CHAPTER 14 | Chemical Equilibrium: Equal but Opposite Reaction Rates

14.1. Collect and Organize
For two reversible reactions, we are given the reaction profiles (Figure P14.1). The profile for the conversion of A to B shows that reactant A has a lower free energy than product B. The profile for the conversion of C to D shows that C has a higher free energy than D. From the profiles, we are to determine which reaction has the larger \( k_f \), the smaller \( k_r \), and the larger value of \( K_c \).

Analyze
The magnitude of the rate constant is inversely related to the magnitude of the activation energy, \( E_a \). The reaction with the larger \( k_f \), smaller \( k_r \), and the larger \( K_c \) is that reaction with the lowest \( E_a \) for the forward reaction and where \( k_f > k_r \).

Solve
The reaction \( C \rightarrow D \) has the larger \( k_f \), the smaller \( k_r \), and the larger \( K_c \) (because it has the lowest activation energy for the forward direction).

Think about It
Remember that a large \( k \) (rate constant) means that the reaction is fast and therefore the reaction has a low activation energy.

14.2. Collect and Organize
From Figure P14.2, depicting the molar concentrations of A (red spheres) and B (blue spheres) over time, we are to determine whether the reaction reaches equilibrium, in what direction that equilibrium is achieved (\( A \rightarrow B \) or \( B \rightarrow A \)), and what is the value of the equilibrium constant.

Analyze
(a) At equilibrium, the relative concentrations of A and B do not change.
(b) From Figure P14.2, we see that more A is present at the beginning of the reaction, but more B is present at later times.
(c) The equilibrium constant can be calculated from the concentrations of A and B at equilibrium:
\[
K_c = \frac{[\text{product}]}{[\text{reactant}]} = \frac{16 M}{24 M} = 0.667
\]

Solve
(a) No. Because the last two boxes in Figure P14.2 do not contain the same number of A and B, we cannot tell whether this reaction reaches equilibrium.
(b) \( A \rightarrow B \)
(c) If we assume that the last box in Figure P14.2 represents equilibrium, then
\[
K_c = \frac{[B]}{[A]} = \frac{24 M}{16 M} = 1.5
\]

Think about It
Equilibrium could be approached in this system starting with B reacting to give A. If we write that reaction as \( B \rightarrow A \), \( K_c \) would be
\[
K_c = \frac{[A]}{[B]} = \frac{16 M}{24 M} = 0.667
\]

14.3. Collect and Organize
From Figure P16.3, showing 26 blue spheres (product B) and 13 red spheres (reactant A), we are to write the chemical equation of the equilibrium reaction and calculate the value of \( K_c \).
Chemical Equilibrium

Analyze
(a) In this reaction, A is transformed into B. We represent a system at equilibrium by using double-headed reaction arrows between the reactants and products. We will assume that one molecule of A produces one molecule of B in the reaction.
(b) The value of $K_c$ is the ratio of the concentration of the products (number of B spheres) and the concentration of the reactants (number of A spheres) raised to their respective stoichiometric coefficients from the balanced chemical equation.

Solve
(a) $A \rightarrow B$
(b) $K_c = \frac{26}{13} = 2.0$

Think about It
If the chemical equation were written as $2A \rightarrow B$, then $K_c$ would be

$$K_c = \frac{[B]}{[A]^2} = \frac{26}{(13)^2} = 0.15$$

14.4. Collect and Organize
We are to determine whether the reaction mixture depicted in Figure P14.4 is at equilibrium by comparing the reaction quotient to the given equilibrium constant. If the reaction mixture is not at equilibrium, we are to predict the direction in which it shifts in order to achieve equilibrium.

Analyze
Figure P14.4 shows 18 red spheres (A), 24 blue spheres (B), and 10 blue-red pairs (AB). If the reaction quotient $Q = \frac{[AB]}{[A][B]}$ is equal to 3.0, then the reaction is at equilibrium. If $Q$ is less than 3.0, the reaction shifts to the right. If $Q$ is greater than 3.0, the reaction shifts to the left.

Solve

$$Q = \frac{10}{18 \times 24} = 0.023$$

This reaction is not at equilibrium, as $Q \neq K$, and because $Q < K$, the reaction shifts to the right to attain equilibrium.

Think about It
When equilibrium is attained, the number of A, B, and AB molecules remains constant even though, at the molecular level, the conversions of A and B to AB and AB to A and B continue (but at equal rates).

14.5. Collect and Organize
By comparing the relative distributions of reactants A and B with product AB at two different temperatures, as shown in Figure P14.5, we can determine whether the reaction is endothermic or exothermic.

Analyze
From the equation

$$\Delta G = -RT \ln K = \Delta H - T \Delta S$$

we see that as temperature rises for an exothermic reaction, $\Delta G$ becomes less negative and therefore $K$ decreases. If, however, the temperature is raised on an endothermic reaction, $\Delta G$ becomes more negative and $K$ increases. Therefore, if products increase upon raising the temperature, the reaction is endothermic; if products decrease, the reaction is exothermic.
Solve
At 300 K the equilibrium mixture is 6 A, 10 B, and 5 AB. This gives an equilibrium constant of
\[ K_{300K} = \frac{5}{6 \times 10} = 0.083 \]
At 400 K, the equilibrium mixture is 3 A, 7 B, and 8 AB. This gives an equilibrium constant of
\[ K_{400K} = \frac{8}{3 \times 7} = 0.38 \]
As temperature increases for this reaction, \( K \) increases, indicating that more products form at higher temperatures, so this reaction is endothermic.

Think about It
We assume in this problem that the difference in entropy for the two temperatures at which this reaction is run is minimal, so only \( \Delta H \) contributes to the difference in \( \Delta G \) at the two temperatures.

14.6. Collect and Organize
From the Arrhenius plot of \( \ln K_c \) versus \( 1/T \) (Figure P14.6), we are to determine whether the reaction is endothermic or exothermic.

Analyze
The Arrhenius equation is
\[ \ln K_c = \frac{-\Delta H^*/R}{1/T} + \frac{\Delta S^*/R}{R} \]
where \( y = \ln K_c, x = 1/T, m = -\Delta H^*/R, \) and \( b = \Delta S^*/R. \)

Solve
The slope \((m)\) of the graph is positive, so \( \Delta H^*/R \) is negative. The reaction is exothermic.

Think about It
If the \( y \)-axis in Figure P14.6 showed values of \( \ln K_c \), we would be able to calculate the slope of the line and therefore estimate the value of \( \Delta H \) for the reaction.

14.7. Collect and Organize
We are asked to determine from Figure P14.7 whether the reaction depicted reaches equilibrium.

Analyze
Equilibrium is a state where the composition of the reaction is not changing.

Solve
A reaction is at equilibrium when the rate of the forward reaction equals the rate of the reverse reaction. As a result, the concentration of neither the products nor the reactants will change at equilibrium. In Figure P14.7, we see that both the concentrations of the reactants and the products level off after 50 microseconds. This is the point of equilibrium. At 20 microseconds the concentrations of the reactants and the products are still changing, so at this point, the reaction is not at equilibrium.

Think about It
Chemical equilibrium is a dynamic process. At the molecular level the forward and reverse reactions are still occurring. Because they occur at the same rate, however, we observe no macroscopic changes in the concentrations of the reactants and products in the mixture.
14.8. **Collect and Organize**  
For the reaction rates shown in Figure P14.7, we are asked how the forward and reverse rates at 30 µs compare for the forward and the reverse reactions.

**Analyze**  
We see on the plot that the concentration of the product B is higher than the concentration of the reactant A at 30 µs, so the reaction is well on its way to formation of product B from reactant A. The reaction, however, has not yet come to equilibrium, where the rate of the forward reaction is equal to the rate of the reverse reaction.

**Solve**  
Because the reaction is still making product B and losing reactant A, the rate of the forward reaction must still be larger than the rate of the reverse reaction.

**Think about It**  
When the reaction reaches equilibrium, the concentrations of the reactants and products are unchanging. For this reaction, equilibrium occurs after 50 µs.

14.9. **Collect and Organize**  
We are to describe an everyday experience of dynamic equilibrium.

**Analyze**  
In a dynamic equilibrium, the forward and reverse processes occur at the same rate so that we observe no changes in the concentrations of reactants and products.

**Solve**  
Any process in which something is removed and replaced immediately would be an example. A common example is that of an unopened soda bottle in which the dissolved carbon dioxide is continuously entering the gas phase at the same rate at which undissolved carbon dioxide enters the liquid phase in a dynamic equilibrium process.

**Think about It**  
Once the soda bottle is opened, however, the rate of CO₂ escaping the liquid phase is faster than the rate of CO₂ entering the liquid phase, and the soda eventually goes flat.

14.10. **Collect and Organize**  
We consider whether the sum of the concentrations of reactants equals the sum of the concentrations of the products at equilibrium.

**Analyze**  
Equilibrium is defined by an unchanging composition of a reaction mixture brought about by the rate of the forward reaction equaling the rate of the reverse reaction.

**Solve**  
No. The reaction may heavily favor either products or reactants. The definition of equilibrium does not specify the distribution of the reactants and products.

**Think about It**  
At any given temperature for a reaction at equilibrium, the value of $K_c$ does not change. The ratio $[\text{products}]^x/[\text{reactants}]^y$ (where $x$ and $y$ are stoichiometric coefficients from the balanced chemical equation) does not change.

14.11. **Collect and Organize**  
For a reaction where $k_f > k_r$, we are to determine whether $K$ is greater than, less than, or equal to 1.
Chapter 14

Analyze
The equilibrium constant defined in terms of the rate constants for a reaction is

\[ K = \frac{k_f}{k_r} \]

Solve
When \( k_f > k_r \), \( K \) is greater than 1.

Think about It
When \( K > 1 \), more products are present at equilibrium than reactants.

14.12. Collect and Organize
Using the relationship between \( K \) and \( k_f \) and \( k_r \), we are to explain why \( K \) may be large even though \( k_f \) and \( k_r \) are small.

Analyze
The equilibrium constant defined in terms of the rate constants for a reaction is

\[ K = \frac{k_f}{k_r} \]

Solve
The ratio \( k_f \) to \( k_r \) determines the magnitude of \( K \). For example, if \( k_f = 1 \times 10^{-2} \) and \( k_r = 1 \times 10^{-8} \), then

\[ K = \frac{1 \times 10^{-2}}{1 \times 10^{-8}} = 1 \times 10^6 \]

Think about It
Likewise, if \( k_f \) and \( k_r \) are both large, the value of \( K \) might be small, as in the following example:

\[ K = \frac{1 \times 10^6}{1 \times 10^9} = 1 \times 10^{-3} \]

14.13. Collect and Organize
For the decomposition of \( \text{N}_2\text{O} \) to \( \text{N}_2 \) and \( \text{O}_2 \), we are to identify the species present after 1 day from the given molar masses. The initial reaction mixture contains \( ^{15}\text{N}_2\text{O}, \text{N}_2, \) and \( \text{O}_2 \).

Analyze
The only isotope in the reaction for oxygen is \( ^{16}\text{O} \), but for nitrogen both \( ^{15}\text{N} \) and \( ^{14}\text{N} \) are present at the beginning of the reaction. After 1 day, the \( ^{14}\text{N} \) will be incorporated into \( \text{N}_2\text{O} \) and \( ^{15}\text{N} \) will be incorporated into \( \text{N}_2 \).

Solve

<table>
<thead>
<tr>
<th>Molar Mass</th>
<th>Compound</th>
<th>How Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>( ^{14}\text{N}_2 )</td>
<td>Originally present</td>
</tr>
<tr>
<td>29</td>
<td>( ^{15}\text{N}^{14}\text{N} )</td>
<td>From decomposition of ( ^{15}\text{N}^{14}\text{NO} )</td>
</tr>
<tr>
<td>30</td>
<td>( ^{15}\text{N}_2 )</td>
<td>From decomposition of ( ^{15}\text{N}_2\text{O} )</td>
</tr>
<tr>
<td>32</td>
<td>( \text{O}_2 )</td>
<td>Originally present</td>
</tr>
<tr>
<td>44</td>
<td>( ^{14}\text{N}_2\text{O} )</td>
<td>From combination of ( ^{14}\text{N}_2 ) and ( \text{O}_2 )</td>
</tr>
<tr>
<td>45</td>
<td>( ^{15}\text{N}^{14}\text{NO} )</td>
<td>From combination of ( ^{15}\text{N}^{14}\text{N} ) and ( \text{O}_2 )</td>
</tr>
<tr>
<td>46</td>
<td>( ^{15}\text{N}_2\text{O} )</td>
<td>Originally present</td>
</tr>
</tbody>
</table>

Think about It
The redistribution of \( ^{15}\text{N} \) from \( \text{N}_2\text{O} \) to \( \text{N}_2 \) and of \( ^{14}\text{N} \) from \( \text{N}_2 \) to \( \text{N}_2\text{O} \) demonstrates that both forward and reverse reactions occur in a dynamic equilibrium process.
14.14. **Collect and Organize**  
From the equation  
\[ 2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g) \]  
and starting the reaction with \(^{13}\text{CO}, \^{12}\text{CO}_2\), and \(\text{O}_2\) we are to identify the compounds present after 1 day and explain their appearance.

**Analyze**  
The masses of the atoms combine to give the molar masses of the compounds seen in the reaction mixture:  
\[ \begin{align*}  
^{12}\text{C} & = 12 \text{ g/mol} \\
^{13}\text{C} & = 13 \text{ g/mol} \\
^{16}\text{O} & = 16 \text{ g/mol} \text{(the most abundant O isotope)} 
\end{align*} \]

**Solve**  
The compounds matched with their molar masses are as follows:  
- 28 g/mol = \(^{12}\text{CO}\)
- 29 g/mol = \(^{13}\text{CO}\)
- 32 g/mol = \(^{16}\text{O}_2\)
- 44 g/mol = \(^{12}\text{CO}_2\)
- 45 g/mol = \(^{13}\text{CO}_2\)

The reaction mixture initially contains \(^{13}\text{CO}, \^{12}\text{CO}_2\), and \(^{16}\text{O}_2\). The \(^{12}\text{CO}\) is produced in the reaction mixture through the reverse reaction  
\[ 2 \^{12}\text{CO}_2 \rightarrow \text{O}_2 + 2 \^{12}\text{CO} \]

and the \(^{13}\text{CO}_2\) is produced through the forward reaction  
\[ 2 \^{13}\text{CO} + \text{O}_2 \rightarrow 2 \^{13}\text{CO}_2 \]

**Think about It**  
A reaction, even at equilibrium, is dynamic and isotopically labeled elements will, to some extent, be scrambled throughout the reactants and products.

14.15. **Collect and Organize**  
From the rate laws and rate constants for the forward and reverse reactions for  
\[ \text{A} \rightleftharpoons \text{B} \]
we are to calculate the value of the equilibrium constant.

**Analyze**  
At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction. The equilibrium constant is the ratio of the concentrations of the products raised to their coefficients to the concentrations of the reactants raised to their respective coefficients.

**Solve**  
For the reaction \(\text{A} \rightleftharpoons \text{B}\) we are given that the forward reaction is first order in \(\text{A}\):  
\[ \text{Rate}_f = k_1[\text{A}], \text{ where } k_1 = 1.50 \times 10^{-2} \text{ s}^{-1} \]

and that the reverse reaction is first order in \(\text{B}\):  
\[ \text{Rate}_r = k_{-1}[\text{B}], \text{ where } k_{-1} = 4.50 \times 10^{-2} \text{ s}^{-1} \]

At equilibrium, \(\text{rate}_f = \text{rate}_r\), so  
\[ k_1[\text{A}] = k_{-1}[\text{B}] \]

Rearranging this to give the equilibrium constant expression allows us to solve for \(K_c\):  
\[ K_c = \frac{[\text{B}]}{[\text{A}]} = \frac{k_1}{k_{-1}} = \frac{1.50 \times 10^{-2} \text{ s}^{-1}}{4.50 \times 10^{-2} \text{ s}^{-1}} = 0.333 \]
Think about It
For the reverse equilibrium \( B \rightleftharpoons A \)
the equilibrium constant is \( 1/0.333 \), or 3.00.

14.16. Collect and Organize
Given the equilibrium constant \( K_c = 8.7 \times 10^6 \) and the rate constant for the reverse reaction \( \left( k_r = 0.54 \ M^{-1} \ s^{-1} \right) \) for
\[
2 \text{ NO}(g) + \text{ O}_2(g) \rightarrow 2 \text{ NO}_2(g)
\]
we are to calculate the rate constant for the forward reaction.

Analyze
At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction, or
\[
k_f [\text{NO}]^2[\text{O}_2] = k_r [\text{NO}_2]^2
\]
Rearranging gives the equilibrium constant expression:
\[
K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = \frac{k_r}{k_f}
\]
Therefore, \( k_f = K_c \times k_r \).

Solve
\[
k_f = 8.7 \times 10^6 \times 0.54 \ M^{-1} \ s^{-1} = 4.7 \times 10^6 \ M^{-1} \ s^{-1}
\]

Think about It
Because the equilibrium constant is large, it is consistent that \( k_f > k_r \).

14.17. Collect and Organize
From the equation relating \( K_c \) and \( K_p \), we can determine under what conditions \( K_c = K_p \).

Analyze
The equation relating \( K_c \) and \( K_p \) is
\[
K_p = K_c (RT)^{\Delta n}
\]

Solve
\( K_p \) equals \( K_c \) when \( \Delta n = 0 \). This is true when the number of moles of gaseous products equals the number of moles of gaseous reactants in the balanced chemical equation.

Think about It
The value of \( K_p \) may also be less than \( K_c \) (for \( \Delta n < 0 \)) or greater than \( K_c \) (for \( \Delta n > 0 \)).

14.18. Collect and Organize
We are asked to determine at which temperature the values of \( K_c \) and \( K_p \) are equal for the reaction of nitrogen with oxygen to give gaseous NO.

Analyze
The equation relating \( K_c \) and \( K_p \) is
\[
K_p = K_c (RT)^{\Delta n}
\]

Solve
For this reaction \( \Delta n = 0 \), so the value of \( (RT)^{\Delta n} = 1 \). This means that
\[
K_p = K_c (RT)^{\Delta n} = K_c (RT)^0 = K_c \times 1
\]
\[
K_p = K_c
\]
Therefore, \( K_c \) and \( K_p \) are equal at all temperatures.
Think about It
As we saw in Problem 14.17, $K_c$ equals $K_p$ only when $\Delta n = 0$.

14.19. Collect and Organize
Given three reactions involving nitrogen oxides, we are to write $K_c$ and $K_p$ expressions for each reaction.

