

15 Chemical Equilibrium

Visualizing Concepts

- 15.1 (a) $k_f > k_r$. According to the Arrhenius equation [14.19], $k = Ae^{-E_a/RT}$. As the magnitude of E_a increases, k decreases. On the energy profile, E_a is the difference in energy between the starting point and the energy at the top of the barrier. Clearly this difference is smaller for the forward reaction, so $k_f > k_r$.
- (b) From the Equation [15.5], the equilibrium constant = k_f/k_r . Since $k_f > k_r$, the equilibrium constant for the process shown in the energy profile is greater than 1.
- 15.2 Yes. The first box is pure reactant A. As the reaction proceeds, some A changes to B. In the fourth and fifth boxes, the relative amounts (concentrations) of A and B are constant. Although the reaction is ongoing the rates of $A \rightarrow B$ and $B \rightarrow A$ are equal, and the relative amounts of A and B are constant.
- 15.3 *Analyze.* Given box diagram and reaction type, determine whether $K > 1$ for the equilibrium mixture depicted in the box.
- Plan.* Assign species in the box to reactants and products. Write an equilibrium expression in terms of concentrations. Find the relationship between numbers of molecules and concentration. Calculate K .
- Solve.* Let red = A, blue = X, red and blue pairs = AX. (The colors of A and X are arbitrary.) There are 3A, 2B, and 8AX in the box.
- $M = \text{mol/L}$. Since moles is a counting unit for particles, mol ratios and particle ratios are equivalent. We can use numbers of particles in place of moles in the molarity formula. $V = 1 \text{ L}$, so in this case, $[A] = \text{number of A particles}$.
- $$K = \frac{[AX]}{[A][X]}; [AX] = 8/V = 8; [A] = 3/V = 3; [X] = 2/V = 2. K = \frac{8}{[3][2]} = \frac{8}{6} = 1.33$$
- 15.4 *Analyze/Plan.* Given that element A = red and element B = blue, evaluate the species in the reactant and product boxes, and write the reaction. Answer the remaining questions based on the balanced equation. *Solve.*
- (a) reactants: $4A_2 + 4B$; products: $4A_2B$
balanced equation: $A_2 + B \rightarrow A_2B$
- (b) $K_c = \frac{[A_2B]}{[A_2][B]}$
- (c) $\Delta n = \Sigma n(\text{prod}) - \Sigma n(\text{react}) = 1 - 2 = -1$.
- (d) $K_p = K_c(RT)^{\Delta n}$, Equation [15.14].
If you have a balanced equation, calculate Δn . Use Equation [15.14] to calculate K_p from K_c , or vice versa.

- 15.5 Your friend is not correct. By definition, a reaction at equilibrium has forward and reverse reactions happening simultaneously at the same rate. So, the faster the forward reaction, the faster the reverse reaction. The equilibrium constant for the reaction is the algebraic ratio of the rate constant for the forward reaction and the rate constant for the reverse reaction, k_f/k_r . The magnitude of the equilibrium constant, K , depends on the relative rate constants, not the speed of the reactions.
- 15.6 The statement is vaguely correct. If $K_c = 1.5 \times 10^6$, the arithmetic *product* of the concentrations of all product molecules is 1.5×10^6 times the *product* of the concentrations of all reactant molecules. (It does not mean that the sum of all product molecules is 1.5×10^6 times the sum of all reactant molecules.)
- 15.7 *Analyze/Plan.* The reaction with the largest equilibrium constant has the largest ratio of products to reactants. Count product and reactant molecules. Calculate ratios and compare. *Solve.*

$$K = \frac{[\text{C}_2\text{H}_4\text{X}_2]}{[\text{C}_2\text{H}_4][\text{X}_2]}. \text{ Use numbers of molecules as an adequate measure of concentration.}$$

(While the volume terms don't cancel, they are the same for all parts. For the purpose of comparison, we can ignore volume.) *Solve.*

$$(a) \quad 8 \text{ C}_2\text{H}_4\text{Cl}_2, \quad 2 \text{ Cl}_2, \quad 2 \text{ C}_2\text{H}_4. \quad K = \frac{8}{(2)(2)} = 2$$

$$(b) \quad 6 \text{ C}_2\text{H}_4\text{Br}_2, \quad 4 \text{ Br}_2, \quad 4 \text{ C}_2\text{H}_4. \quad K = \frac{6}{(4)(4)} = 0.375 = 0.4$$

$$(c) \quad 3 \text{ C}_2\text{H}_4\text{I}_2, \quad 7 \text{ I}_2, \quad 7 \text{ C}_2\text{H}_4. \quad K = \frac{3}{(7)(7)} = 0.0612 = 0.06$$

From the smallest to the largest equilibrium constant, $(c) < (b) < (a)$.

Check. By inspection, there are the fewest product molecules and the most reactant molecules in (c); most product and least reactant in (a).

- 15.8 *Analyze.* Given box diagrams, reaction type, and value of K_c , determine whether each reaction mixture is at equilibrium.

Plan. Analyze the contents of each box, express them as concentrations (see Solution 5.3). Write the equilibrium expression, calculate Q for each mixture, and compare it to K_c . If $Q = K$, the mixture is at equilibrium. If $Q < K$, the reaction shifts right (more product). If $Q > K$, the reaction shifts left (more reactant).

$$\text{Solve. } K_c = \frac{[\text{AB}]^2}{[\text{A}_2][\text{B}_2]}.$$

For this reaction, $\Delta n = 0$, so the volume terms cancel in the equilibrium expression. In this case, the number of each kind of particle can be used as a representation of moles (see Solution 5.3) and molarity.

$$(a) \quad \text{Mixture (i): } 1\text{A}_2, 1\text{B}_2, 6\text{AB}; \quad Q = \frac{6^2}{(1)(1)} = 36$$

$Q > K_c$, the mixture is not at equilibrium.

$$\text{Mixture (ii): } 3A_2, 2B_2, 3AB; Q = \frac{3^2}{(3)(2)} = 1.5$$

$Q = K_c$, the mixture is at equilibrium.

$$\text{Mixture (iii): } 3A_2, 3B_2, 2AB; Q = \frac{2^2}{(3)(3)} = 0.44$$

$Q < K_c$, the mixture is not at equilibrium.

(b) Mixture (i) proceeds toward reactants.

Mixture (iii) proceeds toward products.

- 15.9 For the reaction $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$, $\Delta n = 0$ and $K_p = K_c$. We can evaluate the equilibrium expression in terms of concentration. Also since $\Delta n = 0$, the volume terms in the expression cancel and we can use number of particles as a measure of moles and molarity. The mixture contains 2A, 4AB and 2A₂.

$$K_c = \frac{[A][AB]}{[A_2][B]} = \frac{(2)(4)}{(2)(2)} = 2; B = 2$$

2 B atoms should be added to the diagram.

- 15.10 *Analyze.* Given the diagram and reaction type, calculate the equilibrium constant K_c .

Plan. Analyze the contents of the cylinder. Express them as concentrations, using number of particles as a measure of moles, and $V = 2$ L. Write the equilibrium expression in terms of concentration and calculate K_c . *Solve.*

- (a) The mixture contains 2A₂, 2B, 4AB. $[A_2] = 2/2 = 1$, $[B] = 2/2 = 1$, $[AB] = 4/2 = 2$.

$$K_c = \frac{[AB]^2}{[A_2][B]^2} = \frac{(2)^2}{(1)(1)^2} = 4$$

- (b) A decrease in volume favors the reaction with fewer particles. This reaction has two particles in products and three in reactants, so a decrease in volume favors products. The number of AB (product) molecules will increase.

Note that a change in volume does not change the value of K_c . If V decreases, the number of AB molecules must increase in order to maintain the equilibrium value of K_c .

- 15.11 If temperature increases, K of an endothermic reaction increases and K of an exothermic reaction decreases. Calculate the value of K for the two temperatures and compare. For this reaction, $\Delta n = 0$ and $K_p = K_c$. We can ignore volume and use number of particles as a measure of moles and molarity. $K_c = [A][AB]/[A_2][B]$

$$(1) \quad 300 \text{ K, } 3A, 5AB, 1A_2, 1B; K_c = (3)(5)/(1)(1) = 15$$

$$(2) \quad 500 \text{ K, } 1A, 3AB, 3A_2, 3B; K_c = (1)(3)/(3)(3) = 0.33$$

K_c decreases as T increases, so the reaction is exothermic.

- 15.12 (a) Exothermic. In both reaction mixtures (orange and blue), $[AB]$ decreases as T increases.

- (b) In the reaction, there are fewer moles of gas in products than reactants, so greater pressure favors production of products. At any single temperature, $[AB]$ is greater at $P = y$ than at $P = x$. Since the concentration of the product, AB , is greater at $P = y$, $P = y$ is the greater pressure.

Equilibrium; The Equilibrium Constant (sections 15.1 – 15.4)

- 15.13 *Analyze/Plan.* Given the forward and reverse rate constants, calculate the equilibrium constant using Equation [15.5]. At equilibrium, the rates of the forward and reverse reactions are equal. Write the rate laws for the forward and reverse reactions and use their equality to answer part (b). *Solve.*

$$(a) \quad K_c = \frac{k_f}{k_r}, \text{ Equation [15.5];} \quad K_c = \frac{4.7 \times 10^{-3} \text{ s}^{-1}}{5.8 \times 10^{-1} \text{ s}^{-1}} = 8.1 \times 10^{-3}$$

$$\text{For this reaction, } K_p = K_c = 8.1 \times 10^{-3}$$

$$(b) \quad \text{rate}_f = \text{rate}_r; k_f[A] = k_r[B]$$

Since $k_f < k_r$, in order for the two rates to be equal, $[A]$ must be greater than $[B]$ and the partial pressure of A is greater than the partial pressure of B .

- 15.14 (a) $K_c = \frac{[C][D]}{[A][B]}$; if K_c is large, the numerator of the K_c expression is much greater than the denominator and products will predominate at equilibrium.

- (b) $K_c = k_f/k_r$; if K_c is large, k_f is larger than k_r and the forward reaction has the greater rate constant.

