is a valuable nitrogenous fertiliser.

$$2NH_3 + CO_2 \xrightarrow{150 \circ C} NH_2CONH_2 + H_2O$$
  
urea

### 7. Ammonia as a reducing agent :

#### (i) Reduction of chlorine to hydrogen chloride

When chlorine reacts with ammonia, it is reduced to HCl, which further combines with excess of ammonia and forms NH<sub>4</sub>Cl.

### (a) When ammonia is in excess,

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$
  

$$6NH_3 + 6HCl \rightarrow 6NH_4Cl$$
  

$$\therefore \quad 8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$
  
(excess)

#### **Observation**:

The yellowish-green colour of chlorine disappears and white fumes of ammonium chloride are formed.

(b) When chlorine is in excess, then the products are hydrogen chloride and yellow coloured highly explosive liquid nitrogen trichloride.

$$NH_3 + 3Cl_2 \rightarrow 3HCl + NCl_3$$

#### These reactions show that :

- · Chlorine has a great affinity for hydrogen.
- · Ammonia is a reducing agent.

#### (ii) Reduction of metallic oxides

Ammonia reduces heated metallic oxides to give metals, water vapour and nitrogen.

Procedure : Pass ammonia gas over heated copper oxide in a hard glass tube.

#### **Reaction :**

 $2NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2\uparrow$ black reddish gas solid brown solid

**Observation :** The black copper oxide is reduced to reddish brown copper.

Similarly, Ammonia reduces heated yellow lead monoxide to greyish metallic lead.

> $3PbO + 2NH_3 \rightarrow 3Pb + 3H_2O + N_2$ (yellow) (greyish)

Collection of gas : Nitrogen is collected over water in a gas jar (Fig. 9.8).

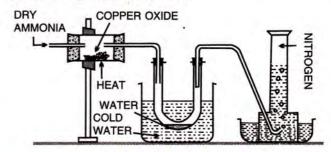


Fig. 9.8 Reducing action of ammonia

The water formed is collected in the U-tube and is tested with anhydrous copper sulphate which turns blue.

**Note**: This reaction proves that ammonia is made up of nitrogen and hydrogen and is, therefore, a nitrogen hydride.

# 9.7 TESTS FOR AMMONIA GAS AND AMMONIUM ION

Ammonia gas can easily be recognised by the following characteristics :

- (1) It has a sharp characteristic odour.
- (2) It turns
  - · moist red litmus blue,
  - · moist turmeric paper brown
  - phenolphthalein solution pink.
- (3) It gives dense white fumes with conc. hydrochloric acid.

 $NH_3 + HCl \rightarrow NH_4Cl.$ 

- (4) When NH<sub>3</sub> gas is passed through copper sulphate solution blue precipitate is formed which changes to deep blue solution on passing the gas in excess.
- (5) All ammonium salts generally produce ammonia gas when warmed with alkali like sodium hydroxide.
- (6) Ammonium salt gives brown colour or precipitates with Nessler's solution K<sub>2</sub>HgI<sub>4</sub> (a slightly alkaline solution of potassium mercuric iodide made by adding KOH).

## 9.8 USES OF AMMONIA

 Liquid ammonia is used as a refrigerant in ice plants. Liquid ammonia takes a lot of energy to vaporize (5700 calories per mole at -33 °C). This heat is taken from the surrounding bodies which are consequently cooled down.

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

The main refrigerants used are freon chlorofluoro carbon (CFC). They deplete ozone

layer and also contribute to global warming. Thus these refrigerants are harmful to life. The chlorofluoro carbons are decomposed by the ultraviolet rays to highly reactive chlorine which is produced in the atomic form.

 $CF_2Cl_2(g) \xrightarrow{Ultraviolet} CF_2Cl(g) + Cl(g)$ (free radical)

The free radical [Cl] reacts with ozone and chlorine monoxide is formed.

 $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$ 

This causes depletion of ozone. Chlorine monoxide further reacts with atomic oxygen and produces more free chlorine radicals.

$$ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$$

Again this free radical [Cl] destroys ozone and the process continues thereby giving rise to **ozone depletion**.

