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Chapter-2 Manufacture of Basic Chemicals

Introduction, Manufacture of Ammonia, Physico- Chemical Principles (In Ammonia Manufacture)

Introduction

The chemical industries in India stand apart in all manufacturing industries in terms of their utility to common man and importance to the nation. Many of their products are used in manufacturing industries in India. For example, chemical industries supply materials for de preparation of food materials, drugs, polymers, textiles, dyes, building material, Ammonia, sulphuric acid and nitric acid are we of the chemicals produced by the preparation of other chemicals

Manufacture of Ammonia

Principle

The manufacture of ammonia is based on the principle, that, nitrogen and hydrogen react in the volume ratio 1:3 under pressure and at an optimum temperature, in presence of a catalyst.

Reaction

$$N2 \quad + \quad 3H2 \quad \rightleftharpoons \quad 2NH3$$

(1 vol) (3 vol) (2Vol)

Process

Depending upon the source of reactants viz. hydrogen and nitrogen, the processes are named as (1) Haber process (ii) Modified Bosch-Haber Process

1. Haber Process - In this process, nitrogen is obtained from liquid air and hydrogen is obtained from steam, hydrocarbon or electrolytic process.

2. Modified Bosch-Haber Process- This process is sometimes also called Bosch-Haber process. In this process, nitrogen is obtained from producer gas (CO+ N) and hydrogen is obtained from water gas ($CO+H_2$) The main limitation of Haber process is that the yield of ammonia is low about 8%. The yield of ammonia by Bosch-Haber process is about 19%, So Bosch-Haber process is preferred to Haber process

Manufacture of Ammonia by Modified Bosch-Haber Process This is described below. It is carried out in a Ni-V-Cr steel converter is used The reaction is carried out at about 550°C under 300 atmosphere pressure using a catalyst (Fe2O3).

Raw Materials

Nitrogen gas and hydrogen gas are the basic raw materials required for synthesis of ammonia. Different methods are used to obtain these gases. Hydrogen Gas: It is obtained from any one of the following sources (1) from water (CO + H_2) (ii) from coke oven gas (iii) from naphtha (iv) by reacting natural steam (v) by electrolysis of water. Nitrogen Gas: It is obtained from any one of the following sources (1) from producer (CO+N_2) (ii) from air

In modified Bosch - Haber process hydrogen gas and nitrogen gas are obtained water gas and producer gas respectively.

Water Gas is produced from coke and steam as C (coke) and H_2O (steam)Producer gas is produced from coke and air

Manufacture of Basic Chemical

Reaction -In A mixture of water gas and producer gas is passed in an oxidation tower. The Co from water gas and producer gas is converted to CO; by steam using iron oxide catalyst, promoted with Cr2O3, and CeO_2 heated at 450°C.

The reaction is exothermic. Due to the heat produced, the reaction can continue even at low temperature, hence the temperature is kept 450°C The gaseous mixture of CO_2, H_2, Ny and CO is cooled in a heat exchanger and compressed to 25 atmosphere pressure. The unwanted gases CO, and CO are removed in a scrubber as follows the CO_2 is removed by dissolving it in water under pressure CO_2 + H_2O and The solution of cuprous formate is boiled with the gaseous mixture to remove CO and recycled.

The Reaction in The Converter. The mixture of pure N2, and H2, in the ratio 1:3 is further compressed to 200-300 atmospheres in a compressor and then passed through oil filters to remove oil, if any. Then the mixture of gases (N_2, H_2) is passed over finely divided iron catalyst (with molybdenum as promoter) kept at 500°C in Ni-V-Cr steel converter. The catalyst in the granular form is kept in the central portion of the converter. The gases are heated to 500°C and passed through the catalyst. Following reaction takes place in the converter.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \ +92 \text{ kJ}$$

The reaction is exothermic and can continue, even at lower temperature. The required temperature is maintained by adjusting the speed of entering gases.

Separation Of Ammonia from The Unconverted Gases

The outgoing mixture of gases contain 8% NH_3, and unconverted N_2 and H_2. The mixture is cooled first by circulating cold water and then by ammonia refrigeration at -15°C. Liquid NH_3, is collected in a storage tank. The unconverted gas mixture (N_2, H_2) is compressed to 300 atmospheres and then mixed with fresh compressed gas mixture in the compressor and recirculated.

