CHAPTER 15 EQUILIBRIUM: THE EXTENT OF CHEMICAL REACTIONS

CHEMICAL CONNECTIONS BOXED READING PROBLEM

B15.1   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

15.1   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).

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

15.7   The equilibrium constant expression is $K = p_{O_2}$ (remember the activity of solids is 1). If the temperature remains
constant, K remains constant. If the initial amount of Li_2O_2 present was sufficient to reach equilibrium, the
pressure of O_2 obtained will be constant, regardless of how much $Li_2O_2(s)$ is present.

15.8   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
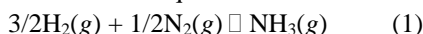concentration of product HI increases, which means that Q increases as a function of time.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad Q = \frac{p_{HI}^2}{p_{H_2}\, p_{I_2}}$$
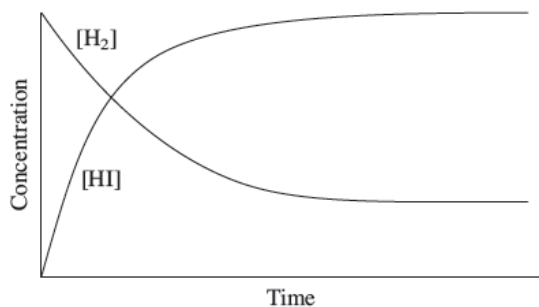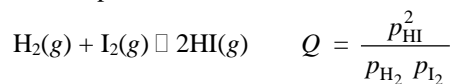
The value of Q increases as a function of time until it reaches the value of K.
b) No, Q would still increase with time because the $[I_2]$ would decrease in exactly the same way as $[H_2]$ decreases.

15.11   <u>Plan:</u> Write the reaction and then the expression for Q.
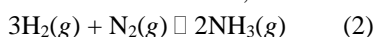   <u>Solution:</u>
        The balanced equation for the first reaction is
        $3/2H_2(g) + 1/2N_2(g) \rightleftharpoons NH_3(g)$ (1)
        The coefficient in front of NH_3 is fixed at 1 mole according to the description.   The reaction quotient for this

        reaction is $Q_1 = \dfrac{p_{NH_3}}{p_{H_2}^{3/2} p_{N_2}^{1/2}}$.

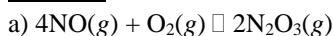   In the second reaction, the coefficient in front of N_2 is fixed at 1 mole.
        $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ (2)

        The reaction quotient for this reaction is $Q_2 = \dfrac{p_{NH_3}^2}{p_{H_2}^3 p_{N_2}}$

        Q_2 is equal to Q_1^2.

15.12   <u>Plan:</u> Remember that $Q = \dfrac{a_C^c a_D^d}{a_A^a a_B^b}$ 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.
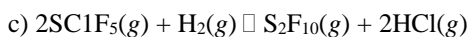   <u>Solution:</u>
        a) $4NO(g) + O_2(g) \rightleftharpoons 2N_2O_3(g)$

            $Q = \dfrac{p_{N_2O_3}^2}{p_{NO}^4 p_{O_2}}$

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

            $Q = \dfrac{p_{SO_2F_2}^3}{p_{SF_6} p_{SO_3}^2}$

        c) $2SClF_5(g) + H_2(g) \rightleftharpoons S_2F_{10}(g) + 2HCl(g)$
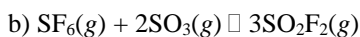
            $Q = \dfrac{p_{S_2F_{10}} p_{HCl}^2}{p_{SClF_5}^2 p_{H_2}}$

15.14   <u>Plan:</u> Remember that Q will be determined using pressures in place of activities when the species in the chemical
        reaction are all gases.
        <u>Solution:</u>
        a) $2NO_2Cl(g) \rightleftharpoons 2NO_2(g) + Cl_2(g)$

            $Q = \dfrac{p_{NO_2}^2 p_{Cl_2}}{p_{NO_2Cl}^2}$

        b) $2POCl_3(g) \rightleftharpoons 2PCl_3(g) + O_2(g)$
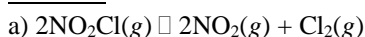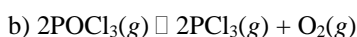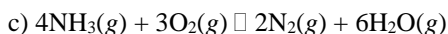
            $Q = \dfrac{p_{PCl_3}^2 p_{O_2}}{p_{POCl_3}^2}$

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

            $Q = \dfrac{p_{N_2}^2 p_{H_2O}^6}{p_{NH_3}^4 p_{O_2}^3}$

15.16   <u>Plan:</u> 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.
        <u>Solution:</u>

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

The given reaction $1/2S_2(g) + H_2(g) \rightleftharpoons H_2S(g)$ 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.

$$K_{(a)} = (1/K)^{1/2} = \dfrac{p_{H_2S}}{p_{H_2}\, p_{S_2}^{1/2}}$$

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

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

$$K_{(b)} = (K_c)^{5/2} = \dfrac{p_{H_2}^5\, p_{S_2}^{5/2}}{p_{H_2S}^5}$$
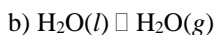
$$K_{(b)} = (1.6\text{x}10^{-2})^{5/2} = 3.23817\text{x}10^{-5} = \mathbf{3.2\text{x}10^{-5}}$$

15.18   Plan: The activity of pure solids and pure liquids is 1, so they do not appear
in the reaction quotient expression. Remember that stoichiometric coefficients are used as exponents in the
expression for the reaction quotient.
Solution:
a) $2Na_2O_2(s) + 2CO_2(g) \rightleftharpoons 2Na_2CO_3(s) + O_2(g)$

$$Q = \dfrac{p_{O_2}}{p_{CO_2}^2}$$

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

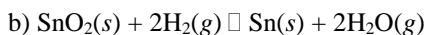$$Q = p_{H_2O}$$

c) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
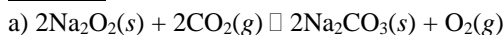
$$Q = p_{NH_3}\, p_{HCl}$$

