# CHAPTER 17 EQUILIBRIUM: THE EXTENT OF CHEMICAL REACTIONS

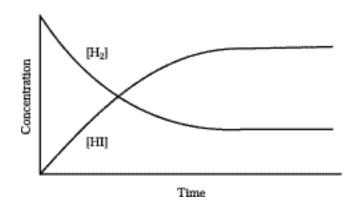
#### END-OF-CHAPTER PROBLEMS

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).

$$K_{\rm c} = \frac{[{\rm products}]}{[{\rm reactants}]}$$

- 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.  $K = \frac{[\text{products}]}{[\text{reactants}]}$
- 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.
- a) On the graph, the concentration of HI increases at twice the rate that H<sub>2</sub> decreases because the stoichiometric ratio in the balanced equation is 1H<sub>2</sub>: 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<sub>2</sub> and I<sub>2</sub> decrease and the concentration of product HI increases, which means that *Q* increases as a function of time.

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



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

$$Q_{\text{c(form)}} = \frac{\left[\text{NO}\right]}{\left[\text{N}_2\right]^{1/2} \left[\text{O}_2\right]^{1/2}}$$

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

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

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

17.11 Plan: Write the reaction and then the expression for Q. Remember that  $Q = \frac{\left[C\right]^{c}\left[D\right]^{d}}{\left[A\right]^{a}\left[B\right]^{b}}$  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:

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<sub>3</sub> is fixed at 1 mole according to the description. The reaction quotient for this

reaction is 
$$Q_1 = \frac{\left[\text{NH}_3\right]}{\left[\text{H}_2\right]^{\frac{3}{2}}\left[\text{N}_2\right]^{\frac{1}{2}}}$$
.

In the second reaction, the coefficient in front of N<sub>2</sub> is fixed at 1 mole.

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

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

 $Q_2$  is equal to  ${Q_1}^2$ .

17.12 Plan: Remember that  $Q_c = \frac{\left[C\right]^c \left[D\right]^d}{\left[A\right]^a \left[B\right]^b}$  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:

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

$$Q_{c} = \frac{\left[N_{2}O_{3}\right]^{2}}{\left[NO\right]^{4}\left[O_{2}\right]}$$

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

$$Q_{c} = \frac{\left[SO_{2}F_{2}\right]^{3}}{\left[SF_{6}\right]\left[SO_{3}\right]^{2}}$$

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

$$Q_{c} = \frac{\left[S_{2}F_{10}\right]\left[HCI\right]^{2}}{\left[SCIF_{5}\right]^{2}\left[H_{2}\right]}$$

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

$$Q_{c} = \frac{\left[\text{CO}_{2}\right]^{4} \left[\text{H}_{2}\text{O}\right]^{6}}{\left[\text{C}_{2}\text{H}_{6}\right]^{2} \left[\text{O}_{2}\right]^{7}}$$

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

$$Q_{c} = \frac{\left[\text{CF}_{4}\right]\left[\text{HF}\right]^{4}}{\left[\text{CH}_{4}\right]\left[\text{F}_{2}\right]^{4}}$$

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

$$Q_{c} = \frac{\left[SO_{2}\right]^{2} \left[O_{2}\right]}{\left[SO_{3}\right]^{2}}$$

- 17.14 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  $K_c = \frac{\left[H_2\right]^2 \left[S_2\right]}{\left[H_2S\right]^2}$

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.

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

$$K_{c (a)} = (1/1.6 \times 10^{-2})^{1/2} = 7.90569 = 7.9$$

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.

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

$$K_{c (b)} = (1.6x10^{-2})^{5/2} = 3.23817x10^{-5} = 3.2x10^{-5}$$

17.15 
$$K_{c} = \frac{[N_{2}][H_{2}O]^{2}}{[NO]^{2}[H_{2}]^{2}}$$

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

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

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

$$K_c = [K_c]^{-2} = (6.5 \times 10^2)^{-2} = 2.36686 \times 10^{-6} = 2.4 \times 10^{-6}$$

17.16 <u>Plan:</u> 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) 
$$2\text{Na}_2\text{O}_2(s) + 2\text{CO}_2(g) \leftrightarrows 2\text{Na}_2\text{CO}_3(s) + \text{O}_2(g)$$

$$Q_{c} = \frac{\left[O_{2}\right]}{\left[CO_{2}\right]^{2}}$$

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

$$Q_c = [NH_3][HCl]$$

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

$$Q_{c} = \frac{\left[ \mathbf{H}_{2} \mathbf{SO}_{4} \right]}{\left\lceil \mathbf{SO}_{3} \right\rceil}$$

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

$$Q_{\rm c} = [{\rm O}_2]$$

$$Q_{c} = [O_{2}]$$
  
c)  $S_{8}(s) + 24F_{2}(g) \leftrightarrows 8SF_{6}(g)$ 

$$Q_{c} = \frac{\left[SF_{6}\right]^{8}}{\left[F_{2}\right]^{24}}$$

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

a) 
$$4HCl(g) + O_2(g) \stackrel{\leftarrow}{\Rightarrow} 2Cl_2(g) + 2H_2O(g)$$

$$Q_{c} = \frac{\left[\text{Cl}_{2}\right]^{2} \left[\text{H}_{2}\text{O}\right]^{2}}{\left[\text{HCl}\right]^{4} \left[\text{O}_{2}\right]}$$

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

$$Q_{c} = \frac{\left[O_{2}\right]^{3}}{\left[F_{2}\right]^{10}}$$

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

$$Q_{c} = \frac{\left[SO_{2}\right]\left[HF\right]^{4}}{\left[SF_{4}\right]}$$

d)  $2\text{MoO}_3(s) + 6\text{XeF}_2(g) \leftrightarrows 2\text{MoF}_6(l) + 6\text{Xe}(g) + 3\text{O}_2(g)$ 

$$Q_{c} = \frac{\left[Xe\right]^{6} \left[O_{2}\right]^{3}}{\left[XeF_{2}\right]^{6}}$$

- 17.19 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.

$$Q_{1} = \frac{\left[\text{CIF}\right]^{2}}{\left[\text{Cl}_{2}\right]\left[\text{F}_{2}\right]}$$

$$Q_{1} = \frac{\left[\text{CIF}\right]^{2}}{\left[\text{Cl}_{2}\right]\left[\text{F}_{2}\right]}$$

$$Q_{2} = \frac{\left[\text{CIF}_{3}\right]^{2}}{\left[\text{CIF}\right]^{2}\left[\text{F}_{2}\right]^{2}}$$

$$Q_{2} = \frac{\left[\text{CIF}_{3}\right]^{2}}{\left[\text{CIF}\right]^{2}\left[\text{F}_{2}\right]^{2}}$$

$$Q_{2} = \frac{\left[\text{CIF}_{3}\right]^{2}}{\left[\text{CIF}\right]^{2}\left[\text{F}_{2}\right]^{2}}$$

$$Q_{2} = \frac{\left[\text{CIF}_{3}\right]^{2}}{\left[\text{CIF}\right]^{2}\left[\text{F}_{2}\right]^{2}}$$

$$Q_{2} = \frac{\left[\text{CIF}_{3}\right]^{2}}{\left[\text{CIF}\right]^{2}\left[\text{F}_{2}\right]^{3}}$$

