

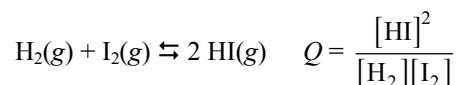
# CHAPTER 17 EQUILIBRIUM: THE EXTENT OF CHEMICAL REACTIONS

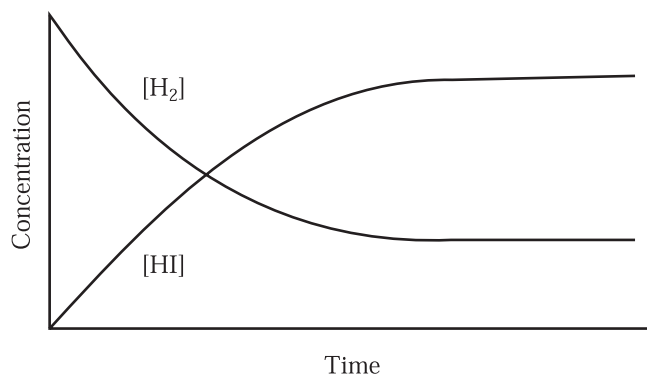
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- 17.1 If the rate of the forward reaction exceeds the rate of reverse reaction, products are formed faster than they are consumed. The change in reaction conditions results in more products and less reactants. A change in reaction conditions can result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

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

- 17.2 The faster the rate and greater the yield, the more useful the reaction will be to the manufacturing process.
- 17.3 A system at equilibrium continues to be very dynamic at the molecular level. Reactant molecules continue to form products, but at the same rate that the products decompose to re-form the reactants.
- 17.4 If  $K$  is very large, the reaction goes nearly to completion. A large value of  $K$  means that the numerator is much larger than the denominator in the  $K$  expression. A large numerator, relative to the denominator, indicates that most of the reactants have reacted to become products. 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.
- 17.5 The reaction is exothermic because the energy of the reactants is greater than the energy of products. The products would be favored and be present at equilibrium at higher concentrations than the reactants because a lower energy state is favored. The change in energy looks large on the graph so the product concentrations are much larger than the reactant concentrations and  $K$  is large.
- 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  $K = [\text{O}_2]$ . If the temperature remains constant,  $K$  remains constant. If the initial amount of  $\text{Li}_2\text{O}_2$  present was sufficient to reach equilibrium, the amount of  $\text{O}_2$  obtained will be constant, regardless of how much  $\text{Li}_2\text{O}_2(\text{s})$  is present.
- 17.8 On the graph, the concentration of HI increases at twice the rate that  $\text{H}_2$  decreases because the stoichiometric ratio in the balanced equation is 1  $\text{H}_2$  : 2 HI.  
 $Q$  for a reaction is the ratio of concentrations of products to concentrations of reactants. As the reaction progresses the concentration of reactants decrease and the concentration of products increase, which means that  $Q$  increases as a function of time.

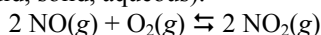




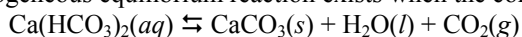
The value of  $Q$  increases as a function of time until it reaches the value of  $K$ .

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).

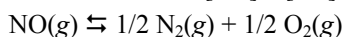


A heterogeneous equilibrium reaction exists when the components of the reaction are in different phases.



- 17.10  $1/2 \text{N}_2(g) + 1/2 \text{O}_2(g) \rightleftharpoons \text{NO}(g)$

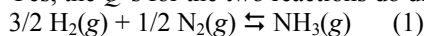
$$Q_{c(\text{form})} = \frac{[\text{NO}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}}$$



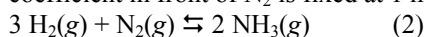
$$Q_{c(\text{decomp})} = \frac{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}}{[\text{NO}]}$$

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

- 17.11 Yes, the  $Q$ 's for the two reactions do differ. The balanced equation for the first reaction is



The coefficient in front of  $\text{NH}_3$  is fixed at 1 mole according to the description. In the second reaction, the coefficient in front of  $\text{N}_2$  is fixed at 1 mole.

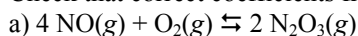


The reaction quotients for the two equations and their relationship are:

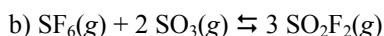
$$Q_1 = \frac{[\text{NH}_3]}{[\text{H}_2]^{3/2} [\text{N}_2]^{1/2}} \quad Q_2 = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]}$$

$$Q_2 = Q_1^2$$

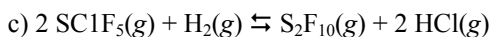
- 17.12 Check that correct coefficients from balanced equation are included as exponents in the mass action expression.



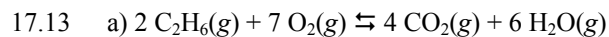
$$Q_c = \frac{[\text{N}_2\text{O}_3]^2}{[\text{NO}]^4 [\text{O}_2]}$$



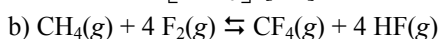
$$Q_c = \frac{[\text{SO}_2\text{F}_2]^3}{[\text{SF}_6] [\text{SO}_3]^2}$$



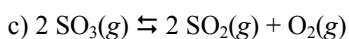
$$Q_c = \frac{[\text{S}_2\text{F}_{10}][\text{HCl}]^2}{[\text{SClF}_3]^2[\text{H}_2]}$$



$$Q_c = \frac{[\text{CO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{C}_2\text{H}_6]^2 [\text{O}_2]^7}$$

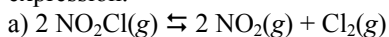


$$Q_c = \frac{[\text{CF}_4][\text{HF}]^4}{[\text{CH}_4][\text{F}_2]^4}$$

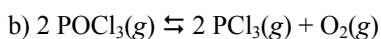


$$Q_c = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2}$$

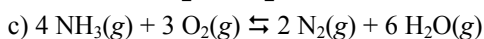
17.14 Check that correct coefficients from the balanced equation are included as exponents in the mass action expression.



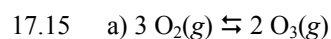
$$Q_c = \frac{[\text{NO}_2]^2 [\text{Cl}_2]}{[\text{NO}_2\text{Cl}]^2}$$



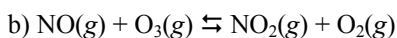
$$Q_c = \frac{[\text{PCl}_3]^2 [\text{O}_2]}{[\text{POCl}_3]^2}$$



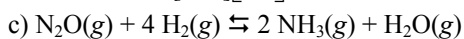
$$Q_c = \frac{[\text{N}_2]^2 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^3}$$



$$Q_c = \frac{[\text{O}_3]^2}{[\text{O}_2]^3}$$



$$Q_c = \frac{[\text{NO}_2][\text{O}_2]}{[\text{NO}][\text{O}_3]}$$



$$Q_c = \frac{[\text{NH}_3]^2 [\text{H}_2\text{O}]}{[\text{N}_2\text{O}][\text{H}_2]^4}$$

17.16 The  $Q$  for the original reaction is  $Q_{\text{ref}} = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2}$

a) The given reaction  $\frac{1}{2} \text{S}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{g})$  is the reverse reaction of the original reaction multiplied by a factor of  $1/2$ . The equilibrium constant for the reverse reaction is the inverse of the original constant. When a reaction is multiplied by a factor,  $K$ , the new equation is equal to the  $K$  of the original equilibrium raised to a power equal to the factor. For the reaction given in part a), take  $(1/K)^{1/2}$ .

$$Q_a = (1 / Q_{\text{ref}})^{1/2} = \frac{[\text{H}_2\text{S}]}{[\text{S}_2]^{1/2} [\text{H}_2]}$$

$$K = (1 / 1.6 \times 10^{-2})^{1/2} = 7.90569 = \mathbf{7.9}$$

b) The given reaction  $5 \text{H}_2\text{S}(\text{g}) \rightleftharpoons 5 \text{H}_2(\text{g}) + 5/2 \text{S}_2(\text{g})$  is the original reaction multiplied by  $5/2$ . Take the original  $K$  to the  $5/2$  power to find  $K$  of given reaction.

$$Q_a = (Q_{\text{ref}})^{5/2} = \frac{[\text{H}_2]^5 [\text{S}_2]^{5/2}}{[\text{H}_2\text{S}]^5}$$

$$K = (1.6 \times 10^{-2})^{5/2} = 3.23817 \times 10^{-5} = \mathbf{3.2 \times 10^{-5}}$$

17.17  $Q_{\text{c(ref)}} = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2 [\text{H}_2]^2}$

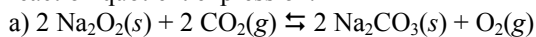
a)  $Q_c = [Q_{\text{c(ref)}}]^{1/2} = \frac{[\text{N}_2]^{1/2} [\text{H}_2\text{O}]}{[\text{NO}][\text{H}_2]}$

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

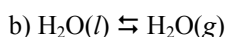
b)  $Q_c = [Q_{\text{c(ref)}}]^{-2} = \frac{[\text{NO}]^4 [\text{H}_2]^4}{[\text{N}_2]^2 [\text{H}_2\text{O}]^4}$

$$K_c = [K_{\text{c(ref)}}]^{-2} = (6.5 \times 10^2)^{-2} = 2.36686 \times 10^{-6} = \mathbf{2.4 \times 10^{-6}}$$

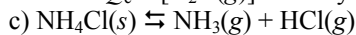
17.18 The concentration of solids and pure liquids do not change, so their concentration terms are not written in the reaction quotient expression.



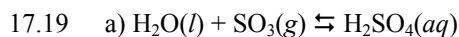
$$Q_c = \frac{[\text{O}_2]}{[\text{CO}_2]^2}$$



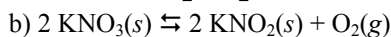
$$Q_c = [\text{H}_2\text{O}(\text{g})] \quad \text{Only the gaseous water is used. The “(g)” is for emphasis.}$$



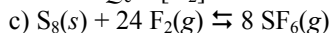
$$Q_c = [\text{NH}_3][\text{HCl}]$$



$$Q_c = \frac{[\text{H}_2\text{SO}_4]}{[\text{SO}_3]}$$

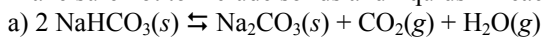


$$Q_c = [\text{O}_2]$$

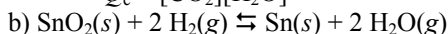


$$Q_c = \frac{[\text{SF}_6]^8}{[\text{F}_2]^{24}}$$

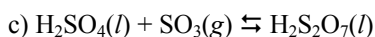
17.20 Make sure not to include solids and liquids in reaction quotient.



