

Haber Process for Ammonia Synthesis

Jayant M Modak



Jayant M Modak is Professor and Chairman at the Department of Chemical Engineering, Indian Institute of Science. His research interests include modeling, optimization and control of reactors, engineering analysis of fermentation processes and biohydrometallurgy.

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 saltpetre, saltpetre from human and animal urine, and later ammonia recovered from coke manufacture were some of the important sources of fixed nitrogen [1]. 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 (essentially sea bird droppings) 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.

Keywords

Haber process, ammonia, nitrogen fixation, catalyst.

Synthetic ammonia produced from reaction between nitrogen and hydrogen is the base from which virtually all nitrogen-containing products are derived.

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 30 tons/day was set up by the German chemical giant BASF (Badische Aniline und Soda Fabrik) in Oppau, Germany [2]. 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 130 million tonnes [3] and is the sixth largest chemical produced (*Chemical and Engineering News*, 1996). Ammonia is a major raw material for industry and agriculture as summarized in *Table 1*.

Chemical Reaction and Equilibrium

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

$$K_{\text{eq}} = \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}} \quad (2)$$

Industry	Use
Fertilizer	Production of: ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$; ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$; ammonium nitrate, NH_4NO_3 ; urea, $(\text{NH}_2)_2\text{CO}$
Chemicals	Synthesis of: nitric acid, HNO_3 which is used in making explosives such as TNT (2,4,6-trinitrotoluene), nitroglycerine which is also used as a vasodilator (a substance that dilates blood vessels) and PETN (pentaerythritol nitrate); sodium hydrogen carbonate (sodium bicarbonate), NaHCO_3 ; sodium carbonate, Na_2CO_3 ; hydrogen cyanide (hydrocyanic acid), HCN ; hydrazine, N_2H_4 (used in rocket propulsion systems).
Explosives	Ammonium nitrate, NH_4NO_3
Fibres & plastics	nylon, $-\text{[(CH}_2)_4\text{-CO-NH-(CH}_2)_6\text{-NH-CO]}-$, and other polyamides.
Refrigeration	Used for making ice, large scale refrigeration plants, air-conditioning units in buildings and plants.
Pharmaceuticals	Used in the manufacture of drugs such as sulfonamide which inhibit the growth and multiplication of bacteria that require <i>p</i> -aminobenzoic acid (PABA) for the biosynthesis of folic acids; anti-malarials and vitamins such as the B vitamins nicotinamide (niacinamide) and thiamine.
Pulp & paper	Ammonium hydrogen sulfite, NH_4HSO_3 , enables some hardwoods to be used
Mining & metallurgy	Used in nitriding (bright annealing) steel; used in zinc and nickel extraction.
Cleaning	Ammonia in solution is used as a cleaning agent such as in 'cloudy ammonia'.

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) and backward direction (ammonia decomposition). The reaction is accompanied by decrease in volume because there is a decrease in number of moles of gas from 2 to 1. By Le Chatelier's Principle (see *Box 1*): (i) increasing the pressure causes the equilibrium to shift to the right resulting in a higher yield of ammonia since there is a pressure drop accompanying the transformation (ii) decreasing the temperature also causes the equilibrium position to move to the right again resulting in

Table 1. Uses of ammonia.

Box 1. 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 minimise, or counteract, the effect of the disturbance. For a reversible chemical reaction, Chatelier's principle has several important implications as given below:

- (i) If the concentration of a reactant is increased, the equilibrium position shifts to use up the added reactants by producing more products.
- (ii) 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 (1). 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.
- (iii) 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 (1). 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.

a higher yield of ammonia since the reaction is exothermic (releases heat). *Figures 1A and B* show the effect of temperature and pressure on the equilibrium mole fraction of ammonia. It can be seen that the ammonia mole fraction decreases as the temperature is increased (*Figure 1A*) while it increases as the pressure is increased (*Figure 1B*).

