if a reaction has an equal number of moles of gas on both sides of the chemical equation, then a change in volume produces no effect on the equilibrium.

adding an inert gas to the mixture at a fixed volume has no effect on the equilibrium.

14.20 If the temperature of a system at equilibrium is changed, the system shifts in a direction to counter that change. So, if the temperature is increased, the reaction shifts in the direction that tends to decrease the temperature and vice versa.

In an exothermic chemical reaction,
increasing the temperature causes the reaction to shift left and the value of the equilibrium constant decreases.

decreasing the temperature causes the reaction to shift right and the value of the equilibrium constant increases.

In an endothermic chemical reaction,
increasing the temperature causes the reaction to shift right and the equilibrium constant increases.

decreasing the temperature causes the reaction to shift left and the equilibrium constant decreases.

Problems by Topic
Equilibrium and the Equilibrium Constant

14.21 The equilibrium constant is defined as the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients.

(a) \[ K = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} \]

(b) \[ K = \frac{[NO][Br_2]}{[BrNO]^2} \]

(c) \[ K = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2} \]

(d) \[ K = \frac{[CO_2]^2}{[CO][O_2]} \]

14.22 The equilibrium constant is defined as the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients.

(a) \[ K = \frac{[H_2][I_2]}{[H_2S]^2} \]

(b) \[ K = \frac{[COCl_3]}{[CO][Cl_2]} \]

14.23 With an equilibrium constant of \(1.4 \times 10^{-5}\), the value of the equilibrium constant is small, therefore, the concentration of reactants will be greater than the concentration of products. This is independent of the initial concentration of the reactants and products.

14.24 Figure a at equilibrium has \(8 \text{C}_2\text{H}_4\text{Cl}_2, 2 \text{Cl}_2, \) and \(2 \text{C}_2\text{H}_4\).

Figure b at equilibrium has \(6 \text{C}_2\text{H}_4\text{Br}_2, 4 \text{Br}_2, \) and \(4 \text{C}_2\text{H}_4\).

Figure c at equilibrium has \(3 \text{C}_2\text{H}_4\text{I}_2, 7 \text{I}_2, \) and \(7 \text{C}_2\text{H}_4\).

Since the equilibrium constant is concentration of products/concentration of reactants, the equilibrium situation which has the largest concentration of products will have the largest equilibrium constant. Therefore, \(K_{\text{Cl}_2} > K_{\text{Br}_2} > K_{\text{I}_2}\).
14.25  
(i) has $10 \text{H}_2$ and $10 \text{I}_2$
(ii) has $7 \text{H}_2$ and $7 \text{I}_2$ and $6 \text{HI}$
(iii) has $5 \text{H}_2$ and $5 \text{I}_2$ and $10 \text{HI}$
(iv) has $4 \text{H}_2$ and $4 \text{I}_2$ and $12 \text{HI}$
(v) has $3 \text{H}_2$ and $3 \text{I}_2$ and $14 \text{HI}$
(vi) has $3 \text{H}_2$ and $3 \text{I}_2$ and $14 \text{HI}$

(a) Concentration of (v) and (vi) are the same, so the system reached equilibrium at (v).
(b) If a catalyst was added to the system, the system would reach the conditions at (v) sooner since a catalyst speeds up the reaction but does not change the equilibrium conditions.
(c) The final figure (vi) would have the same amount of reactants and products since a catalyst speeds up the reaction, but does not change the equilibrium concentrations.

14.26 The equilibrium constant gives us the ratio of products to reactants at equilibrium, it does not say how long it takes to reach equilibrium. So after 15 minutes, if the smaller equilibrium constant has more products, then the kinetics of that reaction are faster.

14.27  
(a) If you reverse the reaction, invert the equilibrium constant. So $K' = \frac{1}{K_p} = \frac{1}{2.26 \times 10^4} = 4.42 \times 10^{-5}$. The reactants will be favored.
(b) If you multiply the coefficients in the equation by a factor, raise the equilibrium constant to the same factor. So $K' = (K_p)^{1/2} = (2.26 \times 10^4)^{1/2} = 1.50 \times 10^2$. The products will be favored.
(c) Begin with the reverse of the reaction and invert the equilibrium constant.

14.28  
(a) The reaction is multiplied by $1/2$, so raise the value of the equilibrium constant to $1/2$. $K' = (K_p)^{1/2} = (2.26 \times 10^4)^{1/2} = 1.5 \times 10^2$. The products will be favored.
(b) The reaction is multiplied by 3, so raise the value of the equilibrium constant to 3. $K' = (K_p)^3 = (2.2 \times 10^6)^3 = 1.1 \times 10^{19}$. The products will be favored.
(c) Begin with the reverse of the reaction and invert the equilibrium constant.

To find the equilibrium constant for reaction 3, you need to combine reactions 1 and 2 to get reaction 3. Begin by reversing reaction 2, then multiply reaction 1 by 2 and add the two new reactions. When you add reactions you multiply the values of $K$.

14.29  
$\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)$  
$K_1 = \frac{1}{K_p} = \frac{1}{2.1 \times 10^{30}} = 4.76 \times 10^{-31}$

$2 \text{NO}(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{NOBr}(g)$  
$K_2 = (K_p)^2 = (5.3)^2 = 28.09$

$\text{N}_2(g) + \text{O}_2(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{NOBr}(g)$  
$K_3 = K_1K_2 = (4.76 \times 10^{-31})(28.09) = 1.3 \times 10^{-29}$
To find the equilibrium constant for reaction 3, you need to combine reactions 1 and 2 to get reaction 3. Begin by multiplying reaction 1 by 2 and then reverse reaction 2 and add the two new reactions. When you add reactions you multiply the values of $K$.

$$
2\text{A(s)} \rightleftharpoons 3\text{B(g)} + 2\text{C(g)} \quad K_1 = (K_p)^2 = (0.0334)^2 = 1.1 \times 10^{-3}
$$

$$
\text{B(g)} + 2\text{C(g)} \rightleftharpoons 3\text{D(g)} \quad K_2 = \frac{1}{K_p} = \frac{1}{0.425} = 2.35
$$

$$
2\text{A(s)} \rightleftharpoons 3\text{D(g)} \quad K' = K_1 K_2 = (1.1 \times 10^{-3})(0.425) = 4.68 \times 10^{-4}
$$

### $K_p$, $K_c$, and Heterogeneous Equilibria

14.30  

(a) Given: $K_p = 6.26 \times 10^{-22}$  

Conceptual Plan: $K_p \rightarrow K_c$  

Solution: $\Delta n = \text{mol product gas} - \text{mol reactant gas} = 2 - 1 = 1$  

$$
K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{6.26 \times 10^{-22}}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1})^1} = 2.56 \times 10^{-23}
$$

