Pearson

Exercises

Review Questions

1. How does a developing fetus get oxygen in the womb?
2. What is dynamic equilibrium? Why is it called *dynamic*?
3. Give the general expression for the equilibrium constant of the following generic reaction:

$$aA + bB \rightleftharpoons cC + dD$$

4. What is the significance of the equilibrium constant? What does a large equilibrium constant tell us about a reaction? A small one?
5. What happens to the value of the equilibrium constant for a reaction if the reaction equation is reversed? Multiplied by a constant?
6. If two reactions sum to an overall reaction, and the equilibrium constants for the two reactions are K_1 and K_2 what is the equilibrium constant for the overall reaction?
7. Explain the difference between K_c and K_p. For a given reaction, how are the two constants related?
8. What units should you use when expressing concentrations or partial pressures in the equilibrium constant? What are the units of K_p and K_c? Explain.
9. Why do we omit the concentrations of solids and liquids from equilibrium expressions?
10. Does the value of the equilibrium constant depend on the initial concentrations of the reactants and products? Do the equilibrium concentrations of the reactants and products depend on their initial concentrations? Explain.
11. Explain how you might deduce the equilibrium constant for a reaction in which you know the initial concentrations of the reactants and products and the equilibrium concentration of only one reactant or product.
12. What is the definition of the reaction quotient (Q) for a reaction? What does Q measure?
13. What is the value of Q when each reactant and product is in its standard state? (See Section 9.10 for the definition of standard states.)
14. In what direction does a reaction proceed for each condition: a. $Q < K$; b. $Q > K$; and c. $Q = K$?
15. Many equilibrium calculations involve finding the equilibrium concentrations of reactants and products given their initial concentrations and the equilibrium constant. Outline the general procedure used in solving these kinds of problems.
16. In equilibrium problems involving equilibrium constants that are small relative to the initial concentrations of reactants, we can often assume that the quantity x (which represents how far the reaction proceeds toward products) is small. When this assumption is made, we can ignore the quantity x when it is subtracted from a large number but not when it is multiplied by a large number. In other words, $2.5 - x \approx 2.5$, but $2.5x \neq 2.5$. Explain why we can ignore a small x in the first case but not in the second.
17. What happens to a chemical system at equilibrium when equilibrium is disturbed?
18. What is the effect of a change in concentration of a reactant or product on a chemical reaction initially at equilibrium?
19. What is the effect of a change in volume on a chemical reaction (that includes gaseous reactants or products) initially at equilibrium?
20. What is the effect of a temperature change on a chemical reaction initially at equilibrium? How does the effect differ for an exothermic reaction compared to an endothermic one?

Problems by Topic

Note: Answers to all odd-numbered Problems can be found in Appendix III. Exercises in the Problems by Topic section *are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.*

Equilibrium and the Equilibrium Constant Expression

21. Write an expression for the equilibrium constant of each chemical equation:

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

b. $2\ BrNO(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$

c. $CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + 4\ H_2(g)$

d. $2\ CO(g) + O_2(g) \rightleftharpoons 2\ CO_2(g)$

22. Find and fix each mistake in the equilibrium constant expressions:

a. $2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g) \qquad K_c = \dfrac{[H_2][S_2]}{[H_2S]}$

b. $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad K_c = \dfrac{[CO][Cl_2]}{[COCl_2]}$

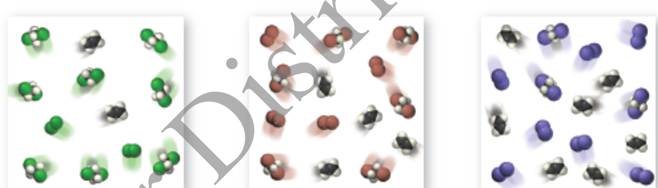
23. When this reaction comes to equilibrium, will the concentrations of the reactants or products be greater? Does the answer to this question depend on the initial concentrations of the reactants and products?

$$A(g) + B(g) \rightleftharpoons 2\ C(g) \quad K_c = 1.4 \times 10^{-5}$$

24. Ethene (C_2H_4) can be halogenated by this reaction:

$$C_2H_4(g) + X_2(g) \rightleftharpoons C_2H_4X(g)$$

where X_2 can be Cl_2 (green), Br_2 (brown), or I_2 (purple). Examine the three figures representing equilibrium concentrations in this reaction at the same temperature for the three different halogens. Rank the equilibrium constants for the three reactions from largest to smallest.



a. b. c.

25. H_2 and I_2 are combined in a flask and allowed to react according to the reaction:

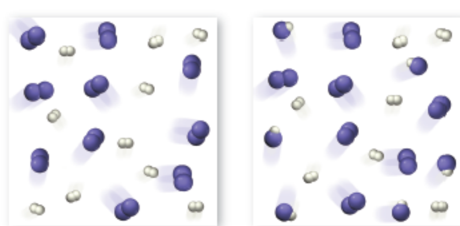
$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

Examine the figures (sequential in time) and answer the questions:

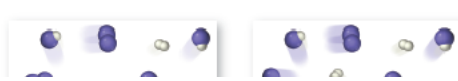
a. Which figure represents the point at which equilibrium is reached?

