

Ammonia Synthesis from Haber - Bosch Process by using Le Chatelier's Principal

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Abstract— Ammonia production is a high energy and capital-intensive industry as it obliges high temperature (410-510°C) and also high pressure (160-280 bar) for its daily processes. Two moles of ammonia are obtained by reacting one mole of nitrogen and three moles of hydrogen gases in the existence of conventional catalyst which is magnetite (Fe₃O₄). The process to produce ammonia is known as Haber-Bosch process which was developed and patented by Fritz Haber and Carl Bosch in 1916. Since then more work on ammonia production was carried out with the goal to achieve higher ammonia yield.

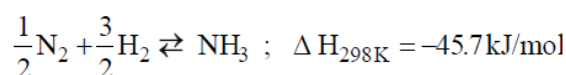
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I. INTRODUCTION

Fixed nitrogen from the air is the major ingredient of fertilizers which makes intensive food production possible. During the development of inexpensive nitrogen fixation processes, many principles of chemical and high-pressure processes were clarified and the field of chemical engineering emerged. Before synthetic nitrogen fixation, wastes and manures of various types or their decomposition products, and ammonium sulfate, which is a by-product from the coking of coal, were the primary sources of agricultural nitrogen. Chilean saltpeter, saltpeter from human and animal urine, and later ammonia recovered from coke manufacture were some of the important sources of fixed nitrogen. During the first decade of the twentieth century, the worldwide demand for nitrogen-based fertilizers far exceeded the existent supply. The largest source of the chemicals necessary for fertilizer production was found in a huge guano deposit that was 220 miles in length and five feet thick, located along the coast of Chile. Scientists had long desired to solve the problem of the world's dependence on this fast disappearing natural source of ammonia and nitrogenous compounds. Priestly and Cavendish passed electric sparks through air and produced nitrates by dissolving the oxides of nitrogen thus formed in alkalis. Commercial development of this process had proved elusive, for much electrical energy was consumed at low efficiency. Nitrogen had been fixed as calcium cyanamide, but the process was too expensive except for producing chemicals requiring the cyanamide configuration. Other processes, such as thermal processing to mixed oxides of nitrogen (NO_x), cyanide formation, aluminum nitride formation and decomposition to ammonia, etc., showed little commercial promise although they were technically possible. It was Fritz Haber, along with Carl Bosch, who finally solved this problem. Haber invented a large-scale catalytic synthesis of ammonia from elemental hydrogen and nitrogen gas, reactants which are abundant and inexpensive. By using high temperature (around 500°C), high pressure (approximately 150-200 ATM), and an iron catalyst, Haber could force relatively unreactive gaseous nitrogen and hydrogen to combine into ammonia. This furnished the essential precursor for many important substances, particularly fertilizers and

explosives used in mining and warfare. Bosch, with his technical ingenuity, developed suitable high-pressure equipment and production methods for large-scale production of ammonia. The collaborative efforts of Haber and Bosch made the commercial high-pressure synthesis of ammonia possible by 1913. The first commercial plant with a capacity of 33 tons/day was set up by the German chemical giant BASF (Badische Anilin- und Soda-Fabrik) in Oppau, Germany. This energy-intensive process has undergone considerable modification in recent years, resulting in prices which have not escalated as rapidly as energy prices in general. Today, synthetic ammonia produced from reaction between nitrogen and hydrogen is the base from which virtually all nitrogen-containing products are derived. The worldwide production of ammonia exceeds 150 million tonnes and is the sixth largest chemical produced (Chemical and Engineering News, 1996).

Ammonia synthesis from nitrogen and hydrogen is a reversible reaction and can be described by the overall reaction – (1).



And the equilibrium constant for the reaction is defined as

$$K_{eq} = \frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}}$$

The formation of ammonia is an exothermic reaction with considerable release of heat. The reaction is a reversible reaction, that is, it can proceed both in forward direction (ammonia synthesis)

II. MATERIALS & METHODS

A. Materials

Raw material requirement consists of a source of hydrogen, the nitrogen is obtained from air, and the feed stock supplies the hydrogen. The production of ammonia depends upon cost and operability of available raw material for hydrogen. Different raw materials for hydrogen can be-

Wood	Liquid petroleum gas
Coal	Naphtha
Natural gas	Refinery gas
Electrolysis of water	Fuel oil
Coke oven gas	Crude oil

B. Method

The principal manufacturing methods that are used for synthetic ammonia production are steam water gas process, the steam hydrocarbon process, the coke oven gas process & electrolysis of water.

Much research work is still diverted to find cheaper manufacturing methods. Many new plants use ethanol amine to remove carbon dioxide from gas streams instead of high pressure water.

