Unit-1 : Manufacture of Heavy Chemicals

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CONTENTS OF SYLLABUS : ***(B.Sc.-III, Sem-V)*** **(8 Lectures)**

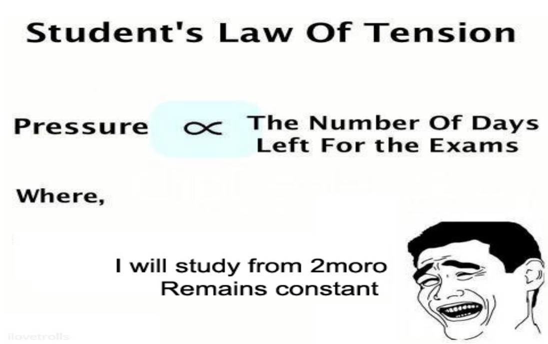
- **Le Chatelier's principle : (Not in syllabus)**
  Effect of changes in the **T, P, C and catalyst** on position of equilibrium
- **Physicochemical Principles:**
  a) Haber's Process b) Contact Process
  c) Ostwald's Process & d) Solvay Process
- **Manufacturing Process:**
  a) Haber's Process (Manufacturing of NH_3) & b) Contact Process (Manufacturing of H_2SO_4)
  c) Ostwald's Process (Manufacturing of HNO_3) & d) Solvay Process (Manufacturing of Na_2CO_3)

"When you focus on problem, you will have more problems. But when focus on possibility, you will have more opportunity."

Dr. APJ Abdul Kalam

"When the student is ready, the teacher will appear"

"a good student could learn more from a bad teacher than a bad student from even a skilled teacher"



Q.1) State Le Chatelier's Principle. Explain the effect of changes in the following factors on position of equilibrium;

i) Concentration ii) Pressure iii) Temperature iv) Catalyst

Or Write short note on 'Le chatelier's Principle & shift in equilibrium'

Ans. Statement : If a stress is applied to a system at equilibrium, the system will change to relieve that stress and reestablish the equilibrium.

Or Whenever a system in equilibrium is subjected **to a change i.**e. change in temperature or pressure or concentration, the equilibrium shifts in that direction so as **to nullify the effect of that change.**

Factors affecting on position of equilibrium:

1) Effect of Concentration
2) Effect of Pressure
3) Effect of Temperature
4) Effect of Catalyst

1) Effect of Concentration:

When a reactant or product is **added to a system at equilibrium**, the system **shifts away from the added component**. (moves in a direction that uses up the excess component)

But if a **reactant or product is removed**, the system **shifts toward the removed component.**

Concentration Changes:

- Add more reactant ➔ ***Equilibrium Shift to products side***
- Remove reactants ➔ ***Equilibrium Shift to reactants side***
- Add more product ➔ ***Equilibrium Shift to reactants side***
- Remove products ➔ ***Equilibrium Shift to products side***

2) Effect of Pressure:

This is **applicable for gaseous reactions.** We have, at constant volume and constant temperature,

$$P \propto n \qquad \text{(Since, } PV = nRT\text{)}$$

Thus, equilibrium systems affects only with **<u>unequal</u> moles of gaseous reactants and products.**

Example:

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{\text{Catalyst}} 2NH_{3(g)} + 22800\text{Cal}$$

In the forward reaction (synthesis of ammonia), the number of moles of gaseous components is decreasing. i.e.,

$$\Delta n_g = (n_P - n_R)$$

where, n_P = No. of moles of gaseous products = 2
n_R = No. of moles of gaseous reactants = 1+3 = 4

$$\Delta n_g = (2) - (1+3) = -2$$

Thus, the synthesis of ammonia in Haber process is favored by **increasing the pressure** of the system. Industrially, 200 - 250 atm. of pressure is employed.

3) **Effect of Temperature:**

When heat is added to a system at equilibrium, the system shifts in a direction **that uses up the excess heat.**

A reaction that absorbs heat is **endothermic** & a reaction that produces heat is **exothermic**.

Temperature Changes for Exothermic & Endothermic Reactions:

Consider heat as a product in **exothermic reactions.**

A + B = AB + Heat

- Add **heat** ➔ ***Equilibrium Shift to reactants side***
- Remove **heat** ➔ ***Equilibrium Shift to products side***

Consider heat as a reactant in **endothermic reactions.**

A + B + Heat = AB

- Add **heat** ➔ ***Equilibrium Shift to products side***
- Remove **heat** ➔ ***Equilibrium Shift to reactants side***

4) **Effect of Catalyst:**

Certain chemical reactions favor the formation of product at low temperature but it slows down the rate of reaction. Therefore according to Le-Chatelier's principle, **suitable catalyst is used to increase the rate of reaction.**
e.g. In Haber process, **Finely divided iron oxide (Fe_2O_3)** together with small amount of **Molybdenum (promoter)** is used as catalyst which **increases the rate of reaction.**

Remark: The chemicals which are consumed on large commercial scale are known as 'Heavy chemicals' e.g.H_2SO_4, HNO_3, NH_3, Na_2CO_3 etc.

Q.2) State Le Chatelier's Principle. Explain physicochemical principles involved in Haber Process. (5Marks)

OR Write note on physicochemical principles involved in the manufacturing of ammonia (NH_3).

