

CHAPTER 20. The Properties of Acids and Bases

20-1. Nitric acid is a strong acid, so

$$[\text{H}_3\text{O}^+] = [\text{NO}_3^-] = 0.60 \text{ M}$$

and

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14} \text{ M}^2}{0.60 \text{ M}} = 1.7 \times 10^{-14} \text{ M}$$

20-2. Barium hydroxide, $\text{Ba}(\text{OH})_2(aq)$, is a strong base, so

$$[\text{Ba}^{2+}] = 0.25 \text{ M}$$

$$[\text{OH}^-] = (2)(0.25 \text{ M}) = 0.50 \text{ M}$$

and

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14} \text{ M}^2}{0.50 \text{ M}} = 2.0 \times 10^{-14} \text{ M}$$

20-3. See the text.

20-4. Because sodium hydroxide is a strong base, the hydroxide concentration of 6.0 M $\text{NaOH}(aq)$ is

$$[\text{OH}^-] = 6.0 \text{ M}$$

When the solution is diluted to 75.0 mL, the concentration is now given by

$$[\text{OH}^-] = (6.0 \text{ M}) \left(\frac{20.0 \text{ mL}}{75.0 \text{ mL}} \right) = 1.6 \text{ M}$$

The value of $[\text{H}_3\text{O}^+]$ is calculated by using the ion-product constant of water:

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} \text{ M}^2}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14} \text{ M}^2}{1.6 \text{ M}} = 6.3 \times 10^{-15} \text{ M}$$

The pH of the solutions is

$$\text{pH} = -\log([\text{H}_3\text{O}^+]/\text{M}) = -\log(6.3 \times 10^{-15}) = 14.20$$

20-5. Using the relation $\text{pH} = 14.00 - \text{pOH}$, we have for the two solutions

$$\text{pH}_1 = 14.00 - \text{pOH}_1 \quad \text{and} \quad \text{pH}_2 = 14.00 - \text{pOH}_2$$

Thus, $\Delta\text{pH} = -\Delta\text{pOH}$. The ratio of the $\text{OH}^- (aq)$ concentrations is 1×10^4 , and so

$$\begin{aligned} \Delta\text{pOH} &= \text{pOH}_2 - \text{pOH}_1 = -\log([\text{OH}]_2/M) - (-\log([\text{OH}]_1/M)) \\ &= -\log \frac{[\text{OH}]_2/M}{[\text{OH}]_1/M} = -\log(1 \times 10^4) = -4.0 \end{aligned}$$

or 4 pH units.

20-6. Because $\text{pH} + \text{pOH} = 14.00$, $\text{pOH} = 14.00 - 12 = 2$, and

$$[\text{OH}^-] = 10^{-\text{pOH}} \text{ M} = 10^{-2} \text{ M} = 1 \times 10^{-2} \text{ M}$$

20-7. For formic acid,

$$[\text{H}_3\text{O}^+]/M = 10^{-\text{pH}} = 10^{-2.08} = 8.3 \times 10^{-3}$$

The percentage of the formic acid molecules dissociated is given by

$$\% \text{ dissociated} = \frac{8.3 \times 10^{-3} \text{ M}}{0.40 \text{ M}} \times 100 = 2.1\%$$

For hydrocyanic acid,

$$[\text{H}_3\text{O}^+]/M = 10^{-\text{pH}} = 10^{-4.80} = 1.6 \times 10^{-5}$$

The percentage of the hydrocyanic acid molecules dissociated is given by

$$\% \text{ dissociated} = \frac{1.6 \times 10^{-5} \text{ M}}{0.40 \text{ M}} \times 100 = 4.0 \times 10^{-3}\%$$

20-8. We set up a concentration table

Concentration	$\text{C}_6\text{H}_5\text{COOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{C}_6\text{H}_5\text{COO}^-(aq)$
Initial	0.250 M		–		$\approx 0 \text{ M}$		0 M
Change	– x		–		+ x		+ x
Equilibrium	$0.250 \text{ M} - x$		–		x		x

The equilibrium-constant expression is

$$\frac{x^2}{0.250 \text{ M} - x} = 6.3 \times 10^{-5} \text{ M}$$

Arranging this equation in the standard form of a quadratic equation, we have

$$x^2 + (6.3 \times 10^{-5} \text{ M})x - 1.575 \times 10^{-5} \text{ M}^2 = 0$$

The two roots of this equation are $x = 4.0 \times 10^{-3} \text{ M}$ and $x = -8.0 \times 10^{-3} \text{ M}$. Rejecting the negative root as physically impossible, we have

$$\begin{aligned} [\text{H}_3\text{O}^+] &= [\text{C}_6\text{H}_5\text{COO}^-] = x = 4.0 \times 10^{-3} \text{ M} \\ [\text{C}_6\text{H}_5\text{COOH}] &= 0.250 \text{ M} - x = 0.246 \text{ M} \end{aligned}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14} \text{ M}^2}{4.0 \times 10^{-3} \text{ M}} = 2.5 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log([\text{H}_3\text{O}^+]/\text{M}) = 2.40$$

20-9. Use the equation $\text{p}K_a = -\log(K_a/\text{M})$ to write

$$K_a/\text{M} = 10^{-0.78} = 0.17$$

or $K_a = 0.17 \text{ M}$.

20-10. The molecular mass of acetylsalicylic acid is 180.16. Therefore, the molarity of the solution is

$$M = \frac{(324 \text{ mg}) \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) \left(\frac{1 \text{ mol}}{180.16 \text{ g}} \right)}{0.1000 \text{ L}} = 0.0180 \text{ M}$$

The value of K_a is

$$K_a = 10^{-3.48} \text{ M} = 3.3 \times 10^{-4} \text{ M}$$

To calculate $[\text{H}_3\text{O}^+]$, we set up a concentration table

Concentration	acid(aq)	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	anion(aq)
Initial	0.0180 M		–		$\approx 0 \text{ M}$		0 M
Change	– x		–		+ x		+ x
Equilibrium	0.0180 M – x		–		x		x

The equilibrium-constant expression is

$$\frac{x^2}{0.0180 \text{ M} - x} = 3.3 \times 10^{-4} \text{ M}$$

Solving for x using the method of successive approximations gives $x = [\text{H}_3\text{O}^+] = 2.3 \times 10^{-3} \text{ M}$ after three iterations, and so

$$\text{pH} = -\log([\text{H}_3\text{O}^+]/\text{M}) = -\log(2.3 \times 10^{-3}) = 2.64$$

