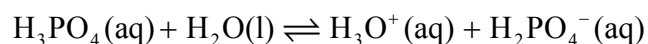


CHAPTER 11

AQUEOUS EQUILIBRIA

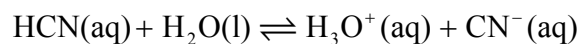
- 11.2** (a) When solid sodium dihydrogen phosphate is added to a solution of phosphoric acid, the following equilibrium



shifts to the left to relieve the stress resulting from the increased H_2PO_4^- .

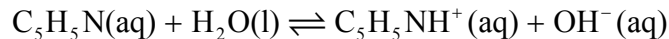
Consequently, $[\text{H}_3\text{O}^+]$ decreases and the pH increases.

- (b) When HBr, a strong acid, is added to a solution of HCN, the percentage of HCN that is deprotonated decreases because the following equilibrium



shifts to the left to relieve the stress imposed by the increased H_3O^+ supplied by the HBr.

- (c) When pyridinium chloride ($\text{C}_5\text{H}_5\text{NHCl}$) is added to a solution of pyridine, the following equilibrium



shifts to the left to relieve the stress resulting from the increased $\text{C}_5\text{H}_5\text{NH}^+$. Consequently, the $[\text{OH}^-]$ decreases. Because $[\text{H}_3\text{O}^+][\text{OH}^-]$ is constant, $[\text{H}_3\text{O}^+]$ must increase and the pH consequently decreases.

- 11.4** (a) The reaction is $\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CN}^-(\text{aq})$.

Concentration

(mol · L ⁻¹)	HCN(aq)	+ H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+ CN ⁻ (aq)
initial	0.075	—		0	0.045
change	-x	—		+x	+x
equilibrium	0.075 - x	—		x	0.045 + x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(x)(0.045 + x)}{(0.075 - x)}$$

$$4.9 \times 10^{-10} \approx \frac{[\text{H}_3\text{O}^+](0.045)}{(0.075)}$$

$$[\text{H}_3\text{O}^+] \approx 8.2 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1}$$

(b) 0.50 M NaCl will have no effect:

Concentration

(mol · L ⁻¹)	NH ₂ NH ₂ (aq)	+ H ₂ O(l)	⇌	NH ₂ NH ₃ ⁺ (aq)	+ OH ⁻ (aq)
initial	0.20	0		0	
change	-x	—		+x	+x
equilibrium	0.20 - x	—		x	x

$$K_b = \frac{[\text{NH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{NH}_2\text{NH}_2]}$$

$$1.7 \times 10^{-6} = \frac{[\text{OH}^-]^2}{0.20}$$

$$[\text{OH}^-] = \sqrt{3.4 \times 10^{-7}} = 5.8 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{5.8 \times 10^{-4}} = 1.7 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1}$$

(c) Setup is similar to part (a).

$$K_a = 4.9 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{(x)(0.030 + x)}{(0.015 - x)}$$

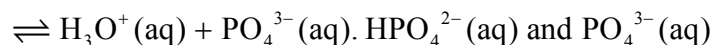
$$4.9 \times 10^{-10} \approx \frac{[\text{H}_3\text{O}^+][0.030]}{(0.015)}$$

$$[\text{H}_3\text{O}^+] = 2.5 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1}$$

(d) When the concentrations of a weak base and its conjugate acid are equal, the pOH equals the pK_b . Therefore, the pOH of hydrazine = $pK_b = 5.77$, and

$$\begin{aligned} \text{pH} &= 14.00 - \text{pOH} = 14.00 - 5.77 = 8.23. [\text{H}_3\text{O}^+] = 10^{-8.23} \\ &= 5.9 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$

11.6 In each case, the equilibrium involved is $\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$



are conjugate acid and base; therefore, the pH calculation is most easily performed with the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \left(\frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \right)$$

For H_3PO_4 , $\text{p}K_{a3} = 12.68$

(a)

$$\text{pH} = 12.68 + \log \left(\frac{0.25 \text{ mol} \cdot \text{L}^{-1}}{0.17 \text{ mol} \cdot \text{L}^{-1}} \right) = 12.85; \text{pOH} = 14.00 - 12.85 = 1.15$$

(b)

$$\text{pH} = 12.68 + \log \left(\frac{0.42 \text{ mol} \cdot \text{L}^{-1}}{0.66 \text{ mol} \cdot \text{L}^{-1}} \right) = 12.48; \text{pOH} = 14.00 - 12.48 = 1.52$$

(c)

$$\text{pH} = 12.68 + \log \left(\frac{0.12 \text{ mol} \cdot \text{L}^{-1}}{0.12 \text{ mol} \cdot \text{L}^{-1}} \right) = 12.68; \text{pOH} = 14.00 - 12.68 = 1.32$$

11.8 molarity of $\text{NaBrO} = \left(\frac{7.50 \text{ g NaBrO}}{118.90 \text{ g/mol}} \right) \left(\frac{1}{0.100 \text{ L}} \right) = 0.631 \text{ mol} \cdot \text{L}^{-1}$

Concentration

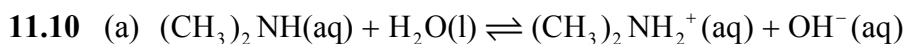
(mol · L ⁻¹)	H ₂ O(l)	+ HBrO(aq)	⇌	H ₃ O ⁺ (aq)	+	BrO ⁻ (aq)
initial	—	0.50		0		0.631
change	—			+x		+x
equilibrium	—	0.50 - x		x		0.631 + x

$$K_a = 2.0 \times 10^{-9} = \frac{[\text{H}_3\text{O}^+][\text{BrO}^-]}{[\text{HBrO}]} = \frac{x(0.631 + x)}{0.50 - x} \approx \frac{0.631x}{0.50}$$

$$x = [\text{H}_3\text{O}^+] = 1.6 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.6 \times 10^{-9}) = 8.80$$

$$\text{Change in pH is } 8.80 - 4.50 = 4.30$$



$$\text{total volume } 400 \text{ mL} = 0.400 \text{ L}$$

$$\text{moles of } (\text{CH}_3)_2\text{NH} = (0.100 \text{ L})(0.020 \text{ mol} \cdot \text{L}^{-1})$$

$$= 2.0 \times 10^{-3} \text{ mol } (\text{CH}_3)_2\text{NH}$$

$$\text{moles of } (\text{CH}_3)_2\text{NH}_2\text{Cl} = (0.300 \text{ L})(0.030 \text{ mol} \cdot \text{L}^{-1})$$

$$= 9.0 \times 10^{-3} \text{ mol } (\text{CH}_3)_2\text{NH}_2\text{Cl}$$

$$\text{initial } [(\text{CH}_3)_2\text{NH}] = \frac{2.0 \times 10^{-3} \text{ mol}}{0.400 \text{ L}} = 5.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{initial } [(\text{CH}_3)_2\text{NH}_2\text{Cl}] = \frac{9.0 \times 10^{-3} \text{ mol}}{0.400 \text{ L}} = 2.3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

Concentration

(mol · L ⁻¹)	H ₂ O(l)	+ (CH ₃) ₂ NH(aq)	⇌	(CH ₃) ₂ NH ₂ ⁺ (aq)	+	OH ⁻ (aq)
initial	—	5.0 × 10 ⁻³		2.3 × 10 ⁻²		0
change	—	-x		+x		+x
equilibrium	—	5.0 × 10 ⁻³ - x		2.3 × 10 ⁻² + x		x

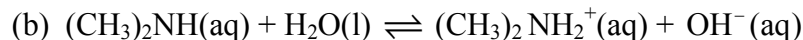
$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]} = \frac{(2.3 \times 10^{-2} + x)(x)}{(5.0 \times 10^{-3} - x)} \cong \frac{(2.3 \times 10^{-2})(x)}{(5.0 \times 10^{-3})}$$

$$= 5.4 \times 10^{-4}$$

$$x = 1.2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cong [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.2 \times 10^{-4}) = 3.92$$

$$\text{pH} = 14.00 - 3.92 = 10.08$$



$$\text{Total volume } 75 \text{ mL} = 0.0750 \text{ L}$$

$$\text{moles of } (\text{CH}_3)_2\text{NH} = (0.065 \text{ L})(0.010 \text{ mol} \cdot \text{L}^{-1})$$

$$= 6.5 \times 10^{-4} \text{ mol } (\text{CH}_3)_2\text{NH}$$

$$\text{moles of } (\text{CH}_3)_2\text{NH}_2\text{Cl} = (0.010 \text{ L})(0.150 \text{ mol} \cdot \text{L}^{-1})$$

$$= 1.5 \times 10^{-3} \text{ mol } (\text{CH}_3)_2\text{NH}_2\text{Cl}$$

$$\text{initial } [(\text{CH}_3)_2\text{NH}_2\text{Cl}] = \frac{1.5 \times 10^{-3} \text{ mol}}{0.0750 \text{ L}} = 2.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{and } [(\text{CH}_3)_2\text{NH}] = \frac{6.5 \times 10^{-4} \text{ mol}}{0.0750 \text{ L}} = 8.7 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

As in part (a),

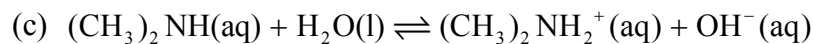
$$K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]} = \frac{(2.0 \times 10^{-2} + x)(x)}{(8.7 \times 10^{-3} - x)} \approx \frac{(2.0 \times 10^{-2})(x)}{(8.7 \times 10^{-3})}$$

$$= 5.4 \times 10^{-4}$$

$$x = 2.3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cong [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(2.3 \times 10^{-4}) = 3.64$$

$$\text{pH} = 14.00 - 3.64 = 10.36$$



$$\text{Total volume} = 175 \text{ mL} = 0.175 \text{ L}$$

$$\text{moles of } (\text{CH}_3)_2\text{NH} = (0.050 \text{ L})(0.015 \text{ mol} \cdot \text{L}^{-1})$$

$$= 7.5 \times 10^{-4} \text{ mol } (\text{CH}_3)_2\text{NH}$$

$$\text{moles of } (\text{CH}_3)_2\text{NH}_2\text{Cl} = (0.125 \text{ L})(0.015 \text{ mol} \cdot \text{L}^{-1})$$

$$= 1.9 \times 10^{-3} \text{ mol } (\text{CH}_3)_2 \text{NH}_2 \text{Cl}$$

$$\text{initial } [(\text{CH}_3)_2 \text{NH}_2 \text{Cl}] = \frac{1.9 \times 10^{-3} \text{ mol}}{0.175 \text{ L}} = 1.1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{and } [(\text{CH}_3)_2 \text{NH}] = \frac{7.5 \times 10^{-4} \text{ mol}}{0.175 \text{ L}} = 4.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$K_b = \frac{[(\text{CH}_3)_2 \text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2 \text{NH}]} = \frac{(1.1 \times 10^{-2} + x)(x)}{(4.3 \times 10^{-3} - x)} = \frac{(1.1 \times 10^{-2})(x)}{(4.3 \times 10^{-3})}$$

$$= 5.4 \times 10^{-4}$$

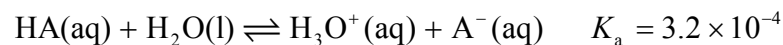
$$x = 2.1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cong [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(2.1 \times 10^{-4}) = 3.68$$

$$\text{pH} = 14.00 - 3.68 = 10.32$$

11.12 HA = acetylsalicylic acid

A^- = conjugate base of acetylsalicylic acid



We will use the following formula to evaluate the ratio of $[\text{A}^-]$ to $[\text{HA}]$ at equilibrium:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

The formula is derived in this way:

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

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

$$\begin{aligned} \text{pH} &= \text{p} \left(\frac{K_a [\text{HA}]}{[\text{A}^-]} \right) \\ &= \text{p}K_a - \log \frac{[\text{HA}]}{[\text{A}^-]} \\ &= \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \end{aligned}$$