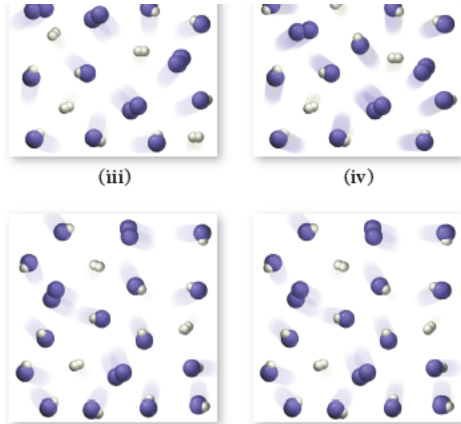
b. How would the series of figures change in the presence of a catalyst?

c. Would there be different amounts of reactants and products in the final figure (vi) in the presence of a catalyst?



(i) (ii)





(iii) (iv) (v) (vi)

26. A chemist trying to synthesize a particular compound attempts two different synthesis reactions. The equilibrium constants for the two reactions are 23.3 and 2.2×10^4 at room temperature. However, upon carrying out both reactions for 15 minutes, the chemist finds that the reaction with the smaller equilibrium constant produces more of the desired product. Explain how this might be possible.

27. This reaction has an equilibrium constant of $K_p = 2.26 \times 10^4$ at 298 K:

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

Calculate K_p for each reaction and predict whether reactants or products will be favored at equilibrium:

a. $CH_3OH(g) \rightleftharpoons CO(g) + 2\,H_2(g)$

b. $\frac{1}{2}CO(g) + H_2(g) \rightleftharpoons \frac{1}{2}CH_3OH(g)$

c. $2\,CH_3OH(g) \rightleftharpoons 2\,CO(g) + 4\,H_2(g)$

28. This reaction has an equilibrium constant of $K_p = 2.2 \times 10^6$ at 298 K:

$$2\,COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g)$$

Calculate K_p for each reaction and predict whether reactants or products will be favored at equilibrium:

a. $COF_2(g) \rightleftharpoons \frac{1}{2}CO_2(g) + \frac{1}{2}CF_4(g)$

b. $6\,COF_2(g) \rightleftharpoons 3\,CO_2(g) + 3\,CF_4(g)$

c. $2\,CO_2(g) + 2\,CF_4(g) \rightleftharpoons 4\,COF_2(g)$

29. Consider the reactions and their respective equilibrium constants:

$$NO(g) + \tfrac{1}{2}Br_2(g) \rightleftharpoons NOBr(g) \qquad K_p = 5.3$$
$$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g) \qquad K_p = 2.1 \times 10^{30}$$

Use these reactions and their equilibrium constants to predict the equilibrium constant for the following reaction:

$$N_2(g) + O_2(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g)$$

30. Use the following reactions and their equilibrium constants to predict the equilibrium constant for this reaction: $2A(s) \rightleftharpoons 3D(g)$

$$A(s) \rightleftharpoons \tfrac{1}{2}B(g) + C(g) \qquad K_1 = 0.0334$$
$$3\,D(g) \rightleftharpoons B(g) + 2C(g) \qquad K = 2.35$$

K_p, K_c, and Heterogeneous Equilibria

31. Calculate K_c for each reaction

a. $I_2(g) \rightleftharpoons 2\,I(g) \quad K_p = 6.26 \times 10^{-22}$(at 298 K)

b. $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)$

c. $I_2(g) + Cl_2(g) \rightleftharpoons 2\,ICl(g)\quad K_p = 81.9(\text{at } 298\text{ K})$

32. Calculate K_p for each reaction.

a. $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)\quad K_c = 5.9 \rightleftharpoons 10^{-3}(\text{at } 298\text{ K})$

b. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)\quad K_c = 3.7 \times 10^{8}(\text{at } 298\text{ K})$

c. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)\quad K_c = 4.10 \times 10^{-31}(\text{at } 298\text{ K})$

33. Write an equilibrium expression for each chemical equation involving one or more solid or liquid reactants or products.

a. $CO_3^{\,2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^{\,-}(aq) + OH^-(aq)$

b. $2\,KClO_3(s) \rightleftharpoons 2\,KCl(s) + 3\,O_2(g)$

c. $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

d. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^{\,+}(aq) + OH^-(aq)$

34. Find and fix the mistake in the equilibrium expression:

$$PCl_5(g) \rightleftharpoons PCl_3(l) + Cl_2(g)\quad K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Relating the Equilibrium Constant to Equilibrium Concentrations and Equilibrium Partial Pressures

35. Consider the reaction:

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

An equilibrium mixture of this reaction at a certain temperature has $[CO] = 0.105\text{ M}$, $[H_2] = 0.114\text{ M}$, and $[CH_3OH] = 0.185\text{ M}$. What is the value of the equilibrium constant (K_c) at this temperature?

36. Consider the reaction:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

An equilibrium mixture of this reaction at a certain temperature has $NH_4HS(s) = 0.278\text{ M}$ and $[H_2S] = 0.355\text{ M}$.. What is the value of the equilibrium constant (K_c) at this temperature?

37. Consider the reaction:

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

Complete the table. Assume that all concentrations are equilibrium concentrations in M.

T (K)	$[N_2]$	$[H_2]$	$[NH_3]$	K_c
500	0.115	0.105	0.439	________
575	0.110	________	0.128	9.6
775	0.120	0.140	________	0.0584

38. Consider the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

Complete the table. Assume that all concentrations are equilibrium concentrations in M.

