CHAPTER 11

AQUEOUS EQUILIBRIA

11.1 (a) When solid sodium acetate is added to an acetic acid solution, the

concentration of H_3O^+ decreases because the equilibrium

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

shifts to the left to relieve the stress imposed by the increase of $[C_2H_3O_2^-]$

(Le Chatelier's principle).

(b) When HCl is added to a benzoic acid solution, the percentage of

benzoic acid that is deprotonated decreases because the equilibrium

$$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5CO_2^-(aq)$$

shifts to the left to relieve the stress imposed by the increased $[H_3O^+]$ (Le

Chatelier's principle).

(c) When solid NH_4Cl is added to an ammonia solution, the

concentration of OH^- decreases because the equilibrium

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ shifts to the left to relieve the

stress imposed by the increased $[NH_4^+]$ (Le Chatelier's principle).

Because $[OH^-]$ decreases, $[H_3O^+]$ increases and pH decreases.

11.3 (a) $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$; $pK_a = pH - \log \dfrac{[A^-]}{[HA]}$. If $[A^-] = [HA]$, then

$pK_a = pH.$

$pH = pK_a = 3.08, \quad K_a = 8.3 \times 10^{-4}$

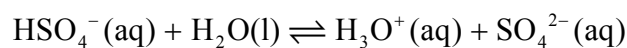(b) Let $x = [\text{lactate ion}] = [L^{-1}]$ and $y = [H_3O^+]$

Concentration

$$(\text{mol} \cdot \text{L}^{-1}) \quad \text{HL(aq)} \quad + \quad \text{H}_2\text{O(l)} \quad \rightleftharpoons \quad \text{H}_3\text{O}^+\text{(aq)} \quad + \quad \text{L}^-\text{(aq)}$$

initial	$2x$	—	—	x
change	$-y$	—	$+y$	$+y$
equilibrium	$2x - y$	—	y	$y + x$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{L}^-]}{[\text{HL}]} = \frac{(y)(y+x)}{(2x-y)} \cong \frac{(y)(x)}{(2x)} = 8.3 \times 10^{-4}$$

$$y = 2(8.3 \times 10^{-4}) \cong 1.7 \times 10^{-3} \; \text{mol} \cdot \text{L}^{-1} \cong [\text{H}_3\text{O}^+]$$

$$\text{pH} \approx 2.77$$

11.5 In each case, the equilibrium involved is

$$\text{HSO}_4^-\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{SO}_4^{2-}\text{(aq)}$$

$\text{HSO}_4^-\text{(aq)}$ and $\text{SO}_4^{2-}\text{(aq)}$ are conjugate acid and base; therefore, the pH calculation is most easily performed with the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = \text{p}K_a + \log\left(\frac{[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}\right)$$

(a) $\text{pH} = 1.92 + \log\left(\dfrac{0.25 \; \text{mol} \cdot \text{L}^{-1}}{0.5 \; \text{mol} \cdot \text{L}^{-1}}\right) = 1.62, \quad \text{pOH} = 14.00 - 1.62 = 12.38$

(b) $\text{pH} = 1.92 + \log\left(\dfrac{0.10 \; \text{mol} \cdot \text{L}^{-1}}{0.50 \; \text{mol} \cdot \text{L}^{-1}}\right) = 1.22, \quad \text{pOH} = 12.78$

(c) $\text{pH} = \text{p}K_a = 1.92, \quad \text{pOH} = 12.08$

See solution to Exercise 11.3.

11.7 $\left(\dfrac{0.356 \; \text{g NaF}}{0.050 \; \text{L}}\right)\left(\dfrac{1 \; \text{mol NaF}}{41.99 \; \text{g NaF}}\right) = 0.17 \; \text{mol} \cdot \text{L}^{-1}$

Concentration

$$(\text{mol} \cdot \text{L}^{-1}) \quad \text{HF(aq)} \quad + \quad \text{H}_2\text{O(l)} \quad \rightleftharpoons \quad \text{H}_3\text{O}^+\text{(aq)} \quad + \quad \text{F}^-\text{(aq)}$$

initial	0.40	—	0	0.17

change $-x$ — $+x$ $+x$

equilibrium $0.40 - x$ — x $0.17 + x$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(0.17 + x)}{(0.40 - x)} \approx \frac{(x)(0.17)}{(0.40)} = 3.5 \times 10^{-4}$$

$$x \cong 8.2 \times 10^{-4} \ \text{mol} \cdot \text{L}^{-1} \cong [H_3O^+]$$

$$pH = -\log[H_3O^+] = -\log(8.2 \times 10^{-4}) = 3.09$$

$$\text{change in pH} = 3.09 - 1.93 = 1.16$$

11.9   (a) $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$

total volume = 100 mL = 0.100 L

moles of HCN = $0.0300 \ \text{L} \times 0.050 \ \text{mol} \cdot \text{L}^{-1} = 1.5 \times 10^{-3}$ mol HCN

moles of NaCN = $0.0700 \ \text{L} \times 0.030 \ \text{mol} \cdot \text{L}^{-1} = 2.1 \times 10^{-3}$ mol NaCN

$$\text{initial } [HCN]_0 = \frac{1.5 \times 10^{-3} \ \text{mol}}{0.100 \ \text{L}} = 1.5 \times 10^{-2} \ \text{mol} \cdot \text{L}^{-1}$$

$$\text{initial } [CN^-]_0 = \frac{2.1 \times 10^{-3} \ \text{mol}}{0.100 \ \text{L}} = 2.1 \times 10^{-2} \ \text{mol} \cdot \text{L}^{-1}$$

Concentration

$(\text{mol} \cdot \text{L}^{-1})$ $HCN(aq)$ + $H_2O(l)$ $\llcorner$ $H_3O^+(aq)$ + $CN^-(aq)$

initial 1.5×10^{-2} —   0 2.1×10^{-2}

change $-x$ — $+x$ $+x$

equilibrium $1.5 \times 10^{-2} - x$ — x $2.1 \times 10^{-2} + x$

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(2.1 \times 10^{-2} + x)}{(1.5 \times 10^{-2} - x)} \approx \frac{(x)(2.1 \times 10^{-2})}{(1.5 \times 10^{-2})} = 4.9 \times 10^{-10}$$

$$x \approx 3.5 \times 10^{-10} \ \text{mol} \cdot \text{L}^{-1} \approx [H_3O^+]$$

$$pH = -\log[H_3O^+] = -\log(3.5 \times 10^{-10}) = 9.46$$

(b) The solution here is the same as for part (a), except for the initial concentrations:

$$[\text{HCN}]_0 = \frac{0.0400 \text{ L} \times 0.030 \text{ mol} \cdot \text{L}^{-1}}{0.100 \text{ L}} = 1.2 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{CN}^-]_0 = \frac{0.0600 \text{ L} \times 0.050 \text{ mol} \cdot \text{L}^{-1}}{0.100 \text{ L}} = 3.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$K_a = 4.9 \times 10^{-10} = \frac{(x)(3.0 \times 10^{-2})}{(1.2 \times 10^{-2})}$$

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

$$\text{pH} = -\log(2.0 \times 10^{-10}) = 9.71$$

(c) $[\text{HCN}]_0 = [\text{NaCN}]_0$ after mixing; therefore,

$$K_a = 4.9 \times 10^{-10} = \frac{(x)[\text{NaCN}]_0}{[\text{HCN}]_0} = x = [\text{H}_3\text{O}^+]$$

$$\text{pH} = \text{p}K_a = -\log(4.9 \times 10^{-10}) = 9.31$$

11.11 In a solution containing HClO(aq) and $\text{ClO}^-\text{(aq)}$, the following equilibrium occurs:

$$\text{HClO(aq)} + \text{H}_2\text{O(l)} \llcorner \text{H}_3\text{O}^+\text{(aq)} + \text{ClO}^-\text{(aq)}$$

The ratio $[\text{ClO}^-]/[\text{HClO}]$ is related to pH, as given by the Henderson-Hasselbalch equation: $\text{pH} = \text{p}K_a + \log\left(\dfrac{[\text{ClO}^-]}{[\text{HClO}]}\right)$, or

$$\log\left(\frac{[\text{ClO}^-]}{[\text{HClO}]}\right) = \text{pH} - \text{p}K_a = 6.50 - 7.53 = -1.03$$

$$\frac{[\text{ClO}^-]}{[\text{HClO}]} = 9.3 \times 10^{-2}$$

11.13 The rule of thumb we use is that the effective range of a buffer is roughly within plus or minus one pH unit of the $\text{p}K_a$ of the acid. Therefore,

(a) $\text{p}K_a = 3.08$; pH range, 2–4

(b) $\text{p}K_a = 4.19$; pH range, 3–5

(c) $pK_{a3} = 12.68$; pH range, 11.5–13.5

(d) $pK_{a2} = 7.21$; pH range, 6–8

(e) $pK_b = 7.97$, $pK_a = 6.03$; pH range, 5–7

11.15 Choose a buffer system in which the conjugate acid has a pK_a close to the desired pH. Therefore,

(a) $HClO_2$ and $NaClO_2$, $pK_a = 2.00$

(b) NaH_2PO_4 and Na_2HPO_4, $pK_{a2} = 7.21$

(c) $CH_2ClCOOH$ and $NaCH_2ClCO_2$, $pK_a = 2.85$

(d) Na_2HPO_4 and Na_3PO_4, $pK_a = 12.68$

11.17 (a) $HCO_3^- (aq) + H_2O(l) \sqsubset CO_3^{2-} (aq) + H_3O^+ (aq)$

$$K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}, \quad pK_{a2} = 10.25$$

$$pH = pK_{a2} + \log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right)$$

$$\log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right) = pH - pK_{a2} = 11.0 - 10.25 = 0.75$$

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = 5.6$$

(b) $[CO_3^{2-}] = 5.6 \times [HCO_3^-] = 5.6 \times 0.100 \text{ mol} \cdot L^{-1} = 0.56 \text{ mol} \cdot L^{-1}$

moles of CO_3^{2-} = moles of $K_2CO_3 = 0.56 \text{ mol} \cdot L^{-1} \times 1 \text{ L} = 0.56 \text{ mol}$

mass of $K_2CO_3 = 0.56 \text{ mol} \times \left(\frac{138.21 \text{ g } K_2CO_3}{1 \text{ mol } K_2CO_3}\right) = 77 \text{ g } K_2CO_3$

(c) $[HCO_3^-] = \frac{[CO_3^{2-}]}{5.6} = \frac{0.100 \text{ mol} \cdot L^{-1}}{5.6} = 1.8 \times 10^{-2} \text{ mol} \cdot L^{-1}$

moles of HCO_3^- = moles of $KHCO_3 = 1.8 \times 10^{-2} \text{ mol} \cdot L^{-1} \times 1 \text{ L}$

$$= 1.8 \times 10^{-2} \text{ mol}$$

mass $KHCO_3 = 1.8 \times 10^{-2}$ mol $\times 100.12$ g·mol$^{-1} = 1.8$ g $KHCO_3$

(d) $[CO_3{}^{2-}] = 5.6 \times [HCO_3{}^{-}]$

moles of

$HCO_3{}^{-}$ = moles $KHCO_3 = 0.100$ mol·L$^{-1} \times 0.100$ L $= 1.00 \times 10^{-2}$ mol.

