

10. False: The spontaneity of a reaction depends on enthalpy changes as well as entropy changes.
11. False: The pH of acetic acid is greater than 1.
12. False: The hypochlorite ion is a weaker base than ammonia.
13. False: Metal oxides form basic solutions while nonmetal oxides form acidic solutions.
14. False: Potassium sulfate forms a neutral solution.
15. True
16. True
17. False: The pH at the equivalence point depends on the type of acid and base involved.
18. True
19. False: Buffering action occurs during the flat portions of the graph.
20. True
21. False: An effective acid–base buffer contains approximately equal amounts of a weak acid and its conjugate base.
22. True
23. (b)
24. (b)
25. (e)
26. (b)
27. (b)
28. (c)
29. (b)
30. (e)
31. (c)
32. (c)
33. (d)
34. (c)
35. (e)
36. (c)
37. (b)
38. (a)
39. (d)
40. (d)
41. (e)

UNIT 4 REVIEW

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Understanding Concepts

$$1. \frac{[\text{SO}_{2(g)}]^2[\text{O}_{2(g)}]}{[\text{SO}_{3(g)}]^2} = K$$

$$= \frac{1}{279}$$

$$K = 3.58 \times 10^{-3}$$

The equilibrium constant for the given reaction has a value of 3.58×10^{-3} .

$$2. K = \frac{[\text{NO}_{(g)}]^2}{[\text{N}_{2(g)}][\text{O}_{2(g)}]}$$

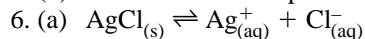
$$= \frac{[0.15]^2}{[0.63][0.21]}$$

$$K = 1.7 \times 10^{-3}$$

The equilibrium constant is 1.7×10^{-3} .

3. (a) [CO] decreases
- (b) [CO] decreases
- (c) [CO] increases

- (d) [CO] no effect
 (e) [CO] no effect
 (f) [CO] increases
 (g) [CO] decreases
4. (Sample answers) The equilibrium methanol concentration can be increased by:
- removing methanol as it is produced,
 - increasing the concentration of the reactants,
 - increasing the pressure on the system,
 - decreasing the volume of the reaction chamber,
 - cooling the reaction chamber.
5. (a) An increase in pressure shifts the equilibrium to the right, favouring the production of ammonium carbamate.
 (b) An increase in temperature and a reduction of pressure favour the production of urea.



$$K_{sp} = [\text{Ag}_{(aq)}^+][\text{Cl}_{(aq)}^-]$$

$$K_{sp} = 1.8 \times 10^{-10}$$

$$[\text{Ag}_{(aq)}^+] = [\text{Cl}_{(aq)}^-]$$

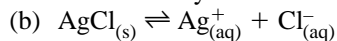
$$1.8 \times 10^{-10} = [\text{Ag}_{(aq)}^+]^2$$

$$[\text{Ag}_{(aq)}^+] = 1.3 \times 10^{-5} \text{ mol/L}$$

$$[\text{AgCl}_{(aq)}] = [\text{Ag}_{(aq)}^+]$$

$$[\text{AgCl}_{(aq)}] = 1.3 \times 10^{-5} \text{ mol/L}$$

The solubility of silver chloride is 1.3×10^{-5} .



$$K_{sp} = [\text{Ag}_{(aq)}^+][\text{Cl}_{(aq)}^-]$$

$$K_{sp} = 1.8 \times 10^{-10}$$

$$\text{If } [\text{Cl}_{(aq)}^-] = 0.015 \text{ mol/L}$$

$$1.8 \times 10^{-10} = [\text{Ag}_{(aq)}^+][0.015]$$

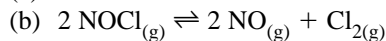
$$[\text{Ag}_{(aq)}^+] = 1.2 \times 10^{-8} \text{ mol/L}$$

$$[\text{AgCl}_{(aq)}] = [\text{Ag}_{(aq)}^+]$$

The solubility of silver chloride in 0.015 mol/L $\text{NaCl}_{(aq)}$ is 1.2×10^{-8} .

7. The synthesis of ammonia is exothermic. An increase in temperature results in a decrease in the value of the equilibrium constant. This observation implies that the concentration of ammonia decreases and the concentrations of nitrogen and hydrogen increase with a temperature increase. This result can only occur if the energy term is on the right side of the chemical equation.

8. (a) reactants

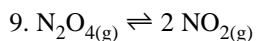


$$\frac{[\text{NO}_{(g)}]^2[\text{Cl}_{2(g)}]}{[\text{NOCl}_{(g)}]^2} = 1.60 \times 10^{-5}$$

$$\frac{[0.10]^2[0.10]}{[\text{NOCl}_{(g)}]^2} = 1.60 \times 10^{-5}$$

$$[\text{NOCl}_{(g)}] = 7.91 \text{ mol/L}$$

The equilibrium concentration of $\text{NOCl}_{(g)}$ is 7.91 mol/L.



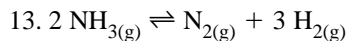
$$\frac{[\text{NO}_{2(g)}]^2}{[\text{N}_2\text{O}_{4(g)}]} = 6.13 \times 10^{-3}$$

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

$$= \frac{[4.00 \times 10^{-3}]^2}{[8.00 \times 10^{-4}]}$$

$$Q = 0.0200$$

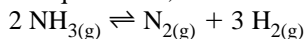
Since $Q \neq 6.13 \times 10^{-3}$, the system is not at equilibrium. The system will become less reddish-brown as it shifts to approach equilibrium.



$$\frac{[\text{N}_{2(g)}][\text{H}_{2(g)}]^3}{[\text{NH}_{3(g)}]^2} = 1.60 \times 10^{-3}$$

ICE Table for the Decomposition of Ammonia			
	$2 \text{NH}_{3(g)} \rightleftharpoons$	$\text{N}_{2(g)} +$	$3 \text{H}_{2(g)}$
Initial concentration (mol/L)	0.20	0.00	0.00
Change in concentration (mol/L)	$-2x$	$+x$	$+3x$
Equilibrium concentration (mol/L)	$0.20 - 2x$	x	$3x$

At equilibrium,



$$\frac{[\text{N}_{2(g)}][\text{H}_{2(g)}]^3}{[\text{NH}_{3(g)}]^2} = 1.60 \times 10^{-3}$$

$$\frac{[x][3x]^3}{[0.20 - 2x]^2} = 1.60 \times 10^{-3}$$

$$\frac{x^4}{(0.20 - 2x)^2} = 5.926 \times 10^{-3} \text{ (extra digits carried)}$$

$$\sqrt{\frac{x^4}{(0.20 - 2x)^2}} = \sqrt{5.926 \times 10^{-3}}$$

$$\frac{x^2}{0.20 - 2x} = 0.770$$

$$x^2 + 0.154x - 0.00154 = 0$$

$$x = \frac{-0.154 \pm \sqrt{(0.154)^2 - 4(1)(-0.00154)}}{2(1)}$$

$$x = 0.3229$$

$$[\text{NH}_{3(g)}] = 0.20 - 2x$$

$$= 0.20 - 2(0.3229)$$

$$[\text{NH}_{3(g)}] = 0.14 \text{ mol/L}$$

$$[\text{H}_{2(g)}] = 3x$$

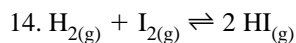
$$= 3(0.3229)$$

$$[\text{H}_{2(g)}] = 0.97 \text{ mol/L}$$

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

$$[\text{N}_{2(\text{g})}] = 0.32 \text{ mol/L}$$

The equilibrium concentrations of nitrogen, hydrogen, and ammonia are 0.32 mol/L, 0.097 mol/L, and 0.14 mol/L.



