CHAPTER 17 EQUILIBRIUM: THE EXTENT OF CHEMICAL REACTIONS

FOLLOW–UP PROBLEMS

17.1A Plan: First, balance the equations and then write the reaction quotient. Products appear in the numerator of the reaction quotient and reactants appear in the denominator; coefficients in the balanced reaction become exponents.

Solution:

a) Balanced equation: $4NH_3(g) + 5O_2(g) \rightleftarrows 4NO(g) + 6H_2O(g)$

Reaction quotient: $Q_c = \dfrac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$

b) Balanced equation: $2NO_2(g) + 7H_2(g) \rightleftarrows 2NH_3(g) + 4H_2O(l)$

Reaction quotient: $Q_c = \dfrac{[NH_3]^2}{[NO_2]^2[H_2]^7}$

c) Balanced equation: $2KClO_3(s) \rightleftarrows 2KCl(s) + 3O_2(g)$

Reaction quotient: $Q_c = [O_2]^3$

17.1B Plan: First, balance the equations and then write the reaction quotient. Products appear in the numerator of the reaction quotient and reactants appear in the denominator; coefficients in the balanced reaction become exponents.

Solution:

a) Balanced equation: $CH_4(g) + CO_2(g) \rightleftarrows 2CO(g) + 2H_2\ (g)$

Reaction quotient: $Q_c = \dfrac{[CO]^2[H_2]^2}{[CH_4][CO_2]}$

b) Balanced equation: $2H_2S(g) + SO_2(g) \rightleftarrows 2S(s) + 2H_2O(g)$

Reaction quotient: $Q_c = \dfrac{[H_2O]^2}{[H_2S]^2[SO_2]}$

c) Balanced equation: $HCN(aq) + NaOH(aq)\ (s) \rightleftarrows NaCN(aq) + H_2O(l)$

Reaction quotient: $Q_c = \dfrac{[NaCN]}{[HCN][NaOH]}$

17.2A Plan: Add the individual steps to find the overall equation, canceling substances that appear on both sides of the equation. Write the reaction quotient for each step and the overall equation. Multiply the reaction quotients for each step and cancel terms to obtain the overall reaction quotient.

Solution:

(1) $Br_2(g) \rightleftarrows 2Br(g)$

(2) $Br(g) + H_2(g) \rightleftarrows HBr(g) + H(g)$

(3) $\underline{H(g) + Br(g) \rightleftarrows HBr(g)\qquad}$

$Br_2(g) + \cancel{2Br(g)} + H_2(g) + \cancel{H(g)} \rightleftarrows \cancel{2Br(g)} + 2HBr(g) + \cancel{H(g)}$

Canceling the reactants leaves the overall equation as $Br_2(g) + H_2(g) \rightleftarrows 2HBr(g)$.

Write the reaction quotients for each step:

$$Q_{c1} = \frac{[Br]^2}{[Br_2]} \qquad Q_{c2} = \frac{[HBr][H]}{[Br][H_2]} \qquad Q_{c3} = \frac{[HBr]}{[H][Br]}$$

and for the overall equation:

$$Q_c = \frac{[HBr]^2}{[H_2][Br_2]}$$

Multiplying the individual Q_c's and canceling terms gives

$$Q_{c1}\ Q_{c2}\ Q_{c3} = \frac{\left[\text{Br}\right]^2}{\left[\text{Br}_2\right]} \text{ x } \frac{\left[\text{HBr}\right]\left[\text{H}\right]}{\left[\text{Br}\right]\left[\text{H}_2\right]} \text{ x } \frac{\left[\text{HBr}\right]}{\left[\text{H}\right]\left[\text{Br}\right]} = \frac{\left[\text{HBr}\right]^2}{\left[\text{H}_2\right]\left[\text{Br}_2\right]}$$

The product of the multiplication of the three individual reaction quotients equals the overall reaction quotient.

17.2B Plan: Add the individual steps to find the overall equation, canceling substances that appear on both sides of the equation. Write the reaction quotient for each step and the overall equation. Multiply the reaction quotients for each step and cancel terms to obtain the overall reaction quotient.

Solution:

(1) $H_2(g) + ICl(g) \leftrightarrows HI(g) + HCl(g)$

(2) $\underline{HI(g) + ICl(g) \leftrightarrows I_2(g) + HCl(g)}$

$$H_2(g) + 2ICl(g) + \cancel{HI(g)} \leftrightarrows \cancel{HI(g)} + 2HCl(g) + I_2(g)$$

Canceling the reactants leaves the overall equation as $H_2(g) + 2ICl(g) \leftrightarrows 2HCl(g) + I_2(g)$

Write the reaction quotients for each step:

$$Q_{c1} = \frac{[HI][HCl]}{[H_2][ICl]} \qquad Q_{c2} = \frac{[I_2][HCl]}{[HI][ICl]}$$

and for the overall equation:

$$Q_c = \frac{[HCl]^2[I_2]}{[H_2][ICl]^2}$$

Multiplying the individual Q_c's and canceling terms gives

$$Q_{c1}\ Q_{c2} = \frac{[HI][HCl]}{[H_2][ICl]} \text{ x } \frac{[I_2][HCl]}{[HI][ICl]} = \frac{[HCl]^2[I_2]}{[H_2][ICl]^2}$$

The product of the multiplication of the two individual reaction quotients equals the overall reaction quotient.

17.3A Plan: When a reaction is multiplied by a factor, the equilibrium constant is raised to a power equal to the factor. When a reaction is reversed, the reciprocal of the equilibrium constant is used as the new equilibrium constant.

Solution:

a) All coefficients have been multiplied by the factor 1/2 so the equilibrium constant should be raised to the 1/2 power (which is the square root).

For reaction a) $K_c = (7.6\text{x}10^8)^{½} = 2.7568\text{x}10^4 = \mathbf{2.8x10^4}$

b) The reaction has been reversed so the new K_c is the reciprocal of the original equilibrium constant. The reaction has also been multiplied by a factor of 2/3, so the reciprocal of the original K_c must be raised to the 2/3 power.

For reaction b) $K_c = \left(\frac{1}{7.6\text{ x }10^8}\right)^{\frac{2}{3}} = 1.20076\text{x}10^{-6} = \mathbf{1.2x10^{-6}}$

17.3B Plan: When a reaction is multiplied by a factor, the equilibrium constant is raised to a power equal to the factor. When a reaction is reversed, the reciprocal of the equilibrium constant is used as the new equilibrium constant.

Solution:

a) All coefficients have been multiplied by the factor 2. Additionally, the reaction has been reversed. Therefore, the reciprocal of the equilibrium constant should be raised to the 2 power.

For reaction a) $K_c = (1/1.3\text{x}10^{-2})^2 = 5917.1598 = \mathbf{5.9x10^3}$

b) All coefficients have been multiplied by the factor 1/4 so the equilibrium constant should be raised to the 1/4 power.

For reaction b) $K_c = (1.3\text{x}10^{-2})^{1/4} = 0.33766 = 0.\mathbf{34}$

17.4A Plan: K_p and K_c for a reaction are related through the ideal gas equation as shown in $K_P = K_c(RT)^{\Delta n}$. Find Δn_{gas}, the change in the number of moles of gas between reactants and products (calculated as products minus reactants). Then, use the given K_c to solve for K_p.

Solution:
The total number of product moles of gas is 1 and the total number of reactant moles of gas is 2.

$\Delta n = 1 - 2 = -1$

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

$K_P = 1.67[(0.0821 \text{ atm•L/mol•K})(500. \text{ K})]^{-1}$

$K_P = 0.040682095 = \mathbf{4.07x10^{-2}}$

17.4B Plan: K_p and K_c for a reaction are related through the ideal gas equation as shown in $K_P = K_c(RT)^{\Delta n}$. Find Δn_{gas}, the change in the number of moles of gas between reactants and products (calculated as products minus reactants). Then, use the given K_P to solve for K_c.
Solution:
The total number of product moles of gas is 3 and the total number of reactant moles of gas is 5.

$\Delta n = 3 - 5 = -2$

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

$K_P = K_c(RT)^{-2}$

$K_P(RT)^2 = K_c$

$K_c = (3.0x10^{-5})\ [(0.0821 \text{ atm•L/mol•K})(1173 \text{ K})]^2 = 0.27822976 = \mathbf{0.28}$

17.5A Plan: Write the reaction quotient for the reaction and calculate Q_c for each circle. Compare Q_c to K_c to determine the direction needed to reach equilibrium. If $Q_c > K_c$, reactants are forming. If $Q_c < K_c$, products are forming.
Solution:

The reaction quotient is $\frac{[Y]}{[X]}$.

Circle 1: $Q_c = \frac{[Y]}{[X]} = \frac{[3]}{[9]} = 0.33$

Since $Q_c < K_c$ (0.33 < 1.4), the reaction will shift to the **right** to reach equilibrium

Circle 2: $Q_c = \frac{[Y]}{[X]} = \frac{[7]}{[5]} = 1.4$

Since $Q_c = K_c$ (1.4 = 1.4), there is **no change** in the reaction direction. The reaction is at equilibrium now.

Circle 3: $Q_c = \frac{[Y]}{[X]} = \frac{[8]}{[4]} = 2.0$

Since $Q_c > K_c$ (2.0 > 1.4), the reaction will shift to the **left** to reach equilibrium

17.5B Plan: Write the reaction quotient for the reaction and calculate Q_c for each circle. Compare Q_c to K_c to determine the direction needed to reach equilibrium. If $Q_c > K_c$, reactants are forming. If $Q_c < K_c$, products are forming.
Solution:

The reaction quotient is $\frac{[D]}{[C]^2}$.

Circle 1: $Q_c = \frac{[D]}{[C]^2} = \frac{[5]}{[3]^2} = 0.56$

According to the problem, circle 1 is at equilibrium. Therefore, $K_c = 0.56$.

Circle 2: $Q_c = \frac{[D]}{[C]^2} = \frac{[6]}{[3]^2} = 0.67$

Since $Q_c > K_c$ (0.67 > 0.56), the reaction will shift to the **left** to reach equilibrium.

Circle 3: $Q_c = \frac{[D]}{[C]^2} = \frac{[7]}{[4]^2} = 0.44$

Since $Q_c < K_c$ (0.44 < 0.56), the reaction will shift to the **right** to reach equilibrium

17.6A Plan: To decide whether CH_3Cl or CH_4 are forming while the reaction system moves toward equilibrium, calculate Q_p and compare it to K_p. If $Q_p > K_p$, reactants are forming. If $Q_p < K_p$, products are forming.
Solution:

$$Q_P = \frac{P_{CH_3Cl}P_{HCl}}{P_{CH_4}P_{Cl_2}} = \frac{(0.24\text{ atm})(0.47\text{ atm})}{(0.13\text{ atm})(0.035\text{ atm})} = 24.7912 = 25$$

K_p for this reaction is given as 1.6x10^4. Q_p is smaller than K_p ($Q_p < K_p$) so more products will form. **CH_3Cl** is one of the products forming.

17.6B <u>Plan:</u> To determine whether the reaction is at equilibrium or, if it is not at equilibrium, which direction to will proceed, calculate Q_c and compare it to K_c. If $Q_c > K_c$, the reaction will proceed to the left. If $Q_c < K_c$, the reaction will proceed to the right.

<u>Solution:</u>

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left[\frac{1.2\text{ mol}}{2.0\text{ L}}\right]^2}{\left[\frac{3.4\text{ mol}}{2.0\text{ L}}\right]^2\left[\frac{1.5\text{ mol}}{2.0\text{ L}}\right]} = 0.166089965 = 0.17$$

The system is **not at equilibrium**. K_c for this reaction is given as 4.2 x 10^{-2}. Q_c is larger than K_c ($Q_c > K_c$) so the reaction will proceed to the **left**.

17.7A <u>Plan:</u> The information given includes the balanced equation, initial pressures of both reactants, and the equilibrium pressure for one reactant. First, set up a reaction table showing initial partial pressures for reactants and 0 for product. The change to get to equilibrium is to react some of reactants to form some product. Use the equilibrium quantity for O_2 and the expression for O_2 at equilibrium to solve for the change. From the change find the equilibrium partial pressure for NO and NO_2. Calculate K_p using the equilibrium values.

<u>Solution:</u>

Pressures (atm)	$2NO(g)$	+	$O_2(g)$	⇆	$2NO_2(g)$
Initial	1.000		1.000		0
Change	–2x		–x		+2x
Equilibrium	1.000 – 2x		1.000 – x		2x

At equilibrium P_{O_2} = 0.506 atm = 1.000 – x; so x = 1.000 – 0.506 = 0.494 atm

P_{NO} = 1.000 – 2x = 1.000 – 2(0.494) = 0.012 atm

P_{NO_2} = 2x = 2(0.494) = 0.988 atm

Use the equilibrium pressures to calculate K_p.

$$K_P = \frac{P^2_{NO_2}}{P^2_{NO}P_{O_2}} = \frac{(0.988)^2}{(0.012)^2(0.506)} = 1.339679\text{ x}10^4 = \mathbf{1.3x10^4}$$

17.7B <u>Plan:</u> The information given includes the balanced equation, initial concentrations of both reactants, and the equilibrium concentration for one product. First, set up a reaction table showing initial concentrations for reactants and 0 for products. The change to get to equilibrium is to react some of reactants to form some of the products. Use the equilibrium quantity for N_2O_4 and the expression for N_2O_4 at equilibrium to solve for the change. From the change find the equilibrium concentrations for NH_3, O_2, and H_2O. Calculate K_c using the equilibrium values.

<u>Solution:</u>

Pressures (atm)	$4NH_3(g)$ +	$7O_2(g)$	⇆	$2N_2O_4(g)$ +	$6H_2O(g)$
Initial	2.40	2.40		0	0
Change	–4x	–7x		+2x	+6x
Equilibrium	2.40 – 4x	2.40 –7 x		2x	6x

At equilibrium $[N_2O_4]$ = 0.134 M = 2x; so x = 0.0670 M

$[NH_3]$ = 2.40 M – 4(0.0670 M) = 2.13 M

$[O_2]$ = 2.40 M – 7(0.0670 M) = 1.93 M

$[H_2O]$ = 6(0.0670 M) = 0.402 M

Use the equilibrium pressures to calculate K_c.

$$K_c = \frac{[N_2O_4]^2[H_2O]^6}{[NH_3]^4[O_2]^7} = \frac{(0.134)^2(0.402)^6}{(2.13)^4(1.93)^7} = 3.6910\text{x}10^{-8} = \mathbf{3.69x10^{-8}}$$

17.8A Plan: Convert K_c to K_p for the reaction. Write the equilibrium expression for K_p and insert the atmospheric pressures for P_{N_2} and P_{O_2} as their equilibrium values. Solve for P_{NO}.

Solution:

The conversion of K_c to K_p: $K_p = K_c(RT)^{\Delta n}$. For this reaction $\Delta n = 0$, so $K_p = K_c$.

$$K_P = \frac{P_{N_2}P_{O_2}}{P_{NO}^2} = K_c = 2.3\text{x}10^{30} = \frac{(0.781)(0.209)}{\text{x}^2}$$

$$\text{x} = 2.6640\text{x}10^{-16} = 2.7\text{x}10^{-16}\ \text{atm}$$

The equilibrium partial pressure of NO in the atmosphere is **$2.7\text{x}10^{-16}$ atm**.

17.8B Plan: Write the equilibrium expression for K_p and insert the partial pressures for PH_3 and P_2 as their equilibrium values. Solve for the partial pressure of H_2.

Solution:

$$K_P = \frac{(P_{P_2})(P_{H_2})^3}{(P_{PH_3})^2} = \sqrt[3]{\frac{K_P(P_{PH_3})^2}{(P_{P_2})}} = P_{H_2} = \sqrt[3]{\frac{(19.6)(0.112)^2}{(0.215)}} = 1.0457 = \mathbf{1.05\ atm}$$

17.9A Plan: Find the initial molarity of HI by dividing moles of HI by the volume. Set up a reaction table and use the variables to find equilibrium concentrations in the equilibrium expression.

Solution:

$$M_{HI} = \frac{\text{moles HI}}{\text{volume}} = \frac{2.50\ \text{mol}}{10.32\ \text{L}} = 0.242248\ M$$

Concentration (M)	$2HI(g)$	$\leftrightarrows$	$H_2(g)$	+	$I_2(g)$
Initial	0.242248		0		0
Change	–2x		+x		+x
Equilibrium	0.242248 – 2x		x		x

Set up equilibrium expression:

$$K_c = 1.26\text{x}10^{-3} = \frac{[H_2][I_2]}{[HI]^2} = \frac{[\text{x}][\text{x}]}{[0.242248 - 2\text{x}]^2}$$ Take the square root of each side.

$$3.54965\text{x}10^{-2} = \frac{[\text{x}]}{[0.242248 - 2\text{x}]}$$

x = $8.59895\text{x}10^{-3} - 7.0993\text{x}10^{-2}$ x

x = $8.02895\text{x}10^{-3} = 8.03\text{x}10^{-3}$

$[H_2] = [I_2] =$ **$8.02\text{x}10^{-3}$ *M***

17.9B Plan: Find the initial molarities of Cl_2O and H_2O by dividing moles by the volume of the flask. Set up a reaction table and use the variables to find equilibrium concentrations in the equilibrium expression.

