Natubhai V. Patel College of Pure & Applied Sciences

S. Y. B.Sc. (Industrial chemistry)

C-214: Chemical Process Industries

UNIT 2B

SYLLABUS

INDUSTRIAL GASES: Hydrogen, Oxygen, Nitrogen, Carbon dioxide and Sulfur dioxide

INDUSTRIAL GASES

2.13 INTRODUCTION

The gases, which are very important for the different industries are hydrogen, Oxygen, Nitrogen, Carbon dioxide and sulfur dioxide.

2.14 HYDROGEN [H_2]

2.14.1 Manufacture

There are several method is known for **production of hydrogen gas**.

1. Electrolytic process.
2. Lane process or iron steam process.
3. Bosch process or water gas-steam process.
4. Steam hydrocarbon process.
5. Liquefaction of coal gas and coke oven gas.

1) Electrolytic Process

Pure hydrogen can be manufacture **by electrolysis of brine or water**. Since water is non-conductor of electricity, hence it has to be made conductor by addition of small quantities of pure H_2SO_4 or KOH or $Ba(OH)_2$. Hydrogen gas (2 volumes) and Oxygen gas (1 volume) are simultaneously liberated at cathode and anode respectively

2) Lane Process

Hydrogen is manufactured by **exothermic reaction** between red hot **iron and steam**. The continuity of production with the help of same mass of iron is maintained by reducing with the water gas the iron oxide produced by the iron steam reaction and repeating the cycle of oxidation and reduction.

3) Bosch Process

In preparing hydrogen, **only water gas** instead of mixture of water gas and producer gas (to prepare the mixture 3 volumes of hydrogen and 1 volumes of nitrogen) is taken.

4) Cracking of Hydrocarbon / Steam H.C. Process

The raw material used in this process is mostly liquid **methane or propane** gas, which are obtained from **natural gas or from coke oven gas**. The **catalyst** used is finely divided **nickel**. The temperature of the endothermic reaction is maintained **815°C**. The temperature maintained at this level by internal combustion process i.e. by allowing a part of methane to undergo oxidation with oxygen.

$$CH_4 + H_20 \xrightarrow{Ni/815^0C} CO + 3H_2 \qquad \Delta H = 48{,}900 \text{ cal.}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \Delta H = -191{,}800 \text{ cal.}$$

The combination of reactions results in exothermic.

$$12CH_4 + 5H_2O + 5O_2 \longrightarrow 29H_2 + 9CO + 3CO_2 \qquad \Delta H = -20{,}400 \text{ cal.}$$

Using propane as a raw material the reaction is

$C_3H_8 + 3H_2O \longrightarrow 3CO + 7H_2 \quad \Delta H = 129{,}270$ cal.

The temperature is maintained at 850°C either by external heating or by internal combustion.

5) Liquefaction of coke-oven gas

In this process the **coke oven gas** is first **purified** from H_2S, HCN, NH_3, CO_2 and light oil. Then the gas is **compressed** to **250 to 300 psi** and scrubbed in a pressure bubble cap tower with dilute NH_3 to remove CO_2 and HCN. Remaining CO_2 is removed by passing gas through NaOH (alkali) scrubber. Then gas is dry and again compressed and cooled, to remove ethylene and methane (Tc = -82.85° C & P_c = 45.6 atm.) Then the gas is further compressed and cooled so that nitrogen is liquefied with Tc = -147. 13° C & Pc = 33.49 atm and the hydrogen remains in the gaseous condition with Tc = -239.9° C and Pc = 12.8 atm. Then the pure hydrogen gas is cooled and stored.

2.14.2 Uses

- In fertilizer industries to produce NH_3 which is converted into $(NH_4)_2SO_4$, urea and HNO_3
- In hydrogenation of oils to make fats or in hardening of fatty oils
- In hydrogenating coal, low temperature carbonization tar and water gas to produce gasoline
- In hydrogenating water gas to produce methanol
- In production of HCl, which is used in large quantity in industries
- For filling in metrological balloons which are essential for upper air observation to guide the air flights
- In making oxy-hydrogen flame used for melting of platinum, quartz and in auto welding of lead
- In producing an inert media and in making tungsten filaments for electric lamps, mixture of nitrogen and hydrogen is used

2.15 OXYGEN [O_2] & NITROGEN [N_2]

Before discussing the uses and manufacturing process of oxygen & nitrogen we summarized the **kinetic theory of gases**.