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

Initial concentrations are

$$[\text{H}_{2(\text{g})}]_{\text{initial}} = \frac{2.00 \text{ mol}}{5.00 \text{ L}}$$

$$[\text{H}_{2(\text{g})}]_{\text{initial}} = 0.400 \text{ mol/L}$$

$$[\text{I}_{2(\text{g})}]_{\text{initial}} = \frac{1.00 \text{ mol}}{5.00 \text{ L}}$$

$$[\text{I}_{2(\text{g})}]_{\text{initial}} = 0.200 \text{ mol/L}$$

$$[\text{HI}_{(\text{g})}]_{\text{initial}} = 0.0 \text{ mol/L}$$

ICE Table for the Formation of $\text{HI}_{(\text{g})}$			
	$\text{H}_{2(\text{g})} +$	$\text{I}_{2(\text{g})} \rightleftharpoons$	$2 \text{HI}_{(\text{g})}$
Initial concentration (mol/L)	0.400	0.200	0.000
Change in concentration (mol/L)	$-x$	$-x$	$+2x$
Equilibrium concentration (mol/L)	$0.400 - x$	$0.200 - x$	$2x$

At equilibrium,

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

$$\frac{(2x)^2}{(0.400 - x)(0.200 - x)} = 49.7$$

$$4x^2 = (49.7)(0.400 - x)(0.200 - x)$$

$$x^2 = (12.425)(0.0800 - 0.6x + x^2) \quad (\text{extra digits carried})$$

$$x^2 - 0.6525x + 0.0870 = 0$$

$$x = \frac{0.6525 \pm \sqrt{0.6525^2 - 4(0.0870)(1)}}{2(1)}$$

$$x = 0.46565 \text{ or } 0.18725 \quad (\text{extra digits carried})$$

The root 0.46565 is rejected as it exceeds the initial amount of hydrogen.

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

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

$$= 2 \times 0.18725$$

$$[\text{HI}_{(\text{g})}] = 0.375 \text{ mol/L}$$

$$[\text{H}_{2(\text{g})}] = 0.400 - x$$

$$= 0.400 - 0.18725$$

$$\begin{aligned}
 [\text{H}_{2(\text{g})}] &= 0.213 \text{ mol/L} \\
 [\text{I}_{2(\text{g})}] &= 0.200 - x \\
 &= 0.200 - 0.18725 \\
 [\text{I}_{2(\text{g})}] &= 0.013 \text{ mol/L}
 \end{aligned}$$

The equilibrium concentrations of hydrogen, iodine, and hydrogen iodide are 0.213 mol/L, 0.013 mol/L, and 0.375 mol/L, respectively.

15. At equilibrium,

$$\begin{aligned}
 2 \text{SO}_{3(\text{g})} &\rightleftharpoons 2 \text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \\
 \frac{[\text{SO}_{2(\text{g})}]^2 [\text{O}_{2(\text{g})}]}{[\text{SO}_{3(\text{g})}]^2} &= 6.9 \times 10^{-7} \\
 \frac{[2x]^2 [x]}{[0.200 - 2x]^2} &= 6.9 \times 10^{-7} \\
 \frac{4x^3}{(0.200 - 2x)^2} &= 6.9 \times 10^{-7}
 \end{aligned}$$

Assuming $0.200 - 2x \doteq 0.200 \dots$

$$\begin{aligned}
 \frac{4x^3}{(0.200)^2} &\doteq 6.9 \times 10^{-7} \\
 \frac{4x^3}{0.040} &\doteq 6.9 \times 10^{-7} \\
 100x^3 &\doteq 6.9 \times 10^{-7} \\
 x^3 &\doteq 6.9 \times 10^{-5} \\
 x &= 1.904 \times 10^{-3} \quad (\text{extra digits carried}) \\
 [\text{SO}_{3(\text{g})}] &= 0.200 - 2x \\
 &= 0.200 - 2(1.904 \times 10^{-3}) \\
 [\text{SO}_{3(\text{g})}] &= 0.20 \text{ mol/L} \\
 [\text{O}_{2(\text{g})}] &= 1.9 \times 10^{-3} \text{ mol/L} \\
 [\text{SO}_{2(\text{g})}] &= 2(1.904 \times 10^{-3}) \\
 [\text{SO}_{2(\text{g})}] &= 3.8 \times 10^{-3} \text{ mol/L}
 \end{aligned}$$

The equilibrium concentrations of sulfur trioxide, oxygen, and sulfur dioxide are 0.20 mol/L, 1.9×10^{-3} mol/L, and 3.8×10^{-3} mol/L, respectively.

$$\begin{aligned}
 16. K_{\text{sp}} &= [\text{Ca}_{(\text{aq})}^{2+}][\text{SO}_{4(\text{aq})}^{2-}] \\
 K_{\text{sp}} &= 7.1 \times 10^{-5} \\
 x^2 &= 7.1 \times 10^{-5} \\
 x &= 8.4 \times 10^{-3}
 \end{aligned}$$

The molar solubility of calcium sulfate is 8.4×10^{-3} mol/L.

ICE Table for the Dissolving of Calcium Sulfate			
	$\text{CaSO}_{4(\text{s})} \rightleftharpoons$	$\text{Ca}_{(\text{aq})}^{2+} +$	$\text{SO}_{4(\text{aq})}^{2-}$
Initial concentration (mol/L)			
Change in concentration (mol/L)		+x	+x
Equilibrium concentration (mol/L)			

$$x = 8.4 \times 10^{-3} \text{ mol/L}$$

The molar solubility of calcium sulfate is $8.4 \times 10^{-3} \text{ mol/L}$.

$$17. \quad K_{\text{sp}} = [\text{Pb}_{(\text{aq})}^{2+}][\text{Cl}_{(\text{aq})}^{-}]^2$$

$$K_{\text{sp}} = 1.2 \times 10^{-5}$$

$$(x)(2x)^2 = 1.2 \times 10^{-5}$$

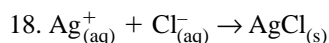
$$4x^3 = 1.2 \times 10^{-5}$$

$$x = 0.01442 \quad (\text{extra digits carried})$$

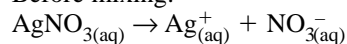
$$[\text{Cl}_{(\text{aq})}^{-}] = 2 \times 0.01442$$

$$[\text{Cl}_{(\text{aq})}^{-}] = 0.029 \text{ mol/L}$$

The molar concentration of chloride ions is 0.029 mol/L.



