10.9: The Haber-Bosch Reaction Can Be Surface Catalyzed

10.9.1: The Haber-Bosch Process for Synthesis of Ammonia

An example of an industrial catalytic process is the Haber-Bosch process. Karl Bosch (1874–1940) was a German chemical engineer who was responsible for designing the process that took advantage of Fritz Haber's discoveries regarding the N_2 + H_2/NH_3 equilibrium to make ammonia synthesis via this route cost-effective. He received the Nobel Prize in Chemistry in 1931 for his work. The industrial process is called either the Haber process or the Haber-Bosch process. used to synthesize ammonia via the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

with

$$\Delta H_{rxn} = -91.8\ kJ/mol$$

Because the reaction converts 4 mol of gaseous reactants to only 2 mol of gaseous product, Le Chatelier's principle predicts that the formation of NH_3 will be favored when the pressure is increased. The reaction is exothermic, however (ΔH_{rxn} = −91.8 kJ/mol), so the equilibrium constant decreases with increasing temperature, which causes an equilibrium mixture to contain only relatively small amounts of ammonia at high temperatures ($10.9.1$). Taken together, these considerations suggest that the maximum yield of NH_3 will be obtained if the reaction is carried out at as low a temperature and as high a pressure as possible. Unfortunately, at temperatures less than approximately 300°C, where the equilibrium yield of ammonia would be relatively high, the reaction is too *slow* to be of any commercial use. The industrial process, therefore, uses a mixed oxide (Fe_2O_3/K_2O) catalyst that enables the reaction to proceed at a significant rate at temperatures of 400°C–530°C, where the formation of ammonia is less unfavorable than at higher temperatures.

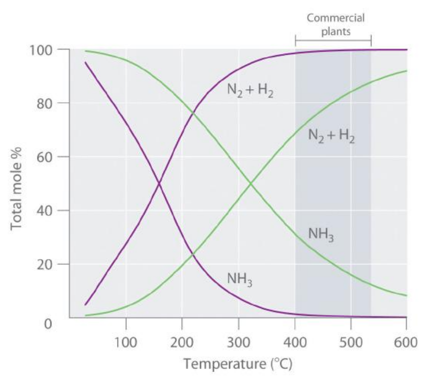

Figure $10.9.1$ Effect of Temperature and Pressure on the Equilibrium Composition of Two Systems that Originally Contained a 3:1 Mixture of Hydrogen and Nitrogen: At all temperatures, the total pressure in the systems was initially either 4 atm (purple curves) or 200 atm (green curves). Note the dramatic decrease in the proportion of NH_3 at equilibrium at higher temperatures in both cases, as well as the large increase in the proportion of NH_3 at equilibrium at any temperature for the system at higher pressure (green) versus lower pressure (purple). Commercial plants that use the Haber-Bosch process to synthesize ammonia on an industrial scale operate at temperatures of 400°C–530°C (indicated by the darker gray band) and total pressures of 130–330 atm.

Because of the low value of the equilibrium constant at high temperatures (e.g., K = 0.039 at 800 K), there is no way to produce an equilibrium mixture that contains large proportions of ammonia at high temperatures. We can, however, control the temperature and the pressure while using a catalyst to convert a fraction of the N_2 and H_2 in the reaction mixture to NH_3, as is done in the Haber-Bosch process. This process also makes use of the fact that the product—ammonia—is less volatile than the reactants. Because NH_3 is a liquid at room temperature at pressures greater than 10 atm, cooling the reaction mixture causes NH_3 to condense from the vapor as liquid ammonia, which is easily separated from unreacted N_2 and H_2. The unreacted gases are recycled until the complete conversion of hydrogen and nitrogen to ammonia is eventually achieved. Figure $10.9.2$ is a simplified layout of a Haber-Bosch process plant.

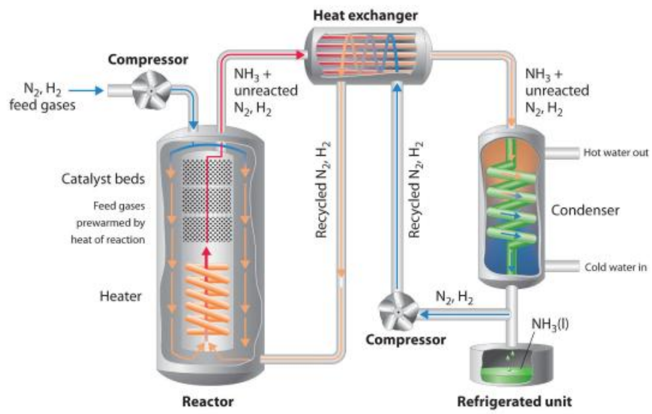

Figure 10.9.2 A Schematic Diagram of an Industrial Plant for the Production of Ammonia via the Haber-Bosch Process: A 3:1 mixture of gaseous H_2 and N_2 is compressed to 130–330 atm, heated to 400°C–530°C, and passed over an Fe_2O_3/K_2O catalyst, which results in partial conversion to gaseous NH_3. The resulting mixture of gaseous NH_3, H_2, and N_2 is passed through a heat exchanger, which uses the hot gases to prewarm recycled N_2 and H_2, and a condenser to cool the NH_3, giving a liquid that is readily separated from unreacted N_2 and H_2. (Although the normal boiling point of NH_3 is −33°C, the boiling point increases rapidly with increasing pressure, to 20°C at 8.5 atm and 126°C at 100 atm.) The unreacted N_2 and H_2 are recycled to form more NH_3.