Analyze
The $K_c$ expression uses concentration (molarity) units for the reactants and the products, whereas the $K_p$ expression uses partial pressure. The $K$ expression for a balanced chemical reaction takes the general form

$$wA + xB \rightleftharpoons yC + zD$$

$$K_c = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

and

$$K_p = \frac{(P_c)^y(P_d)^z}{(P_a)^w(P_b)^x}.$$

Solve

(a) $K_c = \frac{[N_2O_4]}{[N_2][O_2]^2}$ and $K_p = \frac{P_{N_2O_4}}{P_{N_2}P_{O_2}^2}$

(b) $K_c = \frac{[NO_2][N_2]O}{[NO]^3}$ and $K_p = \frac{P_{NO_2}}{(P_{N_2}O)^3}$

(c) $K_c = \frac{[N_2]^2[O_2]}{[N_2]O}$ and $K_p = \frac{(P_{N_2})^2(P_{O_2})}{(P_{N_2}O)^2}$

Think about It
$K_c$ uses concentration units (usually in moles per liter), whereas $K_p$ uses partial pressure units (usually in atmospheres).

14.20. Collect and Organize
For three balanced reactions, we are to write the equilibrium constant expressions.

Analyze
The $K_c$ expression uses concentration (molarity) units for the reactants and the products, whereas the $K_p$ expression uses partial pressure. The $K$ expression for a balanced chemical reaction takes the general form

$$wA + xB \rightleftharpoons yC + zD$$

$$K_c = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

and

$$K_p = \frac{(P_c)^y(P_d)^z}{(P_a)^w(P_b)^x}.$$

Solve

(a) $K_c = \frac{[ClO][O_2]}{[Cl][O_3]}$ and $K_p = \frac{P_{ClO}}{(P_{Cl})(P_{O_2})}$

(b) $K_c = \frac{[Cl_2][O_2]}{[ClO]^2}$ and $K_p = \frac{P_{Cl_2}}{(P_{ClO})^2}$

(c) $K_c = \frac{[O_2]^3}{[O_3]^2}$ and $K_p = \frac{(P_{O_2})^3}{(P_{O_3})^2}$
**Think about It**

$K_c$ uses concentration units (usually moles per liter), whereas $K_p$ uses partial pressure units (usually atmospheres).

### 14.21. Collect and Organize

Given a plot of the concentration versus time for the decomposition of $\text{N}_2\text{O}$ to $\text{N}_2$ and $\text{O}_2$ (Figure P14.21), we are to estimate the value of $K_c$.

**Analyze**

The amounts of $\text{N}_2\text{O}$, $\text{N}_2$, and $\text{O}_2$ are given in concentration units and the form of the $K_c$ expression is

$$K_c = \frac{[\text{N}_2][\text{O}_2]^{1/2}}{[\text{N}_2\text{O}]}$$

The concentrations of each species at equilibrium can be read from the graph as those concentrations that are no longer changing with time. This occurs after 5 s and gives $[\text{N}_2] = 0.00030 \text{ M}$, $[\text{O}_2] = 0.00014 \text{ M}$, and $[\text{N}_2\text{O}] = 7.10 \times 10^{-6} \text{ M}$.

**Solve**

$$K_c = \frac{[\text{N}_2][\text{O}_2]^{1/2}}{[\text{N}_2\text{O}]} = \frac{(0.00030 \text{ M})(0.00014 \text{ M})^{1/2}}{(7.10 \times 10^{-6} \text{ M})} = 0.50$$

**Think about It**

Because this equilibrium constant is neither high nor low, at equilibrium the distribution of the reactants and products is expected to be roughly equal. A general rule is that if $K < 0.01$, the reactants are favored in the equilibrium, and if $K > 100$, the products are favored in the equilibrium.

### 14.22. Collect and Organize

From the concentrations of $\text{O}_2$, $\text{NO}$, and $\text{NO}_2$ at equilibrium shown in Figure P14.22, we are to estimate $K_c$ for

$$2 \text{ NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ NO}_2(g).$$

**Analyze**

Equilibrium is achieved when the concentrations of the reactants and products in the reaction mixture no longer change. For this reaction this is at $[\text{O}_2] = 0.007 \text{ M}$, $[\text{NO}_2] = 0.006 \text{ M}$, and $[\text{NO}] = 0.004 \text{ M}$.
The equilibrium constant expression for this reaction is

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

Solve

\[
K_c = \frac{(0.006 \text{ M})^2}{(0.004 \text{ M})(0.007 \text{ M})} = 300
\]

Think about It
Because \(K_c\) is greater than 1, the product is favored in this reaction.

14.23. Collect and Organize
Given the balanced chemical equation and the equilibrium partial pressures of all species in the decomposition reaction of \(\text{H}_2\text{S}\) to give \(\text{H}_2\) and \(\text{S}\), we are to calculate the value of \(K_p\) for the reaction.

Analyze
The form of the \(K_p\) expression for this reaction is

\[
K_p = \frac{P_{\text{H}_2}P_{\text{S}}}{P_{\text{H}_2\text{S}}}
\]

Solve

\[
K_p = \frac{(0.045 \text{ atm})(0.030 \text{ atm})}{(0.020 \text{ atm})^2} = 0.068
\]

Think about It
Remember that equilibrium constants, \(K\), do not have any units.

14.24. Collect and Organize
Given the partial pressures for \(\text{H}_2\text{O}\), \(\text{H}_2\), and \(\text{O}_2\) for the equilibrium reaction

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

we are to calculate the value of \(K_p\).

Analyze
The \(K_p\) expression for this reaction is

\[
K_p = \frac{P_{\text{H}_2}^2P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2}
\]
14.25. Collect and Organize
Given the equilibrium molar concentrations of $N_2$, $O_2$, and NO, we are to calculate $K_c$ for
$$N_2(g) + O_2(g) \rightleftharpoons 2 \text{NO}(g)$$

Analyze
The equilibrium constant expression for this reaction is
$$K_c = \frac{[\text{NO}]^2}{[N_2][O_2]}$$

Solve
$$K_c = \frac{(3.1 \times 10^{-3} M)^2}{(3.3 \times 10^{-3} M)(5.8 \times 10^{-3} M)} = 0.50$$

Think about It
Be careful to account for the coefficients in the mass action equation when calculating $K_c$. In this problem, we must be sure to square the equilibrium concentration of NO.

14.26. Collect and Organize
Given the equilibrium molar concentrations of $N_2O_4$ and NO$_2$, we are to calculate $K_c$ for the reaction
$$2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$$

Analyze
The equilibrium constant expression for this reaction is
$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

Solve
$$K_c = \frac{(2.9 \times 10^{-3} M)}{(4.2 \times 10^{-3} M)^2} = 160$$

Think about It
Be careful to account for the coefficients in the mass action equation when calculating $K_c$. In this problem, we must be sure to square the equilibrium concentration of NO$_2$.

14.27. Collect and Organize
Given the initial moles of H$_2$O and CO and the moles of CO$_2$ present at equilibrium, we are to determine $K_c$ for
$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$
Chemical Equilibrium

Analyze
Because the ratios of reactants and products are 1:1:1:1, we do not need the volume of the vessel because that volume would cancel in the final $K_c$ expression. We can therefore simply use the mole amounts. Furthermore, we can calculate the amounts of reactants and products present at equilibrium from the initial amounts of the reactants, the given moles of the product CO$_2$ formed ($8.3 \times 10^{-3}$ mol), and the stoichiometry of the reaction.

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>H$_2$O(g) + CO(g) ⇌ H$_2$(g) + CO$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (mol)</td>
<td>0.0150</td>
</tr>
<tr>
<td>Change (mol)</td>
<td>−x</td>
</tr>
<tr>
<td>Equilibrium (mol)</td>
<td>0.0150 − x</td>
</tr>
</tbody>
</table>

At equilibrium, we know that [CO$_2$] = $x = 8.3 \times 10^{-3}$ mol. This gives

- $H_2O = CO = 0.0150 − x = 0.0067$ mol
- $H_2 = CO_2 = x = 8.3 \times 10^{-3}$ mol

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{(8.3 \times 10^{-3} \text{ mol})(8.3 \times 10^{-3} \text{ mol})}{(0.0067 \text{ mol})(0.0067 \text{ mol})} = 1.5$$

Think about It
We must have a balanced chemical reaction so that we can stoichiometrically relate the quantity of products to the reactants and correctly calculate the value of the equilibrium constant.

14.28. Collect and Organize
Given the initial moles of NO and H$_2$ contained in a 100 mL vessel along with the concentration of NO at equilibrium, we are to calculate the value of $K_c$ for

$$2 \text{H}_2(\text{g}) + 2 \text{NO}(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$$

Analyze
The initial concentrations of the reactants are

- $\frac{2.60 \times 10^{-2} \text{ mol NO}}{0.100 \text{ L}} = 0.260 \text{ M NO}$
- $\frac{1.30 \times 10^{-2} \text{ mol H}_2}{0.100 \text{ L}} = 0.130 \text{ M H}_2$

Because we are given the [NO] at equilibrium, we can calculate the amount of NO reacted. From that we can calculate by stoichiometry the equilibrium concentrations of H$_2$, H$_2$O, and N$_2$ and calculate the value of $K_c$ for the reaction.

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>H$_2$(g) + 2 NO(g) ⇌ 2 H$_2$O(g) + N$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.130</td>
</tr>
<tr>
<td>Change</td>
<td>−2x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.130 − 2x</td>
</tr>
</tbody>
</table>

At equilibrium, we know that [NO] = 0.161 M, so

$$[\text{NO}] = 0.161 \text{ M} = 0.260 - 2x$$

$$x = 0.0495$$
Therefore, the equilibrium amounts of all species are

\[
\begin{align*}
[H_2] &= 0.130 - 2x = 0.031 \, M \\
[NO] &= 0.161 \, M \\
[H_2O] &= 2x = 0.0990 \, M \\
[N_2] &= x = 0.0495 \, M
\end{align*}
\]

\[
K_c = \frac{[H_2O]^2 [N_2]}{[H_2]^2 [NO]} = \frac{(0.0990 \, M)^2 (0.0495 \, M)}{(0.031 \, M)^2 (0.161 \, M)^2} = 19
\]

**Think about It**
We must have a balanced chemical reaction so that we can stoichiometrically relate the quantity of products to the reactants and to correctly calculate the value of the equilibrium constant.

**14.29. Collect and Organize**
We are given \(K_p = 32\) for the following reaction at 298 K:

\[A(g) + B(g) \rightleftharpoons AB(g)\]

We are to calculate the value of \(K_c\), which we can do using the relationship

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

**Analyze**
The change in the number of moles of gas for this reaction (\(\Delta n\)) is

\[1 \text{ mol AB} - (1 \text{ mol A} + 1 \text{ mol B}) = -1\]

**Solve**

\[
32 = K_c \times \left( \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 298 \text{ K} \right)^{-1}
\]

\[K_c = 780\]

**Think about It**
When \(\Delta n\) is positive, \(K_p\) is greater than \(K_c\), but when \(\Delta n\) is negative, \(K_p\) is less than \(K_c\). When \(\Delta n\) is zero, \(K_p\) equals \(K_c\).

**14.30. Collect and Organize**
We are given \(K_c = 6.0 \times 10^4\) for the following reaction at 500 K:

\[CD(g) \rightleftharpoons C(g) + D(g)\]

We are to calculate the value of \(K_p\), which we can do using the relationship

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

**Analyze**
The change in the number of moles of gas for this reaction (\(\Delta n\)) is

\[(1 \text{ mol C} + 1 \text{ mol D}) - (1 \text{ mol CD}) = 1\]

**Solve**

\[
K_p = 6.0 \times 10^4 \times \left( \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 500 \text{ K} \right)^1
\]

\[K_p = 2.5 \times 10^6\]

**Think about It**
When \(\Delta n\) is positive, \(K_p\) is greater than \(K_c\), but when \(\Delta n\) is negative, \(K_p\) is less than \(K_c\). When \(\Delta n\) is zero, \(K_p\) equals \(K_c\).
14.31. **Collect and Organize**

We are given \( K_p = 1.45 \times 10^{-5} \) for the following reaction at 500°C:

\[
N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)
\]

We are to calculate the value of \( K_c \).

**Analyze**

Rearranging the equation relating \( K_p \) and \( K_c \) to solve for \( K_c \) gives

\[
K_c = \frac{K_p}{(RT)^{\Delta n}}
\]

The change in the number of moles is

\[
(2 \text{ mol NH}_3) - (1 \text{ mol N}_2 + 3 \text{ mol H}_2) = -2
\]

The temperature in kelvins is \( 500 + 273 = 773 \text{ K} \).

**Solve**

\[
K_c = \frac{1.45 \times 10^{-5}}{\left( \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 773 \text{ K} \right)^{-2}} = 0.0583
\]

**Think about It**

Here, \( K_p < K_c \) because \( \Delta n \) is negative. When \( \Delta n = 0 \), \( K_p = K_c \).

14.32. **Collect and Organize**

Given \( K_c = 5 \times 10^5 \) for the following reaction at 298 K,

\[
2 \text{ CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ CO}_2(g)
\]

we are to calculate the value of \( K_p \), which we can do using the relationship

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

**Analyze**

The change in the number of moles of gas for this reaction (\( \Delta n \)) is

\[
(2 \text{ mol CO}_2) - (2 \text{ mol CO} + 1 \text{ mol O}_2) = -1
\]

**Solve**

\[
K_p = 5 \times 10^5 \times \left( \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} \right)^{-1} = 2 \times 10^4
\]

**Think about It**

The lower value of \( K_p \) is consistent with \( \Delta n \) being negative.

14.33. **Collect and Organize**

We are asked to determine in which of the three reactions the values of \( K_c \) and \( K_p \) are equal.

**Analyze**

\( K_p \) and \( K_c \) are equal when \( \Delta n = 0 \) in the relationship

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

where \( \Delta n \) is the change in the number of moles of gas in the reaction:

\[
\Delta n = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants})
\]
Chapter 14

Solve
(a) $\Delta n = 2 - 3 = -1$
(b) $\Delta n = 1 - 1 = 0$
(c) $\Delta n = 2 - 2 = 0$
Reactions (b) and (c) have $K_p = K_c$. Only reaction (a) has $K_p \neq K_c$.

Think about It
Remember that $\Delta n$ is the difference in the moles of gaseous products and gaseous reactants. In reaction (b), Fe(s) and FeO(s) are not considered.

14.34. Collect and Organize
For three reactions we are to determine for which the values of $K_c$ and $K_p$ are different.

Analyze
$K_p$ and $K_c$ are different when $\Delta n \neq 0$ in the relationship
$$K_p = K_c \left( \frac{RT}{\Delta n} \right)^{\Delta n}$$
where $\Delta n$ is the change in the number of moles of gas in the reaction:
$$\Delta n = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants})$$

Solve
(a) $\Delta n = 2 - 1 = 1$
(b) $\Delta n = 2 - 3 = -1$
(c) $\Delta n = 3 - 2 = 1$
For all three reactions (a–c), $K_p \neq K_c$.

Think about It
For reactions (a) and (c), $K_p > K_c$, whereas for reaction (b), $K_p < K_c$.

14.35. Collect and Organize
Given $K_c = 5.0$ for the following reaction at 327°C (600 K)
$$\text{Cl}_2(g) + \text{CO}(g) \rightleftharpoons \text{COCl}_2(g)$$
we are to calculate the value of $K_p$ at 325°C. We can use the relationship
$$K_p = K_c \left( \frac{RT}{\Delta n} \right)^{\Delta n}$$

Analyze
For this reaction
$$\Delta n = (1 \text{ mol COCl}_2) - (1 \text{ mol Cl}_2 + 1 \text{ mol CO}) = -1$$

Solve
$$K_p = 5.0 \times \left( \frac{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 598 \text{ K}}{1} \right)^{-1} = 0.10$$

Think about It
Because $\Delta n$ is negative, the value of $K_p$ is less than that of $K_c$.

14.36. Collect and Organize
Given $K_p = 3.45$ for the following reaction at 298 K:
$$\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{NO}(g) + \text{SO}_3(g)$$
we are to calculate the value of $K_c$ for the reverse reaction. We can use the relationships

$$K_p = K_c (RT)^{\Delta n}$$

$$K_{\text{reverse}} = \frac{1}{K_{\text{forward}}}$$

**Analyze**

For this reaction

$$\Delta n = (1 \text{ mol NO} + 1 \text{ mol SO}_3) - (1 \text{ mol SO}_2 + 1 \text{ mol NO}_2) = 0$$

**Solve**

Because $\Delta n = 0$,

$$K_p = K_c (RT)^0 = K_c \times 1$$

and the value of $K_c = K_p$, so $K_c = 3.45$ for the forward reaction. For the reverse reaction,

$$K_{\text{reverse}} = \frac{1}{K_{\text{forward}}} = \frac{1}{3.45} = 0.290$$

**Think about It**

Only when $\Delta n \neq 0$ would $K_c$ and $K_p$ be different in value.

14.37. **Collect and Organize**

We consider how $K$ changes when the coefficients of a balanced reaction are scaled up or down.

**Analyze**

To answer the question, let’s consider the following reactions:

(1) $2 \text{ A} + \text{ B} \rightleftharpoons \text{ C}$

(2) $4 \text{ A} + 2 \text{ B} \rightleftharpoons 2 \text{ C}$

The equilibrium constant expressions for the reactions are

$$K_1 = \frac{[\text{C}]}{[\text{A}]^2[B]}$$

$$K_2 = \frac{[\text{C}]^2}{[\text{A}]^2[B]}$$

These are related by

$$K_2 = (K_1)^2$$

**Solve**

When we scale the coefficients of a reaction up or down, the new value of the equilibrium constant is the first $K$ raised to the power of the scaling constant.

**Think about It**

Scaling reaction 1 by $\frac{1}{3}$ gives

$$\frac{2}{3} \text{ A} + \frac{1}{3} \text{ B} \rightleftharpoons \frac{1}{3} \text{ C}$$

$$K = \frac{[\text{C}]^{1/3}}{[\text{A}]^{2/3}[\text{B}]^{1/3}}$$

14.38. **Collect and Organize**

We are to explain why the temperature and a written form of the equilibrium equation are needed when reporting the value of $K$.

**Analyze**

As we saw in Problem 14.37, scaling a chemical equation up or down changed the value of the equilibrium constant. Temperature and the value of $K$ are related through Gibbs free energy:

$$\frac{\Delta G}{RT} = \ln K$$
**Solve**
The temperature and form of the equilibrium reaction must be given with a value of \( K \) because both the stoichiometric scaling of the reaction and the temperature change the value of \( K \).

**Think about It**
From the Gibbs free energy equation, we see that the value of \( K \) increases with an increase in temperature for a spontaneous reaction (negative \( \Delta G \)) and decreases with an increase in temperature for a nonspontaneous reaction (positive \( \Delta G \)).

14.39. **Collect and Organize**
Given the equilibrium constant for the reaction of 1 mol I\(_2\)(g) with 1 mol Br\(_2\)(g) to give 2 mol IBr(g), we are to calculate the value of the equilibrium constant for the reaction of \( \frac{1}{2} \) mol of I\(_2\) and Br\(_2\) to give 1 mol of IBr.