- 15.15 *Analyze/Plan.* Follow the logic in Sample Exercises 15.1 and 15.6. *Solve.*

$$(a) \quad K_c = \frac{[N_2O][NO_2]}{[NO]^3}$$

$$(b) \quad K_c = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

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

$$(d) \quad K_c = \frac{[H^+][F^-]}{[HF]}$$

$$(e) \quad K_c = \frac{[Ag^+]^2}{[Zn^{2+}]}$$

$$(f) \quad K_c = [H^+][OH^-]$$

$$(g) \quad K_c = [H^+][OH^-]$$

homogeneous: (a), (b), (d), (f), (g); heterogeneous: (c), (e)

$$15.16 \quad (a) \quad K_c = \frac{[O_2]^3}{[O_3]^2} \quad (b) \quad K_c = \frac{1}{[Cl_2]^2}$$

$$(c) \quad K_c = \frac{[C_2H_6]^2[O_2]}{[C_2H_4]^2[H_2O]^2}$$

$$(d) \quad K_c = \frac{[CH_4]}{[H_2]^2}$$

$$(e) \quad K_c = \frac{[Cl_2]^2}{[HCl]^4[O_2]}$$

$$(f) \quad K_c = \frac{[CO_2]^{16}[H_2O]^{18}}{[O_2]^{25}}$$

$$(g) \quad K_c = \frac{[CO_2]^{16}}{[O_2]^{25}}$$

homogeneous: (a), (c); heterogeneous: (b), (d), (e), (f), (g)

- 15.17 *Analyze.* Given the value of K_c or K_p , predict the contents of the equilibrium mixture.
Plan. If K_c or $K_p \gg 1$, products dominate; if K_c or $K_p \ll 1$, reactants dominate. *Solve.*
 (a) mostly reactants ($K_c \ll 1$)
 (b) mostly products ($K_p \gg 1$)
- 15.18 (a) equilibrium lies to right, favoring products ($K_p \gg 1$)
 (b) equilibrium lies to left, favoring reactants ($K_c \ll 1$)
- 15.19 No, the equilibrium constant can never be a negative number. The equilibrium constant is a ratio of concentrations of products to concentration of reactants, or of partial pressures of reactants to partial pressures of products. Concentrations and partial pressures are never negative, and neither is K . (Or, K is a ratio of rate constants, which also cannot have negative values.)
- 15.20 The equilibrium constant can never be zero. By definition, a reaction at equilibrium has forward and reverse reactions occurring at equal (non-zero) rates. The equilibrium constant is a ratio of the rate constants for the forward and reverse reactions, and rate constants are non-zero numbers. The equilibrium constant is also a ratio of concentrations (or partial pressures) of products to concentrations (or partial pressures) of reactants. Both products and reactants must be present in finite amounts. This means that both the numerator and denominator must have nonzero values, and the ratio, K , is always nonzero.
- 15.21 *Analyze/Plan.* Follow the logic in Sample Exercise 15.2. *Solve.*
 $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g}), K_c = 0.042. \Delta n = 1 - 2 = -1$
 $K_p = K_c(\text{RT})^{\Delta n} = 0.042(\text{RT})^{-1} = 0.042/\text{RT}$
 $K_p = \frac{0.042}{(0.08206)(500)} = 0.001024 = 1.0 \times 10^{-3}$
- 15.22 $\text{SO}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2\text{Cl}_2(\text{g}), K_p = 34.5. \Delta n = 1 - 2 = -1$
 $K_p = K_c(\text{RT})^{\Delta n}; 34.5 = K_c(\text{RT})^{-1} = K_c/\text{RT};$
 $K_c = 34.5 \text{ RT} = 34.5(0.08206)(303) = 857.81 = 858$
- 15.23 *Analyze.* Given K_c for a chemical reaction, calculate K_c for the reverse reaction.
Plan. Evaluate which species are favored by examining the magnitude of K_c . The equilibrium expressions for the reaction and its reverse are the reciprocals of each other, and the values of K_c are also reciprocal. *Solve.*
 (a) For the reaction as written, $K_c < 1$, which means that reactants are favored. At this temperature, the equilibrium favors NO and Br_2 .
 (b) $K_c(\text{forward}) = \frac{[\text{NOBr}]^2}{[\text{NO}]^2[\text{Br}_2]} = 1.3 \times 10^{-2}$
 $K_c(\text{reverse}) = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} = \frac{1}{1.3 \times 10^{-2}} = 76.92 = 77$
 (c) $K_{c2}(\text{reverse}) = \frac{[\text{NO}][\text{Br}_2]^{1/2}}{[\text{NOBr}]} = (K_c(\text{reverse}))^{1/2} = (76.92)^{1/2} = 8.8$

15.24 $2\text{H}_2(\text{g}) + \text{S}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{S}(\text{g})$, $K_c = 1.08 \times 10^7$ at 700°C . $\Delta n = 2 - 3 = -1$.

(a) $K_p = K_c(\text{RT})^{\Delta n} = 700^\circ\text{C} + 273 = 973 \text{ K}$.

$$K_p = 1.08 \times 10^7 (\text{RT})^{-1} = \frac{1.08 \times 10^7}{(0.08206)(973)} = 1.35 \times 10^5$$

(b) Both K_p and K_c are much greater than one, so the product, H_2S , is favored at equilibrium. The equilibrium mixture contains mostly H_2S .

(c) $\text{H}_2(\text{g}) + \frac{1}{2} \text{S}_2(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{g})$; $K_{c2} = \frac{[\text{H}_2\text{S}]}{[\text{H}_2][\text{S}_2]^{1/2}}$

$$K_{c2} = (K_c)^{1/2} = (1.08 \times 10^7)^{1/2} = 3.29 \times 10^3$$

$$K_{p2} = (K_p)^{1/2} = (1.35 \times 10^5)^{1/2} = 368$$

15.25 *Analyze.* Given K_p for a reaction, calculate K_p for a related reaction.

Plan. The algebraic relationship between the K_p values is the same as the algebraic relationship between equilibrium expressions.

Solve. $K_p = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} \times P_{\text{O}_2}^{1/2}} = 1.85$

(a) $K_p = \frac{P_{\text{SO}_2} \times P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} = \frac{1}{1.85} = 0.541$

(b) $K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = (1.85)^2 = 3.4225 = 3.42$

(c) $K_p = K_c(\text{RT})^{\Delta n}$; $\Delta n = 2 - 3 = -1$; $T = 1000 \text{ K}$

$$K_p = K_c(\text{RT})^{-1} = K_c/\text{RT}; K_c = K_p(\text{RT})$$

$$K_c = 3.4225(0.08206)(1000) = 280.85 = 281$$

15.26 $K_p = \frac{P_{\text{HCl}}^4 \times P_{\text{O}_2}}{P_{\text{Cl}_2}^2 \times P_{\text{H}_2\text{O}}^2} = 0.0752$

(a) $K_p = \frac{P_{\text{Cl}_2}^2 \times P_{\text{H}_2\text{O}}^2}{P_{\text{HCl}}^4 \times P_{\text{O}_2}} = \frac{1}{0.0752} = 13.298 = 13.3$

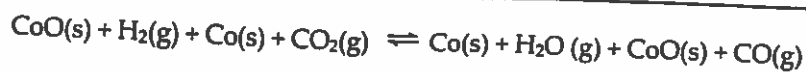
(b) $K_p = \frac{P_{\text{HCl}}^2 \times P_{\text{O}_2}^{1/2}}{P_{\text{Cl}_2} \times P_{\text{H}_2\text{O}}} = (0.0752)^{1/2} = 0.2742 = 0.274$

(c) $K_p = K_c(\text{RT})^{\Delta n}$; $\Delta n = 2.5 - 2 = 0.5$; $T = 480^\circ\text{C} + 273 = 753 \text{ K}$

$$K_p = K_c(\text{RT})^{1/2}, K_c = K_p/(\text{RT})^{1/2} = 0.2742/[0.08206 \times 753]^{1/2} = 0.03488 = 0.0349$$

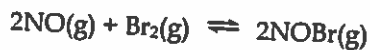
15.27 *Analyze/Plan.* Follow the logic in Sample Exercise 15.5. *Solve.*



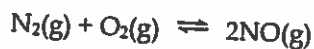


$$K_c = K_1 \times K_2 = 67 \times \frac{1}{490} = 0.1367 = 0.14$$

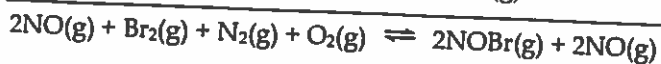
15.28



$$K_1 = 2.0$$



$$K_2 = \frac{1}{2.1 \times 10^{30}}$$



$$K_c = K_1 \times K_2 = 2.0 \times \frac{1}{2.1 \times 10^{30}} = 9.524 \times 10^{-31} = 9.5 \times 10^{-31}$$

15.29

Pure solids and liquids are normally excluded from equilibrium-constant expressions because their concentrations are constant. Molar concentration is the ratio of moles of substance to volume occupied by substance. For a pure solid or liquid, if moles increase, volume occupied increases (and vice versa), so the concentration remains the same.

An alternate explanation involves the use of activities to express amounts of the various reactants and products in an equilibrium mixture. By definition, the activity of a pure solid or liquid is one, and it need not appear in the equilibrium-constant expression.

15.30

Concentration of solvent is normally excluded from liquid-phase equilibrium-constant expressions because solvents do not usually participate in the chemical reaction and their concentrations do not change. This constant is incorporated into the value of the equilibrium constant.

15.31

Analyze/Plan. Follow the logic in Sample Exercise 15.6. *Solve.*

$$(a) \quad K_p = P_{\text{O}_2}$$

$$(b) \quad K_c = [\text{Hg(soln)}]^4[\text{O}_2(\text{soln})]$$

15.32

$$(a) \quad K_p = 1/P_{\text{SO}_2}$$

$$(b) \quad K_c = \frac{[\text{Na}_2\text{SO}_3]}{[\text{Na}_2\text{O}][\text{SO}_2]}$$

Calculating Equilibrium Constants (section 15.5)

15.33

Analyze/Plan. Calculate molarity of reactants and products. Follow the logic in Sample Exercise 15.8 using concentrations rather than pressures. *Solve.*

$$[\text{CH}_3\text{OH}] = \frac{0.0406 \text{ mol}}{2.00 \text{ L}} = 0.0203 \text{ M}$$

$$[\text{CO}] = \frac{0.170 \text{ mol CO}}{2.00 \text{ L}} = 0.0850 \text{ M}; \quad [\text{H}_2] = \frac{0.302 \text{ mol H}_2}{2.00 \text{ L}} = 0.151 \text{ M}$$

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{0.0203}{(0.0850)(0.151)^2} = 10.4743 = 10.5$$

$$15.34 \quad K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]_2} = \frac{(4.79 \times 10^{-4})(4.79 \times 10^{-4})}{(3.53 \times 10^{-3})^2} = 0.018413 = 0.0184$$

15.35 *Analyze/Plan.* Follow the logic in Sample Exercise 15.8. *Solve.*



$$K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 \times P_{\text{Cl}_2}} = \frac{(0.28)^2}{(0.095)^2 (0.171)} = 50.80 = 51$$

(b) $K_p = K_c(\text{RT})^{\Delta n}$; $\Delta n = 2 - 3 = -1$; $K_p = K_c(\text{RT})^{-1} = K_c/(\text{RT})$

$$K_c = K_p(\text{RT}) = 50.80(0.08206 \times 500) = 2.1 \times 10^3$$

15.36 (a) $K_p = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} \times P_{\text{Cl}_2}} = \frac{1.30 \text{ atm}}{0.124 \text{ atm} \times 0.157 \text{ atm}} = 66.8$

(b) Since $K_p > 1$, products (the numerator of the K_p expression) are favored over reactants (the denominator of the K_p expression).

(c) $K_p = K_c(\text{RT})^{\Delta n}$; $\Delta n = 1 - 2 = -1$; $K_p = K_c(\text{RT})^{-1} = K_c/(\text{RT})$

$$K_c = K_p(\text{RT}) = 66.8(0.08206 \times 450) = 2.5 \times 10^3$$

15.37 *Analyze/Plan.* Follow the logic in Sample Exercise 15.9. Since the container volume is 1.0 L, mol = M. *Solve.*

(a) First calculate the change in [NO], $0.062 - 0.10 = -0.038 = -0.04 \text{ M}$. From the stoichiometry of the reaction, calculate the changes in the other pressures. Finally, calculate the equilibrium pressures.

	$2\text{NO}(\text{g})$	+	$2\text{H}_2(\text{g})$	\rightleftharpoons	$\text{N}_2(\text{g})$	+	$2\text{H}_2\text{O}(\text{g})$
initial	0.10 M		0.050 M		0 M		0.10 M
change	-0.038 M		-0.038 M		+0.019 M		+0.038 M
equil.	0.062 M		0.012 M		0.019 M		0.138 M

Strictly speaking, the change in [NO] has two decimal places and thus one sig fig. This limits equilibrium pressures to one sig fig for all but H_2O , and K_c to one sig fig. We compute the extra figures and then round.