Before mixing:



$$[\text{AgNO}_{3(\text{aq})}] = [\text{Ag}_{(\text{aq})}^{+}]$$

$$[\text{AgNO}_{3(\text{aq})}] = 0.010 \text{ mol/L}$$

$$[\text{Cl}_{(\text{aq})}^{-}] = 2.2 \times 10^{-4} \text{ mol/L}$$

After mixing:

$$250.0 \text{ mL} + 250.0 \text{ mL} = 500.0 \text{ mL}$$

Concentrations after mixing:

$$[\text{Ag}_{(\text{aq})}^{+}] = 0.010 \text{ mol/L} \times \frac{250.0 \text{ mL}}{500.0 \text{ mL}}$$

$$[\text{Ag}_{(\text{aq})}^{+}] = 0.0050 \text{ mol/L}$$

$$[\text{Cl}_{(\text{aq})}^{-}] = 2.2 \times 10^{-4} \text{ mol/L} \times \frac{250.0 \text{ mL}}{500.0 \text{ mL}}$$

$$[\text{Cl}_{(\text{aq})}^{-}] = 1.1 \times 10^{-4} \text{ mol/L}$$



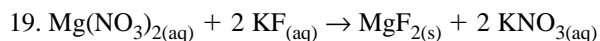
$$Q = [\text{Ag}_{(\text{aq})}^{+}][\text{Cl}_{(\text{aq})}^{-}]$$

$$= (0.0050)(1.1 \times 10^{-4})$$

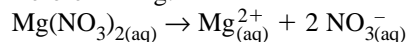
$$Q = 5.5 \times 10^{-7}$$

$$K_{\text{sp}} = 1.8 \times 10^{-10}$$

Q is greater than K_{sp} . Therefore, a precipitate will form.



Before mixing:



$$[\text{Mg}(\text{NO}_3)_{2(\text{aq})}] = [\text{Mg}_{(\text{aq})}^{2+}]$$

$$[\text{Mg}(\text{NO}_3)_{2(\text{aq})}] = 0.015 \text{ mol/L}$$

$$[\text{KF}_{(\text{aq})}] = [\text{F}_{(\text{aq})}^{-}]$$

$$[\text{KF}_{(\text{aq})}] = 0.10 \text{ mol/L}$$

After mixing:

$$300 \text{ mL} + 100 \text{ mL} = 400 \text{ mL}$$

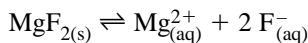
Concentrations after mixing:

$$[\text{Mg}_{(\text{aq})}^{2+}] = 0.015 \text{ mol/L} \times \frac{100 \text{ mL}}{400 \text{ mL}}$$

$$[\text{Mg}_{(\text{aq})}^{2+}] = 3.75 \times 10^{-3} \text{ mol/L} \quad (\text{extra digits carried})$$

$$[\text{F}_{(\text{aq})}^{-}] = 0.10 \text{ mol/L} \times \frac{300 \text{ mL}}{400 \text{ mL}}$$

$$[\text{F}_{(\text{aq})}^{-}] = 0.075 \text{ mol/L}$$



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

$$= (3.75 \times 10^{-3})(0.075)^2$$

$$Q = 2.1 \times 10^{-5}$$

$$K_{\text{sp}} = 6.4 \times 10^{-9}$$

Q is larger than K_{sp} . Therefore, a precipitate does form.

20. Solubility refers to the amount of a compound that dissolves in a given volume of solution. The solubility product, however, is the product of the concentration of the ions released when a compound dissolves.
21. Compounds that release calcium or sulfate ions will decrease the solubility of calcium sulfate. Some examples are calcium chloride, calcium nitrate, sodium sulfate, and potassium sulfate.
22. (a) Entropy is positive. The liquid state is more random than the solid state.
 (b) Entropy is negative. The products are less random due to the formation of the precipitate.
 (c) Entropy is negative. The formation of two molecules of the same substance HOCl is more ordered than the left side.
 (d) Entropy is positive. The gases on the right side of the equation are more randomly arranged than solid ammonium chloride.
23. $2 \text{NaCl}_{(\text{s})} \rightarrow 2 \text{Na}_{(\text{g})} + \text{Cl}_{2(\text{g})}$

The decomposition of sodium chloride is endothermic ($\Delta H > 0$). The entropy change is positive, $\Delta S > 0$, since the products are more random than the reactant.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = + - (+)(+)$$

Since the reaction does not occur spontaneously at room temperature, ΔG must be positive. Consequently, the temperature must be small enough so that the ΔH term in the equation is greater than $T\Delta S$.

$$24. \Delta H^{\circ} = [\Delta H^{\circ}_{\text{f}(\text{NH}_4\text{Cl}_{(\text{aq})})}] - [\Delta H^{\circ}_{\text{f}(\text{NH}_4\text{Cl}_{(\text{s})})}]$$

$$= [1 \text{ mol } (-299.7 \text{ kJ/mol})] - [1 \text{ mol } (-314.4 \text{ kJ/mol})]$$

$$= [-299.7 \text{ kJ}] - [-314.4 \text{ kJ}]$$

$$\Delta H^{\circ} = +14.7 \text{ kJ}$$

$$\Delta S^{\circ} = [S^{\circ}_{(\text{NH}_4\text{Cl}_{(\text{aq})})}] - [S^{\circ}_{(\text{NH}_4\text{Cl}_{(\text{s})})}]$$

$$= [1 \text{ mol } (169.9 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol } (94.6 \text{ J/mol}\cdot\text{K})]$$

$$= [169.9 \text{ J/K}] - [94.6 \text{ J/K}]$$

$$\Delta S^{\circ} = 75.3 \text{ J/K}$$

$$\Delta S^{\circ} = 75.3 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta S^{\circ} = 0.0753 \text{ kJ/K}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$= 14.7 \text{ kJ} - (298 \text{ K})(0.0753 \text{ kJ/K})$$

$$\Delta G^{\circ} = -7.7 \text{ kJ}$$

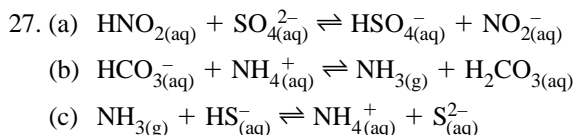
The standard Gibbs free energy change associated with this reaction is -7.7 kJ. Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of -7.7 kJ of free energy is made available to do useful work for each mole of solid ammonium chloride that reacts.

$$\begin{aligned}
 25. \Delta H^\circ &= [\Delta H^\circ_{\text{f}(\text{CO}_{2(\text{g})})} + 2 \Delta H^\circ_{\text{f}(\text{H}_2\text{O}_{(\text{g})})}] - [\Delta H^\circ_{\text{f}(\text{CH}_4(\text{g}))} + 2 \Delta H^\circ_{\text{f}(\text{O}_{2(\text{g})})}] \\
 &= [1 \text{ mol} + (-393.5 \text{ kJ/mol}) + 2 \text{ mol} \times (-241.8 \text{ kJ/mol})] - [(-74.4 \text{ kJ/mol}) + 2 \text{ mol} \times (0)] \\
 &= [-877.1 \text{ kJ/mol}] - [-74.4 \text{ kJ}] \\
 \Delta H^\circ &= -802.7 \text{ kJ} \\
 \Delta S^\circ &= [S^\circ_{(\text{CO}_{2(\text{g})})} + 2 S^\circ_{(\text{H}_2\text{O}_{(\text{g})})}] - [S^\circ_{(\text{CH}_4(\text{g}))} + 2 S^\circ_{(\text{O}_{2(\text{g})})}] \\
 &= [1 \text{ mol} \times (213.78 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (188.84 \text{ J/mol}\cdot\text{K})] - [(186.3 \text{ J/mol}\cdot\text{K}) + 2 \text{ mol} \times (205.14 \text{ J/mol}\cdot\text{K})] \\
 &= [591.46 \text{ J/K}] - [596.58 \text{ J/K}] \\
 \Delta S^\circ &= -5.12 \text{ J/K} \\
 \Delta S^\circ &= -5.12 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
 \Delta S^\circ &= -0.00512 \text{ kJ/K} \\
 \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
 &= -802.7 \text{ kJ} - (298\text{K})(-0.00512 \text{ kJ/K}) \\
 \Delta G^\circ &= -801.2 \text{ kJ}
 \end{aligned}$$

