Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier’s principle

As we saw in the previous section, 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 \( K \). 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 \( Q \leq K \)) or the reactants (if \( Q \geq K \)) until \( Q \) returns to the same value as \( K \). This process is described by Le Chatelier’s principle.

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 \( Q = K \).

Predicting the Direction of a Reversible Reaction

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 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 Fe(SCN)²⁺ should decrease, increasing the concentration of SCN⁻ part way back to its original concentration, and increasing the concentration of Fe³⁺ above its initial equilibrium concentration.
Figure (PageIndex{1}): (a) The test tube contains 0.1 M \(\ce{Fe^{3+}}\). (b) Thiocyanate ion has been added to solution in (a), forming the red \(\ce{Fe(SCN)^{2+}}\) ion. 
\[
\ce{Fe^{3+}(aq) + SCN^-(aq) &\rightleftharpoons Fe(SCN)^{2+}(aq)}
\]
(c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN\(^-\) as the white solid \(\ce{AgSCN}\). 
\[
\ce{Ag^+(aq) + SCN^-(aq) &\rightleftharpoons AgSCN(s)}
\]
The decrease in the SCN\(^-\) concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the \(\ce{Fe(SCN)^{2+}}\). (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:
\[
\ce{H_2(g) + I_2(g) &\rightleftharpoons 2HI(g)}
\]
\[K_c = 50.0 \text{ at } 400°C\]
The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with \(\ce{[H_2]} = \ce{[I_2]} = 0.221 \; \text{M}\) and \(\ce{[HI]} = 1.563 \; \text{M}\) is at equilibrium; for this mixture, \(\ce{Q_c = K_c = 50.0}\).
If \(\ce{H_2}\) is introduced into the system so quickly that its concentration doubles before it begins to react (new \(\ce{[H_2]} = 0.442 \; \text{M}\)), the reaction will shift so that a new equilibrium is reached, at which
\[
\begin{align*}
\ce{Q_c} &= \dfrac{[\ce{HI}]^2}{\ce{[H_2]} \ce{[I_2]}} \\
&= \dfrac{(1.692)^2}{(0.374)(0.153)} \\
&= 50.0 = K_c
\end{align*}
\]
We have stressed this system by introducing additional \(\ce{H_2}\). The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess \(\ce{H_2}\), reducing the amount of uncombined \(\ce{I_2}\), and forming additional \(\ce{HI}\).

**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 \(\ce{NO}\), \(\ce{O_2}\), and \(\ce{NO_2}\) are at equilibrium:

\[
\ce{2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)} \tag{15.7.3}
\]

The formation of additional amounts of \(\ce{NO_2}\) decreases the total number of molecules in the system because each time two molecules of \(\ce{NO_2}\) form, a total of three molecules of \(\ce{NO}\) and \(\ce{O_2}\) 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 \(\ce{NO_2}\) into \(\ce{NO}\) and \(\ce{O_2}\), which tends to restore the pressure.

Now consider this reaction:

\[
\ce{N_2(g) + O_2(g) \rightleftharpoons 2NO(g)} \tag{15.7.4}
\]

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.

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### 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.

\[
\ce{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)} \quad \Delta H=\text{\textbackslash{}mathrm{−9.4\;kJ\;{(exothermic)}}} \tag{15.7.5}
\]

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

\[
\ce{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)} + \text{heat} \tag{15.7.6}
\]
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 H₂ and I₂ 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 H₂ has increased and the concentrations of H₂ and I₂ 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 \(\ce{N2O4(g)} \rightleftharpoons 2\ce{NO2(g)}\) in this reaction

\[
\ce{N2O4(g) \rightleftharpoons 2NO2(g)}; \Delta H = \text{57.20 kJ}\]

The positive \(\Delta H\) value tells us that the reaction is endothermic and could be written

\[
\ce{heat + \ce{N2O4(g) \rightleftharpoons 2NO2(g)}}
\]

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown \(\ce{NO2}\) 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 \(\ce{N2O4}\) increases, and the concentration of brown \(\ce{NO2}\) decreases, causing the brown color to fade.

The overview of how different disturbances affect the reaction equilibrium properties is tabulated in Table \(\PageIndex{1}\).