15.20   Plan: The activity of pure solids and pure liquids is 1, so they do not appear
in the reaction quotient expression. Remember that stoichiometric coefficients are used as exponents in the
expression for the reaction quotient.
Solution:
a) $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$

$$Q = p_{CO_2}\, p_{H_2O}$$

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

$$Q = \dfrac{p_{H_2O}^2}{p_{H_2}^2}$$

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

$$Q = \dfrac{1}{p_{SO_3}}$$

15.23   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.

$$(1)\ Cl_2(g) + F_2(g) \rightleftharpoons \cancel{2ClF(g)} \qquad\qquad Q_1 = \frac{p_{ClF}^2}{p_{Cl_2}\, p_{F_2}}$$

$$\underline{(2)\ \cancel{2ClF(g)} + 2F_2(g) \rightleftharpoons 2ClF_3(g)} \qquad\qquad Q_2 = \frac{p_{ClF_3}^2}{p_{ClF}^2\, p_{F_2}^2}$$

$$\text{Overall: } Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g) \qquad\qquad Q_{overall} = \frac{p_{ClF_3}^2}{p_{Cl_2}\, p_{F_2}^3}$$
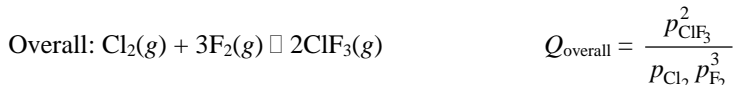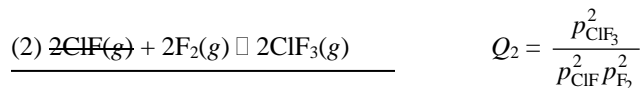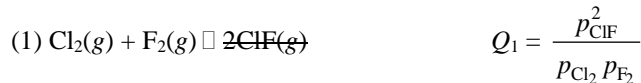
b) The reaction quotient for the overall reaction, $Q_{overall}$, determined from the reaction is:

$$Q_{overall} = \frac{p_{ClF_3}^2}{p_{Cl_2}\, p_{F_2}^3}$$

$$Q_{overall} = Q_1 Q_2^2 = \left(\frac{p_{ClF}^2}{p_{Cl_2}\, p_{F_2}}\right)\left(\frac{p_{ClF_3}^2}{p_{ClF}^2\, p_{F_2}^2}\right) = \frac{p_{ClF_3}^2}{p_{Cl_2}\, p_{F_2}^3}$$

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

15.26   a) $K = K_c(RT)^{\Delta n}$. Since Δn = amount (mol) gaseous products – amount (mol) 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. **K_c is smaller than K**.
b) Assuming that $RT > 1$ (which occurs when $T > 12.0\ K$, because 0.08314 (R) x 12.0 = 1), **$K > K_c$** if the amount (mol) of gaseous products exceeds the amount (mol) of gaseous reactants. $K < K_c$ when the amount (mol) of gaseous reactants exceeds the amount (mol) of gaseous product.

15.27   Plan: Δn_{gas} = moles gaseous products – moles gaseous reactants.
Solution:
a) Amount (mol) of <u>gaseous</u> reactants = 0; amount (mol) of <u>gaseous</u> products = 3; $\Delta n_{gas} = 3 - 0 = \mathbf{3}$
b) Amount (mol) of <u>gaseous</u> reactants = 1; amount (mol) of <u>gaseous</u> products = 0; $\Delta n_{gas} = 0 - 1 = \mathbf{-1}$
c) Amount (mol) of <u>gaseous</u> reactants = 0; amount (mol) of <u>gaseous</u> products = 3; $\Delta n_{gas} = 3 - 0 = \mathbf{3}$

15.29   Plan: First, determine Δn for the reaction and then calculate K_c using $K = K_c(RT)^{\Delta n}$.
Solution:
a) Δn = moles gaseous products – moles gaseous reactants = $1 - 2 = -1$
$$K = K_c(RT)^{\Delta n}$$
$$K_c = \frac{K}{(RT)^{\Delta n}} = \frac{3.9 \times 10^{-2}}{[(0.08314)(1000.)]^{-1}} = 3.24246 = \mathbf{3.2}$$
b) Δn = moles gaseous products – moles gaseous reactants = $1 - 1 = 0$
$$K_c = \frac{K}{(RT)^{\Delta n}} = \frac{28.5}{[(0.08314)(500.)]^{0}} = \mathbf{28.5}$$

15.31   Plan: First, determine Δn for the reaction and then calculate K using $K = K_c(RT)^{\Delta n}$.
Solution:
a) Δn = moles gaseous products – moles gaseous reactants = $2 - 1 = 1$
$$K = K_c(RT)^{\Delta n} = (6.1 \times 10^{-3})[(0.08314)(298)]^1 = 0.15113 = \mathbf{0.15}$$
b) Δn = moles gaseous products – moles gaseous reactants = $2 - 4 = -2$
$$K = K_c(RT)^{\Delta n} = (2.4 \times 10^{-3})[(0.08314)(1000.)]^{-2} = 3.4721 \times 10^{-7} = \mathbf{3.5 \times 10^{-7}}$$

15.33   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).