The standard Gibbs free energy change associated with this reaction is -801.2 kJ. Since ΔG° is negative, the reaction is spontaneous under standard conditions and will proceed to the right as written. A total of -801.2 kJ of free energy is made available to do useful work for each mole of methane that burns.

$$\begin{aligned}
 26. \text{C}_2\text{H}_5\text{OH}_{(\text{l})} &\rightarrow \text{C}_2\text{H}_5\text{OH}_{(\text{g})} \\
 T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\
 &= [\Delta H^\circ_{\text{f}(\text{C}_2\text{H}_5\text{OH}_{(\text{g})})} - \Delta H^\circ_{\text{f}(\text{C}_2\text{H}_5\text{OH}_{(\text{l})})}] \\
 &= (-235.2 \text{ kJ/mol}) - (-277.7 \text{ kJ/mol}) \\
 T &= 42.5 \text{ kJ} \\
 \Delta S^\circ &= [S^\circ_{(\text{C}_2\text{H}_5\text{OH}_{(\text{g})})} - S^\circ_{(\text{C}_2\text{H}_5\text{OH}_{(\text{l})})}] \\
 &= (+282.70 \text{ J/mol}\cdot\text{K}) - (+160.7 \text{ J/mol}\cdot\text{K}) \\
 \Delta S^\circ &= 122 \text{ J/mol}\cdot\text{K} \\
 \Delta S^\circ &= 122 \text{ J/K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\
 \Delta S^\circ &= 0.122 \text{ kJ/K} \\
 T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\
 &= \frac{42.5 \text{ kJ}}{0.122 \text{ kJ/K}} \\
 T &= 348 \text{ K} \\
 t &= (T - 273^\circ\text{C}) \\
 &= (348 \text{ K} - 273^\circ\text{C}) \\
 t &= 75^\circ\text{C}
 \end{aligned}$$

The normal condensation point of ethanol is 75°C .



28. (a) endothermic
 (b) The increase in K_w with temperature implies that the hydrogen ion concentration also increases. Consequently, the pH decreases.

29. $[H^+]_{(aq)} \text{rainwater} = 10^{-5.6}$
 $[H^+]_{(aq)} \text{rainwater} = 2.51 \times 10^{-6} \text{ mol/L}$ (extra digits carried)

$$[H^+]_{(aq)} \text{acidic rainwater} = 10^{-4.0}$$

$$[H^+]_{(aq)} \text{acidic rainwater} = 1 \times 10^{-4} \text{ mol/L}$$

$$\frac{1 \times 10^{-4} \text{ mol/L}}{2.51 \times 10^{-6} \text{ mol/L}} = 40$$

The acidic rainwater is 40 times more acidic than normal rainwater.

30. $[H^+]_{(aq)} \text{cola} = 10^{-2.7}$
 $[H^+]_{(aq)} \text{cola} = 2 \times 10^{-3} \text{ mol/L}$
 $\text{pOH} = 14 - 2.7$
 $\text{pOH} = 11.3$

$$[OH^-]_{(aq)} \text{cola} = 10^{-11.3}$$

$$[OH^-]_{(aq)} \text{cola} = 5 \times 10^{-12} \text{ mol/L}$$

The hydrogen and hydroxide ion concentrations in cola are $2 \times 10^{-3} \text{ mol/L}$ and $5 \times 10^{-12} \text{ mol/L}$, respectively.

31. 5.9%
 $\text{HOCN}_{(aq)} \rightleftharpoons H^+_{(aq)} + \text{OCN}^-_{(aq)}$

$$K_a = \frac{[H^+]_{(aq)}[\text{OCN}^-_{(aq)}]}{[\text{HOCN}_{(aq)}]}$$

$$[H^+]_{(aq)} = (5.9 \times 10^{-3})(0.100 \text{ mol/L})$$

$$[H^+]_{(aq)} = 5.9 \times 10^{-4}$$

ICE Table for the Ionization of $\text{HOCN}_{(aq)}$			
	$\text{HOCN}_{(aq)} \rightleftharpoons$	$H^+_{(aq)} +$	$\text{OCN}^-_{(aq)}$
Initial concentration (mol/L)	0.100	0.000	0.000
Change in concentration (mol/L)	-5.9×10^{-4}	5.9×10^{-4}	5.9×10^{-4}
Equilibrium concentration (mol/L)	$0.100 - 5.9 \times 10^{-4}$	5.9×10^{-4}	5.9×10^{-4}

$$K_a = \frac{[H^+]_{(aq)}[\text{OCN}^-_{(aq)}]}{[\text{HOCN}_{(aq)}]}$$

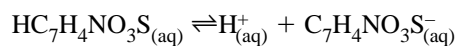
$$= \frac{(5.9 \times 10^{-4})^2}{0.100 - 5.9 \times 10^{-4}}$$

$$K_a = 3.5 \times 10^{-6}$$

The K_a for cyanic acid is 3.5×10^{-6} .

32.

ICE Table for the Ionization of $\text{HC}_7\text{H}_4\text{NO}_3\text{S}_{(aq)}$			
	$\text{HC}_7\text{H}_4\text{NO}_3\text{S}_{(aq)} \rightleftharpoons$	$H^+_{(aq)} +$	$\text{C}_7\text{H}_4\text{NO}_3\text{S}^-_{(aq)}$
Initial concentration (mol/L)	0.500	0.000	0.000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.500 - x$	x	x



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{C}_7\text{H}_4\text{NO}_3\text{S}_{(\text{aq})}^-]}{[\text{HC}_7\text{H}_4\text{NO}_3\text{S}_{(\text{aq})}]}$$

$$\frac{x^2}{0.500 - x} = 2.1 \times 10^{-12}$$

Predicting whether $0.100 - x \doteq 0.100 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_a} = \frac{0.100 \text{ mol/L}}{2.1 \times 10^{-12}}$$

$$>100$$

Therefore, we assume that $0.500 - x \doteq 0.500$.

$$\frac{x^2}{(0.500)} \doteq 2.1 \times 10^{-12}$$

$$x^2 \doteq 1.05 \times 10^{-12} \text{ (extra digits carried)}$$

$$x = 1.1 \times 10^{-6}$$

The 5% rule justifies the assumption.

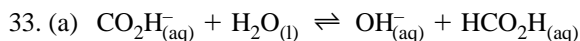
$$[\text{H}_{(\text{aq})}^+] = 1.1 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_{(\text{aq})}^+]$$

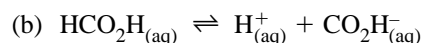
$$= -\log[1.1 \times 10^{-6}]$$

$$\text{pH} = 5.99$$

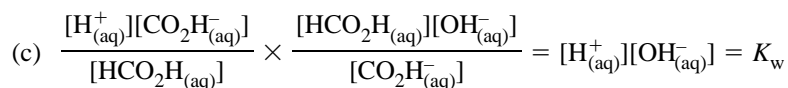
The pH of the saccharin solution is 5.99.



$$\frac{[\text{HCO}_2\text{H}_{(\text{aq})}][\text{OH}_{(\text{aq})}^-]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]}$$

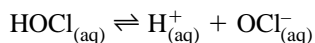


$$\frac{[\text{H}_{(\text{aq})}^+][\text{CO}_2\text{H}_{(\text{aq})}^-]}{[\text{HCO}_2\text{H}_{(\text{aq})}]}$$



34.