Solution:

$$\text{Molarity of } Cl_2O = \frac{\text{moles } Cl_2O}{\text{volume}} = \frac{6.15\ \text{mol}}{5.00\ \text{L}} = 1.23\ M$$

$$\text{Molarity of } H_2O = \frac{\text{moles } H_2O}{\text{volume}} = \frac{6.15\ \text{mol}}{5.00\ \text{L}} = 1.23\ M$$

Concentration (M)	$Cl_2O(g)$ +	$H_2O(g)$	$\leftrightarrows$	$2HOCl\ (g)$
Initial	1.23	1.23		0
Change	–x	–x		+2x
Equilibrium	1.23 – x	1.23 – x		2x

Set up equilibrium expression:

$$K_c = 0.18 = \frac{[HOCl]^2}{[Cl_2O][H_2O]} = \frac{[2\text{x}]^2}{[1.23 - \text{x}][1.23 - \text{x}]}$$

Take the square root of each side.

$$0.424264068 = \frac{[2x]}{[1.23 - x]}$$

$0.521844804 - 0.424264068x = 2x$

$0.521844804 = 2.424264068x$

$x = 0.215259000 = 0.21\ M$

$[Cl_2O] = [H_2O] = 1.23\ M - 0.21\ M = \mathbf{1.02\ M}$

$[HOCl] = 2(0.21\ M) = \mathbf{0.42\ M}$

17.10A <u>Plan:</u> Find the molarity of I_2 by dividing moles of I_2 by the volume. First set up the reaction table, then set up the equilibrium expression. To solve for the variable, x, first assume that x is negligible with respect to initial concentration of I_2. Check the assumption by calculating the % error. If the error is greater than 5%, calculate x using the quadratic equation. The next step is to use x to determine the equilibrium concentrations of I_2 and I.

<u>Solution:</u>

$$[I_2]_{init} = \frac{0.50\text{ mol}}{2.5\text{ L}} = 0.20\ M$$

a) Equilibrium at 600 K

Concentration (M)	$I_2(g)$	$\leftrightarrows$	$2I(g)$
Initial	0.20		0
Change	$-x$		$+2x$
Equilibrium	$0.20 - x$		$2x$

Equilibrium expression: $K_c = \dfrac{[I]^2}{[I_2]} = 2.94\text{x}10^{-10}$

$$\frac{[2x]^2}{[0.20 - x]} = 2.94\text{x}10^{-10}$$ Assume x is negligible so $0.20 - x \approx 0.20$

$$\frac{[2x]^2}{[0.20]} = 2.94\text{x}10^{-10}$$

$4x^2 = (2.94\text{x}10^{-10})\ (0.20)$; $x = 3.834\text{x}10^{-6} = 3.8\text{x}10^{-6}$

Check the assumption by calculating the % error:

$\dfrac{3.8\text{x}10^{-6}}{0.20}(100) = 0.0019\%$ which is smaller than 5%, so the assumption is valid.

At equilibrium $[I]_{eq} = 2x = 2(3.8\text{x}10^{-6}) = 7.668\text{x}10^{-6} = \mathbf{7.7x10^{-6}\ M}$ and

$[I_2]_{eq} = 0.20 - x = 0.20 - 3.834\text{x}10^{-6} = 0.199996 = \mathbf{0.20\ M}$

b) Equilibrium at 2000 K

Equilibrium expression: $K_c = \dfrac{[I]^2}{[I_2]} = 0.209$

$$\frac{[2x]^2}{[0.20 - x]} = 0.209$$ Assume x is negligible so $0.20 - x$ is approximately 0.20

$$\frac{[2x]^2}{[0.20]} = 0.209$$

$4x^2 = (0.209)(0.20)$

$x = 0.102225 = 0.102$

Check the assumption by calculating the % error:

$\dfrac{0.102}{0.20}(100) = 51\%$ which is larger than 5% so the assumption is not valid. Solve using quadratic equation.

$$\frac{[2x]^2}{[0.20 - x]} = 0.209$$

$$4x^2 + 0.209x - 0.0418 = 0$$

$$x = \frac{-0.209 \pm \sqrt{(0.209)^2 - 4(4)(-0.0418)}}{2(4)} = 0.0793857 \text{ or } -0.1316$$

Choose the positive value, x = 0.079
At equilibrium $[I]_{eq}$ = 2x = 2(0.079) = 0.15877 = **0.16 *M*** and
$[I_2]_{eq}$ = 0.20 – x = 0.20 – 0.079 = 0.12061 = **0.12 *M***

17.10B Plan: First set up the reaction table, then set up the equilibrium expression. To solve for the variable, x, first assume that x is negligible with respect to initial partial pressure of PCl_5. Check the assumption by calculating the % error. If the error is greater than 5%, calculate x using the quadratic equation. The next step is to use x to determine the equilibrium partial pressure of PCl_5.

Solution:

a) Equilibrium at a PCl_5 partial pressure of 0.18 atm:

Partial Pressure (atm)	$PCl_5(g)$ ⇆	$PCl_3(g)$ +	$Cl_2(g)$
Initial	0.18	0	0
Change	–x	+x	+x
Equilibrium	0.18 – x	x	x

Equilibrium expression: $K_P = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = 3.4\text{x}10^{-4}$

$\frac{(x)(x)}{(0.18 - x)} = 3.4\text{x}10^{-4}$ Assume x is negligible so 0.18 – x ≈ 0.18

$\frac{(x)(x)}{(0.18)} = 3.4\text{x}10^{-4}$

$x^2 = (3.4\text{x}10^{-4})(0.18)$; x = 0.0078230428 = $7.8\text{x}10^{-3}$

Check the assumption by calculating the % error:

$\frac{7.8\text{x}10^{-3}}{0.18}(100)$= 4.3% which is smaller than 5%, so the assumption is valid.

At equilibrium $[PCl_5]_{eq}$ = 0.18 *M* – 7.8 x 10^{-3} *M* = **0.17 *M***

b) Equilibrium at a PCl_5 partial pressure of 0.18 atm:

Partial Pressure (atm)	$PCl_5(g)$ ⇆	$PCl_3(g)$ +	$Cl_2(g)$
Initial	0.025	0	0
Change	–x	+x	+x
Equilibrium	0.025 – x	x	x

Equilibrium expression: $K_P = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = 3.4\text{x}10^{-4}$

$\frac{(x)(x)}{(0.025 - x)} = 3.4\text{x}10^{-4}$ Assume x is negligible so 0.025 – x ≈ 0.025

$\frac{(x)(x)}{(0.025)} = 3.4\text{x}10^{-4}$

$x^2 = (3.4\text{x}10^{-4})(0.025)$; x = 0.002915476= $2.9\text{x}10^{-3}$

Check the assumption by calculating the % error:

$\frac{2.9\text{x}10^{-3}}{0.025}(100)$ = 12% which is larger than 5%, so the assumption is NOT valid. Solve using quadratic equation.

$\frac{(x)(x)}{(0.025 - x)} = 3.4\text{x}10^{-4}$

$$x^2 + 3.4\text{x}10^{-4}x - 8.5\text{x}10^{-6} = 0$$

$$x = \frac{+8.5\text{x}10^{-6} \pm \sqrt{(3.4\text{x}10^{-4})^2 - 4(1)(-8.5\text{x}10^{-6})}}{2(1)} = 0.002750428051 \text{ or } -0.003090428051$$

Choose the positive value, $x = 0.0028\ M$; At equilibrium $[PCl_5]_{eq} = 0.025\ M - 0.0028\ M =$ **$0.022\ M$**

17.11A <u>Plan:</u> Calculate the initial concentrations (molarity) of each substance. For part (a), calculate Q_c and compare to given K_c. If $Q_c > K_c$ then the reaction proceeds to the left to make reactants from products. If $Q_c < K_c$ then the reaction proceeds to right to make products from reactants. For part (b), use the result of part (a) and the given equilibrium concentration of PCl_5 to find the equilibrium concentrations of PCl_3 and Cl_2.

<u>Solution:</u>

Initial concentrations: $[PCl_5] = \dfrac{0.1050 \text{ mol}}{0.5000 \text{ L}} = 0.2100\ M$

$$[PCl_3] = [Cl_2] = \frac{0.0450 \text{ mol}}{0.5000 \text{ L}} = 0.0900\ M$$

a) $Q_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{[0.0900][0.0900]}{[0.2100]} = 0.038571 = 0.0386$

Q_c, 0.0386, is less than K_c, 0.042, so the reaction will proceed to the **right** to make more products.

b) To reach equilibrium, concentrations will increase for the products, PCl_3 and Cl_2, and decrease for the reactant, PCl_5.

Concentration (M)	$PCl_5(g)$	$\leftrightarrows$	$PCl_3(g)$	+	$Cl_2(g)$
Initial	0.2100		0.0900		0.0900
Change	–x		+x		+x
Equilibrium	0.2100 – x		0.0900 + x		0.0900 + x

$[PCl_5] = 0.2065 = 0.2100 - x$; $x = 0.0035\ M$

$[PCl_3] = [Cl_2] = 0.0900 + x = 0.0900 + 0.0035 =$ **$0.0935\ M$**

17.11B <u>Plan:</u> For part (a), calculate Q_P and compare to given K_P. If $Q_P > K_P$ then the reaction proceeds to the left to make reactants from products. If $Q_P < K_P$ then the reaction proceeds to right to make products from reactants. For part (b), set up a reaction table and use the variables to find equilibrium concentrations in the equilibrium expression.

<u>Solution:</u>

$$Q_P = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(0.750)^2}{(0.500)(0.500)} = 2.25$$

Q_P, 2.25, is greater than K_P, 8.44×10^{-3}, so the reaction will proceed to the **left** to make more reactants.

To reach equilibrium, concentrations will increase for the reactants, N_2 and O_2, and decrease for the product, NO.

Pressure (atm)	$N_2(g)$ +	$O_2(g)$	$\leftrightarrows$	$2NO(g)$
Initial	0.500	0.500		0.750
Change	+x	+x		–2x
Equilibrium	0.500 + x	0.500 + x		0.750 – 2 x

$$K_P = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(0.750 - 2x)^2}{(0.500 + x)(0.500 + x)} = 8.44\text{x}10^{-3}$$

Take the square root of each side.

$$\frac{(0.750 - 2x)}{(0.500 + x)} = 0.0919$$

$0.750 - 2x = 0.0460 + 0.0919x$

$0.704 = 2.0919x$

$x = 0.337\ M$

$[N_2] = [O_2] = 0.500\ M + 0.337\ M =$ **$0.837\ M$**

$[NO] = 0.750\ M - 2(0.337\ M) =$ **$0.076\ M$**

17.12A Plan: Examine each change for its impact on Q_c. Then decide how the system would respond to re-establish equilibrium.

Solution:

$$Q_c = \frac{[SiF_4][H_2O]^2}{[HF]^4}$$

a) Decreasing $[H_2O]$ leads to $Q_c < K_c$, so the reaction would shift to make more products from reactants. Therefore, the SiF_4 concentration, as a product, would **increase**.

b) Adding liquid water to this system at a temperature above the boiling point of water would result in an increase in the concentration of water vapor. The increase in $[H_2O]$ increases Q_c to make it greater than K_c To re-establish equilibrium products will be converted to reactants and the $[SiF_4]$ will **decrease**.

c) Removing the reactant HF increases Q_c, which causes the products to react to form more reactants. Thus, $[SiF_4]$ **decreases**.

d) Removal of a solid product has no impact on the equilibrium; $[SiF_4]$ **does not change**.

Check: Look at each change and decide which direction the equilibrium would shift using Le Châtelier's principle to check the changes predicted above.

a) Remove product, equilibrium shifts to right.
b) Add product, equilibrium shifts to left.
c) Remove reactant, equilibrium shifts to left.
d) Remove solid reactant, equilibrium does not shift.

17.12B Plan: Examine each change for its impact on Q_c. Then decide how the system would respond to re-establish equilibrium.

Solution:

$$Q_c = \frac{[CO][H_2]}{[H_2O]}$$

a) Adding carbon, a solid reactant, has no impact on the equilibrium. [CO] **does not change**.

b) Removing water vapor, a reactant, increases Q_c, which causes the products to react to form more reactants. Thus, [CO] **decreases**.

c) Removing the product H_2 decreases Q_c, which causes the reactants to react to form more products. Thus, [CO] **increases**.

d) Adding water vapor, a reactant, decreases Q_c, which causes the reactants to react to form more products. Thus, [CO] **increases**.

Check: Look at each change and decide which direction the equilibrium would shift using Le Châtelier's principle to check the changes predicted above.

a) Add solid reactant, equilibrium does not shift.
b) Remove reactant, equilibrium shifts to the left.
c) Remove product, equilibrium shifts to the right.
d) Add reactant, equilibrium shifts to the right.

17.13A Plan: Changes in pressure (and volume) affect the concentration of gaseous reactants and products. A decrease in pressure, i.e., increase in volume, favors the production of more gas molecules whereas an increase in pressure favors the production of fewer gas molecules. Examine each reaction to decide whether more or fewer gas molecules will result from producing more products. If more gas molecules result, then the pressure should be increased (volume decreased) to reduce product formation. If fewer gas molecules result, then pressure should be decreased to produce more reactants.

Solution:

a) In $2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$ three molecules of gas form two molecules of gas, so there are fewer gas molecules in the product. **Decreasing pressure** (increasing volume) will decrease the product yield.

b) In $4NH_3(g) + 5O_2(g) \leftrightarrows 4NO(g) + 6H_2O(g)$ 9 molecules of reactant gas convert to 10 molecules of product gas. **Increasing pressure** (decreasing volume) will favor the reaction direction that produces fewer moles of gas: towards the reactants and away from products.

c) In $CaC_2O_4(s) \leftrightarrows CaCO_3(s) + CO(g)$ there are no reactant gas molecules and one product gas molecule. The yield of the products will decrease when volume decreases, which corresponds to a **pressure increase**.

17.13B <u>Plan:</u> Changes in pressure (and volume) affect the concentration of gaseous reactants and products. A decrease in pressure, i.e., increase in volume, favors the production of more gas molecules whereas an increase in pressure favors the production of fewer gas molecules. Examine each reaction to determine if a decrease in pressure will shift the reaction toward the products (resulting in an increase in the yield of products) or toward the reactants (resulting in a decrease in the yield of products).

<u>Solution:</u>

a) In $CH_4(g) + CO_2(g) \rightleftarrows 2CO(g) + 2H_2(g)$ two molecules of gas form four molecules of gas, so there are more gas molecules in the product. Decreasing pressure (increasing volume) will shift the reaction to the right, **increasing** the product yield.

b) In $NO(g) + CO_2(g) \rightleftarrows NO_2(g) + CO(g)$ 2 molecules of reactant gas convert to 2 molecules of product gas. Decreasing pressure (increasing volume) will have **no effect** on this reaction or on the amount of product produced because the number of moles of gas does not change.

c) In $2H_2S(g) + SO_2(g) \rightleftarrows 3S(s + 2H_2O(g)$ three molecules of reactant gas convert to 2 molecules of product gas. Decreasing pressure (increasing volume) will shift the reaction toward the reactants, **decreasing** the product yield.

17.14A <u>Plan:</u> A decrease in temperature favors the exothermic direction of an equilibrium reaction. First, identify whether the forward or reverse reaction is exothermic from the given enthalpy change. $\Delta H < 0$ means the forward reaction is exothermic, and $\Delta H > 0$ means the reverse reaction is exothermic. If the forward reaction is exothermic then a decrease in temperature will shift the equilibrium to make more products from reactants and increase K_p. If the reverse reaction is exothermic then a decrease in temperature will shift the equilibrium to make more reactants from products and decrease K_p.

<u>Solution:</u>

a) $\Delta H < 0$ so the forward reaction is exothermic. A decrease in temperature increases the partial pressure of products and decreases the partial pressures of reactants, so P_{H_2} **decreases**. With increases in product pressures and decreases in reactant pressures, $\boldsymbol{K_p}$ **increases**.

b) $\Delta H > 0$ so the reverse reaction is exothermic. A decrease in temperature decreases the partial pressure of products and increases the partial pressures of reactants, so P_{N_2} **increases**. $\boldsymbol{K_p}$ **decreases** with decrease in product pressures and increase in reactant pressures.

c) $\Delta H < 0$ so the forward reaction is exothermic. Decreasing temperature **increases** P_{PCl_5} and **increases** $\boldsymbol{K_p}$.

17.14B <u>Plan:</u> A decrease in temperature favors the exothermic direction of an equilibrium reaction. First, identify whether the forward or reverse reaction is exothermic from the given enthalpy change. $\Delta H < 0$ means the forward reaction is exothermic, and $\Delta H > 0$ means the reverse reaction is exothermic. If the forward reaction is exothermic then a decrease in temperature will shift the equilibrium to make more products from reactants and increase K_p. If the reverse reaction is exothermic then an increase in temperature will shift the equilibrium to make more products from reactants and increase K_p.

<u>Solution:</u>

a) $\Delta H > 0$ so the reverse reaction is exothermic. An **increase in temperature** will increase the partial pressure of products and decrease the partial pressures of reactants. $\boldsymbol{K_p}$ **increases** with an increase in product pressures and a decrease in reactant pressures.

b) $\Delta H < 0$ so the forward reaction is exothermic. A **decrease in temperature** increases the partial pressure of products and decreases the partial pressures of reactants. With increases in product pressures and decreases in reactant pressures, $\boldsymbol{K_p}$ **increases**.

c) $\Delta H > 0$ so the reverse reaction is exothermic. An **increase in temperature** increases the partial pressure of products and decreases the partial pressures of reactants. $\boldsymbol{K_p}$ **increases** with an increase in product pressures and a decrease in reactant pressures.

17.15A <u>Plan:</u> Given the balanced equilibrium equation, it is possible to set up the appropriate equilibrium expression (Q_c). For the equation given $\Delta n = 0$ meaning that $K_p = K_c$. The value of K may be found for scene 1, and values for Q may be determined for the other two scenes. The reaction will shift towards the reactant side if $Q > K$, and the reaction will shift towards the product side if $Q < K$. The reaction is exothermic ($\Delta H < 0$), thus, heat may be considered a product. Increasing the temperature adds a product and decreasing the temperature removes a product.