Because the final total volume is the same for both

$KHCO_3$ and K_2CO_3, the number of moles of K_2CO_3 required is

$5.6 \times 1.00 \times 10^{-2}$ mol $= 5.6 \times 10^{-2}$ mol.

Thus,

volume of K_2CO_3 solution $= \dfrac{5.6 \times 10^{-2}\ \text{mol}}{0.200\ \text{mol·L}^{-1}} = 0.28$ L $= 2.8 \times 10^2$ mL

11.19 (a) $pH = pK_a + \log\left(\dfrac{[CH_3CO_2{}^{-}]}{[CH_3COOH]}\right)$ (see Exercise 11.23)

$pH = pK_a + \log\left(\dfrac{0.100}{0.100}\right) = 4.75$ (initial pH)

final pH: $(0.0100\ \text{L})(0.950\ \text{mol·L}^{-1}) = 9.50 \times 10^{-3}$ mol NaOH (strong

base) produces 9.50×10^{-3} mol $CH_3CO_2{}^{-}$ from CH_3COOH

0.100 mol·L$^{-1} \times 0.100$ L $= 1.00 \times 10^{-2}$ mol CH_3COOH initially
0.100 mol·L$^{-1} \times 0.100$ L $= 1.00 \times 10^{-2}$ mol $CH_3CO_2{}^{-}$ initially

After adding NaOH:

$[CH_3COOH] = \dfrac{(1.00 \times 10^{-2} - 9.5 \times 10^{-3})\ \text{mol}}{0.110\ \text{L}} = 5 \times 10^{-3}$ mol·L^{-1}

$[CH_3CO_2{}^{-}] = \dfrac{(1.00 \times 10^{-2} + 9.5 \times 10^{-3})\ \text{mol}}{0.110\ \text{L}} = 1.77 \times 10^{-1}$ mol·L^{-1}

$pH = 4.75 + \log\left(\dfrac{1.77 \times 10^{-1}\ \text{mol·L}^{-1}}{5 \times 10^{-3}\ \text{mol·L}^{-1}}\right) = 4.75 + 1.5 = 6.3$

(b) $(0.0200\ \text{L})(0.100\ \text{mol·L}^{-1}) = 2.00 \times 10^{-3}$ mol HNO_3 (strong acid)

produces

2.00×10^{-3} mol CH_3COOH from $CH_3CO_2{}^{-}$.
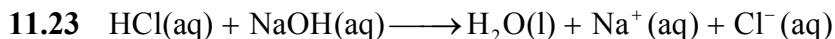
After adding HNO_3 [see part (a) of this exercise]:
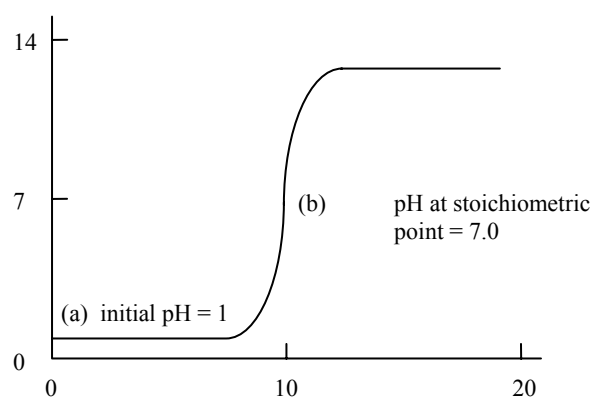
$$[CH_3COOH] = \frac{(1.00 \times 10^{-2} + 2.00 \times 10^{-3}) \text{ mol}}{0.120 \text{ L}} = 1.00 \times 10^{-1} \text{ mol} \cdot L^{-1}$$

$$[CH_3CO_2^{-}] = \frac{(1.00 \times 10^{-2} - 2.00 \times 10^{-3}) \text{ mol}}{0.120 \text{ L}} = 6.7 \times 10^{-2} \text{ mol} \cdot L^{-1}$$

$$pH = 4.75 + \log\left(\frac{6.7 \times 10^{-2} \text{ mol} \cdot L^{-1}}{1.00 \times 10^{-1} \text{ mol} \cdot L^{-1}}\right) = 4.75 - 0.17 = 4.58$$

$$\Delta pH = -0.17$$

11.21

11.23 $HCl(aq) + NaOH(aq) \longrightarrow H_2O(l) + Na^+(aq) + Cl^-(aq)$

(a) $V_{HCl} = (\frac{1}{2})(25.0 \text{ mL})\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)\left(\frac{0.110 \text{ mol NaOH}}{1 \text{ L}}\right)$

$\left(\frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}}\right)\left(\frac{1 \text{ L HCl}}{0.150 \text{ mol HCl}}\right)$

$= 9.17 \times 10^{-3} \text{ L HCl}$

(b) $2 \times 9.17 \times 10^{-3} \text{ L} = 0.0183 \text{ L}$

(c) volume $= (0.0250 + 0.0183) \text{ L} = 0.0433 \text{ L}$

$$[Na^+] = (0.0250 \text{ L})\left(\frac{0.110 \text{ mol NaOH}}{1 \text{ L}}\right)\left(\frac{1 \text{ mol Na}^+}{1 \text{ mol NaOH}}\right)\left(\frac{1}{0.0433 \text{ L}}\right)$$

$$= 0.0635 \text{ mol} \cdot L^{-1}$$

(d) number of moles of H_3O^+ (from acid) $= (0.0200 \text{ L})\left(\dfrac{0.150 \text{ mol}}{1 \text{ L}}\right)$

$$= 3.00 \times 10^{-3} \text{ mol } H_3O^+$$

number of moles of OH^- (from base) $= (0.0250 \text{ L})\left(\dfrac{0.110 \text{ mol Na}^+}{1 \text{ L}}\right)$

$$= 2.75 \times 10^{-3} \text{ mol } OH^-$$

excess $H_3O^+ = (3.00 - 2.75) \times 10^{-3} \text{ mol} = 2.5 \times 10^{-4} \text{ mol } H_3O^+$

$$[H_3O^+] = \dfrac{2.5 \times 10^{-4} \text{ mol}}{0.0450 \text{ L}} = 5.6 \times 10^{-3} \text{ mol} \cdot L^{-1}$$

$$pH = -\log(5.6 \times 10^{-3}) = 2.25$$

11.25 The moles of OH^- added are equivalent to the number of moles of HA present:

$$\left(0.0350 \text{ mol} \cdot L^{-1}\right)\left(0.050 \text{ L}\right) = 0.0182 \text{ mol } OH^-,$$

$\therefore$ 0.0182 mol of HA were present in solution.

$$\text{molar mass} = \dfrac{4.25 \text{ g}}{0.0182 \text{ mol}} = 234 \text{ g} \cdot \text{mol}^{-1}$$

11.27 mass of pure NaOH $= (0.0342 \text{ L HCl})\left(\dfrac{0.0695 \text{ mol HCl}}{1 \text{ L HCl}}\right)$

$$\left(\dfrac{1 \text{ mol NaOH}}{1 \text{ mol HCl}}\right)\left(\dfrac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}}\right)\left(\dfrac{300 \text{ mL}}{25.0 \text{ mL}}\right)$$

$$= 1.14 \text{ g}$$

$$\text{percent purity} = \dfrac{1.14 \text{ g}}{1.592 \text{ g}} \times 100\% = 71.7\%$$

11.29 (a) $pOH = -\log(0.110) = 0.959$, $pH = 14.00 - 0.959 = 13.04$

(b) initial moles of OH^- (from base) $= (0.0250 \text{ L})\left(\dfrac{0.110 \text{ mol}}{1 \text{ L}}\right)$

$$= 2.75 \times 10^{-3} \text{ mol } OH^-$$

$$\text{moles of } H_3O^+ \text{ added} = (0.0050 \text{ L})\left(\frac{0.150 \text{ mol}}{1 \text{ L}}\right) = 7.5 \times 10^{-4} \text{ mol } H_3O^+$$

$$\text{excess } OH^- = (2.75 - 0.75) \times 10^{-3} \text{ mol} = 2.00 \times 10^{-3} \text{ mol } OH^-$$

$$[OH^-] = \frac{2.00 \times 10^{-3} \text{ mol}}{0.030 \text{ L}} = 0.067 \text{ mol} \cdot L^{-1}$$

$$pOH = -\log(0.067) = 1.17, \ pH = 14.00 - 1.17 = 12.83$$

(c) $\text{moles of } H_3O^+ \text{ added} = 2 \times 7.5 \times 10^{-4} \text{ mol} = 1.50 \times 10^{-3} \text{ mol } H_3O^+$

$$\text{excess } OH^- = (2.75 - 1.50) \times 10^{-3} \text{ mol} = 1.25 \times 10^{-3} \text{ mol } OH^-$$

$$[OH^-] = \frac{1.25 \times 10^{-3} \text{ mol}}{0.035 \text{ L}} = 0.036 \text{ mol} \cdot L^{-1}$$

$$pOH = -\log(0.036) = 1.44, \ pH = 14.00 - 1.44 = 12.56$$

(d) $pH = 7.00$

$$V_{HCl} = (2.75 \times 10^{-3} \text{ mol NaOH})\left(\frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}}\right)\left(\frac{1 \text{ L HCl}}{0.150 \text{ mol HCl}}\right)$$
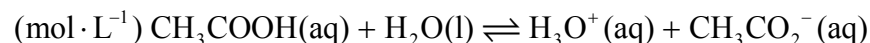
$$= 0.0183 \text{ L}$$

(e) $[H_3O^+] = (0.0050 \text{ L})\left(\frac{0.150 \text{ mol}}{1 \text{ L}}\right)\left(\frac{1}{(0.0250 + 0.0183 + 0.0050) \text{ L}}\right)$

$$= 0.016 \text{ mol} \cdot L^{-1}$$

$$pH = -\log(0.016) = 1.80$$

(f) $[H_3O^+] = \left(\frac{0.010 \text{ L}}{0.0533 \text{ L}}\right)\left(\frac{0.150 \text{ mol}}{1 \text{ L}}\right) = 0.028 \text{ mol} \cdot L^{-1}$

$$pH = -\log(0.028) = 1.55$$

11.31 (a) Concentration

$$(\text{mol} \cdot L^{-1}) \ CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

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

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$x^2 = 1.8 \times 10^{-6}$

$x = 1.3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} = [\text{H}_3\text{O}^+]$

initial pH $= -\log(1.3 \times 10^{-3}) = 2.89$

(b) moles of $\text{CH}_3\text{COOH} = (0.0250 \text{ L})(0.10 \text{ M})$
$$= 2.50 \times 10^{-3} \text{ mol CH}_3\text{COOH}$$

moles of NaOH $= (0.0100 \text{ L})(0.10 \text{ M}) = 1.0 \times 10^{-3} \text{ mol OH}^-$

After neutralization,

$$\frac{1.50 \times 10^{-3} \text{ mol CH}_3\text{COOH}}{0.0350 \text{ L}} = 4.29 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3\text{COOH}$$

$$\frac{1.0 \times 10^{-3} \text{ mol CH}_3\text{CO}_2^-}{0.0350 \text{ L}} = 2.86 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3\text{CO}_2^-$$

Then consider equilibrium, $K_a = \dfrac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2]}{[\text{CH}_3\text{COOH}]}$

Concentration

$(\text{mol} \cdot \text{L}^{-1})$ $\text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{CH}_3\text{CO}_2^-\text{(aq)}$

	CH₃COOH	H₂O	H₃O⁺	CH₃CO₂⁻
initial	4.29×10^{-2}	—	0	2.86×10^{-2}
change	$-x$	—	$+x$	$+x$
equilibrium	$4.29 \times 10^{-2} - x$	—	x	$2.86 \times 10^{-2} + x$

$1.8 \times 10^{-5} = \dfrac{(x)(x + 2.86 \times 10^{-2})}{(4.29 \times 10^{-2} - x)}$; assume $+x$ and $-x$ negligible.

