

15. CHEMICAL EQUILIBRIUM

■ Solutions to Exercises

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

- 15.1 Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	CO(g)	+	H ₂ O(g)		CO ₂ (g)	+	H ₂ (g)
Starting	1.00		1.00		0		0
Change	-x		-x		+x		+x
Equilibrium	(1.00 - x)		(1.00 - x)		x		x = 0.43

Because we are given that $x = 0.43$ in the statement of the problem, we can use that to calculate the equilibrium amounts of the reactants and products:

$$\text{Equilibrium amount CO} = 1.00 - 0.43 = 0.57 \text{ mol}$$

$$\text{Equilibrium amount H}_2\text{O} = 1.00 - 0.43 = 0.57 \text{ mol}$$

$$\text{Equilibrium amount CO}_2 = x = 0.43 \text{ mol}$$

$$\text{Equilibrium amount H}_2 = x = 0.43 \text{ mol}$$

- 15.2 For the equation $2\text{NO}_2 + 7\text{H}_2 \rightarrow 2\text{NH}_3 + 4\text{H}_2\text{O}$, the expression for the equilibrium constant, K_c , is

$$K_c = \frac{[\text{NH}_3]^2 [\text{H}_2\text{O}]^4}{[\text{NO}_2]^2 [\text{H}_2]^7}$$

Notice that each concentration term is raised to a power equal to that of its coefficient in the chemical equation.

For the equation $\text{NO}_2 + 7/2\text{H}_2 \rightarrow \text{NH}_3 + 2\text{H}_2\text{O}$, the expression for the equilibrium constant, K_c , is

$$K_c = \frac{[\text{NH}_3][\text{H}_2\text{O}]^2}{[\text{NO}_2][\text{H}_2]^{7/2}}$$

Note the correspondence between the power and coefficient for each molecule.

- 15.3 The chemical equation for the reaction is



The expression for the equilibrium constant for this reaction is

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

We obtain the concentration of each substance by dividing the moles of substance by its volume. The equilibrium concentrations are as follows: $[\text{CO}] = 0.057 \text{ M}$, $[\text{H}_2\text{O}] = 0.057 \text{ M}$, $[\text{CO}_2] = 0.043 \text{ M}$, and $[\text{H}_2] = 0.043 \text{ M}$. Substituting these values into the equation for the equilibrium constant gives

$$K_c = \frac{(0.043)(0.043)}{(0.057)(0.057)} = 0.569 = 0.57$$

- 15.4 Use the table approach, and give the starting, change, and equilibrium concentrations of each by dividing moles by volume in liters.

Conc. (M)	2H ₂ S(g)		2H ₂ (g)	+	S ₂ (g)
Starting	0.0100		0		0
Change	-2x		+2x (= 0.00285)		+x
Equilibrium	0.0100 - 2x		2x		x

Because the problem states that 0.00285 M H₂ was formed, we can use the 0.00285 M to calculate the other concentrations. The S₂ molarity should be one-half that, or 0.001425 M, and the H₂S molarity should be 0.0100 - 0.00285, or 0.00715 M. Substituting into the equilibrium expression gives

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2} = \frac{(0.00285)^2 (0.001425)}{(0.00715)^2} = 2.26 \times 10^{-4} = 2.3 \times 10^{-4}$$

- 15.5 Use the expression that relates K_c to K_p:

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

The Δn term is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants. In this case, $\Delta n = (2 - 1) = 1$, and K_p is

$$K_p = (3.26 \times 10^{-2}) (0.0821 \times 464)^1 = 1.241 = 1.24$$

- 15.6 For a heterogeneous equilibrium, the concentration terms for liquids and solids are omitted because such concentrations are constant at a given temperature and are incorporated into the measured value of K_c. For this case, K_c is defined

$$K_c = \frac{[\text{Ni}(\text{CO})_4]}{[\text{CO}]^4}$$

- 15.7 Because the equilibrium constant is very large ($> 10^4$), the equilibrium mixture will contain mostly products. Rearrange the K_c expression to solve for [NO₂].

$$\begin{aligned} [\text{NO}_2] &= \sqrt{K_c [\text{O}_2] [\text{NO}]^2} = \sqrt{(4.0 \times 10^{13}) (2.0 \times 10^{-6}) (2.0 \times 10^{-6})^2} = 1.78 \times 10^{-2} \\ &= 1.8 \times 10^{-2} = 0.018 \text{ M} \end{aligned}$$

- 15.8 First, divide moles by volume in liters to convert to molar concentrations, giving 0.00015 M CO_2 and 0.010 M CO . Substitute these values into the reaction quotient and calculate Q .

$$Q = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(0.010)^2}{(0.00015)} = 0.6\bar{6}6 = 0.67$$


Because $Q = 0.67$ and is less than K_c , the reaction will go to the right, forming more CO .

- 15.9 Rearrange the K_c expression, and substitute for K_c ($= 0.0415$) and the given moles per 1.00 L to solve for moles per 1.00 L of PCl_5 .

$$\begin{aligned} [\text{PCl}_5] &= \frac{[\text{PCl}_3][\text{Cl}_2]}{K_c} = \frac{(0.020)(0.020)}{0.0415} = 9.63 \times 10^{-3} \\ &= 9.6 \times 10^{-3} \text{ mol/ 1.00 L} \end{aligned}$$

Because the volume is 1.00 L, the moles of $\text{PCl}_5 = 0.0096$ mol.

- 15.10 Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$		$2\text{HI}(\text{g})$
Starting	0.500		0.500		0
Change	-x		-x		+2x
Equilibrium	0.500 - x		0.500 - x		2x

Substitute the equilibrium concentrations into the expression for K_c ($= 49.7$).

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}; 49.7 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)} = \frac{(2x)^2}{(0.500 - x)^2}$$

Taking the square root of both sides of the right-hand equation and solving for x gives:

$$\pm 7.05 = \frac{2x}{(0.500 - x)}, \text{ or } \pm 7.05(0.500 - x) = 2x$$

(continued)

Using the positive root, $x = 0.390$.

Using the negative root, $x = 0.698$ (this must be rejected because 0.698 is greater than the 0.500 starting number of moles).

Substituting $x = 0.390$ mol into the last line of the table to solve for equilibrium concentrations gives these amounts: 0.11 mol H_2 , 0.11 mol I_2 , and 0.78 mol HI.

- 15.11 Use the table approach for starting, change, and equilibrium concentrations of each species.

Conc. (M)	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Starting	1.00		0		0
Change	-x		+x		+x
Equilibrium	$1.00 - x$		x		x

Substitute the equilibrium concentration expressions from the table into the equilibrium equation, and solve for x using the quadratic formula.

$$[\text{PCl}_3][\text{Cl}_2] = K_c \times [\text{PCl}_5] = 0.0211(1.00 - x) = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(-0.0211)}}{2} = \frac{-0.0211 \pm 0.2913}{2}$$

$$x = -0.1562 \text{ (impossible; reject), or } x = 0.13509 = 0.135 \text{ M (logical)}$$

Solve for the equilibrium concentrations using $x = 0.135$ M: $[\text{PCl}_5] = 0.86$ M, $[\text{Cl}_2] = 0.135$ M, and $[\text{PCl}_3] = 0.135$ M.

- 15.12 a. Increasing the pressure will cause a net reaction to occur from right to left, and more CaCO_3 will form.
- b. Increasing the concentration of hydrogen will cause a net reaction to occur from right to left, forming more Fe and H_2O .

- 15.13 a. Because there are equal numbers of moles of gas on each side of the equation, increasing the pressure will not increase the amount of product.
- b. Because the reaction increases the number of moles of gas, increasing the pressure will decrease the amount of product.
- c. Because the reaction decreases the number of moles of gas, increasing the pressure will increase the amount of product.
- 15.14 Because this is an endothermic reaction and absorbs heat, high temperatures will be more favorable to the production of carbon monoxide.
- 15.15 Because this is an endothermic reaction and absorbs heat, high temperatures will give the best yield of carbon monoxide. Because the reaction increases the number of moles of gas, decreasing the pressure will also increase the yield.

■ Answers to Concept Checks

- 15.1 The statement that when reactant A decreases by an amount x , product C increases by amount x implies that A and C have the same coefficients. The statement that when reactant B decreases by an amount x , product C increases by amount $2x$ implies that the coefficient of C is twice that of B. Therefore, the coefficient of A is twice that of B. The simplest equation satisfying these conditions is $2A + B \rightarrow 2C$.
- 15.2 To answer this question, find the relationship between the two species present using the equilibrium constant expression and its value. For the first reaction, $A(g) \rightleftharpoons B(g)$, with $K = 2$, this becomes

$$K = 2 = \frac{[B]}{[A]}$$

This reduces to $[B] = 2[A]$. This corresponds to the container that has twice as many balls of one color than the other color, namely container IV. Here, the blue molecules are B (eight of them), and the red molecules are A (four of them).

For the second reaction, $X(g) \rightleftharpoons 2Y(g)$, with $K = 6$, this becomes

$$K = 6 = \frac{[Y]^2}{[X]}$$

This reduces to $[Y]^2 = 6[X]$. This corresponds to container I, where there are six of each color molecule. Since there are the same numbers of each molecule, you cannot determine which color corresponds to which molecule.

(continued)

For the third reaction, $2 \text{C(g)} \rightleftharpoons \text{D(g)}$, with $K = 1$, this becomes

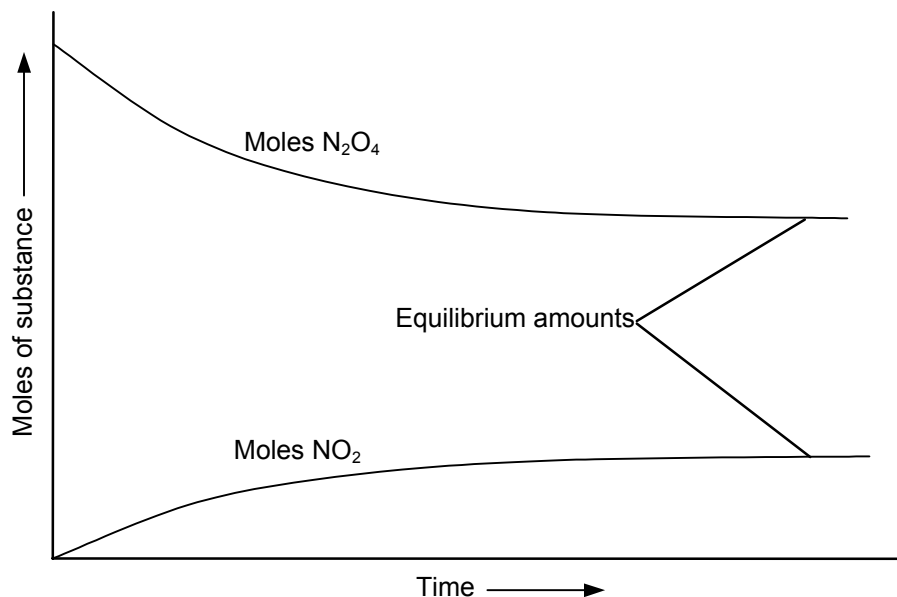
$$K = 1 = \frac{[\text{D}]}{[\text{C}]^2}$$

This reduces to $[\text{C}]^2 = [\text{D}]$. This corresponds to container II. The red balls (nine of them) correspond to molecule D, and the blue balls (three of them) correspond to molecule C.