In the **gaseous state** molecules have **two tendencies**

(1) Repulsion Tendency,

(2) Attraction Tendency.

The **liquid form** is obtained when the kinetic energy and the potential energy of the substance is approximately equal.

Critical temperature is the temperature below which any gas can be liquefied by increasing the pressure. Above the critical temperature any gas cannot be liquefied by compression. Therefore air should be cooled at very high pressure and low temperature for cooling purpose material used is liquid CO_2, SO_2 liquid Freon.

Oxygen in pure condition is obtained as a byproduct in the manufacture of H_2 by electrolytic process. It is usually manufactured by rectification of liquid air, N_2 obtained simultaneously.

2.15.1 Analysis of Air

Oxygen [O_2] ⟶ 20.99 % by weight

Nitrogen [N_2] ⟶ 78.01 % by weight

Argon [Ar] ⟶ 00.94 % by weight

Hydrogen [H_2] ⟶ 0.01 % by weight

Carbon dioxide [CO_2] ⟶ 0.03 to 0.07 % by wt

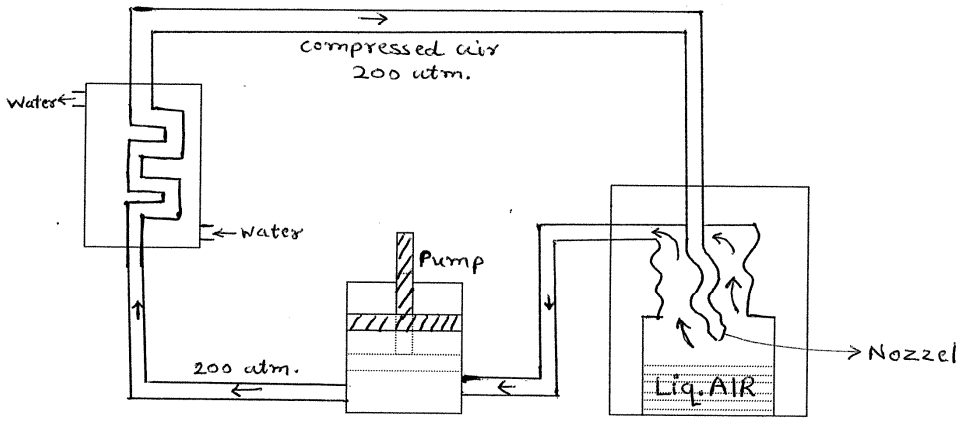
Neon [Ne] ⟶ 0.0015 % by weight

He & Kr ⟶ 0.01 to 0.02 % by weight

2.15.2 Liquefaction of air By Joule - Thomson effect

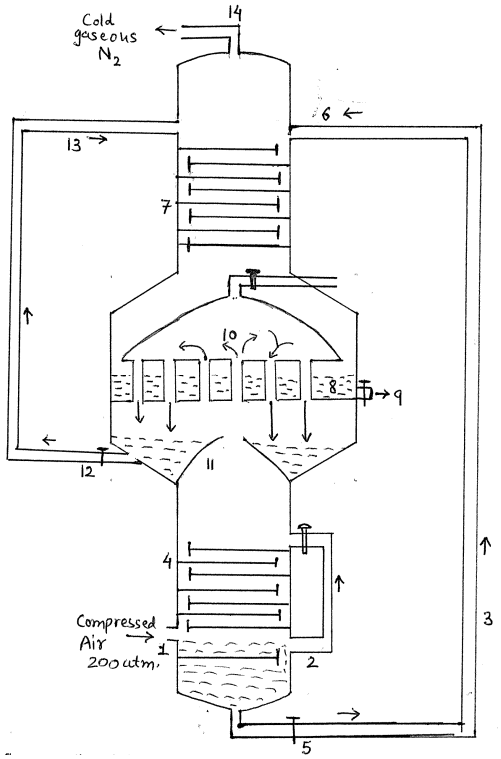
Air free from CO_2 compressed to **200 atm**. pressure is **cooled** by water and freed from condensed water passing through heat exchangers. There is a valve ending in a nozzle at the end of the inner coil. The gas is allowed to **suddenly expand** by opening the valve. By this expansion the air is cooled to a certain temperature and formed liquid air. The air which is

not liquefied is taken out in the compressor and **again compressed at 200 atm**. pressure for liquefaction.