$[\text{H}_3\text{O}^+] = x = 2.7 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ and pH $= -\log(2.7 \times 10^{-5}) = 4.56$
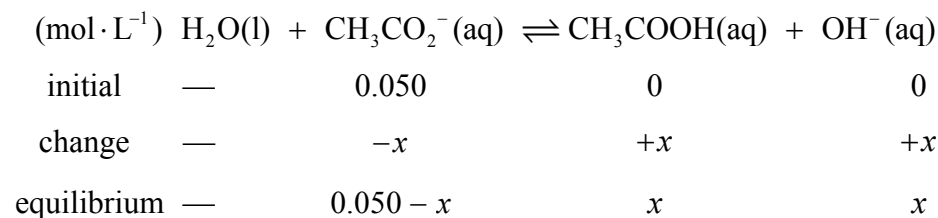
(c) Because acid and base concentrations are equal, their volumes are equal at the stoichiometric point. Therefore, 25.0 mL NaOH is required to reach the stoichiometric point and 12.5 mL NaOH is required to reach the half stoichiometric point.

(d) At the half stoichiometric point, pH $= \text{p}K_a = 4.75$

(e) 25.0 mL; see part (c)

(f) The pH is that of 0.050 M NaCH_3CO_2.

Concentration

$$(mol \cdot L^{-1}) \quad H_2O(l) \;+\; CH_3CO_2^{-}(aq) \;\rightleftharpoons\; CH_3COOH(aq) \;+\; OH^{-}(aq)$$

initial	—	0.050	0	0
change	—	$-x$	$+x$	$+x$
equilibrium	—	$0.050 - x$	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$
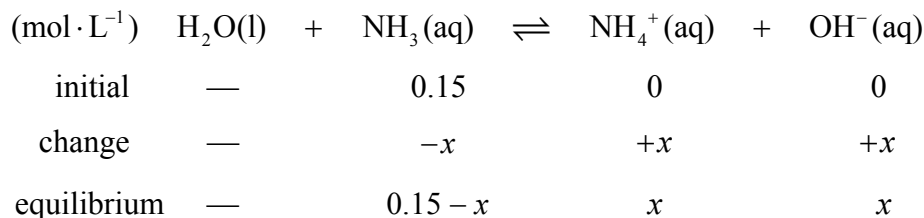
$$x^2 = 2.8 \times 10^{-11}$$

$$x = 5.3 \times 10^{-6} \; mol \cdot L^{-1} = [OH^{-}]$$

$$pOH = 5.28, \; pH = 14.00 - 5.28 = 8.72$$

11.33 (a) $K_b = \dfrac{[NH_4^{+}][OH^{-}]}{[NH_3]} = 1.8 \times 10^{-5}$

Concentration

$$(mol \cdot L^{-1}) \quad H_2O(l) \;+\; NH_3(aq) \;\rightleftharpoons\; NH_4^{+}(aq) \;+\; OH^{-}(aq)$$

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

$$1.8 \times 10^{-5} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$[OH^{-}] = x = 1.6 \times 10^{-3} \; mol \cdot L^{-1}$$

$$pOH = 2.80, \; initial \; pH = 14.00 - 2.80 = 11.20$$

(b) initial moles of

$$NH_3 = (0.0150 \; L)(0.15 \; mol \cdot L^{-1}) = 2.3 \times 10^{-3} \; mol \; NH_3$$

$$moles \; of \; HCl = (0.0150 \; L)(0.10 \; mol \cdot L^{-1}) = 1.5 \times 10^{-3} \; mol \; HCl$$

$$\frac{(2.3 \times 10^{-3} - 1.5 \times 10^{-3}) \; mol \; NH_3}{0.0300 \; L} = 2.7 \times 10^{-2} \; mol \cdot L^{-1} \; NH_3$$

$$\frac{1.5 \times 10^{-3} \; mol \; HCl}{0.0300 \; L} = 5.0 \times 10^{-2} \; mol \cdot L^{-1} \; HCl \approx 5.0 \times 10^{-2} \; mol \cdot L^{-1} \; NH_4^{+}$$

Then consider the equilibrium:

Concentration

$$(mol \cdot L^{-1}) \quad H_2O(l) \quad + \quad NH_3(aq) \quad \rightleftharpoons \quad NH_4^+(aq) \quad + \quad OH^-(aq)$$

initial	—	2.7×10^{-2}	5.0×10^{-2}	0
change	—	$-x$	$+x$	$+x$
equilibrium	—	$2.7 \times 10^{-2} - x$	$5.0 \times 10^{-2} + x$	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

$$= \frac{(x)(5.0 \times 10^{-2} + x)}{(2.7 \times 10^{-2} - x)}; \text{ assume that } +x \text{ and } -x \text{ are negligible}$$

$[OH^-] = x = 9.7 \times 10^{-6} \text{ mol} \cdot L^{-1}$ and $pOH = 5.01$

Therefore, $pH = 14.00 - 5.01 = 8.99$

(c) At the stoichiometric point, moles of NH_3 = moles of HCl

$$\text{volume HCl added} = \frac{(0.15 \text{ mol} \cdot L^{-1} \ NH_3)(0.0150 \text{ L})}{0.10 \text{ mol} \cdot L^{-1} \ HCl} = 0.0225 \text{ L HCl}$$

Therefore, halfway to the stoichiometric point, volume HCl added

$= 22.5/2 = 11.25 \text{ mL}$

(d) At half stoichiometric point, $pOH = pK_b$ and $pOH = 4.75$

Therefore, $pH = 14.00 - 4.75 = 9.25$

(e) 22.5 mL; see part (c)

(f) $NH_4^+(aq) + H_2O(l) \sqsubset H_3O^+(aq) + NH_3(aq)$

The initial moles of NH_3 have now been converted to moles of NH_4^+ in a

$(15 + 22.5 = 37.5)$ mL volume:

$$[NH_4^+] = \frac{2.25 \times 10^{-3} \text{ mol}}{0.0375 \text{ L}} = 0.060 \text{ mol} \cdot L^{-1}$$

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

Concentration

$$(mol \cdot L^{-1}) \quad NH_4^+(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad H_3O^+(aq) \quad + \quad NH_3(aq)$$

initial	0.060	—	0	0
change	$-x$	—	$+x$	$+x$

equilibrium $0.060 - x$ — x x

$$K_a = 5.6 \times 10^{-10} = \frac{x^2}{0.060 - x} \approx \frac{x^2}{0.060}$$

$$x = [H_3O^+] = 5.8 \times 10^{-6} \ mol \cdot L^{-1}$$

$$pH = -\log(5.8 \times 10^{-6}) = 5.24$$

11.35 At the stoichiometric point, the volume of solution will have doubled; therefore, the concentration of $CH_3CO_2^-$ will be 0.10 M. The equilibrium is

Concentration

$(mol \cdot L^{-1})$ $CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons HCH_3CO_2(aq) + OH^-(aq)$

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

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

$$K_b = \frac{[HCH_3CO_2][OH^-]}{[CH_3CO_2^-]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} = 5.6 \times 10^{-10}$$

$$x = 7.5 \times 10^{-6} \ mol \cdot L^{-1} = [OH^-]$$

$$pOH = -\log(7.5 \times 10^{-6}) = 5.12, \ pH = 14.00 - 5.12 = 8.88$$

From Table 11.2, we see that this pH value lies within the range for phenolphthalein, so that indicator would be suitable; the others would not.

11.37 Exercise 11.31: thymol blue or phenolphthalein; Exercise 11.33: methyl red or bromocresol green.

11.39 (a) To reach the first stoichiometric point, we must add enough solution to neutralize one H^+ on the H_3AsO_4. To do this, we will require $0.0750 \ L \times 0.137 \ mol \cdot L^{-1} = 0.0103 \ mol \ OH^-$. The volume of base required will be given by the number of moles of base required, divided by

the concentration of base solution:

$$\frac{0.0750 \text{ L} \times 0.137 \text{ mol} \cdot \text{L}^{-1}}{0.275 \text{ mol} \cdot \text{L}^{-1}} = 0.0374 \text{ L or } 37.4 \text{ mL}$$

(b) and (c) To reach the second stoichiometric point will require double the amount calculated in (a), or 74.8 mL, and the third stoichiometric point will be reached with three times the amount added in (a), or 112 mL.

11.41 (a) The base HPO_3^{2-} is the fully deprotonated form of phosphorous acid H_3PO_3 (the remaining H attached to P is not acidic). It will require an equal number of moles of HNO_3 to react with HPO_3^{2-}, in order to reach the first stoichiometric point (formation of $H_2PO_3^-$). The value will be

given by $\dfrac{0.0355 \text{ L} \times 0.158 \text{ mol} \cdot \text{L}^{-1}}{0.255 \text{ mol} \cdot \text{L}^{-1}} = 0.0220 \text{ L or } 22.0 \text{ mL}$

(b) To reach the second stoichiometric point would require double the amount of solution calculated in (a), or 44.0 mL.

11.43 (a) This value is calculated as described in Example 10.12. First we calculate the molarity of the starting phosphorous acid solution:

$\dfrac{0.122 \text{ g}}{81.99 \text{ g} \cdot \text{mol}^{-1}} \Big/ 0.0500 \text{ L} = 0.0298 \text{ mol} \cdot \text{L}^{-1}$. We then use the first acid

dissociation of phosphorous acid as the dominant equilibrium. The K_{a1} is 1.0×10^{-2}. Let H_2P represent the fully-protonated phosphorus acid.