15.35   Plan: To decide if the reaction is at equilibrium, calculate Q and compare it to K. If $Q = K$, then the reaction is at equilibrium. If $Q > K$, then the reaction proceeds to the left to produce more reactants. If $Q < K$, then the reaction proceeds to the right to produce more products.
Solution:

$$Q = \frac{p_{H_2} p_{Br_2}}{p_{HBr}^2} = \frac{(0.010)(0.010)}{(0.20)^2} = 2.5 \times 10^{-3} > K = 4.18 \times 10^{-9}$$

$Q > K$, 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 will decrease until $Q = K$.

15.38   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.

15.40   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 [reactant]$_{initial}$ is very small, or when [reactant]$_{change}$ is relatively large due to a large K.

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

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left[1.87 \times 10^{-3}\right]^2}{\left[6.50 \times 10^{-5}\right]\left[1.06 \times 10^{-3}\right]} = 50.753 = \mathbf{50.8}$$

15.43   Plan: Calculate the initial concentration of PCl_5 from the given amount (mol) 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 mol/L
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*)	$PCl_5(g)$	⇌	$PCl_3(g)$	+	$Cl_2(g)$
Initial	0.075		0		0
Change	–x		+x		+x
Equilibrium	0.075 – x		x		x

15.45   <u>Plan</u>: Two of the three equilibrium pressures are known, as is K. Construct an equilibrium expression and solve
for p_{NOCl}.
<u>Solution</u>:

$$K = 6.5 \times 10^4 \ = \ \frac{p_{NOCl}^2}{p_{NO}^2 \, p_{Cl_2}}$$

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

$$P_{NOCl} \ = \ \sqrt{(6.5 \times 10^4)(0.35)^2 (0.10)} \ = 28.2179 \text{ bar} = \textbf{28 bar}$$

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

15.47   <u>Plan</u>: Use the balanced equation to write an equilibrium expression and to define x. Set up a reaction table,
substitute into the K expression, and solve for x.
<u>Solution</u>:

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

x = [NH₄HS] reacting (–x), and the amount of H₂S and of NH₃ forming (+x) since there is a 1:1:1 mole
ratio between the reactant and products.
(It is not necessary to include the NH₄HS as it is a solid with activity=1).

Pressure (bar)	NH₄HS(s)	$\square$	H₂S(g)	+	NH₃(g)
Initial	—		0		0
Change	—		+x		+x
Equilibrium	—		x		x

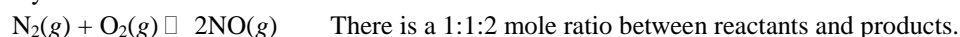$$K = 0.11 = (p_{H_2S})(p_{NH_3}) \qquad \text{(The solid NH}_4\text{HS is not included.)}$$
$$0.11 = (x)(x)$$
$$x = \ p_{NH_3} \ = \ 0.33166 = \textbf{0.33 bar}$$

15.49   <u>Plan</u>: 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.
<u>Solution</u>:
The initial concentrations of N₂ and O₂ are (0.20 mol/1.0 L) = 0.20 mol/L and (0.15 mol/1.0 L) = 0.15 mol/L,
respectively.

$$N_2(g) + O_2(g) \ \square \ 2NO(g) \qquad \text{There is a 1:1:2 mole ratio between reactants and products.}$$

Concentration (mol/L)	N₂(g)	+	O₂(g)	$\square$	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	

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

Assume $0.20 \text{ mol/L} - x \approx 0.20 \text{ mol/L}$ and $0.15 \text{ mol/L} - x \approx 0.15 \text{ mol/L}$

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

x = 1.753568×10⁻³ mol/L
[NO] = 2x = 2(1.753568×10⁻³ mol/L) = 3.507136×10⁻³ mol/L= **3.5×10⁻³ mol/L**
(Since (1.8×10⁻³)/(0.15) < 0.05, the assumption is OK.)

15.51   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 mol/L
        $[H_2]$ = (0.00623 mol)/(1.50 L) = 0.0041533 mol/L
        $[I_2]$ = (0.00414 mol)/(1.50 L) = 0.00276 mol/L
Equilibrium concentration of H_2 is greater than the initial, so the reaction moves in the forward direction.
2 HI(g) ⇌ $H_2(g)$ + $I_2(g)$ There is a 2:1:1 mole ratio between reactants and products.

Concentration (mol/L)	2 HI(g)	⇌	$H_2(g)$	+	$I_2(g)$	
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 mol/L
$[I_2]_{eq}$ = 0.00276 + x = 0.00276 + 0.0005167 = 0.0032767 mol/L= **0.00328 mol/L I_2**
$[HI]_{eq}$ = 0.0162667 – 2x = 0.0162667 – 2(0.0005167) = 0.0152333 mol/L= **0.0152 mol/L HI**

15.53   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 mol/L

Concentration (mol/L)	2ICl(g)	⇌	$I_2(g)$	+	$Cl_2(g)$
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 mol/L= **0.0200 mol/L**
$[ICl]_{eq}$ = 0.100 – 2x = 0.100 – 2(0.0199397) = 0.0601206 mol/L= **0.060 mol/L ICl**

15.55   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:
$4NH_3(g) + 3O_2(g) ⇌ 2N_2(g) + 6H_2O(g)$
Initial $[NH_3]$ = Initial $[O_2]$ = (0.0150 mol)/(1.00 L) = 0.0150 mol/L

| Concentration (mol/L) | 4NH₃(g) | + | 3O₂(g) | ⇌ | 2N₂(g) | + | 6H₂O(g) |

Concentration (mol/L)	$4NH_3(g)$	+	$3O_2(g)$	⇌	$2N_2(g)$	+	$6H_2O(g)$
Initial	0.0150		0.0150		0		0
Change	–4x		–3x		+2x		+6x
Equilibrium	0.0150 – 4		0.0150 – 3x		+2x		+6x

$[N_2]_{eq} = 2x = 1.96\text{x}10^{-3}$ mol/L

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

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

$[NH_3]_{eq} = 0.0150 – 4x = 0.0150 – 4(9.80\text{x}10^{-4}) = 1.1080\text{x}10^{-2}$ mol/L

$[O_2]_{eq} = 0.0150 – 3x = 0.0150 – 3(9.80\text{x}10^{-4}) = 1.2060\text{x}10^{-2}$ mol/L

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

15.58   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.

