

## 13.E: Fundamental Equilibrium Concepts (Exercises)

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### 13.E.1: 13.1: Chemical Equilibria Exercises

#### 13.E.1.1: Q13.1.1

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

#### 13.E.1.2: S13.1.1

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

#### 13.E.1.3: Q13.1.2

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

#### 13.E.1.4: Q13.1.3

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

#### 13.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.

#### 13.E.1.6: Q13.1.4

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

#### 13.E.1.7: Q13.1.5

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

#### 13.E.1.8: S13.1.5

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

### 13.E.2: 13.2: Equilibrium Constant Exercises

#### 13.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.

#### 13.E.2.2: Q13.2.2

Explain why an equilibrium between  $\text{Br}_2(l)$  and  $\text{Br}_2(g)$  would not be established if the container were not a closed vessel shown below:

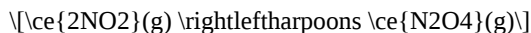


#### 13.E.2.3: S13.2.2

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  $\text{Br}_2$  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.

#### 13.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  $\text{NO}_2$  or with pure  $\text{N}_2\text{O}_4$ ?



#### 13.E.2.5: Q13.2.4

Among the solubility rules previously discussed is the statement: All chlorides are soluble except  $\text{Hg}_2\text{Cl}_2$ ,  $\text{AgCl}$ ,  $\text{PbCl}_2$ , and  $\text{CuCl}$ .

#### 13.E.2.6: Q13.2.5

- (a) Write the expression for the equilibrium constant for the reaction represented by the equation  $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.
- (b) Write the expression for the equilibrium constant for the reaction represented by the equation  $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightleftharpoons \text{PbCl}_2(\text{s})$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.

#### 13.E.2.7: S13.2.5

(a)  $K_c = [\text{Ag}^+][\text{Cl}^-] < 1$ .  $\text{AgCl}$  is insoluble; thus, the concentrations of ions are much less than 1 M; (b)  $K_c = \frac{1}{[\text{Pb}^{2+}][\text{Cl}^-]^2} > 1$  because  $\text{PbCl}_2$  is insoluble and formation of the solid will reduce the concentration of ions to a low level ( $< 1$  M).

#### 13.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.

- Write the expression for the equilibrium constant for the reaction represented by the equation  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.
- Write the expression for the equilibrium constant for the reaction represented by the equation  $3\text{Ba}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightleftharpoons \text{Ba}_3(\text{PO}_4)_2(\text{s})$ . Is  $K_c > 1$ ,  $< 1$ , or  $\approx 1$ ? Explain your answer.

#### 13.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:  $3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{g})$ . 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.

#### 13.E.2.10: S13.2.7

Since  $K_c = \frac{[\text{C}_6\text{H}_6]}{[\text{C}_2\text{H}_2]^3}$ , a value of  $K_c \approx 10$  means that  $\text{C}_6\text{H}_6$  predominates over  $\text{C}_2\text{H}_2$ . In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

#### 13.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  $\text{KI}(\text{aq}) + \text{I}_2(\text{aq}) \rightleftharpoons \text{KI}_3(\text{aq})$  give the same expression for the reaction quotient.  $\text{KI}_3$  is composed of the ions  $\text{K}^+$  and  $\text{I}_3^-$ .

#### 13.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  $\approx 1$  for a titration reaction?

#### 13.E.2.13: S13.2.9

$K_c > 1$

#### 13.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  $\approx 1$  for a useful precipitation reaction?

### 13.E.2.15: Q13.2.11

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

- $\text{CH}_4(g) + \text{Cl}_2(g) \rightleftharpoons \text{CH}_3\text{Cl}(g) + \text{HCl}(g)$
- $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)$
- $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$
- $\text{BaSO}_3(s) \rightleftharpoons \text{BaO}(s) + \text{SO}_2(g)$
- $\text{P}_4(g) + 5 \text{O}_2(g) \rightleftharpoons \text{P}_4\text{O}_{10}(s)$
- $\text{Br}_2(g) \rightleftharpoons 2 \text{Br}(g)$
- $\text{CH}_4(g) + 2 \text{O}_2(g) \rightleftharpoons \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$
- $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}(s) \rightleftharpoons \text{CuSO}_4(s) + 5 \text{H}_2\text{O}(g)$

### 13.E.2.16: S13.2.11

$$(a) Q_c = \frac{[\text{CH}_3\text{Cl}][\text{HCl}]}{[\text{CH}_4][\text{Cl}_2]}; (b) Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}; (c) Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}; (d) Q_c = [\text{SO}_2]; (e) Q_c = \frac{1}{[\text{P}_4][\text{O}_2]^5}; (f) Q_c = \frac{[\text{Br}]^2}{[\text{Br}_2]}; (g) Q_c = \frac{[\text{CO}_2]}{[\text{CH}_4][\text{O}_2]^2}; (h) Q_c = [\text{H}_2\text{O}]^5$$

### 13.E.2.17: Q13.2.12

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

- $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$
- $4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$
- $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$
- $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$
- $\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$
- $2 \text{Pb}(\text{NO}_3)_2(s) \rightleftharpoons 2 \text{PbO}(s) + 4 \text{NO}_2(g) + \text{O}_2(g)$
- $2 \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(l)$
- $\text{S}_8(g) \rightleftharpoons 8 \text{S}(g)$