ICE Table for the Ionization of $\text{HOCl}_{(\text{aq})}$			
	$\text{HOCl}_{(\text{aq})} \rightleftharpoons$	$\text{H}_{(\text{aq})}^+ +$	$\text{OCl}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.100	0.000	0.000
Change in concentration (mol/L)	$-x$	$+x$	$+x$
Equilibrium concentration (mol/L)	$0.100 - x$	x	x



$$K_a = \frac{[\text{H}_{(\text{aq})}^+][\text{OCl}_{(\text{aq})}^-]}{[\text{HOCl}_{(\text{aq})}]}$$

$$\frac{x^2}{0.100 - x} = 2.9 \times 10^{-8}$$

Predicting whether $0.100 - x \doteq 0.100 \dots$

$$\frac{[\text{HA}]_{\text{initial}}}{K_{\text{a}}} = \frac{0.100 \text{ mol/L}}{2.9 \times 10^{-8}}$$

$$>100$$

Therefore, we assume that $0.100 - x \doteq 0.100$.

$$\frac{x^2}{(0.100)} \doteq 2.9 \times 10^{-8}$$

$$x^2 \doteq 2.9 \times 10^{-8}$$

$$x = 5.39 \times 10^{-5} \quad (\text{extra digits carried})$$

The 5% rule justifies the assumption.

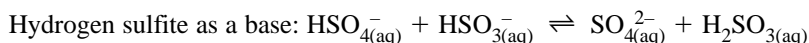
$$[\text{H}_{(\text{aq})}^+] = 5.4 \times 10^{-5} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_{(\text{aq})}^+]$$

$$= -\log[5.39 \times 10^{-5}]$$

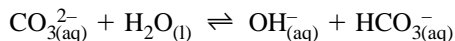
$$\text{pH} = 4.27$$

The pH of the hypochlorous acid solution is 4.27.

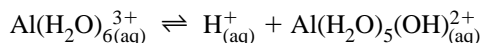


36. Despite having identical molar concentrations, solutions of these compounds differ in pH because the hydrogen sulfite ion, $\text{HSO}_{4(\text{aq})}^-$, is a stronger acid than the hydrogen sulfite ion, $\text{HSO}_{3(\text{aq})}^-$.

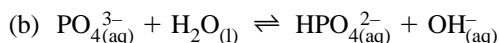
37. (a) Calcium carbonate would raise soil pH because the hydrolysis of the carbonate ion releases hydroxide ions:



(b) Alum lowers soil pH due to the hydrolysis of the aluminum ion:



38. (a) Sodium phosphate solution is likely to be basic.



ICE Table for the Hydrolysis of Phosphate				
	$\text{PO}_{4(\text{aq})}^{3-} +$	$\text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$	$\text{HPO}_{4(\text{aq})}^{2-} +$	$\text{OH}_{(\text{aq})}^-$
Initial concentration (mol/L)	0.10	—	0.00	0.00
Change in concentration (mol/L)	—x	—	+x	+x
Equilibrium concentration (mol/L)	$0.10 - x$	—	x	x

$$K_{\text{b}} = \frac{K_{\text{w}}}{K_{\text{a}}}$$

$$= \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-13}}$$

$$K_{\text{b}} = 2.3 \times 10^{-2}$$

$$K_{\text{b}} = \frac{[\text{HPO}_{4(\text{aq})}^{2-}][\text{OH}_{(\text{aq})}^-]}{[\text{PO}_{4(\text{aq})}^{3-}]}$$

$$K_b = 2.3 \times 10^{-2}$$

$$\frac{x^2}{0.10 - x} = 2.3 \times 10^{-2}$$

$$x^2 = 2.3 \times 10^{-2} (0.10 - x)$$

$$x^2 = 2.3 \times 10^{-3} - 2.3 \times 10^{-2}x$$

$$x^2 + 2.3 \times 10^{-2}x - 2.3 \times 10^{-3} = 0$$

$$x = \frac{-2.3 \times 10^{-2} \pm \sqrt{(2.3 \times 10^{-2})^2 - 4(-2.3 \times 10^{-3})}}{2}$$

$$x = 0.0378 \text{ (the only positive root) (extra digits carried)}$$

$$[\text{OH}_{(\text{aq})}^-] = 0.0378 \text{ mol/L}$$

$$\text{pOH} = -\log[0.0378]$$

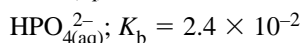
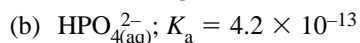
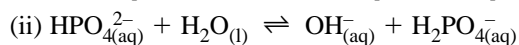
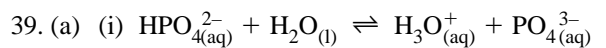
$$= 1.42$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14.0 - 1.42$$

$$\text{pH} = 12.58$$

The pH of the phosphate solution is 12.58.



K_b for the hydrogen phosphate ion is larger than K_a .

(c) Since $K_b > K_a$, a solution of Na_2HPO_4 is basic.

40. (a) <7

(b) >7

(c) <7

(d) >7

(e) >7

(f) 7

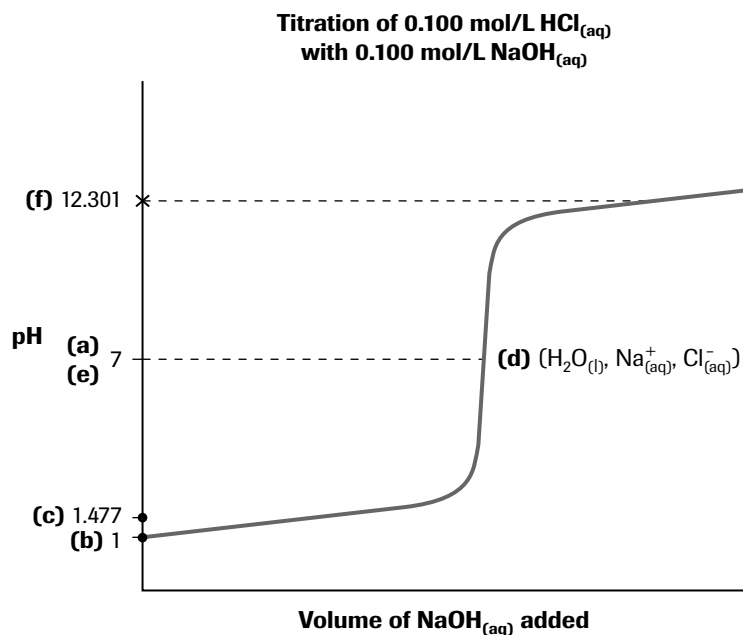
41.

	Lewis acid:	Lewis base:
(a)	$\text{HCl}_{(\text{g})}$	$\text{NH}_{3(\text{g})}$
(b)	$\text{Cu}_{(\text{aq})}^{2+}$	$\text{H}_2\text{O}_{(\text{l})}$
(c)	$\text{Al}(\text{OH})_3$	$\text{OH}_{(\text{aq})}^-$

42.

Type of titration	pH at equivalence point
strong acid/strong base	7
strong acid/weak base	6
weak acid/strong base	9

43.