Check: Substitute into the equation and confirm that you get the original value of $K_p$.  

$$
K_p = K_c (RT)^{\Delta n} = (2.56 \times 10^{-23})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \times 298 \text{ K})^1 = 6.26 \times 10^{-22}
$$

(b) Given: $K_p = 7.7 \times 10^{-24}$  

Conceptual Plan: $K_p \rightarrow K_c$  

Solution: $\Delta n = \text{mol product gas} - \text{mol reactant gas} = 4 - 2 = 2$  

$$
K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{7.7 \times 10^{-24}}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \times 298 \text{ K})^2} = 1.3 \times 10^{-22}
$$

Check: Substitute into the equation and confirm that you get the original value of $K_p$.  

$$
K_p = K_c (RT)^{\Delta n} = (1.3 \times 10^{-22})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \times 298 \text{ K})^2 = 7.7 \times 10^{-24}
$$

(c) Given: $K_p = 81.9$  

Conceptual Plan: $K_p \rightarrow K_c$  

Solution: $\Delta n = \text{mol product gas} - \text{mol reactant gas} = 2 - 2 = 0$  

$$
K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{81.9}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \times 298 \text{ K})^0} = 81.9
$$

Check: Substitute into the equation and confirm that you get the original value of $K_p$.  

$$
K_p = K_c (RT)^{\Delta n} = (81.9)(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \times 298 \text{ K})^0 = 81.9
$$
(b) Given: \( K_c = 3.7 \times 10^8 \) \( T = 298 \text{K} \) Find: \( K_p \\
Conceptual Plan: \( K_p \rightarrow K_c \\
K_p = K_c \frac{(RT)^n}{\text{mol} \cdot \text{K}} \\
Solution: \Delta n = \text{mol product gas} - \text{mol reactant gas} = 2 - 4 = -2 \\
K_p = K_c \frac{(RT)^n}{\text{mol} \cdot \text{K}} = 3.7 \times 10^8 \frac{0.08206 \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \frac{298 \text{K}}{2} = 6.2 \times 10^5 \\
Check: \text{Substitute into the equation and confirm that you get the original value of } K_p \\
K_p \cdot 6.2 \times 10^5 = K_c (RT)^n = 3.7 \times 10^8 \frac{0.08206 \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \frac{298 \text{K}}{2} \\
(c) Given: \( K_c = 4.10 \times 10^{-31} \) \( T = 298 \text{K} \) Find: \( K_p \\
Conceptual Plan: \( K_p \rightarrow K_c \\
K_p = K_c \frac{(RT)^n}{\text{mol} \cdot \text{K}} \\
Solution: \Delta n = \text{mol product gas} - \text{mol reactant gas} = 2 - 2 = 0 \\
K_p = K_c \frac{(RT)^n}{\text{mol} \cdot \text{K}} = 4.10 \times 10^{-31} \frac{0.08206 \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \frac{298 \text{K}}{0} = 4.10 \times 10^{-31} \\
Check: \text{Substitute into the equation and confirm that you get the original value of } K_p \\
K_p \cdot 4.10 \times 10^{-31} = K_c (RT)^n = 4.10 \times 10^{-31} \frac{0.08206 \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \frac{298 \text{K}}{0} \\

Relating the Equilibrium Constant to Equilibrium Concentrations and Equilibrium Partial Pressures

14.35 Given: At equilibrium: \([\text{CO}] = 0.105 \text{M}, [\text{H}_2] = 0.114 \text{M}, [\text{CH}_3\text{OH}] = 0.185 \text{M} \) Find: \( K_c \\
Conceptual Plan: Balanced reaction \rightarrow \text{equilibrium expression} \rightarrow K_c \\
Solution: \( K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{0.185}{(0.105)(0.114)^2} = 136 \\
Check: \text{The answer is reasonable since the concentration of products is greater than the concentration of reactants and the equilibrium constant should be greater than 1.} \\
14.36 Given: At equilibrium: \([\text{NH}_3] = 0.278 \text{M}, [\text{H}_2\text{S}] = 0.355 \text{M} \) Find: \( K_c \\
Conceptual Plan: Balanced reaction \rightarrow \text{equilibrium expression} \rightarrow K_c \\
Solution: \text{Since NH}_3\text{HS is a solid, it is omitted from the equilibrium expression.} \\
K_c = \frac{[\text{NH}_3][\text{H}_2\text{S}]}{[\text{H}_2\text{O}]} = 0.278(0.355) = 0.0987 \\
Check: \text{The answer is reasonable since the concentration of products is less than 1M, the equilibrium constant is less than 1.} \\
14.37 At 500K: Given: At equilibrium: \([\text{N}_2] = 0.115 \text{M}, [\text{H}_2] = 0.105 \text{M}, \text{and } [\text{NH}_3] = 0.439 \) Find: \( K_c \\

Chapter 14 Chemical Equilibrium

Conceptual Plan: Balanced reaction $\rightarrow$ equilibrium expression $\rightarrow K_c$

Solution: $K_c = \frac{[HN_3]^2}{[N_2][H_3]^3}$

Check: The value is reasonable since the concentration of products is greater than the concentration of reactants.

At 575K: Given: At equilibrium: $[N_2] = 0.110M, [NH_3] = 0.128, K_c = 9.6$ Find: $[H_2]$

Conceptual Plan: Balanced reaction $\rightarrow$ equilibrium expression $\rightarrow [H_2]$

Solution: $K_c = \frac{[NH_3]^2}{[N_2][H_3]^3}$

Check: Plug the value for $x$ back into the equilibrium expression, and check the value.

At 575K: Given: At equilibrium: $[N_2] = 0.110M, [NH_3] = 0.128, K_c = 9.6$ Find: $[NH_3]$

Conceptual Plan: Balanced reaction $\rightarrow$ equilibrium expression $\rightarrow [NH_3]$

Solution: $K_c = \frac{[NH_3]^2}{[N_2][H_3]^3}$

Check: Plug the value for $x$ back into the equilibrium expression, and check the value.

At 775K: Given: At equilibrium: $[N_2] = 0.120M, [H_2] = 0.140, K_c = 0.0584$ Find: $[NH_3]$

Conceptual Plan: Balanced reaction $\rightarrow$ equilibrium expression $\rightarrow [NH_3]$

Solution: $K_c = \frac{[NH_3]^2}{[N_2][H_3]^3}$

Check: Plug the value for $x$ back into the equilibrium expression, and check the value.

At 25°C: Given: At equilibrium: $[H_2] = 0.0355M, [I_2] = 0.0388M, and [HI] = 0.922$ Find: $K_c$

Conceptual Plan: Balanced reaction $\rightarrow$ equilibrium expression $\rightarrow K_c$

Solution: $K_c = \frac{[HI]^2}{[H_2][I_2]^2}$

Check: The value is reasonable since the concentration of products is greater than the concentration of reactants.