2.15.3 Linde's process (For Manufacture of Oxygen and Nitrogen)

Air is freed from CO_2 and dust by washing with caustic potash solution. Then the air is compressed to **200atm**. pressure, the condensed water is removed by solid KOH or activated alumina.



1. Entering of compressed air at 200 atm.
2. Accumulated liquid rich in O_2
3. Cooled and liquid air entering tower
4. Lower (power) rectifying column
5. Exit valve for liquid O_2 40%
6. Liquid entering upper rectifying column
7. Upper rectifying column
8. Accumulated liquid O_2
9. Exit value for 99% O_2
10. Condensed tubes & domes for lower column
11. Condensed overhead from lower column rich in N_2
12. Return valve for flow to upper column
13. N_2 rich liquid entry upper column
14. Cold gaseous N_2

Then the compressed air enters the inner coil of the **heat interchanger** (not shown in the figure). The main part of the plant is a **double column** (rectifying) one above the other. After the compressed air passes through interchanger for many times the air reaches the liquefaction point. Their air passes in the **lower column**, through the side, but after liquefaction point has been reached liquid air enters, in the lower column and undergoes rectification and by oxygen rich liquid air collects at the bottom of the column and nitrogen rich air enters in the dome through the pipes. A liquid richer in nitrogen rich liquid rises through another pipe and enters itself in the **upper column** through the other side. In the upper column, an exchanges between down coming liquid richer and richer in oxygen and rising gas richer and richer in nitrogen resulting to complete separation of nitrogen and

oxygen. Nitrogen obtains in gas form at the top and oxygen obtained in liquid form at the bottom of the column.

2.15.4 Uses of oxygen

- It is used to produce oxyacetylene flame to cutting and welding the metals
- It is used in L.D. process for steel production
- Used for artificial respiration in case of patients
- It is used for mountain climbers and high attitude aero planes flights

2.15.5 Uses of nitrogen

- It is mainly used in manufacture of synthetic ammonia.
- It is also used in making nitrogen oxide. It is applied to create inert atmosphere.

2.16 CARBON DIOXIDE [CO_2]

2.16.1 Sources of CO_2

- In the production of H_2 by steam water gas 16% pure CO_2 is obtained.
- In manufacture of alcohol (ethanol) by the fermentation process. 99.9 % pure CO_2 is obtained.
- In calcinations of $CaCO_3$ 40% CO_2 is obtained

$$CaCO_3 \xrightarrow{1000°C} CaO + CO_2 \ (40\%)$$

- By burning of carbonaceous materials

$$C + O_2 \longrightarrow CO_2 \ (10 \text{ to } 18\% \text{ Pure})$$

2.16.2 Purification

Carbon dioxide obtained in impure state can be **purified by different ways**. There are two main categories for purification of carbon dioxide.