Ozone layer acts as a blanket in the atmosphere above 16 km height from the earths surface. It absorbs the harmful ultraviolet rays coming from the Sun and thus protects life on earth.

#### Advantages of Ammonia as refrigerant

- (i) Ammonia is environmentally compatible. It does not deplete ozone layer and does not contribute the global warming.
- (ii) It has superior thermodynamic qualities as a result ammonia refrigeration systems use less electricity.
- (iii) Ammonia has a recognizable odour and so leaks are not likely to escape.

#### Ammonia has some disadvantage.

It is not compatible with copper, so it cannot be used in any system with copper pipes. Ammonia is poisonous in high concentration although it is easily detectable due to its peculiar smell and also being lighter than air goes up in the atmosphere not affecting the life too much on earth.

2. Ammonia solution is used as an important laboratory reagent in qualitative analysis as it gives characteristic coloured metallic hydroxide precipitates.

- 3. Aqueous NH<sub>3</sub> emulsifies or dissolves fats, grease, etc. so it is used :
  - (i) to remove grease and perspiration stains from clothes,
  - (ii) for cleaning tiles, windows, etc.

#### 4. Ammonia is used in the manufacture of :

- (a) **nitrogenous fertilisers** like ammonium sulphate, diammonium hydrogen phosphate, ammonium nitrate and urea.
- (b) **explosives** like ammonium nitrate. Ammonium nitrate decomposes explosively leaving no residue behind

 $NH_4NO_3 \xrightarrow{\Delta} N_2O(g) + 2H_2O(vap.)$ 

(c) other ammonium salts such as ammonium carbonate (used as smelling salt for reviving a fainted person), ammonium chloride – used in dry cells and in the preparation of nitrogen gas.

 $NaNO_2(aq) + NH_4Cl(aq) \rightarrow NaCl(aq) + NH_4NO_2(aq.)$ Sodium nitrite

> $NH_4NO_2(aq) \xrightarrow{\Delta} N_2(g) + 2H_2O(g)$ Ammonium nitrite

- (d) nylon and rayon, and sodium cyanamide, plastics, dyes, organic chemicals, explosives and wood pulp.
- (e) sodium carbonate by Solvay process. This process involves the interaction of ammonia, carbon dioxide, and sodium chloride in water solution resulting in the precipitation of sodium hydrogen carbonate.

 $NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 \downarrow + NH_4Cl$ 

The sodium hydrogen carbonate is separated and ignited to obtain sodium carbonate.

 $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2\uparrow$ 

(f) nitric acid by the Ostwald process.

#### 9.9 MANUFACTURE OF NITRIC ACID

A German chemist Ostwald, in 1914, developed **Ostwald process**.

The process is explained in three steps :

A mixture of dry air (free from carbon dioxide and dust particles) and dry ammonia in the ratio of 10 : 1 by volume, is first compressed and then passed into the **catalytic chamber** containing platinum gauze as catalyst at about 800°C (Fig. 9.9).

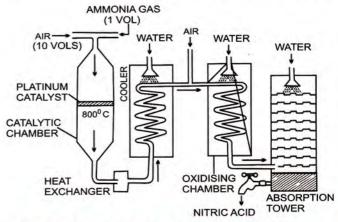


Fig. 9.9 Manufacture of nitric acid by Ostwald process

This results in the oxidation of ammonia into nitrogen monoxide (Nitric oxide).

$$4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O} + \text{Heat}$$

The reaction is **exothermic** and the heat evolved maintains the temperature of the catalytic chamber.

The hot gases are then passed through a heat exchanger, where they are mixed with air and passed into another cooling chamber called **oxidising chamber**.

# Step II : Oxidation of nitric oxide in oxidation chamber

In this chamber, nitric oxide combines with oxygen to form nitrogen dioxide at about 50°C.

$$2NO(g) + O_2(g) \xrightarrow{50^{\circ}C} 2NO_2(g)$$

#### Step III : Absorption of nitrogen dioxide in water

The nitrogen dioxide together with the remaining air (sometimes more air is added at this stage) is passed through the **absorption tower** (a steel tower filled with quartz stone packed in layers), from the top of which warm water trickles.