20-11. The molecular mass of aniline is 93.13. Therefore, the molarity of the solution is

$$M = \frac{(3.50 \text{ g}) \left(\frac{1 \text{ mol}}{93.13 \text{ g}} \right)}{0.1000 \text{ L}} = 0.376 \text{ M}$$

To calculate $[\text{OH}^-]$, we set up a concentration table

Concentration	$\text{C}_6\text{H}_5\text{NH}_2(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{C}_6\text{H}_5\text{NH}_3^+(aq)$	+	$\text{OH}^-(aq)$
Initial	0.376 M		–		0 M		$\approx 0 \text{ M}$
Change	– x		–		+ x		+ x
Equilibrium	0.376 M – x		–		x		x

The equilibrium-constant expression is (using K_b from Table 20.5)

$$\frac{x^2}{0.376 \text{ M} - x} = K_b = 7.4 \times 10^{-10} \text{ M}$$

Solving for x using the method of successive approximations gives
 $x = [\text{OH}^-] = 1.7 \times 10^{-5} \text{ M} = [\text{C}_6\text{H}_5\text{NH}_3^+]$. Thus,

$$[\text{OH}^-] = [\text{C}_6\text{H}_5\text{NH}_3^+] = 1.7 \times 10^{-5} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{NH}_2] = 0.376 \text{ M} - 1.7 \times 10^{-5} \text{ M} = 0.376 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14} \text{ M}^2}{1.7 \times 10^{-5} \text{ M}} = 5.9 \times 10^{-10} \text{ M}$$

and

$$\text{pH} = -\log([\text{H}_3\text{O}^+]/\text{M}) = 9.23$$

20-12. The conjugate acid of each species has one more hydrogen atom than the base.

(a) $\text{HCN}(aq)$; (b) $\text{H}_2\text{SO}_4(aq)$; (c) $\text{HSO}_3^-(aq)$

20-13. The conjugate acid has one more hydrogen atom than the base. The hydrogen atom is bonded to the nitrogen atom as in ammonia and amines: $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_3^+(aq)$. We use

$$\text{p}K_a = 14.00 - \text{p}K_b = 14.00 - 3.40 = 10.60$$

$$K_a = 10^{-\text{p}K_a} \text{ M} = 2.5 \times 10^{-11} \text{ M}$$

20-14. (a) Acidic. $\text{HCN}(aq)$ is an acid.

(b) Neutral. $\text{KClO}_3(aq)$ consists of a neutral cation and a neutral anion.

(c) Acidic. $\text{FeCl}_3(aq)$ is acidic because of the reactions described by



20-15. (a) Basic. $\text{NH}_4\text{CN}(aq)$ consists of an acidic cation and a basic anion, but $\text{CN}^-(aq)$ is a stronger base ($K_b = 1.6 \times 10^{-5} \text{ M}$) than $\text{NH}_4^+(aq)$ is an acid ($K_a = 5.6 \times 10^{-10} \text{ M}$).

(b) Basic. $\text{CH}_3\text{NH}_2(aq)$ is a weak base.

(c) Acidic. $\text{Pb}^{2+}(aq)$ is an acidic cation and $\text{NO}_3^-(aq)$ is a neutral anion.

20-16. The equation for the reaction is



We set up a concentration table to calculate $[\text{H}_3\text{O}^+]$

Concentration	$[\text{Tl}(\text{H}_2\text{O})_6]^{3+}(aq)$	$+$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	$+$	$[\text{Tl}(\text{OH})(\text{H}_2\text{O})_5]^{2+}(aq)$
Initial	0.25 M		—		$\approx 0 \text{ M}$		0 M
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.25 \text{ M} - x$		—		x		x

The equilibrium-constant expression is

$$\frac{x^2}{0.25 \text{ M} - x} = 7.0 \times 10^{-2} \text{ M}$$

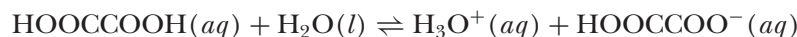
where $K_a = 7.0 \times 10^{-2}$ M from Table 20.8. Solving for x using the method of successive approximations (about five or six iterations) or the quadratic formula gives

$$x = [\text{H}_3\text{O}^+] = 0.10 \text{ M}$$

and

$$\text{pH} = -\log([\text{H}_3\text{O}^+]/\text{M}) = 1.00$$

- 20-17. The values of $\text{p}K_{a_1}$ and $\text{p}K_{a_2}$ for oxalic acid are 1.25 and 3.81, respectively (Table 20.9). Using $K_a = 10^{-\text{p}K_a}$ M gives values of $K_{a_1} = 0.056$ M and $K_{a_2} = 1.5 \times 10^{-4}$ M. The first dissociation step is represented by



We set up a concentration table to calculate $[\text{H}_3\text{O}^+]$

Concentration	$\text{H}_2\text{C}_2\text{O}_4(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{HC}_2\text{O}_4^-(aq)$
Initial	0.250 M		—		≈ 0 M		0 M
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.250 \text{ M} - x$		—		x		x

The first equilibrium-constant expression is

$$\frac{x^2}{0.250 \text{ M} - x} = 0.052 \text{ M}$$

Solving for x using the method of successive approximations (several iterations) gives

$$x = [\text{H}_3\text{O}^+] = 0.094 \text{ M} = [\text{HOOC}(\text{COO}^-)]$$

Now set up a concentration table for the second dissociation

Concentration	$\text{HC}_2\text{O}_4^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{C}_2\text{O}_4^{2-}(aq)$
Initial	0.094 M		—		0.094 M		0 M
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.094 \text{ M} - x$		—		$0.094 \text{ M} + x$		x

The equilibrium-constant expression is

$$\frac{(x)(0.094 \text{ M} + x)}{0.094 \text{ M} - x} = 1.5 \times 10^{-4} \text{ M}$$

Neglecting x with respect to 0.094 M gives $x = 1.5 \times 10^{-4}$ M. Thus, we have

$$[\text{OOC}(\text{COO})^{2-}] = 1.5 \times 10^{-4} \text{ M}$$

$$[\text{HOOC}(\text{COO}^-)] = 0.094 \text{ M}$$

$$[\text{HOOC}(\text{COOH})] = 0.250 \text{ M} - 0.094 \text{ M} = 0.156 \text{ M}$$

$$[\text{H}_3\text{O}^+] = 0.094 \text{ M} + 1.5 \times 10^{-4} \text{ M} = 0.094 \text{ M}$$

$$\text{pH} = -\log 0.094 = 1.03$$

Notice that the pH after the second dissociation is the same as that after the first dissociation, namely, 1.03, because $K_{a_1} \gg K_{a_2}$.

