17.1 MODERN CHEMICAL MANUFACTURERS

LEARNING OUTCOME
THE STUDENTS SHOULD BE ABLE TO

17.1 State and show the manufacture of ammonia by Haber's process (principle and flowsheet diagram).
17.2 State and show the manufacture of nitric acid by Ostwald's process (principle and flow-sheet diagram).
17.3 State and show the manufacture of sulphuric acid by the contact process (principle and flow-sheet diagram).
17.4 State and show the manufacture of sodium hydroxide by Diaphragm Cell (principle and flow-sheet diagram).
17.5 State and show the manufacture of sodium carbonate by ammonia soda or the Solvay process (principle and flow-sheet diagram).

Modern chemical manufacturers are companies that produce chemicals on an industrial scale for use in a wide range of industries, including pharmaceuticals, agriculture, electronics, and construction. These manufacturers use advanced technologies, automation, and sustainable practices to create raw materials and speciality chemicals. They serve key sectors like healthcare, agriculture, and manufacturing, focusing on efficiency, innovation, and environmental safety.

17.1.1 Manufacture of Ammonia by Haber's Process

Principle

- Nitrogen does not combine with hydrogen under ordinary conditions.
- But when a mixture of nitrogen and hydrogen in the ratio 1:3 by volume is heated to about 450°C under a pressure of 200-900 atmospheres in the presence of finely divided Iron as a catalyst and Molybdenum as a promoter, ammonia is obtained.

$$N_2(g) + 3\,H_2(g) \underset{200\text{-}900\text{ atm}}{\overset{450^oC,\ Fe\text{-}Mo}{\rightleftharpoons}} 2\,NH_3(g) + 92.6\text{ KJ/mol}$$

Conditions for maximum yield of ammonia:

Since the reaction is reversible, exothermic and occurs with diminution in volume, according to Le-Chatelier's principle, it is favoured by the following conditions.

a) **High pressure**: It has been shown that at a particular temperature, the yield of ammonia increases with increasing pressure.
b) **Low temperature**: As the reaction is exothermic, it is favoured by low temperature. But if the temperature is too low the reaction will be too slow. Therefore, an optimum temperature of 450°C is used.
c) **High concentration**: If the reactants are used in excess, a larger amount of products is formed. Hence, pure reactants are used, and one of the reactants is used in excess.
d) **Presence of a catalyst**: Finely divided iron is used as a catalyst to speed up the reaction under given conditions. To increase the efficiency of the catalyst, Molybdenum is used as a promoter. Moreover, the purity of the reactants is essential to avoid poisoning the catalyst.

Flow sheet diagram:

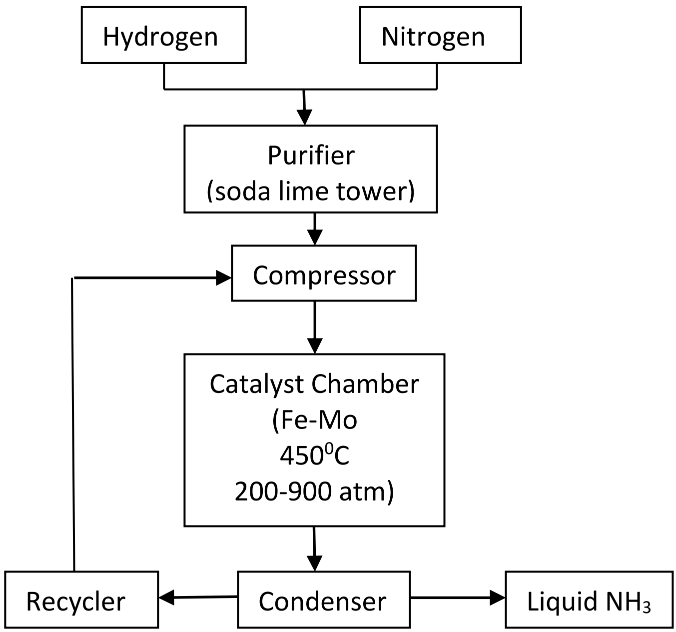


Fig: Flow sheet diagram for the manufacture of Ammonia by Haber's Process

1. Prof. Dr. Fritz Haber won the Noble prize in
   a. 1908 b. 1913 c. 1931 d. 1918
2. In the reaction $N_2 + H_2 \rightleftharpoons NH_3$, the formation of ammonia is favoured by
   a. Increase in pressure and decrease in temperature
   b. Decrease in pressure and increase in temperature
   c. Increase in pressure and increase in temperature
   d. Decrease in temperature and decrease in pressure