The nitrogen dioxide and oxygen present in the air react with water to form nitric acid.

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 $4\mathrm{NO}_2(\mathrm{g}) + 2\mathrm{H}_2\mathrm{O}(l) + \mathrm{O}_2(\mathrm{g}) \rightarrow 4\mathrm{HNO}_3 \ (\mathrm{aq.}).$ 

The nitric acid obtained at the bottom of the tower is concentrated above 50%.

The above acid on further distillation gives 68% nitric acid. This acid is **concentrated nitric** acid which is used in laboratories.

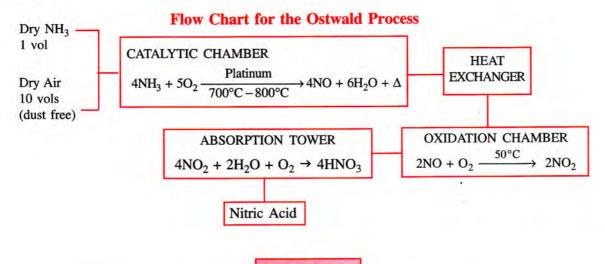
#### Concentration of nitric acid

Nitric acid up to 98% (fuming nitric acid) is obtained by distilling 68% HNO<sub>3</sub> over conc. sulphuric acid.

Pure 100% nitric acid is obtained by strongly cooling the 98% acid, when colourless crystals of pure nitric acid get separated at  $-42^{\circ}$ C.

Note : In the manufacture of nitric acid,

- (i) Higher ratio of air is used because oxygen is only 1/5th in air and it is required in all the three chambers.
- (ii) Quartz is acid resistant and when packed in layers it helps in dissolving nitrogen dioxide uniformly in water.



EXERCISE

- 1. (a) Is ammonia more dense or less dense than air?
  - (b) What property of ammonia is demonstrated by the Fountain Experiment?
  - (c) Write the balanced equation for the reaction between ammonia and sulphuric acid.
- 2. Pick the odd member from the list giving reasons:
  - (a) Ammonia, sulphur dioxide, hydrogen chloride, carbon dioxide.
  - (b) Copper oxide, aluminium oxide, sodium oxide, magnesium oxide.
- 3. The following reactions are carried out :
  - A : Nitrogen + metal  $\rightarrow$  compound X.
  - $B: X + water \rightarrow ammonia + another compound.$
  - C: Ammonia + metal oxide  $\rightarrow$  metal + water + N<sub>2</sub>.

One metal that can be used for reaction A is magnesium.

- (a) Write the formula of the compound X formed.
- (b) Write the correctly balanced equation for reaction B where X is the compound formed.

- (c) What property of ammonia is demonstrated by reaction C?
- A gas 'P' gives dense white fumes with chlorine. Its aqueous solution gives a blue colour with copper (II) hydroxide. (a) Name the gas P. (b) Give its formula. (c) Give three uses of P.
- 5. Ammonia solution in water gives a blue precipitate when it combines with a solution of copper salt. The blue precipitate further dissolves in excess of ammonia solution to give azure blue solution. Explain with equation.
- 6. Give chemical equation(s) to prove that NH<sub>3</sub> contains nitrogen and hydrogen ?
- 7. Copy and complete the following equations.
  - (a)  $AIN + H_2O \rightarrow$  (b)  $2NH_3 + 3PbO \rightarrow$
  - (c)  $\text{NH}_3 + 3\text{Cl}_2 \rightarrow$  (d)  $\text{NH}_3 + \text{CO}_2 \rightarrow$ 
    - (i) Which property of ammonia is illustrated by equation (c)?