- 15.3 The concentration of each substance initially doubles. This means that each concentration factor in the reaction quotient expression is double that in the initial equilibrium mixture. Because this expression contains $[\text{CO}][\text{H}_2]^2$ in the denominator, the denominator increases by a factor of 2^3 . However, the numerator contains only $[\text{CH}_3\text{OH}]$, which merely doubles. So, the reaction quotient equals two divided by two cubed, or one-quarter, times the equilibrium constant. To approach the equilibrium constant, the numerator of the reaction quotient must increase, and the denominator must decrease. This means that more CH_3OH must be produced. The reaction goes from left to right.
- 15.4 The equilibrium constant expression is $[\text{C}]/([\text{A}][\text{B}])$. A new equilibrium is attained in which the equilibrium constant expression is $[\text{C}']/([\text{A}'][\text{B}']) = [\text{C}']/(2[\text{A}]2[\text{B}])$, where primes indicate new equilibrium concentrations. The value of the equilibrium constant expression, though, must remain fixed in value, so $[\text{C}']/(2[\text{A}]2[\text{B}])$ equals $[\text{C}]/([\text{A}][\text{B}])$. This means that the new concentration of C, or $[\text{C}]'$, must be four times larger than the original equilibrium value. Thus, the concentration of C is quadrupled.
- 15.5 For an exothermic reaction, as the temperature is increased, the reaction shifts towards the reactant side to absorb the heat and counteract the temperature increase. This corresponds to the case where there are mostly reactant molecules and very few product molecules, namely container I. At lower temperatures, the reaction shifts towards the product side to release heat. This corresponds to the case where there is a larger proportion of product molecules to reactant molecules, namely container II.

■ Answers to Review Questions

- 15.1 A reasonable graph showing the decrease in concentration of $\text{N}_2\text{O}_4(\text{g})$ and the increase in concentration of $\text{NO}_2(\text{g})$ is shown below:



At first, the concentration of N_2O_4 is large, and the rate of the forward reaction is large, but then as the concentration of N_2O_4 decreases, the rate of the forward reaction decreases. In contrast, the concentration of NO_2 builds up from zero to a low concentration. Thus, the initial rate of the reverse reaction is zero, but it steadily increases as the concentration of NO_2 increases. Eventually, the two rates become equal when the reaction reaches equilibrium. This is a dynamic equilibrium because both the forward and reverse reactions are occurring at all times even though there is no net change in concentration at equilibrium.

- 15.2 The 1.0 mol of $\text{H}_2(\text{g})$ and 1.0 mol of $\text{I}_2(\text{g})$ in the first mixture reach equilibrium when the amounts of reactants decrease to 0.50 mol each and when the amount of product increases to 1.0 mol. The total number of moles of the reactants at the start is 2.0 mol, which is the same number of moles as in the second mixture, the 2.0 mol of HI that is to be allowed to come to equilibrium. The second mixture should produce the same number of moles of H_2 , I_2 , and HI at equilibrium because, if the total number of moles is constant, it should not matter from which direction an equilibrium is approached.

15.3 The equilibrium constant for a gaseous reaction can be written using partial pressures instead of concentrations because all the reactants and products are in the same vessel. Therefore, at constant temperature, the pressure, P , is proportional to the concentration, n/V . (The ideal gas law says that $P = [n/V]RT$).

15.4 The addition of reactions 1 and 2 yields reaction 3:



The rule states that, if a given equation can be obtained from the sum of other equations, the equilibrium constant for the given equation equals the product of the other equilibrium constants. Thus, K for reaction 3 is

$$K = K_1 \times K_2 = (4.9 \times 10^4) \times (1.0 \times 10^{-14}) = 4.9 \times 10^{-10}$$

- 15.5 a. Homogeneous equilibrium. All substances are gases and thus exist in one phase, a mixture of gases.
- b. Heterogeneous equilibrium. The two copper compounds are solids, but the other substances are gases. This fulfills the definition of a heterogeneous equilibrium.
- c. Homogeneous equilibrium. All substances are gases and thus exist in one phase, a mixture of gases.
- d. Heterogeneous equilibrium. The two copper-containing substances are solids, but the other substances are gases. This fulfills the definition of a heterogeneous equilibrium.
- 15.6 Pure liquids and solids can be ignored in an equilibrium-constant expression because their concentrations do not change. (If a solid is present, it has not dissolved in any gas or solution present.) In effect, concentrations of liquids and solids are incorporated into the value of K_c , as discussed in the chapter.
- 15.7 A qualitative interpretation of the equilibrium constant involves using the magnitude of the equilibrium constant to predict the relative amounts of reactants and products at equilibrium. If K_c is around one, the equilibrium mixture contains appreciable amounts (same order of magnitude) of reactants and products. If K_c is large, the equilibrium mixture is mostly products. If K_c is small, the equilibrium mixture is mostly reactants. The type of reaction governs what "large" and "small" values are; but for some types of reactions, "large" might be no less than 10^2 to 10^4 , whereas "small" might be no more than 10^{-4} to 10^{-2} .

- 15.8 The reaction quotient, Q_c , is an expression that has the same form as the equilibrium-constant expression but whose concentrations are not necessarily equilibrium concentrations. It is useful in determining whether a reaction mixture is at equilibrium or, if not, what direction the reaction will go as it approaches equilibrium.
- 15.9 The ways in which the equilibrium composition of a mixture can be altered are (1) changing concentrations by removing some of the products and/or some of the reactants, (2) changing the partial pressure of a gaseous reactant and/or a gaseous product, and (3) changing the temperature of the reaction mixture. (Adding a catalyst cannot alter the equilibrium concentration, but can affect only the rate of reaction.)
- 15.10 The role of the platinum is that of a catalyst; it provides conditions (a surface) suitable for speeding up the attainment of equilibrium. The platinum has no effect on the equilibrium composition of the mixture even though it greatly increases the rate of reaction.
- 15.11 In some cases, a catalyst can affect the product in a reaction because it affects only the rate of one reaction out of several reactions that are possible. If two reactions are possible, and the uncatalyzed rate of one is much slower but is the only reaction that is catalyzed, then the products with and without a catalyst will be different. The Ostwald process is a good example. In the absence of a catalyst, NH_3 burns in O_2 to form only N_2 and H_2O , even though it is possible for NH_3 to react to form NO and H_2O . Ostwald found that adding a platinum catalyst favors the formation of the NO and H_2O almost to the exclusion of the N_2 and H_2O .
- 15.12 Four ways in which the yield of ammonia can be improved are (1) removing the gaseous NH_3 from the equilibrium by liquefying it, (2) increasing the nitrogen or hydrogen concentration, (3) increasing the total pressure on the mixture (the moles of gas decrease), and (4) lowering the temperature (ΔH° is negative, so heat is evolved). Each causes a shift to the right in accordance with Le Chatelier's principle.

■ Answers to Conceptual Problems

- 15.13 For each three moles of H_2 that react, two moles of ammonia form. The mole ratio is

$$\frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2}$$

If x mol H_2 react, then the amount of ammonia that forms is

$$x \text{ mol H}_2 \times \frac{2 \text{ mol NH}_3}{3 \text{ mol H}_2} = \frac{2x}{3} \text{ mol NH}_3$$

- 15.14 The addition of a pure liquid does not affect an equilibrium. (The pure liquid does not appear in the equilibrium constant; in effect, the concentration of the liquid does not change.) Thus, the amount of water vapor does not change appreciably. (More precisely, the amount of vapor decreases slightly because the liquid takes up more room in the container.) If, instead, you add water vapor to the container, vapor condenses until the original vapor pressure is restored. Thus, the amount of liquid water in the container increases.
- 15.15 Hydrogen, H_2 , is the limiting reactant, so the maximum amount of CH_3OH that could form is one mol. However, because the reaction comes to equilibrium before it can go to completion, less than one mol of CH_3OH forms. The answer is a.
- 15.16 The system must exist as an equilibrium mixture of all four substances. The reaction can be represented as



If you pass $\text{H}_2(\text{g})$ over iron oxide, the reaction shifts to the right, and metallic iron and water vapor form. If, instead, you pass water vapor over metallic iron, the reaction shifts to the left, and iron oxide and H_2 will form. An excess of one reactant pushes the reaction in the opposite direction.

- 15.17 a. The equilibrium constant expression for this reaction is

$$K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 2.0$$

The equilibrium case is where the reaction quotient, Q , is equal to the equilibrium constant, K . This occurs in picture III, where

$$Q = \frac{(2)(4)}{(2)^2} = 2.0 = K$$

- b. For picture I, the reaction quotient is

$$Q = \frac{(2)(2)}{(4)^2} = 0.25 < K$$

Since $Q < K$, the reaction shifts towards the product ($\text{H}_2 + \text{I}_2$) side.

For picture II, the reaction quotient is

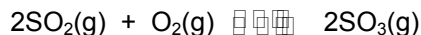
$$Q = \frac{(4)(4)}{(4)^2} = 1.0 < K$$

Since $Q < K$, the reaction shifts towards the product ($\text{H}_2 + \text{I}_2$) side.

- 15.18 Equilibrium has been reached when the concentration of reactants and products is constant. The equilibrium region on the graph is where the lines flatten out indicating the concentrations of reactants and products are not changing. At equilibrium, the concentration of A is approaching 2.0 M, and the concentration of B is approaching 1.0 M. Substituting into the equilibrium constant expression gives

$$K_c = \frac{[B]}{[A]^2} = \frac{1.0}{(2.0)^2} = 0.25$$

- 15.19 a. When the volume is doubled, the pressure is reduced by one-half. A decrease in pressure results in the equilibrium shifting to the side of the reaction with the greater number of moles of gas. Note that in this reaction, there are two moles of gas reactants versus one mole of gas products. Since the pressure has been reduced, the reaction will shift to the left, towards the side of the reaction with the greater number of moles of gas.
- b. Since the reaction has been shifted to the left, the concentrations of A and B will increase, while the concentration of C will decrease.
- 15.20 For an endothermic reaction, as the temperature lowers, the reaction shifts towards the reactant side, producing heat and counteracting the lowering of the temperature. This corresponds to container I, where there is a smaller proportion of product molecules to reactant molecules. In terms of the reaction quotient, Q , the lower temperature corresponds to the container with the smaller value of Q (container I).
- 15.21 The formation of SO_3 can be represented by the following reaction:



The first condition mentioned is the oxygen-enriched air. The higher concentration of O_2 drives the reaction to the right, increasing the yield of SO_3 . Next, the reaction temperature is 420°C . Since the reaction is exothermic, the elevated temperature drives the reaction to the left, decreasing the yield of SO_3 . The vanadium(V) oxide catalyst affects the rate of the reaction, but not the amount of SO_3 that forms at equilibrium. Finally, the SO_3 that forms in the reaction is absorbed by concentrated sulfuric acid and removed from the system. This causes the reaction to shift to the right, forming more SO_3 .


Another condition that can be explored is a change in pressure. Since there are more moles of gas on the left side, an increase in pressure (or decrease in volume) should cause more SO_3 to form.

- 15.22 If you start with 1.00 mol CH_3OH , there will be 0.100 mol CH_3OH present at equilibrium. Assume the reaction could go to completion. Starting with 1.00 mol CO and 2.00 mol H_2 , stoichiometry shows you would obtain 1.00 mol CH_3OH . Therefore, 1.00 mol CH_3OH is chemically equivalent to 1.00 mol CO and 2.00 mol H_2 . At equilibrium, starting either with 1.00 mol CO and 2.00 mol H_2 or with 1.00 mol CH_3OH gives the same equilibrium mixture, one containing 0.100 mol CH_3OH .