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



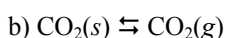
$$Q_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2}$$



$$Q_c = \frac{1}{[\text{SO}_3]}$$

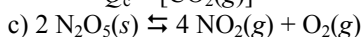
17.21 a)  $2 \text{Al}(s) + 2 \text{NaOH}(aq) + 6 \text{H}_2\text{O}(l) \rightleftharpoons 2 \text{Na}[\text{Al}(\text{OH})_4](aq) + 3 \text{H}_2(g)$

$$Q_c = \frac{[\text{Na}[\text{Al}(\text{OH})_4]]^2 [\text{H}_2]^3}{[\text{NaOH}]^2}$$



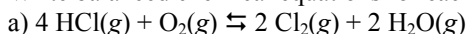
$$Q_c = [\text{CO}_2(g)]$$

Only the gaseous carbon dioxide is used. The “(g)” is for emphasis.

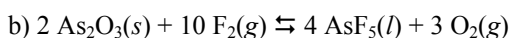


$$Q_c = [\text{NO}_2]^4[\text{O}_2]$$

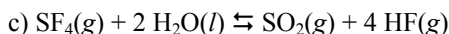
17.22 Write balanced chemical equations for each reaction, and then write the appropriate equilibrium expression.



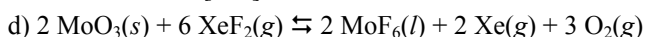
$$Q_c = \frac{[\text{Cl}_2]^2 [\text{H}_2\text{O}]^2}{[\text{HCl}]^4 [\text{O}_2]}$$



$$Q_c = \frac{[\text{O}_2]^3}{[\text{F}_2]^{10}}$$

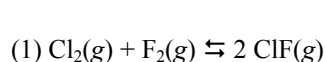


$$Q_c = \frac{[\text{SO}_2][\text{HF}]^4}{[\text{SF}_4]}$$

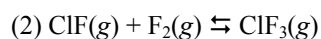


$$Q_c = \frac{[\text{Xe}]^2 [\text{O}_2]^3}{[\text{XeF}_2]^6}$$

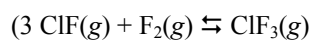
17.23 a) The balanced equations and corresponding reaction quotients are given below. Note the second equation must occur twice to get the appropriate overall equation.



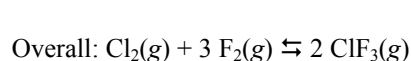
$$Q_1 = \frac{[\text{ClF}]^2}{[\text{Cl}_2][\text{F}_2]}$$



$$Q_2 = \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]}$$



$$Q_2 = \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]}$$



$$Q_{\text{overall}} = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

b) The second equation occurs twice, thus it could simply be multiplied by two and its reaction quotient squared. The reaction quotient for the overall reaction,  $Q_{\text{overall}}$ , determined from the reaction is:

$$Q_{\text{overall}} = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

$$Q_{\text{overall}} = Q_1 Q_2^2 = Q_1 Q_2 Q_2 = \frac{[\text{ClF}]^2}{[\text{Cl}_2][\text{F}_2]^3} \times \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]} \times \frac{[\text{ClF}_3]}{[\text{ClF}][\text{F}_2]} = \frac{[\text{ClF}_3]^2}{[\text{Cl}_2][\text{F}_2]^3}$$

17.24 Concentration and pressure of gas are directly proportional as long as the temperature is constant:  $C = n/V = P/RT$ .

17.25  $K_c$  and  $K_p$  are related by the equation  $K_c = K_p(RT)^{-\Delta n}$ , 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  $K_c \neq K_p$ .

17.26 a) Since  $\Delta n =$  number of moles gaseous products - number of moles gaseous reactants,  $\Delta n$  is a positive integer. If  $\Delta n$  is a positive integer, then  $(RT)^{-\Delta n}$  is less than 1. Thus,  $K_p$  must be larger since it is multiplied by a fraction that is less than 1 gives  $K_c$ .  **$K_c$  is smaller than  $K_p$ .**

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

17.27 a) Number of moles of gaseous reactants = 0; Number of moles of gaseous products = 3;  $\Delta n = 3 - 0 = 3$

b) Number of moles of gaseous reactants = 1; Number of moles of gaseous products = 0;  $\Delta n = 0 - 1 = -1$

c) Number of moles of gaseous reactants = 0; Number of moles of gaseous products = 3;  $\Delta n = 3 - 0 = 3$

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

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

a)  $\Delta n =$  Number of product gas moles - Number of reactant gas moles =  $1 - 2 = -1$

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

This assumes that 1000 has at least 2 significant figures.

b)  $\Delta n =$  Number of product gas moles - Number of reactant gas moles =  $1 - 1 = 0$

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

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

a)  $\Delta n =$  Number of product gas moles - Number of reactant gas moles =  $2 - 2 = 0$

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

b)  $\Delta n =$  Number of product gas moles - Number of reactant gas moles =  $2 - 3 = -1$

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

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

a)  $\Delta n =$  Number of product gas moles - Number of reactant gas moles =  $2 - 1 = 1$

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

b)  $\Delta n =$  Number of product gas moles - Number of reactant gas moles =  $2 - 4 = -2$

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

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

a)  $\Delta n =$  Number of product gas moles - Number of reactant gas moles =  $2 - 2 = 0$

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

b)  $\Delta n =$  Number of product gas moles - Number of reactant gas moles =  $2 - 3 = -1$

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

- 17.33 When  $Q < K$ , the reaction proceeds to the **right** to form more products. The reaction quotient and equilibrium constant are determined by  $[\text{products}] / [\text{reactants}]$ . For  $Q$  to increase and reach the value of  $K$ , the concentration of products (numerator) must increase in relation to the concentration of reactants (denominator).
- 17.34 Reactant and product concentrations are constant over time. The forward reaction rate equals the reverse reaction rate. The reaction quotient equals the equilibrium constant:  $Q = K$ .
- 17.35 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.

$$Q_p = \frac{P_{\text{H}_2} P_{\text{Br}_2}}{P_{\text{HBr}}^2} = (0.010)(0.010) / (0.20)^2 = 2.5 \times 10^{-3} > K_p = 4.18 \times 10^{-9}$$

$Q_p > K_p$ , thus, the reaction is **not** at equilibrium and will proceed to the **left** (towards the reactants).

17.36 
$$Q_p = \frac{P_{\text{NO}}^2 P_{\text{Br}_2}}{P_{\text{NOBr}}^2} = (0.10)^2(0.10) / (0.10)^2 = 0.10 < K_p = 60.6$$

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

- 17.37 There is insufficient information to calculate the partial pressures of each gas ( $T$  is not given). There is sufficient information to determine the concentrations and hence  $Q_c$ . Convert the  $K_p$  given to  $K_c$  using  $K_p = K_c(RT)^{\Delta n}$ . Compare the  $Q_c$  to the  $K_c$  just calculated and make a prediction.

$$\Delta n = \text{Number of product gas moles} - \text{Number of reactant gas moles} = 2 - 2 = 0$$

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.)

$$Q_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.62 / 2.0][0.43 / 2.0]}{[0.13 / 2.0][0.56 / 2.0]} = 3.662 \text{ (unrounded)} > K_c = 2.7$$

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

- 17.38 At equilibrium, equal concentrations of  $\text{CFCl}_3$  and  $\text{HCl}$  exist, regardless of starting reactant concentrations. The equilibrium concentrations of  $\text{CFCl}_3$  and  $\text{HCl}$  would still be equal if unequal concentrations of  $\text{CCl}_4$  and  $\text{HF}$  were used. This occurs only when the two products have the same coefficients in the balanced equation. Otherwise, more of the product with the larger coefficient will be produced.

- 17.39 When  $x$  mol of  $\text{CH}_4$  reacts,  $2x$  mol of  $\text{H}_2\text{O}$  also reacts to form  $x$  mol of  $\text{CO}_2$  and  $4x$  mol of  $\text{H}_2$ . The final (equilibrium) concentration of each reactant is the initial concentration minus the amount that reacts. The final (equilibrium) concentration of each product is the initial concentration plus the amount that forms.

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

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

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[1.87 \times 10^{-3}]^2}{[6.50 \times 10^{-5}][1.06 \times 10^{-3}]} = 50.753 = \mathbf{50.8}$$

$$17.42 \quad K_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{[0.114][0.342]^3}{[0.0225]^2} = 9.0077875 = \mathbf{9.01}$$

17.43 The reaction table requires that the initial  $[\text{PCl}_5]$  be calculated:  $[\text{PCl}_5] = 0.15 \text{ mol}/2.0 \text{ L} = 0.075 \text{ M}$   
 $x = [\text{PCl}_5]$  reacting (-x), and the amount of  $\text{PCl}_3$  and of  $\text{Cl}_2$  forming (+x).

Concentration (M)	$\text{PCl}_5(\text{g})$	$\rightleftharpoons$	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial	0.075		0		0
Change	-x		+x		+x
Equilibrium	$0.075 - x$		x		x

17.44 The reaction table requires that the initial  $[\text{H}_2]$  and  $[\text{F}_2]$  be calculated:  $[\text{H}_2] = 0.10 \text{ mol} / 0.50 \text{ L} = 0.20 \text{ M}$ ;  
 $[\text{F}_2] = 0.050 \text{ mol} / 0.50 \text{ L} = 0.10 \text{ M}$

$x = [\text{H}_2]$  reacting

Concentration (M)	$\text{H}_2(\text{g})$	+	$\text{F}_2(\text{g})$	$\rightleftharpoons$	$2\text{HF}(\text{g})$
Initial	0.20		0.10		0
Change	-x		-x		+2 x
Equilibrium	$0.20 - x$		$0.10 - x$		2 x

17.45 Construct an equilibrium expression and solve for  $P_{\text{NOCl}}$ .

$$K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 P_{\text{Cl}_2}} = 6.5 \times 10^4$$

$$P_{\text{NOCl}} = \sqrt{K_p P_{\text{NO}}^2 P_{\text{Cl}_2}} = \sqrt{(6.5 \times 10^4)(0.35)^2 (0.10)} = 28.2179 = \mathbf{28 \text{ atm}}$$

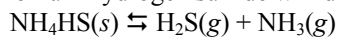
A high pressure for NOCl is expected because the  $K_p$  indicates that the reaction proceeds largely to the right, i.e., to the formation of products.

