15.6: Controlling the Products of Reactions

> ◑ **Learning Objectives**
>
> - To understand different ways to control the products of a reaction.

Whether in the synthetic laboratory or in industrial settings, one of the primary goals of modern chemistry is to control the identity and quantity of the products of chemical reactions. For example, a process aimed at synthesizing ammonia is designed to maximize the amount of ammonia produced using a given amount of energy. Alternatively, other processes may be designed to minimize the creation of undesired products, such as pollutants emitted from an internal combustion engine. To achieve these goals, chemists must consider the competing effects of the reaction conditions that they can control.

One way to obtain a high yield of a desired compound is to make the reaction rate of the desired reaction much faster than the reaction rates of any other possible reactions that might occur in the system. Altering reaction conditions to control reaction rates, thereby obtaining a single product or set of products, is called kinetic controlThe altering of reaction conditions to control reaction rates, thereby obtaining a single desired product or set of products. A second approach, called thermodynamic control. The altering of reaction conditions so that a single desired product or set of products is present in significant quantities at equilibrium., consists of adjusting conditions so that at equilibrium only the desired products are present in significant quantities.

An example of thermodynamic control 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:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{15.6.1a}$$

with

$$\Delta H_{rxn} = -91.8 \ kJ/mol \tag{15.6.1b}$$

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 (Figure 15.6.1). 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.
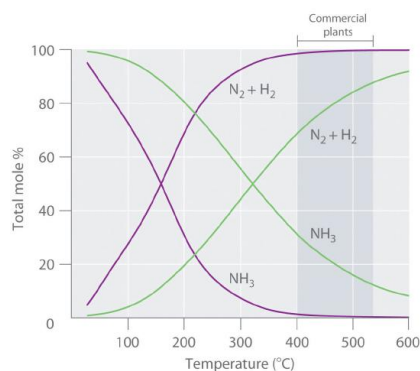
Figure 15.6.1 Effect of Temperature and Pressure on the Equilibrium Composition of Two Systems that Originally Contained a 3:1 Mixture of Hydrogen and Nitrogen At all temperatures, the total pressure in the systems was initially either 4 atm (purple curves) or 200 atm (green curves). Note the dramatic *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 complete conversion of hydrogen and nitrogen to ammonia is eventually achieved. Figure 15.6.2 is a simplified layout of a Haber-Bosch process plant.
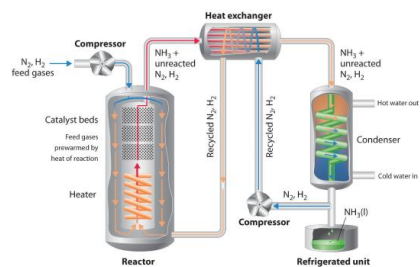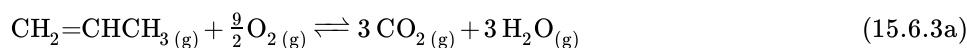

Figure 15.6.2 A Schematic Diagram of an Industrial Plant for the Production of Ammonia via the Haber-Bosch Process A 3:1 mixture of gaseous H_2 and N_2 is compressed to 130–330 atm, heated to 400°C–530°C, and passed over an Fe_2O_3/K_2O catalyst, which results in partial conversion to gaseous NH_3. The 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.

The Sohio acrylonitrile process, in which propene and ammonia react with oxygen to form acrylonitrile, is an example of a kinetically controlled reaction:

$$CH_2{=}CHCH_{3\,(g)} + NH_{3\,(g)} + \tfrac{3}{2}O_{2\,(g)} \rightleftharpoons CH_2{=}CHC\equiv N_{(g)} + 3\,H_2O_{(g)} \qquad (15.6.2)$$
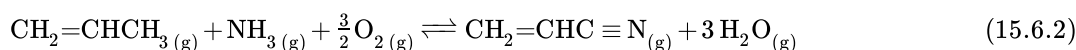
Like most oxidation reactions of organic compounds, this reaction is highly exothermic ($\Delta H° = -519$ kJ/mol) and has a very large equilibrium constant ($K = 1.2 \times 10^{94}$). Nonetheless, the reaction shown in Equation 15.43 is not the reaction a chemist would expect to occur when propene or ammonia is heated in the presence of oxygen. Competing combustion reactions that produce CO_2 and N_2 from the reactants, such as those shown in Equation 15.6.3 and Equation 15.6.4, are even more exothermic and have even larger equilibrium constants, thereby reducing the yield of the desired product, acrylonitrile:
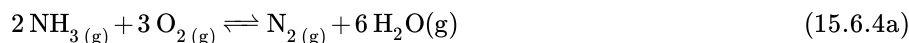
$$CH_2{=}CHCH_{3\,(g)} + \tfrac{9}{2}O_{2\,(g)} \rightleftharpoons 3\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad (15.6.3a)$$

with

$$\Delta H° = -1926.1 \ \ kJ/mol \qquad (15.6.3b)$$

and

$$K = 4.5 \times 10^{338} \qquad (15.6.3\text{c})$$

$$2\,NH_{3\,(g)} + 3\,O_{2\,(g)} \rightleftharpoons N_{2\,(g)} + 6\,H_2O(g) \qquad (15.6.4\text{a})$$

with

$$\Delta H^{\circ} = -1359.2\ kJ/mol, \qquad (15.6.4\text{c})$$

and

$$K = 4.4 \times 10^{234} \qquad (15.6.4\text{c})$$

propene   acrylonitrile
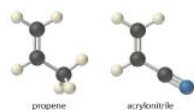
In fact, the formation of acrylonitrile in Equation 15.6.2. is accompanied by the release of approximately 760 kJ/mol of heat due to partial combustion of propene during the reaction.

The Sohio process uses a catalyst that selectively accelerates the rate of formation of acrylonitrile without significantly affecting the reaction rates of competing combustion reactions. Consequently, acrylonitrile is formed more rapidly than CO_2 and N_2 under the optimized reaction conditions (approximately 1.5 atm and 450°C). The reaction mixture is rapidly cooled to prevent further oxidation or combustion of acrylonitrile, which is then washed out of the vapor with a liquid water spray. Thus controlling the kinetics of the reaction causes the desired product to be formed under conditions where equilibrium is not established. In industry, this reaction is carried out on an enormous scale. Acrylonitrile is the building block of the polymer called *polyacrylonitrile*, found in all the products referred to collectively as *acrylics*, whose wide range of uses includes the synthesis of fibers woven into clothing and carpets.

Note the Pattern

Controlling the amount of product formed requires that both thermodynamic and kinetic factors be considered.

Example 15.6.1

Recall that methanation is the reaction of hydrogen with carbon monoxide to form methane and water:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad (15.6.1)$$

This reaction is the reverse of the steam reforming of methane described in Example 14. The reaction is exothermic ($\Delta H^{\circ} = -206$ kJ/mol), with an equilibrium constant at room temperature of $K_p = 7.6 \times 10^{24}$. Unfortunately, however, CO and H_2 do not react at an appreciable rate at room temperature. What conditions would you select to maximize the amount of methane formed per unit time by this reaction?

Given: balanced chemical equation and values of ΔH° and K

Asked for: conditions to maximize yield of product

Strategy:

Consider the effect of changes in temperature and pressure and the addition of an effective catalyst on the reaction rate and equilibrium of the reaction. Determine which combination of reaction conditions will result in the maximum production of methane.

