

18. (a)  
19. (c)  
20. (a)

## CHAPTER 7 REVIEW

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### Understanding Concepts

- Chemical equilibrium is a dynamic equilibrium between the reactants and products of a chemical reaction in a closed system.
  - Chemical equilibrium depends on the rate of the two opposing processes being equal.
- Two ways to describe the relative amounts of reactants and products are percent reaction and the equilibrium law expression.
- A soft drink is in a non-equilibrium state when it is open.
  - A soft drink is in an equilibrium state when it is closed.
- When a chemical system at equilibrium is disturbed by a change in a property, the system adjusts in a way that opposes the change.
- Given the size of the equilibrium constant, the amount of water present at equilibrium far exceeds the amount of hydrogen and oxygen. For all practical purposes, this reaction is complete.
- Variables commonly manipulated to shift the position of the equilibrium include: concentration, temperature, volume/pressure.
- An increase in volume of a container results in a decrease in pressure. Conversely, a decrease in volume results in an increase in pressure.
- An increase in the concentration of reactants as well as a decrease in the concentration of products can improve yield.
- approx. 100%

$$2 \text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2 \text{H}_2\text{O}_{(\text{g})}$$

$$K = \frac{[\text{H}_2\text{O}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}]^2[\text{O}_{2(\text{g})}]}$$
  - approx. 67%

$$\text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \rightleftharpoons \text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})}$$

$$K = \frac{[\text{CO}_{2(\text{g})}][\text{H}_{2(\text{g})}]}{[\text{CO}_{(\text{g})}][\text{H}_2\text{O}_{(\text{g})}]}$$
  - <10%

$$\text{N}_{2(\text{g})} + 3 \text{H}_{2(\text{g})} \rightleftharpoons 2 \text{NH}_{3(\text{g})}$$

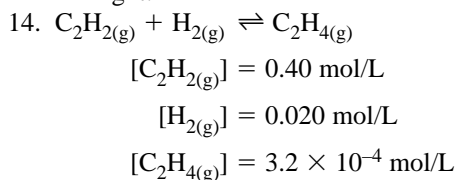
$$K = \frac{[\text{NH}_{3(\text{g})}]^2}{[\text{N}_{2(\text{g})}][\text{H}_{2(\text{g})}]^3}$$
- $$2 \text{NO}_{2(\text{g})} \rightleftharpoons \text{N}_2\text{O}_{4(\text{g})}$$

$$K = \frac{[\text{N}_2\text{O}_{4(\text{g})}]}{[\text{NO}_{2(\text{g})}]^2}$$
  - $$\frac{[\text{N}_2\text{O}_{4(\text{g})}]}{[0.050]^2} = 1.15$$

$$[\text{N}_2\text{O}_{4(\text{g})}] = 2.9 \times 10^{-3} \text{ mol/L}$$

The concentration of dinitrogen tetroxide is  $2.9 \times 10^{-3} \text{ mol/L}$ .
  - An increase in the nitrogen dioxide concentration will shift the equilibrium to the right.
- left
  - left
  - right
  - no effect
  - no effect

12. (a) Conditions that would increase the yield of ethene include:
- increasing the temperature.
  - decreasing the pressure on the system, or conversely, increasing the volume.
  - increasing the concentration of ethane.
  - removing the products as quickly as they form.
- (b) Conditions that would increase the yield of methanol include:
- decreasing the temperature.
  - increasing the pressure on the system, or conversely, decreasing the volume.
  - increasing the concentration of the reactants.
  - removing methanol as quickly as it forms.
13. (a) The addition of  $\text{CuSO}_4$  increases the concentration of copper(II) ions. The system shifts to the right to remove excess copper(II) ions.
- (b) The reverse reaction is favoured when the temperature is decreased, causing the system to shift to the left.
- (c) The addition of a solid has no effect on the equilibrium because condensed phases are not included in the equilibrium law expression.
- (d) A decrease in volume (increase in pressure) favours the reverse reaction, shifting the equilibrium to the left.
- (e) Silver ions from the silver nitrate combine with chloride ions from the equilibrium to produce a silver chloride precipitate. The system adjusts by favouring the forward reaction, which produces more chloride.
- (f) A volume change has no effect on this equilibrium because the same number of moles of gas are on each side of the chemical equation.
- (g) Iron(III) ions released from  $\text{Fe}(\text{NO}_3)_3$  favour the formation of more  $\text{FeSCN}_{(\text{aq})}^{2+}$ , shifting the equilibrium to the right.