We can conclude then that ammonia synthesis as per equation (1) is an equilibrium reaction that is favoured by low temperature and high pressure. Equilibrium conditions is 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. Since the reaction cannot be moved to the RHS at low temperature, we increase the temperature, which in turn



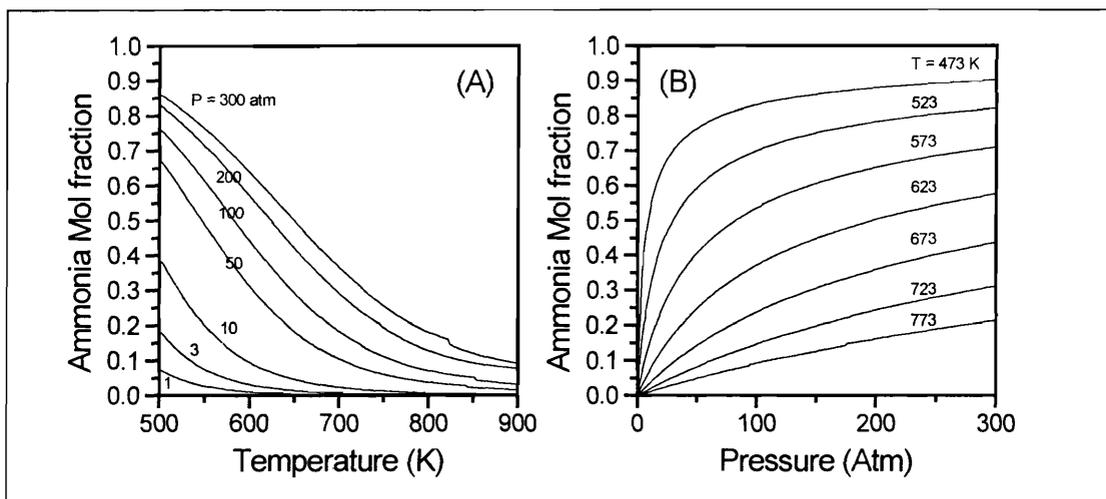
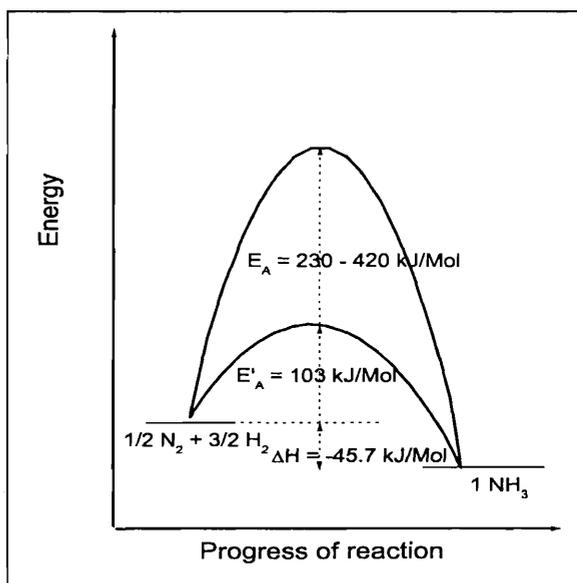


Figure 1. Mole fraction of ammonia at equilibrium from an initial mixture of 1:3 N_2/H_2 gas at (A) at different temperatures for fixed value of pressure (B) at different pressures at fixed value of temperature.

unfortunately drives the reverse reaction! This is clearly a vicious circle. This is where the role of the iron catalyst comes in. *Figure 2* 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 N_2 and H_2 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

Figure 2. Effect of catalyst on the activation energy of the ammonia synthesis.



Box 2. Catalyst and Rate of Reaction

Activation energy of a reaction, E_a , is the minimum amount of energy reactant molecules must possess in order to form products. On 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. (Figure 2). The lower the activation energy, the faster will be the rate of the reaction. enthalpy change, ΔH , is the amount of energy absorbed or released during the transformation of the reactants to products, and on 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 (ΔH is negative), while during an endothermic one energy is absorbed (ΔH 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.

the equilibrium conversion is large enough to be useful. The reaction rate depends on the temperature as well as conversion of the reactants. Figure 3 shows 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