### 13.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.

- $2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g)$   $K_c = 17$ ;  $[\text{NH}_3] = 0.20 \text{ M}$ ,  $[\text{N}_2] = 1.00 \text{ M}$ ,  $[\text{H}_2] = 1.00 \text{ M}$
- $2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g)$   $K_P = 6.8 \times 10^4$ ; initial pressures:  $\text{NH}_3 = 3.0 \text{ atm}$ ,  $\text{N}_2 = 2.0 \text{ atm}$ ,  $\text{H}_2 = 1.0 \text{ atm}$
- $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$   $K_c = 0.230$ ;  $[\text{SO}_3] = 0.00 \text{ M}$ ,  $[\text{SO}_2] = 1.00 \text{ M}$ ,  $[\text{O}_2] = 1.00 \text{ M}$
- $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$   $K_P = 16.5$ ; initial pressures:  $\text{SO}_3 = 1.00 \text{ atm}$ ,  $\text{SO}_2 = 1.00 \text{ atm}$ ,  $\text{O}_2 = 1.00 \text{ atm}$
- $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$   $K_c = 4.6 \times 10^4$ ;  $[\text{NO}] = 1.00 \text{ M}$ ,  $[\text{Cl}_2] = 1.00 \text{ M}$ ,  $[\text{NOCl}] = 0 \text{ M}$
- $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)$   $K_P = 0.050$ ; initial pressures:  $\text{NO} = 10.0 \text{ atm}$ ,  $\text{N}_2 = \text{O}_2 = 5 \text{ atm}$

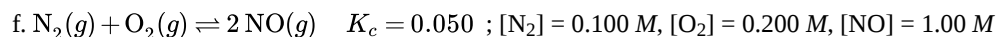
### 13.E.2.19: S13.2.13

(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

### 13.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.

- $2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g)$   $K_c = 17$ ;  $[\text{NH}_3] = 0.50 \text{ M}$ ,  $[\text{N}_2] = 0.15 \text{ M}$ ,  $[\text{H}_2] = 0.12 \text{ M}$
- $2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g)$   $K_P = 6.8 \times 10^4$ ; initial pressures:  $\text{NH}_3 = 2.00 \text{ atm}$ ,  $\text{N}_2 = 10.00 \text{ atm}$ ,  $\text{H}_2 = 10.00 \text{ atm}$
- $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$   $K_c = 0.230$ ;  $[\text{SO}_3] = 2.00 \text{ M}$ ,  $[\text{SO}_2] = 2.00 \text{ M}$ ,  $[\text{O}_2] = 2.00 \text{ M}$
- $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$   $K_P = 6.5 \text{ atm}$ ; initial pressures:  $\text{SO}_2 = 1.00 \text{ atm}$ ,  $\text{O}_2 = 1.130 \text{ atm}$ ,  $\text{SO}_3 = 0 \text{ atm}$
- $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$   $K_P = 2.5 \times 10^3$ ; initial pressures:  $\text{NO} = 1.00 \text{ atm}$ ,  $\text{Cl}_2 = 1.00 \text{ atm}$ ,  $\text{NOCl} = 0 \text{ atm}$



### 13.E.2.21: Q13.2.15

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



If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium?  $P(\text{NH}_3) = 93 \text{ atm}$ ,  $P(\text{N}_2) = 48 \text{ atm}$ , and  $P(\text{H}_2) = 52$

### 13.E.2.22: S13.2.15

The system will shift toward the reactants to reach equilibrium.

### 13.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?



$[\text{SO}_2\text{Cl}_2] = 0.12 \text{ M}$ ,  $[\text{Cl}_2] = 0.16 \text{ M}$  and  $[\text{SO}_2] = 0.050 \text{ M}$ .  $K_c$  for the reaction is 0.078.

### 13.E.2.24: Q13.2.17

Which of the systems described in [Exercise](#) give homogeneous equilibria? Which give heterogeneous equilibria?

### 13.E.2.25: S13.2.17

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

### 13.E.2.26: Q13.2.18

Which of the systems described in [Exercise](#) give homogeneous equilibria? Which give heterogeneous equilibria?

### 13.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)?

### 13.E.2.28: S13.2.19

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

### 13.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)?

### 13.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  $K_c$ .

- $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$   $K_c = 0.50$  at  $400^\circ \text{C}$
- $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$   $K_c = 50.2$  at  $448^\circ \text{C}$
- $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}(s) \rightleftharpoons \text{Na}_2\text{SO}_4(s) + 10 \text{H}_2\text{O}(g)$   $K_P = 4.08 \times 10^{-25}$  at  $25^\circ \text{C}$
- $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$   $K_P = 0.122$  at  $50^\circ \text{C}$

### 13.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)  $K_c = 4.60 \times 10^{-3}$

### 13.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  $K_c$ .

- $\text{Cl}_2(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{BrCl}(g)$   $K_c = 4.7 \times 10^{-2}$  at  $25^\circ \text{C}$
- $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$   $K_P = 48.2$  at  $500^\circ \text{C}$
- $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}(s) \rightleftharpoons \text{CaCl}_2(s) + 6 \text{H}_2\text{O}(g)$   $K_P = 5.09 \times 10^{-44}$  at  $25^\circ \text{C}$
- $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$   $K_P = 0.196$  at  $60^\circ \text{C}$

### 13.E.2.33: Q13.2.22

What is the value of the equilibrium constant expression for the change  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$  at 30 °C?

### 13.E.2.34: S13.2.22

$$K_P = P_{\text{H}_2\text{O}} = 0.042. \quad (13.E.1)$$

### 13.E.2.35: Q13.2.23

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

### 13.E.2.36: Q13.2.24

Write the reaction quotient expression for the ionization of  $\text{NH}_3$  in water.

### 13.E.2.37: S13.2.24

$$Q_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{HN}_3]} \quad (13.E.2)$$

### 13.E.2.38: Q13.2.25

What is the approximate value of the equilibrium constant  $K_P$  for the change  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(l) \rightleftharpoons \text{C}_2\text{H}_5\text{OC}_2\text{H}_5(g)$  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.)

## 13.E.3: 13.3: Shifting Equilibria Exercises

### 13.E.3.1: Q13.3.1

The following equation represents a reversible decomposition:



Under what conditions will decomposition in a closed container proceed to completion so that no  $\text{CaCO}_3$  remains?

### 13.E.3.2: S13.3.1

The amount of  $\text{CaCO}_3$  must be so small that  $P_{\text{CO}_2}$  is less than  $K_P$  when the  $\text{CaCO}_3$  has completely decomposed. In other words, the starting amount of  $\text{CaCO}_3$  cannot completely generate the full  $P_{\text{CO}_2}$  required for equilibrium.