Physico- Chemical Principles (In Ammonia Manufacture)

Synthetically ammonia is formed by the following reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH3 \quad +92\ kJ$$

The reaction is reversible. The forward reaction is exothermic and backward reaction. is endothermic. During formation of NH_3, there is decrease in volume. According to Le -Chatelier principle; percentage of ammonia formation at equilibrium will to increase in pressure and decrease in temperature. Equilibrium constant K, for the above reaction depends upon the temp and pressure

Effect of Temperature-

The increase the temperature, we find that the system tries decrease it Similarly, if we decrease the temperature, the system tries to increase formation of ammonia is an exothermic reaction, therefore, it is favored by low temperature. the decrease in percentage of ammonia at equilibrium temperature is increased. Effect of Temperature on Equilibrium

Temperature (°C)	350	400	450	500	550
% of NHs (at 200 atm) →	37.5	24.9	16.4	10.4	6.9

The equilibrium constant (K) remains constant at a given temperature. It increases with increase in temperature and decreases with decrease in temperature., the conversion of NHI is more at lower temperature. But at lower temperature, the rate of reaction is very slow. Therefore, in the converter optimum temperature is kept and rate of reaction is increased by using a catalyst.

Effect of Pressure:

In the above reaction there is decrease in volume during forward reaction. Therefore, if we increase the pressure, the equilibrium shifts the number of moles and hence the volume decreases. If we increase the pressure, we find such a direction that that more amount of NH_3, is formed. In general, a reaction which is accompanied by decrease in volume is favoured by increase in the pressure. % of ammonia as a function of pressure at different temperatures.

At 200ºC and pressures above 750 atm there is an almost 100% conversion of reactants to the ammonia product. Since there are difficulties associated with taking larger amounts of materials at this high pressure, lower pressures of around 200 atm are used industrially. By using a pressure of around 200 atm and a temperature of about 500°C, the yield of ammonia is 10-20%, while costs and safety concerns in the building and during operation of the plant are minimised

Effect of Catalyst: When a chemical process is used for commercial application, time factor is important. Maximum yield of the desired product has to be obtained in minimum possible time. An exothermic reversible chemical reaction is favoured by low temperature but at low temperature time required to reach the equilibrium is very long.

In industrial process, usually a temperature is found out such that yield will be more. and the equilibrium will be reached sufficiently faster. This temperature is called as optimum temperature. During the process, optimum temperature is kept and a catalyst is used.

In the manufacture of ammonia, the optimum temperature for the above reaction is 500°C. In the absence of catalyst, the equilibrium is reached in 2 hours at 500°C when 80% reaction is complete. When a catalyst is used at 500°C, the rate is increased 4 times, so the equilibrium is reached in 1/2 hour. This makes the process economical. Hence finely divided iron is used as a catalyst in the manufacture of ammonia. A small quantity of Al_20_3, (3%) and K_2O (1%) or Mo is added to the catalyst and they increase the percentage conversion of ammonia.

A catalyst does not shift the equilibrium to the left or right and hence does not change the magnitude of equilibrium constant. The catalyst only helps the equilibrium to establish in a shorter time.

The favorable conditions for the better yield of ammonia are

Temperature - 500°C

Pressure - 200 to 300 atm

Catalyst - Finely divided iron

Proportion of gases - N, to 1_2-13

Uses of Ammonia

(1) Agricultural industries are the major users of ammonia. Ammonia is a very valuable source of nitrogen that is essential for plant growth.

2) Ammonia is used in the production of liquid fertilizer solutions which consists of ammonia, ammonium nitrate, urea and aqua ammonia. It is also used by the Fertilizer industry to produce ammonium and nitrate salts.

3) Ammonia and urea are used as a source of protein in livestock feeds for ram animals such as cattle, sheep and goats. Ammonia can also be used as an anti-fungal agent on certain fruits and as preservative.

4) Dissociated ammonia is used in such metal treating operations as carbonitriding, bright annealing, sintering, sodium hydride descaling atomic hydrogen welding and other applications where protective atmospheres a required.

5) Ammonia is used in the manufacture of nitric acid; certain alkalies such as soda a dyes, pharmaceuticals such as sulfa drugs, vitamins and cosmetics, synthetic textile fiber such as nylon, polyurethanes.

6) The petroleum industry utilizes ammonia in neutralizing the acid constituents of crude oil and for protection of equipment from corrosion. Ammonia is used in the mining industry for extraction of metals such as copper, nickel and molybdenum from their or

References: According to the new revised syllabus of Savitribai Phule Pune University from June 2021, Text book of Industrial chemistry for T.Y. B.Sc. course (CH- 505), Sem-V Manali Publication, Nirali Publication and google images