17.46  $\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g})$

$$Q_p = \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} = 0.262$$

$$P_{\text{CH}_4} = Q_p P_{\text{H}_2}^2 = (0.262)(1.22)^2 = 0.38996 = \mathbf{0.390 \text{ atm}}$$

17.47 The ammonium hydrogen sulfide will decompose to produce hydrogen sulfide and ammonia gas until  $K_p = 0.11$ :



$$Q_p = P_{\text{H}_2\text{S}} P_{\text{NH}_3} = 0.11$$

$$P_{\text{H}_2\text{S}} = P_{\text{NH}_3}$$

$$P_{\text{NH}_3} = \sqrt{Q_p} = 0.33166 = \mathbf{0.33 \text{ atm}}$$

17.48  $2 \text{H}_2\text{S}(\text{g}) \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{S}_2(\text{g})$

$$[\text{H}_2\text{S}] = 0.45 \text{ mol} / 3.0 \text{ L} = 0.15 \text{ M}$$

Concentration (M)	$2 \text{H}_2\text{S}(\text{g})$	$\rightleftharpoons$	$2 \text{H}_2(\text{g})$	$\text{S}_2(\text{g})$
Initial	0.15		0	0
Change	-x		+2 x	+ x
Equilibrium	$0.15 - 2x$		2 x	x

$$Q_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{[2x]^2 [x]}{[0.15 - 2x]^2} = 9.30 \times 10^{-8}$$



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

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

$$x = 8.0575 \times 10^{-4} M \text{ (unrounded)}$$

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

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

- 17.49 The initial concentrations of  $N_2$  and  $O_2$  are  $(0.20 \text{ mol}/1.0 \text{ L}) = 0.20 M$  and  $(0.15 \text{ mol}/1.0 \text{ L}) = 0.15 M$ , respectively.

	$N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$		
Concentration (M)	$N_2(g)$	$O_2(g)$	$2 NO(g)$
Initial	0.20	0.15	0
Change	-x	-x	+ 2x
Equilibrium	$0.20 - x$	$0.15 - x$	2x

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

Assume  $0.20 M - x \approx 0.20 M$  and  $0.15 M - x \approx 0.15 M$

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

$$x = 1.753568 \times 10^{-3} M \text{ (unrounded)}$$

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

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

- 17.50  $2 NO_2(g) \rightleftharpoons 2 NO(g) + O_2(g)$
- |                |             |                      |           |          |
|----------------|-------------|----------------------|-----------|----------|
| Pressure (atm) | $2 NO_2(g)$ | $\rightleftharpoons$ | $2 NO(g)$ | $O_2(g)$ |
| Initial        | 0.75        |                      | 0         | 0        |
| Change         | - 2x        |                      | + 2x      | + x      |
| Equilibrium    | $0.75 - 2x$ |                      | 2x        | x        |

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

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

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

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

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

- 17.51 First, determine the initial concentration of  $H_2$  and the change,  $x$ , to reach equilibrium.

Initial (unrounded) concentrations:

$$[HI] = (0.0244 \text{ mol}) / (1.50 \text{ L}) = 0.0162667$$

$$[H_2] = (0.00623 \text{ mol}) / (1.50 \text{ L}) = 0.0041533$$

$$[I_2] = (0.00414 \text{ mol}) / (1.50 \text{ L}) = 0.00276 M$$

Concentration (M)	$2 HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
Initial	0.0162667		0.0041533		0.00276
Change	-2x		+x		+x
Equilibrium	$0.0162667 - 2x$		$0.0041533 + x$		$0.00276 + x$

$$[H_2]_{eq} = 0.00467 = 0.0041533 + x$$

$$x = 0.0005167 M \text{ (unrounded)}$$

$$[I_2]_{eq} = 0.00276 + x = 0.0032767 = \mathbf{0.00328 M I_2}$$

$$[HI]_{eq} = 0.0162667 - 2x = 0.0152333 = \mathbf{0.0152 M HI}$$

17.52 Initial concentrations:

$$[A] = (1.75 \times 10^{-3} \text{ mol}) / (1.00 \text{ L}) = 1.75 \times 10^{-3} \text{ M}$$

$$[B] = (1.25 \times 10^{-3} \text{ mol}) / (1.00 \text{ L}) = 1.25 \times 10^{-3} \text{ M}$$

$$[C] = (6.50 \times 10^{-4} \text{ mol}) / (1.00 \text{ L}) = 6.50 \times 10^{-4} \text{ M}$$

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

$$[A]_{\text{eq}} = 2.15 \times 10^{-3} = 1.75 \times 10^{-3} - x$$

$$x = -0.00040$$

$$[B]_{\text{eq}} = 1.25 \times 10^{-3} + 2x = \mathbf{4.5 \times 10^{-4} \text{ M B}}$$

$$[C]_{\text{eq}} = 6.50 \times 10^{-4} + x = \mathbf{2.5 \times 10^{-4} \text{ M C}}$$

17.53 Construct a reaction table, using  $[ICl]_{\text{init}} = (0.500 \text{ mol} / 5.00 \text{ L}) = 0.100 \text{ M}$ , and substitute the equilibrium concentrations into the equilibrium expression.

Concentration (M)	2 ICl(g)	$\rightleftharpoons$	I <sub>2</sub> (g)	+	Cl <sub>2</sub> (g)
Initial	0.100		0		0
Change	-2 x		+x		+x
Equilibrium	$0.100 - 2x$		x		x

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

Take the square root of each side:

$$\frac{[x]}{[0.100 - 2x]} = \sqrt{0.110} = 0.331662 \text{ (unrounded)}$$

$$x = 0.0331662 - 0.663324 x$$

$$1.663324 x = 0.0331662$$

$$x = 0.0199397$$

$$[I_2]_{\text{eq}} = [Cl_2]_{\text{eq}} = \mathbf{0.0200 \text{ M}}$$

$$[ICl]_{\text{eq}} = 0.100 - 2x = 0.601206 = \mathbf{0.060 \text{ M ICl}}$$

17.54 Concentration (M)  $SCl_2(g) + 2 C_2H_4(g) \rightleftharpoons S(CH_2CH_2Cl)_2(g)$

Initial	0.675	0.973	0
Change	- x	- 2 x	+ x
Equilibrium	$0.675 - x$	$0.973 - 2x$	x

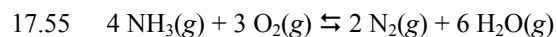
$$[S(CH_2CH_2Cl)_2]_{\text{eq}} = x = 0.350 \text{ M}$$

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

$$[C_2H_4]_{\text{eq}} = 0.973 - 2x = 0.273 \text{ M}$$

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

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



To find the equilibrium constant, determine the equilibrium concentrations of each reactant and product and insert into the equilibrium expression. Since  $[\text{N}_2]$  increases from 0 to  $1.96 \times 10^{-3} \text{ M}$ , the concentration of  $\text{H}_2\text{O}$  gas will increase by 3 times as much (stoichiometric ratio is  $6 \text{H}_2\text{O} : 2 \text{N}_2$ ) and the concentration of products will decrease by a factor equivalent to the stoichiometric ratio (2 for  $\text{NH}_3$  and  $3/2$  for  $\text{O}_2$ ). Since the volume is 1.00 L, the concentrations are equal to the number of moles present.

Concentration (M)	4 $\text{NH}_3(\text{g})$	+	3 $\text{O}_2(\text{g})$	$\rightleftharpoons$	2 $\text{N}_2(\text{g})$	+	6 $\text{H}_2\text{O}(\text{g})$
Initial	0.0150		0.0150		0		0
Change	- 4 x		- 3 x		+ 2 x		+ 6 x
Equilibrium	0.0150 - 4 x		0.0150 - 3 x		+ 2 x		+ 6 x

All intermediate concentration values are unrounded.

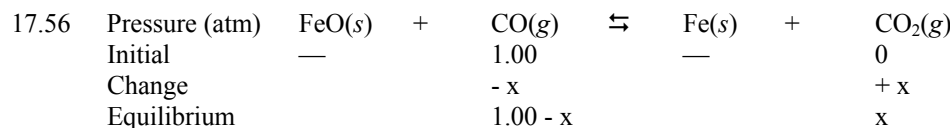
$$[\text{H}_2\text{O}]_{\text{eq}} = (6 \text{ mol H}_2\text{O}/2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 5.8800 \times 10^{-3} \text{ M}$$

$$[\text{NH}_3]_{\text{eq}} = (0.0150 \text{ mol NH}_3/1.00 \text{ L}) - (4 \text{ mol NH}_3/2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 1.1080 \times 10^{-2} \text{ M}$$

$$[\text{O}_2]_{\text{eq}} = (0.0150 \text{ mol O}_2/1.00 \text{ L}) - (3 \text{ mol O}_2/2 \text{ mol N}_2) (1.96 \times 10^{-3}) = 1.2060 \times 10^{-2} \text{ M}$$

$$K_c = \frac{[\text{N}_2]^2 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^3} = \frac{[1.96 \times 10^{-3}]^2 [5.8800 \times 10^{-3}]^6}{[1.1080 \times 10^{-2}]^4 [1.2060 \times 10^{-2}]^3} = 6.005859 \times 10^{-6} = \mathbf{6.01 \times 10^{-6}}$$

If values for concentrations were rounded to calculate  $K_c$ , the answer is  $5.90 \times 10^{-6}$ .



$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = 0.403 = \frac{x}{1.00 - x}$$

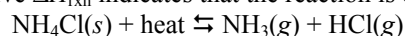
$$x = 0.28724 = \mathbf{0.287 \text{ atm CO}_2}$$

$$1.00 - x = 1.00 - 0.28724 = 0.71276 = \mathbf{0.71 \text{ atm CO}}$$

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

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

17.59 A positive  $\Delta H_{\text{rxn}}$  indicates that the reaction is endothermic, and that heat is consumed in the reaction:



a) The addition of heat 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)** best represents the mixture.

b) When heat is removed, the reaction shifts to the left to offset that disturbance. Therefore,  $\text{NH}_3$  and  $\text{HCl}$  molecules combine to form more reactant and container **(A)** best represents the mixture.