Given that $\text{pH} = 4.67$ and $K_a = 3.2 \times 10^{-4}$ ($\text{p}K_a = 3.49$),

$$4.67 = 3.49 + \log \frac{[A^-]}{[HA]}$$

$$1.18 = \log \frac{[A^-]}{[HA]}$$

Taking antilogs of both sides of this equation gives

$$15 = \frac{[A^-]}{[HA]}$$

11.14 (a) $pK_a = 3.37$, pH range ≈ 2 to 4

(b) $pK_a = 3.75$, pH range ≈ 3 to 5

(c) $pK_{a2} = 10.25$, pH range ≈ 9 to 11

(d) $pK_b = 4.75$, $pK_a = 9.25$, pH range ≈ 8 to 10

(e) $pK_b = 8.75$, $pK_a = 5.25$, pH range ≈ 4 to 6

11.16 (a) C_6H_5COOH and $NaC_6H_5CO_2$, $pK_a = 4.19$

(b) NH_4Cl and NH_3 , $pK_b = 4.75$, $pK_a = 9.25$

(c) CH_3COOH and $NaCH_3CO_2$, $pK_a = 4.75$

(d) $(C_2H_5)_3NHCl$ and $(C_2H_5)_3N$, $pK_b = 2.99$, $pK_a = 11.01$

11.18 $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$

$$K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$pH = pK_{a3} + \log \frac{[PO_4^{3-}]}{[HPO_4^{2-}]} \text{ (see Exercise 11.12)}$$

$$\log \frac{[PO_4^{3-}]}{[HPO_4^{2-}]} = pH - pK_{a3}; pK_{a3} = 12.68$$

$$(a) \log \frac{[PO_4^{3-}]}{[HPO_4^{2-}]} = 12.00 - 12.68 = -0.68$$

$$\frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 0.21$$

(b)

$$\begin{aligned}\text{molarity of PO}_4^{3-} &= 0.21 \times \text{molarity of HPO}_4^{2-} = 0.21 \times 0.100 \text{ mol} \cdot \text{L}^{-1} \\ &= 2.1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}\end{aligned}$$

$$\begin{aligned}\text{moles of PO}_4^{3-} &= \text{moles of K}_3\text{PO}_4 = 2.1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \times 1 \text{ L} \\ &= 2.1 \times 10^{-2} \text{ mol}\end{aligned}$$

$$\text{mass of K}_3\text{PO}_4 = 2.1 \times 10^{-2} \text{ mol} \times \frac{212.27 \text{ g K}_3\text{PO}_4}{1 \text{ mol K}_3\text{PO}_4} = 4.46 \text{ g K}_3\text{PO}_4$$

$$(c) \quad \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 0.21 = \frac{0.100 \text{ mol} \cdot \text{L}^{-1}}{x \text{ mol} \cdot \text{L}^{-1}} = \frac{0.100 \text{ mol}}{x \text{ mol}} = \frac{0.100 \text{ mol K}_3\text{PO}_4}{x \text{ mol K}_2\text{HPO}_4}$$

$$x \text{ mol K}_2\text{HPO}_4 = \frac{0.100 \text{ mol}}{0.21} = 0.48 \text{ mol K}_2\text{HPO}_4$$

$$\begin{aligned}\text{mass of K}_2\text{HPO}_4 &= 0.48 \text{ mol K}_2\text{HPO}_4 \times \frac{174.18 \text{ g K}_2\text{HPO}_4}{1 \text{ mol K}_2\text{HPO}_4} \\ &= 84 \text{ g K}_2\text{HPO}_4\end{aligned}$$

$$\begin{aligned}(d) \quad \text{moles of K}_3\text{PO}_4 \text{ required} &= 0.21 \times \text{moles of K}_2\text{HPO}_4 \\ &= 0.21 \times 0.0500 \text{ L}\end{aligned}$$

$$\times 0.100 \text{ mol} \cdot \text{L}^{-1} = 1.1 \times 10^{-3} \text{ mol}$$

$$\text{volume of K}_3\text{PO}_4 \text{ solution} = \frac{1.1 \times 10^{-3} \text{ mol}}{0.150 \text{ mol} \cdot \text{L}^{-1}} = 7.3 \times 10^{-3} \text{ L} = 7.3 \text{ mL}$$

11.20 (a) The initial pH is found by:

$$\begin{aligned}\text{pH} &= \text{p}K_{a1} + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \\ &= 7.21 + \log \frac{0.150 \text{ M}}{0.100 \text{ M}} \\ &= 7.39\end{aligned}$$

$$(0.0800 \text{ L})(0.0100 \text{ mol} \cdot \text{L}^{-1}) = 8.00 \times 10^{-4} \text{ mol NaOH (strong base),}$$

$$\text{producing } 8.0 \times 10^{-4} \text{ mol HPO}_4^{2-} \text{ from H}_2\text{PO}_4^-$$

$$(0.150 \text{ mol} \cdot \text{L}^{-1})(0.100 \text{ L}) = 1.50 \times 10^{-2} \text{ mol HPO}_4^{2-} \text{ (initially)}$$

$$(0.100 \text{ mol} \cdot \text{L}^{-1})(0.100 \text{ L}) = 1.00 \times 10^{-2} \text{ mol H}_2\text{PO}_4^- \text{ (initially)}$$

After adding NaOH:

$$[\text{HPO}_4^{2-}] = \frac{(1.50 \times 10^{-2} + 8.00 \times 10^{-4}) \text{ mol}}{0.180 \text{ L}} = 8.78 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{H}_2\text{PO}_4^-] = \frac{(1.00 \times 10^{-2} - 8.00 \times 10^{-4}) \text{ mol}}{0.180 \text{ L}} = 5.1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HPO}_4^-]}{[\text{H}_2\text{PO}_4^{2-}]}$$

$$\text{pH} = 7.21 + \log \frac{(8.78 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1})}{(5.1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1})} = 7.21 + 0.24 = 7.45$$

$$\Delta\text{pH} = +0.06$$

$$\text{(b) } (0.0100 \text{ L})(1.0 \text{ mol} \cdot \text{L}^{-1}) = 1.0 \times 10^{-2} \text{ mol HNO}_3 \text{ (strong acid),}$$

producing $1.0 \times 10^{-2} \text{ mol H}_2\text{PO}_4^-$ from HPO_4^{2-}

$$\text{molarity of HPO}_4^{2-} = \frac{(1.5 \times 10^{-2} - 1.0 \times 10^{-2}) \text{ mol}}{0.110 \text{ L}} = 5 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

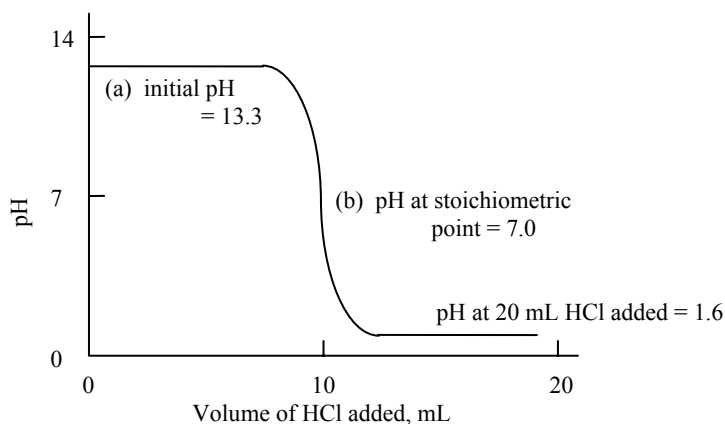
$$\text{molarity of H}_2\text{PO}_4^- = \frac{(1.0 \times 10^{-2} + 1.0 \times 10^{-2}) \text{ mol}}{0.110 \text{ L}} = 1.8 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HPO}_4^-]}{[\text{H}_2\text{PO}_4^{2-}]}$$

$$\text{pH} = 7.21 + \log \frac{(5 \times 10^{-2} \text{ mol} \cdot \text{L})}{(1.8 \times 10^{-1} \text{ mol} \cdot \text{L})} = 7.21 - 0.6 = 6.6$$

$$\Delta\text{pH} = 6.6 - 7.39 = -0.8$$

11.22



$$\text{Initial molarity of OH}^- = 2 \times 0.10 \text{ mol} \cdot \text{L}^{-1} = 0.20 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(0.20) = 0.70, \text{pH} = 14.00 - 0.70 = 13.30$$

$$\begin{aligned} \mathbf{11.24} \quad (\text{a}) \quad V_{\text{HCl}} &= \left(\frac{25.0 \text{ mL}}{2} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{0.215 \text{ mol KOH}}{1 \text{ L KOH}} \right) \\ &\quad \times \left(\frac{1 \text{ mol HCl}}{1 \text{ mol KOH}} \right) \left(\frac{1 \text{ L HCl}}{0.116 \text{ mol HCl}} \right) \\ &= 0.0232 \text{ L HCl} = 23.2 \text{ mL HCl} \end{aligned}$$

$$(\text{b}) \quad 2 \times 0.0232 \text{ L} = 0.0464 \text{ L} = 46.4 \text{ mL HCl}$$

$$(\text{c}) \quad \text{In HCl, } [\text{HCl}]_0 = [\text{Cl}^-]$$

$$\text{volume} = (0.0250 + 0.0464) \text{ L} = 0.0714 \text{ L}$$

$$\begin{aligned} \text{molarity of Cl}^- &= (0.0464 \text{ L}) \left(\frac{0.116 \text{ mol Cl}^-}{1 \text{ L}} \right) \left(\frac{1}{0.0714 \text{ L}} \right) \\ &= 0.0754 \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$

$$\begin{aligned} (\text{d}) \quad \text{number of moles of H}_3\text{O}^+ \text{ (from acid)} &= (0.0400 \text{ L})(0.116 \text{ mol} \cdot \text{L}^{-1}) \\ &= 4.64 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{number of moles of OH}^- \text{ (from base)} &= (0.0250 \text{ L})(0.215 \text{ mol} \cdot \text{L}^{-1}) \\ &= 5.38 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{excess OH}^- = (5.38 - 4.64) \times 10^{-3} \text{ mol} = 7.4 \times 10^{-4} \text{ mol}$$

$$\text{volume solution} = (0.0400 + 0.0250) \text{ L} = 0.0650 \text{ L}$$

$$[\text{OH}^-] = \frac{7.4 \times 10^{-4} \text{ mol}}{0.0650 \text{ L}} = 0.011 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(0.011) = 1.96$$

$$\text{pH} = 14.00 - 1.96 = 12.04$$

$$\mathbf{11.26} \quad (\text{a})$$

$$M = \frac{m}{n} = \frac{0.483 \text{ g}}{0.250 \text{ M} \times 42.0 \text{ mL}} = \frac{0.483 \text{ g}}{0.250 \text{ mol} \times \text{L}^{-1} \times 0.0420 \text{ L}} = 46.0 \text{ g} \cdot \text{mol}^{-1}$$

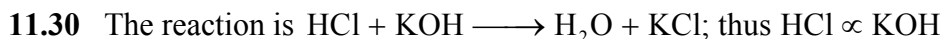
$$(\text{b}) \quad \text{pK}_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{pH at the midpoint of the titration} = 3.75$$

Comparing to values listed in Table 10.1, the acid is most likely formic acid (HCOOH).



$$\begin{aligned} & \text{mass of pure Ba(OH)}_2 \\ &= (0.0176 \text{ L HCl}) \left(\frac{0.0935 \text{ mol HCl}}{1 \text{ L HCl}} \right) \left(\frac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol HCl}} \right) \\ & \quad \left(\frac{171.36 \text{ g Ba(OH)}_2}{1 \text{ mol Ba(OH)}_2} \right) \left(\frac{250 \text{ mL}}{35.0 \text{ mL}} \right) \\ &= 1.01 \text{ g} \end{aligned}$$

$$\text{percentage purity} = \frac{1.01 \text{ g}}{1.331 \text{ g}} \times 100\% = 75.9\%$$



(a) Initial : $[\text{OH}^-] = 0.215 \text{ mol} \cdot \text{L}^{-1}$

$$\text{pOH} = -\log(0.215) = 0.668$$

$$\text{pH} = 14.00 - \text{pOH} = 13.33$$

(b) After addition of 5.0 mL of $0.116 \text{ mol} \cdot \text{L}^{-1}$ HCl:

$$\begin{aligned} & (0.0250 \text{ L base}) \left(\frac{0.215 \text{ mol KOH}}{1 \text{ L base}} \right) - (0.0050 \text{ L}) \left(\frac{0.116 \text{ mol HCl}}{1 \text{ L}} \right) \\ &= 4.80 \times 10^{-3} \text{ mol KOH unreacted} \end{aligned}$$

$$[\text{OH}^-] = \frac{4.80 \times 10^{-3} \text{ mol OH}^-}{0.0300 \text{ L}} = 0.16 \text{ mol} \cdot \text{L}^{-1} \text{ OH}^-$$

$$\text{pOH} = -\log(0.16) = 0.80$$

$$\text{pH} = 14.00 - 0.80 = 13.20$$

(c) After addition of 10.0 mL of $0.116 \text{ mol} \cdot \text{L}^{-1}$ HCl:

$$\begin{aligned} & (0.0250 \text{ L base}) \left(\frac{0.215 \text{ mol KOH}}{1 \text{ L base}} \right) - (0.0100 \text{ L}) \left(\frac{0.116 \text{ mol HCl}}{1 \text{ L}} \right) \\ &= 4.22 \times 10^{-3} \text{ mol KOH unreacted} \end{aligned}$$

$$[\text{OH}^-] = \frac{4.22 \times 10^{-3} \text{ mol OH}^-}{0.0350 \text{ L}} = 0.121 \text{ mol} \cdot \text{L}^{-1} \text{ OH}^-$$

$$\text{pOH} = -\log(0.121) = 0.917$$

$$\text{pH} = 14.00 - 0.917 = 13.08$$

(d) At the stoichiometric point:

For the reaction of a strong acid with a strong base, the pH at the stoichiometric point is the same as the pH for pure water. Therefore, the pH = 7.0.