Solution:

The products are highly favored at equilibrium, but the rate at which equilibrium is reached is too slow to be useful. You learned in Chapter 14 that the reaction rate can often be increased dramatically by increasing the temperature of the reactants. Unfortunately, however, because the reaction is quite exothermic, an increase in temperature will shift the equilibrium to the left, causing more reactants to form and relieving the stress on the system by absorbing the added heat. If we increase the temperature too much, the equilibrium will no longer favor methane formation. (In fact, the equilibrium constant for this reaction is very temperature sensitive, decreasing to only 1.9×10^{-3} at 1000°C.) To increase the reaction rate, we can try to find a catalyst that will operate at

lower temperatures where equilibrium favors the formation of products. Higher pressures will also favor the formation of products because 4 mol of gaseous reactant are converted to only 2 mol of gaseous product. Very high pressures should not be needed, however, because the equilibrium constant favors the formation of products. Thus optimal conditions for the reaction include carrying it out at temperatures greater than room temperature (but not too high), adding a catalyst, and using pressures greater than atmospheric pressure.

Industrially, catalytic methanation is typically carried out at pressures of 1–100 atm and temperatures of 250°C–450°C in the presence of a nickel catalyst. (At 425°C°C, K_p is 3.7 × 10^3, so the formation of products is still favored.) The synthesis of methane can also be favored by removing either H_2O or CH_4 from the reaction mixture by condensation as they form.

Exercise

As you learned in Example 10, the water–gas shift reaction is as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \qquad (15.6.2)$$

K_p = 0.106 and ΔH = 41.2 kJ/mol at 700 K. What reaction conditions would you use to maximize the yield of carbon monoxide?

Answer: high temperatures to increase the reaction rate and favor product formation, a catalyst to increase the reaction rate, and atmospheric pressure because the equilibrium will not be greatly affected by pressure

Summary

Changing conditions to affect the reaction rates to obtain a single product is called **kinetic control** of the system. In contrast, **thermodynamic control** is adjusting the conditions to ensure that only the desired product or products are present in significant concentrations at equilibrium.

Key Takeaway

- Both kinetic and thermodynamic factors can be used to control reaction products.

Conceptual Problems

1. A reaction mixture will produce either product A or B depending on the reaction pathway. In the absence of a catalyst, product A is formed; in the presence of a catalyst, product B is formed. What conclusions can you draw about the forward and reverse rates of the reaction that produces A versus the reaction that produces B in (a) the absence of a catalyst and (b) the presence of a catalyst?

2. Describe how you would design an experiment to determine the equilibrium constant for the synthesis of ammonia:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
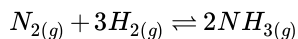
   The forward reaction is exothermic ($\Delta H°$ = −91.8 kJ). What effect would an increase in temperature have on the equilibrium constant?

3. What effect does a catalyst have on each of the following?

   1. the equilibrium position of a reaction
   2. the rate at which equilibrium is reached
   3. the equilibrium constant?

4. How can the ratio Q/K be used to determine in which direction a reaction will proceed to reach equilibrium?

5. Industrial reactions are frequently run under conditions in which competing reactions can occur. Explain how a catalyst can be used to achieve reaction selectivity. Does the ratio Q/K for the selected reaction change in the presence of a catalyst?

Numerical Problems

1. The oxidation of acetylene via 2C$_2$H$_2$ (g) + 5O$_2$(g) $\rightleftharpoons$ 4 CO$_2$(g) + 2 H$_2$O(l) has $\Delta H°$ = −2600 kJ. What strategy would you use with regard to temperature, volume, and pressure to maximize the yield of product?

2. The oxidation of carbon monoxide via CO(g) + 1/2 O$_2$(g) $\rightleftharpoons$ CO$_2$(g) has $\Delta H°$ = −283 kJ. If you were interested in maximizing the yield of CO$_2$, what general conditions would you select with regard to temperature, pressure, and volume?

3. You are interested in maximizing the product yield of the system $2SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ $K = 280$ and $\Delta H° = -158$ kJ. What general conditions would you select with regard to temperature, pressure, and volume? If SO_2 has an initial concentration of 0.200 M and the amount of O_2 is stoichiometric, what amount of SO_3 is produced at equilibrium?

Answer

1. Use low temperature and high pressure (small volume).

2.
3.

Contributors

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