T (°C)	$[H_2]$	$[I_2]$	$[HI]$	K_c
25	0.0355	0.0388	0.922	________

340	________	0.0455	0.387	9.6
445	0.0485	0.0468	________	50.2

39. Consider the reaction:

$$2\ \mathrm{NO}(g) + \mathrm{Br_2}(g) \rightleftharpoons 2\ \mathrm{NOBr}(g) \quad K_p = 28.4 \text{ at } 298\ \mathrm{K}$$

In a reaction mixture at equilibrium, the partial pressure of NO is 108 torr and that of Br_2 is 126 torr. What is the partial pressure of NOBr in this mixture?

40. Consider the reaction:

$$\mathrm{SO_2Cl_2}(g) \rightleftharpoons \mathrm{SO_2} + \mathrm{Cl_2}(g) \quad K_p = 2.91 \times 10^3 \text{ at } 298\ \mathrm{K}$$

In a reaction at equilibrium, the partial pressure of SO_2 is 137 torr and that of CL_2 is 285 torr. What is the partial pressure of SO_2Cl_2 in this mixture?

41. For the reaction $\mathrm{A}(g) \rightleftharpoons 2\ \mathrm{B}(g)$, a reaction vessel initially contains only A at a pressure of $P_A = 1.32$ atm. At equilibrium, $P_A = 0.25$ atm. Calculate the value of K_p. (Assume no changes in volume or temperature.)

42. For the reaction $2\ \mathrm{A}(g) \rightleftharpoons \mathrm{B}(g) + 2\ \mathrm{C}(g)$, a reaction vessel initially contains only A at a pressure of $P_A = 225$ mmHg. At equilibrium, $P_A = 55$ mmHg. Calculate the value of K_p. (Assume no changes in volume or temperature.)

43. Consider the reaction:

$$\mathrm{Fe^{3+}}(aq) + \mathrm{SCN^-}(aq) \rightleftharpoons \mathrm{FeSCN^{2+}}(aq)$$

A solution is made containing an initial $[\mathrm{Fe^{3+}}]$ of 1.0×10^{-3} M and an initial $[\mathrm{SCN^-}]$ of 8.0×10^{-4} M. At equilibrium, $[\mathrm{FeSCN^{2+}}] = 1.7 \times 10^{-4}$M. Calculate the value of the equilibrium constant (K_c).

44. Consider the reaction:

$$\mathrm{SO_2Cl_2}(g) \rightleftharpoons \mathrm{SO_2}(g) + \mathrm{Cl_2}(g)$$

A reaction mixture is made containing an initial $[\mathrm{SO_2Cl_2}]$ of 0.020 M. At equilibrium, $[\mathrm{Cl_2}] = 1.2 \times 10^{-2}$M. Calculate the value of the equilibrium constant (K_c).

45. Consider the reaction:

$$\mathrm{H_2}(g) + \mathrm{I_2}(g) \rightleftharpoons 2\ \mathrm{HI}(g)$$

A reaction mixture in a 3.67 L flask at a certain temperature initially contains 0.763 g H_2 and 96.9 g I_2, At equilibrium, the flask contains 90.4 g HI. Calculate the equilibrium constant (K_c) for the reaction at this temperature.

46. Consider the reaction:

$$\mathrm{CO}(g) + 2\ \mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_3OH}(g)$$

A reaction mixture in a 5.19 L flask at a certain temperature contains 26.9 g CO and 2.34 g H_2. At equilibrium, the flask contains 8.65 g CH_3OH. Calculate the equilibrium constant (K_c) for the reaction at this temperature.

The Reaction Quotient and Reaction Direction

47. Consider the reaction:

$$\mathrm{NH_4HS}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{H_2S}(g)$$

At a certain temperature, $K_c = 8.5 \times 10^{-3}$. A reaction mixture at this temperature containing solid NH_4HS has $[\mathrm{NH_3}] = 0.166$ M and $[\mathrm{H_2S}] = 0.166$ M. Will more of the solid form, or will some of the existing solid decompose as equilibrium is reached?

48. Consider the reaction:

$$2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g) \quad K_p = 2.4 \times 10^{-4} \text{ at } 1073\ K$$

A reaction mixture contains 0.112 atm of H_2, 0.055 atm of S_2, and 0.445 atm of H_2S. Is the reaction mixture at equilibrium? If not, in what direction will the reaction proceed?

49. Silver sulfate dissolves in water according to the reaction:

$$Ag_2SO_4(s) \rightleftharpoons 2\ Ag^+(aq) + SO_4^{2-}(aq)$$
$$K_c = 1.1 \times 10^{-5} \text{ at } 298\ K$$

A 1.5-L solution contains 6.55 g of dissolved silver sulfate. If additional solid silver sulfate is added to the solution, will it dissolve?

50. Nitrogen dioxide reacts with itself according to the reaction:

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_p = 6.7 \text{ at } 298\ K$$

A 2.25-L container contains 0.055 mol of NO_2 and 0.082 mol of N_2O_4 at 298 K. Is the reaction at equilibrium? If not, in what direction will the reaction proceed?

