The Learning Objective of this Module is to understand the differences between the information that thermodynamics and kinetics provide about a system.

Because thermodynamics deals with state functions, it can be used to describe the overall properties, behavior, and equilibrium composition of a system. It is not concerned with the particular pathway by which physical or chemical changes occur, however, so it cannot address the rate at which a particular process will occur. Although thermodynamics provides a significant constraint on what can occur during a reaction process, it does not describe the detailed steps of what actually occurs on an atomic or a molecular level.

**Note**

Thermodynamics focuses on the energetics of the products and the reactants, whereas kinetics focuses on the pathway from reactants to products.

Table 18.4 gives the numerical values of the equilibrium constant (K) that correspond to various approximate values of \( \Delta G^\circ \). Note that \( \Delta G^\circ \geq +10 \text{ kJ/mol} \) or \( \Delta G^\circ \leq -10 \text{ kJ/mol} \) ensures that an equilibrium lies essentially all the way to the left or to the right, respectively, under standard conditions, corresponding to a reactant-to-product ratio of approximately 10,000:1 (or vice versa). Only if \( \Delta G^\circ \) is quite small (±10 kJ/mol) are significant amounts of both products and reactants present at equilibrium. Most reactions that we encounter have equilibrium constants substantially greater or less than 1, with the equilibrium strongly favoring either products or reactants. In many cases, we will encounter reactions that are strongly favored by thermodynamics but do not occur at a measurable rate. In contrast, we may encounter reactions that are not thermodynamically favored under standard conditions but nonetheless do occur under certain nonstandard conditions.

<table>
<thead>
<tr>
<th>( \Delta G^\circ ) (kJ/mol)</th>
<th>K</th>
<th>Physical Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>( 3 \times 10^{-88} )</td>
<td>For all intents and purposes, the reaction does not proceed in the forward direction: only reactants are present at equilibrium.</td>
</tr>
<tr>
<td>100</td>
<td>( 3 \times 10^{-18} )</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>( 2 \times 10^{-2} )</td>
<td>Both forward and reverse reactions occur: significant amounts of both products and reactants are present at equilibrium.</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>-10</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>-100</td>
<td>( 3 \times 10^{17} )</td>
<td>For all intents and purposes, the forward reaction proceeds to completion: only products are present at equilibrium.</td>
</tr>
<tr>
<td>-500</td>
<td>( 4 \times 10^{87} )</td>
<td></td>
</tr>
</tbody>
</table>
A typical challenge in industrial processes is a reaction that has a large negative value of $\Delta G^\circ$ and hence a large value of $K$ but that is too slow to be practically useful. In such cases, mixing the reactants results in only a physical mixture, not a chemical reaction. An example is the reaction of carbon tetrachloride with water to produce carbon dioxide and hydrochloric acid, for which $\Delta G^\circ$ is $-232 \text{ kJ/mol}$:

$$[\text{CCl}_4(\text{l})+2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_2(\text{g})+2\text{HCl}(\text{g})]$$

The value of $K$ for this reaction is $5 \times 10^{40}$ at 25°C, yet when $\text{CCl}_4$ and water are shaken vigorously at 25°C, nothing happens: the two immiscible liquids form separate layers, with the denser $\text{CCl}_4$ on the bottom. In comparison, the analogous reaction of $\text{SiCl}_4$ with water to give $\text{SiO}_2$ and $\text{HCl}$, which has a similarly large equilibrium constant, occurs almost explosively. Although the two reactions have comparable thermodynamics, they have very different kinetics!