■ Solutions to Practice Problems

Note on significant figures: If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

- 15.23 Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$\text{PCl}_5(\text{g})$		$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Starting	2.500		0		0
Change	-x		+x		+x
Equilibrium	2.500 - x		x = 0.338		x

Since the equilibrium amount of PCl_3 is given in the problem, this tells you $x = 0.338$. The equilibrium amounts for the other substances can now be determined.

$$\text{Equilibrium amount } \text{Cl}_2 = x = 0.338 \text{ mol}$$

$$\text{Equilibrium amount } \text{PCl}_5 = 2.500 - x = 2.500 - 0.338 = 2.162 \text{ mol}$$

Therefore, the amounts of the substances in the equilibrium mixture are 2.162 mol PCl_5 , 0.338 mol PCl_3 , and 0.338 mol Cl_2 .

- 15.24 Because the amount of NO_2 at the start is zero, the 0.90 mol of NO_2 at equilibrium must also equal the change, x , in the moles of N_2O_3 . Use the table approach, and insert the starting, change, and equilibrium number of moles:

Amt. (mol)	$\text{N}_2\text{O}_3(\text{g})$		$\text{NO}_2(\text{g})$	+	$\text{NO}(\text{g})$
Starting	3.00		0		0
Change	-x		+x		+x
Equilibrium	3.00 - x		x = 0.90		x

(continued)


Since the equilibrium amount of NO_2 is given in the problem, this tells you $x = 0.90$. The equilibrium amounts for the other substances can now be determined.

$$\text{Equilibrium amount NO} = x = 0.90 \text{ mol}$$

$$\text{Equilibrium amount N}_2\text{O}_3 = 3.00 - x = 3.00 - 0.90 = 2.10 \text{ mol}$$

Therefore, the amounts of the substances in the equilibrium mixture are 2.10 mol N_2O_3 , 0.90 mol NO_2 , and 0.90 mol NO .

- 15.25 Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$		$2\text{NH}_3(\text{g})$
Starting	0.600		1.800		0
Change	-x		-3x		+2x
Equilibrium	$0.600 - x$		$1.800 - 3x$		$2x = 0.048$


Since the equilibrium amount of NH_3 is given in the problem, this tells you $x = 0.024$. The equilibrium amounts for the other substances can now be determined.

$$\text{Equilibrium amount N}_2 = 0.600 - 0.024 = 0.576 \text{ mol}$$

$$\text{Equilibrium amount H}_2 = 1.800 - 3 \times (0.024) = 1.728 \text{ mol}$$

Therefore, the amounts of the substances in the equilibrium mixture are 0.576 mol N_2 , 1.728 mol H_2 , and 0.048 mol NH_3 .

- 15.26 Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$2\text{NO}(\text{g})$	+	$\text{Br}_2(\text{g})$		$2\text{NOBr}(\text{g})$
Starting	0.0524		0.0262		0
Change	-2x		-x		+2x
Equilibrium	$0.0524 - 2x$		$0.0262 - x$		$2x = 0.0311$

Since the equilibrium amount of NOBr is given in the problem, this tells you $x = 0.01555$. The equilibrium amounts for the other substances can now be determined.

$$\text{Equilibrium amount NO} = 0.0524 - 2 \times (0.01555) = 0.02130 = 0.0213 \text{ mol}$$

$$\text{Equilibrium amount Br}_2 = 0.0262 - 0.01555 = 0.01065 = 0.0107 \text{ mol}$$

Therefore, the amounts of the substances in the equilibrium mixture are 0.0213 mol NO , 0.0107 mol Br_2 , and 0.0311 mol NOBr .

- 15.27 Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$2\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	\rightleftharpoons	$2\text{SO}_3(\text{g})$
Starting	0.0400		0.0200		0
Change	-2x		-x		+2x
Equilibrium	$0.0400 - 2x$		$0.0200 - x$		$2x (= 0.0296)$

Therefore, $x = 0.0148$, and the amounts of substances at equilibrium are 0.0104 mol SO_2 , 0.0052 mol O_2 , and 0.0296 mol SO_3 .

- 15.28 Use the table approach, and give the starting, change, and equilibrium number of moles of each.

Amt. (mol)	$\text{CO}(\text{g})$	+	$2\text{H}_2(\text{g})$	\rightleftharpoons	$\text{CH}_3\text{OH}(\text{g})$
Starting	0.1500		0.3000		0
Change	-x		-2x		+x
Equilibrium	$0.1500 - x$ (= 0.1187)		$0.3000 - 2x$		x

Because $0.1500 - x = 0.1187$, $x = 0.0313$. Therefore, the amounts of substances at equilibrium are 0.1187 mol CO , 0.2374 mol H_2 , and 0.0313 mol CH_3OH .

15.29 a. $K_c = \frac{[\text{NO}_2][\text{NO}]}{[\text{N}_2\text{O}_3]}$

b. $K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2}$

c. $K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]}$

d. $K_c = \frac{[\text{P}(\text{NH}_2)_3][\text{HCl}]^3}{[\text{PCl}_3][\text{NH}_3]^3}$

15.30 a. $K_c = \frac{[\text{N}_2][\text{H}_2]^2}{[\text{N}_2\text{H}_4]}$

b. $K_c = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$

c. $K_c = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2 [\text{H}_2]^2}$

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

- 15.31 The reaction is $2\text{H}_2\text{S}(\text{g}) + 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + 2\text{SO}_2(\text{g})$

15.32 The reaction is $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$

15.33 When the reaction is halved, the equilibrium-constant expression is

$$K_c = \frac{[\text{NO}_2]^2 [\text{O}_2]^{1/2}}{[\text{N}_2\text{O}_5]}$$

When the reaction is then reversed, the equilibrium-constant expression becomes

$$K_c = \frac{[\text{N}_2\text{O}_5]}{[\text{NO}_2]^2 [\text{O}_2]^{1/2}}$$

15.34 When the reaction is halved, the equilibrium-constant expression is

$$K_c = \frac{[\text{NH}_3]^2 [\text{O}_2]^{5/2}}{[\text{NO}]^2 [\text{H}_2\text{O}]^3}$$

When the reaction is then reversed, the equilibrium-constant expression becomes

$$K_c = \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{5/2}}$$

15.35 Because $K_c = 1.84$ for $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$, the value of K_c for $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ must be the reciprocal of K_c for the first reaction. Mathematically, this can be shown as follows:

$$\text{Forward: } K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 1.84$$

$$\text{Reverse: } K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{1}{\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}} = \frac{1}{K_c(\text{f})}$$

Thus, for the reverse reaction, K_c is calculated as follows:

$$K_c = 1 \div 1.84 = 5.434 \times 10^{-1} = 0.543$$

- 15.36 Because $K_c = 27.8$ for $\text{CS}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{S}$, the value of K_c for $\frac{1}{2}\text{CS}_2 + 2\text{H}_2 \rightleftharpoons \frac{1}{2}\text{CH}_4 + \text{H}_2\text{S}$, the second (2) reaction, must be the square root of K_c for the first (1) reaction. Mathematically, this can be shown as follows:

$$K_c(1) = \frac{[\text{CH}_4][\text{H}_2\text{S}]^2}{[\text{CS}_2][\text{H}_2]^4}$$

$$K_c(2) = \frac{[\text{CH}_4]^{1/2}[\text{H}_2\text{S}]}{[\text{CS}_2]^{1/2}[\text{H}_2]^2} = \left[\frac{[\text{CH}_4][\text{H}_2\text{S}]^2}{[\text{CS}_2][\text{H}_2]^4} \right]^{1/2} = [K_c(1)]^{1/2}$$

Thus, for the second (2) reaction, K_c is calculated as follows:

$$K_c = \sqrt{27.8} = 5.272 = 5.27$$

- 15.37 First, calculate the molar concentrations of each of the compounds in the equations:

$$[\text{H}_2] = 0.488 \text{ mol H}_2 \div 6.00 \text{ L} = 0.081\text{33 M}$$

$$[\text{I}_2] = 0.206 \text{ mol I}_2 \div 6.00 \text{ L} = 0.034\text{33 M}$$

$$[\text{HI}] = 2.250 \text{ mol HI} \div 6.00 \text{ L} = 0.375\text{0 M}$$

Now, substitute into the K_c expression:

$$K_c = \frac{(0.3750)^2}{(0.08133)(0.03433)} = 50.\text{36} = 50.4$$

- 15.38 First, calculate the molar concentrations of each of the compounds in the equilibrium:

$$[\text{PCl}_5] = 0.0126 \text{ mol PCl}_5 \div 4.00 \text{ L} = 0.0031\text{50 M}$$

$$[\text{PCl}_3] = 0.0148 \text{ mol PCl}_3 \div 4.00 \text{ L} = 0.0037\text{00 M}$$

$$[\text{Cl}_2] = 0.0870 \text{ mol Cl}_2 \div 4.00 \text{ L} = 0.021\text{75 M}$$

Now, substitute these into the expression for K_c :

$$K_c = \frac{0.003150}{(0.003700)(0.02175)} = 39.\text{14} = 39.1$$

15.39 Substitute the following concentrations into the K_c expression:

$$[\text{SO}_3] = 0.0296 \text{ mol} \div 2.000 \text{ L} = 0.01480 \text{ M}$$

$$[\text{SO}_2] = 0.0104 \text{ mol} \div 2.000 \text{ L} = 0.005200 \text{ M}$$

$$[\text{O}_2] = 0.0052 \text{ mol} \div 2.000 \text{ L} = 0.00260 \text{ M}$$

$$K_c = \frac{(0.01480)^2}{(0.005200)^2(0.00260)} = 3.1 \times 10^3 = 3.1 \times 10^3$$

15.40 Substitute the following concentrations into the K_c expression:


$$[\text{CH}_3\text{OH}] = 0.0313 \text{ mol} \div 1.50 \text{ L} = 0.02086 \text{ M}$$

$$[\text{CO}] = 0.1187 \text{ mol} \div 1.50 \text{ L} = 0.07913 \text{ M}$$

$$[\text{H}_2] = 0.2374 \text{ mol} \div 1.50 \text{ L} = 0.1582$$

$$K_c = \frac{(0.02086)}{(0.07913)(0.1582)^2} = 10.53 = 10.5$$

15.41 For each mole of NOBr that reacts, $(1.000 - 0.094 = 0.906)$ mol remains. Starting with 2.00 mol NOBr, 2×0.906 mol NOBr, or 1.812 mol NOBr, remain. Because the volume is 1.00 L, the concentration of NOBr at equilibrium is 1.812 M. Assemble a table of starting, change, and equilibrium concentrations:

Conc. (M)	2NOBr(g)		2NO(g)	+	Br ₂ (g)
Starting	2.00		0		0
Change	-2x		+2x		+x
Equilibrium	2.00 - 2x (= 1.812)		2x		x

Because $2.00 - 2x = 1.812$, $x = 0.094 \text{ M}$. Therefore, the equilibrium concentrations are $[\text{NOBr}] = 1.812 \text{ M}$, $[\text{NO}] = 0.188 \text{ M}$, and $[\text{Br}_2] = 0.094 \text{ M}$.

$$K_c = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} = \frac{(0.188 \text{ M})^2(0.094 \text{ M})}{(1.812 \text{ M})^2} = 1.01 \times 10^{-3} = 1.0 \times 10^{-3}$$

- 15.42 A decomposition of 6.0 percent of NO_2 means that $0.060 \times 2.00 \text{ mol} = 0.12 \text{ mol}$ was decomposed, leaving 1.88 mol at equilibrium. Because the concentration at the start was $2.00 \text{ mol}/80.0 \text{ L}$, or 0.0250 M , the concentration at equilibrium is $1.88 \text{ mol}/80.0 \text{ L}$, or 0.0235 M . Assemble a table of starting, change, and equilibrium concentrations:

Conc. (M)	$2\text{NO}_2(\text{g})$	\rightleftharpoons	$2\text{NO}(\text{g})$	+	$\text{O}_2(\text{g})$
Starting	0.0250		0		0
Change	-2x		+2x		+x
Equilibrium	$0.0250 - 2x$ (= 0.0235)		2x		x

Because $0.0250 - 2x = 0.0235 \text{ M}$, $x = 0.00075 \text{ M}$; thus, $[\text{NO}_2] = 0.0235 \text{ M}$, $[\text{NO}] = 0.0015 \text{ M}$, and $[\text{O}_2] = 0.00075 \text{ M}$. The value of K_c is

$$K_c = \frac{(0.0015)^2(0.00075)}{(0.0235)^2} = 3.055 \times 10^{-6} = 3.1 \times 10^{-6}$$

15.43 a. $K_p = \frac{P_{\text{HBr}}^2}{P_{\text{H}_2} P_{\text{Br}_2}}$

b. $K_p = \frac{P_{\text{CH}_4} P_{\text{H}_2\text{S}}^2}{P_{\text{CS}_2} P_{\text{H}_2}^4}$

c. $K_p = \frac{P_{\text{H}_2\text{O}}^2 P_{\text{Cl}_2}^2}{P_{\text{HCl}}^4 P_{\text{O}_2}}$

d. $K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} P_{\text{H}_2}^2}$

15.44 a. $K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$

b. $K_p = \frac{P_{\text{NOBr}}^2}{P_{\text{NO}}^2 P_{\text{Br}_2}}$

c. $K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}}$

d. $K_p = \frac{P_{\text{NO}}^4 P_{\text{H}_2\text{O}}^6}{P_{\text{NH}_3}^4 P_{\text{O}_2}^5}$

- 15.45 There are three mol of gaseous product for every five mol of gaseous reactant, so $\Delta n = 3 - 5 = -2$. Using this, calculate K_p from K_c :

$$K_p = K_c(RT)^{\Delta n} = 0.28 (0.0821 \times 1173)^{-2} = 3.019 \times 10^{-5} = 3.0 \times 10^{-5}$$

- 15.46 There is one mol of gaseous product for every three mol of gaseous reactant, so $\Delta n = 1 - 3 = -2$. Using this, calculate K_p from K_c :

$$K_p = K_c(RT)^{\Delta n} = 10.5 (0.0821 \times 500)^{-2} = 6.231 \times 10^{-3} = 6.23 \times 10^{-3}$$

- 15.47 For each one mol of gaseous product, there are 1.5 mol of gaseous reactants; thus, $\Delta n = 1 - 1.5 = -0.5$. Using this, calculate K_c from K_p :

$$\begin{aligned} K_c &= \frac{K_p}{(RT)^{\Delta n}} = \frac{6.55}{(0.0821 \times 900)^{-0.5}} = 6.55 \times (0.0821 \times 900)^{0.5} \\ &= 56.303 = 56.3 \end{aligned}$$

- 15.48 For each one mol of gaseous product, there is 0.5 mol of gaseous reactant; thus, $\Delta n = 1 - 0.5 = 0.5$. Using this, calculate K_c from K_p :

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{7.55 \times 10^{-2}}{(0.0821 \times 1115)^{0.5}} = 7.891 \times 10^{-3} = 7.89 \times 10^{-3}$$

15.49 a. $K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]}$

b. $K_c = \frac{[\text{CO}_2]}{[\text{CO}]}$

c. $K_c = \frac{[\text{CO}_2]}{[\text{SO}_2][\text{O}_2]^{1/2}}$

d. $K_c = [\text{Pb}^{2+}][\text{I}^-]^2$

15.50 a. $K_c = [\text{NH}_3][\text{HCl}]$

b. $K_c = \frac{[\text{CO}_2][\text{N}_2]^2}{[\text{N}_2\text{O}]^2}$

c. $K_c = [\text{H}_2\text{O}][\text{CO}_2]$

d. $K_c = \frac{1}{[\text{Fe}^{3+}][\text{OH}^-]^3}$

- 15.51 a. Not complete; K_c is very small (10^{-31}), indicating very little reaction.

- b. Nearly complete; K_c is very large (10^{21}), indicating nearly complete reaction.

- 15.52 a. Nearly complete; K_c is very large (10^{113}), indicating nearly complete reaction.

- b. Not complete; K_c is very small (10^{-16}), indicating very little reaction.

- 15.53 K_c is extremely small, indicating very little reaction at room temperature. Because the decomposition of HF yields equal amounts of H_2 and F_2 , at equilibrium $[H_2] = [F_2]$. So, for the decomposition of HF,

$$K_c = \frac{[H_2][F_2]}{[HF]^2} = \frac{[H_2]^2}{[HF]^2}$$

$$[H_2] = K_c^{1/2} [HF] = (1.0 \times 10^{-95})^{1/2} (1.0 \text{ M}) = 3.16 \times 10^{-48} = 3.2 \times 10^{-48} \text{ mol/L}$$

This result does agree with what is expected from the very small magnitude of K_c .

- 15.54 K_c is extremely large, indicating nearly complete reaction at room temperature. The problem states that, at equilibrium, $[SO_2] = [O_2]$. So for the reaction of SO_2 ,

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[SO_3]^2}{[SO_2]^3}$$

Solving for $[SO_2]$

$$[SO_2] = \left[\frac{[SO_3]^2}{K_c} \right]^{1/3} = \left[\frac{(1.0)^2}{8.0 \times 10^{35}} \right]^{1/3} = 1.07 \times 10^{-12} = 1.1 \times 10^{-12} \text{ M}$$

This agrees with what we expect from the magnitude of K_c .

- 15.55 Calculate Q , the reaction quotient, and compare it to the equilibrium constant ($K_c = 3.07 \times 10^{-4}$). If Q is larger, the reaction will go to the left; smaller, the reaction will go to the right; equal, the reaction is at equilibrium. In all cases, Q is found by combining these terms:

$$Q = \frac{[NO]^2 [Br_2]}{[NOBr]^2}$$

$$\text{a. } Q = \frac{(0.0162)^2 (0.0123)}{(0.0720)^2} = 6.226 \times 10^{-4} = 6.23 \times 10^{-4}$$

$Q > K_c$. The reaction should go to the left.

$$\text{b. } Q = \frac{(0.0159)^2 (0.0139)}{(0.121)^2} = 2.400 \times 10^{-4} = 2.40 \times 10^{-4}$$

$Q < K_c$. The reaction should go to the right.

(continued)

$$\text{c. } Q = \frac{(0.0134)^2(0.0181)}{(0.103)^2} = 3.0\textbf{6}3 \times 10^{-4} = 3.06 \times 10^{-4}$$

$Q = K_c$. The reaction should be at equilibrium.

$$\text{d. } Q = \frac{(0.0121)^2(0.0105)}{(0.0472)^2} = 6.9\textbf{0}0 \times 10^{-4} = 6.90 \times 10^{-4}$$

$Q > K_c$. The reaction should go to the left.

- 15.56 Calculate Q , the reaction quotient, and compare it to the equilibrium constant ($K_c = 3.59$). If Q is larger, the reaction will go to the left; smaller, the reaction will go to the right; equal, the reaction is at equilibrium. In all cases, Q is found by combining these terms:

$$Q = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2}$$

$$\text{a. } Q = \frac{(1.43)(1.12)^4}{(1.26)(1.32)^2} = 1.0\textbf{2}49 = 1.02$$

$Q < K_c$. The reaction should go to the right.

$$\text{b. } Q = \frac{(1.15)(1.73)^4}{(1.25)(1.52)^2} = 3.5\textbf{6}6 = 3.57$$

$Q = K_c$. The reaction should be at equilibrium.

$$\text{c. } Q = \frac{(1.15)(1.85)^4}{(1.20)(1.31)^2} = 6.5\textbf{4}1 = 6.54$$

$Q > K_c$. The reaction should go to the left.

$$\text{d. } Q = \frac{(1.23)(1.91)^4}{(1.56)(1.43)^2} = 5.1\textbf{3}14 = 5.13$$

$Q > K_c$. The reaction should go to the left.

- 15.57 Calculate Q , the reaction quotient, and compare it to the equilibrium constant. If Q is larger, the reaction will go to the left, and vice versa. Q is found by combining these terms:

$$Q = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{(0.020)}{(0.010)(0.010)^2} = 20.0 (>10.5)$$

The reaction goes to the left.

- 15.58 Calculate Q , the reaction quotient, and compare it to the equilibrium constant. If Q is larger, the reaction will go to the left, and vice versa. Q is found by combining these terms:

$$Q = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.40)^2}{(0.20)^2(0.10)} = 40.0 (>0.0417)$$

The reaction goes to the left.

- 15.59 Substitute into the expression for K_c and solve for $[\text{COCl}_2]$:

$$K_c = 1.23 \times 10^3 = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{[\text{COCl}_2]}{(0.012)(0.025)}$$


$$[\text{COCl}_2] = (1.23 \times 10^3)(0.012)(0.025) = 0.369 = 0.37 \text{ M}$$

- 15.60 Substitute into the expression for K_c and solve for $[\text{NO}]$:

$$K_c = 0.0025 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{[\text{NO}]^2}{(0.031)(0.023)}$$

$$[\text{NO}] = [(0.0025)(0.031)(0.023)]^{1/2} = 1.33 \times 10^{-3} = 1.3 \times 10^{-3} \text{ M}$$

- 15.61 Divide moles of substance by the volume of 5.0 L to obtain concentration. The starting concentrations are $3.0 \times 10^{-4} \text{ M}$ for both $[\text{I}_2]$ and $[\text{Br}_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$\text{I}_2(\text{g})$	+	$\text{Br}_2(\text{g})$		$2 \text{ IBr}(\text{g})$
Starting	3.0×10^{-4}		3.0×10^{-4}		0
Change	-x		-x		+2x
Equilibrium	$(3.0 \times 10^{-4}) - x$		$(3.0 \times 10^{-4}) - x$		2x

(continued)

Substituting into the equilibrium-constant expression gives

$$K_c = 1.2 \times 10^2 = \frac{[\text{IBr}]^2}{[\text{I}_2][\text{Br}_2]} = \frac{(2x)^2}{(3.0 \times 10^{-4} - x)(3.0 \times 10^{-4} - x)}$$

Taking the square root of both sides yields

$$10.95 = \frac{(2x)}{(3.0 \times 10^{-4} - x)}$$


Rearranging and simplifying the right side gives

$$(3.0 \times 10^{-4} - x) = \frac{(2x)}{10.95} = (0.182 x)$$

$$x = 2.53 \times 10^{-4} \text{ M}$$

Thus, $[\text{I}_2] = [\text{Br}_2] = 4.70 \times 10^{-5} = 4.7 \times 10^{-5} \text{ M}$, and $[\text{IBr}] = 5.06 \times 10^{-4} = 5.1 \times 10^{-4} \text{ M}$.

- 15.62 Divide moles of substance by the volume of 8.00 L to obtain concentration. The starting concentrations are 0.10625 M for both $[\text{N}_2]$ and $[\text{O}_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$		$2\text{NO}(\text{g})$
Starting	0.10625		0.10625		0
Change	-x		-x		+2x
Equilibrium	0.10625 - x		0.10625 - x		2x

$$K_c = 0.0123 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(0.10625 - x)(0.10625 - x)}$$

Taking the square root of both sides gives

$$0.1109 = \frac{(2x)}{(0.10625 - x)}$$

Rearranging and simplifying the right side yields

$$(0.10625 - x) = \frac{(2x)}{0.1109} = (18.03 x)$$

$$x = 5.583 \times 10^{-3} \text{ M}$$

Thus $[\text{N}_2] = [\text{O}_2] = 0.1006 = 0.101 \text{ M}$, and $[\text{NO}] = 1.116 \times 10^{-2} = 1.12 \times 10^{-2} \text{ M}$.