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

51. Consider the reaction and the associated equilibrium constant:

$$aA(g) \rightleftharpoons bB(g) \quad K_c = 4.0$$

Find the equilibrium concentrations of A and B for each value of a and b. Assume that the initial concentration of A in each case is 1.0 M and that no B is present at the beginning of the reaction.

a. $a = 1; b = 1$

b. $a = 2; b = 2$

c. $a = 1; b = 2$

52. Consider the reaction and the associated equilibrium constant:

$$aA(g) + bB(g) \rightleftharpoons cC(g) \quad K_c = 5.0$$

Find the equilibrium concentrations of A, B, and C for each value of a, b, and c. Assume that the initial concentrations of A and B are each 1.0 M and that no product is present at the beginning of the reaction.

a. $a = 1; b = 1; c = 2$

b. $a = 1; b = 1; c = 1$

c. $a = 2; b = 1; c = 1$ (set up equation for x; don't solve)

53. For the reaction, $K_c = 0.513$ at 500 K.

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

If a reaction vessel initially contains an N_2O_4 concentration of 0.0500 M at 500 K, what are the equilibrium concentrations of N_2O_4 and NO_2 at 500 K?

54. For the reaction, $K_c = 255$ at 1000 K.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

If a reaction mixture initially contains a CO concentration of 0.1500 M and a Cl_2 concentration of 0.175 M at 1000 K, what are the equilibrium concentrations of CO, Cl_2, and $COCl_2$ at 1000 K?

55. Consider the reaction:

$$NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g) \quad K_c = 4.0 \times 10^3 \text{ at } 1500\ K$$

$$NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g) \quad K_c = 4.0 \times 10^3 \text{ at } 1500 \text{ K}$$

If a mixture of solid nickel (II) oxide and 0.20 M carbon monoxide comes to equilibrium at 1500 K, what is the equilibrium concentration of CO_2?

56. Consider the reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 102 \text{ at } 500 \text{ K}$$

If a reaction mixture initially contains 0.110 M CO and 0.110 M H_2O, what is the equilibrium concentration of each of the reactants and products?

57. Consider the reaction:

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq) \quad K_c = 1.8 \times 10^{-5} \text{ at } 25\,^\circ\text{C}$$

If a solution initially contains 0.210 M $HC_2H_3O_2$, what is the equilibrium concentration of H_3O^+ at 25 °C?

58. Consider the reaction:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g) \quad K_c = 2.99 \times 10^{-7} \text{ at } 277^\circ \text{ C}$$

If a reaction mixture initially contains 0.175 M SO_2Cl_2, what is the equilibrium concentration of Cl_2 at $227\,^\circ\text{C}$?

59. Consider the reaction:

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_p = 1.11 \times 10^{-4} \text{ at } 150 \text{ K}$$

A reaction mixture initially contains a Br_2 partial pressure of 755 torr and a Cl_2 partial pressure of 735 torr at 150 K. Calculate the equilibrium partial pressure of BrCl.

60. Consider the reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_p = 0.0611 \text{ at } 2000 \text{ K}$$

A reaction mixture initially contains a CO partial pressure of 1344 torr and a H_2O partial pressure of 1766 torr at 2000 K. Calculate the equilibrium partial pressures of each of the products.

61. Consider the reaction:

$$A(g) \rightleftharpoons B(g) + C(g)$$

Find the equilibrium concentrations of A, B, and C for each value of K_c. Assume that the initial concentration of A in each case is 1.0 M and that the reaction mixture initially contains no products. Make any appropriate simplifying assumptions.

a. $K_c = 1.0$

b. $K_c = 0.010$

c. $K_c = 1.0 \times 10^{-5}$

62. Consider the reaction:

$$A(g) \rightleftharpoons 2\,B(g)$$

Find the equilibrium partial pressures of A and B for each value of K. Assume that the initial partial pressure of B in each case is 1.0 atm and that the initial partial pressure of A is 0.0 atm. Make any appropriate simplifying assumptions.

a. $K_c = 1.0$

b. $K_c = 1.0 \times 10^{-4}$

c. $K_c = 1.0 \times 10^5$

Le Châtelier's Principle

63. Consider this reaction at equilibrium:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance:

a. $COCl_2$ is added to the reaction mixture.

b. Cl_2 is added to the reaction mixture.

c. $COCl_2$ is removed from the reaction mixture.

64. Consider this reaction at equilibrium:

$$2\ BrNO(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$$

Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

a. NO is added to the reaction mixture.

b. BrNO is added to the reaction mixture.

c. Br_2 is removed from the reaction mixture.

65. Consider this reaction at equilibrium:

$$2\ KClO_3(s) \rightleftharpoons 2\ KCl(s) + 3\ O_2(g)$$

Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

a. O_2 is removed from the reaction mixture.

b. KCl is added to the reaction mixture.

c. $KClO_3$ is added to the reaction mixture.

d. O_2 is added to the reaction mixture.

66. Consider this reaction at equilibrium:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

a. C is added to the reaction mixture.

b. H_2O is condensed and removed from the reaction mixture.

c. CO is added to the reaction mixture.

d. H_2 is removed from the reaction mixture.