There are also many reactions for which $\Delta G^\circ << 0$ but that do not occur as written because another possible reaction occurs more rapidly. For example, consider the reaction of lead sulfide with hydrogen peroxide. One possible reaction is as follows:

$$[\text{PbS}(\text{s})+4\text{H}_2\text{O}_2(\text{l}) \rightleftharpoons \text{PbO}_2(\text{s})+\text{SO}_2(\text{g})+4\text{H}_2\text{O}(\text{l})]$$

for which $\Delta G^\circ$ is $-886 \text{ kJ/mol}$ and $K$ is $10^{161}$. Yet when lead sulfide is mixed with hydrogen peroxide, the ensuing vigorous reaction does not produce $[\text{PbO}_2]$ and $[\text{SO}_2]$. Instead, the reaction that actually occurs is as follows:

$$[\text{PbS}(\text{s})+4\text{H}_2\text{O}_2(\text{l}) \rightleftharpoons \text{PbSO}_4(\text{s})+4\text{H}_2\text{O}(\text{l})]$$

This reaction has a $\Delta G^\circ$ value of $-1181 \text{ kJ/mol}$, within the same order of magnitude as the reaction in Equation 18.43, but it occurs much more rapidly.

Now consider reactions with $\Delta G^\circ > 0$. Thermodynamically, such reactions do not occur spontaneously under standard conditions. Nonetheless, these reactions can be made to occur under nonstandard conditions. An example is the reduction of chromium(III) chloride by hydrogen gas:

$$[\text{CrCl}_3(\text{s})+\frac{1}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{CrCl}_2(\text{s})+\text{HCl}(\text{g})]$$

At 25°C, $\Delta G^\circ = 35 \text{ kJ/mol}$ and $K_p = 7 \times 10^{-7}$. However, at 730°C, $\Delta G^\circ = -52 \text{ kJ/mol}$ and $K_p = 5 \times 10^2$; at this elevated temperature, the reaction is a convenient way of preparing chromium(II) chloride in the laboratory. Moreover, removing HCl gas from the system drives the reaction to completion, as predicted by Le Châtelier’s principle. Although the reaction is not thermodynamically spontaneous under standard conditions, it becomes spontaneous under nonstandard conditions.

There are also cases in which a compound whose formation appears to be thermodynamically prohibited can be prepared using a different reaction. The reaction for the preparation of chlorine monoxide from its component elements, for example, is as follows:

$$[\text{O}_2(\text{g})+\text{Cl}_2(\text{g}) \rightleftharpoons \text{Cl}_2\text{O}(\text{g})]$$

for which $\Delta G^\circ_f$ is $97.9 \text{ kJ/mol}$. The large positive value of $\Delta G^\circ_f$ for this reaction indicates that mixtures of chlorine and oxygen do not react to any extent to form Cl$_2$O. Nonetheless, Cl$_2$O is easily prepared using the reaction

$$[\text{HgO}(\text{s})+2\text{Cl}_2(\text{g}) \rightleftharpoons \text{Cl}_2\text{O}(\text{g})+\text{HgCl}_2(\text{s})]$$

which has a $\Delta G^\circ$ of $-22.2 \text{ kJ/mol}$ and a $K_p$ of approximately $1 \times 10^4$. 

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Finally, the ΔG° values for some reactions are so positive that the only way to make them proceed in the desired direction is to supply external energy, often in the form of electricity. Consider, for example, the formation of metallic lithium from molten lithium chloride:

\[
\text{LiCl(l)} \rightleftharpoons \text{Li(l)} + \frac{1}{2}\text{Cl}_2(g) \tag{18.48}
\]

Even at 1000°C, ΔG is very positive (324 kJ/mol), and there is no obvious way to obtain lithium metal using a different reaction. Hence in the industrial preparation of metallic lithium, electrical energy is used to drive the reaction to the right.

**Note**

A reaction that does not occur under standard conditions can be made to occur under nonstandard conditions, such as by driving the reaction to completion using Le Châtelier’s principle or by providing external energy.