- 15.63 Divide moles of substance by the volume of 1.25 L to obtain concentration. The starting concentration is 1.00 M for $[\text{CO}_2]$, but the concentration of carbon, a solid, is omitted. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$\text{CO}_2(\text{g})$	+	$\text{C}(\text{s})$	\rightleftharpoons	$2\text{CO}(\text{g})$
Starting	1.00				0
Change	-x				+2x
Equilibrium	$1.00 - x$				2x

Substituting into the equilibrium expression for K_c gives

$$K_c = 14.0 = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(2x)^2}{(1.00 - x)}$$

Rearranging and solving for x yields

$$14.0 - 14.0x = 4x^2$$

$$4x^2 + 14.0x - 14.0 = 0 \text{ (quadratic equation)}$$

Using the solution to the quadratic equation gives

$$x = \frac{-14.0 \pm \sqrt{(14.0)^2 - 4(4)(-14.0)}}{2(4)}$$

$$x = -4.31 \text{ (impossible; reject), or } x = 0.8117 = 0.812 \text{ M (logical)}$$

Thus, $[\text{CO}_2] = 0.19 \text{ M}$, and $[\text{CO}] = 1.62 \text{ M}$.

- 15.64 Divide moles of substance by the volume of 4.0 L to obtain concentration. The starting concentrations are 0.10 M for both $[\text{PCl}_3]$ and $[\text{Cl}_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{PCl}_5(\text{g})$
Starting	0.10		0.10		0
Change	-x		-x		+x
Equilibrium	$0.10 - x$		$0.10 - x$		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 49 = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{x}{(0.10 - x)(0.10 - x)}$$

(continued)

Rearranging and solving for x yields

$$49(0.10 - x)^2 = 49(x^2 - 0.20x + 0.010) = x$$

$$49x^2 - 10.8x + 0.49 = 0 \text{ (quadratic equation)}$$


Using the solution to the quadratic equation gives

$$x = \frac{10.8 \pm \sqrt{(10.8)^2 - 4(49)(0.49)}}{2(49)}$$

$$x = 0.157 \text{ (impossible; reject), or } x = 0.06389 = 0.064 \text{ M (logical)}$$

Thus, $[\text{PCl}_3] = [\text{Cl}_2] = 0.036 \text{ M}$, and $[\text{PCl}_5] = 0.064 \text{ M}$; the vessel contains 0.18 mol PCl_3 , 0.18 mol Cl_2 , and 0.32 mol PCl_5 .

- 15.65 Divide moles of substance by the volume of 10.00 L to obtain concentration. The starting concentrations are 0.1000 M for $[\text{CO}]$ and 0.3000 M for $[\text{H}_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	CO(g)	+	$3\text{H}_2\text{(g)}$		$\text{CH}_4\text{(g)}$	+	$\text{H}_2\text{O(g)}$
Starting	0.1000		0.3000		0		0
Change	-x		-3x		+x		+x
Equilibrium	0.1000 - x		0.3000 - 3x		x		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 3.92 = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{x^2}{(0.1000 - x)[3(0.1000 - x)]^3}$$

$$= \frac{x^2}{27(0.1000 - x)^4}$$

Multiplying both sides by 27 and taking the square root of both sides gives

$$10.29 = \frac{x}{(0.1000 - x)^2}$$

Or,

$$10.29x^2 - 3.058x + 0.1029 = 0$$

(continued)

Using the solution to the quadratic equation yields

$$x = \frac{3.058 \pm \sqrt{(-3.058)^2 - 4(10.29)(0.1029)}}{2(10.29)}$$

$$x = 0.2585 \text{ (can't be } > 0.1000, \text{ so reject), or } x = 0.03868 = 0.0387 \text{ M (use)}$$

Thus, $[\text{CO}] = 0.0613 \text{ M}$, $[\text{H}_2] = 0.1839 \text{ M}$, $[\text{CH}_4] = 0.0387 \text{ M}$, and $[\text{H}_2\text{O}] = 0.0387 \text{ M}$.

- 15.66 Divide moles of substance by the volume of 2.00 L to obtain concentration. The starting concentrations are 0.500 M for $[\text{N}_2]$ and 1.50 M for $[\text{H}_2]$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$\text{N}_2(\text{g})$	+	$3\text{H}_2(\text{g})$	\rightleftharpoons	$2\text{NH}_3(\text{g})$
Starting	0.500		1.50		0
Change	-x		-3x		+2x
Equilibrium	0.500 - x		1.50 - 3x		2x

Substituting into the equilibrium expression for K_c gives

$$K_c = 0.159 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2x)^2}{(0.500 - x)(1.50 - 3x)^3}$$

$$= \frac{(2x)^2}{(0.500 - x)3^3(0.500 - x)^3}$$

Combining the value of K_c and 3^3 from the right-hand term gives

$$(3^3)(0.159) = \frac{(2x)^2}{(0.500 - x)^4}$$

Taking the square root of both sides gives

$$2.072 = \frac{2x}{(0.5000 - x)^2}$$

$$0.5180 - 2.072x + 2.072x^2 = 2x$$

$$2.072x^2 - 4.072x + 0.5180 = 0 \text{ (quadratic equation)}$$

(continued)

Using the solution to the quadratic equation yields

$$x = \frac{4.072 \pm \sqrt{(-4.072)^2 - 4(2.072)(0.5180)}}{2(2.072)}$$

$x = 1.829$ (larger than 0.500, so reject), or $x = 0.1367$ M (logical; use)

Thus, $[N_2] = 0.3633 = 0.363$ M, $[H_2] = 1.0899 = 1.09$ M,
and $[NH_3] = 0.2734 = 0.273$ M.

15.67 Forward direction

15.68 a. Forward direction

b. Reverse direction

15.69 a. A pressure increase has no effect because the number of moles of reactants equals that of products.

b. A pressure increase has no effect because the number of moles of reactants equals that of products.

c. A pressure increase causes the reaction to go to the left because the number of moles of reactants is less than that of products.

15.70 a. Pressure increase

b. Pressure increase

c. Pressure decrease

15.71 The fraction would not increase because an increase in temperature decreases the amounts of products of an exothermic reaction.

15.72 The decomposition would be favorable at high temperatures because an increase in temperature increases the amounts of products of an endothermic reaction.

15.73 The value of ΔH° is calculated from the ΔH°_f values below each substance in the reaction:



$$\Delta H^\circ = -967.2 + (-91.8) - 66.4 = -1125.4 \text{ kJ/2 mol } NO_2$$

The equilibrium constant will decrease with temperature because raising the temperature of an exothermic reaction will cause the reaction to go farther to the left.

- 15.74 The value of ΔH° is calculated from the ΔH°_f values below each substance in the reaction:



$$\Delta H^\circ = 117 - (-40) - (-74.9) = 231.9 = 232 \text{ kJ/mol CH}_4$$

The equilibrium constant will increase with temperature because raising the temperature of an endothermic reaction will cause the reaction to go farther to the right.

- 15.75 Because the reaction is exothermic, the formation of products will be favored by low temperatures. Because there are more molecules of gaseous products than of gaseous reactants, the formation of products will be favored by low pressures.
- 15.76 Because the reaction is exothermic, the formation of products will be favored by low temperatures. Because there are more molecules of gaseous reactants than of gaseous products, the formation of products will be favored by high pressures.

■ Solutions to General Problems

- 15.77 Substitute the concentrations into the equilibrium expression to calculate K_c .

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{(0.015)}{(0.096)(0.191)^2} = 4.28 = 4.3$$

- 15.78 Substitute the concentrations into the equilibrium expression to calculate K_c .

$$K_c = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = \frac{(0.0160)}{(0.0056)(0.0021)^{1/2}} = 62.3 = 62$$

- 15.79 Assume 100.00 g of gas: 90.55 g are CO, and 9.45 g are CO₂. The moles of each are

$$90.55 \text{ g CO} \times \frac{1 \text{ mol CO}}{28.01 \text{ g CO}} = 3.2328 \text{ mol CO}$$

$$9.45 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} = 0.2147 \text{ mol CO}_2$$

(continued)

Total moles of gas = $(3.2328 + 0.2147) \text{ mol} = 3.4475 \text{ mol}$. Use the ideal gas law to convert to the volume of gaseous solution:

$$V = \frac{nRT}{P} = \frac{(3.4475 \text{ mol})(0.082057 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(850 + 273)\text{K}}{1.000 \text{ atm}} = 317.69 \text{ L}$$

The concentrations are

$$[\text{CO}] = \frac{3.2328 \text{ mol CO}}{317.69 \text{ L}} = 0.010176 \text{ M}$$

$$[\text{CO}_2] = \frac{0.2147 \text{ mol CO}_2}{317.69 \text{ L}} = 6.758 \times 10^{-4} \text{ M}$$

Find K_c by substituting into the equilibrium expression:

$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(0.010176)^2}{(6.758 \times 10^{-4})} = 0.1532 = 0.153$$

15.80 Assume 100.0 g of gas: 65.8 g are NO_2 , and 34.2 g are N_2O_4 . The moles of each are

$$65.8 \text{ g NO}_2 \times \frac{1 \text{ mol NO}_2}{46.01 \text{ g NO}_2} = 1.430 \text{ mol}$$

$$34.2 \text{ g N}_2\text{O}_4 \times \frac{1 \text{ mol N}_2\text{O}_4}{92.01 \text{ g N}_2\text{O}_4} = 0.3717 \text{ mol}$$

Total moles of gas = $(1.430 + 0.3717) \text{ mol} = 1.802 \text{ mol}$. Use the ideal gas law to convert to the volume of gaseous solution:

$$V = \frac{nRT}{P} = \frac{(1.802 \text{ mol})(0.082057 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(25 + 273)\text{K}}{1.00 \text{ atm}} = 44.06 \text{ L}$$

The concentrations are

$$[\text{NO}_2] = \frac{1.430 \text{ mol NO}_2}{44.06 \text{ L}} = 0.03246 \text{ M}$$

$$[\text{N}_2\text{O}_4] = \frac{0.3717 \text{ mol N}_2\text{O}_4}{44.06 \text{ L}} = 0.008436 \text{ M}$$

(continued)

Find K_c by substituting into the equilibrium expression:

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.03246)^2}{(0.008436)} = 0.1248 = 0.125 \text{ M}$$

- 15.81 After calculating the concentrations after mixing, calculate Q , the reaction quotient, and compare it with K_c .

$$[\text{N}_2] = [\text{H}_2] = 1.00 \text{ mol} \div 2.00 \text{ L} = 0.500 \text{ M}$$

$$[\text{NH}_3] = 2.00 \text{ mol} \div 2.00 \text{ L} = 1.00 \text{ M}$$

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(1.00)^2}{(0.500)(0.500)^3} = 16.00 = 16.0$$

Because Q is greater than K_c , the reaction will go in the reverse direction (to the left) to reach equilibrium.