Concentration

$(\text{mol} \cdot \text{L}^{-1})$	$H_2P(aq)$	$+ H_2O(l)$	$\rightleftharpoons HP^-(aq)$	$+ H_3O^+(aq)$
initial	0.0298	—	0	0
change	$-x$	—	$+x$	$+x$
final	$0.0298 - x$	—	$+x$	$+x$

$$K_a = \frac{[H_3O^+][HP^-]}{[H_2P]} = 1.0 \times 10^{-2}$$

$$1.0 \times 10^{-2} = \frac{x \cdot x}{0.0298 - x} = \frac{x^2}{0.0298 - x}$$

If we assume $x \ll 0.0298,$ then the equation becomes

$$x^2 = (1.0 \times 10^{-2})(0.0298) = 2.98 \times 10^{-4}$$

$$x = 1.73 \times 10^{-2}$$

Because this value is more than 10% of 0.0400, the full quadratic solution should be undertaken. The equation is
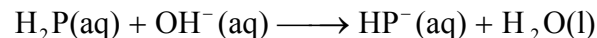
$$x^2 = (1.0 \times 10^{-2})(0.0298 - x) \text{ or}$$

$$x^2 + (1.0 \times 10^{-2} x) - (2.98 \times 10^{-4}) = 0$$

Using the quadratic formula, we obtain $x = 0.013.$

$$pH = 1.89$$

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

$$H_2P(aq) + OH^-(aq) \longrightarrow HP^-(aq) + H_2O(l)$$

moles of $H_2P = (0.0298 \text{ mol} \cdot L^{-1})(0.0500 \text{ L}) = 1.49 \times 10^{-3} \text{ mol}$

moles of $OH^- = (0.00500 \text{ L})(0.175 \text{ mol} \cdot L^{-1}) = 8.76 \times 10^{-4} \text{ mol}$

8.75×10^{-3} mol OH^- will react completely with 1.49×10^{-3} mol H_2P to give 8.75×10^{-3} mol HP^- with 6.1×10^{-4} moles of H_2P remaining.

$$[H_2P] = \frac{6.1 \times 10^{-4} \text{ mol}}{0.0565 \text{ L}} = 0.0109 \text{ mol} \cdot L^{-1}$$

$$[HP^-] = \frac{8.75 \times 10^{-3} \text{ mol}}{0.0565 \text{ L}} = 0.0155 \text{ mol} \cdot L^{-1}$$

Concentration

$(\text{mol} \cdot L^{-1})$	$H_2P(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HP^-(aq)$	+	$H_3O^+(aq)$
initial	0.0109		—		0.0155		0
change	$-x$		—		$+x$		$+x$
final	$0.0109 - x$		—		$0.0155 + x$		$+x$

The calculation is performed as in part (a):

$$1.0 \times 10^{-2} = \frac{(0.0155 + x)x}{0.0109 - x}$$

$$x = 1.08 \times 10^{-2}$$

$$pH = 1.96$$

(c) moles of $H_2P = 1.49 \times 10^{-3}$

moles of $OH^- = 8.75 \times 10^{-4} + 8.75 \times 10^{-4} = 1.75 \times 10^{-3}$

Following the reaction between H_2P and OH^-, 0 mol of H_2P remain and 2.62×10^{-4} mol OH^- remain.

$[OH^-] = 4.37 \times 10^{-3}$ M, $\therefore$ $[H_3O^+] = 2.29 \times 10^{-12}$ M.

1.49×10^{-3} mol of HP^- remain, $[HP^-] = \dfrac{1.49 \times 10^{-3} \text{ mol}}{0.060 \text{ L}} = 2.48 \times 10^{-2}$ M

Concentration

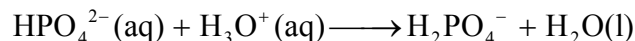| $(mol \cdot L^{-1})$	HP^-	$+$	H_3O^+	$\rightleftharpoons$	H_2P	$+$	H_2O
initial	2.48×10^{-2}		2.29×10^{-12}		0		—
change	$-x$		$-x$		$+x$		—
final	$2.48 \times 10^{-2} - x$		$2.29 \times 10^{-12} - x$		x		—

The calculation is performed as in part (a):

$$100 = \frac{x}{\left(2.48 \times 10^{-2} - x\right)\left(2.29 \times 10^{-12} - x\right)}$$

Using the quadratic equation, we find $x = 5.6 \times 10^{-16}$,

$[H_3O] = 2.29 \times 10^{-12}$, and $pH = -\log(2.29 \times 10^{-12}) = 11.6$

11.45 (a) The reaction of the base Na_2HPO_4 with the strong acid will be taken to completion first:

$$HPO_4{}^{2-}(aq) + H_3O^+(aq) \longrightarrow H_2PO_4{}^- + H_2O(l)$$

Initially, moles of

$HPO_4{}^{2-} =$ moles of $H_3O^+ = 0.0500 \text{ L} \times 0.275 \text{ mol} \cdot L^{-1} = 0.0138$ mol

Because this reaction proceeds with no excess base or acid, we are dealing

with a solution that can be viewed as being composed of $H_2PO_4^-$. The

problem then becomes one of estimating the pH of this solution, which

can be done from the relationship

$pH = \frac{1}{2}(pK_{a1} + pK_{a2})$

$pH = \frac{1}{2}(2.12 + 7.21) = 4.66$

(b) This reaction proceeds as in (a), but there is more strong acid

available, so the excess acid will react with $H_2PO_4^-$ to produce H_3PO_4.

Addition of the first 50.0 mL of acid solution will convert all the HPO_4^{2-}

into $H_2PO_4^-$. The additional 25.0 mL of the strong acid will react with

$H_2PO_4^-$:

$H_2PO_4^-(aq) + H_3O^+(aq) \longrightarrow H_3PO_4(aq) + H_2O(l)$
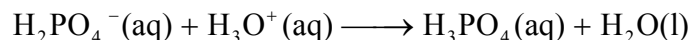
0.0138 mol $H_2PO_4^-$ will react with 0.006 88 mol H_3O^+ to give 0.0069

mol H_3PO_4 with 0.069 mol $H_2PO_4^-$ in excess. The concentrations will

be

$[H_3PO_4] = [H_2PO_4^-] = \dfrac{0.0069 \text{ mol}}{0.125 \text{ L}} = 0.055.$ The appropriate relationship

to use is then

Concentration

$(mol \cdot L^{-1})$	$H_3PO_4(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$H_2PO_4^-(aq)$	$+$	$H_3O^+(aq)$
initial	0.055		—		0.055		0
change	$-x$		—		$+x$		$+x$
final	$0.055 - x$		—		$0.055 + x$		$+x$

$K_{a1} = \dfrac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}$

Because the equilibrium constant is not small compared to 0.055, the full

quadratic solution must be calculated:

$x^2 + 0.055x = 7.6 \times 10^{-3} (0.055 - x)$

$x^2 + 0.063x - 4.2 \times 10^{-4} = 0$

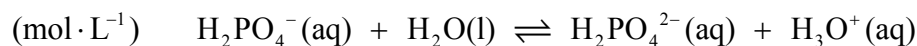$x = 1.6 \times 10^{-3}$

$pH = -\log(1.6 \times 10^{-3}) = 2.80$

(c) The reaction of Na_2HPO_4 with strong acid goes only halfway to completion. 0.275 mol of HPO_4^{2-} will react with

$(0.025 \text{ L} \times 0.275 \text{ mol} \cdot \text{L}^{-1}) = 6.9 \times 10^{-3}$ mol HCl to produce 6.9×10^{-3} mol

$H_2PO_4^-$ and leave 6.9×10^{-3} HPO_4^{2-} unreacted.

6.9×10^{-3} mol $\div$ 0.075 L = 0.092 mol $\cdot$ L^{-1}

Concentration

$(\text{mol} \cdot \text{L}^{-1})$	$H_2PO_4^-$ (aq)	+ H_2O(l)	$\rightleftharpoons$	$H_2PO_4^{2-}$ (aq)	+ H_3O^+ (aq)
intial	0.092	—		0.092	0
change	$-x$	—		$+x$	$+x$
final	$0.092 - x$	—		$0.092 + x$	$+x$

$K_{a2} = 6.2 \times 10^{-8} = \dfrac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]}$

$\dfrac{[0.092 + x][H_3O^+]}{[0.092 - x]} = 6.2 \times 10^{-8}$

assuming $x \ll$ than 0.092

$x = [H_3O^+] = 6.2 \times 10^{-8}$

$pH = -\log(6.2 \times 10^{-8}) = 7.21$

11.47 (a) The solubility equilibrium is $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$.

$[Ag^+] = [Br^-] = 8.8 \times 10^{-7}$ mol $\cdot$ L$^{-1} = S = $ solubility

$K_{sp} = [Ag^+][Br^-] = (8.8 \times 10^{-7})(8.8 \times 10^{-7}) = 7.7 \times 10^{-13}$

(b) The solubility equilibrium is $PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$

$[Pb^{2+}] = 1.3 \times 10^{-7}$ mol $\cdot$ L$^{-1} = S$, $[CrO_4^{2-}] = 1.3 \times 10^{-7}$ mol $\cdot$ L$^{-1} = S$

$K_{sp} = [Pb^{2+}][CrO_4^{2-}] = (1.3 \times 10^{-7})(1.3 \times 10^{-7}) = 1.7 \times 10^{-14}$

(c) The solubility equilibrium is $Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\,OH^-(aq)$

$[Ba^{2+}] = 0.11\,mol \cdot L^{-1} = S, \quad [OH^-] = 0.22\,mol \cdot L^{-1} = 2S$

$K_{sp} = [Ba^{2+}][OH^-]^2 = (0.11)(0.22)^2 = 5.3 \times 10^{-3}$

(d) The solubility equilibrium is $MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,F^-(aq)$

$[Mg^{2+}] = 1.2 \times 10^{-3}\,mol \cdot L^{-1} = S, \quad [F^-] = 2.4 \times 10^{-3}\,mol \cdot L^{-1} = 2S$

$K_{sp} = [Mg^{2+}][F^-]^2 = (1.2 \times 10^{-3})(2.4 \times 10^{-3})^2 = 6.9 \times 10^{-9}$

11.49 (a) Equilibrium equation: $Ag_2S(s) \rightleftharpoons 2\,Ag^+(aq) + S^{2-}(aq)$

$K_{sp} = [Ag^+]^2[S^{2-}] = (2S)^2(S) = 4S^3 = 6.3 \times 10^{-51}$

$S = 1.2 \times 10^{-17}\,mol \cdot L^{-1}$

(b) Equilibrium equation: $CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$

$K_{sp} = [Cu^{2+}][S^{2-}] = S \times S = S^2 = 1.3 \times 10^{-36}$
$S = 1.1 \times 10^{-18}\,mol \cdot L^{-1}$

(c) Equilibrium equation: $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

$K_{sp} = [Ca^{2+}][CO_3^{2-}] = S \times S = S^2 = 8.7 \times 10^{-9}$
$S = 9.3 \times 10^{-5}\,mol \cdot L^{-1}$

11.51 $Tl_2CrO_4(s) \rightleftharpoons 2\,Tl^+(aq) + CrO_4^{2-}(aq)$

$[CrO_4^{2-}] = S = 6.3 \times 10^{-5}\,mol \cdot L^{-1}$
$[Tl^+] = 2S = 2(6.3 \times 10^{-5})\,mol \cdot L^{-1}$
$K_{sp} = [Tl^+]^2[CrO_4^{2-}] = (2S)^2 \times (S)$
$K_{sp} = [2(6.3 \times 10^{-5})]^2 \times (6.3 \times 10^{-5}) = 1.0 \times 10^{-12}$

11.53 (a)

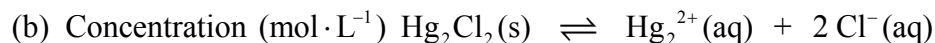| Concentration $(mol \cdot L^{-1})$	$AgCl(s)$	$\rightleftharpoons$	$Ag^+(aq)$	$+$	$Cl^-(aq)$
initial	—		0		0.20
change	—		$+S$		$+S$
equilibrium	—		S		$S + 0.20$

$K_{sp} = [Ag^+][Cl^-] = (S) \times (S + 0.20) = 1.6 \times 10^{-10}$

Assume S in $(S + 0.20)$ is negligible, so $0.20\,S = 1.6 \times 10^{-10}$

$S = 8.0 \times 10^{-10}\ \text{mol} \cdot \text{L}^{-1} = [Ag^+] =$ molar solubility of AgCl in
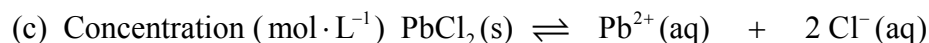
0.15 M NaCl