(b) $K_c = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2[\text{H}_2]^2} = \frac{(0.019)(0.138)^2}{(0.062)^2(0.012)^2} = \frac{(0.02)(0.14)^2}{(0.06)^2(0.01)^2} = 653.7 = 7 \times 10^2$

15.38 (a) Calculate the initial concentrations of $\text{H}_2(\text{g})$ and $\text{Br}_2(\text{g})$ and the equilibrium concentration of $\text{H}_2(\text{g})$. $M = \text{mol/L}$.

$$[\text{H}_2]_{\text{init}} = 1.374 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.0159 \text{ g H}_2} \times \frac{1}{2.00 \text{ L}} = 0.34079 = 0.341 \text{ M}$$

$$[\text{Br}_2] = 70.31 \text{ g Br}_2 \times \frac{1 \text{ mol Br}_2}{159.81 \text{ g Br}_2} \times \frac{1}{2.00 \text{ L}} = 0.21998 = 0.220 \text{ M}$$

$$[\text{H}_2]_{\text{equil}} = 0.566 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.0159 \text{ g H}_2} \times \frac{1}{2.00 \text{ L}} = 0.14038 = 0.140 \text{ M}$$

	H ₂ (g)	+	Br ₂ (g)	⇌	2HBr(g)
initial	0.34079 M		0.21998 M		0
change	-0.20041 M		-0.20041 M		+2(0.20041) M
equil.	0.14038 M		0.01957 M		0.40082 M

The change in H₂ is (0.34079 - 0.14038 = 0.20041 = 0.200). The changes in [Br₂] and [HBr] are set by stoichiometry, resulting in the equilibrium concentrations shown in the table.

$$(b) \quad K_c = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]} = \frac{(0.40082)^2}{(0.14038)(0.01957)} = \frac{(0.401)^2}{(0.140)(0.020)} = 58.48 = 58$$

The equilibrium concentration of Br₂ has 3 decimal places and 2 sig figs, so the value of K_c has 2 sig figs.

- 15.39 *Analyze/Plan.* Follow the logic in Sample Exercise 15.9, using partial pressures, rather than concentrations. *Solve.*

$$(a) \quad P = nRT/V; P_{\text{CO}_2} = 0.2000 \text{ mol} \times \frac{500 \text{ K}}{2.000 \text{ L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 4.1030 = 4.10 \text{ atm}$$

$$P_{\text{H}_2} = 0.1000 \text{ mol} \times \frac{500 \text{ K}}{2.000 \text{ L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 2.0515 = 2.05 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = 0.1600 \times \frac{500 \text{ K}}{2.000 \text{ L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 3.2824 = 3.28 \text{ atm}$$

- (b) The change in P_{H₂O} is 3.51 - 3.28 = 0.2276 = 0.23 atm. From the reaction stoichiometry, calculate the change in the other pressures and the equilibrium pressures.

	CO ₂ (g)	+	H ₂ (g)	⇌	CO(g)	+	H ₂ O(g)
initial	4.10 atm		2.05 atm		0 atm		3.28 atm
change	-0.23 atm		-0.23 atm		+0.23		+0.23 atm
equil	3.87 atm		1.82 atm		0.23 atm		3.51 atm

$$(c) \quad K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} \times P_{\text{H}_2}} = \frac{(0.23)(3.51)}{(3.87)(1.82)} = 0.1146 = 0.11$$

Without intermediate rounding, equilibrium pressures are P_{H₂O} = 3.51, P_{CO} = 0.2276, P_{H₂} = 1.8239, P_{CO₂} = 3.8754 and K_p = 0.1130 = 0.11, in good agreement with the value above.

$$(d) \quad K_p = K_c(RT)^{\Delta n}; \Delta n = 2 - 2 = 0; K_p = K_c(RT)^0; K_c = K_p = 0.11$$

- 15.40 (a)

	N ₂ O ₄ (g)	⇌	2NO ₂ (g)
initial	1.500 atm		1.000 atm
change	+0.244 atm		-0.488 atm
equil	1.744 atm		0.512 atm

The change in P_{NO_2} is $(1.000 - 0.512) = -0.488$ atm, so the change in $P_{\text{N}_2\text{O}_4}$ is $+(0.488/2) = +0.244$ atm.

$$(b) \quad K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(0.512)^2}{(1.744)} = 0.1503 = 0.150$$

$$(c) \quad K_p = K_c(RT)^{\Delta n}; \Delta n = 2 - 1 = 1; K_p = K_c(RT)^1 = K_c(RT)$$

$$K_c = K_p/(RT) = 0.1503/(0.08206 \times 298) = 6.15 \times 10^{-3}$$

15.41 *Analyze/Plan.* Follow the logic in Sample Exercise 15.9. $mM = 10^{-3} M$

	X(aq)	+	Y(aq)	\rightleftharpoons	XY(aq)
initial	1.0 mM		1.0 mM		0
change	-0.80 mM		-0.80 mM		+0.80 mM
equil.	0.20 mM		0.20 mM		0.80 mM

$$K_c = \frac{[\text{XY}]}{[\text{X}][\text{Y}]} = \frac{(0.80 \times 10^{-3})}{(0.20 \times 10^{-3})(0.20 \times 10^{-3})} = 2.0 \times 10^4$$

15.42 The initial concentrations of drug candidate and protein are the same in the two experiments, and the two reactions have the same stoichiometry. At equilibrium, the concentration of B-protein complex is greater than the concentration of A-protein complex, so drug B is the better choice for further research. Calculation of equilibrium constants for the two reactions confirms this conclusion.

	A(aq)	+	protein(aq)	\rightleftharpoons	A-protein(aq)
initial	$2.00 \times 10^{-6} \text{ mM}$		$1.50 \times 10^{-6} \text{ mM}$		0
change	$-1.00 \times 10^{-6} \text{ mM}$		$-1.00 \times 10^{-6} \text{ mM}$		$+1.00 \times 10^{-6} \text{ mM}$
equil.	$1.00 \times 10^{-6} \text{ mM}$		$0.50 \times 10^{-6} \text{ mM}$		$1.00 \times 10^{-6} \text{ mM}$

$$K_c = \frac{[\text{A-protein}]}{[\text{A}][\text{protein}]} = \frac{(1.00 \times 10^{-6})}{(1.00 \times 10^{-6})(0.50 \times 10^{-6})} = 2.0 \times 10^6$$

	B(aq)	+	protein(aq)	\rightleftharpoons	B-protein(aq)
initial	$2.00 \times 10^{-6} \text{ mM}$		$1.50 \times 10^{-6} \text{ mM}$		0
change	$-1.40 \times 10^{-6} \text{ mM}$		$-1.40 \times 10^{-6} \text{ mM}$		$+1.40 \times 10^{-6} \text{ mM}$
equil.	$0.60 \times 10^{-6} \text{ mM}$		$0.10 \times 10^{-6} \text{ mM}$		$1.40 \times 10^{-6} \text{ mM}$

$$K_c = \frac{[\text{B-protein}]}{[\text{B}][\text{protein}]} = \frac{(1.40 \times 10^{-6})}{(0.60 \times 10^{-6})(0.10 \times 10^{-6})} = 2.3 \times 10^7$$

Applications of Equilibrium Constants (section 15.6)

- 15.43 (a) A reaction quotient is the result of the law of mass action for a general set of concentrations, whereas the equilibrium constant requires equilibrium concentrations.
- (b) In the direction of more products, to the right.

- (c) If $Q_c = K_c$, the system is at equilibrium; the concentrations used to calculate Q must be equilibrium concentrations.
- 15.44 (a) If the value of Q_c equals the value of K_c , the system is at equilibrium.
 (b) In the direction of less products (more reactants), to the left.
 (c) $Q_c = 0$ if the concentration of any product is zero.

15.45 *Analyze/Plan.* Follow the logic in Sample Exercise 15.10. We are given molarities, so we calculate Q directly and decide on the direction to equilibrium. *Solve.*

$$K_c = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = 2.19 \times 10^{-10} \text{ at } 100^\circ\text{C}$$

(a) $Q = \frac{(3.3 \times 10^{-6})(6.62 \times 10^{-6})}{(2.00 \times 10^{-3})} = 1.1 \times 10^{-8}; Q > K$

The reaction will proceed left to attain equilibrium.

(b) $Q = \frac{(1.1 \times 10^{-7})(2.25 \times 10^{-6})}{(4.50 \times 10^{-2})} = 5.5 \times 10^{-12}; Q < K$

The reaction will proceed right to attain equilibrium.

(c) $Q = \frac{(1.48 \times 10^{-6})^2}{(0.0100)} = 2.19 \times 10^{-10}; Q = K$

The reaction is at equilibrium.

15.46 Calculate the reaction quotient in each case, compare with

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3} = 4.51 \times 10^{-5}$$

(a) $Q = \frac{(98)^2}{(45)(55)^3} = 1.3 \times 10^{-3}$

Since $Q > K_p$, the reaction will shift toward reactants to achieve equilibrium.

(b) $Q = \frac{(57)^2}{(143)(0)^3} = \infty$

Since $Q > K_p$, reaction must shift toward reactants to achieve equilibrium. There must be some H_2 present to achieve equilibrium. In this example, the only source of H_2 is the decomposition of NH_3 .

(c) $Q = \frac{(13)^2}{(27)(82)^3} = 1.1 \times 10^{-5}; Q$ is only slightly less than K_p , so the reaction will shift slightly toward products to achieve equilibrium.

15.47 *Analyze/Plan.* Follow the logic in Sample Exercise 15.11. We are given concentrations, so write the K_c expression and solve for $[\text{Cl}_2]$. Change molarity to partial pressure using the ideal gas equation and the definition of molarity. *Solve.*

$$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]}; [\text{Cl}_2] = \frac{K_c[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2]} = \frac{(0.078)(0.108)}{0.052} = 0.16200 = 0.16 \text{ M}$$

$$PV = nRT, P = \frac{n}{V}RT; \frac{n}{V} = M; P = M RT; T = 100^\circ\text{C} + 273 = 373 \text{ K}$$

$$P_{\text{Cl}_2} = \frac{0.16200 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 373 \text{ K} = 4.959 = 5.0 \text{ atm}$$

$$\text{Check. } K_c = \frac{(0.052)(0.162)}{(0.108)} = 0.078. \text{ Our values are self-consistent.}$$

$$15.48 \quad K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}}; P_{\text{SO}_3} = (K_p \times P_{\text{SO}_2}^2 \times P_{\text{O}_2})^{1/2} = [(0.345)(0.135)^2(0.455)]^{1/2} = 0.0535 \text{ atm}$$

