CHAPTER 6

CHEMICAL EQUILIBRIUM

Characteristics of Chemical Equilibrium

10. $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g) \quad K = \frac{[H_2][CO_2]}{[H_2O][CO]} = 2.0$

K is a unitless number because there is an equal number of moles of product gases as moles of reactant gases in the balanced equation. Therefore, we can use units of molecules per liter instead of moles per liter to determine K.

We need to start somewhere, so let's assume 3 molecules of CO react. If 3 molecules of CO react, then 3 molecules of H_2O must react, and 3 molecules each of H_2 and CO_2 are formed. We would have 6 – 3 = 3 molecules of CO, 8 – 3 = 5 molecules of H_2O, 0 + 3 = 3 molecules of H_2, and 0 + 3 = 3 molecules of CO_2 present. This will be an equilibrium mixture if K = 2.0:

$$K = \frac{\left(\frac{3\text{ molecules } H_2}{L}\right)\left(\frac{3\text{ molecules } CO_2}{L}\right)}{\left(\frac{5\text{ molecules } H_2O}{L}\right)\left(\frac{3\text{ molecules } CO}{L}\right)} = \frac{3}{5}$$

Because this mixture does not give a value of K = 2.0, this is not an equilibrium mixture. Let's try 4 molecules of CO reacting to reach equilibrium.

Molecules CO remaining = 6 – 4 = 2 molecules of CO
Molecules H_2O remaining = 8 – 4 = 4 molecules of H_2O
Molecules H_2 present = 0 + 4 = 4 molecules of H_2
Molecules CO_2 present = 0 + 4 = 4 molecules of CO_2

$$K = \frac{\left(\frac{4\text{ molecules } H_2}{L}\right)\left(\frac{4\text{ molecules } CO_2}{L}\right)}{\left(\frac{4\text{ molecules } H_2O}{L}\right)\left(\frac{2\text{ molecules } CO}{L}\right)} = 2.0$$

Because K = 2.0 for this reaction mixture, we are at equilibrium.

11. When equilibrium is reached, there is no net change in the amount of reactants and products present because the rates of the forward and reverse reactions are equal to each other. The first diagram has 4 A_2B molecules, 2 A_2 molecules, and 1 B_2 molecule present. The second diagram has 2 A_2B molecules, 4 A_2 molecules, and 2 B_2 molecules. Therefore, the first diagram cannot represent equilibrium because there was a net change in reactants and products. Is the second diagram the equilibrium mixture? That depends on whether there is a net change between reactants and products when going from the second diagram to the third diagram. The third diagram contains the same number and type of molecules as the second diagram, so the second diagram is the first illustration that represents equilibrium.

The reaction container initially contained only A_2B. From the first diagram, 2 A_2 molecules and 1 B_2 molecule are present (along with 4 A_2B molecules). From the balanced reaction, these 2 A_2 molecules and 1 B_2 molecule were formed when 2 A_2B molecules decomposed. Therefore, the initial number of A_2B molecules present equals 4 + 2 = 6 molecules A_2B.

12. No, equilibrium is a dynamic process. Both reactions

$$H_2O + CO \rightarrow H_2 + CO_2 \quad \text{and} \quad H_2 + CO_2 \rightarrow H_2O + CO$$

are occurring at equal rates. Thus ^{14}C atoms will be distributed between CO and CO_2.

13. No, it doesn't matter which direction the equilibrium position is reached. Both experiments will give the same equilibrium position because both experiments started with stoichiometric amounts of reactants or products.

14. a. This experiment starts with only H_2 and N_2, and no NH_3 present. From the initial mixture diagram, there is three times as many H_2 as N_2 molecules. So the green line, at the highest initial concentration is the H_2 plot, the blue line is the N_2 plot, and the pink line, which has an initial concentration of zero, is the NH_3 plot.

b. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; when a reaction starts with only reactants present initially, the reactant concentrations decrease with time while the product concentrations increase with time. This is seen in the various plots. Also notice that the H_2 concentration initially decreases more rapidly as compared to the initial decrease in N_2 concentration. This is due to the stoichiometry in the balanced equation, which dictates that for every 1 molecule of N_2 that reacts, 3 molecules of H_2 must also react. One would expect the NH_3 plot to initially increase faster than the N_2 plot decreases (due to the 2 : 1 mole ratio in the balanced equation), and for the H_2 plot to initially decrease faster than the NH_3 plot increases (due to the 3 : 2 mole ratio). This is seen in the various plots.

c. Equilibrium is reached when the rate of the forward reaction equals the rate of the reverse reaction. At this time, there is no net change in any of the reactant and product concentrations; so the various plots indicate equilibrium has been reached when their concentrations no longer change with time (when the plots reach a plateau).

15. $2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g) \quad K = 1.6 \times 10^{-5}$

The expression for K is the product concentrations divided by the reactant concentrations. When K has a value much less than one, the product concentrations are relatively small, and the reactant concentrations are relatively large.

$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g) \quad K = 1 \times 10^{31}$

When K has a value much greater than one, the product concentrations are relatively large, and the reactant concentrations are relatively small. In both cases, however, the rate of the forward reaction equals the rate of the reverse reaction at equilibrium (this is a definition of equilibrium).

The Equilibrium Constant

16. When reactants and products are all in the same phase, these are homogeneous equilibria. Heterogeneous equilibria involve more than one phase. In general, for a homogeneous gas-phase equilibrium, all reactants and products are included in the K expression. In heterogeneous equilibria, equilibrium does not depend on the amounts of pure solids or liquids present. The amounts of solids and liquids present are not included in K expressions; they just have to be present. On the other hand, gases and solutes are always included in K expressions. Solutes have (aq) written after them.

17. K and K_p are equilibrium constants as determined by the law of mass action. For K, concentration units of mol/L are used, and for K_p, partial pressures in units of atm are used (generally). Q is called the reaction quotient. Q has the exact same form as K or K_p, but instead of equilibrium concentrations, initial concentrations are used to calculate the Q value. We use Q to determine if a reaction is at equilibrium. When Q = K (or when $Q_p = K_p$), the reaction is at equilibrium. When $Q \neq K$, the reaction is not at equilibrium, and one can deduce the net change that must occur for the system to get to equilibrium.

18. The equilibrium constant is a number that tells us the relative concentrations (pressures) of reactants and products at equilibrium. An equilibrium position is a set of concentrations that satisfies the equilibrium constant expression. More than one equilibrium position can satisfy the same equilibrium constant expression.

    Table 6.1 of the text illustrates this nicely. Each of the three experiments in Table 6.1 has different equilibrium positions; that is, each experiment has different equilibrium concentrations. However, when these equilibrium concentrations are inserted into the equilibrium constant expression, each experiment gives the same value for K. The equilibrium position depends on the initial concentrations one starts with. Since there are an infinite number of initial conditions, there are an infinite number of equilibrium positions. However, each of these infinite equilibrium positions will always give the same value for the equilibrium constant (assuming temperature is constant).

19. Solids and liquids do not appear in equilibrium expressions. Only gases and dissolved solutes appear in equilibrium expressions.

    a. $K = \frac{[H_2O]}{[NH_3]^2[CO_2]}; \quad K_p = \frac{P_{H_2O}}{P_{NH_3}^2 \times P_{CO_2}}$

    b. $K = [N_2][Br_2]^3; \quad K_p = P_{N_2} \times P_{Br_2}^3$

    c. $K = [O_2]^3; \quad K_p = P_{O_2}^3$

    d. $K = \frac{[H_2O]}{[H_2]}; \quad K_p = \frac{P_{H_2O}}{P_{H_2}}$

20. $K_p = K(RT)^{\Delta n}$, where Δn equals the difference in the sum of the coefficients between gaseous products and gaseous reactants (Δn = mol gaseous products – mol gaseous reactants). When Δn = 0, then $K_p = K$. In Exercise 19, only reaction d has Δn = 0, so only reaction d has $K_p = K$.

21. $K_p = K(RT)^{\Delta n}$, where Δn = sum of gaseous product coefficients – sum of gaseous reactant coefficients. For this reaction, Δn = 3 – 1 = 2.

$$K = \frac{[CO][H_2]^2}{[CH_3OH]} = \frac{(0.24)(1.1)^2}{(0.15)} = 1.9$$

$$K_p = K(RT)^2 = 1.9(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 600.\text{ K})^2 = 4.6 \times 10^3$$

22. $H_2(g) + Br_2(g) \rightleftharpoons 2\ HBr(g) \quad K_p = \frac{P_{HBr}^2}{(P_{H_2})(P_{Br_2})} = 3.5 \times 10^4$

a. $HBr \rightleftharpoons 1/2\ H_2 + 1/2\ Br_2 \quad K_p^{'} = \frac{(P_{H_2})^{1/2}(P_{Br_2})^{1/2}}{P_{HBr}} = \left(\frac{1}{K_p}\right)^{1/2} = \left(\frac{1}{3.5 \times 10^4}\right)^{1/2}$

$= 5.3 \times 10^{-3}$

b. $2\ HBr \rightleftharpoons H_2 + Br_2 \quad K_p^{''} = \frac{(P_{H_2})(P_{Br_2})}{P_{HBr}^2} = \frac{1}{K_p} = \frac{1}{3.5 \times 10^4} = 2.9 \times 10^{-5}$

c. $1/2\ H_2 + 1/2\ Br_2 \rightleftharpoons HBr \quad K_p^{'''} = \frac{P_{HBr}}{(P_{H_2})^{1/2}(P_{Br_2})^{1/2}} = (K_p)^{1/2} = 190$

23. $[N_2O] = \frac{2.00 \times 10^{-2}\text{ mol}}{2.00\text{ L}}$; $[N_2] = \frac{2.80 \times 10^{-4}\text{ mol}}{2.00\text{ L}}$; $[O_2] = \frac{2.50 \times 10^{-5}\text{ mol}}{2.00\text{ L}}$

$$K = \frac{[N_2O]^2}{[N_2]^2[O_2]} = \frac{\left(\frac{2.00 \times 10^{-2}}{2.00}\right)^2}{\left(\frac{2.80 \times 10^{-4}}{2.00}\right)^2\left(\frac{2.50 \times 10^{-5}}{2.00}\right)} = \frac{(1.00 \times 10^{-2})^2}{(1.40 \times 10^{-4})^2(1.25 \times 10^{-5})}$$

$= 4.08 \times 10^8$

If the given concentrations represent equilibrium concentrations, then they should give a value of $K = 4.08 \times 10^8$.

$$\frac{(0.200)^2}{(2.00 \times 10^{-4})^2(0.00245)} = 4.08 \times 10^8$$

Because the given concentrations when plugged into the equilibrium constant expression give a value equal to K (4.08×10^8), this set of concentrations is a system at equilibrium

24. $K_p = K(RT)^{\Delta n}$, $K = \dfrac{K_p}{(RT)^{\Delta n}}$; $\Delta n = 2 - 3 = -1$; $K = \dfrac{0.25}{(0.08206 \times 1100)^{-1}} = 23$

25. $[NO] = \dfrac{4.5 \times 10^{-3}\text{ mol}}{3.0\text{ L}} = 1.5 \times 10^{-3}\,M$; $[Cl_2] = \dfrac{2.4\text{ mol}}{3.0\text{ L}} = 0.80\,M$

$$[NOCl] = \frac{1.0\text{ mol}}{3.0\text{ L}} = 0.33\,M; \quad K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(1.5 \times 10^{-3})^2(0.80)}{(0.33)^2} = 1.7 \times 10^{-5}$$

26. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$; with only reactants present initially, the net change that must occur to reach equilibrium is a conversion of reactants into products. At constant volume and temperature, $n \propto P$. Thus if x atm of N_2 reacts to reach equilibrium, then $3x$ atm of H_2 must also react to form $2x$ atm of NH_3 (from the balanced equation). Let's summarize the problem in a table that lists what is present initially, what change in terms of x that occurs to reach equilibrium, and what is present at equilibrium (initial + change). This table is typically called an ICE table for *i*nitial, *c*hange, and *e*quilibrium.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

	$N_2(g)$	$3\,H_2(g)$		$2\,NH_3(g)$
Initial	1.00 atm	2.00 atm		0
	x atm of N_2 reacts to reach equilibrium			
Change	$-x$	$-3x$	→	$+2x$
Equil.	$1.00 - x$	$2.00 - 3x$		$2x$

From the setup: $P_{total} = 2.00\text{ atm} = P_{N_2} + P_{H_2} + P_{NH_3}$

$$2.00\text{ atm} = (1.00 - x) + (2.00 - 3x) + 2x = 3.00 - 2x, \quad x = 0.500\text{ atm}$$

$$P_{H_2} = 2.00 - 3x = 2.00 - 3(0.500) = 0.50\text{ atm}$$

$$K_p = \frac{(2x)^2}{(1.00 - x)(2.00 - 3x)^3} = \frac{[2(0.500)]^2}{(1.00 - 0.500)[2.00 - 3(0.500)]^3} = \frac{(1.00)^2}{(0.50)(0.50)^3} = 16$$

27. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \quad K_p = \dfrac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$

To determine K_p, we must determine the equilibrium partial pressures of each gas. Initially, $P_{PCl_5} = 0.50$ atm and $P_{PCl_3} = P_{Cl_2} = 0$ atm. To reach equilibrium, some of the PCl_5 reacts to produce some PCl_3 and Cl_2, all in a 1 : 1 mole ratio. We must determine the change in partial pressures necessary to reach equilibrium. Because moles $\propto$ P at constant V and T, if we let x = atm of PCl_5 that reacts to reach equilibrium, this will produce x atm of PCl_3 and x atm of Cl_2 at equilibrium. The equilibrium partial pressures of each gas will be the initial partial pressure of each gas plus the change necessary to reach equilibrium. The equilibrium partial pressures are:

P_{PCl_5} = 0.50 atm – x, $P_{PCl_3} = P_{Cl_2} = x$

Now we solve for x using the information in the problem:

$P_{total} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2}$, 0.84 atm = 0.50 – $x + x + x$, 0.84 atm = 0.50 + x,

x = 0.34 atm

The equilibrium partial pressures are:

P_{PCl_5} = 0.50 – 0.34 = 0.16 atm, $P_{PCl_3} = P_{Cl_2}$ = 0.34 atm

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{(0.34)(0.34)}{(0.16)} = 0.72$$

$$K = \frac{K_p}{(RT)^{\Delta n}},\ \Delta n = 2 - 1 = 1;\ K_p = \frac{0.72}{(0.08206)(523)} = 0.017$$

28. $$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}} = \frac{(3.1 \times 10^{-2})^2}{(0.85)(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

$$\frac{(0.167)^2}{(0.525)(0.00761)^3} = 1.21 \times 10^3$$

When the given partial pressures in atmospheres are plugged into the K_p expression, the value does not equal the K_p value of 3.8 × 10^4. Therefore, one can conclude that the given set of partial pressures does not represent a system at equilibrium.