- (ii) What important fertiliser is prepared from equation (d)? State the conditions.
- 8. What do you observe when ammonium hydroxide is added to the aqueous solution of :
  - (a) FeSO<sub>4</sub>, (b) Iron (III) chloride,
  - (c) Lead nitrate, (d) Zinc nitrate ?
- 9. Give a chemical test to distinguish between the following:
  - (a) Ammonium chloride and sodium chloride,
  - (b) Ferric salt and ferrous salt,
  - (c) Sodium sulphate and ammonium sulphate.
- 10. Give balanced equations for the following conversions :
  - (a) Ammonia to nitrogen using an acidic gas,
  - (b) Ammonia to brown gas,
  - (c) Ammonia to nitrogen trichloride,
  - (d) Ammonia solution to an amphoteric hydroxide,
  - (e) A nitride of a trivalent metal to ammonia,
  - (f) Lead oxide to lead.
- 11. Name :
  - (a) the gas which is prepared by Haber's Process,
  - (b) two gases which give dense white fumes with ammonia,
  - (c) one salt of ammonia in each case which is used in :(i) dry cell (ii) explosives (iii) medicine,
  - (d) an acidic gas which reacts with a basic gas liberating a neutral gas,
  - (e) a metallic chloride soluble in ammonium hydroxide,
  - (f) the gas obtained when ammonia burns in an atmosphere of oxygen without any catalyst,
  - (g) a nitride of a divalent metal which reacts with warm water liberating ammonia,
  - (h) an amphoteric oxide reduced by the basic gas,
  - (i) a white salt produced by an acid gas and a basic gas.
- 12. When ammonium hydroxide is added to solution B, a pale blue precipitate is formed. This pale blue precipitate dissolves in excess ammonium hydroxide giving an inky blue solution. What is the cation [positive ion] present in solution B? What is the probable colour of solution B.
- 13. When an ammonium salt is warmed with sodium hydroxide solution, ammonia gas is evolved. State three ways in which you could identify this gas.
- 14. A gas 'A' reacts with another gas 'B' in the presence of a catalyst to give a colourless gas 'C'. The gas 'C' when comes in contact with air produces a brown gas 'D'. The solution of 'A' in water turns red litmus blue. Explain the observations.

- **15.** (a) Name the common refrigerent. How does it deplete ozone layer ?
  - (b) What is the alternative of chlorofluoro carbon?
  - (c) State the advantages and disadvantages of using ammonia as refrigerent?
- 16. Name a compound prepared by ammonia and is used as :
  - (a) Explosive, (b) Fertilizers,
  - (c) Medicine, (d) Laboratory reagent.
- 17. Ammonia is used in the Ostwald process,
  - (a) Give the source of reactants used in this process.
  - (b) Name the catalyst used in the process.
  - (c) Name the oxidising agent used in this process.
  - (d) What is the ratio of ammonia and air taken in this process ?
  - (e) Why is quartz used in this process ?
- 18. Write the equation for the action of heat on :

(a) Ammonium chloride, (b) Ammonium nitrate.State whether each reaction is an example of thermal decomposition or thermal dissociation.

- **19.** (a) Which feature of ammonia molecule leads to the formation of the ammonium ion when ammonia dissolves in water ?
  - (b) Name the other ion formed when ammonia dissolves in water.
  - (c) Give one test that can be used to detect the presence of the ion produced in (b).
- **20.** (a) Of the two gases, ammonia and hydrogen chloride, which is more dense ? Name the method of collection of this gas.
  - (b) Give one example of a reaction between the above two gases which produces a solid compound.
  - (c) Write a balanced equation for a reaction in which ammonia is oxidized by :
    - (i) a metal oxide,
    - (ii) a gas which is not oxygen.

#### 2008

- (a) Write equation for the following : Aluminium nitride and water.
- (b) Choose the correct from the following : Ammonia can be obtained by adding water to
  - A: Ammonium chloride,
  - B: Ammonium nitrite,
  - C: Magnesium nitride,
  - D: Magnesium nitrate.

- 2009
- (a) Name the gas evolved in each case [formula is not acceptable]. The gas that burns in oxygen with a green flame.
- (b) Write a fully balanced equation for Magnesium nitride is treated with warm water.
- (c) Identify the substance 'O' based on the information given — The white crystalline solid 'Q' is soluble in water. It liberates a pungent smelling gas when heated with sodium hydroxide solution.