Solution:

a) K_p requires the equilibrium value of P for each gas. The pressure may be found from $P = nRT/V$.

$$K_p = \frac{P_{CD}^2}{P_{C_2}P_{D_2}} = \frac{\left(\frac{n_{CD}RT}{V}\right)^2}{\left(\frac{n_{C_2}RT}{V}\right)\left(\frac{n_{D_2}RT}{V}\right)}$$

This equation may be simplified because for the sample R, T, and V are constant. Using scene 1:

$$K_p = \frac{n_{CD}^2}{n_{C_2}n_{D_2}} = \frac{(4)^2}{(2)(2)} = \mathbf{4}$$

b) Scene 2: $Q_p = \frac{n_{CD}^2}{n_{C_2}n_{D_2}} = \frac{(6)^2}{(1)(1)} = 36$

$Q > K$ so the reaction will shift to the **left** (towards the reactants).

Scene 3: $Q_p = \frac{n_{CD}^2}{n_{C_2}n_{D_2}} = \frac{(2)^2}{(3)(3)} = 0.44$

$Q < K$ so the reaction will shift to the **right** (towards the products).

c) Increasing the temperature is equivalent to adding a product (heat) to the equilibrium. The reaction will shift to consume the added heat. The reaction will shift to the left (towards the reactants). However, since there are 2 moles of gas on each side of the equation, the shift has **no effect** on total moles of gas.

17.15B Plan: Write the equilibrium expression for the reaction. Count the number of each type of particle in the first scene and use this information to calculate the value of K at T_1. Follow a similar procedure to calculate the value of K at T_2. Determine if K at T_1 is larger or smaller than K at T_2. Use this information to determine the sign of ΔH for the reaction.

Solution:

a) $K = \frac{[AB]}{[A][B]}$

Calculating K at T_1:

$K = \frac{[3]}{[2][2]} = \mathbf{0.75}$

b) Going from the scene at T_1 to the scene at T_2, the number of product molecules decreases. This decreases the value of K. The problem states that $T_2 < T_1$, so as the temperature decreases, K also decreases. The fact that both the temperature and the value of K decreased suggests that this is an endothermic reaction, with $\mathbf{\Delta H > 0}$.

c) Calculating K at T_2:

$K = \frac{[2]}{[3][3]} = \mathbf{0.22}$

CHEMICAL CONNECTIONS BOXED READING PROBLEM

B17.1 Plan: To control the pathways, the first enzyme specific for a branch is inhibited by the end product of that branch.

Solution:

a) The enzyme that is inhibited by F is the first enzyme in that branch, which is **enzyme 3**.

b) Enzyme **6** is inhibited by I.

c) If F inhibited enzyme 1, then neither branch of the reaction would take place once enough F was produced.

d) If F inhibited enzyme 6, then the second branch would not take place when enough F was made.

END–OF–CHAPTER PROBLEMS

17.1 If the rate of the forward reaction exceeds the rate of reverse reaction, products are formed faster than they are consumed. The change in reaction conditions results in more products and less reactants. A change in reaction conditions can result from a change in concentration or a change in temperature. If concentration changes, product concentration increases while reactant concentration decreases, but the K_c remains unchanged because the *ratio* of products and reactants remains the same. If the increase in the forward rate is due to a change in temperature, the rate of the reverse reaction also increases. The equilibrium ratio of product concentration to reactant concentration is no longer the same. Since the rate of the forward reaction increases more than the rate of the reverse reaction, K_c increases (numerator, [products], is larger and denominator, [reactants], is smaller).

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

17.2 The faster the rate and greater the yield, the more useful the reaction will be to the manufacturing process.

17.3 A system at equilibrium continues to be very dynamic at the molecular level. Reactant molecules continue to form products, but at the same rate that the products decompose to re-form the reactants.

17.4 If K is very large, the reaction goes nearly to completion. A large value of K means that the numerator is much larger than the denominator in the K expression. A large numerator, relative to the denominator, indicates that most of the reactants have reacted to become products. $K = \dfrac{[\text{products}]}{[\text{reactants}]}$

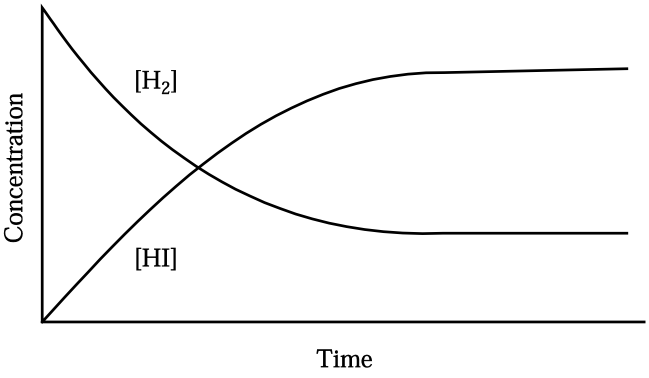
17.5 One cannot say with certainty whether the value of K for the phosphorus plus oxygen reaction is large or small (although it likely is large). However, it is certain that the reaction proceeds very fast.

17.6 **No**, the value of Q is determined by the mass action expression with arbitrary concentrations for products and reactants. Thus, its value is not constant.

17.7 The equilibrium constant expression is $K = [O_2]$ (we do not include solid substances in the equilibrium expression). If the temperature remains constant, K remains constant. If the initial amount of Li_2O_2 present was sufficient to reach equilibrium, the amount of O_2 obtained will be constant, regardless of how much $Li_2O_2(s)$ is present.

17.8 a) On the graph, the concentration of HI increases at twice the rate that H_2 decreases because the stoichiometric ratio in the balanced equation is $1H_2$: 2HI. Q for a reaction is the ratio of concentrations of products to concentrations of reactants. As the reaction progresses the concentration of reactants H_2 and I_2 decrease and the concentration of product HI increases, which means that Q increases as a function of time.

$$H_2(g) + I_2(g) \leftrightarrows 2HI(g) \qquad Q = \frac{[HI]^2}{[H_2][I_2]}$$



The value of Q increases as a function of time until it reaches the value of K.

b) No, Q would still increase with time because the $[I_2]$ would decrease in exactly the same way as $[H_2]$ decreases.

17.9 A homogeneous equilibrium reaction exists when **all** the components of the reaction are in the same phase (i.e., gas, liquid, solid, aqueous).

$$2NO(g) + O_2(g) \leftrightarrows 2NO_2(g)$$

A heterogeneous equilibrium reaction exists when the components of the reaction are in different phases.

$$Ca(HCO_3)_2(aq) \leftrightarrows CaCO_3(s) + H_2O(l) + CO_2(g)$$

17.10 $1/2N_2(g) + 1/2O_2(g) \leftrightarrows NO(g)$

$$Q_{c(form)} = \frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}}$$

$NO(g) \leftrightarrows 1/2N_2(g) + 1/2O_2(g)$

$$Q_{c(decomp)} = \frac{[N_2]^{1/2}[O_2]^{1/2}}{[NO]}$$

$Q_{c(decomp)} = 1/Q_{c(form)}$, so the constants do differ (they are the reciprocal of each other).

17.11 <u>Plan:</u> Write the reaction and then the expression for Q. Remember that $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced equation.

<u>Solution:</u>

The balanced equation for the first reaction is

$3/2H_2(g) + 1/2N_2(g) \leftrightarrows NH_3(g)$ (1)

The coefficient in front of NH_3 is fixed at 1 mole according to the description. The reaction quotient for this reaction is $Q_1 = \frac{[NH_3]}{[H_2]^{3/2}[N_2]^{1/2}}$.

In the second reaction, the coefficient in front of N_2 is fixed at 1 mole.

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

The reaction quotient for this reaction is $Q_2 = \frac{[NH_3]^2}{[H_2]^3[N_2]}$

Q_2 is equal to Q_1^2.

17.12 <u>Plan:</u> Remember that $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced equation.

<u>Solution:</u>

a) $4NO(g) + O_2(g) \leftrightarrows 2N_2O_3(g)$

$$Q_c = \frac{[N_2O_3]^2}{[NO]^4[O_2]}$$

b) $SF_6(g) + 2SO_3(g) \leftrightarrows 3SO_2F_2(g)$

$$Q_c = \frac{[SO_2F_2]^3}{[SF_6][SO_3]^2}$$

c) $2SC1F_5(g) + H_2(g) \leftrightarrows S_2F_{10}(g) + 2HCl(g)$

$$Q_c = \frac{[S_2F_{10}][HCl]^2}{[SClF_5]^2[H_2]}$$

17.13 a) $2C_2H_6(g) + 7O_2(g) \leftrightarrows 4CO_2(g) + 6H_2O(g)$

$$Q_c = \frac{[CO_2]^4[H_2O]^6}{[C_2H_6]^2[O_2]^7}$$

b) $CH_4(g) + 4F_2(g) \leftrightarrows CF_4(g) + 4HF(g)$

$$Q_c = \frac{[CF_4][HF]^4}{[CH_4][F_2]^4}$$

c) $2SO_3(g) \leftrightarrows 2SO_2(g) + O_2(g)$

$$Q_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

17.14 Plan: Remember that $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are the stoichiometric coefficients in the balanced equation.

Solution:

a) $2NO_2Cl(g) \leftrightarrows 2NO_2(g) + Cl_2(g)$

$$Q_c = \frac{[NO_2]^2[Cl_2]}{[NO_2Cl]^2}$$

b) $2POCl_3(g) \leftrightarrows 2PCl_3(g) + O_2(g)$

$$Q_c = \frac{[PCl_3]^2[O_2]}{[POCl_3]^2}$$

c) $4NH_3(g) + 3O_2(g) \leftrightarrows 2N_2(g) + 6H_2O(g)$

$$Q_c = \frac{[N_2]^2[H_2O]^6}{[NH_3]^4[O_2]^3}$$

17.15 a) $3O_2(g) \leftrightarrows 2O_3(g)$

$$Q_c = \frac{[O_3]^2}{[O_2]^3}$$

b) $NO(g) + O_3(g) \leftrightarrows NO_2(g) + O_2(g)$

$$Q_c = \frac{[NO_2][O_2]}{[NO][O_3]}$$

c) $N_2O(g) + 4H_2(g) \leftrightarrows 2NH_3(g) + H_2O(g)$

$$Q_c = \frac{[NH_3]^2[H_2O]}{[N_2O][H_2]^4}$$

17.16 Plan: Compare each equation with the reference equation to see how the direction and coefficients have changed. If a reaction has been reversed, the *K* value is the reciprocal of the *K* value for the reference reaction. If the coefficients have been changed by a factor *n*, the *K* value is equal to the original *K* value raised to the *nth* power.

Solution:

a) The K for the original reaction is $K_c = \dfrac{[H_2]^2[S_2]}{[H_2S]^2}$

The given reaction $1/2S_2(g) + H_2(g) \leftrightarrows H_2S(g)$ is the reverse reaction of the original reaction and the coefficients of the original reaction have been multiplied by a factor of 1/2. The equilibrium constant for the reverse reaction is the reciprocal (1/K) of the original constant. The K value of the original reaction is raised to the 1/2 power.

$$K_{c\,(a)} = (1/K_c)^{1/2} = \frac{[H_2S]}{[S_2]^{1/2}[H_2]}$$

$$K_{c\,(a)} = (1/1.6\text{x}10^{-2})^{1/2} = 7.90569 = \mathbf{7.9}$$

b) The given reaction $5H_2S(g) \leftrightarrows 5H_2(g) + 5/2S_2(g)$ is the original reaction multiplied by 5/2. Take the original K to the 5/2 power to find K of given reaction.

$$K_{c\,(b)} = (K_c)^{5/2} = \frac{[H_2]^5[S_2]^{5/2}}{[H_2S]^5}$$

$$K_{c\,(b)} = (1.6\text{x}10^{-2})^{5/2} = 3.23817\text{x}10^{-5} = \mathbf{3.2x10^{-5}}$$

17.17 $K_c = \dfrac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$

a) $K_{c\,(a)} = [K_c]^{1/2} = \dfrac{[N_2]^{1/2}[H_2O]}{[NO][H_2]}$

Thus, $K_{c\,(a)} = [K_c]^{1/2} = (6.5\text{x}10^2)^{1/2} = 25.495 = \mathbf{25}$

b) $K_c = [K_c]^{-2} = \dfrac{[NO]^4[H_2]^4}{[N_2]^2[H_2O]^4}$

$K_c = [K_c]^{-2} = (6.5\text{x}10^2)^{-2} = 2.36686\text{x}10^{-6} = \mathbf{2.4x10^{-6}}$

17.18 Plan: The concentration of solids and pure liquids do not change, so their concentration terms are not written in the reaction quotient expression. Remember that stoichiometric coefficients are used as exponents in the expression for the reaction quotient.

Solution:

a) $2Na_2O_2(s) + 2CO_2(g) \leftrightarrows 2Na_2CO_3(s) + O_2(g)$

$$Q_c = \frac{[O_2]}{[CO_2]^2}$$

b) $H_2O(l) \leftrightarrows H_2O(g)$

$Q_c = [H_2O(g)]$ Only the gaseous water is used. The “(g)” is for emphasis.

c) $NH_4Cl(s) \leftrightarrows NH_3(g) + HCl(g)$

$Q_c = [NH_3][HCl]$

17.19 a) $H_2O(l) + SO_3(g) \leftrightarrows H_2SO_4(aq)$

$$Q_c = \frac{[H_2SO_4]}{[SO_3]}$$

b) $2KNO_3(s) \leftrightarrows 2KNO_2(s) + O_2(g)$

$Q_c = [O_2]$

c) $S_8(s) + 24F_2(g) \leftrightarrows 8SF_6(g)$

$$Q_c = \frac{[SF_6]^8}{[F_2]^{24}}$$

17.20 Plan: The concentration of solids and pure liquids do not change, so their concentration terms are not written in the reaction quotient expression. Remember that stoichiometric coefficients are used as exponents in the expression for the reaction quotient.

Solution:

a) $2NaHCO_3(s) \leftrightarrows Na_2CO_3(s) + CO_2(g) + H_2O(g)$

$Q_c = [CO_2][H_2O]$

b) $SnO_2(s) + 2H_2(g) \leftrightarrows Sn(s) + 2H_2O(g)$

$$Q_c = \frac{[H_2O]^2}{[H_2]^2}$$

c) $H_2SO_4(l) + SO_3(g) \leftrightarrows H_2S_2O_7(l)$

$$Q_c = \frac{1}{[SO_3]}$$

17.21 a) $2Al(s) + 2NaOH(aq) + 6H_2O(l) \leftrightarrows 2Na[Al(OH)_4](aq) + 3H_2(g)$

$$Q_c = \frac{[Na[Al(OH)_4]]^2[H_2]^3}{[NaOH]^2}$$

b) $CO_2(s) \leftrightarrows CO_2(g)$

$Q_c = [CO_2(g)]$ Only the gaseous carbon dioxide is used. The "(*g*)" is for emphasis.

c) $2N_2O_5(s) \leftrightarrows 4NO_2(g) + O_2(g)$

$Q_c = [NO_2]^4[O_2]$

17.22 Write balanced chemical equations for each reaction, and then write the appropriate equilibrium expression.

a) $4HCl(g) + O_2(g) \leftrightarrows 2Cl_2(g) + 2H_2O(g)$

$$Q_c = \frac{[Cl_2]^2[H_2O]^2}{[HCl]^4[O_2]}$$

b) $2As_2O_3(s) + 10F_2(g) \leftrightarrows 4AsF_5(l) + 3O_2(g)$

$$Q_c = \frac{[O_2]^3}{[F_2]^{10}}$$

c) $SF_4(g) + 2H_2O(l) \leftrightarrows SO_2(g) + 4HF(g)$

$$Q_c = \frac{[SO_2][HF]^4}{[SF_4]}$$

d) $2MoO_3(s) + 6XeF_2(g) \leftrightarrows 2MoF_6(l) + 6Xe(g) + 3O_2(g)$

$$Q_c = \frac{[Xe]^6[O_2]^3}{[XeF_2]^6}$$

17.23 Plan: Add the two equations, canceling substances that appear on both sides of the equation. Write the Q_c expression for each of the steps and for the overall equation. Since the individual steps are added, their Q_c's are multiplied and common terms are canceled to obtain the overall Q_c.

Solution:

a) The balanced equations and corresponding reaction quotients are given below. Note the second equation must be multiplied by 2 to get the appropriate overall equation.

(1) $Cl_2(g) + F_2(g) \leftrightarrows \cancel{2ClF(g)}$ $\qquad Q_1 = \dfrac{[ClF]^2}{[Cl_2][F_2]}$

(2) $\cancel{2ClF(g)} + 2F_2(g) \leftrightarrows 2ClF_3(g)$ $\qquad Q_2 = \dfrac{[ClF_3]^2}{[ClF]^2[F_2]^2}$

Overall: $Cl_2(g) + 3F_2(g) \leftrightarrows 2ClF_3(g)$ $\qquad Q_{\text{overall}} = \dfrac{[ClF_3]^2}{[Cl_2][F_2]^3}$

b) The reaction quotient for the overall reaction, Q_{overall}, determined from the reaction is:

$$Q_{\text{overall}} = \frac{[ClF_3]^2}{[Cl_2][F_2]^3}$$

$$Q_{\text{overall}} = Q_1 Q_2^{\,2} = \frac{[ClF]^2}{[Cl_2][F_2]} \text{ x } \frac{[ClF_3]^2}{[ClF]^2[F_2]^2} = \frac{[ClF_3]^2}{[Cl_2][F_2]^3}$$

17.24 According to the ideal gas equation, $PV = nRT$. Concentration and pressure of gas are directly proportional as long as the temperature is constant: $C = n/V = P/RT$.

17.25 K_c and K_p are related by the equation $K_p = K_c(RT)^{\Delta n}$, where Δn represents the change in the number of moles of gas in the reaction (moles gaseous products – moles gaseous reactants). When Δn is zero (no change in number of moles of gas), the term $(RT)^{\Delta n}$ equals 1 and $K_c = K_p$. When Δn is not zero, meaning that there is a change in the number of moles of gas in the reaction, then $K_c \neq K_p$.