Volume HCl at the stoichiometric point:

$$(0.0250 \text{ L KOH}) \left(\frac{0.215 \text{ mol KOH}}{1 \text{ L KOH}} \right) \left(\frac{1 \text{ mol HCl}}{1 \text{ mol KOH}} \right) \left(\frac{1 \text{ L HCl}}{0.116 \text{ mol HCl}} \right) \\ = 0.0463 \text{ L HCl}$$

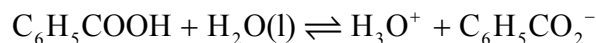
(e) After addition of 5.0 mL of acid beyond the stoichiometric point,

$$(0.0050 \text{ L}) \left(\frac{0.116 \text{ mol HCl}}{1 \text{ L}} \right) \left(\frac{1}{(0.0463 + 0.0050 + 0.0250) \text{ L}} \right) \\ = 0.0076 \text{ mol} \cdot \text{L}^{-1} \text{ H}_3\text{O}^+ \\ \text{pH} = -\log(0.0076) = 2.12$$

(f) After addition of 10 mL of acid beyond the stoichiometric point,

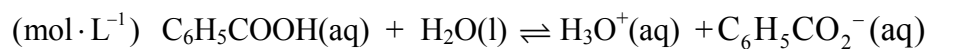
$$(0.010 \text{ L}) \left(\frac{0.116 \text{ mol HCl}}{1 \text{ L}} \right) \left(\frac{1}{(0.0463 + 0.010 + 0.0250) \text{ L}} \right) \\ = 0.014 \text{ mol} \cdot \text{L}^{-1} \text{ H}_3\text{O}^+ \\ \text{pH} = -\log(0.014) = 1.85$$

11.32 (a) Initial pH of 0.20 M $\text{C}_6\text{H}_5\text{COOH}$ ($K_a = 6.5 \times 10^{-5}$)



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

Concentration



initial	0.20	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.20 - x$	—	x	x

$$6.5 \times 10^{-5} = \frac{(x)(x)}{0.20 - x} \cong \frac{x^2}{0.20}$$

$$x = [\text{H}_3\text{O}^+] = 3.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(3.6 \times 10^{-3}) = 2.44$$

$$\begin{aligned} \text{(b) initial moles of } \text{C}_6\text{H}_5\text{COOH} &= (0.0300 \text{ L})(0.20 \text{ mol} \cdot \text{L}^{-1}) \\ &= 6.0 \times 10^{-3} \text{ mol } \text{C}_6\text{H}_5\text{COOH} \end{aligned}$$

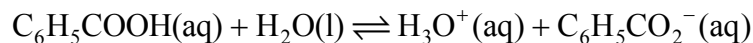
$$\begin{aligned} \text{moles of KOH} &= (0.0150 \text{ L})(0.30 \text{ mol} \cdot \text{L}^{-1}) = 4.5 \times 10^{-3} \text{ mol KOH} \\ &= \text{mol } \text{C}_6\text{H}_5\text{CO}_2^- \end{aligned}$$

$$\begin{aligned} \text{moles } \text{C}_6\text{H}_5\text{OH remaining} &= 6.0 \times 10^{-3} \text{ mol} - 4.5 \times 10^{-3} \text{ mol} \\ &= 1.5 \times 10^{-3} \text{ mol} \end{aligned}$$

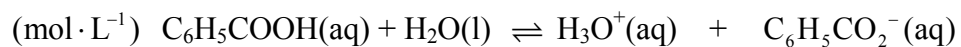
$$\frac{1.5 \times 10^{-3} \text{ mol } \text{C}_6\text{H}_5\text{COOH}}{0.0450 \text{ L}} = 3.3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ } \text{C}_6\text{H}_5\text{COOH}$$

$$\text{and } \frac{4.5 \times 10^{-3} \text{ mol } \text{C}_6\text{H}_5\text{CO}_2^-}{0.0450 \text{ L}} = 0.10 \text{ mol} \cdot \text{L}^{-1} \text{ } \text{C}_6\text{H}_5\text{O}_2^-$$

Then, consider the equilibrium



Concentration



initial	3.3×10^{-2}	—	0	0.10
change	$-x$	—	$+x$	$+x$
equilibrium	$3.3 \times 10^{-2} - x$	—	x	$0.10 + x$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$6.5 \times 10^{-5} = \frac{(x)(x + 0.10)}{(3.3 \times 10^{-2} - x)}; +x \text{ and } -x \text{ are negligible}$$

$$[\text{H}_3\text{O}^+] = x = 2.1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{and pH} = -\log(2.1 \times 10^{-5}) = 4.68$$

(c)

$$0.0300 \text{ L} \left(\frac{0.20 \text{ mol C}_6\text{H}_5\text{COOH}}{\text{L}} \right) \left(\frac{1 \text{ mol KOH}}{1 \text{ mol C}_6\text{H}_5\text{COOH}} \right) \\ \times \left(\frac{\text{L}}{0.30 \text{ mol KOH}} \right)$$

$$= 0.020 \text{ L or 20 mL}$$

20 mL to the stoichiometric point, so halfway to the stoichiometric point uses 10 mL.

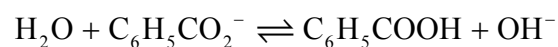
(d) At half-stoichiometric point, $\text{pH} = \text{p}K_{\text{a}}$

$$\text{and pH} = -\log(6.5 \times 10^{-5}) = 4.19$$

(e) 20 mL, as calculated in part (c).

(f) Concentration of $\text{KC}_6\text{H}_5\text{O}_2$ at the stoichiometric point is

$$\frac{6.0 \times 10^{-3} \text{ mol}}{0.050 \text{ L}} = 0.12 \text{ mol} \cdot \text{L}^{-1}$$



$$K_{\text{b}} = \frac{K_{\text{w}}}{K_{\text{a}}} = \frac{1.00 \times 10^{-14}}{6.5 \times 10^{-5}} = 1.5 \times 10^{-10}$$

Concentration

(mol · L ⁻¹)	H ₂ O +	C ₆ H ₅ CO ₂ ⁻	⇌	C ₆ H ₅ COOH	+	OH ⁻
initial	—	0.10		0		0
change	—	-x		+x		+x
equilibrium	—	0.10 - x		x		x

$$K_{\text{b}} = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{CO}_2^-]} = 1.5 \times 10^{-10} = \frac{(x)(x)}{0.12 - x} \approx \frac{x^2}{0.12}$$

$$[\text{OH}^-] = x = 4.2 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

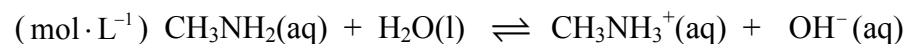
$$\text{pOH} = 5.38; \text{pH} = 14.00 - 5.38 = 8.62$$

11.34 (a) Initial pH of 0.25 M CH_3NH_2



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

Concentration



initial	0.25	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.25 - x$	—	x	x

$$3.6 \times 10^{-4} = \frac{x^2}{0.25 - x} \approx \frac{x^2}{0.25}$$

$$[\text{OH}^-] = x = 9.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = -\log(9.5 \times 10^{-3}) = 2.02$$

$$\therefore \text{pH} = 14.00 - 2.02 = 11.98$$

$$\begin{aligned} \text{(b) initial moles of } \text{CH}_3\text{NH}_2 &= (0.0500 \text{ L})(0.25 \text{ mol} \cdot \text{L}^{-1}) \\ &= 1.3 \times 10^{-2} \text{ mol } \text{CH}_3\text{NH}_2 \end{aligned}$$

$$\text{moles of HCl} = (0.0150 \text{ L})(0.35 \text{ mol} \cdot \text{L}^{-1}) = 5.3 \times 10^{-3} \text{ mol HCl}$$

After neutralization:

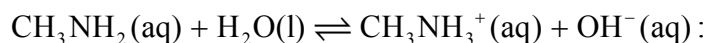
$$\text{molarity of } \text{CH}_3\text{NH}_2 = \frac{1.3 \times 10^{-2} \text{ mol} - 5.3 \times 10^{-3} \text{ mol}}{0.0650 \text{ L}}$$

$$= 0.1 \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3\text{NH}_2$$

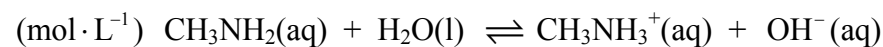
$$\text{molarity of } \text{CH}_3\text{NH}_3^+ = \frac{5.3 \times 10^{-3} \text{ mol } \text{CH}_3\text{NH}_3^+}{0.0650 \text{ L}}$$

$$= 8.2 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3\text{NH}_3^+$$

Then, consider the equilibrium



Concentration



initial	0.1	—	8.2×10^{-2}	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.1 - x$	—	$8.2 \times 10^{-2} + x$	x

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = 3.6 \times 10^{-4} = \frac{(x)(x + 8.2 \times 10^{-2})}{(0.1 - x)};$$

$+x$ and $-x$ are negligible

$$[\text{OH}^-] = x = 4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ and } \text{pOH} = 3.4$$

$$\therefore \text{pH} = 14.00 - 3.4 = 10.6$$

(c) At the stoichiometric point, the volume of acid needed, V_A , is

$$\begin{aligned} V_A &= (0.050 \text{ L base}) \left(\frac{0.25 \text{ mol base}}{1 \text{ L base}} \right) \left(\frac{1 \text{ mol acid}}{1 \text{ mol base}} \right) \left(\frac{1 \text{ L acid}}{0.35 \text{ mol acid}} \right) \\ &= 36 \times 10^{-3} \text{ L HCl} = 36 \text{ mL} \end{aligned}$$

Therefore, the half-stoichiometric point $= \frac{1}{2}(36 \text{ mL}) = 18 \text{ mL}$

(d) At the half-stoichiometric point, $\text{pOH} = \text{p}K_b$

$$\text{and } \text{pOH} = -\log(3.6 \times 10^{-4}) = 3.44$$

$$\text{pH} = 14.00 - 3.44 = 10.56$$

(e) 36 mL HCl; see part (c)

$$(f) V_{\text{total}} = V_A + V_B = 36 + 50.0 = 86 \text{ mL}$$

The solution contains

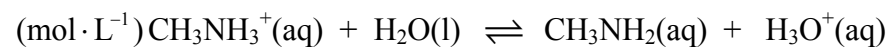
$$(0.050 \text{ L}) \left(\frac{0.25 \text{ mol base}}{1 \text{ L base}} \right) \left(\frac{1}{86 \times 10^{-3} \text{ L}} \right)$$

$$= 0.15 \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3\text{NH}_3^+ \text{ as } \text{CH}_3\text{NH}_3\text{Cl}$$



$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{3.6 \times 10^{-4}} = 2.8 \times 10^{-11}$$

Concentration



initial	0.15	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.15 - x$	—	x	x

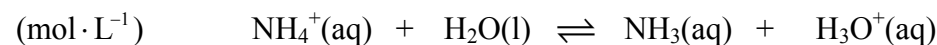
$$2.8 \times 10^{-11} = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$[\text{H}_3\text{O}^+] = x = 2.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(2.0 \times 10^{-6}) = 5.69$$

- 11.36** At the stoichiometric point, the volume of solution will have doubled; therefore, the concentration of NH_4^+ will be 0.10 M. The equilibrium is

Concentration



initial	0.10	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.10 - x$	—	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} = 5.6 \times 10^{-10}$$

$$x = 7.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(7.5 \times 10^{-6}) = 5.12$$

From Table 11.2, we see that this pH value lies within the range for (a) bromocresol green (3.8 to 5.4), and (b) methyl red (4.8 to 6.0). Phenol red (pH range: 6.6 to 8.0) and thymol blue (ranges of 1.2 to 2.8 for red-yellow change and 8.0 to 9.6 for yellow-blue change) are unsuitable.

- 11.38** Exercise 11.32; thymol blue; Exercise 11.34: methyl red.

11.40 (a) To reach the first stoichiometric point, we must add enough solution to neutralize one H^+ on the H_2SO_3 . To do this, we will require

$0.125 \text{ L} \times 0.197 \text{ mol} \cdot \text{L}^{-1} = 0.0246 \text{ mol}$ of OH^- . The volume of base required will be given by the number of moles of base required, divided by the concentration of base solution:

$$\frac{0.125 \text{ L} \times 0.197 \text{ mol} \cdot \text{L}^{-1}}{0.123 \text{ mol} \cdot \text{L}^{-1}} = 0.200 \text{ L or } 2.00 \times 10^2 \text{ mL.}$$

(b) To reach the second stoichiometric point will require double the amount calculated in (a), or $4.00 \times 10^2 \text{ mL}$.

11.42 (a) The exercise begins with the fully deprotonated base PO_4^{3-} and is essentially the opposite situation from beginning with the polyprotic acid H_3PO_4 . It will require an equal number of moles of HCl to react with PO_4^{3-} in order to reach the first equivalence point. The value will be

given by
$$\frac{0.0888 \text{ L} \times 0.233 \text{ mol} \cdot \text{L}^{-1}}{0.0848 \text{ mol} \cdot \text{L}^{-1}} = 0.244 \text{ L or } 244 \text{ mL.}$$

(b) To reach the second equivalence point would require double the amount of solution calculated in (a), or 488 mL.

(c) To reach, the third equivalence point would require triple the amount of solution calculated in (a), or 732 mL.