29. $K_p = \dfrac{P^4_{H_2}}{P^4_{H_2O}}$; $P_{total} = P_{H_2O} + P_{H_2}$, 36.3 torr = 15.0 torr + P_{H_2}, P_{H_2} = 21.3 torr

Because l atm = 760 torr: $$K_p = \frac{\left(21.3\ \text{torr} \times \dfrac{1\ \text{atm}}{760\ \text{torr}}\right)^4}{\left(15.0\ \text{torr} \times \dfrac{1\ \text{atm}}{760\ \text{torr}}\right)^4} = 4.07$$

Note: Solids and pure liquids are not included in K expressions.

30. $S_8(g) \rightleftharpoons 4\ S_2(g)$ $\quad K_p = \dfrac{P^4_{S_2}}{P_{S_8}}$

Initially: P_{S_8} = 1.00 atm and P_{S_2} = 0 atm

Change: Because 0.25 atm of S_8 remain at equilibrium, 1.00 atm – 0.25 atm = 0.75 atm of S_8 must have reacted in order to reach equilibrium. Because there is a 4 : 1 mole ratio between

S_2 and S_8 (from the balanced reaction), 4(0.75 atm) = 3.0 atm of S_2 must have been produced when the reaction went to equilibrium (moles and pressure are directly related at constant T and V).

Equilibrium: P_{S_8} = 0.25 atm, P_{S_2} = 0 + 3.0 atm = 3.0 atm; Solving for K_p:

$$K_p = \frac{(3.0)^4}{0.25} = 3.2 \times 10^2$$

31. $K = \frac{[H_2]^2[O_2]}{[H_2O]^2}$, $2.4 \times 10^{-3} = \frac{(1.9 \times 10^{-2})^2[O_2]}{(0.11)^2}$, $[O_2] = 0.080\ M$

Mol O_2 = 2.0 L × $\frac{0.080\ \text{mol}\ O_2}{L}$ = 0.16 mol O_2

32. $K_P = \frac{P^2_{NOBr}}{P^2_{NO} \times P_{Br_2}}$, $109 = \frac{(0.0768)^2}{P^2_{NO} \times 0.0159}$, P_{NO} = 0.0583 atm

33. When solving equilibrium problems, a common method to summarize all the information in the problem is to set up a table. We commonly call this table an ICE table because it summarizes *i*nitial concentrations, *c*hanges that must occur to reach equilibrium, and *e*quilibrium concentrations (the sum of the initial and change columns). For the change column, we will generally use the variable *x*, which will be defined as the amount of reactant (or product) that must react to reach equilibrium. In this problem, the reaction must shift right to reach equilibrium because there are no products present initially. Therefore, *x* is defined as the amount of reactant SO_3 that reacts to reach equilibrium, and we use the coefficients in the balanced equation to relate the net change in SO_3 to the net change in SO_2 and O_2. The general ICE table for this problem is:

$$2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g) \qquad K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

	$2\ SO_3(g)$		$2\ SO_2(g)$	$O_2(g)$
Initial	12.0 mol/3.0 L		0	0
	Let *x* mol/L of SO_3 react to reach equilibrium.			
Change	$-x$	→	$+x$	$+x/2$
Equil.	$4.0 - x$		x	$x/2$

From the problem, we are told that the equilibrium SO_2 concentration is 3.0 mol/3.0 L = 1.0 *M* ($[SO_2]_e = 1.0\ M$). From the ICE table setup, $[SO_2]_e = x$, so $x = 1.0$. Solving for the other equilibrium concentrations: $[SO_3]_e = 4.0 - x = 4.0 - 1.0 = 3.0\ M$; $[O_2] = x/2 = 1.0/2 = 0.50\ M$.

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(1.0\ M)^2(0.50\ M)}{(3.0\ M)^2} = 0.056$$

Alternate method: Fractions in the change column can be avoided (if you want) be defining *x* differently. If we were to let 2*x* mol/L of SO_3 react to reach equilibrium, then the ICE table setup is:

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

	$2\ SO_3(g)$	$\rightleftharpoons$	$2\ SO_2(g)$	+	$O_2(g)$
Initial	4.0 *M*		0		0
	Let 2*x* mol/L of SO_3 react to reach equilibrium.				
Change	$-2x$	$\rightarrow$	$+2x$		$+x$
Equil.	$4.0 - 2x$		$2x$		x

Solving: $2x = [SO_2]_e = 1.0\ M$, $x = 0.50\ M$; $[SO_3]_e = 4.0 - 2(0.50) = 3.0\ M$; $[O_2]_e = x$
$= 0.50\ M$

These are exactly the same equilibrium concentrations as solved for previously, thus K will be the same (as it must be). The moral of the story is to define *x* in a manner that is most comfortable for you. Your final answer is independent of how you define *x* initially.

34. The general ICE table for this problem is:

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

	$2\ NO_2(g)$	$\rightleftharpoons$	$2\ NO(g)$	+	$O_2(g)$
Initial	8.0 mol/1.0 L		0		0
	Let *x* mol/L of NO_2 react to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x/2$
Equil.	$8.0 - x$		x		$x/2$

Note that we must use the coefficients in the balanced equation to determine the amount of products produced when *x* mol/L of NO_2 reacts to reach equilibrium. In the problem, we are told that $[NO]_e = 2.0\ M$. From the set-up, $[NO]_e = x = 2.0\ M$. Solving for the other concentrations: $[NO]_e = 8.0 - x = 8.0 - 2.0 = 6.0\ M$; $[O_2]_e = x/2 = 2.0/2 = 1.0\ M$. Calculating K:

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2} = \frac{(2.0\ M)^2\ (1.0\ M)}{(6.0\ M)^2} = 0.11$$

Equilibrium Calculations

35. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \quad K_p = P_{CO_2} = 1.04$ atm

We only need to calculate the initial partial pressure of CO_2 and compare this value to 1.04 atm. At this temperature, all CO_2 will be in the gas phase.

a. $$PV = nRT,\ Q = P_{CO_2} = \frac{n_{CO_2}RT}{V} = \frac{\frac{58.4\text{ g } CO_2}{44.01\text{ g/mol}} \times \frac{0.08206\text{ L atm}}{\text{K mol}} \times 1173\text{K}}{50.0\text{ L}} =$$

$2.55\text{ atm} > K_p$

Reaction will shift to the left because $Q > K_p$; the mass of CaO will decrease.

b. $Q = P_{CO_2} = \dfrac{(23.76)(0.08206)(1173)}{(44.01)(50.0)} = 1.04 \text{ atm} = K_p$

At equilibrium because $Q = K_p$; mass of CaO will not change.

c. Mass of CO_2 is the same as in part b. $P = 1.04 \text{ atm} = K_P$. At equilibrium; mass of CaO will not change.

d. $Q = P_{CO_2} = \dfrac{(4.82)(0.08206)(1173)}{(44.01)(50.0)} = 0.211 \text{ atm} < K_p$

Reaction will shift to the right because $Q < K_p$; the mass of CaO will increase.

36. Determine Q for each reaction, compare this value to K_p (= 0.0900), and then determine which direction the reaction shifts to reach equilibrium. Note that for this reaction, $K = K_p$ because $\Delta n = 0$.

a. $Q = \dfrac{P_{HOCl}^2}{P_{H_2O} \times P_{Cl_2O}} = \dfrac{(1.00 \text{ atm})^2}{(1.00 \text{ atm})(1.00 \text{ atm})} = 1.00$

$Q > K_p$, so the reaction shifts left to reach equilibrium.

b. $Q = \dfrac{(21.0 \text{ torr})^2}{(200. \text{ torr})(49.8 \text{ torr})} = 4.43 \times 10^{-2} < K_p$

The reaction shifts right to reach equilibrium. *Note*: Because Q and K_p are unitless, we can use any pressure units when determining Q without changing the numerical value.

c. $Q = \dfrac{(20.0 \text{ torr})^2}{(296 \text{ torr})(15.0 \text{ torr})} = 0.0901 \approx K_p$; at equilibrium

37. $H_2O(g) + Cl_2O(g) \rightarrow 2\ HOCl(g) \qquad K = \dfrac{[HOCl]^2}{[H_2O][Cl_2O]} = 0.0900$

Use the reaction quotient Q to determine which way the reaction shifts to reach equilibrium. For the reaction quotient, initial concentrations given in a problem are used to calculate the value for Q. If Q < K, then the reaction shifts right to reach equilibrium. If Q > K, then the reaction shifts left to reach equilibrium. If Q = K, then the reaction does not shift in either direction because the reaction is already at equilibrium.

a. $Q = \dfrac{[HOCl]_0^2}{[H_2O]_0[Cl_2O]_0} = \dfrac{\left(\dfrac{1.0 \text{ mol}}{1.0 \text{ L}}\right)^2}{\left(\dfrac{0.10 \text{ mol}}{1.0 \text{ L}}\right)\left(\dfrac{0.10 \text{ mol}}{1.0 \text{ L}}\right)} = 1.0 \times 10^2$

Q > K, so the reaction shifts left to produce more reactants in order to reach equilibrium.

b. $$Q = \frac{\left(\frac{0.084\,\text{mol}}{2.0\,\text{L}}\right)^2}{\left(\frac{0.98\,\text{mol}}{2.0\,\text{L}}\right)\left(\frac{0.080\,\text{mol}}{2.0\,\text{L}}\right)} = 0.090 = K;\quad \text{at equilibrium}$$

c. $$Q = \frac{\left(\frac{0.25\,\text{mol}}{3.0\,\text{L}}\right)^2}{\left(\frac{0.56\,\text{mol}}{3.0\,\text{L}}\right)\left(\frac{0.0010\,\text{mol}}{3.0\,\text{L}}\right)} = 110$$

$Q > K$, so the reaction shifts to the left to reach equilibrium.

38. Because only reactants are present initially, the reaction must proceed to the right to reach equilibrium. Summarizing the problem in a table:

	$N_2(g)$	+ $O_2(g)$	$\rightleftharpoons$ $2\,NO(g)$	$K_p = 0.050$
Initial	0.80 atm	0.20 atm	0	
	x atm of N_2 reacts to reach equilibrium			
Change	$-x$	$-x$	$+2x$	
Equil.	$0.80 - x$	$0.20 - x$	$2x$	

$$K_p = 0.050 = \frac{P_{NO}^2}{P_{N_2} \times P_{O_2}} = \frac{(2x)^2}{(0.80 - x)(0.20 - x)},\quad 0.050[0.16 - (1.00)x + x^2] = 4x^2$$

$$4x^2 = 8.0 \times 10^{-3} - (0.050)x + (0.050)x^2,\quad (3.95)x^2 + (0.050)x - 8.0 \times 10^{-3} = 0$$

Solving using the quadratic formula (see Appendix 1 of the text):

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-0.050 \pm [(0.050)]^2 - 4(3.95)(-8.0 \times 10^{-3})]^{1/2}}{2(3.95)}$$

$x = 3.9 \times 10^{-2}$ atm or $x = -5.2 \times 10^{-2}$ atm; only $x = 3.9 \times 10^{-2}$ atm makes sense (x cannot be negative), so the equilibrium NO concentration is:

$$P_{NO} = 2x = 2(3.9 \times 10^{-2}\ \text{atm}) = 7.8 \times 10^{-2}\ \text{atm}$$

39.

	$2\,SO_2(g)$	+ $O_2(g)$	$\rightleftharpoons$	$2\,SO_3(g)$	$K_p = 0.25$
Initial	0.50 atm	0.50 atm		0	
	$2x$ atm of SO_2 reacts to reach equilibrium				
Change	$-2x$	$-x$	$\rightarrow$	$+2x$	
Equil.	$0.50 - 2x$	$0.50 - x$		$2x$	

$$K_p = 0.25 = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}} = \frac{(2x)^2}{(0.50 - 2x)^2(0.50 - x)}$$

This will give a cubic equation. Graphing calculators can be used to solve this expression. If you don't have a graphing calculator, an alternative method for solving a cubic equation is to use the method of successive approximations (see Appendix 1 of the text). The first step is to guess a value for x. Because the value of K is small (K < 1), not much of the forward reaction will occur to reach equilibrium. This tells us that x is small. Let's guess that x = 0.050 atm. Now we take this estimated value for x and substitute it into the equation everywhere that x appears except for one. For equilibrium problems, we will substitute the estimated value for x into the denominator, and then solve for the numerator value of x. We continue this process until the estimated value of x and the calculated value of x converge on the same number. This is the same answer we would get if we were to solve the cubic equation exactly. Applying the method of successive approximations and carrying extra significant figures:

$$\frac{4x^2}{[0.50-2(0.050)]^2 - [0.50-(0.050)]} = \frac{4x^2}{(0.40)^2(0.45)} = 0.25,\ x = 0.067$$

$$\frac{4x^2}{[0.50-2(0.067)]^2\,[0.50-(0.067)]} = \frac{4x^2}{(0.366)^2(0.433)} = 0.25,\ x = 0.060$$

$$\frac{4x^2}{(0.38)^2(0.44)} = 0.25,\ x = 0.063;\quad \frac{4x^2}{(0.374)^2(0.437)} = 0.25,\quad x = 0.062$$

The next trial gives the same value for x = 0.062 atm. We are done except for determining the equilibrium concentrations. They are:

$P_{SO_2} = 0.50 - 2x = 0.50 - 2(0.062) = 0.376 = 0.38$ atm

$P_{O_2} = 0.50 - x = 0.438 = 0.44$ atm; $P_{SO_3} = 2x = 0.124 = 0.12$ atm

40. $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$ K = 1.1×10^3

Before	0.020 *M*	0.10 *M*		0	
	Let 0.020 mol/L Fe^{3+} react completely (K is large; products dominate).				
Change	–0.020	–0.020	→	+0.020	React completely
After	0	0.08		0.020	New initial
	x mol/L $FeSCN^{2+}$ reacts to reach equilibrium				
Change	$+x$	$+x$	←	$-x$	
Equil.	x	$0.08 + x$		$0.020 - x$	

$$K = 1.1 \times 10^3 = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{0.020 - x}{(x)(0.08 + x)} \approx \frac{0.020}{(0.08)x}$$

$x = 2 \times 10^{-4}$ *M*; x is 1% of 0.020. Assumptions are good by the 5% rule.