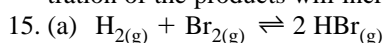


$$Q = \frac{[\text{C}_2\text{H}_{4(\text{g})}]}{[\text{C}_2\text{H}_{2(\text{g})}][\text{H}_{2(\text{g})}]}$$

$$= \frac{[3.2 \times 10^{-4}]}{[0.40][0.020]}$$

$$Q = 0.040$$

Since the value of  $Q$  is less than the value of  $K$  (0.072), the reaction is not at equilibrium. In order to attain equilibrium, the reaction will shift to the right (as written). The concentration of the reactants will decrease and the concentration of the products will increase.



Initial concentrations are

$$[\text{HBr}_{2(\text{g})}] = 0.00$$

$$[\text{H}_{2(\text{g})}] = [\text{Br}_{2(\text{g})}]$$

$$= \frac{8.00 \text{ mol}}{2.00 \text{ L}}$$

$$[\text{H}_{2(\text{g})}] = 4.00 \text{ mol/L}$$

ICE Table for the Formation of $\text{HBr}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{Br}_{2(\text{g})} \rightleftharpoons$	$2 \text{HBr}_{(\text{g})}$
Initial concentration (mol/L)	4.00	4.00	0.00
Change in concentration (mol/L)	-x	-x	-2x
Equilibrium concentration (mol/L)	$4.00 - x$	$4.00 - x$	$2x$

At equilibrium,

$$K = \frac{[\text{HBr}_{(g)}]^2}{[\text{H}_{2(g)}][\text{Br}_{2(g)}]}$$

$$\frac{(2x)^2}{(4.00 - x)^2} = 12.0$$

$$\sqrt{\frac{(2x)^2}{(4.00 - x)^2}} = \sqrt{12.0}$$

$$\frac{2x}{4.00 - x} = 3.464 \quad (\text{extra digits carried})$$

$$2x = 3.464(4.00 - x)$$

$$x = 2.536$$

$$[\text{HBr}_{(g)}] = 2x$$

$$= 2(2.536)$$

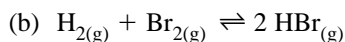
$$[\text{HBr}_{(g)}] = 5.07 \text{ mol/L}$$

$$[\text{H}_{2(g)}] = [\text{Br}_{2(g)}]$$

$$= 4.00 - x$$

$$[\text{H}_{2(g)}] = 1.46 \text{ mol/L}$$

The equilibrium concentrations of hydrogen, bromine, and hydrogen bromide are 1.46 mol/L, 1.46 mol/L, and 5.07 mol/L, respectively.



Initial concentrations are

$$[\text{HBr}_{(g)}] = 0.00$$

$$[\text{H}_{2(g)}] = [\text{Br}_{2(g)}]$$

$$= \frac{12.00 \text{ mol}}{2.00 \text{ L}}$$

$$[\text{H}_{2(g)}] = 6.00 \text{ mol/L}$$

ICE Table for the Formation of $\text{HBr}_{(g)}$				
	$\text{H}_{2(g)}$	$+$	$\text{Br}_{2(g)} \rightleftharpoons$	$2 \text{HBr}_{(g)}$
Initial concentration (mol/L)	6.00		6.00	0.000
Change in concentration (mol/L)	-x		-x	+2x
Equilibrium concentration (mol/L)	6.00 - x		6.00 - x	2x