11.44 (a) This value is calculated as described in section 10.12. First we calculate the molarity of the starting oxalic acid solution:

$$\frac{0.242 \text{ g}}{90.03 \text{ g} \cdot \text{mol}^{-1}} \bigg/ 0.0500 \text{ L} = 0.0538 \text{ mol} \cdot \text{L}^{-1}. \text{ We then use the first acid}$$

dissociation of oxalic acid as the dominant equilibrium. The K_{a1} is 5.9×10^{-2} . Let H_2Ox represent the fully protonated oxalic acid:

Concentration

(mol · L ⁻¹)	H ₂ Ox (aq)	+ H ₂ O(l)	⇌	HOx ⁻ (aq)	+ H ₃ O ⁺ (aq)
initial	0.0538	—		0	0
change	-x	—		+x	+x
final	0.0538 - x	—		+x	+x

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HOx}^-]}{[\text{H}_2\text{Ox}]} = 5.9 \times 10^{-2}$$

$$5.9 \times 10^{-2} = \frac{x \cdot x}{0.0538 - x} = \frac{x^2}{0.0538 - x}$$

Because the equilibrium constant is reasonably large, the full quadratic solution should be undertaken. The equation is

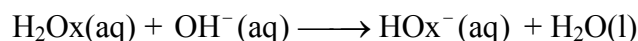
$$x^2 = (5.9 \times 10^{-2})(0.0538 - x) \text{ or}$$

$$x^2 + 5.9 \times 10^{-2}x - 3.17 \times 10^{-3} = 0$$

Using the quadratic formula, we obtain $x = 0.034$.

$$\text{pH} = 1.47$$

(b) First, carry out the reaction between oxalic acid and the strong base to completion:



$$\text{moles of H}_2\text{Ox} = (0.0538 \text{ mol} \cdot \text{L}^{-1})(0.0500 \text{ L}) = 2.69 \times 10^{-3} \text{ mol}$$

$$\text{moles of OH}^- = (0.0150 \text{ L})(0.150 \text{ mol} \cdot \text{L}^{-1}) = 2.25 \times 10^{-3} \text{ mol}$$

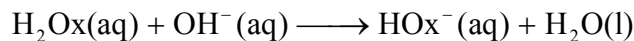
This amount of base will partially neutralize one H⁺ present in H₂Ox. At this point, 0.440×10^{-3} mol of H₂O_x and 2.25×10^{-3} mol of HO_x⁻ are present in solution, so

$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{HO}_x^-]}{[\text{H}_2\text{O}_x]} = 1.23 + \log \frac{2.25}{0.44}$$

$$= 1.94$$

(c) The total amount of OH⁻ added will be 15.0 mL + 5.00 mL = 20.00 mL. The moles of OH⁻ = (0.0200 L)(0.150 mol · L⁻¹) = 3.00×10^{-3} mol.

Because there are 2.69×10^{-3} moles of H₂Ox, the first deprotonation will be complete:

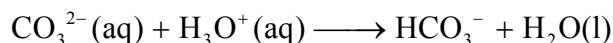


The excess base will be $(3.00 \times 10^{-3} \text{ mol}) - (2.69 \times 10^{-3} \text{ mol}) = 0.31 \times 10^{-3} \text{ mol}$ and the amount of HOx^- will be $2.69 \times 10^{-3} \text{ mol}$. This base can then react with HOx^- to form Ox^{2-} . Because the stoichiometry is 1 : 1, the amount of HOx^- that reacts is $7.5 \times 10^{-4} \text{ mol}$, giving that number of moles of Ox^{2-} and leaving $3.1 \times 10^{-4} \text{ mol}$ of HOx^- .

The pH is then:

$$\begin{aligned} \text{pH} &= \text{p}K_{a2} + \log \frac{[\text{O}_x^{2-}]}{[\text{HO}_x^-]} = 4.19 + \log \frac{0.31}{2.38} \\ &= 3.30 \end{aligned}$$

- 11.46** (a) The reaction of the base Na_2CO_3 with the strong acid will be taken to completion first.



$$\text{moles of } \text{CO}_3^{2-} = 0.0750 \text{ L} \times 0.0995 \text{ mol} \cdot \text{L}^{-1} = 7.46 \times 10^{-3} \text{ mol}$$

$$\text{moles of } \text{H}_3\text{O}^+ = 0.0250 \text{ L} \times 0.130 \text{ mol} \cdot \text{L}^{-1} = 3.25 \times 10^{-3} \text{ mol}$$

There is excess carbonate ion, so all of the strong acid will be consumed, generating a starting solution with residual CO_3^{2-} and product HCO_3^- (bicarbonate ion). Because the reaction stoichiometry is 1 : 1,

$3.25 \times 10^{-3} \text{ mol}$ of HCO_3^- will be formed; this will leave

$(7.46 \times 10^{-3} \text{ mol}) - (3.25 \times 10^{-3} \text{ mol}) = 4.21 \times 10^{-3} \text{ mol } \text{CO}_3^{2-}$. This places the concentrations of the species in the second buffer region of carbonic acid. The concentrations will be

$$[\text{HCO}_3^-] = \frac{3.25 \times 10^{-3} \text{ mol}}{0.100 \text{ L}} = 0.0325 \text{ mol} \cdot \text{L}^{-1};$$

$$[\text{CO}_3^{2-}] = \frac{4.21 \times 10^{-3} \text{ mol}}{0.100 \text{ L}} = 0.0421 \text{ mol} \cdot \text{L}^{-1}.$$

The equilibrium of interest is

Concentration

(mol · L ⁻¹)	CO ₃ ²⁻ (aq)	+ H ₂ O(l)	⇌	HCO ₃ ⁻ (aq)	+ OH ⁻ (aq)
initial	0.0421	—		0.0325	0
change	-x	—		+x	+x
final	0.0421 - x			0.0325 + x	+x

The K_{b1} for CO₃²⁻ is given by $\frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.8 \times 10^{-4}$, where K_{a2}

is the second acid dissociation constant of H₂CO₃.

The solution is set up as follows.

$$K_{b1} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

$$1.8 \times 10^{-4} = \frac{(0.0325 + x)x}{0.0421 - x}$$

If $x \ll 0.0325$, then the problem simplifies to

$$1.8 \times 10^{-4} = \frac{0.0325x}{0.0421}$$

$$x = 2.3 \times 10^{-4}$$

Because x is less than 5% of 0.0325, the assumption was valid.

$$x = [\text{OH}^-], \text{ so } -\log x = \text{pOH} = 3.64$$

$$\text{pH} = 14.00 - 3.64 = 10.36$$

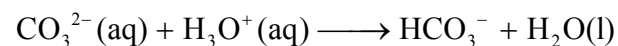
(b) The reaction proceeds as in (a) but now there is more strong acid:

$$\text{moles of H}_3\text{O}^+ = 0.0550 \text{ L} \times 0.130 \text{ mol} \cdot \text{L}^{-1} = 7.15 \times 10^{-3} \text{ mol}$$

The moles of CO₃²⁻ initially is the same as in (a) at 7.46×10^{-3} mol.

There is not enough strong acid present to convert all of the CO₃²⁻ to

HCO₃⁻ so some CO₃²⁻ will remain. The setup is the same as in (a):



$$\text{moles of CO}_3^{2-} = 0.0300 \text{ L} \times 0.175 \text{ mol} \cdot \text{L}^{-1} = 7.46 \times 10^{-3} \text{ mol}$$

$$\text{moles of H}_3\text{O}^+ = 0.0550 \text{ L} \times 0.130 \text{ mol} \cdot \text{L}^{-1} = 7.15 \times 10^{-3} \text{ mol}$$

There is excess carbonate ion, so all of the strong acid will be consumed, generating a starting solution with residual CO_3^{2-} and product HCO_3^- (bicarbonate ion). Because the reaction stoichiometry is 1 : 1, 7.15×10^{-3} mol of HCO_3^- will be formed; this will leave $(7.46 \times 10^{-3} \text{ mol}) - (7.15 \times 10^{-3} \text{ mol}) = 3.1 \times 10^{-4} \text{ mol } \text{CO}_3^{2-}$. This places the concentrations of the species in the second buffer region of carbonic acid. The concentrations will be

$$[\text{CO}_3^{2-}] = \frac{3.1 \times 10^{-4} \text{ mol}}{0.140 \text{ L}} = 2.2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}; [\text{HCO}_3^-] = \frac{7.15 \times 10^{-3} \text{ mol}}{0.140 \text{ L}} = 0.0510 \text{ mol} \cdot \text{L}^{-1}$$

The equilibrium of interest is

Concentration

	$(\text{mol} \cdot \text{L}^{-1})$	$\text{CO}_3^{2-}(\text{aq})$	$+$	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{HCO}_3^-(\text{aq})$	$+$	$\text{OH}^-(\text{aq})$
initial		2.2×10^{-3}		—		0.0510		0
change		$-x$		—		$+x$		$+x$
final		$2.2 \times 10^{-3} - x$				$0.0510 + x$		$+x$

The K_{b1} for CO_3^{2-} is given by $\frac{K_{\text{w}}}{K_{\text{a2}}} = \frac{1.00 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.8 \times 10^{-4}$, where K_{a2}

is the second acid dissociation constant of H_2CO_3 .

The solution is set up as follows:

$$K_{\text{b1}} = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

$$1.8 \times 10^{-4} = \frac{(0.0510 + x)(x)}{(2.2 \times 10^{-3} - x)}$$

If $x \ll 2.2 \times 10^{-3}$, then the problem simplifies to

$$1.8 \times 10^{-4} = \frac{0.0510x}{2.2 \times 10^{-3}}$$

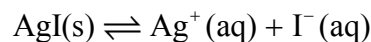
$$x = 7.8 \times 10^{-6}$$

Because x is less than 5% of 2.2×10^{-3} , the assumption was valid.

$$x = [\text{OH}^-], \text{ so } -\log x = \text{pOH} = 5.10$$

$$\text{pH} = 14.00 - 5.10 = 8.90$$

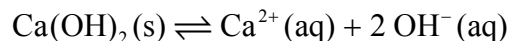
11.48 (a) The solubility equilibrium is



$$[\text{Ag}^+] = [\text{I}^-] = 9.1 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1} = S \text{ (molar solubility)}$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-] = (9.1 \times 10^{-9})^2 = 8.3 \times 10^{-17}$$

(b) The solubility equilibrium is



$$[\text{Ca}^{2+}] = 0.011 \text{ mol} \cdot \text{L}^{-1} = S$$

$$[\text{OH}^-] = 0.022 \text{ mol} \cdot \text{L}^{-1} = 2S$$

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = (0.011)(0.022)^2 = 5.3 \times 10^{-6}$$

(c) The solubility equilibrium is

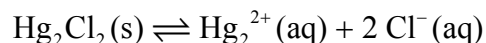


$$[\text{Ag}^+] = 8.1 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} = 3S$$

$$[\text{PO}_4^{3-}] = 2.7 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} = S$$

$$K_{\text{sp}} = [\text{Ag}^+]^3[\text{PO}_4^{3-}] = (8.1 \times 10^{-6})^3(2.7 \times 10^{-6}) = 1.4 \times 10^{-21}$$

(d) The solubility equilibrium is



$$[\text{Hg}_2^{2+}] = 5.2 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} = S$$

$$[\text{Cl}^-] = 1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} = 2S$$

$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (5.2 \times 10^{-7})(1.0 \times 10^{-6})^2 = 5.2 \times 10^{-19}$$

11.50 (a) S = molar solubility; $\text{PbSO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$

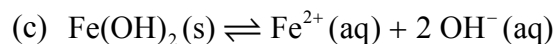
$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = S \times S = S^2 = 1.6 \times 10^{-8}$$

$$S = 1.3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

(b) $\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons 2 \text{Ag}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = (2S)^2 \times S = 4S^3 = 6.2 \times 10^{-12}$$

$$S = 1.2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

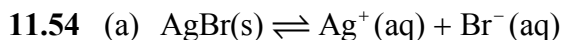


$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^{-}]^2 = S \times (2S)^2 = 4S^3 = 1.6 \times 10^{-14}$$

$$S = 1.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

11.52 S = molar solubility The reaction is $\text{Ce}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Ce}^{3+}(\text{aq}) + 3 \text{OH}^{-}(\text{aq})$

$$K_{\text{sp}} = [\text{Ce}^{3+}][\text{OH}^{-}]^3 = S \times (3S)^3 = 27S^4 = 27(5.2 \times 10^{-6})^4 = 2.0 \times 10^{-20}$$



$S = \text{mol} \cdot \text{L}^{-1}$ of AgBr that dissolve = $[\text{Ag}^{+}]$

Concentration

(mol · L ⁻¹)	AgBr(s)	\rightleftharpoons Ag ⁺ (aq) +	Br ⁻ (aq)
initial	—	0	0.050
change	—	+ S	+ S
equilibrium	—	S	0.050 + S

$$0.050 + S = [\text{Br}^{-}]$$

$$K_{\text{sp}} = [\text{Ag}^{+}][\text{Br}^{-}]$$

$$7.7 \times 10^{-13} = (S) \times (0.050 + S) = (S) \times (0.050)$$

$$S = 1.5 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1} = [\text{Ag}^{+}] = \text{molar solubility of AgBr in } 0.050 \text{ M}$$

NaBr



Concentration

(mol · L ⁻¹)	MgCO ₃ (s)	\rightleftharpoons Mg ²⁺ (aq) +	CO ₃ ²⁻ (aq)
initial	—	0	1.0×10^{-3}
change	—	+ S	+ S
equilibrium	—	S	$1.0 \times 10^{-3} + S$

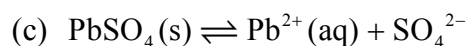
$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{CO}_3^{2-}] = (S) \times (1.0 \times 10^{-3} + S) = 1.0 \times 10^{-5}$$

$$S^2 + 1.0 \times 10^{-3} S - 1.0 \times 10^{-5} = 0$$

$$S = 2.7 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} = [\text{Mg}^{2+}]$$

= molar solubility of MgCO_3 in 1.0×10^{-3}

M Na_2CO_3



Concentration

(mol · L ⁻¹)	$\text{PbSO}_4(s)$	\rightleftharpoons	$\text{Pb}^{2+}(aq)$	$+$	$\text{SO}_4^{2-}(aq)$
initial	—		0		0.25
change	—		+S		+S
equilibrium	—		S		0.25 + S
$K_{\text{sp}} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = S \times (0.25 + S) = 1.6 \times 10^{-8}$					