15.59   A positive $\Delta_r H$ indicates that the reaction is endothermic, and that heat is consumed in the reaction:
$NH_4Cl(s) + \mathbf{heat} \rightleftharpoons NH_3(g) + HCl(g)$
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.

15.63   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.

15.65   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 F₂** (one mole of gas) is present as the reaction shifts towards the right.
b) **More C₂H₂ and H₂** form (four moles of gas) and **less CH₄** (two moles of gas) is present as the reaction shifts towards the right.

15.67   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 a smaller amount (mol) 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 amount (mol) of reactant and product gas , 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 a smaller amount (mol) 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.

15.69   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 a larger amount (mol) of gas, while decreasing the container volume results in a shift in the direction that forms a smaller amount (mol) of gas.
Solution:
a) Because the amount (mol) of reactant gas ($4H_2$) equals the amount (mol) of product gas ($4H_2O$), 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.

15.71   Plan: An increase in temperature (addition of heat) causes a shift in the equilibrium <u>away</u> from the side of the reaction with heat. Recall that a negative value of $\Delta_r H°$ indicates an exothermic reaction, while a positive value of $\Delta_r H°$ indicates an endothermic reaction.
Solution:
a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) + heat$ $\Delta_r H° = –90.7$ kJ/mol
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) $C(s) + H_2O(g) + heat \rightleftharpoons CO(g) + H_2(g)$ $\Delta_r H° = 131$ kJ/mol
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) $2NO_2(g) + heat \rightleftharpoons 2NO(g) + O_2(g)$
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) $2C(s) + O_2(g) \rightleftharpoons 2CO(g) + heat$
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**.

15.73   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.
Solution:

$K_{298} = K_1 = 1.80$ $T_1 = 298$ K
$K_{500} = K_2 = ?$ $T_2 = 500.$ K $R = 8.314$ J/mol•K

$$\Delta_r H° = \left(\frac{0.32 \text{ kJ}}{1 \text{ mol DH}} \right)(2 \text{ DH})\left(\frac{10^3 \text{ J}}{1 \text{ kJ}} \right) = 6.4 \times 10^2 \text{ J/mol}$$

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

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

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

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

15.76 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 a larger amount (mol) of gas, while decreasing the container volume (pressure increases) results in a shift in the direction that forms a smaller amount (mol) of gas. Adding a reactant causes a shift in the direction of products.
Solution:
a) $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g) + $ heat
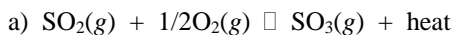
The forward reaction is exothermic ($\Delta_r H°$ is negative), so it is favored by **lower temperatures**. Lower temperatures will cause a shift to the right, the heat side of the reaction. The amount (mol) of gas as products ($1SO_3$) is smaller than as reactants ($1SO_2(g) + 1/2O_2$), so products are favored by **higher pressure**. High pressure will cause a shift in equilibrium to the side with the smaller amount (mol) of gas.

b) Addition of O_2 would **decrease Q** since $Q = \dfrac{p_{SO_3}}{p_{SO_2} \, p_{O_2}^{1/2}}$, 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**.

15.78 a) $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ The mole ratio $H_2:N_2 = 3:1$; at equilibrium, if $N_2 = x$, $H_2 = 3x$;
$p_{NH_3} = 50.$ bar

$$K = \frac{\left(p_{NH_3}\right)^2}{\left(p_{N_2}\right)\left(p_{H_2}\right)^3} = 1.00\times10^{-4}$$

$$K = \frac{\left(50.\right)^2}{\left(x\right)\left(3x\right)^3} = 1.00\times10^{-4}$$

x = 31.02016 = **31 bar N_2**
3x = 3(31.02016) = 93.06049 = **93 bar H_2**
$p_{total} = p_{nitrogen} + p_{hydrogen} + p_{ammonia} = $ (31.02016 bar) + (93.06049 bar) + (50. bar)
= 174.08065 bar= **174 bar total**

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

$$K = \frac{\left(50.\right)^2}{\left(x\right)\left(6x\right)^3} = 1.00\times10^{-4}$$

x = 18.445 = **18 bar N_2**
6x = 6(18.445) = 110.67 = **111 bar H_2**
$p_{total} = p_{nitrogen} + p_{hydrogen} + p_{ammonia} = $ (18.445 bar) + (110.67 bar) + (50. bar)
= 179.115 bar= **179 bar 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.

15.81   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 (mol/L)	NH$_2$COONH$_4$(s)	⇌	2NH$_3$(g)	+	CO$_2$(g)
Initial	7.80 g		0		0
Change	—		+2x		+x
Equilibrium	—		2x		x

The solid has an activity of 1 and, as long as some is present, is not included in the K_c expression.