- 15.82 To calculate the concentrations after mixing, the volume can be assumed to be 1.00 L, symbolized as V . Because the volumes in the numerator and denominator cancel each other, it does not matter. Assume a 1.00-L volume and calculate Q , the reaction quotient, and compare it with K_c .

$$[\text{I}_2] = [\text{Br}_2] = 0.0010 \text{ mol/1.00 L}$$

$$[\text{IBr}] = 0.200 \div 1.00 \text{ L} = 0.200 \text{ mol/1.00 L}$$

$$Q = \frac{[\text{IBr}]^2}{[\text{I}_2][\text{Br}_2]} = \frac{(0.200 \text{ mol/1.00 L})^2}{(0.0010 \text{ mol/1.00 L})(0.0010 \text{ mol/1.00 L})} = 4.00 \times 10^4$$

Because Q is greater than K_c , the reaction will go in the reverse direction (to the left) to reach equilibrium.

- 15.83 To calculate the concentrations after mixing, assume the volume to be 1.00 L, symbolized as V . Because the volumes in the numerator and denominator cancel each other, they do not matter. Assume a 1.00-L volume and calculate Q , the reaction quotient, and compare it with K_c .

$$[\text{CO}] = [\text{H}_2\text{O}] = [\text{CO}_2] = [\text{H}_2] = 1.00 \text{ mol/1.00 L}$$

$$Q = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(1.00 \text{ mol/1.00 L})(1.00 \text{ mol/1.00 L})}{(1.000 \text{ mol/1.00 L})(1.00 \text{ mol/1.00 L})} = 1.00$$

Because Q is greater than K_c , the reaction will go in the reverse direction (left) to reach equilibrium.

- 15.84 After calculating the concentrations after mixing, calculate Q , the reaction quotient, and compare it with K_c .

$$[\text{CO}] = 0.10 \text{ mol} \div 2.0 \text{ L} = 0.050 \text{ M}$$

$$[\text{H}_2] = 0.20 \text{ mol} \div 2.0 \text{ L} = 0.10 \text{ M}$$

$$[\text{CH}_3\text{OH}] = 0.50 \text{ mol} \div 2.0 \text{ L} = 0.25 \text{ M}$$

$$Q = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{(0.25)}{(0.050)(0.10)^2} = 5.00 \times 10^2 = 5.0 \times 10^2$$

Because Q is greater than K_c , the reaction will go in the reverse direction (left) to reach equilibrium.

- 15.85 Assemble a table of starting, change, and equilibrium concentrations, letting $2x$ = the change in $[\text{HBr}]$.

Conc. (M)	2HBr(g)	\rightleftharpoons	$\text{H}_2\text{(g)}$	+	$\text{Br}_2\text{(g)}$
Starting	0.010		0		0
Change	-2x		+x		+x
Equilibrium	$0.010 - 2x$		x		x

$$K_c = 0.016 = \frac{[\text{H}_2][\text{Br}_2]}{[\text{HBr}]^2} = \frac{(x)(x)}{(0.010 - 2x)^2}$$


$$0.126 = \frac{(x)}{(0.010 - 2x)}$$

$$1.26 \times 10^{-3} - (2.52 \times 10^{-1})x = x$$

$$x = (1.26 \times 10^{-3}) \div 1.252 = 1.006 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M}$$

Therefore, $[\text{HBr}] = 0.008 \text{ M}$, or 0.008 mol ; $[\text{H}_2] = 0.0010 \text{ M}$, or 0.0010 mol ; and $[\text{Br}_2] = 0.0010 \text{ M}$, or 0.0010 mol .

- 15.86 The starting concentration of $[\text{IBr}] = 0.010 \text{ mol} \div 1.0 \text{ L} = 0.010 \text{ M}$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	2IBr(g)		$\text{I}_2\text{(g)}$	+	$\text{Br}_2\text{(g)}$
Starting	0.010		0		0
Change	-2x		+x		+x
Equilibrium	$0.010 - 2x$		x		x

$$K_c = 0.026 = \frac{[\text{I}_2][\text{Br}_2]}{[\text{IBr}]^2} = \frac{(x)(x)}{(0.010 - 2x)^2}$$


$$0.161 = \frac{(x)}{(0.010 - 2x)}$$

$$1.61 \times 10^{-3} - (3.22 \times 10^{-1})x = x$$

$$x = (1.61 \times 10^{-3}) \div 1.322 = 1.217 \times 10^{-3} = 1.2 \times 10^{-3} \text{ M}$$

Therefore, $[\text{IBr}] = 0.0076 \text{ M}$, or 0.008 mol ; $[\text{I}_2] = 0.00121 \text{ M}$, or 0.0012 mol ; and $[\text{Br}_2] = 0.00121 \text{ M}$, or 0.0012 mol .

- 15.87 The starting concentration of $\text{COCl}_2 = 1.00 \text{ mol} \div 25.00 \text{ L} = 0.0400 \text{ M}$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$\text{COCl}_2\text{(g)}$		$\text{Cl}_2\text{(g)}$	+	CO(g)
Starting	0.0400		0		0
Change	-x		+x		+x
Equilibrium	$0.0400 - x$		x		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 8.05 \times 10^{-4} = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{(x)(x)}{(0.0400 - x)}$$

Rearranging and solving for x yields

$$3.22 \times 10^{-5} - (8.05 \times 10^{-4})x - x^2 = 0$$

$$x^2 + (8.05 \times 10^{-4})x - 3.22 \times 10^{-5} = 0 \text{ (quadratic equation)}$$

(continued)

Using the solution to the quadratic equation gives

$$x = \frac{-(8.05 \times 10^{-4}) \pm \sqrt{(8.05 \times 10^{-4})^2 - 4(1)(-3.22 \times 10^{-5})}}{2(1)}$$

$$x = -6.09 \times 10^{-3} \text{ (impossible; reject), or } x = 5.286 \times 10^{-3} \text{ (logical; use)}$$

$$\begin{aligned} \text{Percent dissociation} &= (\text{change} \div \text{starting}) \times 100\% = (0.005286 \div 0.0400) \times 100\% \\ &= 13.21 = 13.2 \text{ percent} \end{aligned}$$

- 15.88 The starting concentration of $\text{N}_2\text{O}_4 = 0.0300 \text{ mol} \div 1.00 \text{ L} = 0.0300 \text{ M}$. Assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	$\text{N}_2\text{O}_4(\text{g})$	\rightleftharpoons	$2\text{NO}_2(\text{g})$
Starting	0.0300		0
Change	-x		+2x
Equilibrium	$0.0300 - x$		2x

Substituting into the equilibrium expression for K_c gives

$$K_c = 0.125 = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x)^2}{(0.0300 - x)}$$

Rearranging and solving for x yields

$$4x^2 + 0.125x - 3.75 \times 10^{-3} = 0 \text{ (quadratic equation)}$$


Using the solution to the quadratic equation gives

$$x = \frac{-(0.125) \pm \sqrt{(0.125)^2 - 4(4)(-3.75 \times 10^{-3})}}{2(4)}$$

$$x = -5.00 \times 10^{-2} \text{ (impossible; reject), or } x = 1.875 \times 10^{-2} \text{ M (logical)}$$

$$\begin{aligned} \text{Percent dissociation} &= (\text{change} \div \text{starting}) \times 100\% = (0.01875 \div 0.0300) \times 100\% \\ &= 62.50 = 62.5 \text{ percent} \end{aligned}$$

- 15.89 Using 1.00 mol/10.00 L, or 0.100 M, and 4.00 mol/10.00 L, or 0.400 M, for the respective starting concentrations for CO and H₂, assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	CO(g)	+	3H ₂ (g)		CH ₄ (g)	+	H ₂ O(g)
Starting	0.100		0.400		0		0
Change	-x		-3x		+x		+x
Equilibrium	0.100 - x		0.400 - 3x		x		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 3.92 = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{x^2}{(0.100 - x)(0.400 - 3x)^3}$$


$$f(x) = \frac{x^2}{(0.100 - x)(0.400 - 3x)^3}$$

Because K_c is > 1 (> 50 percent reaction), choose x = 0.05 (about half of CO reacting), and use that for the first entry in the table of x, f(x), and interpretations:

x	f(x)	Interpretation
0.05	3.20	x > 0.05
0.06	8.45	x < 0.06
0.055	5.18	x < 0.055
0.0525	4.07	x < 0.0525 (but close)
0.052	3.87	f(x) of 3.87 ≅ 3.92

At equilibrium, concentrations and moles are CO: 0.048 M and 0.48 mol; H₂: 0.244 M and 2.44 mol; CH₄: 0.052 M and 0.52 mol; and H₂O: 0.052 M and 0.52 mol.

- 15.90 Using 1.00 mol/10.00 L, or 0.100 M, and 4.00 mol/10.00 L, or 0.400 M, for the respective starting concentrations for N₂ and H₂, assemble a table of starting, change, and equilibrium concentrations.

Conc. (M)	N ₂ (g)	+	3H ₂ (g)		2NH ₃ (g)
Starting	0.100		0.400		0
Change	-x		-3x		+2x
Equilibrium	0.100 - x		0.400 - 3x		2x

(continued)

Substituting into the equilibrium expression for K_c gives

$$K_c = 0.153 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2x)^2}{(0.100 - x)(0.400 - 3x)^3}$$

$$f(x) = \frac{4x^2}{(0.100 - x)(0.400 - 3x)^3}$$

Because K_c is < 1 (< 50 percent reaction), choose $x = 0.010$ (about 10 percent of N_2 reacting), and use that for the first entry in the table of x , $f(x)$, and interpretations:

x	$f(x)$	Interpretation
0.010	0.0877	x too small
0.020	0.5089	x too big
0.015	0.237	x still too big
0.012	0.136	$x < 0.153$ (but close)
0.013	0.1651	$f(x)$ of .1651 $\cong 0.153$
0.0125	0.150	best $f(x)$

At equilibrium, concentrations and moles are N_2 : 0.087 M and 0.87 mol; H_2 : 0.362 M and 3.62 mol; and NH_3 : 0.025 M and 0.25 mol.

15.91 The dissociation is endothermic.

15.92 The value of K_c and the ratio of products to reactants decrease with temperature, so the reaction must be exothermic.

15.93 For $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$, K_p is defined in terms of pressures as

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

But by the ideal gas law, where $[i] = \text{mol/L}$,

$$P_i = (n_i RT)/V, \text{ or } P_i = [i] RT$$

Substituting the right-hand equality into the K_p expression gives

$$K_p = \frac{[\text{NH}_3]^2 (RT)^2}{[\text{N}_2] (RT) [\text{H}_2]^3 (RT)^3} = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3} (RT)^{-2}$$

$$K_p = K_c (RT)^{-2}, \text{ or } K_c = K_p (RT)^2$$

15.94 For $\text{COCl}_2 \rightleftharpoons \text{CO} + \text{Cl}_2$, K_p is defined in terms of pressure as

$$K_p = \frac{P_{\text{CO}} P_{\text{Cl}_2}}{P_{\text{COCl}_2}}$$

Substituting $[i]RT = P$ for each term as in the above problem yields

$$K_p = \frac{[\text{CO}](RT)[\text{Cl}_2](RT)}{[\text{COCl}_2](RT)} = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}(RT)$$

$$K_p = K_c RT, \text{ or } K_c = K_p / (RT)$$

15.95 a. The change in the number of moles of gas for the reaction is $\Delta n = 2 - 1 = 1$. Using this, calculate K_p from K_c :

$$K_p = K_c (RT)^{\Delta n} = 0.153 (0.08206 \times 1123)^1 = 14.099 = 14.1$$

b. Use the table approach, and give the starting, change, and equilibrium pressures in atm.

