Sample Exercise 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for $K_c$ for the following reactions:

(a) $2 \text{O}_3(\text{g}) \rightleftharpoons 3 \text{O}_2(\text{g})$

(b) $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{NOCl}(\text{g})$

(c) $\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag(NH}_3)_2^+(aq)$

Solution

Analyze We are given three equations and are asked to write an equilibrium-constant expression for each.

Plan Using the law of mass action, we write each expression as a quotient having the product concentration terms in the numerator and the reactant concentration terms in the denominator. Each concentration term is raised to the power of its coefficient in the balanced chemical equation.

Solve

(a) $K_c = \frac{[\text{O}_2]^3}{[\text{O}_3]^2}$

(b) $K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]}$

(c) $K_c = \frac{[\text{Ag(NH}_3)_2^+]^1}{[\text{Ag}^+][\text{NH}_3]^2}$

Practice Exercise

Write the equilibrium-constant expression $K_c$ for (a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$,

(b) $\text{Cd}^{2+}(aq) + 4 \text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$

Answer: (a) $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$  

(b) $K_c = \frac{[\text{CdBr}_4^{2-}]}{[\text{Cd}^{2+}][\text{Br}^-]^4}$
Sample Exercise 15.2 Converting between $K_c$ and $K_p$

For the Haber process,

$$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$$

$K_c = 9.60$ at 300 °C. Calculate $K_p$ for this reaction at this temperature.

Solution

**Analyze** We are given $K_c$ for a reaction and asked to calculate $K_p$.

**Plan** The relationship between $K_c$ and $K_p$ is given by Equation 15.14. To apply that equation, we must determine $\Delta n$ by comparing the number of moles of product with the number of moles of reactants (Equation 15.15).

$$K_p = K_c(RT)^{\Delta n} \quad [15.14]$$

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant}) \quad [15.15]$$

**Solve** With 2 mol of gaseous products (2 NH$_3$) and 4 mol of gaseous reactants, (1 N$_2$ + 3 H$_2$), $\Delta n = 2 - 4 = 2$. (Remember that $\Delta$ functions are always based on *products minus reactants.*) The temperature is $273 + 300 = 573$ K. The value for the ideal-gas constant, $R$, is 0.08206 L-atm/mol-K. Using $K_c = 9.60$, we therefore have

$$K_p = K_c(RT)^{\Delta n} = \frac{(9.60)(0.08206 \times 573)^{-2}}{(0.08206 \times 573)^2} = 4.34 \times 10^{-3}$$

**Practice Exercise**

For the equilibrium $2 \text{SO}_3(\text{g}) \rightleftharpoons 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$, $K_c$ is $4.08 \times 10^{-3}$ at 1000 K. Calculate the value for $K_p$.

**Answer:** 0.335
Sample Exercise 15.3 Interpreting the Magnitude of an Equilibrium Constant

The following diagrams represent three systems at equilibrium, all in the same-size containers. (a) Without doing any calculations, rank the systems in order of increasing $K_c$. (b) If the volume of the containers is 1.0 L and each sphere represents 0.10 mol, calculate $K_c$ for each system.

Solution

**Analyze** We are asked to judge the relative magnitudes of three equilibrium constants and then to calculate them.

**Plan** (a) The more product present at equilibrium, relative to reactant, the larger the equilibrium constant. (b) The equilibrium constant is given by Equation 15.8.

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$  \[15.8\]  

 products  \[15.8\]  

 reactants
Sample Exercise 15.3 Interpreting the Magnitude of an Equilibrium Constant

Continued

Solve
(a) Each box contains 10 spheres. The amount of product in each varies as follows: (i) 6, (ii) 1, (iii) 8. Therefore, the equilibrium constant varies in the order (ii) < (i) < (iii), from smallest (most reactant) to largest (most products).
(b) In (i) we have 0.60 mol/L product and 0.40 mol/L reactant, \( K_c = \frac{0.60}{0.40} = 1.5 \). (You will get the same result by merely dividing the number of spheres of each kind: 6 spheres/4 spheres = 1.5.) In (ii) we have 0.10 mol/L product and 0.90 mol/L reactant, giving \( K_c = \frac{0.10}{0.90} = 0.11 \) (or 1 sphere/9 spheres = 0.11). In (iii) we have 0.80 mol/L product and 0.20 mol/L reactant, giving \( K_c = \frac{0.80}{0.20} = 4.0 \) (or 8 spheres/2 spheres = 4.0). These calculations verify the order in (a).