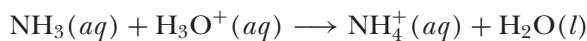
CHAPTER 21. Buffers and the Titration of Acids and Bases

21-1. We can use the Henderson–Hasselbalch equation, Equation 21.7.

$$\text{pH} \approx \text{p}K_{\text{a}} + \log \frac{[\text{base}]_0}{[\text{acid}]_0} = 4.74 + \log \frac{0.30 \text{ M}}{0.85 \text{ M}} = 4.29$$

where $\text{p}K_{\text{a}} = 4.74$. (See Table 20.4.)

21-2. (a) The equation for the reaction that takes place is



The initial pH is given by Equation 21.7. (See Example 21-1.)

$$\text{pH} \approx \text{p}K_{\text{a}} + \log \frac{[\text{base}]_0}{[\text{acid}]_0} = 9.25 + \log \frac{0.500 \text{ M}}{0.500 \text{ M}} = 9.25$$

The initial number of millimoles of $\text{NH}_3(aq)$ is given by

$$\left(\begin{array}{l} \text{mmol of NH}_3 \\ \text{before HCl addition} \end{array} \right) = (0.500 \text{ M})(100.0 \text{ mL}) = 50.0 \text{ mmol}$$

The number of millimoles of $\text{HCl}(aq)$ added is

$$\text{mmol of HCl added} = (10.0 \text{ mL})(0.250 \text{ M}) = 2.50 \text{ mmol}$$

The number of millimoles of $\text{NH}_3(aq)$ after the addition of $\text{HCl}(aq)$ is given by

$$\left(\begin{array}{l} \text{mmol of NH}_3 \\ \text{after HCl addition} \end{array} \right) = 50.0 \text{ mmol} - 2.50 \text{ mmol} = 47.5 \text{ mmol}$$

The initial number of millimoles of $\text{NH}_4^+(aq)$ is given by

$$\left(\begin{array}{l} \text{mmol of NH}_4^+ \\ \text{before HCl addition} \end{array} \right) = (0.500 \text{ M})(100.0 \text{ mL}) = 50.0 \text{ mmol}$$

The number of millimoles of $\text{NH}_4^+(aq)$ after the addition of $\text{HCl}(aq)$ is given by

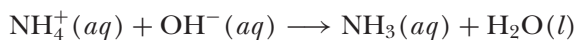
$$\left(\begin{array}{c} \text{mmol of } \text{NH}_4^+ \\ \text{after HCl addition} \end{array} \right) = 50.0 \text{ mmol} + 2.50 \text{ mmol} = 52.5 \text{ mmol}$$

We can use the number of millimoles of each in Equation 21.7 because both have the same volume. The pH is now

$$\text{pH} \approx 9.25 + \log \frac{47.5 \text{ mmol}}{52.5 \text{ mmol}} = 9.21$$

for a change of -0.04 pH units.

(b) The equation for the reaction that takes place is



The number of millimoles of $\text{NaOH}(aq)$ added is

$$\text{mmol of NaOH added} = (10.0 \text{ mL})(0.250 \text{ M}) = 2.50 \text{ mmol}$$

The number of millimoles of $\text{NH}_4^+(aq)$ after the addition of $\text{KOH}(aq)$ is given by

$$\text{millimoles of } \text{NH}_4^+(aq) = 50.0 \text{ mmol} - 2.50 \text{ mmol} = 47.5 \text{ mmol}$$

The number of millimoles of $\text{NH}_4^+(aq)$ after the $\text{NaOH}(aq)$ addition is

$$\text{millimoles of } \text{NH}_4^+(aq) = 50.0 \text{ mmol} + 2.50 \text{ mmol} = 52.5 \text{ mmol}$$

The pH is now

$$\text{pH} \approx 9.25 + \log \frac{52.5 \text{ mmol}}{47.5 \text{ mmol}} = 9.29$$

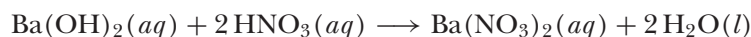
for a change of $+0.04$ pH units.

21-3. See the text.

21-4. Referring to Figure 21.7 or Table 21.2, we see that the pH is between 3 and 4.

21-5. Figure 21.11 shows that the pH of the equivalence point is around 5, so we choose an indicator that changes around this value. Figure 21.7 or Table 21.2 shows that bromcresol green and bromcresol purple can be used.

21-6. The equation for the reaction that takes place is



The initial pH is given by

$$[\text{OH}^-] = (2)(0.200 \text{ M}) = 0.400 \text{ M}$$

$$\text{pOH} = 0.40 \quad \text{and} \quad \text{pH} = 14.00 - \text{pOH} = 13.60$$

We will do the calculation for the addition of 10.0 milliliters of 0.300 M $\text{HNO}_3(aq)$ in detail. The initial number of millimoles of $\text{OH}^-(aq)$ in 30.0 milliliters of 0.200 M $\text{Ba}(\text{OH})_2(aq)$ is

$$\text{mmol of } \text{OH}^- \text{ initially present} = (2)(30.0 \text{ mL})(0.200 \text{ M}) = 12.00 \text{ mmol}$$

The number of millimoles of $\text{H}_3\text{O}^+(aq)$ in 10.0 milliliters of 0.300 M $\text{HNO}_3(aq)$ is

$$\text{mmol of H}_3\text{O}^+ \text{ added} = (10.0 \text{ mL})(0.300 \text{ M}) = 3.00 \text{ mmol}$$

The number of millimoles of $\text{OH}^-(aq)$ remaining after the addition is

$$\text{mmol of OH}^- \text{ unreacted} = 12.00 \text{ mmol} - 3.00 \text{ mmol} = 9.00 \text{ mmol}$$

The total volume of the solution is $30.0 \text{ mL} + 10.0 \text{ mL} = 40.0 \text{ mL}$, so the concentration of unreacted $\text{OH}^-(aq)$ is

$$[\text{OH}^-] = \frac{9.00 \text{ mmol}}{40.0 \text{ mL}} = 0.225 \text{ M}$$

The pOH of the solutions is $-\log(0.225) = 0.65$ and the pH is

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 0.65 = 13.35$$

Continuing in a like manner, we can set up the following table that gives the pH of the solution as a function of the volume of 0.300 M $\text{HNO}_3(aq)$ added to the 30.00 mL of 0.200 M $\text{Ba}(\text{OH})_2(aq)$.

