4.E: Fundamental Equilibrium Concepts (Exercises)

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4.E.1: 13.1: Chemical Equilibria Exercises

4.E.1.1: Q13.1.1

What does it mean to describe a reaction as “reversible”?

4.E.1.2: S13.1.1

The reaction can proceed in both the forward and reverse directions.

4.E.1.3: Q13.1.2

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

4.E.1.4: Q13.1.3

If a reaction is reversible, when can it be said to have reached equilibrium?

4.E.1.5: S13.1.3

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the reactions continue to occur, but at equivalent rates.

4.E.1.6: Q13.1.4

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

4.E.1.7: Q13.1.5

If the concentrations of products and reactants are equal, is the system at equilibrium?

4.E.1.8: S13.1.5

The concept of equilibrium does not imply equal concentrations, though it is possible.

4.E.2: 13.2: Equilibrium Constant Exercises

4.E.2.1: Q13.2.1

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

4.E.2.2: Q13.2.2

Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown below:

4.E.2.3: S13.2.2

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

4.E.2.4: Q13.2.3

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

\[\ce{2NO2}(g) \rightleftharpoons \ce{N2O4}(g)\]

4.E.2.5: Q13.2.4

Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

4.E.2.6: Q13.2.5

1. (a) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
2. (b) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathrm{Pb^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) \rightleftharpoons \mathrm{PbCl_2}(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

4.E.2.7: S13.2.5

(a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*; (b) $K_c = \dfrac{1}{[\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).

4.E.2.8: Q13.2.6

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

a. Write the expression for the equilibrium constant for the reaction represented by the equation $\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
b. Write the expression for the equilibrium constant for the reaction represented by the equation $3\,\mathrm{Ba^{2+}}(aq) + 2\,\mathrm{PO_4^{3-}}(aq) \rightleftharpoons \mathrm{Ba_3(PO_4)_2}(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

4.E.2.9: Q13.2.7

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3\,\mathrm{C_2H_2}(g) \longrightarrow \mathrm{C_6H_6}(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

4.E.2.10: S13.2.7

Since $K_c = \dfrac{[\mathrm{C_6H_6}]}{[\mathrm{C_2H_2}]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

4.E.2.11: Q13.2.8

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $\mathrm{KI}(aq) + \mathrm{I_2}(aq) \rightleftharpoons \mathrm{KI_3}(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^-.

4.E.2.12: Q13.2.9

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

4.E.2.13: S13.2.9

$K_c > 1$

4.E.2.14: Q13.2.10

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

4.E.2.15: Q13.2.11

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$
b. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$
c. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
d. $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$
e. $P_4(g) + 5\,O_2(g) \rightleftharpoons P_4O_{10}(s)$
f. $Br_2(g) \rightleftharpoons 2\,Br(g)$
g. $CH_4(g) + 2\,O_2(g) \rightleftharpoons CO_2(g) + 2\,H_2O(l)$
h. $CuSO_4 \cdot 5\,H_2O(s) \rightleftharpoons CuSO_4(s) + 5\,H_2O(g)$

4.E.2.16: S13.2.11

(a) $Q_c = \frac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$; (b) $Q_c = \frac{[NO]^2}{[N_2][O_2]}$; (c) $Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (d) Q_c = [SO_2]; (e) $Q_c = \frac{1}{[P_4][O_2]^5}$; (f) $Q_c = \frac{[Br]^2}{[Br_2]}$; (g) $Q_c = \frac{[CO_2]}{[CH_4][O_2]^2}$; (h) Q_c = [H_2O]^5

4.E.2.17: Q13.2.12

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$
b. $4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g)$
c. $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
d. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
e. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
f. $2\,Pb(NO_3)_2(s) \rightleftharpoons 2\,PbO(s) + 4\,NO_2(g) + O_2(g)$
g. $2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(l)$
h. $S_8(g) \rightleftharpoons 8\,S(g)$

4.E.2.18: S13.2.12

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad K_c = 17$; [NH_3] = 0.20 *M*, [N_2] = 1.00 *M*, [H_2] = 1.00 *M*
b. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 3.0 atm, N_2 = 2.0 atm, H_2 = 1.0 atm
c. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_c = 0.230$; [SO_3] = 0.00 *M*, [SO_2] = 1.00 *M*, [O_2] = 1.00 *M*
d. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_P = 16.5$; initial pressures: SO_3 = 1.00 atm, SO_2 = 1.00 atm, O_2 = 1.00 atm
e. $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_c = 4.6 \times 10^4$; [NO] = 1.00 *M*, [Cl_2] = 1.00 *M*, [NOCl] = 0 *M*
f. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad K_P = 0.050$; initial pressures: NO = 10.0 atm, N_2 = O_2 = 5 atm

