

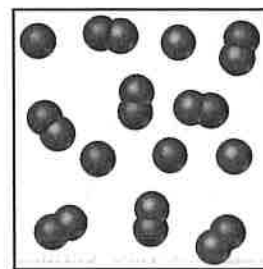
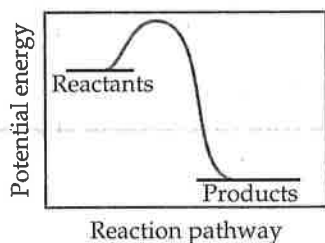
- Write the equilibrium-constant expression for a heterogeneous reaction.
- Calculate an equilibrium constant from concentration measurements.
- Predict the direction of a reaction given the equilibrium constant and the concentrations of reactants and products.
- Calculate equilibrium concentrations given the equilibrium constant and all but one equilibrium concentration.
- Calculate equilibrium concentrations given the equilibrium constant and the starting concentrations.
- Understand how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position.

## KEY EQUATIONS

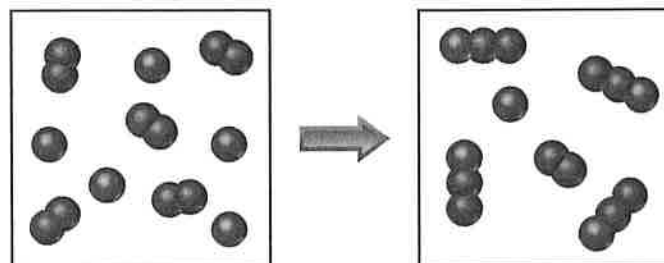
- $K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$  [15.8] The equilibrium-constant expression for a general reaction of the type  $aA + bB \rightleftharpoons dD + eE$ ; the concentrations are equilibrium concentrations only
- $K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$  [15.11] The equilibrium-constant expression in terms of equilibrium partial pressures
- $K_p = K_c(RT)^{\Delta n}$  [15.14] Relating the equilibrium constant based on pressures to the equilibrium constant based on concentration
- $Q_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$  [15.22] The reaction quotient. The concentrations are for any time during a reaction. If the concentrations are equilibrium concentrations, then  $Q_c = K_c$ .

VISUALIZING CONCEPTS *(May wait to do 1-10 till the end--they are conceptual)*

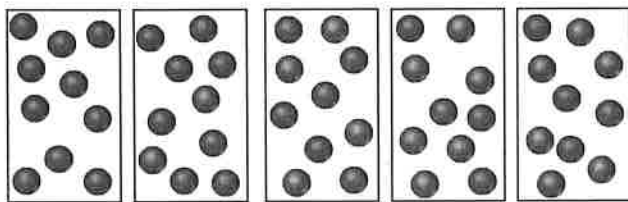
- 15.1 (a) Based on the following energy profile, predict whether  $k_f > k_r$  or  $k_f < k_r$ . (b) Using Equation 15.5, predict whether the equilibrium constant for the process is greater than 1 or less than 1. [Section 15.1]



- 15.4 The following diagram represents a reaction shown going to completion. (a) Letting A = red spheres and B = blue spheres, write a balanced equation for the reaction. (b) Write the equilibrium-constant expression for the reaction. (c) Assuming that all of the molecules are in the gas phase, calculate  $\Delta n$ , the change in the number of gas molecules that accompanies the reaction. (d) How can you calculate  $K_p$  if you know  $K_c$  at a particular temperature? [Section 15.2]

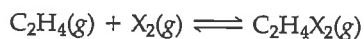


- 15.2 The following diagrams represent a hypothetical reaction  $A \rightarrow B$ , with A represented by red spheres and B represented by blue spheres. The sequence from left to right represents the system as time passes. Do the diagrams indicate that the system reaches an equilibrium state? Explain. [Sections 15.1 and 15.2]