Before the equivalence point

Volume $\text{HNO}_3(aq)$ added/mL	$\text{H}_3\text{O}^+(aq)$ added/mmol	Unreacted $\text{OH}^-(aq)$ /mmol	Total volume of solution/mL	$[\text{OH}^-]/\text{M}$	pH
0	0	12.00	30.0	0.00	13.60
10.0	3.00	9.00	40.0	0.23	13.35
20.0	6.00	6.00	50.0	0.12	13.08
30.0	9.00	3.00	60.0	0.050	12.70
39.5	11.85	0.15	69.5	0.0022	11.33

The equivalence point occurs at

$$\text{moles of HNO}_3 = 2 \times \text{moles of Ba}(\text{OH})_2 = (2)(30.0 \text{ mL})(0.200 \text{ M})$$

or $M_{\text{HNO}_3} V_{\text{HNO}_3} = (2)(30.0 \text{ mL})(0.200 \text{ M})$. Solving for the volume of $\text{HNO}_3(aq)$ required gives

$$V_{\text{HNO}_3} = \frac{(2)(0.200 \text{ M})(30.00 \text{ mL})}{0.300 \text{ M}} = 40.0 \text{ mL}$$

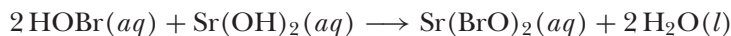
At the equivalence point

Volume $\text{HNO}_3(aq)$ added/mL	$\text{H}_3\text{O}^+(aq)$ added/mmol	Unreacted $\text{OH}^-(aq)$ /mmol	Total volume of solution/mL	$[\text{OH}^-]/\text{M}$	pH
40.0	12.00	7.00×10^{-6}	70.0	1.00×10^{-7}	7.00

Beyond the equivalence point, we have excess $\text{H}_3\text{O}^+(aq)$. Some points are

Volume $\text{HNO}_3(aq)$ added/mL	$\text{H}_3\text{O}^+(aq)$ added/mmol	Unreacted $\text{H}_3\text{O}^+(aq)$ /mmol	Total volume of solution/mL	$[\text{H}_3\text{O}^+]/\text{M}$	pH
40.5	12.15	0.15	70.5	0.0021	2.67
50.0	15.0	3.00	80.0	0.038	1.43
60.0	18.0	6.00	90.0	0.067	1.18

21-7. The equation for the reaction that takes place is



The initial number of millimoles of $\text{HOBr}(aq)$ is given by

$$\text{millimoles of HOBr}(aq) = (0.500 \text{ M})(250.0 \text{ mL}) = 125 \text{ mmol}$$

The number of millimoles of $\text{Sr}(\text{OH})_2(aq)$ required to neutralize the $\text{HOBr}(aq)$ is

$$\text{millimoles of Sr}(\text{OH})_2 = (125 \text{ mmol HOBr}) \left(\frac{1 \text{ mmol Sr}(\text{OH})_2}{2 \text{ mmol HOBr}} \right) = 62.5 \text{ mmol}$$

The volume of $\text{Sr}(\text{OH})_2(aq)$ required is

$$V = \frac{62.5 \text{ mmol}}{0.275 \text{ mmol} \cdot \text{mL}^{-1}} = 227 \text{ mL}$$

At the equivalence point, we have essentially a solution of $\text{BrO}^-(aq)$ with a total volume of $250.0 \text{ mL} + 227 \text{ mL} = 477 \text{ mL}$. The number of millimoles of $\text{BrO}^-(aq)$ is given by

$$\text{millimoles of BrO}^-(aq) = \text{initial millimoles of HOBr}(aq) = 125 \text{ mmol}$$

and its concentration is

$$M = \frac{125 \text{ mmol}}{477 \text{ mL}} = 0.262 \text{ M BrO}^-(aq)$$

Now set up a concentration table

Concentration	$\text{BrO}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HOBr}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.262 M		–		0 M		$\approx 0 \text{ M}$
Change	$-x$		–		$+x$		$+x$
Equilibrium	$0.262 \text{ M} - x$		–		x		x

The equilibrium-constant expression is

$$\frac{x^2}{0.262 \text{ M} - x} = K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14} \text{ M}^2}{2.8 \times 10^{-9} \text{ M}} = 3.6 \times 10^{-6} \text{ M}$$

Solving for x using the method of successive approximations gives $x = 9.7 \times 10^{-4} \text{ M} = [\text{OH}^-]$. The pOH of the solution is 3.01 and the pH of the solution is

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.01 = 10.99$$

21-8. The number of millimoles of $\text{NaOH}(aq)$ added is

$$\text{mmol of NaOH added} = (30.0 \text{ mL})(0.100 \text{ M}) = 3.00 \text{ mmol}$$

The number of millimoles of $\text{CH}_3\text{COOH}(aq)$ in the solution before the addition of $\text{NaOH}(aq)$ is 5.00 millimoles. The number of millimoles of $\text{CH}_3\text{COOH}(aq)$ after the addition of 30.0 mL of 0.100 M $\text{NaOH}(aq)$ is

$$\text{mmol of CH}_3\text{COOH after NaOH addition} = 5.00 \text{ mmol} - 3.00 \text{ mmol} = 2.00 \text{ mmol}$$

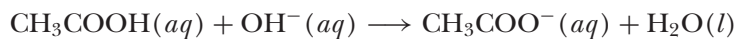
Furthermore,

$$\text{mmol of CH}_3\text{COO}^- \text{ produced} = \text{mmol of NaOH added} = 3.00 \text{ mmol}$$

As in Example 21-8, we can use Equation 21.7 to write

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]_0}{[\text{acid}]_0} = 4.74 + \log \frac{3.00 \text{ mmol}}{2.00 \text{ mmol}} = 4.92$$