Comment Imagine a drawing that represents a reaction with a very small or very large value of \( K_c \). For example, what would the drawing look like if \( K_c = 1 \times 10^{-5} \)? In that case there would need to be 100,000 reactant molecules for only 1 product molecule. But then, that would be impractical to draw.

Practice Exercise
For the reaction \( \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}) \), \( K_p = 794 \) at 298 K and \( K_p = 55 \) at 700 K. Is the formation of HI favored more at the higher or lower temperature?

Answer: at the lower temperature because \( K_p \) is larger at the lower temperature
Sample Exercise 15.4 Evaluating an Equilibrium Constant When an Equation is Reversed

For the reaction

\[ \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) \]

that is run at 25 °C, \( K_c = 1 \times 10^{-30} \). Use this information to write the equilibrium-constant expression and calculate the equilibrium constant for the reaction

\[ 2 \text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \]

Solution

**Analyze** We are asked to write the equilibrium-constant expression for a reaction and to determine the value of \( K_c \) given the chemical equation and equilibrium constant for the reverse reaction.

**Solve**

Writing products over reactants, we have

Both the equilibrium-constant expression and the numerical value of the equilibrium constant are the reciprocals of those for the formation of NO from \( \text{N}_2 \) and \( \text{O}_2 \):

Plan The equilibrium-constant expression is a quotient of products over reactants, each raised to a power equal to its coefficient in the balanced equation. The value of the equilibrium constant is the reciprocal of that for the reverse reaction.

\[
K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2}
\]

\[
K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{1}{1 \times 10^{-30}} = 1 \times 10^{30}
\]
Sample Exercise 15.4 Evaluating an Equilibrium Constant When an Equation is Reversed

Continued

Comment Regardless of the way we express the equilibrium among NO, N₂, and O₂, at it lies on the side that favors N₂ and O₂. Thus, the equilibrium mixture will contain mostly N₂ and O₂ with very little NO present.

Practice Exercise

For \( \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \), \( K_p = 4.34 \times 10^{-3} \) at 300 °C. What is the value of \( K_p \) for the reverse reaction?

Answer: \( 2.30 \times 10^2 \)
Sample Exercise 15.5 Combining Equilibrium Expressions

Given the reactions

\[
\begin{align*}
\text{HF}(aq) & \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq) & K_c = 6.8 \times 10^{-4} \\
\text{H}_2\text{C}_2\text{O}_4(aq) & \rightleftharpoons 2 \text{H}^+(aq) + \text{C}_2\text{O}_4^{2-}(aq) & K_c = 3.8 \times 10^{-6}
\end{align*}
\]

determine the value of \( K_c \) for the reaction

\[
2 \text{HF}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \rightleftharpoons 2 \text{F}^-(aq) + \text{H}_2\text{C}_2\text{O}_4(aq)
\]

Solution

**Analyze** We are given two equilibrium equations and the corresponding equilibrium constants and are asked to determine the equilibrium constant for a third equation, which is related to the first two.

**Plan** We cannot simply add the first two equations to get the third. Instead, we need to determine how to manipulate the equations to come up with the steps that will add to give us the desired equation.
Sample Exercise 15.5 Combining Equilibrium Expressions

Continued

Solve

If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get

\[ 2 \text{HF}(aq) \rightleftharpoons 2 \text{H}^+(aq) + 2 \text{F}^-(aq) \quad K_c = (6.8 \times 10^{-4})^2 = 4.6 \times 10^{-7} \]

Reversing the second equation and again making the corresponding change to its equilibrium constant (taking the reciprocal) gives

\[ 2 \text{H}^+(aq) + \text{C}_2\text{O}_4^{2-}(aq) \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4(aq) \quad K_c = \frac{1}{3.8 \times 10^{-6}} = 2.6 \times 10^5 \]