17.26 a) $K_p = K_c(RT)^{\Delta n}$. Since Δn = number of moles gaseous products – number of moles gaseous reactants, Δn is a positive integer for this reaction. If Δn is a positive integer, then $(RT)^{\Delta n}$ is greater than 1. Thus, K_c is multiplied by a number that is greater than 1 to give K_p. **K_c is smaller than K_p.**

b) Assuming that $RT > 1$ (which occurs when $T > 12.2$ K, because 0.0821 (R) x 12.2 = 1), **$K_p > K_c$** if the number of moles of gaseous products exceeds the number of moles of gaseous reactants. $K_p < K_c$ when the number of moles of gaseous reactants exceeds the number of moles of gaseous product.

17.27 Plan: Δn_{gas} = moles gaseous products – moles gaseous reactants.

Solution:

a) Number of moles of gaseous reactants = 0; number of moles of gaseous products = 3; $\Delta n_{\text{gas}} = 3 - 0 = \mathbf{3}$

b) Number of moles of gaseous reactants = 1; number of moles of gaseous products = 0; $\Delta n_{\text{gas}} = 0 - 1 = \mathbf{-1}$

c) Number of moles of gaseous reactants = 0; number of moles of gaseous products = 3; $\Delta n_{\text{gas}} = 3 - 0 = \mathbf{3}$

17.28 a) $\Delta n_{\text{gas}} = \mathbf{1}$ b) $\Delta n_{\text{gas}} = \mathbf{-3}$ c) $\Delta n_{\text{gas}} = \mathbf{1}$

17.29 Plan: First, determine Δn for the reaction and then calculate K_c using $K_p = K_c(RT)^{\Delta n}$.

Solution:

a) Δn = moles gaseous products – moles gaseous reactants = 1 – 2 = –1

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

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{3.9\text{x}10^{-2}}{[(0.0821)(1000.)]^{-1}} = 3.2019 = \mathbf{3.2}$$

b) Δn = moles gaseous products – moles gaseous reactants = 1 – 1 = 0

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{28.5}{[(0.0821)(500.)]^{0}} = \mathbf{28.5}$$

17.30 First, determine Δn for the reaction and then calculate K_c using $K_p = K_c(RT)^{\Delta n}$.

a) Δn = moles gaseous products – moles gaseous reactants = 2 – 2 = 0

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{49}{[(0.0821)(730.)]^{0}} = \mathbf{49}$$

b) Δn = moles gaseous products – moles gaseous reactants = 2 – 3 = –1

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{2.5\text{x}10^{10}}{[(0.0821)(500.)]^{-1}} = 1.02625\text{x}10^{12} = \mathbf{1.0x10^{12}}$$

17.31 <u>Plan:</u> First, determine Δn for the reaction and then calculate K_p using $K_p = K_c(RT)^{\Delta n}$.

<u>Solution:</u>

a) Δn = moles gaseous products – moles gaseous reactants = 2 – 1 = 1

$K_p = K_c(RT)^{\Delta n} = (6.1\text{x}10^{-3})[(0.0821)(298)]^1 = 0.14924 = \mathbf{0.15}$

b) Δn = moles gaseous products – moles gaseous reactants = 2 – 4 = – 2

$K_p = K_c(RT)^{\Delta n} = (2.4\text{x}10^{-3})[(0.0821)(1000.)]^{-2} = 3.5606\text{x}10^{-7} = \mathbf{3.6x10^{-7}}$

17.32 First, determine Δn for the reaction and then calculate K_p using $K_p = K_c(RT)^{\Delta n}$.

a) Δn = moles gaseous products – moles gaseous reactants = 2 – 2 = 0

$K_p = K_c(RT)^{\Delta n} = (0.77)[(0.0821)(1020.)]^0 = \mathbf{0.77}$

b) Δn = moles gaseous products – moles gaseous reactants = 2 – 3 = –1

$K_p = K_c(\text{RT})^{\Delta n} = (1.8\text{x}10^{-56})[(0.0821)\ (570.)]^{-1} = 3.8464\text{x}10^{-58} = \mathbf{3.8x10^{-58}}$

17.33 When $Q < K$, the reaction proceeds to the **right** to form more products. The reaction quotient and equilibrium constant are determined by [products]/[reactants]. For Q to increase and reach the value of K, the concentration of products (numerator) must increase in relation to the concentration of reactants (denominator).

17.34 a) The reaction is 2D ↔ E and $K_c = \frac{[\text{E}]}{[\text{D}]^2}$.

Concentration of D = Concentration of E = $(3\text{ spheres})\left(\frac{0.0100\text{ mol}}{1\text{ sphere}}\right)\left(\frac{1}{1.00\text{ L}}\right) = 0.0300\ M$

$$K_c = \frac{[\text{E}]}{[\text{D}]^2} = \frac{[0.0300]}{[0.0300]^2} = 33.3333 = 33.3$$

b) In Scene B the concentrations of D and E are both 0.0300 mol/0.500 L = 0.0600 M

$$Q_c = \frac{[\text{E}]}{[\text{D}]^2} = \frac{[0.0600]}{[0.0600]^2} = 16.66666 = 16.7$$

B is not at equilibrium. Since $Q_c < K_c$, the reaction will proceed to the right.

In Scene C, the concentration of D is still 0.0600 M and the concentration of E is 0.0600 mol/0.500 L = 0.120 M

$$Q_c = \frac{[\text{E}]}{[\text{D}]^2} = \frac{[0.120]}{[0.0600]^2} = 33.3333 = 33.3$$

Since $Q_c = K_c$ in Scene C, the reaction is at equilibrium.

17.35 <u>Plan:</u> To decide if the reaction is at equilibrium, calculate Q_p and compare it to K_p. If $Q_p = K_p$, then the reaction is at equilibrium. If $Q_p > K_p$, then the reaction proceeds to the left to produce more reactants. If $Q_p < K_p$, then the reaction proceeds to the right to produce more products.

Solution:

$$Q_p = \frac{P_{H_2} P_{Br_2}}{P^2_{HBr}} = \frac{(0.010)(0.010)}{(0.20)^2} = 2.5x10^{-3} > K_p = 4.18x10^{-9}$$

$Q_p > K_p$, thus, the reaction is **not** at equilibrium and will proceed to the **left** (towards the reactants). Thus, the numerator will decrease in size as products are consumed and the denominator will increase in size as more reactant is produced. Q_p will decrease until $Q_p = K_p$.

17.36 $$Q_p = \frac{P^2_{NO} P_{Br_2}}{P^2_{NOBr}} = \frac{(0.10)^2(0.10)}{(0.10)^2} = 0.10 < K_p = 60.6$$

$Q_p < K_p$ Thus, the reaction is **not** at equilibrium and will proceed to the **right** (towards the products).

17.37 There is insufficient information to calculate the partial pressures of each gas (T is not given). There is sufficient information to determine the concentrations and hence Q_c. Convert the K_p given to K_c using $K_p = K_c(RT)^{\Delta n}$. Compare the Q_c to the K_c just calculated and make a prediction.
Δn = moles gaseous products – moles gaseous reactants = 2 – 2 = 0
Since $\Delta n = 0$, $K_p = K_c = 2.7$ (Note: If Δn had any other value, we could not finish the calculation without the temperature.)

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.62/2.0][0.43/2.0]}{[0.13/2.0][0.56/2.0]} = 3.662 > K_c = 2.7$$

$Q_c > K_c$ Thus, the reaction is **not** at equilibrium and will proceed to the **left** (towards the reactants).

17.38 At equilibrium, equal concentrations of $CFCl_3$ and HCl exist, regardless of starting reactant concentrations. The equilibrium concentrations of $CFCl_3$ and HCl would still be equal if unequal concentrations of CCl_4 and HF were used. This occurs only when the two products have the same coefficients in the balanced equation. Otherwise, more of the product with the larger coefficient will be produced.

17.39 When x mol of CH_4 reacts, 2x mol of H_2O also reacts to form x mol of CO_2 and 4x mol of H_2. This is based on the 1:2:1:4 mole ratio in the reaction. The final (equilibrium) concentration of each reactant is the initial concentration minus the amount that reacts. The final (equilibrium) concentration of each product is the initial concentration plus the amount that forms.

17.40 a) The approximation applies when the change in concentration from initial to equilibrium is so small that it is insignificant. This occurs when K is small and initial concentration is large.
b) This approximation will not work when the change in concentration is greater than 5%. This can occur when $[\text{reactant}]_{\text{initial}}$ is very small, or when $[\text{reactant}]_{\text{change}}$ is relatively large due to a large K.

17.41 Plan: Since all equilibrium concentrations are given in molarities and the reaction is balanced, construct an equilibrium expression and substitute the equilibrium concentrations to find K_c.
Solution:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{[1.87x10^{-3}]^2}{[6.50x10^{-5}][1.06x10^{-3}]} = 50.753 = \mathbf{50.8}$$

17.42 $$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{[0.114][0.342]^3}{[0.0225]^2} = 9.0077875 = \mathbf{9.01}$$

17.43 Plan: Calculate the initial concentration of PCl_5 from the given number of moles and the container volume; the reaction is proceeding to the right, consuming PCl_5 and producing products. There is a 1:1:1 mole ratio between the reactants and products.
Solution:
Initial $[PCl_5]$ = 0.15 mol/2.0 L = 0.075 M
Since there is a 1:1:1 mole ratio in this reaction:

x = [PCl_5] reacting (–x), and the amount of PCl_3 and of Cl_2 forming (+x).

Concentration (*M*)	$PCl_5(g)$	$\leftrightarrows$	$PCl_3(g)$	+	$Cl_2(g)$
Initial	0.075		0		0
Change	–x		+x		+x
Equilibrium	0.075 – x		x		x

17.44 The reaction table requires that the initial [H_2] and [F_2] be calculated: [H_2] = 0.10 mol/0.50 L = 0.20 *M*; [F_2] = 0.050 mol/0.50 L = 0.10 *M*.

x = [H_2] = [F_2] reacting (–x); 2x = [HF] forming (+2x)

Concentration (*M*)	$H_2(g)$	+	$F_2(g)$	$\leftrightarrows$	$2HF(g)$
Initial	0.20		0.10		0
Change	–x		–x		+2x
Equilibrium	0.20 – x		0.10 – x		2x

17.45 Plan: Two of the three equilibrium pressures are known, as is K_p. Construct an equilibrium expression and solve for P_{NOCl}.

Solution:

$$K_p = 6.5\text{x}10^4 = \frac{P_{NOCl}^2}{P_{NO}^2 P_{Cl_2}}$$

$$6.5\text{x}10^4 = \frac{P^2{}_{NOCl}}{(0.35)^2(0.10)}$$

$$P_{NOCl} = \sqrt{\left(6.5\text{x}10^4\right)(0.35)^2(0.10)} = 28.2179 = \mathbf{28\ atm}$$

A high pressure for NOCl is expected because the large value of K_p indicates that the reaction proceeds largely to the right, i.e., to the formation of products.

17.46 $C(s) + 2H_2(g) \leftrightarrows CH_4(g)$

$$K_p = \frac{P_{CH_4}}{P_{H_2}^2} = 0.262$$

$$P_{CH_4} = K_p P_{H_2}^2 = (0.262)(1.22)^2 = 0.38996 = \mathbf{0.390\ atm}$$

17.47 Plan: Use the balanced equation to write an equilibrium expression and to define x. Set up a reaction table, substitute into the K_p expression, and solve for x.

Solution:

$NH_4HS(s) \leftrightarrows H_2S(g) + NH_3(g)$

x = [NH_4HS] reacting (–x), and the amount of H_2S and of NH_3 forming (+x) since there is a 1:1:1 mole ratio between the reactant and products.

(It is not necessary to calculate the molarity of NH_4HS since, as a solid, it is not included in the equilibrium expression.)

Concentration (*M*)	$NH_4HS(s)$	$\leftrightarrows$	$H_2S(g)$	+	$NH_3(g)$
Initial	—		0		0
Change	–x		+x		+x
Equilibrium	—		x		x

$K_p = 0.11 = (P_{H_2S})(P_{NH_3})$ (The solid NH_4HS is not included.)

0.11 = (x)(x)

x = P_{NH_3} = = 0.33166 = **0.33 atm**

17.48 $2H_2S(g) \leftrightarrows 2H_2(g) + S_2(g)$

$[H_2S]$ = 0.45 mol/3.0 L = 0.15 *M*

Concentration (*M*)	$2H_2S(g)$	$\leftrightarrows$	$2H_2(g)$	+	$S_2(g)$
Initial	0.15		0		0
Change	–2x		+2x		+x
Equilibrium	0.15 – 2x		2x		x

$$K_c = 9.30\text{x}10^{-8} = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{[2\text{x}]^2[\text{x}]}{[0.15 - 2\text{x}]^2}$$

Assuming 0.15 *M* – 2 x ≈ 0.15 *M*

$$9.30\text{x}10^{-8} = \frac{[2\text{x}]^2[\text{x}]}{[0.15]^2} = \frac{4\text{x}^3}{0.15^2}$$

x = $8.0575\text{x}10^{-4}$ *M*

$[H_2]$ = 2x = 2 ($8.0575\text{x}10^{-4}$ *M*) = $1.6115\text{x}10^{-3}$ = **$1.6\text{x}10^{-3}$ *M***

(Since $(1.6\text{x}10^{-3})/(0.15) < 0.05$, the assumption is OK.)

17.49 Plan: Use the balanced equation to write an equilibrium expression. Find the initial concentration of each reactant from the given amounts and container volume, use the balanced equation to define x and set up a reaction table, substitute into the equilibrium expression, and solve for x, from which the concentration of NO is calculated.

Solution:

The initial concentrations of N_2 and O_2 are (0.20 mol/1.0 L) = 0.20 *M* and (0.15 mol/1.0 L) = 0.15 *M*, respectively.

$N_2(g) + O_2(g) \leftrightarrows 2NO(g)$ There is a 1:1:2 mole ratio between reactants and products.

Concentration (*M*)	$N_2(g)$	+	$O_2(g)$	$\leftrightarrows$	$2NO(g)$	
Initial	0.20		0.15		0	
Change	–x		–x		+2x	(1:1:2 mole ratio)
Equilibrium	0.20 – x		0.15 – x		2x	

$$K_c = 4.10\text{x}10^{-4} = \frac{[NO]^2}{[N_2][O_2]} = \frac{[2\text{x}]^2}{[0.20 - \text{x}][0.15 - \text{x}]}$$

Assume 0.20 *M* – x ≈ 0.20 *M* and 0.15 *M* – x ≈ 0.15 *M*

$$4.10\text{x}10^{-4} = \frac{4\text{x}^2}{[0.20][0.15]}$$

x = $1.753568\text{x}10^{-3}$ *M*

[NO] = 2x = 2($1.753568\text{x}10^{-3}$ *M*) = $3.507136\text{x}10^{-3}$ = **$3.5\text{x}10^{-3}$ *M***

(Since $(1.8\text{x}10^{-3})/(0.15) < 0.05$, the assumption is OK.)

17.50 $2NO_2(g) \leftrightarrows 2NO(g) + O_2(g)$

Pressure (atm)	$2NO_2(g)$	$\leftrightarrows$	$2NO(g)$	+	$O_2(g)$
Initial	0.75		0		0
Change	– 2x		+2x		+x
Equilibrium	0.75 – 2x		2x		x

$$K_p = 4.48\text{x}10^{-13} = \frac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2} = \frac{(2\text{x})^2(\text{x})}{(0.75 - 2\text{x})^2}$$

Assume 0.75 atm – 2x ≈ 0.75 atm

$$4.48\text{x}10^{-13} = \frac{(4\text{x}^2)(\text{x})}{(0.75)^2} = \frac{(4\text{x}^3)}{(0.75)^2}$$

x = $3.979\text{x}10^{-5}$ atm = **$4.0\text{x}10^{-5}$ atm O_2**

$P_{NO} = 2x = 2(3.979\text{x}10^{-5}\text{ atm}) = 7.958\text{x}10^{-5} = \mathbf{8.0x10^{-5}\ atm\ NO}$

17.51 Plan: Find the initial concentration of each reactant and product from the given amounts and container volume, use the balanced equation to define x, and set up a reaction table. The equilibrium concentration of H_2 is known, so x can be calculated and used to find the other equilibrium concentrations.

Solution:

Initial concentrations:

[HI] = (0.0244 mol)/(1.50 L) = 0.0162667 *M*
$[H_2]$ = (0.00623 mol)/(1.50 L) = 0.0041533 *M*
$[I_2]$ = (0.00414 mol)/(1.50 L) = 0.00276 *M*

$2\ HI(g) \rightleftarrows H_2(g) + I_2(g)$ There is a 2:1:1 mole ratio between reactants and products.

Concentration (*M*)	2 HI(*g*)	$\rightleftarrows$	$H_2(g)$	+	$I_2(g)$	
Initial	0.0162667		0.0041533		0.00276	
Change	–2x		+x		+x	2:1:1 mole ratio
Equilibrium	0.0162667 – 2x		0.0041533 + x		0.00276 + x	

$[H_2]_{eq}$ = 0.00467 = 0.0041533 + x
x = 0.0005167 *M*
$[I_2]_{eq}$ = 0.00276 + x = 0.00276 + 0.0005167 = 0.0032767 = **0.00328 *M* I_2**
$[HI]_{eq}$ = 0.0162667 – 2x = 0.0162667 – 2(0.0005167) = 0.0152333 = **0.0152 *M* HI**

17.52 Initial concentrations:

[A] = $(1.75\text{x}10^{-3}$ mol)/(1.00 L) = $1.75\text{x}10^{-3}$ *M*
[B] = $(1.25\text{x}10^{-3}$ mol)/(1.00 L) = $1.25\text{x}10^{-3}$ *M*
[C] = $(6.50\text{x}10^{-4}$ mol)/(1.00 L) = $6.50\text{x}10^{-4}$ *M*

Concentration (*M*)	A(*g*)	$\rightleftarrows$	2B(*g*)	+	C(*g*)
Initial	$1.75\text{x}10^{-3}$		$1.25\text{x}10^{-3}$		$6.50\text{x}10^{-4}$
Change	– x		+ 2x		+x
Equilibrium	$1.75\text{x}10^{-3}$ – x		$1.25\text{x}10^{-3}$ + 2x		$6.50\text{x}10^{-4}$ + x

$[A]_{eq} = 2.15\text{x}10^{-3} = 1.75\text{x}10^{-3} - x$
x = –0.00040
$[B]_{eq} = 1.25\text{x}10^{-3} + 2x = \mathbf{4.5x10^{-4}}$ ***M***
$[C]_{eq} = 6.50\text{x}10^{-4} + x = \mathbf{2.5x10^{-4}}$ ***M***

17.53 Plan: Use the balanced equation to write an equilibrium expression. Find the initial concentration of ICl from the given amount and container volume, use the balanced equation to define x and set up a reaction table, substitute into the equilibrium expression, and solve for x, from which the equilibrium concentrations can be calculated.