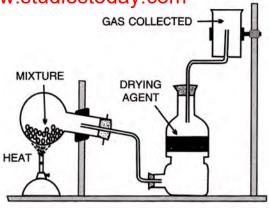
#### 2010

- (a) Complete the blanks (i) to (v) in the passage given, using the following words. [Ammonium, reddish brown, hydroxyl, nitrogen dioxide, ammonia, dirty green, alkaline, acidic]. In the presence of a catalyst nitrogen and hydrogen combine to give (i) ...... gas. When the same gas is passed through water it foris a solution, which will be (ii) ...... in nature, and will contain the ions (iii) ...... and (iv) ...... A (v) ...... coloured precipitate of iron [II] hydroxide is formed when the above solution is added to iron [II] sulphate solution.
- (b) State your observation when in the absence of catalyst, ammonia is burnt in an atmosphere of oxygen.
- (c) Give the equation for the reaction ammonium chloride is heated with sodium hydroxide.
- (d) In the manutacture of ammonia
  - (i) Name the process
  - (ii) State the ratio of the reactants take
  - (iii) State the catalyst used
  - (iv) Give the equation for the manufacture of the gas

     ammonia.
- (e) Write a relevant equation to show that ammonia acts as a reducing agent.
- (f) Name two gases which can be used to study the fountain experiment. State the common property demonstrated by the fountain experiment.

#### 2011

- (a) State what is observed when Ammonium hydroxide is first added in a small quantity and then in excess to a solution of copper sulphate.
- (b) The diagram below shows the set up for the laboratory preparation of a pungent alkaline gas.



- (i) Name the gas collected in the jar.
- (ii) Give a balanced equation for the above preparation.
- (iii) State how the above gas is collected.
- (iv) Name the drying agent used.
- (v) State how you will find out that the jar is full of the pungent gas.
- (c) Write a balanced chemical equation Chlorine reacts with excess of ammonia.
- (d) State your observation Water is added to the product formed, when Al is burnt in a jar of nitrogen gas.

#### 2012

- (a) Name The gas produced when excess ammonia reacts with chlorine.
- (b) Rewrite the correct statement with the missing word/s : Magnesium nitride reacts with water to liberate ammonia.
- (c) Give balanced equation for the reaction : Ammonia and oxygen in the presence of a catalyst.
- (d) The following question are based on the preparation of ammonia gas in the laboratory :
  - Explain why ammonium nitrate is not used in the preparation of ammonia.
  - (ii) Name the compound normally used as a drying agent during the process.
  - (iii) How is ammonia gas collected. Explain why it is not collected over water.

#### 2013

- (a) State one appropriate observation for : Excess of chlorine gas is reacted with ammonia gas.
- (b) Nitrogen gas can be obtained by heating :
  - (i) Ammonium nitrate
  - (ii) Ammonium nitrite
  - (iii) Magnesium nitride
  - (iv) Ammonium chlorde

- (c)<sup>\*</sup> State two relevant observations for : Ammonium hydroxide solution is added to zinc nitrate solution slowly and then in excess.
- (d) Give a balanced equation for : Reduction of hot copper (II) oxide to copper using ammonia gas.
- (e) Copy and complete the following table relating to important industrial process :

Name of the process	Temperature	Catalyst	Equation for the catalyzed reaction
Haber's process			William March 1

(f) Identify : An alkaline gas which produces dense white fumes when reacted with HCl gas.

#### 2014

(a) Fill in the blank from the choices given in bracket : Ammonia gas is collected by ...... [upward displacement of air, downward displacement of water, downward displacment of air].

- (b) Write balanced equation for : Action of warm water on magnesium nitride.
- (c) Distinguish between the following pairs of compounds using the test given in bracket :
  - (i) Iron [II] sulphate and iron [III] sulphate (using ammonium hydroxide).
  - (ii) A lead salt and a zinc salt (using excess ammonium hydroxide).
- (d) State your observation : Calcium hydroxide is heated with ammonium chloride crystals.
- (e) Name the other ion formed when ammonia dissolves in water. Give one test that can be used to detect the presence of the ion produced.
- (f) State the conditions required for : Catalytic oxidation of ammonia to nitric oxide.