At 340°C: Given: At equilibrium: $[I_2] = 0.0455$, and $[HI] = 0.387, K_c = 9.6$ Find: $[H_2]$

Conceptual Plan: Balanced reaction $\rightarrow$ equilibrium expression $\rightarrow [H_2]$

Solution: $K_c = \frac{[HI]^2}{[H_2][I_2]^2}$

Check: Plug the value for $x$ back into the equilibrium expression, and check the value.

At 445°C: Given: At equilibrium: $[H_2] = 0.0485M, [I_2] = 0.0468, K_c = 50.2$ Find: $[HI]$

Conceptual Plan: Balanced reaction $\rightarrow$ equilibrium expression $\rightarrow [HI]$

Solution: $K_c = \frac{[HI]^2}{[H_2][I_2]^2}$

Check: Plug the value for $x$ back into the equilibrium expression, and check the value.

Given: $P_{NO} = 108$ torr; $P_{Br_2} = 126$ torr, $K_p = 28.4$ Find: $P_{NOBr}$

Conceptual Plan: torr $\rightarrow \text{arm and then balanced reaction} \rightarrow \text{equilibrium expression} \rightarrow P_{NOBr}$

Solution: $P_{NO} = 108 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.1421 \text{ atm}$ $P_{Br_2} = 126 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.1658$

Check: Plug the value for $x$ back into the equilibrium expression, and check the value.

Given: $P_{NO} = 108 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.1421 \text{ atm}$ $P_{Br_2} = 126 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.1658$

Source: $\frac{P_{NO}}{P_{NOBr}}$ $\times \frac{P_{Br_2}}{x} = \frac{28.4}{x} = 0.308 \text{ atm} = 234 \text{ torr}$

Check: Plug the value for $x$ back into the equilibrium expression, and check the value.

Source: $\frac{P_{NO}}{P_{NOBr}}$ $\times \frac{P_{Br_2}}{x} = \frac{28.4}{x} = 0.308 \text{ atm} = 234 \text{ torr}$

Check: Plug the value for $x$ back into the equilibrium expression, and check the value.

Source: $\frac{P_{NO}}{P_{NOBr}}$ $\times \frac{P_{Br_2}}{x} = \frac{28.4}{x} = 0.308 \text{ atm} = 234 \text{ torr}$
14.40  Given: \( P_{SO_2} = 137 \) torr, \( P_{Cl_2} = 285 \) torr, \( K_p = 2.91 \times 10^3 \) Find: \( P_{SOCl_2} \)

Conceptual Plan: \( 1 \text{ atm} \rightarrow \text{torr} \) and then balanced reaction \( \rightarrow \) equilibrium expression \( \rightarrow P_{SOCl_2} \)

Solution: \( P_{SO_2} = 137 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.1803 \text{ atm} \)
\( P_{Cl_2} = 285 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.3750 \text{ atm} \)
\( K_p = \frac{P_{SOCl_2}}{P_{SO_2}P_{Cl_2}} = 2.91 \times 10^3 \)
\( x = \frac{2.91 \times 10^3}{(0.1803)(0.3750)} \approx 0.0177 \text{ torr} \)

Check: Plug the value for \( x \) back into the equilibrium expression, and check the value.

14.41  Given: \( [Fe^{3+}]_{\text{initial}} = 1.0 \times 10^{-3} \text{ M}; [SCN^-]_{\text{initial}} = 8.0 \times 10^{-4} \text{ M}; [FeSCN^{2+}]_{\text{eq}} = 1.7 \times 10^{-4} \text{ M} \) Find: \( K_c \)

Conceptual Plan:
1. Prepare ICE table
2. Calculate concentration change for known value
3. Calculate concentration changes for other reactants/products
4. Determine equilibrium concentration
5. Write the equilibrium expression and determine \( K_c \)

Solution: \( Fe^{3+}(aq) + SCN^- (aq) \rightarrow FeSCN^{2+}(aq) \)

\[
\begin{array}{c|c|c|c}
 & [Fe^{3+}] & [SCN^-] & [FeSCN^{2+}] \\
\hline I & 1.0 \times 10^{-3} & 8.0 \times 10^{-4} & 0.00 \\
 C & -1.7 \times 10^{-4} & -1.7 \times 10^{-4} & +1.7 \times 10^{-4} \\
 E & 8.3 \times 10^{-4} & 6.3 \times 10^{-4} & 1.7 \times 10^{-4} \\
 K_c = \frac{[Fe^{3+}][SCN^-]}{[Fe^{3+}][SCN^-]} = \frac{(1.7 \times 10^{-4})(8.3 \times 10^{-4})}{(6.3 \times 10^{-4})(6.3 \times 10^{-4})} = 3.3 \times 10^2 \\
\end{array}
\]

14.42  Given: \( [SO_2Cl_2]_{\text{initial}} = 0.020 \text{ M}; [Cl_2]_{\text{eq}} = 1.2 \times 10^{-2} \text{ M} \) Find: \( K_c \)

Conceptual Plan:
1. Prepare ICE table
2. Calculate concentration change for known value
3. Calculate concentration changes for other reactants/products
4. Determine equilibrium concentration
5. Write the equilibrium expression and determine \( K_c \)

Solution: \( SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g) \)

\[
\begin{array}{c|c|c|c}
 & [SO_2Cl_2] & [SO_2] & [Cl_2] \\
\hline I & 0.020 & 0.00 & 0.00 \\
 C & -1.2 \times 10^{-2} & +1.2 \times 10^{-2} & +1.2 \times 10^{-2} \\
 E & 0.0080 & 1.2 \times 10^{-2} & 1.2 \times 10^{-2} \\
 K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{(1.2 \times 10^{-2})(1.2 \times 10^{-2})}{0.0080} = 0.018 \\
\end{array}
\]

14.43  Given: 3.67 L flask, 0.763 g H\(_2\) initial, 96.9 g I\(_2\) initial, 90.4 g HI equilibrium Find: \( K_c \)

Conceptual Plan: \( g \rightarrow \text{mol} \rightarrow M \) and then

1. Prepare ICE table
2. Calculate concentration change for known value
3. Calculate concentration changes for other reactants/products
4. Determine equilibrium concentration
5. Write the equilibrium expression and determine \( K_c \)