Solution:

$[ICl]_{init}$ = (0.500 mol/5.00 L) = 0.100 *M*

Concentration (*M*)	2ICl(*g*)	$\rightleftarrows$	$I_2(g)$	+	$Cl_2(g)$	
Initial	0.100		0		0	
Change	–2x		+x		+x	(2:1:1 mole ratio)
Equilibrium	0.100 – 2x		x		x	

$$K_c = 0.110 = \frac{[I_2][Cl_2]}{[ICl]^2} = \frac{[x][x]}{[0.100 - 2x]^2}$$

$$0.110 = \frac{[x]^2}{[0.100 - 2x]^2}$$ Take the square root of each side:

$$0.331662 = \frac{[x]}{[0.100 - 2x]}$$

x = 0.0331662 – 0.663324x
1.663324x = 0.0331662

x = 0.0199397

$[I_2]_{eq}$ = $[Cl_2]_{eq}$ = x = 0.0199397 = **0.0200 *M***

$[ICl]_{eq}$ = 0.100 – 2x = 0.100 – 2(0.0199397) = 0.0601206 = **0.060 *M* ICl**

17.54

Concentration (*M*)	$SCl_2(g)$	+	$2C_2H_4(g)$	$\leftrightarrows$	$S(CH_2CH_2Cl)_2(g)$
Initial	0.675		0.973		0
Change	– x		– 2x		+x
Equilibrium	0.675 – x		0.973 – 2x		x

$[S(CH_2CH_2Cl)_2]_{eq}$ = x = 0.350 *M*

$[SCl_2]_{eq}$ = 0.675 – x = 0.675 – 0.350 = = 0.325 *M*

$[C_2H_4]_{eq}$ = 0.973 – 2x = 0.973 – 2(0.350) = 0.273 *M*

$$K_c = \frac{[S(CH_2CH_2Cl)_2]}{[SCl_2][C_2H_4]^2} = \frac{[0.350]}{[0.325][0.273]^2} = 14.4497$$

$K_p = K_c(RT)^{\Delta n}$ $\quad\quad$ Δn = 1 mol – 3 mol = –2

$$K_p = (14.4497)\left[(0.0821)(273.2 + 20.0)\right]^{-2} = 0.0249370 = \mathbf{0.0249}$$

17.55 Plan: Use the balanced equation to write an equilibrium expression. Find the initial concentration of each reactant from the given amounts and container volume, use the balanced equation to define x, and set up a reaction table. The equilibrium concentration of N_2 is known, so x can be calculated and used to find the other equilibrium concentrations. Substitute the equilibrium concentrations into the equilibrium expression to find K_c.

Solution:

$4NH_3(g) + 3O_2(g) \leftrightarrows 2N_2(g) + 6H_2O(g)$

Initial $[NH_3]$ = Initial $[O_2]$ = (0.0150 mol)/(1.00 L) = 0.0150 *M*

Concentration (*M*)	$4NH_3(g)$	+	$3O_2(g)$	$\leftrightarrows$	$2N_2(g)$	+	$6H_2O(g)$
Initial	0.0150		0.0150		0		0
Change	–4x		–3x		+2x		+6x
Equilibrium	0.0150 – 4		0.0150 – 3x		+2x		+6x

$[N_2]_{eq} = 2x = 1.96\text{x}10^{-3}$ *M*

x = $(1.96\text{x}10^{-3}$ *M*$)/2 = 9.80\text{x}10^{-4}$ *M*

$[H_2O]_{eq} = 6x = 6(9.80\text{x}10^{-4}) = 5.8800\text{x}10^{-3}$ *M*

$[NH_3]_{eq} = 0.0150 - 4x = 0.0150 - 4(9.80\text{x}10^{-4}) = 1.1080\text{x}10^{-2}$ *M*

$[O_2]_{eq} = 0.0150 - 3x = 0.0150 - 3(9.80\text{x}10^{-4}) = 1.2060\text{x}10^{-2}$ *M*

$$K_c = \frac{[N_2]^2[H_2O]^6}{[NH_3]^4[O_2]^3} = \frac{\left[1.96\text{x}10^{-3}\right]^2\left[5.8800\text{x}10^{-3}\right]^6}{\left[1.1080\text{x}10^{-2}\right]^4\left[1.2060\text{x}10^{-2}\right]^3} = 6.005859\text{x}10^{-6} = \mathbf{6.01x10^{-6}}$$

17.56

Pressure (atm)	$FeO(s)$	+	$CO(g)$	$\leftrightarrows$	$Fe(s)$	+	$CO_2(g)$
Initial	—		1.00		—		0
Change			–x				+x
Equilibrium			1.00 – x				x

$$K_p = \frac{P_{CO_2}}{P_{CO}} = 0.403 = \frac{x}{1.00 - x}$$

x = 0.28724 = **0.287 atm CO_2**

1.00 – x = 1.00 – 0.28724 = 0.71276 = **0.71 atm CO**

17.57 A change in equilibrium conditions such as a change in concentration of a component, a change in pressure (volume), or a change in temperature.

17.58 Equilibrium position refers to the specific concentrations or pressures of reactants and products that exist at equilibrium, whereas equilibrium constant refers to the overall ratio of equilibrium concentrations and not to specific concentrations. Changes in reactant concentration cause changes in the specific equilibrium concentrations of reactants and products (equilibrium position), but not in the equilibrium constant.

17.59 A positive ΔH_{rxn} indicates that the reaction is endothermic, and that heat is consumed in the reaction:

$NH_4Cl(s)$ + **heat** $\leftrightarrows NH_3(g) + HCl(g)$

a) The addition of heat (high temperature) causes the reaction to proceed to the right to counterbalance the effect of the added heat. Therefore, more products form at a higher temperature and container **(B)** with the largest number of product molecules best represents the mixture.

b) When heat is removed (low temperature), the reaction shifts to the left to produce heat to offset that disturbance. Therefore, NH_3 and HCl molecules combine to form more reactant and container **(A)** with the smallest number of product gas molecules best represents the mixture.

17.60 Equilibrium component concentration values may change but the mass action expression of these concentrations is a constant as long as temperature remains constant. Changes in component amounts, pressures (volumes), or addition of a catalyst will not change the value of the equilibrium constant.

17.61 a) $\text{Rate}_f = k_f[\text{reactants}]^x$. An increase in reactant concentration shifts the equilibrium to the right by increasing the initial forward rate. Since $K_{eq} = k_f / k_r$ and k_f and k_r are not changed by changes in concentration, K_{eq} remains constant.

b) A decrease in volume causes an increase in concentrations of gases. The reaction rate for the formation of fewer moles of gases is increased to a greater extent. Again, the k_f and k_r values are unchanged.

c) An increase in temperature increases k_r to a greater extent for an exothermic reaction and thus lowers the K_{eq} value.

d) An endothermic reaction can be written as: reactants + heat $\leftrightarrows$ products. A rise in temperature (increase in heat) favors the forward direction of the reaction, i.e., the formation of products and consumption of reactants. Since K = [products]/[reactants], the addition of heat increases the numerator and decreases the denominator, making K_2 larger than K_1.

17.62 $XY(s) \leftrightarrows X(g) + Y(s)$ Since product Y is a solid substance, addition of solid Y has no effect on the equilibrium position (as long as some Y is present). **Scene A** best represents the system at equilibrium after the addition of two formula units of Y. More Y is present but the amounts of X and XY do not change.

17.63 Plan: If the concentration of a substance in the reaction increases, the equilibrium position will shift to consume some of it. If the concentration of a substance in the reaction decreases, the equilibrium position will shift to produce more of it.

Solution:

a) Equilibrium position shifts **towards products**. Adding a reactant (CO) causes production of more products as the system will act to reduce the increase in reactant by proceeding toward the product side, thereby consuming additional CO.

b) Equilibrium position shifts **towards products**. Removing a product (CO_2) causes production of more products as the system acts to replace the removed product.

c) Equilibrium position **does not shift**. The amount of a solid reactant or product does not impact the equilibrium as long as there is some solid present.

d) Equilibrium position shifts **towards reactants**. When product is added, the system will act to reduce the increase in product by proceeding toward the reactant side, thereby consuming additional CO_2; dry ice is solid carbon dioxide that sublimes to carbon dioxide gas. At very low temperatures, CO_2 solid will not sublime, but since the reaction lists carbon dioxide as a gas, the assumption that sublimation takes place is reasonable.

17.64 a) **no change** b) **no change**
c) **shifts towards the products** d) **shifts towards the reactants**

17.65 Plan: An increase in container volume results in a decrease in pressure (Boyle’s law). Le Châtelier’s principle states that the equilibrium will shift in the direction that forms more moles of gas to offset the decrease in pressure.

Solution:

a) **More F** forms (two moles of gas) and **less F_2** (one mole of gas) is present as the reaction shifts towards the right.

b) **More C_2H_2 and H_2** form (four moles of gas) and **less CH_4** (two moles of gas) is present as the reaction shifts towards the right.

17.66 a) **less $CH_3OH(l)$; more $CH_3OH(g)$**

b) **less CH_4 and NH_3; more HCN and H_2**

17.67 Plan: Decreasing container volume increases the pressure (Boyle’s law). Le Châtelier’s principle states that the equilibrium will shift in the direction that forms fewer moles of gas to offset the increase in pressure.

Solution:

a) There are two moles of reactant gas (H_2 and Cl_2) and two moles of product gas (HCl). Since there is the same number of reactant and product gas moles, there is **no effect** on the amounts of reactants or products.

b) There are three moles of reactant gases (H_2 and O_2) and zero moles of product gas. The reaction will shift to the right to produce fewer moles of gas to offset the increase in pressure. **H_2 and O_2 will decrease** from their initial values before the volume was changed. **More H_2O** will form because of the shift in equilibrium position.

17.68 a) **more CO_2 and H_2O; less C_3H_8 and O_2**

b) **more NH_3 and O_2; less N_2 and H_2O**

17.69 Plan: The purpose of adjusting the volume is to cause a shift in equilibrium to the right for increased product yield. Increasing the volume of the container results in a shift in the direction that forms more moles of gas, while decreasing the container volume results in a shift in the direction that forms fewer moles of gas.

Solution:

a) Because the number of reactant gaseous moles ($4H_2$) equals the product gaseous moles ($4H_2O$), a change in volume will have **no effect** on the yield.

b) The moles of gaseous product (2CO) exceed the moles of gaseous reactant ($1O_2$). A decrease in pressure favors the reaction direction that forms more moles of gas, so **increase** the reaction vessel volume.

17.70 a) **increase volume** b) **decrease volume**

17.71 Plan: An increase in temperature (addition of heat) causes a shift in the equilibrium away from the side of the reaction with heat. Recall that a negative value of $\Delta H^\circ_{\text{rxn}}$ indicates an exothermic reaction, while a positive value of $\Delta H^\circ_{\text{rxn}}$ indicates an endothermic reaction.

Solution:

a) $CO(g) + 2H_2(g) \leftrightarrows CH_3OH(g) + \text{heat}$ $\Delta H^\circ_{\text{rxn}} = -90.7\text{ kJ}$

The reaction is exothermic, so heat is written as a product. The equilibrium shifts to the left, away from heat, towards the reactants, so amount of product **decreases**.

b) $C(s) + H_2O(g) + \text{heat} \leftrightarrows CO(g) + H_2(g)$ $\Delta H^\circ_{\text{rxn}} = 131\text{ kJ}$

The reaction is endothermic, so heat is written as a reactant. The equilibrium shifts to the right, away from heat, towards the products, so amounts of products **increase**.

c) $2NO_2(g) + \text{heat} \leftrightarrows 2NO(g) + O_2(g)$

The reaction is endothermic, so heat is written as a reactant. The equilibrium shifts to the right, away from heat, towards the product, so amounts of products **increase**.

d) $2C(s) + O_2(g) \leftrightarrows 2CO(g) + \text{heat}$

The reaction is exothermic, so heat is written as a product. The equilibrium shifts to the left, away from heat, towards the reactants; amount of product **decreases**.

17.72 a) **decrease** b) **decrease** c) **decrease** d) **increase**

17.73 Plan: The van't Hoff equation shows how the equilibrium constant is affected by a change in temperature. Substitute the given variables into the equation and solve for K_2. Convert $\Delta H^\circ_{\text{rxn}}$ from units of kJ/mol DH to units of J/2 mol DH.

Solution:

$K_{298} = K_1 = 1.80$ $\quad T_1 = 298\text{ K}$

$K_{500} = K_2 = ?$ $\quad T_2 = 500.\text{ K}$ $\quad R = 8.314\text{ J/mol•K}$

$$\Delta H^\circ_{\text{rxn}} = \left(\frac{0.32\text{ kJ}}{1\text{ mol DH}}\right)\left(2\text{ mol DH}\right)\left(\frac{10^3\text{ J}}{1\text{ kJ}}\right) = 6.4\text{x}10^2\text{ J}$$

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

$$\ln\frac{K_2}{1.80} = -\frac{6.4\text{x}10^2\text{ J}}{8.314\text{ J/mol•K}}\left(\frac{1}{500.\text{ K}} - \frac{1}{298\text{ K}}\right)$$

$$\ln\frac{K_2}{1.80} = 0.104360$$

$$\frac{K_2}{1.80} = 1.110$$

$K_2 = (1.80)(1.110) = 1.998 = \mathbf{2.0}$

17.74 The van't Hoff equation shows how the equilibrium constant is affected by a change in temperature. Substitute the given variables into the equation and solve for K_2.

$K_{298} = K_1 = 2.25\text{x}10^4$ $\quad T_1 = 298\text{ K}$ $\quad \Delta H^\circ_{\text{rxn}} = -128\text{ kJ/mol}$

$K_0 = K_2 = ?$ $\quad T_2 = (273 + 0.) = 273\text{ K}$ $\quad R = 8.314\text{ J/mol•K}$

$\Delta H^\circ_{\text{rxn}} = (-128\text{ kJ/mol})(10^3\text{ J/1 kJ}) = -1.28\text{x}10^5\text{ J}$

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

$$\ln\frac{K_2}{2.25\text{x}10^4} = -\frac{-1.28\text{x}10^5\text{ J}}{8.314\text{ J/mol•K}}\left(\frac{1}{273\text{ K}} - \frac{1}{298\text{ K}}\right)$$

$$\ln\frac{K_2}{2.25\text{x}10^4} = 4.731088$$

$$\frac{K_2}{2.25\text{x}10^4} = 1.134189\text{x}10^2$$

$K_2 = (2.25\text{x}10^4)(1.134189\text{x}10^2) = 2.551925\text{x}10^6 = \mathbf{2.55x10^6}$

17.75 $4\text{Fe}_3\text{O}_4(s) + \text{O}_2(g) \leftrightarrows 6\text{Fe}_2\text{O}_3(s)$ $\quad K_\text{p} = 2.5\text{x}10^{87}$ at 298 K

a) $K_\text{p} = \dfrac{1}{P_{\text{O}_2}} = 2.5\text{x}10^{87}$

$P_{\text{O}_2} = \mathbf{4.0x10^{-88}\ atm}$

b) $Q_\text{p} = \dfrac{1}{P_{\text{O}_2}} = 1/(0.21) = 4.7619$

$K_\text{p} > Q_\text{p}$ thus, the reaction will proceed to the **right**.

c) $K_\text{p} = K_\text{c}(RT)^{\Delta n}$

$K_\text{c} = K_\text{p}/(RT)^{\Delta n}$ $\quad \Delta n = 0 - 1 = -1$

$K_\text{c} = (2.5\text{x}10^{87})/[(0.0821)(298)]^{-1} = 6.11645\text{x}10^{88} = \mathbf{6.1x10^{88}}$

17.76 Plan: An increase in temperature (addition of heat) causes a shift in the equilibrium away from the side of the reaction with heat, while a decrease in temperature (removal of heat) causes a shift in the equilibrium towards the side with heat. Increasing the volume of the container (pressure decreases) results in a shift in the direction that forms more moles of gas, while decreasing the container volume (pressure increases) results in a shift in the direction that forms fewer moles of gas. Adding a reactant causes a shift in the direction of products.

Solution:

a) $SO_2(g) + 1/2O_2(g) \leftrightarrows SO_3(g)$ + heat

The forward reaction is exothermic (ΔH°_{rxn} is negative), so it is favored by **lower temperatures**. Lower temperatures will cause a shift to the right, the heat side of the reaction. There are fewer moles of gas as products ($1SO_3$) than as reactants ($1SO_2(g) + 1/2O_2$), so products are favored by **higher pressure**. High pressure will cause a shift in equilibrium to the side with the fewer moles of gas.

b) Addition of O_2 would **decrease *Q*** since $Q = \dfrac{[SO_3]}{[SO_2][O_2]^{1/2}}$, and have **no impact on *K***.

c) To enhance yield of SO_3, a low temperature is used. Reaction rates are slower at lower temperatures, so a catalyst is used **to speed up the reaction**.