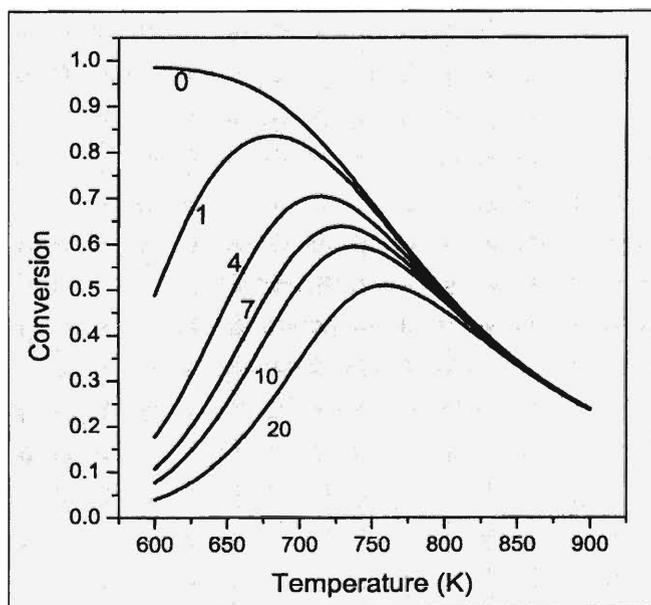


Figure 3. Contours of constant reaction rate (Kg/m³ catalyst/hr) in the conversion-temperature phase plane [4].

Box 3. Current Status of Ammonia Production

The technological improvements in the past 90 years or so has resulted in significant improvement in the yield of ammonia and modern plants usually produce 1000-1500 T/day of ammonia. The plants employ gas velocities of about 10000-20000 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 utilises, in the majority of cases, a triply promoted catalyst operating at temperatures between 400-700°C and pressures over 300 atm. These severe conditions require enormous energy input. There has been a decrease in the synthesis pressure conditions from ~300 to 80 atm, 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 [5] 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 40 atms is thus technically feasible.

conversions increase, the temperature has to be decreased to overcome the limitations posed by the equilibrium (rate equals zero). The ammonia converters today (see *Box 3*) 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.

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 equilibria 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 300°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 75 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 overcame his colleagues' excessive preoccupation with unfavorable equilibrium concentrations. Firstly, he recognized that much higher pressures had to be employed and he constructed a small labora-

Haber recognized that much higher pressures had to be employed and he constructed a small laboratory apparatus for the continuous production of ammonia.

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tory apparatus for the continuous production of ammonia [6]. Secondly, and perhaps more importantly, he developed the concept of a recycle process.

The 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 were 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 (*Figure 3*). 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, space time yield needs to be maximized.

Early in 1909, Haber discovered in finely distributed osmium, a catalyst which yielded 8% ammonia at 175 bar and about 600°C [6]. 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 (*Figure 4*). With this equipment, he demonstrated the production of 80 g of ammonia/hr in July 1909. The catalysts which 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 next two years resulted in solution to the catalyst problem. Iron with a few percent of alumina and a pinch of potassium

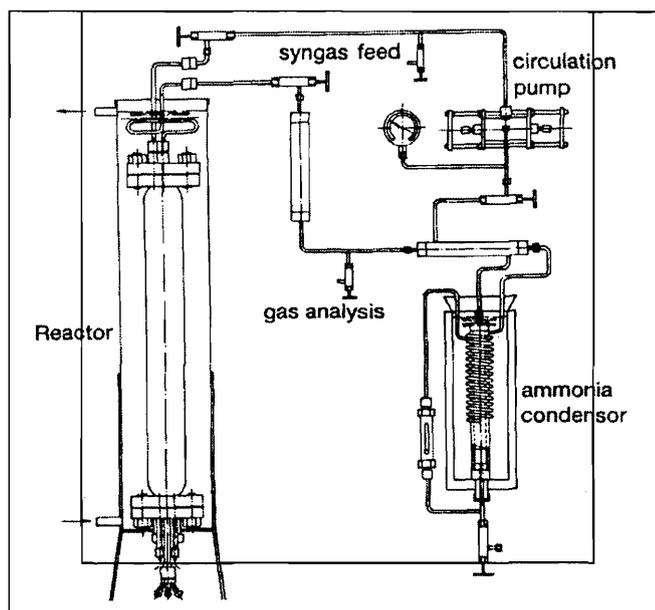


Figure 4. Schematic of recycle apparatus used by Haber for ammonia synthesis [2].

yielded a catalyst with acceptable reproducibility, performance and lifetime. Haber, with his path-breaking work on ammonia synthesis in early twentieth century, led 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.

Suggested Reading

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Address for Correspondence

Jayant M Modak
 Department of Chemical
 Engineering
 Indian Institute of Science
 Bangalore 560012, India.
 Email:
 modak@chemeng.iisc.ernet.in