1. **Describe Haber's process for the manufacture of ammonia. 4/6**
2. Write a balanced chemical equation for the preparation of ammonia by Haber's process. 2
3. Give a balanced chemical equation for the preparation of ammonia from hydrogen and nitrogen. What are the proper conditions for the better yield of ammonia 2
4. Describe the physical and chemical principle for the manufacture of ammonia by Haber's process. Draw a flow sheet diagram for it. 5
5. Discuss the principle and self-explanatory sketch for the manufacture of ammonia by Haber's process. 5
6. Write the necessary physical and chemical principles involved in the manufacture of ammonia gas by Haber's process? 4
7. Describe the principle involved in the manufacture of ammonia by Haber's process. 3
8. Describe the importance of Haber's process in chemical industries. 2

Manufacture of HNO_3 by Ostwald's Process

(Technical Production of HNO_3 by Catalytic Oxidation of NH_3) (VVVI)

Principle

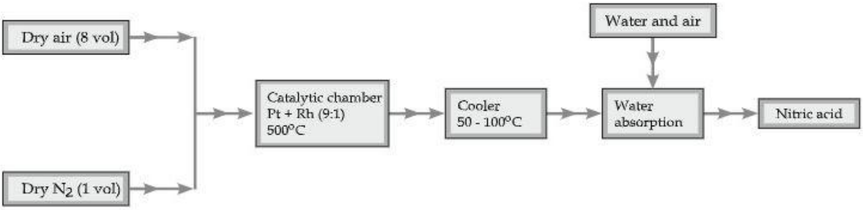
The first and most important step in this process is the catalytic oxidation of ammonia by the oxygen of the air, carried out in the presence of **Platinum gauze heated to 850^{o}C.** Under these conditions, ammonia is oxidized to NO, which is then cooled to about 50^{0}C -100 ^{0}C and air oxidized to NO_2. Nitrogen dioxide is then allowed to react with water and more air to form HNO_3.

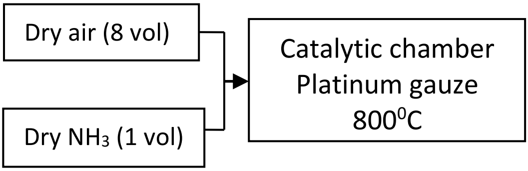
$$4\,NH_3\,(g) + 5\,O_2(g) \longrightarrow 4\,NO\,(g) + 6\,H_2O(g) + 215Kcal$$

$2\,NO\,(g) + O_2(g) \longrightarrow 2\,NO_2\,(g)$

$4\,NO_2\,(g) + O_2\,(g) + 2\,H_2O(l) \longrightarrow 4\,HNO_3(aq)$

Flow sheet diagram





3. The oxide obtained in the catalytic oxidation of ammonia is
   a. NO
   b. NO_2
   c. N_2O
   d. N_2O_5

9. Write the principle and process involved, along with a self-explanatory diagram of the manufacture of nitric acid by catalytic oxidation of ammonia. 6
10. Starting from ammonia, how would you prepare nitric acid? 1
11. Give balanced chemical equations for the preparation of nitric acid from ammonia. 1
12. How is nitric acid prepared from ammonia? 5
13. How is nitric acid manufactured by catalytic oxidation of ammonia? Sketch a well-labelled diagram for it. 5/6
14. Write down the principle and sketch a labelled diagram for the manufacture of nitric acid by the oxidation of ammonia. 6
15. Describe the manufacture of nitric acid by catalytic oxidation of ammonia. 8
16. Write down the manufacture of HNO_3 by the oxidation of ammonia. 5
17. Describe the manufacture of nitric acid by the Ostwald process, giving a neat and labelled diagram. 8

17.1.3 Manufacture of Sulphuric acid by the contact process

Sulphuric acid is a widely used chemical in different industries; therefore, also called the king of chemicals. The amount of sulphuric acid consumed by a country can be taken as the index of its industrial advancement. It is manufactured by the contact process.