17.77 $3H_2(g) + N_2(g) \leftrightarrows 2NH_3(g)$

P_{NH_3} = (41.49%/100%)(110. atm) = 45.639 atm

100.00% – 41.49% = 58.51% $N_2 + H_2$

$P_{H_2} + P_{N_2}$ = (58.51%/100%)(110. atm) = 64.361 atm

P_{H_2} = (3/4)(64.361 atm) = 48.27075 atm

P_{N_2} = (1/4)(64.361 atm) = 16.09025 atm

$$K_p = \frac{\left(P_{NH_3}\right)^2}{\left(P_{H_2}\right)^3\left(P_{N_2}\right)} = \frac{\left(45.639\right)^2}{\left(48.27075\right)^3\left(16.09025\right)} = 1.15095\text{x}10^{-3} = \mathbf{1.15x10^{-3}}$$

17.78 a) $3H_2(g) + N_2(g) \leftrightarrows 2NH_3(g)$ The mole ratio $H_2:N_2$ = 3:1; at equilibrium, if N_2 = x, H_2 = 3x; P_{NH_3} = 50. atm

$$K_p = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3} = 1.00\text{x}10^{-4}$$

$$K_p = \frac{(50.)^2}{(x)(3x)^3} = 1.00\text{x}10^{-4}$$

x = 31.02016 = **31 atm N_2**

3x = 3(31.02016) = 93.06049 = **93 atm H_2**

$P_{total} = P_{nitrogen} + P_{hydrogen} + P_{ammonia}$ = (31.02016 atm) + (93.06049 atm) + (50. atm)
= 174.08065 = **174 atm total**

b) The mole ratio $H_2:N_2$ = 6:1; at equilibrium, if N_2 = x, H_2 = 6x; P_{NH_3} = 50. atm

$$K_p = \frac{(50.)^2}{(x)(6x)^3} = 1.00\text{x}10^{-4}$$

x = 18.445 = **18 atm N_2**

6x = 6(18.445) = 110.67 = **111 atm H_2**

$P_{total} = P_{nitrogen} + P_{hydrogen} + P_{ammonia}$ = (18.445 atm) + (110.67 atm) + (50. atm)
= 179.115 = **179 atm total**

This is not a valid argument. The total pressure in b) is greater than in a) to produce the same amount of NH_3.

17.79 a) **More $CaCO_3$**. Because the forward reaction is exothermic, decreasing the temperature will cause an increase in the amount of $CaCO_3$ formed as the reaction shifts to the right to produce more heat.

b) **Less $CaCO_3$**. The only gas in the equation is a reactant. Increasing the volume (decreasing the pressure) will cause the equilibrium to shift toward the reactant side and the amount of $CaCO_3$ formed decreases.
c) **More $CaCO_3$**. Increasing the partial pressure of CO_2 will cause more $CaCO_3$ to be formed as the reaction shifts to the right to consume the added CO_2.
d) **No change**. Removing half of the initial $CaCO_3$ will have no effect on the amount of $CaCO_3$ formed, because $CaCO_3$ is a solid.

17.80 a) $Q_c = \dfrac{[XY]^2}{[X_2][Y_2]}$

b) Scene A: $Q_c = \dfrac{[0]^2}{[0.4][0.4]} = \mathbf{0}$

Scene B: $Q_c = \dfrac{[0.4]^2}{[0.2][0.2]} = \mathbf{4}$

Scenes C–E: $Q_c = \dfrac{[0.6]^2}{[0.1][0.1]} = 36 = \mathbf{4x10^1}$

c) Time is progressing to the **right**. Frame A must be the earliest time.
d) $K = \mathbf{4x10^1}$
e) **Scene B**. At higher temperatures, the reaction shifts to the left (forming more X_2 and Y_2).
f) **None**. Volume (pressure) has no effect on the position of the equilibrium since there are two moles of gas on each side.

17.81 Plan: Use the balanced equation to write an equilibrium expression and to define x. Set up a reaction table, substitute into the K_c expression, and solve for x. Once the total concentration of the gases at equilibrium is known, the pressure can be found with $PV = nRT$.
Solution:

Concentration (M)	$NH_2COONH_4(s)$	$\leftrightarrows$	$2NH_3(g)$	$+$	$CO_2(g)$
Initial	7.80 g		0		0
Change	—		+2x		+x
Equilibrium	—		2x		x

The solid is irrelevant (as long as some is present) and is not included in the K_c expression.
$K_c = [NH_3]^2[CO_2]$
$K_c = 1.58x10^{-8} = (2x)^2(x)$
$x = 1.580759x10^{-3}\ M$
Total concentration of gases $= 2x + x = 2(1.580759x10^{-3}\ M) + 1.580759x10^{-3}\ M = 4.742277x10^{-3}\ M$
To find total pressure use the ideal gas equation: $PV = nRT$

$$P = \frac{nRT}{V} = \left(\frac{n}{V}\right)RT = MRT$$

$P = (4.742277x10^{-3}\ M)(0.0821\ L•atm/mol•K)(273 + 250.)K = 0.203625 = \mathbf{0.204\ atm}$

17.82 a) (1) $2Ni_3S_2(s) + 7O_2(g) \leftrightarrows$ ~~$6NiO(s)$~~ $+ 4SO_2(g)$
(2) ~~$6NiO(s)$~~ $+ 6H_2(g) \leftrightarrows$ ~~$6Ni(s)$~~ $+ 6H_2O(g)$
(3) ~~$6Ni(s)$~~ $+ 24CO(g) \leftrightarrows 6Ni(CO)_4(g)$

Overall: $2Ni_3S_2(s) + 7O_2(g) + 6H_2(g) + 24CO(g) \leftrightarrows 4SO_2(g) + 6H_2O(g) + 6Ni(CO)_4(g)$
b) As always, the solid is not included in the Q expression.

$$Q_{c(overall)} = \frac{[SO_2]^4[H_2O]^6[Ni(CO)_4]^6}{[O_2]^7[H_2]^6[CO]^{24}}$$

$$Q_1 \text{ x } Q_2 \text{ x } Q_3 = \frac{[SO_2]^4}{[O_2]^7} \text{ x } \frac{[H_2O]^6}{[H_2]^6} \text{ x } \frac{[Ni(CO)_4]^6}{[CO]^{24}} = \frac{[SO_2]^4[H_2O]^6[Ni(CO)_4]^6}{[O_2]^7[H_2]^6[CO]^{24}}$$

17.83 a) Since the volume is 1.00 L, the molarity equals the number of moles present.

	$2NH_3(g)$	$\leftrightarrows$	$N_2(g)$	+	$3H_2(g)$
Initial	0		1.30		1.65
Change	+2x		–x		–3x
Equilibrium	2x = 0.100 *M*		1.30 – x		1.65 – 3x

x = 0.0500 mol

$[N_2]_{eq}$ = (1.30 – 0.0500) *M* = **1.25 *M* N_2**

$[H_2]_{eq}$ = [1.65 – 3(0.0500)] *M* = **1.50 *M* H_2**

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{[1.25][1.50]^3}{[0.100]^2} = 421.875 = \mathbf{422}$$

b) $$K_c = \frac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]} = \frac{[1.50]^{1/2}[1.25]^{3/2}}{[8.34\text{x}10^{-2}]} = 20.523177 = \mathbf{20.5}$$

c) K_c in a) is the square of K_c in b). The balanced equations are different; therefore, the values of K_c are different.

17.84 Plan: Write the equilibrium expression. You are given a value of K_c but the amounts of reactant and product are given in units of pressure. Convert K_c to K_p and use the equilibrium pressures of C_2H_5OH and H_2O to obtain the equilibrium pressure of C_2H_4. An increase in temperature (addition of heat) causes a shift in the equilibrium away from the side of the reaction with heat, while a decrease in temperature (removal of heat) causes a shift in the equilibrium towards the side with heat. Increasing the volume of the container (pressure decreases) results in a shift in the direction that forms more moles of gas, while decreasing the container volume (pressure increases) results in a shift in the direction that forms fewer moles of gas. The van't Hoff equation shows how the equilibrium constant is affected by a change in temperature. Substitute the given variables into the equation and solve for *K* at 450. K.

Solution:

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

Δn = moles gaseous products – moles gaseous reactants = 1 – 2 = –1 (one mol of product, C_2H_5OH, and two mol of reactants, $C_2H_4 + H_2O$)

$K_p = K_c(RT)^{-1} = (9\text{x}10^3)[(0.0821\ \text{L•atm/mol•K})(600.\ \text{K})]^{-1} = 1.82704\text{x}10^2$

Substitute the given values into the equilibrium expression and solve for $P_{C_2H_4}$.

$$K_p = \frac{P_{C_2H_5OH}}{P_{C_2H_4}P_{H_2O}} = \frac{200.}{P_{C_2H_4}(400.)} = 1.8270\text{x}10^2$$

$$P_{C_2H_4} = 2.7367\text{x}10^{-3} = \mathbf{3x10^{-3}\ atm}$$

b) Since ΔH°_{rxn} is negative, the reaction is exothermic and heat is written as a product. To shift the reaction towards the right to yield more ethanol, heat must be removed. A **low temperature** favors an exothermic reaction. The forward direction, towards the production of ethanol, produces the smaller number of moles of gas and is favored by **high pressure**.

c) $K_1 = 9\text{x}10^3$ T_1 = 600. K $\Delta H^\circ_{rxn} = (-47.8\ \text{kJ})\left(\frac{10^3\ \text{J}}{1\ \text{kJ}}\right) = -4.78\text{x}10^4\ \text{J}$

K_2 = ? T_2 = 450. K *R* = 8.314 J/mol•K

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

$$\ln\frac{K_2}{9\text{x}10^3} = -\frac{-4.78\text{x}10^4\ \text{J}}{8.314\ \text{J/mol•K}}\left(\frac{1}{450.\ \text{K}} - \frac{1}{600.\ \text{K}}\right)$$

$$\ln\frac{K_2}{9\text{x}10^3} = 3.1940769$$

$$\frac{K_2}{9\text{x}10^3} = 24.38765$$

$K_2 = (9\text{x}10^3)(24.38765) = 2.1949\text{x}10^5 = \mathbf{2x10^5}$

d) **No**, condensing the C_2H_5OH would not increase the yield. Ethanol has a lower boiling point (78.5°C) than water (100°C). Decreasing the temperature to condense the ethanol would also condense the water, so moles of gas from each side of the reaction are removed. The direction of equilibrium (yield) is unaffected when there is no net change in the number of moles of gas.

17.85 $n/V = M = P/RT = \dfrac{(2.0\text{ atm})}{\left(0.0821\dfrac{\text{L•atm}}{\text{mol•K}}\right)\left((273.2 + 25.0)\text{K}\right)}$ = 0.0816919 M each gas

	$H_2(g)$	+	$CO_2(g)$	⇆	$H_2O(g)$	+	$CO(g)$
Initial	0.0816919		0.0816919		0		0
Change	–x		–x		+x		+x
Equi:	0.0816919 – x		0.0816919 – x		x		x

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} = 0.534 = \frac{[x][x]}{[0.0816919 - x][0.0816919 - x]} = \frac{[x]^2}{[0.0816919 - x]^2}$$

$$(0.534)^{1/2} = 0.730753 = \frac{[x]}{[0.0816919 - x]}$$

x = 0.03449 M

M of H_2 at equilibrium = 0.0816919 – x = 0.0816919 – 0.03449 = 0.0472019 mol/L

Mass (g) of H_2 = $(1.00\text{ L})\left(\dfrac{0.0472019\text{ mol}}{\text{L}}\right)\left(\dfrac{2.016\text{ g}}{1\text{ mol}}\right)$ = 0.095159 = **0.095 g H_2**

17.86 To get the two equations to sum to the desired equation, the first equation must be reversed and doubled. This will result in squaring the reciprocal of its K_c value. The other equation does not need to be changed. Adding the two equations means the new K_c value will be the product of the individual K_c values.

~~$2NO(g)$~~ ⇆ $N_2(g) + O_2(g)$ $K_1 = (K_c)^{-2} = 4.340\text{x}10^{18} = K_2$
$2NO_2(g)$ ⇆ ~~$2NO(g)$~~ $+ O_2(g)$ $K_2 = K_c = 1.1\text{x}10^{-5}$
Overall: $2NO_2(g)$ ⇆ $N_2(g) + 2O_2(g)$ K_c (overall) = $K_1K_2 = 4.774\text{x}10^{13}$ = **$4.8\text{x}10^{13}$ M**

17.87 Plan: Write the equilibrium expression. You are given a value of K_c but the amounts of reactants and product are given in units of pressure. Convert K_c to K_p and use the equilibrium pressures of SO_3 and O_2 to obtain the equilibrium pressure of SO_2. For part b), set up a reaction table and solve for x. The equilibrium concentrations can then be used to find the K_c value at the higher temperature. The concentration of SO_2 is converted to pressure using the ideal gas law, $PV = nRT$.

Solution:

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

Δn = moles gaseous products – moles gaseous reactants = 2 – 3 = –1 (two mol of product, SO_3, and three mol of reactants, 2 SO_2 + O_2)

$K_p = K_c(RT)^{\Delta n} = K_c(RT)^{-1} = (1.7\text{x}10^8)[(0.0821\text{ L•atm/mol•K})(600.\text{ K})]^{-1} = 3.451\text{x}10^6$

$$K_p = \frac{P^2_{SO_3}}{P^2_{SO_2}P_{O_2}} = \frac{(300.)^2}{P^2_{SO_2}(100.)} = 3.451\text{x}10^6$$

P_{SO_2} = 0.016149 = **0.016 atm**

b) Create a reaction table that describes the reaction conditions. Since the volume is 1.0 L, the moles equals the molarity. Note the 2:1:2 mole ratio between SO_2:O_2:SO_3.

Concentration (M)	$2SO_2(g)$	+	$O_2(g)$	⇆	$2SO_3(g)$	
Initial	0.0040		0.0028		0	
Change	–2x		–x		+2x	(2:1:2 mole ratio)
Equilibrium	0.0040 – 2x		0.0028 – x		2x = 0.0020 (given)	

x = 0.0010, therefore:

$[SO_2] = 0.0040 - 2x = 0.0040 - 2(0.0010) = 0.0020\ M$
$[O_2] = 0.0028 - x = 0.0028 - 0.0010 = 0.0018\ M$
$[SO_3] = 2(0.0010) = 0.0020\ M$
Substitute equilibrium concentrations into the equilibrium expression and solve for K_c.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[0.0020]^2}{[0.0020]^2[0.0018]} = 555.5556 = \mathbf{5.6x10^2}$$

The pressure of SO_2 is estimated using the concentration of SO_2 and the ideal gas law (although the ideal gas law is not well behaved at high pressures and temperatures).

$PV = nRT$

$$P_{SO_2} = \frac{nRT}{V} = \frac{(0.0020\text{ mol})\left(0.0821\frac{\text{L•atm}}{\text{mol•K}}\right)(1000.\text{ K})}{(1.0\text{ L})} = 0.1642 = \mathbf{0.16\ atm}$$

17.88 The original concentrations are: (0.350 mol/0.500 L) = 0.700 M for CO and Cl_2.

Concentration (M)	$CO(g)$ +	$Cl_2(g)$	⇆	$COCl_2(g)$
Initial	0.700	0.700		0
Change	– x	– x		+x
Equilibrium	0.700 – x	0.700 – x		x

$$Q_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{[x]}{[0.700 - x][0.700 - x]} = \frac{[x]}{[0.490 - 1.400x + x^2]} = 4.95$$

$4.95x^2 - 7.93x + 2.4255 = 0$

a = 4.95 b = – 7.93 c = 2.4255

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(-7.93) \pm \sqrt{(-7.93)^2 - 4(4.95)(2.4255)}}{2(4.95)}$$

x = 1.19039 or 0.41162959

(The 1.19039 value is not possible because 0.700 – x would be negative.)

$[CO] = [Cl_2] = 0.700 - x = 0.700 - 0.41162959 = 0.28837041 = \mathbf{0.288\ M}$
$[COCl_2] = x = 0.41162959 = \mathbf{0.412\ M}$

17.89 Plan: Set up a reaction table to find the equilibrium amount of $CaCO_3$ after the first equilibrium is established and then the equilibrium amount after the second equilibrium is established.

Solution:

The equilibrium pressure of CO_2 = P_{CO_2} = 0.220 atm.

	$CaCO_3(s)$	⇆	$CaO(s)$	+	$CO_2(g)$
Initial	0.100 mol		0.100 mol		0
Change	– x		– x		+x
Equilibrium	0.100 – x		0.100 – x		x = 0.220 atm (given)

The amount of calcium carbonate solid in the container at the first equilibrium equals the original amount, 0.100 mol, minus the amount reacted to form 0.220 atm of carbon dioxide. The moles of $CaCO_3$ reacted is equal to the number of moles of carbon dioxide produced. Use the pressure of CO_2 and the ideal gas equation to calculate the moles of CO_2 produced:

$PV = nRT$

$$\text{Moles of } CO_2 = n = \frac{PV}{RT}$$

$$n = \frac{(0.220\text{ atm})(10.0\text{ L})}{\left(0.0821\frac{\text{L•atm}}{\text{mol•K}}\right)(385\text{ K})} = 0.0696015\text{ mol } CO_2$$

Moles of $CaCO_3$ reacted = moles of CO_2 produced = 0.0696015 mol

Moles of $CaCO_3$ remaining = initial moles – moles reacted = 0.100 mol $CaCO_3$ – 0.0696015 mol $CaCO_3$
= 0.0304 mol $CaCO_3$ at first equilibrium

As more carbon dioxide gas is added, the system returns to equilibrium by shifting to the left to convert the added carbon dioxide to calcium carbonate to maintain the partial pressure of carbon dioxide at 0.220 atm (K_p). Convert the added 0.300 atm of CO_2 to moles using the ideal gas equation. The moles of CO_2 reacted equals the moles of $CaCO_3$ formed.

$$\text{Moles of CO}_2 = n = \frac{PV}{RT}$$

$$n = \frac{(0.300\text{ atm})(10.0\text{ L})}{\left(0.0821\frac{\text{L}\bullet\text{atm}}{\text{mol}\bullet\text{K}}\right)(385\text{ K})} = 0.09491\text{ mol CO}_2$$

Moles of $CaCO_3$ produced = moles of CO_2 reacted = 0.09491 mol $CaCO_3$

Add the moles of $CaCO_3$ formed in the second equilibrium to the moles of $CaCO_3$ at the first equilibrium position.