At equilibrium,

$$K = \frac{[\text{HBr}_{(g)}]^2}{[\text{H}_{2(g)}][\text{Br}_{2(g)}]}$$

$$\frac{(2x)^2}{(6.00 - x)^2} = 12.0$$

$$\sqrt{\frac{(2x)^2}{(6.00 - x)^2}} = \sqrt{12.0}$$

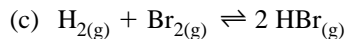
$$\frac{2x}{6.00 - x} = 3.464 \quad (\text{extra digits carried})$$

$$2x = 3.464(6.00 - x)$$

$$x = 3.804$$

$$\begin{aligned}
 [\text{HBr}_{(g)}] &= 2x \\
 &= 2(3.804) \\
 [\text{HBr}_{(g)}] &= 7.61 \text{ mol/L} \\
 [\text{H}_{2(g)}] &= [\text{Br}_{2(g)}] \\
 &= 6.00 - x \\
 [\text{H}_{2(g)}] &= 2.20 \text{ mol/L}
 \end{aligned}$$

The equilibrium concentrations of hydrogen, bromine, and hydrogen bromide are 2.20 mol/L, 2.20 mol/L, and 7.61 mol/L, respectively.



Initial concentrations are

$$\begin{aligned}
 [\text{HBr}_{(g)}] &= 0.00 \\
 [\text{H}_{2(g)}] &= \frac{12.00 \text{ mol}}{2.00 \text{ L}} \\
 [\text{H}_{2(g)}] &= 6.00 \text{ mol/L} \\
 [\text{Br}_{2(g)}] &= \frac{8.00 \text{ mol}}{2.00 \text{ L}} \\
 [\text{Br}_{2(g)}] &= 4.00 \text{ mol/L}
 \end{aligned}$$

ICE Table for the Formation of $\text{HBr}_{(g)}$			
	$\text{H}_{2(g)} +$	$\text{Br}_{2(g)} \rightleftharpoons$	$2 \text{HBr}_{(g)}$
Initial concentration (mol/L)	6.00	4.00	0.00
Change in concentration (mol/L)	-x	-x	+2x
Equilibrium concentration (mol/L)	6.00 - x	4.00 - x	2x

At equilibrium,

$$K = \frac{[\text{HBr}_{(g)}]^2}{[\text{H}_{2(g)}][\text{Br}_{2(g)}]}$$

$$\frac{(2x)^2}{(6.00 - x)(4.00 - x)} = 12.0$$

$$\frac{4x^2}{(6.00 - x)(4.00 - x)} = 12.0$$

$$12.0(6.00 - x)(4.00 - x) = 4x^2 \quad (\text{extra digits carried})$$

$$3(6.00 - x)(4.00 - x) = x^2$$

$$3(24 - 10x + x^2) = x^2$$

$$2x^2 - 30x + 72 = 0$$

$$x^2 - 15x + 36 = 0$$

$$x = \frac{15 \pm \sqrt{15^2 - 4(1)(36)}}{2(1)}$$

$$x = 12.0 \text{ or } 3.00$$

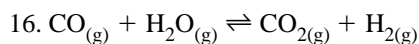
$x = 12.0$  gives a negative concentration, which is meaningless.

$$\therefore x = 3.00$$

$$[\text{HBr}_{(g)}] = 2x$$

$$\begin{aligned}
 &= 2(3.00) \\
 &= 6.00 \text{ mol/L} \\
 &\quad [\text{H}_{2(\text{g})}][\text{Br}_{2(\text{g})}] \\
 &= 6.00 - x \\
 [\text{HBr}_{(\text{g})}] &= 3.00 \text{ mol/L} \\
 [\text{Br}_{2(\text{g})}] &= 4.00 - x \\
 [\text{Br}_{2(\text{g})}] &= 1.00 \text{ mol/L}
 \end{aligned}$$

The equilibrium concentrations of hydrogen, bromine, and hydrogen bromide are 3.00 mol/L, 1.00 mol/L, and 6.00 mol/L, respectively.



