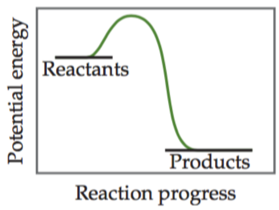
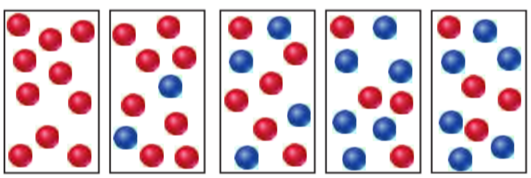
Chemical Equilibrium
Problem Set

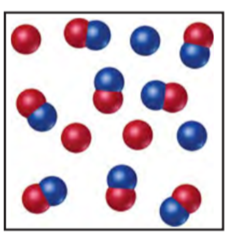
15.1 **(a)** Based on the following energy profile, predict whether $k_f > k_r$ or $k_f < k_r$. **(b)** Using Equation 15.5, predict whether the equilibrium constant for the process is greater than 1 or less than 1. [Section 15.1]



15.2 The following diagrams represent a hypothetical reaction $A \longrightarrow B$, 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]



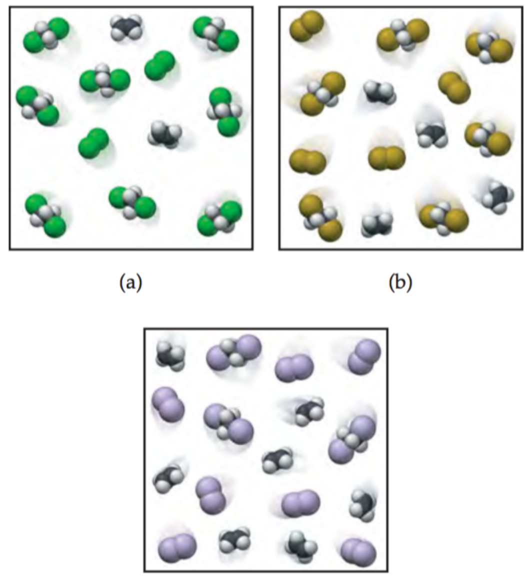
15.5 A friend says that the faster the reaction, the larger the equilibrium constant. Is your friend correct? Why or why not? [Sections 15.1 and 15.2]

15.6 A certain chemical reaction has $K_c = 1.5 \times 10^6$. Does this mean that at equilibrium there are 1.5×10^6 times as many product molecules as reactant molecules? Explain. [Sections 15.1 and 15.2]

15.7 Ethene (C_2H_4) reacts with halogens (X_2) by the following reaction:

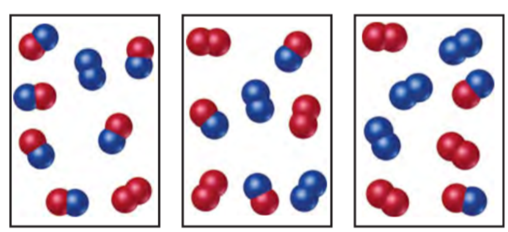
$$C_2H_4(g) + X_2(g) \rightleftharpoons C_2H_4X_2(g)$$

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]



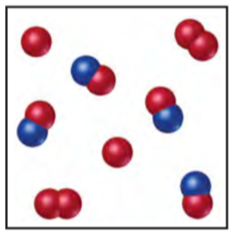
(a) (b) (c)

15.8 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]

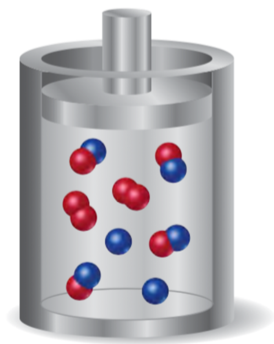


(i) (ii) (iii)

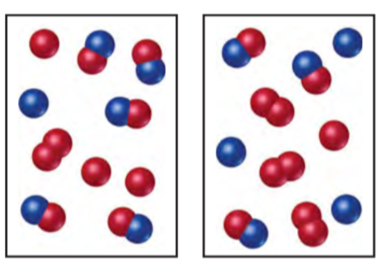
15.9 The reaction $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$ has an equilibrium constant of $K_p = 2$. The accompanying diagram shows a mixture containing A atoms (red), A_2 molecules, and AB molecules (red and blue). How many B atoms should be added to the diagram to illustrate an equilibrium mixture?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