$x = [Fe^{3+}] = 2 \times 10^{-4}$ *M*; $[SCN^-] = 0.08 + 2 \times 10^{-4} = 0.08$ *M*

$[FeSCN^{2+}] = 0.020 - 2 \times 10^{-4} = 0.020$ *M*

41. $H_2O(g) + Cl_2O(g) \rightleftharpoons 2\ HOCl(g)$ $\qquad K = 0.090 = \dfrac{[HOCl]^2}{[H_2O][Cl_2O]}$

a. The initial concentrations of H_2O and Cl_2O are:

$$\frac{1.0\ \text{g H}_2\text{O}}{1.0\ \text{L}} \times \frac{1\ \text{mol}}{18.0\ \text{g}} = 5.6 \times 10^{-2}\ \text{mol/L};\quad \frac{2.0\ \text{g Cl}_2\text{O}}{1.0\ \text{L}} \times \frac{1\ \text{mol}}{86.9\ \text{g}} = 2.3 \times 10^{-2}\ \text{mol/L}$$

Because only reactants are present initially, the reaction must proceed to the right to reach equilibrium. Summarizing the problem in a table:

	$H_2O(g)$	+	$Cl_2O(g)$	$\rightleftharpoons$	2 HOCl(g)
Initial	$5.6 \times 10^{-2}\ M$		$2.3 \times 10^{-2}\ M$		0
	x mol/L of H_2O reacts to reach equilibrium				
Change	$-x$		$-x$	→	$+2x$
Equil.	$5.6 \times 10^{-2} - x$		$2.3 \times 10^{-2} - x$		$2x$

$$K = 0.090 = \frac{(2x)^2}{(5.6 \times 10^{-2} - x)(2.3 \times 10^{-2} - x)}$$

$$1.16 \times 10^{-4} - (7.11 \times 10^{-3})x + (0.090)x^2 = 4x^2$$

$(3.91)x^2 + (7.11 \times 10^{-3})x - 1.16 \times 10^{-4} = 0$ (We carried extra significant figures.)

Solving using the quadratic formula (see Appendix 1 of the text):

$$x = \frac{-7.11 \times 10^{-3} \pm (5.06 \times 10^{-5} + 1.81 \times 10^{-3})^{1/2}}{7.82} = 4.6 \times 10^{-3}\ M \text{ or } -6.4 \times 10^{-3}\ M$$

A negative answer makes no physical sense; we can't have less than nothing. Thus $x = 4.6 \times 10^{-3}\ M$.

$[HOCl] = 2x = 9.2 \times 10^{-3}\ M$; $[Cl_2O] = 2.3 \times 10^{-2} - x = 0.023 - 0.0046 = 1.8 \times 10^{-2}\ M$

$[H_2O] = 5.6 \times 10^{-2} - x = 0.056 - 0.0046 = 5.1 \times 10^{-2}\ M$

b.

	$H_2O(g)$	+	$Cl_2O(g)$	$\rightleftharpoons$	2 HOCl(g)
Initial	0		0		1.0 mol/2.0 L = 0.50 M
	$2x$ mol/L of HOCl reacts to reach equilibrium				
Change	$+x$		$+x$	←	$-2x$
Equil.	x		x		$0.50 - 2x$

$$K = 0.090 = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{(0.50 - 2x)^2}{x^2}$$

The expression is a perfect square, so we can take the square root of each side:

$$0.30 = \frac{0.50 - 2x}{x}, \quad (0.30)x = 0.50 - 2x,\ (2.30)x = 0.50$$

$x = 0.217\ M$ (We carried extra significant figures.)

$x = [H_2O] = [Cl_2O] = 0.217 = 0.22\ M$; $[HOCl] = 0.50 - 2x = 0.50 - 0.434 = 0.07\ M$

42. Q = 1.00, which is less than K. The reaction shifts to the right to reach equilibrium. Summarizing the equilibrium problem in a table:

	$SO_2(g)$	+	$NO_2(g)$	$\rightleftharpoons$	$SO_3(g)$	+	$NO(g)$	$K = 3.75$
Initial	$0.800\ M$		$0.800\ M$		$0.800\ M$		$0.800\ M$	
	x mol/L of SO_2 reacts to reach equilibrium							
Change	$-x$		$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$0.800 - x$		$0.800 - x$		$0.800 + x$		$0.800 + x$	

Plug the equilibrium concentrations into the equilibrium constant expression:

$$K = \frac{[SO_3][NO]}{[SO_2][NO_2]},\ 3.75 = \frac{(0.800 + x)^2}{(0.800 - x)^2}$$; take the square root of both sides and solve for x:

$$\frac{0.800 + x}{0.800 - x} = 1.94,\ 0.800 + x = 1.55 - (1.94)x,\ (2.94)x = 0.75,\ x = 0.26\ M$$

The equilibrium concentrations are:

$[SO_3] = [NO] = 0.800 + x = 0.800 + 0.26 = 1.06\ M$; $[SO_2] = [NO_2] = 0.800 - x = 0.54\ M$

43. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K_p = 1.16 = P_{CO_2}$

Some of the 20.0 g of $CaCO_3$ will react to reach equilibrium. The amount that reacts is the quantity of $CaCO_3$ required to produce a CO_2 pressure of 1.16 atm (from the K_p expression).

$$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{1.16\ \text{atm} \times 10.0\ \text{L}}{\frac{0.08206\ \text{L atm}}{\text{K mol}} \times 1073\text{K}} = 0.132\ \text{mol } CO_2$$

$$\text{Mass } CaCO_3 \text{ reacted} = 0.132\ \text{mol } CO_2 \times \frac{1\ \text{mol } CaCO_3}{\text{mol } CO_2} \times \frac{100.09\ \text{g}}{\text{mol } CaCO_3} = 13.2\ \text{g } CaCO_3$$

$$\text{Mass \% } CaCO_3 \text{ reacted} = \frac{13.2\ \text{g}}{20.0\ \text{g}} \times 100 = 66.0\%$$

44. $K = \dfrac{[HF]^2}{[H_2][F_2]} = \dfrac{(0.400M)^2}{(0.0500M)(0.0100M)}$ = 320.; 0.200 mol F_2/5.00 L = 0.0400 *M* F_2 added

After F_2 has been added, the concentrations of species present are [HF] = 0.400 *M*, $[H_2] = [F_2]$ = 0.0500 *M*. Q = $(0.400)^2/(0.0500)^2$ = 64.0; because Q < K, the reaction will shift right to reestablish equilibrium.

	$H_2(g)$	$+$	$F_2(g)$	$\rightleftharpoons$	$2\ HF(g)$
Initial	0.0500 *M*		0.0500 *M*		0.400 *M*
	x mol/L of F_2 reacts to reach equilibrium				
Change	$-x$		$-x$	$\rightarrow$	$+2x$
Equil.	$0.0500 - x$		$0.0500 - x$		$0.400 + 2x$

$K = 320. = \dfrac{(0.400 + 2x)^2}{(0.0500 - x)^2}$; taking the square root of each side:

$17.9 = \dfrac{0.400 + 2x}{0.0500 - x}$, $0.895 - (17.9)x = 0.400 + 2x$, $(19.9)x = 0.495$, $x = 0.0249$ mol/L

[HF] = 0.400 + 2(0.0249) = 0.450 *M*; $[H_2] = [F_2]$ = 0.0500 – 0.0249 = 0.0251 *M*

45. The assumption comes from the value of K being much less than 1. For these reactions, the equilibrium mixture will not have a lot of products present; mostly reactants are present at equilibrium. If we define the change that must occur in terms of *x* as the amount (molarity or partial pressure) of a reactant that must react to reach equilibrium, then *x* must be a small number because K is a very small number. We want to know the value of *x* in order to solve the problem, so we don't assume *x* = 0. Instead, we concentrate on the equilibrium row in the ICE table. Those reactants (or products) that have equilibrium concentrations in the form of $0.10 - x$ or $0.25 + x$ or $3.5 - 3x$, etc., is where an important assumption can be made. The assumption is that because K << 1, *x* will be small (*x* << 1), and when we add *x* or subtract *x* from some initial concentration, it will make little or no difference. That is, we assume that $0.10 - x \approx 0.10$ or $0.25 + x \approx 0.25$ or $3.5 - 3x \approx 3.5$, etc.; we assume that the initial concentration of a substance is equal to the final concentration. This assumption makes the math much easier and usually gives a value of *x* that is well within 5% of the true value of *x* (we get about the same answer with a lot less work).

We check the assumptions for validity using the 5% rule. From doing a lot of these calculations, it is found that when an assumption such as $0.20 - x \approx 0.20$ is made, if *x* is less than 5% of the number the assumption was made against, then our final answer is within acceptable error limits of the true value of *x* (as determined when the equation is solved exactly). For our example above ($0.20 - x \approx 0.20$), if $(x/0.20) \times 100 \le 5\%$, then our assumption is valid by the 5% rule. If the error is greater than 5%, then we must solve the equation exactly or use a math trick called the method of successive approximations. See Appendix 1 for details regarding the method of successive approximations, as well as for a review in solving quadratic equations exactly.

46. a. The reaction must proceed to products to reach equilibrium because only reactants are present initially. Summarizing the problem in a table:

	$2\ NOCl(g)$	$\rightleftharpoons$	$2\ NO(g)\ +$	$Cl_2(g)$	$K = 1.6 \times 10^{-5}$
Initial	$\frac{2.0\ \text{mol}}{2.0\ \text{L}} = 1.0\ M$		0	0	
	$2x$ mol/L of NOCl reacts to reach equilibrium				
Change	$-2x$	$\rightarrow$	$+2x$	$+x$	
Equil.	$1.0 - 2x$		$2x$	x	

$$K = 1.6 \times 10^{-5} = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(2x)^2(x)}{(1.0 - 2x)^2}$$

If we assume that $1.0 - 2x \approx 1.0$ (from the small size of K, we know that the product concentrations will be small, so x will be small), then:

$$1.6 \times 10^{-5} = \frac{4x^3}{1.0^2},\quad x = 1.6 \times 10^{-2}\ M; \text{ now we must check the assumption.}$$

$$1.0 - 2x = 1.0 - 2(0.016) = 0.97 = 1.0 \text{ (to proper significant figures)}$$

Our error is about 3%, that is, $2x$ is 3.2% of 1.0 M. Generally, if the error we introduce by making simplifying assumptions is less than 5%, we go no further, the assumption is said to be valid. We call this the 5% rule. Solving for the equilibrium concentrations:

$$[NO] = 2x = 0.032\ M;\ [Cl_2] = x = 0.016\ M;\ [NOCl] = 1.0 - 2x = 0.97\ M \approx 1.0\ M$$

Note: If we were to solve this cubic equation exactly (a longer process), we get $x = 0.016$. This is the exact same answer we determined by making a simplifying assumption. We saved time and energy. Whenever K is a very small value, always make the assumption that x is small. If the assumption introduces an error of less than 5%, then the answer you calculated making the assumption will be considered the correct answer.

b. There is a little trick we can use to solve this problem in order to avoid solving a cubic equation. Because K for this reaction is very small (K << 1), the reaction will contain mostly reactants at equilibrium (the equilibrium position lies far to the left). We will let the products react to completion by the reverse reaction, and then we will solve the forward equilibrium problem to determine the equilibrium concentrations. Summarizing these steps in a table:

	$2\ NOCl(g)$	$\rightleftharpoons$	$2\ NO(g)\ +$	$Cl_2(g)$	$K = 1.6 \times 10^{-5}$
Before	0		$2.0\ M$	$1.0\ M$	
	Let 1.0 mol/L Cl_2 react completely.				(K is small, reactants dominate.)
Change	+2.0	$\leftarrow$	−2.0	−1.0	React completely
After	2.0		0	0	New initial conditions
	$2x$ mol/L of NOCl reacts to reach equilibrium				
Change	$-2x$	$\rightarrow$	$+2x$	$+x$	
Equil.	$2.0 - 2x$		$2x$	x	

$$K = 1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(2.0-2x)^2} \approx \frac{4x^3}{2.0^2} \qquad \text{(assuming } 2.0 - 2x \approx 2.0\text{)}$$

$x^3 = 1.6 \times 10^{-5}$, $x = 2.5 \times 10^{-2}$ *M*; assumption good by the 5% rule ($2x$ is 2.5% of 2.0).

[NOCl] = 2.0 – 0.050 = 1.95 *M* = 2.0 *M*; [NO] = 0.050 *M*; [Cl_2] = 0.025 *M*

Note: If we do not break this problem into two parts (a stoichiometric part and an equilibrium part), then we are faced with solving a cubic equation. The setup would be:

	2 NOCl	$\rightleftharpoons$	2 NO	+	Cl_2
Initial	0		2.0 *M*		1.0 *M*
Change	$+2y$	←	$-2y$		$-y$
Equil.	$2y$		$2.0 - 2y$		$1.0 - y$

$$1.6 \times 10^{-5} = \frac{(2.0-2y)^2(1.0-y)}{(2y)^2}$$

If we say that y is small to simplify the problem, then:

$$1.6 \times 10^{-5} = \frac{2.0^2}{4y^2}\text{; We get } y = 250. \text{ This is impossible!}$$

To solve this equation, we cannot make any simplifying assumptions; we have to find a way to solve a cubic equation. Or we can use some chemical common sense and solve the problem the easier way.

c. $2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)$

	2 NOCl(g)	$\rightleftharpoons$	2 NO(g)	+	Cl_2(g)
Initial	1.0 *M*		1.0 *M*		0
	$2x$ mol/L NOCl reacts to reach equilibrium				
Change	$-2x$	→	$+2x$		$+x$
Equil.	$1.0 - 2x$		$1.0 + 2x$		x

$$1.6 \times 10^{-5} = \frac{(1.0+2x)^2(x)}{(1.0-2x)^2} \approx \frac{(1.0)^2(x)}{(2.0)^2} \qquad \text{(assuming } 2x \ll 1.0\text{)}$$

$x = 1.6 \times 10^{-5}$ *M*; Assumptions are great ($2x$ is 3.2×10^{-3}% of 1.0).