21-9. The equation for the reaction is



At the equivalence point, the number of moles of $\text{OH}^-(aq)$ added is equal to the number of moles of acid present or

$$(0.100 \text{ M}) V_{\text{base}} = (0.200 \text{ M})(25.00 \text{ mL})$$

$$V_{\text{base}} = \frac{(0.200 \text{ M})(25.00 \text{ mL})}{0.100 \text{ M}} = 50.0 \text{ mL}$$

Therefore, 5.0 mL of $\text{NaOH}(aq)$ has been added in excess of that needed to reach the equivalence point. The concentration of excess $\text{OH}^-(aq)$ is

$$[\text{OH}^-] = \frac{(0.100 \text{ M})(5.0 \text{ mL})}{25.0 \text{ mL} + 55.0 \text{ mL}} = 6.25 \times 10^{-3} \text{ M}$$

and $\text{pOH} = 2.20$. Thus, $\text{pH} = 14.00 - \text{pOH} = 11.80$.

21-10. The equation for the reaction is

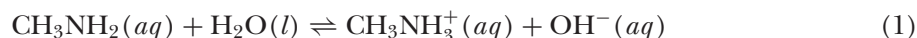


This equation is the reverse of the equation that describes $\text{C}_5\text{H}_5\text{NH}^+(aq)$ acting as an acid. Thus, the equilibrium constant is

$$K = \frac{1}{K_a} = \frac{1}{5.9 \times 10^{-6} \text{ M}} = 1.7 \times 10^5 \text{ M}^{-1}$$

where we have taken the value of K_a from Table 20.6.

21-11. (a) Before the addition of any $\text{HBr}(aq)$, we have a solution containing 100.0 mL of 0.250 M $\text{CH}_3\text{NH}_2(aq)$ that reacts with $\text{H}_2\text{O}(l)$ according to



Now set up a concentration table

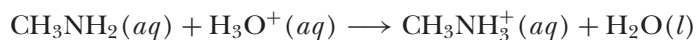
Concentration	$\text{CH}_3\text{NH}_2(aq)$	$+$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{CH}_3\text{NH}_3^+(aq)$	$+$	$\text{OH}^-(aq)$
Initial	0.250 M		—		0 M		$\approx 0 \text{ M}$
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.250 \text{ M} - x$		—		x		x

The equilibrium-constant expression is

$$K_b = \frac{x^2}{0.250 \text{ M} - x} = 4.6 \times 10^{-4} \text{ M}$$

Solving for x using the method of successive approximations gives $x = 0.0105 \text{ M} = [\text{OH}^-]$, so the pOH is 1.98 and the pH is 12.02.

(b) 15.0 mL of 0.500 M HBr(aq) is equivalent to adding 7.50 mmol of HBr(aq). The original solution contained (100.0 mL)(0.250 M) = 25.0 mmol CH₃NH₂(aq). The equation for the reaction is



The value of K_c for this reaction as written is given by

$$K_c = \frac{1}{K_a} = \frac{K_b}{K_w} = 4.6 \times 10^{10} \text{ M}^{-1}$$

Because K_c for this reaction is large, essentially all the HBr(aq) added goes to form CH₃NH₃⁺(aq). Thus, after the addition of the HBr(aq), we have 7.50 mmol of CH₃NH₃⁺(aq) and 25.00 mmol – 7.50 mmol = 17.50 mmol CH₃NH₂(aq) as the principal species in solution. The resulting solution is a buffer, and so we can apply the Henderson-Hasselbalch equation. The pH is

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]_0}{[\text{acid}]_0} = 10.66 + \log \frac{[\text{CH}_3\text{NH}_2]_0}{[\text{CH}_3\text{NH}_3^+]_0} = 10.66 + \log \frac{17.50 \text{ mmol}}{7.50 \text{ mmol}} = 11.03$$

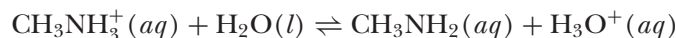
(c) At this point, we have added (25.0 mL)(0.500 M) = 12.50 mmol HBr(aq). Because the original amount of CH₃NH₂(aq) was 25.00 mmol (see part b above), we are at the midpoint of the titration and [CH₃NH₂]₀ = [CH₃NH₃⁺]₀. Because both K_a and K_b are small, we have

$$\text{pH} \approx \text{p}K_a = 10.66$$

(d) At this point, we have added (35.0 mL)(0.500 M) = 17.50 mmol HBr(aq), and so we are slightly past the midpoint along the titration curve. Because the original amount of CH₃NH₂(aq) was 25.00 mmol (see part b above), we have 25.00 mmol – 17.50 mmol = 7.50 mmol CH₃NH₂(aq) and 17.5 mmol of CH₃NH₃⁺(aq). Once again, we apply the Henderson-Hasselbalch equation to obtain

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]_0}{[\text{acid}]_0} = 10.66 + \log \frac{[\text{CH}_3\text{NH}_2]_0}{[\text{CH}_3\text{NH}_3^+]_0} = 10.66 + \log \frac{7.50 \text{ mmol}}{17.50 \text{ mmol}} = 10.29$$

(e) Here we have added (50.0 mL)(0.500 M) = 25.00 mmol of HBr(aq). Because this is equal to the number of millimoles of CH₃NH₂(aq) originally present, we are at the equivalence point of the titration and all the CH₃NH₂(aq) is converted to CH₃NH₃⁺(aq) according to equation 1 above. Thus, we now have a problem involving the solution of the weak acid CH₃NH₃⁺(aq) that dissociates according to the equation



Because the total volume of the solution is 100.0 mL + 50.0 mL = 150.0 mL,

$$[\text{CH}_3\text{NH}_3^+] = \frac{25.00 \text{ mmol}}{150.0 \text{ mL}} = 0.167 \text{ M}$$

Ignoring the autoprotonation reaction of water, the concentration table for this equation is

Concentration	CH ₃ NH ₃ ⁺ (aq)	+ H ₂ O(l)	⇌	CH ₃ NH ₂ (aq)	+ H ₃ O ⁺ (aq)
Initial	0.167 M	–		0 M	≈ 0 M
Change	–x	–		+x	+x
Equilibrium	0.167 M – x	–		x	x