Or Apply Le Chatelier's Principle to following reaction;

$$N_{2(g)} + 3H_{2(g)} \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} 2NH_{3(g)} + 22800\text{Cal}$$

Ans. Le Chatelier's Principle: If a stress is applied to a system at equilibrium, the system will change to relieve that stress and reestablish the equilibrium. **(1Mark)**

Or Whenever a system in equilibrium is subjected **to a change i.**e. change in temperature or pressure or concentration, the equilibrium shifts in that direction so as **to nullify the effect of that change.**

Physiochemical Principles involved in Haber Process: **(1Mark)**

$$N_{2(g)} + 3H_{2(g)} \overset{\text{Catalyst}}{\rightleftharpoons} 2NH_{3(g)} + 22800\text{Cal}$$

(1Volume) + (3Volume) **(2Volume)**

In Haber process, reaction is **reversible** and forward reaction is **exothermic,** associated with **decrease in volume.** The **maximum yield of ammonia** would be obtained by maintaining some optimum reaction conditions such as;

1) Temperature 3) Pressure
2) Concentration and 4) Use of suitable catalyst

1) Effect of Temperature: **(1Mark)**

Forward reaction is **exothermic therefore** according to Le-Chatelier's principle, decrease **in temperature** favors the formation of ammonia, but it **decreases the rate** of reaction. Hence, to increase the reaction rate, **suitable catalyst must be used** and the requirement of optimum temperature is **at about 500-550^{0}C.**

2) Effect of Catalyst: **(1Mark)**

Though low temperature favors the formation of ammonia, it slows down the rate of reaction. Therefore according to Le-Chatelier's principle, **suitable catalyst is used to increase the rate of reaction.**

Finely divided iron oxide (Fe_2O_3) together with small amount of **Molybdenum (promoter)** is used as catalyst which **increases the rate of reaction.** Osmium is a much **better catalyst** for the reaction but is **very expensive.**

3) Effect of Pressure: **(1Mark)**

By applying the **law of mass action** to the following reaction, **in terms of partial pressure**

$$N_{2(g)} + 3H_{2(g)} \overset{\text{Catalyst}}{\rightleftharpoons} 2NH_{3(g)} + 22800\text{Cal}$$

(1Volume) + (3Volume) **(2Volume)**

According to **law of mass action,** we have

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \cdot P^3_{H_2}}$$

Where, K_p= equilibrium constant

As forward reaction results with **decrease in volume,** therefore according to Le-Chatelier's principle, the formation of ammonia **requires the higher pressure** and the requirement of optimum pressure is **at about 200-250atm.**

4) Effect of Concentration: (1Mark)

By applying the **law of mass action** to the following reaction, **in terms of concentration,**

$$N_{2(g)} + 3H_{2(g)} \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} 2NH_{3(g)} + 22800Cal$$

(1mole) + (3mole) **(2mole)**

According to **law of mass action,** we have

$$K_c = \frac{[NH_3]^2}{\{[N_2] \cdot [H_2]^3\}}$$

Where, K_c = equilibrium constant

Therefore, according to Le-Chatelier's principle, maximum yield of ammonia can be obtained by passing the nitrogen and hydrogen gases at **the proportion of 1:3 ($N_2 : H_2$).**

5) Space velocity / Rate of flow / Time of contact:

The conversion reaction depends upon the time of contact of reacting gases with catalyst. Hence, to get good conversion, these gases are recirculated over the catalyst repeatedly.

Thus, according to physicochemical principle, the optimum conditions for the Haber's process are,

i) Temperature: **500-550^{0}C**
ii) Pressure: **200-250atm.**
iii) Catalyst: finely divided **Fe_2O_3 with promoter (Mo).**
iv) Conc. i.e. Proportion of gases **1:3 ($N_2 : H_2$)**
v) Repeatedly circulation of reacting gases over catalyst

2) Contact Process:

Q.3) Write note on physicochemical principles involved in Contact Process.

OR Explain physicochemical principles involved in the manufacturing of sulphuric acid (H_2SO_4) (5Mark)

Ans. Contact process involves the following steps (reactions) : **(1Mark)**

1) Preparation of sulphur dioxide by burning high grade sulphur or iron pyrites.

$$S_{(s)} + O_{2(g)} \xrightarrow{\text{Burning}} SO_{2(g)} + 70{,}920\text{cal}$$

$$\underset{\text{Iron pyrites}}{4FeS_{2(s)}} + 11O_2 \longrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)} + 82{,}340\text{cal}$$

2) Oxidation of sulphur dioxide by air in the presence of catalyst to give sulphur trioxide.

$$2SO_{2\,(g)} + O_{2(g)} \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} 2SO_{3(g)} + 45{,}000\text{cal}$$

3) Formation of oleum by dissolving sulphur trioxide in 98% sulphuric acid.

$$SO_{3(g)} + H_2SO_{4(l)} \longrightarrow \underset{\text{oleum}}{H_2S_2O_{7(l)}}$$

4) Preparation of sulphuric acid of nay concentration by diluting oleum with water.

$$H_2O_{(l)} + \underset{\text{oleum}}{H_2S_2O_{7(l)}} \longrightarrow \underset{\text{sulphuric acid}}{2H_2SO_{4(l)}}$$

Physiochemical Principle: The yield of sulphuric acid by this process depends upon **the catalytic oxidation of SO_2 to SO_3 by atmospheric oxygen.** **(1Mark)**

$$\underset{(2\text{Volume})}{2SO_{2(g)}} + \underset{(1\text{Volume})}{O_{2(g)}} \overset{\text{Catalyst}}{\rightleftharpoons} \underset{(2\text{Volume})}{2SO_{3(g)}} + 45{,}000\text{cal}$$

The reaction is **reversible** and forward reaction is **exothermic,** associated with **decrease in volume.** The maximum yield of sulphuric acid is obtained by maintaining some optimum reaction conditions such as;

1) Temperature
2) Pressure
3) Concentration and
4) Use of suitable catalyst

1) Effect of Temperature: **(1Mark)**

Forward reaction is **exothermic, therefore** according to Le-Chatelier's principle, **decrease in temperature** favors the formation of sulphuric acid but it **decreases the rate** of reaction. Hence, to increase the reaction rate, **suitable catalyst must be used** and the requirement of optimum temperature is **at about 425-450^{0}C.** Experimentally, it is observed that at 434^{0}C, 99% reaction is completed.