$$[\text{CO}_{(\text{g})}] = 4.00 \text{ mol/L}$$

$$[\text{H}_2\text{O}_{(\text{g})}] = 2.00 \text{ mol/L}$$

$$[\text{CO}_{2(\text{g})}] = 4.00 \text{ mol/L}$$

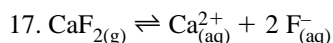
$$[\text{H}_{2(\text{g})}] = 2.00 \text{ mol/L}$$

$$Q = \frac{[\text{CO}_{2(\text{g})}][\text{H}_{2(\text{g})}]}{[\text{CO}_{(\text{g})}][\text{H}_2\text{O}_{(\text{g})}]}$$

$$= \frac{[4.00][2.00]}{[4.00][2.00]}$$

$$Q = 1$$

Since the value of  $Q$  is less than the value of  $K$  (4.00), the reaction is not at equilibrium. In order to attain equilibrium, the reaction will shift to the right (as written). The concentration of the reactants will decrease and the concentration of the products will increase.



$$n_{\text{CaF}_{2(\text{s})}} = \frac{26.76 \times 10^{-3} \text{ g}}{78.08 \text{ g/mol}}$$

$$n_{\text{CaF}_{2(\text{s})}} = 3.4273 \times 10^{-4} \text{ mol} \quad (\text{extra digits carried})$$

$$[\text{CaF}_{2(\text{aq})}] = [\text{Ca}_{(\text{aq})}^{2+}]$$

$$= \frac{3.4273 \times 10^{-4} \text{ mol}}{1.00 \text{ L}}$$

$$[\text{CaF}_{2(\text{aq})}] = 3.4273 \times 10^{-4} \text{ mol/L}$$

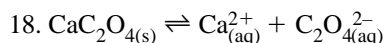
$$[\text{F}_{(\text{aq})}^-] = 2[\text{Ca}_{(\text{aq})}^{2+}]$$

$$[\text{F}_{(\text{aq})}^-] = 6.8546 \times 10^{-4} \text{ mol/L}$$

$$\begin{aligned}
 K_{\text{sp}} &= [\text{Ca}_{(\text{aq})}^{2+}][\text{F}_{(\text{aq})}^-]^2 \\
 &= [3.4273 \times 10^{-4}][6.8546 \times 10^{-4}]^2
 \end{aligned}$$

$$K_{\text{sp}} = 1.61 \times 10^{-10}$$

The  $K_{\text{sp}}$  for calcium fluoride is  $1.61 \times 10^{-10}$ .



$$K_{\text{sp}} = [\text{Ca}_{(\text{aq})}^{2+}][\text{C}_2\text{O}_4(\text{aq})^{2-}]$$

$$K_{\text{sp}} = 2.3 \times 10^{-9}$$

$$[\text{Ca}_{(\text{aq})}^{2+}] = [\text{C}_2\text{O}_4(\text{aq})^{2-}]$$

$$2.3 \times 10^{-9} = [\text{Ca}_{(\text{aq})}^{2+}]^2$$

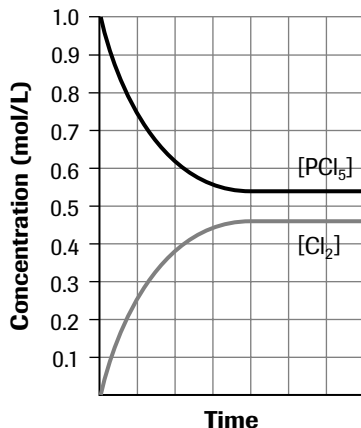
$$[\text{Ca}_{(\text{aq})}^{2+}] = 4.8 \times 10^{-5} \text{ mol/L}$$

$$\begin{aligned}
 [\text{CaC}_2\text{O}_{4(\text{aq})}] &= [\text{Ca}_{(\text{aq})}^{2+}] \\
 &= 4.8 \times 10^{-5} \text{ mol/L}
 \end{aligned}$$

The molar solubility of calcium oxalate is  $4.8 \times 10^{-5} \text{ mol/L}$ .