$K_c = [NH_3]^2[CO_2]$
$K_c = 1.58 \times 10^{-8} = (2x)^2(x)$
$x = 1.580759 \times 10^{-3}$ mol/L
Total concentration of gases = 2x + x = 2(1.580759$\times 10^{-3}$ mol/L) + 1.580759$\times 10^{-3}$ mol/L = 4.742277$\times 10^{-3}$ mol/L
To find total pressure use the ideal gas equation: $PV = nRT$

$$p = \frac{nRT}{V} = \left(\frac{n}{V}\right)RT = cRT$$

$P = (4.742277 \times 10^{-3}$ mol/L)(0.08314 L•bar/mol•K)(273 + 250.)K = 0.206205 bar = **0.206 bar**

15.84   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 and use the equilibrium pressures of C$_2$H$_5$OH and H$_2$O to obtain the equilibrium pressure of C$_2$H$_4$. 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) $K = K_c(RT)^{\Delta n}$
Δn = amount (mol) gaseous products – amount (mol) gaseous reactants = 1 – 2 = –1 (one mol of product, C$_2$H$_5$OH, and two mol of reactants, C$_2$H$_4$ + H$_2$O)
$K = K_c(RT)^{-1} = (9 \times 10^3)[(0.08314$ L•bar/mol•K)(600. K)]$^{-1}$ = 1.8042$\times 10^2$
Substitute the given values into the equilibrium expression and solve for $p_{C_2H_4}$.

$$K = \frac{p_{C_2H_5OH}}{p_{C_2H_4}\, p_{H_2O}} = \frac{200.}{p_{C_2H_4}\,(400.)} = 1.8042 \times 10^2$$

$$p_{C_2H_4} = 2.7713 \times 10^{-3} = \textbf{3} \times \textbf{10}^{-3}\ \textbf{bar}$$

b) Since $\Delta_r H°$ 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 amount (mol) of gas and is favored by **high pressure**.

c) $K_1 = 9 \times 10^3$ $T_1 = 600.$ K $\Delta_r H° = (-47.8$ kJ/mol$)\left(\dfrac{10^3\ J}{1\ kJ}\right) = -4.78 \times 10^4$ J/mol

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

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

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

$$\ln \frac{K_2}{9\times10^3} = 3.1940769$$

$$\frac{K_2}{9\times10^3} = 24.38765$$

$$K_2 = (9\times10^3)(24.38765) = 2.1949\times10^5 = \mathbf{2\times10^5}$$

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 amount (mol) of gas.

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

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

$$K = K_c(RT)^{\Delta n} = K_c(RT)^{-1} = (1.7\times10^8)[(0.08314 \text{ L•bar/mol•K})(600.\text{ K})]^{-1} = 3.4079\times10^6$$

$$K = \frac{p_{SO_3}^2}{p_{SO_2}^2\, p_{O_2}} = \frac{(300.)^2}{p_{SO_2}^2\,(100.)} = 3.4079\times10^6$$

$$p_{SO_2} = 0.016251 = \mathbf{0.016\ bar}$$

b) Create a reaction table that describes the reaction conditions. Since the volume is 1.0 L, the amount (mol) equals the concentration (mol/L). Note the 2:1:2 mole ratio between $SO_2:O_2:SO_3$.

Concentration (mol/L)	$2SO_2(g)$	+	$O_2(g)$	⇌	$2SO_3(g)$	
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:
$[SO_2] = 0.0040 – 2x = 0.0040 – 2(0.0010) = 0.0020$ mol/L
$[O_2] = 0.0028 – x = 0.0028 – 0.0010 = 0.0018$ mol/L
$[SO_3] = 2(0.0010) = 0.0020$ mol/L
Substitute equilibrium concentrations into the equilibrium expression and solve for K_c.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.0020)^2}{(0.0020)^2(0.0018)} = 555.5556 = \mathbf{5.6\times10^2}$$

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).

$$pV = nRT$$

$$p_{SO_2} = \frac{nRT}{V} = \frac{(0.0020 \text{ mol})\left(0.08314\dfrac{\text{L•bar}}{\text{mol•K}}\right)(1000.\text{ K})}{(1.0 \text{ L})} = 0.1663 = \mathbf{0.17\ bar}$$

15.89   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 $CO_2 = p_{CO_2} = 0.220$ bar.

	$CaCO_3(s)$	$\rightleftharpoons$	$CaO(s)$	$+$	$CO_2(g)$
Initial	0.100 mol		0.100 mol		0
Change	$-x$		$-x$		$+x$
Equilibrium	$0.100 - x$		$0.100 - x$		$x = 0.220$ bar (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 bar of carbon dioxide. The amount (mol) of $CaCO_3$ reacted is equal to the amount (mol) of carbon dioxide produced. Use the pressure of CO_2 and the ideal gas equation to calculate the amount (mol) of CO_2 produced:
$$pV = nRT$$

Amount (mol) of $CO_2 = n = \dfrac{pV}{RT}$

$$n = \frac{(0.220 \text{ bar})(10.0 \text{ L})}{\left(0.08314 \dfrac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}\right)(385 \text{ K})} = 0.068731 \text{ mol } CO_2$$

Amount (mol) of $CaCO_3$ reacted = amount (mol) of CO_2 produced = 0.068731 mol
Amount (mol) of $CaCO_3$ remaining = initial amount (mol) amount (mol) reacted = 0.100 mol $CaCO_3$ – 0.068731 mol $CaCO_3$

$$= 0.0313 \text{ mol } CaCO_3 \text{ at first equilibrium}$$

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 bar (K). Convert the added 0.300 bar of CO_2 to moles using the ideal gas equation. The amount (mol) of CO_2 reacted equals the amount (mol) of $CaCO_3$ formed.