2) Effect of Catalyst: **(1Mark)**

Though low temperature favors the formation of SO_3, it slows down the rate of reaction. Therefore, according to Le-Chatelier's principle, suitable catalyst is used to increase the rate of reaction.

The commonly used catalysts are Fe_2O_3, finely divided Pt and V_2O_5.

The good results obtained by using **Pt as catalyst** but it is **expensive** and also easily **poisoned by impurities.** Therefore, **V_2O_5 is preferred.**

$$V_2O_{5\,(s)} + SO_{2(g)} \longrightarrow SO_{3(g)} + V_2O_{4\,(s)}$$

Vanadium pentaoxide

3) Effect of Pressure: **(1Mark)**

By applying law of mass action to following reaction in terms of partial pressure,

$$\underset{(2\text{Volume}) + (1\text{Volume})}{2SO_{2(g)} + O_{2(g)}} \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} \underset{(2\text{Volume})}{2SO_{3(g)}} + 45{,}000\text{cal}$$

According to **law of mass action,** we have

$$Kp = \frac{P^2{}_{SO_3}}{[P^2{}_{SO_2} \cdot P_{O_2}]}$$

Where, K_p= equilibrium constant

SO_3 is **strongly adsorbed on the surface of catalyst** at high pressure therefore incoming gases diffuse through such layer. As forward reaction results with **decrease in volume,** therefore according to Le-Chatelier's principle, the formation of SO_3 **requires the higher pressure** and the requirement of optimum pressure is **at about 1.5- 1.7 atm.**

4) Effect of Concentration: **(1Mark)**

By applying the **law of mass action** to the following reaction, **in terms of concentration,**

$$\underset{(2\text{mole}) + (1\text{mole})}{2SO_{2(g)} + O_{2(g)}} \overset{\text{Catalyst}}{\rightleftharpoons} \underset{(2\text{mole})}{2SO_{3(g)}} + 45{,}000\text{cal}$$

According to **law of mass action,** we have

$$K_c = \frac{[SO_3]^2}{\{[SO_2]^2 . [O_2]\}}$$

Where, K_c= equilibrium constant

Therefore, according to Le-Chatelier's principle, maximum yield of sulphuric acid can be obtained by passing SO_2 and O_2 gases at the **proportion of 2:3(SO_2 : O_2)**

5) Space velocity / Rate of flow / Time of contact:

The time of contact of the reacting gases with the catalyst must be carefully controlled and thus space velocity is adjusted.

Thus, according to physicochemical principle, the optimum conditions for the maximum yield of SO_3 are:

i) Temperature: **425-450^{0}C**
ii) Pressure: **1.5-1.7 atm.**
iii) Catalyst: **V_2O_5 or Pt.**
iv) Proportion of gases **2:3 (SO_2 : O_2)**
v) Appreciable space velocity

Q. 4) What are different industrial methods of manufacturing sulphuric acid? Write the chemical reactions and physiochemical principles involved in contact process. (10Marks)

Ans. The different industrial methods of manufacturing sulphuric acid are

a) The Lead Chambers Process
b) The Contact Process **(2Mark)**

Chemical reactions: Refer above answer (Q.3) **(3Mark)**

Physiochemical: Refer above answer(Q.3) **(5Mark)**

All of us do not have equal Talent. But, all of us have Equal Opportunities to develop our Talents….

Q.5) Give detailed account of the manufacture of ammonia by Haber's process OR Explain manufacturing of ammonia by Haber's process . (5Marks) OR Write short note on: 'Haber process'.

Ans. Manufacture of ammonia by Haber's process: Ammonia is manufactured by Haber's synthetic method which is most important one and **about 90% of ammonia** is manufactured by this process today.

<u>Principle</u>: In Haber process, ammonia is prepared be catalytic combination of nitrogen and hydrogen as **1:3 ratio** under optimum temperature and pressure. **(1Mark)**

$$N_{2(g)} + 3H_{2\,(g)} \xrightleftharpoons{\text{Catalyst}} 2NH_{3\,(g)} + 22800\text{Cal}$$