**Analyze**
The \( K_c \) expressions for these reactions are

\[
K_{c_1} = \frac{[\text{IBr}]^2}{[\text{I}_2][\text{Br}_2]}
\text{ and }\ K_{c_2} = \frac{[\text{IBr}]}{[\text{I}_2]^{\frac{1}{2}}[\text{Br}_2]^{\frac{1}{2}}}
\]

\( K_{c_2} \) for the second reaction is, therefore, related to that of the first by

\[
K_{c_2} = \left( K_{c_1} \right)^{\frac{1}{2}}
\]

**Solve**

\[
K_{c_2} = \left( K_{c_1} \right)^{\frac{1}{2}} = (120)^{\frac{1}{2}} = 11.0
\]

**Think about It**
When we multiply a chemical reaction by a number, the new value of the equilibrium constant is the first equilibrium constant raised to that number.

14.40. **Collect and Organize**
Given the equilibrium constant for the reaction of 1 mol N\(_2\)(g) with 3 mol H\(_2\)(g) to give 2 mol NH\(_3\)(g), we are to calculate the value of the equilibrium constant for the reaction of \( \frac{1}{2} \) mol of N\(_2\) with \( \frac{3}{2} \) mol of H\(_2\) to give 1 mol of NH\(_3\).

**Analyze**
The \( K_c \) expressions for these reactions are

\[
K_{c_1} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}
\text{ and }\ K_{c_2} = \frac{[\text{NH}_3]}{[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]^{\frac{3}{2}}}
\]

\( K_{c_2} \) for the second reaction is, therefore, related to that of the first by

\[
K_{c_2} = \left( K_{c_1} \right)^{\frac{1}{2}}
\]

**Solve**

\[
K_{c_2} = \left( K_{c_1} \right)^{\frac{1}{2}} = (4.3 \times 10^{-3})^{\frac{1}{2}} = 6.6 \times 10^{-2}
\]

**Think about It**
When we multiply a chemical reaction by a number, the new value of the equilibrium constant is the first equilibrium constant raised to that number.
14.41. Collect and Organize
For the reaction of NO with NO₃, we are to explain how \( K_c \) for the reverse reaction relates to \( K_c \) of the forward reaction by writing their equilibrium constant expressions.

**Analyze**
The form of the equilibrium constant expression for the forward reaction is the ratio of the product of the concentration of the products raised to their stoichiometric coefficients to the product of the concentration of the reactants raised to their stoichiometric coefficients:

\[
K_c = \frac{[\text{products}]^y}{[\text{reactants}]^x}
\]

**Solve**
The form of the equilibrium constant expression for the forward reaction is

\[
K_{c,\text{forward}} = \frac{[\text{NO}_2]^2}{[\text{NO}][\text{NO}_3]}
\]

For the reverse reaction, the equilibrium constant expression is

\[
K_{c,\text{reverse}} = \frac{[\text{NO}][\text{NO}_3]}{[\text{NO}_2]^2}
\]

Examining these two expressions, we see that

\[
K_{c,\text{reverse}} = \frac{1}{K_{c,\text{forward}}}
\]

**Think about It**
Another way to think about this relationship is

\[
K_{c,\text{forward}} \times K_{c,\text{reverse}} = 1
\]

14.42. Collect and Organize
Given \( K_p = 4.5 \times 10^{-5} \) for the reaction

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

at 450°C, we are to calculate \( K_p \) for

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

at the same temperature.

**Analyze**
The \( K_p \) expressions for these reactions are

\[
K_{p_1} = \frac{(\text{NH}_3)^2}{(\text{N}_2)(\text{H}_2)^3} \quad \text{and} \quad K_{p_2} = \frac{(\text{N}_2)(\text{H}_2)^3}{(\text{NH}_3)^2}
\]

\( K_{p_2} \) is, therefore, related to \( K_{p_1} \) by

\[
K_{p_2} = \frac{1}{K_{p_1}}
\]

**Solve**

\[
K_{p_2} = \frac{1}{4.5 \times 10^{-5}} = 2.2 \times 10^4
\]

**Think about It**
When we reverse a reaction, the new equilibrium constant is the inverse of \( K \) for the forward reaction.
14.43. Collect and Organize
For two reactions of different stoichiometry for the reaction of SO\(_2\) with O\(_2\) to produce SO\(_3\), we are to write the equilibrium constant expressions and explain how they are related.

Analyze
Equilibrium constant expressions take the form
\[ wA + xB \rightleftharpoons yC + zD \]
\[ K_c = \frac{[C]^y[D]^z}{[A]^w[B]^x} \]

Solve
The equilibrium expressions for the reactions are
\[ K_c = \frac{[SO_3]}{[SO_2][O_2]^2 \rightleftharpoons N_2\text{(g)} + H_2\text{(g)} \rightleftharpoons \frac{1}{2} N_2\text{(g)} + H_2\text{O}\text{(g)}} \]
These expressions are related by
\[ K'_c = (K_c)^\frac{1}{2} \]

Think about It
If the second reaction were
\[ \frac{1}{2} SO_2\text{(g)} + \frac{1}{2} O_2\text{(g)} \rightleftharpoons \frac{1}{2} SO_3\text{(g)} \]
then
\[ K'_{c2} = \frac{[SO_2]^\frac{1}{2}}{[SO_2]^\frac{1}{2}[O_2]^\frac{1}{2}} \]

14.44. Collect and Organize
Given \( K_c = 0.11 \) for the reaction
\[ 2 \text{NO(g)} + 2 \text{H}_2\text{(g)} \rightleftharpoons \text{N}_2\text{(g)} + 2 \text{H}_2\text{O}\text{(g)} \]
at a given temperature, we are to calculate \( K_c \) for
\[ \text{NO(g)} + \text{H}_2\text{(g)} \rightleftharpoons \frac{1}{2} \text{N}_2\text{(g)} + \text{H}_2\text{O}\text{(g)} \]
at the same temperature.

Analyze
The \( K_c \) expressions for these reactions are
\[ K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} \quad \text{and} \quad K_c = \frac{[N_2]^\frac{1}{2}[H_2O]}{[NO][H_2]} \]
\( K_c \) for the second reaction is, therefore, related to that of the first by
\[ K'_c = \left(K_c\right)^\frac{1}{2} \]

Solve
\[ K'_c = (0.11)^\frac{1}{2} = 0.33 \]

Think about It
When we multiply a chemical reaction by a number, the new value of the equilibrium constant is the first equilibrium constant raised to the number.

14.45. Collect and Organize
Given the value of \( K_c \) for the reaction
\[ 2 \text{SO}_3\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{SO}_2\text{(g)} \]
as \( 2.4 \times 10^{-3} \), we are to calculate \( K_c \) for three other forms of this reaction at the same temperature.
Analyse
When a reaction is multiplied by a factor $x$, the new equilibrium constant is $(K_c)^x$. When a reaction is reversed, the new equilibrium constant is $1/K_c$.

Solve
(a) This reaction is the original equation multiplied by $1/2$. The new $K_c$ is
\[
\left(2.4 \times 10^{-3}\right)^{1/2} = 4.9 \times 10^{-2}
\]
(b) This reaction equation is the reverse of the original equation. The new $K_c$ is
\[
\frac{1}{\left(2.4 \times 10^{-3}\right)} = 420
\]
(c) This reaction equation is the reverse of the original equation multiplied by $1/2$. The new $K_c$ is
\[
\frac{1}{\left(2.4 \times 10^{-3}\right)^{1/2}} = 20
\]

Think about It
Because we can relate the equilibrium constants for different forms of a reaction, we need to tabulate only one of the equilibrium constants. All others can be calculated from that value.

14.46. Collect and Organize
Given the value of $K_c$ for the reaction
\[2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g)\]
as $5 \times 10^{12}$, we are to calculate $K_c$ for three other forms of this reaction at the same temperature.

Analyse
When a reaction is multiplied by a factor $x$, the new equilibrium constant is $(K_c)^x$. When a reaction is reversed, the new equilibrium constant is $1/K_c$.

Solve
(a) This reaction is the original equation multiplied by $1/2$. The new $K_c$ is
\[
\left(5 \times 10^{12}\right)^{1/2} = 2 \times 10^6
\]
(b) This reaction equation is the reverse of the original equation. The new $K_c$ is
\[
\frac{1}{\left(5 \times 10^{12}\right)} = 2 \times 10^{-13}
\]
(c) This reaction equation is the reverse of the original equation multiplied by $1/2$. The new $K_c$ is
\[
\frac{1}{\left(5 \times 10^{12}\right)^{1/2}} = 4 \times 10^{-7}
\]

Think about It
Because we can relate the equilibrium constants for different forms of a reaction, we need to tabulate only one of the equilibrium constants. All others can be calculated from that value.

14.47. Collect and Organize
We are asked to calculate $K$ for a reaction given $K_c$ values for two other reactions. We can add the two equations and reverse the resulting equation and then calculate the equilibrium constant for this new chemical equation.
**Analyze**
The $K_c$ expressions for the reactions and the overall reaction are

\[\begin{align*}
A + 2B &\rightleftharpoons C \quad K_1 = \frac{[C]}{[A][B]^2} = 3.3 \\
C &\rightleftharpoons 2D \quad K_2 = \frac{[D]^2}{[C]} = 0.041 \\
A + 2B &\rightleftharpoons 2D \quad K_3 = \frac{[D]^2}{[A][B]^2}
\end{align*}\]

where $K_3 = K_1 \times K_2$. The equilibrium constant for the reaction

\[2D \rightleftharpoons A + 2B\]

is the inverse of $K_3$.

**Solve**

\[K = \frac{1}{0.041 \times 3.3} = 7.4\]

**Think about It**
When we add reactions, the new equilibrium constant is the product of the equilibrium constants of the reactions that were combined.

14.48. **Collect and Organize**
We are asked to calculate $K$ for a reaction given $K_c$ values for two other reactions. We can add the two equations and reverse the resulting equation and then calculate the equilibrium constant for this new chemical equation.

**Analyze**
The $K_c$ expressions for the reactions and the overall reaction are

\[\begin{align*}
2G &\rightleftharpoons H \quad K_1 = \frac{[H]}{[G]^2} = 3.1 \times 10^{-4} \\
H &\rightleftharpoons 2E + 2F \quad K_2 = \frac{[E][F]^2}{[H]} = 2.8 \times 10^{-2} \\
2G &\rightleftharpoons 2E + 2F \quad K_3 = \frac{[E][F]^2}{[G]^2}
\end{align*}\]

where $K_3 = K_1 \times K_2$. The equilibrium constant for the reaction

\[E + F \rightleftharpoons G\]

will be $\frac{1}{(K_1)^{1/2}}$.

**Solve**

\[K = \frac{1}{(3.1 \times 10^{-4} \times 2.8 \times 10^{-2})^{1/2}} = 340\]

**Think about It**
Remember that when we reverse an equation, the equilibrium constant is the inverse of the forward reaction equilibrium constant.
14.49. **Collect and Organize / Analyze**  
We are to define the term *reaction quotient*.

**Solve**  
The reaction quotient is the ratio of the concentrations of the products raised to their stoichiometric coefficients to the concentrations of reactants raised to their stoichiometric coefficients. The reaction quotient has the same form as the equilibrium constant expression, but the reaction concentrations (or partial pressures) are not necessarily at their equilibrium values.

**Think about It**  
If the reaction quotient, $Q$, is greater than $K$, the reaction mixture must reduce its concentration of products to attain equilibrium. When $Q$ is less than $K$, the reaction mixture must increase its concentration of products to attain equilibrium.

14.50. **Collect and Organize**  
We are asked how, in most cases, the equilibrium constant $K$ and the reaction quotient $Q$ differ for a given equilibrium system.

**Analyze**  
Both $K$ and $Q$ take the form of the ratio of the concentrations of products raised to their stoichiometric coefficients to the concentrations of reactants raised to their stoichiometric coefficients.

**Solve**  
The reaction quotient $Q$ is for a reaction mixture not necessarily at equilibrium. Only if the system is at equilibrium is $Q = K$.

**Think about It**  
If the reaction quotient, $Q$, is greater than $K$, the reaction mixture must reduce its concentration of products to attain equilibrium. When $Q$ is less than $K$, the reaction mixture must increase its concentration of products to attain equilibrium.

14.51. **Collect and Organize**  
We are asked what it means when $Q = K$.

**Analyze**  
Both $K$ and $Q$ take the form of the ratio of the concentrations of products raised to their stoichiometric coefficients to the concentrations of reactants raised to their stoichiometric coefficients.

**Solve**  
When $Q = K$ the system is at equilibrium.

**Think about It**  
Whenever $Q \neq K$, the reaction is not at equilibrium and it adjusts its relative concentrations of reactants and products so that $Q = K$.

14.52. **Collect and Organize**  
We are to explain how comparing numerical values of $K$ and $Q$ allows us to determine whether a reaction is at equilibrium and which direction a reaction will shift to attain equilibrium.

**Analyze**  
Both $K$ and $Q$ take the form of the ratio of the concentrations of products raised to their stoichiometric coefficients to the concentrations of reactants raised to their stoichiometric coefficients.

**Solve**  
When $Q < K$, the reaction shifts to the right, forming more products. When $Q > K$, the reaction shifts to the left, forming more reactants. When $Q = K$, the reaction is at equilibrium.
Think about It
When \( Q \neq K \), the reaction shifts until \( Q = K \). At that point no more changes in the relative concentrations of the reactants and products occur as long as reaction conditions remain constant.

14.53. Collect and Organize
We are asked whether the reaction

\[
A(aq) \rightleftharpoons B(aq)
\]

where \([A(aq)] = 0.10 \, M\), \([B(aq)] = 2.0 \, M\), and \( K = 22 \) is at equilibrium. If the reaction is not at equilibrium, we are to state in which direction the reaction will proceed to reach equilibrium.

Analyze
The reaction quotient (\( Q \)) is

\[
\frac{[B]}{[A]} = Q
\]

where \([B]\) and \([A]\) are the concentrations of A and B in the reaction mixture. If \( Q > K \), the reaction will proceed to the left to reach equilibrium. If \( Q < K \), the reaction will proceed to the right. If \( Q = K \), the reaction is at equilibrium.

Solve
\[
Q = \frac{2.0 \, M}{0.10 \, M} = 20
\]

No, the reaction is not at equilibrium. \( Q < K \), so this reaction proceeds to the right to reach equilibrium.

Think about It
In this reaction, more B forms as the reaction proceeds to equilibrium.

14.54. Collect and Organize
We can compare \( Q \) versus \( K \) to determine in which direction the reaction will shift to attain equilibrium. We are given \( K_c = 3 \times 10^{-3} \).

Analyze
The form of the reaction quotient for this reaction is

\[
Q = \frac{[D][E]}{[C]^2}
\]

If \( Q > K \), the reaction will proceed to the left to reach equilibrium. If \( Q < K \), the reaction will proceed to the right. If \( Q = K \), the reaction is at equilibrium.
Chemical Equilibrium

Solve

\[ Q = \frac{(5 \times 10^{-4} \, M)(5 \times 10^{-4} \, M)}{(5 \times 10^{-4} \, M)^2} = 1 \]

Because, \( Q > K \) (3 × 10⁻³), this reaction proceeds to the left to reach equilibrium, forming more of reactant C.

Think about It

To calculate the amount of each reactant and product at equilibrium, we solve for \( x \) in the following equation:

\[ K_c = 3 \times 10^{-3} = \frac{(5 \times 10^{-4} \, M - x)^2}{(5 \times 10^{-4} \, M + x)^2} \]

14.55. Collect and Organize

Given two sets of reactant and product concentrations for the reaction of A and B to form C (where \( K_p = 1.00 \)), we are to determine whether either reaction mixture is at equilibrium. The temperature is 300 K.

Analyze

These systems are at equilibrium when \( Q = K_p = 1.00 \). For the reaction where A, B, and C are expressed in terms of molarity, we must convert \( K_p \) to \( K_c \) by using

\[ K_p = K_c (RT)^{\Delta_n} \]

where for this reaction \( \Delta n = -1 \).

Solve

(a) \( Q_p = \frac{1.0 \, \text{atm}}{(1.0 \, \text{atm})(1.0 \, \text{atm})} = 1.0 \)

This reaction mixture is at equilibrium.

(b) Rearranging the equation to solve for \( K_c \) gives

\[ K_c = \frac{K_p}{(RT)^{\Delta_n}} = \frac{1.00}{\left[ \frac{0.08206 \, \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 300 \, \text{K} \right]^1} = 24.6 \]

\[ Q_c = \frac{1.0 \, M}{(1.0 \, M)(1.0 \, M)} = 1.0 \]

Because \( Q_c < K_c \), this reaction mixture is not at equilibrium and shifts to the right to attain equilibrium.

Think about It

Both \( K_p \) and \( K_c \) are close to 1, and so these reaction mixtures have roughly equal proportions of reactants and products when they reach equilibrium.
14.56. **Collect and Organize**

For the reaction

\[ A(g) + B(g) \rightleftharpoons C(g) \]

for which \( K_p = 1.00 \) at 300 K, we are to calculate \( Q \) for different partial pressures or concentrations of A, B, and C to determine in which direction each reaction mixture will proceed to reach equilibrium.

**Analyze**

If \( Q > K \), the reaction will proceed to the left to reach equilibrium; if \( Q < K \), the reaction will proceed to the right; if \( Q = K \), the reaction is at equilibrium. Because we are given \( K_p \) for the reaction, we have to calculate \( K_c \) for the conditions of part b from the relationship

\[ K_p = K_c (RT)^\Delta n \]

**Solve**

(a) \( Q_p = \frac{(P_C)}{(P_A)(P_B)} = \frac{1.0 \text{ atm}}{(1.0 \text{ atm})(0.50 \text{ atm})} = 2.0 \)

For this reaction mixture, \( Q > K \), so the reaction proceeds to the left.

(b) \( K_c = \frac{K_p}{(RT)^\Delta n} \)

where \( R = 0.8206 \text{ (L \cdot atm)/(mol \cdot K)} \), \( T = 300 \text{ K} \), and \( \Delta n = 1 - 2 = -1 \).

\[ K_c = \frac{1.00}{\left[\frac{0.8206 \text{ L \cdot atm}}{\text{mol \cdot K}}\right]\left(300 \text{ K}\right)^{-1}} = 24.6 \]

\[ Q_c = \frac{1.0 M}{1.0 M \times 1.0 M} = 1.0 \]

For this reaction mixture, \( Q < K \), so the reaction proceeds to the right.

**Think about It**

Because \( K_c \) and \( K_p \) are both greater than 1, the products are favored for this reaction.

14.57. **Collect and Organize**

By comparing \( Q \) versus \( K \) for the reaction of \( N_2 \) with \( O_2 \) to form \( NO \), we can determine in which direction the reaction will proceed to attain equilibrium.

**Analyze**

The form of the reaction quotient for this reaction is

\[ Q_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} \]

Because \( \Delta n = 0 \) for this reaction, \( K_p = K_c = 1.5 \times 10^{-3} \).

**Solve**

\[ Q_p = \frac{(1.00 \times 10^{-3})^2}{(1.00 \times 10^{-3})(1.00 \times 10^{-3})} = 1.00 \]

Because \( Q > K \), the system is not at equilibrium and proceeds to the left.

