

4.4: Shifting Equilibria - Le Chatelier's Principle

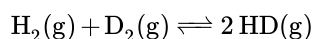
Learning Objectives

- Predict whether reactants or products are favored in a given reaction based on the equilibrium constant
- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

Reversible reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). In this section, you will learn to predict whether reactants or products are favored at equilibrium, and how to predict the direction a reaction will proceed when its equilibrium is disturbed.

4.4.1: Relating K to the Reaction Mixture Composition

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:



The equilibrium constant expression for this reaction is

$$K = \frac{[\text{HD}]^2}{[\text{H}_2][\text{D}_2]}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2 , D_2 , and HD contains significant concentrations of both product and reactants.

Figure 4.4.1 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants \rightleftharpoons products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations ??? and ???), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

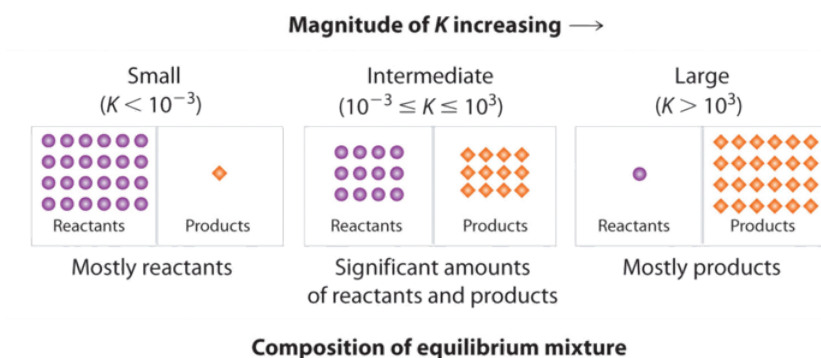


Figure 4.4.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K , the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

✓ Example 4.4.1

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ $K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$ $K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$ $K_{(298K)} = 5.9 \times 10^{55}$

Strategy:

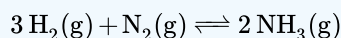
Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

- a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
- b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
- c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

? Exercise 4.4.1

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:



Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
 - $K_{177^\circ C} = 2.6 \times 10^3$, and
 - $K_{327^\circ C} = 4.1$.
- a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
 - b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C



Video which Discusses What Does K Tell us About a Reaction?: https://youtu.be/39-456o3O_4

4.4.2: Predicting the Direction of a Reversible Reaction

We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K . If a system at equilibrium is subjected to a perturbation or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K . To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K .

This process is described by Le Chatelier's principle: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q ; the reaction will shift to re-establish $Q = K$.

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure 4.4.1 is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $\text{Fe}(\text{SCN})^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.

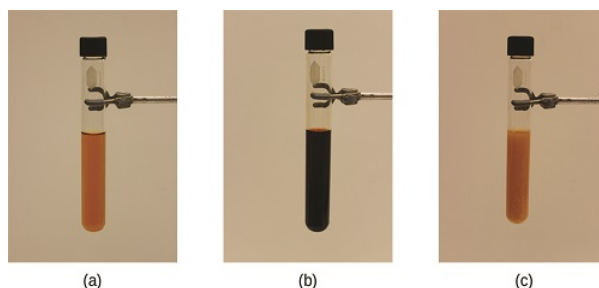


Figure 4.4.1: (a) The test tube contains 0.1 M Fe^{3+} . (b) Thiocyanate ion has been added to solution in (a), forming the red $\text{Fe}(\text{SCN})^{2+}$ ion. $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{SCN})^{2+}(\text{aq})$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN^- as the white solid AgSCN . $\text{Ag}^+(\text{aq}) + \text{SCN}^-(\text{aq}) \rightleftharpoons \text{AgSCN}(\text{s})$. The decrease in the SCN^- concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $\text{Fe}(\text{SCN})^{2+}$. (credit: modification of work by Mark Ott).

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:



$$K_c = 50.0 \text{ at } 400^\circ \text{C} \quad (4.4.2)$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400°C with $[\text{H}_2] = [\text{I}_2] = 0.221 \text{ M}$ and $[\text{HI}] = 1.563 \text{ M}$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[\text{H}_2] = 0.442 \text{ M}$), the reaction will shift so that a new equilibrium is reached, at which

- $[\text{H}_2] = 0.374 \text{ M}$,
- $[\text{I}_2] = 0.153 \text{ M}$, and
- $[\text{HI}] = 1.692 \text{ M}$.

This gives:

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \quad (4.4.3)$$

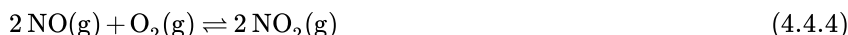
We have stressed this system by introducing additional H_2 . The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2 , reducing the amount of uncombined I_2 , and forming additional HI .

4.4.3: Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO , O_2 , and NO_2 are at equilibrium:



The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2 , which tends to restore the pressure.

Now consider this reaction:

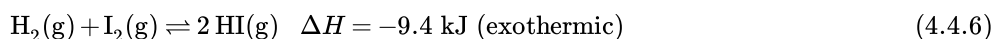


Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

4.4.4: Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.



Because this reaction is exothermic, we can write it with heat as a product.



Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI . Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357°C to 50.0 at 400°C .

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction



The positive ΔH value tells us that the reaction is endothermic and could be written



At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

4.4.5: Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation



A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

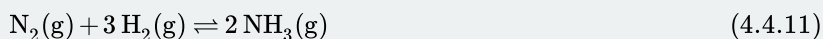
Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures.



The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.



Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, "During peace time a scientist belongs to the World, but during war time he belongs to his country."¹ Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

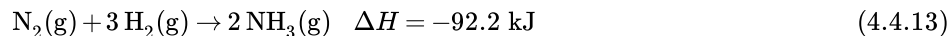
It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2 , H_2 , and NH_3 are at equilibrium or are coming to equilibrium.



The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2 , H_2 , and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2 , no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:



Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures.

Summary

The magnitude of an equilibrium constant will allow you to predict whether the reactants or products will be in excess when the system is at equilibrium. Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Table 4.4.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. Herrlich, P. "The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?" *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

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