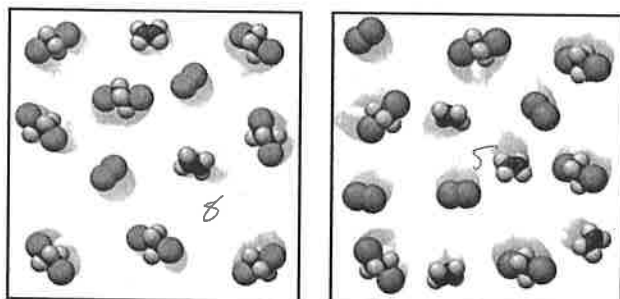


- 15.3 The following diagram represents an equilibrium mixture produced for a reaction of the type  $A + X \rightleftharpoons AX$ . If the volume is 1 L, is  $K$  greater or smaller than 1? [Section 15.2]

- 15.5 Ethene ( $C_2H_4$ ) reacts with halogens ( $X_2$ ) by the following reaction:

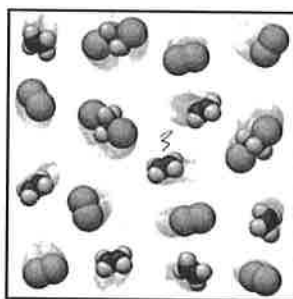


The following figures represent the concentrations at equilibrium at the same temperature when  $X_2$  is  $Cl_2$  (green),  $Br_2$  (brown), and  $I_2$  (purple). List the equilibria from smallest to largest equilibrium constant. [Section 15.3]



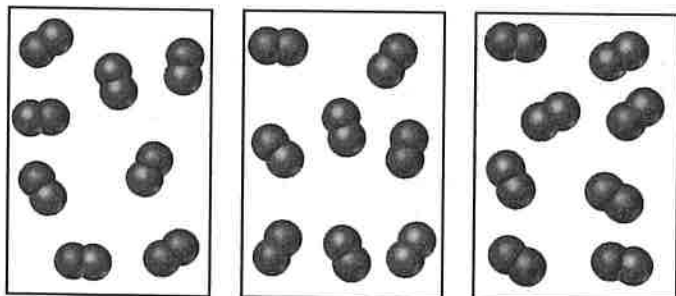
(a)

(b)



(c)

- 15.6 The reaction  $A_2 + B_2 \rightleftharpoons 2 AB$  has an equilibrium constant  $K_c = 1.5$ . The following diagrams represent reaction mixtures containing  $A_2$  molecules (red),  $B_2$  molecules (blue), and  $AB$  molecules. (a) Which reaction mixture is at equilibrium? (b) For those mixtures that are not at equilibrium, how will the reaction proceed to reach equilibrium? [Sections 15.5 and 15.6]

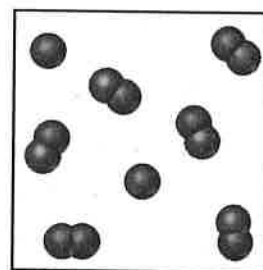


(i)

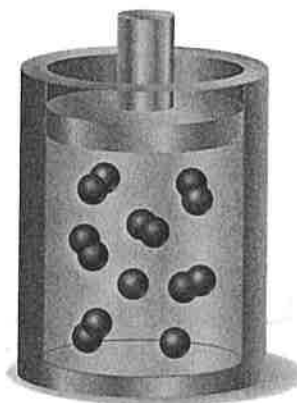
(ii)

(iii)

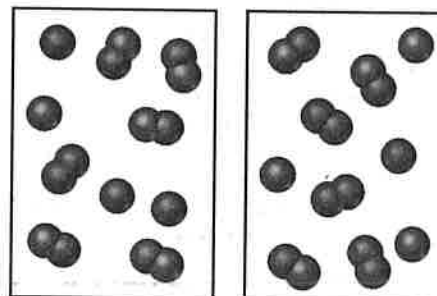
- 15.7 The reaction  $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$  has an equilibrium constant of  $K_p = 2$ . The accompanying diagram shows a mixture containing  $A$  atoms (red),  $A_2$  molecules, and  $AB$  molecules (red and blue). How many  $B$  atoms should be added to the diagram to illustrate an equilibrium mixture? [Section 15.6]