(a) 7

(b) 1

(c) $V_{\text{HCl remaining}} = 5.00 \text{ mL}$

$$C_{\text{HCl after addition of NaOH}} = 0.100 \text{ mol/L} \times \frac{5 \text{ mL}}{15 \text{ mL}}$$

$$C_{\text{HCl after addition of NaOH}} = 0.0333 \text{ mol/L}$$

$$\text{pH} = -\log 0.0333$$

$$\text{pH} = 1.477$$

The pH after adding 5.00 mL of base is 1.477.

(d) H₂O_(l), Cl⁻_(aq), Na⁺_(aq)

(e) 7

(f) $V_{\text{NaOH remaining}} = 5.00 \text{ mL}$

$$C_{\text{NaOH}} = 0.100 \text{ mol/L} \times \frac{5.00 \text{ mL}}{25.00 \text{ mL}}$$

$$= 0.0200 \text{ mol/L}$$

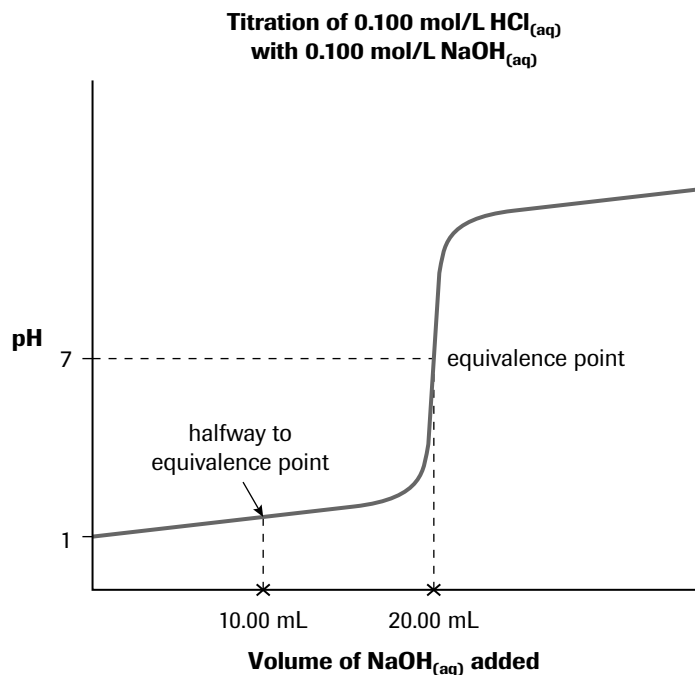
$$\text{pOH} = -\log 0.0200$$

$$\text{pOH} = 1.699$$

$$\text{pH} = 12.301$$

The pH after adding 15.00 mL of base is 12.301.

44.



(a) 1

(b) $V_{\text{HCl remaining}} = 10.00 \text{ mL}$

$$C_{\text{HCl after addition of NaOH}} = 0.100 \text{ mol/L} \times \frac{10.00 \text{ mL}}{30.00 \text{ mL}}$$

$$C_{\text{HCl after addition of NaOH}} = 0.0333 \text{ mol/L}$$

$$\text{pH} = -\log 0.0333$$

$$\text{pH} = 1.477$$

The pH after adding 10.00 mL of base is 1.477.

(c) $V_{\text{HCl remaining}} = 0.10 \text{ mL}$

$$C_{\text{HCl after addition of NaOH}} = 0.100 \text{ mol/L} \times \frac{0.10 \text{ mL}}{39.90 \text{ mL}}$$

$$C_{\text{HCl after addition of NaOH}} = 2.506 \times 10^{-4} \text{ mol/L} \quad (\text{extra digits carried})$$

$$\text{pH} = -\log 2.506 \times 10^{-4}$$

$$\text{pH} = 3.601$$

The pH after adding 19.90 mL of base is 3.601.

(d) $V_{\text{HCl remaining}} = 0.01 \text{ mL}$

$$C_{\text{HCl after addition of NaOH}} = 0.01 \text{ mol/L} \times \frac{0.01 \text{ mL}}{39.99 \text{ mL}}$$

$$C_{\text{HCl after addition of NaOH}} = 2.5006 \times 10^{-6} \text{ mol/L} \quad (\text{extra digits carried})$$

$$\text{pH} = -\log 2.5006 \times 10^{-6}$$

$$\text{pH} = 4.602$$

The pH after adding 19.99 mL of base is 4.602.

(e) $V_{\text{NaOH remaining}} = 0.01 \text{ mL}$

$$C_{\text{NaOH}} = 0.100 \text{ mol/L} \times \frac{0.01 \text{ mL}}{40.01 \text{ mL}}$$

$$C_{\text{NaOH}} = 2.499 \times 10^{-5} \text{ mol/L} \quad (\text{extra digits carried})$$

$$\text{pOH} = -\log 2.499 \times 10^{-5}$$

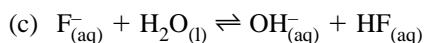
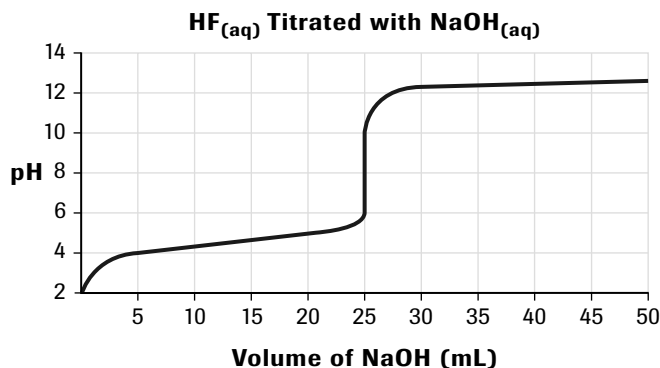
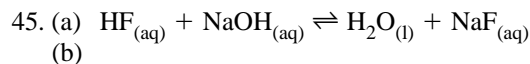
$$\text{pOH} = 4.600$$

$$\text{pH} = 9.400$$

The pH after adding 20.01 mL of base is 9.400.

$$\begin{aligned} \text{(f)} \quad V_{\text{NaOH remaining}} &= 5.00 \text{ mL} \\ C_{\text{NaOH}} &= 0.100 \text{ mol/L} \times \frac{5.00 \text{ mL}}{45.00 \text{ mL}} \\ C_{\text{NaOH}} &= 11 \times 10^{-2} \text{ mol/L} \\ \text{pOH} &= 1.954 \\ \text{pH} &= 12.046 \end{aligned}$$

The pH after adding 25.00 mL of base is 12.046.



Small additions of hydroxide are consumed by the reverse reaction of the equilibrium.

- (d) The pH at the equivalence point will be greater than 7: basic.
46. (a) The bottom curve represents the titration of a strong acid with sodium hydroxide solution. The strongest acid has the lowest initial pH.
 (b) The top curve represents the titration of the acid with the smallest K_a value. The weakest acid will have the highest initial pH.
 (c) At the equivalence point, the moles of acid present equal the moles of base added.
- 47.

methyl red	orange (red in transition to yellow)
thymolphthalein	colourless
bromothymol blue	green (blue in transition to yellow)
indigo carmine	yellow

48. Thymolphthalein

49. The molar concentration of sodium acetate should also be 0.5 mol/L. Dissolve 1.5 g of anhydrous sodium acetate in enough distilled water to make 50 mL of solution. Combine this solution with 50 mL of 0.5 mol/L acetic acid.
50. (a) Bromothymol blue changes colour during the steep portion of the graph.
 (b) The colour change of phenolphthalein is within the steep portion of the graph.
51. (a) Equilibrium shifts to the left.
 (b) Equilibrium shifts to the right.
 (c) Equilibrium shifts to the left.