The equilibrium-constant expression is

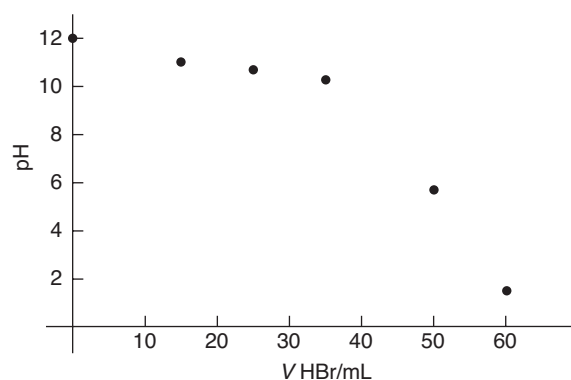
$$K_a = \frac{x^2}{0.167 \text{ M} - x} = 2.2 \times 10^{-11} \text{ M}$$

Solving for x using the method of successive approximations gives $x = 1.9 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$, so the pH is 5.72.

(f) 60.0 mL of 0.500 M $\text{HBr}(aq)$ is equivalent to adding 30.0 mmol of $\text{HBr}(aq)$. Because the original solution contained 25.00 mmol of $\text{CH}_3\text{NH}_2(aq)$, we are now past the equivalence point and have added an excess of $30.00 \text{ mmol} - 25.00 \text{ mmol} = 5.00 \text{ mmol}$ of $\text{HBr}(aq)$. Because the value of K_a for the methylammonium ion is small, we can neglect the $\text{H}_3\text{O}^+(aq)$ coming from the dissociation of the $\text{CH}_3\text{NH}_3^+(aq)$ and write

$$[\text{H}_3\text{O}^+] \approx \frac{5.00 \text{ mmol}}{60.0 \text{ mL} + 100.0 \text{ mL}} = 0.0313$$

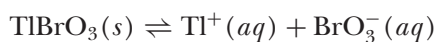
and the pH is 1.51. The titration curve is



An appropriate indicator would be one that changes color around $\text{pH} = 6$: methyl red or bromocresol purple.

CHAPTER 22. Solubility and Precipitation Reactions

22-1. The chemical equation that describes the solubility equilibrium is



The K_{sp} expression is

$$K_{\text{sp}} = [\text{Tl}^+][\text{BrO}_3^-] = 1.1 \times 10^{-4} \text{ M}^2$$

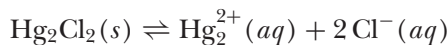
The solubility of $\text{TlBrO}_3(s)$ in pure water, s , is given by $s = [\text{Tl}^+] = [\text{BrO}_3^-]$. Thus,

$$\begin{aligned} K_{\text{sp}} = s^2 &= 1.1 \times 10^{-4} \text{ M}^2 \\ s &= 1.05 \times 10^{-2} \text{ M} \end{aligned}$$

The solubility in grams per liter is

$$\text{solubility} = (1.05 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1})(332.29 \text{ g}\cdot\text{mol}^{-1}) = 3.5 \text{ g}\cdot\text{L}^{-1}$$

22-2. The chemical equation that describes the solubility equilibrium is



Thus, from the equation stoichiometry, the solubility, s , is

$$s = [\text{Hg}_2^{2+}] = \frac{1}{2} [\text{Cl}^-]$$

Substitution into the K_{sp} expression yields

$$K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = (s)(2s)^2 = 1.4 \times 10^{-18} \text{ M}^2$$

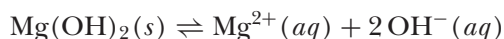
Solving for s yields

$$s = 7.05 \times 10^{-7} \text{ M}$$

The solubility of $\text{Hg}_2\text{Cl}_2(s)$ in grams per liter is

$$s = (7.05 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}) \left(\frac{472.09 \text{ g Hg}_2\text{Cl}_2}{1 \text{ mol Hg}_2\text{Cl}_2} \right) = 3.3 \times 10^{-4} \text{ g}\cdot\text{L}^{-1}$$

22-3. The chemical equation that describes the solubility equilibrium is



Thus, from the equation stoichiometry, the solubility, s , is

$$s = [\text{Mg}^{2+}] = \frac{1}{2} [\text{OH}^-]$$

and

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (s)(2s)^2 = 5.6 \times 10^{-12} \text{ M}^2$$

$$s = 1.12 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 2s = 2.24 \times 10^{-4} \text{ M}$$

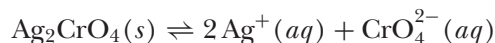
The pOH is

$$\text{pOH} = -\log(2.24 \times 10^{-4}) = 3.65$$

and

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.65 = 10.35$$

22-4. The chemical equation that describes the solubility equilibrium is



$$s = [\text{CrO}_4^{2-}]$$

$$[\text{Ag}^+] = 2s + 0.65 \text{ M}$$

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (0.65 \text{ M} + 2s)^2(s) = 1.1 \times 10^{-12} \text{ M}^3$$

We can neglect $2s$ with respect to 0.65 M to obtain

$$\begin{aligned} s &= 2.60 \times 10^{-12} \text{ M} \\ &= (2.60 \times 10^{-12} \text{ mol}\cdot\text{L}^{-1}) \left(\frac{331.73 \text{ g Ag}_2\text{CrO}_4}{1 \text{ mol Ag}_2\text{CrO}_4} \right) = 8.6 \times 10^{-10} \text{ g}\cdot\text{L}^{-1} \end{aligned}$$

22-5. The sum of the two equations given is



$$K_{\text{c}} = K_{\text{sp}}K_{\text{f}} = (1.8 \times 10^{-10} \text{ M}^2)(2.0 \times 10^7 \text{ M}^{-2}) = 3.6 \times 10^{-3}$$

We set up a concentration table

Concentration	$\text{AgCl}(s)$	$+ 2\text{NH}_3(aq)$	\rightleftharpoons	$[\text{Ag}(\text{NH}_3)_2]^+(aq)$	$+ \text{Cl}^-(aq)$
Initial	—	0.100 M		0 M	0.100 M
Change	—	$-2x$		$+x$	$+x$
Equilibrium	—	$0.100 \text{ M} - 2x$		x	$0.100 \text{ M} + x$