Press. (atm)	C(s)	+	CO ₂ (g)	\rightleftharpoons	2CO(g)
Starting			1.50		0
Change			-x		+2x
Equilibrium			1.50 - x		2x

Substituting into the equilibrium-constant expression gives

$$K_p = 14.10 = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(2x)^2}{(1.50 - x)}$$

Rearranging and solving for x gives a quadratic equation.

$$4x^2 + 14.10x - 21.15 = 0$$

Using the quadratic formula gives

$$x = \frac{-14.10 \pm \sqrt{(14.10)^2 - (4)(4)(-21.15)}}{2(4)}$$

$$x = 1.135 \text{ (positive root)}$$

(continued)

Thus, at equilibrium, the pressures of CO and CO₂ are

$$P_{\text{CO}_2} = 1.50 - 1.135 = 0.365 = 0.37 \text{ atm}$$

$$P_{\text{CO}} = 2x = 2(1.135) = 2.270 = 2.27 \text{ atm}$$

- c. Because the reaction is endothermic, the equilibrium will shift to the left, and the pressure of CO will decrease.

- 15.96 a. The change in the number of moles of gas for the reaction is $\Delta n = 2 - 1 = 1$. Using this, calculate K_p from K_c :

$$K_p = K_c(RT)^{\Delta n} = 0.238 (0.08206 \times 1173)^1 = 22.909 = 22.9$$

- b. The total pressure of the system at equilibrium is 6.40 atm. This equals the sum of the pressures of CO and CO₂. Thus, the pressure of CO₂ can be expressed as

$$P_{\text{CO}_2} = 6.40 - P_{\text{CO}}$$

Substituting into the equilibrium-constant expression gives

$$K_p = 22.91 = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{P_{\text{CO}}^2}{6.40 - P_{\text{CO}}}$$

Rearranging and solving for x ($= P_{\text{CO}}$) gives a quadratic equation.

$$x^2 + 22.91x - 146.6 = 0$$

Using the quadratic formula gives

$$x = \frac{-22.91 \pm \sqrt{(22.91)^2 - (4)(1)(-146.6)}}{2(1)}$$

$$x = 5.213 \text{ (positive root)}$$

Thus, at equilibrium, the pressures of CO and CO₂ are

$$P_{\text{CO}_2} = 6.40 - 5.213 = 1.187 = 1.19 \text{ atm}$$

$$P_{\text{CO}} = x = 5.213 = 5.21 \text{ atm}$$

- c. Carbon doesn't appear in the equilibrium expression, so it doesn't have any effect on the position of the equilibrium.

15.97 a. The molar mass of PCl_5 is 208.22 g/mol. Thus, the initial concentration of PCl_5 is

$$\frac{35.8 \text{ g PCl}_5 \times \frac{1 \text{ mol PCl}_5}{208.22 \text{ g PCl}_5}}{5.0 \text{ L}} = 0.0344 \text{ M}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{PCl}_5(\text{g})$
Starting	0		0		0.0344
Change	x		x		- x
Equilibrium	x		x		0.0344 - x

Substituting into the equilibrium-constant expression gives

$$K_c = 4.1 = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{0.0344 - x}{x^2}$$

Rearranging and solving for x gives a quadratic equation.

$$4.1x^2 + x - 0.0344 = 0$$

Using the quadratic formula gives

$$x = \frac{-1 \pm \sqrt{(1)^2 - (4)(4.1)(-0.0344)}}{2(4.1)}$$

$$x = 0.0306 \text{ (positive root)}$$

Thus, at equilibrium, $[\text{PCl}_3] = [\text{Cl}_2] = x = 0.031 \text{ M}$. The concentration of PCl_5 is

$$[\text{PCl}_5] = 0.0344 - x = 0.0344 - 0.0306 = 0.0038 = 0.004 \text{ M}.$$

b. The fraction of PCl_5 decomposed is

$$\text{fraction decomposed} = \frac{0.0306 \text{ M}}{0.0344 \text{ M}} = 0.889 = 0.89$$

c. There would be a greater pressure, so less PCl_5 would decompose in order to minimize the increase in pressure.

15.98 a. The total pressure at equilibrium is

$$P_{\text{NH}_3} + P_{\text{H}_2\text{S}} = 0.660 \text{ atm}$$

Since the pressures of NH_3 and H_2S are equal, this gives

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = \frac{0.660 \text{ atm}}{2} = 0.330 \text{ atm}$$

The equilibrium-constant expression is

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} = (0.330)^2 = 0.1089 = 0.109$$

b. Since $P_{\text{H}_2\text{S}} = 3P_{\text{NH}_3}$, the equilibrium-constant expression becomes


$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} = 3P_{\text{NH}_3}^2 = 0.1089$$

$$P_{\text{NH}_3} = \sqrt{\frac{0.1089}{3}} = 0.1905 = 0.191 \text{ atm}$$

The partial pressure of H_2S is

$$P_{\text{H}_2\text{S}} = 3(0.1905) = 0.5715 = 0.572 \text{ atm}$$

c. Use the table approach, and give the starting, change, and equilibrium pressures in atm.

Press. (atm)	$\text{NH}_4\text{HS(s)}$		$\text{NH}_3\text{(g)}$	+	$\text{H}_2\text{S(g)}$
Starting			0.750		0.500
Change			-x		-x
Equilibrium			0.750 - x		0.500 - x

Substituting into the equilibrium-constant expression gives

$$K_p = P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}} = (0.750 - x)(0.500 - x) = 0.1089$$

(continued)

Rearranging and solving for x gives a quadratic equation.

$$x^2 - 1.250x + 0.2661 = 0$$

Using the quadratic formula gives

$$x = \frac{-(-1.250) \pm \sqrt{(-1.250)^2 - (4)(1)(0.2661)}}{2(1)}$$

$$x = 0.2721 \text{ (negative root)}$$

Thus, at equilibrium, the partial pressures of NH_3 and H_2S are

$$P_{\text{NH}_3} = 0.750 - 0.2721 = 0.4779 = 0.478 \text{ atm}$$

$$P_{\text{H}_2\text{S}} = 0.500 - 0.2721 = 0.2279 = 0.228 \text{ atm}$$

For NH_4HS , use the ideal gas equation to convert atm (= x) to moles.

$$n = \frac{PV}{RT} = \frac{(0.2721 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.01113 = 0.0111 \text{ mol}$$

15.99 The initial moles of SbCl_5 (molar mass 299.01 g/mol) are

$$65.4 \text{ g SbCl}_5 \times \frac{1 \text{ mol SbCl}_5}{299.01 \text{ g SbCl}_5} = 0.2187 \text{ mol}$$

The initial pressure of SbCl_5 is

$$P = \frac{nRT}{V} = \frac{(0.2187 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(468 \text{ K})}{5.00 \text{ L}} = 1.680 \text{ atm}$$

(continued)

Use the table approach, and give the starting, change, and equilibrium pressures in atm.

Press. (atm)	$\text{SbCl}_5(\text{g})$	\rightleftharpoons	$\text{SbCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Starting	1.680		0		0
Change	-x		x		x
Equilibrium	(1.680)(0.642)		(1.680)(0.358)		(1.680)(0.358)

At equilibrium, 35.8 percent of the SbCl_5 is decomposed, so $x = (1.680)(0.358)$ in this table. The equilibrium-constant expression is

$$K_p = \frac{P_{\text{SbCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{SbCl}_5}} = \frac{(1.680 \times 0.358)^2}{1.680 \times 0.642} = 0.3354 = 0.335$$

- 15.100 Use the table approach, and give the starting, change, and equilibrium concentrations. The volume of the system is 1.00 L.

Conc. (M)	$\text{SO}_2(\text{g})$	+	$1/2\text{O}_2(\text{g})$	\rightleftharpoons	$\text{SO}_3(\text{g})$
Starting	0.0216		0.0148		0
Change	-x		-1/2x		+x (= 0.0175)
Equilibrium	0.0216 - 0.0175 = 0.00410		0.0148 - 1/2(0.0175) = 0.00605		0.0175

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = \frac{0.0175}{(0.00410)(0.00605)^{1/2}} = 54.87 = 54.9$$

15.101 a. The initial concentration of SO_2Cl_2 (molar mass 134.97 g/mol) is

$$\frac{8.25 \text{ g SO}_2\text{Cl}_2 \times \frac{1 \text{ mol SO}_2\text{Cl}_2}{134.97 \text{ g SO}_2\text{Cl}_2}}{1.00 \text{ L}} = 0.06112 \text{ M}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{SO}_2\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{SO}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$
Starting	0.06112		0		0
Change	-x		x		x
Equilibrium	0.06112 - x		x		x

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{x^2}{(0.06112 - x)} = 0.045$$

Rearranging and solving for x gives a quadratic equation.

$$x^2 + 0.045x - 0.0027506 = 0$$

Using the quadratic formula gives

$$x = \frac{- (0.045) \pm \sqrt{(0.045)^2 - (4)(1)(-0.0027506)}}{2(1)}$$

$$x = 0.03456 \text{ (positive root)}$$

The concentrations at equilibrium are $[\text{SO}_2] = [\text{Cl}_2] = x = 0.034 \text{ M}$. For SO_2Cl_2 ,

$$[\text{SO}_2\text{Cl}_2] = 0.06112 - x = 0.06112 - 0.03456 = 0.02655 = 0.027 \text{ M}.$$

b. The fraction of SO_2Cl_2 decomposed is

$$\text{Fraction decomposed} = \frac{0.03456 \text{ M}}{0.06112 \text{ M}} = 0.565 = 0.57$$

(continued)

- c. This would shift the equilibrium to the left and decrease the fraction of SO_2Cl_2 that has decomposed.

15.102a. The initial concentration of COCl_2 (molar mass 98.91 g/mol) is

$$\frac{6.55 \text{ g COCl}_2 \times \frac{1 \text{ mol COCl}_2}{98.91 \text{ g COCl}_2}}{1.00 \text{ L}} = 0.06622 \text{ M}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	$\text{COCl}_2(\text{g})$	\rightleftharpoons	$\text{CO}(\text{g})$	+	$\text{Cl}_2(\text{g})$
Starting	0.06622		0		0
Change	-x		x		x
Equilibrium	$0.06622 - x$		x		x

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{x^2}{(0.06622 - x)} = 0.0046$$

Rearranging and solving for x gives a quadratic equation.

$$x^2 + 0.0046x - 3.046 \times 10^{-4} = 0$$

Using the quadratic formula gives

$$x = \frac{-(0.0046) \pm \sqrt{(0.0046)^2 - (4)(1)(-3.046 \times 10^{-4})}}{2(1)}$$

$$x = 0.0153 \text{ (positive root)}$$

The concentrations at equilibrium are $[\text{CO}] = [\text{Cl}_2] = x = 0.015 \text{ M}$. For COCl_2 ,

$$[\text{COCl}_2] = 0.06622 - x = 0.06622 - 0.0153 = 0.0509 = 0.051 \text{ M}.$$


(continued)

- b. The fraction of COCl_2 decomposed is

$$\text{Fraction decomposed} = \frac{0.0153 \text{ M}}{0.06622 \text{ M}} = 0.231 = 0.23$$

- c. This would shift the equilibrium to the left and decrease the fraction of COCl_2 that has decomposed.