Solution:
\[
\begin{align*}
\text{Initial:} & \quad \text{H}_2: 0.3785 \text{ mol H}_2; \quad \text{I}_2: 0.3818 \text{ mol I}_2; \quad \text{HI: 0.3818 mol HI} \\
\text{Equilibrium:} & \quad \text{H}_2: 0.103 \text{ M} \quad \text{H}_2; \quad \text{I}_2: 0.104 \text{ M} \quad \text{I}_2; \quad \text{HI: 0.193 M} \\
\text{Molar mass:} & \quad \text{H}_2: 2.016 \text{ g H}_2; \quad \text{I}_2: 253.8 \text{ g I}_2; \quad \text{HI: 127.9 g HI} \\
\text{Conversion:} & \quad \text{H}_2: 96.9 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 0.3818 \text{ mol H}_2 \quad \text{H}_2; \quad \text{I}_2: 96.9 \text{ g I}_2 \times \frac{1 \text{ mol I}_2}{253.8 \text{ g I}_2} = 0.3818 \text{ mol I}_2 \quad \text{I}_2; \quad \text{HI: 90.4 \ g HI} \times \frac{1 \text{ mol HI}}{127.9 \text{ g HI}} = 0.7068 \text{ mol HI} \quad \text{HI} \\
\text{Volume:} & \quad \text{3.67 L} \\
\text{Molarity:} & \quad \text{H}_2: \frac{0.3785 \text{ mol H}_2}{3.67 \text{ L}} \quad \text{H}_2; \quad \text{I}_2: \frac{0.3818 \text{ mol I}_2}{3.67 \text{ L}} \quad \text{I}_2; \quad \text{HI: \frac{0.07068 \text{ mol HI}}{3.67 \text{ L}} = 0.193 M} \\
\end{align*}
\]
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14.44  Given: 5.19 L flask, 26.9 g CO initial, 2.34 g H₂ initial, 8.65 g CH₃OH equilibrium  Find: \( K_c \)

Conceptual Plan: g \( \rightarrow \) mol \( \rightarrow \) M and then

1. Prepare ICE table
2. Calculate concentration change for known value
3. Calculate concentration changes for other reactants/products
4. Determine equilibrium concentration
5. Write the equilibrium expression and determine \( K_c \)

Solution: 26.9 g CO x \( \frac{1 \text{ mol CO}}{28.01 \text{ g CO}} = \frac{0.9604 \text{ mol CO}}{5.19 \text{ L}} = 0.185 \text{ M} \)

2.34 \( \text{g H}_2 \) x \( \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 1.161 \text{ mol H}_2 \)

8.65 \( \text{g CH}_3\text{OH} \) x \( \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} = 0.2720 \text{ mol CH}_3\text{OH} \)

\[ \text{CO(g)} + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) \]

Since CH₃OH gained 0.0520 M, CO had to lose 0.0520 since the stoichiometry is 1:1 and H₂ had to lose 0.104 since the stoichiometry is 2:1.

The Reaction Quotient and Reaction Direction

14.45  Given: \( K_c = 8.5 \times 10^{-3} \); [NH₃] = 0.166 M; [H₂S] = 0.166 M  Find: Will solid form or decompose?

Conceptual Plan: Calculate Q \( \rightarrow \) compare Q and \( K_c \)

Solution: Q = [NH₃][H₂S] = (0.166)(0.166) = 0.0276

\( Q = 0.0276 \) and \( K_c = 8.5 \times 10^{-3} \) so Q > \( K_c \) and the reaction will shift to the left, so more solid will form.

14.46  Given: \( K_p = 2.4 \times 10^{-4} \); \( P_{H_2} = 0.112 \text{ atm} \); \( P_{H_2S} = 0.055 \text{ atm} \); \( P_{H_2} = 0.445 \text{ atm} \)  Find: Is the reaction at equilibrium?

Conceptual Plan: Calculate Q \( \rightarrow \) compare Q and \( K_p \)

Solution: Q = \( \frac{P_{H_2}}{P_{H_2S}^2} \times \frac{P_{H_2}}{P_{H_2}} = \frac{0.112}{(0.055)^2} = 3.48 \times 10^{-3} \)  Q = 3.48 \( \times 10^{-3} \) and \( K_p = 2.4 \times 10^{-4} \) so Q > \( K_p \), the system is not at equilibrium, and the reaction will shift to the left.

14.47  Given: 6.55 g Ag₂SO₄; 1.5 L solution, \( K_c = 1.1 \times 10^{-5} \)  Find: Will more solid dissolve?

Conceptual Plan: g Ag₂SO₄ \( \rightarrow \) mol Ag₂SO₄ \( \rightarrow \) [Ag₂SO₄] \( \rightarrow \) [Ag⁺][SO₄²⁻] \( \rightarrow \) calculate Q and compare to \( K_c \)

\[ 1 \text{ mol Ag}_2\text{SO}_4 \quad \text{mol Ag}_2\text{SO}_4 \]

\[ 311.81 \text{ g} \quad 1 \text{ mol Ag}_2\text{SO}_4 \]

\[ 0.0210 \text{ mol Ag}_2\text{SO}_4 \]

0.0210 mol Ag₂SO₄ = 0.0140 M Ag₂SO₄

\[ [\text{Ag}^+] = 2[\text{Ag}_2\text{SO}_4] = 2(0.0140 \text{ M}) = 0.0280 \text{ M [SO}_4^{2^-}] = [\text{Ag}_2\text{SO}_4] = 0.0140 \text{ M} \]

\[ Q = [\text{Ag}^+][\text{SO}_4^{2-}] = (0.0280)(0.0140) = 1.1 \times 10^{-5} \]
Chapter 14 Chemical Equilibrium

Q = K_v so the system is at equilibrium and is a saturated solution. Therefore, if more solid is added it will not dissolve.

14.48 Given: \( K_p = 6.7 \) at 298 K; 2.25 L flask; \( \text{NO}_2 = 0.055 \) mol; \( \text{N}_2\text{O}_4 = 0.082 \) mol Find: Is the reaction at equilibrium?

Conceptual Plan: \( K_p \rightarrow K_c \) and mol \( \rightarrow M \) and then calculate Q and compare to \( K_c \).

\[
K_c = \frac{K_v \cdot (RT)^{a_n}}{M = \frac{\text{mol}}{V}}
\]

Solution: \( K_c = \frac{K_p \cdot (RT)^{a_n}}{[\text{NO}_2]} = \frac{0.082 \text{ mol}}{0.055 \text{ mol}} = 1.49 \)

\[
Q = \frac{[\text{NO}_2]}{[\text{NO}_2]} = \frac{0.082 \text{ mol}}{2.25 \text{ L}} = 0.036
\]

Q < \( K_c \), the reaction is not at equilibrium and will shift to the right.

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

14.49 (a) Given: \( [\text{A}] = 1.0 \) M, \( [\text{B}] = 0.0 \) \( K_c = 4.0; a = 1, b = 1 \) Find: \( [\text{A}], [\text{B}] \) at equilibrium

Conceptual Plan: Prepare an ICE table, calculate Q, compare Q and \( K_c \) predict the direction of the reaction, represent the change with \( x \), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \( x \). Determine \( [\text{A}] \) and \( [\text{B}] \).