**Think about It**

For this problem \( K_p = K_c \). This is not always the case, so be careful to notice which value is provided for \( K \) and in what units the amounts of the reactants and products are expressed.
14.58. **Collect and Organize**

Given $K_p = 4.3 \times 10^{-4}$ at 650 K for the reaction of $N_2$ with $H_2$ to produce $NH_3$, we can use the amounts of the reactants and products present to calculate $Q$ and then compare that value to $K_c$ to determine whether more ammonia will form in the reaction (reaction shifts to the right).

**Analyze**

Because the amounts of $N_2$, $H_2$, and $NH_3$ are expressed in terms of molarity, we need to find the value of $K_c$ from $K_p$ by using the equation

$$K_p = K_c \left(\frac{RT}{\Delta n}\right)^{\Delta n}$$

**Solve**

For this reaction, $\Delta n = -2$ and $K_c$ is

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{4.3 \times 10^{-4}}{(0.08206 \text{ L\cdot atm mol}^{-1} \text{K}^{-1} \times 650 \text{ K})^{-2}} = 1.2$$

The reaction quotient is

$$Q_c = \frac{(0.00020 \text{ M})^2}{(0.010 \text{ M})(0.030 \text{ M})^3} = 0.15$$

For this reaction mixture, $Q_c < K_c$, so the reaction proceeds to the right. Yes, more ammonia will form.

**Think about It**

If we had not converted $K_p$ to $K_c$, we would have reached the opposite conclusion that less ammonia would be present once the reaction attained equilibrium.

4.59. **Collect and Organize**

Given initial concentrations of the reactants $X$ and $Y$ and product $Z$ and the value of the equilibrium constant ($K_c = 1.00$ at 350 K), we can use the reaction quotient to determine in which direction the reaction will shift to reach equilibrium.

**Analyze**

The reaction quotient for this reaction has the form

$$Q_c = \frac{[Z]}{[X][Y]}$$

**Solve**

$$Q_c = \frac{[Z]}{[X][Y]} = \frac{0.2 \text{ M}}{0.2 \text{ M} \times 0.2 \text{ M}} = 5$$

Because $Q_c > K_c$, the reaction proceeds to the left (a), producing more $X$ and $Y$.

**Think about It**

To calculate the equilibrium concentration of each reactant and product, we solve for $x$ in the equation

$$1.00 = \frac{0.2 - x}{(0.2 + x)^3}$$

14.60. **Collect and Organize**

From the result of Problem 14.59, we are to determine how the concentration of reactant $X$ changes from the initial conditions to equilibrium.

**Analyze**

We determined in Problem 14.59 that the equilibrium shifts to the left.
Solve
The concentration of X increases when the equilibrium shifts to the left.

Think about It
At equilibrium, this reaction has a decreased concentration of product Z.

14.61. Collect and Organize
For the dissolution of CuS to give Cu$^{2+}$ and S$^{2-}$ in aqueous solution, we are asked to write the $K_c$ expression.

Analyze
Because any pure solids or liquids do not change in concentration during a reaction, their “concentrations” do not appear in the mass action (equilibrium constant) expression.

Solve
$$K_c = [Cu^{2+}][S^{2-}]$$

Think about It
Because the reactant in the dissolution reaction is a pure solid, only the concentrations of the products influence the position of the equilibrium.

14.62. Collect and Organize
For the heterogeneous equilibrium reaction
$$Al_2O_3(s) + 3 H_2O(l) \rightleftharpoons 2 Al^{3+}(aq) + 6 OH^-(aq)$$
we are to write the $K_c$ expression.

Analyze
Because any pure solids or liquids do not change in concentration during a reaction, their “concentrations” do not appear in the mass action (equilibrium constant) expression.

Solve
$$K_c = [Al^{3+}][OH^-]^6$$

Think about It
Because both reactants are either pure solids or pure liquids for this reaction, only the concentrations of the products influence the equilibrium.

14.63. Collect and Organize
For the decomposition reaction of CaCO$_3$ to CO$_2$ and CaO, we are to explain why [CaCO$_3$] and [CaO] do not appear in the $K_c$ expression.

Analyze
The $K_c$ expression includes the concentrations of the reactants and products that may change during the reaction attaining equilibrium.

Solve
The concentrations (expressed as densities) of pure solids (CaCO$_3$ and CaO) do not change during the reaction to attain equilibrium, and so they do not appear in the equilibrium constant expression.

Think about It
The form of $K_c$ for this reaction is simply $K_c = [CO_2]$. 
14.64. **Collect and Organize**

For the decomposition of NaHCO₃ to Na₂CO₃, CO₂, and H₂O we are to identify the number of partial pressure terms that are part of the $K_p$ expression.

**Analyze**

The decomposition of NaHCO₃ is described by the stoichiometric equation

$$2 \text{NaHCO}_3(s) \rightleftharpoons \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$$

In the equilibrium expression, pure liquids and solids do not appear, so the only species that will appear in the $K_p$ expression are CO₂ and H₂O.

The reaction involves the breaking of bonds to form CO₂ from CO₃²⁻, so we expect this reaction to be endothermic. If we increase the temperature, more products will form in this reaction by Le Châtelier’s principle.

**Solve**

The $K_p$ expression for the decomposition reaction of sodium bicarbonate is

$$K_p = \left( P_{\text{CO}_2} \right) \times \left( P_{\text{H}_2\text{O}} \right)$$

Therefore, the $K_p$ expression has two partial pressure terms.

**Think about It**

If the water formed in this reaction were in the liquid form, the $K_p$ expression would simply be

$$K_p = \left( P_{\text{CO}_2} \right)$$

14.65. **Collect and Organize**

We are asked whether the value of $K$ increases when more reactants are added to a reaction already at equilibrium.

**Analyze**

The general form of the equilibrium constant expression for a reaction is

$$wA + xB \rightleftharpoons yC + zD$$

$$K = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

**Solve**

No, the equilibrium constant is not changed when the concentration of the reactants is increased. The relative concentrations of the reactants and products in that case adjust until they achieve the value of $K$. The value of the equilibrium constant is affected only by temperature.

**Think about It**

The value of the reaction quotient $Q$ decreases below the value of $K$ when reactants are added to a system previously at equilibrium, and the reaction shifts to the right.

14.66. **Collect and Organize**

Given that adding reactants shifts a reaction to the right, we are to determine how adding a reactant to a reaction mixture affects the rates of the forward and reverse reactions.

**Analyze**

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. For the reaction $A \rightarrow B$, the forward and reverse rate expressions are

$$\text{Rate}_f = k_f[A]$$

$$\text{Rate}_r = k_r[B]$$
Solve
When a reactant is first added to a reaction mixture at equilibrium, the forward rate will increase in relation to the reverse rate because we have increased the concentration of A in the rate equation, thereby increasing rate_f. As more product B is formed, the rate, increases as rate_f decreases as A is used up in the reaction. Eventually, rate_f = rate_r and the reaction again reaches equilibrium.

Think about it
Be sure to remember that it is the overall rate_f that is equal to rate_r at equilibrium. It is not true that the rate constants, k_f and k_r, are equal.

14.67. Collect and Organize
Given that the K for the binding of CO to hemoglobin is larger than that for the binding of O_2 to hemoglobin, we are to explain how the treatment of CO poisoning by administering pure O_2 to a patient works.

Analyze
By giving a patient pure O_2 to breathe, we increase the partial pressure of O_2 to which the hemoglobin in the patient’s blood is exposed. This oxygen can displace the CO bound to the hemoglobin through application of Le Châtelier’s principle.

Solve
Combining the two equations, we can write the expression for the displacement of CO bound to hemoglobin by O_2:

\[
\text{Hb(CO)}_4 \rightleftharpoons \text{Hb} + 4 \text{ CO(g)}
\]

\[
\text{Hb} + 4 \text{O}_2(g) \rightleftharpoons \text{Hb(O}_2)_4
\]

\[
\text{Hb(CO)}_4 + 4 \text{O}_2(g) \rightleftharpoons \text{Hb(O}_2)_4 + 4 \text{CO(g)}
\]

As the concentration of O_2 increases, the reaction shifts to the right and the CO on the hemoglobin is displaced.

Think about it
If we were given the values of the equilibrium constants for the reactions, we could calculate the new equilibrium constant for the overall reaction.

14.68. Collect and Organize
We consider the effect of atmospheric pressure on the value of K_p for the reaction

\[
2 \text{NO}_2(g) \rightleftharpoons \text{N}_2 \text{O}_4(g)
\]

Analyze
Even though Los Angeles and Denver have different atmospheric pressures, the reaction will not be affected, because the concentrations or partial pressures of the reactions are assumed to be the same.

Solve
A lower pressure in Denver than in Los Angeles at the same temperature does not change the value of K_p. Only temperature affects the value of the equilibrium constant.

Think about it
As we will see later in the chapter, the value of K_p is dependent on the value of the free energy, as shown by the equation \( \Delta G^\circ = -RT \ln K \). The free energy is affected by temperature, as shown by \( \Delta G^\circ = \Delta H^\circ -T\Delta S^\circ \), and so truly the only parameter that affects K is the temperature.

14.69. Collect and Organize
We are to interpret Henry’s law through Le Châtelier’s principle.
Analyze
The dissolution of a gas (let’s use oxygen in this example) in a liquid (let’s use water) can be written as a chemical equation:

\[ \text{O}_2(g) \rightleftharpoons \text{O}_2(aq) \]

Solve
According to Le Châtelier’s principle, an increase in the partial pressure (or concentration) of \( \text{O}_2 \) above the water shifts the equilibrium to the right so that more oxygen becomes dissolved in the water. This is consistent with Henry’s law.

Think about It
The solubilities of different gases in a liquid are different from each other, but all gases are more soluble in a liquid when present at higher partial pressures.

Collect and Organize
We are to explain why adding an inert gas to a reaction mixture does not change the position of equilibrium for the following reaction:

\[ 2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g) \]

Analyze
The equilibrium concentrations of reactants and products are expressed by the equilibrium constant equation:

\[ K_p = \frac{\left( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2}{\frac{P_{\text{O}_2}}{P_{\text{CO}}}} \]

Solve
Adding an inert gas to a reaction at equilibrium does not change the relative partial pressures of the reactant gases. The partial pressure of the inert gas does not appear in the equilibrium constant expression, and so the position of the equilibrium is unaffected.

\[ 2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g) \]

\[ P_{\text{total}} = 0.9 \]
\[ P_{\text{CO}} = 0.6 \]
\[ P_{\text{O}_2} = 0.3 \]

\[ P_{\text{total}} = 0.6 \]
\[ P_{\text{CO}_2} = 0.6 \]
Chapter 14

Think about It
In this equilibrium mixture, adding either CO or O₂ shifts the equilibrium to the right, whereas adding CO₂ shifts the equilibrium to the left.

14.71. Collect and Organize
Of four reactions, we are to determine which will shift its equilibrium to form more products when the mixture is compressed to half its original volume.

Analyze
Decreasing the volume by half doubles the partial pressures of all the gaseous reactants and products in the reactions. This would cause a shift in the position of the equilibrium toward the side of the reaction with the fewer number of moles of gas.

Solve
(a) This equilibrium shifts to the left, forming more reactants.
(b) This equilibrium shifts to the right, forming more products.
(c) This equilibrium shifts neither to the left nor to the right, as the number of moles of gas is the same on both sides of the equation.
(d) This equilibrium shifts to the right, forming more products.
Reactions (b) and (d) will form more products when the volume of the mixture is decreased by half.

Think about It
The opposite shifts occur in the position of the equilibrium when the volumes of the reaction mixtures are increased.

14.72. Collect and Organize
Of four reactions, we are to determine which will shift its equilibrium to form more products when the volume of the reaction mixture is doubled.

Analyze
Doubling the volume of a reaction will decrease the pressure, which causes the equilibrium to shift toward the side of the reaction that has the greater number of moles of gas.

Solve
(a) This equilibrium will shift to the left, forming more reactants.
(b) This equilibrium will not change.
(c) This equilibrium will shift to the right, forming more products.
(d) This equilibrium will shift to the right, forming more products.
Reactions (c) and (d) will form more products when the volume of the reaction mixture at equilibrium is increased.
**Think about It**
The opposite shifts in equilibrium occur if the volume is decreased to increase the pressure, which favors the side of the reaction with the fewer numbers of moles of gas.

14.73. **Collect and Organize**
We are to predict the effect on the position of the equilibrium

\[ 2 \text{O}_3(g) \rightleftharpoons 3 \text{O}_2(g) \]

with various changes in concentration and volume.

**Analyze**
Increasing the concentration of a reactant shifts the equilibrium to the right, whereas increasing the concentration of a product shifts the equilibrium to the left. An increase in volume decreases the pressure and shifts the equilibrium toward the side of the reaction with the greater moles of gas.

**Solve**
(a) Increasing the concentration of the reactant, \( \text{O}_3 \), shifts the equilibrium to the right, increasing the concentration of the product, \( \text{O}_2 \).
(b) Increasing the concentration of the product, \( \text{O}_2 \), shifts the equilibrium to the left, increasing the concentration of the reactant, \( \text{O}_3 \).
(c) Decreasing the volume of the reaction to 1/10 its original volume shifts the equilibrium to the left, increasing the concentration of the reactant, \( \text{O}_3 \).

**Think about It**
Adding \( \text{O}_2 \) and decreasing the volume cause the same shift in the position of the equilibrium.

14.74. **Collect and Organize**
We are to predict the effect on the position of the equilibrium

\[ 2 \text{NO}_2(g) \rightleftharpoons \text{NO}(g) + \text{NO}_3(g) \]

with various changes in concentration and volume.

**Analyze**
Increasing the concentration of a reactant shifts the equilibrium to the right, whereas increasing the concentration of a product shifts the equilibrium to the left. An increase in volume decreases the pressure and shifts the equilibrium toward the side of the reaction with the greater moles of gas.

**Solve**
(a) Increasing the concentration of the product, \( \text{NO} \), shifts the equilibrium to the left.
(b) Increasing the concentration of the reactant, \( \text{NO}_2 \), shifts the equilibrium to the right.
(c) Because the moles of gaseous products equal the moles of gaseous reactants, increasing the volume of the reaction has no effect on the position of the equilibrium.

**Think about It**
Increasing the concentration of \( \text{NO}_3 \) has the same effect on the equilibrium as increasing the concentration of \( \text{NO} \).

14.75. **Collect and Organize**
We are to determine how decreasing the partial pressure of \( \text{O}_2 \) affects the equilibrium

\[ 2 \text{SO}_2(g)+\text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g) \]

**Analyze**
According to Le Châtelier’s principle, increasing the partial pressure or concentration of a reactant shifts the equilibrium to the right. Decreasing the partial pressure of a reactant, then, shifts the equilibrium to the left.
Solve
Decreasing the partial pressure of O₂ in this reaction shifts the equilibrium to the left.

Think about It
At equilibrium, then, we have less SO₃ product when we reduce the partial pressure of O₂ in the reaction mixture.

14.76. Collect and Organize
We are asked to predict how the concentrations of H₂, Cl₂, and HCl in the equilibrium
\[ \text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{HCl}(g) \]
will be affected if the equilibrium constant for the reaction of ammonia with hydrochloric acid
\[ \text{NH}_3(g) + \text{HCl}(g) \rightleftharpoons \text{NH}_4\text{Cl}(s) \]
is much higher than that of the first reaction.

Analyze
If the \( K \) for the reaction of NH₃ with HCl is much larger than that of H₂ with Cl₂, then adding NH₃ to a reaction mixture of H₂, Cl₂, and HCl will substantially remove HCl from that equilibrium mixture.

Solve
When NH₃ reacts with HCl to remove HCl from the equilibrium mixture, the reaction to form HCl will shift to the right. Because 2 mol of HCl is produced in the reaction of H₂ with Cl₂, the relative concentrations of H₂ and Cl₂ will decrease at half the rate at which HCl decreases.

Think about It
By removing a product of a reaction through using a large-\( K \) process, we can drive even a low-\( K \) process to completion.

14.77. Collect and Organize
For three processes at equilibrium, we are to determine which shows an increased yield of product C at increasing temperatures.

Analyze
Endothermic processes have heat as a reactant. When the temperature is raised for these reactions, the equilibrium shifts to the right, increasing the amount of product C formed.

Solve
Reaction (a) is the only endothermic process (\( \Delta H > 0 \)), so it is the only process for which the product yield increases with increasing temperature.

Think about It
Temperature changes do not affect the amount of product formed for reaction (b), for which \( \Delta H = 0 \).

14.78. Collect and Organize
For three processes at equilibrium, we are to determine which shows a decreased yield of product Z at increasing temperatures.

Analyze
Exothermic processes have heat as a product. When the temperature is raised for these reactions, the equilibrium shifts to the left, decreasing the amount of products formed.

Solve
Reaction (c) is the only exothermic process (\( \Delta H < 0 \)), so it is the only process for which the product yield decreases as the temperature of the reaction is raised.

Think about It
Temperature changes do not affect the amount of product formed for reaction (b), for which \( \Delta H = 0 \).
Chemical Equilibrium

14.79. **Collect and Organize**
We are to explain why equilibrium calculations are simpler when no product is present at the start of the reaction and when the value of the equilibrium constant, $K$, is very small.

**Analyze**
When no product is present, the reaction can only proceed to products; no reverse reaction can occur. When $K$ is very small, the reaction does not proceed very far to the right. The concentrations of products formed once the reaction achieves equilibrium are very small.

**Solve**
When no products are present at the beginning of a reaction, we know that, no matter what the value of the equilibrium constant, the reaction will proceed to the right, so the equilibrium expression for the reaction is

$$X + Y \rightleftharpoons Z$$

$$K = \frac{x}{([X] - x)([Y] - x)}$$

We do not have to determine the reaction quotient for this situation because $Q = 0 < K$.

When $K$ is very small, the amount of reactants transformed into products is small, and so at equilibrium the concentration of the reactants is approximately equal to the initial concentrations. This means that the approximation

$$K = \frac{x}{([X] - x)([Y] - x)} = \frac{x}{([X])([Y])}$$

for the reaction

$$X + Y \rightleftharpoons Z$$

is valid. This makes our calculations easier and avoids having to use the quadratic equation.

**Think about It**
The assumption is considered valid if $x < 5\%$ for the value of both A and B.

14.80. **Collect and Organize**
For the reaction of 2 mol NO with 1 mol O₂ to give 2 mol NO₂, we are to determine whether the quadratic equation could be used to solve for $[\text{NO}_2]_\text{eq}$.