Now we have two equations that sum to give the net equation, and we can multiply the individual \( K_c \) values to get the desired equilibrium constant.

\[
\begin{align*}
2 \text{HF}(aq) & \rightleftharpoons 2 \text{H}^+(aq) + 2 \text{F}^-(aq) \quad K_c = 4.6 \times 10^{-7} \\
2 \text{H}^+(aq) + \text{C}_2\text{O}_4^{2-}(aq) & \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4(aq) \quad K_c = 2.5 \times 10^5 \\
2 \text{HF}(aq) + \text{C}_2\text{O}_4^{2-}(aq) & \rightleftharpoons 2 \text{F}^-(aq) + \text{H}_2\text{C}_2\text{O}_4(aq) \quad K_c = (4.6 \times 10^{-7})(2.6 \times 10^5) = 0.12
\end{align*}
\]
Sample Exercise 15.5 Combining Equilibrium Expressions

Continued

Practice Exercise

Given that, at 700 K, $K_p = 54.0$ for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, determine the value of $K_p$ for the reaction $2 \text{NH}_3(\text{g}) + 3 \text{I}_2(\text{g}) \rightleftharpoons 6 \text{HI}(\text{g}) + \text{N}_2(\text{g})$ at 700 K.

Answer:

\[
\frac{(54.0)^3}{1.04 \times 10^{-4}} = 1.51 \times 10^9
\]
Sample Exercise 15.6 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Write the equilibrium-constant expression $K_c$ for

(a) $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(l)$

(b) $\text{SnO}_2(s) + 2 \text{CO}(g) \rightleftharpoons \text{Sn}(s) + 2 \text{CO}_2(g)$

**Solution**

**Analyze** We are given two chemical equations, both for heterogeneous equilibria, and asked to write the corresponding equilibrium-constant expressions.

**Plan** We use the law of mass action, remembering to omit any pure solids and pure liquids from the expressions.

**Solve**

(a) The equilibrium-constant expression is

$$K_c = \frac{[\text{CO}]}{[\text{CO}_2][\text{H}_2]}$$

Because $\text{H}_2\text{O}$ appears in the reaction as a liquid, its concentration does not appear in the equilibrium-constant expression.

(b) The equilibrium-constant expression is

$$K_c = \frac{[\text{CO}_2]^2}{[\text{CO}]^2}$$

Because $\text{SnO}_2$ and Sn are pure solids, their concentrations do not appear in the equilibrium-constant expression.
Sample Exercise 15.6 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Continued

Practice Exercise

Write the following equilibrium-constant expressions:

(a) \( K_c \) for \( \text{Cr}(s) + 3 \text{Ag}^+(aq) \rightleftharpoons \text{Cr}^{3+}(aq) + 3 \text{Ag}(s) \)

(b) \( K_p \) for \( 3 \text{Fe}(s) + 4 \text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_3\text{O}_4(s) + 4 \text{H}_2(g) \)

Answer: (a) \( K_c = \frac{[\text{Cr}^{3+}]}{[\text{Ag}^+]^3} \)  
(b) \( K_p = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2\text{O}})^4} \)
Sample Exercise 15.7 Analyzing a Heterogeneous Equilibrium

Each of these mixtures was placed in a closed container and allowed to stand:

(a) CaCO$_3$(s)
(b) CaO(s) and CO$_2$(g) at a pressure greater than the value of $K_p$
(c) CaCO$_3$(s) and CO$_2$(g) at a pressure greater than the value of $K_p$
(d) CaCO$_3$(s) and CaO(s)

Determine whether or not each mixture can attain the equilibrium

$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$

Solution

**Analyze** We are asked which of several combinations of species can establish an equilibrium between calcium carbonate and its decomposition products, calcium oxide and carbon dioxide.

**Plan** For equilibrium to be achieved, it must be possible for both the forward process and the reverse process to occur. For the forward process to occur, there must be some calcium carbonate present. For the reverse process to occur, there must be both calcium oxide and carbon dioxide. In both cases, either the necessary compounds may be present initially or they may be formed by reaction of the other species.