(assume S in (0.25 + S) is negligible)

$$0.25S = 1.6 \times 10^{-8}$$

$S = 6.4 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$ = molar solubility of PbSO_4 in 0.25 M Na_2SO_4

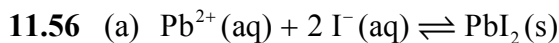


Concentration

(mol · L ⁻¹)	$\text{Ni(OH)}_2(s)$	\rightleftharpoons	$\text{Ni}^{2+}(aq)$	$+$	$\text{OH}^-(aq)$
initial	—		0.125		0
change	—		+S		+2S
equilibrium	—		0.125 + S		2S
$K_{\text{sp}} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 6.5 \times 10^{-18} = (S + 0.125) \times (2S)^2$					

(assume S in (S + 0.125) is negligible)

$S = 3.6 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$ = molar solubility of Ni(OH)_2 in 0.125 M NiSO_4



Concentration ($\text{mol} \cdot \text{L}^{-1}$)	Pb^{2+}	I^{-}
initial	0.0020	0
change	0	+x
equilibrium	0.0020	x [Pb(NO ₃) ₂ is soluble]

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = 1.4 \times 10^{-8} = (0.0020)(x)^2$$

$$\text{molarity of } \text{I}^{-} = x = \sqrt{\frac{1.4 \times 10^{-8}}{0.002}} = 2.6 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

(b) mass of KI =

$$\left(\frac{2.6 \times 10^{-3} \text{ mol KI}}{1 \text{ L}} \right) (0.0250 \text{ L}) \left(\frac{166.00 \text{ g KI}}{1 \text{ mol KI}} \right) = 1.1 \times 10^{-2} \text{ g KI}$$



$$K_{\text{sp}} = [\text{Ag}^{+}]^2[\text{CO}_3^{2-}] = 6.2 \times 10^{-12}$$

$$\begin{aligned} Q_{\text{sp}} &= \left[\frac{(1.00)(0.010)}{1.01} \right]^2 \left[\frac{(0.0050)(0.10)}{1.01} \right] \\ &= 4.9 \times 10^{-8} \end{aligned}$$

A precipitate will form because $Q_{\text{sp}} > K_{\text{sp}}$.



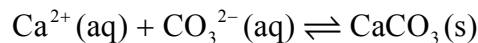
$$K_{\text{sp}} = [\text{Ag}^{+}][\text{Cl}^{-}] = 1.6 \times 10^{-10}$$

$$\begin{aligned} Q_{\text{sp}} &= \left[\frac{(0.0033)(1.0)}{0.050} \right] \left[\frac{(0.0049)(0.0030)}{0.050} \right] \\ &= 1.9 \times 10^{-5} \end{aligned}$$

A precipitate will form because $Q_{\text{sp}} > K_{\text{sp}}$.

11.60 (a) $\frac{1 \text{ mL}}{20 \text{ drops}} \times 7 \text{ drops} = 0.35 \text{ mL} = 3.5 \times 10^{-4} \text{ L}$

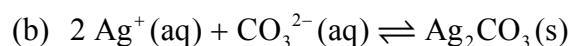
$$\begin{aligned} (3.5 \times 10^{-4} \text{ L})(0.0029 \text{ mol} \cdot \text{L}^{-1}) &= 1.0 \times 10^{-6} \text{ mol K}_2\text{CO}_3 \\ &= 1.0 \times 10^{-6} \text{ mol CO}_3^{2-} \end{aligned}$$



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

$$Q_{\text{sp}} = \left[\frac{(0.0250)(0.0018)}{0.0254} \right] \left[\frac{1.0 \times 10^{-6}}{0.0254} \right] = 7.0 \times 10^{-8}$$

will precipitate because $Q_{\text{sp}} (7.0 \times 10^{-8}) > K_{\text{sp}} (8.7 \times 10^{-9})$



$$\frac{1 \text{ mL}}{20 \text{ drops}} \times 10 \text{ drops} = 0.5 \text{ mL} = 5 \times 10^{-4} \text{ L}$$

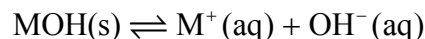
$$(5 \times 10^{-4} \text{ L})(0.010 \text{ mol} \cdot \text{L}^{-1}) = 5 \times 10^{-6} \text{ mol Na}_2\text{CO}_3 = 5 \times 10^{-6} \text{ mol CO}_3^{2-}$$

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

$$Q_{\text{sp}} = \left[\frac{(0.0100)(0.0040)}{0.0105} \right]^2 \left[\frac{5 \times 10^{-6}}{0.0105} \right] = 7 \times 10^{-9}$$

will precipitate because $Q_{\text{sp}} (7 \times 10^{-9}) > K_{\text{sp}} (6.2 \times 10^{-12})$

11.62 For MOH:



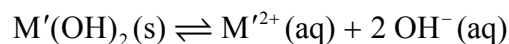
$$K_{\text{sp}} = [\text{M}^+][\text{OH}^-]$$

$$1.0 \times 10^{-12} = (1.0 \times 10^{-3})[\text{OH}^-]$$

$$[\text{OH}^-] = 1.0 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pOH} = 9, \text{pH} = 5$$

For $\text{M}'(\text{OH})_2$:



$$K_{\text{sp}} = [\text{M}'^{2+}][\text{OH}^-]^2$$

$$1.0 \times 10^{-12} = (1.0 \times 10^{-3})[\text{OH}^-]^2$$

$$[\text{OH}^-] = \sqrt{\frac{1.0 \times 10^{-12}}{1.0 \times 10^{-3}}} = 3.2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

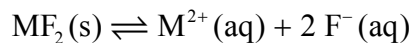
$$\text{pOH} = 4.5, \text{pH} = 9.5$$

MOH precipitates first at pH = 5, whereas $M'(OH)_2$ does not precipitate until pH = 9.5.

11.64 The K_{sp} values are

CaF ₂	4.0×10^{-11}
BaF ₂	1.7×10^{-6}
CaCO ₃	8.7×10^{-9}
BaCO ₃	8.1×10^{-9}

The difference in these numbers suggests that there is a greater solubility difference between the fluorides, and therefore this anion should give a better separation. Because different numbers of ions are involved, it is instructive to convert the K_{sp} values into molar solubility. For the fluorides the reaction is

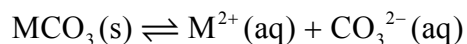


Change $+x$ $+2x$

$$K_{sp} = x(2x)^2$$

Solving for x for CaF₂ gives 0.000 22 M and 0.0075 M for BaF₂.

For the carbonates:

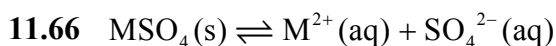


$+x$ $+x$

$$K_{sp} = x^2$$

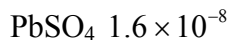
Solving this for CaCO₃ gives 9.3×10^{-5} M and 9.0×10^{-5} M for BaCO₃.

Clearly, of the K_{sp} values given, the solubility difference is greatest between the two fluorides, and F^{-} is the better choice of anion. The solubilities of the two carbonates are almost identical, so this would not be a good choice.



$$K_{sp} = [M^{2+}][SO_4^{2-}]$$

The K_{sp} values are BaSO₄ 1.1×10^{-10}



(a) For BaSO_4 , the maximum concentration of sulfate that allows all the Ba^{2+} to remain in solution is given by

$$1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (0.010)[\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = 1.1 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$

Similarly, for PbSO_4 :

$$1.6 \times 10^{-8} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (0.010)[\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = 1.6 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

(b) The BaSO_4 is less soluble and will be essentially all precipitated when the PbSO_4 begins to precipitate. The concentration of SO_4^{2-} required for the Pb^{2+} to precipitate will be $1.6 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. We can calculate the concentration of Ba^{2+} at this concentration of sulfate ion:

$$1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = [\text{Ba}^{2+}][1.6 \times 10^{-6}]$$

$$[\text{Ba}^{2+}] = 6.9 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$



$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^{-}]^3 = 2.0 \times 10^{-39}$$

S = molar solubility

(a) $\text{pH} = 11.0$; $\text{pOH} = 3.0$; $[\text{OH}^{-}] = 1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$

$$[\text{Fe}^{3+}](1.0 \times 10^{-3})^3 = 2.0 \times 10^{-39}$$

$$S = \frac{2.0 \times 10^{-39}}{1.0 \times 10^{-9}} = 2.0 \times 10^{-30} \text{ mol} \cdot \text{L}^{-1} = [\text{Fe}^{3+}]$$

= molar solubility of $\text{Fe}(\text{OH})_3$ at $\text{pH} = 11.0$

(b) $\text{pH} = 3.0$; $\text{pOH} = 11.0$; $[\text{OH}^{-}] = 1.0 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1}$

$$[\text{Fe}^{3+}](1.0 \times 10^{-11})^3 = 2.0 \times 10^{-39}$$

$$S = \frac{2.0 \times 10^{-39}}{1.0 \times 10^{-33}} = 2.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1} = [\text{Fe}^{3+}]$$

= molar solubility of $\text{Fe}(\text{OH})_3$ at $\text{pH} = 3.0$



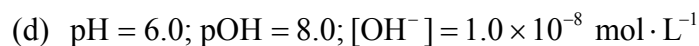
$$K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^{-}]^2 = 1.6 \times 10^{-14}$$

$$\text{pH} = 8.0; \text{pOH} = 6.0; [\text{OH}^{-}] = 1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{Fe}^{2+}](1.0 \times 10^{-6})^2 = 1.6 \times 10^{-14}$$

$$S = \frac{1.6 \times 10^{-14}}{1.0 \times 10^{-12}} = 1.6 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} = [\text{Fe}^{2+}]$$

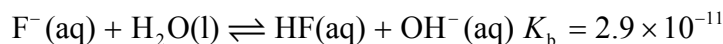
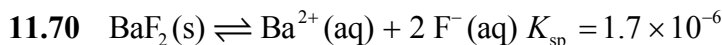
= molar solubility of $\text{Fe}(\text{OH})_2$ at $\text{pH} = 8.0$



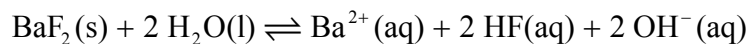
$$[\text{Fe}^{2+}](1.0 \times 10^{-8})^2 = 1.6 \times 10^{-14}$$

$$S = \frac{1.60 \times 10^{-14}}{1.0 \times 10^{-16}} = 1.6 \times 10^2 \text{ mol} \cdot \text{L}^{-1} = [\text{Fe}^{2+}]$$

= molar solubility of $\text{Fe}(\text{OH})_2$ at $\text{pH} = 6.0$



(a) Multiply the second equilibrium equation by 2 and add to the first equilibrium equation:



$$K = K_{\text{sp}} K_{\text{b}}^2 = (1.7 \times 10^{-6}) \times (2.9 \times 10^{-11})^2 = 1.4 \times 10^{-27}$$

$$(b) \quad S = \text{molar solubility} \quad K = [\text{Ba}^{2+}][\text{HF}]^2[\text{OH}^{-}]^2$$

$$1.4 \times 10^{-27} = (S)(2S)^2(1.0 \times 10^{-7})^2 \quad (\text{at } \text{pH} = 7.0, [\text{OH}^{-}] = 1 \times 10^{-7} \text{ M})$$

$$1.4 \times 10^{-13} = 4S^3$$

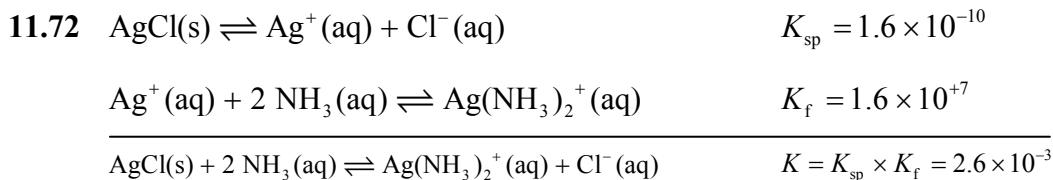
$$S = [\text{Ba}^{2+}] = 3.3 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} = \text{molar solubility of } \text{BaF}_2 \text{ at } \text{pH} = 7.0$$

$$(c) \quad K = [\text{Ba}^{2+}][\text{HF}]^2[\text{OH}^{-}]^2$$

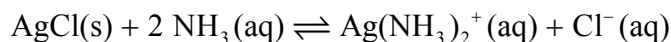
$$1.4 \times 10^{-27} = (S)(2S)^2(1.0 \times 10^{-10})^2 \quad (\text{at } \text{pH} = 4.0)$$

$$1.4 \times 10^{-7} = 4S^3$$

$$S = [\text{Ba}^{2+}] = 3.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} = \text{molar solubility of } \text{BaF}_2 \text{ at } \text{pH} = 4.0$$



$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$



$$\text{Equilibrium concentration} \quad \text{---} \quad 1.0 - 2S \quad \quad S \quad \quad S$$

$$K = \frac{S^2}{(1.0 - 2S)^2} = 2.6 \times 10^{-3}$$

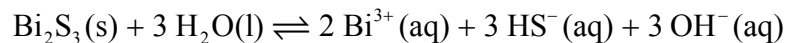
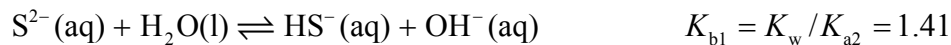
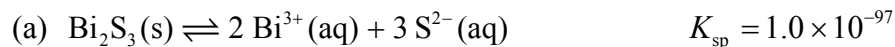
$$\frac{S}{1.0 - 2S} = \sqrt{2.6 \times 10^{-3}} = 5.1 \times 10^{-2}$$

$$S = 5.1 \times 10^{-2} - 0.10 S$$

$$1.10 S = 5.1 \times 10^{-2}$$

$$S = 4.6 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

11.74 The calculation for the solubility of the sulfides can be seen to be pH dependent, due to the equilibrium between S^{2-} and HS^- in aqueous solution. The solubilities of metal sulfides can be calculated as a function of pH quantitatively, as shown below.



