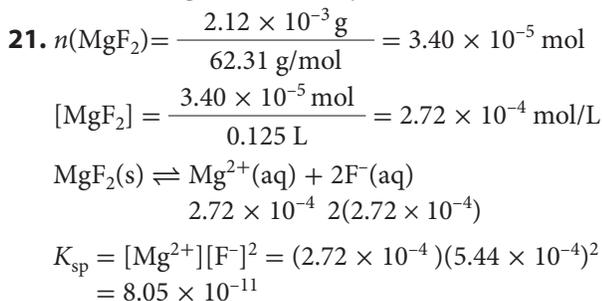


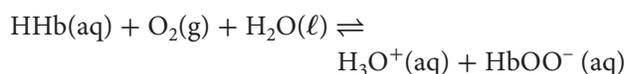
The pH would change from 9.26 to 9.00, which shows the buffering effect of the system.



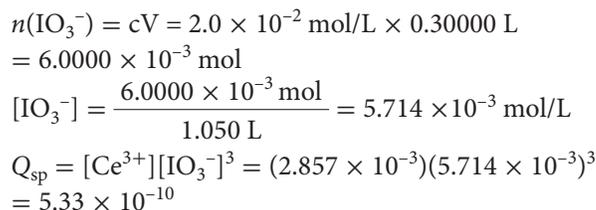
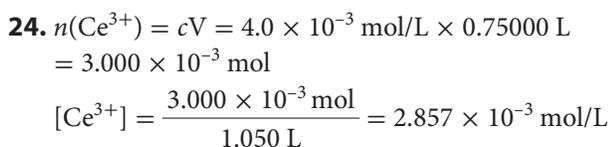
22. a. The pH range is from 4.5 to 5.

b. These ended up being good choices for this unknown solution, as it narrowed the pH to a relatively small range. If the unknown was a base or outside this pH range, the choice would not have been a good one.

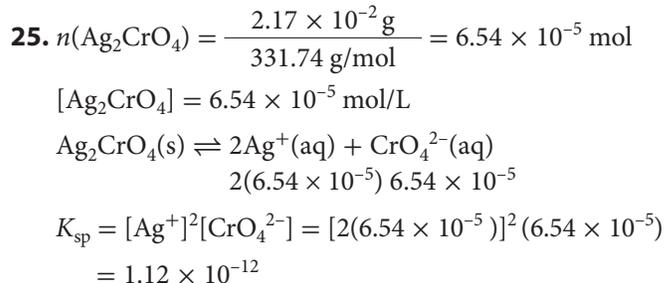
23. Hemoglobin HHb(aq), and the oxygenated form oxyhemoglobin, HbOO⁻(aq) react as follows:



Because the hydronium ions are part of this equilibrium process, the pH of the blood plays a critical role in the ability of hemoglobin to combine with oxygen. If the blood pH becomes too acidic, the equilibrium will shift to the left, which will cause the hemoglobin to lose the ability to combine with the oxygen. If the blood pH becomes too basic, the hemoglobin will attach to more and more oxygen, but then loses its ability to release the oxygen when it reaches the cell site that is in need of the oxygen. Blood pH must remain as close to 7.4 as possible to have a balance of oxygen pick up and release in the body.



Since $Q_{\text{sp}} = 5.3 \times 10^{-10}$, which is larger than K_{sp} for the solid, a precipitate will form.



Answers to Unit 4 Review Questions (Student textbook pages 569-73)

1. a

2. e

3. d

4. a

5. c

6. b

7. e

8. a

9. e

10. b

11. a. $K_{\text{eq}} = [\text{CO}_2]$

b. $K_{\text{eq}} = \frac{[\text{HCl}]^2}{[\text{Cl}_2][\text{HI}]^2}$

c. $K_{\text{eq}} = \frac{1}{[\text{HCl}][\text{NH}_3]}$

d. $K_{\text{eq}} = \frac{[\text{H}_2\text{O}][\text{Cl}_2]}{[\text{HCl}]^2[\text{O}_2]^{1/2}}$

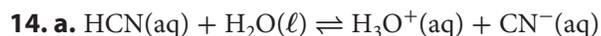
12. a. $\text{CH}_3\text{COO}^-(\text{aq})$ and $\text{CH}_3\text{COOH}(\text{aq})$; $\text{HSO}_3^-(\text{aq})$ and $\text{SO}_3^{2-}(\text{aq})$

b. $\text{CN}^-(\text{aq})$ and $\text{HCN}(\text{aq})$; $\text{H}_2\text{O}(\ell)$ and $\text{OH}^-(\text{aq})$

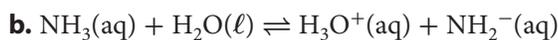
c. $\text{HSO}_4^-(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$; $\text{HCO}_3^-(\text{aq})$ and $\text{H}_2\text{CO}_3(\text{aq})$

d. $\text{CH}_3\text{COOH}(\text{aq})$ and $\text{CH}_3\text{COO}^-(\text{aq})$; $\text{HPO}_4^{2-}(\text{aq})$ and $\text{H}_2\text{PO}_4^-(\text{aq})$

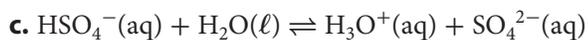
13. Since $\text{HNO}_2(\text{aq})$ is a stronger acid than $\text{HSO}_4^-(\text{aq})$, the reaction will progress toward the stronger acid, therefore, the reverse reaction is favoured.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_2^-]}{[\text{NH}_3]}$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

