Questions and Problems

The Concept of Equilibrium and the Equilibrium Constant

Review Questions

14.1 Define equilibrium. Give two examples of a dynamic equilibrium.

14.2 Explain the difference between physical equilibrium and chemical equilibrium. Give two examples of each.

14.3 What is the law of mass action?

14.4 Briefly describe the importance of equilibrium in the study of chemical reactions.

Equilibrium Constant Expressions

Review Questions

14.5 Define homogeneous equilibrium and heterogeneous equilibrium. Give two examples of each.

14.6 What do the symbols K_c and K_P represent?

14.7 Write the expressions for the equilibrium constants K_P of the following thermal decomposition reactions:

(a) $2NaHCO_3(s) \rightleftharpoons$
$Na_2CO_3(s) + CO_2(g) + H_2O(g)$

(b) $2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g)$

14.8 Write equilibrium constant expressions for K_c, and for K_P, if applicable, for the following processes:

(a) $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$

(b) $3O_2(g) \rightleftharpoons 2O_3(g)$

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

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

(e) $HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$

(f) $2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$

14.9 Write the equilibrium constant expressions for K_c and K_P, if applicable, for the following reactions:

(a) $2NO_2(g) + 7H_2(g) \rightleftharpoons 2NH_3(g) + 4H_2O(l)$

(b) $2ZnS(s) + 3O_2(g) \rightleftharpoons 2ZnO(s) + 2SO_2(g)$

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

(d) $C_6H_5COOH(aq) \rightleftharpoons$
$C_6H_5COO^-(aq) + H^+(aq)$

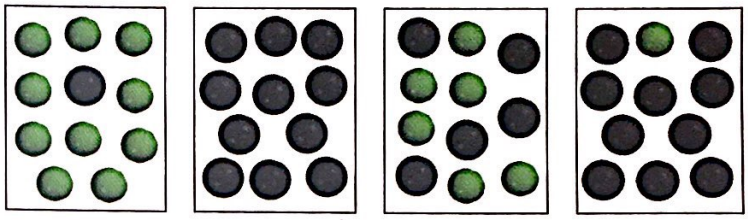
14.10 Write the equation relating K_c to K_P, and define all the terms.

14.11 What is the rule for writing the equilibrium constant for the overall reaction involving two or more reactions?

14.12 Give an example of a multiple equilibria reaction.

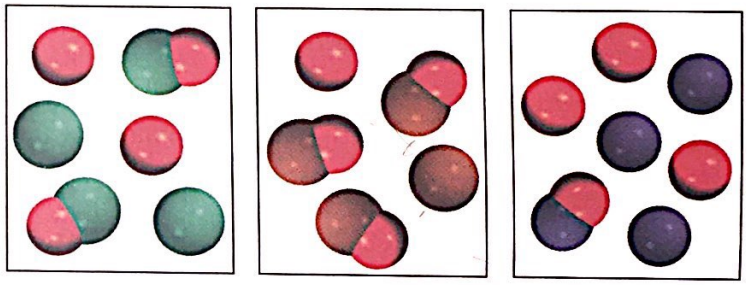
Problems

14.13 The equilibrium constant for the reaction A $\rightleftharpoons$ B is $K_c = 10$ at a certain temperature. (1) Starting with only reactant A, which of the diagrams shown here best represents the system at equilibrium? (2) Which of the diagrams best represents the system at equilibrium if $K_c = 0.10$? Explain why you can calculate K_c in each case without knowing the volume of the container. The gray spheres represent the A molecules and the green spheres represent the B molecules.



(a) (b) (c) (d)

• **14.14** The following diagrams represent the equilibrium state for three different reactions of the type A + X $\rightleftharpoons$ AX (X = B, C, or D):



A + B $\rightleftharpoons$ AB A + C $\rightleftharpoons$ AC A + D $\rightleftharpoons$ AD

(a) Which reaction has the largest equilibrium constant? (b) Which reaction has the smallest equilibrium constant?

• 14.15 The equilibrium constant (K_c) for the reaction

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

is 4.17×10^{-34} at 25°C. What is the equilibrium constant for the reaction

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

at the same temperature?

• **14.16** Consider the following equilibrium process at 700°C:

$$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g)$$

Analysis shows that there are 2.50 moles of H_2, 1.35×10^{-5} mole of S_2, and 8.70 moles of H_2S present in a 12.0-L flask. Calculate the equilibrium constant K_c for the reaction.

