

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.

6. (a) $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}_{(aq)}^+ + \text{Cl}_{(aq)}^-$

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

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

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

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

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

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

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

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

(b) $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}_{(aq)}^+ + \text{Cl}_{(aq)}^-$

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

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

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

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

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

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

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

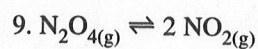
(b) $2 \text{NOCl}_{(g)} \rightleftharpoons 2 \text{NO}_{(g)} + \text{Cl}_{2(g)}$

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

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

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

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



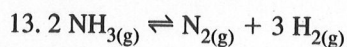
$$\frac{[\text{NO}_{2(g)}]^2}{[\text{N}_2\text{O}_{4(g)}]} = 6.13 \times 10^{-3}$$

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

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

$$Q = 0.0200$$

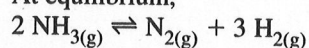
Since $Q \neq 6.13 \times 10^{-3}$, the system is not at equilibrium. The system will become less reddish-brown as it shifts to approach equilibrium.



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

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,



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

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

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

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

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

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

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

$$x = 0.3229$$

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

$$= 0.20 - 2(0.3229)$$

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

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

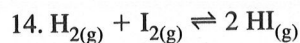
$$= 3(0.3229)$$

$$[\text{H}_{2(g)}] = 0.097 \text{ mol/L}$$

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

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

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.

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

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

$$= 2 \times 0.18725$$

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

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

$$= 0.400 - 0.18725$$

$$[\text{H}_{2(\text{g})}] = 0.213 \text{ mol/L}$$

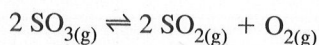
$$[\text{I}_{2(\text{g})}] = 0.200 - x$$

$$= 0.200 - 0.18725$$

$$[\text{I}_{2(\text{g})}] = 0.013 \text{ mol/L}$$

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,



$$\frac{[\text{SO}_{2(\text{g})}]^2 [\text{O}_{2(\text{g})}]}{[\text{SO}_{3(\text{g})}]^2} = 6.9 \times 10^{-7}$$

$$\frac{[2x]^2 [x]}{[0.200 - 2x]^2} = 6.9 \times 10^{-7}$$

$$\frac{4x^3}{(0.200 - 2x)^2} = 6.9 \times 10^{-7}$$

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

$$\frac{4x^3}{(0.200)^2} \doteq 6.9 \times 10^{-7}$$

$$\frac{4x^3}{0.040} \doteq 6.9 \times 10^{-7}$$

$$100x^3 \doteq 6.9 \times 10^{-7}$$

$$x^3 \doteq 6.9 \times 10^{-5}$$

$$x = 1.904 \times 10^{-3} \quad (\text{extra digits carried})$$

$$\begin{aligned} [\text{SO}_{3(\text{g})}] &= 0.200 - 2x \\ &= 0.200 - 2(1.904 \times 10^{-3}) \end{aligned}$$

$$[\text{SO}_{3(\text{g})}] = 0.20 \text{ mol/L}$$

$$[\text{O}_{2(\text{g})}] = 1.9 \times 10^{-3} \text{ mol/L}$$

$$[\text{SO}_{2(\text{g})}] = 2(1.904 \times 10^{-3})$$

$$[\text{SO}_{2(\text{g})}] = 3.8 \times 10^{-3} \text{ mol/L}$$

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.

$$16. K_{\text{sp}} = [\text{Ca}_{(\text{aq})}^{2+}][\text{SO}_{4(\text{aq})}^{2-}]$$

$$K_{\text{sp}} = 7.1 \times 10^{-5}$$

$$x^2 = 7.1 \times 10^{-5}$$

$$x = 8.4 \times 10^{-3}$$

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

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

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

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

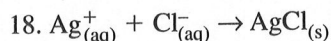
$$4x^3 = 1.2 \times 10^{-5}$$

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

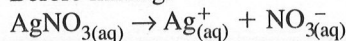
$$[\text{Cl}_{(aq)}^-] = 2 \times 0.01442$$

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

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



Before mixing:



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

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

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

After mixing:

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

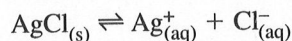
Concentrations after mixing:

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

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

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

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



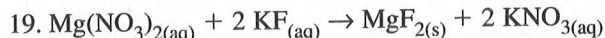
$$Q = [\text{Ag}_{(aq)}^+][\text{Cl}_{(aq)}^-]$$

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

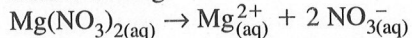
$$Q = 5.5 \times 10^{-7}$$

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

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



Before mixing:



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

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

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

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

After mixing:

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

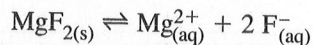
Concentrations after mixing:

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

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

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

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



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

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

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

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

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 $T\Delta S$.

$$\begin{aligned} 24. \Delta H^{\circ} &= [\Delta H^{\circ}_{\text{f}(\text{NH}_4\text{Cl}_{(\text{aq})})}] - [\Delta H^{\circ}_{\text{f}(\text{NH}_4\text{Cl}_{(\text{s})})}] \\ &= [1 \text{ mol} (-299.7 \text{ kJ/mol})] - [1 \text{ mol} (-314.4 \text{ kJ/mol})] \\ &= [-299.7 \text{ kJ}] - [-314.4 \text{ kJ}] \end{aligned}$$

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

$$\begin{aligned} \Delta S^{\circ} &= [S^{\circ}_{(\text{NH}_4\text{Cl}_{(\text{aq})})}] - [S^{\circ}_{(\text{NH}_4\text{Cl}_{(\text{s})})}] \\ &= [1 \text{ mol} (169.9 \text{ J/mol}\cdot\text{K})] - [1 \text{ mol} (94.6 \text{ J/mol}\cdot\text{K})] \\ &= [169.9 \text{ J/K}] - [94.6 \text{ J/K}] \end{aligned}$$

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

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

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

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

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

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