<u>Flow Sheet Diagram</u>: **(2Marks)**

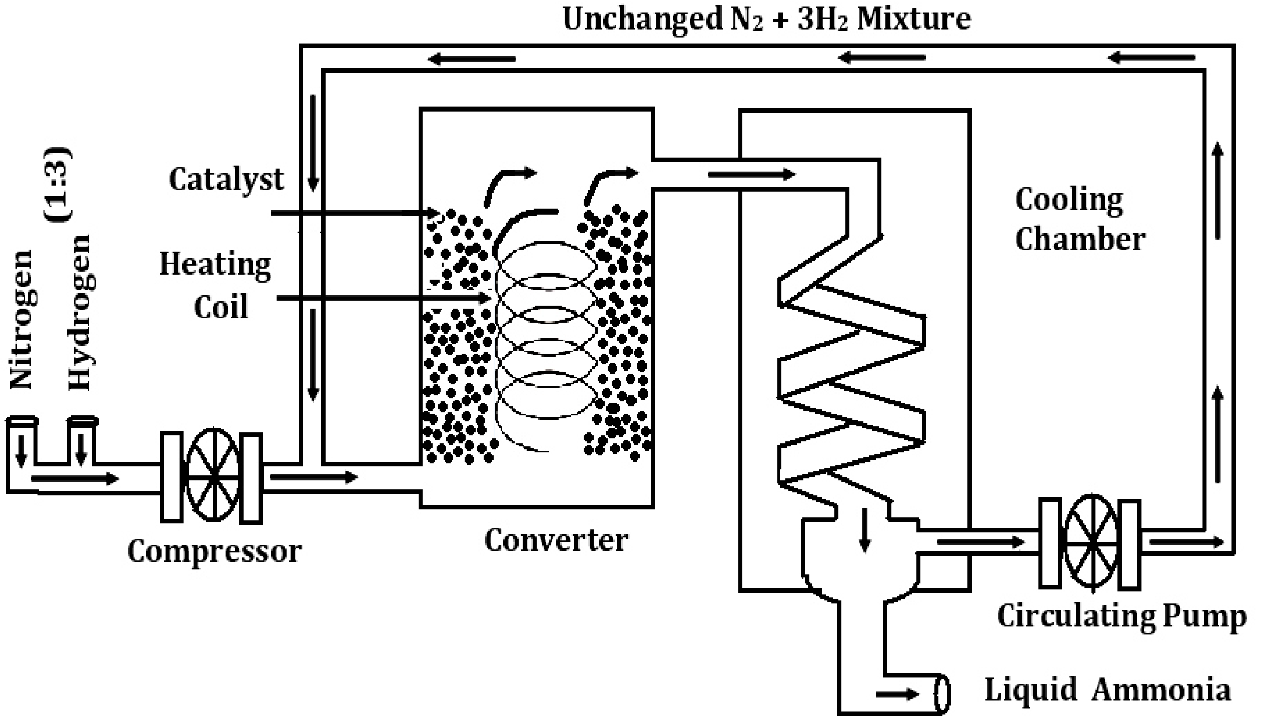


Fig. Manufacturing of Ammonia By Haber's Process

The process involves following **important steps, (3Mark : Each Step- 1Mark)**

1) Preparation and purification of the reacting gases.
2) The reaction in the converter.
3) Separation of ammonia from the unreacted gases.

1) Preparation and purification of the reacting gases : **(1Mark)**

a) The mixture of nitrogen and hydrogen in the **proportion of 1:3** is obtained by mixing proper quantities of **water gas (H_2O + CO), producer gas (N_2 + CO), steam** and passing this mixture over iron oxide as a catalyst at 550^0C.

b) The CO from water gas and producer gas reacts with steam to form hydrogen gas,

$$CO_{(g)} + H_2O_{(l)} \xrightarrow[550^oC]{Fe_2O_3} H_{2(g)} + CO_{2\,(g)} + 10{,}000cal$$

c) CO_2 is **removed by dissolving it in water** under pressure and traces of CO are removed by NaOH solution under pressure.

d) The purified gases are brought in the proper proportion, dried, compressed to 200atm pressure and passed through converter.

2) The reaction in the converter: **(1Mark)**

a) It consists of electrically heated catalyst which is first heated to 500-550^0C.

b) When reaction is started and it **being an exothermic,** the optimum temperature can be maintained by only **controlling the speed of entering nitrogen and hydrogen gases.**

c) In presence of Fine iron powder (used as catalyst) & Mo (promoter), N_2 & H_2 gases react according to the equation,

$$N_{2(g)} + 3H_{2\,(g)} \underset{}{\overset{Catalyst}{\rightleftharpoons}} 2NH_{3\,(g)} + 22800Cal$$

3) Separation of ammonia from the unreacted gases: **(1Mark)**

a) The ammonia formed is then cooled to condensate into liquid state.

b) The unchanged gases i.e. nitrogen and hydrogen are compressed and passed back to the circulatory system.

Advantages / Significance of Haber Process:

The important significance of this process is that **nothing is lost** and **about 8% ammonia** is obtained at each circulation **and it is very pure.**

Confidence and Hard Work is the BEST MEDICINE to kill the disease called Failure, it will make you Successful Person

DREAM *is not that which you see while sleeping,*

it is something that does not let you sleep. - Dr. APJ Kalam sir

Q.6) Give detailed account of the manufacture of sulphuric acid by contact process. OR Explain manufacturing of sulphuric acid by contact process. (5M) OR Write short note on: Contact Process.

Ans. Sulphuric acid is the most important inorganic heavy chemical and is known as ***'King of chemicals'***.