• 14.17 What is K_P at 1273°C for the reaction

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

if K_c is 2.24×10^{22} at the same temperature?

Difficulty Levels: • Easy •• Medium ••• Difficult.

•• **14.48** The equilibrium constant K_c for the reaction

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

is 4.2 at 1650°C. Initially 0.80 mol H_2 and 0.80 mol CO_2 are injected into a 5.0-L flask. Calculate the concentration of each species at equilibrium.

Factors That Affect Chemical Equilibrium

Review Questions

14.49 Explain Le Châtelier's principle. How can this principle help us maximize the yields of reactions?

14.50 Use Le Châtelier's principle to explain why the equilibrium vapor pressure of a liquid increases with increasing temperature.

14.51 List four factors that can shift the position of an equilibrium. Only one of these factors can alter the value of the equilibrium constant. Which one is it?

14.52 Does the addition of a catalyst have any effects on the position of an equilibrium?

Problems

• 14.53 Consider the following equilibrium system involving SO_2, Cl_2, and SO_2Cl_2 (sulfuryl dichloride):

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

Predict how the equilibrium position would change if (a) Cl_2 gas were added to the system; (b) SO_2Cl_2 were removed from the system; (c) SO_2 were removed from the system. The temperature remains constant.

• **14.54** Heating solid sodium bicarbonate in a closed vessel establishes the following equilibrium:

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

What would happen to the equilibrium position if (a) some of the CO_2 were removed from the system; (b) some solid Na_2CO_3 were added to the system; (c) some of the solid $NaHCO_3$ were removed from the system? The temperature remains constant.

• 14.55 Consider the following equilibrium systems:

(a) $A \rightleftharpoons 2B$ $\quad \Delta H° = 20.0$ kJ/mol
(b) $A + B \rightleftharpoons C$ $\quad \Delta H° = -5.4$ kJ/mol
(c) $A \rightleftharpoons B$ $\quad \Delta H° = 0.0$ kJ/mol

Predict the change in the equilibrium constant K_c that would occur in each case if the temperature of the reacting system were raised.

• **14.56** What effect does an increase in pressure have on each of the following systems at equilibrium? The temperature is kept constant and, in each case, the reactants are in a cylinder fitted with a movable piston.

(a) $A(s) \rightleftharpoons 2B(s)$
(b) $2A(l) \rightleftharpoons B(l)$
(c) $A(s) \rightleftharpoons B(g)$
(d) $A(g) \rightleftharpoons B(g)$
(e) $A(g) \rightleftharpoons 2B(g)$

•• 14.57 Consider the equilibrium

$$2I(g) \rightleftharpoons I_2(g)$$

What would be the effect on the position of equilibrium of (a) increasing the total pressure on the system by decreasing its volume; (b) adding I_2 to the reaction mixture; and (c) decreasing the temperature?

• **14.58** Consider the following equilibrium process:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \quad \Delta H° = 92.5 \text{ kJ/mol}$$

Predict the direction of the shift in equilibrium when (a) the temperature is raised; (b) more chlorine gas is added to the reaction mixture; (c) some PCl_3 is removed from the mixture; (d) the pressure on the gases is increased; (e) a catalyst is added to the reaction mixture.

• 14.59 Consider the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H° = -198.2 \text{ kJ/mol}$$

Comment on the changes in the concentrations of SO_2, O_2, and SO_3 at equilibrium if we were to (a) increase the temperature; (b) increase the pressure; (c) increase SO_2; (d) add a catalyst; (e) add helium at constant volume.

• **14.60** In the uncatalyzed reaction

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

the pressure of the gases at equilibrium are $P_{N_2O_4} = 0.377$ atm and $P_{NO_2} = 1.56$ atm at 100°C. What would happen to these pressures if a catalyst were added to the mixture?

•• 14.61 Consider the gas-phase reaction

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

Predict the shift in the equilibrium position when helium gas is added to the equilibrium mixture (a) at constant pressure and (b) at constant volume.

•• **14.62** Consider the following equilibrium reaction in a closed container:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

What will happen if (a) the volume is increased; (b) some CaO is added to the mixture; (c) some $CaCO_3$ is removed; (d) some CO_2 is added to the mixture; (e) a few drops of a NaOH solution are added to the mixture; (f) a few drops of a HCl solution are added to the mixture (ignore the reaction between CO_2 and water); (g) temperature is increased

Additional Problems

• 14.63 Consider the statement: "The equilibrium constant of a reacting mixture of solid NH_4Cl and gase