52.

$$[\text{CO}_2\text{H}_{(\text{aq})}^-] = 0.15 \text{ mol/L}$$

$$[\text{HCO}_2\text{H}_{(\text{aq})}] = 0.25 \text{ mol/L}$$

$$\text{HCO}_2\text{H}_{(\text{aq})} \rightleftharpoons \text{H}_{(\text{aq})}^+ + \text{CO}_2\text{H}_{(\text{aq})}^-$$

$$\frac{[\text{H}_{(\text{aq})}^+][\text{CO}_2\text{H}_{(\text{aq})}^-]}{[\text{HCO}_2\text{H}_{(\text{aq})}]} = 1.8 \times 10^{-4}$$

$$[\text{H}_{(\text{aq})}^+] = K_a \frac{[\text{HCO}_2\text{H}_{(\text{aq})}]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]}$$

$$= 1.8 \times 10^{-4} \times \frac{0.25 \text{ mol/L}}{0.15 \text{ mol/L}}$$

$$[\text{H}_{(\text{aq})}^+] = 3.0 \times 10^{-4}$$

$$\text{pH} = -\log [1.8 \times 10^{-4}]$$

$$\text{pH} = 3.52$$

The addition of $\text{H}_{(\text{aq})}^+$...

$$[\text{H}_{(\text{aq})}^+]_{\text{added}} = 0.10 \text{ mol/L}$$

$$[\text{HCO}_2\text{H}_{(\text{aq})}]_{\text{final}} = (0.25 + 0.10) \text{ mol/L}$$

$$[\text{HCO}_2\text{H}_{(\text{aq})}]_{\text{final}} = 0.35 \text{ mol/L}$$

$$[\text{CO}_2\text{H}_{(\text{aq})}^-]_{\text{final}} = (0.15 - 0.10) \text{ mol/L}$$

$$[\text{CO}_2\text{H}_{(\text{aq})}^-]_{\text{final}} = 0.05 \text{ mol/L}$$

$$[\text{H}_{(\text{aq})}^+] = K_a \frac{[\text{HCO}_2\text{H}_{(\text{aq})}]}{[\text{CO}_2\text{H}_{(\text{aq})}^-]}$$

$$= 1.8 \times 10^{-4} \times \frac{0.35}{0.05}$$

$$[\text{H}_{(\text{aq})}^+] = 1.26 \times 10^{-3} \quad (\text{extra digits carried})$$

$$\text{pH} = 2.90$$

The change in pH is 3.52 – 2.90.

$$\Delta\text{pH} = 0.62$$

53. (a) $n_{\text{Ag}_2\text{SO}_4} = \frac{0.25 \text{ g}}{311.80 \text{ g/mol}}$

$$n_{\text{Ag}_2\text{SO}_4} = 8.0 \times 10^{-4} \text{ mol}$$

(b) molar solubility of Ag_2SO_4

$$= \frac{8.0 \times 10^{-4} \text{ mol}}{50.00 \times 10^{-3}}$$

$$= 0.016 \text{ mol/L}$$

(c) $[\text{Ag}_{(\text{aq})}^+] = 0.032 \text{ mol/L}$

(d) $[\text{SO}_{4(\text{aq})}^{2-}] = 0.016 \text{ mol/L}$

(e) $K_{\text{sp}} = [\text{Ag}_{(\text{aq})}^+]^2[\text{SO}_{4(\text{aq})}^{2-}]$

(f) $K_{\text{sp}} = [\text{Ag}_{(\text{aq})}^+]^2[\text{SO}_{4(\text{aq})}^{2-}]$

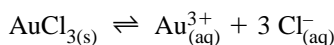
$$= [0.032]^2[0.016]$$

$$K_{\text{sp}} = 1.6 \times 10^{-5}$$

- (g) The accepted value for the solubility product of silver sulfate is 1.2×10^{-5} . The perfect difference between the calculated value and the accepted value is 33%. Given the large difference, the calculated value is judged to be unacceptable. (Note: Large errors in K_{sp} experiments are quite common.)
54. (a) Volume of unreacted acid = 17.40 mL
- $$C_{\text{HCl}} = 17.40 \text{ mL} \times 1.00 \text{ mol/L}$$
- $$C_{\text{HCl}} = 17.4 \text{ mmol}$$
- The amount of unreacted acid is 17.4 mmol.
- (b) 7.60 mL of HCl reacted.
- $$n_{\text{HCl}} = 7.60 \text{ mL} \times 1.00 \text{ mol/L}$$
- $$n_{\text{HCl}} = 7.60 \text{ mmol}$$
- 2:1 ratio, therefore
- $$n_{\text{CaCO}_3} = 3.80 \text{ mmol}$$
- The amount of calcium carbonate in the shell was 3.80 mmol.
- (c) $m_{\text{CaCO}_3} = 3.80 \text{ mmol} \times 100.09 \text{ g/mol}$
- $$m_{\text{CaCO}_3} = 0.380 \text{ g}$$
- The mass of calcium carbonate in the shell was 0.380 g.
- $$\% \text{CaCO}_3 = \frac{0.38}{0.45}$$
- $$\% \text{CaCO}_3 = 84\%$$
- The percent by mass of calcium carbonate in the shell is 84%.
- (d) Grinding the shell increases its surface area, allowing the reaction with acid to occur more quickly.
- (e) The contents of the flask are boiled to remove dissolved carbon dioxide from the solution and to ensure that the reaction with the acid is complete.
- (f) The addition of water dilutes the acid but does not alter the moles of acid present. The amount of base added depends only on the amount of acid.
55. (a) $n_{\text{KH(IO}_3)_2} = \frac{1.00 \text{ g}}{263.01 \text{ g/mol}}$
- $$n_{\text{KH(IO}_3)_2} = 3.802 \times 10^{-3} \text{ mol}$$
- $$n_{\text{KH(IO}_3)_2} = n_{\text{NaOH used}}$$
- $$C_{\text{NaOH}} = \frac{3.802 \times 10^{-3} \text{ mol}}{25.54 \times 10^{-3} \text{ mol}}$$
- $$C_{\text{NaOH}} = 0.185 \text{ mol/L}$$
- The concentration of the sodium hydroxide solution is 0.185 mol/L.
- (b) Since this is a titration of a strong acid with a strong base, the pH change at the equivalence point is large. The pH range of both indicators falls well within the pH change that occurs.
- (c) Boiling the water removes dissolved carbon dioxide that could combine with the hydroxide ions.
- (d) The test tube prevents atmospheric carbon dioxide from dissolving into the solution.
56. (a) Maintaining a high pressure inside the washing machine forces the equilibrium to shift to the right – the side with fewer gas molecules.
- (b) Fresh-air circulation systems must be installed in CO_2 dry-cleaning facilities to ensure that workers and customers are not exposed to excessive levels of carbon dioxide. Periodic monitoring of carbon dioxide levels should occur on a regular basis. In the extreme, a sudden leak of CO_2 could suffocate everyone in the facility.
- (c) Carbon dioxide is an ideal dry-cleaning solvent. It is a nonpolar molecule that is just as effective in dissolving grease and oil as the organic solvents currently used in the dry-cleaning process. It is nonflammable, almost chemically inert, and does not harm the ozone layer as many dry-cleaning solvents do. Once the washing cycle is complete, carbon dioxide can be evaporated, leaving behind the residue of the cleaning process. The “clean”

gas is then collected and can be used for the next cleaning cycle. The clean clothing can be packaged immediately because no drying is required, saving considerable time.