### 13.E.3.3: Q13.3.2

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

### 13.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?

### 13.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.

### 13.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  $\text{Fe}(\text{OH})_3$  precipitated? Explain your answer.

### 13.E.3.7: Q13.3.5

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



Is an equilibrium among  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  established under these conditions? Explain your answer.

### 13.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.

### 13.E.3.9: Q13.3.6

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide,  $\text{SO}_3$ , from sulfur dioxide,  $\text{SO}_2$ , and oxygen,  $\text{O}_2$ , shown here. At high temperatures, the rate of formation of  $\text{SO}_3$  is higher, but the equilibrium amount (concentration or partial pressure) of  $\text{SO}_3$  is lower than it would be at lower temperatures.



- Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
- Is the reaction endothermic or exothermic?

### 13.E.3.10: Q13.3.7a

Suggest four ways in which the concentration of hydrazine,  $\text{N}_2\text{H}_4$ , could be increased in an equilibrium described by the following equation:

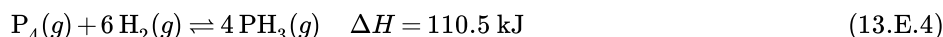


### 13.E.3.11: S13.3.7a

Add  $\text{N}_2$ ; add  $\text{H}_2$ ; decrease the container volume; heat the mixture.

### 13.E.3.12: Q13.3.7b

Suggest four ways in which the concentration of  $\text{PH}_3$  could be increased in an equilibrium described by the following equation:



### 13.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?

- $2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g) \quad \Delta H = 92 \text{ kJ}$
- $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g) \quad \Delta H = 181 \text{ kJ}$
- $2 \text{O}_3(g) \rightleftharpoons 3 \text{O}_2(g) \quad \Delta H = -285 \text{ kJ}$
- $\text{CaO}(s) + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s) \quad \Delta H = -176 \text{ kJ}$

### 13.E.3.14: S13.3.8

(a)  $\Delta T$  increase = shift right,  $\Delta P$  increase = shift left; (b)  $\Delta T$  increase = shift right,  $\Delta P$  increase = no effect; (c)  $\Delta T$  increase = shift left,  $\Delta P$  increase = shift left; (d)  $\Delta T$  increase = shift left,  $\Delta P$  increase = shift right.

### 13.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?

- $2 \text{H}_2\text{O}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{O}_2(g) \quad \Delta H = 484 \text{ kJ}$
- $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \quad \Delta H = -92.2 \text{ kJ}$
- $2 \text{Br}(g) \rightleftharpoons \text{Br}_2(g) \quad \Delta H = -224 \text{ kJ}$
- $\text{H}_2(g) + \text{I}_2(s) \rightleftharpoons 2 \text{HI}(g) \quad \Delta H = 53 \text{ kJ}$

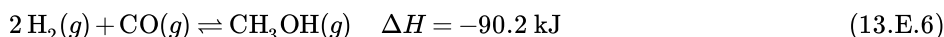
### 13.E.3.16: Q13.3.10

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:



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



- b. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if more  $\text{H}_2$  is added?  
 c. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if  $\text{CO}$  is removed?  
 d. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if  $\text{CH}_3\text{OH}$  is added?  
 e. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if the temperature of the system is increased?  
 f. What will happen to the concentrations of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_3\text{OH}$  at equilibrium if more catalyst is added?

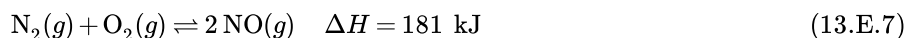
### 13.E.3.17: S13.3.10

- a.  $K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2]^2 [\text{CO}]}$ ;  
 b.  $[\text{H}_2]$  increases,  $[\text{CO}]$  decreases,  $[\text{CH}_3\text{OH}]$  increases;  
 c.  $[\text{H}_2]$  increases,  $[\text{CO}]$  decreases,  $[\text{CH}_3\text{OH}]$  decreases;  
 d.  $[\text{H}_2]$  increases,  $[\text{CO}]$  increases,  $[\text{CH}_3\text{OH}]$  increases;  
 e.  $[\text{H}_2]$  increases,  $[\text{CO}]$  increases,  $[\text{CH}_3\text{OH}]$  decreases;  
 f. no changes.

### 13.E.3.18: Q13.3.11

Nitrogen and oxygen react at high temperatures.

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

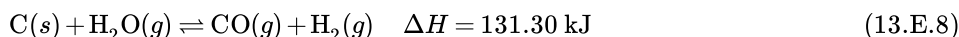


- b. What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if more  $\text{O}_2$  is added?  
 c. What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if  $\text{N}_2$  is removed?  
 d. What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if  $\text{NO}$  is added?  
 e. What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  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  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if the temperature of the system is increased?  
 g. What will happen to the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium if a catalyst is added?

### 13.E.3.19: Q13.3.12

Water gas, a mixture of  $\text{H}_2$  and  $\text{CO}$ , 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



- b. What will happen to the concentration of each reactant and product at equilibrium if more  $\text{C}$  is added?  
 c. What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2\text{O}$  is removed?  
 d. What will happen to the concentration of each reactant and product at equilibrium if  $\text{CO}$  is added?  
 e. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

### 13.E.3.20: S13.3.12

- (a)  $K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$ ; (b)  $[\text{H}_2\text{O}]$  no change,  $[\text{CO}]$  no change,  $[\text{H}_2]$  no change; (c)  $[\text{H}_2\text{O}]$  decreases,  $[\text{CO}]$  decreases,  $[\text{H}_2]$  decreases;  
 (d)  $[\text{H}_2\text{O}]$  increases,  $[\text{CO}]$  increases,  $[\text{H}_2]$  decreases; (f)  $[\text{H}_2\text{O}]$  decreases,  $[\text{CO}]$  increases,  $[\text{H}_2]$  increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