$$K = K_{\text{sp}} \cdot K_{\text{b1}}^3 = 2.8 \times 10^{-97}$$

$$\text{At } [\text{H}_3\text{O}^+] = 1.00 \text{ mol} \cdot \text{L}^{-1}, [\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{Bi}^{3+}]^2 [\text{HS}^-]^3 [\text{OH}^-]^3 = 2.8 \times 10^{-97}$$

$$[\text{Bi}^{3+}]^2 [\text{HS}^-]^3 [1.00 \times 10^{-14}]^3 = 2.8 \times 10^{-97}$$

$$[\text{Bi}^{3+}]^2 [\text{HS}^-]^3 = 2.8 \times 10^{-55}$$

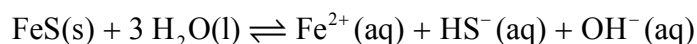
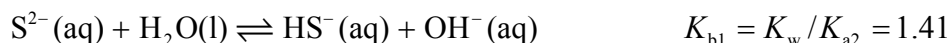
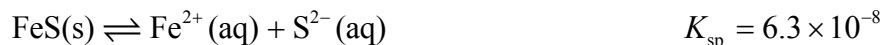
If we let x be the number of moles of Bi_2S_3 that dissolve in one L, the concentration of Bi^{3+} will be $2x$ and of HS^- will be $3x$:

$$(2x)^2 (3x)^3 = 2.8 \times 10^{-55}$$

$$x = 4.8 \times 10^{-12} \text{ mol} \cdot \text{L}^{-1}$$

Bi_2S_3 is insoluble in 1.00 M HNO_3 .

(b) A similar procedure is used for FeS :



$$K = K_{\text{sp}} \cdot K_{\text{bl}} = 8.9 \times 10^{-8}$$

At $[\text{H}_3\text{O}^+] = 1.00 \text{ mol} \cdot \text{L}^{-1}$, $[\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol} \cdot \text{L}^{-1}$

$$[\text{Fe}^{2+}][\text{HS}^-][\text{OH}^-] = 8.9 \times 10^{-8}$$

$$[\text{Fe}^{2+}][\text{HS}^-][1.00 \times 10^{-14}]^3 = 8.9 \times 10^{-8}$$

$$[\text{Fe}^{2+}][\text{HS}^-] = 8.9 \times 10^6$$

If we let x be the number of moles of FeS that dissolve in one L, the concentration of Fe^{2+} will be x and of HS^- will also be x :

$$x^2 = 8.9 \times 10^6$$

$$x = 3.0 \times 10^3 \text{ mol} \cdot \text{L}^{-1}$$

FeS is soluble in 1.00 M HNO_3 .

11.76 Both ZnCl_2 and MgCl_2 are soluble, giving M^{2+} cations and Cl^- ions in solution. If OH^- is added, both will precipitate M(OH)_2 . However, if you continue to add OH^- , the formation of the complex ion Zn(OH)_4^{2-} will occur; thus Zn(OH)_2 will redissolve but the Mg(OH)_2 will remain insoluble.

- 11.78** (a) 1.00 L of solution will have a mass of 8.9×10^2 g and will contain 2.7×10^2 g NH_3 ($17.03 \text{ g} \cdot \text{mol}^{-1}$) or 15.8 moles. The concentration will be approximately 15.8 M. (b) The K_b value for NH_3 is 1.8×10^{-5} . We can set up the typical relationship:

Concentration

(mol · L ⁻¹)	$\text{NH}_3(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{NH}_4^+(\text{aq})$	+	$\text{OH}^-(\text{aq})$
initial	15.8		—		0		0
change	$-x$		—		$+x$		$+x$
equilibrium	$15.8 - x$		—		$+x$		$+x$

$$\frac{x^2}{15.8 - x} = 1.8 \times 10^{-5}$$

assume x is small compared to 15.8

$$x^2 = (1.8 \times 10^{-5})(15.8) = 2.8 \times 10^{-4}$$

$$x = 1.7 \times 10^{-2}$$

The assumption was good. $[\text{NH}_3] \cong 15.8 \text{ M}$; $[\text{NH}_4\text{OH}] = 1.7 \times 10^{-2} \text{ M}$

(c) 1.00 g AgNO_3 ($169.88 \text{ g} \cdot \text{mol}^{-1}$) = $5.89 \times 10^{-3} \text{ mol AgNO}_3$

$$[\text{AgNO}_3] = 5.89 \times 10^{-3} \text{ M}$$

The K_{sp} of AgOH is 1.5×10^{-8} .

To precipitate the 5.89×10^{-3} moles of Ag^+ present, we will need to have at least $5.89 \times 10^{-3} \text{ mol}$ of OH^- . However, from the K_{sp} value of

1.5×10^{-8} , we can calculate that the molar solubility of AgOH will be

$$1.2 \times 10^{-4} \text{ M} \left(\sqrt{1.5 \times 10^{-8}} \right), \text{ which is about 2.0\% of the amount of Ag}$$

present. In order to precipitate the Ag^+ so that less than 1% of the Ag^+ is present in solution, we will need to have a slightly higher concentration of OH^- .



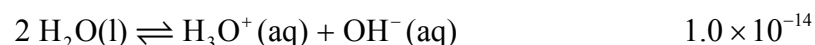
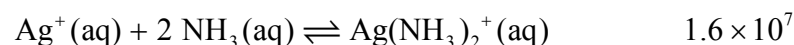
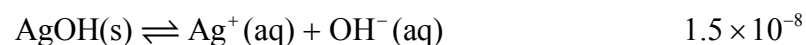
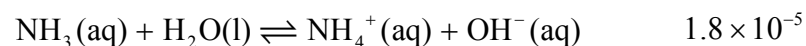
$$1.5 \times 10^{-8} = [\text{Ag}^+][\text{OH}^-] = [5.89 \times 10^{-5}][\text{OH}^-]$$

$$[\text{OH}^-] = 2.5 \times 10^{-4} \text{ M}$$

We need $5.89 \times 10^{-3} \text{ mol} + 2.5 \times 10^{-4} \text{ mol} = 6.14 \times 10^{-3} \text{ mol}$ to ensure that at equilibrium at least 99% of the Ag^+ has precipitated.

$$(6.14 \times 10^{-3} \text{ mol})(40.00 \text{ g} \cdot \text{mol}^{-1}) = 0.246 \text{ g NaOH}$$

(d) The equilibria that we need to satisfy simultaneously include



We begin with the condition that all the silver must be dissolved and that 99% must be in the form of the complex ion.

$$[\text{Ag}(\text{NH}_3)_2^+] = 0.99 \times (5.89 \times 10^{-3}) = 5.83 \times 10^{-3}$$

$$[\text{Ag}^+] = 0.01 \times (5.89 \times 10^{-3}) = 5.89 \times 10^{-5}$$

We can calculate $[\text{OH}^-]$ from the K_{sp} relationship:

$$[5.89 \times 10^{-5}][\text{OH}^-] = 1.5 \times 10^{-8}$$

$$[\text{OH}^-] = 2.5 \times 10^{-4}$$

And $[\text{H}_3\text{O}^+]$ from K_{w} :

$$[\text{H}_3\text{O}^+][2.5 \times 10^{-4}] = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 3.9 \times 10^{-11}$$

We can calculate $[\text{NH}_3]$ from the K_{f} relationship:

$$\frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.6 \times 10^7$$

$$[\text{NH}_3] = 2.5 \times 10^{-3}$$

And NH_4^+ from the K_{b} expression for NH_3 :

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

$$[\text{NH}_4^+] = 1.8 \times 10^{-4}$$

These values satisfy all of the equilibrium constants involved reasonably well (within the significant figures).

$$[\text{Ag}(\text{NH}_3)_2^+] = 5.83 \times 10^{-3}$$

$$[\text{Ag}^+] = 5.89 \times 10^{-5}$$

$$[\text{NH}_4^+] = 1.8 \times 10^{-4}$$

$$[\text{NH}_3] = 2.5 \times 10^{-3}$$

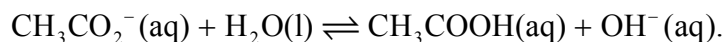
$$[\text{OH}^-] = 2.5 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+] = 3.9 \times 10^{-11}$$

The total amount of ammonia/ammonium that must be added will be

$6 \cdot 5.83 \times 10^{-3} \text{ mol} + 1.8 \times 10^{-4} \text{ mol} + 2.5 \times 10^{-3} \text{ mol} = 3.8 \times 10^{-2} \text{ mol}$. This amount will be supplied by $(3.8 \times 10^{-2} \text{ mol}) \div 15.8 \text{ mol} \cdot \text{L}^{-1} = 2.4 \times 10^{-3} \text{ L}$ or 2.4 mL. This will be a negligible volume addition to the 1.00 L of solution.

11.80 (a) The reaction is



Concentration

(mol · L ⁻¹)	$\text{CH}_3\text{CO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$			
initial	0.026	—	0	0
change	-x	—	+x	+x
equilibrium	0.026 - x	—	x	x

$$K_b = \frac{K_w}{K_a} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.026 - x} \approx \frac{x^2}{0.026}$$

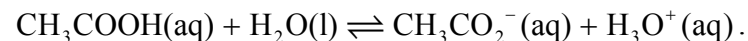
$$K_b = 5.6 \times 10^{-10}$$

$$[\text{OH}^-] = x = \sqrt{1.44 \times 10^{-11}} = 3.8 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

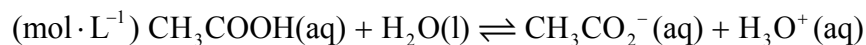
$$\text{and } \text{pOH} = -\log(3.8 \times 10^{-6}) = 5.42$$

$$\text{pH} = 14.00 - 5.42 = 8.58$$

(b) The reaction is



Concentration



initial	0.040	—	0	0
change	$-x$	—	$+x$	$+x$
equilibrium	$0.040 - x$	—	x	x

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.040 - x} \approx \frac{x^2}{0.040} = 1.8 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = \sqrt{0.040 \times 1.8 \times 10^{-5}} = 8.5 \times 10^{-4}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(8.5 \times 10^{-4}) = 3.1$$

$$(c) (0.026 \text{ mol} \cdot \text{L}^{-1})(0.150 \text{ L}) = 3.9 \times 10^{-3} \text{ mol CH}_3\text{CO}_2^-$$

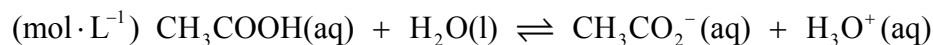
$$\text{molarity of CH}_3\text{CO}_2^- = \frac{3.9 \times 10^{-3} \text{ mol}}{0.150 \text{ L} + 0.200 \text{ L}} = 1.1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{moles of CH}_3\text{COOH} = (0.020 \text{ mol} \cdot \text{L}^{-1})(0.200 \text{ L}) = 4.0 \times 10^{-3} \text{ mol}$$

$$\text{molarity of CH}_3\text{COOH} = \frac{4.0 \times 10^{-3} \text{ mol}}{0.150 \text{ L} + 0.200 \text{ L}} = 1.1 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

and, after mixing:

Concentration



initial	1.1×10^{-2}	—	1.1×10^{-2}	0
change	$-x$	—	$+x$	$+x$
equilibrium	$1.1 \times 10^{-2} - x$	—	$1.1 \times 10^{-2} + x$	x

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(1.1 \times 10^{-2} + x)(x)}{1.1 \times 10^{-2} - x}$$

$$1.8 \times 10^{-5} = \frac{(1.1 \times 10^{-2})x}{1.1 \times 10^{-2}} = x$$

$$[\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

11.82 The concentration of acid in the bottle of trichloroacetic acid buffer is found by:

$$\text{pH} = \text{p}K_a - \log \frac{[\text{CCl}_3\text{COOH}]}{[\text{CCl}_3\text{COO}^-]}$$

$$2.95 = 0.52 - \log \frac{[\text{CCl}_3\text{COOH}]}{0.200 \text{ M}}$$

$$[\text{CCl}_3\text{COOH}] = 7.43 \times 10^{-4} \text{ M}$$

To increase the pH of the buffer to 3.00, more conjugate base will need to be added. The concentration of conjugate base needed to reach a pH of 3.00 is given by:

$$3.00 = 0.52 - \log \frac{7.43 \times 10^{-4} \text{ M}}{[\text{CCl}_3\text{COO}^-]}$$

$$[\text{CCl}_3\text{COO}^-] = 0.224 \text{ M}$$

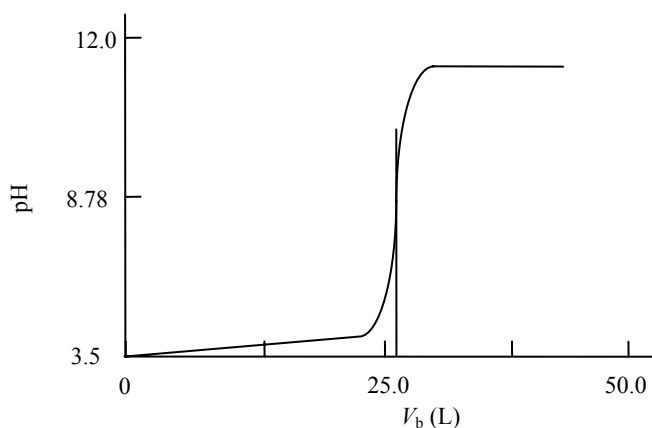
So the concentration of the conjugate base needs to be increased by 0.024 M by adding:

$$(0.024 \text{ M})(0.150 \text{ L}) = 3.6 \times 10^{-3} \text{ mol}$$

or

$$(3.6 \times 10^{-3} \text{ mol})(185.37 \text{ g} \cdot \text{mol}^{-1}) = 0.67 \text{ g of sodium trichloroacetate}$$