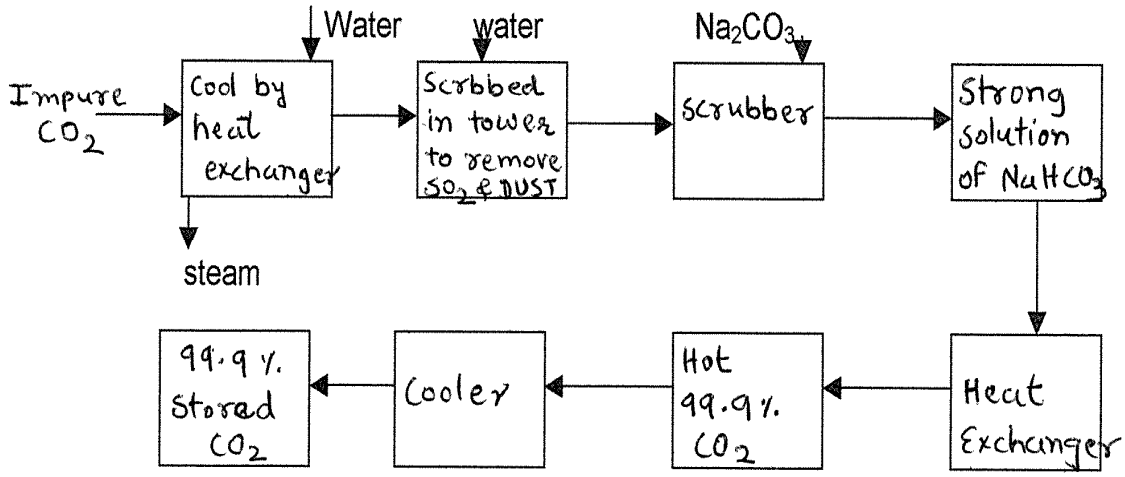
1. Purification of high % CO_2 containing gas.
2. Purification of low % CO_2 containing gas.

1) Purification of high % CO_2 containing gas

In this method **impure gas** is first **compressed** to **80psi** pressure and passes through a scrubber where it is treated with **$KMnO_4$** to remove organic matters. The gas is then **dehydrated** by passing through silica gel or activated alumina or conc. H_2SO_4, in **scrubber.** Then the gas passes through an oil scrubber to remove bad odour of gas. Then the gas is, **compressed** in two stages, 80 psi to 300 psi and 300 psi to 900 psi. When the gas is compressed and supplied then 300 psi is sufficient, when liquid is produced the gas is compressed to 900 psi. For this purpose the temperature is brought down much below **31.1°C**. After compression by cooling of CO_2, the liquid is stored at -10° C temperature. If the liquid CO_2 is passes through an expansion tank and pressure is released then the solid CO_2 is formed at -40° C temperature.

2) Purification of low % CO_2 containing gas

In this method **18% hot CO_2** gas passes through **exchanger** to lower the temperature. Then it is passed, through a **scrubber** from top, of which the water is percolated to remove SO_2 and dust particles. Then the gas passes through **two packed towers** where the gas is scrubbed with Na_2CO_3 solution and absorbed in it to form $NaHCO_3$ solution in **second tower**. Solution is heated in heat exchanger to remove absorbed carbon dioxide. This carbon dioxide is then cooled in cooler and stored.



2.16.3 Uses

- As solid CO_2 in refrigeration process
- Liquid CO_2 is needed in carbonated.
- Used in creating inert atmosphere.
- Gaseous CO_2 used as a neutralizing agent
- Gaseous CO_2 is the basic raw material for production of Na_2CO_3, $NaHCO_3$ & other carbonates products