15. As written the reaction is exothermic, as heat is given off in the process. The K_{eq} value will decrease as the system will shift to the left, decreasing the concentration of products (i.e., the numerator) while increasing the concentrations of reactants (i.e., the denominator), causing the value of the fraction to decrease.
16. Since pressure is being applied to the closed system, the reaction will shift to the left (a side that has fewer moles of gas molecules)
17. The structure of carbon monoxide is so similar that of oxygen that carbon monoxide is able to bind to the protein hemoglobin, which normally carries oxygen in the blood. The equilibrium constant for the reaction of hemoglobin with carbon monoxide is much larger than the equilibrium constant for the reaction with oxygen. Due to the fact that hemoglobin binds more readily with carbon monoxide than with oxygen, breathing even small concentrations of carbon monoxide can be a problem. Arterial blood pumped from the heart to the cells and organs would carry too little oxygen, and so the cells would not get enough oxygen to carry out their life processes.
18. Dissociation refers to the breaking of chemical bonds without looking at whether the result is ions in solution or neutral fragments of the original material. However, ionization refers to the process where ions are formed, usually by the actions of solvent molecules. Weak acids and bases dissociate and ionize, but strong acids and bases simply ionize.
19. NH_3 can be amphiprotic as it can form NH_4^+ or NH_2^- ; HSO_4^- can be amphiprotic as it can form H_2SO_4 or SO_4^{2-} ; H_2PO_4^- can be amphiprotic as it can form HPO_4^{2-} or H_3PO_4 . Other possibilities also exist.
20. a. Syngas is the name given to the mixture of carbon monoxide and hydrogen gas obtained from the methane in natural gas.

b. Syngas is the source of hydrogen gas used in the Haber-Bosch process

c. When syngas is passed over a catalyst at a pressure of 5 to 10 MPa and a temperature of approximately 250°C, methanol and heat form.

21. All pure liquids have a constant concentration, and so there is no need to include the value in the equilibrium constant expression that monitors how concentrations change.
22. a. The reverse direction will be favoured as 9 moles of gas on the reactant side of the equation take up less space than 10 moles of gas that are on the product side.
- b. Adding a reactant will favour the formation of product, so equilibrium will shift to the right.
- c. Adding product will favour the formation of reactants, so equilibrium will shift to the left.
- d. Adding an inert gas will have no effect on the position of equilibrium.
- e. Increasing the total volume will favour the reaction that takes up more space, so the forward reaction will be favoured.
23. addition of $\text{PCl}_3(\text{g})$; addition of $\text{Cl}_2(\text{g})$; increased pressure; decreased volume; remove $\text{PCl}_5(\text{g})$ as it forms

24.

| | $[\text{A}_2]$ | $[\text{B}_2]$ | $[\text{AB}]$ |
|----------|----------------|----------------|----------------------------|
| I | 1.00 | 1.00 | 0 |
| C | $-x$ | $-x$ | $+2x = 2.5 \times 10^{-2}$ |
| E | $1.00 - x$ | $1.00 - x$ | 2.5×10^{-2} |

$$2x = 2.5 \times 10^{-2}$$

$$x = 1.125 \times 10^{-2}$$

$$1.00 - x = 1.00 - (1.125 \times 10^{-2})$$

$$1.00 - x = 0.9875$$

Equilibrium concentrations:

$$[\text{A}_2] = 0.9875 \text{ mol/L}$$

$$[\text{B}_2] = 0.9875 \text{ mol/L}$$

$$[\text{AB}] = 2.5 \times 10^{-2} \text{ mol/L}$$

$$\begin{aligned} K_{\text{eq}} &= \frac{[\text{AB}]^2}{[\text{A}][\text{B}]} \\ &= \frac{(2.5 \times 10^{-2})^2}{(0.9875)(0.9875)} \\ &= 6.4 \times 10^{-4} \end{aligned}$$

25. $\text{pH} = -\log [\text{H}_3\text{O}^+]$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
 $[\text{H}_3\text{O}^+] = 10^{-4.15}$
 $[\text{H}_3\text{O}^+] = 7.08 \times 10^{-5}$

$$\begin{aligned} \text{percent dissociation} &= \frac{[\text{HA}]_{\text{dissociated}}}{[\text{HA}]_{\text{initial}}} \times 100\% \\ &= \frac{(7.08 \times 10^{-5})}{0.100} \times 100\% \\ &= 0.0708\% \\ &= 0.071\% \end{aligned}$$

26.

| | [CO ₂] | [H ₂] | [CO] | [H ₂ O] |
|----------|--|--|------|--------------------|
| I | $\frac{2.34 \text{ mol}}{2.00 \text{ L}} = 1.17 \frac{\text{mol}}{\text{L}}$ | $\frac{2.34 \text{ mol}}{2.00 \text{ L}} = 1.17 \frac{\text{mol}}{\text{L}}$ | 0 | 0 |
| C | -x | -x | x | x |
| E | 1.17 - x | 1.17 - x | x | x |

$$K_{\text{eq}} = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$$

$$1.29 = \frac{x \cdot x}{(1.17 - x)(1.17 - x)}$$

$$1.29 = \frac{x^2}{(1.17 - x)^2}$$

$$\sqrt{1.29} = \sqrt{\frac{x^2}{(1.17 - x)^2}}$$

$$1.113578 = \frac{x}{1.17 - x}$$

$$1.113578(1.17 - x) = x$$

$$1.3288 - 1.113578x = x$$

$$2.113578x = 1.3288$$

$$x = 0.6287$$

$$x = 0.629$$

27. Moles of NH₃ in the solution:

$$n = cV$$

$$= \left(0.100 \frac{\text{mol}}{\mathcal{L}}\right) \left(30.00 \text{ mL}\right) \left(\frac{1 \mathcal{L}}{1000 \text{ mL}}\right)$$

$$= 3.00 \times 10^{-3} \text{ mol NH}_3$$

Therefore, 3.00 × 10⁻³ mol HCl must be added to reach the equivalence point.