Amount (mol) of $CO_2 = n = \dfrac{pV}{RT}$

$$n = \frac{(0.300 \text{ bar})(10.0 \text{ L})}{\left(0.08314 \dfrac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}\right)(385 \text{ K})} = 0.09372 \text{ mol } CO_2$$

Amount (mol) of $CaCO_3$ produced = amount (mol) of CO_2 reacted = 0.09372 mol $CaCO_3$
Add the amount (mol) of $CaCO_3$ formed in the second equilibrium to the amount (mol) of $CaCO_3$ at the first equilibrium position.
Amount (mol) of $CaCO_3$ = amount (mol) at first equilibrium + amount (mol) formed in second equilibrium

$$= 0.0313 \text{ mol} + 0.09372 = 0.12502 \text{mol } CaCO_3$$

Mass (g) of $CaCO_3 = \left(0.12502 \text{ mol } CaCO_3\right)\left(\dfrac{100.09 \text{ g } CaCO_3}{1 \text{ mol } CaCO_3}\right) = 12.514 = \textbf{12.5 g } \textbf{CaCO}_3$

15.93   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:
$S_2F_{10}(g) \rightleftharpoons SF_4(g) + SF_6(g)$
The reaction is described by the following equilibrium expression:

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

At the first equilibrium, $[S_2F_{10}] = 0.50$ mol/L 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, $[S_2F_{10}] = 2.5$ mol/L 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:

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

15.95   <u>Plan:</u> 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.
<u>Solution:</u>
a) Calculate the partial pressures of oxygen and carbon dioxide because volumes are proportional to the amount (mol) 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 $V_{CO_2} + V_{O_2} + V_{N_2} = 10.0 + 1.00 + 50.0 = 61.0$.

$$p_{CO_2} = \left(\frac{10.0 \text{ mol CO}_2}{61.0 \text{ mol gas}}\right)(4.0 \text{ bar}) = 0.6557377 \text{ bar}$$

$$p_{O_2} = \left(\frac{1.00 \text{ mol O}_2}{61.0 \text{ mol gas}}\right)(4.0 \text{ bar}) = 0.06557377 \text{ bar}$$

Use the partial pressures and given K to find p_{CO}.
$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

$$K = \frac{p_{CO}^2 \, p_{O_2}}{p_{CO_2}^2} = \frac{p_{CO}^2 \,(0.06557377)}{(0.6557377)^2} = 1.4 \times 10^{-28}$$

$$p_{CO} = 3.0299 \times 10^{-14} = \mathbf{3.0 \times 10^{-14} \text{ bar}}$$

b) $pV = nRT$

$$\frac{n_{CO}}{V} = \frac{p}{RT} = \frac{\left(3.0299 \times 10^{-14} \text{ bar}\right)}{\left(0.08314 \dfrac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}}\right)(800 \text{ K})} = 4.55542 \times 10^{-16} \text{ mol/L}$$

$$\text{Concentration (pg/L) of CO} = \left(\frac{4.55572 \times 10^{-16} \text{ mol CO}}{\text{L}}\right)\left(\frac{28.01 \text{ g CO}}{1 \text{ mol CO}}\right)\left(\frac{1 \text{ pg}}{10^{-12} \text{ g}}\right) = 0.01276 \text{ pg/L} = \mathbf{0.013 \text{ pg}}$$

CO/L

15.97   <u>Plan:</u> Write a reaction table given that p_{CH_4} (init) $= p_{CO_2}$ (init) $= 10.0$ bar, substitute equilibrium values into the equilibrium expression, and solve for p_{H_2}.

<u>Solution:</u>
a)
Pressure (bar)	$CH_4(g)$	$+$	$CO_2(g)$	$\rightleftharpoons$	$2CO(g)$	$+$	$2H_2(g)$
Initial	10.0		10.0		0		0
Change	$-x$		$-x$		$+2x$		$+2x$
Equilibrium	$10.0 - x$		$10.0 - x$		$2x$		$2x$

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

15-14

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

A quadratic is necessary:

$4x^2 + (1.8836135 \times 10^3 \, x) - 1.8836135 \times 10^4 = 0$

$a = 4 \quad b = 1.8836135 \times 10^3 \quad c = -1.8836135 \times 10^4$

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

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

$x = 9.796209$

$p_{H_2} = 2x = 2(9.796209) = 19.592419$ bar

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

The percent yield is $\dfrac{19.592418 \text{ bar}}{20.0 \text{ bar}}(100\%) = 97.96209 \% = \textbf{98.0\%}$.

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

$$K = \frac{p_{CO}^2 \, p_{H_2}^2}{p_{CH_4} \, p_{CO_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 2.626 \times 10^7$$

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

A quadratic is needed:

$4x^2 + (5.124451 \times 10^3 \, x) - 5.124451 \times 10^4 = 0$

$a = 4 \qquad b = 5.124451 \times 10^3 \qquad c = -5.124451 \times 10^4$

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

$x = 9.923144$

$p_{H_2} = 2x = 2(9.923144) = 19.84629$ bar

If the reaction proceeded entirely to completion, the partial pressure of H_2 would be 20.0 bar (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 $\dfrac{19.84629 \text{ bar}}{20.0 \text{ bar}}(100\%) = 99.23145 \% = \textbf{99.0\%}$.

c) van't Hoff equation:

$K_1 = 3.548 \times 10^6 \qquad\qquad T_1 = 1200. \text{ K} \qquad \Delta_r H^\circ = ?$

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

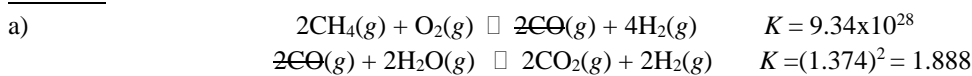$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{2.626 \times 10^7}{3.548 \times 10^6} = -\frac{\Delta_r H^\circ}{\left(8.314 \dfrac{\text{J}}{\text{mol·K}}\right)}\left(\frac{1}{1200. \text{ K}} - \frac{1}{1300. \text{ K}}\right)$$

$2.0016628 = \Delta_r H^\circ \, (7.710195 \times 10^{-6}) \text{mol/J}$

$\Delta_r H^\circ = 2.0016628/(7.710195 \times 10^{-6} \text{ mol/J}) = 2.5961247 \times 10^5 \text{ J/mol} = \textbf{2.60} \times \textbf{10}^5 \textbf{ J/mol}$