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

$$Q_{\text{overall}} = \frac{\left[\text{ClF}_{3}\right]^{2}}{\left[\text{Cl}_{2}\right]\left[\text{F}_{2}\right]^{3}}$$

$$Q_{\text{overall}} = Q_{1}Q_{2}^{2} = \frac{\left[\text{ClF}\right]^{2}}{\left[\text{Cl}_{2}\right]\left[\text{F}_{2}\right]} \quad \text{x} \quad \frac{\left[\text{ClF}_{3}\right]^{2}}{\left[\text{ClF}\right]^{2}\left[\text{F}_{2}\right]^{2}} = \frac{\left[\text{ClF}_{3}\right]^{2}}{\left[\text{Cl}_{2}\right]\left[\text{F}_{2}\right]^{3}}$$

- 17.20 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.
- 17.21  $K_c$  and  $K_p$  are related by the equation  $K_p = K_c (RT)^{\Delta n}$ , where  $\Delta n$  represents the change in the number of moles of gas in the reaction (moles gaseous products moles gaseous reactants). When  $\Delta n$  is zero (no change in number of moles of gas), the term  $(RT)^{\Delta n}$  equals 1 and  $K_c = K_p$ . When  $\Delta n$  is not zero, meaning that there is a change in the number of moles of gas in the reaction, then  $K_c \neq K_p$ .
- 17.22 a)  $K_p = K_c(RT)^{\Delta n}$ . Since  $\Delta n =$  number of moles gaseous products number of moles gaseous reactants,  $\Delta n$  is a positive integer for this reaction. If  $\Delta n$  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.
- 17.23 Plan:  $\Delta n_{\text{gas}} = \text{moles gaseous products} \text{moles gaseous reactants.}$ Solution:
  - a) Number of moles of gaseous reactants = 0; number of moles of gaseous products = 3;  $\Delta n_{\rm gas} = 3 0 = 3$
  - b) Number of moles of gaseous reactants = 1; number of moles of gaseous products = 0;  $\Delta n_{\rm gas} = 0 1 = -1$
  - c) Number of moles of gaseous reactants = 0; number of moles of gaseous products = 3;  $\Delta n_{\rm gas} = 3 0 = 3$

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

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

a) 
$$\Delta n =$$
 moles gaseous products – moles gaseous reactants = 1 – 2 = –1  $K_p = K_c (RT)^{\Delta n}$ 

$$K_{\rm c} = \frac{K_{\rm p}}{(RT)^{\Delta n}} = \frac{3.9 \times 10^{-2}}{[(0.0821)(1000.)]^{-1}} = 3.2019 = 3.2$$

b)  $\Delta n =$  moles gaseous products – moles gaseous reactants = 1 – 1 = 0

$$K_{\rm c} = \frac{K_{\rm p}}{(RT)^{\Delta n}} = \frac{28.5}{[(0.0821)(500.)]^0} = 28.5$$

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

a)  $\Delta n = \text{moles gaseous products} - \text{moles gaseous reactants} = 2 - 2 = 0$ 

$$K_{\rm c} = \frac{K_{\rm p}}{(RT)^{\Delta n}} = \frac{49}{[(0.0821)(730.)]^0} = 49$$

b)  $\Delta n$  = moles gaseous products – moles gaseous reactants = 2 – 3 = –1

$$K_{\rm c} = \frac{K_{\rm p}}{(RT)^{\Delta n}} = \frac{2.5 \text{x} 10^{10}}{\left[ (0.0821)(500.) \right]^{-1}} = 1.02625 \text{x} 10^{12} = \mathbf{1.0x} \mathbf{10^{12}}$$

- 17.27 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).
- 17.28 a) The reaction is  $2D \leftrightarrow E$  and  $K_c = \frac{[E]}{[D]^2}$ .

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

$$K_{\rm c} = \frac{[\rm E]}{[\rm D]^2} = \frac{[0.0300]}{[0.0300]^2} = 33.3333 = 33.3$$

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

$$Q_{\rm c} = \frac{[\rm E]}{[\rm D]^2} = \frac{[0.0600]}{[0.0600]^2} = 16.66666 = 16.7$$

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

$$Q_{\rm c} = \frac{[\rm E]}{[\rm D]^2} = \frac{[0.120]}{[0.0600]^2} = 33.3333 = 33.3$$

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

17.29 Plan: 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:

$$Q_{\rm p} = \frac{{\rm P}_{\rm H_2} {\rm P}_{\rm Br_2}}{{\rm P}_{\rm HBr}^2} = \frac{(0.010)(0.010)}{{(0.20)}^2} = 2.5 {\rm x} 10^{-3} > K_{\rm p} = 4.18 {\rm x} 10^{-9}$$

 $Q_p > K_p$ , 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  $Q_p = K_p$ .

17.30 
$$Q_{\rm p} = \frac{P_{\rm NO}^2 P_{\rm Br_2}}{P_{\rm NOBr}^2} = \frac{(0.10)^2 (0.10)}{(0.10)^2} = 0.10 < K_{\rm p} = 60.6$$

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

17.31 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.

 $\Delta n$  = moles gaseous products – moles gaseous reactants = 2 – 2 = 0

Since  $\Delta n = 0$ ,  $K_p = K_c = 2.7$  (Note: If  $\Delta n$  had any other value, we could not finish the calculation without the temperature.)

$$Q_{c} = \frac{[\text{CO}_{2}][\text{H}_{2}]}{[\text{CO}][\text{H}_{2}\text{O}]} = \frac{[0.62/2.0][0.43/2.0]}{[0.13/2.0][0.56/2.0]} = 3.662 > K_{c} = 2.7$$

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

- 17.32 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.
- 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.
- 17.34 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:

$$K_{\rm c} = \frac{{\rm [HI]}^2}{{\rm [H_2][I_2]}} = \frac{{\rm [1.87x10^{-3}]}^2}{{\rm [6.50x10^{-5}][1.06x10^{-3}]}} = 50.753 =$$
**50.8**

17.35 
$$K_{c} = \frac{\left[N_{2}\right]\left[H_{2}\right]^{3}}{\left[NH_{3}\right]^{2}} = \frac{\left[0.114\right]\left[0.342\right]^{3}}{\left[0.0225\right]^{2}} = 9.0077875 = 9.01$$

17.36 <u>Plan:</u> Calculate the initial concentration of PCl<sub>5</sub> from the given number of moles and the container volume; the reaction is proceeding to the right, consuming PCl<sub>5</sub> and producing products. There is a 1:1:1 mole ratio between the reactants and products.