[Cl_2] = 1.6×10^{-5} *M* and [NOCl] = [NO] = 1.0 *M* d.

	$2\,NOCl(g)$	⇌	$2\,NO(g)$	+	$Cl_2(g)$	
Before	0		$3.0\ M$		$1.0\ M$	
	Let 1.0 mol/L Cl_2 react completely.					
Change	+2.0	←	–2.0		–1.0	React completely
After	2.0		1.0		0	New initial
	$2x$ mol/L NOCl reacts to reach equilibrium					
Change	$-2x$	→	$+2x$		$+x$	
Equil.	$2.0 - 2x$		$1.0 + 2x$		x	

$$1.6 \times 10^{-5} = \frac{(1.0+2x)^2(x)}{(2.0-2x)^2} \approx \frac{x}{4.0};\quad \text{solving: } x = 6.4 \times 10^{-5}\ M$$

Assumptions are great ($2x$ is 1.3×10^{-2}% of 1.0).

$[Cl_2] = 6.4 \times 10^{-5}\ M$; $[NOCl] = 2.0\ M$; $[NO] = 1.0\ M$

e.

	$2\,NOCl(g)$	⇌	$2\,NO(g)$	+	$Cl_2(g)$	
Before	$2.0\ M$		$2.0\ M$		$1.0\ M$	
	Let 1.0 mol/L Cl_2 react completely.					
Change	+2.0	←	–2.0		–1.0	React completely
After	4.0		0		0	New initial
	$2x$ mol/L NOCl reacts to reach equilibrium					
Change	$-2x$	→	$+2x$		$+x$	
Equil.	$4.0 - 2x$		$2x$		x	

$$1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(4.0-2x)^2} \approx \frac{4x^3}{16},\ x = 4.0 \times 10^{-2}\ M;\quad \text{assumption good (2\% error).}$$

$[Cl_2] = 0.040\ M$; $[NO] = 0.080\ M$; $[NOCl] = 4.0 - 2(0.040) = 3.92\ M \approx 3.9\ M$

f.

	$2\,NOCl(g)$	⇌	$2\,NO(g)$	+	$Cl_2(g)$	
Before	$1.00\ M$		$1.00\ M$		$1.00\ M$	
	Let 1.00 mol/L NO react completely (the limiting reagent).					
Change	+1.00	←	–1.00		–0.500	React completely
After	2.00		0		0.50	New initial
	$2x$ mol/L NOCl reacts to reach equilibrium					
Change	$-2x$	→	$+2x$		$+x$	
Equil.	$2.00 - 2x$		$2x$		$0.50 + x$	

$$K = \frac{(2x)^2(0.50+x)}{(2.00-2x)^2} \approx \frac{4x^2(0.50)}{(2.00)^2} = 1.6 \times 10^{-5},\ x = 5.7 \times 10^{-3}\ M$$

Assumptions are good (x is 1.1% of 0.50).

[NO] = $2x = 1.1 \times 10^{-2}$ *M*; $[Cl_2] = 0.50 + 0.0057 = 0.51$ *M*

[NOCl] = 2.00 – 2(0.0057) = 1.99 *M*

47. $2\ CO_2(g) \rightleftharpoons 2\ CO(g) + O_2(g) \qquad K = \dfrac{[CO]^2[O_2]}{[CO_2]^2} = 2.0 \times 10^{-6}$

	$2\ CO_2(g)$		$2\ CO(g)$	$O_2(g)$
Initial	2.0 mol/5.0 L		0	0
	$2x$ mol/L of CO_2 reacts to reach equilibrium			
Change	$-2x$	→	$+2x$	$+x$
Equil.	$0.40 - 2x$		$2x$	x

$K = 2.0 \times 10^{-6} = \dfrac{[CO]^2[O_2]}{[CO_2]^2} = \dfrac{(2x)^2(x)}{(0.40 - 2x)^2}$; assuming $2x << 0.40$ (K is small, so x is small.)

$$2.0 \times 10^{-6} \approx \frac{4x^3}{(0.40)^2}, \quad 2.0 \times 10^{-6} = \frac{4x^3}{0.16}, \quad x = 4.3 \times 10^{-3}\ M$$

Checking assumption: $\dfrac{2(4.3 \times 10^{-3})}{0.40} \times 100 = 2.2\%$; assumption is valid by the 5% rule.

$[CO_2] = 0.40 - 2x = 0.40 - 2(4.3 \times 10^{-3}) = 0.39$ *M*

$[CO] = 2x = 2(4.3 \times 10^{-3}) = 8.6 \times 10^{-3}$ *M*; $[O_2] = x = 4.3 \times 10^{-3}$ *M*

48. a. The reaction must proceed to products to reach equilibrium because no product is present initially. Summarizing the problem in a table where x atm of N_2O_4 reacts to reach equilibrium:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad K_p = 0.25$$

	$N_2O_4(g)$		$2\ NO_2(g)$
Initial	4.5 atm		0
Change	$-x$	→	$+2x$
Equil.	$4.5 - x$		$2x$

$K_p = \dfrac{P_{NO_2}^2}{P_{N_2O_4}} = \dfrac{(2x)^2}{4.5 - x} = 0.25$, $4x^2 = 1.125 - (0.25)x$, $4x^2 + (0.25)x - 1.125 = 0$

We carried extra significant figures in this expression (as will be typical when we solve an expression using the quadratic formula). Solving using the quadratic formula (see Appendix 1 of text):

$$x = \frac{-0.25 \pm [(0.25)^2 - 4(4)(-1.125)]^{1/2}}{2(4)} = \frac{-0.25 \pm 4.25}{8}, \ x = 0.50$$

(Other value is negative.)

$P_{NO_2} = 2x = 1.0$ atm; $P_{N_2O_4} = 4.5 - x = 4.0$ atm

b. The reaction must shift to reactants (shift left) to reach equilibrium.

	$N_2O_4(g)$	$\rightleftharpoons$	$2\ NO_2(g)$
Initial	0		9.0 atm
Change	$+x$	←	$-2x$
Equil.	x		$9.0 - 2x$

$K_p = \dfrac{(9.0 - 2x)^2}{x} = 0.25$, $4x^2 - (36.25)x + 81 = 0$ (carrying extra significant figures)

Solving: $x = \dfrac{-(-36.25) \pm [(-36.25)^2 - 4(4)(81)]^{1/2}}{2(4)}$, $x = 4.0$ atm

The other value, 5.1, is impossible. $P_{N_2O_4} = x = 4.0$ atm; $P_{NO_2} = 9.0 - 2x = 1.0$ atm

c. No, we get the same equilibrium position starting with either pure N_2O_4 or pure NO_2 in stoichiometric amounts.

d. From part a, the equilibrium partial pressures are $P_{NO_2} = 1.0$ atm and $P_{N_2O_4} = 4.0$ atm. Halving the container volume will increase each of these partial pressures by a factor of 2. $Q = (2.0)^2/8.0 = 0.50$. Because $Q > K_p$, the reaction will shift left to reestablish equilibrium.

	$N_2O_4(g)$	$\rightleftharpoons$	$2\ NO_2(g)$
Initial	4.0 atm		1.0 atm
New Initial	8.0		2.0
Change	$+x$	←	$-2x$
Equil.	$8.0 + x$		$2.0 - 2x$

$K_p = \dfrac{(2.0 - 2x)^2}{8.0 + x} = 0.25$, $4x^2 - (8.25)x + 2.0 = 0$ (carrying extra sig. figs.)

Solving using the quadratic formula: $x = 0.28$ atm

$P_{N_2O_4} = 8.0 + x = 8.3$ atm; $P_{NO_2} = 2.0 - 2x = 1.4$ atm

49. a. $K_p = K(RT)^{\Delta n} = 4.5\times10^9\left(\dfrac{0.08206\,\text{L atm}}{\text{K mol}} \times 373\,\text{K}\right)^{-1}$, where $\Delta n = 1 - 2 = -1$

$K_p = 1.5 \times 10^8$

b. K_p is so large that at equilibrium we will have almost all $COCl_2$. Assume $P_{total} \approx P_{COCl_2} \approx 5.0$ atm.

	$CO(g)$	$+\ Cl_2(g)$	$\rightleftharpoons$	$COCl_2(g)$	$K_p = 1.5 \times 10^8$
Initial	0	0		5.0 atm	
	x atm $COCl_2$ reacts to reach equilibrium				
Change	$+x$	$+x$	←	$-x$	
Equil.	x	x		$5.0 - x$	

$K_p = 1.5 \times 10^8 = \dfrac{5.0 - x}{x^2} \approx \dfrac{5.0}{x^2}$ (Assuming $5.0 - x \approx 5.0$.)

Solving: $x = 1.8 \times 10^{-4}$ atm. Check assumptions: $5.0 - x = 5.0 - 1.8 \times 10^{-4} = 5.0$ atm. Assumptions are good (well within the 5% rule).

$P_{CO} = P_{Cl_2} = 1.8 \times 10^{-4}$ atm and $P_{COCl_2} = 5.0$ atm

50. This is a typical equilibrium problem except that the reaction contains a solid. Whenever solids and liquids are present, we basically ignore them in the equilibrium problem.

$$NH_4OCONH_2(s) \rightleftharpoons 2\ NH_3(g) + CO_2(g) \qquad K_p = 2.9 \times 10^{-3}$$

Initial	–		0	0

Some NH_4OCONH_2 decomposes to produce $2x$ atm of NH_3 and x atm of CO_2.

Change	–	→	$+2x$	$+x$
Equil.	–		$2x$	x

$K_p = 2.9 \times 10^{-3} = P_{NH_3}^2 \times P_{CO_2} = (2x)^2(x) = 4x^3$

$x = \left(\dfrac{2.9 \times 10^{-3}}{4}\right)^{1/3} = 9.0 \times 10^{-2}$ atm; $P_{NH_3} = 2x = 0.18$ atm; $P_{CO_2} = x = 9.0 \times 10^{-2}$ atm

$P_{total} = P_{NH_3} + P_{CO_2} = 0.18 \text{ atm} + 0.090 \text{ atm} = 0.27$ atm

Le Châtelier's Principle

51. a. Left b. Right c. Left

d. No effect; the reactant and product concentrations/partial pressures are unchanged.

e. No effect; because there are equal numbers of product and reactant gas molecules, a change in volume has no effect on this equilibrium position.

f. Right; a decrease in temperature will shift the equilibrium to the right because heat is a product in this reaction (as is true in all exothermic reactions).

52. a. Shift to left

b. Shift to right; because the reaction is endothermic (heat is a reactant), an increase in temperature will shift the equilibrium to the right.

c. No effect; the reactant and product concentrations/partial pressures are unchanged.

d. Shift to right

e. Shift to right; because there are more gaseous product molecules than gaseous reactant molecules, the equilibrium will shift right with an increase in volume.

53. a. Right b. Right c. No effect; He(g) is neither a reactant nor a product.

d. Left; because the reaction is exothermic, heat is a product:

$$CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g) + \text{heat}$$

Increasing T will add heat. The equilibrium shifts to the left to use up the added heat.

e. No effect; because the moles of gaseous reactants equals the moles of gaseous products (2 mol versus 2 mol), a change in volume will have no effect on the equilibrium.

54. a. The moles of SO_3 will increase because the reaction will shift left to use up some of the added $O_2(g)$.

b. Increase; because there are fewer reactant gas molecules than product gas molecules, the reaction shifts left with a decrease in volume.

c. No effect; the partial pressures of sulfur trioxide, sulfur dioxide, and oxygen are unchanged, so the reaction is still at equilibrium.

d. Increase; heat + 2 $SO_3 \rightleftharpoons 2\ SO_2 + O_2$; decreasing T will remove heat, shifting this endothermic reaction to the left to add heat.

e. Decrease

55. An endothermic reaction, where heat is a reactant, will shift right to products with an increase in temperature. The amount of $NH_3(g)$ will increase as the reaction shifts right, so the smell of ammonia will increase.

56. a. Doubling the volume will decrease all concentrations by a factor of one-half.

$$Q = \frac{\frac{1}{2}[\text{FeSCN}^{2+}]_{eq}}{\left(\frac{1}{2}[\text{Fe}^{3+}]_{eq}\right)\left(\frac{1}{2}[\text{SCN}^{-}]_{eq}\right)} = 2\text{ K},\ \ Q > K$$

The reaction will shift to the left to reestablish equilibrium.

b. Adding Ag^+ will remove SCN^- through the formation of AgSCN(s). The reaction will shift to the left to produce more SCN^-.

c. Removing Fe^{3+} as $Fe(OH)_3(s)$ will shift the reaction to the left to produce more Fe^{3+}.

d. Reaction shifts to the right as Fe^{3+} is added.

57. Only statement d is correct. Addition of a catalyst has no effect on the equilibrium position; the reaction just reaches equilibrium more quickly. Statement a is false for reactants that are either solids or liquids (adding more of these has no effect on the equilibrium). Statement b is false always. If temperature remains constant, then the value of K is constant. Statement c is false for exothermic reactions where an increase in temperature decreases the value of K.

58. A change in volume will change the partial pressure of all reactants and products by the same factor. The shift in equilibrium depends on the number of gaseous particles on each side. An increase in volume will shift the equilibrium to the side with the greater number of particles in the gas phase. A decrease in volume will favor the side with lesser gas-phase particles. If there are the same number of gas-phase particles on each side of the reaction, a change in volume will not shift the equilibrium.

When we change the pressure by adding an unreactive gas, we do not change the partial pressures (or concentrations) of any of the substances in equilibrium with each other since the volume of the container did not change. If the partial pressures (and concentrations) are unchanged, the reaction is still at equilibrium.

59. $H^+ + OH^- \rightarrow H_2O$; sodium hydroxide (NaOH) will react with the H^+ on the product side of the reaction. This effectively removes H^+ from the equilibrium, which will shift the reaction to the right to produce more H^+ and CrO_4^{2-}. Because more CrO_4^{2-} is produced, the solution turns yellow.

60. As temperature increases, the value of K decreases. This is consistent with an exothermic reaction. In an exothermic reaction, heat is a product, and an increase in temperature shifts the equilibrium to the reactant side (as well as lowering the value of K).

61. a. No effect; adding more of a pure solid or pure liquid has no effect on the equilibrium position.

b. Shifts left; HF(g) will be removed by reaction with the glass. As HF(g) is removed, the reaction will shift left to produce more HF(g).

c. Shifts right; as $H_2O(g)$ is removed, the reaction will shift right to produce more $H_2O(g)$.