67. Each reaction is allowed to come to equilibrium, and then the volume is changed as indicated. Predict the effect (shift right, shift left, or no effect) of the indicated volume change.

a. $I_2(g) \rightleftharpoons 2\ I(g)$ (volume is increased)

b. $2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g)$ (volume is decreased)

c. $I_2(g) + Cl_2(g) \rightleftharpoons 2\ ICl(g)$ (volume is decreased)

68. Each reaction is allowed to come to equilibrium, and then the volume is changed as indicated. Predict the effect (shift right, shift left, or no effect) of the indicated volume change.

a. $CO(g) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ (volume is decreased)

b. $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ (volume is increased)

c. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (volume is increased)

69. This reaction is endothermic:

$$C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$$

Predict the effect (shift right, shift left, or no effect) of increasing and decreasing the reaction temperature. How does the value of the equilibrium constant depend on temperature?

70. This reaction is exothermic:

$$C_6H_{12}O_6(6) + 6\ O_2(g) \rightleftharpoons 6\ CO_2(g) + 6\ H_2O(g)$$

Predict the effect (shift right, shift left, or no effect) of increasing and decreasing the reaction temperature. How does the value of the equilibrium constant depend on temperature?

71. Coal, which is primarily carbon, can be converted to natural gas, primarily CH_4, by the exothermic reaction:

$$C(s) + 2\,H_2(g) \rightleftharpoons CH_4(g)$$

Which disturbance favors CH_4 at equilibrium?

a. adding more C to the reaction mixture
b. adding more H_2 to the reaction mixture
c. raising the temperature of the reaction mixture
d. lowering the volume of the reaction mixture
e. adding a catalyst to the reaction mixture
f. adding neon gas to the reaction mixture

72. Coal can be used to generate hydrogen gas (a potential fuel) by the endothermic reaction:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

If this reaction mixture is at equilibrium, predict whether each disturbance will result in the formation of additional hydrogen gas, the formation of less hydrogen gas, or have no effect on the quantity of hydrogen gas.

a. adding C to the reaction mixture
b. adding H_2O to the reaction mixture
c. raising the temperature of the reaction mixture
d. increasing the volume of the reaction mixture
e. adding a catalyst to the reaction mixture
f. adding an inert gas to the reaction mixture

Cumulative Problems

73. Carbon monoxide replaces oxygen in oxygenated hemoglobin according to the reaction:

$$HbO_2(aq) + CO(aq) \rightleftharpoons HbCO(aq) + O_2(aq)$$

a. Use the reactions and associated equilibrium constants at body temperature to find the equilibrium constant for the reaction just shown.

$$Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq) \quad K_c = 1.8$$
$$Hb(aq) + CO(aq) \rightleftharpoons HbCO(aq) \quad K_c = 306$$

b. Suppose that an air mixture becomes polluted with carbon monoxide at a level of 0.10%. Assuming the air contains 20.0% oxygen and that the oxygen and carbon monoxide ratios that dissolve in the blood are identical to the ratios in the air, what is the ratio of HbCO to HbO_2 in the bloodstream? Comment on the toxicity of carbon monoxide.

74. Nitrogen monoxide is a pollutant in the lower atmosphere that irritates the eyes and lungs and leads to the formation of acid rain. Nitrogen monoxide forms naturally in the atmosphere according to the endothermic reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad K_p = 4.1 \times 10^{-31} \text{ at } 298\text{ K}$$

Use the ideal gas law to calculate the concentrations of nitrogen and oxygen present in air at a pressure of 1.0 atm and a temperature of 298 K. Assume that nitrogen composes 78% of air by volume and that oxygen composes 21% of air. Find the "natural" equilibrium concentration of NO in air in units of molecules/cm^3. How would you expect this concentration to change in an automobile engine in which combustion is occurring?

75. The reaction $CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$ has $K_p = 5.78$ at 1200 K.

a. Calculate the total pressure at equilibrium when 4.45 g of CO_2 is introduced into a 10.0-L container and heated to 1200 K in the presence of 2.00 g of graphite.
b. Repeat the calculation of part a in the presence of 0.50 g of graphite.

76. A mixture of water and graphite is heated to 600 K. When the system comes to equilibrium, it contains 0.13 mol of H_2, 0.13 mol of CO, 0.43 mol of H_2O, and some graphite. Some O_2 is added to the system, and a spark is applied so that the H_2 reacts completely with the O_2. Find the amount of CO in the flask when the system returns to equilibrium.

77. At 650 K, the reaction $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$ has $K_p = 0.026$. A 10.0-L container at 650 K has 1.0 g of MgO(s) and CO_2 at $P = 0.0260$ atm. The container is then compressed to a volume of 0.100 L. Find the mass of MgO(s) that is formed.

78. A system at equilibrium contains $I_2(g)$ at a pressure of 0.21 atm and I(g) at a pressure of 0.23 atm. The system is then compressed to half its volume. Find the pressure of each gas when the system returns to equilibrium.