- 15.8 The following diagram represents the equilibrium state for the reaction  $A_2(g) + 2 B(g) \rightleftharpoons 2 AB(g)$ . (a) Assuming the volume is 1 L, calculate the equilibrium constant,  $K_c$ , for the reaction. (b) If the volume of the equilibrium mixture is decreased, will the number of  $AB$  molecules increase or decrease? [Sections 15.5 and 15.7]



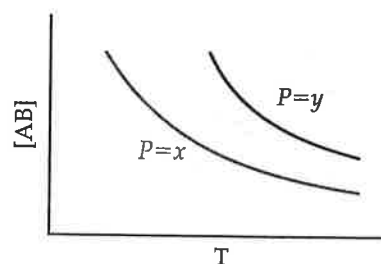
- 15.9 The following diagrams represent equilibrium mixtures for the reaction  $A_2 + B \rightleftharpoons A + AB$  at (1) 300 K and (2) 500 K. The  $A$  atoms are red, and the  $B$  atoms are blue. Is the reaction exothermic or endothermic? [Section 15.7]



(a)

(b)

- 15.10 The following graph represents the yield of the compound  $AB$  at equilibrium in the reaction  $A(g) + B(g) \rightleftharpoons AB(g)$ .



- (a) Is this reaction exothermic or endothermic? (b) Is  $P = x$  greater or smaller than  $P = y$ ? [Section 15.7]

## EXERCISES

## Equilibrium; The Equilibrium Constant

15.11 Suppose that the gas-phase reactions  $A \rightarrow B$  and  $B \rightarrow A$  are both elementary processes with rate constants of  $3.8 \times 10^{-2} \text{ s}^{-1}$  and  $3.1 \times 10^{-1} \text{ s}^{-1}$ , respectively. (a) What is the value of the equilibrium constant for the equilibrium  $A(g) \rightleftharpoons B(g)$ ? (b) Which is greater at equilibrium, the partial pressure of A or the partial pressure of B? Explain.

15.12 Consider the reaction  $A + B \rightleftharpoons C + D$ . Assume that both the forward reaction and the reverse reaction are elementary processes and that the value of the equilibrium constant is very large. (a) Which species predominate at equilibrium, reactants or products? (b) Which reaction has the larger rate constant, the forward or the reverse? Explain.

15.13 Write the expression for  $K_c$  for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.

- (a)  $3 \text{ NO}(g) \rightleftharpoons \text{N}_2\text{O}(g) + \text{NO}_2(g)$   
 (b)  $\text{CH}_4(g) + 2 \text{ H}_2\text{S}(g) \rightleftharpoons \text{CS}_2(g) + 4 \text{ H}_2(g)$   
 (c)  $\text{Ni}(\text{CO})_4(g) \rightleftharpoons \text{Ni}(s) + 4 \text{ CO}(g)$   
 (d)  $\text{HF}(aq) \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq)$   
 (e)  $2 \text{ Ag}(s) + \text{Zn}^{2+}(aq) \rightleftharpoons 2 \text{ Ag}^+(aq) + \text{Zn}(s)$

15.14 Write the expressions for  $K_c$  for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.

- (a)  $2 \text{ O}_3(g) \rightleftharpoons 3 \text{ O}_2(g)$   
 (b)  $\text{Ti}(s) + 2 \text{ Cl}_2(g) \rightleftharpoons \text{TiCl}_4(l)$   
 (c)  $2 \text{ C}_2\text{H}_4(g) + 2 \text{ H}_2\text{O}(g) \rightleftharpoons 2 \text{ C}_2\text{H}_6(g) + \text{O}_2(g)$   
 (d)  $\text{C}(s) + 2 \text{ H}_2(g) \rightleftharpoons \text{CH}_4(g)$   
 (e)  $4 \text{ HCl}(aq) + \text{O}_2(g) \rightleftharpoons 2 \text{ H}_2\text{O}(l) + 2 \text{ Cl}_2(g)$