62. When the volume of a reaction container is increased, the reaction itself will want to increase its own volume by shifting to the side of the reaction that contains the most molecules of gas. When the molecules of gas are equal on both sides of the reaction, then the reaction will remain at equilibrium no matter what happens to the volume of the container.

a. Reaction shifts left (to reactants) because the reactants contain 4 molecules of gas compared with 2 molecules of gas on the product side.

b. Reaction shifts right (to products) because there are more product molecules of gas (2) than reactant molecules (1).

c. No change because there are equal reactant and product molecules of gas.

d. Reaction shifts right.

e. Reaction shifts right to produce more $CO_2(g)$. One can ignore the solids and only concentrate on the gases because gases occupy a relatively huge volume compared with solids. We make the same assumption when liquids are present (only worry about the gas molecules).

Additional Exercises

63. $5.63\text{ g } C_5H_6O_3 \times \dfrac{1\,\text{mol}\,C_5H_6O_3}{114.10\text{ g}} = 0.0493\text{ mol } C_5H_6O_3$ initially

Total moles of gas = $n_{total} = \dfrac{P_{total}V}{RT} = \dfrac{1.63\,\text{atm} \times 2.50\text{ L}}{\dfrac{0.08206\text{ L atm}}{\text{K mol}} \times 473\text{ K}} = 0.105$ mol
at equilibrium

	$C_5H_6O_3(g)$	$\rightleftharpoons$	$C_2H_6(g)$ +	$3\ CO(g)$
Initial	0.0493 mol		0	0
	Let x mol $C_5H_6O_3$ react to reach equilibrium.			
Change	$-x$	$\rightarrow$	$-x$	$-3x$
Equil.	$0.0493 - x$		x	$3x$

0.105 mol total = $0.0493 - x + x + 3x = 0.0493 + 3x$, $x = 0.0186$ mol

$$K = \frac{[C_2H_6][CO]^3}{[C_5H_6O_3]} = \frac{\left[\dfrac{0.0186\,\text{mol}\,C_2H_6}{2.50\text{ L}}\right]\left[\dfrac{3(0.0186)\,\text{mol}\,CO}{2.50\text{ L}}\right]^3}{\left[\dfrac{(0.0493 - 0.0186)\,\text{mol}\,C_5H_6O_3}{2.50\text{ L}}\right]} = 6.74 \times 10^{-6}$$

64. a.

$$\begin{array}{ll}
Na_2O(s) \rightleftharpoons 2\,Na(l) + 1/2\,O_2(g) & K_1 \\
2\,Na(l) + O_2(g) \rightleftharpoons Na_2O_2(s) & 1/K_3 \\
\hline
Na_2O(s) + 1/2\,O_2(g) \rightleftharpoons Na_2O_2(s) & K = (K_1)(1/K_3)
\end{array}$$

$$K = \frac{2 \times 10^{-25}}{5 \times 10^{-29}} = 4 \times 10^3$$

b.

$$\begin{array}{ll}
NaO(g) \rightleftharpoons Na(l) + 1/2\,O_2(g) & K_2 \\
Na_2O(s) \rightleftharpoons 2\,Na(l) + 1/2\,O_2(g) & K_1 \\
2\,Na(l) + O_2(g) \rightleftharpoons Na_2O_2(s) & 1/K_3 \\
\hline
NaO(g) + Na_2O(s) \rightleftharpoons Na_2O_2(s) + Na(l) & K = K_2(K_1)(1/K_3) = 8 \times 10^{-2}
\end{array}$$

c.

$$\begin{array}{ll}
2\,NaO(g) \rightleftharpoons 2\,Na(l) + O_2(g) & K_2^2 \\
2\,Na(l) + O_2(g) \rightleftharpoons Na_2O_2(s) & 1/K_3 \\
\hline
2\,NaO(g) \rightleftharpoons Na_2O_2(s) & K = K_2^2(1/K_3) = 8 \times 10^{18}
\end{array}$$

65.

$O(g) + NO(g) \rightleftharpoons NO_2(g)$	$K = 1/6.8 \times 10^{-49} = 1.5 \times 10^{48}$
$NO_2(g) + O_2(g) \rightleftharpoons NO(g) + O_3(g)$	$K = 1/5.8 \times 10^{-34} = 1.7 \times 10^{33}$
$O_2(g) + O(g) \rightleftharpoons O_3(g)$	$K = (1.5 \times 10^{48})(1.7 \times 10^{33}) = 2.6 \times 10^{81}$

66. Assuming 100.00 g naphthalene:

$$93.71\text{ C} \times \frac{1\,\text{mol C}}{12.011\,\text{g}} = 7.802\text{ mol C}$$

$$6.29\text{ g H} \times \frac{1\,\text{mol H}}{1.008\,\text{g}} = 6.24\text{ mol H};\quad \frac{7.802}{6.24} = 1.25$$

Empirical formula = $(C_{1.25}H) \times 4 = C_5H_4$; molar mass = $\frac{32.8\text{ g}}{0.256\text{ mol}}$ = 128 g/mol

Because the empirical mass (64.08 g/mol) is one-half of 128, the molecular formula is $C_{10}H_8$.

	$C_{10}H_8(s)$	$\rightleftharpoons$	$C_{10}H_8(g)$	$K = 4.29 \times 10^{-6} = [C_{10}H_8]$
Initial	–		0	
Equil.	–		x	

$K = 4.29 \times 10^{-6} = [C_{10}H_8] = x$

Mol $C_{10}H_8$ sublimed = 5.00 L × 4.29×10^{-6} mol/L = 2.15×10^{-5} mol $C_{10}H_8$ sublimed

Mol $C_{10}H_8$ initially = 3.00 g × $\frac{1\,\text{mol}\,C_{10}H_8}{128.16\,\text{g}}$ = 2.34×10^{-2} mol $C_{10}H_8$ initially

Percent $C_{10}H_8$ sublimed = $\frac{2.15 \times 10^{-5}\text{ mol}}{2.34 \times 10^{-2}\text{ mol}} \times 100 = 0.0919\%$

67.

	$NH_3(g)$	+	$H_2S(g)$	$\rightleftharpoons$	$NH_4HS(s)$	$K = 400. = \frac{1}{[NH_3][H_2S]}$
Initial	$\frac{2.00\,\text{mol}}{5.00\,\text{L}}$		$\frac{2.00\,\text{mol}}{5.00\,\text{L}}$		–	
	x mol/L of NH_3 reacts to reach equilibrium					
Change	$-x$		$-x$		–	
Equil.	$0.400 - x$		$0.400 - x$		–	

$$K = 400. = \frac{1}{(0.400 - x)(0.400 - x)},\quad 0.400 - x = \left(\frac{1}{400.}\right)^{1/2} = 0.0500,\quad x = 0.350\ M$$

Mol NH_4HS(s) produced = 5.00 L $\times \dfrac{0.350\,\text{mol}\,NH_3}{\text{L}} \times \dfrac{1\,\text{mol}\,NH_4HS}{\text{mol}\,NH_3}$ = 1.75 mol

Total mol NH_4HS(s) = 2.00 mol initially + 1.75 mol produced = 3.75 mol total

3.75 mol NH_4HS $\times \dfrac{51.12\,\text{g}\,NH_4HS}{\text{mol}\,NH_4HS}$ = 192 g NH_4HS

$[H_2S]_e = 0.400\ M - x = 0.400\ M - 0.350\ M = 0.050\ M\ H_2S$

$$P_{H_2S} = \frac{n_{H_2S}RT}{V} = \frac{n_{H_2S}}{V} \times RT = \frac{0.050\,\text{mol}}{\text{L}} \times \frac{0.08206\,\text{L atm}}{\text{K mol}} \times 308.2\ \text{K} = 1.3\ \text{atm}$$

68. $SO_2Cl_2(g) \rightleftharpoons Cl_2(g) + SO_2(g)$

	$SO_2Cl_2(g)$		$Cl_2(g)$	$SO_2(g)$	
Initial	P_0		0	0	P_0 = initial pressure of SO_2Cl_2
Change	$-x$	$\rightarrow$	$+x$	$+x$	
Equil.	$P_0 - x$		x	x	

$P_{total} = 0.900\ \text{atm} = P_0 - x + x + x = P_0 + x$

$\dfrac{x}{P_0} \times 100 = 12.5,\ \ P_0 = (8.00)x$

Solving: $0.900 = P_0 + x = (9.00)x,\ \ x = 0.100$ atm

$x = 0.100\ \text{atm} = P_{Cl_2} = P_{SO_2}$; $P_0 - x = 0.800 - 0.100 = 0.700\ \text{atm} = P_{SO_2Cl_2}$

$$K_p = \frac{P_{Cl_2} \times P_{SO_2}}{P_{SO_2Cl_2}} = \frac{(0.100)^2}{0.700} = 1.43 \times 10^{-2}$$

69. a. $2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$ $K_p = 0.25$

	$2\,NaHCO_3(s)$		$Na_2CO_3(s)$	$CO_2(g)$	$H_2O(g)$
Initial	–		–	0	0

$NaHCO_3$(s) decomposes to form x atm each of CO_2(g) and H_2O(g) at equilibrium.

	$2\,NaHCO_3(s)$		$Na_2CO_3(s)$	$CO_2(g)$	$H_2O(g)$
Change	–	$\rightarrow$	–	$+x$	$+x$
Equil.	–		–	x	x

$K_p = 0.25 = P_{CO_2} \times P_{H_2O}$, $0.25 = x^2$, $x = P_{CO_2} = P_{H_2O} = 0.50$ atm

b. $$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{(0.50\,\text{atm})(1.00\,\text{L})}{(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1})(398\,\text{K})} = 1.5 \times 10^{-2}\ \text{mol}\ CO_2$$

Mass of Na_2CO_3 produced:

$$1.5 \times 10^{-2} \text{ mol CO}_2 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{\text{mol CO}_2} \times \frac{106.0 \text{ g Na}_2\text{CO}_3}{\text{mol Na}_2\text{CO}_3} = 1.6 \text{ g Na}_2\text{CO}_3$$

Mass of $NaHCO_3$ reacted:

$$1.5 \times 10^{-2} \text{ mol CO}_2 \times \frac{2 \text{ mol NaHCO}_3}{\text{mol CO}_2} \times \frac{84.01 \text{ g NaHCO}_3}{\text{mol}} = 2.5 \text{ g NaHCO}_3$$

Mass of $NaHCO_3$ remaining = 10.0 – 2.5 = 7.5 g

c. $$10.0 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} \times \frac{1 \text{ mol CO}_2}{2 \text{ mol NaHCO}_3} = 5.95 \times 10^{-2} \text{ mol CO}_2$$

When all the $NaHCO_3$ has just been consumed, we will have 5.95×10^{-2} mol CO_2 gas at a pressure of 0.50 atm (from a).

$$V = \frac{nRT}{P} = \frac{(5.95 \times 10^{-2} \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(398 \text{ K})}{0.50 \text{ atm}} = 3.9 \text{ L}$$

70. $$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K_p = 5.3 \times 10^5$$

	N_2	$3H_2$		$2NH_3$	
Initial	0	0		P_0	P_0 = initial pressure of NH_3
	$2x$ atm of NH_3 reacts to reach equilibrium				
Change	$+x$	$+3x$	←	$-2x$	
Equil.	x	$3x$		$P_0 - 2x$	

From problem, $P_0 - 2x = \dfrac{P_0}{2.00}$, so $P_0 = (4.00)x$

$$K_p = \frac{[(4.00)x - 2x]^2}{(x)(3x)^3} = \frac{[(2.00)x]^2}{(x)(3x)^3} = \frac{(4.00)x^2}{27x^4} = \frac{4.00}{27x^2} = 5.3 \times 10^5, \quad x = 5.3 \times 10^{-4} \text{ atm}$$

$P_0 = (4.00)x = 4.00(5.3 \times 10^{-4} \text{ atm}) = 2.1 \times 10^{-3}$ atm

71. a. $$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K_p = (P_{PCl_3} \times P_{Cl_2})/P_{PCl_5}$$

	PCl_5		PCl_3	Cl_2	
Initial	P_0		0	0	P_0 = initial PCl_5 pressure
Change	$-x$	→	$+x$	$+x$	
Equil.	$P_0 - x$		x	x	

$P_{total} = P_0 - x + x + x = P_0 + x = 358.7$ torr

$$P_0 = \frac{n_{PCl_5}RT}{V} = \frac{\dfrac{2.4156 \text{ g}}{208.22 \text{ g/mol}} \times \dfrac{0.08206 \text{ L atm}}{\text{K mol}} \times 523.2 \text{ K}}{2.000 \text{ L}} = 0.2490 \text{ atm (or 189.2 torr)}$$

$x = P_{total} - P_0 = 358.7 - 189.2 = 169.5$ torr

$$P_{PCl_3} = P_{Cl_2} = 169.5 \text{ torr} \times \frac{1\,\text{atm}}{760\,\text{torr}} = 0.2230 \text{ atm}$$

$$P_{PCl_5} = 189.2 - 169.5 = 19.7 \text{ torr} \times \frac{1\,\text{atm}}{760\,\text{torr}} = 0.0259 \text{ atm}$$

$$K_p = \frac{(0.2230)^2}{0.0259} = 1.92$$

b. $P_{Cl_2} = \dfrac{n_{Cl_2}RT}{V} = \dfrac{0.250 \times 0.08206 \times 523.2}{2.000} = 5.37$ atm Cl_2 added

	$PCl_5(g)$	⇌	$PCl_3(g)$	+	$Cl_2(g)$	
Initial	0.0259 atm		0.2230 atm		0.2230 atm	(from a)
	Adding 0.250 mol Cl_2 increases P_{Cl_2} by 5.37 atm.					
Initial'	0.0259		0.2230		5.59	
Change	+0.2230	←	–0.2230		–0.2230	React completely
After	0.2489		0		5.37	New initial
Change	$-x$	→	$+x$		$+x$	
Equil.	$0.2489 - x$		x		$5.37 + x$	

$$\frac{(5.37 + x)(x)}{(0.2489 - x)} = 1.92, \quad x^2 + (7.29)x - 0.478 = 0$$

Solving using the quadratic formula: $x = 0.0650$ atm

$P_{PCl_3} = 0.0650$ atm; $P_{PCl_5} = 0.2489 - 0.0650 = 0.1839$ atm; $P_{Cl_2} = 5.37 + 0.0650$
$= 5.44$ atm

72.

$$\begin{array}{ll} 2\,C(g) \rightleftharpoons 2\,A(g) + 2\,B(g) & K_1 = (1/3.50)^2 = 8.16 \times 10^{-2} \\ 2\,A(g) + D(g) \rightleftharpoons C(g) & K_2 = 7.10 \\ \hline C(g) + D(g) \rightleftharpoons 2\,B(g) & K = K_1 \times K_2 = 0.579 \end{array}$$

$K_p = K(RT)^{\Delta n}$, $\Delta n = 2 - (1 + 1) = 0$; because $\Delta n = 0$, $K_p = K = 0.579$.