Solution: \( \text{A(g)} \rightarrow \text{B(g)} \)

<table>
<thead>
<tr>
<th>( [\text{A}] )</th>
<th>( [\text{B}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0 0.00</td>
</tr>
<tr>
<td>C</td>
<td>-x x</td>
</tr>
<tr>
<td>E</td>
<td>1-x x</td>
</tr>
</tbody>
</table>

\[
Q = \frac{[\text{B}]}{[\text{A}]} = \frac{x}{1} = 0 \quad Q < K \text{ therefore, the reaction will proceed to the right by } x.
\]

\[
K_c = \frac{[\text{B}]^a}{[\text{A}]^b} = \frac{(x)^a}{(1-x)^b} = 4.0 \quad x = 0.80
\]

Check: Plug the values into the equilibrium expression: \( K_c = 0.80 = 4.0 \).

(b) Given: \( [\text{A}] = 1.0 \) M, \( [\text{B}] = 0.0 \) \( K_c = 4.0; a = 2, b = 2 \) Find: \( [\text{A}], [\text{B}] \) at equilibrium

Conceptual Plan: Prepare an ICE table, calculate Q, compare Q and \( K_c \) predict the direction of the reaction, represent the change with \( x \), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \( x \). Determine \( [\text{A}] \) and \( [\text{B}] \).

Solution: \( 2 \text{A(g)} \rightarrow 2 \text{B(g)} \)

<table>
<thead>
<tr>
<th>( [\text{A}] )</th>
<th>( [\text{B}] )</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0 0.00</td>
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<tr>
<td>C</td>
<td>-2x 2x</td>
</tr>
<tr>
<td>E</td>
<td>1-2x 2x</td>
</tr>
</tbody>
</table>

\[
Q = \frac{[\text{B}]^2}{[\text{A}]^2} = \frac{1}{(1-2x)^2} = 0 \quad Q < K \text{ therefore, the reaction will proceed to the right by } x.
\]

\[
K_c = \frac{[\text{B}]^2}{[\text{A}]^2} = \frac{1}{(1-2x)^2} = 4.0 \quad x = 0.33
\]

Check: Plug the values into the equilibrium expression: \( K_c = \frac{(0.66)^2}{(0.33)^2} = 4.0 \).
Given: \([A] = 1.0\ M, [B] = 1.0, [C] = 0.0\)
\(K_c = 5.0; a = 2, b = 1, c = 1\)  
Find: \([A], [B], [C]\) at equilibrium

Conceptual Plan: Prepare an ICE table, calculate \(Q\), compare \(Q\) and \(K\), predict the direction of the reaction, represent the change with \(x\), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \(x\).

Solution:  
\[
\begin{array}{c|c|c|c|c}
& A & B & C \\
I & 1.0 & 1.0 & 0.0 \\
C & -2x & -x & x \\
E & 1 - 2x & 1 - x & x \\
\end{array}
\]

\(Q = \frac{[C]^2}{[A]^2[B]} = \frac{(1)(1)}{1 - 2x} = 5.0\)

\(-20x^2 + 40x^2 - 26x + 5.0 = 0.\) Solve by using successive approximations or a cubic equation calculator found on the internet.

\(x = 0.3396 = 0.34\)

\([A] = 1 - 2x = 0.32\ M; [B] = 1 - x = 0.66\ M; [C] = x = 0.34\ M.\)

Check: Plug the values into the equilibrium expression: \(K_c = \frac{[C]^2}{[A]^2[B]} = \frac{(0.34)^2}{(0.32)^2(0.66)} = 5.0.\)

Given: \([N_2O_4] = 0.0500\ M, \,[NO_2] = 0.0\) \(K_c = 0.513\)  
Find: \([N_2O_4], [NO_2]\) at equilibrium

Conceptual Plan: Prepare an ICE table, calculate \(Q\), compare \(Q\) and \(K\), predict the direction of the reaction, represent the change with \(x\), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \(x\).

Determine \([N_2O_4]\) and \([NO_2]\).

Solution:  
\[
\begin{array}{c|c|c|c|c}
& N_2O_4 & NO_2 \\
I & 0.0500 & 0.00 \\
C & -x & 2x \\
E & 0.0500 - x & 2x \\
\end{array}
\]

\(Q = \frac{[NO_2]^2}{[N_2O_4]^2} = \frac{(2x)}{(0.0500 - x)^2} = 0.513\)

\(-b \pm \sqrt{b^2 - 4ac} = -0.513 \pm \sqrt{(0.513)^2 - 4(0.02565)} = -0.513 \pm \sqrt{0.6735}

\[2x = \frac{-0.1667 \text{ or } x = 0.0385}{2(4)}\]

\([N_2O_4] = 0.0500 - 0.0385 = 0.0115\ M; [NO_2] = 2x = 2(0.0385) = 0.0770\ M.\)

Check: Plug the values into the equilibrium expression: \(K_c = \frac{[NO_2]^2}{[N_2O_4]^2} = \frac{(0.0770)^2}{(0.0115)} = 5.15.\)

Given: \([CO] = 0.1500\ M, [Cl_2] = 0.175, [COCl_2] = 0.0\) \(K_c = 255\)  
Find: \([CO], [Cl_2], [COCl_2]\) at equilibrium

Conceptual Plan: Prepare an ICE table, calculate \(Q\), compare \(Q\) and \(K\), predict the direction of the reaction, represent the change with \(x\), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \(x\).

Determine \([CO], [Cl_2], \text{ and } [COCl_2]\).

Solution:  
\[
\begin{array}{c|c|c|c|c}
& CO & Cl_2 & COCl_2 \\
I & 0.1500 & 0.175 & 0.0 \\
C & -x & x & x \\
E & 0.1500 - x & 0.175 - x & x \\
\end{array}
\]

\(Q = \frac{[CO][Cl_2]^2}{[COCl_2]^2} = \frac{(0.1500)(0.175)}{(0.1500 - x)(0.175 - x)} = 0.175\)

\(-b \pm \sqrt{b^2 - 4ac} = -255 \pm \sqrt{(255)^2 - 4(83.875x + 6.69375)} = -255 \pm \sqrt{83.875x + 6.69375}\)

\[x = 0.00770 \text{ or } x = 0.00770\]
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\[-b \pm \sqrt{b^2 - 4ac} \over 2a = \frac{-(-83.875) \pm \sqrt{(-83.875)^2 - 4(255)(6.69375)}}{2(255)}\]

\[x = 0.1927 \text{ or } x = 0.1362, \text{ therefore, } x = 0.1362.\]

\[[\text{CO}] = 0.1500 - 0.1362 = 0.01377 \text{ M}\]

\[[\text{Cl}_2] = 0.175 - 0.1362 = 0.03878 \text{ M}\]

\[[\text{COCl}_2] = x = 0.1362 \text{ M}\]

Check: Plug the values into the equilibrium expression:

\[K_c = \frac{[\text{CO}_2]}{[\text{CO}] [\text{Cl}_2]} = \frac{(0.1362)}{(0.01377)(0.03878)} = 255.\]

14.53 Given: \[[\text{CO}] = 0.20 \text{ M}, [\text{CO}_2] = 0.0 \text{ M}, K_c = 4.0 \times 10^3 \text{ Find: [CO}_2\text{ ] at equilibrium}\]

Conceptual Plan: Prepare an ICE table, calculate \(Q\), compare \(Q\) and \(K_c\) predict the direction of the reaction, represent the change with \(x\), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \(x\).