15.15 When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?

- (a)  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ NO}(g); K_c = 1.5 \times 10^{-10}$   
 (b)  $2 \text{ SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ SO}_3(g); K_p = 2.5 \times 10^9$

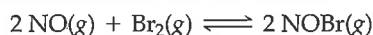
15.16 Which of the following reactions lies to the right, favoring the formation of products, and which lies to the left, favoring formation of reactants?

- (a)  $2 \text{ NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ NO}_2(g); K_p = 5.0 \times 10^{12}$   
 (b)  $2 \text{ HBr}(g) \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g); K_c = 5.8 \times 10^{-18}$

15.17 If  $K_c = 0.042$  for  $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$  at 500 K, what is the value of  $K_p$  for this reaction at this temperature?

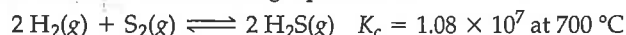
15.18 Calculate  $K_c$  at 303 K for  $\text{SO}_2(g) + \text{Cl}_2(g) \rightleftharpoons \text{SO}_2\text{Cl}_2(g)$  if  $K_p = 34.5$  at this temperature.

15.19 The equilibrium constant for the reaction



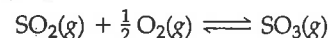
is  $K_c = 1.3 \times 10^{-2}$  at 1000 K. (a) Calculate  $K_c$  for  $2 \text{ NOBr}(g) \rightleftharpoons 2 \text{ NO}(g) + \text{Br}_2(g)$ . (b) At this temperature does the equilibrium favor NO and Br<sub>2</sub>, or does it favor NOBr?

15.20 Consider the following equilibrium:



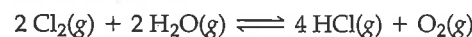
(a) Calculate  $K_p$ . (b) Does the equilibrium mixture contain mostly H<sub>2</sub> and S<sub>2</sub> or mostly H<sub>2</sub>S?

15.21 At 1000 K,  $K_p = 1.85$  for the reaction



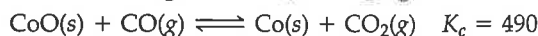
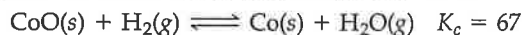
(a) What is the value of  $K_p$  for the reaction  $\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{ O}_2(g)$ ? (b) What is the value of  $K_p$  for the reaction  $2 \text{ SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ SO}_3(g)$ ? (c) What is the value of  $K_c$  for the reaction in part (b)?

15.22 Consider the following equilibrium, for which  $K_p = 0.0752$  at 480 °C:



(a) What is the value of  $K_p$  for the reaction  $4 \text{ HCl}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{ Cl}_2(g) + 2 \text{ H}_2\text{O}(g)$ ? (b) What is the value of  $K_p$  for the reaction  $\text{Cl}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons 2 \text{ HCl}(g) + \frac{1}{2} \text{ O}_2(g)$ ? (c) What is the value of  $K_c$  for the reaction in part (b)?

15.23 The following equilibria were attained at 823 K:

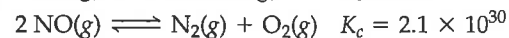
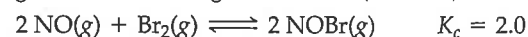


Based on these equilibria, calculate the equilibrium constant for  $\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$  at 823 K.

15.24 Consider the equilibrium



Calculate the equilibrium constant  $K_p$  for this reaction, given the following information (at 298 K):



15.25 Mercury(I) oxide decomposes into elemental mercury and elemental oxygen:  $2 \text{ Hg}_2\text{O}(s) \rightleftharpoons 4 \text{ Hg}(l) + \text{O}_2(g)$

(a) Write the equilibrium-constant expression for this reaction in terms of partial pressures. (b) Explain why we normally exclude pure solids and liquids from equilibrium-constant expressions.