Solution:

Initial  $[PCl_5] = 0.15 \text{ mol}/2.0 \text{ L} = 0.075 \text{ M}$ 

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)	$PCl_5(g)$	≒	$PCl_3(g)$	+	$\operatorname{Cl}_2(g)$
Initial <u>Change</u>	0.075 -x		0 +x		0 +x
Equilibrium	0.075 - x		X		X

The reaction table requires that the initial  $[H_2]$  and  $[F_2]$  be calculated:  $[H_2] = 0.10 \text{ mol}/0.50 \text{ L} = 0.20 \text{ M}$ ;  $[F_2] = 0.050 \text{ mol}/0.50 \text{ L} = 0.10 \text{ M}$ .

$$x = [H_2] = [F_2] \text{ reacting } (-x); \ 2x = [HF] \text{ forming } (+2x)$$

Concentration  $(M)$   $H_2(g)$  +  $F_2(g)$   $\leftrightarrows$   $2HF(g)$ 

Initial  $0.20$   $0.10$   $0$ 

Change  $-x$   $-x$   $+2x$ 

Equilibrium  $0.20 - x$   $0.10 - x$   $2x$ 

17.38 Plan: Two of the three equilibrium pressures are known, as is  $K_p$ . Construct an equilibrium expression and solve for  $P_{\text{NOCI}}$ . Solution:

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

$$6.5 \times 10^4 = \frac{P_{\text{NOCI}}^2}{(0.35)^2 (0.10)}$$

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

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.

17.39 
$$C(s) + 2H_2(g) \leftrightarrows CH_4(g)$$
  

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

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

17.40 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.)

17.41 
$$2H_2S(g) \leftrightarrows 2H_2(g) + S_2(g)$$

$$[H_2S] = 0.45 \text{ mol/} 3.0 \text{ L} = 0.15 M$$

Concentration (M) 
$$2H_2S(g) \Rightarrow 2H_2(g) + S_2(g)$$
  
Initial  $0.15 \Rightarrow 0 \Rightarrow 0$   
Change  $-2x \Rightarrow +2x \Rightarrow +x$   
Equilibrium  $0.15-2x \Rightarrow 2x \Rightarrow x$ 

$$K_{c} = 9.30 \times 10^{-8} = \frac{\left[H_{2}\right]^{2} \left[S_{2}\right]}{\left[H_{2}S\right]^{2}} = \frac{\left[2 \times \right]^{2} \left[x\right]}{\left[0.15 - 2 \times \right]^{2}}$$

Assuming  $0.15 M - 2 x \approx 0.15 M$ 

$$9.30x10^{-8} = \frac{\left[2\,x\right]^2\left[x\right]}{\left[0.15\right]^2} = \frac{4\,x^3}{0.15^2}$$

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

$$[H_2] = 2x = 2 (8.0575x10^{-4} M) = 1.6115x10^{-3} = 1.6x10^{-3} M$$

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

17.42 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.

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

$$Concentration (M) \qquad N_2(g) \qquad + \qquad O_2(g) \qquad \leftrightarrows 2NO(g)$$
Initial 
$$0.20 \qquad 0.15 \qquad 0$$

$$Change \qquad -x \qquad -x \qquad +2x \qquad (1:1:2 \text{ mole ratio})$$
Equilibrium 
$$0.20 - x \qquad 0.15 - x \qquad 2x$$

$$K_c = 4.10x10^{-4} = \frac{\left[NO\right]^2}{\left[N_2\right]\left[O_2\right]} = \frac{\left[2x\right]^2}{\left[0.20 - x\right]\left[0.15 - x\right]}$$

$$Assume \quad 0.20 \ M - x \approx 0.20 \ M \qquad \text{and} \qquad 0.15 \ M - x \approx 0.15 \ M$$

$$4.10x10^{-4} = \frac{4x^2}{\left[0.20\right]\left[0.15\right]}$$

$$x = 1.753568x10^{-3} \ M$$

$$[NO] = 2x = 2(1.753568x10^{-3} \ M) = 3.507136x10^{-3} = 3.5x10^{-3} \ M$$

$$(Since (1.8x10^{-3})/(0.15) < 0.05, \text{ the assumption is OK.})$$

17.43 
$$2NO_2(g) \Rightarrow 2NO(g) + O_2(g)$$

Pressure (atm) 
$$2NO_2(g)$$
  $\Rightarrow$   $2NO(g)$  +  $O_2(g)$  Initial 0.75 0 0 0

Change  $-2x$   $+2x$   $+x$ 

Equilibrium 0.75 - 2x  $2x$   $x$ 

$$K_{\rm p} = 4.48 \times 10^{-13} = \frac{P_{\rm NO}^2 P_{\rm O_2}}{P_{\rm NO_2}^2} = \frac{(2x)^2 (x)}{(0.75 - 2x)^2}$$

Assume  $0.75 \text{ atm} - 2x \approx 0.75 \text{ atm}$ 

$$4.48x10^{-13} = \frac{\left(4x^2\right)\!\left(x\right)}{\left(0.75\right)^2} = \frac{\left(4x^3\right)}{\left(0.75\right)^2}$$

$$x = 3.979 \times 10^{-5} \text{ atm} = 4.0 \times 10^{-5} \text{ atm } O_2$$
  
 $P_{NO} = 2 \times 2 = 2(3.979 \times 10^{-5} \text{ atm}) = 7.958 \times 10^{-5} = 8.0 \times 10^{-5} \text{ atm NO}$ 

17.44 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:

$$0.110 = \frac{\left[x\right]^2}{\left[0.100 - 2x\right]^2}$$
 Take the square root of each side: 
$$0.331662 = \frac{\left[x\right]}{\left[0.100 - 2x\right]}$$
 
$$x = 0.0331662 - 0.663324x$$
 
$$1.663324x = 0.0331662$$
 
$$x = 0.0199397$$
 
$$[I_2]_{eq} = [CI_2]_{eq} = x = 0.0199397 = \textbf{0.0199} \textbf{M}$$
 
$$[ICI]_{eq} = 0.100 - 2x = 0.100 - 2(0.0199397) = 0.0601206 = \textbf{0.0601} \textbf{M} \textbf{ICI}$$