15.49 *Analyze/Plan.* Follow the logic in Sample Exercise 15.11. In each case, change given masses to molarities solve for the equilibrium molarity of the desired component, and calculate mass of that substance present at equilibrium. *Solve.*

$$(a) \quad K_c = \frac{[\text{Br}]^2}{[\text{Br}_2]} = 1.04 \times 10^{-3}$$

$$[\text{Br}_2] = \frac{0.245 \text{ g Br}_2}{0.200 \text{ L}} \times \frac{1 \text{ mol Br}_2}{159.8 \text{ g Br}_2} = 0.007666 = 0.00767 \text{ M}$$

$$[\text{Br}] = (K_c [\text{Br}_2])^{1/2} = [(1.04 \times 10^{-3})(0.007666)]^{1/2} = 0.002824 = 0.00282 \text{ M}$$

$$\frac{0.002824 \text{ mol Br}}{\text{L}} \times 0.200 \text{ L} \times \frac{79.90 \text{ g Br}}{\text{mol}} = 0.0451 \text{ g Br(g)}$$

$$\text{Check. } K_c = (0.002824)^2 / (0.007666) = 1.04 \times 10^{-3}$$

$$(b) \quad K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 55.3; [\text{HI}] = (K_c [\text{H}_2][\text{I}_2])^{1/2}$$

$$[\text{H}_2] = \frac{0.056 \text{ g H}_2}{2.00 \text{ L}} \times \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 0.01389 = 0.014 \text{ M}$$

$$[\text{I}_2] = \frac{4.36 \text{ g I}_2}{2.00 \text{ L}} \times \frac{1 \text{ mol I}_2}{253.8 \text{ g I}_2} = 0.008589 = 0.00859 \text{ M}$$

$$[\text{HI}] = [(55.3)(0.01389)(0.008589)]^{1/2} = 0.08122 = 0.081 \text{ M}$$

$$0.08122 \text{ M HI} \times 2.00 \text{ L} \times \frac{127.9 \text{ g HI}}{\text{mol HI}} = 20.78 = 21 \text{ g HI}$$

$$\text{Check. } K_c = \frac{(0.08122)^2}{(0.01389)(0.008589)} = 55.3$$

$$15.50 \quad (a) \quad K_c = \frac{[\text{I}]^2}{[\text{I}_2]} = 3.1 \times 10^{-5}$$

$$[\text{I}] = \frac{2.67 \times 10^{-2} \text{ g I}}{10.0 \text{ L}} \times \frac{1 \text{ mol I}}{126.9 \text{ g I}} = 2.1040 \times 10^{-5} = 2.10 \times 10^{-5} \text{ M}$$

$$[I_2] = \frac{[I]^2}{K_c} = \frac{(2.104 \times 10^{-5})^2}{3.1 \times 10^{-5}} = 1.428 \times 10^{-5} = 1.43 \times 10^{-5} M$$

$$\frac{1.428 \times 10^{-5} \text{ mol } I_2}{L} \times 10.0 L \times \frac{253.8 \text{ g } I_2}{\text{mol } I_2} = M = 0.0362 \text{ g } I_2$$

$$\text{Check. } K_c = \frac{(2.104 \times 10^{-5})^2}{1.428 \times 10^{-5}} = 3.1 \times 10^{-5}$$

$$(b) \quad PV = nRT; P = \frac{gRT}{MM V}$$

$$P_{SO_3} = \frac{1.17 \text{ g } SO_3}{80.06 \text{ g/mol}} \times \frac{0.08206 \text{ L-atm}}{\text{K-mol}} \times \frac{700 \text{ K}}{2.00 \text{ L}} = 0.4197 = 0.420 \text{ atm}$$

$$P_{O_2} = \frac{0.105 \text{ g } O_2}{32.00 \text{ g/mol}} \times \frac{0.08206 \text{ L-atm}}{\text{K-mol}} \times \frac{700 \text{ K}}{2.00 \text{ L}} = 0.09424 = 0.0942 \text{ atm}$$

$$K_p = 3.0 \times 10^4 = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}; P_{SO_2} = [P_{SO_3}^2 / (K_p)(P_{O_2})]^{1/2}$$

$$P_{SO_2} = [(0.4197)^2 / (3.0 \times 10^4)(0.09424)]^{1/2} = 7.894 \times 10^{-3} = 7.9 \times 10^{-3} \text{ atm}$$

$$\text{g } SO_2 = \frac{MM PV}{RT} = \frac{64.06 \text{ g } SO_2}{\text{mol } SO_2} \times \frac{\text{K-mol}}{0.08206 \text{ L-atm}} \times \frac{7.894 \times 10^{-3} \text{ atm} \times 2.00 \text{ L}}{700 \text{ K}}$$

$$= 0.01761 = 0.018 \text{ g } SO_2$$

$$\text{Check. } K_p = [(0.4197)^2 / (7.894 \times 10^{-3})^2(0.09424)] = 3.0 \times 10^4$$

15.51 *Analyze/Plan.* Follow the logic in Sample Exercise 15.12. Since molarity of NO is given directly, we can construct the equilibrium table straight away. *Solve.*

	$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$	$K_c = \frac{[N_2][O_2]}{[NO]^2} = 2.4 \times 10^3$	
initial	0.175 M	0	0
change	-2x	+x	+x
equil.	0.175 - 2x	+x	+x

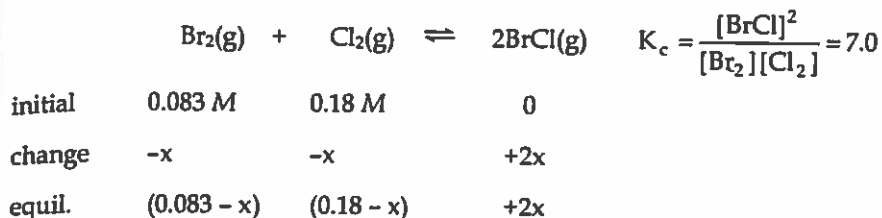
$$2.4 \times 10^3 = \frac{x^2}{(0.175 - 2x)^2}; (2.4 \times 10^3)^{1/2} = \frac{x}{0.175 - 2x}$$

$$x = (2.4 \times 10^3)^{1/2} (0.175 - 2x); x = 8.573 - 97.98x; 98.98x = 8.573, x = 0.08662 = 0.087 M$$

$$[N_2] = [O_2] = 0.087 M; [NO] = 0.175 - 2(0.08662) = 0.00177 = 0.002 M$$

$$\text{Check. } K_c = (0.08662)^2 / (0.00177)^2 = 2.4 \times 10^3$$

15.52 $[\text{Br}_2] = 0.25 \text{ mol}/3.0 \text{ L} = 0.08333 = 0.083 \text{ M}$; $[\text{Cl}_2] = 0.55 \text{ mol}/3.0 \text{ L} = 0.1833 = 0.18 \text{ M}$



$$7.0 = \frac{(2x)^2}{(0.08333 - x)(0.1833 - x)}; \quad 4x^2 = 7.0(0.0153 - 0.2666x + x^2); \quad 0 = 0.1069 - 1.8662x + 3x^2$$

$$x = \frac{1.8662 \pm \sqrt{(-1.8662)^2 - 4(3)(0.1069)}}{2(3)} = 0.06387 = 0.064 \text{ M}$$

(The 0.56 M quadratic solution is not chemically meaningful.)

$$[\text{BrCl}] = 2x = 0.1277 = 0.13 \text{ M}; \quad [\text{Br}_2] = 0.08333 - 0.06387 = 0.01946 = 0.019 \text{ M}$$

$$[\text{Cl}_2] = 0.1833 - 0.06387 = 0.1195 = 0.12 \text{ M}$$

$$\text{Check. } K_c = (0.1277)^2 / (0.01946)(0.1195) = 7.0125 = 7.0$$

- 15.53 *Analyze/Plan.* Write the K_p expression, substitute the stated pressure relationship, and solve for P_{Br_2} . *Solve.*

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

When $P_{\text{NOBr}} = P_{\text{NO}}$, these terms cancel and $P_{\text{Br}_2} = K_p = 0.416 \text{ atm}$. This is true for all cases where $P_{\text{NOBr}} = P_{\text{NO}}$.

- 15.54 $K_c = [\text{NH}_3][\text{H}_2\text{S}] = 1.2 \times 10^{-4}$. Because of the stoichiometry, equilibrium concentrations of H_2S and NH_3 will be equal; call this quantity y . Then, $y^2 = 1.2 \times 10^{-4}$, $y = 0.010954 = 0.011 \text{ M}$.

- 15.55 (a) $\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \quad K_c = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 2.4 \times 10^{-5}$

At equilibrium, $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = x$

$$K_c = 2.4 \times 10^{-5} = x^2; \quad x = 4.9 \times 10^{-3} \text{ M } \text{Ca}^{2+} \text{ and } \text{SO}_4^{2-}$$

- (b) A saturated solution of $\text{CaSO}_4(\text{aq})$ is $4.9 \times 10^{-3} \text{ M}$.

1.4 L of this solution contain:

$$\frac{4.9 \times 10^{-3} \text{ mol}}{\text{L}} \times 1.4 \text{ L} \times \frac{136.14 \text{ g CaSO}_4}{\text{mol}} = 0.9337 = 0.94 \text{ g CaSO}_4$$

A bit more than 1.0 g CaSO_4 is needed in order to have some undissolved $\text{CaSO}_4(\text{s})$ in equilibrium with 1.4 L of saturated solution.

- 15.56 (a) *Analyze/Plan.* If only $\text{PH}_3\text{BCl}_3(\text{s})$ is present initially, the equation requires that the equilibrium concentrations of $\text{PH}_3(\text{g})$ and $\text{BCl}_3(\text{g})$ are equal. Write the K_c expression and solve for $x = [\text{PH}_3] = [\text{BCl}_3]$. *Solve.*

$$K_c = [\text{PH}_3][\text{BCl}_3]; \quad 1.87 \times 10^{-3} = x^2; \quad x = 0.043243 = 0.0432 \text{ M } \text{PH}_3 \text{ and } \text{BCl}_3$$

(b) Since the mole ratios are 1:1:1, mol $\text{PH}_3\text{BCl}_3(\text{s})$ required = mol PH_3 or BCl_3 produced.

$$\frac{0.043243 \text{ mol PH}_3}{\text{L}} \times 0.250 \text{ L} = 0.01081 = 0.0108 \text{ mol PH}_3 = 0.0108 \text{ mol PH}_3\text{BCl}_3$$

$$0.01081 \text{ mol PH}_3\text{BCl}_3 \times \frac{151.2 \text{ g PH}_3\text{BCl}_3}{1 \text{ mol PH}_3\text{BCl}_3} = 1.6346 = 1.63 \text{ g PH}_3\text{BCl}_3$$

In fact, some $\text{PH}_3\text{BCl}_3(\text{s})$ must remain for the system to be in equilibrium, so a bit more than 1.63 g PH_3BCl_3 is needed.

15.57 *Analyze/Plan.* Follow the approach in Solution 15.51. Calculate $[\text{IBr}]$ from mol IBr and construct the equilibrium table.

Solve. $[\text{IBr}] = 0.500 \text{ mol}/2.00 \text{ L} = 0.250 \text{ M}$

Since no I_2 or Br_2 was present initially, the amounts present at equilibrium are produced by the reverse reaction and stoichiometrically equal. Let these amounts equal x . The amount of HBr that reacts is then $2x$. Substitute the equilibrium molarities (in terms of x) into the equilibrium expression and solve for x .

	I_2	+	Br_2	\rightleftharpoons	2IBr	$K_c = \frac{[\text{IBr}]^2}{[\text{I}_2][\text{Br}_2]} = 280$
initial	0 M		0 M		0.250 M	
change	+x M		+x M		-2x M	
equil.	x M		x M		(0.250 - 2x) M	

$$K_c = 280 = \frac{(0.250 - 2x)^2}{x^2}; \text{ taking the square root of both sides}$$

$$16.733 = \frac{0.250 - 2x}{x}; 16.733x + 2x = 0.250; 18.733x = 0.250$$

$$x = 0.013345 = 0.0133 \text{ M}; [\text{I}_2] = [\text{Br}_2] = 0.0133 \text{ M}$$

$$[\text{IBr}] = 0.250 - 2(0.013345) = 0.2233 = 0.223 \text{ M}$$

Check. $\frac{(0.2233)^2}{(0.013345)^2} = 280$. Our values are self-consistent.