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

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

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

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



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

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

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

$$\Delta H_{\text{rxn}}^\circ = [(0.32 \text{ kJ/mol DH}) \times (2 \text{ mol DH})](10^3 \text{ J/1 kJ}) = 6.4 \times 10^2 \text{ J}$$

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

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

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

$$K_2 / 1.80 = 1.11000$$

$$K_2 = (1.80) (1.11000) = 1.99800 = \mathbf{2.0}$$

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

$$K_{298} = K_1 = 2.25 \times 10^4 \quad T_1 = 298 \text{ K} \quad \Delta H_{\text{rxn}}^\circ = -128 \text{ kJ/mol}$$

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

$$\Delta H_{\text{rxn}}^\circ = (-128 \text{ kJ/mol}) (10^3 \text{ J/1 kJ}) = -1.28 \times 10^5 \text{ J}$$

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

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

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

$$K_2 / (2.25 \times 10^4) = 1.134189 \times 10^2$$

$$K_2 = (2.25 \times 10^4) (1.134189 \times 10^2) = 2.5519157 \times 10^6 = \mathbf{2.55 \times 10^6}$$

- 17.75  $4 \text{ Fe}_3\text{O}_4(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 6 \text{ Fe}_2\text{O}_3(\text{s}) \quad K_p = 2.5 \times 10^{87}$  at 298 K

a)  $K_p = \frac{1}{P_{\text{O}_2}} = 2.5 \times 10^{87}$

$$P_{\text{O}_2} = \mathbf{4.0 \times 10^{-88} \text{ atm}}$$

b)  $Q_p = \frac{1}{P_{\text{O}_2}} = 1 / (0.21) = 7.7619$  (unrounded)

$K_p > Q_p$  thus, the reaction will proceed to the **right**.

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

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

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

- 17.76 a) The forward reaction is exothermic, so it is favored by **lower temperatures**. There are fewer moles of gas as products than as reactants, so products are favored by **higher pressure**.
- b) Addition of  $\text{O}_2$  would **decrease  $Q$**  and have **no impact on  $K$** .
- c) To enhance yield of  $\text{SO}_3$ , a low temperature is used. Reaction rates are slower at lower temperatures, so a catalyst is used **to speed up the reaction**.

$$17.77 \quad \text{a) } Q_c = \frac{[XY]^2}{[X_2][Y_2]}$$

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

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

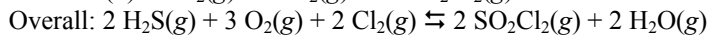
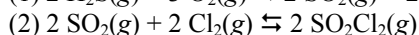
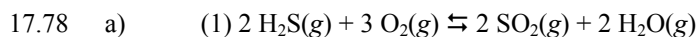
$$\text{Scenes C-E: } Q_c = \frac{[0.6]^2}{[0.1][0.1]} = 36 = \mathbf{4 \times 10^1}$$

c) **left-to-right**. Frame A must be the earliest time.

d)  $K = \mathbf{4 \times 10^1}$

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.



$$\text{b) } Q_1 = \frac{[\text{SO}_2]^2 [\text{H}_2\text{O}]^2}{[\text{H}_2\text{S}]^2 [\text{O}_2]^3} \quad Q_2 = \frac{[\text{SO}_2\text{Cl}_2]^2}{[\text{SO}_2]^2 [\text{Cl}_2]^2}$$

$$Q_{\text{overall}} = \frac{[\text{SO}_2\text{Cl}_2]^2 [\text{H}_2\text{O}]^2}{[\text{H}_2\text{S}]^2 [\text{O}_2]^3 [\text{Cl}_2]^2}$$

$$Q_1 \times Q_2 = \frac{[\text{SO}_2]^2 [\text{H}_2\text{O}]^2}{[\text{H}_2\text{S}]^2 [\text{O}_2]^3} \times \frac{[\text{SO}_2\text{Cl}_2]^2}{[\text{SO}_2]^2 [\text{Cl}_2]^2} = \frac{[\text{SO}_2\text{Cl}_2]^2 [\text{H}_2\text{O}]^2}{[\text{H}_2\text{S}]^2 [\text{O}_2]^3 [\text{Cl}_2]^2}$$

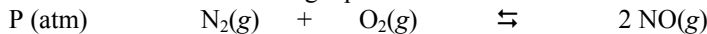
17.79 a) Initially, a total of 6.00 volumes of gas ( $5.00 \text{ N}_2 + 1.00 \text{ O}_2$ ) exist at 5.00 atm and 900. K. The volumes are proportional to moles of gas, so volume fraction equals mole fraction. The initial partial pressures of the two gases are:

$$P_{\text{N}_2} + P_{\text{H}_2} = 5.00 \text{ atm}$$

$$P_{\text{N}_2} = X_{\text{N}_2} P_{\text{tot}} = (5.00 / 6.00) (5.00 \text{ atm}) = 4.16667 \text{ atm (unrounded)}$$

$$P_{\text{H}_2} = X_{\text{H}_2} P_{\text{tot}} = (1.00 / 6.00) (5.00 \text{ atm}) = 0.83333 \text{ atm (unrounded)}$$

The reaction table describing equilibrium is written as follows:



Initial	4.16667		0.83333		0
---------	---------	--	---------	--	---

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

Equilibrium	$(4.16667 - x)$		$(0.83333 - x)$		$2x$
-------------	-----------------	--	-----------------	--	------

Since  $K_p$  is very small, assume that  $[\text{N}_2]_{\text{eq}} = 4.16667 - x = 4.16667$  and  $[\text{H}_2]_{\text{eq}} = 0.83333 - x = 0.83333$ .

$$K_p = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} P_{\text{O}_2}} = \frac{(2x)^2}{(4.16667)(0.83333)} = 6.70 \times 10^{-10}$$

$$x = 2.4116 \times 10^{-5} \text{ (unrounded)}$$

Check assumption: percent error =  $(2.4116 \times 10^{-5} / 4.16667) 100\% = 0.0006\%$ . The assumption is good.

Therefore,  $[\text{NO}]_{\text{eq}} = 2x = 2(2.4116 \times 10^{-5}) = 4.8232 \times 10^{-5} = \mathbf{4.82 \times 10^{-5} \text{ atm}}$

b) Convert atm (P) to concentration (mol/L) using the ideal gas law, assuming that it is applicable at 900. K.

$$n / V = P / RT$$

$$\frac{(4.8232 \times 10^{-5} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(900. \text{ K})} \left(\frac{30.01 \text{ g NO}}{1 \text{ mol NO}}\right) \left(\frac{1 \mu\text{g}}{10^{-6} \text{ g}}\right) = 19.58915 = \mathbf{19.6 \mu\text{g/L}}$$

- 17.80 a) **More CaCO<sub>3</sub>**, because the forward reaction is exothermic, decreasing the temperature will cause an increase in the amount of CaCO<sub>3</sub> formed.  
 b) **Less CaCO<sub>3</sub>**, the only gas in the equation is a reactant. Increasing the volume will cause the equilibrium to shift toward the reactant side and the amount of CaCO<sub>3</sub> formed decrease.  
 c) **More CaCO<sub>3</sub>**, increasing the partial pressure of CO<sub>2</sub> will cause more CaCO<sub>3</sub> to be formed.  
 d) **No change**, removing half of the initial CaCO<sub>3</sub> will have no effect on the amount of CaCO<sub>3</sub> formed, because CaCO<sub>3</sub> is solid.

17.81 Set up reaction table:

Concentration ( <i>M</i> )	NH <sub>2</sub> COONH <sub>4</sub> (s) ⇌	2NH <sub>3</sub>	+	CO <sub>2</sub>
Initial	7.80 g	0		0
Change	—	+ 2 x		+ x
Equilibrium	—	2 x		x

The solid is irrelevant (as long as some is present).

$$K_c = 1.58 \times 10^{-8} = (2x)^2(x); x = 1.580759 \times 10^{-3} \text{ M (unrounded)}$$

$$\text{Total concentration of gases} = 2(1.580759 \times 10^{-3} \text{ M}) + 1.580759 \times 10^{-3} \text{ M} = 4.742277 \times 10^{-3} \text{ M (unrounded)}$$

To find total pressure use the ideal gas equation:

$$P = nRT / V = (n/V) RT = MRT$$

$$P = (4.742277 \times 10^{-3} \text{ M})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(273 + 250.)\text{K} = 0.203625 = \mathbf{0.204 \text{ atm}}$$

17.82 Calculate  $K_c$

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.40][0.10]}{[0.10][0.10]} = 4.0$$

Calculate new concentrations

$$\text{New H}_2 = 0.10 \text{ M} + (0.60 \text{ mol} / 2.0 \text{ L}) = 0.40$$

Concentration ( <i>M</i> )	CO(g) +	H <sub>2</sub> O(g) ⇌	CO <sub>2</sub> (g) +	H <sub>2</sub> (g)
Initial	0.10	0.10	0.40	0.40
Change	x	x	- x	- x
Equilibrium	0.10 + x	0.10 + x	0.40 - x	0.40 - x

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.40 - x][0.40 - x]}{[0.10 + x][0.10 + x]} = \frac{[0.40 - x]^2}{[0.10 + x]^2} = 4.0$$

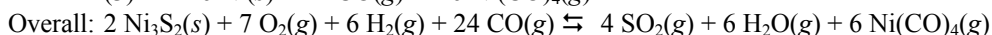
$$\frac{[0.40 - x]}{[0.10 + x]} = 2.0$$

$$x = 0.066667 \text{ (unrounded)}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 0.10 + x = 0.10 + 0.066667 = 0.166667 = \mathbf{0.17 \text{ M}}$$

$$[\text{CO}_2] = [\text{H}_2] = 0.40 - x = 0.40 - 0.066667 = 0.333333 = \mathbf{0.33 \text{ M}}$$