17.45 Concentration (M) 
$$SCl_2(g) + 2C_2H_4(g) \Rightarrow S(CH_2CH_2Cl)_2(g)$$
Initial  $0.675 + 0.973 + 0$ 

$$\frac{Change}{Change} -x -2x +x$$
Equilibrium  $0.675 - x = 0.973 - 2x = x$ 

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

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

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

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

$$K_p = K_c(RT)^{\Delta n} \qquad \Delta n = 1 \text{ mol} - 3 \text{ mol} = -2$$

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

17.46 <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. The equilibrium concentration of N<sub>2</sub> 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:

$$[H_2O]_{eq} = 6x = 6(9.80x10^{-4}) = 5.8800x10^{-3} M$$
  
 $[NH_3]_{eq} = 0.0150 - 4x = 0.0150 - 4(9.80x10^{-4}) = 1.1080x10^{-2} M$   
 $[O_2]_{eq} = 0.0150 - 3x = 0.0150 - 3(9.80x10^{-4}) = 1.2060x10^{-2} M$ 

$$[O_2]_{eq} = 0.0150 - 3x = 0.0150 - 3(9.80x10^{-3}) = 1.2060x10^{-2}M$$

$$[N_2]^2 [H_2O]^6 = [1.96x10^{-3}]^2 [5.8800x10^{-3}]^6 = 6.005850x10^{-6} - 6.01x10^{-6}$$

$$K_{c} = \frac{\left[N_{2}\right]^{2} \left[H_{2}O\right]^{6}}{\left[NH_{3}\right]^{4} \left[O_{2}\right]^{3}} = \frac{\left[1.96 \times 10^{-3}\right]^{2} \left[5.8800 \times 10^{-3}\right]^{6}}{\left[1.1080 \times 10^{-2}\right]^{4} \left[1.2060 \times 10^{-2}\right]^{3}} = 6.005859 \times 10^{-6} = \mathbf{6.01 \times 10^{-6}}$$

17.47 Pressure (atm) FeO(s) + CO(g) 
$$\rightleftharpoons$$
 Fe(s) + CO<sub>2</sub>(g)
Initial - 1.00 - 0
Change -x +x
Equilibrium 1.00 - x

Proceedings: The second second

$$K_{\rm p} = \frac{P_{\rm CO_2}}{P_{\rm CO}} = 0.403 = \frac{\rm x}{1.00 - \rm x}$$

x = 0.28724 = 0.287 atm  $CO_2$ 

1.00 - x = 1.00 - 0.28724 = 0.71276 = 0.71 atm CO

- 17.48 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.
- 17.49 A positive  $\Delta H_{\text{rxn}}$  indicates that the reaction is endothermic, and that heat is consumed in the reaction:  $NH_4Cl(s) + \text{heat} + NH_3(g) + HCl(g)$ 
  - 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.
- 17.50 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.
- 17.51 a) Rate<sub>f</sub> =  $k_f$ [reactants]<sup>x</sup>. An increase in reactant concentration shifts the equilibrium to the right by increasing the initial forward rate. Since  $K = k_f/k_r$  and  $k_f$  and  $k_r$  are not changed by changes in concentration, K 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.
- 17.52 a) An exothermic reaction can be written as: reactants  $\Rightarrow$  products + heat. A rise in temperature (increase in heat) favors the reverse direction of the reaction, i.e., the formation of reactants and consumption of products. Since K = [products]/[reactants], the addition of heat increases the denominator and decreases the numerator, making  $K_2$  smaller than  $K_1$ . Since  $K = k_f/k_r$  and an increase in temperature increases  $k_r$  to a greater extent, the value of K is lower at the increased temperature.
  - b) 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  $K_1$ . For an endothermic reaction,  $k_f$  increases more than  $k_r$  with an increase in temperature and  $K_2 = k_f/k_r$  is larger than  $K_1$ .
- 17.53  $XY(s) \Rightarrow X(g) + Y(s)$  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.
- 17.54 <u>Plan:</u> 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<sub>2</sub>) 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<sub>2</sub>; dry ice is solid

carbon dioxide that sublimes to carbon dioxide gas. At very low temperatures, CO<sub>2</sub> solid will not sublime, but since the reaction lists carbon dioxide as a gas, the assumption that sublimation takes place is reasonable.

17.55 a) **no change** 

- b) no change
- c) shifts towards the products
- d) shifts towards the reactants
- 17.56 <u>Plan:</u> 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.
- 17.57 a) more  $CO_2$  and  $H_2O$ ; less  $C_3H_8$  and  $O_2$ 
  - b) more NH<sub>3</sub> and O<sub>2</sub>; less N<sub>2</sub> and H<sub>2</sub>O
- 17.58 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<sub>2</sub>). A decrease in pressure favors the reaction direction that forms more moles of gas, so **increase** the reaction vessel volume.
- 17.59 a) increase volume b) decrease volume
- 17.60 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  $\Delta H_{rxn}^{\circ}$  indicates an exothermic reaction, while a positive value of  $\Delta H_{rxn}^{\circ}$  indicates an endothermic reaction.

#### Solution:

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

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) 
$$C(s) + H_2O(g) + heat = CO(g) + H_2(g)$$
  $\Delta H_{rxn}^{\circ} = 131 \text{ kJ}$ 

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) 
$$2NO_2(g) + heat = 2NO(g) + O_2(g)$$

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) 
$$2C(s) + O_2(g) = 2CO(g) + heat$$

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**.

- 17.61 a) decrease b) decrease c) decrease d) increase
- 17.62  $4\text{Fe}_3\text{O}_4(s) + \text{O}_2(g) \leftrightarrows 6\text{Fe}_2\text{O}_3(s)$   $K_p = 2.5 \times 10^{87}$  at 298 K a)  $K_p = \frac{1}{P_{\text{O}_2}} = 2.5 \times 10^{87}$

$$P_{\rm O_2} = 4.0 \times 10^{-88} \text{ atm}$$

b) 
$$Q_p = \frac{1}{P_{O_2}} = 1/(0.21) = 4.7619$$

$$K_p > Q_p \text{ thus, the reaction will proceed to the right.}$$
c)  $K_p = K_c (RT)^{\Delta n}$ 

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

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

17.63 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.