15.58 $\text{CaCrO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$ $K_c = [\text{Ca}^{2+}][\text{CrO}_4^{2-}] = 7.1 \times 10^{-4}$

At equilibrium, $[\text{Ca}^{2+}] = [\text{CrO}_4^{2-}] = x$

$$K_c = 7.1 \times 10^{-4} = x^2, x = 0.0266 = 0.027 \text{ M Ca}^{2+} \text{ and CrO}_4^{2-}$$

15.59 *Analyze/Plan.* Follow the logic in sample Exercise 15.12, using torr in place of M . For this reaction, $\Delta n = 0$, and $K_p = K_c$, so we use the more convenient measure of concentration.

	$\text{CH}_4(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$\text{CH}_3\text{I}(\text{g})$	+	$\text{HI}(\text{g})$
initial	105.1 torr		7.96 torr		0 torr		0 torr
change	-x torr		-x torr		+x torr		+x torr
equil	105.1-x torr		7.96-x torr		+x torr		+x torr

$$K_p = 2.26 \times 10^{-4} = \frac{x^2}{(105.1-x)(7.96-x)}; x^2 = 2.26 \times 10^{-4}(836.6 - 113.1x + x^2)$$

$$0.999774x^2 + 0.02555x - 0.18907 = 0; x = \frac{-0.02555 \pm \sqrt{(0.02555)^2 - 4(0.999774)(-0.18907)}}{2(0.999774)}$$

(The negative solution is not chemically meaningful.)

$$x = 0.422 \text{ torr}; \text{ at equilibrium: } P_{\text{CH}_3\text{I}} = P_{\text{HI}} = 0.422 \text{ torr}; P_{\text{CH}_4} = 104.7 \text{ torr}; P_{\text{I}_2} = 7.54 \text{ torr}$$

15.60



initial	0.275 M	3.85 M	0 M	0 M
change	-x M	-x M	+x M	+x M
equil	0.275-x M	3.85-x M	+x M	+x M

$$K_c = 6.68 = \frac{x^2}{(0.275-x)(3.85-x)}; x^2 = 6.68(1.059 - 4.125x + x^2)$$

$$0 = 5.68x^2 - 27.56x + 7.072; x = \frac{27.56 \pm \sqrt{(-27.56)^2 - 4(5.68)(7.072)}}{2(5.68)} = 0.27185 = 0.272 \text{ M}$$

(The 4.58 M quadratic solution is not chemically meaningful.)

$$\frac{0.27185 \text{ mol ethyl acetate}}{\text{L}} \times 15.0 \text{ L} \times \frac{88.10 \text{ g ethyl acetate}}{\text{mol}} = 359.25 = 359 \text{ g ethyl acetate}$$

LeChâtelier's Principle (section 15.7)

15.61 *Analyze/Plan.* Follow the logic in Sample Exercise 15.13. *Solve.*

- Shift equilibrium to the right; more $\text{SO}_3(\text{g})$ is formed, the amount of $\text{SO}_2(\text{g})$ decreases.
- Heating an exothermic reaction decreases the value of K . More SO_2 and O_2 will form, the amount of SO_3 will decrease. This is fundamentally different than shifting the relative amounts of reactants and products to maintain K ; here, the equilibrium position itself changes.
- Since, $\Delta n = -1$, a change in volume will affect the equilibrium position and favor the side with more moles of gas. The amounts of SO_2 and O_2 increase and the amount of SO_3 decreases; equilibrium shifts to the left.
- No effect. Speeds up the forward and reverse reactions equally.
- No effect. Does not appear in the equilibrium expression.
- Shift equilibrium to the right; amounts of SO_2 and O_2 decrease.

15.62 $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

- increase $[\text{NH}_3]$, increase yield NO
- increase $[\text{H}_2\text{O}]$, decrease yield NO

- (c) decrease $[O_2]$, decrease yield NO
 (d) decrease container volume, decrease yield NO (fewer moles gas in reactants)
 (e) add catalyst, no change
 (f) increase temperature, decrease yield NO (reaction is exothermic)
- 15.63 *Analyze/Plan.* Given certain changes to a reaction system, determine the effect on K_p , if any. Only changes in temperature cause changes to the value of K_p . *Solve.*
- (a) no effect (b) no effect (c) no effect
 (d) increase equilibrium constant (e) no effect
- 15.64 (a) The reaction must be endothermic ($+\Delta H$) if heating increases the fraction of products.
 (b) There must be more moles of gas in the products if increasing the volume of the vessel increases the fraction of products.
- 15.65 *Analyze/Plan.* Use Hess's Law, $\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$, to calculate ΔH° . According to the sign of ΔH° , describe the effect of temperature on the value of K . According to the value of Δn , describe the effect of changes to container volume.
Solve.
- (a) $\Delta H^\circ = \Delta H_f^\circ \text{ NO}_2(\text{g}) + \Delta H_f^\circ \text{ N}_2\text{O}(\text{g}) - 3\Delta H_f^\circ \text{ NO}(\text{g})$
 $\Delta H^\circ = 33.84 \text{ kJ} + 81.6 \text{ kJ} - 3(90.37 \text{ kJ}) = -155.7 \text{ kJ}$
- (b) The reaction is exothermic because it has a negative value of ΔH° . The equilibrium constant will decrease with increasing temperature.
- (c) Δn does not equal zero, so a change in volume at constant temperature will affect the fraction of products in the equilibrium mixture. An increase in container volume would favor reactants, while a decrease in volume would favor products.
- 15.66 (a) $\Delta H^\circ = \Delta H_f^\circ \text{ CH}_3\text{OH}(\text{g}) - \Delta H_f^\circ \text{ CO}(\text{g}) - 2\Delta H_f^\circ \text{ H}_2(\text{g})$
 $= -201.2 \text{ kJ} - (-110.5 \text{ kJ}) - 0 \text{ kJ}$
 $= -90.7 \text{ kJ}$
- (b) The reaction is exothermic; an increase in temperature would decrease the value of K and decrease the yield. A low temperature is needed to maximize yield.
- (c) Increasing total pressure would increase the partial pressure of each gas, shifting the equilibrium toward products. The extent of conversion to CH_3OH increases as the total pressure increases.
- 15.67 For this reaction, there are more moles of product gas than moles of reactant gas. An increase in total pressure increases the partial pressure of each gas, shifting the equilibrium towards reactants. An increase in pressure favors formation of ozone.
- 15.68 Increasing levels of atmospheric CO_2 provide an alternate CO_2 source to microorganisms. They need to process fewer environmental pollutants in order to maintain their biomass. Increasing levels of atmospheric CO_2 decrease the effectiveness of microorganism bioremediation.

Additional Exercises

- 15.69 (a) Since both the forward and reverse processes are elementary steps, we can write the rate laws directly from the chemical equation.

$$\text{rate}_f = k_f [\text{CO}][\text{Cl}_2] = \text{rate}_r = k_r [\text{COCl}][\text{Cl}]$$

$$\frac{k_f}{k_r} = \frac{[\text{COCl}][\text{Cl}]}{[\text{CO}][\text{Cl}_2]} = K$$

$$K_c = \frac{k_f}{k_r} = \frac{1.4 \times 10^{-28} \text{ M}^{-1} \text{ s}^{-1}}{9.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}} = 1.5 \times 10^{-39}$$

For a homogeneous equilibrium in the gas phase, we usually write K in terms of partial pressures. In this exercise, concentrations are more convenient because the rate constants are expressed in terms of molarity. For this reaction, the value of K is the same regardless of how it is expressed, because there is no change in the moles of gas in going from reactants to products.

- (b) Since the K is quite small, reactants are much more plentiful than products at equilibrium.
- (c) In order to determine whether the reaction is exothermic or endothermic, We need to know whether an increase in temperature increases or decreases the value of the equilibrium constant, K .



$$\frac{[\text{B}]}{[\text{A}]^2} = 1, [\text{B}] = [\text{A}]^2 \text{ and } [\text{A}] = [\text{B}]^{1/2}$$



$$K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2}^3}{P_{\text{CH}_4} \times P_{\text{H}_2\text{O}}}; P = \frac{g RT}{MM V}; T = 1000 \text{ K}$$

$$P_{\text{CO}} = \frac{8.62 \text{ g}}{28.01 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{1000 \text{ K}}{5.00 \text{ L}} = 5.0507 = 5.05 \text{ atm}$$

$$P_{\text{H}_2} = \frac{2.60 \text{ g}}{2.016 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{1000 \text{ K}}{5.00 \text{ L}} = 21.1663 = 21.2 \text{ atm}$$

$$P_{\text{CH}_4} = \frac{43.0 \text{ g}}{16.04 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{1000 \text{ K}}{5.00 \text{ L}} = 43.9973 = 44.0 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = \frac{48.4 \text{ g}}{18.02 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{1000 \text{ K}}{5.00 \text{ L}} = 44.0811 = 44.1 \text{ atm}$$

$$K_p = \frac{(5.0507)(21.1663)^3}{(43.9973)(44.0811)} = 24.6949 = 24.7$$

$$K_p = K_c(\text{RT})^{\Delta n}, K_c = K_p/(\text{RT})^{\Delta n}; \Delta n = 4 - 2 = 2$$

$$K_c = (24.6949)/[(0.08206)(1000)]^2 = 3.6673 \times 10^{-3} = 3.67 \times 10^{-3}$$

$$15.72 \quad [\text{SO}_2\text{Cl}_2] = \frac{2.00 \text{ mol}}{2.00 \text{ L}} = 1.00 \text{ M}$$

The change in $[\text{SO}_2\text{Cl}_2] = 0.56(1.00 \text{ M}) = 0.56 \text{ M}$

	$\text{SO}_2\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{SO}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$	$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]}$
initial	1.00 M		0		0	
change	-0.56 M		+0.56 M		+0.56 M	
equil.	0.44 M		+0.56 M		+0.56 M	

$$(a) \quad K_c = \frac{(0.56)^2}{0.44} = 0.7127 = 0.71$$

$$(b) \quad K_p = K_c(RT)^{\Delta n}; \Delta n = 2 - 1 = 1; K_p = (0.7127)(0.08206)(303) = 17.7214 = 18$$

$$(c) \quad [\text{SO}_2\text{Cl}_2] = \frac{2.00 \text{ mol}}{15.00 \text{ L}} = 0.13333 = 0.133 \text{ M}; \Delta M = 0.56(0.133) = 0.07466 = 0.075 \text{ M}$$

The equilibrium concentrations are: $[\text{SO}_2\text{Cl}_2] = (0.13333 - 0.07466) \text{ M} = 0.05867 = 0.059 \text{ M}$; $[\text{SO}_2] = 0.07466 = 0.075 \text{ M}$; $[\text{Cl}_2] = 0.07466 = 0.075 \text{ M}$.

$$K_c = \frac{(0.07466)^2}{0.05867} = 0.09501 = 0.095; K_p = (0.09501)(0.08206)(303) = 2.362 = 2.4$$

$$15.73 \quad (a) \quad \text{H}_2(\text{g}) + \text{S}(\text{s}) \rightleftharpoons \text{H}_2\text{S}(\text{g}) \quad K_c = [\text{H}_2\text{S}]/[\text{H}_2]$$

(b) Calculate the molarities of H_2S and H_2 .

$$[\text{H}_2\text{S}] = \frac{0.46 \text{ g}}{34.1 \text{ g/mol}} \times \frac{1}{1.0 \text{ L}} = 0.01349 = 0.013 \text{ M}$$

$$[\text{H}_2] = \frac{0.40 \text{ g}}{2.02 \text{ g/mol}} \times \frac{1}{1.0 \text{ L}} = 0.1980 = 0.20 \text{ M}$$

$$K_c = 0.01349/0.1980 = 0.06812 = 0.068$$

(c) Since S is a pure solid, its concentration doesn't change during the reaction, so [S] does not appear in the equilibrium expression.