Nitrogen required for synthesis gas is obtained usual from an air liquefaction plant. In water gas and natural gas process, nitrogen is obtained in same manufacturing process as hydrogen. Air is added in secondary reforms of natural gas process and reacts with carbon monoxide to furnish carbon dioxide and nitrogen.

Le Chatelier's Principle

- In 1884, the French Chemist Henri Le Chatelier suggested that equilibrium systems tend to compensate for the effects of perturbing influences. When a system at equilibrium is disturbed, the equilibrium position will shift in the direction which tends to minimize, or counteract, the effect of the disturbance. For a reversible chemical reaction, Chatelier's principle has several important implications as given below: If the concentration of a reactant is increased, the equilibrium position shifts to use up the added reactants by producing more products.
- For gaseous reactions, gas pressure is related to the number of gas particles in the system; more gas particles means more gas pressure. Consider a reaction which is accompanied by decrease in number of moles, such as, ammonia synthesis. Increasing the pressure on this equilibrium system will result in the equilibrium position shifting to reduce the pressure, that is, to the side that has the least number of gas particles.
- In an endothermic reaction, energy can be considered as a reactant of the reaction while in an exothermic reaction, energy can be considered as a product of the reaction. Consider an exothermic reaction which is accompanied by release of heat, such as ammonia synthesis. Reducing the temperature of this equilibrium system (removing heat) will result in the equilibrium position shifting to increase the temperature (producing more heat), that is, to shift the equilibrium position to the right

III. RESULTS

A. Effect of Temperature on Equilibrium

Ammonia synthesis according to equation is an equilibrium reaction that is favored by low temperature and high pressure. Equilibrium conditions are only a part of the picture, that is, thermodynamics does not give us any idea about the rate of the reaction. The reaction does not proceed at ambient temperature because nitrogen requires a lot of energy to dissociate. In the gas phase this dissociation occurs only at around 3000°C. Even the hydrogen molecule, which has a weaker molecular bond, only dissociates markedly at temperatures above 1000°C. Thus, the reaction cannot be performed at lower temperature because it needs high energy, and if we increase the temperature to a high level, the reverse reaction predominates! This is clearly a vicious circle. This is where the role of the iron catalyst shows the energy profiles for ammonia synthesis in the absence and presence of the catalyst. The hydrogen and nitrogen molecules lose their translational degrees of freedom when bound to the catalyst surface. This reduces the activation energy dramatically and thus makes the forward reaction go faster. This means we can do away with extremely high temperature conditions. Also, the use of lower temperature reaction conditions means there is limited reverse reaction which is energy saving as well.

This does not mean that we can go down to ambient temperatures! We still need reasonably high temperatures (250–400°C) to dissociate the N₂ and H₂ reactant molecules, even with the use of a catalyst. The use of a catalyst essentially provides a good trade-off. It accelerates the reaction sufficiently so that we can obtain ammonia at conditions where the equilibrium conversion is large enough to be useful. The reaction rate depends on the temperature as well as conversion of the reactants. contours of reaction rate in the phase plane of conversion of reactants and temperature for different reaction rate values, namely 0, 1, 4, 7, 10 and 20 kg ammonia/ m³ catalyst/hr. The contour of rate = 0 is the relationship between conversion and temperature at equilibrium. It can be seen that at low conversion, higher temperatures can be maintained to achieve higher reaction rates. However, as the conversions increase, the temperature has to be decreased to overcome the limitations posed by the equilibrium (rate equals zero). The ammonia converters today combine the catalyst section and heat exchanger to achieve desired temperature profiles to strike a balance between higher rates of reaction and constraints posed by the equilibrium considerations.

B. Catalyst and Rate of Reaction

Activation energy of a reaction, E_a , is the minimum amount of energy that reactant molecules must possess in order to form products. In an Energy Profile diagram, the activation energy is the energy difference between the reactants and the peak of the energy profile diagram, which represents the 'transition state' of the reaction. The lower the activation energy, the faster will be the rate of the reaction. Enthalpy change, H , is the amount of energy absorbed or released during the transformation of the reactants to products, and in the energy profile diagram it is depicted as the energy difference between the reactants and products. During an exothermic reaction energy is released, as the products are lower in energy than the reactants (H is negative), while during an endothermic one energy is absorbed (H is positive). Catalysts speed up the rate of reaction by lowering the activation energy without themselves being consumed during the reaction. A catalyst does not alter the net enthalpy change for the reaction and, therefore, does not alter the equilibrium of the reaction, but merely increases the rate of reaction.