We can write the seven reactions that are involved in the process where ad indicates that the molecule or atom is adsorbed on the catalyst

$$H_2(g) + 2S(s) \rightleftharpoons 2H(ad) \tag{10.9.1}$$

$$N_2(g) \rightleftharpoons N_2(ad) \tag{10.9.2}$$

$$N_2(ad) + 2S(s) \rightleftharpoons 2N(ad) \tag{10.9.3}$$

$$H(ad) + N(ad) \rightleftharpoons NH(ad) \tag{10.9.4}$$

$$NH(ad) + H(ad) \rightleftharpoons NH_2(ad) \tag{10.9.5}$$

$$NH_2(ad) + H(ad) \rightleftharpoons NH_3(ad) \tag{10.9.6}$$

$$NH_3(ad) \rightleftharpoons NH_3(g) \tag{10.9.7}$$

Reaction 10.9.3 is much the slowest, and therefore the rate determining step. Figure 10.9.3 summarizes the reaction scheme.

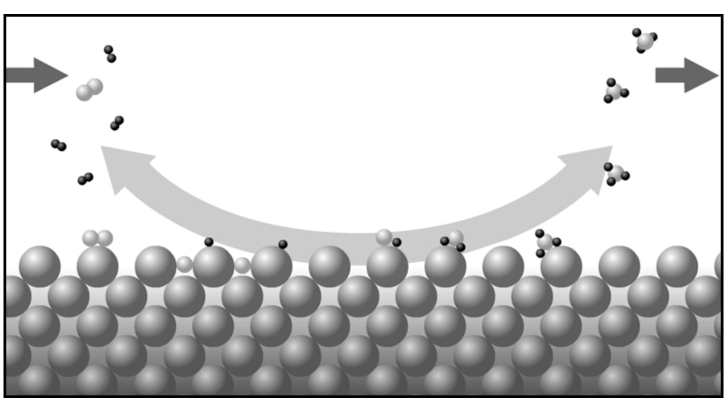

Figure 10.9.3: A representation of the reactions Eqs. 10.9.1 to 10.9.7 with H_2 and N_2 coming in from the left and being adsorbed on the catalyst. The H_2 and N_2 then atomize on the surface of the catalyst, followed by a set of sequential reactions forming NH, NH_2 and finally NH_3 which desorbs from the catalyst as shown on the right

Gerhard Ertl worked out the energetics of the reaction shown in Figure 10.9.4 below shows the amount of energy per mole needed on the catalyst and that which would be needed in the gas phase. Ertl's Nobel Prize speech about his work on the catalytic reactions forming ammonia and other catalytic reactions can be viewed on line.

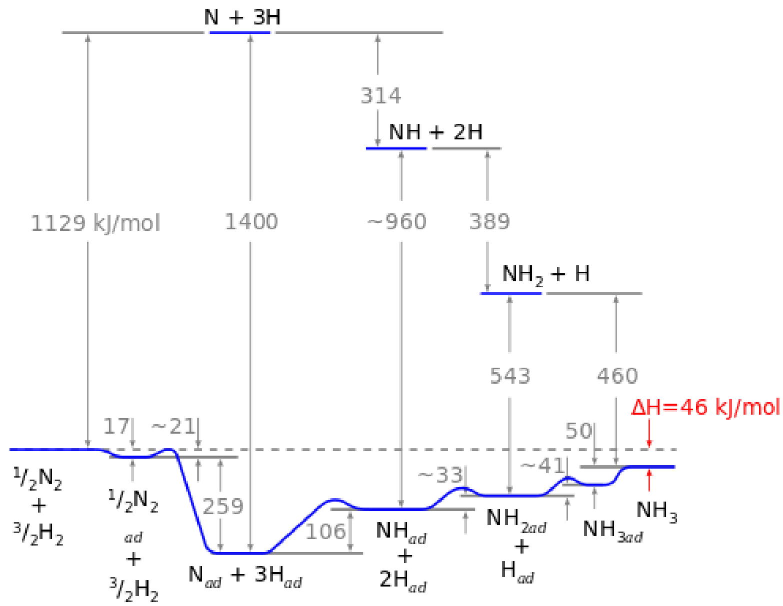

Figure 10.9.4: Ertl's group was able to measure the energy needed for each step of the Bosch-Haber process as opposed to the energy that would be needed in the gas phase.

Further studies of the Fe_2O_3/K_2O catalyst have shown that the rate of the reaction depends on the particular surface on which the reaction is occurring. Figure 10.9.5 shows the reaction rates for the synthesis of ammonia on five different surfaces of the iron.

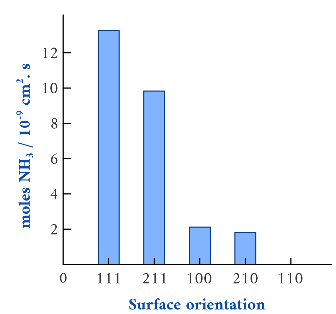

Figure 10.9.5: The rates of ammonia production for various iron catalyst surfaces. (CC BY-NC; Ümit Kaya via LibreTexts)

10.9.1.1: Contributors

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