4.E.2.19: S13.2.13

(a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

4.E.2.20: Q13.2.14

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad K_c = 17$; [NH_3] = 0.50 *M*, [N_2] = 0.15 *M*, [H_2] = 0.12 *M*
b. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 2.00 atm, N_2 = 10.00 atm, H_2 = 10.00 atm
c. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_c = 0.230$; [SO_3] = 2.00 *M*, [SO_2] = 2.00 *M*, [O_2] = 2.00 *M*
d. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_P = 6.5\ \text{atm}$; initial pressures: SO_2 = 1.00 atm, O_2 = 1.130 atm, SO_3 = 0 atm
e. $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_P = 2.5 \times 10^3$; initial pressures: NO = 1.00 atm, Cl_2 = 1.00 atm, NOCl = 0 atm

f. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad K_c = 0.050$; $[N_2]$ = 0.100 *M*, $[O_2]$ = 0.200 *M*, [NO] = 1.00 *M*

4.E.2.21: Q13.2.15

The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

\[\ce{N2}(g)+\ce{3H2}(g) \rightleftharpoons \ce{2NH3}(g)\]

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52

4.E.2.22: S13.2.15

The system will shift toward the reactants to reach equilibrium.

4.E.2.23: Q13.2.16

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

\(\ce{SO2Cl2}(g) \rightleftharpoons \ce{SO2}(g)+\ce{Cl2}(g)\)

$[SO_2Cl_2]$ = 0.12 *M*, $[Cl_2]$ = 0.16 *M* and $[SO_2]$ = 0.050 *M*. K_c for the reaction is 0.078.

4.E.2.24: Q13.2.17

Which of the systems described in Exercise give homogeneous equilibria? Which give heterogeneous equilibria?

4.E.2.25: S13.2.17

(a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

4.E.2.26: Q13.2.18

Which of the systems described in Exercise give homogeneous equilibria? Which give heterogeneous equilibria?

4.E.2.27: Q13.2.19

For which of the reactions in Exercise does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

4.E.2.28: S13.2.19

This situation occurs in (a) and (b).

4.E.2.29: Q13.2.19

For which of the reactions in Exercise does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

4.E.2.30: Q13.2.20

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.50 \text{ at } 400^\circ C$
b. $H_2 + I_2 \rightleftharpoons 2\,HI \quad K_c = 50.2 \text{ at } 448^\circ C$
c. $Na_2SO_4 \cdot 10\,H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10\,H_2O(g) \quad K_P = 4.08 \times 10^{-25} \text{ at } 25^\circ C$
d. $H_2O(l) \rightleftharpoons H_2O(g) \quad K_P = 0.122 \text{ at } 50^\circ C$

4.E.2.31: S13.2.20

(a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

4.E.2.32: Q13.2.21

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a. $Cl_2(g) + Br_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_c = 4.7 \times 10^{-2} \text{ at } 25^\circ C$
b. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \quad K_P = 48.2 \text{ at } 500^\circ C$
c. $CaCl_2 \cdot 6\,H_2O(s) \rightleftharpoons CaCl_2(s) + 6\,H_2O(g) \quad K_P = 5.09 \times 10^{-44} \text{ at } 25^\circ C$
d. $H_2O(l) \rightleftharpoons H_2O(g) \quad K_P = 0.196 \text{ at } 60^\circ C$

4.E.2.33: Q13.2.22

What is the value of the equilibrium constant expression for the change $H_2O(l) \rightleftharpoons H_2O(g)$ at 30 °C?

4.E.2.34: S13.2.22

$$K_P = P_{H_2O} = 0.042. \tag{4.E.1}$$

4.E.2.35: Q13.2.23

Write the expression of the reaction quotient for the ionization of HOCN in water.

4.E.2.36: Q13.2.24

Write the reaction quotient expression for the ionization of NH_3 in water.

4.E.2.37: S13.2.24

$$Q_c = \frac{[NH_4^+][OH^-]}{[HN_3]} \tag{4.E.2}$$

4.E.2.38: Q13.2.25

What is the approximate value of the equilibrium constant K_P for the change $C_2H_5OC_2H_5(l) \rightleftharpoons C_2H_5OC_2H_5(g)$ at 25 °C. (Vapor pressure was described in the previous chapter on liquids and solids; refer back to this chapter to find the relevant information needed to solve this problem.)

4.E.3: 13.3: Shifting Equilbria Exercises

4.E.3.1: Q13.3.1

The following equation represents a reversible decomposition:

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

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

4.E.3.2: S13.3.1

The amount of $CaCO_3$ must be so small that P_{CO_2} is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full P_{CO_2} required for equilibrium.

4.E.3.3: Q13.3.2

Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.

4.E.3.4: Q13.3.3

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

4.E.3.5: S13.3.3

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

4.E.3.6: Q13.3.4

What would happen to the color of the solution in part (b) of Figure if a small amount of NaOH were added and Fe(OH)3 precipitated? Explain your answer.

4.E.3.7: Q13.3.5

The following reaction occurs when a burner on a gas stove is lit:

\(\ce{CH4}(g)+\ce{2O2}(g)\rightleftharpoons\ce{CO2}(g)+\ce{2H2O}(g)\)

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

4.E.3.8: S13.3.5

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

4.E.3.9: Q13.3.6

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO3, from sulfur dioxide, SO2, and oxygen, O2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO3 is lower than it would be at lower temperatures.

$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g) \tag{4.E.3}$$

a. (a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
b. (b) Is the reaction endothermic or exothermic?