(b) Concentration $(\text{mol} \cdot \text{L}^{-1})$ $Hg_2Cl_2(s)$ $\rightleftharpoons$ $Hg_2^{2+}(aq)$ + $2\,Cl^-(aq)$

initial	—	0	0.150
change	—	$+S$	$+2S$
equilibrium	—	S	$0.150 + 2S$

$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (S) \times (2S + 0.150)^2 = 1.3 \times 10^{-18}$

Assume $2S$ in $(2S + 0.150)$ is negligible, so $0.150S = 1.3 \times 10^{-18}$

$S = 8.7 \times 10^{-18}\ \text{mol} \cdot \text{L}^{-1} = [Hg_2^{2+}] =$ molar solubility of Hg_2Cl_2

in 0.225 M NaCl

(c) Concentration $(\text{mol} \cdot \text{L}^{-1})$ $PbCl_2(s)$ $\rightleftharpoons$ $Pb^{2+}(aq)$ + $2\,Cl^-(aq)$

initial	—	0	$2 \times 0.025 = 0.05$
change	—	$+S$	$+S$
equilibrium	—	S	$S + 0.05$

$K_{sp} = [Pb^{2+}][Cl^-]^2 = S \times (2S + 0.05)^2 = 1.6 \times 10^{-5}$

S may not be negligible relative to 0.05, so the full cubic form may be required. We do it both ways:

For $S^3 + 0.20\,S^2 + (0.0025 \times 10^{-2}\,S) - (1.6 \times 10^{-5}) = 0,$ the solution by standard methods is $S = 4.6 \times 10^{-3}\ \text{mol} \cdot \text{L}^{-1}$.

If S had been neglected, the answer would have been the same, 4.6×10^{-3}, to within two significant figures.

(d) Concentration $(\text{mol} \cdot \text{L}^{-1})$ $Fe(OH)_2(s)$ $\rightleftharpoons$ $Fe^{2+}(aq)$ + $2\,OH^-(aq)$

initial	—	2.5×10^{-3}	0
change	—	$+S$	$+2S$
equilibrium	—	$2.5 \times 10^{-3} + S$	$2S$

$$K_{sp} = [Fe^{2+}][OH^-]^2 = (S + 2.5 \times 10^{-3}) \times (2S)^2 = 1.6 \times 10^{-14}$$

Assume S in $(S + 2.5 \times 10^{-3})$ is negligible, so

$$4S^2 \times (2.5 \times 10^{-3}) = 1.6 \times 10^{-1}.$$

$$S^2 = 1.6 \times 10^{-12}$$

$S = 1.3 \times 10^{-6}$ mol $\cdot$ L^{-1} = molar solubility of Fe(OH)$_2$ in 2.5×10^{-3} M FeCl$_2$

11.55 (a) $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

Concentration (mol $\cdot$ L^{-1})	Ag$^+$	Cl$^-$
initial	0	1.0×10^{-5}
change	$+x$	0
equilibrium	x	1.0×10^{-5}

$$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10} = (x)(1.0 \times 10^{-5})$$
$$x = [Ag^+] = 1.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

(b) mass AgNO$_3$

$$= \left(\frac{1.6 \times 10^{-5} \text{ mol AgNO}_3}{1 \text{ L}} \right)(0.100 \text{ L})\left(\frac{169.88 \text{ g AgNO}_3}{1 \text{ mol AgNO}_3} \right)\left(\frac{1 \text{ } \mu g}{10^{-6} \text{ g}} \right)$$
$$= 2.7 \times 10^2 \text{ } \mu g \text{ AgNO}_3$$

11.57 (a) $Ni^{2+}(aq) + 2 OH^-(aq) \rightleftharpoons Ni(OH)_2(s)$

Concentration (mol $\cdot$ L^{-1})	Ni^{2+}	OH$^-$
initial	0.060	0
change	0	$+x$
equilibrium	0.060	x

$$K_{sp} = [Ni^{2+}][OH^-]^2 = 6.5 \times 10^{-18} = (0.060)(x)^2$$
$$[OH^-] = x = 1.0 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$$
$$pOH = -\log(1.0 \times 10^{-8}) = 8.00, pH = 14.00 - 8.00 = 6.00$$
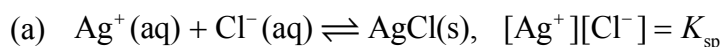
(b) A similar set up for $[Ni^{2+}] = 0.030$ M

gives $x = 1.5 \times 10^{-8}$
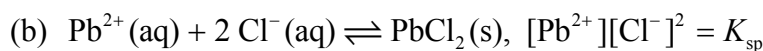
$pOH = -\log(1.5 \times 10^{-8}) = 7.82$

$pH = 14.00 - 7.82 = 6.18$

11.59 $\left(\dfrac{1 \text{ mL}}{20 \text{ drops}}\right) \times 1 \text{ drop} = 0.05 \text{ mL} = 0.05 \times 10^{-3} \text{ L} = 5 \times 10^{-5} \text{ L}$

and $(5 \times 10^{-5} \text{ L})(0.010 \text{ mol} \cdot \text{L}^{-1}) = 5 \times 10^{-7} \text{ mol NaCl} = 5 \times 10^{-7} \text{ mol Cl}^-$

(a) $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s), \quad [Ag^+][Cl^-] = K_{sp}$

$Q_{sp} = \left[\dfrac{(0.010 \text{ L})(0.0040 \text{ mol} \cdot \text{L}^{-1})}{0.010 \text{ L}}\right]\left[\dfrac{5 \times 10^{-7} \text{ mol}}{0.010 \text{ L}}\right] = 2 \times 10^{-7}$

Will precipitate, because $Q_{sp} (2 \times 10^{-7}) > K_{sp} (1.6 \times 10^{-10})$

(b) $Pb^{2+}(aq) + 2 Cl^-(aq) \rightleftharpoons PbCl_2(s), \quad [Pb^{2+}][Cl^-]^2 = K_{sp}$

$Q_{sp} = \left[\dfrac{(0.0100 \text{ L})(0.0040 \text{ mol} \cdot \text{L}^{-1})}{0.010 \text{ L}}\right]\left[\dfrac{5 \times 10^{-7} \text{ mol}}{0.010 \text{ L}}\right]^2 = 1 \times 10^{-11}$

Will not precipitate, because $Q_{sp} (1 \times 10^{-11}) < K_{sp} (1.6 \times 10^{-5})$

11.61 (a) $K_{sp}[Ni(OH)_2] < K_{sp}[Mg(OH)_2] < K_{sp}[Ca(OH)_2]$

This is the order for the solubility products of these hydroxides. Thus, the

order of precipitation is (first to last): $Ni(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$.

(b) $K_{sp}[Ni(OH)_2] = 6.5 \times 10^{-18} = [Ni^{2+}][OH^-]^2$

$[OH^-]^2 = \dfrac{6.5 \times 10^{-18}}{0.0010} = 6.5 \times 10^{-15}$

$[OH^-] = 8.1 \times 10^{-8}$

$pOH = -\log[OH^-] = 7.09 \quad pH \approx 7$

$K_{sp}[Mg(OH)_2] = 1.1 \times 10^{-11} = [Mg^{2+}][OH^-]^2$

$[OH^-] = \sqrt{\dfrac{1.1 \times 10^{-11}}{0.0010}} = 1.0 \times 10^{-4}$

$pOH = -\log(1.0 \times 10^{-4}) = 4.00 \quad pH = 14.00 - 4.00 = 10.00, pH \approx 10$

$K_{sp}[Ca(OH)^2] = 5.5 \times 10^{-6} = [Ca^{2+}][OH^-]^2$

$$[OH^-] = \sqrt{\frac{5.5 \times 10^{-6}}{0.0010}} = 7.4 \times 10^{-2}$$

$$pOH = -\log(7.4 \times 10^{-2}) = 1.13 \quad pH = 14.00 - 1.13 = 12.87, \quad pH \approx 13$$

11.63 The K_{sp} values are

MgF_2	6.4×10^{-9}
BaF_2	1.7×10^{-6}
$MgCO_3$	1.0×10^{-5}
$BaCO_3$	8.1×10^{-9}

The difference in these numbers suggests that there is a greater solubility difference between the carbonates, and thus 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
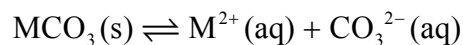
$$MF_2(s) \rightleftharpoons M^{2+}(aq) + 2\ F^-(aq)$$
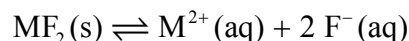
Change $\qquad +x \qquad +2x$

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

Solving this for MgF_2 gives 0.0012 M and for BaF_2 gives 0.0075 M.

For the carbonates:

$$MCO_3(s) \rightleftharpoons M^{2+}(aq) + CO_3^{2-}(aq)$$

$\qquad\qquad\qquad +x \qquad +x$

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

Solving this for $MgCO_3$ gives 0.0032 M and for $BaCO_3$ gives 9.0×10^{-5} M. Clearly, the solubility difference is greatest between the two carbonates, and CO_3^{2-} is the better choice of anion.

11.65 $Cu(IO_3)_2$ ($K_{sp} = 1.4 \times 10^{-7}$) is more soluble than

$Pb(IO_3)_2$ ($K_{sp} = 2.6 \times 10^{-13}$) so Cu^{2+} will remain in solution until

essentially all the $Pb(IO_3)_2$ has precipitated. Thus, we expect very little Pb^{2+} to be the left in solution by the time we reach the point at which $Cu(IO_3)_2$ begins to precipitate.