Manufacturing plant and process: **(1Marks)**

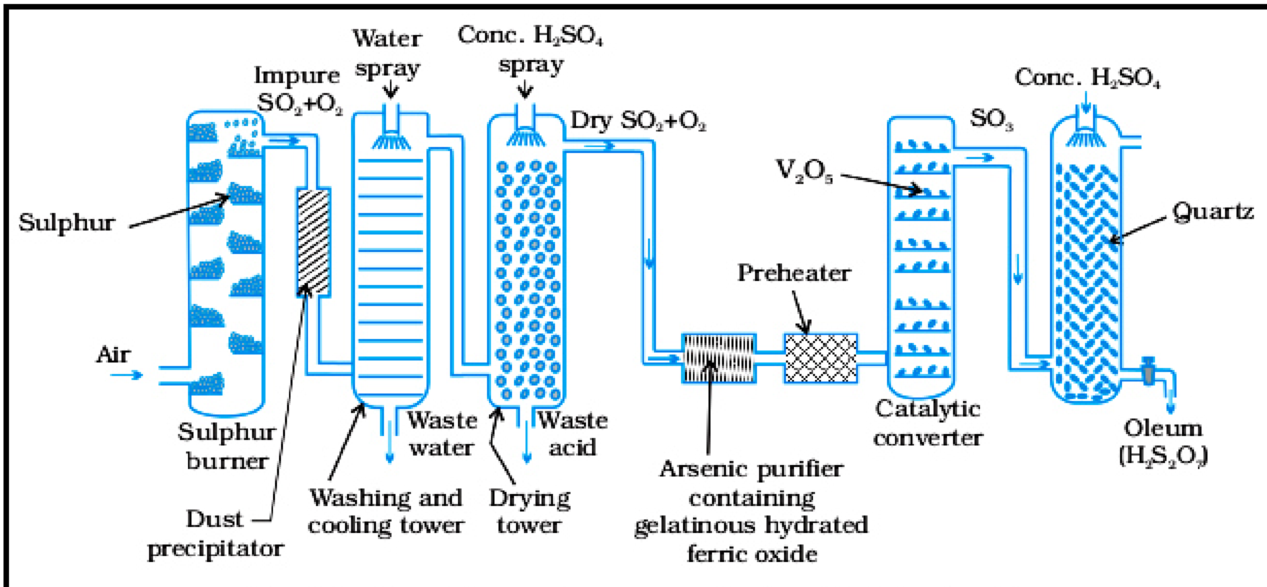
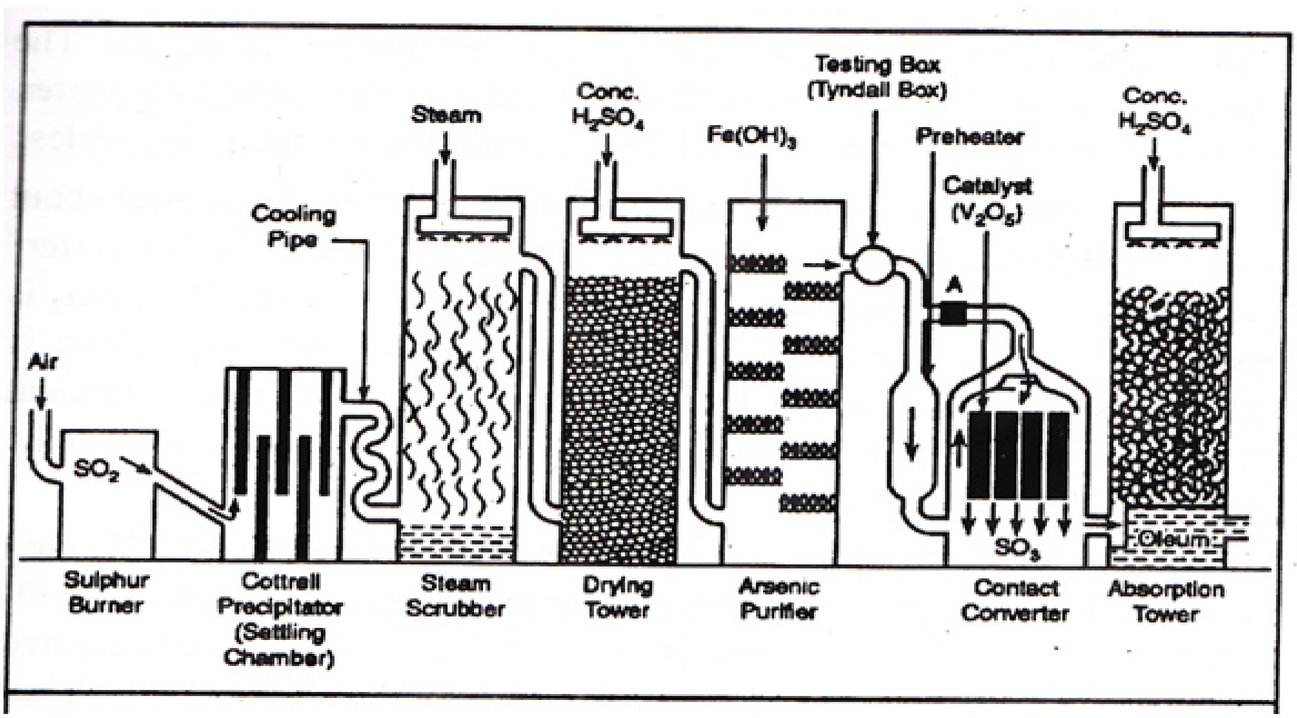


Fig. 7.7: Flow diagram for the manufacture of sulphuric acid



The plant consists of following important units as:

A) Burners B) Purification unit C) Contact converter D) Absorption unit

A) Burners: **(1Mark)**

a) SO_2 is obtained by burning high grade of sulphur or iron pyrites.
b) It is sufficiently pure therefore no need for the further purification.
c) But the gas obtained from **low grade sulphur or pyrite contains impurities** therefore it needs to purify.

$$S_{(s)} + O_{2(g)} \xrightarrow{\text{Burning}} SO_{2(g)} + 70{,}920\text{cal}$$

$$\underset{\text{Iron pyrites}}{4FeS_{2(s)}} + 11O_{2(g)} \longrightarrow 2Fe_2O_{3\,(s)} + 8SO_{2(g)} + 82{,}340\text{cal}$$

B) Purification Unit: **(1Mark)**

a) The gases obtained from the sulphur burner furnace contain impurities like **dust particles, acid fog and arsenic oxide** which **inactive the catalyst.**
b) So, all these impurities are removed **before passing through catalytic converter.**
c) The **fine dust particles** are removed in 'Cottrell precipitator i.e **dust precipitator** '.
d) **Acid fog** is removed by washing with water and sulphuric acid.
e) The gases are then dried by passing through **arsenic purifier** containing gelatinous ferric hydroxide which absorbs arsenous oxide.