4.E.3.10: Q13.3.7a

Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

\[\ce{N2}(g)+\ce{2H2}(g)\rightleftharpoons\ce{N2H4}(g) \hspace{20px} ΔH=\ce{95\:kJ}\]

4.E.3.11: S13.3.7a

Add N_2; add H_2; decrease the container volume; heat the mixture.

4.E.3.12: Q13.3.7b

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4(g) + 6\,H_2(g) \rightleftharpoons 4\,PH_3(g) \quad \Delta H = 110.5\ \text{kJ} \tag{4.E.4}$$

4.E.3.13: Q13.3.8

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad \Delta H = 92\ \text{kJ}$
b. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 181\ \text{kJ}$
c. $2\,O_3(g) \rightleftharpoons 3\,O_2(g) \quad \Delta H = -285\ \text{kJ}$
d. $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \quad \Delta H = -176\ \text{kJ}$

4.E.3.14: S13.3.8

(a) ΔT increase = shift right, ΔP increase = shift left; (b) ΔT increase = shift right, ΔP increase = no effect; (c) ΔT increase = shift left, ΔP increase = shift left; (d) ΔT increase = shift left, ΔP increase = shift right.

4.E.3.15: Q13.3.9

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + O_2(g) \quad \Delta H = 484\ \text{kJ}$
b. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad \Delta H = -92.2\ \text{kJ}$
c. $2\,Br(g) \rightleftharpoons Br_2(g) \quad \Delta H = -224\ \text{kJ}$
d. $H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g) \quad \Delta H = 53\ \text{kJ}$

4.E.3.16: Q13.3.10

Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction:

$$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g). \tag{4.E.5}$$

Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$2\,H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -90.2\text{ kJ} \tag{4.E.6}$$

b. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?
c. What will happen to the concentrations of HH_2, CO, and CH_3OH at equilibrium if CO is removed?
d. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?
e. What will happen to the concentrations of HH_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?
f. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

4.E.3.17: S13.3.10

a. $K_c = \dfrac{[CH_3OH]}{[H_2]^2[CO]}$;
b. $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ increases;
c. $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ decreases;
d. $[H_2]$ increases, [CO] increases, $[CH_3OH]$ increases;
e. $[H_2]$ increases, [CO] increases, $[CH_3OH]$ decreases;
f. no changes.

4.E.3.18: Q13.3.11

Nitrogen and oxygen react at high temperatures.

a. Write the expression for the equilibrium constant (Kc) for the reversible reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 181\ \text{kJ} \tag{4.E.7}$$

b. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?
c. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?
d. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?
e. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
f. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?
g. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

4.E.3.19: Q13.3.12

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

a. Write the expression for the equilibrium constant for the reversible reaction

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad \Delta H = 131.30\text{ kJ} \tag{4.E.8}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more C is added?
c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
d. What will happen to the concentration of each reactant and product at equilibrium if CO is added?
e. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

4.E.3.20: S13.3.12

(a) $K_c = \dfrac{[CO][H_2]}{[H_2O]}$; (b) $[H_2O]$ no change, [CO] no change, $[H_2]$ no change; (c) $[H_2O]$ decreases, [CO] decreases, $[H_2]$ decreases; (d) $[H_2O]$ increases, [CO] increases, $[H_2]$ decreases; (f) $[H_2O]$ decreases, [CO] increases, $[H_2]$ increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

4.E.3.21: Q13.3.13

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$Fe_2O_3(s) + 3\,H_2(g) \rightleftharpoons 2\,Fe(s) + 3\,H_2O(g) \quad \Delta H = 98.7\ \text{kJ} \tag{4.E.9}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?
c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
d. What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?
e. What will happen to the concentration of each reactant and product at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
f. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

4.E.3.22: Q13.3.14

Ammonia is a weak base that reacts with water according to this equation:

\[\ce{NH3}(aq)+\ce{H2O}(l)\rightleftharpoons\ce{NH4+}(aq)+\ce{OH-}(aq)\]

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water and why?

a. Addition of NaOH
b. Addition of HCl
c. Addition of NH_4Cl

4.E.3.23: S13.3.14

Only (b)

4.E.3.24: Q13.3.15

Acetic acid is a weak acid that reacts with water according to this equation:

\[\ce{CH3CO2H}(aq)+\ce{H2O}(aq)\rightleftharpoons\ce{H3O+}(aq)+\ce{CH3CO2-}(aq)\]

Will any of the following increase the percent of acetic acid that reacts and produces $CH_3CO_2^-$ ion?

a. Addition of HCl
b. Addition of NaOH
c. Addition of $NaCH_3CO_2$

4.E.3.25: Q13.3.16

Suggest two ways in which the equilibrium concentration of Ag+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and NO_3^-, in contact with solid AgCl.

\(\ce{Na+}(aq)+\ce{Cl-}(aq)+\ce{Ag+}(aq)+\ce{NO3-}(aq)\rightleftharpoons\ce{AgCl}(s)+\ce{Na+}(aq)+\ce{NO3-}(aq)\)

$$\Delta H = -65.9\ \text{kJ}$$

4.E.3.26: S13.3.16

Add NaCl or some other salt that produces Cl− to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(s).