15.26 Consider the equilibrium  $\text{Na}_2\text{O}(s) + \text{SO}_2(g) \rightleftharpoons \text{Na}_2\text{SO}_3(s)$ . (a) Write the equilibrium-constant expression for this reaction in terms of partial pressures. (b) Why doesn't the concentration of Na<sub>2</sub>O appear in the equilibrium-constant expression?

## Calculating Equilibrium Constants

15.27 Gaseous hydrogen iodide is placed in a closed container at 425 °C, where it partially decomposes to hydrogen and iodine:  $2 \text{ HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$ . At equilibrium it is

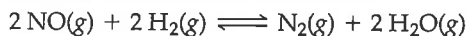
found that  $[\text{HI}] = 3.53 \times 10^{-3} \text{ M}$ ,  $[\text{H}_2] = 4.79 \times 10^{-4} \text{ M}$ , and  $[\text{I}_2] = 4.79 \times 10^{-4} \text{ M}$ . What is the value of  $K_c$  at this temperature?

15.28 Methanol ( $\text{CH}_3\text{OH}$ ) is produced commercially by the catalyzed reaction of carbon monoxide and hydrogen:  $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$ . An equilibrium mixture in a 2.00-L vessel is found to contain 0.0406 mol  $\text{CH}_3\text{OH}$ , 0.170 mol  $\text{CO}$ , and 0.302 mol  $\text{H}_2$  at 500 K. Calculate  $K_c$  at this temperature.

15.29 The equilibrium  $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$  is established at 500 K. An equilibrium mixture of the three gases has partial pressures of 0.095 atm, 0.171 atm, and 0.28 atm for  $\text{NO}$ ,  $\text{Cl}_2$ , and  $\text{NOCl}$ , respectively. Calculate  $K_p$  for this reaction at 500 K.

15.30 Phosphorus trichloride gas and chlorine gas react to form phosphorus pentachloride gas:  $\text{PCl}_3 + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$ . A gas vessel is charged with a mixture of  $\text{PCl}_3(g)$  and  $\text{Cl}_2(g)$ , which is allowed to equilibrate at 450 K. At equilibrium the partial pressures of the three gases are  $P_{\text{PCl}_3} = 0.124$  atm,  $P_{\text{Cl}_2} = 0.157$  atm, and  $P_{\text{PCl}_5} = 1.30$  atm. (a) What is the value of  $K_p$  at this temperature? (b) Does the equilibrium favor reactants or products?

15.31 A mixture of 0.10 mol of  $\text{NO}$ , 0.050 mol of  $\text{H}_2$ , and 0.10 mol of  $\text{H}_2\text{O}$  is placed in a 1.0-L vessel at 300 K. The following equilibrium is established:



At equilibrium  $[\text{NO}] = 0.062$  M. (a) Calculate the equilibrium concentrations of  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ . (b) Calculate  $K_c$ .

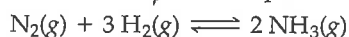
## Applications of Equilibrium Constants

15.35 (a) How does a reaction quotient differ from an equilibrium constant? (b) If  $Q_c < K_c$ , in which direction will a reaction proceed in order to reach equilibrium? (c) What condition must be satisfied so that  $Q_c = K_c$ ?

15.36 (a) How is a reaction quotient used to determine whether a system is at equilibrium? (b) If  $Q_c > K_c$ , how must the reaction proceed to reach equilibrium? (c) At the start of a certain reaction, only reactants are present; no products have been formed. What is the value of  $Q_c$  at this point in the reaction?