C) Contact Converter: **(1Mark)**

a) The purified gases are heated first **to about 300^0C in the 'Pre-heater'** and are then passed through the converter.
b) The reaction being exothermic, the temperature is maintained at **about 450^0C.**

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{\text{Catalyst}} 2SO_{3\,(g)} + 45{,}000\text{cal}$$

D) Absorption Unit: **(1Mark)**

a) The hot gases from converter are passed through 'Heat exchanger' to heat up entering gases.
b) So, SO_3 gas gets cooled before absorbed in conc.H_2SO_4 flowing through the 'Absorption Unit / Tower'.
c) The SO_3 gets absorbed in 98% H_2SO_4 to give 'Oleum'.

$$SO_{3(g)} + \underset{98\%}{H_2SO_{4(l)}} \longrightarrow \underset{\text{Oleum}}{H_2S_2O_{7(l)}}$$

d) The oleum obtained may be diluted with water to get H_2SO_4.

$$H_2O_{(l)} + \underset{\text{Oleum}}{H_2S_2O_{7\,(l)}} \longrightarrow \underset{\text{sulphuric acid}}{2H_2SO_{4\,(l)}}$$

3) <u>Ostwald's Process:</u> (Ammonia Oxidation Process)

♦ Physicochemical Principles of Ostwald's process :

***Q.7) Write note on physicochemical principles involved in* Ostwald's process.**
OR Explain physicochemical principles involved in the manufacturing of nitric acid (HNO_3) ***(5Mark)***

Ans. **Ostwald's process involves the following steps (reactions) :** **(1Mark)**

1) Production of nitric oxide (NO):

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O, \quad \Delta H = -216.6 kcal$$

2) Conversion of nitric oxide (NO) to nitrogen dioxide (NO_2) :

$$2NO + O_2 \longrightarrow 2NO_2, \quad \Delta H = -27.1 kcal$$

3) Absorption of NO_2 into water:

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3, \quad \Delta H = -32.2 kcal$$

<u>Physiochemical Principle:</u>

a) Principle involved in conversion of NH_3 to NO:

$$\underset{(4Vol.)}{4NH_3} + \underset{(5Vol.)}{5O_2} \longrightarrow \underset{(4Vol.)}{4NO} + \underset{(6Vol.)}{6H_2O}, \quad \Delta H = -216.6 kcal$$

i) **Effect of Temperature & catalyst:** This reaction of conversion of NH_3 to NO is exothermic in nature and hence to achieve maximum conversion into gaseous nitric oxide (NO),

a) Reaction is maintained between 750^0C to 900^0C and
b) Suitable catalyst i.e. Pt-Rh (10%) is used

Here, oxygen is adsorbed on the surface of catalyst. The reaction between adsorbed oxygen and NH_3 takes place to convert each NH_3 molecule into NO.

ii) **Effect of Pressure:**
This reaction of conversion of NH_3 to NO is associated with increase in volume and hence according to Le Chatelier's principle, increase in pressure is unfavourable to achieve maximum conversion into gaseous NO. Thus in practice the reaction is carried out at just above the atmospheric pressure to maintain the appropriate flow of gases, contact time, rate of reaction, catalytic effect and combustion temperature.

iii) **Effect of Concentration:** According to Le Chatelier's principle, to achieve maximum conversion into gaseous NO, the proportion of reacting gases, **NH_3** and **air is 1:9** whereas for NH_3 and oxygen is 1:1.25 theoretically. Practically, oxygen is used in little excess.

iv) **Rate of flow of gases:** Appropriate flow of the reacting gases is maintained so as to get more yields.

b) Principle used in oxidation of NO to NO_2 :

$$2NO + O_2 \rightleftharpoons 2NO_2 \quad , \quad \Delta H = -27.1 kcal$$

2Vol. 1Vol. 2Vol.

According to Le Chatelier's principle, to achieve maximum conversion of NO into NO_2,

i) Temperature should be low (below 150^0C) because reaction is exothermic.

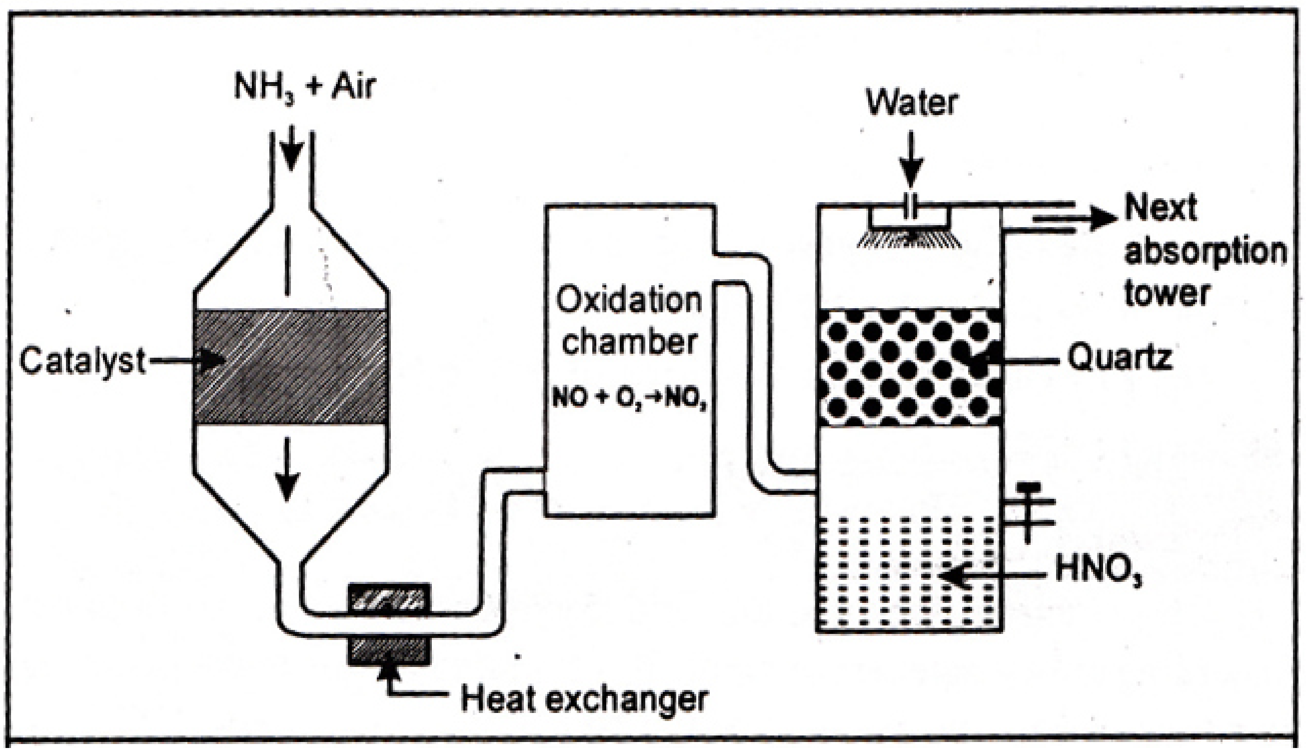
ii) Pressure should be high because decrease in volume is observed.