15.10 The diagram shown here represents the equilibrium state for the reaction $A_2(g) + 2\,B(g) \rightleftharpoons 2\,AB(g)$. **(a)** Assuming the volume is 2 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]



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



(a) (b)

15.13 Suppose that the gas-phase reactions $A \longrightarrow B$ and $B \longrightarrow A$ are both elementary processes with rate constants of $4.7 \times 10^{-3}\ s^{-1}$ and $5.8 \times 10^{-1}\ s^{-1}$, 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.

15.14 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.

15.15 Write the expression for K_c for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.
(a) $3\,NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$
(b) $CH_4(g) + 2\,H_2S(g) \rightleftharpoons CS_2(g) + 4\,H_2(g)$
(c) $Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4\,CO(g)$
(d) $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

15.18 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) $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g);\ K_p = 5.0 \times 10^{12}$
(b) $2\,HBr(g) \rightleftharpoons H_2(g) + Br_2(g);\ K_c = 5.8 \times 10^{-18}$

15.19 Can the equilibrium constant ever be a negative number? Explain.

15.20 Can the equilibrium constant ever be zero? Explain.

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

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

(a) What is the value of K_p for the reaction $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$? **(b)** What is the value of K_p for the reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$? **(c)** What is the value of K_c for the reaction in part (b)?

15.27 The following equilibria were attained at 823 K:

$$CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g) \quad K_c = 67$$
$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \quad K_c = 490$$

Based on these equilibria, calculate the equilibrium constant for $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ at 823 K.

15.29 Explain why we normally exclude pure solids and liquids from equilibrium-constant expressions.

15.30 Explain why we normally exclude solvents from liquid-phase reactions in equilibrium-constant expressions.

15.32 Consider the equilibrium $Na_2O(s) + SO_2(g) \rightleftharpoons Na_2SO_3(s)$. **(a)** Write the equilibrium-constant expression for this reaction in terms of partial pressures. **(b)** All the compounds in this reaction are soluble in water. Rewrite the equilibrium-constant expression in terms of molarities for the aqueous reaction.

15.33 Methanol (CH_3OH) is produced commercially by the catalyzed reaction of carbon monoxide and hydrogen: $CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$. An equilibrium mixture in a 2.00-L vessel is found to contain 0.0406 mol CH_3OH, 0.170 mol CO, and 0.302 mol H_2 at 500 K. Calculate K_c at this temperature.

15.36 Phosphorus trichloride gas and chlorine gas react to form phosphorus pentachloride gas: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$. A 7.5-L gas vessel is charged with a mixture of $PCl_3(g)$ and $Cl_2(g)$, which is allowed to equilibrate at 450 K. At equilibrium the partial pressures of the three gases are $P_{PCl_3} = 0.124$ atm, $P_{Cl_2} = 0.157$ atm, and $P_{PCl_5} = 1.30$ atm. **(a)** What is the value of K_p at this temperature? **(b)** Does the equilibrium favor reactants or products? **(c)** Calculate K_c for this reaction at 450 K.

15.37 A mixture of 0.10 mol of NO, 0.050 mol of H_2, and 0.10 mol of H_2O is placed in a 1.0-L vessel at 300 K. The following equilibrium is established:

$$2\,NO(g) + 2\,H_2(g) \rightleftharpoons N_2(g) + 2\,H_2O(g)$$

At equilibrium [NO] = 0.062 *M*. **(a)** Calculate the equilibrium concentrations of H_2, N_2, and H_2O. **(b)** Calculate K_c.

15.39 A mixture of 0.2000 mol of CO_2, 0.1000 mol of H_2, and 0.1600 mol of H_2O is placed in a 2.000-L vessel. The following equilibrium is established at 500 K:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

(a) Calculate the initial partial pressures of CO_2, H_2, and H_2O. **(b)** At equilibrium $P_{H_2O} = 3.51$ atm. Calculate the equilibrium partial pressures of CO_2, H_2, and CO. **(c)** Calculate K_p for the reaction. **(d)** Calculate K_c for the reaction.