4.E.3.27: Q13.3.17

How can the pressure of water vapor be increased in the following equilibrium?

\[\ce{H2O}(l)\rightleftharpoons\ce{H2O}(g) \hspace{20px} ΔH=\ce{41\:kJ}\]

4.E.3.28: Q13.3.18

Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.

\[\ce{2Ag+}(aq)+\ce{SO4^2-}(aq)\rightleftharpoons\ce{Ag2SO4}(s)\]

Which of the following will occur?

a. Ag^+ or SO_4^{2-} concentrations will not change.
b. The added silver sulfate will dissolve.

c. Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine.
d. The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.

4.E.3.29: S13.3.18

(a)

4.E.3.30: Q13.3.19

The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization $(HX \rightleftharpoons H^+ + X^-)$?

4.E.4: 13.4: Equilibrium Calculations Exercises

4.E.4.1: Q13.4.1

A reaction is represented by this equation: $A(aq) + 2\,B(aq) \rightleftharpoons 2\,C(aq) \quad K_c = 1 \times 10^3$

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations ≤1 *M*, make up two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

4.E.4.2: S13.4.1

$K_c = \frac{[C]^2}{[A][B]^2}$. [A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.

4.E.4.3: Q13.4.2

A reaction is represented by this equation: $2\,W(aq) \rightleftharpoons X(aq) + 2\,Y(aq) \quad K_c = 5 \times 10^{-4}$

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations of ≤1 *M*, make up two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

4.E.4.4: Q13.4.3

What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{4.E.10}$$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

4.E.4.5: S13.4.3

$K_c = 6.00 \times 10^{-2}$

4.E.4.6: Q13.4.4

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3\,H_2(g) + CO(g) \tag{4.E.11}$$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

4.E.4.7: S13.4.4

$K_c = 0.50$

4.E.4.8: Q13.4.5

At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 3.3×10^{-3}% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

$$2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g) \tag{4.E.12}$$

4.E.4.9: Q13.4.6

Calculate the value of the equilibrium constant K_P for the reaction $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

4.E.4.10: S13.4.6

The equilibrium equation is $K_P = 1.9 \times 10^3$

4.E.4.11: Q13.4.7

When heated, iodine vapor dissociates according to this equation:

$$I_2(g) \rightleftharpoons 2\,I(g) \tag{4.E.13}$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

4.E.4.12: Q13.4.8

A sample of ammonium chloride was heated in a closed container.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \tag{4.E.14}$$

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

4.E.4.13: S13.4.8

$K_P = 3.06$

4.E.4.14: Q13.4.9

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the transformation at 60 °C?

$$H_2O(l) \rightleftharpoons H_2O(g) \tag{4.E.15}$$

4.E.4.15: Q13.4.10

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$\begin{array}{ccc} 2\,SO_3(g) \rightleftharpoons & 2\,SO_2(g) + & O_2(g) \\ \_\_\_\_ & \_\_\_\_ & +x \\ \_\_\_\_ & \_\_\_\_ & 0.125\ M \end{array} \tag{4.E.16–4.E.18}$$

(b)

$$\begin{array}{cccc} 4\,NH_3(g) + & 3\,O_2(g) \rightleftharpoons & 2\,N_2(g) + & 6\,H_2O(g) \\ \_\_\_\_ & 3x & \_\_\_\_ & \_\_\_\_ \\ \_\_\_\_ & 0.24\ M & \_\_\_\_ & \_\_\_\_ \end{array} \tag{4.E.19–4.E.21}$$

(c) Change in pressure:

$$\begin{array}{ccc} 2\,CH_4(g) \rightleftharpoons & C_2H_2(g) + & 3\,H_2(g) \\ \_\_\_\_ & x & \_\_\_\_ \\ \_\_\_\_ & 25\text{ torr} & \_\_\_\_ \end{array} \tag{4.E.22–4.E.24}$$

(d) Change in pressure:

$$\begin{array}{cccc} CH_4(g) + & H_2O(g) \rightleftharpoons & CO(g) + & 3\,H_2(g) \\ \_\_\_\_ & x & \_\_\_\_ & \_\_\_\_ \\ \_\_\_\_ & 5\text{ atm} & \_\_\_\_ & \_\_\_\_ \end{array} \tag{4.E.25–4.E.27}$$

(e)

$$\begin{array}{lll} NH_4Cl(s) \rightleftharpoons NH_3(g) + & HCl(g) & (4.E.28) \\ x & \_\_\_\_ & (4.E.29) \\ 1.03 \times 10^{-4}\ M & \_\_\_\_ & (4.E.30) \end{array}$$

(f) change in pressure:

$$\begin{array}{lll} Ni(s) + 4\,CO(g) \rightleftharpoons & Ni(CO)_4(g) & (4.E.31) \\ 4x & \_\_\_\_ & (4.E.32) \\ 0.40\text{ atm} & \_\_\_\_ & (4.E.33) \end{array}$$

4.E.4.16: S13.4.10

a. −2*x*, 2*x*, −0.250 *M*, 0.250 *M*;
b. 4*x*, −2*x*, −6*x*, 0.32 *M*, −0.16 *M*, −0.48 *M*;
c. −2*x*, 3*x*, −50 torr, 75 torr;
d. *x*, − *x*, −3*x*, 5 atm, −5 atm, −15 atm;
e. *x*, 1.03×10^{-4} *M*; (f) *x*, 0.1 atm.