<table>
<thead>
<tr>
<th>Disturbance</th>
<th>Observed Change as Equilibrium is Restored</th>
<th>Direction of Shift</th>
<th>Effect on K</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactant added</td>
<td>added reactant is partially consumed</td>
<td>toward products</td>
<td>none</td>
</tr>
<tr>
<td>product added</td>
<td>added product is partially consumed</td>
<td>toward reactants</td>
<td>none</td>
</tr>
<tr>
<td>decrease in volume/</td>
<td>pressure decreases</td>
<td>toward side with</td>
<td>none</td>
</tr>
<tr>
<td>increase in gas pressure</td>
<td></td>
<td>fewer moles of gas</td>
<td></td>
</tr>
<tr>
<td>increase in volume/</td>
<td>pressure increases</td>
<td>toward side with</td>
<td>none</td>
</tr>
<tr>
<td>decrease in gas pressure</td>
<td></td>
<td>fewer moles of gas</td>
<td></td>
</tr>
<tr>
<td>temperature increase</td>
<td>heat is absorbed</td>
<td>toward products</td>
<td>changes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for endothermic,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>toward reactants</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>for exothermic</td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Disturbance</th>
<th>Observed Change as Equilibrium is Restored</th>
<th>Direction of Shift</th>
<th>Effect on K</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature decrease</td>
<td>heat is given off</td>
<td>toward reactants for endothermic, toward products for exothermic</td>
<td>changes</td>
</tr>
</tbody>
</table>

Example \(\PageIndex{1}\)

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

a. \(\ce{2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)}\): the amount of HgO is doubled.

b. \(\ce{NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)}\): the concentration of \(\ce{H_2S}\) is tripled.

c. \(\ce{n-butane(g) \rightleftharpoons isobutane(g)}\): the concentration of isobutane is halved.

**Given**: equilibrium systems and changes

**Asked for**: equilibrium constant expressions and effects of changes

**Strategy**:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

**Solution**:

Because \(\ce{HgO(s)}\) and \(\ce{Hg(l)}\) are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, \(K = [O_2]\). The equilibrium concentration of \(\ce{O_2}\) is a constant and does not depend on the amount of \(\ce{HgO}\) present. Hence adding more \(\ce{HgO}\) will not affect the equilibrium concentration of \(\ce{O_2}\), so no compensatory change is necessary.

\(\ce{NH_4HS}\) does not appear in the equilibrium constant expression because it is a solid. Thus \(K = [\ce{NH_3}][\ce{H_2S}]\), which means that the concentrations of the products are inversely proportional. If adding \(\ce{H_2S}\) triples the \(\ce{H_2S}\) concentration, for example, then the \(\ce{NH_3}\) concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals \(K\).

For this reaction, \(K = \frac{[\text{isobutane}]}{[\text{n-butane}]}\), so halving the concentration of isobutane means that the n-butane concentration must also decrease by about half if the system is to maintain equilibrium.

**Exercise \(\PageIndex{1}\)**

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

a. \(\ce{HBr (g) + NaH (s) \rightleftharpoons NaBr (s) + H_2(g)}\): the concentration of \(\ce{HBr}\) is decreased by a factor of 3.

b. \(\ce{6Li (s) + N_2(g) \rightleftharpoons 2Li3N(s)}\): the amount of \(\ce{Li}\) is tripled.
c. \(\textbf{SO}_2\text{(g)} + \ce{ Cl_2(g) \rightleftharpoons SO_2Cl_2(l)}\): the concentration of \(\ce{Cl_2}\) is doubled.

**Answer a**
\[
\text{\(K = \dfrac{[H_2]}{[HBr]}\): \([H_2]\text{ must decrease by about a factor of 3.}\)}
\]

**Answer b**
\[
\text{\(K = \dfrac{1}{[N_2]}\): solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.}
\]

**Answer c**
\[
\text{\(K = \dfrac{1}{[SO_2][Cl_2]}\): \([SO_2]\) must decrease by about half.}
\]

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**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

\[
\text{\(\ce{N2(g) + 3H2(g) \rightleftharpoons 2NH3(g)}\) \(\text{\ref{15.7.9}}\)}
\]

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. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements (Equation \(\text{\ref{15.7.9}}\)). 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 ($\text{N}_2$) is nutritionally unavailable to a majority of plants due to the tremendous stability of the nitrogen-nitrogen triple bond. Therefore, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation). Legumes achieve this conversion at ambient temperature by exploiting bacteria equipped with suitable enzymes.

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.” 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.

**Summary**

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.
Footnotes


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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