11.84 (a) $M_a = 0.0329$, $M_b = 0.0257$, $V_a = 20.0$, $V_b = 0.0$ to 50.0



(b) The volume of titrant is calculated from v , which is v_b/v_a where v_a is the volume of the acid and v_b is the volume of the titrant. At the equivalence point $v = 1.28$. $v_a = 20.0 \text{ mL}$, so $v_b = 1.28 \times 20.0 = 25.6 \text{ mL}$

(c) 3.50

(d) 8.78

$$\begin{aligned} 11.86 \quad [\text{NaOH}] &= (0.0118 \text{ L HCl}) \left(\frac{2.05 \text{ mol HCl}}{1 \text{ L HCl}} \right) \\ &\quad \times \left(\frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \right) \left(\frac{1}{0.0050 \text{ L NaOH}} \right) \\ &= 4.8 \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$

11.88 (a) The acidity constant may be found using:

$$K_a = e^{-\Delta G_r / RT}$$

$$\begin{aligned} \Delta G_r &= -269.2 \text{ kJ} \cdot \text{mol}^{-1} - (-293.1 \text{ kJ} \cdot \text{mol}^{-1}) = 23.9 \text{ kJ} \cdot \text{mol}^{-1} \\ &= 23900 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

$$K_a = e^{-23900 \text{ J} \cdot \text{mol}^{-1} / (8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 6.47 \times 10^{-5}$$

(b) Given the acidity constant above, the mass of sodium acetate needed is:

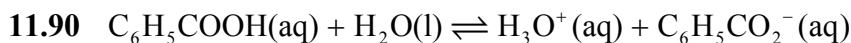
$$pK_a = 10^{-K_a} = 4.76$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 4.0 = 4.19 + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{4.0-4.19} = 0.646$$

$$\text{Given } [\text{HA}] = 1.4 \text{ M}, \quad [\text{A}^-] = 0.646 \times 1.4 \text{ M} = 0.904 \text{ M.}$$

$$\text{and } (0.904 \text{ M})(2.0 \text{ L})(144.11 \text{ g} \cdot \text{mol}^{-1}) = 261 \text{ g}$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\text{p}K_a = \text{pH} - \log \frac{[\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_6\text{H}_5\text{CO}_2^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

$$(a) \text{ pH} = K_a + \log \left\{ \frac{\left[\frac{(0.032 \text{ mol} \cdot \text{L}^{-1})(0.0200 \text{ L})}{0.0700 \text{ L}} \right]}{\left[\frac{(0.022 \text{ mol} \cdot \text{L}^{-1})(0.0500 \text{ L})}{0.0700 \text{ L}} \right]} \right\}$$

$$\text{pH} = 4.19 + \log \frac{9.1 \times 10^{-3}}{1.6 \times 10^{-2}}$$

$$\text{pH} = 4.19 - 0.24 = 3.95 \text{ (initial pH)}$$

(b) $0.054 \text{ mmol HCl} = 5.4 \times 10^{-5} \text{ mol HCl}$ (a strong acid), producing $5.4 \times 10^{-5} \text{ mol C}_6\text{H}_5\text{COOH}$ from $\text{C}_6\text{H}_5\text{CO}_2^-$ (assume no volume change) after adding HCl:

$$[\text{C}_6\text{H}_5\text{COOH}] = 1.6 \times 10^{-2} + \frac{5.4 \times 10^{-5} \text{ mol}}{0.0700 \text{ L}} = 1.6 \times 10^{-2} + 7.7 \times 10^{-4} \\ \approx 1.7 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{C}_6\text{H}_5\text{CO}_2^-] = 9.1 \times 10^{-3} - \frac{5.4 \times 10^{-5} \text{ mol}}{0.0700 \text{ L}} = (9.1 \times 10^{-3}) - (7.7 \times 10^{-4}) \\ = 8.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{and pH} = 4.19 + \log \frac{8.3 \times 10^{-3}}{1.7 \times 10^{-2}}$$

$$\text{pH} = 4.19 - 0.31 = 3.88$$

$$\Delta \text{pH} = 3.88 - 3.95 = -0.07, \text{ that is, a decrease of } 0.07 \text{ pH units}$$

$$(c) [\text{H}_3\text{O}^+] = \frac{5.4 \times 10^{-5} \text{ mol}}{0.070 \text{ L}} = 7.7 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = -\log(7.7 \times 10^{-4}) = 3.11$$

$$\Delta \text{pH} = 7.00 - 3.11 = -3.89, \text{ that is, a decrease of } 3.89 \text{ pH units}$$

(d) $(0.0100 \text{ L})(0.054 \text{ mol} \cdot \text{L}^{-1}) = 5.4 \times 10^{-4} \text{ mol HCl}$ (a strong acid), producing $5.4 \times 10^{-4} \text{ mol C}_6\text{H}_5\text{COOH}$ from $\text{C}_6\text{H}_5\text{CO}_2^-$ after adding HCl:

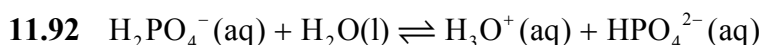
$$\text{molarity of C}_6\text{H}_5\text{COOH} = \frac{(0.022 \text{ mol} \cdot \text{L}^{-1})(0.0500 \text{ L})}{0.0800 \text{ L}} + \frac{5.4 \times 10^{-4} \text{ mol}}{0.0800 \text{ L}} \\ = 2.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$\begin{aligned}\text{molarity of } \text{C}_6\text{H}_5\text{CO}_2^- &= \frac{(0.032 \text{ mol} \cdot \text{L}^{-1})(0.0200 \text{ L})}{0.0800 \text{ L}} - \frac{5.4 \times 10^{-4} \text{ mol}}{0.0800 \text{ L}} \\ &= 1.3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}\end{aligned}$$

$$\text{pH} = 4.19 + \log \frac{1.3 \times 10^{-3}}{2.0 \times 10^{-2}}$$

$$\text{pH} = 4.19 - 1.19 = 3.00$$

$\Delta \text{pH} = [3.00 - 3.95]$, that is, a 0.95 decrease



$$K_{\text{a}2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\text{pH} = \text{p}K_{\text{a}2} + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \quad (\text{see Exercise 11.12})$$

$$7.40 = 7.21 + \log x$$

$$\log x = 0.19$$

$$x = 1.5 = \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

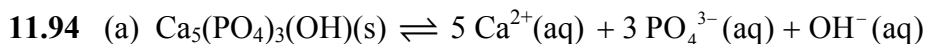
$$\text{molarity of } \text{NaH}_2\text{PO}_4 = 0.10 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{molarity of } \text{Na}_2\text{HPO}_4 = 1.5 \times 0.10 \text{ mol} \cdot \text{L}^{-1}$$

$$= 0.15 \text{ mol} \cdot \text{L}^{-1}, \text{ or } 0.075 \text{ mol/500 mL}$$

(assuming no volume change),

$$\begin{aligned}\text{mass of } \text{Na}_2\text{HPO}_4 &= 0.075 \text{ mol } \text{Na}_2\text{HPO}_4 \times \frac{141.96 \text{ g } \text{Na}_2\text{HPO}_4}{1 \text{ mol } \text{Na}_2\text{HPO}_4} \\ &= 11 \text{ g } \text{Na}_2\text{HPO}_4\end{aligned}$$

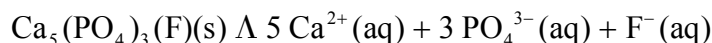


Concentration (mol · L ⁻¹)	Ca ²⁺	PO ₄ ³⁻	OH ⁻
initial	0	0	0
change	+5 <i>S</i>	+3 <i>S</i>	+ <i>S</i>
equilibrium	5 <i>S</i>	3 <i>S</i>	<i>S</i>

$$K_{\text{sp}} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{OH}^-]$$

$$1.0 \times 10^{-36} = (5S)^5 \times (3S)^3 \times (S) = 84\,375 S^9$$

$$S = 2.8 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1} = \text{molar solubility of } \text{Ca}_5(\text{PO}_4)_3\text{OH}$$



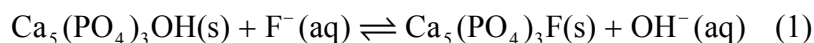
Concentration (mol · L ⁻¹)	Ca ²⁺	PO ₄ ³⁻	F ⁻
initial	0	0	0
change	+5 <i>S</i>	+3 <i>S</i>	+ <i>S</i>
equilibrium	5 <i>S</i>	3 <i>S</i>	<i>S</i>

$$K_{\text{sp}} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{F}^-]$$

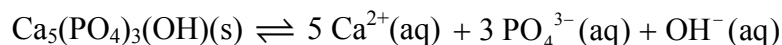
$$1.0 \times 10^{-60} = (5S)^5 \times (3S)^3 \times (S) = 84\,375 S^9$$

$$S = 6.1 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1} = [\text{F}^-] = \text{molar solubility of } \text{Ca}_5(\text{PO}_4)_3\text{F}$$

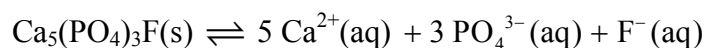
(b) The overall equation for which we wish to find the free energy change is



It can be obtained by combining the two equations given:



$$K = 1.0 \times 10^{-36} \quad (2)$$



$$K = 1.0 \times 10^{-60} \quad (3)$$

Equation (1) = Equation (2) – Equation (3)

$$K_1 = K_2 / K_3 = (1.0 \times 10^{-36}) / (1.0 \times 10^{-60}) = 1.0 \times 10^{24}$$

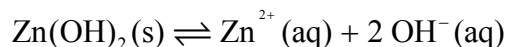
$$\begin{aligned} \Delta G^\circ &= -RT \ln K = -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) \ln (1.0 \times 10^{24}) \\ &= -1.4 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

11.96 (a)

molarity of ZnCl_2 = molarity of Zn^{2+}

$$\begin{aligned} &= (1.36 \text{ mg } \text{ZnCl}_2) \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}} \right) \left(\frac{1 \text{ mol } \text{ZnCl}_2}{136.27 \text{ g}} \right) \left(\frac{1}{0.500 \text{ L}} \right) \\ &= 2.00 \times 10^{-5} \text{ M } \text{ZnCl}_2 \end{aligned}$$

pH = 8.00; pOH = 6.00; molarity of $\text{OH}^- = 1.00 \times 10^{-6} \text{ M}$



$$[\text{Zn}^{2+}][\text{OH}^-]^2 = Q_{\text{sp}}$$

$$(2.00 \times 10^{-5})(1.0 \times 10^{-6})^2 = 2.0 \times 10^{-17} = Q_{\text{sp}}$$

Because $Q_{\text{sp}} (2.0 \times 10^{-17})$ equals $K_{\text{sp}} (2.0 \times 10^{-17})$, no precipitate forms (just barely!)

(b) Because the concentration of hydroxide is higher for (b), we might expect that there would be a precipitate. The corresponding calculation at this pH is

$$[\text{OH}^-] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{Zn}^{2+}][\text{OH}^-]^2 = (2.00 \times 10^{-5})(1.0 \times 10^{-2})^2 = 2.0 \times 10^{-9} = Q_{\text{sp}}$$

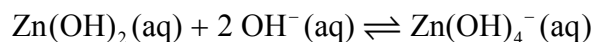
This number exceeds K_{sp} and so we would expect a precipitate to form.

The amount of zinc present in solution can be obtained from

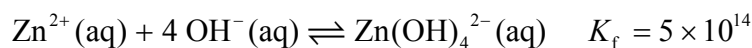
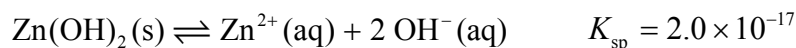
$$[\text{Zn}^{2+}][1.0 \times 10^{-2}]^2 = 2.0 \times 10^{-17}$$

$$[\text{Zn}^{2+}] = 2.0 \times 10^{-13} \text{ M}$$

However, we must also consider the ensuring formation of the complex ion as additional hydroxide ion is added:



The equilibrium constant for this reaction can be obtained by combining the two equilibrium constants for the given reactions:



Adding these two equations gives the desired equilibrium with

$$K = (2.0 \times 10^{-17})(5 \times 10^{14}) = 1 \times 10^{-2}.$$

$$\frac{[\text{Zn(OH)}_4^{2-}]}{[\text{OH}^-]^2} = 1 \times 10^{-2}$$

$$\frac{[\text{Zn(OH)}_4^{2-}]}{(1.0 \times 10^{-2})^2} = 1 \times 10^{-2}$$

$$[\text{Zn(OH)}_4^{2-}] = 1 \times 10^{-6}$$

This represents only about 5% of the zinc present, so the bulk of the zinc will remain as a precipitate.