4.E.4.17: Q13.4.11

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$\begin{array}{llll} 2\,H_2(g) + & O_2(g) \rightleftharpoons & 2\,H_2O(g) & (4.E.34) \\ \_\_\_\_ & \_\_\_\_ & +2x & (4.E.35) \\ \_\_\_\_ & \_\_\_\_ & 1.50\ M & (4.E.36) \end{array}$$

(b)

$$\begin{array}{lllll} CS_2(g) + & 4\,H_2(g) \rightleftharpoons & CH_4(g) + & 2\,H_2S(g) & (4.E.37) \\ x & \_\_\_\_ & \_\_\_\_ & \_\_\_\_ & (4.E.38) \\ 0.020\ M & \_\_\_\_ & \_\_\_\_ & \_\_\_\_ & (4.E.39) \end{array}$$

(c) Change in pressure:

$$\begin{array}{llll} H_2(g) + & Cl_2(g) \rightleftharpoons & 2\,HCl(g) & (4.E.40) \\ x & \_\_\_\_ & \_\_\_\_ & (4.E.41) \\ 1.50\text{ atm} & \_\_\_\_ & \_\_\_\_ & (4.E.42) \end{array}$$

(d) Change in pressure:

$$\begin{array}{lllll} 2\,NH_3(g) + & 2\,O_2(g) \rightleftharpoons & N_2O(g) + & 3\,H_2O(g) & (4.E.43) \\ \_\_\_\_ & \_\_\_\_ & \_\_\_\_ & x & (4.E.44) \\ \_\_\_\_ & \_\_\_\_ & \_\_\_\_ & 60.6\text{ torr} & (4.E.45) \end{array}$$

(e)

$$\begin{array}{lll} NH_4HS(s) \rightleftharpoons NH_3(g) + & H_2S(g) & (4.E.46) \\ x & \_\_\_\_ & (4.E.47) \\ 9.8 \times 10^{-6}\ M & \_\_\_\_ & (4.E.48) \end{array}$$

(f) Change in pressure:

$$\begin{array}{lll} Fe(s) + 5\,CO(g) \rightleftharpoons & Fe(CO)_4(g) & (4.E.49) \\ \_\_\_\_ & x & (4.E.50) \\ \_\_\_\_ & 0.012\text{ atm} & (4.E.51) \end{array}$$

4.E.4.18: Q13.4.12

Why are there no changes specified for Ni in Exercise, part (f)? What property of Ni does change?

4.E.4.19: S13.4.12

Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

4.E.4.20: Q13.4.13

Why are there no changes specified for NH_4HS in Exercise, part (e)? What property of NH_4HS does change?

4.E.4.21: Q13.4.14

Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \quad K_c = 0.50 \text{ at } 400\ ^\circ\mathrm{C} \tag{4.E.52}$$

Calculate the equilibrium molar concentration of NH_3.

4.E.4.22: S13.4.14

$[NH_3] = 9.1 \times 10^{-2}$ *M*

4.E.4.23: Q13.4.16

Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$$\mathrm{H_2} + \mathrm{I_2} \rightleftharpoons 2\,\mathrm{HI} \quad K_c = 50.2 \text{ at } 448\ ^\circ\mathrm{C}$$

4.E.4.24: Q13.4.17

What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$\mathrm{Cl_2}(g) + \mathrm{Br_2}(g) \rightleftharpoons 2\,\mathrm{BrCl}(g) \quad K_P = 4.7 \times 10^{-2} \tag{4.E.53}$$

4.E.4.25: S13.4.17

$P_{BrCl} = 4.9 \times 10^{-2}$ atm

4.E.4.26: Q13.4.18

What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

$$\mathrm{H_2}(g) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{H_2O}(g) + \mathrm{CO}(g) \quad K_P = 1.6 \text{ at } 990\ ^\circ\mathrm{C} \tag{4.E.54}$$

4.E.4.27: Q13.4.12

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$\mathrm{CoO}(s) + \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s) + \mathrm{CO_2}(g) \quad K_c = 4.90 \times 10^2 \text{ at } 550\ ^\circ\mathrm{C}$$

What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100$ *M*?

4.E.4.28: S13.4.12

$[CO] = 2.0 \times 10^{-4}$ *M*

4.E.4.29: Q13.4.13

Carbon reacts with water vapor at elevated temperatures.

$$\mathrm{C}(s) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g) \quad K_c = 0.2 \text{ at } 1000\ ^\circ\mathrm{C}$$

What is the concentration of CO in an equilibrium mixture with $[H_2O] = 0.500$ *M* at 1000 °C?