Principle:

In this industrial process, sulphuric acid is produced in the following steps

1. Production of sulphur dioxide: SO_2 gas can be prepared either byburning sulphur or roasting iron pyrites

   $S + O_2 \rightarrow SO_2$

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

2. Oxidation of SO_2 to SO_3: Sulphur dioxide is oxidised to sulphur trioxide in the presence of the catalyst **vanadium pentoxide at about 450^{o}C and 2 atm** pressure. Since this reaction is carried out in contact with the catalyst, it is also called the **contact process**.

   $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g) + 45$ kcal

18. Why is this process called the contact process?

3. Absorption of SO_3 by conc. sulphuric acid: Sulphur trioxide is allowed to absorb in 98% H_2SO_4, whereby pyrosulphuric acid ($H_2S_2O_7$), called oleum (fuming sulphuric acid), is formed

   $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (Major product)

   $SO_3 + H_2SO_4 \rightarrow H_2S_3O_{10} + H_2O$

4. Dilution of oleum to sulphuric acid: The oleum is carefully pouredinto water with constant stirring to produce sulphuric acid.

   $H_2S_2O_7 + H_2O \rightarrow 2\ H_2SO_4$

Conditions for the optimum yield of H_2SO_4

The formation of SO_3 from SO_2 is a reversible process. The optimum condition for the formation of SO_3 can be explained by Le-Chatelier'sprinciple

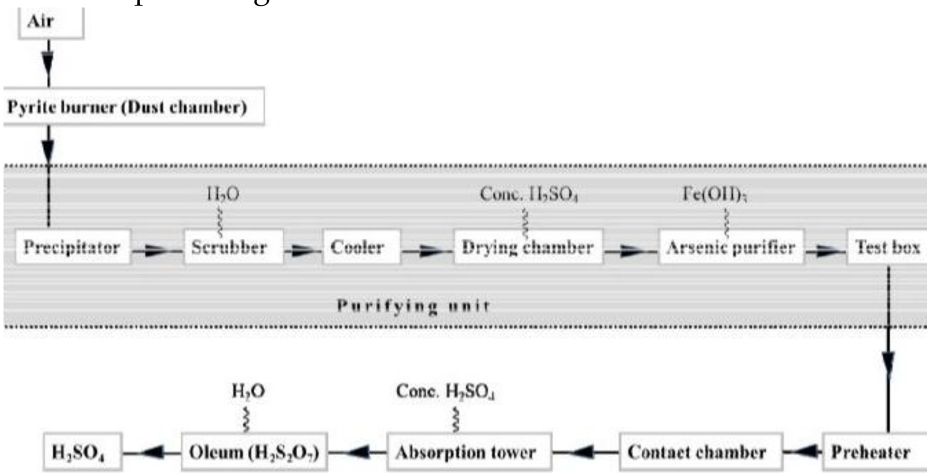
1. **Temperature:** The formation of SO_2 is an exothermic process. So according to Le-Chatelier's principle, the reaction should be carried out at a low temperature. However, too low a temperature makesthe reaction rate too slow. Therefore, an optimum temperature of about 450^o is supplied.

2. **Pressure:** According to the Le-Chatelier's principle, the pressure should be high. But at high pressure, SO_2 and SO_3 might corrode thelining of the vessel. Therefore, an optimum pressure of 2 atm. is used.

3. **Concentration:** High concentrations of reactants are used for thehigher yield of the product.

4. **Catalyst:** The rate of the reaction can be increased by using positivecatalysts such as vanadium pentoxide.

5. **Purity of gas:** Pure gases should be used to protect the catalyst from poisoning.



4. The catalyst used in the contact process is
    a. MnO_2
    b. Cr_2O_3
    c. V_2O_5
    d. Al_2O_3

19. Starting from sulphur, how would you obtain sulphuric acid? (reaction only)
20. Write the chemical reactions involved in the manufacture of sulphuric acid by the contact process.
21. Discuss the principle and stepwise procedure of the manufacture of sulphuricacid by the contact process, giving a self-explanatory sketch.
22. Sulphuric acid is known as the king of chemicals. 2+2
    i) Discuss the principle for the manufacture of this acid industrially.
    ii) Also, mention the optimum conditions for its maximum yield.