The equilibrium-constant expression is

$$K_c = \frac{x(0.100 \text{ M} + x)}{(0.100 \text{ M} - 2x)^2} = 3.6 \times 10^{-3}$$

Neglecting x with respect to 0.100 M gives

$$x = [\text{Ag}(\text{NH}_3)_2^+] = 3.6 \times 10^{-4} \text{ M}$$

If we ignore $\text{Ag}^+(aq)$ from the solubility product expression, we can say that

$$s = [\text{Ag}(\text{NH}_3)_2^+] = 3.6 \times 10^{-4} \text{ M}$$

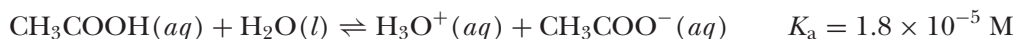
The solubility of AgCl in grams per liter is

$$s = (3.6 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}) \left(\frac{143.32 \text{ g AgCl}}{1 \text{ mol AgCl}} \right) = 0.052 \text{ g}\cdot\text{L}^{-1}$$

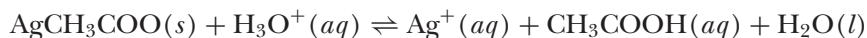
22-6. The relevant reaction equations are



and



Reversing the second equation and adding it to the first equation, we obtain



with

$$K_c = \frac{K_{\text{sp}}}{K_{\text{a}}} = \frac{1.9 \times 10^{-3} \text{ M}^2}{1.8 \times 10^{-5} \text{ M}} = 110 \text{ M}$$

At pH = 4.00, $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-4} \text{ M}$, and so we can set up a concentration table

Concentration	$\text{AgCH}_3\text{COO}(s)$	$+$	$\text{H}_3\text{O}^+(aq)$	\rightleftharpoons	$\text{Ag}^+(aq)$	$+$	$\text{CH}_3\text{COOH}(aq)$	$+$	$\text{H}_2\text{O}(l)$
Initial	—		$1.0 \times 10^{-4} \text{ M}$		0 M		0 M		—
Change	—		none, buffered		$+s$		$+s$		—
Equilibrium	—		$1.0 \times 10^{-4} \text{ M}$		s		s		—

Substituting the equilibrium values into the equilibrium expression, we get

$$K_c = \frac{[\text{Ag}^+][\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^+]} = \frac{s^2}{1.0 \times 10^{-4} \text{ M}} = 110 \text{ M}$$

Taking the positive root, we find that $s = 0.10 \text{ M}$, and so the solubility of $\text{AgCH}_3\text{COO}(s)$ is

$$s = (0.10 \text{ mol}\cdot\text{L}^{-1})(166.9 \text{ g}\cdot\text{mol}^{-1}) = 17 \text{ g}\cdot\text{L}^{-1}$$

22-7. The initial concentrations of $\text{Pb}^{2+}(aq)$ and $\text{I}^-(aq)$ in the 80.0 milliliter mixture of the two solutions are

$$[\text{Pb}^{2+}]_0 = \frac{(0.050 \text{ M})(30.0 \text{ mL})}{80.0 \text{ mL}} = 0.0188 \text{ M}$$

$$[\text{I}^-]_0 = \frac{(0.015 \text{ M})(50.0 \text{ mL})}{80.0 \text{ mL}} = 0.0094 \text{ M}$$

Thus,

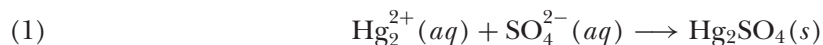
$$Q_{\text{sp}} = [\text{Pb}^{2+}] [\text{I}^-]^2 = (0.0188 \text{ M}) (0.0094 \text{ M})^2 = 1.7 \times 10^{-6} \text{ M}^3$$

and from Table 22.1

$$K_{\text{sp}} = 9.8 \times 10^{-9} \text{ M}^3$$

Because $Q_{\text{sp}} > K_{\text{sp}}$, precipitation will occur.

22-8. The equation for the precipitation reaction is



The number of millimoles of $\text{Hg}_2^{2+} (aq)$ and $\text{SO}_4^{2-} (aq)$ available are

$$\text{millimoles of } \text{Hg}_2^{2+} = (0.025 \text{ M}) (30.0 \text{ mL}) = 0.75 \text{ mmol}$$

$$\text{millimoles of } \text{SO}_4^{2-} = (0.0065 \text{ M}) (20.0 \text{ mL}) = 0.13 \text{ mmol}$$

The corresponding initial concentrations are

$$[\text{Hg}_2^{2+}]_0 = \frac{0.75 \text{ mmol}}{50.0 \text{ mL}} = 0.015 \text{ M}$$

$$[\text{SO}_4^{2-}]_0 = \frac{0.13 \text{ mmol}}{50.0 \text{ mL}} = 0.0026 \text{ M}$$

The reaction quotient for the solubility equilibrium is defined by the reverse of equation (1) as

$$Q_{\text{sp}} = [\text{Hg}_2^{2+}] [\text{SO}_4^{2-}] = (0.015 \text{ M}) (0.0026 \text{ M}) = 3.9 \times 10^{-5} \text{ M}^2$$

and from Table 22.1

$$K_{\text{sp}} = 6.5 \times 10^{-7} \text{ M}^2$$

Because $Q_{\text{sp}} > K_{\text{sp}}$, precipitation will occur. We see that $\text{Hg}_2^{2+} (aq)$ is in excess, and so essentially all the $\text{SO}_4^{2-} (aq)$ precipitates as $\text{Hg}_2\text{SO}_4(s)$. There are 0.13 millimoles of $\text{SO}_4^{2-} (aq)$, and so the mass of the precipitate is

$$\text{mass} = (0.13 \times 10^{-3} \text{ mol Hg}_2\text{SO}_4) \left(\frac{497.25 \text{ g Hg}_2\text{SO}_4}{1 \text{ mol Hg}_2\text{SO}_4} \right) = 0.065 \text{ g}$$

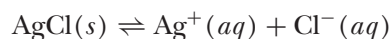
22-9. In order to achieve 99.0% separation, we desire the molarity of either $\text{Cl}^- (aq)$ or $\text{I}^- (aq)$ to be

$$\text{molarity } \text{Cl}^- (aq) = (0.010) (0.225 \text{ M}) = 0.00225 \text{ M}$$