$$15.74 \quad (a) \quad K_p = \frac{P_{\text{Br}_2} \times P_{\text{NO}}^2}{P_{\text{NOBr}}^2}; P = \frac{gRT}{MM \times V}; T = 100^\circ\text{C} + 273 = 373 \text{ K}$$

$$P_{\text{Br}_2} = \frac{4.19 \text{ g}}{159.8 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{373}{5.00 \text{ L}} = 0.16051 = 0.161 \text{ atm}$$

$$P_{\text{NO}} = \frac{3.08 \text{ g}}{30.01 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{373}{5.00 \text{ L}} = 0.62828 = 0.628 \text{ atm}$$

$$P_{\text{NOBr}} = \frac{3.22 \text{ g NOBr}}{109.9 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{373}{5.00 \text{ L}} = 0.17936 = 0.179 \text{ atm}$$

$$K_p = \frac{(0.16051)(0.62828)^2}{(0.17936)^2} = 1.9695 = 1.97 \quad K_p = K_c(RT)^{\Delta n}, \Delta n = 3 - 2 = 1$$

$$K_c = K_p/RT = 1.9695/(0.08206)(373) = 0.064345 = 0.0643$$

- (b) $P_t = P_{\text{Br}_2} + P_{\text{NO}} + P_{\text{NOBr}} = 0.16051 + 0.62828 + 0.17936 = 0.96815 = 0.968 \text{ atm}$
- (c) All NO and Br₂ present at equilibrium came from the decomposition of the original NOBr. The mass of original NOBr is the sum of the masses of all compounds at equilibrium.

$$\text{Original g NOBr} = 4.19 \text{ g Br}_2 + 3.08 \text{ g NO} + 3.22 \text{ g NOBr} = 10.49 \text{ g}$$

15.75 (a)

	A(g)	\rightleftharpoons	2B(g)
initial	0.75 atm		0
change	-0.39 atm		+0.78 atm
equil.	0.36 atm		0.78 atm

$$P_t = P_A + P_B = 0.36 \text{ atm} + 0.78 \text{ atm} = 1.14 \text{ atm}$$

(b) $K_p = \frac{(P_B)^2}{P_A} = \frac{(0.78)^2}{0.36} = 1.690 = 1.7$

- (c) Increasing the volume of the flask favors the reaction with more moles of gas. Doing the reaction in a larger flask maximizes the yield of B.

15.76 (a)

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3} = 4.34 \times 10^{-3}; T = 300^\circ\text{C} + 273 = 573 \text{ K}$$

$$P_{\text{NH}_3} = \frac{gRT}{MM \times V} = \frac{1.05 \text{ g}}{17.03 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{573 \text{ K}}{1.00 \text{ L}} = 2.899 = 2.90 \text{ atm}$$

	N ₂ (g)	+ 3H ₂ (g)	\rightleftharpoons	2NH ₃ (g)
initial	0 atm	0 atm		?
change	x	3x		-2x
equil.	x atm	3x atm		2.899 atm

(Remember, only the change line reflects the stoichiometry of the reaction.)

$$K_p = \frac{(2.899)^2}{(x)(3x)^3} = 4.34 \times 10^{-3}; 27x^4 = \frac{(2.899)^2}{4.34 \times 10^{-3}}; x^4 = 71.725$$

$$x = 2.910 = 2.91 \text{ atm} = P_{\text{N}_2}; P_{\text{H}_2} = 3x = 8.730 = 8.73 \text{ atm}$$

$$g_{\text{N}_2} = \frac{MM \times PV}{RT} = \frac{28.02 \text{ g N}_2}{\text{mol N}_2} \times \frac{\text{mol} \cdot \text{K}}{0.08206 \text{ L} \cdot \text{atm}} \times \frac{2.910 \text{ atm} \times 1.00 \text{ L}}{573 \text{ K}} = 1.73 \text{ g N}_2$$

$$g_{\text{H}_2} = \frac{2.016 \text{ g H}_2}{\text{mol H}_2} \times \frac{\text{mol} \cdot \text{K}}{0.08206 \text{ L} \cdot \text{atm}} \times \frac{8.730 \text{ atm} \times 1.00 \text{ L}}{573 \text{ K}} = 0.374 \text{ g H}_2$$

- (b) The initial $P_{\text{NH}_3} = 2.899 \text{ atm} + 2(2.910 \text{ atm}) = 8.719 = 8.72 \text{ atm}$

$$g_{\text{NH}_3} = \frac{17.03 \text{ g NH}_3}{\text{mol NH}_3} \times \frac{\text{mol} \cdot \text{K}}{0.08206 \text{ L} \cdot \text{atm}} \times \frac{8.719 \text{ atm} \times 1.00 \text{ L}}{573 \text{ K}} = 3.16 \text{ g NH}_3$$

- (c) $P_t = P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3} = 2.910 \text{ atm} + 8.730 \text{ atm} + 2.899 \text{ atm} = 14.54 \text{ atm}$

15.77	$2\text{IBr} \rightleftharpoons \text{I}_2 + \text{Br}_2$
initial	0.025 atm 0 0
change	-2x x x
equil.	(0.025 - 2x) atm x x

$$K_p = 8.5 \times 10^{-3} = \frac{P_{\text{I}_2} \times P_{\text{Br}_2}}{P_{\text{IBr}}^2} = \frac{x^2}{(0.025 - 2x)^2}; \text{ Taking the square root of both sides}$$

$$\frac{x}{0.025 - 2x} = (8.5 \times 10^{-3})^{1/2} = 0.0922; x = 0.0922(0.025 - 2x)$$

$$x + 0.184x = 0.002305; 1.184x = 0.002305; x = 0.001947 = 1.9 \times 10^{-3}$$

$$\text{At equilibrium, } P_{\text{I}_2} = P_{\text{Br}_2} = x = 1.9 \times 10^{-3} \text{ atm}$$

$$P_{\text{IBr}} \text{ at equilibrium} = 0.025 - 2(1.947 \times 10^{-3}) = 0.02111 = 0.021 \text{ atm}$$

Check. $K_p = (0.001947)^2 / (0.02111)^2 = 8.5 \times 10^{-3}$; the calculated concentrations are self-consistent.

15.78 (a) $K_p = 0.052$; $K_p = K_c(RT)^{\Delta n}$; $\Delta n = 2 - 0 = 2$; $K_c = K_p / (RT)^2$
 $K_c = 0.052 / [0.08206(333)]^2 = 6.964 \times 10^{-5} = 7.0 \times 10^{-5}$

(b) PH_3BCl_3 is a solid and its concentration is taken as a constant, C.

$$[\text{BCl}_3] = \frac{0.0500 \text{ g BCl}_3}{1.500 \text{ L}} \times \frac{\text{mol BCl}_3}{117.17 \text{ g BCl}_3} = 2.8449 \times 10^{-4} = 2.84 \times 10^{-4} \text{ M BCl}_3$$

	$\text{PH}_3\text{BCl}_3 \rightleftharpoons \text{PH}_3 + \text{BCl}_3$
initial	C 0 M $2.84 \times 10^{-4} \text{ M}$
change	+x M +x M
equil.	C +x M $(2.84 \times 10^{-4} + x) \text{ M}$

$$K_c = [\text{PH}_3][\text{BCl}_3]; 6.964 \times 10^{-5} = x(2.84 \times 10^{-4} + x); x^2 + 2.84 \times 10^{-4}x - 6.964 \times 10^{-5} = 0$$

$$x = \frac{-2.84 \times 10^{-4} \pm [(2.84 \times 10^{-4})^2 - 4(1)(-6.964 \times 10^{-5})]^{1/2}}{2(1)} = 0.008204 = 8.2 \times 10^{-3} \text{ M PH}_3$$

$$\text{Check. } K_c = (8.2 \times 10^{-3})(2.84 \times 10^{-4} + 8.2 \times 10^{-3}) = 7.0 \times 10^{-5}.$$

15.79 $K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}}; P_t = 0.614 \text{ atm}$

If the equilibrium amounts of NH_3 and H_2S are due solely to the decomposition of $\text{NH}_4\text{HS}(s)$, the equilibrium pressures of the two gases are equal, and each is 1/2 of the total pressure.

$$P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = 0.614 \text{ atm} / 2 = 0.307 \text{ atm}$$

$$K_p = (0.307)^2 = 0.0943$$

$$15.80 \quad \text{Initial } P_{\text{SO}_3} = \frac{gRT}{MMV} = \frac{0.831 \text{ g}}{80.07 \text{ g/mol}} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{1100 \text{ K}}{1.00 \text{ L}} = 0.9368 = 0.937 \text{ atm}$$

	2SO_3	\rightleftharpoons	2SO_2	$+$	O_2
initial	0.9368 atm		0		0
change	-2x		+2x		+x
equil.	0.9368-2x		2x		x
[equil.]	0.2104 atm		0.7264 atm		0.3632 atm

$$P_t = (0.9368 - 2x) + 2x + x; 0.9368 + x = 1.300 \text{ atm}; x = 1.300 - 0.9368 = 0.3632 = 0.363 \text{ atm}$$

$$K_p = \frac{P_{\text{SO}_2}^2 \times P_{\text{O}_2}}{P_{\text{SO}_3}^2} = \frac{(0.7264)^2 (0.3632)}{(0.2104)^2} = 4.3292 = 4.33$$

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

$$K_c = K_p/RT = 4.3292 / [(0.08206)(1100)] = 0.04796 = 0.0480$$

$$15.81 \quad \text{In general, the reaction quotient is of the form } Q = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 \times P_{\text{Cl}_2}}$$

$$(a) \quad Q = \frac{(0.11)^2}{(0.15)^2 (0.31)} = 1.7$$

$Q > K_p$. The mixture is not at equilibrium. It will shift to the left and produce more reactants as it moves toward equilibrium.

$$(b) \quad Q = \frac{(0.050)^2}{(0.12)^2 (0.10)} = 1.7$$

$Q > K_p$. The mixture is not at equilibrium. It will shift to the left and produce more reactants as it moves toward equilibrium.

$$(c) \quad Q = \frac{(5.10 \times 10^{-3})^2}{(0.15)^2 (0.20)} = 5.8 \times 10^{-3}$$

$Q < K_p$. The mixture is not at equilibrium. It will shift to the right and produce more products as it moves toward equilibrium.

$$15.82 \quad K_c = [\text{CO}_2] = 0.0108; [\text{CO}_2] = \frac{g \text{ CO}_2}{44.01 \text{ g/mol}} \times \frac{1}{10.0 \text{ L}}$$

In each case, calculate $[\text{CO}_2]$ and determine the position of the equilibrium.

$$(a) \quad [\text{CO}_2] = \frac{4.25 \text{ g}}{44.01 \text{ g/mol}} \times \frac{1}{10.0 \text{ L}} = 9.657 \times 10^{-3} = 9.66 \times 10^{-3} \text{ M}$$

$Q = 9.66 \times 10^{-3} < K_c$. The reaction proceeds to the right to achieve equilibrium and the amount of $\text{CaCO}_3(\text{s})$ decreases.

$$(b) \quad [\text{CO}_2] = \frac{5.66 \text{ g CO}_2}{44.01 \text{ g/mol}} \times \frac{1}{10.0 \text{ L}} = 0.0129 \text{ M}$$

$Q = 0.0129 > K_c$. The reaction proceeds to the left to achieve equilibrium and the amount of $\text{CaCO}_3(\text{s})$ increases.

- (c) 6.48 g CO₂ means [CO₂] > 0.0129 M; Q > 0.0129 > K_c, the amount of CaCO₃ increases.