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

The forward reaction is exothermic ( $\Delta H_{\text{rxn}}^{\circ}$  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<sub>2</sub> would **decrease** Q since  $Q = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$ , and have **no impact on** K.
- c) To enhance yield of SO<sub>3</sub>, a low temperature is used. Reaction rates are slower at lower temperatures, so a catalyst is used to speed up the reaction.
- a)  $3H_2(g) + N_2(g) \implies 2NH_3(g)$  The mole ratio  $H_2: N_2 = 3:1$ ; at equilibrium, if  $N_2 = x$ ,  $H_2 = 3x$ ;  $P_{\rm NH_3} = 50$ . atm

$$K_{p} = \frac{\left(P_{\text{NH}_{3}}\right)^{2}}{\left(P_{\text{N}_{2}}\right)\left(P_{\text{H}_{2}}\right)^{3}} = 1.00 \text{x} 10^{-4}$$

$$K_{p} = \frac{\left(50.\right)^{2}}{\left(x\right)\left(3x\right)^{3}} = 1.00 \text{x} 10^{-4}$$

$$K_{\rm p} = \frac{\left(50.\right)^2}{\left(x\right)\left(3x\right)^3} = 1.00 \text{x} 10^{-4}$$

$$x = 31.02016 = 31 \text{ atm } N_2$$

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

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (31.02016 \text{ atm}) + (93.06049 \text{ atm}) + (50. \text{ atm})$$
  
= 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

$$K_{\rm p} = \frac{\left(50.\right)^2}{\left(x\right)\left(6x\right)^3} = 1.00x10^{-4}$$

$$x = 18.445 = 18$$
 atm  $N_2$ 

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

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (18.445 \text{ atm}) + (110.67 \text{ atm}) + (50. \text{ atm})$$

= 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<sub>3</sub>.

a) You are given a value of  $K_c$  but the amounts of reactant and product is given in units of pressure. 17.65 Convert  $K_c$  to  $K_p$ .

$$K_p = K_c(RT)^{\Delta n}$$
  $\Delta n = 1 - 2 = -1$  (1 mol of product,  $C_2H_5OH$  and 2 mol of reactants,  $C_2H_4 + 1$ 

 $H_2O)$  $K_p = K_c (RT)^{-1} = (9 \text{ x } 10^3)[(0.0821 \text{ L-atm/mol-K}) (600. \text{ K})]^{-1} = 1.8270 \text{ x } 10^2 \text{ (unrounded)}$ Substitute the given values into the equilibrium expression and solve for  $P_{C_2H_4}$ .

$$K_{\rm p} = \frac{P_{\rm C_2H_5OH}}{P_{\rm C_2H_4}P_{\rm H_2O}} = \frac{200.}{P_{\rm C_2H_4} (400.)} = 1.8270 \text{ x } 10^2$$
$$P_{\rm C_2H_4} = 2.7367 \text{ x } 10^{-3} = 3 \text{ x } 10^{-3} \text{ atm}$$

- b) The forward direction, towards the production of ethanol, produces the least number of moles of gas and is favored by **high pressure**. A **low temperature** favors an exothermic reaction.
- c) 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.

17.66 a) 
$$Q_{c} = \frac{\left[XY\right]^{2}}{\left[X_{2}\right]\left[Y_{2}\right]}$$
  
b) Scene A:  $Q_{c} = \frac{\left[0\right]^{2}}{\left[0.4\right]\left[0.4\right]} = \mathbf{0}$   
Scene B:  $Q_{c} = \frac{\left[0.4\right]^{2}}{\left[0.2\right]\left[0.2\right]} = \mathbf{4}$   
Scenes C-E:  $Q_{c} = \frac{\left[0.6\right]^{2}}{\left[0.1\right]\left[0.1\right]} = 36 = \mathbf{4x10^{1}}$ 

- c) Time is progressing to the **right**. Frame A must be the earliest time.
- d)  $K = 4 \times 10^{1}$
- 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.

17.67 
$$n/V = M = P/RT = \frac{(2.0 \text{ atm})}{(0.0821 \frac{\text{L*atm}}{\text{mol*K}})((273.2 + 25.0) \text{K})} = 0.0816919 M \text{ each gas}$$

$$\frac{\text{H}_2(g)}{\text{Initial}} + \frac{\text{CO}_2(g)}{0.0816919} + \frac{\text{H}_2\text{O}(g)}{0} + \frac{\text{CO}(g)}{0}$$

$$\frac{\text{Change}}{\text{Initial}} - \frac{x}{\sqrt{200816919}} + \frac{x}{\sqrt{200816919}} + \frac{x}{\sqrt{200816919}} + \frac{x}{\sqrt{200816919}} + \frac{x}{\sqrt{200816919}} = \frac{x}{\sqrt{200816919}$$

17.68 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.

$$\frac{2\text{NO}(g)}{2} \leftrightarrows \text{N}_2(g) + \text{O}_2(g)$$
  $K_1 = (K_c)^{-2} = 4.340 \times 10^{18} = K_2$   
 $2\text{NO}_2(g) \leftrightarrows \frac{2\text{NO}(g)}{2} + \text{O}_2(g)$   $K_2 = K_c = 1.1 \times 10^{-5}$ 

Overall: 
$$2NO_2(g) = N_2(g) + 2O_2(g)$$
  $K_c \text{ (overall)} = K_1K_2 = 4.774 \times 10^{13} = 4.8 \times 10^{13} M$ 

17.69 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) 
$$K_{\rm p} = K_{\rm c} (RT)^{\Delta n}$$

 $\Delta n$  = moles gaseous products – moles gaseous reactants = 2 – 3 = –1 (two mol of product, SO<sub>3</sub>, and three mol of reactants, 2 SO<sub>2</sub> + O<sub>2</sub>)

$$K_{p} = K_{c}(RT)^{\Delta n} = K_{c}(RT)^{-1} = (1.7 \times 10^{8})[(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(600. \text{ K})]^{-1} = 3.451 \times 10^{6}$$

$$K_{p} = \frac{P_{SO_{3}}^{2}}{P_{SO_{2}}^{2} P_{O_{2}}} = \frac{(300.)^{2}}{P_{SO_{2}}^{2} (100.)} = 3.451 \times 10^{6}$$

$$P_{SO_2} = 0.016149 = 0.016$$
 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  $SO_2:O_2:SO_3$ .

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  $K_c$ .

$$K_{\rm c} = \frac{\left[{\rm SO_3}\right]^2}{\left[{\rm SO_2}\right]^2 \left[{\rm O_2}\right]} = \frac{\left[0.0020\right]^2}{\left[0.0020\right]^2 \left[0.0018\right]} = 555.5556 = 5.6x10^2$$

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).

$$PV = nRT$$

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

17.70 <u>Plan:</u> Set up a reaction table to find the equilibrium amount of CaCO<sub>3</sub> 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		<u>+x</u>
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<sub>3</sub> reacted is equal to the number of moles of carbon dioxide produced. Use the pressure of CO<sub>2</sub> and the ideal gas equation to calculate the moles of CO<sub>2</sub> produced:

$$PV = nRT$$

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.