	$C(g)$	+	$D(g)$	⇌	$2\,B(g)$
Initial	1.50 atm		1.50 atm		0
Equil.	$1.50 - x$		$1.50 - x$		$2x$

$$0.579 = K = \frac{(2x)^2}{(1.50 - x)(1.50 - x)} = \frac{(2x)^2}{(1.50 - x)^2}$$

$$\frac{2x}{1.50 - x} = (0.579)^{1/2} = 0.761, \ x = 0.413 \text{ atm}$$

P_B (at equilibrium) = $2x = 2(0.413) = 0.826$ atm

$P_{total} = P_C + P_D + P_B = 2(1.50 - 0.413) + 0.826 = 3.00$ atm

$$P_B = \chi_B P_{total}, \ \chi_B = \frac{P_B}{P_{total}} = \frac{0.826 \text{ atm}}{3.00 \text{ atm}} = 0.275$$

73. $3\ H_2(g) + N_2(g) \rightleftharpoons 2\ NH_3(g)$

Initial	$[H_2]_0$	$[N_2]_0$		0
	x mol/L of N_2 reacts to reach equilibrium			
Change	$-3x$	$-x$	$\rightarrow$	$+2x$
Equil.	$[H_2]_0 - 3x$	$[N_2]_0 - x$		$2x$

From the problem:

$[NH_3]_e = 4.0\ M = 2x, \ x = 2.0\ M; \ [H_2]_e = 5.0\ M = [H_2]_0 - 3x; \ [N_2]_e = 8.0\ M = [N_2]_0 - x$

$5.0\ M = [H_2]_0 - 3(2.0\ M), \ [H_2]_0 = 11.0\ M; \ 8.0\ M = [N_2]_0 - 2.0\ M, \ [N_2]_0 = 10.0\ M$

74. a. $$P_{PCl_5} = \frac{n_{PCl_5}RT}{V} = \frac{\dfrac{2.450\text{g } PCl_5}{208.22\text{g/mol}} \times \dfrac{0.08206\text{L atm}}{\text{K mol}} \times 600.\text{K}}{0.500\text{L}} = 1.16 \text{ atm}$$

b. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K_p = \dfrac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = 11.5$

Initial	1.16 atm		0	0
	x atm of PCl_5 reacts to reach equilibrium			
Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$1.16 - x$		x	x

$$K_p = \frac{x^2}{1.16 - x} = 11.5, \ x^2 + (11.5)x - 13.3 = 0$$

Using the quadratic formula: $x = 1.06$ atm

$P_{PCl_5} = 1.16 - 1.06 = 0.10$ atm

c. $P_{PCl_3} = P_{Cl_2} = 1.06$ atm; $P_{PCl_5} = 0.10$ atm

$P_{total} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} = 0.10 + 1.06 + 1.06 = 2.22$ atm

d. Percent dissociation = $\dfrac{x}{1.16} \times 100 = \dfrac{1.06}{1.16} \times 100 = 91.4\%$

75. a. $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$ $K_p = 1 \times 10^{-31} = \dfrac{P_{NO}^2}{P_{N_2} \times P_{O_2}} = \dfrac{P_{NO}^2}{(0.8)(0.2)}$

$P_{NO} = 1 \times 10^{-16}$ atm

In 1.0 cm³ of air: $n_{NO} = \dfrac{PV}{RT} = \dfrac{(1 \times 10^{-16}\ \text{atm})(1.0 \times 10^{-3}\ \text{L})}{\left(\dfrac{0.08206\ \text{L atm}}{\text{K mol}}\right)(298\ \text{K})} = 4 \times 10^{-21}$ mol NO

$$\frac{4 \times 10^{-21}\ \text{mol NO}}{\text{cm}^3} \times \frac{6.02 \times 10^{23}\ \text{molecules}}{\text{mol NO}} = \frac{2 \times 10^3\ \text{molecules NO}}{\text{cm}^3}$$

b. There is more NO in the atmosphere than we would expect from the value of K. The answer must lie in the rates of the reaction. At 25°C, the rates of both reactions:

$$N_2 + O_2 \rightarrow 2\ NO \quad \text{and} \quad 2\ NO \rightarrow N_2 + O_2$$

are so slow that they are essentially zero. Very strong bonds must be broken; the activation energy is very high. Therefore, the reaction essentially doesn't occur at low temperatures. Nitric oxide, however, can be produced in high-energy or high-temperature environments because the production of NO is endothermic. In nature, some NO is produced by lightning and the primary manmade source is automobiles. At these high temperatures, K will increase, and the rates of the reaction will also increase, resulting in a higher production of NO. Once the NO gets into a more normal temperature environment, it doesn't go back to N_2 and O_2 because of the slow rate.

76. a.

	$2\ AsH_3(g)$	$\rightleftharpoons$	$2\ As(s)$	+	$3\ H_2(g)$
Initial	392.0 torr		–		0
Equil.	392.0 - 2x		–		3x

$P_{total} = 488.0$ torr $= 392.0 - 2x + 3x$, $x = 96.0$ torr

$P_{H_2} = 3x = 3(96.0) = 288$ torr; $P_{AsH_3} = 392.0 - 2(96.0) = 200.0$ torr

b. $K_p = \dfrac{(P_{H_2})^3}{(P_{AsH_3})^2} = \dfrac{(288)^3}{(200.0)^2} = 597\ \text{torr} \times \dfrac{1\ \text{atm}}{760\ \text{torr}} = 0.786$ atm $= 0.786$

77. $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ $K_p = \dfrac{P_{NO_2}^2}{P_{N_2O_4}} = \dfrac{(1.20)^2}{0.34} = 4.2$

Doubling the volume decreases each partial pressure by a factor of 2 (P = nRT/V).
$P_{NO_2} = 0.600$ atm and $P_{N_2O_4} = 0.17$ atm are the new partial pressures.

$Q = \dfrac{(0.600)^2}{0.17} = 2.1$, $Q < K$; equilibrium will shift to the right.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

	$N_2O_4(g)$	$2\,NO_2(g)$
Initial	0.17 atm	0.600 atm
Equil.	$0.17 - x$	$0.600 + 2x$

$K_p = 4.2 = \dfrac{(0.600 + 2x)^2}{(0.17 - x)}$, $4x^2 + (6.6)x - 0.354 = 0$ (carrying extra sig. figs.)

Solving using the quadratic formula: $x = 0.052$ atm

$P_{NO_2} = 0.600 + 2(0.052) = 0.704$ atm; $P_{N_2O_4} = 0.17 - 0.052 = 0.12$ atm

Challenge Problems

78. P_0 (for O_2) = $n_{O_2}RT/V$ = (6.400 g × 0.08206 × 684 K)/(32.00 g/mol × 2.50 L) = 4.49 atm

	$CH_4(g)$ +	$2\,O_2(g)$	→	$CO_2(g)$ +	$2\,H_2O(g)$
Change	$-x$	$-2x$	→	$+x$	$+2x$

	$CH_4(g)$ +	$3/2\,O_2(g)$	→	$CO(g)$ +	$2\,H_2O(g)$
Change	$-y$	$-3/2\,y$	→	$+y$	$+2y$

Amount of O_2 reacted = 4.49 atm – 0.326 atm = 4.16 atm O_2

$2x + 3/2\,y = 4.16$ atm O_2 and $2x + 2y = 4.45$ atm H_2O

Solving using simultaneous equations:

$$\begin{array}{rcl} 2x + 2y &=& 4.45 \\ \underline{-2x - (3/2)y} &=& \underline{-4.16} \\ (0.50)y &=& 0.29, \quad y = 0.58 \text{ atm} = P_{CO} \end{array}$$

$2x + 2(0.58) = 4.45$, $x = \dfrac{4.45 - 1.16}{2} = 1.65$ atm $= P_{CO_2}$

79. $4.72\text{ g } CH_3OH \times \dfrac{1\text{ mol}}{32.04\text{ g}} = 0.147\text{ mol } CH_3OH$ initially

Graham's law of effusion: $\dfrac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\dfrac{M_2}{M_1}}$

$$\frac{\text{Rate}_{H_2}}{\text{Rate}_{CH_3OH}} = \sqrt{\frac{M_{CH_3OH}}{M_{H_2}}} = \sqrt{\frac{32.04}{2.016}} = 3.987$$

The effused mixture has 33.0 times as much H_2 as CH_3OH. When the effusion rate ratio is multiplied by the equilibrium mole ratio of H_2 to CH_3OH, the effused mixture will have 33.0 times as much H_2 as CH_3OH. Let n_{H_2} and n_{CH_3OH} equal the equilibrium moles of H_2 and CH_3OH, respectively.

$$33.0 = 3.987 \times \frac{n_{H_2}}{n_{CH_3OH}}, \quad \frac{n_{H_2}}{n_{CH_3OH}} = 8.28$$

	$CH_3OH(g)$	$\rightleftharpoons$	$CO(g)$	$+ 2\,H_2(g)$
Initial	0.147 mol		0	0
Change	$-x$	$\rightarrow$	$+x$	$+2x$
Equil.	$0.147 - x$		x	$2x$

From the ICE table, $8.28 = \dfrac{n_{H_2}}{n_{CH_3OH}} = \dfrac{2x}{0.147 - x}$

Solving: $x = 0.118$ mol

$$K = \frac{[CO][H_2]^2}{[CH_3OH]} = \frac{\left(\frac{0.118\,\text{mol}}{1.00\,\text{L}}\right)\left(\frac{2(0.118\,\text{mol})}{1.00\,\text{L}}\right)^2}{\frac{(0.147 - 0.118)\,\text{mol}}{1.00\,\text{L}}} = 0.23$$

80. a. Because density (mass/volume) decreases while the mass remains constant (mass is conserved in a chemical reaction), volume must increase. The volume increases because the number of moles of gas increases ($V \propto n$ at constant T and P).

$$\frac{\text{Density(initial)}}{\text{Density(equil.)}} = \frac{4.495\,\text{g/L}}{4.086\,\text{g/L}} = 1.100 = \frac{V_{\text{equil.}}}{V_{\text{initial}}} = \frac{n_{\text{equil.}}}{n_{\text{initial}}}$$

Assuming an initial volume of 1.000 L:

$$4.495\text{ g NOBr} \times \frac{1\,\text{mol NOBr}}{109.91\,\text{g}} = 0.04090 \text{ mol NOBr initially}$$

	$2\,NOBr(g)$	$\rightleftharpoons$	$2\,NO(g)$	$+\ Br_2(g)$
Initial	0.04090 mol		0	0
Change	$-2x$	$\rightarrow$	$+2x$	$+x$
Equil.	$0.04090 - 2x$		$2x$	x

$$\frac{n_{\text{equil.}}}{n_{\text{initial}}} = \frac{0.04090 - 2x + 2x + x}{0.04090} = 1.100; \quad \text{solving: } x = 0.00409 \text{ mol}$$

If the initial volume is 1.000 L, then the equilibrium volume will be 1.110(1.000 L) = 1.110 L. Solving for the equilibrium concentrations:

$$[\text{NOBr}] = \frac{0.03272\,\text{mol}}{1.100\,\text{L}} = 0.02975\,M; \quad [\text{NO}] = \frac{0.00818\,\text{mol}}{1.100\,\text{L}} = 0.00744\,M$$

$$[\text{Br}_2] = \frac{0.00409\,\text{mol}}{1.100\,\text{L}} = 0.00372\,M$$

$$K = \frac{(0.00744)^2(0.00372)}{(0.02975)^2} = 2.33 \times 10^{-4}$$

b. The argon gas will increase the volume of the container. This is because the container is a constant-pressure system, and if the number of moles increases at constant T and P, the volume must increase. An increase in volume will dilute the concentrations of all gaseous reactants and gaseous products. Because there are more moles of product gases versus reactant gases (3 mol versus 2 mol), the dilution will decrease the numerator of K more than the denominator will decrease. This causes Q < K and the reaction shifts right to get back to equilibrium.

Because temperature was unchanged, the value of K will not change. K is a constant as long as temperature is constant.

81.

	$N_2(g)$	+ $O_2(g)$	$\rightleftharpoons$ $2\,NO(g)$
Equil.	$(3.7)p$	p	x

Let:
equilibrium $P_{O_2} = p$
equilibrium $P_{N_2} = (78/21)P_{O_2} = (3.7)p$
equilibrium $P_{NO} = x$
equilibrium $P_{NO_2} = y$

$$K_p = 1.5 \times 10^{-4} = \frac{P_{NO}^2}{P_{O_2} \times P_{N_2}}$$

	N_2	+ $2\,O_2$	$\rightleftharpoons$ $2\,NO_2$
Equil.	$(3.7)p$	p	y

$$K_p = 1.0 \times 10^{-5} = \frac{P_{NO_2}^2}{P_{O_2}^2 \times P_{N_2}}$$

We want $P_{NO_2} = P_{NO}$ at equilibrium, so $x = y$.

Taking the ratio of the two K_p expressions:

$$\frac{\dfrac{P_{NO}^2}{P_{O_2} \times P_{N_2}}}{\dfrac{P_{NO_2}^2}{P_{O_2}^2 \times P_{N_2}}} = \frac{1.5 \times 10^{-4}}{1.0 \times 10^{-5}};\ \text{because } P_{NO} = P_{NO_2}:\ P_{O_2} = \frac{1.5 \times 10^{-4}}{1.0 \times 10^{-5}} = 15 \text{ atm}$$

Air is 21 mol % O_2, so: $P_{O_2} = (0.21)P_{total}$, $P_{total} = \dfrac{15 \text{ atm}}{0.21} = 71 \text{ atm}$

To solve for the equilibrium concentrations of all gases (not required to answer the question), solve one of the K_p expressions where $p = P_{O_2} = 15$ atm.