15.83		CO ₂ (g)	+	H ₂ (g)	⇌	CO(g)	+	H ₂ O(g)
	initial	1.50 mol		1.50 mol		0		0
	change	-x		-x		+x		+x
	equil.	(1.50 - x)mol		(1.50 - x)mol		x		x

Since Δn = 0, the volume terms cancel and we can use moles in place of molarity in the K expression.

$$K_c = 0.802 = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{x^2}{(1.50 - x)^2}$$

Take the square root of both sides.

$$(0.802)^{1/2} = x/(1.50 - x); 0.8955(1.50 - x) = x$$

$$1.3433 = 1.8955x, x = 0.7087 = 0.709 \text{ mol}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 0.7087 \text{ mol}/3.00 \text{ L} = 0.236 \text{ M}$$

$$[\text{CO}_2] = [\text{H}_2] = (1.50 - 0.709) \text{ mol}/3.00 \text{ L} = 0.264 \text{ M}$$

15.84 (a) $[\text{CO}_2] = \frac{25.0 \text{ g CO}_2}{44.01 \text{ g/mol}} \times \frac{1}{3.00 \text{ L}} = 0.18935 = 0.189 \text{ M}$

		C(s)	+	CO ₂ (g)	⇌	2CO(g)
	initial	excess		0.189		0
	change	-x		-x		+2x
	equil.			0.189 - x		+2x

$$K_c = 1.9 = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(2x)^2}{0.189 - x}; 4x^2 = 1.9(0.189 - x); 4x^2 + 1.9x - 0.36 = 0.$$

Solve the quadratic for x.

$$x = \frac{-1.9 \pm \sqrt{(1.9)^2 - 4(4)(-0.36)}}{2(4)} = 0.14505 = 0.15 \text{ M}$$

$$[\text{CO}] = 2x = 2(0.14505) = 0.2901 = 0.29 \text{ M}$$

$$\frac{0.2901 \text{ mol CO}}{\text{L}} \times 3.00 \text{ L} \times \frac{28.01 \text{ g CO}}{\text{mol}} = 24.38 = 24 \text{ g CO}$$

- (b) The amount of C(s) consumed is related to x. Change M to mol to g C.

$$\frac{0.14505 \text{ mol}}{\text{L}} \times 3.00 \text{ L} \times 12.01 \text{ g} = 5.226 = 5.2 \text{ g C consumed}$$

- (c) A smaller vessel at the same temperature increases the total pressure of the mixture. The equilibrium shifts to form fewer total moles of gas, which favors reactants. The yield of CO product will be smaller in a smaller vessel.
- (d) The two K_c values are 0.133 at 298 K and 1.9 at 1000 K. The reaction is endothermic, because K is larger at higher temperature.

$$15.85 \quad K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = 6.0 \times 10^2$$

If P_{CO} is 150 torr, P_{CO_2} can never exceed $760 - 150 = 610$ torr. Then $Q = 610/150 = 4.1$. Since this is far less than K , the reaction will shift in the direction of more product. Reduction will therefore occur.

- 15.86 The anecdote tells us that increasing the volume of the reaction container, the furnace, had no effect on the amount of unreacted CO(g), the amount of CO(g) expelled. This is true for reactions that have the same number of moles of gaseous products and reactants, as this one does. It also means that $K_p = K_c$.

15.87 (a)

	$\text{CCl}_4(\text{g}) \rightleftharpoons \text{C}(\text{s}) + 2\text{Cl}_2(\text{g})$
initial	2.00 atm 0 atm
change	-x atm +2x atm
equil.	(2.00-x) atm 2x atm

$$K_p = 0.76 = \frac{P_{\text{Cl}_2}^2}{P_{\text{CCl}_4}} = \frac{(2x)^2}{(2.00-x)}$$

$$1.52 - 0.76x = 4x^2; \quad 4x^2 + 0.76x - 1.52 = 0$$

Using the quadratic formula, $a = 4$, $b = 0.76$, $c = -1.52$

$$x = \frac{-0.76 \pm \sqrt{(0.76)^2 - 4(4)(-1.52)}}{2(4)} = \frac{-0.76 + 4.99}{8} = 0.5287 = 0.53 \text{ atm}$$

$$\text{Fraction CCl}_4 \text{ reacted} = \frac{x \text{ atm}}{2.00 \text{ atm}} = \frac{0.5287}{2.00} = 0.264 = 26\%$$

(b) $P_{\text{Cl}_2} = 2x = 2(0.5287) = 1.06 \text{ atm}$

$$P_{\text{CCl}_4} = 2.00 - x = 2.00 - 0.5287 = 1.47 \text{ atm}$$

15.88 (a) $Q = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} \times P_{\text{Cl}_2}} = \frac{(0.20)}{(0.50)(0.50)} = 0.80$

0.80 (Q) > 0.0870 (K), the reaction proceeds to the left.

(b)

	$\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$
initial	0.50 atm 0.50 atm 0.20 atm
change	+x atm +x atm -x atm
equil.	(0.50 + x) atm (0.50 + x) atm (0.20 - x) atm

(Since the reaction proceeds to the left, P_{PCl_5} must decrease and P_{PCl_3} and P_{Cl_2} must increase.)

$$K_p = 0.0870 = \frac{(0.20-x)}{(0.50+x)(0.50+x)}; \quad 0.0870 = \frac{(0.20-x)}{(0.250+1.00x+x^2)}$$

$$0.0870(0.250 + 1.00x + x^2) = 0.20 - x; \quad -0.17825 + 1.0870x + 0.0870x^2 = 0$$

$$x = \frac{-1.0870 \pm \sqrt{(1.0870)^2 - 4(0.0870)(-0.17825)}}{2(0.0870)} = \frac{-1.0870 + 1.1152}{0.174} = 0.162$$

$$P_{\text{PCl}_3} = (0.50 + 0.162) \text{ atm} = 0.662 \quad P_{\text{Cl}_2} = (0.50 + 0.162) \text{ atm} = 0.662 \text{ atm}$$

$$P_{\text{PCl}_5} = (0.20 - 0.162) \text{ atm} = 0.038 \text{ atm}$$

To two decimal places, the pressures are 0.66, 0.66 and 0.04 atm, respectively. When substituting into the K_p expression, pressures to three decimal places yield a result much closer to 0.0870.

- (c) Increasing the volume of the container favors the process where more moles of gas are produced, so the reverse reaction is favored and the equilibrium shifts to the left; the mole fraction of Cl_2 increases.
- (d) For an exothermic reaction, increasing the temperature decreases the value of K ; more reactants and fewer products are present at equilibrium and the mole fraction of Cl_2 increases.

15.89 *Analyze/Plan.* Calculate the equilibrium pressures of H_2 , I_2 , and HI , use them to calculate K_p . Set up a new equilibrium table and calculate new equilibrium pressures.

Solve.

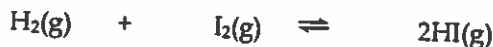
$$\frac{P}{n} = \frac{RT}{V} = \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{731 \text{ K}}{5.00} = 11.997 \frac{\text{atm}}{\text{mol}}$$

$$P_{\text{H}_2} = P_{\text{I}_2} = 0.112 \text{ mol} \times 11.997 \frac{\text{atm}}{\text{mol}} = 1.344 = 1.34 \text{ atm}$$

$$P_{\text{HI}} = 0.775 \text{ mol} \times 11.997 \frac{\text{atm}}{\text{mol}} = 9.298 = 9.30 \text{ atm}$$

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}); \quad K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} \times P_{\text{I}_2}} = \frac{(9.298)^2}{(1.344)^2} = 47.861 = 47.9$$

$$P_{\text{HI}} (\text{added}) = 0.200 \text{ mol} \times \frac{11.997 \text{ atm}}{\text{mol}} = 2.3994 = 2.40 \text{ atm}$$



initial	1.34 atm	1.34 atm	9.30 atm + 2.40 atm
change	+x atm	+x atm	-2x atm
equil.	(1.34+x) atm	(1.34+x) atm	(11.70-2x) atm

$$K_p = 47.86 = \frac{(11.70-2x)^2}{(1.34+x)^2}. \quad \text{Take the square root of both sides:}$$

$$6.918 = \frac{11.70 - 2x}{1.34 + x}; 9.270 + 6.918x = 11.70 - 2x; 8.918x = 2.430; x = 0.27248 = 0.272$$

$$P_{H_2} = P_{I_2} = 1.34 + 0.272 = 1.612 = 1.61 \text{ atm}; P_{HI} = 11.70 - 2(0.272) = 11.156 = 11.16 \text{ atm}$$

$$\text{Check. } \frac{(11.156)^2}{(1.612)^2} = 47.89 = 47.9$$

15.90

- (a) Since the volume of the vessel = 1.00 L, mol = M. The reaction will proceed to the left to establish equilibrium.

	$A(g) +$	$2B(g) \rightleftharpoons$	$2C(g)$
initial	0 M	0 M	1.00 M
change	+x M	+2x M	-2x M
equil.	x M	2x M	(1.00 - 2x) M

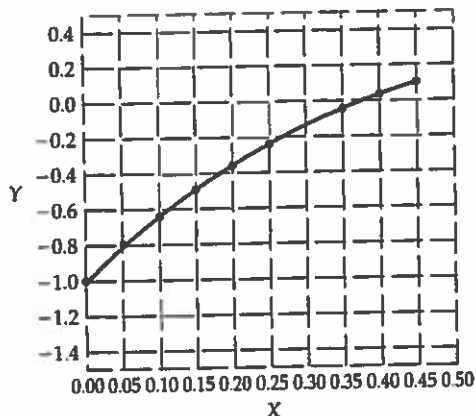
At equilibrium, $[C] = (1.00 - 2x) M$, $[B] = 2x M$.

- (b) x must be less than 0.50 M (so that $[C]$, $1.00 - 2x$, is not less than zero).

(c)
$$K_c = \frac{[C]^2}{[A][B]^2}; \frac{(1.00 - 2x)^2}{(x)(2x)^2} = 0.25$$

$$1.00 - 4x + 4x^2 = 0.25(4x)^2; x^3 - 4x^2 + 4x - 1 = 0$$

(d)



X	Y
0.0	-1.000
0.05	-0.810
0.10	-0.639
0.15	-0.487
0.20	-0.352
0.25	-0.234
0.35	-0.047
0.40	+0.024
0.45	+0.081
-0.383	0.00

- (e) From the plot, $x \approx 0.383 M$

$$[A] = x = 0.383 M; [B] = 2x = 0.766 M$$

$$[C] = 1.00 - 2x = 0.234 M$$

Using the K_c expression as a check:

$$K_c = 0.25; \frac{(0.234)^2}{(0.383)(0.766)^2} = 0.24; \text{ the estimated values are reasonable.}$$

$$15.91 \quad K_p = \frac{P_{\text{O}_2} \times P_{\text{CO}}^2}{P_{\text{CO}_2}^2} \approx 1 \times 10^{-13}; P_{\text{O}_2} = (0.03)(1 \text{ atm}) = 0.03 \text{ atm}$$

$$P_{\text{CO}} = (0.002)(1 \text{ atm}) = 0.002 \text{ atm}; P_{\text{CO}_2} = (0.12)(1 \text{ atm}) = 0.12 \text{ atm}$$

$$Q = \frac{(0.03)(0.002)^2}{(0.12)^2} = 8.3 \times 10^{-6} = 8 \times 10^{-6}$$

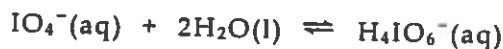
Since $Q > K_p$, the system will shift to the left to attain equilibrium. Thus a catalyst that promoted the attainment of equilibrium would result in a lower CO content in the exhaust.