### 13.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



- What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?
- What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2\text{O}$  is removed?
- What will happen to the concentration of each reactant and product at equilibrium if  $\text{H}_2$  is added?
- 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?
- What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

### 13.E.3.22: Q13.3.14

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



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

- Addition of NaOH
- Addition of HCl
- Addition of  $\text{NH}_4\text{Cl}$

### 13.E.3.23: S13.3.14

Only (b)

### 13.E.3.24: Q13.3.15

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

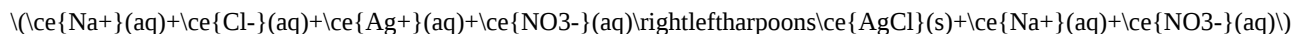


Will any of the following increase the percent of acetic acid that reacts and produces  $\text{CH}_3\text{CO}_2^-$  ion?

- Addition of HCl
- Addition of NaOH
- Addition of  $\text{NaCH}_3\text{CO}_2$

### 13.E.3.25: Q13.3.16

Suggest two ways in which the equilibrium concentration of  $\text{Ag}^+$  can be reduced in a solution of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Ag}^+$ , and  $\text{NO}_3^-$ , in contact with solid AgCl.



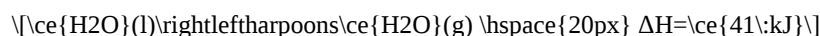
$$\Delta H = -65.9 \text{ kJ}$$

### 13.E.3.26: S13.3.16

Add NaCl or some other salt that produces  $\text{Cl}^-$  to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(s).

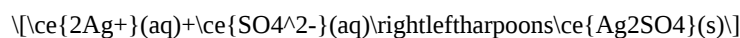
### 13.E.3.27: Q13.3.17

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



### 13.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.



Which of the following will occur?

- $\text{Ag}^+$  or  $\text{SO}_4^{2-}$  concentrations will not change.
- The added silver sulfate will dissolve.



- c. Additional silver sulfate will form and precipitate from solution as  $\text{Ag}^+$  ions and  $\text{SO}_4^{2-}$  ions combine.  
 d. The  $\text{Ag}^+$  ion concentration will increase and the  $\text{SO}_4^{2-}$  ion concentration will decrease.

### 13.E.3.29: S13.3.18

(a)

### 13.E.3.30: Q13.3.19

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

## 13.E.4: 13.4: Equilibrium Calculations Exercises

### 13.E.4.1: Q13.4.1

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

- Write the mathematical expression for the equilibrium constant.
- Using concentrations  $\leq 1 \text{ M}$ , make up two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

### 13.E.4.2: S13.4.1

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

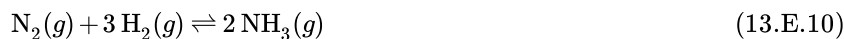
### 13.E.4.3: Q13.4.2

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

- Write the mathematical expression for the equilibrium constant.
- Using concentrations of  $\leq 1 \text{ M}$ , make up two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

### 13.E.4.4: Q13.4.3

What is the value of the equilibrium constant at  $500^\circ\text{C}$  for the formation of  $\text{NH}_3$  according to the following equation?



An equilibrium mixture of  $\text{NH}_3(g)$ ,  $\text{H}_2(g)$ , and  $\text{N}_2(g)$  at  $500^\circ\text{C}$  was found to contain  $1.35 \text{ M H}_2$ ,  $1.15 \text{ M N}_2$ , and  $4.12 \times 10^{-1} \text{ M NH}_3$ .

### 13.E.4.5: S13.4.3

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

### 13.E.4.6: Q13.4.4

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



What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations:  $\text{CH}_4$ ,  $0.126 \text{ M}$ ;  $\text{H}_2\text{O}$ ,  $0.242 \text{ M}$ ;  $\text{CO}$ ,  $0.126 \text{ M}$ ;  $\text{H}_2$ ,  $1.15 \text{ M}$ , at a temperature of  $760^\circ\text{C}$ ?

A  $0.72\text{-mol}$  sample of  $\text{PCl}_5$  is put into a  $1.00\text{-L}$  vessel and heated. At equilibrium, the vessel contains  $0.40 \text{ mol}$  of  $\text{PCl}_3(g)$  and  $0.40 \text{ mol}$  of  $\text{Cl}_2(g)$ . Calculate the value of the equilibrium constant for the decomposition of  $\text{PCl}_5$  to  $\text{PCl}_3$  and  $\text{Cl}_2$  at this temperature.

### 13.E.4.7: S13.4.4

$$K_c = 0.50$$

### 13.E.4.8: Q13.4.5

At  $1 \text{ atm}$  and  $25^\circ\text{C}$ ,  $\text{NO}_2$  with an initial concentration of  $1.00 \text{ M}$  is  $3.3 \times 10^{-3}\%$  decomposed into  $\text{NO}$  and  $\text{O}_2$ . Calculate the value of the equilibrium constant for the reaction.



#### 13.E.4.9: Q13.4.6

Calculate the value of the equilibrium constant  $K_P$  for the reaction  $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$  from these equilibrium pressures: NO, 0.050 atm;  $\text{Cl}_2$ , 0.30 atm; NOCl, 1.2 atm.

#### 13.E.4.10: S13.4.6

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

#### 13.E.4.11: Q13.4.7

When heated, iodine vapor dissociates according to this equation:



At 1274 K, a sample exhibits a partial pressure of  $\text{I}_2$  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.

#### 13.E.4.12: Q13.4.8

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



At equilibrium, the pressure of  $\text{NH}_3(g)$  was found to be 1.75 atm. What is the value of the equilibrium constant  $K_P$  for the decomposition at this temperature?