**Solve** Equilibrium can be reached in all cases except (c) as long as sufficient quantities of solids are present. (a) CaCO$_3$ simply decomposes, forming CaO(s) and CO$_2$(g) until the equilibrium pressure of CO$_2$ is attained. There must be enough CaCO$_3$, however, to allow the CO$_2$ pressure to reach equilibrium. (b) CO$_2$ continues to combine with CaO until the partial pressure of the CO$_2$ decreases to the equilibrium value. (c) There is no CaO present, so equilibrium cannot be attained because there is no way the CO$_2$ pressure can decrease to its equilibrium value (which would require some of the CO$_2$ to react with CaO). (d) The situation is essentially the same as in (a): CaCO$_3$ decomposes until equilibrium is attained. The presence of CaO initially makes no difference.
Sample Exercise 15.7 Analyzing a Heterogeneous Equilibrium

Continued

Practice Exercise

When added to Fe$_3$O$_4$(s) in a closed container, which one of the following substances — H$_2$(g), H$_2$O(g), O$_2$(g) — allows equilibrium to be established in the reaction 3 Fe(s) + 4 H$_2$O(g) $\rightleftharpoons$ Fe$_3$O$_4$(s) + 4 H$_2$(g)?

Answer: H$_2$(g)
Sample Exercise 15.8 Calculating $K$ When All Equilibrium Concentrations Are Known

After a mixture of hydrogen and nitrogen gases in a reaction vessel is allowed to attain equilibrium at 472 °C, it is found to contain 7.38 atm H₂, 2.46 atm N₂, and 0.166 atm NH₃. From these data, calculate the equilibrium constant $K_p$ for the reaction

$$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$$

Solution

**Analyze** We are given a balanced equation and equilibrium partial pressures and are asked to calculate the value of the equilibrium constant.

**Plan** Using the balanced equation, we write the equilibrium-constant expression. We then substitute the equilibrium partial pressures into the expression and solve for $K_p$.

**Solve**

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

**Practice Exercise**

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C: $[\text{CH}_3\text{COOH}] = 1.65 \times 10^{-2} \text{ M}$; $[\text{H}^+] = 5.44 \times 10^{-4} \text{ M}$; and $[\text{CH}_3\text{COO}^-] = 5.44 \times 10^{-4} \text{ M}$. Calculate the equilibrium constant $K_c$ for the ionization of acetic acid at 25 °C. The reaction is

$$\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$$

**Answer:** $1.79 \times 10^{-5}$
Sample Exercise 15.9 Calculating $K$ from Initial and Equilibrium Concentrations

A closed system initially containing $1.000 \times 10^{-3} \, M \, H_2$ and $2.000 \times 10^{-3} \, M \, I_2$ at 448 °C is allowed to reach equilibrium, and at equilibrium the HI concentration is $1.87 \times 10^{-3} \, M$. Calculate $K_c$ at 448 °C for the reaction taking place, which is

$$H_2(g) + I_2(g) \rightleftharpoons 2 \text{HI}(g)$$

Solution

Analyze We are given the initial concentrations of $H_2$ and $I_2$ and the equilibrium concentration of HI. We are asked to calculate the equilibrium constant $K_c$ for $H_2(g) + I_2(g) \rightleftharpoons 2 \text{HI}(g)$.

Solve First, we tabulate the initial and equilibrium concentrations of as many species as we can. We also provide space in our table for listing the changes in concentrations. As shown, it is convenient to use the chemical equation as the heading for the table.