The concentration of IO_3^- at which Cu^{2+} begins to precipitate will be given by
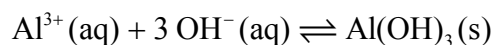
$$K_{sp} = [Cu^{2+}][IO_3^-]^2 = 1.4 \times 10^{-7} = [0.0010][IO_3^-]^2$$
$$[IO_3^-] = 0.012 \ mol \cdot L^{-1}$$

The concentration of Pb in solution when the $[IO_3^-] = 0.012 \ mol \cdot L^{-1}$ is given by

$$K_{sp} = [Pb^{2+}][IO_3^-]^2 = 2.6 \times 10^{-13} = [Pb^{2+}][0.012]^2$$
$$[Pb^{2+}] = 1.8 \times 10^{-9} \ mol \cdot L^{-1}$$

11.67 (a) $pH = 7.0; [OH^-] = 1.0 \times 10^{-7} \ mol \cdot L^{-1}$

$$Al^{3+}(aq) + 3 \ OH^-(aq) \rightleftharpoons Al(OH)_3(s)$$
$$[Al^{3+}][OH^-]^3 = K_{sp} = 1.0 \times 10^{-33}$$
$$S \times (10^{-7})^3 = 1.0 \times 10^{-33}$$
$$S = \frac{1.0 \times 10^{-33}}{1 \times 10^{-21}} = 1.0 \times 10^{-12} \ mol \cdot L^{-1} = [Al^{3+}]$$
$$= \text{molar solubility of } Al(OH)_3 \text{ at } pH = 7.0$$

(b) $pH = 4.5; pOH = 9.5; [OH^-] = 3.2 \times 10^{-10} \ mol \cdot L^{-1}$
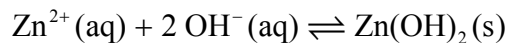
$$[Al^{3+}][OH^-]^3 = K_{sp} = 1.0 \times 10^{-33}$$
$$S \times (3.2 \times 10^{-10})^3 = 1.0 \times 10^{-33}$$
$$S = \frac{1.0 \times 10^{-33}}{3.3 \times 10^{-29}} = 3.1 \times 10^{-5} \ mol \cdot L^{-1} = [Al^{3+}]$$
$$= \text{molar solubility of } Al(OH)_3 \text{ at } pH = 4.5$$

(c) $pH = 7.0; [OH^-] = 1.0 \times 10^{-7} \ mol \cdot L^{-1}$

$$Zn^{2+}(aq) + 2 \ OH^-(aq) \rightleftharpoons Zn(OH)_2(s)$$
$$[Zn^{2+}][OH^-]^2 = K_{sp} = 2.0 \times 10^{-17}$$

$$S \times (1.0 \times 10^{-7})^2 = 2.0 \times 10^{-17}$$

$$S = \frac{2.0 \times 10^{-17}}{1.0 \times 10^{-14}} = 2.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} = [\text{Zn}^{2+}]$$
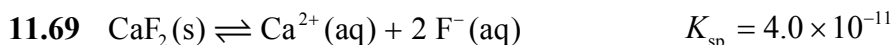
$$= \text{molar solubility of Zn(OH)}_2 \text{ at pH} = 7.0$$

(d) pH = 6.0; pOH = 8.0; $[\text{OH}^-] = 1.0 \times 10^{-8}$ mol · L^{-1}

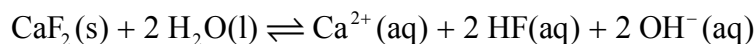$$[\text{Zn}^{2+}][\text{OH}^-]^2 = 2.0 \times 10^{-17} = K_{sp}$$

$$S \times (1.0 \times 10^{-8})^2 = 2.0 \times 10^{-17}$$

$$S = \frac{2.0 \times 10^{-17}}{1.0 \times 10^{-16}} = 2.0 \times 10^{-1} = 0.20 \text{ mol} \cdot \text{L}^{-1} = [\text{Zn}^{2+}]$$

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

11.69 $\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{ F}^-(aq)$ $\qquad K_{sp} = 4.0 \times 10^{-11}$

$\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq)$ $\qquad K_b(\text{F}^-) = 2.9 \times 10^{-11}$

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

$\text{CaF}_2(s) + 2 \text{ H}_2\text{O}(l) \rightleftharpoons \text{Ca}^{2+}(aq) + 2 \text{ HF}(aq) + 2 \text{ OH}^-(aq)$

$K = K_w \cdot K_b^2 = (4.0 \times 10^{-11})(2.9 \times 10^{-11})^2 = 3.4 \times 10^{-32}$

(b) The calculation of K_{sp} is complicated by the fact that the anion of the salt is part of a weak base-acid pair. If we wish to solve the equation algebraically, then we need to consider which equilibrium is the dominant one at pH = 7.0, for which $[\text{H}_3\text{O}^+] = 1 \times 10^{-7}$.

To determine whether F$^-$ or HF is the dominant species at this pH (if either), consider the base hydrolysis reaction:

$\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq)$ $\qquad K_b = 2.9 \times 10^{-11}$
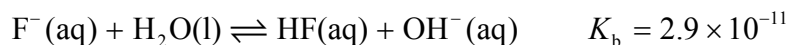
$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$$

$$2.9 \times 10^{-11} = \frac{[\text{HF}][1 \times 10^{-7}]}{[\text{F}^-]}$$

$$\frac{[\text{HF}]}{[\text{F}^-]} = \frac{2.9 \times 10^{-11}}{1 \times 10^{-7}} = 3 \times 10^{-4}$$

Given that the ratio of HF to F^- is on the order of 10^{-4} to 1, the F^- species is still dominant. The appropriate equation to use is thus the original one for the K_{sp} of $CaF_2(s)$:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \quad K_{sp} = 4.0 \times 10^{-11}$$
$$K_{sp} = [Ca^{2+}][F^-]^2$$
$$4.0 \times 10^{-11} = x(2x)^2 = 4x^3$$
$$x = 2.2 \times 10^{-4}$$

molar solubility $= 2.2 \times 10^{-4} \; mol \cdot L^{-1}$

(c) At

$pH = 3.0, [H_3O^+] = 1 \times 10^{-3} \; mol \cdot L^{-1}$ and $[OH^-] = 1 \times 10^{-11} \; mol \cdot L^{-1}$.

Under these conditions

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

$$2.9 \times 10^{-11} = \frac{[HF][1 \times 10^{-11}]}{[F^-]}$$

$$\frac{[HF]}{[F^-]} = \frac{2.9 \times 10^{-11}}{1 \times 10^{-11}} = 3$$

$$[HF] = 3[F^-]$$

As can be seen, at pH 3.0 the amounts of F^- and HF are comparable, so the protonation of F^- to form HF cannot be ignored. The relation $2[Ca^{2+}] = [F^-] + [HF]$ is required by the mass balance as imposed by the stoichiometry of the dissolution equilibrium.

$$2[Ca^{2+}] = [F^-] + 3[F^-]$$
$$2[Ca^{2+}] = 4[F^-]$$
$$[Ca^{2+}] = 2[F^-]$$
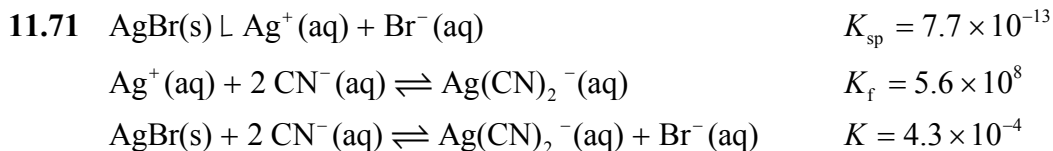
Using this with K_{sp} relationship:

$$(2[F^-])[F^-]^2 = 4.0 \times 10^{-11}$$
$$2[F^-]^3 = 4.0 \times 10^{-11}$$
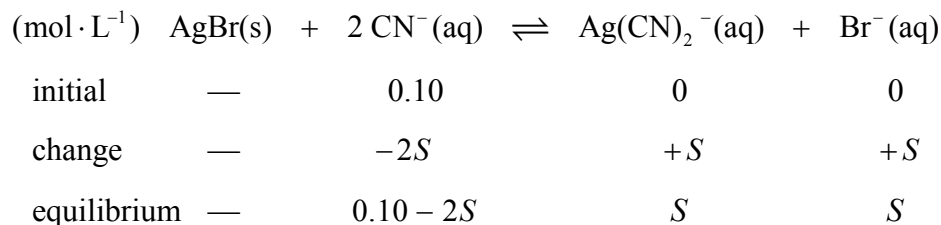$$[F^-] = 2 \times 10^{-4}$$
$$[Ca^{2+}] = (2)(2 \times 10^{-4}) = 4 \times 10^{-4} mol \cdot L^{-1}$$

The solubility is about double that at pH = 7.0.

11.71 $AgBr(s) \sqsubset Ag^+(aq) + Br^-(aq)$ $\qquad\qquad K_{sp} = 7.7 \times 10^{-13}$

$Ag^+(aq) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$ $\qquad\qquad K_f = 5.6 \times 10^8$

$AgBr(s) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) + Br^-(aq)$ $\qquad K = 4.3 \times 10^{-4}$

Hence, $K = \dfrac{[Ag(CN)_2^-][Br^-]}{[CN^-]^2} = 4.3 \times 10^{-4}$

Concentration

(mol·L^{-1})	AgBr(s)	+	2 CN$^-$(aq)	$\rightleftharpoons$	Ag(CN)$_2^-$(aq)	+	Br$^-$(aq)
initial	—		0.10		0		0
change	—		$-2S$		$+S$		$+S$
equilibrium	—		$0.10 - 2S$		S		S

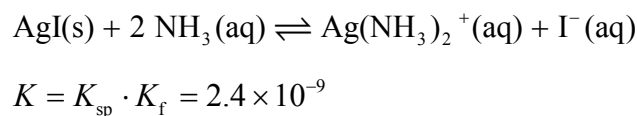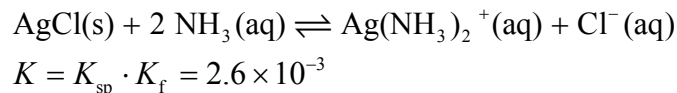$\dfrac{[Ag(CN)_2^-][Br^-]}{[CN^-]^2} = \dfrac{S^2}{(0.10 - 2S)^2} = 4.3 \times 10^{-4}$

$\dfrac{S}{0.10 - 2S} = \sqrt{4.3 \times 10^{-4}} = 2.1 \times 10^{-2}$

$S = (2.1 \times 10^{-3}) - (4.2 \times 10^{-2}\,S)$

$1.042S = 2.1 \times 10^{-3}$

$S = 2.0 \times 10^{-3} \text{ mol·L}^{-1} = \text{molar solubility of AgBr}$

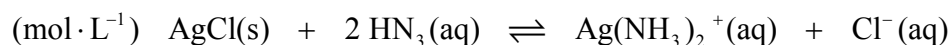**11.73** The two salts can be distinguished by their solubility in NH_3. The equilibria that are pertinent are

$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$
$K = K_{sp} \cdot K_f = 2.6 \times 10^{-3}$

$AgI(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + I^-(aq)$

$K = K_{sp} \cdot K_f = 2.4 \times 10^{-9}$

For example, let's consider the solubility of these two salts in 1.00 M NH_3 solution:

For AgCl $K = \dfrac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = 2.6 \times 10^{-3}$

Concentration

$$(\mathrm{mol \cdot L^{-1}}) \quad \mathrm{AgCl(s)} \ + \ 2\,\mathrm{HN_3(aq)} \ \rightleftharpoons \ \mathrm{Ag(NH_3)_2}{}^+(aq) \ + \ \mathrm{Cl^-(aq)}$$

	AgCl(s)	$2\,\mathrm{HN_3(aq)}$	$\mathrm{Ag(NH_3)_2}{}^+(aq)$	$\mathrm{Cl^-(aq)}$
initial	—	1.00	0	0
change	—	$-2x$	$+x$	$+x$
final	—	$1.00 - 2x$	$+x$	$+x$

$$K = \frac{[\mathrm{Ag(NH_3)_2}{}^+][\mathrm{Cl^-}]}{[\mathrm{NH_3}]^2} = 2.6 \times 10^{-3}$$

$$2.6 \times 10^{-3} = \frac{[x][x]}{[1.00 - 2x]^2} = \frac{x^2}{[1.00 - 2x]^2}$$

$$0.051 = \frac{x}{1.00 - 2x}$$

$$x = 0.046$$

0.046 mol AgCl will dissolve in 1.00 L of aqueous solution. The molar mass of AgCl is

$143.32 \ \mathrm{g \cdot mol^{-1}}$; this corresponds to 0.046

$\mathrm{mol \cdot L^{-1}} \times 142.32 \ \mathrm{g \cdot mol^{-1}} = 6.5 \ \mathrm{g \cdot L^{-1}}$.