Solution:

\[
\begin{align*}
\text{NiO(s)} + \text{CO}(g) & \rightleftharpoons \text{Ni(s)} + \text{CO}_2(g) \\
\text{I} & 0.20 \quad 0.0 \\
\text{C} & -x \quad x \\
\text{E} & 0.10 \quad -x \quad x \\
\text{x} & x \\
\text{Q} = [\text{CO}_2] & \quad 0 \\
[\text{CO}] & \quad (0.20) \\
\text{K_c} & \quad \frac{x}{(0.20 - x)} = 4.0 \times 10^3 \quad 4.0 \times 10^3(0.20 - x) = x \\
x & = 0.100 \\
[\text{CO}_2] & = 0.199 \text{ M}
\end{align*}
\]

Check: Since the equilibrium constant is so large, the reaction goes essentially to completion, therefore, it is reasonable that the concentration of product is 0.199 M.

14.54 Given: \[[\text{CO}] = 0.110 \text{ M}, [\text{H}_2\text{O}] = 0.110 \text{ M}, [\text{CO}_2] = 0.0 \text{ M}, [\text{H}_2] = 0.0 \text{ M}, K_c = 10^2 \text{ Find: [CO}_2\text{ ] at equilibrium}\]

Conceptual Plan: Prepare an ICE table, calculate \(Q\), compare \(Q\) and \(K_c\) predict the direction of the reaction, represent the change with \(x\), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \(x\). Determine \([\text{CO}_2]\), \([\text{Cl}_2]\), and \([\text{COCl}_2]\).

Solution:

\[
\begin{align*}
\text{CO(g)} + \text{H}_2\text{O}(g) & \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \\
\text{I} & 0.110 \quad 0.110 \quad 0.0 \quad 0.0 \\
\text{C} & -x \quad -x \\
\text{E} & 0.110-x \quad 0.110 \quad -x \quad x \\
\text{Q} = [\text{CO}_2][\text{H}_2] & \quad 0 \\
[\text{CO}][\text{H}_2\text{O}] & \quad (0.110)(0.110) \\
\text{K_c} = [\text{CO}_2][\text{H}_2\text{O}] & \quad \frac{x}{(0.110 - x)(0.110 - x)} = 102 \\
\sqrt{(0.110 - x)(0.110 - x)} & \quad \sqrt{102} \\
x & = 0.110 - x = \pm 10.0995 \\
\pm 10.0995(0.110 - x) & = x \\
x & = 0.10009 \text{ or } x = 0.22099, \text{ therefore, } x = 0.100. \\
[\text{CO}] = [\text{H}_2\text{O}] = 0.110 \quad - 0.100 = 0.010 = 0.010 \text{ M} \\
[\text{H}_2] = [\text{CO}_2] = x = 0.100 = 0.100 \text{ M}
\end{align*}
\]

Check: Plug the values into the equilibrium expression:

\[K_c = \frac{[\text{CO}_2] \cdot [\text{H}_2\text{O}]}{[\text{CO}] \cdot [\text{H}_2]} = \frac{(0.100)(0.100)}{(0.110)(0.110)} = 101.2 = 1.0 \times 10^2; \text{ within 1% of true value, answers are valid.}\]
Given: \([\text{HC}_2\text{H}_3\text{O}_2] = 0.210\text{M}, [\text{H}_2\text{O}] = 0.0, [\text{C}_2\text{H}_3\text{O}_2^-] = 0.0, K_c = 1.8 \times 10^{-5}\)

Find: \([\text{HC}_2\text{H}_3\text{O}_2]\), \([\text{H}_2\text{O}^+]\), \([\text{C}_2\text{H}_3\text{O}_2^-]\) at equilibrium

Conceptual Plan: Prepare an ICE table, calculate \(Q\), compare \(Q\) and \(K_c\) predict the direction of the reaction, represent the change with \(x\), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \(x\). Determine \([\text{CO}]\), \([\text{Cy}]\), and \([\text{COCl}_2]\).

Solution:

\[
\begin{array}{c|c|c|c|c|c}
 & \text{HC}_2\text{H}_3\text{O}_2(aq) & +\text{H}_2\text{O}(l) & \rightleftharpoons & \text{H}_2\text{O}^+(aq) & + \text{C}_2\text{H}_3\text{O}_2^-(aq) \\
I & 0.210 & 0.0 & 0.0 & & \\
C & \cdot x & x & x & & \\
E & 0.210-x & x & x & & \\
\end{array}
\]

\[Q = \frac{[\text{H}_2\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{0}{0.210} = 0\]

\(Q < K_c\) therefore, the reaction will proceed to the right by \(x\).

\[K_c = \frac{[\text{H}_2\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(x)}{(0.210 - x)} = 1.8 \times 10^{-5}\]

Assume \(x\) is small compared to 0.210.

\[x^2 = 0.210(1.8 \times 10^{-5})\]

\[x = 0.00194 \quad \text{check assumption:} \quad 0.00194 \times 100 = 0.194\%; \text{assumption valid.}\]

\[\text{[H}_2\text{O}^+] = \text{[C}_2\text{H}_3\text{O}_2^-] = x = 0.00194 \text{M}\]

\[\text{[HC}_2\text{H}_3\text{O}_2^-] = 0.210 - 0.00194 = 0.2081 = 0.208 \text{M}\]

Check: Plug the values into the equilibrium expression:

\[K_c = \frac{(0.00194)(0.00194)}{0.208} = 1.81 \times 10^{-5};\]

the answer is the same to 2 significant figures with the true value, answers are valid.

Given: \([\text{SO}_2\text{Cl}_2] = 0.175\text{M}, [\text{SO}_2] = 0.0, [\text{Cl}_2] = 0.0, K_c = 2.99 \times 10^{-7}\)

Find: \([\text{SO}_2\text{Cl}_2], [\text{SO}_2], [\text{Cl}_2]\) at equilibrium

Conceptual Plan: Prepare an ICE table, calculate \(Q\), compare \(Q\) and \(K_c\) predict the direction of the reaction, represent the change with \(x\), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \(x\). Determine \([\text{SO}_2\text{Cl}_2], [\text{SO}_2],\) and \([\text{Cl}_2]\).