c) Absorption of NO_2 into water:

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3 \quad , \quad \Delta H = -32.2 kcal$$

According to Le Chatelier's principle, to achieve maximum absorption of NO_2 into water can be controlled by cooling the gases because of their exothermic nature. The rate of absorption is increased by increasing number of absorption units.

♦ **Manufacturing Process of Ostwald's process :**



Manufacturing Process of Ostwald's process involves following units;

1) **Reacting gases:** A mixture of anhydrous ammonia and dry air in the ratio **1: 9** is fed to the catalyst chamber as shown in fig.

2) **Catalytic Chamber:** In this chamber, reacting gases when passing through Pt-Rh gauze which is preheated to about 700^0C react with each other and ammonia is rapidly oxidized to nitric oxide.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O, \quad \Delta H = -216.6 kcal$$

3) **Heat Exchanger:** The produced gases are cooled by heat exchangers and passed into oxidation chamber.
4) **Oxidation Chamber :** In this chamber, nitric oxide further oxidized to NO_2 by cooling below 200^0C,

$$2NO + O_2 \longrightarrow 2NO_2 , \quad \Delta H = -27.1 kcal$$

NO_2 is further cooled and passed through absorption towers

5) **Absorption Towers :** Absorption towers are filled with broken quartz, in which water sprayed from the top continuously. Here, NO_2 is absorbed into water to form nitric acid.

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3 , \quad \Delta H = -32.2 kcal$$

6) Finally the dilute nitric acid is collected and further concentrated (about 68.4%) by distillation.

4) Solvay Process : (Ammonia-soda process)

♦ Physicochemical Principles of Solvay Process:

Solvay process involves following set of reactions as given below;

(a) $CaCO_3 \longrightarrow CaO + CO_2\uparrow$ $\quad \Delta H = + 43.4$ kcal

(b) $C + O_2 \longrightarrow CO_2\uparrow$ $\quad \Delta H = - 96.5$ kcal

(c) $CaO + H_2O \longrightarrow Ca(OH)_2$ $\quad \Delta H = - 15.9$ kcal

(d) $NH_3 + H_2O \longrightarrow NH_4OH$ $\quad \Delta H = - 8.4$ kcal

(e) $2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$ $\quad \Delta H = - 22.1$ kcal

(f) $(NH_4)_2CO_3 + CO_2 + H_2O \longrightarrow 2NH_4HCO_3$

(g) $NaCl + NH_4HCO_3 \longrightarrow NH_4Cl + NaHCO_3$

(h) $2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2\uparrow + H_2O$ $\quad \Delta H = + 30.7$ kcal

(i) $2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$ $\quad \Delta H = + 10.7$ kcal