#### 13.E.4.13: S13.4.8

$K_P = 3.06$

#### 13.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?



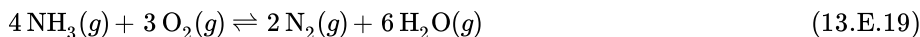
#### 13.E.4.15: Q13.4.10

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

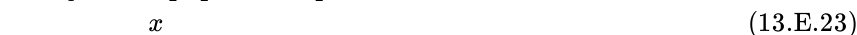
(a)



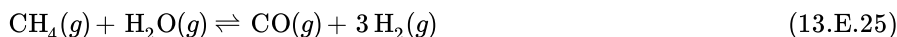
(b)



(c) Change in pressure:



(d) Change in pressure:



(e)



$$x \quad \text{_____} \quad (13.E.29)$$

$$1.03 \times 10^{-4} M \quad \text{_____} \quad (13.E.30)$$

(f) change in pressure:



$$4x \quad \text{_____} \quad (13.E.32)$$

$$0.40 \text{ atm} \quad \text{_____} \quad (13.E.33)$$

#### 13.E.4.16: S13.4.10

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

#### 13.E.4.17: Q13.4.11

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

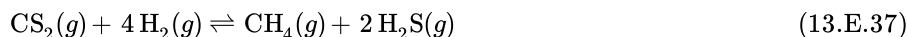
(a)



$$\text{_____} \quad \text{_____} \quad + 2x \quad (13.E.35)$$

$$\text{_____} \quad \text{_____} \quad 1.50 M \quad (13.E.36)$$

(b)



$$x \quad \text{_____} \quad \text{_____} \quad \text{_____} \quad (13.E.38)$$

$$0.020 M \quad \text{_____} \quad \text{_____} \quad \text{_____} \quad (13.E.39)$$

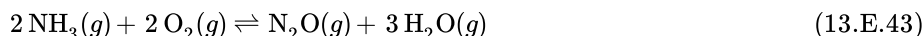
(c) Change in pressure:



$$x \quad \text{_____} \quad \text{_____} \quad (13.E.41)$$

$$1.50 \text{ atm} \quad \text{_____} \quad \text{_____} \quad (13.E.42)$$

(d) Change in pressure:



$$\text{_____} \quad \text{_____} \quad \text{_____} \quad x \quad (13.E.44)$$

$$\text{_____} \quad \text{_____} \quad \text{_____} \quad 60.6 \text{ torr} \quad (13.E.45)$$

(e)



$$x \quad \text{_____} \quad \text{_____} \quad (13.E.47)$$

$$9.8 \times 10^{-6} M \quad \text{_____} \quad (13.E.48)$$

(f) Change in pressure:



$$\text{_____} \quad \text{_____} \quad x \quad (13.E.50)$$

$$\text{_____} \quad \text{_____} \quad 0.012 \text{ atm} \quad (13.E.51)$$

#### 13.E.4.18: Q13.4.12

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

### 13.E.4.19: S13.4.12

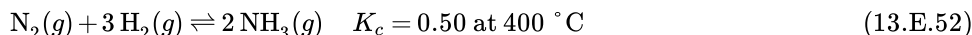
Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

### 13.E.4.20: Q13.4.13

Why are there no changes specified for  $\text{NH}_4\text{HS}$  in [Exercise](#), part (e)? What property of  $\text{NH}_4\text{HS}$  does change?

### 13.E.4.21: Q13.4.14

Analysis of the gases in a sealed reaction vessel containing  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$  at equilibrium at  $400^\circ\text{C}$  established the concentration of  $\text{N}_2$  to be  $1.2\text{ M}$  and the concentration of  $\text{H}_2$  to be  $0.24\text{ M}$ .



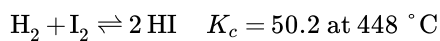
Calculate the equilibrium molar concentration of  $\text{NH}_3$ .

### 13.E.4.22: S13.4.14

$$[\text{NH}_3] = 9.1 \times 10^{-2}\text{ M}$$

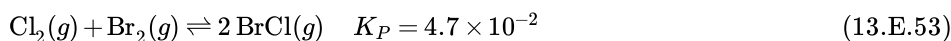
### 13.E.4.23: Q13.4.16

Calculate the number of moles of  $\text{HI}$  that are at equilibrium with  $1.25\text{ mol}$  of  $\text{H}_2$  and  $1.25\text{ mol}$  of  $\text{I}_2$  in a  $5.00\text{-L}$  flask at  $448^\circ\text{C}$ .



### 13.E.4.24: Q13.4.17

What is the pressure of  $\text{BrCl}$  in an equilibrium mixture of  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{BrCl}$  if the pressure of  $\text{Cl}_2$  in the mixture is  $0.115\text{ atm}$  and the pressure of  $\text{Br}_2$  in the mixture is  $0.450\text{ atm}$ ?

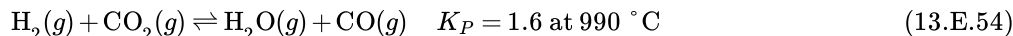


### 13.E.4.25: S13.4.17

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

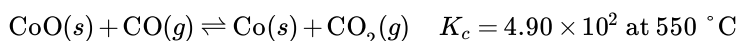
### 13.E.4.26: Q13.4.18

What is the pressure of  $\text{CO}_2$  in a mixture at equilibrium that contains  $0.50\text{ atm}$   $\text{H}_2$ ,  $2.0\text{ atm}$  of  $\text{H}_2\text{O}$ , and  $1.0\text{ atm}$  of  $\text{CO}$  at  $990^\circ\text{C}$ ?



### 13.E.4.27: Q13.4.12

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



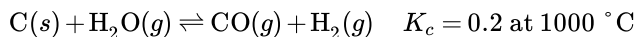
What concentration of  $\text{CO}$  remains in an equilibrium mixture with  $[\text{CO}_2] = 0.100\text{ M}$ ?

### 13.E.4.28: S13.4.12

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

### 13.E.4.29: Q13.4.13

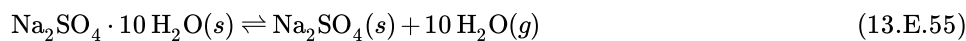
Carbon reacts with water vapor at elevated temperatures.