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

$$n = \frac{(0.300 \text{ atm})(10.0 \text{ L})}{\left(0.0821 \frac{\text{L•atm}}{\text{mol•K}}\right)(385 \text{ K})} = 0.09491 \text{ mol } CO_2$$

Moles of CaCO<sub>3</sub> produced = moles of CO<sub>2</sub> reacted = 0.09491 mol CaCO<sub>3</sub>

Add the moles of CaCO<sub>3</sub> formed in the second equilibrium to the moles of CaCO<sub>3</sub> at the first equilibrium position.

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

Mass (g) of CaCO<sub>3</sub> = 
$$(0.12531 \text{ mol CaCO}_3) \left( \frac{100.09 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \right) = 12.542 = 12.5 \text{ g CaCO}_3$$

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

17.72 The first equation is in the correct form, but the second equation must be reversed. Reversing the equation leads to the reciprocal of the *K* value.

to the reciprocal of the 
$$K$$
 value.  

$$\frac{1/2H_2(g)}{1/2H_2(g)} + 1/2O_2(g) \leftrightarrows HO(g)$$

$$K_{c1} = 0.58$$

$$\frac{H(g) \leftrightarrows \frac{1/2H_2(g)}{1/2H_2(g)} \qquad K_{c2} = (K_{c2})^{-1} = (1.6\times10^{-3})^{-1} = 625$$
Overall:  $H(g) + 1/2O_2(g) \leftrightarrows HO(g)$ 

$$K_{c(overall)} = K_{c1} \times (K_{c2})^{-1}$$

$$= 0.58 \times 625 = 362.5 = 3.6\times10^2$$

- 17.73 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  $V_{\text{CO}_2} + V_{\text{O}_2} + V_{\text{N}_2} = 10.0 + 1.00 + 50.0 = 61.0$ .

$$P_{\text{CO}_2} = \left(\frac{10.0 \text{ mol CO}_2}{61.0 \text{ mol gas}}\right) (4.0 \text{ atm}) = 0.6557377 \text{ atm}$$

$$P_{\text{O}_2} = \left(\frac{1.00 \text{ mol O}_2}{61.0 \text{ mol gas}}\right) (4.0 \text{ atm}) = 0.06557377 \text{ atm}$$

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

$$2\text{CO}_2(g) \leftrightarrows 2\text{CO}(g) + \text{O}_2(g)$$

$$K_p = \frac{P_{\text{CO}}^2 P_{\text{O}_2}}{P_{\text{CO}_2}^2} = \frac{P_{\text{CO}}^2 \left(0.06557377\right)}{\left(0.6557377\right)^2} = 1.4\text{x}10^{-28}$$

$$P_{\rm CO} = 3.0299 \times 10^{-14} = 3.0 \times 10^{-14} \text{ atm}$$

b) 
$$PV = nRT$$

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

 $Concentration (pg/L) of CO = \left(\frac{4.61312x10^{-16} \ mol \ CO}{L}\right) \left(\frac{28.01 \ g \ CO}{1 \ mol \ CO}\right) \left(\frac{1 \ pg}{10^{-12} \ g}\right) = 0.01292 = \textbf{0.013} \ \textbf{pg} \ \textbf{CO/L}$ 

17.74 a)  $Fe^{2+} + 2Fe^{3+}$ 

b)  $(0.050 \text{ mol H}_2\text{O})/(1.0 \text{ L}) = 0.050 M\text{ H}_2\text{O}$ 

$$K_{c} = \frac{\left[H_{2}\right]^{4}}{\left[H_{2}O\right]^{4}} = 5.1 = \frac{\left[4x\right]^{4}}{\left[0.050 - 4x\right]^{4}}$$

$$1.50277 = \frac{\left[4x\right]}{\left[0.050 - 4x\right]}$$

 $x = (7.50553x10^{-3} \text{ mol/L})(1.0 \text{ L}) = 7.50553x10^{-3} \text{ mol Fe}_3\text{O}_4 \text{ reacting}$ Mass Fe<sub>3</sub>O<sub>4</sub> =  $(7.50553x10^{-3})(231.55 \text{ g Fe}_3\text{O}_4/1 \text{ mol Fe}_3\text{O}_4) = 1.7494 =$ **1.7 \text{ g Fe}\_3\text{O}\_4** 

17.75 
$$M_2(g) + N_2(g) \iff 2MN(g)$$

$$K_{\rm c} = \frac{\left[\rm MN\right]^2}{\left[\rm M_2\right]\left[\rm N_2\right]}$$

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

$$K_{\rm c} = \frac{\left[0.40\right]^2}{\left[0.20\right][0.20]} = 4.0$$

Scene B:

$$K_{\rm c} = 4.0 = \frac{\left[2x\right]^2}{\left[0.60 - x\right][0.30 - x]}$$

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

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

$$3.6x = 0.72$$

$$x = 0.20 M$$

$$[M_2] = 0.60 - x = 0.60 - 0.20 = 0.40 M$$

$$[N_2] = 0.30 - x = 0.30 - 0.20 = 0.10 M$$

$$[MN] = 2x = 2(0.20 M) = 0.40 M$$

## 17.76 Calculate $K_c$ .

$$K_{\rm c} = \frac{[{\rm CO}_2][{\rm H}_2]}{[{\rm CO}][{\rm H}_2{\rm O}]} = \frac{[0.40][0.10]}{[0.10][0.10]} = 4.0$$

Calculate new concentrations.

New H<sub>2</sub> = 
$$0.10 M + (0.60 \text{ mol/} 2.0 \text{ L}) = 0.40 M$$

Concentration ( <i>M</i> )	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	<u>-x</u>
Equilibrium	0.10 + x	0.10 + x	0.40 - x	0.40 - x

$$\begin{split} K_{\rm c} &= \frac{\left[{\rm CO}_2\right]\left[{\rm H}_2\right]}{\left[{\rm CO}\right]\left[{\rm H}_2{\rm O}\right]} = \frac{\left[0.40-{\rm x}\right]\left[0.40-{\rm x}\right]}{\left[0.10+{\rm x}\right]\left[0.10+{\rm x}\right]} = \frac{\left[0.40-{\rm x}\right]^2}{\left[0.10+{\rm x}\right]^2} = 4.0\\ &\frac{\left[0.40-{\rm x}\right]}{\left[0.10+{\rm x}\right]} = 2.0\\ {\rm x} &= 0.066667\\ {\rm [CO]} &= \left[{\rm H}_2{\rm O}\right] = 0.10+{\rm x} = 0.10+0.066667 = 0.166667 = \textbf{0.17}~\textbf{\textit{M}}\\ {\rm [CO}_2] &= \left[{\rm H}_2\right] = 0.40-{\rm x} = 0.40-0.066667 = 0.333333 = \textbf{0.33}~\textbf{\textit{M}} \end{split}$$

- 17.77 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<sub>3</sub>, increasing the temperature).
- 17.78 <u>Plan:</u> 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  $P_{\rm H_2}$ .