(c) We can use the relationship from part (b) to determine the concentration of hydroxide ion required to complex with all of the zinc ions ($2.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$).

$$\frac{[\text{Zn}(\text{OH})_4^{2-}]}{[\text{OH}^-]^2} = 1 \times 10^{-2}$$

$$\frac{2.0 \times 10^{-5}}{[\text{OH}^-]^2} = 1 \times 10^{-2}$$

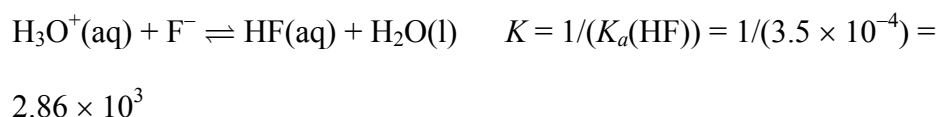
$$[\text{OH}^-] = 0.04$$

$$\text{pH} = 12.6$$

11.98 In addition to the reaction corresponding to the dissolution of $\text{BaF}_2(\text{s})$:



The buffer will provide a source of $\text{H}_3\text{O}^{+}(\text{aq})$ ions that will allow the reaction:



These two coupled reactions give two equilibrium expressions, which must be simultaneously satisfied:

$$[\text{F}^{-}]^2 [\text{Ba}^{2+}] = 1.7 \times 10^{-6} \quad \text{and} \quad \frac{[\text{HF}]}{[\text{H}_3\text{O}^{+}][\text{F}^{-}]} = 2.86 \times 10^3$$

Given that all fluoride ions come from $\text{BaF}_2(\text{s})$ and wind up as either $\text{F}^{-}(\text{aq})$ or $\text{HF}(\text{aq})$, and that for every one mole of $\text{Ba}^{2+}(\text{aq})$ generated two moles of $\text{F}^{-}(\text{aq})$ are also produced, we can write a third equation which relates the concentration of the fluoride containing species to the concentration of dissolved barium: $[\text{Ba}^{2+}] = \frac{1}{2}([\text{F}^{-}] + [\text{HF}])$.

In the end, the concentration of $\text{Ba}^{2+}(\text{aq})$ will be equal to the solubility of $\text{BaF}_2(\text{s})$. To determine the equilibrium concentration of $\text{Ba}^{2+}(\text{aq})$, we first

determine $[\text{H}_3\text{O}^+]$, which is fixed by the buffer system, and then use the three simultaneous equations above to solve for $[\text{Ba}^{2+}]_{\text{eq}}$.

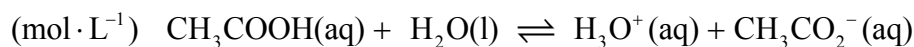
The buffer determines the equilibrium concentration of $\text{H}_3\text{O}^+(\text{aq})$. The initial concentration of $\text{H}_3\text{O}^+(\text{aq})$ and $\text{NaCH}_3\text{CO}_2(\text{aq})$ are:

$$[\text{H}_3\text{O}^+]_i = \frac{(0.055 \text{ L})(0.15 \text{ mol} \cdot \text{L}^{-1})}{0.10 \text{ L}} = 0.0825 \text{ M} \quad \text{and}$$

$$[\text{CH}_3\text{CO}_2^-]_i = \frac{(0.045 \text{ L})(0.65 \text{ mol} \cdot \text{L}^{-1})}{0.10 \text{ L}} = 0.293 \text{ M}.$$

To determine their equilibrium concentrations we solve using the familiar method:

Concentration



initial	0	—	0.0825	0.293
change	+ x	—	− x	− x
equilibrium	x	—	$0.0825 - x$	$0.292 - x$

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]} = \frac{(0.0825 - x)(0.292 - x)}{(x)}$$

Rearranging this expression we obtain:

$$0.024072 - 0.3745x + x^2 = 0.$$

Using the quadratic formula we find $x = 0.082493$, and $[\text{H}_3\text{O}^+] = 7.1 \times 10^{-6} \text{ M}$

With this equilibrium concentration of $\text{H}_3\text{O}^+(\text{aq})$ we revisit the three simultaneous equations from above, namely

$$[\text{F}^-]^2[\text{Ba}] = 1.7 \times 10^{-6};$$

$$[\text{Ba}^{2+}] = \frac{1}{2}([\text{F}^-] + [\text{HF}]); \text{ and}$$

$$\frac{[\text{HF}]}{[\text{H}_3\text{O}^+][\text{F}^-]} = 2.86 \times 10^3.$$

Due to the presence of the buffer, $[\text{H}_3\text{O}^+] = 7.1 \times 10^{-6}$

and this last equation simplifies to

$$\frac{[\text{HF}]}{[\text{F}^-]} = 2.03 \times 10^{-2}.$$

Rearranging these three simultaneous equations we find:

$$[\text{Ba}^{2+}] = \frac{1.7 \times 10^{-6}}{[\text{F}^-]^2}, \quad [\text{HF}] = [\text{F}^-] \times (2.03 \times 10^{-2}), \quad \text{and}$$

$$[\text{Ba}^{2+}] = \frac{1}{2}([\text{F}^-] + [\text{HF}])$$

$$= \frac{1.7 \times 10^{-6}}{[\text{F}^-]^2} = \frac{1}{2} \left[[\text{F}^-] + ([\text{F}^-] \times (2.03 \times 10^{-2})) \right].$$

Solving this expression for $[\text{F}^-]$:

$$[\text{F}^-] = \sqrt[3]{\frac{3.4 \times 10^{-6}}{1.0203}} = 1.49 \times 10^{-2}.$$

The equilibrium concentration of $\text{Ba}^{2+}(\text{aq})$ is then:

$$[\text{Ba}^{2+}] = \frac{1.7 \times 10^{-6}}{[\text{F}^-]^2} = \frac{1.7 \times 10^{-6}}{(1.49 \times 10^{-2})^2} = 7.62 \times 10^{-3} \text{ M}$$

Therefore, the solubility of $\text{BaF}_2(\text{s})$ is $7.6 \times 10^{-3} \text{ M}$

11.100 The K_{sp} values are 1.3×10^{-36} for CuS and 1.3×10^{-15} for MnS . Because the form of the K_{sp} reaction is essentially the same for both compounds, the numbers are comparable directly. MnS is more soluble than CuS and so will remain in solution as the CuS precipitates. CuS will begin to precipitate at $[\text{S}^{2-}] = 6.5 \times 10^{-36} \text{ mol} \cdot \text{L}^{-1}$ as calculated from

$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{S}^{2-}] = 1.3 \times 10^{-36}$$

$$0.20[\text{S}^{2-}] = 1.3 \times 10^{-36}$$

$$[\text{S}^{2-}] = 6.5 \times 10^{-36} \text{ mol} \cdot \text{L}^{-1}$$

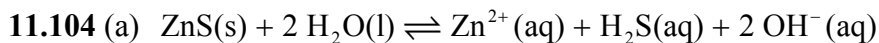
11.102 $\text{HgS}(\text{s}) \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$

$$K_{\text{sp}} = [\text{Hg}^{2+}][\text{S}^{2-}] = S^2 = 1.6 \times 10^{-52}$$

$$S = \sqrt{1.6 \times 10^{-52}} = 1.3 \times 10^{-26} \text{ mol} \cdot \text{L}^{-1} = [\text{Hg}^{2+}]$$

$$\text{and } (1.3 \times 10^{-26} \text{ mol} \cdot \text{L}^{-1}) \left(\frac{6.022 \times 10^{23} \text{ ions}}{1 \text{ mol}} \right) = \frac{7.8 \times 10^{-3} \text{ ions}}{1 \text{ L}}$$

The reciprocal gives the number of liters per ion = $1.3 \times 10^2 \text{ L/ion}$



$$K = K_{\text{sp}} \cdot K_{\text{b1}} \cdot K_{\text{b2}} = K_{\text{sp}} \cdot \frac{K_{\text{w}}}{K_{\text{a2}}} \cdot \frac{K_{\text{w}}}{K_{\text{a1}}} \\ = 1.6 \times 10^{-24} \cdot \frac{1.00 \times 10^{-14}}{7.1 \times 10^{-15}} \cdot \frac{1.00 \times 10^{-14}}{1.3 \times 10^{-7}} = 1.7 \times 10^{-31}$$

(b) $[\text{Zn}^{2+}][\text{H}_2\text{S}][\text{OH}^{-}]^2 = 1.7 \times 10^{-31}$

at pH = 7.00, $[\text{OH}^{-}] = 1.0 \times 10^{-7}$

$$[\text{Zn}^{2+}](0.10)(1.0 \times 10^{-7})^2 = 1.7 \times 10^{-31}$$

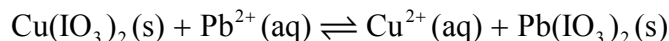
$$[\text{Zn}^{2+}] = 1.7 \times 10^{-16} \text{ mol} \cdot \text{L}^{-1}$$

(c) at pH = 10.00, $[\text{OH}^{-}] = 1.0 \times 10^{-4}$

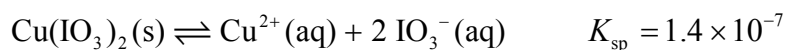
$$[\text{Zn}^{2+}](0.10)(1.0 \times 10^{-4})^2 = 1.7 \times 10^{-31}$$

$$[\text{Zn}^{2+}] = 1.7 \times 10^{-22} \text{ mol} \cdot \text{L}^{-1}$$

11.106 (a) Both $\text{Cu}(\text{IO}_3)_2$ and $\text{Pb}(\text{IO}_3)_2$ are insoluble compounds, but a small amount of dissolution to give the M^{2+} and IO_3^{-} ions in solution should occur. The question then becomes one of determining where the equilibrium lies between Cu^{2+} ions, $\text{Cu}(\text{IO}_3)_2(\text{s})$, Pb^{2+} ions, and $\text{Pb}(\text{IO}_3)_2(\text{s})$ in this system. The relevant equation is



This information can be obtained from the K_{sp} values:



The first reaction minus the second is the process we want, giving a K value for the overall reaction of

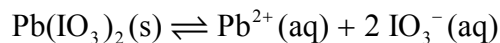
$$K = \frac{1.4 \times 10^{-7}}{2.6 \times 10^{-13}} = 5.4 \times 10^5$$

The form of this equilibrium expression is $K = \frac{[\text{Cu}^{2+}]}{[\text{Pb}^{2+}]}$. Because the ratio

of Cu^{2+} ions to Pb^{2+} ions is 5.4×10^5 , this will represent quantitative

conversion of the copper iodate to the lead iodate (for 99.99% conversion, the ratio would be $99.99 \div 0.01 = 1 \times 10^4$). Although the thermodynamic analysis indicates that the replacement will take place, it does not tell us how fast it will occur.

(b) The IO_3^- concentration will be determined by the $\text{Pb}(\text{IO}_3)_2$ dissolution equilibrium because that is the least soluble species:



$$K_{\text{sp}} = 2.6 \times 10^{-13} = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = x(2x)^2$$

$$4x^3 = 2.6 \times 10^{-13}$$

$$x = 4.0 \times 10^{-5}$$

The IO_3^- concentration is $2x = 2(4.0 \times 10^{-5}) = 8.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$.

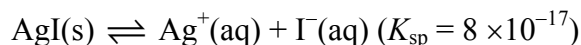
(c) The free energy of the displacement reaction is calculated from the K of the reaction determined in (a).

$$\Delta G^\circ = -RT \ln K$$

$$= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K}) \ln(5.4 \times 10^5)$$

$$= -32.72 \text{ kJ} \cdot \text{mol}^{-1}$$

11.108 The dissolution reaction of interest is:



The change in the equilibrium constant of this reaction with temperature

can be predicted using: $\ln \left(\frac{K_2}{K_1} \right) = \frac{\Delta H_r^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$. The standard enthalpy

for the dissolution reaction can be found using the table of thermodynamic values in the back of the text:

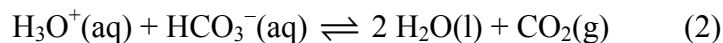
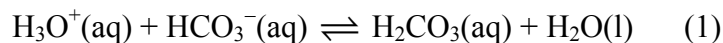
$$\begin{aligned} \Delta H_r^\circ &= 50.38 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - (-61.84 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &= 112.22 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

The solubility constant at 85°C is then found:

$$\ln\left(\frac{K_2}{8 \times 10^{-17}}\right) = \frac{112,220 \text{ J} \cdot \text{mol}^{-1}}{8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \left(\frac{1}{298 \text{ K}} - \frac{1}{358 \text{ K}} \right)$$

$$K_2 = 1.6 \times 10^{-13}$$

11.110 The two equations of interest are:



(a) During exercise, an increase in the amount of carbon dioxide in the muscle will shift reaction (2) above toward reactants, increasing the amount of $\text{H}_3\text{O}^+(\text{aq})$ thereby decreasing the pH. (b) and (c) During hyperventilation, $\text{CO}_2(\text{g})$ is expelled from the body at a rapid rate, shifting reaction (2) toward products and increasing the pH of the blood. The resulting condition is known as respiratory alkalosis and can be remedied by breathing into a paper bag, allowing some of the expelled $\text{CO}_2(\text{g})$ to be reabsorbed into the blood.