Second, we calculate the change in HI concentration, which is the difference between the equilibrium and initial values:

$$\text{Change in [HI]} = 1.87 \times 10^{-3} \, M - 0 = 1.87 \times 10^{-3} \, M$$

Plan We construct a table to find equilibrium concentrations of all species and then use the equilibrium concentrations to calculate the equilibrium constant.
Sample Exercise 15.9 Calculating $K$ from Initial and Equilibrium Concentrations

Continued

Third, we use the coefficients in the balanced equation to relate the change in [HI] to the changes in [H$_2$] and [I$_2$]:

\[
\left( 1.87 \times 10^{-3} \frac{\text{mol HI}}{\text{L}} \right) \left( \frac{1 \text{ mol H}_2}{2 \text{ mol HI}} \right) = 0.935 \times 10^{-3} \frac{\text{mol H}_2}{\text{L}} \\
\left( 1.87 \times 10^{-3} \frac{\text{mol HI}}{\text{L}} \right) \left( \frac{1 \text{ mol I}_2}{2 \text{ mol HI}} \right) = 0.935 \times 10^{-3} \frac{\text{mol I}_2}{\text{L}}
\]

Fourth, we calculate the equilibrium concentrations of H$_2$ and I$_2$, using initial concentrations and changes in concentration. The equilibrium concentration equals the initial concentration minus that consumed:

[H$_2$] = 1.000 \times 10^{-3} M - 0.935 \times 10^{-3} M = 0.065 \times 10^{-3} M

[I$_2$] = 2.000 \times 10^{-3} M - 0.935 \times 10^{-3} M = 1.065 \times 10^{-3} M

Our table now looks like this (with equilibrium concentrations in blue for emphasis):

<table>
<thead>
<tr>
<th>Reaction</th>
<th>H$_2$(g)</th>
<th>I$_2$(g)</th>
<th>2 HI(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration (M)</td>
<td>1.000 \times 10^{-3}</td>
<td>2.000 \times 10^{-3}</td>
<td>0</td>
</tr>
<tr>
<td>Change in concentration (M)</td>
<td>-0.935 \times 10^{-3}</td>
<td>-0.935 \times 10^{-3}</td>
<td>+1.87 \times 10^{-3}</td>
</tr>
<tr>
<td>Equilibrium concentration (M)</td>
<td>0.065 \times 10^{-3}</td>
<td>1.065 \times 10^{-3}</td>
<td>1.87 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Notice that the entries for the changes are negative when a reactant is consumed and positive when a product is formed.
Finally, we use the equilibrium-constant expression to calculate the equilibrium constant:

\[
K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51
\]

**Comment** The same method can be applied to gaseous equilibrium problems to calculate \(K_p\), in which case partial pressures are used as table entries in place of molar concentrations. Your instructor may refer to this kind of table as an ICE chart, where ICE stands for Initial – Change – Equilibrium.

**Practice Exercise**

Sulfur trioxide decomposes at high temperature in a sealed container: \(2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)\) Initially, the vessel is charged at 1000 K with \(\text{SO}_3(g)\) at a partial pressure of 0.500 atm. At equilibrium the \(\text{SO}_3\) partial pressure is 0.200 atm. Calculate the value of \(K_p\) at 1000 K.

**Answer:** 0.338
Sample Exercise 15.10 Predicting the Direction of Approach to Equilibrium

At 448 °C the equilibrium constant $K_c$ for the reaction

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$$

is 50.5. Predict in which direction the reaction proceeds to reach equilibrium if we start with $2.0 \times 10^{-2}$ mol of HI, $1.0 \times 10^{-2}$ mol of H$_2$, and $3.0 \times 10^{-2}$ of I$_2$ in a 2.00-L container.

Solution

Analyze We are given a volume and initial molar amounts of the species in a reaction and asked to determine in which direction the reaction must proceed to achieve equilibrium.

Plan We can determine the starting concentration of each species in the reaction mixture. We can then substitute the starting concentrations into the equilibrium-constant expression to calculate the reaction quotient, $Q_c$. Comparing the magnitudes of the equilibrium constant, which is given, and the reaction quotient will tell us in which direction the reaction will proceed.