- 15.92 The patent claim is false. A catalyst does not alter the position of equilibrium in a system, only the rate of approach to the equilibrium condition.

Integrative Exercises

- 15.93 Calculate the initial $[\text{IO}_4^-]$, and then construct an equilibrium table to determine $[\text{H}_4\text{IO}_6^-]$ at equilibrium.

$$M_c \times V_c = M_d \times L_d; \frac{0.905 \text{ M} \times 25.0 \text{ mL}}{500.0 \text{ mL}} = M_d = 0.04525 = 0.0453 \text{ M IO}_4^-$$



initial	0.0453 M	0
change	-x	+x
equil.	0.0453 - x	+x

$$K_c = 3.5 \times 10^{-2} = \frac{[\text{H}_4\text{IO}_6^-]}{[\text{IO}_4^-]} = \frac{x}{(0.0453 - x)}$$

Because K_c is relatively large and $[\text{IO}_4^-]$ is relatively small, we cannot assume x is small relative to 0.0453.

$$0.035(0.04525 - x) = x; 0.001584 - 0.035x = x; 0.001584 = 1.035x$$

$$x = 0.001584/1.035 = 0.001530 = 0.0015 \text{ M H}_4\text{IO}_6^- \text{ at equilibrium}$$

- 15.94 (a) $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- (b) $K_c = [\text{Ag}^+][\text{Cl}^-]$
- (c) Using thermodynamic data from Appendix C, calculate ΔH for the reaction in part (a).

$$\Delta H^\circ = \Delta H_f^\circ \text{Ag}^+(\text{aq}) + \Delta H_f^\circ \text{Cl}^-(\text{aq}) - \Delta H_f^\circ \text{AgCl}(\text{s})$$

$$\Delta H^\circ = 105.90 \text{ kJ} - 167.2 \text{ kJ} - (-127.0 \text{ kJ}) = 65.7 \text{ kJ}$$

The reaction is endothermic (heat is a reactant), so the solubility of $\text{AgCl}(\text{s})$ in $\text{H}_2\text{O}(\text{l})$ will increase with increasing temperature.

- (d) Calculate the solubility of $\text{AgCl}(\text{s})$ in pure water as $[\text{Ag}^+]$, in 0.100 M $\text{NaCl}(\text{aq})$ as $[\text{Ag}^+]$, and in 0.100 M $\text{NaCl}(\text{aq})$ as $[\text{AgCl}_2]^-$.

In pure water, let $[Ag^+] = [Cl^-] = x$; $K_c = [Ag^+][Cl^-] = x^2 = 1.6 \times 10^{-10}$

$$x = (1.6 \times 10^{-10})^{1/2}; [Ag^+] = 1.3 \times 10^{-5} M [Ag^+]$$

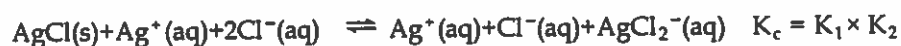
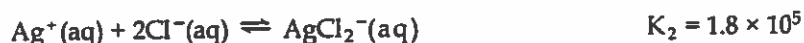
In 0.100 M NaCl(aq), assuming no formation of $[AgCl_2^-]$,

$$[Ag^+] = x, [Cl^-] = 0.100 + x; K_c = [Ag^+][Cl^-] = x(0.100 + x) = 1.6 \times 10^{-10}$$

Assuming x is small relative to 0.100, $0.100x = 1.6 \times 10^{-10}$,

$$x = 1.6 \times 10^{-9} M [Ag^+]$$

To account for complexation, the formation of soluble $AgCl_2^-$, sum the two reactions and calculate K for the overall process.



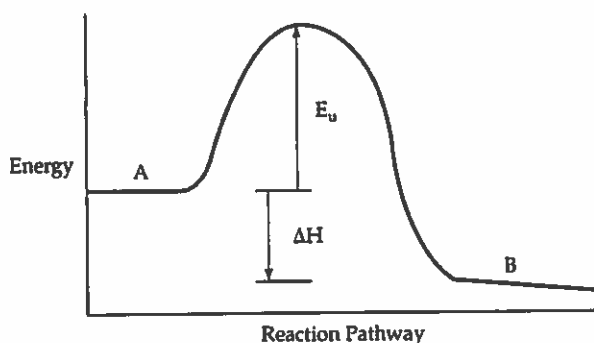
$$K_c = [AgCl_2^-] / [Cl^-]; [AgCl_2^-] = x, [Cl^-] = 0.100 - x$$

Assuming x is small relative to 0.100, $2.9 \times 10^{-5} = x / (0.100)$;

$$x = 2.9 \times 10^{-6} M [AgCl_2^-]$$

These calculations show that the "solubility" of AgCl, the concentration of any soluble silver species, is actually greatest in pure water, $1.3 \times 10^{-5} M [Ag^+]$. In 0.100 M NaCl, complexation causes the solubility of silver, $2.9 \times 10^{-6} M [AgCl_2^-]$, to be greater than that predicted by the common ion effect alone, $1.6 \times 10^{-9} M [Ag^+]$, but not as great as its solubility in pure water.

- 15.95 Consider the energy profile for an exothermic reaction.



The activation energy in the forward direction, $E_{a,f}$, equals E_u , and the activation energy in the reverse reaction, $E_{a,r}$, equals $E_u - \Delta H$. (The same is true for an endothermic reaction because the sign of ΔH is the positive and $E_{a,r} < E_{a,f}$). For the reaction in question,

$$K = \frac{k_f}{k_r} = \frac{A_f e^{-E_{a,f}/RT}}{A_r e^{-E_{a,r}/RT}}$$

Since the ln form of the Arrhenius equation is easier to manipulate, we will consider ln K.

$$\ln K = \ln \left(\frac{k_f}{k_r} \right) = \ln k_f - \ln k_r = \frac{-E_{af}}{RT} + \ln A_f - \left[\frac{-E_{ar}}{RT} + \ln A_r \right]$$

Substituting E_u for E_{af} and $(E_u - \Delta H)$ for E_{ar}

$$\ln K = \frac{-E_u}{RT} + \ln A_f - \left[\frac{-(E_u - \Delta H)}{RT} + \ln A_r \right]; \ln K = \frac{-E_u + (E_u - \Delta H)}{RT} + \ln A_f - \ln A_r$$

$$\ln K = \frac{-\Delta H}{RT} + \ln \frac{A_f}{A_r}$$

For the catalyzed reaction, $E_{cat} < E_u$ and $E_{af} = E_{cat}$, $E_{ar} = E_{cat} - \Delta H$. The catalyst does not change the value of ΔH .

$$\ln K_{cat} = \frac{-E_{cat} + (E_{cat} - \Delta H)}{RT} + \ln A_f - \ln A_r$$

$$\ln K_{cat} = \frac{-\Delta H}{RT} + \ln \frac{A_f}{A_r}$$

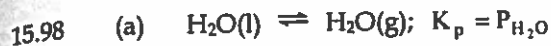
Thus, assuming A_f and A_r are not changed by the catalyst, $\ln K = \ln K_{cat}$ and $K = K_{cat}$.

- 15.96 (a) For the reaction $\text{SO}_2(l) \rightarrow \text{SO}_2(g)$, $K_p = P_{\text{SO}_2}$. From the phase diagram, as T increases P_{SO_2} and K_p increase. For an endothermic reaction, K increases as T increases. The phase diagram tells us that the vaporization of $\text{SO}_2(l)$ is an endothermic process.
- (b) Read P_{SO_2} from the liquid-gas line on the phase diagram at 0°C and 100°C . Note that the pressure axis of the phase diagram is logarithmic with respect to pressure, but linear with respect to $\log P$. In terms of $\log P$, the axis labels would be -1, 0, 1 and 2. The $\log P$ values at 0°C and 100°C are approximately 0.25 and 1.4. The values of P_{SO_2} and K_p are $10^{0.25}$ and $10^{1.4}$, 1.8 and 25, respectively.
- (c) It is not possible to calculate an equilibrium constant between the gas and liquid phases in the supercritical region, because they do not exist separately in this region. That is, the gas and liquid phases are indistinguishable in the supercritical region.
- (d) Gases are most ideal at high temperature and low pressure. The red dot at slightly greater than 240°C is the point where $\text{SO}_2(g)$ most closely approaches ideal behavior.
- (e) The point near 15°C is the one at the lowest temperature, but it is also at low pressure. In general, the closer the pressure and temperature conditions are to the point of phase transition, the less ideal the behavior of the gas (because it is nearly a liquid). This describes the point near 115°C and 20 atm, which is at relatively high pressure and near the liquid-gas line.

- 15.97 Mole % = pressure %. Since the total pressure is 1 atm, mol %/100 = mol fraction = partial pressure. $K_p = P_{\text{CO}}^2 / P_{\text{CO}_2}$.

Temp (K)	P_{CO_2} (atm)	P_{CO} (atm)	K_P
1123	0.0623	0.9377	14.1
1223	0.0132	0.9868	73.8
1323	0.0037	0.9963	2.7×10^2
1473	0.0006	0.9994	1.7×10^3 (2×10^3)

Because K grows larger with increasing temperature, the reaction must be endothermic in the forward direction.

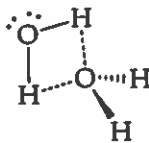


(b) At 30°C , the vapor pressure of $\text{H}_2\text{O}(\text{l})$ is 31.82 torr. $K_p = P_{\text{H}_2\text{O}} = 31.82$ torr

$$K_p = 31.82 \text{ torr} \times 1 \text{ atm}/760 \text{ torr} = 0.041868 = 0.04187 \text{ atm}$$

(c) From part (b), the value of K_p is the vapor pressure of the liquid at that temperature. By definition, vapor pressure = atmospheric pressure = 1 atm at the normal boiling point. $K_p = 1$ atm

15.99 (a) VSEPR indicates that each O atom has four electron domains about it and thus adopts tetrahedral geometry. One O atom has two covalent bonds to H and two hydrogen bonds to H atoms on the second water molecule. The O atom on the second water molecule has two nonbonding electron pairs. The water dimer is not symmetrical.



(b) Hydrogen-bonding is the intermolecular interaction involved in water dimer formation.

(c) Water dimer formation is exothermic, since the value of K decreases as temperature increases.

15.100 The O_2 -binding reaction occurs in aqueous solution, so we will write a K_c expression. The amount of $\text{O}_2(\text{g})$ will appear as a pressure. By convention, reactions which involve gaseous and aqueous substances have mixed equilibrium expressions written in terms of both pressures and molar concentrations.

$$K_c = \frac{[\text{Hb} \cdot (\text{O}_2)_4]}{P_{\text{O}_2}^4 \times [\text{Hb}]}$$

The *P50 value* is the partial pressure at which 50% of the hemoglobin is saturated with $\text{O}_2(\text{g})$. At this partial pressure, the concentrations of O_2 -bound hemoglobin and free hemoglobin are equal, $[\text{Hb} \cdot (\text{O}_2)_4] = [\text{Hb}]$. Substitute the two *P50* values into the K_c expression and compare the values for fetal and adult hemoglobin.

$$\text{at P50, } K_{\text{CF}} = \frac{1}{P_{\text{O}_2}^4} = \frac{1}{19^4} = 7.7 \times 10^{-6}; \quad K_{\text{CA}} = \frac{1}{P_{\text{O}_2}^4} = \frac{1}{26.8^4} = 1.94 \times 10^{-6}$$

Comparing the two values, $K_{\text{CF}}/K_{\text{CA}} = 7.7 \times 10^{-6}/1.94 \times 10^{-6} \approx 4$. The equilibrium constant for O_2 -binding by fetal hemoglobin is approximately four times that by adult hemoglobin.