- 17.83 a) (1)  $2 \text{ Ni}_3\text{S}_2(\text{s}) + 7 \text{ O}_2(\text{g}) \rightleftharpoons 6 \text{ NiO}(\text{s}) + 4 \text{ SO}_2(\text{g})$   
 (2)  $6 \text{ NiO}(\text{s}) + 6 \text{ H}_2(\text{g}) \rightleftharpoons 6 \text{ Ni}(\text{s}) + 6 \text{ H}_2\text{O}(\text{g})$   
 (3)  $6 \text{ Ni}(\text{s}) + 24 \text{ CO}(\text{g}) \rightleftharpoons 6 \text{ Ni}(\text{CO})_4(\text{g})$



b) As always, the solid is not included in the  $Q$  expression.

$$Q_{c(\text{overall})} = \frac{[\text{SO}_2]^4 [\text{H}_2\text{O}]^6 [\text{Ni}(\text{CO})_4]^6}{[\text{O}_2]^7 [\text{H}_2]^6 [\text{CO}]^{24}}$$

$$Q_1 \times Q_2 \times Q_3 = \frac{[\text{SO}_2]^4}{[\text{O}_2]^7} \times \frac{[\text{H}_2\text{O}]^6}{[\text{H}_2]^6} \times \frac{[\text{Ni}(\text{CO})_4]^6}{[\text{CO}]^{24}} = \frac{[\text{SO}_2]^4 [\text{H}_2\text{O}]^6 [\text{Ni}(\text{CO})_4]^6}{[\text{O}_2]^7 [\text{H}_2]^6 [\text{CO}]^{24}}$$

17.84 a) Convert  $K_c$  to  $K_p$ , substitute the given values into the equilibrium expression and solve for  $P_{\text{C}_2\text{H}_4}$ .

$$K_p = K_c(\text{RT})^{\Delta n} = K_c(\text{RT})^{-1} = (9 \times 10^3)[(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(600. \text{ K})]^{-1} = 1.8270 \times 10^2 \text{ (unrounded)}$$

$$K_p = \frac{P_{\text{C}_2\text{H}_5\text{OH}}}{P_{\text{C}_2\text{H}_4} P_{\text{H}_2\text{O}}} = \frac{200.}{P_{\text{C}_2\text{H}_4} (400.)} = 1.8270 \times 10^2$$

$$P_{\text{C}_2\text{H}_4} = 2.7367 \times 10^{-3} = \mathbf{3 \times 10^{-3} \text{ atm}}$$

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) Use van't Hoff's equation to find  $K_c$  at a different temperature.

$$K_1 = 9 \times 10^3 \quad T_1 = 600. \text{ K} \quad \Delta H_{\text{rxn}}^\circ = (-47.8 \text{ kJ/mol}) (10^3 \text{ J/1 kJ}) = -4.78 \times 10^4 \text{ J/mol}$$

$$K_2 = ? \quad T_2 = 450. \text{ K} \quad R = 8.314 \text{ J/mol}\cdot\text{K}$$

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

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

$$\ln \frac{K_2}{9 \times 10^3} = 3.194$$

$$K_2 / 9 \times 10^3 = 24.37765$$

$$K_2 = (9 \times 10^3)(24.37765) = 2.19 \times 10^5 = \mathbf{2 \times 10^5}$$

d) **No**, condensing the  $\text{C}_2\text{H}_5\text{OH}$  would not increase the yield. Ethanol has a lower boiling point ( $78.5^\circ\text{C}$ ) than water ( $100^\circ\text{C}$ ). Decreasing the temperature to condense the ethanol would also condense the water, so moles of gas from each side of the reaction are removed. The direction of equilibrium (yield) is unaffected when there is no net change in the number of moles of gas.

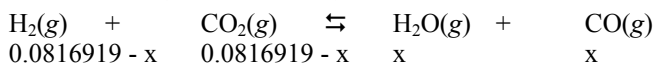
17.85 a) Birds flying north and south is not a good example of an equilibrium. At any one time, the rates of movement in either direction are not equal. Generally, the birds are only moving in one direction or the other.

b) This situation is an example of equilibrium. Carts move in and out of the store, but the number of carts inside and outside remains about constant.

c) A tug-of-war is not a good example of an equilibrium because eventually the ribbon goes all the way to one side.

d) Vaporization of stew and condensation on the lid is an example of equilibrium. Water exists both as a gas and liquid and the quantities of each phase remain about constant.

$$17.86 \quad n/V = M = PV / RT = \frac{(2.0 \text{ atm})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)((273.2 + 25.0) \text{ K})} = 0.0816919 \text{ M each gas (unrounded)}$$



$$0.0816919 - x \quad 0.0816919 - x \quad x \quad x$$

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = 0.534 = \frac{[x][x]}{[0.0816919 - x][0.0816919 - x]} = \frac{[x]^2}{[0.0816919 - x]^2}$$

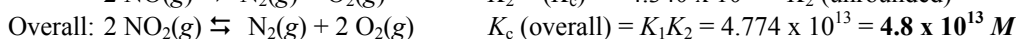
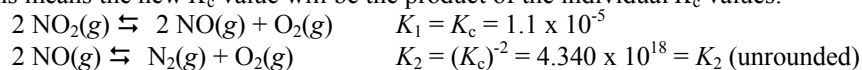
$$(0.534)^{1/2} = 0.730753 = \frac{[x]}{[0.0816919 - x]}$$

$$x = 0.03449 \text{ (unrounded)}$$

$$\text{Mass H}_2 [(0.0816919 - 0.03449) \text{ mol/L}](1.00 \text{ L}) (2.016 \text{ g H}_2/\text{mol}) = 0.095159 = \mathbf{0.095 \text{ g H}_2}$$



- 17.87 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.



- 17.88 a)  $2 \text{BrCl}(g) \rightleftharpoons \text{Br}_2(g) + \text{Cl}_2(g)$

$$\text{b) } Q_A = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2}$$

c)  $Q_A$  increases and  $Q_B$  decreases, until  $Q_A = 1/Q_B$  at equilibrium.

d) In container A, BrCl molecules decompose to form Br<sub>2</sub> and Cl<sub>2</sub> with an equilibrium constant of  $K_A$ , while in container B, Br<sub>2</sub> and Cl<sub>2</sub> molecules will form BrCl molecules with an equilibrium constant of  $K_B$ . At constant temperature,  $K_A = 1/K_B$ . Since the total Br mass and Cl mass is initially identical, identical amounts of BrCl, Cl<sub>2</sub>, and Br<sub>2</sub> will be formed at equilibrium in each container.

- 17.89 a) Convert  $K_c$  to  $K_p$ , substitute given values into the equilibrium expression and solve for  $P_{\text{SO}_2}$  ( $\Delta n = 2 - 3 = -1$ ).

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

$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} = \frac{(300.)^2}{P_{\text{SO}_2}^2 (100.)} = 3.451 \times 10^6$$

$$P_{\text{SO}_2} = 0.016149 = \mathbf{0.016 \text{ atm}}$$

b) Create a reaction table that describes the reaction conditions. Since the volume is 1.0 L, the moles equals the molarity.

Concentration (M)	2 SO <sub>2</sub> (g)	+	O <sub>2</sub> (g)	$\rightleftharpoons$	2 SO <sub>3</sub> (g)
Initial	0.0040		0.0028		0
Change	-2 x		-x		+2 x
Equilibrium	0.0040 - 2 x		0.0028 - x		2 x = 0.0020

$$x = 0.0010, \text{ therefore, } [\text{SO}_2] = 0.0020 \text{ M, } [\text{O}_2] = 0.0018 \text{ M, and } [\text{SO}_3] = 0.0020 \text{ M}$$

The change in concentration for O<sub>2</sub> is half the amount of SO<sub>3</sub> because 1 mol of O<sub>2</sub> reacts to form 2 moles of SO<sub>3</sub>. Substitute equilibrium concentrations into the equilibrium expression and solve for  $K_c$ .

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{[0.0020]^2}{[0.0020]^2 [0.0018]} = 555.5556 = \mathbf{5.6 \times 10^2}$$

The pressure of SO<sub>2</sub> is estimated using the concentration of SO<sub>2</sub> and the ideal gas law (although the ideal gas law is not well behaved at high pressures and temperatures).

$$P_{\text{SO}_2} = nRT / V = \frac{(0.0020 \text{ mol}) \left( 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (1000. \text{ K})}{(1.0 \text{ L})} = 0.1642 = \mathbf{0.16 \text{ atm}}$$

17.90 The original concentrations are:  $(0.350 \text{ mol} / 0.500 \text{ L}) = 0.700 \text{ M}$  for CO and Cl<sub>2</sub>.

Concentration (M)	CO(g) +	Cl <sub>2</sub> (g)	⇌	COCl <sub>2</sub> (g)
Initial	0.700	0.700		0
Change	- x	- x		+ x
Equilibrium	0.700 - x	0.700 - x		x

$$Q_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{[x]}{[0.700 - x][0.700 - x]} = \frac{[x]}{[0.490 - 1.400x + x^2]} = 4.95$$

$$4.95 x^2 - 7.93 x + 2.4255 = 0 \text{ (unrounded)}$$

$$a = 4.95 \quad b = -7.93 \quad c = 2.4255$$

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

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

$$x = 1.19039 \text{ or } 0.41162959 \text{ (unrounded)}$$

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

$$[\text{CO}] = [\text{Cl}_2] = 0.700 - 0.41162959 = 0.288370409 = \mathbf{0.288 \text{ M}}$$

$$[\text{COCl}_2] = x = \mathbf{0.412 \text{ M}}$$

17.91 The equilibrium constant for the reaction is  $K_p = P_{\text{CO}_2} = 0.220 \text{ atm}$

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.

$$\text{Moles CaCO}_3 = \text{moles CO}_2 = n = PV / RT$$

$$n = \frac{(0.220 \text{ atm})(10.0 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(385 \text{ K})} = 0.06960 \text{ mol CaCO}_3 \text{ lost (unrounded)}$$

$$0.100 \text{ mol CaCO}_3 - 0.06960 \text{ mol CaCO}_3$$

As more carbon dioxide gas is added, the system returns to equilibrium by converting the added carbon dioxide to calcium carbonate to maintain the partial pressure of carbon dioxide at 0.220 atm. Convert the added 0.300 atm of CO<sub>2</sub> to moles. The moles of CO<sub>2</sub> reacted equals the moles of CaCO<sub>3</sub> formed. Add to the moles of CaCO<sub>3</sub> at the first equilibrium position and convert to grams.