Solve

The initial concentrations are

- $[\text{HI}] = 2.0 \times 10^{-2} \text{ mol/2.00 L} = 1.0 \times 10^{-2} \text{ M}$
- $[\text{H}_2] = 1.0 \times 10^{-2} \text{ mol/2.00 L} = 5.0 \times 10^{-3} \text{ M}$
- $[\text{I}_2] = 3.0 \times 10^{-2} \text{ mol/2.00 L} = 1.5 \times 10^{-2} \text{ M}$

The reaction quotient is therefore

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because $Q_c < K_c$, the concentration of HI must increase and the concentrations of H$_2$ and I$_2$ must decrease to reach equilibrium; the reaction as written proceeds left to right to attain equilibrium.
Sample Exercise 15.10 Predicting the Direction of Approach to Equilibrium

Continued

Practice Exercise

At 1000 K the value of $K_p$ for the reaction $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$ is 0.338. Calculate the value for $Q_p$, and predict the direction in which the reaction proceeds toward equilibrium if the initial partial pressures are $P_{\text{SO}_3} = 0.16 \text{ atm}$; $P_{\text{SO}_2} = 0.41 \text{ atm}$; $P_{\text{O}_2} = 2.5 \text{ atm}$.

**Answer:** $Q_p = 16$; $Q_p > K_p$, and so the reaction will proceed from right to left, forming more $\text{SO}_3$. 
Sample Exercise 15.11 Calculating Equilibrium Concentrations

For the Haber process, $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, $K_p = 1.45 \times 10^{-5}$ at 500 °C. In an equilibrium mixture of the three gases at 500 °C, the partial pressure of $\text{H}_2$ is 0.928 atm and that of $\text{N}_2$ is 0.432 atm. What is the partial pressure of $\text{NH}_3$ in this equilibrium mixture?

Solution

Analyze We are given an equilibrium constant, $K_p$, and the equilibrium partial pressures of two of the three substances in the equation ($\text{N}_2$ and $\text{H}_2$), and we are asked to calculate the equilibrium partial pressure for the third substance ($\text{NH}_3$).

Solve We tabulate the equilibrium pressures:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Equilibrium pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{N}_2$</td>
<td>0.432</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>0.928</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

Because we do not know the equilibrium pressure of $\text{NH}_3$, we represent it with $x$. At equilibrium the pressures must satisfy the equilibrium-constant expression:

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

We now rearrange the equation to solve for $x$:

$x^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}$

$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3}$ atm = $P_{\text{NH}_3}$
Sample Exercise 15.11 Calculating Equilibrium Concentrations

Continued

**Check** We can always check our answer by using it to recalculate the value of the equilibrium constant:

\[ K_p = \frac{(2.24 \times 10^{-3})^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5} \]

**Practice Exercise**

At 500 K the reaction \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \) has \( K_p = 0.497 \). In an equilibrium mixture at 500 K, the partial pressure of \( \text{PCl}_5 \) is 0.860 atm and that of \( \text{PCl}_3 \) is 0.350 atm. What is the partial pressure of \( \text{Cl}_2 \) in the equilibrium mixture?

*Answer:* 1.22 atm
Sample Exercise 15.12 Calculating Equilibrium Concentration from Initial Concentrations

A 1.000-L flask is filled with 1.000 mol of H\(_2\)(g) and 2.000 mol of I\(_2\)(g) at 447 °C. The value of the equilibrium constant \(K_c\) for the reaction

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \]

at 448 °C is 50.5. What are the equilibrium concentrations of H\(_2\), I\(_2\), and HI in moles per liter?

Solution

Analyze We are given the volume of a container, an equilibrium constant, and starting amounts of reactants in the container and are asked to calculate the equilibrium concentrations of all species.

Solve First, we note the initial concentrations of H\(_2\) and I\(_2\):

\[ [\text{H}_2] = 1.000 \text{ M} \] and \[ [\text{I}_2] = 2.000 \text{ M} \]

Second, we construct a table in which we tabulate the initial concentrations:

<table>
<thead>
<tr>
<th>Initial concentration (M)</th>
<th>(\text{H}_2) (g)</th>
<th>(\text{I}_2) (g)</th>
<th>(\text{HI}) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration (M)</td>
<td>1.000</td>
<td>2.000</td>
<td>0</td>
</tr>
<tr>
<td>Change in concentration (M)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium concentration (M)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Plan In this case we are not given any of the equilibrium concentrations. We must develop some relationships that relate the initial concentrations to those at equilibrium. The procedure is similar in many regards to that outlined in Sample Exercise 15.9, where we calculated an equilibrium constant using initial concentrations.
Sample Exercise 15.12 Calculating Equilibrium Concentration from Initial Concentrations