4.E.4.30: Q13.4.14

Sodium sulfate 10−hydrate, $\mathrm{Na_2SO_4 \cdot 10\,H_2O}$, dehydrates according to the equation

$$\mathrm{Na_2SO_4 \cdot 10\,H_2O}(s) \rightleftharpoons \mathrm{Na_2SO_4}(s) + 10\,\mathrm{H_2O}(g) \tag{4.E.55}$$

with $K_p = 4.08 \times 10^{-25}$ at 25°C. What is the pressure of water vapor at equilibrium with a mixture of $\mathrm{Na_2SO_4 \cdot 10\,H_2O}$ and $\mathrm{NaSO_4}$?

4.E.4.31: S13.4.14

$P_{H_2O} = 3.64 \times 10^{-3}$ atm

4.E.4.32: Q13.4.15

Calcium chloride 6−hydrate, $CaCl_2{\cdot}6H_2O$, dehydrates according to the equation

$$\mathrm{CaCl_2 \cdot 6\,H_2O}(s) \rightleftharpoons \mathrm{CaCl_2}(s) + 6\,\mathrm{H_2O}(g) \quad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ\mathrm{C}$$

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2{\cdot}6H_2O$ and $CaCl_2$?

4.E.4.33: Q13.4.16

A student solved the following problem and found the equilibrium concentrations to be $[SO_2]$ = 0.590 *M*, $[O_2]$ = 0.0450 *M*, and $[SO_3]$ = 0.260 *M*. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

$$2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g) \quad K_c = 4.32$$

What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3]$ = 0.500 *M*, $[SO_2]$ = 0 *M*, and $[O_2]$ = 0.350 *M*?

4.E.4.34: S13.4.16

Calculate *Q* based on the calculated concentrations and see if it is equal to K_c. Because *Q* does equal 4.32, the system must be at equilibrium.

4.E.4.35: Q13.4.16

A student solved the following problem and found $[N_2O_4]$ = 0.16 *M* at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 *M*?

$$2\,\mathrm{NO_2}(g) \rightleftharpoons \mathrm{N_2O_4}(g) \quad K_c = 160 \tag{4.E.56}$$

Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g) \quad K_c = 1.07 \times 10^{-5} \text{ in chloroform}$$

(b) Show that the change is small enough to be neglected.

4.E.4.36: S13.4.16

(a)

- $[NO_2]$ = 1.17 × 10^{-3} *M*
- $[N_2O_4]$ = 0.128 *M*

(b) Percent error $= \dfrac{5.87 \times 10^{-4}}{0.129} \times 100\% = 0.455\%$. The change in concentration of N_2O_4 is far less than the 5% maximum allowed.

4.E.4.37: Q13.4.17

Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.

a. Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.

$$\mathrm{COCl_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{Cl_2}(g) \quad K_c = 2.2 \times 10^{-10} \tag{4.E.57}$$

b. Show that the change is small enough to be neglected.

4.E.4.38: Q13.4.18

Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

$2\,\mathrm{H_2S}(g) \rightleftharpoons 2\,\mathrm{H_2}(g) + \mathrm{S_2}(g) \quad K_P = 2.2 \times 10^{-6}$

(b) Show that the change is small enough to be neglected.

4.E.4.39: S13.4.18

(a)

- $[H_2S]$ = 0.810 atm
- $[H_2]$ = 0.014 atm
- $S_2]$ = 0.0072 atm

(b) The 2*x* is dropped from the equilibrium calculation because 0.014 is negligible when subtracted from 0.824. The percent error associated with ignoring 2*x* is $\frac{0.014}{0.824} \times 100\% = 1.7\%$, which is less than allowed by the “5% test.” The error is, indeed, negligible.

4.E.4.40: Q13.4.19

What are all concentrations after a mixture that contains $[H_2O]$ = 1.00 *M* and $[Cl_2O]$ = 1.00 *M* comes to equilibrium at 25 °C?

$$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\,\mathrm{HOCl}(g) \quad K_c = 0.0900 \tag{4.E.58}$$

4.E.4.41: Q13.4.20

What are the concentrations of PCl_5, PCl_3, and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[PCl_5]$ = 2.00 *M*?

$$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \quad K_c = 0.0211 \tag{4.E.59}$$

4.E.4.42: S13.4.20

$[PCl_3]$ = 1.80 *M*; $[PC_3]$ = 0.195 *M*; $[PCl_3]$ = 0.195 *M*.

4.E.4.43: Q13.4.21

Calculate the pressures of all species at equilibrium in a mixture of NOCl, NO, and Cl_2 produced when a sample of NOCl with a pressure of 10.0 atm comes to equilibrium according to this reaction:

$$2\,\mathrm{NOCl}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \quad K_P = 4.0 \times 10^{-4} \tag{4.E.60}$$

4.E.4.44: Q13.4.22

Calculate the equilibrium concentrations of NO, O_2, and NO_2 in a mixture at 250 °C that results from the reaction of 0.20 *M* NO and 0.10 *M* O_2. (Hint: *K* is large; assume the reaction goes to completion then comes back to equilibrium.)

$$2\,\mathrm{NO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g) \quad K_c = 2.3 \times 10^5 \text{ at } 250\ ^\circ\mathrm{C} \tag{4.E.61}$$