Moles of $CaCO_3$ = moles at first equilibrium + moles formed in second equilibrium
= 0.0304 mol + 0.09491 = 0.12531mol $CaCO_3$

$$\text{Mass (g) of CaCO}_3 = (0.12531\text{ mol CaCO}_3)\left(\frac{100.09\text{ g CaCO}_3}{1\text{ mol CaCO}_3}\right) = 12.542 = \mathbf{12.5\ g\ CaCO_3}$$

17.90 a) $C_2H_4(g) + 3O_2(g) \leftrightarrows 2CO_2(g) + 2H_2O(g)$
b) $4NO_2(g) + 6H_2O(g) \leftrightarrows 4NH_3(g) + 7O_2(g)$

17.91 $C_2H_2(g) + H_2(g) \leftrightarrows C_2H_4(g)$

$$\Delta H^\circ_{\text{rxn}} = \Sigma m\,\Delta H^\circ_{\text{products}} - \Sigma n\,\Delta H^\circ_{\text{reactants}}$$
$$= \{1\,\Delta H^\circ_f\,[C_2H_4(g)]\} - \{1\,\Delta H^\circ_f\,[C_2H_2(g)] + 1\,\Delta H^\circ_f\,[H_2(g)]\}$$
$$= [(1\text{ mol})(52.47\text{ kJ/mol})] - [(1\text{ mol})(227\text{ kJ/mol}) + (1\text{ mol})(0.0\text{ kJ/mol})]$$
$$= -174.53\text{ kJ}$$

$$\ln\frac{K_{300}}{K_{2000}} = -\frac{\Delta H^\circ_{\text{rxn}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{K_{300}}{2.9\text{x}10^8} = -\frac{(-174.53\text{ kJ/mol})}{\left(8.314\frac{\text{J}}{\text{mol}\bullet\text{K}}\right)}\left(\frac{1}{300.\text{ K}} - \frac{1}{2000.\text{ K}}\right)\left(\frac{10^3\text{ J}}{1\text{ kJ}}\right)$$

$$\ln\frac{K_{300}}{2.9\text{x}10^8} = 59.478189$$

$$\frac{K_{300}}{2.9\text{x}10^8} = 6.77719\text{x}10^{25}$$

$K_{300} = (2.9\text{x}10^8)(6.77719\text{x}10^{25}) = 1.9654\text{x}10^{34} = \mathbf{2.0x10^{34}}$

17.92 $M_2(g) + N_2(g) \leftrightarrows 2MN(g)$ $\qquad K_c = \dfrac{[MN]^2}{[M_2][N_2]}$

Scene A: Concentrations: $[M_2] = [N_2] = 0.20\ M$; $[MN] = 0.40\ M$

$$K_c = \frac{[0.40]^2}{[0.20][0.20]} = 4.0$$

Scene B:

Concentration (M)	$M_2(g)$	+	$N_2(g)$	$\leftrightarrows$	$2MN(g)$
Initial	0.60		0.30		0

Change	– x	– x	+2x
Equilibrium	0.60 – x	0.30 – x	2x

$$K_c = 4.0 = \frac{[2x]^2}{[0.60 - x][0.30 - x]}$$

$$4.0 = \frac{4x^2}{0.18 - 0.90\,x + x^2}$$

$4x^2 = 0.72 - 3.6x + 4x^2$

$3.6x = 0.72$

$x = 0.20\ M$

$[M_2] = 0.60 - x = 0.60 - 0.20 = \mathbf{0.40}\ \boldsymbol{M}$

$[N_2] = 0.30 - x = 0.30 - 0.20 = \mathbf{0.10}\ \boldsymbol{M}$

$[MN] = 2x = 2(0.20\ M) = \mathbf{0.40}\ \boldsymbol{M}$

17.93 Plan: Use the balanced reaction to write the equilibrium expression. The equilibrium concentration of S_2F_{10} is used to write an expression for the equilibrium concentrations of SF_4 and SF_6.

Solution:

$S_2F_{10}(g) \leftrightarrows SF_4(g) + SF_6(g)$

The reaction is described by the following equilibrium expression:

$$K_c = \frac{[SF_4][SF_6]}{[S_2F_{10}]}$$

At the first equilibrium, $[S_2F_{10}] = 0.50\ M$ and $[SF_4] = [SF_6] = x$ ($[SF_4]:[SF_6] = 1:1$).

$$K_c = \frac{[SF_4][SF_6]}{[S_2F_{10}]} = \frac{[x][x]}{[0.50]}$$

$x^2 = 0.50K_c$

$[SF_4] = [SF_6] = x = \sqrt{0.50K_c}$

At the second equilibrium, $[S_2F_{10}] = 2.5\ M$ and $[SF_4] = [SF_6] = x$.

$$K_c = \frac{[SF_4][SF_6]}{[S_2F_{10}]} = \frac{[x][x]}{[2.5]}$$

$x^2 = 2.5K_c$

$[SF_4] = [SF_6] = x = \sqrt{2.5K_c}$

Thus, the concentrations of SF_4 and SF_6 increase by a factor of:

$$\frac{\sqrt{2.5K_c}}{\sqrt{0.50K_c}} = \frac{\sqrt{2.5}}{\sqrt{0.50}} = 2.236 = \mathbf{2.2}$$

17.94 Calculate K_c.

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.40][0.10]}{[0.10][0.10]} = 4.0$$

Calculate new concentrations.

New $H_2 = 0.10\ M + (0.60\text{ mol}/2.0\text{ L}) = 0.40\ M$

Concentration (M)	$CO(g)$ +	$H_2O(g)$ $\leftrightarrows$	$CO_2(g)$ +	$H_2(g)$
Initial	0.10	0.10	0.40	0.40
Change	+x	+x	–x	–x
Equilibrium	0.10 + x	0.10 + x	0.40 – x	0.40 – x

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.40 - x][0.40 - x]}{[0.10 + x][0.10 + x]} = \frac{[0.40 - x]^2}{[0.10 + x]^2} = 4.0$$

$$\frac{[0.40 - x]}{[0.10 + x]} = 2.0$$

$x = 0.066667$

$[CO] = [H_2O] = 0.10 + x = 0.10 + 0.066667 = 0.166667 = \mathbf{0.17\ \mathit{M}}$

$[CO_2] = [H_2] = 0.40 - x = 0.40 - 0.066667 = 0.333333 = \mathbf{0.33\ \mathit{M}}$

17.95 Plan: Use the volume fraction of O_2 and CO_2 to find the partial pressure of each gas and substitute these pressures into the equilibrium expression to find the partial pressure of CO. Use $PV = nRT$ to convert the partial pressure of CO to moles per liter and then convert to pg/L.

Solution:

a) Calculate the partial pressures of oxygen and carbon dioxide because volumes are proportional to moles of gas, so volume fraction equals mole fraction. Assume that the amount of carbon monoxide gas is small relative to the other gases, so the total volume of gases equals $V_{CO_2} + V_{O_2} + V_{N_2} = 10.0 + 1.00 + 50.0 = 61.0$.

$$P_{CO_2} = \left(\frac{10.0\text{ mol }CO_2}{61.0\text{ mol gas}}\right)(4.0\text{ atm}) = 0.6557377\text{ atm}$$

$$P_{O_2} = \left(\frac{1.00\text{ mol }O_2}{61.0\text{ mol gas}}\right)(4.0\text{ atm}) = 0.06557377\text{ atm}$$

Use the partial pressures and given K_p to find P_{CO}.

$2CO_2(g) \rightleftarrows 2CO(g) + O_2(g)$

$$K_p = \frac{P_{CO}^2 P_{O_2}}{P_{CO_2}^2} = \frac{P_{CO}^2(0.06557377)}{(0.6557377)^2} = 1.4\text{x}10^{-28}$$

$P_{CO} = 3.0299\text{x}10^{-14} = \mathbf{3.0x10^{-14}\ atm}$

b) $PV = nRT$

$$\frac{n_{CO}}{V} = \frac{P}{RT} = \frac{(3.0299\text{x}10^{-14}\text{ atm})}{\left(0.0821\frac{\text{L•atm}}{\text{mol•K}}\right)(800\text{ K})} = 4.61312\text{x}10^{-16}\text{ mol/L}$$

$$\text{Concentration (pg/L) of CO} = \left(\frac{4.61312\text{x}10^{-16}\text{ mol CO}}{\text{L}}\right)\left(\frac{28.01\text{ g CO}}{1\text{ mol CO}}\right)\left(\frac{1\text{ pg}}{10^{-12}\text{ g}}\right) = 0.01292 = \mathbf{0.013\ pg\ CO/L}$$

17.96 Although the yield is favored by low temperature, the rate of formation is not. In fact, ammonia forms so slowly at low temperatures that the process becomes uneconomical. In practice, a compromise is achieved that optimizes yield and rate (high pressure, continual removal of NH_3, increasing the temperature).

17.97 Plan: Write a reaction table given that P_{CH_4} (init) = P_{CO_2} (init) = 10.0 atm, substitute equilibrium values into the equilibrium expression, and solve for P_{H_2}.

Solution:

a) Pressure (atm)	$CH_4(g)$	+	$CO_2(g)$	$\rightleftarrows$	$2CO(g)$	+	$2H_2(g)$
Initial	10.0		10.0		0		0
Change	–x		–x		+2x		+2x
Equilibrium	10.0 – x		10.0 – x		2x		2x

$$K_p = \frac{P_{CO}^2 P_{H_2}^2}{P_{CH_4} P_{CO_2}} = \frac{(2x)^2(2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0\ - x)^2} = 3.548\text{x}10^6 \quad \text{(take square root of each side)}$$

$$\frac{(2x)^2}{(10.0\ - x)} = 1.8836135\text{x}10^3$$

A quadratic is necessary:

$4x^2 + (1.8836135\text{x}10^3\ x) - 1.8836135\text{x}10^4 = 0$

$a = 4 \quad b = 1.8836135\text{x}10^3 \quad c = -1.8836135\text{x}10^4$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-1.8836135\text{x}10^3 \pm \sqrt{\left(1.8836135\text{x}10^3\right)^2 - 4(4)\left(-1.8836135\text{x}10^4\right)}}{2(4)}$$

$x = 9.796209$

$P_{H_2} = 2x = 2(9.796209) = 19.592419$ atm

If the reaction proceeded entirely to completion, the partial pressure of H_2 would be 20.0 atm (pressure is proportional to moles, and twice as many moles of H_2 form for each mole of CH_4 or CO_2 that reacts).

The percent yield is $\frac{19.592418 \text{ atm}}{20.0 \text{ atm}}(100\%) = 97.96209 = \mathbf{98.0\%}$.

b) Repeat the calculations for part a) with the new K_p value. The reaction table is the same.

$$K_p = \frac{P_{CO}^2 P_{H_2}^2}{P_{CH_4} P_{CO_2}} = \frac{(2x)^2(2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 2.626\text{x}10^7$$

$$\frac{(2x)^2}{(10.0 - x)} = 5.124451\text{x}10^3$$

A quadratic is needed:

$4x^2 + (5.124451\text{x}10^3\ x) - 5.124451\text{x}10^4 = 0$

$a = 4 \qquad b = 5.124451\text{x}10^3 \qquad c = -5.124451\text{x}10^4$

$$x = \frac{-5.124451\text{x}10^3 \pm \sqrt{\left(5.124451\text{x}10^3\right)^2 - 4(4)\left(-5.124451\text{x}10^4\right)}}{2(4)}$$

$x = 9.923144$

$P_{H_2} = 2x = 2(9.923144) = 19.84629$ atm

If the reaction proceeded entirely to completion, the partial pressure of H_2 would be 20.0 atm (pressure is proportional to moles, and twice as many moles of H_2 form for each mole of CH_4 or CO_2 that reacts).

The percent yield is $\frac{19.84629 \text{ atm}}{20.0 \text{ atm}}(100\%) = 99.23145 = \mathbf{99.0\%}$.

c) van't Hoff equation:

$K_1 = 3.548\text{x}10^6 \qquad T_1 = 1200.\text{ K} \qquad \Delta H^\circ_{rxn} = ?$

$K_2 = 2.626\text{x}10^7 \qquad T_2 = 1300.\text{ K} \qquad R = 8.314 \text{ J/mol•K}$

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

$$\ln\frac{2.626\text{x}10^7}{3.548\text{x}10^6} = -\frac{\Delta H^\circ_{rxn}}{\left(8.314 \frac{\text{J}}{\text{mol•K}}\right)}\left(\frac{1}{1200.\text{ K}} - \frac{1}{1300.\text{ K}}\right)$$

$2.0016628 = \Delta H^\circ_{rxn}\,(7.710195\text{x}10^{-6})$

$\Delta H^\circ_{rxn} = 2.0016628/7.710195\text{x}10^{-6} = 2.5961247\text{x}10^5 = \mathbf{2.60x10^5\ J/mol}$

(The subtraction of the $1/T$ terms limits the answer to three significant figures.)

17.98 a) $C_3H_8(g) + 3H_2O(g) \leftrightarrows \cancel{3CO(g)} + 7H_2(g) \qquad K'_{p1} = K_p = 8.175\text{x}10^{15}$

$\cancel{3CO(g)} + 3H_2O(g) \leftrightarrows 3CO_2(g) + 3H_2(g) \qquad K'_{p2} = (K_{p2})^3 = (0.6944)^3 = 0.33483368$

(Overall): $C_3H_8(g) + 6H_2O(g) \leftrightarrows 3CO_2(g) + 10H_2(g)$

b) $K_{p(overall)} = K'_{p1} \text{ x } K'_{p2} = (8.175\text{x}10^{15})(0.33483368) = 2.737265\text{x}10^{15} = \mathbf{2.737x10^{15}}$

c) $K_p = \dfrac{\left(P_{CO_2}\right)^3\left(P_{H_2}\right)^{10}}{\left(P_{C_3H_8}\right)\left(P_{H_2O}\right)^6}$

The partial pressures of each reactant are proportional to the moles, and the limiting reactant may be determined from the partial pressures.

$P_{C_3H_8\text{ (initial)}}$ = (1.00/5.00) x 5.0 atm = 1.0 atm

$P_{H_2O\text{(initial)}}$ = (4.00/5.00) x 5.0 atm = 4.0 atm (limiting reactant)

$P_{CO_2\text{(formed)}}$ = 4.0 atm H_2O x (3 mol CO_2/6 mol H_2O) = 2.0 atm

$P_{H_2\text{(formed)}}$ = 4.0 atm H_2O x (10 mol H_2/6 mol H_2O) = 6.6667 atm

$P_{C_3H_8\text{ (remaining)}}$ = 1.0 atm C_3H_8 – [4.0 atm H_2O x (1 mol C_3H_8/6 mol H_2O)] = 0.3333 atm

$P_{H_2O\text{(remaining)}}$ = 0.00 atm (limiting reactant)

$P_{\text{Total}} = P_{CO_2} + P_{H_2} + P_{C_3H_8} + P_{H_2O}$ = 2.0 atm + 6.6667 atm + 0.3333 atm + 0.00 atm = **9.0 atm**

d) Percent $C_3H_{8\text{(unreacted)}}$ = [0.3333 atm/1.0 atm] x 100% = 33.33% = **30%**

17.99 Plan: Add the two reactions to obtain the overall reaction. Multiply the second equation by 2 to cancel the moles of CO produced in the first reaction. K_p for the second reaction is then $(K_p)^2$. K_p for the overall reaction is equal to the product of the K_p values for the two individual reactions. Calculate K_c using $K_p = K_c(RT)^{\Delta n}$.

Solution:

a)

$$2CH_4(g) + O_2(g) \rightleftarrows \cancel{2CO}(g) + 4H_2(g) \qquad K_p = 9.34\text{x}10^{28}$$
$$\cancel{2CO}(g) + 2H_2O(g) \rightleftarrows 2CO_2(g) + 2H_2(g) \qquad K_p = (1.374)^2 = 1.888$$

$$2CH_4(g) + O_2(g) + 2H_2O(g) \rightleftarrows 2CO_2(g) + 6H_2(g)$$

b) $K_p = (9.34\text{x}10^{28})(1.888) = 1.76339\text{x}10^{29} = \mathbf{1.76x10^{29}}$

c) Δn = moles gaseous products – moles gaseous reactants = 8 – 5 = 3

(8 moles of product gas – 5 moles of reactant gas)

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

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.76339\text{x}10^{29}}{[(0.0821\text{ atm•L/mol•K})(1000)]^3} = 3.18654\text{x}10^{23} = \mathbf{3.19x10^{23}}$$

d) The initial total pressure is given as 30. atm. To find the final pressure use the relationship between pressure and number of moles of gas: $n_{\text{initial}}/P_{\text{initial}} = n_{\text{final}}/P_{\text{final}}$

Total mol of gas initial = 2.0 mol CH_4 + 1.0 mol O_2 + 2.0 mol H_2O = 5.0 mol

Total mol of gas final = 2.0 mol CO_2 + 6.0 mol H_2 = 8.0 mol (from mole ratios)

$$P_{\text{final}} = (30.\text{ atm reactants})\left(\frac{8\text{ mol products}}{5\text{ mol reactants}}\right) = \mathbf{48\text{ atm}}$$

17.100 Plan: Write an equilibrium expression. Use the balanced equation to define x and set up a reaction table, substitute into the equilibrium expression, and solve for x, from which the pressure of N or H is calculated. Convert log K_p to K_p. Convert pressures to moles using the ideal gas law, $PV = nRT$. Convert moles to atoms using Avogadro's number.