79. Consider the exothermic reaction:

$$C_2H_4(g) + Cl_2(g) \rightleftharpoons C_2H_4Cl_2(g)$$

If you were trying to maximize the amount of $C_2H_4Cl_2$ produced, which tactic might you try? Assume that the reaction mixture reaches equilibrium.

a. increasing the reaction volume
b. removing $C_2H_4Cl_2$ from the reaction mixture as it forms
c. lowering the reaction temperature
d. adding Cl_2

80. Consider the endothermic reaction:

$$C_2H_4(g) + I_2(g) \rightleftharpoons C_2H_4I_2(g)$$

If you were trying to maximize the amount of $C_2H_4I_2$ produced, which tactic might you try? Assume that the reaction mixture reaches equilibrium.

a. decreasing the reaction volume
b. removing I_2 from the reaction mixture
c. raising the reaction temperature
d. adding C_2H_4 to the reaction mixture

81. Consider the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

A reaction mixture at equilibrium at 175 K contains $P_{H_2} = 0.958$ atm, $P_{I_2} = 0.877$ atm, and $P_{HI} = 0.020$ atm. A second reaction mixture, also at 175 K, contains $P_{H_2} = P_{I_2} = 0.621$ atm, and $P_{HI} = 0.101$ atm. Is the second reaction at equilibrium? If not, what will be the partial pressure of HI when the reaction reaches equilibrium at 175 K?

82. Consider the reaction:

$$2\ H_2S(g) + SO_2(g) \rightleftharpoons 3\ S(s) + 2\ H_2O(g)$$

A reaction mixture initially containing 0.500 M H_2S and 0.500 M SO_2 contains 0.0011 M H_2O at a certain temperature. A second reaction mixture at the same temperature initially contains $[H_2S] = 0.250$ M and $[SO_2] = 0.325$ M. Calculate the equilibrium concentration of H_2O in the second mixture at this temperature.

83. Ammonia can be synthesized according to the reaction:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) \quad K_p = 5.3 \times 10^{-5} \text{ at } 725\ K$$

A 200.0-L reaction container initially contains 1.27 kg of N_2 and 0.310 kg of H_2 at 725 K. Assuming ideal gas behavior, calculate the mass of NH_3 (in g) present in the reaction mixture at equilibrium. What is the percent yield of the reaction under these conditions?

84. Hydrogen can be extracted from natural gas according to the reaction:

$$CH_4(g) + CO_2(g) \rightleftharpoons 2\ CO(g) + 2\ H_2(g) \quad K_p = 45 \times 10^2 \text{ at } 825\ K$$

An 85.0-L reaction container initially contains 22.3 kg of CH_4 and 55.4 kg of CO_2 at 825 K. Assuming ideal gas behavior, calculate the mass of H_2 (in g) present in the reaction mixture at equilibrium. What is the percent yield of the reaction under these conditions?

85. The system described by the reaction: $CO(g) + Cl(g) \rightleftharpoons COCl_2(g)$ is at equilibrium at a given temperature when $P_{co} = 0.30$ atm, $P_{cl_2} = 0.10$ atm, and $P_{cocl_2} = 0.60$ atm. Pressure of $Cl_2(g) = 0.40$ atm is added. Find the pressure of CO when the system returns to equilibrium.

86. A reaction vessel at 27 °C contains a mixture of $SO_2(P = 3.00\text{ atm})$ and $O_2(P = 1.00\text{ atm})$. When a catalyst is added, this reaction takes place: $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$.
At equilibrium, the total pressure is 3.75 atm. Find the value of K_c.

87. At 70 K, CCl_4 decomposes to carbon and chlorine. The K_p for the decomposition is 0.76. Find the starting pressure of CCl_4 at this temperature that will produce a total pressure of 1.0 atm at equilibrium.

88. The equilibrium constant for the reaction $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$ is 3.0. Find the amount of NO_2 that must be added to 2.4 mol of SO_2 in order to form 1.2 mol of SO_3 at equilibrium.

89. A sample of $CaCO_3(s)$ is introduced into a sealed container of volume 0.654 L and heated to 1000 K until equilibrium is reached. The K_p for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is 3.9×10^{-2} at this temperature. Calculate the mass of CaO(s) that is present at equilibrium.

90. An equilibrium mixture contains N_2O_4, ($P = 0.28$) and NO_2 ($P = 1.1$ atm) at 350 K. The volume of the container is doubled at constant temperature. Calculate the equilibrium pressures of the two gases when the system reaches a new equilibrium.

91. Carbon monoxide and chlorine gas react to form phosgene:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \quad K_p = 3.10 \text{ at } 700\text{ K}$$

If a reaction mixture initially contains 215 torr of CO and 245 torr of Cl_2, what is the mole fraction of $COCl_2$ when equilibrium is reached?

92. Solid carbon can react with gaseous water to form carbon monoxide gas and hydrogen gas. The equilibrium constant for the reaction at 700.0 K is $K_p = 1.60 \times 10^{-3}$. If a 1.55 L reaction vessel initially contains 145 torr of water at 700.0 K in contact with excess solid carbon, find the percent by mass of hydrogen gas of the gaseous reaction mixture at equilibrium.

Challenge Problems

93. Consider the reaction:

$$2\ NO(g) + O_2(g) \rightleftharpoons 2\ NO_2(g)$$

a. A reaction mixture at 175 K initially contains 522 torr of NO and 421 torr of O_2. At equilibrium, the total pressure in the reaction mixture is 748 torr. Calculate K_p at this temperature.

b. A second reaction mixture at 175 K initially contains 255 torr of NO and 185 torr of O_2. What is the equilibrium partial pressure of NO_2 in this mixture?

94. Consider the reaction:

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) \quad K_p = 0.355 \text{ at } 950\text{ K}$$

A 2.75-L reaction vessel at 950 K initially contains 0.100 mol of SO_2 and 0.100 mol of O_2. Calculate the total pressure (in atmospheres) in the reaction vessel when equilibrium is reached.