Volume HCl added:

$$n = cV$$

$$V = \frac{n}{c}$$

$$= \frac{3.00 \times 10^{-3} \text{ mol}}{0.100 \frac{\text{mol}}{\text{L}}}$$

$$= 0.0300 \mathcal{L} \left(\frac{1000 \text{ mL}}{1 \mathcal{L}}\right)$$

$$= 30.0 \text{ mL}$$

Total volume of solution:

$$30.00 \text{ mL} + 30.00 \text{ mL} = 60.00 \text{ mL}$$

Concentration of NH₄Cl:

$$c = \frac{3.00 \times 10^{-3} \text{ mol}}{60.00 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= 5.00 \times 10^{-2} \frac{\text{mol}}{\text{L}}$$

| | [NH ₄ ⁺] | [H ₂ O] | [NH ₃] | [H ₃ O ⁺] |
|----------|---------------------------------|--------------------|--------------------|----------------------------------|
| I | 5.000 × 10 ⁻² | | 0.00 | 0.000 |
| C | -x | | +x | +x |
| E | (5.000 × 10 ⁻²) - x | | x | x |

$$K_{\text{a}} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.05000 - x}$$

$$(5.6 \times 10^{-10})(0.05000 - x) = x^2$$

$$(2.8 \times 10^{-11})(5.6 \times 10^{-10} x) = x^2$$

$$x^2 + (5.6 \times 10^{-10} x) - (2.8 \times 10^{-11}) = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-5.6 \times 10^{-10} \pm \sqrt{(5.6 \times 10^{-10})^2 - 4(1)(-2.8 \times 10^{-11})}}{2 \times 1}$$

$$= \frac{-5.6 \times 10^{-10} \pm 1.0583 \times 10^{-5}}{2}$$

$$= \pm 5.291 \times 10^{-6}$$

A concentration cannot be negative so use the positive value.

$$[\text{H}_3\text{O}^+] = 5.291 \times 10^{-6} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$= -\log (5.291 \times 10^{-6})$$

$$= 5.27$$

$$\text{pH} = 5.27$$

28. a. shift to the left

b. shift to the right

c. shift to the left

d. no change

e. no change, but equilibrium would be established quicker

29. If possible, one or more of the products could be removed or added, without opening the system to the environment (i.e., through injection by syringe), and if there is a change in the system, it was at equilibrium. Otherwise, if there was a difference in the number

of moles of gas in the system, affecting a pressure or volume change would allow for an equilibrium system to react to this change. If any of these are applied and there is no change to the system, it was a reaction that had gone to completion.

30. Change 1: increase the heat added to the system

Change 2: add more H₂O(g) to the system

Change 3: remove H₂(g) or O₂(g), or remove both

Change 4: decrease pressure by increasing the total volume of the container.

31.

| | [H ₂] | [Cl ₂] | [HCl] |
|----------|-------------------|--------------------|-------|
| I | 2.00 | 2.00 | 0.00 |
| C | -x | -x | +2x |
| E | 2.00 - x | 2.00 - x | 2x |

$$K_{\text{eq}} = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]}$$

$$50.00 = \frac{(2x)^2}{(2.00 - x)(2.00 - x)}$$

$$50.00 = \frac{4x^2}{4.00 - 4x + x^2}$$

$$50.00(4.00 - 4x + x^2) = 4x^2$$

$$200.00 - 200.0x + 50.00x^2 = 4x^2$$

$$46.00x^2 - 200.0x + 200.0 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{200.0 \pm \sqrt{200.0^2 - 4(46.00)(200.0)}}{2(46.00)}$$

$$= \frac{200 \pm 56.5685}{92.00}$$

$$= 2.7887 \text{ or } 1.559$$

The value 2.7887 cannot be used because it would make the equilibrium value of the reactants negative numbers. Use 1.559.

$$[\text{HCl}] = 2x$$

$$[\text{HCl}] = 2(1.559)$$

$$= 3.118$$

$$[\text{HCl}] = 3.12 \frac{\text{mol}}{\text{L}}$$

32.

| | [NH ₃] | [N ₂] | [H ₂] |
|----------|--------------------|-------------------|-------------------|
| I | 1.00 | 0.00 | 0.00 |
| C | -2x | +x | +3x |
| E | 1.00 - 2x | x | 3x |

$$K_{\text{eq}} = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$$

$$4.2 \times 10^{-3} = \frac{x(3x)^3}{(1.00 - 2x)^2}$$

$$= \frac{27x^4}{(1.00 - 2x)^2}$$

$$\sqrt{4.2 \times 10^{-3}} = \sqrt{\frac{27x^4}{(1.00 - 2x)^2}}$$

$$6.4807 \times 10^{-2} = \frac{5.196x^2}{1.00 - 2x}$$

$$6.4807 \times 10^{-2} - 0.12961x = 5.196x^2$$

$$5.196x^2 + 0.12961x - 6.4807 \times 10^{-2} = 0$$

$$x = \frac{-0.12961 \pm \sqrt{0.12961^2 - 4(5.196)(-6.4807 \times 10^{-2})}}{2(5.196)}$$

$$= \frac{-0.12961 \pm 1.1678}{10.392}$$

The negative value cannot be used so use only the positive.

$$x = 0.099$$

$$x = 0.100$$

$$[\text{H}_2] = 3x$$

$$[\text{H}_2] = 3(0.100)$$

$$[\text{H}_2] = 0.300 \text{ mol}$$

The answer can be given in moles because the reaction took place in a 1 L container.

33. Many possibilities exist, but all reports should include the detailed information of the chemistry of the equilibrium in their chosen system.

34. Many possible answers exist, but most students will choose to use a titration with a strong base to the equivalence point and a pH meter. At the equivalence point for a strong acid, the pH will be 7.00, but for a weak acid, the pH will be larger than 7.00.