Continued

Third, we use the stoichiometry of the reaction to determine the changes in concentration that occur as the reaction proceeds to equilibrium. The H₂ and I₂ concentrations will decrease as equilibrium is established and that of HI will increase. Let’s represent the change in concentration of H₂ by x. The balanced chemical equation tells us the relationship between the changes in the concentrations of the three gases. For each x mol of H₂ that reacts, x mol of I₂ are consumed and 2x mol of HI are produced:

Fourth, we use initial concentrations and changes in concentrations, as dictated by stoichiometry, to express the equilibrium concentrations. With all our entries, our table now looks like this:

| Initial concentration (M) | 1.000 | 2.000 | 0 |
| Change in concentration (M) | -x | -x | +2x |
| Equilibrium concentration (M) | | | |

| Initial concentration (M) | 1.000 | 2.000 | 0 |
| Change in concentration (M) | -x | -x | +2x |
| Equilibrium concentration (M) | 1.000 - x | 2.000 - x | 2x |
Sample Exercise 15.12 Calculating Equilibrium Concentration from Initial Concentrations

Continued

Fifth, we substitute the equilibrium concentrations into the equilibrium-constant expression and solve for $x$:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

If you have an equation-solving calculator, you can solve this equation directly for $x$. If not, expand this expression to obtain a quadratic equation in $x$:

$$4x^2 = 50.5(x^2 - 3.000x + 2.000)$$
$$46.5x^2 - 151.5x + 101.0 = 0$$

Solving the quadratic equation (Appendix A.3) leads to two solutions for $x$:

$$x = \frac{-(-151.5) \pm \sqrt{(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

When we substitute $x = 2.323$ into the expressions for the equilibrium concentrations, we find negative concentrations of $\text{H}_2$ and $\text{I}_2$. Because a negative concentration is not chemically meaningful, we reject this solution. We then use to find the equilibrium concentrations:

$$[\text{H}_2] = 1.000 - x = 0.065 \text{ M}$$
$$[\text{I}_2] = 2.000 - x = 1.065 \text{ M}$$
$$[\text{HI}] = 2x = 1.87 \text{ M}$$
Sample Exercise 15.12 Calculating Equilibrium Concentration from Initial Concentrations

Continued

**Check** We can check our solution by putting these numbers into the equilibrium constant expression to assure that we correctly calculate the equilibrium constant:

\[
K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.87)^2}{(0.065)(1.065)} = 51
\]

**Comment** Whenever you use a quadratic equation to solve an equilibrium problem, one of the solutions to the equation will give you a value that leads to negative concentrations and thus is not chemically meaningful. Reject this solution to the quadratic equation.

**Practice Exercise**

For the equilibrium \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \), the equilibrium constant \( K_p \) is 0.497 at 500 K. A gas cylinder at 500 K is charged with \( \text{PCl}_5(g) \) at an initial pressure of 1.66 atm. What are the equilibrium pressures of \( \text{PCl}_5, \text{PCl}_3, \) and \( \text{Cl}_2 \) at this temperature?

**Answer:** \( P_{\text{PCl}_5} = 0.967 \text{ atm} \), \( P_{\text{PCl}_3} = P_{\text{Cl}_2} = 0.693 \text{ atm} \)
Sample Exercise 15.13 Using Le Châtelier’s Principle to Predict Shifts in Equilibrium

Consider the equilibrium

\[ \text{N}_2\text{O}_4(g) \leftrightharpoons 2 \text{NO}_2(g) \quad \Delta H^\circ = 58.0 \text{ kJ} \]

In which direction will the equilibrium shift when (a) N2O4 is added, (b) NO2 is removed, (c) the pressure is increased by addition of N2(g), (d) the volume is increased, (e) the temperature is decreased?

Solution

Analyze We are given a series of changes to be made to a system at equilibrium and are asked to predict what effect each change will have on the position of the equilibrium.