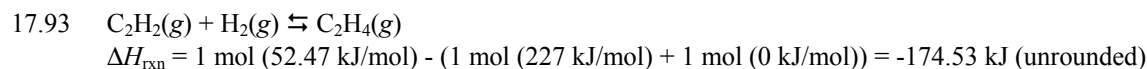
$$\text{Moles CaCO}_3 = \text{moles CO}_2 = n = PV / RT$$

$$n = \frac{(0.300 \text{ atm})(10.0 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(385 \text{ K})} = 0.09491 \text{ mol CaCO}_3 \text{ formed (unrounded)}$$

$$\text{Mass CaCO}_3 = [(0.100 - 0.06960 + 0.09491) \text{ mol CaCO}_3](100.09 \text{ g CaCO}_3 / \text{mol CaCO}_3) \\ = 12.542 = 12.5 \text{ g CaCO}_3$$

17.92 a)  $\text{C}_2\text{H}_4(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

b)  $4 \text{NO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g}) \rightleftharpoons 4 \text{NH}_3(\text{g}) + 7 \text{O}_2(\text{g})$



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

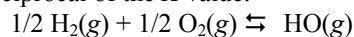
$$\ln \frac{K_{300}}{2.9 \times 10^8} = -\frac{(-174.53 \text{ kJ/mol})}{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)} \left( \frac{1}{300. \text{ K}} - \frac{1}{2000. \text{ K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right)$$

$$\ln \frac{K_{300}}{2.9 \times 10^8} = 59.478$$

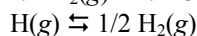
$$\frac{K_{300}}{2.9 \times 10^8} = 6.7759 \times 10^{25}$$

$$K_{300} = (2.9 \times 10^8) (6.7759 \times 10^{25}) = 1.9650 \times 10^{34} = \mathbf{2.0 \times 10^{34}}$$

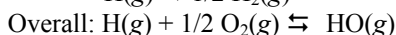
17.94 The first equation is in the correct form, but the second equation must be reversed. Reversing the equation leads to the reciprocal of the  $K$  value.



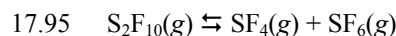
$$K_{c1} = 0.58$$



$$K'_{c2} = (K_{c2})^{-1} = 6.25 \times 10^2 \text{ (unrounded)}$$



$$K_{c(\text{overall})} = K_{c1} \times (K'_{c2})^{-1} = 362.5 = \mathbf{3.6 \times 10^2}$$



The reaction is described by the following equilibrium expression:

$$K_c = \frac{[\text{SF}_4][\text{SF}_6]}{[\text{S}_2\text{F}_{10}]}$$

At the first equilibrium,  $[\text{S}_2\text{F}_{10}] = 0.50 \text{ M}$  and  $[\text{SF}_4] = [\text{SF}_6] = x$ . Therefore, the concentrations of  $\text{SF}_4$  and  $\text{SF}_6$  can be expressed mathematically as

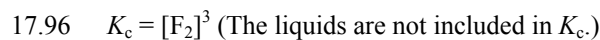
$$[\text{SF}_4] = [\text{SF}_6] = \sqrt{0.50K_c}$$

At the first equilibrium,  $[\text{S}_2\text{F}_{10}] = 2.5 \text{ M}$  and  $[\text{SF}_4] = [\text{SF}_6] = x$ . Therefore, the concentrations of  $\text{SF}_4$  and  $\text{SF}_6$  can be expressed mathematically as

$$[\text{SF}_4] = [\text{SF}_6] = \sqrt{2.5K_c}$$

Thus, the concentrations of  $\text{SF}_4$  and  $\text{SF}_6$  increase by a factor of

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



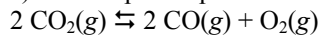
$$[\text{F}_2] = \sqrt[3]{2 \times 10^{-104}} = 2.7144 \times 10^{-35} = \mathbf{3 \times 10^{-35} \text{ M}}$$

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

$$P_{\text{CO}_2} = (10.0 \text{ mol CO}_2 / 61.0 \text{ mol gas}) (4.0 \text{ atm}) = 0.6557377 \text{ atm (unrounded)}$$

$$P_{\text{O}_2} = (1.00 \text{ mol O}_2 / 61.0 \text{ mol gas}) (4.0 \text{ atm}) = 0.06557377 \text{ atm (unrounded)}$$

a) Use the partial pressures and given  $K_p$  to find  $P_{\text{CO}}$ .



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

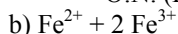
$$P_{\text{CO}} = 3.0299 \times 10^{-14} = \mathbf{3.0 \times 10^{-14} \text{ atm}}$$

b) Convert partial pressure to moles per liter using the ideal gas equation, and then convert moles of CO to grams.

$$n_{\text{CO}} / V = P / RT = \frac{(3.0299 \times 10^{-14} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(800 \text{ K})} = 4.6131 \times 10^{-16} \text{ mol/L (unrounded)}$$

$$(4.6131 \times 10^{-16} \text{ mol/L}) (28.01 \text{ g CO/mol CO}) (1 \text{ pg} / 10^{-12} \text{ g}) = 0.01292 = \mathbf{0.013 \text{ pg CO/L}}$$

17.98 a)  $3 \text{ O.N. (Fe)} + 4 \text{ O.N. (O)} = 0$   
 $3 \text{ O.N. (Fe)} + 4(-2) = 0$   
 $3 \text{ O.N. (Fe)} = 8$   
 $\text{O.N. (Fe)} = \mathbf{8/3}$



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

$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} = 5.1 = \frac{[4x]^4}{[0.050 - 4x]^4}$$

$$1.50277 = \frac{[4x]}{[0.050 - 4x]} \text{ (unrounded)}$$

$$x = (7.50553 \times 10^{-3} \text{ mol/L}) (1.0 \text{ L}) = 7.50553 \times 10^{-3} \text{ mol Fe}_3\text{O}_4 \text{ reacting (unrounded)}$$

$$\text{Mass Fe}_3\text{O}_4 = (7.50553 \times 10^{-3}) (231.55 \text{ g Fe}_3\text{O}_4 / 1 \text{ mol Fe}_3\text{O}_4) = 1.7494 = \mathbf{1.7 \text{ g Fe}_3\text{O}_4}$$

17.99 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  $\text{NH}_3$ , increases the temperature).

17.100 a) Write a reaction table given that  $P_{\text{CH}_4}(\text{init}) = P_{\text{CO}_2}(\text{init}) = 10.0 \text{ atm}$ , substitute equilibrium values into the equilibrium expression, and solve for  $P_{\text{H}_2}$ .

Pressure (atm)	$\text{CH}_4(\text{g})$	+	$\text{CO}_2(\text{g})$	$\rightleftharpoons$	$2 \text{ CO}(\text{g})$	+	$2 \text{ H}_2(\text{g})$
Initial	10.0		10.0		0		0
Change	- x		- x		+ 2 x		+ 2 x
Equilibrium	$10.0 - x$		$10.0 - x$		2 x		2 x

$$K_p = \frac{P_{\text{CO}}^2 P_{\text{H}_2}^2}{P_{\text{CH}_4} P_{\text{CO}_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 3.548 \times 10^6$$

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

A quadratic is necessary:

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

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

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

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

$$x = 9.796209 \text{ (unrounded)}$$

$$P(\text{hydrogen}) = 2x = 2(9.796209) = 19.592418 \text{ atm (unrounded)}$$

If the reaction proceeded entirely to completion, the partial pressure of  $\text{H}_2$  would be 20.0 atm (pressure is proportional to moles, and twice as many moles of  $\text{H}_2$  form for each mole of  $\text{CH}_4$  or  $\text{CO}_2$  that reacts).

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

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

$$K_p = \frac{P_{\text{CO}}^2 P_{\text{H}_2}^2}{P_{\text{CH}_4} P_{\text{CO}_2}} = \frac{(2x)^2 (2x)^2}{(10.0 - x)(10.0 - x)} = \frac{(2x)^4}{(10.0 - x)^2} = 2.626 \times 10^7$$

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

A quadratic is needed:

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

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

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

$$x = 9.923138 \text{ (unrounded)}$$

$$P(\text{hydrogen}) = 2x = 2(9.923138) = 19.846276 \text{ atm (unrounded)}$$

If the reaction proceeded entirely to completion, the partial pressure of  $\text{H}_2$  would be 20.0 atm (pressure is proportional to moles, and twice as many moles of  $\text{H}_2$  form for each mole of  $\text{CH}_4$  or  $\text{CO}_2$  that reacts).

The percent yield is  $(19.846276 \text{ atm} / 20.0 \text{ atm}) \times 100\% = 99.23138 = \mathbf{99.0\%}$ .

c) van't Hoff equation:

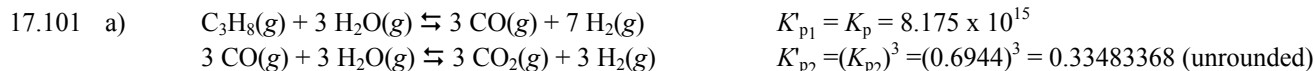
$$\ln \frac{K_{1200}}{K_{1300}} = -\frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

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

$$-2.0016628 = -\Delta H(7.710195 \times 10^{-6})$$

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

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



(Overall):  $\text{C}_3\text{H}_8(\text{g}) + 6 \text{H}_2\text{O}(\text{g}) \rightleftharpoons 3 \text{CO}_2(\text{g}) + 10 \text{H}_2(\text{g})$

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

c)  $K_p = \frac{(P_{\text{CO}_2})^3 (P_{\text{H}_2})^{10}}{(P_{\text{C}_3\text{H}_8})(P_{\text{H}_2\text{O}})^6}$

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

$$P_{\text{C}_3\text{H}_8(\text{initial})} = (1.00 / 5.00) \times 5.0 \text{ atm} = 1.0 \text{ atm} \quad 1.0 \text{ atm} / 1 = 1.0$$

$$P_{\text{H}_2\text{O}(\text{initial})} = (4.00 / 5.00) \times 5.0 \text{ atm} = 4.0 \text{ atm} \quad 4.0 \text{ atm} / 6 = 0.67 = \text{limiting reactant.}$$

$$P_{\text{CO}_2(\text{formed})} = 4.0 \text{ atm} \times (3 \text{ mol CO}_2 / 6 \text{ mol H}_2\text{O}) = 2.0 \text{ atm}$$

$$P_{\text{H}_2(\text{formed})} = 4.0 \text{ atm} \times (10 \text{ mol H}_2 / 6 \text{ mol H}_2\text{O}) = 6.6667 \text{ atm (unrounded)}$$