15.37 At 100 °C the equilibrium constant for the reaction  $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$  has the value  $K_c = 2.19 \times 10^{-10}$ . Are the following mixtures of  $\text{COCl}_2$ ,  $\text{CO}$ , and  $\text{Cl}_2$  at 100 °C at equilibrium? If not, indicate the direction that the reaction must proceed to achieve equilibrium. (a)  $[\text{COCl}_2] = 2.00 \times 10^{-3}$  M,  $[\text{CO}] = 3.3 \times 10^{-6}$  M,  $[\text{Cl}_2] = 6.62 \times 10^{-6}$  M; (b)  $[\text{COCl}_2] = 4.50 \times 10^{-2}$  M,  $[\text{CO}] = 1.1 \times 10^{-7}$  M,  $[\text{Cl}_2] = 2.25 \times 10^{-6}$  M; (c)  $[\text{COCl}_2] = 0.0100$  M,  $[\text{CO}] = [\text{Cl}_2] = 1.48 \times 10^{-6}$  M

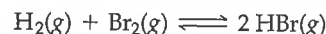
15.38 As shown in Table 15.2,  $K_p$  for the equilibrium



is  $4.51 \times 10^{-5}$  at 450 °C. For each of the mixtures listed here, indicate whether the mixture is at equilibrium at 450 °C. If it is not at equilibrium, indicate the direction (toward product or toward reactants) in which the mixture must shift to achieve equilibrium.

- (a) 98 atm  $\text{NH}_3$ , 45 atm  $\text{N}_2$ , 55 atm  $\text{H}_2$   
 (b) 57 atm  $\text{NH}_3$ , 143 atm  $\text{N}_2$ , no  $\text{H}_2$   
 (c) 13 atm  $\text{NH}_3$ , 27 atm  $\text{N}_2$ , 82 atm  $\text{H}_2$ .

15.32 A mixture of 1.374 g of  $\text{H}_2$  and 70.31 g of  $\text{Br}_2$  is heated in a 2.00-L vessel at 700 K. These substances react as follows:



At equilibrium the vessel is found to contain 0.566 g of  $\text{H}_2$ . (a) Calculate the equilibrium concentrations of  $\text{H}_2$ ,  $\text{Br}_2$ , and  $\text{HBr}$ . (b) Calculate  $K_c$ .

15.33 A mixture of 0.2000 mol of  $\text{CO}_2$ , 0.1000 mol of  $\text{H}_2$ , and 0.1600 mol of  $\text{H}_2\text{O}$  is placed in a 2.000-L vessel. The following equilibrium is established at 500 K:



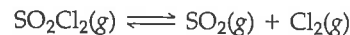
(a) Calculate the initial partial pressures of  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$ . (b) At equilibrium  $P_{\text{H}_2\text{O}} = 3.51$  atm. Calculate the equilibrium partial pressures of  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{CO}$ . (c) Calculate  $K_p$  for the reaction.

15.34 A flask is charged with 1.500 atm of  $\text{N}_2\text{O}_4(g)$  and 1.00 atm  $\text{NO}_2(g)$  at 25 °C, and the following equilibrium is achieved:



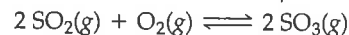
After equilibrium is reached, the partial pressure of  $\text{NO}_2$  is 0.512 atm. (a) What is the equilibrium partial pressure of  $\text{N}_2\text{O}_4$ ? (b) Calculate the value of  $K_p$  for the reaction.

15.39 At 100 °C,  $K_c = 0.078$  for the reaction



In an equilibrium mixture of the three gases, the concentrations of  $\text{SO}_2\text{Cl}_2$  and  $\text{SO}_2$  are 0.108 M and 0.052 M, respectively. What is the partial pressure of  $\text{Cl}_2$  in the equilibrium mixture?

15.40 At 900 K the following reaction has  $K_p = 0.345$ :

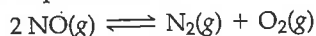


In an equilibrium mixture the partial pressures of  $\text{SO}_2$  and  $\text{O}_2$  are 0.135 atm and 0.455 atm, respectively. What is the equilibrium partial pressure of  $\text{SO}_3$  in the mixture?