Often reactions that are not thermodynamically spontaneous under standard conditions can be made to occur spontaneously if coupled, or connected, in some way to another reaction for which ΔG° << 0. Because the overall value of ΔG° for a series of reactions is the sum of the ΔG° values for the individual reactions, virtually any unfavorable reaction can be made to occur by chemically coupling it to a sufficiently favorable reaction or reactions. In the preparation of chlorine monoxide from mercuric oxide and chlorine (Equation 18.47), we have already encountered one example of this phenomenon of coupled reactions, although we did not describe it as such at the time. We can see how the chemical coupling works if we write Equation 18.47 as the sum of three separate reactions:

\[
\begin{align}
\frac{1}{2}\text{O}_2(g) + \text{Cl}_2(g) &\rightleftharpoons \text{Cl}_2O(g) & \Delta G^\circ &= 97.9 \text{ kJ/mol } \tag{1} \\
\text{HgO(s)} &\rightleftharpoons \text{Hg(l)} + \frac{1}{2}\text{O}_2(g) & \Delta G^\circ &= 58.5 \text{ kJ/mol } \tag{2} \\
\text{Hg(l)} + \text{Cl}_2(g) &\rightleftharpoons \text{HgCl}_2(s) & \Delta G^\circ &= -178.6 \text{ kJ/mol } \tag{3} \\
\text{HgO(s)} + 2\text{Cl}_2(g) &\rightleftharpoons \text{Cl}_2O(g) + \text{HgCl}_2(s) & \Delta G^\circ_{\text{rxn}} &= -22.2 \text{ kJ/mol } \\
\end{align}
\]

Comparing the ΔG° values for the three reactions shows that reaction 3 is so energetically favorable that it more than compensates for the other two energetically unfavorable reactions. Hence the overall reaction is indeed thermodynamically spontaneous as written.

**Note**

By coupling reactions, a reaction that is thermodynamically nonspontaneous can be made spontaneous.

**Example 15**
Bronze Age metallurgists were accomplished practical chemists who unknowingly used coupled reactions to obtain metals from their ores. Realizing that different ores of the same metal required different treatments, they heated copper oxide ore in the presence of charcoal (carbon) to obtain copper metal, whereas they pumped air into the reaction system if the ore was copper sulfide. Assume that a particular copper ore consists of pure cuprous oxide (Cu$_2$O). Using the $\Delta G^\circ_f$ values given for each, calculate

a. $\Delta G^\circ$ and $K_p$ for the decomposition of Cu$_2$O to metallic copper and oxygen gas [$\Delta G^\circ_f$(Cu$_2$O)=-146.0 kJ/mol].

b. $\Delta G^\circ$ and $K_p$ for the reaction of Cu$_2$O with carbon to produce metallic copper and carbon monoxide [$\Delta G^\circ_f$(CO)=-137.2 kJ/mol].

**Given:** reactants and products, $\Delta G^\circ_f$ values for Cu$_2$O and CO, and temperature

**Asked for:** $\Delta G^\circ$ and $K_p$ for the formation of metallic copper from Cu$_2$O in the absence and presence of carbon

**Strategy:**

A. Write the balanced equilibrium equation for each reaction. Using the “products minus reactants” rule, calculate $\Delta G^\circ$ for the reaction.

B. Substitute appropriate values into Equation 18.36 to obtain $K_p$.

**SOLUTION**

A The chemical equation for the decomposition of cuprous oxide is as follows:

\[
\text{Cu}_2\text{O(s)} \rightleftharpoons 2\text{Cu(s)} + \frac{1}{2}\text{O}_2(g)
\]

The substances on the right side of this equation are pure elements in their standard states, so their $\Delta G^\circ_f$ values are zero. $\Delta G^\circ$ for the reaction is therefore

\[
\begin{align}
\Delta G^\circ &= \left[2\Delta G^\circ_f(\text{Cu}) + \frac{1}{2}\Delta G^\circ_f(\text{O}_2)\right] - \Delta G^\circ_f(\text{Cu}_2\text{O}) \\
&= \left[2(0 \text{ kJ/mol}) + \frac{1}{2}(0 \text{ kJ/mol})\right] - (1 \text{ mol})(-146.0 \text{ kJ/mol}) \\
&= 146.0 \text{ kJ}
\end{align}
\]

B Rearranging and substituting the appropriate values into Equation 18.36,

\[
\begin{align}
\ln K_p &= -\frac{\Delta G^\circ}{RT} = -\frac{(146.0 \text{ kJ})(1000 \text{ J/kJ})}{(8.314 \text{ J/K})(298.15 \text{ K})} = -58.90 \\
K_p &= 2.6 \times 10^{-26}
\end{align}
\]