35. a. Moles of HOCl:

$$n_{\text{HOCl}} = cV$$

$$= \left(0.100 \frac{\text{mol}}{\text{L}}\right) \left(25.00 \text{ mL}\right) \left(\frac{1\text{L}}{1000 \text{ mL}}\right)$$

$$= 0.002500 \text{ mol}$$

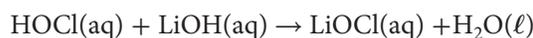
Moles of LiOH at 10.00 mL:

$$= 3.00 \times 10^{-3} \text{ mol NH}_3$$

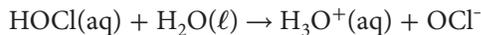
$$n_{\text{LiOH}} = cV$$

$$= \left(0.100 \frac{\text{mol}}{\text{L}}\right) \left(10.00 \text{ mL}\right) \left(\frac{1\text{L}}{1000 \text{ mL}}\right)$$

$$= 0.001000 \text{ mol}$$



| | [HOCl] | [LiOH] | [LiOCl] |
|----------------|-----------|-----------|-----------|
| I (mol) | 0.002500 | 0.001000 | 0.0000 |
| C (mol) | -0.001000 | -0.001000 | +0.001000 |
| E (mol) | 0.001500 | 0.0000 | 0.001000 |



$$K_{\text{eq}} = 4.0 \times 10^{-8}$$

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]}$$

$$4.0 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+] \left(\frac{0.00100 \text{ mol}}{0.035 \text{ L}} \right)}{\frac{0.00150 \text{ mol}}{0.035 \text{ L}}}$$

$$[\text{H}_3\text{O}^+] = \frac{(4.0 \times 10^{-8})(0.001500)}{0.00100}$$

$$[\text{H}_3\text{O}^+] = 6.0 \times 10^{-8} \frac{\text{mol}}{\text{L}}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$= -\log 6.0 \times 10^{-8}$$

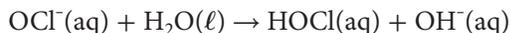
$$= 7.22$$

- b.** At the equivalence point, enough LiOH has been added to convert all of the HOCl to $\text{Li}^+ + \text{OCl}^-$. Therefore, the concentration of the OCl^- ions is:

$$c_{\text{OCl}^-} = \frac{0.002500 \text{ mol}}{0.035 \text{ L}}$$

$$= 0.0714286 \frac{\text{mol}}{\text{L}}$$

The OCl^- acts as a weak base and the reaction with water is:



$$K_{\text{b}} = 2.5 \times 10^{-7}$$

$1000 K_{\text{b}} = 2.5 \times 10^{-4} \ll 0.0714286 \text{ mol/L}$ so use the approximation

| | [OCl ⁻] | [OH ⁻] | [HOCl] |
|----------|---------------------|--------------------|--------|
| I | 0.0714286 | 0.00 | 0.00 |
| C | -x | +x | +x |
| E | 0.0714286 | x | x |

$$K_{\text{b}} = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$$

$$2.5 \times 10^{-7} = \frac{(x)(x)}{(0.0714286)}$$

$$2.5 \times 10^{-7} (0.0714286) = x^2$$

$$1.7857 \times 10^{-8} = x^2$$

$$x = 1.3363 \times 10^{-4}$$

$$[\text{OH}^-] = x$$

$$[\text{OH}^-] = 1.3363 \times 10^{-4}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$= -\log 1.3363 \times 10^{-4}$$

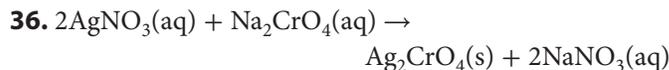
$$= 3.8741$$

$$\text{pH} = 14.0 - \text{pOH}$$

$$= 14.0 - 3.8741$$

$$= 10.126$$

$$= 10.13$$



Moles of Ag^+ :

$$n_{\text{AgNO}_3} = \frac{m}{M}$$

$$= \frac{0.74 \text{ g}}{169.88 \frac{\text{g}}{\text{mol}}}$$

$$= 4.356 \times 10^{-3} \text{ mol}$$

$$n_{\text{Ag}^+} = 4.356 \times 10^{-3} \text{ mol}$$

Concentration of Ag^+ :

$$c = \frac{n}{V}$$

$$= \frac{4.356 \times 10^{-3} \text{ mol}}{1.75 \text{ L}}$$

$$[\text{Ag}^+] = 2.4891 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

Moles of CrO_4^{2-} :

$$n_{\text{Na}_2\text{CrO}_4} = \frac{m}{M}$$

$$= \frac{0.27 \text{ g}}{161.98 \frac{\text{g}}{\text{mol}}}$$

$$= 1.6669 \times 10^{-3} \text{ mol}$$

$$n_{\text{CrO}_4^{2-}} = 1.6669 \times 10^{-3} \text{ mol}$$

Concentration of CrO_4^{2-} :

$$c = \frac{n}{V}$$

$$= \frac{1.6669 \times 10^{-3} \text{ mol}}{1.75 \text{ L}}$$

$$[\text{CrO}_4^{2-}] = 9.525 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

$$Q_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$= (2.4891 \times 10^{-3})^2 (9.515 \times 10^{-4})$$

$$= 5.90 \times 10^{-9}$$

$Q_{\text{sp}} = 5.9 \times 10^{-9}$, which exceeds the actual K_{sp} value, so a solid will form.

37. If the sodium iodide concentration is kept between 8.2×10^{-11} mol/L and 1.27×10^{-6} mol/L, any precipitate that forms will be the lesser soluble solid, silver iodide. Therefore, any solid that forms when the sodium iodide solution is diluted to this value and added will indicate the presence of silver ions. If there is no precipitate, then there were no silver ions. When the concentration of sodium iodide in solution reaches 1.27×10^{-6} mol/L, any remaining silver ions will only be present in a concentration of 1×10^{-11} mol/L, too small a value for any additional solid to precipitate out of solution. Now, if a larger concentration of sodium iodide is added, any solid that forms will be due to the presence of copper(I) ions in solution.