What is the concentration of  $\text{CO}$  in an equilibrium mixture with  $[\text{H}_2\text{O}] = 0.500\text{ M}$  at  $1000^\circ\text{C}$ ?

### 13.E.4.30: Q13.4.14

Sodium sulfate 10-hydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , dehydrates according to the equation



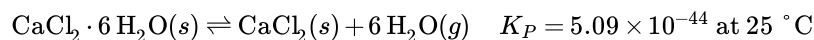
with  $K_p = 4.08 \times 10^{-25}$  at  $25^\circ\text{C}$ . What is the pressure of water vapor at equilibrium with a mixture of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{NaSO}_4$ ?

13.E.4.31: S13.4.14

$$P_{\text{H}_2\text{O}} = 3.64 \times 10^{-3} \text{ atm}$$

13.E.4.32: Q13.4.15

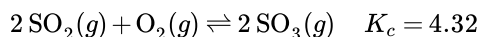
Calcium chloride 6-hydrate,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , dehydrates according to the equation



What is the pressure of water vapor at equilibrium with a mixture of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CaCl}_2$ ?

13.E.4.33: Q13.4.16

A student solved the following problem and found the equilibrium concentrations to be  $[\text{SO}_2] = 0.590 \text{ M}$ ,  $[\text{O}_2] = 0.0450 \text{ M}$ , and  $[\text{SO}_3] = 0.260 \text{ M}$ . How could this student check the work without reworking the problem? The problem was: For the following reaction at  $600^\circ\text{C}$ :



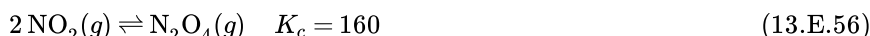
What are the equilibrium concentrations of all species in a mixture that was prepared with  $[\text{SO}_3] = 0.500 \text{ M}$ ,  $[\text{SO}_2] = 0 \text{ M}$ , and  $[\text{O}_2] = 0.350 \text{ M}$ ?

13.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.

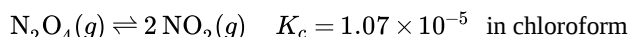
13.E.4.35: Q13.4.16

A student solved the following problem and found  $[\text{N}_2\text{O}_4] = 0.16 \text{ M}$  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  $\text{N}_2\text{O}_4$  in a mixture formed from a sample of  $\text{NO}_2$  with a concentration of  $0.10 \text{ M}$ ?



Assume that the change in concentration of  $\text{N}_2\text{O}_4$  is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in  $1.00 \text{ L}$  of a solution prepared from  $0.129 \text{ mol}$  of  $\text{N}_2\text{O}_4$  with chloroform as the solvent.



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

13.E.4.36: S13.4.16

(a)

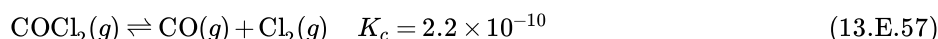
- $[\text{NO}_2] = 1.17 \times 10^{-3} \text{ M}$
- $[\text{N}_2\text{O}_4] = 0.128 \text{ M}$

(b) Percent error =  $\frac{5.87 \times 10^{-4}}{0.129} \times 100\% = 0.455\%$ . The change in concentration of  $\text{N}_2\text{O}_4$  is far less than the 5% maximum allowed.

13.E.4.37: Q13.4.17

Assume that the change in concentration of  $\text{COCl}_2$  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  $\text{COCl}_2$  with an initial concentration of  $0.3166 \text{ M}$ .

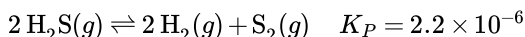


b. Show that the change is small enough to be neglected.

### 13.E.4.38: Q13.4.18

Assume that the change in pressure of  $\text{H}_2\text{S}$  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  $\text{H}_2\text{S}$  with an initial pressure of 0.824 atm.



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

### 13.E.4.39: S13.4.18

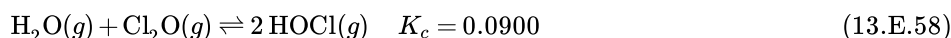
(a)

- $[\text{H}_2\text{S}] = 0.810 \text{ atm}$
- $[\text{H}_2] = 0.014 \text{ atm}$
- $[\text{S}_2] = 0.0072 \text{ atm}$

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

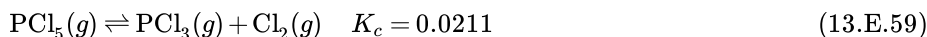
### 13.E.4.40: Q13.4.19

What are all concentrations after a mixture that contains  $[\text{H}_2\text{O}] = 1.00 \text{ M}$  and  $[\text{Cl}_2\text{O}] = 1.00 \text{ M}$  comes to equilibrium at  $25^\circ\text{C}$ ?



### 13.E.4.41: Q13.4.20

What are the concentrations of  $\text{PCl}_5$ ,  $\text{PCl}_3$ , and  $\text{Cl}_2$  in an equilibrium mixture produced by the decomposition of a sample of pure  $\text{PCl}_5$  with  $[\text{PCl}_5] = 2.00 \text{ M}$ ?

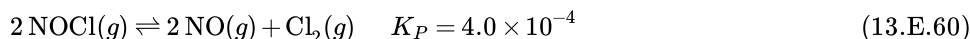


### 13.E.4.42: S13.4.20

$[\text{PCl}_3] = 1.80 \text{ M}$ ;  $[\text{PCl}_5] = 0.195 \text{ M}$ ;  $[\text{Cl}_2] = 0.195 \text{ M}$ .