For AgI, the same calculation gives $x = 4.9 \times 10^{-5} \ \mathrm{mol \cdot L^{-1}}$. The molar mass of AgI is $234.77 \ \mathrm{g \cdot mol^{-1}}$, giving a solubility of

$4.9 \times 10^{-5} \ \mathrm{mol \cdot L^{-1}} \times 234.77 \ \mathrm{g \cdot mol^{-1}} = 0.023 \ \mathrm{g \cdot L^{-1}}$.

Thus, we could treat a 0.10 g sample of the compound with 20.0 mL of 1.00 M $\mathrm{NH_3}$. The AgCl would all dissolve, whereas practically none of the AgI would.

Note: AgI is also slightly yellow in color, whereas AgCl is white, so an initial distinction could be made based upon the color of the sample.

**11.75** In order to use qualitative analyses, the sample must first be dissolved. This can be accomplished by digesting the sample with concentrated $\mathrm{HNO_3}$ and then diluting the resulting solution. HCl or $\mathrm{H_2SO_4}$ could not be used, because some of the metal compounds formed would be insoluble, whereas all of the nitrates would dissolve. Once the sample is

dissolved and diluted, an aqueous solution containing chloride ions can be introduced. This should precipitate the Ag^+ as AgCl but would leave the bismuth and nickel in solution, as long as the solution was acidic. The remaining solution can then be treated with H_2S. In acidic solution, Bi_2S_3 will precipitate but NiS will not. Once the Bi_2S_3 has been precipitated, the pH of the solution can be raised by addition of base. Once this is done, NiS should precipitate.

11.77 The suggested reaction is:

$$C_6H_5CH_2CH(CH_3)NH_3^+ + H_2O \rightleftharpoons C_6H_5CH_2CH(CH_3)NH_2 + H_3O^+,$$
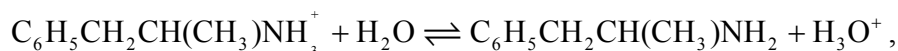
$$pK_a = 10.89$$

$$K_a = 1.288 \times 10^{-11} = \frac{[C_6H_5CH_2CH(CH_3)NH_2][H_3O^+]}{[C_6H_5CH_2CH(CH_3)NH_3^+]}$$

Given a pH of 1.7, $[H_3O^+] = 10^{-1.7} = 0.020$. Substituting this value into the equation above we obtain the ratio:

$$\frac{[C_6H_5CH_2CH(CH_3)NH_2]}{[C_6H_5CH_2CH(CH_3)NH_3^+]} = \frac{1.288 \times 10^{-11}}{0.020} = 6.45 \times 10^{-10}$$

11.79 The relation to use is $pH = pK_a + \log\frac{[\text{Base form}]}{[\text{Acid form}]}$. The K_a value for acetic acid is 1.8×10^{-5} and $pK_a = 4.74$. Because we are adding acid, the pH will fall upon the addition and we want the final pH to be no more than 0.20 pH units different from the initial pH, or 4.54.

$$4.54 = 4.74 + \log\frac{[\text{Base form}]}{[\text{Acid form}]}$$

$$-0.20 = \log\frac{[\text{Base form}]}{[\text{Acid form}]}$$

$$\frac{[\text{Base form}]}{[\text{Acid form}]} = 0.63$$

We want the concentration of the base form to be 0.63 times that of the acid form. We do not know the initial number of moles of base or acid

forms, but we know that the two amounts were equal. Let C = initial number of moles of acetic acid and the initial number of moles of sodium acetate. The number of moles of H_3O^+ to be added (in the form of HCl(aq)) is $0.001\,00\,L \times 6.00\,mol \cdot L^{-1} = 0.006\,00\,mol$. The total final volume will be 0.1010 L.

$$\frac{\dfrac{C - 0.006\,00}{0.1010\,L}}{\dfrac{C + 0.006\,00}{0.1010\,L}} = 0.63$$

$$\frac{C - 0.006\,00}{C + 0.006\,00} = 0.63$$

$$C - 0.006\,00 = 0.63(C + 0.006\,00)$$

$$C - 0.006\,00 = 0.63\,C + 0.003\,78$$

$$0.37\,C = 0.009\,78$$

$$C = 0.026$$

The initial buffer solution must contain at least 0.026 mol acetic acid and 0.026 mol sodium acetate. The concentration of the initial solution will then be $0.026\,mol \div 0.100\,L = 0.260\,M$ in both acetic acid and sodium acetate.

11.81 It stands to reason that if the solution desired has a higher pH than the one available, we should add conjugate base (sodium benzoate). The solution available on the shelf has a [A⁻]/[HA] ratio of:

$$pH = 3.95 = pKa + \log\frac{[A^-]}{[HA]} = 4.19 + \log\frac{[A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{3.95-4.19} = 0.575$$

If $[A^-] = 0.200\,M$ as advertised on the label, then $[HA] = \dfrac{0.200\,M}{0.575} = 0.348\,M$

The desired solution will have a [A⁻]/[HA] ratio of:

$$pH = 4.35 = pKa + \log\frac{[A^-]}{[HA]} = 4.19 + \log\frac{[A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{4.35-4.19} = 1.45$$

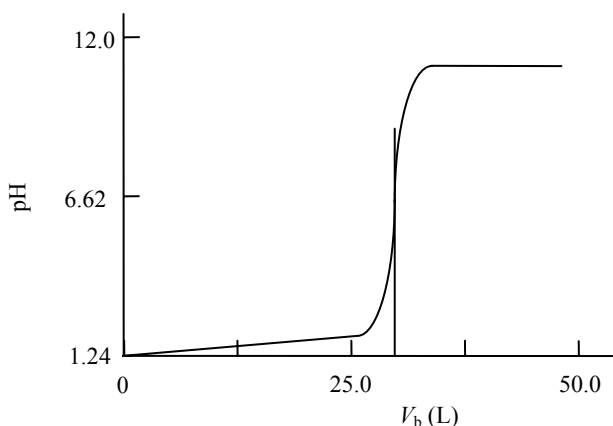To achieve this ratio, we must increase $[A^-]$. Fixing $[HA]$ at 0.348 M, the concentration of $[A^-]$ needed is: $[A^-] = 1.45 \times 0.348$ M $= 0.502$ M.

Therefore, $[A^-]$ needs to increase by: 5.02 M – 0.200 M = 0.302 M.
To determine the number of grams of conjugate base needed:
$$(0.302 \text{ M})(0.100 \text{ L}) = 0.0302 \text{ mol}$$
$$(0.0302 \text{ mol})(144.04 \text{ g} \cdot \text{mol}^{-1}) = 4.35 \text{ g}$$

11.83 (a) $M_a = 0.0567$, $M_b = 0.0296$, $V_a = 15.0$, $V_b = 0.0$ to 50.0

(b) 28.6 mL

(c) 1.24

(d) Because this is a titration of a strong acid with a strong base, the pH at the equivalence point will be 7.00.

11.85 The strong acid, HCl, will protonate the HCO_2^- ion.

moles of HCl $= 0.0040$ L $\times 0.070$ mol $\cdot$ L^{-1} $= 2.8 \times 10^{-4}$ mol HCl (H$^+$)

moles of HCO_2^- $= 0.0600$ L $\times 0.10$ mol $\cdot$ L^{-1} $= 6.0 \times 10^{-3}$ mol HCO_2^-
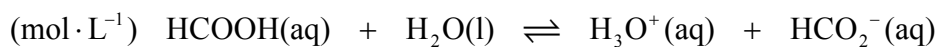
After protonation, there are

$(6.0 - 0.28) \times 10^{-3}$ mol HCO_2^- $= 5.7 \times 10^{-3}$ mol HCO_2^-

and 2.8×10^{-4} mol HCOOH.

$$[HCO_2^-] = \frac{5.7 \times 10^{-3} \text{ mol}}{0.0640 \text{ L}} = 8.9 \times 10^{-2} \text{ mol} \cdot L^{-1}$$

$$[HCOOH] = \frac{2.8 \times 10^{-4} \text{ mol}}{0.0640 \text{ L}} = 4.4 \times 10^{-3} \text{ mol} \cdot L^{-1}$$

Concentration

$(mol \cdot L^{-1})$	$HCOOH(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	$+$	$HCO_2^-(aq)$
initial	4.4×10^{-3}		—		0		8.9×10^{-2}
change	$-x$		—		$+x$		$+x$
equilibrium	$4.4 \times 10^{-3} - x$		—		x		$8.9 \times 10^{-2} + x$

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2^-]}{[HCOOH]} = \frac{(x)(8.9 \times 10^{-2} + x)}{(4.4 \times 10^{-3} - x)}$$

Assume that $+x$ and $-x$ are negligible; so $1.8 \times 10^{-4} = \dfrac{(8.9 \times 10^{-2}) \times (x)}{4.4 \times 10^{-3}}$

$$= 20.2x$$

$$[H_3O^+] = x = 8.9 \times 10^{-6} \text{ mol} \cdot L^{-1}$$
$$[HCOOH] = (4.4 \times 10^{-3}) - (8.9 \times 10^{-6}) \approx 4.4 \times 10^{-3} \text{ mol} \cdot L^{-1}$$
$$pH = -\log(8.9 \times 10^{-6}) = 5.05$$

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

$$K_a = e^{-\Delta G_r / R \cdot T}$$

$$\Delta G_r = -369.31 \text{ kJ} \cdot mol^{-1} - (-396.46 \text{ kJ} \cdot mol^{-1}) = 27.15 \text{ kJ} \cdot mol^{-1}$$

$$= 27150 \text{ J} \cdot mol^{-1}$$

$$K_a = e^{-27150 \text{ J} \cdot mol^{-1} / (8.3145 \text{ J} \cdot K^{-1} \cdot mol^{-1})(298 \text{ K})} = 1.74 \times 10^{-5}$$

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

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

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = 4.8 = 4.76 + \log \frac{[A^-]}{[HA]}$$

$$\frac{[\text{A}^-]}{[\text{HA}]} = 10^{4.8-4.76} = 1.10$$

Given $[\text{HA}] = 1.0$ M, $[\text{A}^-] = 1.10 \times 1.0$ M $= 1.10$ M.

and $(1.10 \text{ M})(2.5 \text{ L})(82.04 \text{ g} \cdot \text{mol}^{-1}) = 225$ g

11.89 Let novocaine $= \text{N}$; $\text{N(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HN}^+\text{(aq)} + \text{OH}^-\text{(aq)}$

$$K_b = \frac{[\text{HN}^+][\text{OH}^-]}{[\text{N}]}$$

$$\text{p}K_a = \text{p}K_w - \text{p}K_b = 14.00 - 5.05 = 8.95$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{N}]}{[\text{HN}^+]}\right)$$

$$\log\left(\frac{[\text{N}]}{[\text{HN}^+]}\right) = \text{pH} - \text{p}K_a = 7.4 - 8.95 = -1.55$$

Therefore, the ratio of the concentrations of novocaine and its conjugate

acid is $[\text{N}]/[\text{HN}^+] = 10^{-1.55} = 2.8 \times 10^{-2}$.