- 15.103a. First, determine the initial concentration of the dimer assuming complete reaction. The reaction can be described as $2\text{A} \rightarrow \text{D}$. Therefore, the initial concentration of dimer is one-half of the concentration of monomer, or $2.0 \times 10^{-4} \text{ M}$. Next, allow the dimer to dissociate into the monomer in equilibrium. Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	D(g)		2A(g)
Starting	2.0×10^{-4}		0
Change	-x		2x
Equilibrium	$2.0 \times 10^{-4} - x$		2x

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[\text{A}]^2}{[\text{D}]} = \frac{(2x)^2}{(2.0 \times 10^{-4} - x)} = \frac{1}{3.2 \times 10^4} = 3.125 \times 10^{-5}$$

Rearranging and solving for x gives a quadratic equation.

$$4x^2 + (3.125 \times 10^{-5})x - (6.250 \times 10^{-9}) = 0$$

Using the quadratic formula gives

$$x = \frac{-(3.125 \times 10^{-5}) \pm \sqrt{(3.125 \times 10^{-5})^2 - (4)(4)(-6.250 \times 10^{-9})}}{2(4)}$$

$$x = 3.58 \times 10^{-5} \text{ (positive root)}$$

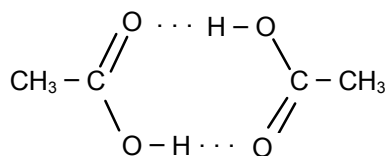
(continued)

Thus, the concentrations at equilibrium are

$$[\text{CH}_3\text{COOH}] = 2x = 2(3.58 \times 10^{-5}) = 7.16 \times 10^{-5} = 7.2 \times 10^{-5} \text{ M}$$


$$[\text{Dimer}] = 2.0 \times 10^{-4} - 3.58 \times 10^{-5} = 1.64 \times 10^{-4} = 1.6 \times 10^{-4} \text{ M}$$

- b. Some hydrogen bonding can occur that results in a more stable system. The proposed structure of the dimer is



- c. An increase in the temperature would facilitate bond breaking and would decrease the amount of dimer. We could also use a Le Chatelier-type argument.

- 15.104a. First, determine the initial pressure of the dimer assuming complete reaction. The reaction can be described as $2A \rightarrow D$. Therefore, the initial pressure of the dimer is one-half of the pressure of monomer, or 3.75×10^{-3} atm. Next, allow the dimer to dissociate into the monomer in equilibrium. Use the table approach, and give the starting, change, and equilibrium pressures.

Press. (atm)	D(g)		2A(g)
Starting	3.75×10^{-3}		0
Change	-x		2x
Equilibrium	$3.75 \times 10^{-3} - x$		2x

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{P_A^2}{P_D} = \frac{(2x)^2}{(3.75 \times 10^{-3} - x)} = \frac{1}{1.3 \times 10^3} = 7.692 \times 10^{-4}$$

Rearranging and solving for x gives a quadratic equation.

$$4x^2 + (7.692 \times 10^{-4})x - (2.885 \times 10^{-6}) = 0$$

(continued)

Using the quadratic formula gives

$$x = \frac{-(7.692 \times 10^{-4}) \pm \sqrt{(7.692 \times 10^{-4})^2 - (4)(4)(-2.885 \times 10^{-6})}}{2(4)}$$

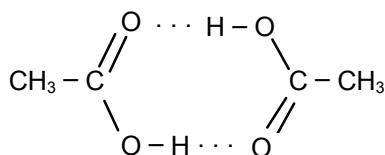
$$x = 7.59 \times 10^{-4} \text{ (positive root)}$$

Thus, the concentrations at equilibrium are

$$[\text{CH}_3\text{COOH}] = 2x = 2(7.59 \times 10^{-4}) = 1.52 \times 10^{-3} = 1.5 \times 10^{-3} \text{ atm}$$

$$[\text{Dimer}] = 3.75 \times 10^{-3} - 7.59 \times 10^{-4} = 2.99 \times 10^{-3} = 3.0 \times 10^{-3} \text{ atm}$$

- b. Some hydrogen bonding can occur that results in a more stable system. The proposed structure of the dimer is



- c. A decrease in the temperature would decrease bond breaking in the dimer, so this would decrease the amount of dimer.

15.105 The molar mass of Br_2 is 159.82 g/mol. Thus, the initial concentration of Br_2 is

$$\frac{18.22 \text{ g Br}_2 \times \frac{1 \text{ mol Br}_2}{159.82 \text{ g Br}_2}}{1.00 \text{ L}} = 0.1140 \text{ M}$$

Use the table approach, and give the starting, change, and equilibrium concentrations.

Conc. (M)	2NO(g)	+	$\text{Br}_2\text{(g)}$	\rightleftharpoons	2NOBr(g)
Starting	0.112		0.1140		0
Change	-2x		-x		2x
Equilibrium	0.112 - 2x		0.1140 - x		2x (= 0.0824 M)
	= 0.02960		= 0.07280		= 0.0824

(continued)

Substituting into the equilibrium-constant expression gives

$$K_c = \frac{[\text{NOBr}]^2}{[\text{NO}]^2[\text{Br}_2]} = \frac{(0.0824)^2}{(0.02960)^2(0.07280)} = 106.4 = 1.1 \times 10^2$$

15.106 The molar mass of Br_2 is 159.82 g/mol. Thus, the initial moles of Br_2 are


$$1.52 \text{ g Br}_2 \times \frac{1 \text{ mol Br}_2}{159.82 \text{ g Br}_2} = 9.511 \times 10^{-3} \text{ mol}$$

The initial pressures of NO and Br_2 are

$$P_{\text{NO}} = \frac{nRT}{V} = \frac{(0.0322 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{1.00 \text{ L}} = 0.7874 \text{ atm}$$

$$P_{\text{Br}_2} = \frac{nRT}{V} = \frac{(9.511 \times 10^{-3} \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{1.00 \text{ L}} = 0.2326 \text{ atm}$$

Use the table approach, and give the starting, change, and equilibrium pressures.

Press. (atm)	2NO(g)	+	$\text{Br}_2\text{(g)}$		2NOBr(g)
Starting	0.7874		0.2326		0
Change	-2x		-x		2x
Equilibrium	0.7874 - 2x = 0.3494		0.2326 - x = 0.0136		2x (= 0.438 atm) = 0.438

Substituting into the equilibrium-constant expression gives

$$K_p = \frac{P_{\text{NOBr}}^2}{P_{\text{NO}}^2 P_{\text{Br}_2}} = \frac{(0.438)^2}{(0.3494)^2(0.0136)} = 115.5 = 1.2 \times 10^2$$

■ Solutions to Cumulative-Skills Problems

15.107 For $\text{Sb}_2\text{S}_3(\text{s}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{Sb}(\text{s}) + 3\text{H}_2\text{S}(\text{g})$ [$+3\text{Pb}^{2+} \rightarrow 3\text{PbS}(\text{s}) + 6\text{H}^+$]:

$$\text{Starting M of H}_2(\text{g}) = 0.0100 \text{ mol} \div 2.50 \text{ L} = 0.00400 \text{ M H}_2$$

$$1.029 \text{ g PbS} \div 239.26 \text{ g PbS/mol H}_2\text{S} = 4.3007 \times 10^{-3} \text{ mol H}_2\text{S}$$

$$4.3007 \times 10^{-3} \text{ mol H}_2\text{S} \div 2.50 \text{ L} = [1.7203 \times 10^{-3}] = \text{M of H}_2\text{S}$$

Conc. (M)	$3\text{H}_2(\text{g})$	+	$\text{Sb}_2\text{S}_3(\text{s})$	\rightleftharpoons	$3\text{H}_2\text{S}(\text{g})$	+	$2\text{Sb}(\text{s})$
Starting	0.00400				0		
Change	-0.0017203				+0.0017203		
Equilibrium	0.0022797				0.0017203		

Substituting into the equilibrium expression for K_c gives

$$K_c = \frac{[\text{H}_2\text{S}]^3}{[\text{H}_2]^3} = \frac{(0.0017203)^3}{(0.0022797)^3} = 0.4297 = 0.430$$

15.108 For $\text{LaCl}_3 + \text{H}_2\text{O} \rightleftharpoons \text{LaOCl}(\text{s}) + 2\text{HCl}(\text{g})$ [$+2\text{Ag}^+ \rightarrow 2\text{AgCl}(\text{s}) + 2\text{H}^+$]:

$$\text{Starting M of H}_2\text{O}(\text{g}) = 0.0250 \text{ mol} \div 1.25 \text{ L} = 0.0200 \text{ M H}_2\text{O}$$

$$3.59 \text{ g AgCl} \div 143.32 \text{ g AgCl/mol AgCl} = 0.025048 \text{ mol AgCl}$$

$$0.025048 \text{ mol AgCl} \div 1.25 \text{ L} = 0.020039 \text{ M}$$

Conc. (M)	$\text{H}_2\text{O}(\text{g})$	+	$\text{LaCl}_3(\text{s})$	\rightleftharpoons	$2\text{HCl}(\text{g})$	+	$\text{LaOCl}(\text{s})$
Starting	0.0200				0		
Change	-0.0100195				+0.020039		
Equilibrium	0.0099805				0.020039		

$$K_c = \frac{[\text{HCl}]^2}{[\text{H}_2\text{O}]} = \frac{(0.020039)^2}{(0.0099805)} = 4.023 \times 10^{-2} = 4.02 \times 10^{-2}$$

15.109 For $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$:

$$\text{Starting M of } \text{PCl}_5 = 0.0100 \text{ mol} \div 2.00 \text{ L} = 0.00500 \text{ M}$$

Conc. (M)	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Starting	0.00500		0		0
Change	-x		+x		+x
Equilibrium	$0.00500 - x$		x		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 4.15 \times 10^{-2} = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(x)(x)}{(0.00500 - x)}$$

$$x^2 + (4.15 \times 10^{-2})x - 2.075 \times 10^{-4} = 0 \text{ (quadratic)}$$

Solving the quadratic equation gives $x = -4.60 \times 10^{-2}$ (impossible) and $x = 4.51 \times 10^{-3} \text{ M}$ (use).

$$\text{Total M of gas} = 0.00451 + 0.00451 + 0.00049 = 0.009510 \text{ M}$$

$$P = (n/V)RT = (0.009510 \text{ M})[0.082057 \text{ L}\cdot\text{atm}/(\text{K}\cdot\text{mol})](523 \text{ K})$$

$$= 0.4081 = 0.408 \text{ atm}$$

15.110 For $\text{SbCl}_5(\text{g}) \rightleftharpoons \text{SbCl}_3(\text{g}) + \text{Cl}_2(\text{g})$:

$$\text{Starting M of } \text{SbCl}_5 = 0.0125 \text{ mol} \div 3.50 \text{ L} = 0.003571 \text{ M}$$

Conc. (M)	$\text{SbCl}_5(\text{g})$	\rightleftharpoons	$\text{SbCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Starting	0.003571		0		0
Change	-x		+x		+x
Equilibrium	$0.003571 - x$		x		x

Substituting into the equilibrium expression for K_c gives

$$K_c = 2.50 \times 10^{-2} = \frac{[\text{SbCl}_3][\text{Cl}_2]}{[\text{SbCl}_5]} = \frac{(x)(x)}{(0.003571 - x)}$$

(continued)

$$x^2 + (2.50 \times 10^{-2})x - 8.927 \times 10^{-5} = 0 \text{ (quadratic)}$$

Solving the quadratic equation gives $x = -2.817 \times 10^{-2}$ (impossible) and $x = 3.17 \times 10^{-3}$ M (use).

$$\text{Total M of gas} = 0.00317 + 0.00317 + 0.00040 = 0.006740 \text{ M}$$

$$\begin{aligned} P &= (n/V)RT = (0.00674 \text{ M})[0.082057 \text{ L}\cdot\text{atm}/(\text{K}\cdot\text{mol})](521 \text{ K}) \\ &= 0.2881 = 0.288 \text{ atm} \end{aligned}$$

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Number of Pages: 51
Number of Words: 9,394 (approx.)
Number of Characters: 53,548 (approx.)