Solution:

a) The initial pressure of N_2 is 200. atm. Log K_p = –43.10; $K_p = 10^{-43.10} = 7.94328\text{x}10^{-44}$

Pressure (atm)	$N_2(g)$	$\rightleftarrows$	$2N(g)$
Initial	200.		0
Change	–x		+2x
Equilibrium	200 – x		2x

$$K_p = \frac{\left(P_N\right)^2}{\left(P_{N_2}\right)} = 7.94328\text{x}10^{-44}$$

$$\frac{(2x)^2}{(200. - x)} = 7.94328\text{x}10^{-44} \qquad \text{Assume } 200. - x \cong 200.$$

$$\frac{(2x)^2}{(200)} = 7.94328\text{x}10^{-44}$$

$4x^2 = 1.588656\text{x}10^{-41}$

$x = 1.992897\text{x}10^{-21}$

$P_N = 2x = 2(1.992897\text{x}10^{-21}) = 3.985795\text{x}10^{-21} = \mathbf{4.0x10^{-21}\ atm}$

b) $\text{Log } K_p = -17.30$; $K_p = 10^{-17.30} = 5.01187\text{x}10^{-18}$

Pressure (atm)	$H_2(g)$	$\leftrightarrows$	$2H(g)$
Initial	600.		0
Change	$-x$		$+2x$
Equilibrium	$600 - x$		$2x$

$$K_p = \frac{(P_H)^2}{(P_{H_2})} = 5.01187\text{x}10^{-18}$$

$$\frac{(2x)^2}{(600. - x)} = 5.01187\text{x}10^{-18}$$ Assume $600. - x \cong 600.$

$$\frac{(2x)^2}{(600)} = 5.01187\text{x}10^{-18}$$

$4x^2 = 3.007122\text{x}10^{-15}$

$x = 2.741862\text{x}10^{-8}$

$P_H = 2x = 2(2.741862\text{x}10^{-8}) = 5.48372\text{x}10^{-8} = \mathbf{5.5x10^{-8}}$

c) $PV = nRT$

$$\text{Moles of N atoms} = \frac{PV}{RT} = \frac{(3.985795\text{x}10^{-21}\text{atm})(1.00\text{ L})}{\left(0.0821\frac{\text{L•atm}}{\text{mol•K}}\right)(1000.\text{ K})} = 4.85481\text{x}10^{-15}\text{ mol}$$

$$\text{Number of N atoms} = (4.85481\text{x}10^{-23}\text{ mol N atoms})\left(\frac{6.022\text{x}10^{23}\text{ N atoms}}{1\text{ mol N atoms}}\right) = 29.2356 = \mathbf{29\ N\ atoms/L}$$

$$\text{Moles of H atoms} = \frac{PV}{RT} = \frac{(5.48372\text{x}10^{-8}\text{atm})(1.00\text{ L})}{\left(0.0821\frac{\text{L•atm}}{\text{mol•K}}\right)(1000.\text{ K})} = 6.67932\text{x}10^{-10}\text{ mol}$$

$$\text{Number of H atoms} = (6.67932\text{x}10^{-10}\text{ mol H atoms})\left(\frac{6.022\text{x}10^{23}\text{ H atoms}}{1\text{ mol H atoms}}\right)$$

$$= 4.022\text{x}10^{14} = \mathbf{4.0x10^{14}\ H\ atoms/L}$$

d) The more reasonable step is $\mathbf{N_2(g) + H(g) \rightarrow NH(g) + N(g)}$. With only twenty-nine N atoms in 1.0 L, the first reaction would produce virtually no NH(g) molecules. There are orders of magnitude more N_2 molecules than N atoms, so the second reaction is the more reasonable step.

17.101 a) Scenes B and D represent equilibrium.

b) C, A, B = D

$$\text{c) [Y]} = (4\text{ spheres})\left(\frac{0.025\text{ mol}}{1\text{ sphere}}\right)\left(\frac{1}{0.40\text{ L}}\right) = 0.25\ M$$

$$[Z] = (8\text{ spheres})\left(\frac{0.025\text{ mol}}{1\text{ sphere}}\right)\left(\frac{1}{0.40\text{ L}}\right) = 0.50\ M$$

$$K_c = \frac{[Z]^2}{[Y]} = \frac{[0.50]^2}{[0.25]} = \mathbf{1.0}$$

17.102 The K is very small, thus the reaction will shift to the right to reach equilibrium. To simplify the calculations, assume the equilibrium shifts entirely to the left, and then a little material reacts to reach equilibrium. Shifting entirely to the left gives $[H_2S] = 0.600$, and $[H_2] = [S_2] = 0$.

	$2H_2S(g)$	$\leftrightarrows$	$2H_2(g)$	+	$S_2(g)$
Initial	0.600 M		0 M		0 M
Change	$-2x$		$+2x$		$+x$
Equilibrium	$0.600 - 2x$		$2x$		x

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = 9.0x10^{-8}$$

$$\frac{[2x]^2[x]}{[0.600 - 2x]^2} = 9.0x10^{-8}$$ Assume 2x is small compared to 0.600 M.

$$\frac{[2x]^2[x]}{[0.600]^2} = 9.0x10^{-8}$$

$x = 2.008x10^{-3}$ (assumption justified)

$[H_2S] = 0.600 - 2x = 0.600 - 2(2.008x10^{-3}) = 0.595984 = \mathbf{0.596\ \mathit{M}\ H_2S}$

$[H_2] = 2x = 2(2.008x10^{-3}) = 4.016x10^{-3} = \mathbf{4.0x10^{-3}\ \mathit{M}\ H_2}$

$[S_2] = x = 2.008x10^{-3} = \mathbf{2.0x10^{-3}\ \mathit{M}\ S_2}$

17.103 Plan: Write an equilibrium expression. Use the balanced equation to define x and set up a reaction table, substitute into the equilibrium expression, and solve for x, from which the equilibrium pressures of the gases are calculated. Add the equilibrium pressures of the three gases to obtain the total pressure. Use the relationship $K_p = K_c(RT)^{\Delta n}$ to find K_c.

Solution:

a)

Pressure (atm)	$N_2(g)$	+	$O_2(g)$	$\leftrightarrows$	$2NO(g)$
Initial	0.780		0.210		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.780 - x$		$0.210 - x$		$2x$

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = 4.35x10^{-31}$$

$$\frac{(2x)^2}{(0.780 - x)(0.210 - x)} = 4.35x10^{-31}$$ Assume x is small because K is small.

$$\frac{(2x)^2}{(0.780)(0.210)} = 4.35x10^{-31}$$

$x = 1.33466x10^{-16}$

Based on the small amount of nitrogen monoxide formed, the assumption that the partial pressures of nitrogen and oxygen change to an insignificant degree holds.

$P_{nitrogen}$ (equilibrium) = $(0.780 - 1.33466x10^{-16})$ atm = $\mathbf{0.780\ atm\ N_2}$

P_{oxygen} (equilibrium) = $(0.210 - 1.33466x10^{-16})$ atm = $\mathbf{0.210\ atm\ O_2}$

P_{NO} (equilibrium) = $2(1.33466x10^{-16})$ atm = $2.66933x10^{-16}$ = $\mathbf{2.67x10^{-16}\ atm\ NO}$

b) The total pressure is the sum of the three partial pressures:

0.780 atm + 0.210 atm + $2.67x10^{-16}$ atm = **0.990 atm**

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

Δn = moles gaseous products – moles gaseous reactants = 2 – 2 = 0

(two moles of product NO and two moles of reactants N_2 and O_2)

$K_p = K_c(RT)^0$

$K_c = K_p =$ $\mathbf{4.35x10^{-31}}$ because there is no net increase or decrease in the number of moles of gas in the course of the reaction.

17.104 a) $K_p = K_c(RT)^{\Delta n}$ $n = 2 - (2 + 1) = -1$

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

$$K_c = \frac{\left(1.3\text{x}10^4\right)}{\left[(0.0821)(457)\right]^{-1}} = 4.877561\text{x}10^5 = \mathbf{4.9x10^5}$$

b) $\Delta H^\circ_{\text{rxn}} = \sum[\,\Delta H^\circ_{\text{f(products)}}\,] - \sum[\,\Delta H^\circ_{\text{f(reactants)}}\,]$

$\Delta H^\circ_{\text{rxn}} = \{2\,\Delta H^\circ_{\text{f}}\,[\text{NO}_2(g)]\} - \{2\,\Delta H^\circ_{\text{f}}\,[\text{NO}(g)] + 1\,\Delta H^\circ_{\text{f}}\,[\text{O}_2(g)]\}$

$= [(2 \text{ mol})(33.2 \text{ kJ/mol})] - [(2 \text{ mol})(90.29 \text{ kJ/mol}) + (1 \text{ mol})(0.0 \text{ kJ/mol})]$

$= -114.18 =$ **– 114.2 kJ**

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

$$\ln\frac{6.4\text{x}10^9}{4.877561\text{x}10^5} = -\frac{-114.18 \text{ kJ}}{8.314 \text{ J/mol•K}}\left(\frac{1}{T_2} - \frac{1}{457\,\text{K}}\right)\left(\frac{10^3\text{ J}}{1\text{ kJ}}\right)$$

$$9.4819931 = 13{,}733\left(\frac{1}{T_2} - \frac{1}{457\,\text{K}}\right)$$

$T_2 = 347.389 =$ $\mathbf{3.5x10^2\ K}$

17.105 Plan: Use the equation $K_p = K_c(RT)^{\Delta n}$ to find K_p. The value of K_c for the formation of HI is the reciprocal of the K_c value for the decomposition of HI. Use the equation $\Delta H^\circ_{\text{rxn}} = \sum[\,\Delta H^\circ_{\text{f(products)}}\,] - \sum[\,\Delta H^\circ_{\text{f(reactants)}}\,]$ to find the value of $\Delta H^\circ_{\text{rxn}}$. Use the van't Hoff equation as a second method of calculating $\Delta H^\circ_{\text{rxn}}$.

Solution:

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

Δn = moles gaseous products – moles gaseous reactants = 2 – 2 = 0

(2 mol product ($1\text{H}_2 + 1\text{I}_2$) – 2 mol reactant (HI) = 0)

$K_p = K_c(RT)^0 = 1.26\text{x}10^{-3}(RT)^0 =$ $\mathbf{1.26x10^{-3}}$

b) The equilibrium constant for the reverse reaction is the reciprocal of the equilibrium constant for the forward reaction:

$$K_{\text{formation}} = \frac{1}{K_{\text{decomposition}}} = \frac{1}{1.26\text{x}10^{-3}} = 793.65 = \mathbf{794}$$

c) $\Delta H^\circ_{\text{rxn}} = \sum[\,\Delta H^\circ_{\text{f(products)}}\,] - \sum[\,\Delta H^\circ_{\text{f(reactants)}}\,]$

$\Delta H^\circ_{\text{rxn}} = \{1\,\Delta H^\circ_{\text{f}}\,[\text{H}_2(g)] + 1\,\Delta H^\circ_{\text{f}}\,[\text{I}_2(g)]\} - \{2\,\Delta H^\circ_{\text{f}}\,[\text{HI}(g)]\}$

$\Delta H^\circ_{\text{rxn}} = [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})] - [(2 \text{ mol})(25.9 \text{ kJ/mol})]$

$\Delta H^\circ_{\text{rxn}} =$ **– 51.8 kJ**

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

$K_1 = 1.26\text{x}10^{-3}$; $K_2 = 2.0\text{x}10^{-2}$, $T_1 = 298$ K; $T_2 = 729$ K

$$\ln\frac{2.0\text{x}10^{-2}}{1.26\text{x}10^{-3}} = -\frac{\Delta H^\circ_{\text{rxn}}}{8.314 \text{ J/mol•K}}\left(\frac{1}{729\text{ K}} - \frac{1}{298\text{ K}}\right)$$

$2.764621 = 2.38629\text{x}10^{-4}\ \Delta H^\circ_{\text{rxn}}$

$\Delta H^\circ_{\text{rxn}}$ = 1.1585x10^4 = **1.2x10^4 J/mol**

17.106 $C_5H_{11}OH + CH_3COOH \leftrightarrows CH_3COOC_5H_{11} + H_2O$
Removing water should help to increase the yield of banana oil. Both isopentyl alcohol and acetic acid are more soluble in water than isopentyl acetate. Thus, removing water will increase the concentration of both reactants and cause a shift in equilibrium towards the products.

17.107 Q(g) $\leftrightarrows$ R(g) $\quad K = \dfrac{[R]}{[Q]}$

For Scene A at equilibrium:

$$K = \frac{[R]}{[Q]} = \frac{[2]}{[6]} = 0.33$$

For Scene B:

	Q(g)	$\leftrightarrows$	R(g)
Initial	10		2
Change	–x		+x
Equilibrium	10 – x		2 + x

$$0.33 = \frac{[2 + x]}{[10 - x]}$$

x = 0.977 = 1
Q = 10 – x = 10 – 1 = **9**; R = 2 + x = 2 + 1 = **3**

17.108 a) $K_p = \left(P_{H_2O}\right)^{10} = 4.08\text{x}10^{-25}$

$P_{H_2O} = \sqrt[10]{4.08\text{x}10^{-25}}$ = 3.6397x10^{-3} = **3.64x10^{-3} atm**

b) (1) Adding more Na_2SO_4(s) will **decrease** the ratio of hydrated form/anhydrous form merely because you are increasing the value of the denominator, not because the equilibrium shifts.
(2) Reducing the container size will **increase** the pressure (concentration) of the water vapor, which will shift the equilibrium to the reactant side. The ratio of hydrated form/anhydrous form will increase.
(3) Adding more water vapor will **increase** the concentration of the water vapor, which will shift the equilibrium to the reactant side. The ratio of hydrated form/anhydrous form will increase.
(4) Adding N_2 gas will not change the partial pressure of the water vapor, so the ratio of hydrated form/anhydrous form **will not change**.

17.109 Plan: Use the balanced equation to write an equilibrium expression. Find the initial concentration of each reactant from the given amounts and container volume, use the balanced equation to define x, and set up a reaction table. The equilibrium concentration of CO is known, so x can be calculated and used to find the other equilibrium concentrations. Substitute the equilibrium concentrations into the equilibrium expression to find K_c. Add the molarities of all of the gases at equilibrium, use (M)(V) to find the total number of moles, and then use $PV = nRT$ to find the total pressure. To find $[CO]_{eq}$ after the pressure is doubled, set up another reaction table in which the initial concentrations are equal to the final concentrations from part a) and add in the additional CO.

Solution:
The reaction is: CO(g) + H_2O(g) $\leftrightarrows$ CO_2(g) + H_2(g)
a) Initial [CO] and initial [H_2O] = 0.100 mol/20.00 L = 0.00500 M.

	CO	H_2O	$\leftrightarrows$	CO_2	H_2
Initial	0.00500 M	0.00500 M		0	0
Change	–x	–x		+x	+x
Equilibrium	0.00500 – x	0.00500 – x		x	x

$[CO]_{\text{equilibrium}}$ = 0.00500 – x = 2.24x10^{-3} M = [H_2O] (given in problem)
x = 0.00276 M = [CO_2] = [H_2]

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.00276][0.00276]}{[0.00224][0.00224]} = 1.518176 = \mathbf{1.52}$$

b) $M_{total} = [CO] + [H_2O] + [CO_2] + [H_2] = (0.00224\ M) + (0.00224\ M) + (0.00276\ M) + (0.00276\ M)$
$= 0.01000\ M$

$n_{total} = (M_{total})(V) = (0.01000\ \text{mol/L})(20.00\ \text{L}) = 0.2000$ mol total

$PV = nRT$

$$P_{total} = n_{total}RT/V = \frac{(0.2000\,\text{mol})\left(0.08206\,\frac{\text{L•atm}}{\text{mol•K}}\right)((273 + 900.)\,\text{K})}{(20.00\ \text{L})} = 0.9625638 = \mathbf{0.9626\ atm}$$

c) Initially, an equal number of moles must be added = **0.2000 mol CO**

d) Set up a table with the initial concentrations equal to the final concentrations from part a), and then add 0.2000 mol CO/20.00 L = 0.01000 *M* to compensate for the added CO.

	CO	H_2O	CO_2	H_2
Initial	0.00224 *M*	0.00224 *M*	0.00276 *M*	0.00276 *M*
Added CO	0.01000 *M*			
Change	–x	–x	+x	+x
Equilibrium	0.01224 – x	0.00224 – x	0.00276 + x	0.00276 + x

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.00276 + x][0.00276 + x]}{[0.01224 - x][0.00224 - x]} = 1.518176$$

$$\frac{\left[7.6176\text{x}10^{-6} + 5.52\text{x}10^{-3}\,x + x^2\right]}{2.74176\text{x}10^{-5} - 1.448\text{x}10^{-2}\,x + x^2} = 1.518176$$

$7.6176\text{x}10^{-6} + 5.52\text{x}10^{-3}x + x^2 = (1.518176)(2.74176\text{x}10^{-5} - 1.448\text{x}10^{-2}x + x^2)$

$7.6176\text{x}10^{-6} + 5.52\text{x}10^{-3}x + x^2 = 4.162474\text{x}10^{-5} - 0.021983x + 1.518176x^2$

$0.518176x^2 - 0.027503x + 3.400714\text{x}10^{-5} = 0$

$a = 0.518176 \quad b = -0.027503 \quad c = 3.400714\text{x}10^{-5}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(-0.027503) \pm \sqrt{(-0.027503)^2 - 4(0.518176)(3.400714\text{x}10^{-5})}}{2(0.518176)}$$

$x = 1.31277\text{x}10^{-3}$

$[CO] = 0.01224 - x = 0.01224 - (1.31277\text{x}10^{-3}) = 0.01092723 = \mathbf{0.01093}$ ***M***

17.110 a) At point A the sign of $\Delta H°$ is negative for the reaction graphite → diamond. An increase in temperature at constant pressure will cause the formation of more graphite. Therefore, the equation must look like this: graphite → diamond + heat, and adding heat shifts the equilibrium to the reactant side.

b) Diamond is denser than graphite. The slope of the diamond-graphite line is positive. An increase in pressure favors the formation of diamond.