Solution:

$$K_{\rm p} = \frac{P_{\rm CO}^2 P_{\rm H_2}^2}{P_{\rm CH_4} P_{\rm CO_2}} = \frac{\left(2x\right)^2 \left(2x\right)^2}{\left(10.0 - x\right) \left(10.0 - x\right)} = \frac{\left(2x\right)^4}{\left(10.0 - x\right)^2} = 3.548 \times 10^6 \text{ (take square root of each side)}$$

$$\frac{\left(2x\right)^2}{\left(10.0 - x\right)} = 1.8836135x10^3$$

A quadratic is necessary:

$$4x^{2} + (1.8836135x10^{3} x) - 1.8836135x10^{4} = 0$$
  
 $a = 4$   $b = 1.8836135x10^{3}$   $c = -1.8836135x10^{4}$ 

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

$$x = \frac{-1.8836135x10^3 \pm \sqrt{\left(1.8836135x10^3\right)^2 - 4(4)\left(-1.8836135x10^4\right)}}{2(4)}$$

x = 9.796209

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

If the reaction proceeded entirely to completion, the partial pressure of H<sub>2</sub> would be 20.0 atm (pressure is proportional to moles, and twice as many moles of H<sub>2</sub> form for each mole of CH<sub>4</sub> or CO<sub>2</sub> that reacts).

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

b) Repeat the calculations for part a) with the new 
$$K_p$$
 value. The reaction table is the same. 
$$K_p = \frac{P_{\rm CO}^2 P_{\rm H_2}^2}{P_{\rm CH_4} P_{\rm CO_2}} = \frac{\left(2x\right)^2 \left(2x\right)^2}{\left(10.0-x\right) \left(10.0-x\right)} = \frac{\left(2x\right)^4}{\left(10.0-x\right)^2} = 2.626 \times 10^7$$

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

A quadratic is needed:

$$4x^{2} + (5.124451x10^{3} x) - 5.124451x10^{4} = 0$$
  
 $a = 4$   $b = 5.124451x10^{3}$   $c = -5.124451x10^{4}$ 

$$x = \frac{-5.124451x10^3 \pm \sqrt{\left(5.124451x10^3\right)^2 - 4\left(4\right)\left(-5.124451x10^4\right)}}{2\left(4\right)}$$

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

If the reaction proceeded entirely to completion, the partial pressure of H<sub>2</sub> would be 20.0 atm (pressure is proportional to moles, and twice as many moles of H<sub>2</sub> form for each mole of CH<sub>4</sub> or CO<sub>2</sub> that reacts).

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

c) van't Hoff equation:

$$\begin{split} K_1 &= 3.548 \text{x} 10^6 & T_1 &= 1200. \text{ K} & \Delta H_{\text{rxn}}^{\circ} &= ? \\ K_2 &= 2.626 \text{x} 10^7 & T_2 &= 1300. \text{ K} & R &= 8.314 \text{ J/mol} \bullet \text{K} \\ \ln \frac{K_2}{K_1} &= -\frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \frac{2.626 \text{x} 10^7}{3.548 \text{x} 10^6} &= -\frac{\Delta H_{\text{rxn}}^{\circ}}{\left( 8.314 \frac{\text{J}}{\text{mol} \bullet \text{K}} \right)} \left( \frac{1}{1200. \text{ K}} - \frac{1}{1300. \text{ K}} \right) \end{split}$$

$$2.0016628 = \Delta H_{\rm rxn}^{\circ} (7.710195 \times 10^{-6})$$

$$\Delta H_{\rm rxn}^{\circ} = 2.0016628/7.710195 {\rm x} 10^{-6} = 2.5961247 {\rm x} 10^{5} = \textbf{2.60} {\rm x} \textbf{10}^{\rm 5} \; \textbf{J/mol}$$

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

17.79 <u>Plan:</u> 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:

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

- $2\text{CH}_4(g) + \text{O}_2(g) + 2\text{H}_2\text{O}(g) \leftrightarrows 2\text{CO}_2(g) + 6\text{H}_2(g)$ b)  $K_p = (9.34 \times 10^{28})(1.888) = 1.76339 \times 10^{29} = \textbf{1.76} \times \textbf{10}^{\textbf{29}}$
- c)  $\Delta n$  = moles gaseous products moles gaseous reactants = 8 5 = 3
- (8 moles of product gas 5 moles of reactant gas)

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

$$K_{\rm c} = \frac{K_{\rm p}}{(RT)^{\Delta n}} = \frac{1.76339 \times 10^{29}}{\left[ (0.0821 \text{ atm} \cdot \text{L/mol} \cdot \text{K})(1000) \right]^3} = 3.18654 \times 10^{23} = 3.19 \times 10^{23}$$

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 =  $2.0 \text{ mol CH}_4 + 1.0 \text{ mol O}_2 + 2.0 \text{ mol H}_2\text{O} = 5.0 \text{ mol}$ Total mol of gas final =  $2.0 \text{ mol CO}_2 + 6.0 \text{ mol H}_2 = 8.0 \text{ mol}$  (from mole ratios)

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

17.80 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.

$$Log K_n = -43.10$$

$$\text{Log } K_{\text{p}} = -43.10;$$
  $K_{\text{p}} = 10^{-43.10} = 7.94328 \text{x} 10^{-44}$ 

Pressure (atm)

$$N_2($$

$$\begin{array}{lll} & & & & \\ & & & \\ & & & \\ &$$

- d) The more reasonable step is  $N_2(g) + H(g) \rightarrow NH(g) + N(g)$ . 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.
- 17.81 a) Scenes B and D represent equilibrium.

 $= 4.022 \times 10^{14} = 4.0 \times 10^{14} \text{ H atoms/L}$ 

b) 
$$C$$
,  $A$ ,  $B = D$ 

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

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

$$K_{\rm c} = \frac{[{\rm Z}]^2}{[{\rm Y}]} = \frac{[0.50]^2}{[0.25]} = 1.0$$

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

17.82 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  $[H_2] = [S_2] = 0$ .