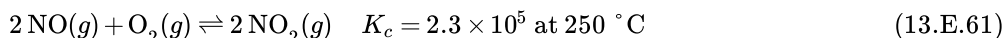
### 13.E.4.43: Q13.4.21

Calculate the pressures of all species at equilibrium in a mixture of  $\text{NOCl}$ ,  $\text{NO}$ , and  $\text{Cl}_2$  produced when a sample of  $\text{NOCl}$  with a pressure of 10.0 atm comes to equilibrium according to this reaction:



### 13.E.4.44: Q13.4.22

Calculate the equilibrium concentrations of  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{NO}_2$  in a mixture at  $250^\circ\text{C}$  that results from the reaction of  $0.20 \text{ M NO}$  and  $0.10 \text{ M O}_2$ . (Hint:  $K$  is large; assume the reaction goes to completion then comes back to equilibrium.)

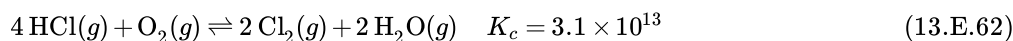


### 13.E.4.45: S13.4.22

- $[\text{NO}_2] = 0.19 \text{ M}$
- $[\text{NO}] = 0.0070 \text{ M}$
- $[\text{O}_2] = 0.0035 \text{ M}$

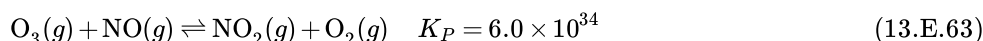
### 13.E.4.46: Q13.4.23

Calculate the equilibrium concentrations that result when  $0.25 \text{ M O}_2$  and  $1.0 \text{ M HCl}$  react and come to equilibrium.



### 13.E.4.47: Q13.4.24

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



What is the pressure of  $\text{O}_3$  remaining after a mixture of  $\text{O}_3$  with a pressure of  $1.2 \times 10^{-8}$  atm and  $\text{NO}$  with a pressure of  $1.2 \times 10^{-8}$  atm comes to equilibrium? (Hint:  $K_P$  is large; assume the reaction goes to completion then comes back to equilibrium.)

### 13.E.4.48: S13.4.24

$$P_{\text{O}_3} = 4.9 \times 10^{-26} \text{ atm}$$

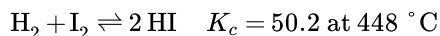
### 13.E.4.49: Q13.4.24

Calculate the pressures of  $\text{NO}$ ,  $\text{Cl}_2$ , and  $\text{NOCl}$  in an equilibrium mixture produced by the reaction of a starting mixture with 4.0 atm  $\text{NO}$  and 2.0 atm  $\text{Cl}_2$ . (Hint:  $K_P$  is small; assume the reverse reaction goes to completion then comes back to equilibrium.)



### 13.E.4.50: Q13.4.25

Calculate the number of grams of  $\text{HI}$  that are at equilibrium with 1.25 mol of  $\text{H}_2$  and 63.5 g of iodine at 448 °C.




### 13.E.4.51: S13.4.25

507 g

### 13.E.4.52: Q13.4.26

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

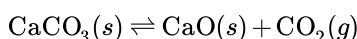
 Three Lewis structures are shown. The first is labeled, "n dash Butane," and has a C H subscript 3 single bonded to a C H subscript 2 group. This C H subscript 2 group is single bonded to another C H subscript 2 group which is single bonded to a C H subscript 3 group. The second is labeled, "iso dash 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.

$$K_P = 2.5 \text{ at } 25^\circ \text{C}$$

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

### 13.E.4.53: Q13.4.27

What is the minimum mass of  $\text{CaCO}_3$  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  $\text{CaCO}_3$  at that temperature?



### 13.E.4.54: S13.4.27

330 g

### 13.E.4.55: Q13.4.28

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



Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of  $\text{H}_2$ , 2.00 mol of  $\text{CO}_2$ , 0.750 mol of  $\text{H}_2\text{O}$ , and 1.00 mol of  $\text{CO}$  to a 5.00-L container at 990 °C.

### 13.E.4.56: Q13.4.29

At 25 °C and at 1 atm, the partial pressures in an equilibrium mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are  $P_{\text{N}_2\text{O}_4} = 0.70$  atm and  $P_{\text{NO}_2} = 0.30$  atm.

- Predict how the pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  will change if the total pressure increases to 9.0 atm. Will they increase, decrease, or remain the same?
- Calculate the partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  when they are at equilibrium at 9.0 atm and 25 °C.

### 13.E.4.57: S13.4.29

(a) Both gases must increase in pressure.

(b)  $P_{\text{N}_2\text{O}_4} = 8.0 \text{ atm}$  and  $P_{\text{NO}_2} = 1.0 \text{ atm}$

### 13.E.4.58: Q13.4.30

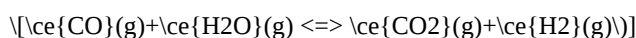
In a 3.0-L vessel, the following equilibrium partial pressures are measured:  $\text{N}_2$ , 190 torr;  $\text{H}_2$ , 317 torr;  $\text{NH}_3$ ,  $1.00 \times 10^3$  torr.



- How will the partial pressures of  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  change if  $\text{H}_2$  is removed from the system? Will they increase, decrease, or remain the same?
- 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.

### 13.E.4.59: Q13.4.31

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



- On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of  $\text{CO}$ , 0.30 mol of water vapor, and 0.90 mol of  $\text{H}_2$  in a liter. How many moles of  $\text{CO}_2$  were there in the equilibrium mixture?
- Maintaining the same temperature, additional  $\text{H}_2$  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  $\text{CO}$ , 0.30 mol of water vapor, and 1.2 mol of  $\text{H}_2$  in a liter. How many moles of  $\text{CO}_2$  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.

### 13.E.4.60: S13.4.31

(a) 0.33 mol.

(b)  $[\text{CO}]^2 = 0.50 \text{ M}$  Added  $\text{H}_2$  forms some water to compensate for the removal of water vapor and as a result of a shift to the left after  $\text{H}_2$  is added.