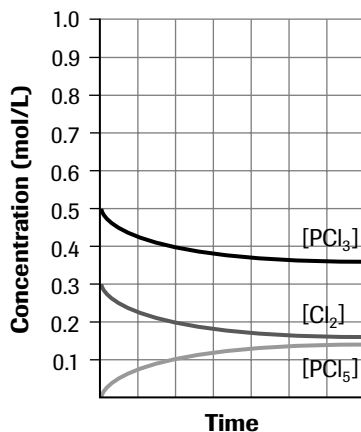
### Applying Inquiry Skills

19. (a)



The concentrations of PCl<sub>3</sub> and Cl<sub>2</sub> both begin at zero, increase, and level off at 0.46 mol/L.

(b)

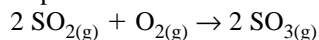


20. (a) The addition of a common ion (chloride) will shift a system in the direction that consumes the common ion.  
 (b) Both hydrochloric acid and sodium chloride had a similar effect on the equilibrium. Although the amounts of both chemicals increased in regular increments, the concentration of the chloride ion does not increase regularly. The addition of the solid NaCl increases the chloride solution at a faster rate than adding a solution of hydrochloric acid because the total volume does not change. An improvement to the experiment could be to use two solids, such as NaCl and NaBr, or two solutions, such as HCl<sub>(aq)</sub> and HBr<sub>(aq)</sub>.

### Making Connections

21. The tungsten and iodine reaction to produce tungsten(II) iodide is exothermic. A high temperature of the system forces the equilibrium to shift to the left, depositing tungsten on the filament. This deposition reverses the tendency of the tungsten to be lost gradually from the filament. The presence of the halogen (iodine) helps to establish an equilibrium, which at high temperature, restores the filament.  
 22. The unreacted reagents should be pumped back into the process to make more ammonia.  
 23. Most of the sulfuric acid manufactured is produced using the Contact Process, a process involving the catalytic oxidation of sulfur dioxide, SO<sub>2</sub>, to sulfur trioxide, SO<sub>3(g)</sub>.  
 I.  $\text{S}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow \text{SO}_{2(\text{g})}$   
 II.  $2 \text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2 \text{SO}_{3(\text{g})}$   
 III.  $\text{SO}_{3(\text{g})} + \text{H}_2\text{SO}_{4(\text{l})} \rightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l})$   
 IV.  $\text{H}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}_{(\text{l})} \rightarrow 2 \text{H}_2\text{SO}_{4(\text{l})}$

The oxidation of sulfur dioxide to sulfur trioxide in step III above is an exothermic reaction, and according to Le Châtelier's principle, higher temperatures will force the equilibrium position to shift to the left, favouring the production of sulfur dioxide. Lower temperatures would favour the production of sulfur trioxide and result in a higher yield. However, the rate of reaching equilibrium at the lower temperatures is extremely low. A higher temperature would mean equilibrium is established more rapidly but the yield of sulfur trioxide is lower. A temperature of 450°C is a compromise, whereby a faster reaction rate results in a slightly lower yield. Similarly, at higher pressures, the equilibrium position shifts to the side of the equation in which there are the least numbers of gaseous molecules.



According to Le Châtelier's principle, higher pressure favours the right-hand side. Higher pressure results in a higher yield of sulfur trioxide. A vanadium catalyst is also used in this reaction in order to speed up the rate of the reaction.

24. (a) The increase in pressure as the diver descends, shifts the equilibrium to the right, forcing more gaseous nitrogen into solution.
- (b) The decrease in water pressure on the diver as he/she ascends, shifts the equilibrium to the left, favouring gaseous nitrogen.

### Extension

25. An increase in temperature shifts this equilibrium to the left, increasing the concentration of nitrogen dioxide and decreasing the concentration of dinitrogen tetroxide. As a result, high temperatures are associated with lower values of the equilibrium constant.  $K = 1250$  corresponds to 0°C and  $K = 200$  corresponds to 25°C.