**Analyze**
The equilibrium constant expression for this reaction is

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

If $[\text{NO}_2]_i = A$, $[\text{NO}]_i = B$, and $[\text{O}_2]_i = C$, the RICE table for this equilibrium would be

<table>
<thead>
<tr>
<th>Reaction</th>
<th>2 NO(g)</th>
<th>+</th>
<th>O₂(g)</th>
<th>⇄</th>
<th>NO₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>B</td>
<td>C</td>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Change</td>
<td>-2x</td>
<td>+x</td>
<td></td>
<td>+2x</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>B - 2x</td>
<td>C + x</td>
<td></td>
<td>A + 2x</td>
<td></td>
</tr>
</tbody>
</table>

and the equilibrium constant expression would be

$$K_c = \frac{[A + 2x]^2}{[B - 2x]^2[C - x]}$$

**Solve**
No, this equilibrium constant expression would require us to use a cubic equation to solve for $[\text{NO}_2]$. 
Think about It
If the equilibrium constant is very small, however, the following assumption might be possible, which would allow us to use the quadratic equation to solve for $[\text{NO}_2]$.

$$K_c = \frac{[\text{A}^2 + 2\text{x}]^2}{[\text{B} - 2\text{x}]^2[C - \text{x}]} = \frac{[\text{A} + 2\text{x}]^2}{[\text{B}]^2[C]}$$

14.81. Collect and Organize
For the decomposition of $\text{PCl}_5$ to $\text{PCl}_3$ and $\text{Cl}_2$ ($K_p = 23.6$ at 500 K), we are to calculate the equilibrium partial pressures given the initial partial pressures of $\text{PCl}_5$ and $\text{PCl}_3$. We are also to determine how the concentration of $\text{PCl}_3$ and $\text{PCl}_5$ change when more $\text{Cl}_2$ is added to the system already at equilibrium.

Analyze
(a) To calculate the partial pressures of all the species present, we set up a RICE table. Because the initial partial pressure of $\text{Cl}_2$ is 0.0 atm, we know that the reaction proceeds to the right to attain equilibrium.
(b) To determine how the equilibrium shifts when $\text{Cl}_2$ is added, we apply Le Châtelier’s principle.

Solve
(a)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\text{PCl}_5(g)$</th>
<th>$\text{PCl}_3(g)$</th>
<th>$\text{Cl}_2(g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.560 atm</td>
<td>0.500 atm</td>
<td>0.00 atm</td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.560 $-x$</td>
<td>0.500 $+x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

After placing these values into the equilibrium constant expression, we can solve for $x$ by using the quadratic formula:

$$23.6 = \frac{(0.500 + x)(x)}{(0.560 - x)}$$

$$x^2 + 24.1x - 13.216 = 0$$

$$x = 0.536 \text{ or } -24.6$$

Because $0.500 + x$ would be negative if $x = -24.6$, the actual root for this problem is $x = 0.536$. The equilibrium partial pressures of $\text{PCl}_5$, $\text{PCl}_3$, and $\text{Cl}_2$ are

- $P_{\text{PCl}_3} = 0.560 - 0.536 = 0.024$ atm
- $P_{\text{PCl}_5} = 0.500 + 0.536 = 1.036$ atm
- $P_{\text{Cl}_2} = 0.536$ atm

(b) When the partial pressure of $\text{Cl}_2$ is increased, the partial pressure (or concentration) of $\text{PCl}_3$ decreases and the partial pressure of $\text{PCl}_5$ increases.

Think about It
Because $K > 1$, the products of this reaction are favored.

14.82. Collect and Organize
For an initial partial pressure of $\text{NO}_2$ of 0.900 atm in the reaction

$$2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$$

for which $K_p = 4$ at 298 K, we are to calculate the partial pressures of $\text{NO}_2$ and $\text{N}_2\text{O}_4$ at equilibrium.
Chemical Equilibrium

Analyze
To solve this problem, we need to set up a RICE table. Because no initial partial pressure of N₂O₄ is given, we assume that it is initially 0.000 atm. The equilibrium constant expression for this reaction is

$$K_p = \frac{P_{N_2O_4}}{P_{NO_2}}$$

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>2 NO₂(g) ⇌ N₂O₄(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_NO₂</td>
<td>0.900 atm</td>
</tr>
<tr>
<td>P_N₂O₄</td>
<td>0.000 atm</td>
</tr>
</tbody>
</table>

Initial

<table>
<thead>
<tr>
<th>Change</th>
<th>-2x</th>
<th>+x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium</td>
<td>0.900 − 2x</td>
<td>x</td>
</tr>
</tbody>
</table>

After placing these values into the equilibrium constant expression, we can solve for $x$ by using the quadratic formula:

$$4 = \frac{x}{(0.900 - 2x)^2}$$

$$4 = \frac{x}{0.81 - 3.6x + 4x^2}$$

$$16x^2 - 15.4x + 3.24 = 0$$

$x = 0.652$ or $0.311$

Because $0.900 - 2x$ would be negative if $x = 0.652$, the actual root for this problem is $x = 0.311$. The equilibrium partial pressures of NO₂ and N₂O₄ are

- $P_{NO_2} = 0.900 - 2x = 0.278$ atm
- $P_{N_2O_4} = x = 0.311$ atm

Think about It
Checking our results should give the value of the equilibrium constant:

$$K_p = \frac{0.311}{(0.278)^2} = 4.0$$

14.83. Collect and Organize
For the initial concentrations of H₂O and Cl₂O as 0.00432 M in the equilibrium reaction

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2 HOCl(g)$$

where $K_c = 0.0900$ at 25°C, we are to calculate the equilibrium concentrations of H₂O, Cl₂O, and HOCl.

Analyze
We first set up a RICE table to solve this problem. We assume here that the initial concentration of HOCl = 0.00 M. The equilibrium constant expression for this reaction is

$$K_c = \frac{[HOCl]^2}{[H_2O][Cl_2O]}$$

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>H₂O(g)</th>
<th>Cl₂O(g)</th>
<th>HOCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.00432 M</td>
<td>0.00432 M</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>−x</td>
<td>−x</td>
<td>+2x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.00432 − x</td>
<td>0.00432 − x</td>
<td>2x</td>
</tr>
</tbody>
</table>
After placing these values into the equilibrium constant expression, we can solve for \( x \) by taking the square root of both sides:

\[
0.0900 = \frac{(2x)^2}{(0.00432 - x)^2} \\
0.300 = \frac{2x}{0.00432 - x} \\
1.296 \times 10^{-3} - 0.30x = 2x
\]

\[x = 5.63 \times 10^{-4}\]

The concentration of all the gases at equilibrium are

\[[\text{H}_2\text{O}] = [\text{Cl}_2\text{O}] = 0.00432 - x = 3.76 \times 10^{-3} \text{ M}\]

\[[\text{HOCl}] = 2x = 1.13 \times 10^{-3} \text{ M}\]

**Think about It**

This reaction, with its equilibrium constant less than 1, favors reactants over product at equilibrium.

14.84. **Collect and Organize**

For an initial partial pressure of \( \text{N}_2 \) of 0.900 atm and of \( \text{H}_2 \) of 0.500 atm, we are to determine the equilibrium partial pressure of \( \text{NH}_3 \) given that \( K_p = 4.3 \times 10^{-4} \) at 648 K for the reaction

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

**Analyze**

To solve this problem, we first need to set up a RICE table. Because no initial partial pressure of \( \text{NH}_3 \) is given, we assume that it is initially 0.000 atm. The equilibrium constant expression for this reaction is

\[K_p = \frac{(p_{\text{NH}_3})^2}{(p_{\text{H}_2})^3(p_{\text{N}_2})}\]

**Solve**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 \text{ H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{ NH}_3(\text{g})</td>
<td>( P_{\text{H}_2} )</td>
<td>( -3x )</td>
<td>( 0.500 - 3x )</td>
</tr>
<tr>
<td></td>
<td>( P_{\text{N}_2} )</td>
<td>( -x )</td>
<td>( 0.900 - x )</td>
</tr>
<tr>
<td></td>
<td>( P_{\text{NH}_3} )</td>
<td>( +2x )</td>
<td>( 2x )</td>
</tr>
</tbody>
</table>

After placing these values into the equilibrium constant expression, we can make simplifying assumptions:

\[4.3 \times 10^{-4} = \frac{(2x)^2}{(0.500 - 3x)^3(0.900 - x)^2} = \frac{(2x)^2}{(0.500)^3(0.900)^2}\]

\[x = 3.48 \times 10^{-3}\]

Checking the assumptions shows that they are both valid (less than 5%).

\[
3 \times 3.48 \times 10^{-3} \times 100 = 2.1\% \quad \text{and} \quad \frac{3.48 \times 10^{-3}}{0.900} \times 100 = 0.4%\]

The partial pressure of ammonia at equilibrium in this reaction mixture is \( 2x = 6.96 \times 10^{-3} \text{ M} \).

**Think about It**

We could expand the equilibrium constant expression to give a cubic equation and solve, but making the simplifying assumptions here helps us to solve the problem more quickly. Remember to always check any simplifying assumptions you make against the 5% rule.
14.85. **Collect and Organize**

Given \( K_p = 2 \times 10^6 \) at 25°C for the reaction of 1 mol of NO with \( \frac{1}{2} \) mol of O\(_2\) to give 1 mol of NO\(_2\), we are to calculate the equilibrium ratio of the partial pressure of NO\(_2\) to that of NO in air, where the partial pressure of oxygen is 0.21 atm.

**Analyze**

The \( K_p \) expression for this reaction is

\[
K_p = \frac{P_{NO_2}}{P_{NO} \times (P_{O_2})^{1/2}}
\]

**Solve**

When \( P_{O_2} = 0.21 \) atm,

\[
K_p = \frac{P_{NO_2}}{P_{NO} \times (0.21)^{1/2}} = 2 \times 10^6
\]

Rearranging this equation to solve for the ratio of the partial pressure of NO\(_2\) to the partial pressure of NO gives

\[
\frac{P_{NO_2}}{P_{NO}} = 2 \times 10^6 \times (0.21)^{1/2} = 9 \times 10^5
\]

**Think about It**

The high value of \( K \) indicates that the product NO\(_2\) is highly favored. This is consistent with the high value we calculated for the ratio of the partial pressures.

14.86. **Collect and Organize**

For the equilibrium describing the reaction of C with H\(_2\)O to give CO and H\(_2\), we are to calculate the equilibrium partial pressures when \( P_{H_2O} = 0.442 \) atm, \( P_{CO} = 5.0 \) atm, and \( K_c = 3.0 \times 10^{-2} \) at 1000°C. We are then to recalculate these pressures when the partial pressures of CO and H\(_2\) are increased by 0.075 atm.

**Analyze**

Because we are working with partial pressures in the equilibrium constant expression, we must convert \( K_c \) into \( K_p \). In the reaction, \( \Delta n = 1 \).

\[
K_p = K_c (RT)^{\Delta n} = 3.0 \times 10^{-2} \times \left( \frac{0.08206 \text{ L·atm}}{\text{mol·K} \times 1273 \text{ K}} \right)^1 = 3.13
\]

For each part of the problem we set up a RICE table. The equilibrium reaction is

\[
C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)
\]

Carbon is a pure solid and does not show up in the equilibrium constant expression:

\[
K_p = \frac{P_{CO} \times P_{H_2}}{P_{H_2O}}
\]

**Solve**

(a)

\[
\begin{array}{c|c|c|c}
\text{Reaction} & P_{H_2O} & P_{CO} & P_{H_2} \\
\hline
\text{Initial} & 0.442 \text{ atm} & 5.0 \text{ atm} & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equilibrium} & 0.442 - x & 5.0 + x & x \\
\end{array}
\]

After placing these values into the equilibrium constant expression, we can solve for \( x \) by using the quadratic formula:
The value of $x = -8.30$ would give negative partial pressures for CO and H$_2$, so $x = 0.167$. The partial pressures of the gases at equilibrium are

$P_{H_2O} = 0.442 - x = 0.275$ atm

$P_{CO} = 5.0 + x = 5.17$ atm, or 5.2 atm

$P_{H_2} = x = 0.167$ atm

(b)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$</th>
<th>$P_{H_2O}$</th>
<th>$P_{CO}$</th>
<th>$P_{H_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium Mixture</td>
<td></td>
<td>0.275 atm</td>
<td>5.17 atm</td>
<td>0.167 atm</td>
</tr>
<tr>
<td>Increase</td>
<td></td>
<td>+0.075 atm</td>
<td>5.245 atm</td>
<td>+0.075 atm</td>
</tr>
<tr>
<td>New Initial</td>
<td></td>
<td>0.275 atm</td>
<td>5.245 atm</td>
<td>0.242 atm</td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td>+x</td>
<td>-x</td>
<td>-x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td>0.275 + x</td>
<td>5.245 - x</td>
<td>0.242 - x</td>
</tr>
</tbody>
</table>

The equilibrium shifts to the left as predicted by Le Châtelier’s principle and confirmed by comparing $Q$ versus $K$.

$Q = \frac{0.242 \times 5.245}{0.275} = 4.62$

After placing these values into the equilibrium constant expression, we can make the simplifying assumption that $x$ is small with respect to 5.245:

$3.13 = \frac{(5.245 - x)(0.242 - x)}{(0.275 + x)} = \frac{(5.245)(0.242 - x)}{(0.275 + x)}$

$8.375x = 0.40854$

$x = 0.0488$

Checking our simplifying assumption shows that it is valid:

$\frac{0.0488 \times 100}{5.245} = 0.9%$

The partial pressures of the gases at equilibrium are

$P_{H_2O} = 0.275 + x = 0.324$ atm

$P_{CO} = 5.245 - x = 5.20$ atm

$P_{H_2} = 0.242 - x = 0.193$ atm

Think about It

Checking our results should give a value close to 3.13, the equilibrium constant value.

For part a: $\frac{5.17 \times 0.167}{0.275} = 3.14$

For part b: $\frac{5.20 \times 0.193}{0.324} = 3.10$

14.87. Collect and Organize

Given that $K_p = 1.5$ at 700°C, we are to calculate $P_{CO_2}$ and $P_{CO}$ at equilibrium for the reaction

$CO_2(g) + C(s) \rightleftharpoons 2 CO(g)$

where the initial partial pressures of CO$_2$ and CO are 5.0 atm and 0.0 atm, respectively.
Analyze
Because carbon is a pure solid, it does not appear in the equilibrium constant expression:

\[ K_p = \frac{(P_{CO})^2}{P_{CO_2}} \]

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CO₂(g) + C(s) ⇌ 2 CO(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_{CO₂}</td>
<td>P_{CO}</td>
</tr>
<tr>
<td>Initial</td>
<td>5.0 atm</td>
</tr>
<tr>
<td>Change</td>
<td>−x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>5.0 − x</td>
</tr>
</tbody>
</table>

After placing these values into the equilibrium constant expression, we can solve for \( x \) by using the quadratic formula:

\[ 1.5 = \frac{(2x)^2}{(5.0 − x)} \]

\[ 4x^2 + 1.5x − 7.5 = 0 \]

\[ x = 1.20 \text{ or } −1.57 \]

The value of \( x = −1.57 \) would give a negative partial pressure for CO, so \( x = 1.20 \). The partial pressures of the gases at equilibrium are

\[ P_{CO} = 2x = 2.4 \text{ atm} \]
\[ P_{CO_2} = 5.0 − x = 3.8 \text{ atm} \]

Think about It
Checking our results should give a value close to 1.5, the equilibrium constant value:

\[ \frac{(2.4)^2}{3.8} = 1.5 \]

14.88. Collect and Organize
Given an equilibrium partial pressure for H₂S of 0.355 atm in the reaction

\[ \text{NH}_4\text{SH(g)} \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S(g)} \]

with \( K_p = 0.126 \) at 24°C, we are to determine the equilibrium partial pressure of NH₃.

Analyze
Because NH₄SH is a solid, it does not appear in the equilibrium constant expression:

\[ K_p = \frac{(P_{NH_3})}{(P_{H_2S})} \]

We are given the values of \( K_p \) and \( P_{H_2S} \) to substitute into the equation to solve for \( P_{NH_3} \).

Solve

\[ P_{NH_3} = \frac{K_p}{P_{H_2S}} = \frac{0.126}{0.355} = 0.355 \text{ atm} \]

Think about It
Because the equilibrium partial pressures of ammonia and hydrogen sulfide in the reaction mixture are equal, we can deduce from their 1:1 stoichiometry in the balanced equation that the initial reaction mixture contained only pure NH₄SH, which was then allowed to decompose in the reaction vessel to give equal amounts of NH₃ and H₂S.
14.89. Collect and Organize
For the decomposition of NO₂ to NO and O₂ when \( P_{O_2} = 0.136 \text{ atm} \) at equilibrium, we are asked to calculate the partial pressures of NO and NO₂ at equilibrium at 1000 K, where \( K_p = 158 \), and to calculate the total pressure in the flask at equilibrium.

Analyze
(a) To calculate the partial pressures of NO and NO₂, we set up a RICE table, where we start with pure NO₂ \((A)\) and end with \( P_{O_2} = 0.136 \text{ atm} = x \) at equilibrium.
(b) The total pressure is
\[
P_t = P_{NO_2} + P_{NO} + P_{O_2}
\]

Solve
(a) Reaction
\[
2 \text{ NO}_2(g) \rightleftharpoons 2 \text{ NO}(g) + \text{ O}_2(g)
\]

<table>
<thead>
<tr>
<th></th>
<th>( P_{NO_2} )</th>
<th>( P_{NO} )</th>
<th>( P_{O_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>( A ) atm</td>
<td>0.00 atm</td>
<td>0.00 atm</td>
</tr>
<tr>
<td>Change</td>
<td>(-2x)</td>
<td>(+2x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>( A - 2x)</td>
<td>(2x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

We know that at equilibrium \( x = 0.136 \text{ atm} \), so
\[
K_p = 158 = \frac{(P_{NO})^2 (P_{O_2})}{(P_{NO_2})^2} = \frac{(2x)^2 (x)}{(P_{NO_2})^2} = \frac{(0.272)^2 (0.136)}{(P_{NO_2})^2}
\]
\[
(P_{NO_2})^2 = \frac{(0.272)^2 \times (0.136)}{158} = 6.37 \times 10^{-5}
\]
\[
P_{NO_2} = (6.37 \times 10^{-5})^{1/2} = 7.98 \times 10^{-3} \text{ atm}
\]
At equilibrium,
\[
P_{NO} = 2x = 0.272 \text{ atm}
\]
\[
P_{O_2} = x = 0.136 \text{ atm}
\]
\[
P_{NO_2} = 7.98 \times 10^{-3} \text{ atm}
\]
(b) \( P_t = 7.98 \times 10^{-3} \text{ atm} + 0.272 \text{ atm} + 0.136 \text{ atm} = 0.416 \text{ atm} \)

Think about It
The amount of NO₂ initially present can also be calculated:
\( A - 2x = 7.98 \times 10^{-3} \text{ atm} \)
Because \( x = 0.136 \text{ atm} \),
\[A = 7.98 \times 10^{-3} + 2 \times 0.136 = 0.280 \text{ atm} \]

14.90. Collect and Organize
Given that \( K_p = 7.69 \) at 830°C for the reaction
\[
2 \text{ SO}_3(g) \rightleftharpoons 2 \text{ SO}_2(g) + \text{ O}_2(g)
\]
in which SO₃ was initially the only compound present and given that the equilibrium partial pressure of SO₃ is 0.100 atm, we are to calculate the partial pressure of oxygen at equilibrium.