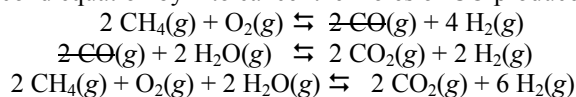
$$P_{\text{C}_3\text{H}_8(\text{remaining})} = 1.0 \text{ atm} - [4.0 \text{ atm} \times (1 \text{ mol C}_3\text{H}_8 / 6 \text{ mol H}_2\text{O})] = 0.3333 \text{ atm (unrounded)}$$

$$P_{\text{H}_2\text{O}(\text{remaining})} = 0.00 \text{ atm (limiting reactant)}$$

$$P_{\text{Total}} = P_{\text{CO}_2} + P_{\text{H}_2} + P_{\text{C}_3\text{H}_8} + P_{\text{H}_2\text{O}} = 2.0 \text{ atm} + 6.6667 \text{ atm} + 0.3333 \text{ atm} + 0.00 \text{ atm} = \mathbf{9.0 \text{ atm}}$$

d) Percent  $\text{C}_3\text{H}_8(\text{unreacted}) = [0.3333 \text{ atm} / 1.0 \text{ atm}] \times 100\% = 33.33\% = \mathbf{30\%}$

17.102 a) Multiply the second equation by 2 to cancel the moles of CO produced in the first reaction.



b)  $K_p = (9.34 \times 10^{28})(1.374)^2 = 1.763276 \times 10^{29} = \mathbf{1.76 \times 10^{29}}$

c)  $\Delta n = 8 - 5 = 3$

$$K_c = (1.763276 \times 10^{29}) / [(0.0821 \text{ atm}\cdot\text{L/mol}\cdot\text{K})(1000 \text{ K})]^3 = 3.18633 \times 10^{23} = \mathbf{3.19 \times 10^{23}}$$

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

Total mol of gas initial = 2.0 mol CH<sub>4</sub> + 1.0 mol O<sub>2</sub> + 2.0 mol H<sub>2</sub>O = 5.0 mol

Total mol of gas final = 2.0 mol CO<sub>2</sub> + 6.0 mol H<sub>2</sub> = 8.0 mol

$P_{\text{final}} = (30. \text{ atm})(8.0 \text{ mol} / 5.0 \text{ mol}) = \mathbf{48 \text{ atm}}$

17.103  $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$

$P_{\text{NH}_3} = (41.49\% / 100\%)(110. \text{ atm}) = 45.639 \text{ atm}$  (unrounded)

$100.00\% - 41.49\% = 58.51\% \text{ N}_2 + \text{H}_2$

$P_{\text{H}_2} + P_{\text{N}_2} = (58.51\% / 100\%)(110. \text{ atm}) = 64.361 \text{ atm}$  (unrounded)

$P_{\text{H}_2} = (3/4)(64.361 \text{ atm}) = 48.27075 \text{ atm}$  (unrounded)

$P_{\text{N}_2} = (1/4)(64.361 \text{ atm}) = 16.09025 \text{ atm}$  (unrounded)

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3 (P_{\text{N}_2})} = \frac{(45.639)^2}{(48.27075)^3 (16.09025)} = 1.15095 \times 10^{-3} = \mathbf{1.15 \times 10^{-3}}$$

17.104 a) Careful reading of the problem indicates that the given  $K_p$  occurs at 1000. K and that the initial pressure of N<sub>2</sub> is 200. atm. Solve the equilibrium expression for  $P_N$ , assuming that  $P_{\text{N}_2}(\text{eq}) = 200. - x$  is about 200.

$$K_p = \frac{(P_N)^2}{(P_{\text{N}_2})} = 10^{-43.10}$$

The exponent, two digits past the decimal point, limits the significant figures.

$$P_N = \sqrt{(200.)10^{-43.10}} = 3.985795 \times 10^{-21} = \mathbf{4.0 \times 10^{-21} \text{ atm}}$$

b)  $K_p = \frac{(P_H)^2}{(P_{\text{H}_2})} = 10^{-17.30}$

The exponent, two digits past the decimal point, limits the significant figures.

$$P_H = \sqrt{(600.)10^{-17.30}} = 5.48372 \times 10^{-8} = \mathbf{5.5 \times 10^{-8} \text{ atm}}$$

c) Convert pressures to moles using the ideal gas law. Convert moles to atoms using Avogadro's number.

$$\begin{aligned} \text{Moles N / L} = P / RT &= \frac{(3.985795 \times 10^{-21} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(1000. \text{K})} \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}}\right) \\ &= 29.2356 = \mathbf{29 \text{ N atoms/L}} \end{aligned}$$

$$\begin{aligned} \text{Moles H / L} = P / RT &= \frac{(5.48372 \times 10^{-8} \text{ atm})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(1000. \text{K})} \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\text{mol}}\right) \\ &= 4.022 \times 10^{14} = \mathbf{4.0 \times 10^{14} \text{ H atoms/L}} \end{aligned}$$

d) The more reasonable step is  $\text{N}_2(\text{g}) + \text{H}(\text{g}) \rightarrow \text{NH}(\text{g}) + \text{N}(\text{g})$ . With only 29 N atoms in 1.0 L, the first reaction would produce virtually no NH(g) molecules. There are orders of magnitude, more N<sub>2</sub> molecules than N atoms, so the second reaction is the more reasonable step.

17.105 a) Since the volume is 1.00 L, the molarity equal the number of moles present.

	$2 \text{ NH}_3(\text{g})$	$\rightleftharpoons$	$\text{N}_2(\text{g})$	+	$3 \text{ H}_2(\text{g})$
Initial	0		1.30		1.65
Change	+2 x		-x		-3 x
Equilibrium	$2 x = 0.100 \text{ M}$		$1.30 - x$		$1.65 - 3 x$

$$x = 0.0500 \text{ mol}$$

$$[\text{N}_2]_{\text{eq}} = (1.30 - 0.0500) \text{ M} = \mathbf{1.25 \text{ M N}_2}$$

$$[\text{H}_2]_{\text{eq}} = [1.65 - 3(0.0500)] \text{ M} = \mathbf{1.50 \text{ M H}_2}$$

$$K_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{[1.25][1.50]^3}{[0.100]^2} = 421.875 = \mathbf{422}$$

$$\text{b) } K_c = \frac{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}{[\text{NH}_3]} = \frac{[1.50]^{1/2}[1.25]^{3/2}}{[8.34 \times 10^{-2}]} = 20.523177 = \mathbf{20.5}$$

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

17.106 a)  $3 \text{ H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{ NH}_3(\text{g})$

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = 1.00 \times 10^{-4}$$

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

$$x = 31.02016 = \mathbf{31 \text{ atm N}_2}$$

$$3x = 3(31.02016) = 93.06048 = \mathbf{93 \text{ atm H}_2}$$

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (31.02016 \text{ atm}) + (93.06048 \text{ atm}) + (50. \text{ atm}) \\ = 174.08064 = \mathbf{174 \text{ atm total}}$$

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

$$x = 18.44 = \mathbf{18 \text{ atm N}_2}$$

$$6x = 6(18.44) = 110.64 = \mathbf{111 \text{ atm H}_2}$$

$$P_{\text{total}} = P_{\text{nitrogen}} + P_{\text{hydrogen}} + P_{\text{ammonia}} = (18.44 \text{ atm}) + (110.64 \text{ atm}) + (50. \text{ atm}) \\ = 179.09 = \mathbf{179 \text{ atm total}}$$

This is not a valid argument. The total pressure in (b) is greater than in (a) to produce the same amount of  $\text{NH}_3$ .

17.107 The equilibrium equation is:  $2 \text{ CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{ CO}_2(\text{g})$

a)	$2 \text{ CO}(\text{g})$	+	$\text{O}_2(\text{g})$	$\rightleftharpoons$	$2 \text{ CO}_2(\text{g})$
Initial	0 atm		0 atm		1.00 atm
Change	+2 x		+x		-2 x
Equilibrium	+2 x		x		$1.00 - 2 x$

$$K_p = \frac{(P_{\text{CO}_2})^2}{(P_{\text{CO}})^2(P_{\text{O}_2})} = 1.00 \times 10^{22}$$

$$\frac{(1.00 - 2x)^2}{(2x)^2(x)} = 1.00 \times 10^{22} \text{ Assume } x \text{ is small compared to } 1.00.$$

$$\frac{(1.00)^2}{(2x)^2(x)} = 1.00 \times 10^{22}$$

$$x = 2.9240 \times 10^{-8} \quad (\text{unrounded}) \quad \text{The assumption is justified.}$$

$$P_{\text{CO}} = 2x = 2(2.9240 \times 10^{-8}) = 5.848 \times 10^{-8} = \mathbf{5.85 \times 10^{-8} \text{ atm}}$$

b) Since  $x$  is so small,  $P_{\text{total}}$  is the carbon dioxide pressure (**1.00 atm**).

c) Set up a new table:

	$2 \text{ CO(g)}$	+	$\text{O}_2\text{(g)}$	$\rightleftharpoons$	$2 \text{ CO}_2\text{(g)}$
Initial	0 atm		0 atm		1.00 atm
Change	+ 2 $x$		+ $x$		- 2 $x$
Equilibrium	+ 2 $x$		$x$		1.00 - 2 $x$

$$2x = (35\% / 100\%) = 0.35$$

$$x = 0.175 \text{ (unrounded)}$$

$$K_p = \frac{(P_{\text{CO}_2})^2}{(P_{\text{CO}})^2 (P_{\text{O}_2})}$$

$$\frac{(1.00 - 2x)^2}{(2x)^2 (x)} = \frac{(1.00 - 2(0.175))^2}{(2(0.175))^2 (0.175)} = 19.70845 = \mathbf{2.0 \times 10^1}$$

d)  $P = (1.00 - 2x) + (2x) + (x) = 1.00 + x = 1.00 + 0.175 = 1.175 = \mathbf{1.18 \text{ atm}}$

e)  $K$  decreases as the temperature increases. The process is **exothermic**.