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

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

Solution:

a) $\qquad$ $2CH_4(g) + O_2(g) \rightleftharpoons 2\cancel{CO}(g) + 4H_2(g)$ $\qquad$ $K = 9.34 \times 10^{28}$

$\qquad$ $\underline{2\cancel{CO}(g) + 2H_2O(g) \rightleftharpoons 2CO_2(g) + 2H_2(g)}$ $\qquad$ $K = (1.374)^2 = 1.888$

$$\mathbf{2CH_4(g) + O_2(g) + 2H_2O(g) \rightleftharpoons 2CO_2(g) + 6H_2(g)}$$

b) $K = (9.34 \times 10^{28})(1.888) = 1.76339 \times 10^{29} = \mathbf{1.76 \times 10^{29}}$

c) Δn = amount (mol) of gaseous products – amount (mol) of gaseous reactants = $8 - 5 = 3$

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

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

$$K_c = \frac{K}{(RT)^{\Delta n}} = \frac{1.76339 \times 10^{29}}{[(0.08314 \text{ bar} \cdot \text{L/mol} \cdot \text{K})(1000)]^3} = 3.01713 \times 10^{23} = \mathbf{3.02 \times 10^{23}}$$

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

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

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

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

15.100 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 to K. Convert pressures to amount (mol) using the ideal gas law, $pV = nRT$. Convert amount (mol) to atoms using Avogadro's number.

Solution:

a) The initial pressure of N_2 is 200. bar. $\qquad$ log K = –43.10; $\qquad$ $K = 10^{-43.10} = 7.94328 \times 10^{-44}$

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

$$K = \frac{(p_N)^2}{(p_{N_2})} = 7.94328 \times 10^{-44}$$

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

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

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

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

$$p_N = 2x = 2(1.992897 \times 10^{-21}) = 3.985795 \times 10^{-21} = \mathbf{4.0 \times 10^{-21} \text{ bar}}$$

b) Log K = –17.30; $\qquad$ $K = 10^{-17.30} = 5.01187 \times 10^{-18}$

Pressure (bar)	$H_2(g)$	$\rightleftharpoons$	$2H(g)$
Initial	600.		0
Change	–x		+2x
Equilibrium	600 – x		2x

$$K = \frac{(p_H)^2}{(p_{H_2})} = 5.01187 \times 10^{-18}$$

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

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

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

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

$p_H = 2x = 2(2.741862\text{x}10^{-8}) = 5.48372\text{x}10^{-8} = \textbf{5.5x10}^{-8}\textbf{ bar}$

c) $pV = nRT$

$$\text{Moles of N atoms} = \frac{pV}{RT} = \frac{\left(3.985795\text{x}10^{-21}\,\text{bar}\right)(1.00\text{ L})}{\left(0.08314\dfrac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}\right)(1000.\text{K})} = 4.794076\text{x}10^{-23}\text{ mol}$$

$$\text{Number of N atoms} = \left(4.794076\text{x}10^{-23}\text{ mol N atoms}\right)\left(\frac{6.022\text{x}10^{23}\text{ N atoms}}{1\text{ mol N atoms}}\right) = 28.8699\text{ atoms/L} = \textbf{29 N}$$

atoms/L

$$\text{Moles of H atoms} = \frac{pV}{RT} = \frac{\left(5.48372\text{x}10^{-8}\,\text{bar}\right)(1.00\text{ L})}{\left(0.08314\dfrac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}\right)(1000.\text{K})} = 6.595766\text{x}10^{-10}\text{ mol}$$

$$\text{Number of H atoms} = \left(6.595766\text{x}10^{-10}\text{ mol H atoms}\right)\left(\frac{6.022\text{x}10^{23}\text{ H atoms}}{1\text{ mol H atoms}}\right)$$

$$= 3.97197\text{x}10^{14} = \textbf{4.0x10}^{14}\textbf{ H atoms/L}$$

d) The more reasonable step is $\textbf{N}_2(g) + \textbf{H}(g) \rightarrow \textbf{NH}(g) + \textbf{N}(g).$ 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.

15.103 <u>Plan:</u> 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 $K = K_c(RT)^{\Delta n}$ to find K_c.
<u>Solution:</u>

a)

Pressure (bar)	$N_2(g)$	+	$O_2(g)$	⇌	$2NO(g)$
Initial	0.780		0.210		0
Change	−x		−x		+2x
Equilibrium	0.780 − x		0.210 − x		2x

$$K = \frac{\left(p_{NO}\right)^2}{\left(p_{N_2}\right)\left(p_{O_2}\right)} = 4.35\text{x}10^{-31}$$

$$\frac{(2x)^2}{(0.780 - x)(0.210 - x)} = 4.35\text{x}10^{-31} \text{ Assume x is small because } K \text{ is small.}$$

$$\frac{(2x)^2}{(0.780)(0.210)} = 4.35\text{x}10^{-31}$$

$x = 1.33466\text{x}10^{-16}$

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) bar = **0.780 bar N₂**

p_{oxygen} (equilibrium) = (0.210 − 1.33466x10⁻¹⁶) bar = **0.210 bar O₂** (assumption justified)

p_{NO} (equilibrium) = 2(1.33466x10⁻¹⁶) bar = 2.66933x10⁻¹⁶ = **2.67x10⁻¹⁶ bar NO**

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

$$0.780 \text{ bar} + 0.210 \text{ bar} + 2.67 \times 10^{-16} \text{ bar} = \textbf{0.990 bar}$$

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

Δn = amount (mol) of gaseous products – amount (mol) of gaseous reactants = 2 – 2 = 0

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

$K = K_c(RT)^0$

$K_c = K = \textbf{4.35} \times \textbf{10}^{-31}$ because there is no net increase or decrease in the amount (mol) of gas in the course of the reaction.