95. Nitrogen monoxide reacts with chlorine gas according to the reaction:

$$2\ NO(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g) \quad K_p = 0.27 \text{ at } 700\text{ K}$$

A reaction mixture initially contains equal partial pressures of NO and Cl_2. At equilibrium, the partial pressure of NOCl is 115 torr. What were the initial partial pressures of NO and Cl_2?

96. At a given temperature, a system containing $O_2(g)$ and some oxides of nitrogen are described by these reactions:

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \quad K_p = 10^4$$
$$2\,NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_p = 0.10$$

A pressure of 1 atm of $N_2O_4(g)$ is placed in a container at this temperature. Predict which, if any, component (other than N_2O_4) will be present at a pressure greater than 0.2 atm at equilibrium.

97. A sample of pure NO_2 is heated to 337 °C, at which temperature it partially dissociates according to the equation:

$$2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)$$

At equilibrium, the density of the gas mixture is 0.520 g/L at 0.750 atm. Calculate K_c for the reaction.

98. When $N_2O_5(g)$ is heated, it dissociates into $N_2O_3(g)$ and $O_2(g)$ according to the reaction:

$$N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g) \quad K_c = 7.75 \text{ at a given temperature}$$

The $N_2O_3(g)$ dissociates to give $N_2O_3(g)$ and $O_2(g)$ according to the reaction:

$$N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g) \quad K_c = 4.00 \text{ at the same temperature}$$

When 4.00 mol of $N_2O_5(g)$ is heated in a 1.00-L reaction vessel to this temperature, the concentration of $O_2(g)$ at equilibrium is 4.50 mol/L. Find the concentrations of all the other species in the equilibrium system.

99. A sample of SO_3 is introduced into an evacuated sealed container and heated to 600 K. The following equilibrium is established:

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

The total pressure in the system is 3.0 atm, and the mole fraction of O_2 is 0.12. Find K_p.

Conceptual Problems

100. A reaction $A(g) \rightleftharpoons B(g)$ has an equilibrium constant of 1.0×10^{-4}. For which of the initial reaction mixtures is the *x is small* approximation most likely to apply?

a. $[A] = 0.0010\ M$; $[B] = 0.00\ M$

b. $[A] = 0.00\ M$; $[B] = 0.10\ M$

c. $[A] = 0.10\ M$; $[B] = 0.10\ M$

d. $[A] = 0.10\ M$; $[B] = 0.00\ M$

101. The reaction $A(g) \rightleftharpoons 2\,B(g)$ has an equilibrium constant of $K_c = 1.0$ at a given temperature. If a reaction vessel contains equal initial amounts (in moles) of A and B, will the direction in which the reaction proceeds depend on the volume of the reaction vessel? Explain.

102. A particular reaction has an equilibrium constant of $K_p = 0.50.$. A reaction mixture is prepared in which all the reactants and products are in their standard states. In which direction will the reaction proceed?

103. Consider the reaction:

$$aA(g) \rightleftharpoons bB(g)$$

Each of the entries in the table represents equilibrium partial pressures of A and B under different initial conditions. What are the values of *a* and *b* in the reaction?

P_A (atm)	P_B (atm)
4.0	2.0
2.0	1.4
1.0	1.0
0.50	0.71

0.25	0.50

104. Consider the simple one-step reaction:

$$A(g) \rightleftharpoons B(g)$$

Since the reaction occurs in a single step, the forward reaction has a rate of $k_{for}[A]$ and the reverse reaction has a rate of $k_{rev}[B]$. What happens to the rate of the forward reaction when we increase the concentration of A? How does this explain the reason behind Le Châtelier's principle?

Questions for Group Work

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

105. The reactions shown here can be combined to sum to the overall reaction $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ by reversing some and/or dividing all the coefficients by a number. As a group, determine how the reactions need to be modified to sum to the overall process. Then have each group member determine the value of K for one of the reactions to be combined. Finally, combine all the values of K to determine the value of K for the overall reaction.

a. $C(s) + O_2(g) \rightarrow CO_2(g) \quad K = 1.363 \times 10^{69}$

b. $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \quad K = 1.389 \times 10^{80}$

c. $2CO(g) + O_2(g) \rightarrow 2CO_2(g) \quad K = 1.477 \times 10^{90}$

106. Consider the reaction: $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$.

a. Write the equilibrium constant expression for this reaction.

If some hydrogen is added, before the reaction shifts:

b. How will the numerator and denominator of the expression in part a compare to the value at equilibrium?

c. Will Q be larger or smaller than K? Why?

d. Will the reaction have to shift forward or backward to retain equilibrium? Explain.

e. Are your answers for b–d consistent with Le Châtelier's principle? Explain.

107. For the reaction $A \rightarrow B$, the ratio of products to reactants at equilibrium is always the same number, no matter how much A or B is initially present. Interestingly, in contrast, the ratio of products to reactants for the reaction $C \rightarrow 2\,D$ does depend on how much of C and D you have initially. Explain this observation. Which ratio is independent of the starting amounts of C and D? Answer in complete sentences.