38. At the equivalence point, the number of moles of H_3O^+ must equal the number of moles of OH^- . Therefore, the number of moles of HCl must equal the number of moles of NaOH.

$$n_{\text{HCl}} = n_{\text{NaOH}}$$

$$c_{\text{HCl}} V_{\text{HCl}} = c_{\text{NaOH}} V_{\text{NaOH}}$$

$$\left(0.225 \frac{\text{mol}}{\text{L}}\right)(32.00 \text{ mL}) = \left(0.185 \frac{\text{mol}}{\text{L}}\right) V_{\text{NaOH}}$$

$$V_{\text{NaOH}} = \frac{\left(0.225 \frac{\text{mol}}{\text{L}}\right)(32.00 \text{ mL})}{\left(0.185 \frac{\text{mol}}{\text{L}}\right)}$$

$$V_{\text{NaOH}} = 38.9189 \text{ mL}$$

$$V_{\text{NaOH}} = 38.9 \text{ mL}$$

39. In a solution of MgCO_3 , the number of Mg ions is equal to the number of ions of CO_3 . Therefore, when calculating the K_{sp} , you can call the concentration of each of the ions, x .

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$$

$$6.82 \times 10^{-6} = (x)(x)$$

$$= x^2$$

$$x = 2.6115 \times 10^{-3}$$

$$[\text{Mg}^{2+}] = [\text{CO}_3^{2-}] = [\text{MgCO}_3] = 2.6115 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

$$m = nM$$

$$= cVM$$

$$= \left(2.6115 \times 10^{-3} \frac{\text{mol}}{\text{L}}\right)(0.500 \text{ L}) \left(84.32 \frac{\text{g}}{\text{mol}}\right)$$

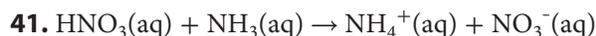
$$= 0.1101 \text{ g}$$

$$= 0.110 \text{ g}$$

40. a. a strong base such as $\text{NaOH}(\text{aq})$ and an indicator such as methyl red or bromocresol green

b. the pH range will be from 4 to 6

c. a pH meter can be used to verify the prediction.



Moles of ammonia:

$$\begin{aligned} n_{\text{NH}_4^+} &= c_{\text{NH}_4^+} V_{\text{NH}_4^+} \\ &= \left(0.100 \frac{\text{mol}}{\text{L}}\right) (25.00 \text{ mL}) = \left(\frac{1 \cancel{\text{L}}}{1000 \cancel{\text{mL}}}\right) \\ &= 2.50 \times 10^{-3} \text{ mol} \end{aligned}$$

At the equivalence point, there are equimolar amounts of HNO_3 and NH_3 in the solution.

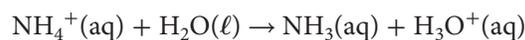
$$\begin{aligned} n_{\text{HNO}_3} &= n_{\text{NH}_3} \\ c_{\text{HNO}_3} V_{\text{HNO}_3} &= c_{\text{NH}_3} V_{\text{NH}_3} \\ \left(0.200 \frac{\text{mol}}{\text{L}}\right) V_{\text{HNO}_3} &= \left(0.100 \frac{\text{mol}}{\text{L}}\right) (25.00 \text{ mL}) \\ V_{\text{HNO}_3} &= \frac{\left(0.100 \frac{\text{mol}}{\text{L}}\right) (25.00 \text{ mL})}{0.200 \frac{\text{mol}}{\text{L}}} \end{aligned}$$

$$V_{\text{HNO}_3} = 12.5 \text{ mL}$$

The total volume is now

$$25.00 \text{ mL} + 12.5 \text{ mL} = 37.5 \text{ mL}$$

The ammonium ion is a weak acid. $K_a = 5.6 \times 10^{-10}$



The concentration of the ammonia is:

$$\begin{aligned} [\text{NH}_3^+] &= \left(\frac{2.5 \times 10^{-3} \text{ mol}}{37.5 \text{ mL}}\right) \left(\frac{1000 \cancel{\text{mL}}}{1 \text{ L}}\right) \\ &= 0.06666 \frac{\text{mol}}{\text{L}} \end{aligned}$$

| | $[\text{NH}_3]$ | $[\text{H}_3\text{O}^+]$ | $[\text{NH}_4^+]$ |
|----------|----------------------------|--------------------------|-------------------|
| I | 0.06666 | 0.00 | 0.00 |
| C | $-x$ | $+x$ | $+x$ |
| E | $0.06666 - x \cong 0.0666$ | x | x |

$1000 K_a = 5.6 \times 10^{-7} \gg 0.06666 \text{ mol/L}$ so the approximation is valid.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

$$5.6 \times 10^{-10} = \frac{(x)(x)}{(0.06666)}$$

$$(0.06666)(5.6 \times 10^{-10}) = x^2$$

$$3.7333 \times 10^{-11} = x^2$$

$$x = 6.1101 = 10^{-6}$$

$$[\text{H}_3\text{O}^+] = 6.1101 \times 10^{-6} \frac{\text{mol}}{\text{L}}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$= -\log(6.1101 \times 10^{-6})$$

$$= -(-5.214)$$

$$= 5.21$$

- 42.** Determine the molar concentration of by dividing by the molar mass of LiF:

$$c = \frac{1.11 \frac{\cancel{\text{g}}}{\text{L}}}{25.94 \frac{\cancel{\text{g}}}{\text{mol}}}$$

$$= 0.04279 \frac{\text{mol}}{\text{L}}$$

$$K_{\text{sp}} = [\text{Li}^+][\text{F}^-]$$

$$= \left(0.04279 \frac{\text{mol}}{\text{L}}\right) \left(0.04279 \frac{\text{mol}}{\text{L}}\right)$$

$$= 0.00183$$

$$= 1.83 \times 10^{-3}$$

- 43.** $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{KCl}(\text{aq}) \rightarrow \text{PbCl}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$