$1.5 \times 10^{-4} = \dfrac{x^2}{15[3.7(15)]}$, $x = P_{NO} = P_{NO_2} = 0.35$ atm

Equilibrium pressures:

$P_{O_2} = 15$ atm; $P_{N_2} = 3.7(15) = 55.5 = 56$ atm; $P_{NO} = P_{NO_2} = 0.35$ atm

82. The first reaction produces equal amounts of SO_3 and SO_2. Using the second reaction, calculate the SO_3, SO_2, and O_2 partial pressures at equilibrium.

	$SO_3(g)$	$\rightleftharpoons$	$SO_2(g)$	+	$1/2\ O_2(g)$	
Initial	P_0		P_0		0	P_0 = initial pressure of SO_3 and SO_2 after first reaction occurs.
Change	$-x$	→	$+x$		$+x/2$	
Equil.	$P_0 - x$		$P_0 + x$		$x/2$	

$P_{total} = P_0 - x + P_0 + x + x/2 = 2P_0 + x/2 = 0.836$ atm

$P_{O_2} = x/2 = 0.0275$ atm, $x = 0.0550$ atm

$2P_0 + x/2 = 0.836$ atm; $2P_0 = 0.836 - 0.0275 = 0.809$ atm, $P_0 = 0.405$ atm

$P_{SO_3} = P_0 - x = 0.405 - 0.0550 = 0.350$ atm; $P_{SO_2} = P_0 + x = 0.405 + 0.0550 = 0.460$ atm

For $2\ FeSO_4(s) \rightleftharpoons Fe_2O_3(s) + SO_3(g) + SO_2(g)$:

$K_p = P_{SO_2} \times P_{SO_3} = (0.460)(0.350) = 0.161$

For $SO_3(g) \rightleftharpoons SO_2(g) + 1/2\ O_2(g)$:

$$K_p = \frac{P_{SO_2} \times P_{O_2}^{1/2}}{P_{SO_3}} = \frac{(0.460)(0.0275)^{1/2}}{(0.350)} = 0.218$$

83. $\frac{2.00\text{g}}{165\text{g/mol}}$ = 0.0121 mol XY (initially)

(0.350)(0.0121 mol) = 4.24×10^{-3} mol XY dissociated

	XY	→	X	+	Y
Initial	0.0121 mol		0		0
Change	–0.00424	→	+0.00424		+0.00424
Equil.	0.0079 mol		0.00424 mol		0.00424 mol

Total moles of gas = 0.0079 + 0.00424 + 0.00424 = 0.0164 mol

$$V \propto n\text{, so: } \frac{V_{\text{final}}}{V_{\text{initial}}} = \frac{n_{\text{final}}}{n_{\text{initial}}} = \frac{0.0164\text{mol}}{0.0121\text{mol}} = 1.36$$

$$V_{\text{initial}} = \frac{nRT}{P} = \frac{(0.0121\text{mol})(0.008206\text{L atm K}^{-1}\text{ mol}^{-1})(298\text{K})}{0.967\text{atm}} = 0.306\text{ L}$$

V_{final} = 0.306 L(1.36) = 0.416 L

Because mass is conserved in a chemical reaction:

$$\text{density (final)} = \frac{\text{mass}}{\text{volume}} = \frac{2.00\text{g}}{0.416\text{L}} = 4.81\text{g/L}$$

$$K = \frac{[X][Y]}{[XY]} = \frac{\left(\frac{0.00424\text{mol}}{0.416\text{L}}\right)^2}{\left(\frac{0.0079\text{mol}}{0.416\text{L}}\right)} = 5.5 \times 10^{-3}$$

84. a. If the volume is increased, equilibrium will shift to the right, so the mole percent of N_2O_5 decomposed will be greater than 0.50%.

b.

	$2\ N_2O_5(g)$	$\rightleftharpoons$	$4\ NO_2(g)$	+	$O_2(g)$
Initial	1.000 atm		0		0
Change	–0.0050	→	+0.010		+0.0025
Equil.	0.995		0.010		0.0025

$$K_p = \frac{(0.010)^4(0.0025)}{(0.995)^2} = 2.5 \times 10^{-11}$$

The new volume is 10.0 times the old volume. Therefore, the initial partial pressure of N_2O_5 will decrease by a factor of 10.0.

$$P_{N_2O_5} = 1.00 \text{ atm} \times \frac{1.00}{10.0} = 0.100 \text{ atm}$$

	$2\ N_2O_5$	$\rightleftharpoons$	$4\ NO_2$	+	O_2
Initial	0.100 atm		0		0
Change	$-2x$	$\rightarrow$	$+4x$		$+x$
Equil.	$0.100 - 2x$		$4x$		x

$$2.5 \times 10^{-11} = \frac{(4x)^4(x)}{(0.100-2x)^2} \approx \frac{(4x)^4(x)}{(0.100)^2}, \quad 2x = 2.0 \times 10^{-3} \text{ atm} = P_{N_2O_5} \text{ decomposed}$$

$$\frac{2.0 \times 10^{-3}}{0.100} \times 100 = 2.0\%\ N_2O_5 \text{ decomposed (moles and P are directly related)}$$

85. $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ $\quad K_p = \dfrac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}} = 6.5 \times 10^{-3}$

<u>1.0 atm</u>	$N_2(g)$	+	$3\ H_2(g)$	$\rightleftharpoons$	$2\ NH_3(g)$
Initial	0.25 atm		0.75 atm		0
Equil.	$0.25 - x$		$0.75 - 3x$		$2x$

$$\frac{(2x)^2}{(0.75-3x)^3(0.25-x)} = 6.5 \times 10^{-3}; \text{ using successive approximations:}$$

$x = 1.2 \times 10^{-2}$ atm; $P_{NH_3} = 2x = 0.024$ atm

<u>10 atm</u>	$N_2(g)$	+	$3\ H_2(g)$	$\rightleftharpoons$	$2\ NH_3(g)$
Initial	2.5 atm		7.5 atm		0
Equil.	$2.5 - x$		$7.5 - 3x$		$2x$

$$\frac{(2x)^2}{(7.5-3x)^3(2.5-x)} = 6.5 \times 10^{-3}; \text{ using successive approximations:}$$

$x = 0.69$ atm; $P_{NH_3} = 1.4$ atm

<u>100 atm</u> Using the same setup as above: $\dfrac{4x^2}{(75-3x)^3(25-x)} = 6.5 \times 10^{-3}$

Solving by successive approximations: $x = 16$ atm; $P_{NH_3} = 32$ atm

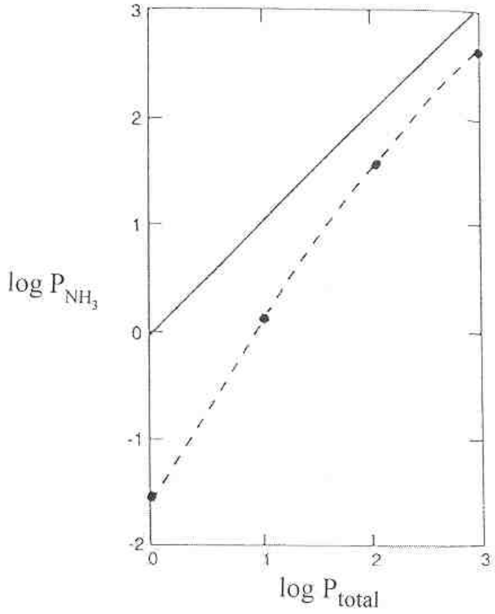
<u>1000 atm</u>

	$N_2(g)$ +	$3\ H_2(g)$ ⇌	$2\ NH_3(g)$
Initial	250 atm	750 atm	0
	Let 250 atm N_2 react completely.		
New initial	0	0	5.0×10^2
Equil.	x	$3x$	$5.0 \times 10^2 - 2x$

$$\frac{(5.0 \times 10^2 - 2x)^2}{(3x)^3 x} = 6.5 \times 10^{-3};\ \text{using successive approximations:}$$

$x = 32$ atm; $P_{NH_3} = 5.0 \times 10^2 - 2x = 440$ atm

The results are plotted as $\log P_{NH_3}$ versus $\log P_{total}$. Notice that as P_{total} increases, a larger fraction of N_2 and H_2 is converted to NH_3, that is, as P_{total} increases (V decreases), the reaction shifts further to the right, as predicted by LeChatelier's principle.



86. a. $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

	N_2O_4		NO_2
Initial	x		0
Change	$-(0.16)x$	$\rightarrow$	$+(0.32)x$
Equil.	$(0.84)x$		$(0.32)x$

$(0.84)x + (0.32)x = 1.5$ atm, $x = 1.3$ atm; $K_p = \dfrac{(0.42)^2}{1.1} = 0.16$

b. $N_2O_4 \rightleftharpoons 2\ NO_2$; $x + y = 1.0$ atm; $\dfrac{y^2}{x} = 0.16$

Equil. x y

Solving: $x = 0.67$ atm $(= P_{N_2O_4})$ and $y = 0.33$ atm $(= P_{NO_2})$

c. $N_2O_4 \rightleftharpoons 2\ NO_2$

	N_2O_4		$2\ NO_2$	
Initial	P_0		0	P_0 = initial pressure of N_2O_4
Change	$-x$	$\rightarrow$	$+2x$	
Equil.	0.67 atm		0.33 atm	

$2x = 0.33$, $x = 0.165$ (using extra sig. figs.)

$P_0 - x = 0.67$, $P_0 = 0.67 + 0.165 = 0.84$ atm; $\dfrac{0.165}{0.84} \times 100 = 20.\%$ dissociated

87. $SO_3(g) \rightleftharpoons SO_2(g) + 1/2\ O_2(g)$

	$SO_3(g)$		$SO_2(g)$	$1/2\ O_2(g)$	
Initial	P_0		0	0	P_0 = initial pressure of SO_3
Change	$-x$	$\rightarrow$	$+x$	$+x/2$	
Equil.	$P_0 - x$		x	$x/2$	

Average molar mass of the mixture is:

$$\text{average molar mass} = \frac{dRT}{P} = \frac{(1.60\ g/L)(0.08206 L\ atm\ K^{-1}\ mol^{-1})(873 K)}{1.80\ atm} = 63.7\ g/mol$$

The average molar mass is determined by:

$$\text{average molar mass} = \frac{n_{SO_3}(80.07 g/mol) + n_{SO_2}(64.07 g/mol) + n_{O_2}(32.00 g/mol)}{n_{total}}$$

Because χ_A = mol fraction of component A = $n_A/n_{total} = P_A/P_{total}$:

$$63.7\ g/mol = = \frac{P_{SO_3}(80.07) + P_{SO_2}(64.07) + P_{O_2}(32.00)}{P_{total}}$$

$P_{total} = P_0 - x + x + x/2 = P_0 + x/2 = 1.80$ atm, $P_0 = 1.80 - x/2$

$$63.7 = \frac{(P_0 - x)(80.07) + x(64.07) + \frac{x}{2}(32.00)}{1.80}$$

$$63.7 = \frac{(1.80 - 3/2\,x)(80.07) + x(64.07) + \frac{x}{2}(32.00)}{1.80}$$

$115 = 144 - (120.1)x + (64.07)x + (16.00)x$, $(40.0)x = 29$, $x = 0.73$ atm

$P_{SO_3} = P_0 - x = 1.80 - (3/2)x = 0.71$ atm; $P_{SO_2} = 0.73$ atm; $P_{O_2} = x/2 = 0.37$ atm

$$K_p = \frac{P_{SO_2} \times P_{O_2}^{1/2}}{P_{SO_3}} = \frac{(0.73)(0.37)^{1/2}}{(0.71)} = 0.63$$

88. a. $89.7 \text{ g } SbCl_5 \times \frac{1 \text{ mol}}{299.1 \text{ g}} = 0.300 \text{ mol } SbCl_5$ initially

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

	$SbCl_5$	$SbCl_3$	Cl_2
Initial	0.300 mol	0	0
Change	–(0.292)(0.300)	+0.0876	+0.0876
Equil.	0.212	0.0876	0.0876 mol

$$K = \frac{\left(\frac{0.0876 \text{ mol}}{15.0 \text{ L}}\right)\left(\frac{0.0876 \text{ mol}}{15.0 \text{ L}}\right)}{\left(\frac{0.212 \text{ mol}}{15.0 \text{ L}}\right)} = 2.41 \times 10^{-3}$$

b. Let x = moles Cl_2 added; reaction shifts left after Cl_2 is added.

Equilibrium moles $SbCl_3$ = 0.0876/2 = 0.0438 mol

Therefore, 0.0438 mol $SbCl_3$ was reacted.

Equilibrium moles $Cl_2 = x + 0.0876 - 0.0438 = x + 0.0438$

Equilibrium moles $SbCl_5$ = 0.212 + 0.0438 = 0.256 mol

$$2.41 \times 10^{-3} = \frac{\left(\frac{x + 0.0438}{15.0}\right)\left(\frac{0.0438}{15.0}\right)}{\left(\frac{0.256}{15.0}\right)};\quad \text{solving:}\quad x = 0.168 \text{ mol } Cl_2 \text{ added}$$

89. $P_4(g) \rightleftharpoons 2\,P_2(g)$ $K_p = 0.100 = \frac{P_{P_2}^2}{P_{P_4}}$; $P_{P_4} + P_{P_2} = P_{total} = 1.00$ atm, $P_{P_4} = 1.00 - P_{P_2}$

Let $y = P_{P_2}$ at equilibrium, then $K_p = \frac{y^2}{1.00 - y} = 0.100$

Solving: $y = 0.270 \text{ atm} = P_{P_2}$; $P_{P_4} = 1.00 - 0.270 = 0.73$ atm

To solve for the fraction dissociated, we need the initial pressure of P_4.