15.105   Plan: Use the equation $K = K_c(RT)^{\Delta n}$ to find K. 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 $\Delta_r H^\circ = \Sigma[\Delta_{f(products)} H^\circ] - \Sigma[\Delta_{f(reactants)} H^\circ]$ to find the value of $\Delta_r H^\circ$. Use the van't Hoff equation as a second method of calculating $\Delta_r H^\circ$.

Solution:

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

Δn = amount (mol) of gaseous products – amount (mol) of gaseous reactants = 2 – 2 = 0

(2 mol product $(1H_2 + 1I_2)$ – 2 mol reactant (HI) = 0)

$K = K_c(RT)^0 = 1.26 \times 10^{-3}(RT)^0 = \textbf{1.26} \times \textbf{10}^{-3}$

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

$$K_{formation} = \frac{1}{K_{decomposition}} = \frac{1}{1.26 \times 10^{-3}} = 793.65 = \textbf{794}$$

c) $\Delta_r H^\circ = \Sigma[\Delta_{f(products)} H^\circ] - \Sigma[\Delta_{f(reactants)} H^\circ]$

$\Delta_r H^\circ = \{1 \Delta_f H^\circ [H_2(g)] + 1 \Delta_f H^\circ [I_2(g)]\} - \{2 \Delta_f H^\circ [HI(g)]\}$

$\Delta_r H^\circ = [(0 \text{ kJ/mol}) + (62.442 \text{ kJ/mol})] - [(2)(25.9 \text{ kJ/mol})]$

$\Delta_r H^\circ = \textbf{10.6 kJ/mol}$

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

$K_1 = 1.26 \times 10^{-3}$; $K_2 = 2.0 \times 10^{-2}$, $T_1 = 298 \text{ K}$; $T_2 = 729 \text{ K}$

$\ln \dfrac{2.0 \times 10^{-2}}{1.26 \times 10^{-3}} = -\dfrac{\Delta_r H^\circ}{8.314 \text{ J/mol•K}}\left(\dfrac{1}{729 \text{ K}} - \dfrac{1}{298 \text{ K}}\right)$

$2.764621 = (2.38629 \times 10^{-4} \text{ mol/J})\, \Delta_r H^\circ$

$\Delta_r H^\circ = 1.1585 \times 10^4 \text{ J/mol} = \textbf{1.2} \times \textbf{10}^4 \textbf{ J/mol}$

15.109   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 $(c)(V)$ to find the total amount (mol), 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: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

a) Initial [CO] and initial $[H_2O]$ = 0.100 mol/20.00 L = 0.00500 mol/L.

concentrations	CO	H₂O	⇌	CO₂	H₂
Initial	0.00500 mol/L	0.00500 mol/L		0	0
Change	–x	–x		+x	+x
Equilibrium	0.00500 – x	0.00500 – x		x	x

$[CO]_{equilibrium} = 0.00500 - x = 2.24 \times 10^{-3} \text{ mol/L} = [H_2O]$ (given in problem)

x = 0.00276 mol/L = $[CO_2]$ = $[H_2]$

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.00276)(0.00276)}{(0.00224)(0.00224)} = 1.518176 = \mathbf{1.52}$$

b) c_{total} = [CO] + [H_2O] + [CO_2] + [H_2] = (0.00224 mol/L) + (0.00224 mol/L) + (0.00276 mol/L) + (0.00276 mol/L)

= 0.01000 mol/L

n_{total} = (c_{total})(V) = (0.01000 mol/L)(20.00 L) = 0.2000 mol total

$pV = nRT$

$$p_{total} = n_{total}RT/V = \frac{(0.2000\,\text{mol})\left(0.08314\,\frac{\text{L•bar}}{\text{mol•K}}\right)\left((273 + 900.)\text{K}\right)}{(20.00\ \text{L})} = 0.9752322\ \text{bar} = \mathbf{0.975\ bar}$$

c) Initially, an equal amount (mol) 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 mol/L to compensate for the added CO.

	CO	H_2O	CO_2	H_2
Initial	0.00224 mol/L	0.00224 mol/L	0.00276 mol/L	0.00276 mol/L
Added CO	0.01000 mol/L			
Change	–x	–x	+x	+x
Equilibrium	0.01224 – x	0.00224 – x	0.00276 + x	0.00276 + x

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.00276 + x)(0.00276 + x)}{(0.00224 - x)(0.00224 - x)} = 1.518176$$

$$\frac{7.6176 \times 10^{-6} + 5.52 \times 10^{-3}\,x\ + x^2}{2.74176 \times 10^{-5} - 1.448 \times 10^{-2}\,x + x^2} = 1.518176$$

$7.6176 \times 10^{-6} + 5.52 \times 10^{-3}x + x^2 = (1.518176)(2.74176 \times 10^{-5} - 1.448 \times 10^{-2}x + x^2)$

$7.6176 \times 10^{-6} + 5.52 \times 10^{-3}x + x^2 = 4.162474 \times 10^{-5} - 0.021983x + 1.518176x^2$

$0.518176x^2 - 0.027503x + 3.400714 \times 10^{-5} = 0$

$a = 0.518176 \quad b = -\,0.027503 \quad c = 3.400714 \times 10^{-5}$

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

$$x = \frac{-(-0.027503) \pm \sqrt{(-0.027503)^2 - 4(0.518176)(3.400714 \times 10^{-5})}}{2(0.518176)}$$

$x = 1.31277 \times 10^{-3}$

$[CO] = 0.01224 - x = 0.01224 - (1.31277 \times 10^{-3}) = 0.01092723 = \mathbf{0.01093\ mol/\ L}$