Analyze
Because we know that the reaction vessel initially contained only SO₃, we know that the initial partial pressures of the products (SO₂ and O₂) were 0.000 atm. We set up a RICE table describing this experiment, keeping in mind that at equilibrium the partial pressure of SO₃ is measured at 0.100 atm.
Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>(A \text{ atm} )</td>
</tr>
<tr>
<td>Change</td>
<td>(A - 2x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.100</td>
</tr>
</tbody>
</table>

where \(A\) is the partial pressure of \(\text{SO}_3\) originally present in the reaction vessel, so that \(A - 2x = 0.100 \text{ atm}\). All we need, however, are the equilibrium partial pressures for the equilibrium constant expression

\[
7.69 = \left(\frac{(2x)^2}{(0.100)^2}\right) \\
0.0769 = 4x^3 \\
x = 0.268
\]

The equilibrium partial pressure of oxygen is \(x = 0.268 \text{ atm}\).

Think about It

The initial partial pressure of \(\text{SO}_3\) in the experiment is \(A = 0.100 + 2x = 0.636 \text{ atm}\).

14.91. Collect and Organize

For the equilibrium reaction

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

the value of \(K_p\) is 0.050 at 2200°C. We are to calculate the partial pressures of \(\text{N}_2\), \(\text{O}_2\), and \(\text{NO}\) at equilibrium given initial partial pressures for these gases of 0.79 atm for \(\text{N}_2\), 0.21 atm for \(\text{O}_2\), and 0.00 atm for \(\text{NO}\).

Analyze

We set up a RICE table to solve this problem. The equilibrium constant expression for this reaction is

\[
K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})}
\]

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.79 atm</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.79 – (x)</td>
</tr>
</tbody>
</table>

After placing these values into the equilibrium constant expression, we can solve for \(x\) by using the quadratic formula:

\[
0.050 = \frac{(2x)^2}{(0.79 - x)(0.21 - x)} \\
0.050 = \frac{4x^2}{0.1659 - x + x^2} \\
3.95x^2 + 0.050x - 0.008295 = 0 \\
x = 0.03993 \text{ or } -0.05260
\]
The value of $x = -0.05260$ would give a negative partial pressure for NO, so $x = 0.03993$. The partial pressures of the gases at equilibrium are

\[
P_{O_2} = 0.21 - x = 0.17 \text{ atm} \\
P_{N_2} = 0.79 - x = 0.75 \text{ atm} \\
P_{NO} = 2x = 0.080 \text{ atm}
\]

**Think about It**
Using these equilibrium partial pressures, we can check our answers, which should give $K_p = 0.050$:

\[
\frac{(0.080)^2}{(0.75)(0.17)} = 0.050
\]

### 14.92. Collect and Organize
For the following reaction

\[
2 \text{NO}_2(g) \rightleftharpoons 2 \text{NO}(g) + \text{O}_2(g)
\]
the value of $K_p$ is $6.5 \times 10^{-6}$ at 450°C. We are to calculate the partial pressures of NO$_2$, NO, and O$_2$ at equilibrium if the initial pressure of NO$_2$ is 0.500 atm.

**Analyze**
We assume that the initial pressures of the other gases in the reaction are 0.000 atm in setting up the RICE table to solve this problem. The equilibrium constant expression for this reaction is

\[
K_p = \frac{(P_{NO})^2}{(P_{NO_2})^2}
\]

**Solve**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>2 NO$_2$(g) \rightleftharpoons 2 NO(g) + O$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>$P_{NO_2}$</td>
</tr>
<tr>
<td>Change</td>
<td>$-2x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.500 – 2x</td>
</tr>
</tbody>
</table>

Because the equilibrium constant is small, this reaction does not proceed very far to the right and we may be able to make a simplifying assumption. After placing these values into the equilibrium constant expression, we can solve for $x$:

\[
6.5 \times 10^{-6} = \frac{(2x)^2(x)}{(0.500 - 2x)^2} = \frac{(2x)^2(x)}{(0.500)^2}
\]

\[
x = 7.41 \times 10^{-3}
\]

Checking this assumption shows that it is valid:

\[
\frac{2 \times 7.41 \times 10^{-3}}{0.500} \times 100 = 3%
\]

The partial pressures of the gases at equilibrium are

\[
P_{NO_2} = 0.500 - 2x = 0.485 \text{ atm} \\
P_{NO} = 2x = 0.0148 \text{ atm} \\
P_{O_2} = x = 0.00741 \text{ atm}
\]

**Think about It**
Our results, which show only a very small amount of product gases being formed, are consistent with the small equilibrium constant for this reaction.
14.93. Collect and Organize
For the following reaction

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

the value of \( K_c \) is \( 2.2 \times 10^{-4} \) at 1400 K. We are to calculate the equilibrium concentration of \( \text{H}_2\text{S} \), given that the initial \( [\text{H}_2\text{S}] \) is 6.00 \( M \).

Analyze
We are told to assume that the initial concentrations of \( \text{H}_2 \) and \( \text{S}_2 \) are 0.00 \( M \). Because the equilibrium constant is small, we may be able to make a simplifying assumption. The equilibrium constant expression for this reaction is

\[ K_c = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2} \]

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>2 ( \text{H}_2\text{S}(g) )</th>
<th>( \rightleftharpoons )</th>
<th>2 ( \text{H}_2(g) ) + ( \text{S}_2(g) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>6.00 ( M )</td>
<td>0.00 ( M )</td>
<td>0.00 ( M )</td>
</tr>
<tr>
<td>Change</td>
<td>(-2x)</td>
<td>(+2x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>6.00 (-2x)</td>
<td>2(x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

Because the equilibrium constant is small, this reaction does not proceed very far to the right and we may be able to make a simplifying assumption. After placing these values into the equilibrium constant expression, we can solve for \( x \):

\[ 2.2 \times 10^{-4} = \frac{(2x)^2(x)}{(6.00 - 2x)^2} = \frac{(2x)^2(x)}{(6.00)^2} \]

\[ x = 0.126 \]

Checking this assumption shows that it is valid:

\[ \frac{2 \times 0.126}{6.00} \times 100 = 4\% \]

The equilibrium \( [\text{H}_2\text{S}] \) is \( 6.00 - 2x = 5.75 \) \( M \).

Think about It
Without the simplifying assumption, we would have to solve a cubic equation.

14.94. Collect and Organize
Given that \( K_c = 6.1 \times 10^{-3} \) at 25°C for the reaction

\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]

and that the equilibrium concentration of \( \text{NO}_2 \) is \( 2.2 \times 10^{-7} \) \( M \), we are to calculate the concentration of \( \text{N}_2\text{O}_4 \) in the air.

Analyze
The equilibrium constant expression for this reaction is

\[ K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \]

Because we are given the values of \( [\text{NO}_2] \) and \( K_c \), we need only solve for \( [\text{N}_2\text{O}_4] \).

Solve

\[ [\text{N}_2\text{O}_4] = \frac{[\text{NO}_2]}{K_c} = \frac{(2.2 \times 10^{-7})^2}{6.1 \times 10^{-3}} = 7.9 \times 10^{-12} \text{ } M \]
Think about It

The equilibrium constant for the reverse reaction would be

\[ K_{\text{reverse}} = \frac{\left[ \text{NO} \right]}{\left[ \text{NO}_2 \right]^2} = \frac{1}{K_c} = 160 \]

14.95. Collect and Organize

For the following reaction, \( K_c = 5.0 \) at 600 K:

\[ \text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \]

We are asked to calculate the partial pressures of the gases at equilibrium given that the initial partial pressures of CO and Cl\(_2\) are 0.265 atm and that of COCl\(_2\) is 0.000 atm.

Analyze

We have to first calculate \( K_p \) from \( K_c \) where \( \Delta n = -1 \):

\[ K_p = K_c (RT) = \frac{5.0}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}} \times 600 \text{ K} = 0.102 \]

We can set up a RICE table to solve for the equilibrium partial pressures of the gases.

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CO(g)</th>
<th>Cl(_2)(g)</th>
<th>COCl(_2)(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>–x</td>
<td>–x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.265 – x</td>
<td>0.265 – x</td>
<td>x</td>
</tr>
</tbody>
</table>

After placing these values into the equilibrium constant expression, we can solve for \( x \) by using the quadratic formula:

\[ 0.102 = \frac{x}{(0.265 - x)^2} \]

\[ 0.102 = \frac{x}{0.0702 - 0.530x + x^2} \]

\[ 0.102x^2 - 1.05406x + 0.00716 = 0 \]

\[ x = 10.33 \text{ or } 0.00680 \]

The value of \( x = 10.33 \) would give negative partial pressures for CO and Cl\(_2\), so \( x = 0.00680 \). The partial pressures of the gases at equilibrium are

\[ P_{\text{CO}} = P_{\text{Cl}_2} = 0.265 - x = 0.258 \text{ atm} \]

\[ P_{\text{COCl}_2} = x = 0.00680 \text{ atm} \]

Think about It

Checking our result, we get the value of \( K_p \):

\[ \frac{0.00680}{(0.258)^2} = 0.102 \]

14.96. Collect and Organize

For the reaction

\[ 2 \text{ CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ CO}_2(g) \]

\( K_c = 1.0 \) at 2000°C. We are to calculate the value of \([\text{CO}] / [\text{CO}_2] \) when \([\text{O}_2] \) at equilibrium is 0.0045 M.
Analyse
The $K_c$ expression for this reaction is

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

Rearranging this expression gives the desired ratio of concentrations:

$$\frac{[\text{CO}]^2}{[\text{CO}_2]^2} = \frac{1}{K_c \times [\text{O}_2]}$$

$$\frac{[\text{CO}]}{[\text{CO}_2]} = \sqrt{\frac{1}{K_c \times [\text{O}_2]}}$$

Solve

$$\frac{[\text{CO}]}{[\text{CO}_2]} = \sqrt{\frac{1}{1.0 \times 0.0045}} = 15$$

Think about it
The equilibrium constant for the reverse reaction would be $1/K_c = 1.0$.

14.97. Collect and Organize
We are to calculate the concentrations of all the gases at equilibrium for the reaction

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

given that the initial concentrations of all the gases are 0.050 M and that $K_c = 5.1$ at 700 K.

Analyse
The equilibrium constant expression for this reaction is

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

We have to use $Q$, the reaction quotient, to determine the direction in which the reaction goes to reach equilibrium:

$$Q = \frac{(0.050)(0.050)}{(0.050)(0.050)} = 1.0$$

$Q < K$, so the reaction proceeds to the right.

Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\text{CO}(g)$</th>
<th>$\text{H}_2\text{O}(g)$</th>
<th>$\rightleftharpoons$</th>
<th>$\text{CO}_2(g)$</th>
<th>$\text{H}_2(g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CO]</td>
<td>0.050 $M$</td>
<td>0.050 $M$</td>
<td></td>
<td>0.050 $M$</td>
<td>0.050 $M$</td>
</tr>
<tr>
<td>Change</td>
<td>$-x$</td>
<td>$-x$</td>
<td></td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.050 - $x$</td>
<td>0.050 - $x$</td>
<td>0.050 + $x$</td>
<td>0.050 + $x$</td>
<td></td>
</tr>
</tbody>
</table>

$$5.1 = \frac{(0.050 + x)^2}{(0.050 - x)^2}$$

Taking the square root of both sides:

$$2.258 = \frac{0.050 + x}{0.050 - x}$$

$$0.1129 - 2.258x = 0.050 + x$$

$$0.0629 = 3.258x$$

$$0.0193 = x$$
The concentrations of the gases at equilibrium are

\[
[\text{CO}] = [\text{H}_2\text{O}] = 0.050 - x = 0.031 \ M
\]
\[
[\text{CO}_2] = [\text{H}_2] = 0.050 + x = 0.069 \ M
\]

**Think about It**
We did not need to use the quadratic formula here because with the concentrations of the reactants equal to each other and the concentrations of the products equal to each other, we could simplify the math by taking the square root of both sides of the equation to solve for \(x\).

14.98. **Collect and Organize**
We are to calculate the concentrations of all the gases at equilibrium for the reaction

\[
\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g)
\]

given that the initial concentrations of \(\text{SO}_2\) and \(\text{NO}_2\) are 0.50 \(M\), the initial concentrations of \(\text{SO}_3\) and \(\text{NO}\) are 0.0050 \(M\), and \(K_c = 2.50\).

**Analyze**
The equilibrium constant expression for this reaction is

\[
K_c = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = 2.50
\]

We have to use \(Q\), the reaction quotient, to determine the direction in which the reaction goes to reach equilibrium:

\[
Q = \frac{(0.0050)(0.0050)}{(0.50)(0.50)} = 1.0 \times 10^{-4}
\]

\(Q < K\), so the reaction proceeds to the right.

**Solve**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\text{SO}_2(g))</th>
<th>+</th>
<th>(\text{NO}_2(g))</th>
<th>(\rightleftharpoons)</th>
<th>(\text{SO}_3(g))</th>
<th>+</th>
<th>(\text{NO}(g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.50 (M)</td>
<td></td>
<td>0.50 (M)</td>
<td>0.0050 (M)</td>
<td>0.0050 (M)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td></td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.50 (-x)</td>
<td>0.50 (-x)</td>
<td>0.0050 (+x)</td>
<td>0.0050 (+x)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
2.50 = \frac{(0.0050 + x)^2}{(0.50 - x)^2}
\]

\[
1.581 = \frac{(0.0050 + x)}{(0.50 - x)}
\]

\[
0.7905 - 1.581x = 0.0050 + x
\]

\[
0.7855 = 2.581x
\]

\[
0.30 = x
\]

The concentrations of the gases at equilibrium are

\[
[\text{SO}_2] = [\text{NO}_2] = 0.50 - x = 0.20 \ M
\]
\[
[\text{SO}_3] = [\text{NO}] = 0.0050 + x = 0.30 \ M
\]

**Think about It**
We did not need to use the quadratic formula here because with the concentrations of the reactants equal to each other and the concentrations of the products equal to each other, we could simplify the math by taking the square root of both sides of the equation to solve for \(x\).

14.99. **Collect and Organize**
We are to calculate the concentrations of all the gases at equilibrium for the reaction

\[
\text{NO}(g) + \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_3(g)
\]
given that the initial amounts of NO and NO₂ are 15 g and 69 g, respectively, contained in a 4.0 L flask. For this reaction at 25°C, \(K_p = 0.535\).

**Analyze**

The equilibrium constant expression for this reaction is

\[
K_c = \frac{[N_2O_3]}{[NO][NO_2]}
\]

We are given the mass of each reactant and can convert those masses to molar concentrations by using the molar mass of the reactants and the volume of the flask to give the initial concentration of the reactants for the RICE table. Because we are given the value of \(K_p\), we will have to calculate the value of \(K_c\) from \(K_p\) by using

\[
K_c = \frac{K_p}{(RT)^\Delta n}
\]

where \(\Delta n = -1\), \(R = 0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}\), and \(T = 298 \text{ K}\). Finally, the flask initially contains only reactants, so we know that the equilibrium will proceed from initial conditions to the right to form products.

**Solve**

The initial concentrations of the reactants are

\[
\begin{align*}
15 \text{ g NO} &\times \frac{1 \text{ mol}}{30.01 \text{ g}} \times \frac{1}{4.0 \text{ L}} = 0.125 \text{ M NO} \\
69 \text{ g NO}_2 &\times \frac{1 \text{ mol}}{46.01 \text{ g}} \times \frac{1}{4.0 \text{ L}} = 0.375 \text{ M NO}_2
\end{align*}
\]

The value of \(K_c\) is

\[
K_c = \frac{K_p}{(RT)^\Delta n} = \frac{0.535}{(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K} \times 298 \text{ K})^{-1}} = 13.08
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>NO(g)</th>
<th>+</th>
<th>NO₂(g)</th>
<th>⇌</th>
<th>N₂O₃(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.125 M</td>
<td></td>
<td>0.375 M</td>
<td></td>
<td>0.0 M</td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(-x)</td>
<td>(+x)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.125 (-x)</td>
<td>0.375 (-x)</td>
<td>(x)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
13.08 = \frac{x}{(0.125-x)(0.375-x)}
\]

\[
13.08 = \frac{x}{(0.046875-0.500x+x^2)}
\]

\[
0.613125 - 6.54x + 13.08x^2 = x
\]

\[
13.08x^2 - 7.54x + 0.613125 = 0
\]

\[
x = 0.09796
\]

The concentrations of the gases at equilibrium are

\[
[\text{NO}] = 0.125 - x = 0.027 \text{ M}
\]

\[
[\text{NO}_2] = 0.375 + x = 0.277 \text{ M}
\]

\[
[N_2O_3] = = x = 0.098 \text{ M}
\]

**Think about It**

This problem is multilayered in that we must realize at the start that \(K_c\) must be calculated from \(K_p\) and that we have to compute the concentrations in moles per liter of each reactant before using the RICE table.
14.100. **Collect and Organize**

For the decomposition reaction of HI into H₂ and I₂, we are to calculate the concentrations of all the gases at equilibrium

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

given that the initial amount of HI is 80.0 g and is contained in a 2.5 L chamber. For this reaction at 400°C, \(K_c = 0.0183\).

**Analyze**

The equilibrium constant expression for this reaction is

\[ K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \]

We are given the mass of the reactant and can convert that mass to the molar concentrations by using the molar mass of HI and the volume of the chamber to give the initial concentration of HI for the RICE table. The flask initially contains only HI as the reactant and no H₂ or I₂ as products, so we know that the equilibrium will proceed from the initial conditions to the right to form products.

**Solve**

The initial concentration of HI is

\[ \frac{80.0 \text{ g HI} \times \frac{1 \text{ mol}}{129.91 \text{ g}} \times \frac{1}{2.5 \text{ L}} = 0.250 \text{ M}}{0.250 \text{ M}} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>2 HI(g)</th>
<th>( \rightleftharpoons )</th>
<th>H₂(g)</th>
<th>+</th>
<th>I₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HI]</td>
<td>0.250 M</td>
<td></td>
<td>0.0 M</td>
<td>+</td>
<td>0.0 M</td>
</tr>
<tr>
<td>Change</td>
<td>-2x</td>
<td></td>
<td>+x</td>
<td>+</td>
<td>x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.250 – 2x</td>
<td></td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

\[ 0.0183 = \frac{x^2}{(0.250 – 2x)^2} \]

\[ 13.08 = \frac{x^2}{(0.0625 – x + 4x^2)} \]

\[ 0.9268x^2 + 0.0183x – 0.00114375 = 0 \]

\[ x = 0.02662 \]

The concentrations of the gases at equilibrium are

\[ [\text{HI}] = 0.250 – 2x = 0.198 \text{ M} \]

\[ [\text{H}_2] = [\text{I}_2] = x = 0.0226 \text{ M} \]

**Think about It**

We cannot make a simplifying assumption in solving this problem because the value of \(x\) that we get from the assumption is 13% compared to the 0.250 M it is subtracted from. Therefore, we must use the quadratic equation for this problem.

14.101. **Collect and Organize**

We are to relate the sign of \(\Delta G^*\) to the magnitude of \(K\).