15.41 (a) At 1285 °C the equilibrium constant for the reaction  $\text{Br}_2(g) \rightleftharpoons 2\text{Br}(g)$  is  $K_c = 1.04 \times 10^{-3}$ . A 0.200-L vessel containing an equilibrium mixture of the gases has 0.245 g  $\text{Br}_2(g)$  in it. What is the mass of  $\text{Br}(g)$  in the vessel? (b) For the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$ ,  $K_c = 55.3$  at 700 K. In a 2.00-L flask containing an equilibrium mixture of the three gases, there are 0.056 g  $\text{H}_2$  and 4.36 g  $\text{I}_2$ . What is the mass of  $\text{HI}$  in the flask?

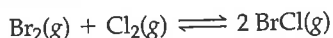
15.42 (a) At 800 K the equilibrium constant for  $\text{I}_2(g) \rightleftharpoons 2\text{I}(g)$  is  $K_c = 3.1 \times 10^{-5}$ . If an equilibrium mixture in a 10.0-L vessel contains  $2.67 \times 10^{-2}$  g of  $\text{I}(g)$ , how many grams of  $\text{I}_2$  are in the mixture? (b) For  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ ,  $K_p = 3.0 \times 10^4$  at 700 K. In a 2.00-L vessel the equilibrium mixture contains 1.17 g of  $\text{SO}_3$  and 0.105 g of  $\text{O}_2$ . How many grams of  $\text{SO}_2$  are in the vessel?

- 15.43 At 2000 °C the equilibrium constant for the reaction



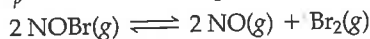
is  $K_c = 2.4 \times 10^3$ . If the initial concentration of NO is 0.200 M, what are the equilibrium concentrations of NO,  $\text{N}_2$ , and  $\text{O}_2$ ?

- 15.44 For the equilibrium



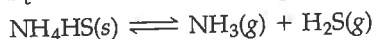
at 400 K,  $K_c = 7.0$ . If 0.25 mol of  $\text{Br}_2$  and 0.25 mol of  $\text{Cl}_2$  are introduced into a 1.0-L container at 400 K, what will be the equilibrium concentrations of  $\text{Br}_2$ ,  $\text{Cl}_2$ , and  $\text{BrCl}$ ?

- 15.45 At 373 K,  $K_p = 0.416$  for the equilibrium



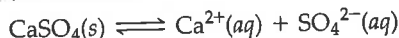
If the pressures of  $\text{NOBr}(g)$  and  $\text{NO}(g)$  are equal, what is the equilibrium pressure of  $\text{Br}_2(g)$ ?

- 15.46 At 218 °C,  $K_c = 1.2 \times 10^{-4}$  for the equilibrium



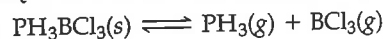
Calculate the equilibrium concentrations of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  if a sample of solid  $\text{NH}_4\text{HS}$  is placed in a closed vessel and decomposes until equilibrium is reached.

- 15.47 Consider the reaction



At 25 °C the equilibrium constant is  $K_c = 2.4 \times 10^{-5}$  for this reaction. (a) If excess  $\text{CaSO}_4(s)$  is mixed with water at 25 °C to produce a saturated solution of  $\text{CaSO}_4$ , what are the equilibrium concentrations of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ? (b) If the resulting solution has a volume of 3.0 L, what is the minimum mass of  $\text{CaSO}_4(s)$  needed to achieve equilibrium?

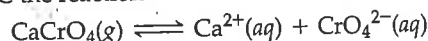
- 15.48 At 80 °C,  $K_c = 1.87 \times 10^{-3}$  for the reaction



(a) Calculate the equilibrium concentrations of  $\text{PH}_3$  and  $\text{BCl}_3$  if a solid sample of  $\text{PH}_3\text{BCl}_3$  is placed in a closed vessel and decomposes until equilibrium is reached. (b) If the flask has a volume of 0.500 L, what is the minimum mass of  $\text{PH}_3\text{BCl}_3(s)$  that must be added to the flask to achieve equilibrium?