4.E.4.45: S13.4.22

- $[NO_2]$ = 0.19 *M*
- [NO] = 0.0070 *M*
- $[O_2]$ = 0.0035 *M*

4.E.4.46: Q13.4.23

Calculate the equilibrium concentrations that result when 0.25 *M* O_2 and 1.0 *M* HCl react and come to equilibrium.

$$4\,\mathrm{HCl}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{Cl_2}(g) + 2\,\mathrm{H_2O}(g) \quad K_c = 3.1 \times 10^{13} \tag{4.E.62}$$

4.E.4.47: Q13.4.24

One of the important reactions in the formation of smog is represented by the equation

$$O_3(g) + NO(g) \rightleftharpoons NO_2(g) + O_2(g) \quad K_P = 6.0 \times 10^{34} \tag{4.E.63}$$

What is the pressure of O_3 remaining after a mixture of O_3 with a pressure of 1.2×10^{-8} atm and NO with a pressure of 1.2×10^{-8} atm comes to equilibrium? (Hint: K_P is large; assume the reaction goes to completion then comes back to equilibrium.)

4.E.4.48: S13.4.24

$P_{O_3} = 4.9 \times 10^{-26}\ \mathrm{atm}$

4.E.4.49: Q13.4.24

Calculate the pressures of NO, Cl_2, and NOCl in an equilibrium mixture produced by the reaction of a starting mixture with 4.0 atm NO and 2.0 atm Cl_2. (Hint: K_P is small; assume the reverse reaction goes to completion then comes back to equilibrium.)

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_P = 2.5 \times 10^3$$

4.E.4.50: Q13.4.25

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2\,HI \quad K_c = 50.2 \text{ at } 448\ ^\circ C$$

4.E.4.51: S13.4.25

507 g

4.E.4.52: Q13.4.26

Butane exists as two isomers, *n*−butane and isobutane.

Three Lewis structures are shown. The first is labeled, “n dash Butane,” and has a C H subscript 3 single bonded to a C H subscript 2 group. This C H subscript 2 group is single bonded to another C H subscript 2 group which is single bonded to a C H subscript 3 group. The second is labeled, “iso dash Butane,” and is composed of a C H group single bonded to three C H subscript 3 groups. The third structure shows a chain of atoms: “C H subscript 3, C H subscript 2, C H subscript 2, C H subscript 3,” a double-headed arrow, then a carbon atom single bonded to three C H subscript 3 groups as well as a hydrogen atom.

K_P = 2.5 at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

4.E.4.53: Q13.4.27

What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.050 for the decomposition reaction of $CaCO_3$ at that temperature?

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

4.E.4.54: S13.4.27

330 g

4.E.4.55: Q13.4.28

The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \tag{4.E.64}$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

4.E.4.56: Q13.4.29

At 25 °C and at 1 atm, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are $P_{N_2O_4} = 0.70\ \mathrm{atm}$ and $P_{NO_2} = 0.30\ \mathrm{atm}$.

a. Predict how the pressures of NO_2 and N_2O_4 will change if the total pressure increases to 9.0 atm. Will they increase, decrease, or remain the same?
b. Calculate the partial pressures of NO_2 and N_2O_4 when they are at equilibrium at 9.0 atm and 25 °C.

4.E.4.57: S13.4.29

(a) Both gases must increase in pressure.

(b) $P_{\mathrm{N_2O_4}} = 8.0\ \mathrm{atm}$ and $P_{\mathrm{NO_2}} = 1.0\ \mathrm{atm}$

4.E.4.58: Q13.4.30

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00 × 10^3 torr.

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{4.E.65}$$

a. How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?
b. Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

4.E.4.59: Q13.4.31

The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

\[\ce{CO}(g)+\ce{H2O}(g) <=> \ce{CO2}(g)+\ce{H2}(g)\)]

a. On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?
b. Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

4.E.4.60: S13.4.31

(a) 0.33 mol.

(b) $[CO]^2$ = 0.50 *M* Added H_2 forms some water to compensate for the removal of water vapor and as a result of a shift to the left after H_2 is added.

4.E.4.61: Q13.4.32a

Antimony pentachloride decomposes according to this equation:

$$\mathrm{SbCl_5}(g) \rightleftharpoons \mathrm{SbCl_3}(g) + \mathrm{Cl_2}(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

4.E.4.62: Q13.4.32b

Consider the reaction between H_2 and O_2 at 1000 K

\[\ce{2H2}(g)+\ce{O2}(g)⇌\ce{2H2O}(g) \hspace{20px} K_P=\dfrac{(P_{\ce{H2O}})^2}{(P_{\ce{O2}})(P_{\ce{H2}})^3}=1.33×10^{20}\]

If 0.500 atm of H_2 and 0.500 atm of O_2 are allowed to come to equilibrium at this temperature, what are the partial pressures of the components?