**Analyze**

The equation relating \(\Delta G^*\) to \(K\) is

\[ \Delta G^* = -RT \ln K \]
Solve
Yes, the value of $\Delta G'$ is positive when $K < 1$. Because $\ln K$ is negative for $K < 1$ and because $\Delta G' = -RT \ln K$, the value of $\Delta G'$ is positive.

Think about It
This means that reactions with $K < 1$ are not spontaneous.

14.102. Collect and Organize
We are to explain why $K_p$ is used in the equation

$$\Delta G' = -RT \ln K$$

for reactions occurring in the gas phase, not $K_c$.

Analyze
If all the reactants and products are in the gas phase, the equilibrium constant can be expressed as $K_p$.

Solve
Because $\Delta G'$ is referenced to standard-state conditions and we can express gas pressures in their standard states, the equilibrium constant $K$ in gaseous reactions can be $K_p$.

Think about It
The equation relating Gibbs free energy and the equilibrium constant $K$ is powerful. We can calculate the value of $K$ by measuring $\Delta G$, or we can determine $\Delta G$ by measuring $K$.

14.103. Collect and Organize
If a reaction starts with 100% reactants, we are to determine in which direction the reaction shifts when it is spontaneous ($\Delta G' < 0$).

Analyze
The equation relating $\Delta G'$ to $K$ is

$$\Delta G' = -RT \ln K$$

Solve
When $\Delta G' < 0$, the $\ln K$ of the reaction is positive, giving $K > 1$. The reaction favors the formation of products, so the reaction will shift to the right.

Think about It
The reaction will proceed to the right until the mixture of reactants and products as expressed in the reaction quotient $Q$ matches the value of the equilibrium constant $K$.

14.104. Collect and Organize
If a reaction starts with 100% products, we are to determine in which direction the reaction shifts when it is spontaneous ($\Delta G' < 0$).
Analyze
The equation relating $\Delta G^\circ$ to $K$ is

$$\Delta G^\circ = -RT \ln K$$

Solve
The $\Delta G^\circ$ for a reaction is expressed for the forward reaction, and because this reaction is spontaneous we know that $K > 1$. This reaction favors product formation. However, $K$ would have to be infinite for the reaction to produce 100% products. Therefore, the reaction will shift slightly to the left to achieve equilibrium.

Think about It
For a reaction in which $\Delta G^\circ > 0$, the equilibrium lies farther to the left than for a reaction for which $\Delta G^\circ < 0$.

Think about It
For a reaction in which $\Delta G^\circ > 0$, the equilibrium lies farther to the left than for a reaction for which $\Delta G^\circ < 0$.

Collect and Organize
Given three reactions with associated $\Delta G^\circ$ values, we are asked to determine which reaction has the largest value of $K$ at 25°C.

Analyze
The equilibrium constant of a reaction is related to the Gibbs free energy through the equation

$$\Delta G^\circ = -RT \ln K$$

Rearranging this equation gives

$$\ln K = \frac{-\Delta G^\circ}{RT}$$

From this we see that the more negative the value of $\Delta G$, the larger $K$ will be.

Solve
Two of the reactions have negative values of $\Delta G^\circ$ and are spontaneous (b and c); they will have $K > 1$. The reaction with the more negative free energy (reaction c) has the largest equilibrium constant.

Think about It
The value of $K$ for reaction (c) is

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{27.9 \text{ kJ}}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K} \times 298 \text{ K}} = 11.26$$

$$K = e^{11.26} = 7.8 \times 10^4$$

Collect and Organize
Given the $\Delta G^\circ$ value for the reaction of $N_2O$ with $O_2$ as 68.9 kJ at 298 K, we are to calculate the value of the equilibrium constant.

Analyze
The equilibrium constant of a reaction is related to the Gibbs free energy through the equation

$$\Delta G^\circ = -RT \ln K$$

Rearranging this equation gives

$$\ln K = \frac{-\Delta G^\circ}{RT}$$
Solve

\[
\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-68.9 \times 10^3 \text{ J/mol N}_2\text{O}}{(8.314 \text{ J/mol} \cdot \text{K}) \times 298 \text{ K}} = -27.81
\]

\[
K = e^{-27.81} = 8.37 \times 10^{-13}
\]

Think about It

Because the free energy of this reaction is positive, the reaction is nonspontaneous and if starting from pure \(\text{N}_2\text{O}\), the reaction proceeds only slightly to the right to give products, as evidenced by its very small equilibrium constant.

14.107. Collect and Organize

For the balanced equilibrium reaction

\[
2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})
\]

for which \(K_p = 3.4\) at 1000 K, we are asked to calculate the enthalpy change of the reaction under standard conditions, to calculate the value of \(K_p\) at 298 K, and finally to calculate the free energy change for the reaction under standard conditions at 298 K to compare it with the value obtained using Appendix 4.

Analyze

(a) The enthalpy of the reaction under standard conditions may be calculated using the values for the enthalpy of formation for the reactants and products in Appendix 4.

\[
\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_{f,\text{products}}^\circ - \sum n \Delta H_{f,\text{reactants}}^\circ
\]

(b) We can calculate the value of the equilibrium constant at 298 K from the value of \(K\) at 1000 K and the enthalpy of the reaction through the equation

\[
\ln \left( \frac{K_{298}}{K_{1000}} \right) = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_{298}} - \frac{1}{T_{1000}} \right)
\]

(c) The value of the equilibrium constant at 298 from part b can be used to calculate the standard free energy of the reaction through

\[
\Delta G_{\text{rxn}}^\circ = -RT \ln K
\]

and the value of the free energy from values in Appendix 4 can be calculated through the following equation for comparison

\[
\Delta G_{\text{rxn}}^\circ = \sum n \Delta G_{f,\text{products}}^\circ - \sum n \Delta G_{f,\text{reactants}}^\circ
\]

Solve

(a) The enthalpy of the reaction under standard conditions is

\[
\Delta H_{\text{rxn}}^\circ = (2 \text{ mol SO}_3)(-395.7 \text{ kJ/mol}) - \left[ (2 \text{ mol SO}_2)(-296.8 \text{ kJ/mol}) + (1 \text{ mol O}_2)(0.0 \text{ kJ/mol}) \right]
\]

\[
\Delta H_{\text{rxn}}^\circ = -197.8 \text{ kJ}
\]

(b) The value of the equilibrium constant at 298 from the calculated value of the enthalpy in part a and from the value of \(K\) at 1000 K is

\[
\ln \left( \frac{K_{298}}{3.4} \right) = \frac{-(-197.8 \times 10^3 \text{ J/mol})}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{298 \text{ K}} - \frac{1}{1000 \text{ K}} \right) = 56.045
\]

\[
\left( \frac{K_{298}}{3.4} \right) = e^{56.045} = 2.188 \times 10^{24}
\]

\[
K_{298} = 7.4 \times 10^{24}
\]

(c) From the value of \(K\) at 298 K, we calculate the free energy at standard conditions:

\[
\Delta G^\circ = -(8.314 \text{ J/mol} \cdot \text{K}) \times (298 \text{ K}) \times \ln(7.4 \times 10^{24}) = -141.9 \text{ kJ/mol}
\]
From the standard free energy values in Appendix 4, the free energy at 298 K is

$$\Delta G_{\text{rxn}} = (2 \text{ mol SO}_3)(-371.1 \text{ kJ/mol}) - [(2 \text{ mol SO}_2)(-300.1 \text{ kJ/mol}) + (1 \text{ mol O}_2)(0.0 \text{ kJ/mol})]$$

$$\Delta G_{\text{rxn}} = -142.0 \text{ kJ}$$

These values are very close to each other.

**Think about It**

This reaction is exothermic, so it makes sense that the equilibrium constant is larger at 298 K than at 1000 K.

14.108. **Collect and Organize**

Given $$K_p = 0.534$$ for the reaction of H$_2$ with CO$_2$ to produce H$_2$O and CO at 700°C, we are to calculate the value of the equilibrium constant, $$K_p$$, at 298 K from the value of the enthalpy of the reaction under standard conditions, then calculate the value of free energy at 298 K from the equilibrium constant at 298 K and compare that answer to the calculated value of $$\Delta G^\circ$$ by using $$\Delta G_f^\circ$$ values from Appendix 4.

**Analyze**

(a) The enthalpy of the reaction under standard conditions may be calculated using the values for the enthalpy of formation for the reactants and products in Appendix 4.

$$\Delta H_{\text{rxn}} = \sum n \Delta H_f^{\text{products}} - \sum n \Delta H_f^{\text{reactants}}$$

We can then calculate the value of the equilibrium constant at 298 K from the value of $$K$$ at 700°C and the enthalpy of the reaction through the equation

$$\ln \left( \frac{K_2}{K_1} \right) = - \frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

(b) The value of the equilibrium constant at 298 K from part a can be used to calculate the standard free energy of the reaction through

$$\Delta G^\circ = -RT \ln K$$

and the value of the free energy from values in Appendix 4 can be calculated through the following equation for comparison:

$$\Delta G_{\text{rxn}} = \sum n \Delta G_f^{\text{products}} - \sum n \Delta G_f^{\text{reactants}}$$

**Solve**

(a) The enthalpy of the reaction under standard conditions is

$$\Delta H_{\text{rxn}} = [(1 \text{ mol H}_2\text{O})(-241.8 \text{ kJ/mol}) + (1 \text{ mol CO})(-110.5 \text{ kJ/mol})]$$

$$- [(1 \text{ mol H}_2)(0.0 \text{ kJ/mol}) + (1 \text{ mol CO}_2)(-393.5 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}} = 41.2 \text{ kJ}$$

The value of the equilibrium constant at 298 K from the calculated value of the enthalpy in part a and from the value of $$K$$ at 973 K (700°C) is

$$\ln \left( \frac{K_{298}}{0.534} \right) = - \frac{(41.2 \times 10^4 \text{ J/mol})}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{298 \text{ K}} - \frac{1}{973 \text{ K}} \right) = -11.54$$

$$\frac{K_{298}}{0.534} = e^{-11.54} = 9.77 \times 10^{-6}$$

$$K_{298} = 5.21 \times 10^{-6}$$

(c) From the value of $$K$$ at 298 K, we calculate the free energy at standard conditions:

$$\Delta G^\circ = -(8.314 \text{ J/mol} \cdot \text{K}) \times (298 \text{ K}) \times \ln(5.21 \times 10^{-6}) = 30.1 \text{ kJ/mol}$$
From the standard free energy values in Appendix 4, the free energy at 298 K is

\[ \Delta G^\circ_{\text{rxn}} = \left[ \begin{array}{c}
(1 \text{ mol H}_2\text{O}) \times (-137.2 \text{ kJ/mol}) + (1 \text{ mol CO}) \times (-228.6 \text{ kJ/mol}) \\
- \left( (1 \text{ mol H}_2) \times (0.0 \text{ kJ/mol}) + (1 \text{ mol CO}_2) \times (-394.4 \text{ kJ/mol}) \right)
\end{array} \right] \]

\[ \Delta G^\circ_{\text{rxn}} = 28.6 \text{ kJ} \]

These values are very close to each other.

**Think about It**
For this reaction, we can also calculate the entropy change from values in Appendix 4. From these values we see that \( \Delta S^\circ = 42.3 \text{ J/mol} \cdot \text{K} \). Thus, this reaction is endothermic but favored by entropy, so at high enough temperature the reaction becomes spontaneous.

14.109. **Collect and Organize**
In this problem we can add two equations to calculate \( \Delta G^\circ \) and \( K_p \) at 298 K for the reaction

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

**Analyze**
To obtain the overall reaction, we simply add the two reactions given and add their \( \Delta G^\circ \) values. We can calculate the value of \( K_c \) by using

\[ \Delta G^\circ = -RT \ln K \]

and from \( K_c \) we can calculate \( K_p \) by using

\[ K_p = K_c \left( RT \right)^{\Delta n} \]

where \( \Delta n \) for this reaction is \(-1\).

**Solve**
Adding the equations gives the overall equation and \( \Delta G^\circ \):

\[ \begin{align*}
\text{N}_2(g) + 2 \text{O}_2(g) & \rightleftharpoons 2 \text{NO}(g) \quad \Delta G^\circ = 173.2 \text{ kJ} \\
2 \text{NO}(g) + \text{O}_2(g) & \rightleftharpoons 2 \text{NO}_2(g) \quad \Delta G^\circ = -69.7 \text{ kJ} \\
\text{N}_2(g) + 2 \text{O}_2(g) & \rightleftharpoons 2 \text{NO}_2(g) \quad \Delta G^\circ = 103.5 \text{ kJ}
\end{align*} \]

Rearranging to calculate \( K_c \),

\[ \ln K = \frac{-103.5 \text{ kJ/mol}}{RT} = \frac{-103.5 \text{ kJ/mol}}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K} \times 298 \text{ K}} = -41.77 \]

\[ K = e^{-41.77} = 7.24 \times 10^{-19} \]

The value of \( K_p \) can now be calculated:

\[ K_p = 7.24 \times 10^{-19} \times \left[ (0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}) \times 298 \text{ K} \right]^{-1} = 2.96 \times 10^{-20} \]

**Think about It**
Because the free-energy change is large and positive, \( K \) is much less than 1 and the reactants are greatly favored over the product at equilibrium.

14.110. **Collect and Organize**
We can add three equations to calculate \( \Delta G^\circ \) and \( K_p \) at 500°C for the reaction

\[ 3 \text{NO}(g) \rightleftharpoons \text{N}_2\text{O}(g) + \text{NO}_2(g) \]

**Analyze**
In adding the equations, we might have to reverse one of the reactions, in which case we have to reverse the sign of \( \Delta G^\circ \) associated with that particular reaction. Combining equations gives us the overall \( \Delta G^\circ \), which gives \( K_p \) through the equation

\[ \Delta G^\circ = -RT \ln K_p \]
Solve
Adding the equations gives the overall $\Delta G_{\text{rxn}}^{\circ}$:

\[
\begin{align*}
2 \text{NO}(g) + \text{O}_2(g) &\rightleftharpoons 2 \text{NO}_2(g) \quad \Delta G^\circ = -69.7 \text{ kJ} \\
2 \text{NO}(g) + \text{N}_2(g) &\rightleftharpoons 2 \text{N}_2\text{O}(g) \quad \Delta G^\circ = 33.8 \text{ kJ} \\
2 \text{NO}(g) &\rightleftharpoons \text{N}_2(g) + \text{O}_2(g) \quad \Delta G^\circ = -173.2 \text{ kJ} \end{align*}
\]

Dividing by 2 gives the desired reaction:

\[
3 \text{NO}(g) \rightleftharpoons \text{N}_2\text{O}(g) + \text{NO}_2(g) \quad \Delta G^\circ = -104.55 \text{ kJ}
\]

The $K_p$ for this reaction is

\[
\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{-(-104.55 \text{ kJ/mol})}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K} \times 773 \text{ K}} = 16.27
\]

\[
K_p = e^{16.27} = 1.16 \times 10^7
\]

Think about It
Because $\Delta G^\circ$ is large and negative for the overall reaction, $K$ is much greater than 1 and the products are greatly favored over the reactants.

14.111. Collect and Organize
Using the relationship

\[
\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{RT} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

we can determine whether a reaction is endothermic or exothermic if the value of $K$ decreases with increasing $T$.

Analyze
In the equation, $K_2 < K_1$, so $\ln(K_2/K_1) < 0$ and $T_2 > T_1$, so $(1/T_2 - 1/T_1) < 0$.

Solve
For $\ln(K_2/K_1)$ to be negative when $(1/T_2 - 1/T_1)$ is also negative, the value of $\Delta H$ must be negative and the reaction must be exothermic.

Think about It
An endothermic reaction, by contrast, shows an increased $K$ with increasing $T$ because $\Delta H > 0$ and thus $\ln(K_2/K_1) > 0$, so $K_2/K_1 > 0$.

14.112. Collect and Organize
Given that the reaction of CO with O$_2$ to give CO$_2$ is exothermic, we are to determine whether $K_p$ increases or decreases with increasing temperature. We can use the relationship

\[
\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{RT} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

Analyze
In this equation $\Delta H$ and, for $T_2 > T_1$, the quantity $1/T_2 - 1/T_1$ are negative.

Solve
When both $\Delta H$ and $(1/T_2 - 1/T_1)$ are negative, $\ln(K_2/K_1)$ is also negative. This gives $K_2 < K_1$. The equilibrium constant decreases for exothermic reactions as the temperature is raised.
Think about It
For an endothermic reaction, however, the equilibrium constant increases as temperature increases.

14.113 Collect and Organize
Given that $K_p$ for the reaction of CO with $H_2O$ increases as the temperature decreases, we can use the relationship

$$\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

to determine whether the reaction is endothermic or exothermic.

Analyze
In the equation $K_2 > K_1$, so $\ln(K_2/K_1) > 0$. Because $T_2 < T_1$, $(1/T_2 - 1/T_1) > 0$.

Solve
For $\ln(K_2/K_1)$ to be positive when $(1/T_2 - 1/T_1)$ is also positive, $\Delta H^\circ$ must be negative and the reaction must be exothermic.

Think about It
An endothermic reaction, by contrast, shows a decreased $K$ with a decrease in temperature.

14.114 Collect and Organize
Given the equation

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$$

and that it is endothermic ($\Delta H^\circ = 206$ kJ), we are to predict whether the value of $K_p$ will increase, decrease, or stay the same as the temperature is raised.

Analyze
By Le Châtelier’s principle, when a reaction is endothermic, heat is a reactant in the chemical process. If we increase the amount of a reactant, we shift the equilibrium to the right.

Solve
Increasing the temperature shifts the equilibrium to the right, and so the value of the equilibrium constant increases.

Think about It
For an exothermic reaction, the opposite occurs: the value of the equilibrium constant decreases as the temperature of the reaction is raised.

14.115 Collect and Organize
Given $\Delta H^\circ = 180.6$ kJ and $K_c = 4.10 \times 10^{-4}$ for the conversion of $N_2$ and $O_2$ to NO at 2000°C, we are to calculate the value of $K_c$ at 25°C.

Analyze
The relationship between equilibrium constants at two different temperatures is given by

$$\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where $\Delta H^\circ$ is the enthalpy of the reaction (in joules per mole), $R$ is the gas constant (in joules per mole per degree kelvin), and $T_1$ and $T_2$ are the temperatures (in kelvins).
Solve

\[
\ln \left( \frac{4.1 \times 10^{-4}}{K_2} \right) = -\frac{8.06 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol K}} \left( \frac{1}{2273 \text{ K}} - \frac{1}{298 \text{ K}} \right)
\]

\[
\ln \left( \frac{4.1 \times 10^{-4}}{K_2} \right) = 63.337
\]

\[
4.1 \times 10^{-4} = e^{63.337} = 3.214 \times 10^{27}
\]

\[
K_2 = 1.3 \times 10^{-31}
\]

Think about It
As we would expect, the equilibrium constant for this endothermic reaction decreases as the reaction is cooled.