Concentration of Pb^{2+} after mixing:

$$c_i V_i = c_f V_f$$

$$\left(2.50 \times 10^{-3} \frac{\text{mol}}{\text{L}}\right) (15.00 \text{ mL}) = c_f (25.00 \text{ mL})$$

$$c_f = \frac{\left(2.50 \times 10^{-3} \frac{\text{mol}}{\text{L}}\right) (15.00 \cancel{\text{mL}})}{(25.00 \cancel{\text{mL}})}$$

$$c_f = 1.50 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

Concentration of Cl^- after mixing:

$$c_i V_i = c_f V_f$$

$$\left(2.10 \times 10^{-2} \frac{\text{mol}}{\text{L}}\right) (10.00 \text{ mL}) = c_f (25.00 \text{ mL})$$

$$c_f = \frac{\left(2.10 \times 10^{-2} \frac{\text{mol}}{\text{L}}\right) (10.00 \cancel{\text{mL}})}{(25.00 \cancel{\text{mL}})}$$

$$c_f = 8.40 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

$$Q_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$= (1.5 \times 10^{-3})(8.40 \times 10^{-3})^2$$

$$= 1.058 \times 10^{-7}$$

$Q_{\text{sp}} = 1.06 \times 10^{-7} < K_{\text{sp}} = 1.7 \times 10^{-5}$ so no precipitate will form.

44. Is there a coloured gas in the mixture? Is there a change in the number of moles of gas from reactants to products? Is an acid either forming or being used up in the process? Can temperature or concentrations easily be monitored?

45. Students should include the following concepts in their paragraph: reversible reaction; closed system, meaning closed to the environment such that there is no ability for materials to come into or escape the system; no change to a physical observable property in the system; constant temperature.

46. Both have product concentrations in the numerator and reactant concentrations in the denominator. Both use the balanced coefficients as exponents on the reactant and product concentrations. Homogeneous equilibrium constants have all materials in the gas phase, and so all are part of the constant. Heterogeneous equilibrium constants involve some materials that are pure liquids or solids, and these materials have constant concentrations and are left out of the equilibrium constant expressions.

47. When a system is composed of gases, using partial pressures to find a K_p value is often easier. This is due to the fact that partial pressures are often more easily measured for gases than molar volumes and concentrations. As long as each gas behaves like an ideal gas, the ideal gas law can be used to find the pressures (or molar volumes if the pressures are known or measured).

48. The choice of graphic organizer will vary, but all choices must include situations such as solving using the quadratic formula, solving by factoring and solving by taking the square root of each side, as well as when each can be used.

49. Student responses will depend on the choice of representation used to illustrate the reaction, but clearly the reaction should illustrate the movement of protons in the reaction between conjugate acid-base pairs.

50. Two possibilities exist: The student can find the pOH and then use $14 - \text{pOH} = \text{pH}$ or they can use $[\text{H}_3\text{O}^+(\text{aq})] = \frac{1 \times 10^{-14}}{[\text{OH}^-(\text{aq})]}$ to first find the hydronium ion concentration and then find the pH.

51. *Sample answer:* A weak acid does not fully dissociate into ions in water, regardless of the amount of acid in solution, whereas a dilute acid simply refers to a low number of moles of acid that is in solution, in either ionic or molecular form.

$$1.15 = \frac{x^2}{(0.500 - x)^2}$$

$$\sqrt{1.15} = \sqrt{\frac{x^2}{(0.500 - x)^2}}$$

$$1.07238 = \frac{x}{0.500 - x}$$

$$1.07238(0.500 - x) = x$$

$$0.53619 - 1.07238x = x$$

$$2.07238x = 0.53619$$

$$x = \frac{0.53619}{2.07238}$$

$$x = 0.25873$$

$$[\text{H}_2] = 0.25873 \frac{\text{mol}}{\text{L}}$$

$$n = cV$$

$$n = \left(0.25873 \frac{\text{mol}}{\cancel{\text{L}}} \right) (2 \cancel{\text{L}})$$

$$n = 0.51746 \text{ mol}$$

$$n = 0.517 \text{ mol}$$

65. $K_{\text{eq}} = 0.0400$

| | [HI] | [H ₂] | [I ₂] |
|----------|-------------|-------------------|-------------------|
| I | 0.200 mol/L | 0.00 | 0.000 |
| C | -2x | +x | +x |
| E | 2.00 - 2x | x | x |

$$K_{\text{eq}} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

$$0.0400 = \frac{(x)(x)}{(2.00 - x)^2}$$

$$0.0400 = \frac{x^2}{(2.00 - x)^2}$$

$$\sqrt{0.0400} = \sqrt{\frac{x^2}{(2.00 - x)^2}}$$

$$0.200 = \frac{x}{2.00 - x}$$

$$0.200(2.00 - x) = x$$

$$0.400 - 0.200x = x$$

$$0.400 = 1.200x$$

$$x = \frac{0.400}{1.200}$$

$$x = 0.3333$$

$$[\text{H}_2] = 0.3333 \frac{\text{mol}}{\text{L}}$$

Because the volume is 1.00 mol, the amount of H₂ gas in the container is: 0.333 mol.

66. Low temperatures may increase the percent yield, but the time needed for the reaction to form enough acid to make it useful would be too long at this temperature. This means that a higher than optimal temperature is used so that the sulfuric acid production is cost effective as a business.
67. The Brønsted-Lowry theory says compounds or ions act as bases because they are combining with hydrogen ions. The reason they are combining with hydrogen ions is that they have lone pairs of electrons - which is what the Lewis theory says. The two theories are consistent.
68. Due to the fact that in the auto-ionization of water, only 1 in 55 million water molecules ionize, even the weakest acids and bases will contribute far more hydroxide and hydronium ions to solution that the contribution due to water ionization does not affect the overall calculations. Even if this was factored in to the calculations, the pH and pOH values would be the same as if the auto-ionization of water was not included.