- 15.49 For the reaction  $\text{I}_2 + \text{Br}_2(g) \rightleftharpoons 2 \text{IBr}(g)$ ,  $K_c = 280$  at 150 °C. Suppose that 0.500 mol  $\text{IBr}$  in a 1.00-L flask is allowed to reach equilibrium at 150 °C. What are the equilibrium concentrations of  $\text{IBr}$ ,  $\text{I}_2$ , and  $\text{Br}_2$ ?

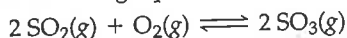
- 15.50 At 25 °C the reaction



has an equilibrium constant  $K_c = 7.1 \times 10^{-4}$ . What are the equilibrium concentrations of  $\text{Ca}^{2+}$  and  $\text{CrO}_4^{2-}$  in a saturated solution of  $\text{CaCrO}_4$ ?

## Le Châtelier's Principle

- 15.51 Consider the following equilibrium, for which  $\Delta H < 0$



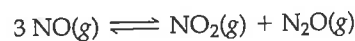
How will each of the following changes affect an equilibrium mixture of the three gases? (a)  $\text{O}_2(g)$  is added to the system; (b) the reaction mixture is heated; (c) the volume of the reaction vessel is doubled; (d) a catalyst is added to the mixture; (e) the total pressure of the system is increased by adding a noble gas; (f)  $\text{SO}_3(g)$  is removed from the system.

- 15.52 Consider  $4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$ ,  $\Delta H = -904.4 \text{ kJ}$ . How does each of the following changes affect the yield of NO at equilibrium? Answer increase, decrease, or no change: (a) increase  $[\text{NH}_3]$ ; (b) increase  $[\text{H}_2\text{O}]$ ; (c) decrease  $[\text{O}_2]$ ; (d) decrease the volume of the container in which the reaction occurs; (e) add a catalyst; (f) increase temperature.

- 15.53 How do the following changes affect the value of the equilibrium constant for a gas-phase exothermic reaction: (a) removal of a reactant or product, (b) decrease in the volume, (c) decrease in the temperature, (d) addition of a catalyst?

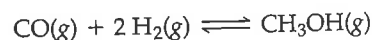
- 15.54 For a certain gas-phase reaction, the fraction of products in an equilibrium mixture is increased by increasing the temperature and increasing the volume of the reaction vessel. (a) What can you conclude about the reaction from the influence of temperature on the equilibrium? (b) What can you conclude from the influence of increasing the volume?

- 15.55 Consider the following equilibrium between oxides of nitrogen



(a) Use data in Appendix C to calculate  $\Delta H^\circ$  for this reaction. (b) Will the equilibrium constant for the reaction increase or decrease with increasing temperature? Explain. (c) At constant temperature would a change in the volume of the container affect the fraction of products in the equilibrium mixture?

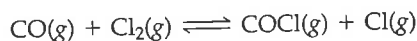
- 15.56 Methanol ( $\text{CH}_3\text{OH}$ ) can be made by the reaction of CO with  $\text{H}_2$ :



(a) Use thermochemical data in Appendix C to calculate  $\Delta H^\circ$  for this reaction. (b) To maximize the equilibrium yield of methanol, would you use a high or low temperature? (c) To maximize the equilibrium yield of methanol, would you use a high or low pressure?

## ADDITIONAL EXERCISES

- 15.57 Both the forward reaction and the reverse reaction in the following equilibrium are believed to be elementary steps:



At 25 °C the rate constants for the forward and reverse reactions are  $1.4 \times 10^{-28} \text{ M}^{-1} \text{ s}^{-1}$  and  $9.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively. (a) What is the value for the equilibrium constant at 25 °C? (b) Are reactants or products more plentiful at equilibrium?