C. Current Status of Ammonia Production

The technological improvements in the past 100 years or so have resulted in significant improvement in the yield of ammonia and modern plants usually produce 1200–1800 T/day of ammonia. The plants employ gas velocities of about 11000–22000 m³ per m³ catalyst per hour and typical conversions obtained are in the range of 8–15% depending on the catalyst. The iron-based industrial ammonia synthesis process utilizes, in the majority of cases, a triply promoted catalyst operating at temperatures between 420–750°C and pressures over 280 atm. These severe conditions require enormous energy input. There has been a decrease in the synthesis pressure conditions from ~300 to 80 at, but this has been due to engineering advances in the construction of the plant. The dominance of iron-based catalyst has recently been challenged by promoted ruthenium catalyst deposited on active graphite. Since ruthenium shows a marked

improvement in activity, it has enabled the lowering of ammonia synthesis temperatures, and consequent lowering of the operating pressures. Operation at synthesis pressures as low as 39 atm is thus technically feasible.

D. Haber's Contributions to Ammonia Synthesis Process

By the turn of the 19th century, complete understanding and application of the law of mass action kinetics and chemical equilibrium enabled chemists to investigate the synthesis of ammonia more systematically. From the equilibrium data measured it was obvious that, at normal pressure, the reaction temperature should be kept well below 290°C in order to obtain even a small percentage of ammonia. For this temperature range, however, no catalyst was available. By increasing the pressure to 70 bar the equilibrium conditions improved, but even at this pressure, and an operating temperature of about 600°C, most known catalysts at that time led to a very low ammonia concentration. It was Haber who finally over-came his colleagues' excessive preoccupation with unfavorable equilibrium concentrations. Firstly, he recognized that much higher pressures had to be employed and he constructed a small laboratory apparatus for the continuous production of ammonia. Secondly, and perhaps more importantly, he developed the concept of a recycle process.

Amount of ammonia formed in a single gas pass is much too small to be of interest for the economic production of ammonia. Haber, therefore, recycled his gas over the catalyst after separating the ammonia formed by condensation. The gas lost by conversion was compensated with a fresh gas input and the mixture was recycled under pressure. This process became the basis for the technical manufacture of ammonia. Since then, the same principle has found widespread application for numerous high-pressure reactions in the organic chemistry sector. Haber's recycle idea changed the previously static conception of process engineering in favor of a more dynamic approach. For the first time, reaction kinetics as well as the thermodynamics of the system was being considered. In addition to chemical equilibrium, Haber recognized that reaction rate was a determining factor in this problem. Instead of simple reaction yield, he concentrated on space-time yield, that is, the amount of ammonia obtained per unit volume of the catalyst per unit time. In this manner it became apparent that the real problem was to find a suitable catalyst so that the maximum amount of product is obtained with minimum volume of the catalyst in the shortest time possible, that is, and space-time yield needs to be maximized.

Early in 1909, Haber discovered in finely distributed osmium, a catalyst which yielded 8-9% ammonia at 170 bars and about 600°C. He also established that uranium could be used as a catalyst. Haber constructed a new laboratory plant which could be operated according to his recycle concept. With this equipment.

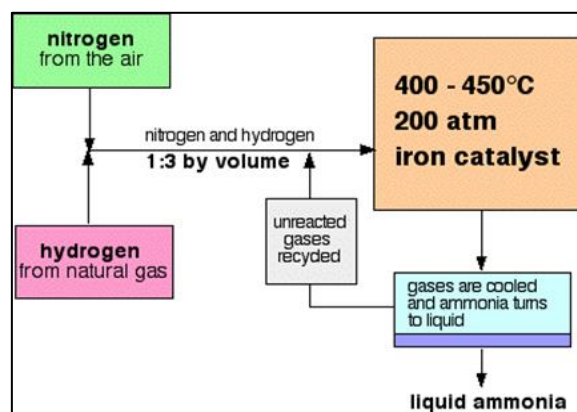


Fig. 1: Block Diagram of Haber Process for Ammonia Synthesis

Haber initially employed were too expensive and unstable to be used in commercial processes. Systematic investigations covering virtually the entire periodic table by Haber, Mittasch and coworkers at BASF for the next two years resulted in a solution to the catalyst problem. Haber, with his path-breaking work on ammonia synthesis in early twentieth century, laid the foundation for the use of catalysts and the application of high pressure technology in chemical industry. Today, this technology finds application in production of many bulk chemicals, urea, methanol, LPDE, oxo-alcohols to name a few. The production of ammonia, with which this technology began, still heads the table in terms of production capacity.

IV. CONCLUSION

As for our discussion we had come to conclusion that from Haber process we can produce the Fertilizer from the ammonia, and it is estimated to be responsible for sustaining one-third of the Earth's population nowadays. Overall Haber process is one of the greatest development in the world and still have a fatal impact on today's industry. The Haber process now produces 454 million tonnes of nitrogen fertilizer per year and it also do a lot of effort on the food supply.

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