18.7: Comparing Thermodynamics and Kinetics

Learning Objectives

- 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 ΔG°. Note that ΔG° ≥ +10 kJ/mol or ΔG° ≤ −10 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 ΔG° 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 18.4 The Relationship between K and ΔG° at 25°C

ΔG° (kJ/mol)	K	Physical Significance
500	3×10^{-88}	For all intents and purposes, the reaction does not proceed in the forward direction: only reactants are present at equilibrium.
100	3×10^{-18}	
10	2×10^{-2}	Both forward and reverse reactions occur: significant amounts of both products and reactants are present at equilibrium.
0	1	
−10	60	
−100	3×10^{17}	For all intents and purposes, the forward reaction proceeds to completion: only products are present at equilibrium.
−500	4×10^{87}	

A typical challenge in industrial processes is a reaction that has a large negative value of ΔG° 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 ΔG° is −232 kJ/mol:

$$CCl_4(l) + 2H_2O(l) \rightleftharpoons CO_2(g) + 2HCl(g) \tag{18.42}$$

The value of K for this reaction is 5×10^{40} at 25°C, yet when CCl_4 and water are shaken vigorously at 25°C, nothing happens: the two immiscible liquids form separate layers, with the denser CCl_4 on the bottom. In comparison, the analogous reaction of $SiCl_4$ with water to give SiO_2 and 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 ΔG° << 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:

$$PbS(s) + 4H_2O_2(l) \rightleftharpoons PbO2(s) + SO_2(g) + 4H_2O(l) \tag{18.43}$$

for which ΔG° is −886 kJ/mol and K is 10^{161}. Yet when lead sulfide is mixed with hydrogen peroxide, the ensuing vigorous reaction does not produce PbO_2 and SO_2. Instead, the reaction that actually occurs is as follows:

$$PbS(s) + 4H_2O_2(l) \rightleftharpoons PbSO_4(s) + 4H_2O(l) \tag{18.7.1}$$

This reaction has a ΔG° value of −1181 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 ΔG° > 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:

$$\mathrm{CrCl_3(s)} + \frac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{CrCl_2(s)} + \mathrm{HCl(g)} \tag{18.45}$$

At 25°C, ΔG° = 35 kJ/mol and $K_p = 7 \times 10^{-7}$. However, at 730°C, ΔG° = −52 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 Chatelier'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:

$$\frac{1}{2}\mathrm{O_2(g)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)} \tag{18.46}$$

for which ΔG°_f is 97.9 kJ/mol. The large positive value of ΔG°_f for this reaction indicates that mixtures of chlorine and oxygen do not react to any extent to form Cl_2O. Nonetheless, Cl_2O is easily prepared using the reaction

$$\mathrm{HgO(s)} + 2\mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)} + \mathrm{HgCl_2(s)} \tag{18.47}$$

which has a ΔG° of −22.2 kJ/mol and a K_p of approximately 1×10^4.

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:

$$\mathrm{LiCl(l)} \rightleftharpoons \mathrm{Li(l)} + \frac{1}{2}\mathrm{Cl_2(g)} \tag{18.48}$$

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 Chatelier'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:

$$\frac{1}{2}\mathrm{O_2(g)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)} \qquad \Delta G^\circ = 97.9\ \mathrm{kJ/mol} \tag{1}$$

$$\mathrm{HgO(s)} \rightleftharpoons \mathrm{Hg(l)} + \frac{1}{2}\mathrm{O_2(g)} \qquad \Delta G^\circ = 58.5\ \mathrm{kJ/mol} \tag{2}$$

$$\mathrm{Hg(l)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{HgCl_2(s)} \qquad \Delta G^\circ = -178.6\ \mathrm{kJ/mol} \tag{3}$$

$$\mathrm{HgO(s)} + 2\mathrm{Cl_2(g)} \rightleftharpoons \mathrm{Cl_2O(g)} + \mathrm{HgCl_2(s)} \qquad \Delta G^\circ_{\mathrm{rxn}} = -22.2\ \mathrm{kJ/mol} \tag{18.7.2}$$

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_2O). Using the ΔG°_f values given for each, calculate

a. $\Delta G°$ and K_p for the decomposition of Cu_2O to metallic copper and oxygen gas [$\Delta G^\circ_f(Cu_2O) = -146.0$ kJ/mol].

b. $\Delta G°$ and K_p for the reaction of Cu_2O with carbon to produce metallic copper and carbon monoxide [$\Delta G^\circ_f(CO) = -137.2$ kJ/mol].