Plan Le Châtelier’s principle can be used to determine the effects of each of these changes.

Solve

(a) The system will adjust to decrease the concentration of the added N2O4, so the equilibrium shifts to the right, in the direction of product.

(b) The system will adjust to the removal of NO2 by shifting to the side that produces more NO2; thus, the equilibrium shifts to the right.

(c) Adding N2 will increase the total pressure of the system, but N2 is not involved in the reaction. The partial pressures of NO2 and N2O4 are therefore unchanged, and there is no shift in the position of the equilibrium.

(d) If the volume is increased, the system will shift in the direction that occupies a larger volume (more gas molecules); thus, the equilibrium shifts to the right.
(e) The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the equation. Decreasing the temperature will shift the equilibrium in the direction that produces heat, so the equilibrium shifts to the left, toward the formation of more $N_2O_4$. Note that only this last change also affects the value of the equilibrium constant, $K$.

**Practice Exercise**

For the reaction

$$\text{PCl}_3(g) \rightleftharpoons \text{PCl}_5(g) + \text{Cl}_2(g) \quad \Delta H^\circ = 87.9 \text{ kJ}$$

in which direction will the equilibrium shift when (a) $\text{Cl}_2(g)$ is removed, (b) the temperature is decreased, (c) the volume of the reaction system is increased, (d) $\text{PCl}_3(g)$ is added?

*Answer: (a) right, (b) left, (c) right, (d) left*
Sample Exercise 15.14 Predicting the Effect of Temperature on $K$

(a) Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$

(b) Determine how the equilibrium constant for this reaction should change with temperature.

Solution

Analyze We are asked to determine the standard enthalpy change of a reaction and how the equilibrium constant for the reaction varies with temperature.

Plan (a) We can use standard enthalpies of formation to calculate $\Delta H^\circ$ for the reaction. (b) We can then use Le Châtelier’s principle to determine what effect temperature will have on the equilibrium constant.

Solve

(a) Recall that the standard enthalpy change for a reaction is given by the sum of the standard molar enthalpies of formation of the products, each multiplied by its coefficient in the balanced chemical equation, less the same quantities for the reactants. (See section 5.7). At 25 °C, $\Delta H^\circ_f$ for NH$_3$(g) is −46.19 kJ/mol. The $\Delta H^\circ_f$ values for H$_2$(g) and N$_2$(g) are zero by definition because the enthalpies of formation of the elements in their normal states at 25 °C are defined as zero. (See section 5.7). Because 2 mol of NH$_3$ is formed, the total enthalpy change is

$$(2 \text{ mol})(-46.19 \text{ kJ/mol}) - 0 = -92.38 \text{ kJ}$$
Sample Exercise 15.14 Predicting the Effect of Temperature on $K$

Continued

(b) Because the reaction in the forward direction is exothermic, we can consider heat a product of the reaction. An increase in temperature causes the reaction to shift in the direction of less $\text{NH}_3$ and more $\text{N}_2$ and $\text{H}_2$. This effect is seen in the values for $K_p$ presented in Table 15.2. Notice that $K_p$ changes markedly with changes in temperature and that it is larger at lower temperatures.

**Comment** The fact that $K_p$ for the formation of $\text{NH}_3$ from $\text{N}_2$ and $\text{H}_2$ decreases with increasing temperature is a matter of great practical importance. To form $\text{NH}_3$ at a reasonable rate requires higher temperatures. At higher temperatures, however, the equilibrium constant is smaller, and so the percentage conversion to $\text{NH}_3$ is smaller. To compensate for this, higher pressures are needed because high pressure favors $\text{NH}_3$ formation.

**Practice Exercise**

Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction

$$2 \text{ POCl}_3(\text{g}) \rightleftharpoons 2 \text{ PCl}_3(\text{g}) + \text{ O}_2(\text{g})$$

Use this result to determine how the equilibrium constant for the reaction should change with temperature.

**Answer:** $\Delta H^\circ = 508.3$ kJ; the equilibrium constant will increase with increasing temperature.