15.44 **(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?

15.45 At 100 °C the equilibrium constant for the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ has the value $K_c = 2.19 \times 10^{-10}$. Are the following mixtures of $COCl_2$, CO, and Cl_2 at 100 °C at equilibrium? If not, indicate the direction that the reaction must proceed to achieve equilibrium. **(a)** $[COCl_2] = 2.00 \times 10^{-3}$ *M*, $[CO] = 3.3 \times 10^{-6}$ *M*, $[Cl_2] = 6.62 \times 10^{-6}$ *M*; **(b)** $[COCl_2] = 4.50 \times 10^{-2}$ *M*, $[CO] = 1.1 \times 10^{-7}$ *M*, $[Cl_2] = 2.25 \times 10^{-6}$ *M*; **(c)** $[COCl_2] = 0.0100$ *M*, $[CO] = [Cl_2] = 1.48 \times 10^{-6}$ *M*

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

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

In an equilibrium mixture of the three gases, the concentrations of SO_2Cl_2 and SO_2 are 0.108 *M* and 0.052 *M*, respectively. What is the partial pressure of Cl_2 in the equilibrium mixture?

15.49 **(a)** At 1285 °C the equilibrium constant for the reaction $Br_2(g) \rightleftharpoons 2\,Br(g)$ is $K_c = 1.04 \times 10^{-3}$. A 0.200-L vessel containing an equilibrium mixture of the gases has 0.245 g $Br_2(g)$ in it. What is the mass of Br(*g*) in the vessel? **(b)** For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_c = 55.3$ at 700 K. In a 2.00-L flask containing an equilibrium mixture of the three gases, there are 0.056 g H_2 and 4.36 g I_2. What is the mass of HI in the flask?

15.51 At 2000 °C the equilibrium constant for the reaction

$$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

is $K_c = 2.4 \times 10^3$. If the initial concentration of NO is 0.175 *M*, what are the equilibrium concentrations of NO, N_2, and O_2?

15.53 At 373 K, $K_p = 0.416$ for the equilibrium

$$2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$$

If the pressures of NOBr(*g*) and NO(*g*) are equal, what is the equilibrium pressure of $Br_2(g)$?

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

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Calculate the equilibrium concentrations of NH_3 and H_2S if a sample of solid NH_4SH is placed in a closed vessel at 218 °C and decomposes until equilibrium is reached.

15.55 Consider the reaction

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

At 25 °C the equilibrium constant is $K_c = 2.4 \times 10^{-5}$ for this reaction. **(a)** If excess $CaSO_4(s)$ is mixed with water at 25 °C to produce a saturated solution of $CaSO_4$, what are the equilibrium concentrations of Ca^{2+} and SO_4^{2-}? **(b)** If the resulting solution has a volume of 1.4 L, what is the minimum mass of $CaSO_4(s)$ needed to achieve equilibrium?

15.57 For the reaction $I_2 + Br_2(g) \rightleftharpoons 2\,IBr(g)$, $K_c = 280$ at 150 °C. Suppose that 0.500 mol IBr in a 2.00-L flask is allowed to reach equilibrium at 150 °C. What are the equilibrium concentrations of IBr, I_2, and Br_2?

15.59 Methane, CH_4, reacts with I_2 according to the reaction $CH_4(g) + I_2(g) \rightleftharpoons CH_3I(g) + HI(g)$. At 630 K, K_p for this reaction is 2.26×10^{-4}. A reaction was set up at 630 K with initial partial pressures of methane of 105.1 torr and of 7.96 torr for I_2. Calculate the pressures, in torr, of all reactants and products at equilibrium.

15.61 Consider the following equilibrium for which $\Delta H < 0$

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

How will each of the following changes affect an equilibrium mixture of the three gases: **(a)** $O_2(g)$ 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)** $SO_3(g)$ is removed from the system?

15.64 For a certain gas-phase reaction, the fraction of products in an equilibrium mixture is increased by either increasing the temperature or by increasing the volume of the reaction vessel. **(a)** Is the reaction exothermic or endothermic? **(b)** Does the balanced chemical equation have more molecules on the reactant side or product side?