Initial 
$$0.600 M 0 M 0 M$$
  
Change  $-2x +2x +x$   
Equilibrium  $0.600 - 2x 2x x$   

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

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

$$\frac{\left[2x\right]^2 \left[x\right]}{\left[0.600\right]^2} = 9.0x10^{-8}$$
 Assume  $0.600 M$ .  

$$\frac{\left[2x\right]^2 \left[x\right]}{\left[0.600\right]^2} = 9.0x10^{-8}$$
 (assumption justified)  

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

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

$$[H_2] = 2x = 2(2.008x10^{-3}) = 4.016x10^{-3} = 4.0 x 10^{-3} M H_2$$

17.83 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  $0.780 - x = 0.210 - x = 2x$ 

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

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

$$\frac{\left(2x\right)^2}{\left(0.780\right)\left(0.210\right)} = 4.35x10^{-31}$$
 $x = 1.33466x10^{-16}$ 

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.

 $P_{\text{nitrogen}}$  (equilibrium) =  $(0.780 - 1.33466 \times 10^{-16})$  atm = **0.780 atm N**<sub>2</sub>

 $P_{\text{oxygen}}$  (equilibrium) =  $(0.210 - 1.33466 \times 10^{-16})$  atm = **0.210 atm O<sub>2</sub>**  $P_{\text{NO}}$  (equilibrium) =  $2(1.33466 \times 10^{-16})$  atm =  $2.66933 \times 10^{-16}$  = **2.67x10<sup>-16</sup> atm NO** 

b) The total pressure is the sum of the three partial pressures:  $0.780 \text{ atm} + 0.210 \text{ atm} + 2.67 \text{x} 10^{-16} \text{ atm} = \textbf{0.990 atm}$ 

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

c) 
$$K_{\rm p} = K_{\rm c} (RT)^{\Delta t}$$

 $\Delta n$  = moles gaseous products – moles gaseous reactants = 2 – 2 = 0

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

$$K_{\rm p} = K_{\rm c}(RT)^0$$

 $K_c = K_p = 4.35 \times 10^{-31}$  because there is no net increase or decrease in the number of moles of gas in the course of the reaction.

17.84 
$$C_5H_{11}OH + CH_3COOH \leftrightarrows CH_3COOC_5H_{11} + H_2O$$

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.

17.85 
$$Q(g) = R(g)$$
  $K = \frac{[R]}{[Q]}$ 

For Scene A at equilibrium:

$$K = \frac{[R]}{[Q]} = \frac{[2]}{[6]} = 0.33$$

For Scene B:

	Q(g)	≒	R(g)
Initial	10		2
Change	-x		+x
Equilibrium	10 - x		2 + x
$0.33 = \frac{[2+x]}{[10-x]}$			

$$x = 0.977 = 1$$

$$Q = 10 - x = 10 - 1 = 9$$
;  $R = 2 + x = 2 + 1 = 3$ 

17.86 a) 
$$K_p = (P_{\text{H}_2\text{O}})^{10} = 4.08 \text{x} 10^{-25}$$

$$P_{\rm H_{2O}} = \sqrt[10]{4.08 {\rm x} 10^{-25}} = 3.6397 {\rm x} 10^{-3} =$$
**3.64 x 10**<sup>-3</sup> atm

- b) (1) Adding more Na<sub>2</sub>SO<sub>4</sub>(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<sub>2</sub> gas will not change the partial pressure of the water vapor, so the ratio of hydrated form/anhydrous form will not change.
- 17.87 <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. 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 = nRTto find the total pressure. To find [CO]<sub>eq</sub> 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  $[H_2O] = 0.100 \text{ mol}/20.00 \text{ L} = 0.00500 \text{ M}$ .

 $x = 0.00276 M = [CO_2] = [H_2]$ 

$$K_{\rm c} = \frac{{
m [CO_2][H_2]}}{{
m [CO][H_2O]}} = \frac{{
m [0.00276][0.00276]}}{{
m [0.00224][0.00224]}} = 1.518176 = 1.52$$

b) 
$$M_{\text{total}} = [\text{CO}] + [\text{H}_2\text{O}] + [\text{CO}_2] + [\text{H}_2] = (0.00224 \, M) + (0.00224 \, M) + (0.00276 \, M) + (0.00276 \, M) + (0.00276 \, M)$$
  
= 0.01000  $M$ 

 $n_{\text{total}} = (M_{\text{total}})(V) = (0.01000 \text{ mol/L})(20.00 \text{ L}) = 0.2000 \text{ mol total}$ 

$$P_{\text{total}} = n_{\text{total}} RT/V = \frac{\left(0.2000 \,\text{mol}\right) \left(0.08206 \frac{\text{L•atm}}{\text{mol•K}}\right) \left(\left(273 + 900.\right) \text{K}\right)}{\left(20.00 \,\text{L}\right)} = 0.9625638 = \textbf{0.9626 atm}$$

- 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.

Initial 0.00224 M 0.00224 M 0.00276 M 0.00276 M 0.00276 M

Added CO 0.01000 M

Change -x -x +x +x +x

Equilibrium 0.01224 - x 0.00224 - x 0.00276 + x 0.00276 + x

$$K_c = \frac{\left[\text{CO}_2\right]\left[\text{H}_2\right]}{\left[\text{CO}\right]\left[\text{H}_2\text{O}\right]} = \frac{\left[0.00276 + x\right]\left[0.00276 + x\right]}{\left[0.01224 - x\right]\left[0.00224 - x\right]} = 1.518176$$

$$\frac{\left[7.6176x10^{-6} + 5.52x10^{-3}x + x^2\right]}{2.74176x10^{-5} - 1.448x10^{-2}x + x^2} = 1.518176$$

$$\frac{2.74176x10^{-6} + 5.52x10^{-3}x + x^2}{2.74176x10^{-5} - 1.448x10^{-2}x + x^2} = 1.518176$$

$$7.6176x10^{-6} + 5.52x10^{-3}x + x^2 = (1.518176)(2.74176x10^{-5} - 1.448x10^{-2}x + x^2)$$

$$7.6176x10^{-6} + 5.52x10^{-3}x + x^2 = 4.162474x10^{-5} - 0.021983x + 1.518176x^2$$

$$0.518176x^2 - 0.027503x + 3.400714x10^{-5} = 0$$

$$a = 0.518176 \quad b = -0.027503 \quad c = 3.400714x10^{-5}$$

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

$$x = \frac{-(-0.027503) \pm \sqrt{(-0.027503)^2 - 4(0.518176)\left(3.400714x10^{-5}\right)}}{2(0.518176)}$$

$$x = 1.31277x10^{-3}$$

$$x = 1.3127/x10^{-3}$$
  
 $[CO] = 0.01224 - x = 0.01224 - (1.31277x10^{-3}) = 0.01092723 = 0.01093 M$