Given: reactants and products, ΔG°_f values for Cu_2O and CO, and temperature

Asked for: $\Delta G°$ and K_p for the formation of metallic copper from Cu_2O in the absence and presence of carbon

Strategy:

A. Write the balanced equilibrium equation for each reaction. Using the "products minus reactants" rule, calculate $\Delta G°$ 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:

$$\mathrm{Cu_2O(s) \rightleftharpoons 2Cu(s) + \tfrac{1}{2}O_2(g)}$$

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

$$\Delta G^\circ = \left[2\Delta G^\circ_f(\mathrm{Cu}) + \frac{1}{2}\Delta G^\circ_f(\mathrm{O_2})\right] - \Delta G^\circ_f(\mathrm{Cu_2O}) \tag{18.7.3}$$

$$= \left[(2\ \mathrm{mol})(0\ \mathrm{kJ/mol}) + \left(\frac{1}{2}\ \mathrm{mol}\right)(0\ \mathrm{kJ/mol})\right] - [(1\ \mathrm{mol})(-146.0\ \mathrm{kJ/mol})] \tag{18.7.4}$$

$$= 146.0\ \mathrm{kJ} \tag{18.7.5}$$

B Rearranging and substituting the appropriate values into Equation 18.36,

$$\ln K_\mathrm{p} = -\frac{\Delta G^\circ}{RT} = -\frac{(146.0\ \mathrm{kJ})(1000\ \mathrm{J/kJ})}{(8.314\ \mathrm{J/K})(298.15\ \mathrm{K})} = -58.90 \tag{18.7.6}$$

$$K_\mathrm{p} = 2.6 \times 10^{-26} \tag{18.7.7}$$

This is a very small number, indicating that Cu_2O does not spontaneously decompose to a significant extent at room temperature.

b.

A The O_2 produced in the decomposition of Cu_2O can react with carbon to form CO:

$$\mathrm{\tfrac{1}{2}O_2(g) + C(s) \rightleftharpoons CO(g)}$$

Because $\Delta G°$ for this reaction is equal to ΔG°_f for CO (−137.2 kJ/mol), it is energetically more feasible to produce metallic copper from cuprous oxide by coupling the two reactions:

$$\mathrm{Cu_2O(s) \rightleftharpoons 2Cu(s) + \frac{1}{2}O_2(g)} \qquad \Delta G^\circ = 146.0\ \mathrm{kJ/mol} \tag{18.7.8}$$

$$\mathrm{\frac{1}{2}O_2(g) + C(s) \rightleftharpoons CO(g)} \qquad \Delta G^\circ = -137.2\ \mathrm{kJ/mol} \tag{18.7.9}$$

$$\mathrm{Cu_2O(s) + C(s) \rightleftharpoons 2Cu(s) + CO(g)} \qquad \Delta G^\circ_f = 8.8\ \mathrm{kJ/mol} \tag{18.7.10}$$

B We can find the corresponding value of K_p:

$$\ln K_\mathrm{p} = -\frac{\Delta G^\circ}{RT} = -\frac{(8.8\ \mathrm{kJ})(1000\ \mathrm{J/kJ})}{(8.314\ \mathrm{J/K})(298.15\ \mathrm{K})} = -3.6 \tag{18.7.11}$$

$$K_\mathrm{p} = 0.03 \tag{18.7.12}$$

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 $\Delta H°$ and $\Delta S°$ 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 ΔG°_f values given to calculate ΔG° and K_p for each reaction.

a. the decomposition of cuprous sulfide to copper metal and elemental sulfur [ΔG°_f (Cu_2S)=−86.2 kJ/mol]

b. the reaction of cuprous sulfide with oxygen gas to produce sulfur dioxide and copper metal [ΔG°_f [$SO_2(g)$] = −300.1 kJ/mol]

Answer:

a. ΔG° = 86.2 kJ/mol; $K_p = 7.90 \times 10^{-16}$

b. ΔG° = −213.9 kJ/mol; $K_p = 2.99 \times 10^{37}$

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