17.108 a) Equilibrium partial pressures for the reactants, nitrogen and oxygen, can be assumed to equal their initial partial pressures because the equilibrium constant is so small that very little nitrogen and oxygen will react to form nitrogen monoxide. After calculating the equilibrium partial pressure of nitrogen monoxide, test this assumption by comparing the partial pressure of nitrogen monoxide with that of nitrogen and oxygen.

$$P_{\text{nitrogen (equilibrium)}} = (0.780 - x) \text{ atm}$$

$$P_{\text{oxygen (equilibrium)}} = (0.210 - x) \text{ atm}$$

$$P_{\text{NO (equilibrium)}} = 2x \text{ atm}$$

$$K_p = \frac{(P_{\text{NO}})^2}{(P_{\text{N}_2})(P_{\text{O}_2})} = 4.35 \times 10^{-31}$$

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

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

$$x = 1.33466 \times 10^{-16} \text{ (unrounded)}$$

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.

$$P_{\text{nitrogen (equilibrium)}} = (0.780 - 1.33466 \times 10^{-16}) \text{ atm} = \mathbf{0.780 \text{ atm N}_2}$$

$$P_{\text{oxygen (equilibrium)}} = (0.210 - 1.33466 \times 10^{-16}) \text{ atm} = \mathbf{0.210 \text{ atm O}_2}$$

$$P_{\text{NO (equilibrium)}} = 2(1.33466 \times 10^{-16}) \text{ atm} = 2.66932 \times 10^{-16} = \mathbf{2.67 \times 10^{-16} \text{ atm NO}}$$

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

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

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

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

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

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

$$K_c = \frac{(1.3 \times 10^4)}{[(0.0821)(457)]^{-1}} = 4.877561 \times 10^5 = \mathbf{4.9 \times 10^5}$$



$$\begin{aligned} \text{b) } \Delta H^\circ_{\text{rxn}} &= \sum[\Delta H^\circ_f(\text{products})] - \sum[\Delta H^\circ_f(\text{reactants})] \\ \Delta H^\circ_{\text{rxn}} &= 2 \Delta H^\circ_f[\text{NO}_2(\text{g})] - 2 \Delta H^\circ_f[\text{NO}(\text{g})] - \Delta H^\circ_f[\text{O}_2(\text{g})] \\ &= 2 \text{ mol } (33.2 \text{ kJ/mol}) - 2 \text{ mol } (90.29 \text{ kJ/mol}) - (0.0) \\ &= -114.18 = \mathbf{-114.2 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \text{c) } \ln \frac{K_2}{K_1} &= -\frac{\Delta H^\circ_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \frac{6.4 \times 10^9}{4.877561 \times 10^5} &= -\frac{-114.18 \text{ kJ}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{T_2} - \frac{1}{457 \text{ K}} \right) \left( \frac{10^3 \text{ J}}{1 \text{ kJ}} \right) \\ T_2 &= 347.389 = \mathbf{3.5 \times 10^2 \text{ K}} \end{aligned}$$

17.110 a) Use the equation  $K_p = K_c(RT)^{\Delta n}$   $\Delta n = 0$

$$K_p = K_c(RT) = K_c = \mathbf{1.26 \times 10^{-3}}$$

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

$$K_c' = 1 / K_c = 1 / (1.26 \times 10^{-3}) = 793.65 = \mathbf{794}$$

$$\begin{aligned} \text{c) } \Delta H^\circ_{\text{rxn}} &= \sum[\Delta H^\circ_f(\text{products})] - \sum[\Delta H^\circ_f(\text{reactants})] \\ \Delta H^\circ_{\text{rxn}} &= \Delta H^\circ_f[\text{H}_2(\text{g})] + \Delta H^\circ_f[\text{I}_2(\text{g})] - 2 \Delta H^\circ_f[\text{HI}(\text{g})] \\ &= 1 \text{ mol } (0 \text{ kJ/mol}) - 1 \text{ mol } (0 \text{ kJ/mol}) - 2 \text{ mol } (25.9 \text{ kJ/mol}) \\ &= \mathbf{-51.8 \text{ kJ}} \end{aligned}$$

$$\begin{aligned} \text{d) } \ln \frac{K_2}{K_1} &= -\frac{\Delta H^\circ_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ \ln \frac{2.0 \times 10^{-2}}{1.26 \times 10^{-3}} &= -\frac{\Delta H^\circ_{\text{rxn}}}{8.314 \text{ J/mol} \cdot \text{K}} \left( \frac{1}{729 \text{ K}} - \frac{1}{298 \text{ K}} \right) \\ \Delta H^\circ_{\text{rxn}} &= 1.1585 \times 10^4 = \mathbf{1.2 \times 10^4 \text{ J/mol}} \end{aligned}$$



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 toward the products.

17.112 a) The enzyme that inhibits F is the one that catalyzes the reaction that produces F. The enzyme is number **5** that catalyzed the reaction from E to F.

b) Enzyme **8** 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.

17.113 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  $[\text{H}_2\text{S}] = 0.600$ , and  $[\text{H}_2] = [\text{S}_2] = 0$

	$\text{H}_2\text{S}(\text{g})$	$\rightleftharpoons$	$2 \text{ H}_2(\text{g})$	+	$\text{S}_2(\text{g})$
Initial	0.600 M		0 M		0 M
Change	-2 x		+2 x		+x
Equilibrium	0.600 - 2 x		+2 x		+x

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = 9.0 \times 10^{-8}$$

$$\frac{[2x]^2 [x]}{[0.600 - 2x]^2} = 9.0 \times 10^{-8} \text{ Assume } 2x \text{ is small compared to } 0.600 \text{ M.}$$

$$\frac{[2x]^2 [x]}{[0.600]^2} = 9.0 \times 10^{-8}$$

$x = 2.008 \times 10^{-3}$  (unrounded) assumption justified

$$[\text{H}_2\text{S}] = 0.600 - 2x = 0.600 - 2(2.008 \times 10^{-3}) = 0.595984 = \mathbf{0.596 \text{ M H}_2\text{S}}$$

$$[\text{H}_2] = 2x = 2(2.008 \times 10^{-3}) = 4.016 \times 10^{-3} = \mathbf{4.0 \times 10^{-3} \text{ M H}_2}$$

$$[\text{S}_2] = x = 2.008 \times 10^{-3} = \mathbf{2.0 \times 10^{-3} \text{ M S}_2}$$

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

$$P_{\text{H}_2\text{O}} = \sqrt[10]{4.08 \times 10^{-25}} = 3.6397 \times 10^{-3} = \mathbf{3.64 \times 10^{-3} \text{ atm}}$$

- b)
- (1) Adding more  $\text{Na}_2\text{SO}_4(\text{s})$  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 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  $\text{N}_2$  gas will not change the partial pressure of the water vapor, so the ratio of hydrated form/anhydrous form will not change.

17.115 The reaction is:  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$

a) Set up a table with the initial CO and initial  $\text{H}_2 = 0.100 \text{ mol} / 20.00 \text{ L} = 0.00500 \text{ M}$ .

	CO	$\text{H}_2\text{O}$	$\text{CO}_2$	$\text{H}_2$
Initial	0.00500 M	0.00500 M	0	0
Change	-x	-x	+x	+x
Equilibrium	0.00500 - x	0.00500 - x	x	x

$$[\text{CO}]_{\text{equilibrium}} = 0.00500 - x = 2.24 \times 10^{-3} \text{ M} = [\text{H}_2\text{O}]$$

$$x = 0.00276 \text{ M} = [\text{CO}_2] = [\text{H}_2]$$

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.00276][0.00276]}{[0.00224][0.00224]} = 1.518176 = \mathbf{1.52}$$

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

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

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

c) Initially, an equal number of moles must be added = **0.2000 mol CO**

d) Set up a table with the initial concentrations equal to the final concentrations from part (a), and then add 0.2000 mol CO / 20.00 L = 0.01000 M to compensate for the added CO.

	CO	$\text{H}_2\text{O}$	$\text{CO}_2$	$\text{H}_2$
Initial	0.00224 M	0.00224 M	0.00276 M	0.00276 M
Added CO	0.01000 M			
Change	-x	-x	+x	+x
Equilibrium	0.01224 - x	0.00224 - x	0.00276 + x	0.00276 + x

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{[0.00276 + x][0.00276 + x]}{[0.01224 - x][0.00224 - x]} = 0.9625638$$

$$\frac{[7.6176 \times 10^{-6} + 5.52 \times 10^{-3}x + x^2]}{2.74176 \times 10^{-5} - 1.448 \times 10^{-2}x + x^2} = 0.9625638$$

$$7.6176 \times 10^{-6} + 5.52 \times 10^{-3}x + x^2 = (0.9625638)(2.74176 \times 10^{-5} - 1.448 \times 10^{-2}x + x^2)$$

$$7.6176 \times 10^{-6} + 5.52 \times 10^{-3}x + x^2 = 2.6391189 \times 10^{-5} - 1.3937923 \times 10^{-2}x + 0.9625638x^2$$

$$0.0374362x^2 + 1.9457923 \times 10^{-2}x - 1.8773589 \times 10^{-5} = 0$$

$$a = 0.0374362 \quad b = 1.9457923 \times 10^{-2} \quad c = -1.8773589 \times 10^{-5}$$

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

$$x = \frac{-(1.9457923 \times 10^{-2}) \pm \sqrt{(1.9457923 \times 10^{-2})^2 - 4(0.0374362)(-1.8773589 \times 10^{-5})}}{2(0.0374362)}$$

$$x = 9.6304567 \times 10^{-4} \text{ (unrounded)}$$

$$[\text{CO}] = 0.01224 - x = 0.01224 - (9.6304567 \times 10^{-4}) = 0.011276954 = \mathbf{0.01128 \text{ M}}$$

- 17.116 a) At point A the sign of  $\Delta H^\circ$  is negative for the reaction graphite  $\rightarrow$  diamond. An increase in temperature at constant pressure will cause the formation of more graphite. Therefore, the equation must look like this: graphite  $\rightarrow$  diamond + heat, and adding heat shifts the equilibrium to the reactant side.
- b) Diamond is denser than graphite. The slope of the diamond-graphite line is positive. An increase in pressure favors the formation of diamond.