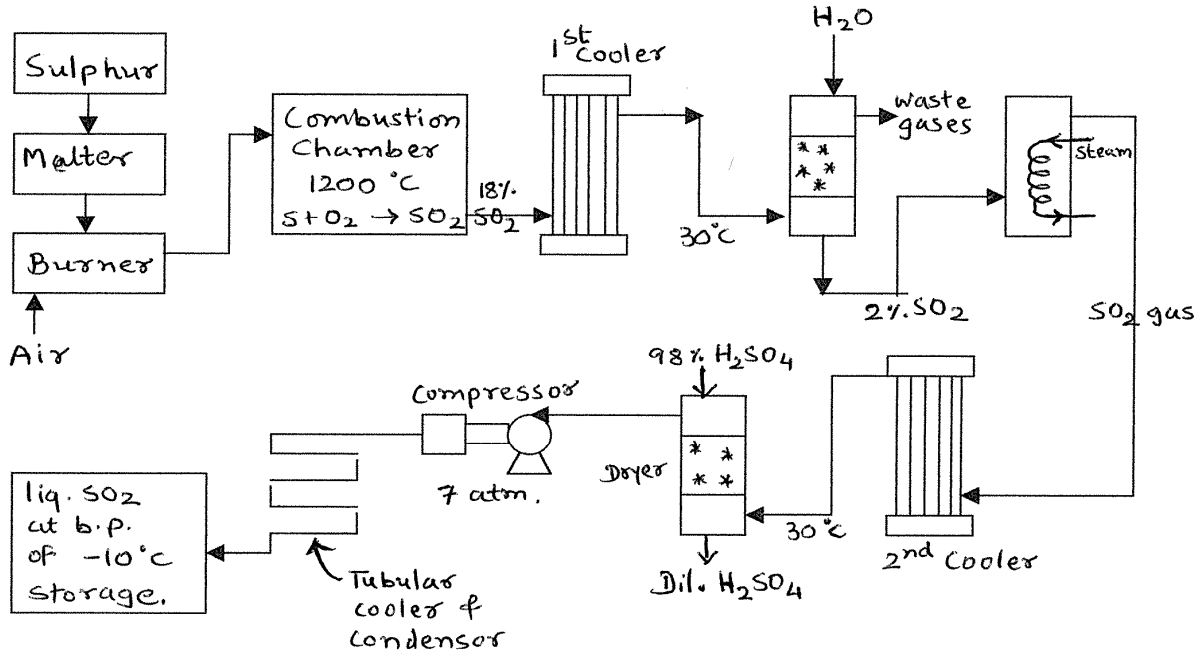
2.17 <u>SULFUR DIOXIDE [SO_2]</u>

2.17.1 Raw material

- Solid sulfur
- Air

2.17.2 Manufacture

Sulfur is first melted in **melter** then it is sent to the **burner** where it is burnt with Air. From the burner it is enters in the combustion chamber where **SO_2 gas** is produced by reaction of **sulfur with oxygen**.



Then the 18% SO_2 from combustion chamber is sent to the **1st cooler** where it is cooled at **30°C**. Then it is passed through **absorber** from top of which water is percolated. Here SO_2

absorbed in water to form liquid and waste gases are taken out. Then 2% SO_2 solution from absorber is enters into the **heat exchanger** where it forms gaseous SO_2 again. The SO_2 gas is sent to the **2nd cooler** and cooled at 30°C again. Then it is dried in drier by treated it with conc. H_2SO_4 acid. Then dry SO_2 gas is **compressed** in compressor at **7 atm**. press and compressed gas passes through a **tabular cooler** and condenser where the SO_2 gas formed in **liquid SO_2 at -10° C** temperature. Then the liquid SO_2 is stored in a storage tank for different purposes.

2.17.3 Uses

- It is used in manufacture of H_2SO_4 acid.
- SO_2 gas is used as bleaching agent in textile and food industry.
- It is used for controlled the fermentation process and paper industry.
- Liquid SO_2 used as a solvent in refining of petroleum fractions.
- Liquid SO_2 is used as a Refrigerant.

2.18 EXERCISE

1. With the help of diagram explain the steps carbonation and ammoniation in Solvay's Ammonia Soda process.
2. With the help of diagram explain manufacture of NaOH by causticizing process
3. Write manufacture of caustic soda by lime soda process
4. Explain manufacture of caustic soda by diaphragm cells
5. Manufacture of sodium hypochlorite
6. Write notes on
   - Nelson cell
   - Hooker cell
   - Castner Kellner cell
   - Membrane cell
   - Leblanc process
   - Baking powder
7. List different methods used to manufacture Hydrogen. Explain steam hydrocarbon process
8. Explain Linde's process for manufacture of Oxygen and Nitrogen
9. Explain methods used to purify CO_2 containing gases
10. Write uses of SO_2 and CO_2
11. Discuss the manufacture of Sulfur dioxide with the help of flow diagram
12. Explain liquefaction of air by Joule – Thomson effect.

2.19 FURTHER READING

1. Industrial chemistry by B. K. Sharma
2. Shreve's chemical process industries by George T. Austin
3. Industrial Chemistry Part 2 by R. K. Das