57. (a) Assuming only Au^{3+} is present ...



Concentrations after mixing:

$$[\text{Au}_{(aq)}^{3+}] = 5.6 \times 10^{-11} \text{ mol/L} \times \frac{1}{2}$$

$$[\text{Au}_{(aq)}^{3+}] = 2.8 \times 10^{-11} \text{ mol/L}$$

$$[\text{Cl}_{(aq)}^{-}] = 0.100 \text{ mol/L} \times \frac{1}{2}$$

$$[\text{Cl}_{(aq)}^{-}] = 5.0 \times 10^{-2} \text{ mol/L}$$

$$Q = [\text{Au}_{(aq)}^{3+}][\text{Cl}_{(aq)}^{-}]^2$$

$$= (2.8 \times 10^{-11})(5.0 \times 10^{-2})^3$$

$$Q = 3.5 \times 10^{-15}$$

$$K_{\text{sp}} = 3.2 \times 10^{-25}$$

Q is larger than K_{sp} . Therefore, a precipitate does form.

- (b) There is so little gold dissolved in seawater that huge quantities of water would have to be processed to extract a measurable amount of gold. This would require investment in an extremely large filtration system. Assuming the gold precipitates could be separated from all the other particulates that are found in seawater, we would then have to extract the gold from the precipitate. Another complication is that the amount of gold that has already precipitated with the existing chloride ions in seawater is unknown. In summary, the extraction of gold from seawater using precipitation is not feasible.

58. (a) $n_{\text{NaOH}} = \frac{24.88 \text{ g}}{40.00 \text{ g/mol}}$

$$n_{\text{NaOH}} = 0.6000 \text{ mol}$$

$$C_{\text{NaOH}_{(aq)}} = \frac{0.6000 \text{ mol}}{0.750 \text{ L}}$$

$$C_{\text{NaOH}_{(aq)}} = 0.800 \text{ mol/L}$$

$$\text{pOH} = -\log 0.800$$

$$\text{pOH} = 0.0969$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 13.903$$

- (b) Safety goggles and chemical-resistant gloves and apron should be worn when preparing this solution.

59. (a) The approximately 2-mm-thick enamel layer that protects teeth is a mineral that has a very low K_{sp} — $\text{Ca}_5(\text{PO}_4)_3\text{OH}_{(s)}$. The action of bacteria, particularly on the sweets we consume, can produce acetic and lactic acids. If the pH drops below 5.5, hydroxide ions are removed from enamel, resulting in demineralization.

- (b) Tooth decay can be prevented by:

- regular brushing to remove food particles, which become nutrients for bacteria, from teeth;
- flossing to remove trapped food particles and plaque in places that the toothbrush cannot reach;
- using toothpastes and fluoride treatments, which add $\text{F}_{(aq)}^{-}$ ions to replace the $\text{OH}_{(aq)}^{-}$ ions, to remineralize teeth with $\text{Ca}_5(\text{PO}_4)_3\text{F}_{(s)}$;
- avoiding sticky, sweet foods because they remain on teeth, providing bacteria with a trapped supply of sugar.
- Some foods, such as milk and other dairy products, actually raise the pH of saliva. They are also rich in calcium and phosphorus and can help remineralize teeth.

60. (a) A decrease in pH corresponds to an increase in the hydrogen ion concentration in the pool water. In response, the system shifts to the left in an effort to consume the excess acid. This produces more hypochlorous acid, which is an eye irritant.

- (b) Raising the pH removes hydrogen ions from the equilibrium. The system responds by producing more hydrogen hypochlorite ions via the forward reaction. The concentration of hypochlorite increases.
- (c) A “shock treatment” involves adding a larger than normal amount of an oxidizing compound like sodium hypochlorite to the pool. These compounds oxidize organic contaminants or ammonia and other nitrogen compounds and sanitize the water.
- (d) A “shock treatment” introduces excess hypochlorite ions to the pool that cause the hypochlorous acid–hypochlorite equilibrium to shift to the left, consuming hydrogen ions in the process. The reduction of hydrogen ions increases the pH of the water.
61. The addition of calcium hydroxide or “slaked lime” has been useful in temporarily reducing the effects of acid deposition in lakes. Calcium hydroxide is relatively inexpensive, readily available in Ontario, nontoxic, and it dissolves readily in water. However, liming a lake can only be a temporary solution. If acid deposition continues, it is not economically feasible to be continually adding calcium hydroxide to lakes. Also, the already existing metal contaminants of the lake pose a possible toxic risk to aquatic life. An alternative strategy would be to reduce the amount of acid deposition contaminating the lakes in the first place.

Extension/Challenge

62. (a) The large value of K suggests that the reaction strongly favours the products of this reaction. Consequently, very little hydrogen sulfide or sulfur dioxide is released.
- (b) An increase in pressure shifts the equilibrium to the side having fewer gas molecules – the right side. The efficiency of the reaction should increase with increasing pressure.
- (c) An increase in temperature favours the reverse reaction, which would decrease the efficiency of the reaction.
63. (a) (i) An increase in pressure increases the yield of sulfur trioxide.
 (ii) The removal of sulfur trioxide increases the yield of sulfur trioxide.
 (iii) Continually adding $\text{SO}_{2(g)}$ and $\text{O}_{2(g)}$ increases the yield of sulfur trioxide.
- (b) The use of a catalyst does not affect the position of the equilibrium because the catalyst increases the rate of both forward and reverse reactions. However, a catalyst does allow more SO_3 to be produced in a given period of time – an increase in the rate of production.
- (c) An increase in temperature shifts the equilibrium to the left. However, it also increases the rate of both reactions, resulting in more SO_3 being produced.
64. (a)

ICE Table for the Solubility of Calcium Carbonate			
	$\text{CaCO}_{3(s)} \rightleftharpoons$	$\text{Ca}^{2+}_{(aq)} +$	$\text{CO}_3^{2-}_{(aq)}$
Initial concentration (mol/L)	–	0.00	0.00
Change in concentration (mol/L)	–	+x	+x
Equilibrium concentration (mol/L)	–	x	x

$$K_{\text{sp}} = [\text{Ca}^{2+}_{(aq)}][\text{CO}_3^{2-}_{(aq)}]$$

$$= 5.0 \times 10^{-9}$$

$$(x)(x) = 5.0 \times 10^{-9}$$

$$x = 7.1 \times 10^{-5}$$

The molar solubility of calcium carbonate is 7.1×10^{-5} mol/L.

(b)
$$n_{\text{CaCO}_3} = \frac{5.00 \text{ g}}{100.0 \text{ g/mol}}$$

$$n_{\text{CaCO}_3} = 0.050 \text{ mol}$$

$$\text{molar solubility} = 7.1 \times 10^{-5} \text{ mol/L}$$

$$V_{\text{water required}} = \frac{0.050 \text{ mol}}{7.1 \times 10^{-5} \text{ mol/L}}$$

$$V_{\text{water required}} = 700 \text{ L}$$

Since the kettle holds 2.0 L of water, it would have to be filled 350 times to dissolve the calcium carbonate scale. This assumes that more scale deposits do not form and that the existing calcium carbonate does not break off during this process.

- (c) Precipitation of calcium carbonate occurs because water cannot hold as much solute when its temperature decreases.
- (d) This is a common problem in hot-water pipes and hot-water heaters.