Answers to Unit 4 Self-Assessment Questions

(Student textbook pages 574-5)

1. b

2. d

$$\begin{aligned} 3. K_{\text{eq}} &= \frac{[\text{H}_2][\text{Cl}_2]}{[\text{HCl}]^2} \\ &= \frac{(4.16 \times 10^{-4})(6.37 \times 10^{-2})}{(2.34 \times 10^{-2})^2} \\ &= 0.04839 \end{aligned}$$

The answer is a.

$$\begin{aligned} 4. K_{\text{eq}} &= \frac{[\text{A}_2][\text{B}_2]}{[\text{AB}]^2} \\ &= \frac{(0.25)(0.25)}{(0.50)^2} \\ &= 0.25 \end{aligned}$$

The answer is b.

5. c

6. d

7. e

8. d

$$9. K_a K_b = 10^{-14}$$

$$\begin{aligned} K_b &= \frac{10^{-14}}{K_a} \\ &= \frac{10^{-14}}{7.2 \times 10^{-9}} \end{aligned}$$

$$= 1.3889 \times 10^{-6}$$

$$= 1.4 \times 10^{-6}$$

The answer is b.

10. a

11. $\text{pH} = -\log [\text{H}_3\text{O}^+]$

$$3.17 = -\log [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-3.17}$$

$$[\text{H}_3\text{O}^+] = 6.7608 \times 10^{-4}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{\text{HA}}$$

$$K_a = \frac{(6.7608 \times 10^{-4})(6.7608 \times 10^{-4})}{0.150}$$

$$K_a = 3.0472 \times 10^{-6}$$

$$K_a = 3.05 \times 10^{-6}$$

12. K_{eq} for reaction 1 will be equal to the square of that written from the second reaction.

13. Pressure will increase until equilibrium is approached.

14. The conclusion is not valid, as the system could simply have a ratio of products to reactants in the gas phase that is the same, which means that the reaction could be at equilibrium and is just not affected by changes in pressure or volume.

15. It is assumed that the inert gas acts like an ideal gas where the particles are considered to take up no volume. Since this is the case, there is no change to the system in terms of pressure or volume based on the reactants and products of the system, and so the position of equilibrium is unaffected by the addition of the inert gas.

16. $K_{\text{eq}} = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]}$

$$= \frac{(3.00)(2.00)}{(4.00)(0.500)}$$

$$= 3.00$$

Add 1.5 mol NO_2 to the 1.50 L container. The $[\text{NO}_2]$ increases by 1.00 mol/L

| | $[\text{SO}_2]$ | $[\text{NO}_2]$ | $[\text{SO}_3]$ | $[\text{NO}]$ |
|----------|-----------------|-----------------|-----------------|---------------|
| I | 4.00 | 1.50 | 3.00 | 2.00 |
| C | $-x$ | $-x$ | $+x$ | $+x$ |
| E | $4.00 - x$ | $1.50 - x$ | $3.00 + x$ | $2.00 + x$ |

$$K_{\text{eq}} = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]}$$

$$3.00 = \frac{(3.00 + x)(2.00 + x)}{(4.00 - x)(1.500 - x)}$$

$$3.00 = \frac{6.00 + 5.00x + x^2}{6.00 - 5.50x + x^2}$$

$$3.00(6.00 - 5.50x + x^2) = (6.00 + 5.00x + x^2)$$

$$18.00 - 16.50x + 3.00x^2 = 6.00 + 5.00x + x^2$$

$$2.00x^2 - 21.50x + 12.00 = 0$$

$$x = \frac{21.50 \pm \sqrt{21.50^2 - 4(2.00)(12.00)}}{2(2.00)}$$

$$x = \frac{21.50 \pm 19.1376}{4}$$

$$x = 0.59 \text{ or } x = 10.159$$

The second value ($x = 10.159$) is not possible because there would be more NO than the total of everything in the container. Therefore, $x = 0.59$.

$$[\text{NO}] = 2.00 + x$$

$$= 2.00 + 0.59$$

$$= 2.59 \frac{\text{mol}}{\text{L}}$$

17. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

| | $[\text{PCl}_5]$ | $[\text{Cl}_2]$ | $[\text{PCl}_3]$ |
|----------|--|-----------------|------------------|
| I | $\frac{0.90 \text{ mol}}{1.50 \text{ L}} = 0.60 \frac{\text{mol}}{\text{L}}$ | 0.00 | 0.00 |
| C | -0.28 | +0.28 | +0.28 |
| E | $\frac{0.48 \text{ mol}}{1.50 \text{ L}} = 0.32 \frac{\text{mol}}{\text{L}}$ | 0.28 | 0.28 |

$$K_{\text{eq}} = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

$$= \frac{(0.28)(0.28)}{(0.32)}$$

$$= 0.245$$

$$= 0.25$$

18.

| | $[\text{Br}_2]$ | $[\text{Cl}_2]$ | $[\text{BrCl}]$ |
|----------|-----------------|-----------------|-----------------|
| I | 4.00 | 4.00 | 0.00 |
| C | $-x$ | $-x$ | $+2x$ |
| E | $4.00 - x$ | $4.00 - x$ | $2x$ |

$$K_{\text{eq}} = \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]}$$

$$47.5 = \frac{(2x)^2}{(4.00 - x)(4.00 - x)}$$

$$47.5 = \frac{(2x)^2}{(4.00 - x)^2}$$

$$\sqrt{47.5} = \sqrt{\frac{(2x)^2}{(4.00 - x)^2}}$$

$$6.892 = \frac{(2x)}{(4.00 - x)}$$

$$6.892(4.00 - x) = (2x)$$

$$27.568 - 6.892x = 2x$$

$$27.568 = 8.892x$$

$$x = \frac{27.568}{8.892}$$

$$x = 3.10$$

$$\begin{aligned} [\text{Br}_2] &= 4.00 - x \\ &= 4.00 - 3.10 \\ &= 0.90 \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{Cl}_2] &= 4.00 - x \\ &= 4.00 - 3.10 \\ &= 0.90 \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{BrCl}] &= 2x \\ &= 2(3.10) \\ &= 6.20 \text{ mol/L} \end{aligned}$$

18. $[\text{Br}_2] = 0.90 \text{ mol/L}$; $[\text{Cl}_2] = 0.90 \text{ mol/L}$;

$$[\text{BrCl}] = 6.20 \text{ mol/L}$$

19. Without balance, the equilibrium systems of the blood will not be able to occur as they would under ideal conditions. Most long term imbalances will lead to a wide variety of health related issues that can cause severe damage to many organs and organ systems. If left untreated, many can lead to damage that cannot be repaired.