108. Solve each of the expressions for x using the quadratic formula and the *x is small* approximation. In which of the following expressions is the *x is small* approximation valid?

a. $x^2/(0.2 - x) = 1.3 \times 10^4$

b. $x^2/(0.2 - x) = 1.3$

c. $x^2/(0.2 - x) = 1.3 \times 10^{-4}$

d. $x^2/(0.01 - x) = 1.3 \times 10^{-4}$

In a complete sentence, describe the factor(s) that tend to make the *x is small* approximation valid in an expression.

109. Have each group member explain to the group what happens if a system at equilibrium is subject to one of the following changes and why.

a. The concentration of a reactant is increased.

b. A solid product is added.

c. The volume is decreased.

d. The temperature is raised.

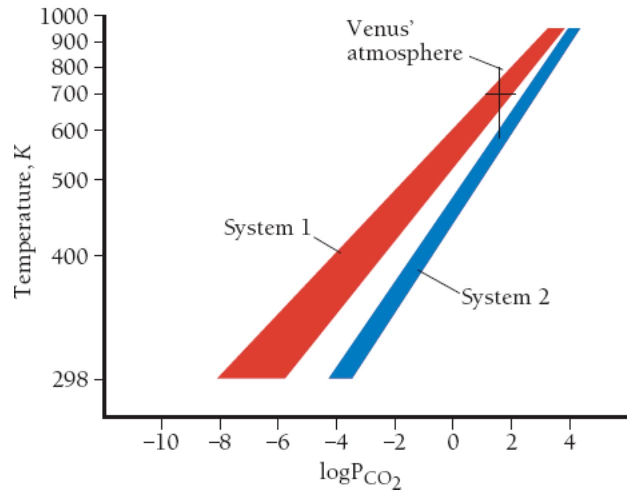
Data Interpretation and Analysis

110. The atmosphere of the planet Venus is almost entirely composed of carbon dioxide (about 96.5% carbon dioxide). The carbon dioxide on Venus could be in equilibrium with carbonate ions in minerals on the planet's crust. Two possible equilibrium systems involve $CaSio_3$ and $MgSiO_3$:

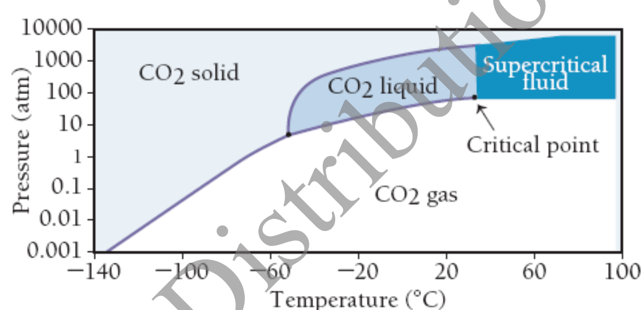
$CaSiO_3(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + SiO_2(s)$ system 1

$MgSiO_3(s) + CaCO_3(s) + SiO_2(s) \rightleftharpoons CaMgSi_2O_6(s) + CO_2(g)$ system 2

The first graph that follows shows the expected pressures of carbon dioxide (in atm) at different temperatures for each of these equilibrium systems. (Note that both axes on this graph are logarithmic.) The second graph is a phase diagram for carbon dioxide. Examine the graphs and answer the questions.



Carbon Dioxide Concentrations for Equilibrium Systems 1 and 2



Carbon Dioxide Phase Diagram

a. The partial pressure of carbon dioxide on the surface of Venus is 91 atm. What is the value of the equilibrium constant (K_p) if the Venusian carbon dioxide is in equilibrium according to system 1? According to system 2?

b. The approximate temperature on the surface of Venus is about 740 K. What is the approximate carbon dioxide concentration for system 1 at this temperature? For system 2? (Use a point at approximately the middle of each colored band, which represents the range of possible values, to estimate the carbon dioxide concentration.)

c. Use the partial pressure of carbon dioxide on the surface of Venus given in part a to determine which of the two equilibrium systems is more likely to be responsible for the carbon dioxide on the surface of Venus.

d. From the carbon dioxide phase diagram, determine the minimum pressure required for supercritical carbon dioxide to form. If the partial pressure of carbon dioxide on the surface of Venus was higher in the distant past, could supercritical carbon dioxide have existed on the surface of Venus?

Answers to Conceptual Connections

Cc 15.1 (**b**) The reaction mixture will contain $[A] = 0.1\ M$ and $[B] = 1.0\ M$ so that $[B]/[A] = 10$.

Cc 15.2 (**b**) The reaction is reversed and divided by two. Therefore, you invert the equilibrium constant and take the square root of the result. $K = (1/0.010)^{1/2} = 10$.

Cc 15.3 **(a)** When $a + b = c + d$, the quantity Δn is zero so that $K_p = K_c(RT)^0$. Since $(RT)^0$ is equal to 1, $K_p = K_c$.

Cc 15.4 **(b)** Since Δn for gaseous reactants and products is zero, $K_p$equalsK_c.

Cc 15.5 **(c)** Because N_2O_4 and NO_2 are both in their standard states, they each have a partial pressure of 1.0

atm. Consequently, $Q_P = 1$. Since $K_p = 0.15, Q_p > K_p$, and the reaction proceeds to the left.

Cc 15.6 **(a)** The *x is small* approximation is most likely to apply to a reaction with a small equilibrium constant and an initial concentration of reactant that is not too small. The bigger the equilibrium constant and the smaller the initial concentration of reactant, the less likely that the *x is small* approximation will apply.

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