4.E.4.63: S13.4.32b

$P_{\mathrm{H_2}} = 8.64 \times 10^{-11}\ \mathrm{atm}$

\(P_{\ce{O2}}=0.250\:\ce{atm}\)

\(P_{\ce{H2O}}=0.500\:\ce{atm}\)

4.E.4.64: Q13.4.33

An equilibrium is established according to the following equation

$$Hg_2^{2+}(aq) + NO_3-(aq) + 3\,H^+(aq) \rightleftharpoons 2\,Hg^{2+}(aq) + HNO_2(aq) + H_2O(l) \quad K_c = 4.6 \tag{4.E.66}$$

What will happen in a solution that is 0.20 *M* each in Hg_2^{2+}, NO_3-, H^+, Hg^{2+}, and HNO_2?

a. Hg_2^{2+} will be oxidized and NO_3- reduced.
b. Hg_2^{2+} will be reduced and NO_3- oxidized.
c. Hg^{2+} will be oxidized and HNO_2 reduced.
d. Hg^{2+} will be reduced and HNO_2 oxidized.
e. There will be no change because all reactants and products have an activity of 1.

4.E.4.65: Q13.4.34

Consider the equilibrium

$$4\,NO_2(g) + 6\,H_2O(g) \rightleftharpoons 4\,NH_3(g) + 7\,O_2(g) \tag{4.E.67}$$

a. What is the expression for the equilibrium constant (K_c) of the reaction?
b. How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
c. If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the pressure of NO_2?
d. If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

4.E.4.66: S13.4.34

(a) $K_c = \dfrac{[NH_3]^4[O_2]^7}{[NO_2]^4[H_2O]^6}$. (b) $[NH_3]$ must increase for Q_c to reach K_c. (c) That decrease in pressure would decrease $[NO_2]$. (d) $P_{O_2} = 49$ torr

4.E.4.67: Q13.4.35

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$HbO_2(aq) + H_3O^+(aq) + CO_2(g) \rightleftharpoons CO_2 - Hb - H^+ + O_2(g) + H_2O(l)$$

1. (a) Write the equilibrium constant expression for this reaction.
2. (b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

4.E.4.68: Q13.4.36

The hydrolysis of the sugar sucrose to the sugars glucose and fructose follows a first-order rate equation for the disappearance of sucrose.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

Rate = $k[C_{12}H_{22}O_{11}]$

In neutral solution, $k = 2.1 \times 10^{-11}$/s at 27 °C. (As indicated by the rate constant, this is a very slow reaction. In the human body, the rate of this reaction is sped up by a type of catalyst called an enzyme.) (Note: That is not a mistake in the equation—the products of the reaction, glucose and fructose, have the same molecular formulas, $C_6H_{12}O_6$, but differ in the arrangement of the atoms in their molecules). The equilibrium constant for the reaction is 1.36×10^5 at 27 °C. What are the concentrations of glucose, fructose, and sucrose after a 0.150 *M* aqueous solution of sucrose has reached equilibrium? Remember that the activity of a solvent (the effective concentration) is 1.

4.E.4.69: S13.4.36

[fructose] = 0.15 *M*

4.E.4.70: Q13.4.37

The density of trifluoroacetic acid vapor was determined at 118.1 °C and 468.5 torr, and found to be 2.784 g/L. Calculate K_c for the association of the acid.

Two Lewis structures are shown in a reaction. The first structure, which is condensed, reads, "2 C F subscript 3 C O subscript 2 H (g)," and is followed by a double-headed arrow. The second structure shows a partially condensed hexagonal ring shape. From the left side, in a clockwise manner, it reads "C F subscript 3 C, single bond, O, single bond, H, dotted line bond, O, double bond, C F subscript 3 C (g), single bond, O, single bond, H, dotted line bond, O, double bond back to the starting compound."

Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of K_P = 1.91 has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

4.E.4.71: S13.4.37

$P_{\mathrm{N_2O_3}} = 1.90\ \mathrm{atm}$ and $P_{\mathrm{NO}} = P_{\mathrm{NO_2}} = 1.90\ \mathrm{atm}$

4.E.4.72: Q13.4.38

A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 *M*; H_2, 0.50 *M*; and NH_3, 0.25 *M*. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 *M*?

4.E.4.73: Q13.4.39

A 0.010 *M* solution of the weak acid HA has an osmotic pressure (see chapter on solutions and colloids) of 0.293 atm at 25 °C. A 0.010 *M* solution of the weak acid HB has an osmotic pressure of 0.345 atm under the same conditions.

(a) Which acid has the larger equilibrium constant for ionization

$$\text{HA } [\mathrm{HA}(aq) \rightleftharpoons \mathrm{A^-}(aq) + \mathrm{H^+}(aq)] \text{ or HB } [\mathrm{HB}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{B^-}(aq)] \text{ ?}$$

(b) What are the equilibrium constants for the ionization of these acids?

(Hint: Remember that each solution contains three dissolved species: the weak acid (HA or HB), the conjugate base (A^- or B^-), and the hydrogen ion (H^+). Remember that osmotic pressure (like all colligative properties) is related to the total number of solute particles. Specifically for osmotic pressure, those concentrations are described by molarities.)

4.E.4.74: S13.4.39

(a) HB ionizes to a greater degree and has the larger K_c.

(b) $K_c(\mathrm{HA}) = 5 \times 10^{-4}$

$K_c(\mathrm{HB}) = 3 \times 10^{-3}$