Solution:

\[
\begin{array}{c|c|c|c|c|c}
 & \text{SO}_2\text{Cl}_2(g) & \rightarrow & \text{SO}_2(g) & + & \text{Cl}_2(g) \\
I & 0.175 & 0.0 & 0.0 & & \\
C & \cdot x & x & x & & \\
E & 0.175-x & x & x & & \\
\end{array}
\]

\[Q = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{0}{0.175} = 0\]

\(Q < K_c\) therefore, the reaction will proceed to the right by \(x\).

\[K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{(x)(x)}{(0.175 - x)} = 2.99 \times 10^{-7}\]

Assume \(x\) is small compared to 0.175.

\[x^2 = 2.99 \times 10^{-7}(0.175)\]

\[x = 2.287 \times 10^{-4} \quad \text{check assumption:} \quad 2.287 \times 10^{-4} \times 100 = 0.13\%; \text{assumption valid.}\]

\[\text{[SO}_2] = \text{[Cl}_2] = x = 2.287 \times 10^{-4} = 2.29 \times 10^{-4} \text{M}\]

\[\text{[SO}_2\text{Cl}_2] = 0.175 - 2.287 \times 10^{-4} = 0.1747 = 0.175 \text{M}\]

Check: Plug the values into the equilibrium expression:

\[K_c = \frac{(0.2287 \times 10^{-4})(2.287 \times 10^{-4})}{(0.175)} = 2.996 \times 10^{-7} = 3.00 \times 10^{-7};\]

this is within 0.01 \times 10^{-7} of the true value, therefore, answers are valid.
Chapter 14 Chemical Equilibrium

14.57 Given: \( P_{Br_2} = 755 \text{ torr} \), \( P_{Cl_2} = 735 \text{ torr} \), \( P_{BrCl} = 0.0 \), \( K_p = 1.11 \times 10^{-4} \) Find: \( P_{BrCl} \) at equilibrium

Conceptual Plan: Torr \( \rightarrow \) atm and then: Prepare an ICE table, calculate \( Q \), compare \( Q \) and \( K_p \), predict the direction of the reaction, represent the change with \( x \), sum the table, determine the equilibrium values, put the equilibrium values in the equilibrium expression, and solve for \( x \). Determine \( P_{BrCl} \)

Solution:

\[
\begin{align*}
P_{Br_2} &= 755 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.9934 \text{ atm} \\
P_{Cl_2} &= 735 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.9671 \text{ atm} \\
\end{align*}
\]

\[
\begin{align*}
\text{Br}_2(g) + Cl_2(g) & \rightleftharpoons 2 \text{BrCl}(g) \\
P_{Br_2} &= 0.9934 \text{ atm} \\
P_{Cl_2} &= 0.9671 \text{ atm} \\
P_{BrCl} &= x \\
\text{I} & \\

\text{C} & \quad -x \\

\text{E} & \quad 0.9934 - x \\

Q &= \frac{P_{BrCl}^2}{P_{Br_2}P_{Cl_2}} = \frac{(2x)^2}{(0.9934)(0.9671)} = 0 \\

\text{Since } Q < K, \text{ the reaction will proceed to the right by } x. \\

\text{Assume } x \text{ is small compared to } 0.9934 \text{ and } 0.9671. \\

K_p &= \frac{(2x)^2}{(0.9934 - x)(0.9671 - x) = 1.11 \times 10^{-4}} \\

x &= 0.00516 \text{ atm} = 3.92 \text{ torr} \\
P_{BrCl} &= 2x = 2(3.92 \text{ torr}) = 7.84 \text{ torr} \\

\text{Check: Plug the values into the equilibrium expression:} \\

K_p &= \frac{(0.9934 - 0.00516)(0.9671 - 0.00516)}{0.9934 - 0.00516} = 1.065 \times 10^{-4} = 1.12 \times 10^{-4}; \\
\text{This is within } 0.01 \times 10^{-4} \text{ of the true value, therefore, answers are valid.}
\]

14.58 Given: \( P_{CO} = 1344 \text{ torr} \), \( P_{H_2}O = 1766 \text{ torr} \), \( P_{CO_2} = 0.0 \), \( P_{H_2} = 0.0 \), \( K_p = 0.0611 \) Find: \( P_{CO_2}/P_{H_2} \) at equilibrium

Conceptual Plan: Torr \( \rightarrow \) atm and then prepare an ICE table, calculate \( Q \), compare \( Q \) and \( K_p \), predict the direction of the reaction, represent the change with \( x \), sum the table, determine the equilibrium values, put the equilibrium values, in the equilibrium expression, and solve for \( x \). Determine \( P_{CO_2} \) and \( P_{H_2} \)

Solution:

\[
\begin{align*}
P_{CO} &= 1344 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.7684 \text{ atm} \\
P_{H_2}O &= 1766 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.3237 \text{ atm} \\
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2(g) + H_2O(g) & \rightleftharpoons CO_2(g) + H_2(g) \\
P_{CO_2} &= 0.0 \text{ atm} \\
P_{H_2}O &= 0.0 \text{ atm} \\
P_{CO} &= 1.7684 \text{ atm} \\
P_{H_2} &= 0.0 \text{ atm} \\
\text{I} & \\

\text{C} & \quad -x \\

\text{E} & \quad 1.7684 - x \\

Q &= \frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2}O} = \frac{(2x)^2}{(1.7684)(2.3237)} = 0 \\

\text{Since } Q < K, \text{ the reaction will proceed to the right by } x. \\

K_p &= \frac{(1.7684 - x)(2.3237 - x)}{(1.7684)(2.3237)} = 0.0611 \\

x &= 0.00408 \text{ or } -0.6671 \text{ so: } x = 0.00408 \\
P_{CO_2} &= P_{H_2} = x = 0.00408 \text{ atm} = 305 \text{ torr} \\

\text{Check: Plug the values into the equilibrium expression:} \\

K_p &= \frac{0.00408^2}{(1.7684 - 0.00408)(2.3237 - 0.00408)} = 0.06108 = 0.061; \\
\text{the answers are the same to two significant figures with the true value, therefore, answers are valid.}
(c) COCl₂ is removed from the reaction mixture: Removing the COCl₂ decreases the concentration of COCl₂ and causes the reaction to shift to the right.

14.62 Given: \(2\text{BrNO}(g) \rightleftharpoons 2\text{NO}(g) + \text{Br}_2(g)\) at equilibrium Find: What is the effect of each of the following?

(a) NO is added to the reaction mixture: Adding NO increases the concentration of NO and causes the reaction to shift to the left.

(b) BrNO is added to the reaction mixture: Adding BrNO increases the concentration of BrNO and causes the reaction to shift to the right.