20. Organizers must include the steps of:

1. Convert the acid dissociation constant to the base ionization constant using K_w .
2. Write and balance the reaction of the ionization for the base.
3. Set up an ICE chart to find expressions for the equilibrium constants for all reactants and products.
4. Use the K_b expression, with the value from step 1 and the equilibrium constants from step 3 to find the concentration of hydroxide ions in solution.
5. Find pOH using the concentration found in step 4.
6. Use $\text{pH} = 14 - \text{pOH}$ to find the pH.

21. $\text{pH} = -\log [\text{H}_3\text{O}^+]$

$$= -\log 0.00750$$

$$= 2.12$$

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

$$= 14 - 2.12$$

$$= 11.88$$

$$[\text{OH}^-][\text{H}_3\text{O}^+] = 10^{-14}$$

$$[\text{OH}^-] = \frac{10^{-14}}{[\text{H}_3\text{O}^+]}$$

$$= \frac{10^{-14}}{0.00750}$$

$$= 1.33333 \times 10^{-12}$$

$$= 1.33 \times 10^{-12}$$

$$\text{pH} = 2.12; \text{pOH} = 11.88;$$

$$[\text{OH}^-] = 1.33 \times 10^{-12} \text{ mol/L}$$

22. $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-$

| | [HCOOH] | [H ₃ O ⁺] | [HCOO ⁻] |
|----------|-----------|----------------------------------|----------------------|
| I | 0.100 | 0.00 | 0.00 |
| C | -x | +x | +x |
| E | 0.100 - x | x | x |

$$K_a = 1.70 \times 10^{-4}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$1.70 \times 10^{-4} = \frac{(x)(x)}{0.100 - x}$$

$$1.70 \times 10^{-4} (0.100 - x) = x^2$$

$$1.70 \times 10^{-5} - 1.70 \times 10^{-4} x = x^2$$

$$x^2 + 1.70 \times 10^{-4} x - 1.70 \times 10^{-5} = 0$$

$$x = \frac{-1.70 \times 10^{-4} \pm \sqrt{(1.70 \times 10^{-4})^2 - 4(1)(-1.70 \times 10^{-5})}}{2(1)}$$

$$x = \frac{-1.70 \times 10^{-4} \pm 8.248 \times 10^{-3}}{2}$$

Use the positive value.

$$x = 4.039 \times 10^{-3}$$

$$\text{pH} = -\log (4.039 \times 10^{-3})$$

$$= 2.3937$$

$$= 2.39$$

23. $\text{B}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{BH}^+(\text{aq}) + \text{HO}^-(\text{aq})$

Concentration of base:

$$c = \frac{n}{V}$$

$$= \left(\frac{m}{M} \right) \frac{1}{V}$$

$$= \frac{3.75 \text{ g}}{101.70 \frac{\text{g}}{\text{mol}}} \frac{1}{1.00 \text{ L}}$$

$$= \frac{0.03687 \text{ mol}}{1 \text{ L}}$$

$$= 0.03687 \frac{\text{mol}}{\text{L}}$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ 9.14 &= -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-9.14} \\ [\text{H}_3\text{O}^+] &= 7.244 \times 10^{-10} \text{ mol/L} \\ [\text{H}_3\text{O}^+][\text{OH}^-] &= 10^{-14} \\ [\text{OH}^-] &= \frac{10^{-14}}{[\text{H}_3\text{O}^+]} \\ [\text{OH}^-] &= \frac{10^{-14}}{7.244 \times 10^{-10}} \\ [\text{OH}^-] &= 1.3804 \times 10^{-5} \end{aligned}$$

| | [B] | [BH ⁺] | [OH ⁻] |
|----------|---|--------------------------|--------------------------|
| I | 0.03687 | 0.00 | 0.00 |
| C | -1.3804×10^{-5} | $+1.3804 \times 10^{-5}$ | $+1.3804 \times 10^{-5}$ |
| E | $0.03687 - 1.3804 \times 10^{-5} = 0.03656$ | 1.3804×10^{-5} | 1.3804×10^{-5} |

$$\begin{aligned} K_b &= \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \\ &= \frac{(1.3804 \times 10^{-5})(1.3804 \times 10^{-5})}{0.03656} \end{aligned}$$

$$K_b = 5.17 \times 10^{-9}$$

24. Moles of NaOH:

$$\begin{aligned} n &= cV \\ &= \left(0.0180 \frac{\text{mol}}{\text{L}}\right) (14.15 \text{ mL}) \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) \\ &= 2.547 \times 10^{-4} \text{ mol} \end{aligned}$$

$$n_{\text{HCl}} = n_{\text{NaOH}} = 2.547 \times 10^{-4} \text{ mol}$$

Initial concentration of HCl:

$$\begin{aligned} c &= \frac{n}{V} \\ &= \left(\frac{2.547 \times 10^{-4} \text{ mol}}{25.00 \text{ mL}}\right) \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) \\ &= 1.0188 \times 10^{-2} \frac{\text{mol}}{\text{L}} \end{aligned}$$

HCl is a strong acid so it dissociates completely.

Therefore the concentration of hydronium ion is the same as the concentration of HCl.

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log (1.0188 \times 10^{-2}) \\ &= 1.99 \end{aligned}$$

25. Water acts as a Brønsted-Lowry base in reactions with acids, such as hydrochloric acid, because it is a proton acceptor. Water functions as a Brønsted-Lowry acid, or a proton donor, in reactions with bases, such as ammonia.