	$P_4(g)$	$\rightleftharpoons$	$2\,P_2(g)$	
Initial	P_0		0	P_0 = initial pressure of P_4
	x atm of P_4 reacts to reach equilibrium			
Change	$-x$	$\rightarrow$	$+2x$	
Equil.	$P_0 - x$		$2x$	

$P_{total} = P_0 - x + 2x = 1.00 \text{ atm} = P_0 + x$

Solving: 0.270 atm = $P_{P_2} = 2x$, $x = 0.135$ atm; $P_0 = 1.00 - 0.135 = 0.87$ atm

$$\text{Fraction dissociated} = \frac{x}{P_0} = \frac{0.135}{0.87} = 0.16\text{, or 16\% of } P_4 \text{ is dissociated to reach equilibrium.}$$

90. a. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$; because the temperature is constant, the value of K will be the same for both container volumes. Since we now the volume in the final mixture, let's calculate K using this mixture. In this final mixture, 2 N_2 molecules, 2 H_2 molecules, and 6 NH_3 molecules are present in a 1.0 L container. Using units of molecules/L for concentrations:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{6\text{ NH}_3\text{ molecules}}{1.00\text{ L}}\right)^2}{\left(\frac{2\text{ N}_2\text{ molecules}}{1.00\text{ L}}\right)\left(\frac{2\text{ H}_2\text{ molecules}}{1.00\text{ L}}\right)^3} = 2.25\frac{\text{L}^2}{\text{molecules}^2}$$

For the K value in typical mol/L units for the concentrations:

$$K = 2.25\,\frac{\text{L}^2}{\text{molecules}^2} \times \left(\frac{6.022\times10^{23}\text{ molecules}}{\text{mol}}\right)^2 = 8.16\times10^{47}\,\frac{\text{L}^2}{\text{mol}^2} = 8.16\times10^{47}$$

b. Because temperature is constant, the initial mixture at the larger volume must also have $K = 2.25\frac{\text{L}^2}{\text{molecules}^2}$. In the initial mixture, there are 2 NH_3 molecules, 4 N_2 molecules, and 8 H_2 molecules in some unknown volume, V.

$$K = 2.25 = \frac{\left(\frac{2\text{ NH}_3\text{ molecules}}{V}\right)^2}{\left(\frac{4\text{ N}_2\text{ molecules}}{V}\right)\left(\frac{8\text{ H}_2\text{ molecules}}{V}\right)^3} = \frac{4V^2}{4(512)} = \frac{V^2}{512}$$

$V = \sqrt{2.25(512)} = 33.9$ L; the volume of the initial container would be 33.9 L.

91. a.

	$2\,NO(g)$	+ $Br_2(g)$	$\rightleftharpoons$	$2\,NOBr(g)$
Initial	98.4 torr	41.3 torr		0
	$2x$ torr of NO reacts to reach equilibrium			
Change	$-2x$	$-x$	$\rightarrow$	$+2x$
Equil.	$98.4 - 2x$	$41.3 - x$		$2x$

$P_{total} = P_{NO} + P_{Br_2} + P_{NOBr} = (98.4 - 2x) + (41.3 - x) + 2x = 139.7 - x$

$P_{total} = 110.5 = 139.7 - x$, $x = 29.2$ torr; $P_{NO} = 98.4 - 2(29.2) = 40.0$ torr $= 0.0526$ atm

$P_{Br_2} = 41.3 - 29.2 = 12.1$ torr $= 0.0159$ atm; $P_{NOBr} = 2(29.2) = 58.4$ torr $= 0.0768$ atm

$$K_p = \frac{P_{NOBr}^2}{P_{NO}^2 \times P_{Br_2}} = \frac{(0.0768\,\text{atm})^2}{(0.0526\,\text{atm})^2(0.0159\,\text{atm})} = 134$$

b.

	$2\,NO(g)$	+ $Br_2(g)$	$\rightleftharpoons$	$2\,NOBr(g)$
Initial	0.30 atm	0.30 atm		0
	$2x$ atm of NO reacts to reach equilibrium			
Change	$-2x$	$-x$	$\rightarrow$	$+2x$
Equil.	$0.30 - 2x$	$0.30 - x$		$2x$

This would yield a cubic equation, which can be difficult to solve unless you have a graphing calculator. Because K_p is pretty large, let's approach equilibrium in two steps: Assume the reaction goes to completion, and then solve the back equilibrium problem.

	$2\,NO$	+ Br_2	$\rightleftharpoons$	$2\,NOBr$	
Before	0.30 atm	0.30 atm		0	
	Let 0.30 atm NO react completely.				
Change	-0.30	-0.15	$\rightarrow$	$+0.30$	React completely
After	0	0.15		0.30	New initial
	$2y$ atm of NOBr reacts to reach equilibrium				
Change	$+2y$	$+y$	$\leftarrow$	$-2y$	
Equil.	$2y$	$0.15 + y$		$0.30 - 2y$	

$$K_p = 134 = \frac{(0.30 - 2y)^2}{(2y)^2(0.15 + y)},\quad \frac{(0.30 - 2y)^2}{(0.15 + y)} = 134 \times 4y^2 = 536y^2$$

If $y << 0.15$: $\dfrac{(0.30)^2}{0.15} \approx 536y^2$ and $y = 0.034$; assumptions are poor (y is 23% of 0.15).

Use 0.034 as an approximation for y, and solve by successive approximations (see Appendix 1):

$$\frac{(0.30-0.068)^2}{0.15+0.034} = 536y^2,\ \ y = 0.023; \qquad \frac{(0.30-0.046)^2}{0.15+0.023} = 536y^2,\ \ y = 0.026$$

$$\frac{(0.30-0.052)^2}{0.15+0.026} = 536y^2,\ \ y = 0.026 \text{ atm}$$ (We have converged on the correct answer.)

So: $P_{NO} = 2y = 0.052$ atm; $P_{Br_2} = 0.15 + y = 0.18$ atm; $P_{NOBr} = 0.30 - 2y = 0.25$ atm

92. Equilibrium lies to the right (K_p values are very large). Let each reaction go to completion initially, and then solve the back equilibrium problems.

	CH_4	+ $2\,O_2$	$\rightarrow$ CO_2	+ $2\,H_2O$
Before	1.50	15.00	0	0
After	0	12.00	1.50	3.00 atm

	$2\,C_2H_6$	+ $7\,O_2$	$\rightarrow$ $4\,CO_2$	+ $6\,H_2O$
Before	2.50	12.00	1.50	3.00
After	0	3.25	6.50	10.50 atm

Thus after we let the two reactions go to completion, we have 3.25 atm O_2, 6.50 atm CO_2, and 10.50 atm H_2O. Let's solve the back equilibrium problems to determine the equilibrium concentrations.

	CH_4	+ $2\,O_2$	$\rightleftharpoons$	CO_2	+ $2\,H_2O$
Initial	0	3.25 atm		6.50 atm	10.50 atm
Change	$+x$	$+2x$	$\leftarrow$	$-x$	$-2x$
Equil.	x	$3.25 + 2x$		$6.50 - x$	$10.50 - 2x$

$$K_p = 1.0 \times 10^4 = \frac{P_{CO_2} \times P_{H_2O}^2}{P_{CH_4} \times P_{O_2}^2} = \frac{(6.50-x)(10.50-2x)^2}{x(3.25+2x)^2} \approx \frac{6.50(10.50)^2}{x(3.25)^2}$$

$x = P_{CH_4} = 6.8 \times 10^{-3}$ atm; assumptions are good.

	$2\,C_2H_6(g)$	+ $7\,O_2(g)$	$\rightleftharpoons$	$4\,CO_2(g)$	+ $6\,H_2O(g)$
Initial	0	3.25 atm		6.50 atm	10.50 atm
Change	$+2x$	$+7x$	$\leftarrow$	$-4x$	$-6x$
Equil.	$2x$	$3.25 + 7x$		$6.50 - 4x$	$10.50 - 6x$

$$K_p = 1.0 \times 10^8 = \frac{P_{CO_2}^4 \times P_{H_2O}^6}{P_{C_2H_6}^2 \times P_{O_2}^7} = \frac{(6.50-4x)^4(10.50-6x)^6}{(2x)^2(3.25+7x)^7} \approx \frac{(6.50)^4(10.50)^6}{4x^2(3.25)^7}$$

$2x = P_{C_2H_6} = 0.079$ atm; assumptions are good.

93. a. $$P_{PCl_5} = \frac{n_{PCl_5}RT}{V} = \frac{0.100\ \text{mol} \times \dfrac{0.08206\ \text{L atm}}{\text{K mol}} \times 480.\ \text{K}}{12.0\ \text{L}} = 0.328\ \text{atm}$$

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$	$K_p = 0.267$
Initial	0.328 atm		0		0	
Change	$-x$	→	$+x$		$+x$	
Equil.	$0.328 - x$		x		x	

$$K_p = \frac{x^2}{0.328 - x} = 0.267,\ x^2 + (0.267)x - 0.08758 = 0\ \text{(carrying extra sig. figs.)}$$

Solving using the quadratic formula: $x = 0.191$ atm

$P_{PCl_3} = P_{Cl_2} = 0.191$ atm; $P_{PCl_5} = 0.328 - 0.191 = 0.137$ atm

b.

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$	
Initial	P_0		0		0	P_0 = initial pressure of PCl_5
Change	$-x$	→	$+x$		$+x$	
Equil.	$P_0 - x$		x		x	

$P_{total} = 2.00\ \text{atm} = (P_0 - x) + x + x = P_0 + x,\ P_0 = 2.00 - x$

$$K_p = \frac{x^2}{P_0 - x} = 0.267;\ \frac{x^2}{2.00 - 2x} = 0.267,\ x^2 = 0.534 - (0.534)x$$

$x^2 + (0.534)x - 0.534 = 0$; solving using the quadratic formula:

$$x = \frac{-0.534 \pm \sqrt{(0.534)^2 + 4(0.534)}}{2} = 0.511\ \text{atm}$$

$P_0 = 2.00 - x = 2.00 - 0.511 = 1.49$ atm; the initial pressure of PCl_5 was 1.49 atm.

$$n_{PCl_5} = \frac{P_{PCl_5}V}{RT} = \frac{(1.49\ \text{atm})(5.00\ \text{L})}{(0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1})(480.\ \text{K})} = 0.189\ \text{mol}\ PCl_5$$

0.189 mol PCl_5 × 208.22 g PCl_5/mol = 39.4 g PCl_5 was initially introduced.

94.

	$CCl_4(g)$	$\rightleftharpoons$	$C(s)$	+	$2\ Cl_2(g)$	$K_p = 0.76$
Initial	P_0		–		0	P_0 = initial pressure of CCl_4
Change	$-x$	→	–		$+2x$	
Equil.	$P_0 - x$		–		$2x$	

$P_{total} = P_0 - x + 2x = P_0 + x = 1.20$ atm

$K_p = \dfrac{(2x)^2}{P_0 - x} = 0.76$, $4x^2 = (0.76)P_0 - (0.76)x$, $P_0 = \dfrac{4x^2 + (0.76)x}{0.76}$; substituting into $P_0 + x = 1.20$:

$\dfrac{4x^2}{0.76} + x + x = 1.20$ atm, $(5.3)x^2 + 2x - 1.20 = 0$; solving using the quadratic formula:

$x = \dfrac{-2 \pm (4 + 25.4)^{1/2}}{2(5.3)} = 0.32\ \text{atm}$; $P_0 + 0.32 = 1.20$, $P_0 = 0.88$ atm

95. $$d = \text{density} = \frac{P \times (\text{molar mass})}{RT} = \frac{P_{O_2}(\text{molar mass}_{O_2}) + P_{O_3}(\text{molar mass}_{O_3})}{RT}$$

$$0.168\ \text{g/L} = \frac{P_{O_2}(32.00\ \text{g/mol}) + P_{O_3}(48.00\ \text{g/mol})}{\dfrac{0.08206\ \text{L atm}}{\text{K mol}} \times 448\ \text{K}},\quad (32.00)P_{O_2} + (48.00)P_{O_3} = 6.18$$

$$P_{total} = P_{O_2} + P_{O_3} = 128\ \text{torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} = 0.168\ \text{atm}$$

We have two equations in two unknowns. Solving using simultaneous equations:

$$\begin{array}{rcr} (32.00)P_{O_2} + (48.00)P_{O_3} & = & 6.18 \\ -(32.00)P_{O_2} - (32.00)P_{O_3} & = & -5.38 \\ \hline (16.00)P_{O_3} & = & 0.80 \end{array}$$

$P_{O_3} = \dfrac{0.80}{16.00} = 0.050$ atm and $P_{O_2} = 0.118$ atm; $K_p = \dfrac{P_{O_3}^2}{P_{O_2}^3} = \dfrac{(0.050)^2}{(0.118)^3} = 1.5$

Marathon Problem

96. Concentration units involve both moles and volume and since both quantities are changing at the same time, we have a complicated system. Let's simplify the setup of the problem initially by only worrying about the changes that occur to the moles of each gas.

	A(g)	+ B(g)	$\rightleftharpoons$	C(g)	K = 130.
Initial	0	0		0.406 mol	
	Let x mol of C(g) react to reach equilibrium				
Change	$+x$	$+x$	←	$-x$	
Equil.	x	x		$0.406 - x$	

Let V_{eq} = the equilibrium volume of the container, so:

$$[A]_{eq} = [B]_{eq} = \frac{x}{V_{eq}} \; ; \; [C]_{eq} = \frac{0.406 - x}{V_{eq}}$$

$$K = \frac{[C]}{[A][B]} = \frac{\frac{0.046 - x}{V_{eq}}}{\frac{x}{V_{eq}} \times \frac{x}{V_{eq}}} = \frac{(0.406 - x)\,V_{eq}}{x^2}$$

From the ideal gas equation: V = nRT/P. To calculate the equilibrium volume from the ideal gas law, we need the total moles of gas present at equilibrium.

At equilibrium: n_{total} = mol A(g) + mol B(g) + mol C(g) = $x + x + 0.406 - x = 0.406 + x$

Therefore: $V_{eq} = \frac{n_{total}RT}{P} = \frac{(0.406 + x)(0.08206\,\text{L atm K}^{-1}\,\text{mol}^{-1})(300.0\,\text{K})}{1.00\,\text{atm}}$

$$V_{eq} = (0.406 + x)24.6\ \text{L/mol}$$

Substituting into the equilibrium expression for V_{eq}:

$$K = 130. = \frac{(0.406 - x)(0.406 + x)24.6}{x^2}$$

Solving for x (we will carry one extra significant figure):

$(130.)x^2 = (0.1648 - x^2)24.6$, $(154.6)x^2 = 4.054$, $x = 0.162$ mol

Solving for the volume of the container at equilibrium:

$$V_{eq} = \frac{(0.406 + 0.162\,\text{mol})(0.08206)(300.0\,\text{K})}{1.00\,\text{atm}} = 14.0\ \text{L}$$