17.1.4 Manufacture of sodium hydroxide by Diaphragm Cell

Principle:

The solution ionizes as follows;

$NaCl \longrightarrow Na^+ + Cl^-$

$H_2O \longrightarrow H^+ + OH^-$

When electricity is passed into the electrolyte solution, following reactions take place in the corresponding electrondes.

Reaction at anode: Graphite or titanium coated ruthenium-titanium oxide can be used as anode material. At anode, Cl^- and OH^- anions go to the anode and compete to get discharged. Diaphragm prevents the entering of hydroxide ions into anode compartment and chloride ions preferentially get discharged forming chlorine gas. The chlorine gas is liberated. The OH^- ions remain intact.

$$2Cl^- \longrightarrow Cl_2 + 2e$$

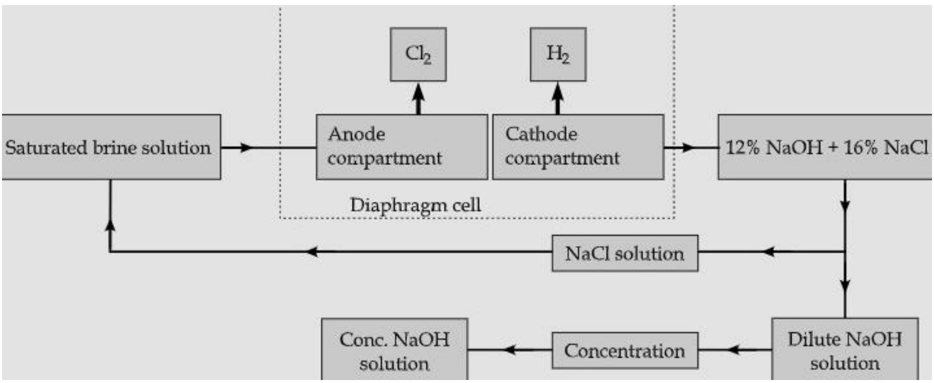
Reaction at cathode: Steel mesh or nickel can be used as cathode. The ion-exchange membrane is used to selectively permit the flow of ions to the cathode compartment. Both H^+ and Na^+ ions go to cathode and compete to get discharged. Out of these two ions, the H^+ ions has lower discharge potential and gets preference to be discharged forming hydrogen gas. The Na^+ ions remain intact in the solution.

$$2H^+ + 2e \longrightarrow H_2$$

Once the electrolysis is over, solution in the cathode compartment contains excess of Na^+ ions and OH^- along with some sodium chloride solution.

Recovery of sodium hydroxide: During the electrolysis process, the solution from the cathode compartment is periodically removed and concentrated whereby sodium chloride gets crystallized leaving behind the concentrated solution of sodium hydroxide. Evaporation of concentrated sodium hydroxide solution up to the dryness gives solid sodium hydroxide. As per the requirement, the solid sodium hydroxide is made granules or pallet for commercial supply.

Flow sheet diagram for manufacture of sodium hydroxide by Diaphragm cell:



17.1.5 Manufacture of sodium carbonate by ammonia soda or *Solvay* process

Principle

Brine solution is saturated is ammonia by bubbling ammonia gas, and the ammonical brine is then treated with carbon dioxide. First, ammonium bicarbonate is formed, which further reacts with sodium chloride to give sodium bicarbonate

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$

Sodium bicarbonate is sparingly soluble in water in the presence of sodium chloride. Hence, sodium bicarbonate formed gets precipitated out, which is separated out by filtration. The sodium bicarbonate is then calcined to get sodium carbonate.