### 13.E.4.61: Q13.4.32a

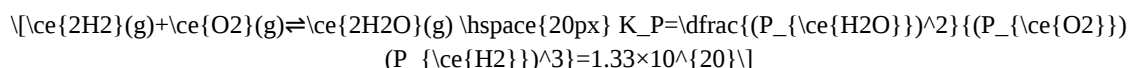
Antimony pentachloride decomposes according to this equation:



An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of  $\text{SbCl}_5$ , 9.14 g of  $\text{SbCl}_3$ , and 2.84 g of  $\text{Cl}_2$ . How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

### 13.E.4.62: Q13.4.32b

Consider the reaction between  $\text{H}_2$  and  $\text{O}_2$  at 1000 K



If 0.500 atm of  $\text{H}_2$  and 0.500 atm of  $\text{O}_2$  are allowed to come to equilibrium at this temperature, what are the partial pressures of the components?

### 13.E.4.63: S13.4.32b

$$P_{\text{H}_2} = 8.64 \times 10^{-11} \text{ atm}$$

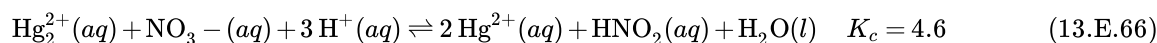
$$P_{\text{O}_2} = 0.250 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = 0.500 \text{ atm}$$



### 13.E.4.64: Q13.4.33

An equilibrium is established according to the following equation

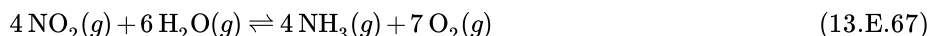


What will happen in a solution that is 0.20 M each in  $\text{Hg}_2^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{H}^+$ ,  $\text{Hg}^{2+}$ , and  $\text{HNO}_2$ ?

- $\text{Hg}_2^{2+}$  will be oxidized and  $\text{NO}_3^-$  reduced.
- $\text{Hg}_2^{2+}$  will be reduced and  $\text{NO}_3^-$  oxidized.
- $\text{Hg}_2^{2+}$  will be oxidized and  $\text{HNO}_2$  reduced.
- $\text{Hg}_2^{2+}$  will be reduced and  $\text{HNO}_2$  oxidized.
- There will be no change because all reactants and products have an activity of 1.

### 13.E.4.65: Q13.4.34

Consider the equilibrium



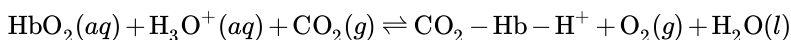
- What is the expression for the equilibrium constant ( $K_c$ ) of the reaction?
- How must the concentration of  $\text{NH}_3$  change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
- If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the pressure of  $\text{NO}_2$ ?
- If the change in the pressure of  $\text{NO}_2$  is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of  $\text{O}_2$  change?

### 13.E.4.66: S13.4.34

(a)  $K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^7}{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}$ . (b)  $[\text{NH}_3]$  must increase for  $Q_c$  to reach  $K_c$ . (c) That decrease in pressure would decrease  $[\text{NO}_2]$ . (d)  $P_{\text{O}_2} = 49$  torr

### 13.E.4.67: Q13.4.35

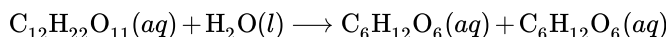
The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin ( $\text{HbO}_2$ ), is partially regulated by the concentration of  $\text{H}_3\text{O}^+$  and dissolved  $\text{CO}_2$  in the blood. Although the equilibrium is complicated, it can be summarized as



- (a) Write the equilibrium constant expression for this reaction.
- (b) Explain why the production of lactic acid and  $\text{CO}_2$  in a muscle during exertion stimulates release of  $\text{O}_2$  from the oxyhemoglobin in the blood passing through the muscle.

### 13.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.



Rate =  $k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$

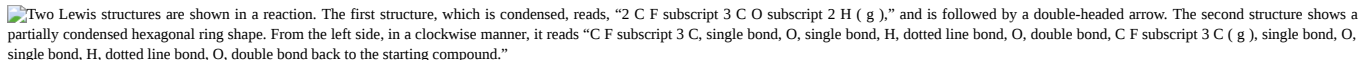
In neutral solution,  $k = 2.1 \times 10^{-11}/\text{s}$  at 27 °C. (As indicated by the rate constant, this is a very slow reaction. In the human body, the rate of this reaction is sped up by a type of catalyst called an enzyme.) (Note: That is not a mistake in the equation—the products of the reaction, glucose and fructose, have the same molecular formulas,  $\text{C}_6\text{H}_{12}\text{O}_6$ , but differ in the arrangement of the atoms in their molecules). The equilibrium constant for the reaction is  $1.36 \times 10^5$  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.

### 13.E.4.69: S13.4.36

[fructose] = 0.15 M

### 13.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.



Liquid  $\text{N}_2\text{O}_3$  is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to  $\text{NO}$  and  $\text{NO}_2$ . At 25 °C, a value of  $K_p = 1.91$  has been established for this decomposition. If 0.236 moles of  $\text{N}_2\text{O}_3$  are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of  $\text{N}_2\text{O}_3(g)$ ,  $\text{NO}_2(g)$ , and  $\text{NO}(g)$ .

### 13.E.4.71: S13.4.37

$P_{\text{N}_2\text{O}_3} = 1.90 \text{ atm}$  and  $P_{\text{NO}} = P_{\text{NO}_2} = 1.90 \text{ atm}$

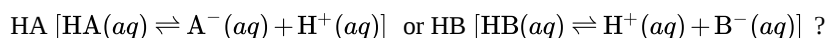
### 13.E.4.72: Q13.4.38

A 1.00-L vessel at 400 °C contains the following equilibrium concentrations:  $\text{N}_2$ , 1.00 M;  $\text{H}_2$ , 0.50 M; and  $\text{NH}_3$ , 0.25 M. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 M?

### 13.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



(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 ( $\text{A}^-$  or  $\text{B}^-$ ), and the hydrogen ion ( $\text{H}^+$ ). 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.)

### 13.E.4.74: S13.4.39

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

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

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

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