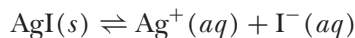
or

$$\text{molarity } \text{I}^- (aq) = (0.010) (0.175 \text{ M}) = 0.00175 \text{ M}$$

The two equations for the solubility of each are



and



The appropriate solubility product expressions are

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10} \text{ M}^2$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-] = 8.5 \times 10^{-17} \text{ M}^2$$

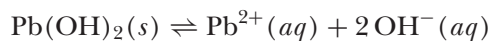
If we use the above values for $[\text{Cl}^-]$ and $[\text{I}^-]$ and solve for $[\text{Ag}^+]$, then

$$[\text{Ag}^+] = \frac{1.8 \times 10^{-10} \text{ M}^2}{0.00225 \text{ M}} = 8.0 \times 10^{-8} \text{ M}$$

$$[\text{Ag}^+] = \frac{8.5 \times 10^{-17} \text{ M}^2}{0.001755 \text{ M}} = 4.8 \times 10^{-14} \text{ M}$$

Thus, $\text{Cl}^-(aq)$ can be separated from $\text{I}^-(aq)$ by adding $\text{Ag}^+(aq)$ at a concentration greater than $4.8 \times 10^{-14} \text{ M}$ but less than $8.0 \times 10^{-8} \text{ M}$.

22-10. The equations for the relevant equilibria are



$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{OH}^-]^2 = 1.4 \times 10^{-20} \text{ M}^3$$

and from Table 22.3



$$K_{\text{f}} = \frac{[\text{Pb}(\text{OH})_3^{-}]}{[\text{OH}^-]} = 0.08$$

The total solubility is given by

$$s = [\text{Pb}(\text{OH})_3^{-}] + [\text{Pb}^{2+}]$$

At $\text{pH} = 14.0$, $[\text{OH}^-] = 1.0 \text{ M}$ and

$$[\text{Pb}^{2+}] = \frac{1.4 \times 10^{-20} \text{ M}^3}{[\text{OH}^-]^2} = \frac{1.4 \times 10^{-20} \text{ M}^3}{1.0 \text{ M}^2} = 1.4 \times 10^{-20} \text{ M}$$

and

$$[\text{Pb}(\text{OH})_3^{-}] = (0.08)[\text{OH}^-] = (0.08)(1.0 \text{ M}) = 0.08 \text{ M}$$

The solubility s is given by

$$s = 0.08 \text{ M} + 1.4 \times 10^{-20} \text{ M} = 0.08 \text{ M}$$

At $\text{pH} = 12.0$, $[\text{OH}^-] = 1.0 \times 10^{-2} \text{ M}$ and

$$s = \frac{1.4 \times 10^{-20} \text{ M}^3}{(1.0 \times 10^{-2} \text{ M})^2} + (0.08)(1.0 \times 10^{-2} \text{ M}) = 8 \times 10^{-4} \text{ M}$$

At pH = 10.0, $[\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$ and

$$s = \frac{1.4 \times 10^{-20} \text{ M}^3}{(1.0 \times 10^{-4} \text{ M})^2} + (0.08)(1.0 \times 10^{-4} \text{ M}) = 8 \times 10^{-6} \text{ M}$$

At pH = 8.0, $[\text{OH}^-] = 1.0 \times 10^{-6} \text{ M}$ and

$$s = \frac{1.4 \times 10^{-20} \text{ M}^3}{(1.0 \times 10^{-6} \text{ M})^2} + (0.08)(1.0 \times 10^{-6} \text{ M}) = 9 \times 10^{-8} \text{ M}$$

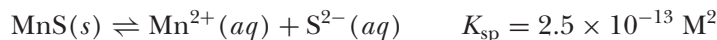
At pH = 6.0, $[\text{OH}^-] = 1.0 \times 10^{-8} \text{ M}$ and

$$s = \frac{1.4 \times 10^{-20} \text{ M}^3}{(1.0 \times 10^{-8} \text{ M})^2} + (0.08)(1.0 \times 10^{-8} \text{ M}) = 1.4 \times 10^{-4} \text{ M}$$

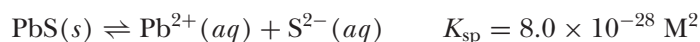
At pH = 4.0, $[\text{OH}^-] = 1.0 \times 10^{-10} \text{ M}$ and

$$s = \frac{1.4 \times 10^{-20} \text{ M}^3}{(1.0 \times 10^{-10} \text{ M})^2} + (0.08)(1.0 \times 10^{-10} \text{ M}) = 1.4 \text{ M}$$

22-11. For $\text{MnS}(s)$, we have that



and for $\text{PbS}(s)$



At pH = 4.0, Equation 22.25 gives

$$[\text{S}^{2-}] = \frac{1.1 \times 10^{-21} \text{ M}^3}{[\text{H}_3\text{O}^+]^2} = \frac{1.1 \times 10^{-21} \text{ M}^3}{(1.0 \times 10^{-4} \text{ M})^2} = 1.1 \times 10^{-13} \text{ M}$$

Thus,

$$[\text{Mn}^{2+}] = \frac{K_{\text{sp}}}{[\text{S}^{2-}]} = \frac{2.5 \times 10^{-13} \text{ M}^2}{1.1 \times 10^{-13} \text{ M}} = 2.3 \text{ M}$$

$$[\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{S}^{2-}]} = \frac{8.0 \times 10^{-28} \text{ M}^2}{1.1 \times 10^{-13} \text{ M}} = 7.3 \times 10^{-15} \text{ M}$$

At pH = 7.0,

$$[\text{S}^{2-}] = \frac{1.1 \times 10^{-21} \text{ M}^3}{(1.0 \times 10^{-7} \text{ M})^2} = 1.1 \times 10^{-7} \text{ M}$$

and

$$[\text{Mn}^{2+}] = \frac{K_{\text{sp}}}{[\text{S}^{2-}]} = \frac{2.5 \times 10^{-13} \text{ M}^2}{1.1 \times 10^{-7} \text{ M}} = 2.3 \times 10^{-6} \text{ M}$$

$$[\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{S}^{2-}]} = \frac{8.0 \times 10^{-28} \text{ M}^2}{1.1 \times 10^{-7} \text{ M}} = 7.3 \times 10^{-21} \text{ M}$$

Reasonable separation can be achieved at pH = 4.0 but not at pH = 7.0.