Overall reaction for the entire process can be written as

$$CaCO_3 + 2NaCl \longrightarrow Na_2CO_3 + CaCl_2$$

From these reactions, it is clear that-

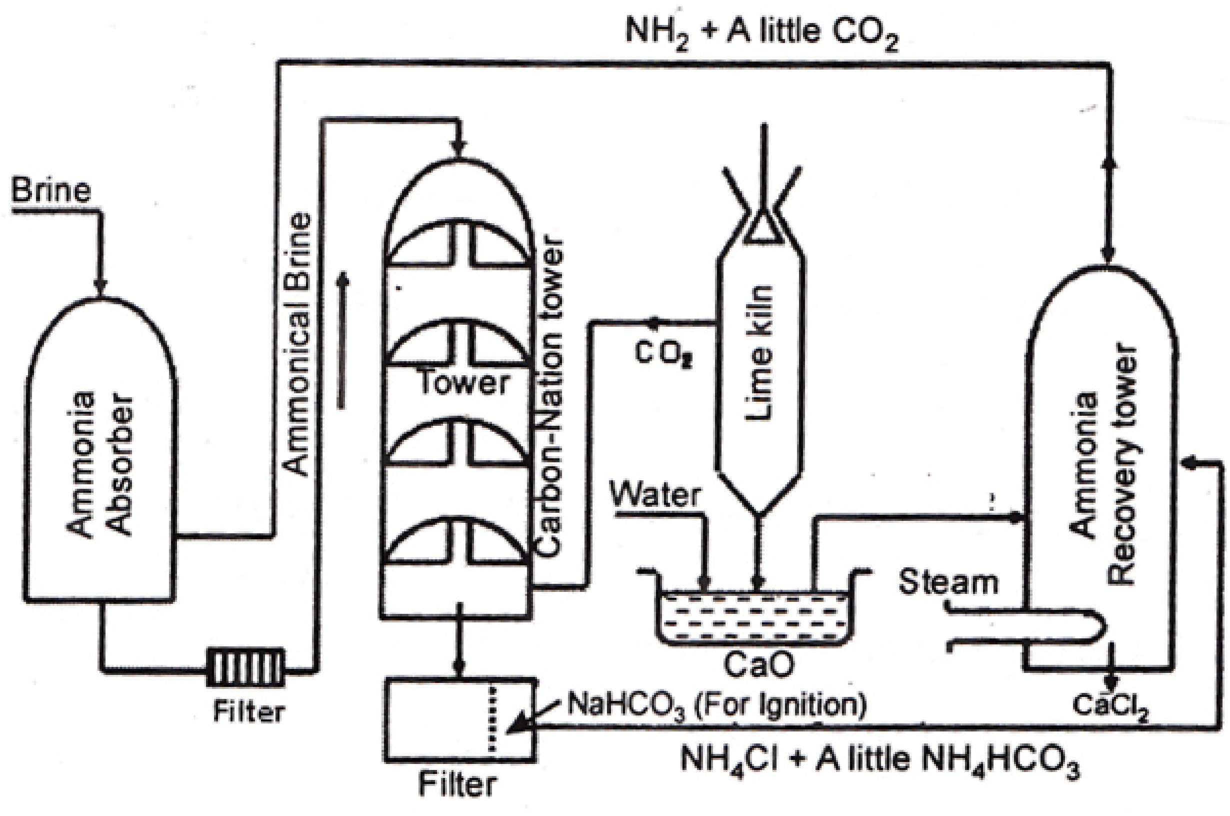
1) **Role of ammonia and CO_2** in this process is important which determines the yield of the final product. Therefore, reactions d, e & f can be written together as;

$$2NH_3 + 2CO_2 + 2H_2O \rightleftharpoons 2NH_4HCO_3 \quad \text{..... (a)}$$

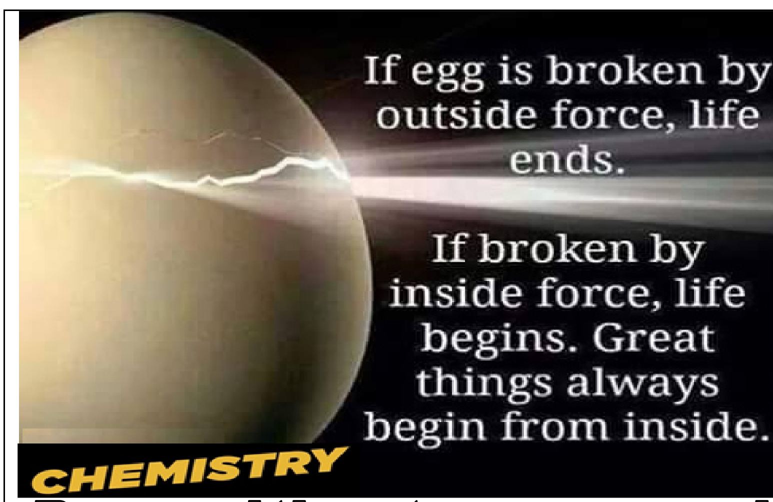
According to Le-chatelier's principle, the overall reaction (a) is **favoured by low temperature** because this reaction is exothermic in nature and it requires dissolution of gases in water.

2) **Precipitation of $NaHCO_3$** is also important to obtain maximum yield of final product so some physicochemical conditions should be maintained as follow;
   a) **Solubility of $NaHCO_3$:** To obtain maximum yield of final product, solubility of sodium bicarbonate should be decreased by maintaining lowest possible temperature.
   b) **Effect of Temperature:** Relatively high temperature (60-65^{0}C) in the beginning is applied so as to have **good crystal growth** and then gradual cooling will facilitate the filtration.

- **Manufacturing Process of Solvay Process:**



1) **Saturation Tank:** In this tank, Brine solution (i.e. saturated NaCl solution) is saturated by absorption of ammonia, which is exothermic and hence water cooling system is fitted. On cooling saturated ammoniacal brine solution is further filtered and pumped at the top of carbonation tower.
2) **Carbonation Tower:** In this tower, ammoniacal brine is trickling down and reacts with CO_2 which is introduced from bottom as shown in fig.
3) **During precipitation of $NaHCO_3$,** temperature is maintained about 20-25^{0}C at the both ends of tower and 45-55^{0}C in the middle by using cooling coils.
4) By shutting off cooling coils $NaHCO_3$ deposited is **dissolved by hot $(NH_4)_2CO_3$ solution formed.**
5) **$(NH_4)_2CO_3$ reacts** with upcoming CO_2 to form NH_4HCO_3 exothermally in the second tower where heat of reaction is removed by cooling coils.
6) **The milky liquid** is collected, allowed to cool and settle in vessel at the bottom.
7) **NH_4HCO_3 is** removed, filtered and pressed. NH_4HCO_3 is further calcined to get Na_2CO_3 (soda ash).
8) **Ammonia Recovery Tower**: The filtrate containing NH_4HCO_3 and NH_4Cl is treated with lime to regenerate NH_3 in **ammonia recovery tower** and circulated back to saturation tower along with little CO_2.
9) Finally, hot Na_2CO_3 (soda ash) from calciner is cooled and packed in bags.



Be positive to your goals

“Without Your Involvement You Can’t Succeed.

With Your Involvement You Can’t Fail.

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