$$NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

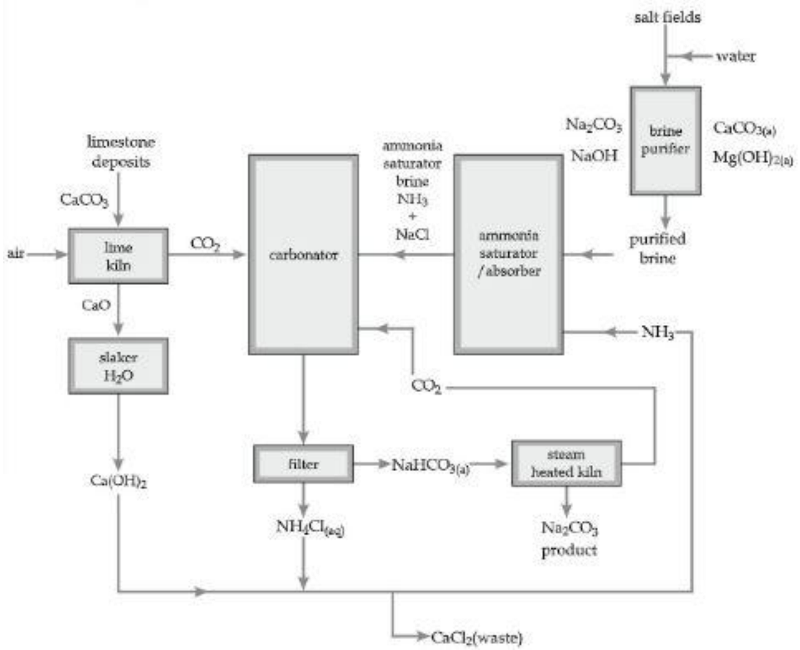


Figure: Flow sheet diagram for the manufacture of Na_2CO_3

Working of the Plant:

1. **Saturation of brine**

In the ammonia absorber, brine solution (about 30% NaCl) is saturated with ammonia gas. Impurities like $CaCl_2$, $MgCl_2$, etc, present in brine are precipitated as hydroxides and carbonates are removed.

$$NH_3 + H_2O \longrightarrow NH_4OH$$

$$MgCl_2 + 2NH_4OH \longrightarrow Mg(OH)_2 \downarrow + 2NH_4Cl$$

$$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$$

$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 + 2NH_4Cl$$

Ammoniated brine is then pumped to the carbonation tower.

2. **Carbonation**

Carbonation tower works on counter current principle.

Ammoniated brine is allowed to trickle down a tower and carbon dioxide is passed from the bottom at about 2 atm pressure and temperature is maintained to about 30 °C. Sodium bicarbonate and ammonium chloride are formed.

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$
$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

Sodium bicarbonate is filtered and filtrate (NH_4Cl with little NH_4HCO_3) is pumped to the ammonia generator.

3. Recovery of ammonia

In ammonia generator, ammonium chloride reacts with lime to generate ammonia gas.

$$NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + NH_3 + H_2O$$
$$NH_4HCO_3 \longrightarrow NH_3 + H_2O + CO_2$$

4. Generation of CO_2

In lime kiln, limestone is heated to produce CO_2 required for carbonation.

$$CaCO_3 \longrightarrow CaO + CO_2$$

CaO is treated with water to get slaked lime and pumped into ammonia generator.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

5. Calcination

Sodium bicarbonate obtained by filtration is heated to get anhydrous sodium carbonate.

6. Crystallization

Aqueous sodium carbonate solution may be subjected to crystallization to get washing soda.

$$Na_2CO_3\ (aq.) \longrightarrow Na_2CO_3.10H_2O$$

5. Which of the following are recycled in the manufacture of sodium Carbonate by Solvay's process?
   a. CO_2 and NH_4Cl c. CO_2 and NH_3
   b. NaCl and CaO d. NaCl and NH_3
6. The processes used for manufacture of sodium carbonate and sodium hydroxide are respectively:

a. Down's Process and Contact process
b. Haber's Process and Solvay process
c. Solvay process and Down's Process
d. Haber's process and Contact Process

7. Which of the following is the correct match

	Compound	Industrial manufacture
i.	Nitric acid	A- Diaphragm Cell
ii.	Sodium hydroxide	B- Ostwald Process
iii.	Sodium carbonate	C- Ammonia -soda Process
iv.	Sulphuric Acid	D- Solvay process
		E- contact Process

a. i-B, ii-C, iii-E, iv- A
b. i-B, ii-A, iii-C, iv- E
c. i-E, ii-A, iii-D, iv-B
d. i-B, ii-A, iii-D, iv-C

*** This note is insufficient. It is to guide you. Study the prescribed textbooks too. ***