14.116. Collect and Organize
Given \( \Delta H^\circ = -92.2 \text{ kJ} \) and \( K_p = 41 \) for the reaction of \( \text{N}_2 \) and \( \text{H}_2 \) to give \( \text{NH}_3 \) at 400 K, we are to calculate the value of \( K_p \) at 700 K.

Analyze
The relationship between equilibrium constants at two different temperatures is given by

\[
\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

where \( \Delta H^\circ \) is the enthalpy of the reaction (in joules per mole), \( R \) is the gas constant (in joules per mole per degree kelvin), and \( T_1 \) and \( T_2 \) are the temperatures (in kelvins).

Solve

\[
\ln \left( \frac{41}{K_2} \right) = -\frac{9.22 \times 10^4 \text{ J/mol}}{8.314 \text{ J/mol K}} \left( \frac{1}{400 \text{ K}} - \frac{1}{700 \text{ K}} \right)
\]

\[
\ln \left( \frac{41}{K_2} \right) = 11.88
\]

\[
\frac{41}{K_2} = e^{11.88} = 1.446 \times 10^5
\]

\[
K_2 = 2.8 \times 10^{-4}
\]

Think about It
As we would expect, the equilibrium constant for this exothermic reaction decreases as the reaction is heated.

14.117. Collect and Organize
Given that \( K_1 = 1.5 \times 10^7 \) at 430°C and \( K_2 = 23 \) at 1000°C, we are to calculate the standard enthalpy of the reaction between \( \text{NO} \) and \( \text{O}_2 \) to produce \( \text{NO}_2 \).

Analyze
We can use the following equation to solve this problem:

\[
\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]
Chemical Equilibrium

Solve

\[ \ln\left(\frac{23}{1.5 \times 10^5}\right) = -\frac{\Delta H^\circ}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{1273 \text{ K}} - \frac{1}{703 \text{ K}}\right) \]

\[ \Delta H^\circ = -1.15 \times 10^5 \text{ J/mol, or } -115 \text{ kJ/mol} \]

Think about It

The result that this reaction, where \( K \) decreases with increasing \( T \), is exothermic is consistent with our answer to Problem 14.112.

14.118. Collect and Organize

Given the \( K_c \) values for the reaction

\[ \text{A} \rightleftharpoons \text{B} \]

at two different temperatures, we are to calculate the enthalpy of the reaction. We have \( K_c = 0.455 \) at 50°C and \( K_c = 0.655 \) at 100°C.

Analyze

The relationship between equilibrium constants at two different temperatures is given by

\[ \ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \]

where \( \Delta H^\circ \) is the enthalpy of the reaction in joules per mole, \( R \) is the gas constant in joules per mole per degree kelvin, and \( T_1 \) and \( T_2 \) are the temperatures in kelvins.

Solve

\[ \ln\left(\frac{0.455}{0.655}\right) = -\frac{\Delta H^\circ}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{323 \text{ K}} - \frac{1}{373 \text{ K}}\right) \]

\[ -0.3643 = -\Delta H^\circ \times (4.992 \times 10^{-5}) \]

\[ \Delta H^\circ = 7.298 \times 10^3 \text{ J/mol, or } 7.30 \text{ kJ/mol} \]

Think about It

Because the value of \( K_c \) increased with increasing temperature, we would expect the enthalpy of this reaction to be positive (endothermic).

14.119. Collect and Organize

Given the percentage of decomposition of \( \text{CO}_2 \) at three temperatures and that each equilibrium mixture begins with 1 atm of \( \text{CO}_2 \), we are to determine whether the reaction is endothermic and then calculate \( K_p \) at each temperature. We are also to comment on the decomposition reaction as a remedy for global warming.

Analyze

The amount of \( \text{CO}_2 \) decomposed increases with increasing temperature. This means that \( K_2 > K_1 \) in the equation

\[ \ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \]

where \( T_2 > T_1 \), so \((1/T_2 - 1/T_1) < 0\). To calculate \( K_p \) for each temperature, we set up a RICE table:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( 2 \text{CO}_2(g) \rightleftharpoons 2 \text{CO}(g) + \text{O}_2(g) )</th>
<th>( P_{\text{CO}_2} )</th>
<th>( P_{\text{CO}} )</th>
<th>( P_{\text{O}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>1 atm</td>
<td>0 atm</td>
<td>0 atm</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>(-2x)</td>
<td>(+2x)</td>
<td>(+x)</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(1 - 2x)</td>
<td>(2x)</td>
<td>(x)</td>
<td></td>
</tr>
</tbody>
</table>
We know that $2x$ is equal to the percent decomposition divided by 100 and that the form of the equilibrium expression is

$$K_p = \frac{(P_{CO})^2 (P_{O_2})}{(P_{CO_2})^2}$$

Because the percent decomposition increases with temperature, the value of $K_p$ is expected to increase as $T$ increases.

**Solve**

Because the value of $K$ increases with increasing temperature, $\ln(K_2/K_1) > 0$. With $(1/T_2 - 1/T_1) < 0$, the value of $\Delta H$ must be positive, so this reaction is endothermic.

At 1500 K, $2x = 0.00048$, $x = 0.00024$, and $1 - 2x = 0.99952$:

$$K_p = \frac{(0.00048)^2 (0.00024)}{(0.99952)^2} = 5.5 \times 10^{-11}$$

At 2500 K, $2x = 0.176$, $x = 0.088$, and $1 - 2x = 0.824$:

$$K_p = \frac{(0.176)^2 (0.088)}{(0.824)^2} = 4.0 \times 10^{-3}$$

At 3000 K, $2x = 0.548$, $x = 0.274$, and $1 - 2x = 0.452$:

$$K_p = \frac{(0.548)^2 (0.274)}{(0.452)^2} = 0.40$$

As predicted, the value of the equilibrium constant increases with increasing temperature. This reaction, however, does not favor products even at very high temperature, so this is not a viable source of CO and is not a remedy to decrease CO$_2$ as a contributor to global warming. Also, the process produces poisonous CO gas.

**Think about It**

By using values in Appendix 4, we can confirm that the reaction is endothermic.

14.120. **Collect and Organize**

For the decomposition of ammonia at 800 K:

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

we are given that the equilibrium concentration of NH$_3$ is 0.0040 M when the 1 L reaction vessel initially contained 2.00 mol NH$_3$. From this information we are to calculate $K_p$ and $K_c$ at 800 K.

**Analyze**

We set up a RICE table to obtain the equilibrium amounts of N$_2$ and H$_2$ so we can compute the value of $K_c$:

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

We can then use the relationship

$$K_p = K_c(RT)^{\Delta n}$$

where $\Delta n = 2$ for this reaction to calculate $K_p$ from $K_c$.

**Solve**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>2 NH$_3$(g) $\rightleftharpoons$ N$_2$(g) + 3 H$_2$(g)</th>
<th>[NH$_3$]</th>
<th>[N$_2$]</th>
<th>[H$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>2.00</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>$-2x$</td>
<td>$+x$</td>
<td>$+3x$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>2.00 $-2x$</td>
<td>$x$</td>
<td>$3x$</td>
<td></td>
</tr>
</tbody>
</table>
We know that $2.00 - 2x = 0.0040$, so $x = 0.998$. Therefore, at equilibrium $[N_2] = x = 0.998$ M and $[H_2] = 3x = 2.994$ M.

$$K_c = \frac{(0.998\text{ M})(2.994\text{ M})^3}{(0.0040)^2} = 1.67 \times 10^6$$

$$K_p = 1.67 \times 10^6 \times \left(\frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 800 \text{ K}\right)^2 = 7.21 \times 10^9$$

**Think about It**
This equilibrium very heavily favors the formation of products, as evidenced by its large equilibrium constant.

### 14.121. Collect and Organize
By combining the two equations given, we can calculate the overall equilibrium constant, $K$, for the reaction and then calculate the concentration of $X^{2–}$ in an equilibrium mixture where $[H_2X]_{eq} = 0.1$ M and $[HCl]_{eq} = [H_3O^+]_{eq} = 0.3$ M.

**Analyze**
When we add equations, the overall equilibrium constant is the product of the individual equilibrium constants. From the overall reaction we can write the equilibrium constant expression and from that solve for $[X^{2–}]$ at equilibrium.

**Solve**

$$
\begin{align*}
H_2X(aq) + H_2O(l) &\rightleftharpoons HX^–(aq) + H_3O^+(aq) & K_1 &= 8.3 \times 10^{-8} \\
HX^–(aq) + H_2O(l) &\rightleftharpoons X^{2–}(aq) + H_3O^+(aq) & K_2 &= 1 \times 10^{-14} \\
H_2X(aq) + 2H_2O(l) &\rightleftharpoons X^{2–}(aq) + 2H_3O^+(aq) & K_3 &= K_1 \times K_2 = 8.3 \times 10^{-22}
\end{align*}
$$

We know that $K_c = 8.3 \times 10^{-22}$, $[H_3O^+] = 0.3$ M, and $[H_2X] = 0.1$ M for the saturated solution. Rearranging the equilibrium constant expression and solving for $[X^{2–}]$ gives

$$
[X^{2–}] = \frac{K_c \times [H_2X]}{[H_3O^+]^2} = \frac{8.3 \times 10^{-22} \times 0.1}{(0.3)^2} = 9 \times 10^{-22} \text{ M}
$$

**Think about It**
Our answer makes sense because with a very small overall equilibrium constant, we expect a very small concentration of product, $X^{2–}$.

### 14.122. Collect and Organize
For the reaction

$$\text{NO}_2(g) + \text{SO}_2(g) \rightleftharpoons \text{NO}(g) + \text{SO}_3(g)$$

we are given the equilibrium concentrations, from which we can calculate $K_c$. We are to calculate the concentrations of all species in the reaction mixture at a new equilibrium after the concentration of $\text{SO}_3$ is increased.

**Analyze**
The $K_c$ expression for this reaction is

$$K_c = \frac{[\text{NO}][\text{SO}_3]}{[\text{NO}_2][\text{SO}_2]} = \frac{(2.00)(0.600)}{(0.100)(0.300)} = 40.0$$

We set up a RICE table where the concentration of $\text{SO}_2$ is increased from the first equilibrium value of 0.300 M to 0.800 M.
### Solve

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\text{NO}_2(g)) + (\text{SO}_2(g)) ⇌ (\text{NO}(g)) + (\text{SO}_3(g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>[0.100 \text{ M} \quad 0.800 \text{ M} \quad 2.00 \text{ M} \quad 0.600 \text{ M}]</td>
</tr>
<tr>
<td>Change</td>
<td>(-x) \quad (-x) \quad (+x) \quad (+x)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>[0.100 - x \quad 0.800 - x \quad 2.00 + x \quad 0.600 + x]</td>
</tr>
</tbody>
</table>

The direction of change is predicted by Le Châtelier’s principle: we increase the concentration of a reactant and the equilibrium shifts to the right. To solve for \(x\) we must expand and solve by the quadratic equation:

\[
40.0 = \frac{(2.00 + x)(0.600 + x)}{(0.100 - x)(0.800 - x)} = \frac{(1.20 + 2.60x + x^2)}{(0.0800 - 0.900x + x^2)}
\]

\[
39.0x^2 - 38.6x + 2.00 = 0
\]

When \(x = 0.935\), the concentrations of \(\text{NO}_2\) and \(\text{SO}_2\) will be negative, so \(x = 0.0549\). The concentrations at equilibrium are

\[
[\text{NO}_2] = 0.100 - x = 0.045 \text{ M}
\]
\[
[\text{SO}_2] = 0.800 - x = 0.745 \text{ M}
\]
\[
[\text{NO}] = 2.00 + x = 2.05 \text{ M}
\]
\[
[\text{SO}_3] = 0.600 + x = 0.655 \text{ M}
\]

### Think about It

To check our answer, we can substitute these concentrations into the \(K_c\) expression:

\[
\frac{(2.05)(0.655)}{(0.745)(0.045)} = 40
\]

14.123. **Collect and Organize**

For the reaction of \(\text{CH}_4\) with \(\text{S}_8\) to form \(\text{CS}_2\) and \(\text{H}_2\), we are to calculate the value of the equilibrium constant by using thermodynamic data from Appendix 4 for the reaction at both 25°C and 500°C.

### Analyze

We have to calculate the value of \(K_p\) from \(\Delta G\) at 500°C. To do so, we must first determine \(\Delta H^\circ\) and \(\Delta S^\circ\) from tabulated values in Appendix 4:

\[
\Delta H^\circ = \left[ (4 \times -115.3) + (8 \times 0.0) \right] - \left[ (4 \times -74.8) - (1 \times 0.0) \right] = 760.4 \text{ kJ}
\]
\[
\Delta S^\circ = \left[ (4 \times 237.8) + (8 \times 130.6) \right] - \left[ (4 \times 186.2) - (1 \times 32.1) \right] = 1219 \text{ J/K}
\]

We can then calculate the value of \(\Delta G_{25^\circ\text{C}}\) and \(\Delta G_{500^\circ\text{C}}\) through

\[
\Delta G_{25^\circ\text{C}} = \Delta H^\circ - T\Delta S^\circ = 760.4 \text{ kJ} - (298 \text{ K} \times 1.219 \text{ kJ/K}) = 397.1 \text{ kJ}
\]
\[
\Delta G_{500^\circ\text{C}} = \Delta H^\circ - T\Delta S^\circ = 760.4 \text{ kJ} - (773 \text{ K} \times 1.219 \text{ kJ/K}) = -181.9 \text{ kJ}
\]

The value of \(K_p\) for each temperature is calculated though the value of \(\Delta G^\circ:\)

\[
\ln K_p = -\frac{\Delta G^\circ}{RT}
\]

### Solve

At 25°C (298 K):

\[
\ln K_p = -\frac{397.1 \text{ kJ/mol}}{\left(\frac{8.314 \times 10^{-3} \text{ kJ}}{\text{mol} \cdot \text{K}}\right) \times 298 \text{ K}} = -160.3
\]

\[
K_p = e^{-160.3} = 2.47 \times 10^{-70}
\]
At 500°C (773 K):

\[
\ln K_p = -\frac{-181.9 \text{ kJ/mol}}{\left(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}\right) \times 773 \text{ K}} = 28.30
\]

\[K_p = e^{28.30} = 1.96 \times 10^{12}\]

**Think about It**
This reaction changed its spontaneity upon heating because it is an endothermic reaction with a favorable entropy change.

14.124. **Collect and Organize**
Given that \(K_c\) is \(1.0 \times 10^5\) at 25°C for the reaction converting CO and \(\text{H}_2\) to \(\text{CO}_2\) and \(\text{H}_2\), we are to calculate the value of \(\Delta G_{\text{rxn}}^\circ\) and predict the sign of \(\Delta H_{\text{rxn}}^\circ\).

**Analyze**
We can calculate \(\Delta G^\circ\) from \(K_c\) by using

\[\Delta G^\circ = -RT \ln K_c\]

To figure out the sign of \(\Delta H^\circ\), we can qualitatively examine first whether entropy is expected to increase or decrease for this reaction. We then can guess the sign of the enthalpy change for the reaction.

**Solve**

\[\Delta G_{\text{rxn}}^\circ = \frac{-8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} \times \ln(1.0 \times 10^5) = -29 \text{ kJ/mol}\]

The entropy of the reaction changes very little since the number of moles of gaseous products equals the number of moles of gaseous reactants. Therefore, \(\Delta S^\circ \approx 0\), so the sign of \(\Delta H^\circ\) is expected to be negative since \(\Delta G = \Delta H^\circ - T \Delta S^\circ\).

**Think about It**
This reaction is spontaneous largely because it is exothermic. Because \(\Delta S^\circ \approx 0\), \(\Delta G_{\text{rxn}}^\circ \approx -29 \text{ kJ/mol}\).

14.125. **Collect and Organize**
Given \(\Delta G^\circ = -418.6 \text{ kJ}\) for the reaction in which \(\text{CaO}\) reacts with \(\text{SO}_2\) in the presence of \(\text{O}_2\) to form solid \(\text{CaSO}_4\), we can calculate \(K\) and then determine the \(P_{\text{SO}_2}\) in this reaction when the partial pressure of oxygen is 0.21 atm.

**Analyze**
To calculate \(K\) from \(\Delta G^\circ\), we use

\[\ln K = \frac{-\Delta G^\circ}{RT}\]

The equilibrium constant expression for the reaction is

\[K_p = \frac{1}{\left(P_{\text{SO}_2}\right)^{1/2}\left(P_{\text{O}_2}\right)^{1/2}}\]

**Solve**

\[\ln K = -\frac{-418.6 \text{ kJ/mol}}{8.314 \times 10^{-3} \text{ kJ/mol} \cdot \text{K} \times 298 \text{ K}} = 168.956\]

\[K = e^{168.956} = 2.38 \times 10^{73}\]
Think about It
Essentially, all the SO\(_2\) is “scrubbed” by the CaO in this reaction, making this an efficient method to remove SO\(_2\) from exhaust gases.

14.126. Collect and Organize
For the reaction

\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)
\]

we are to calculate \(K_p\) at 700°C and find the ratio of \(P_{\text{SO}_2} / P_{\text{SO}_3}\) when \(P_{\text{O}_2}\) at equilibrium is 0.21 atm.

Analyze
First we have to calculate the value of \(K_c\) from \(\Delta G\) at 700°C. To do so, we must first determine \(\Delta H^\circ\) and \(\Delta S^\circ\) from tabulated values in Appendix 4:

\[
\Delta H^\circ = (2 \times -395.7) - [(2 \times -296.8) + (1 \times 0)] = -197.8 \text{ kJ}
\]
\[
\Delta S^\circ = (2 \times 256.8) - [(2 \times 248.2) + (1 \times 205.0)] = -187.8 \text{ J/K}
\]

\[
\Delta G^\circ_{700°C} = \Delta H^\circ - T\Delta S^\circ = -197.8 \text{ kJ} - (973 \text{ K} \times -0.1878 \text{ kJ/K}) = -15.07 \text{ kJ}
\]

From \(\Delta G\), we can calculate \(K_c\):

\[
\ln K_c = \frac{-15.07 \text{ kJ/mol}}{8.314 \times 10^{-3} \text{ kJ/mol·K} \times 973 \text{ K}} = 1.863
\]

\[
K_c = e^{1.863} = 6.443
\]

We can calculate \(K_p\) from \(K_c\) by using

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

where \(\Delta n = -1\) for this reaction.

Solve

\[
K_p = \frac{6.443}{0.08026 \text{ L·atm/mol·K} \times 973} = 0.0807
\]

At equilibrium

\[
K_p = \left(\frac{P_{\text{SO}_2}}{P_{\text{SO}_3}}\right)^2
\]

Rearranging for the ratio \(P_{\text{SO}_2} / P_{\text{SO}_3}\) gives

\[
\frac{P_{\text{SO}_2}}{P_{\text{SO}_3}} = \sqrt{K_p \times P_{\text{O}_2}} = \frac{1}{\sqrt{0.0807 \times 0.21}} = 7.7
\]

Think about It
This equilibrium favors the reactants, and so the ratio of the partial pressure of the reactant SO\(_2\) to the partial pressure of the product SO\(_3\) is greater than 1.