This is a very small number, indicating that Cu$_2$O does not spontaneously decompose to a significant extent at room temperature.

b. A The $\text{O}_2$ produced in the decomposition of Cu$_2$O can react with carbon to form CO:

\[
\frac{1}{2}\text{O}_2(g) + \text{C(s)} \rightleftharpoons \text{CO(g)}
\]
Because $\Delta G^\circ$ for this reaction is equal to $\Delta G^\circ_f$ for CO ($-137.2 \text{ kJ/mol}$), it is energetically more feasible to produce metallic copper from cuprous oxide by coupling the two reactions:

\[
\begin{align*}
\text{Cu}_2\text{O(s)} & \rightleftharpoons 2\text{Cu(s)} + \frac{1}{2}\text{O}_2(g) & \Delta G^\circ &= 146.0 \text{ kJ/mol} \\
\frac{1}{2}\text{O}_2(g) + \text{C(s)} & \rightleftharpoons \text{CO(g)} & \Delta G^\circ &= -137.2 \text{ kJ/mol} \\
\text{Cu}_2\text{O(s)} + \text{C(s)} & \rightleftharpoons 2\text{Cu(s)} + \text{CO(g)} & \Delta G^\circ_f &= 8.8 \text{ kJ/mol}
\end{align*}
\]

B We can find the corresponding value of $K_p$:

\[
\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{(8.8 \text{ kJ})(1000 \text{ J/kJ})}{(8.314 \text{ J/K})(298.15 \text{ K})} = -3.6 \\
K_p = 0.03
\]

Although this value is still less than 1, indicating that reactants are favored over products at room temperature, it is about 24 orders of magnitude greater than $K_p$ for the production of copper metal in the absence of carbon. Because both $\Delta H^\circ$ and $\Delta S^\circ$ are positive for this reaction, it becomes thermodynamically feasible at slightly elevated temperatures (greater than about 80°C). At temperatures of a few hundred degrees Celsius, the reaction occurs spontaneously, proceeding smoothly and rapidly to the right as written and producing metallic copper and carbon monoxide from cuprous oxide and carbon.

Exercise 1

Use the $\Delta G^\circ_f$ values given to calculate $\Delta G^\circ$ and $K_p$ for each reaction.

a. the decomposition of cuprous sulfide to copper metal and elemental sulfur [$\Delta G^\circ_f (\text{Cu}_2\text{S}) = -86.2 \text{ kJ/mol}$]

b. the reaction of cuprous sulfide with oxygen gas to produce sulfur dioxide and copper metal [$\Delta G^\circ_f [\text{SO}_2(g)] = -300.1 \text{ kJ/mol}$]

Answer:

a. $\Delta G^\circ = 86.2 \text{ kJ/mol}; K_p = 7.90 \times 10^{-16}$  
   b. $\Delta G^\circ = -213.9 \text{ kJ/mol}; K_p = 2.99 \times 10^{37}$

Summary

Thermodynamics describes the overall properties, behavior, and equilibrium composition of a system; kinetics describes the rate at which a particular process will occur and the pathway by which it will occur. Whereas thermodynamics tells us what can occur during a reaction process, kinetics tells us what actually occurs on an atomic or a molecular level. A reaction that is not thermodynamically spontaneous under standard conditions can often be made to occur spontaneously.
by varying the reaction conditions; using a different reaction to obtain the same product; supplying external energy, such as electricity; or coupling the unfavorable reaction to another reaction for which ΔG° << 0.

Key Takeaway

• Thermodynamics describes the overall properties, behavior, and equilibrium composition of a system, whereas kinetics describes the particular pathway by which a physical or a chemical change actually occurs.

Conceptual Problem

1. You are in charge of finding conditions to make the reaction A(l) + B(l) → C(l) + D(g) favorable because it is a critical step in the synthesis of your company’s key product. You have calculated that ΔG° for the reaction is negative, yet the ratio of products to reactants is very small. What have you overlooked in your scheme? What can you do to drive the reaction to increase your product yield?

Contributors

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