(c) Br₂ is removed from the reaction mixture: Removing Br₂ decreases the concentration of Br₂ and causes the reaction to shift to the right.

14.63 Given: \(2\text{KClO}_3(s) \rightleftharpoons 2\text{KCl}(s) + 3\text{O}_2(g)\) at equilibrium Find: What is the effect of each of the following?

(a) O₂ is removed from the reaction mixture: Removing the O₂ decreases the concentration of O₂ and causes the reaction to shift to the right.

(b) KCl is added to the reaction mixture: Adding KCl does not cause any change in the reaction. KCl is a solid and the concentration remains constant so the addition of more solid does not change the equilibrium concentration.

(c) KClO₃ is added to the reaction mixture: Adding KClO₃ does not cause any change in the reaction. KClO₃ is a solid and the concentration remains constant so the addition of more solid does not change the equilibrium concentration.

(d) O₂ is added to the reaction mixture: Adding O₂ increases the concentration of O₂ and causes the reaction to shift to the left.

14.64 Given: \(\text{C(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2(g)\) Find: What is the effect of each of the following?

(a) C is added to the reaction mixture: Adding C does not cause any change in the reaction. C is a solid and the concentration remains constant so the addition of more solid does not change the equilibrium concentration.

(b) H₂O is condensed and removed from the reaction mixture: Removing the H₂O decreases the concentration of H₂O and causes the reaction to shift to the left.

(c) CO is added to the reaction mixture: Adding CO increases the concentration of CO and causes the reaction to shift to the left.

(d) H₂ is removed from the reaction mixture: Removing the H₂ decreases the concentration of H₂ and causes the reaction to shift to the right.

14.65 (a) Given: \(\text{I}_2(g) \rightleftharpoons 2\text{l}(g)\) at equilibrium Find: the effect of increasing the volume. The chemical equation has 2 moles of gas on the right and 1 mole of gas on the left. Increasing the volume of the reaction mixture decreases the pressure and causes the reaction to shift to the right (toward the side with more moles of gas particles).

(b) Given: \(2\text{H}_2\text{S(g)} \rightleftharpoons 2\text{H}_2(g) + \text{S}_2(g)\) Find: the effect of decreasing the volume. The chemical equation has 3 moles of gas on the right and 2 moles of gas on the left. Decreasing the volume of the reaction mixture increases the pressure and causes the reaction to shift to the left (toward the side with fewer moles of gas particles).

(c) Given: \(\text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{ICl(g)}\) Find: the effect of decreasing the volume. The chemical equation has 2 moles of gas on the right and 2 moles of gas on the left. Decreasing the volume of the reaction mixture increases the pressure but causes no shift in the reaction because the moles are equal on both sides.

14.66 (a) Given: \(\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)\) Find: the effect of decreasing the volume. The chemical equation has 2 moles of gas on the right and 2 moles of gas on the left. Decreasing the
volume of the reaction mixture increases the pressure but causes no shift in the reaction because the moles are equal on both sides.

(b) Given: $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$ Find: the effect of increasing the volume.
The chemical equation has 2 moles of gas on the left and 1 mole of gas on the right. Increasing the volume of the reaction mixture decreases the pressure and causes the reaction to shift to the left (toward the side with more moles of gas particles).

c) Given: $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ Find: the effect of increasing the volume.
The chemical equation has 1 mole of gas on the right and 0 moles of gas on the left. Increasing the volume of the reaction mixture decreases the pressure and causes the reaction to shift to the right (toward the side with more moles of gas particles).

14.67 Given: $\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g)$ is endothermic. Find: the effect of increasing the temperature.
Since the reaction is endothermic we can think of the heat as a reactant: Increasing the temperature is equivalent to adding a reactant causing the reaction to shift to the right. This will cause an increase in the concentration of products and a decrease in the concentration of reactant; therefore, the value of $K$ will increase.

Find: the effect of decreasing the temperature
Since the reaction is endothermic we can think of the heat as a reactant: Decreasing the temperature is equivalent to removing a reactant causing the reaction to shift to the left. This will cause a decrease in the concentration of products and an increase in the concentration of reactants; therefore, the value of $K$ will decrease.

14.68 Given: $\text{C}_6\text{H}_12\text{O}_6(s) + 6 \text{O}_2(g) \rightleftharpoons 6\text{CO}_2(g) + 6 \text{H}_2\text{O}(g)$ is exothermic.
Find: the effect of increasing the temperature
Since the reaction is exothermic we can think of heat as a product: Increasing the temperature is equivalent to adding a product causing the reaction to shift to the left. This will cause a decrease in the concentration of products and an increase in the concentration of reactant; therefore, the value of $K$ will decrease.

Find: the effect of decreasing the temperature
Since the reaction is exothermic we can think of heat as a product: Decreasing the temperature is equivalent to removing a product causing the reaction to shift to the right. This will cause an increase in the concentration of products and a decrease in the concentration of reactants; therefore, the value of $K$ will increase.

14.69 Given: $\text{C}(s) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_4(g)$ is exothermic. Find: Determine which will favor $\text{CH}_4$.

(a) Adding more $\text{C}$ to the reaction mixture does NOT favor $\text{CH}_4$. Adding $\text{C}$ does not cause any change in the reaction. $\text{C}$ is a solid and the concentration remains constant so the addition of more solid does not change the equilibrium concentration.

(b) Adding more $\text{H}_2$ to the reaction mixture favors $\text{CH}_4$. Adding $\text{H}_2$ increases the concentration of $\text{H}_2$ causing the reaction to shift to the right.

(c) Raising the temperature of the reaction mixture does NOT favor $\text{CH}_4$. Since the reaction is exothermic we can think of heat as a product, raising the temperature is equivalent to adding a product causing the reaction to shift to the left.

(d) Lowering the volume of the reaction mixture favors $\text{CH}_4$. The chemical equation has 1 mole of gas on the right and 2 moles of gas on the left. Decreasing the volume of the reaction mixture increases the pressure and causes the reaction to shift to the right (toward the side with fewer moles of gas particles).

(e) Adding a catalyst to the reaction mixture does NOT favor $\text{CH}_4$. A catalyst added to the reaction mixture only speeds up the reaction, it does not change the equilibrium concentration.

(f) Adding neon gas to the reaction mixture does NOT favor $\text{CH}_4$. Adding an inert gas to a reaction mixture at a fixed volume has no effect on the equilibrium.

14.70 Given: $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$ is endothermic. Find: Determine which will favor $\text{H}_2$.

(a) Adding more $\text{C}$ to the reaction mixture does NOT favor $\text{H}_2$. Adding $\text{C}$ does not cause any change in the reaction. $\text{C}$ is a solid and the concentration remains constant so the addition of more solid does not change the equilibrium concentration.