11.91 $\text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{CH}_3\text{CO}_2{}^-\text{(aq)}$

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

$$\text{pH} = \text{p}K_a + \log\frac{[\text{CH}_3\text{CO}_2{}^-]}{[\text{CH}_3\text{COOH}]} = \text{p}K_a + \log\left(\frac{0.50}{0.150}\right)$$

$$= 4.75 + 0.52 = 5.27 \text{ (initial pH)}$$

(a) $(0.0100 \text{ L})(1.2 \text{ mol} \cdot \text{L}^{-1}) = 1.2 \times 10^{-2}$ mol HCl added (a strong acid)

Produces 1.2×10^{-2} mol CH_3COOH from $\text{CH}_3\text{CO}_2{}^-$ after adding HCl:

$$[\text{CH}_3\text{COOH}] = \frac{(0.100 \text{ L})(0.150 \text{ mol} \cdot \text{L}^{-1})}{0.110 \text{ L}} + \frac{1.2 \times 10^{-2} \text{ mol}}{0.110 \text{ L}}$$

$$= 0.245 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{CH}_3\text{CO}_2{}^-] = \frac{(0.100 \text{ L})(0.50 \text{ mol} \cdot \text{L}^{-1})}{0.110 \text{ L}} - \frac{1.2 \times 10^{-2} \text{ mol}}{0.110 \text{ L}}$$
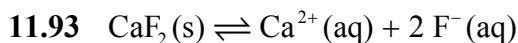
$$= 0.345 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{pH} = 4.75 + \log\left(\frac{0.345}{0.245}\right) = 4.75 + 0.15 = 4.90 \text{ (after adding HCl)}$$

(b) $(0.0500 \text{ L})(0.095 \text{ mol} \cdot \text{L}^{-1}) = 4.7 \times 10^{-3}$ mol NaOH added (a strong base)

Produces 4.7×10^{-3} mol $CH_3CO_2^-$ from CH_3COOH after adding NaOH:

$$[CH_3COOH] = \frac{(0.100 \text{ L})(0.150 \text{ mol} \cdot \text{L}^{-1})}{0.1500 \text{ L}} - \frac{4.7 \times 10^{-3} \text{ mol}}{0.150 \text{ L}}$$
$$= 6.9 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$[CH_3CO_2^-] = \frac{(0.100 \text{ L})(0.50 \text{ mol} \cdot \text{L}^{-1})}{0.150 \text{ L}} + \frac{4.7 \times 10^{-3} \text{ mol}}{0.150 \text{ L}}$$
$$= 3.6 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$$
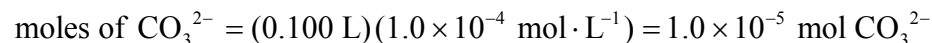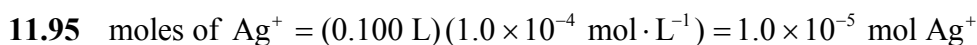
$$\text{pH} = 4.75 + \log\left(\frac{3.6 \times 10^{-1}}{6.9 \times 10^{-2}}\right) = 4.75 + 0.72 = 5.47 \text{ (after adding base)}$$

11.93 $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^-(aq)$

$[Ca^{2+}][F^-]^2 = 4.0 \times 10^{-11}$
$[Ca^{2+}](5 \times 10^{-5})^2 = 4.0 \times 10^{-11}$ $[Ca^{2+}] = 0.016 \text{ mol} \cdot \text{L}^{-1}$

The maximum concentration of $[Ca^{2+}]$ allowed will be $0.016 \text{ mol} \cdot \text{L}^{-1}$.

11.95 moles of $Ag^+ = (0.100 \text{ L})(1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}) = 1.0 \times 10^{-5}$ mol Ag^+

moles of $CO_3^{2-} = (0.100 \text{ L})(1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}) = 1.0 \times 10^{-5}$ mol CO_3^{2-}
$Ag_2CO_3(s) \rightleftharpoons 2\ Ag^+(aq) + CO_3^{2-}(aq)$
$[Ag^+]^2[CO_3^{2-}] = Q_{sp}$
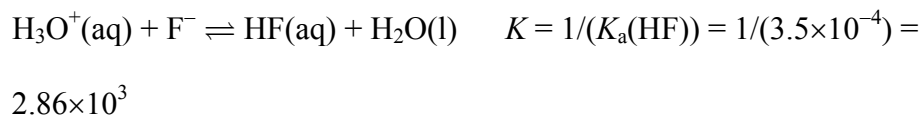$$\left(\frac{1.0 \times 10^{-5}}{0.200}\right)^2\left(\frac{1.0 \times 10^{-5}}{0.200}\right) = 1.3 \times 10^{-13} = Q_{sp}$$

Because Q_{sp} (1.3×10^{-13}) is less than K_{sp} (6.2×10^{-12}), no precipitate will form.

11.97 In addition to the reaction corresponding to the dissolution of $PbF_2(s)$:

$$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ F^-(aq) \qquad K = 3.7 \times 10^{-8}$$
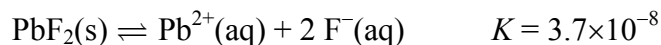
The buffer will provide a source of $H_3O^+(aq)$ ions which will allow the reaction:

$$H_3O^+(aq) + F^- \rightleftharpoons HF(aq) + H_2O(l) \quad K = 1/(K_a(HF)) = 1/(3.5 \times 10^{-4}) =$$

$$2.86 \times 10^3$$

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

$$[F^-]^2[Pb^{2+}] = 1.7 \times 10^{-6} \quad \text{and} \quad \frac{[HF]}{[H_3O^+][F^-]} = 2.86 \times 10^{-3}$$

Given that all fluoride ions come from $PbF_2(s)$ and wind up as either $F^-(aq)$ or $HF(aq)$, and that for every one mole of $Pb^{2+}(aq)$ generated two moles of $F^-(aq)$ are also produced, we can write a third equation which relates the concentration of the fluoride containing species to the concentration of dissolved barium:

$$[Pb^{2+}] = \tfrac{1}{2}([F^-] + [HF]) .$$

In the end, the concentration of $Pb^{2+}(aq)$ will be equal to the solubility of $PbF_2(s)$. To determine the equilibrium concentration of $Pb^{2+}(aq)$, we first determine $[H_3O^+]$, which is fixed by the buffer system, and then use the three simultaneous equations above to solve for $[Pb^{2+}]_{eq}$.

The buffer determines the equilibrium concentration of $H_3O^+(aq)$. The initial concentration of $H_3O^+(aq)$ and $NaCH_3CO_2(aq)$ are:

$$[H_3O^+]_i = \frac{(0.055\ \text{L})(0.15\ \text{mol} \cdot \text{L}^{-1})}{0.10\ \text{L}} = 0.0825\ \text{M} \quad \text{and}$$

$$[CH_3CO_2^-]_i = \frac{(0.045\ \text{L})(0.65\ \text{mol} \cdot \text{L}^{-1})}{0.10\ \text{L}} = 0.293\ \text{M}.$$

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

Concentration

$$(\text{mol} \cdot \text{L}^{-1}) \quad CH_3COOH(aq) \ + \ H_2O(l) \ \rightleftharpoons \ H_3O^+(aq) \ + \ CH_3CO_2^-(aq)$$

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

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3COOH]} = \frac{(0.0825 - x)(0.292 - x)}{(x)}$$

Rearranging this expression we obtain:

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

Using the quadratic formula we find $x = 0.082493$, and $[H_3O^+] = 7.1 \times 10^{-6}$ M

With this equilibrium concentration of H_3O^+(aq) we revisit the three simultaneous equations from above, namely

$$[F^-]^2[Pb] = 3.7 \times 10^{-8};$$

$$[Pb^{2+}] = \tfrac{1}{2}\left([F^-] + [HF]\right); \text{ and}$$

$$\frac{[HF]}{[H_3O^+][F^-]} = 2.86 \times 10^{-3}.$$

Due to the presence of the buffer, $[H_3O^+] = 7.1 \times 10^{-6}$ and this last equation simplifies to

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

Rearranging these three simultaneous equations we find:

$$[Pb^{2+}] = \frac{3.7 \times 10^{-8}}{[F^-]^2}, \quad [HF] = [F^-] \times \left(2.03 \times 10^{-2}\right), \quad \text{and}$$

$$[Pb^{2+}] = \tfrac{1}{2}\left([F^-] + [HF]\right)$$

$$\frac{3.7 \times 10^{-8}}{[F^-]^2} = \tfrac{1}{2}\left[[F^-] + \left([F^-] \times \left(2.03 \times 10^{-2}\right)\right)\right]. \quad \text{Solving this expression for } [F^-]:$$

$$[F^-] = \sqrt[3]{\frac{3.7 \times 10^{-8}}{0.5203}} = 4.14 \times 10^{-3}.$$

The equilibrium concentration of $Pb^{2+}(aq)$ is then:
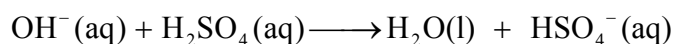
$$[Pb^{2+}] = \frac{3.7 \times 10^{-8}}{[F^-]^2} = \frac{3.7 \times 10^{-8}}{(4.14 \times 10^{-3})^2} = 2.16 \times 10^{-3} \text{ M}$$

Therefore, the solubility of $PbF_2(s)$ is 2.2×10^{-3} M

11.99 The K_{sp} values from Tables 11.5 and 11.7 are

$Cu^{2+}, 1.3 \times 10^{-36}; Co^{2+}, 5 \times 10^{-22}; \quad Cd^{2+}, 4 \times 10^{-29}$. All the salts have the

same expression for K_{sp}, $K_{sp} = [M^{2+}][S^{2-}]$, so the compound with the

smallest K_{sp} will precipitate first, in this case CuS.

11.101 (1) first stoichiometric point:

$$OH^-(aq) + H_2SO_4(aq) \longrightarrow H_2O(l) + HSO_4^-(aq)$$

Then, because the volume of the solution has doubled, $[HSO_4^-] = 0.10$ M,

Concentration

$(mol \cdot L^{-1})$	$HSO_4^-(aq) + H_2O(l)$	$\rightleftharpoons SO_4^{2-}(aq)$	$+ H_3O^+(aq)$
initial	0.10 —	0	0
change	$-x$ —	$+x$	$+x$
equilibrium	$0.10 - x$ —	x	x

$$K_{a2} = 0.012 = \frac{x^2}{0.10 - x}$$

$$0.0012 - 0.012x = x^2$$

$$x^2 + 0.012x - 0.0012 = 0$$

$$x = \frac{-0.012 + \sqrt{(0.012)^2 + (4)(0.0012)}}{2}$$

$$x = [H_3O^+] = 0.029 \text{ mol} \cdot L^{-1}$$

$$pH = -\log(0.029) = 1.54$$

(2) second stoichiometric point:

$HSO_4^-(aq) + OH^-(aq) \longrightarrow SO_4^{2-}(aq) + H_2O(l)$. Because the volume of

the solution has increased by an equal amount,

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Concentration

$(mol \cdot L^{-1})$	$SO_4^{2-}(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$HSO_4^{-}(aq)$	$+$	$OH^-(aq)$
initial	0.067		—		0		1×10^{-7}
change	$-x$		—		$+x$		$+x$
equilibrium	$0.067 - x$		—		x		$1 \times 10^{-7} + x$

$$K_b = 8.3 \times 10^{-3} = \frac{(x)(1 \times 10^{-7} + x)}{0.067 - x}$$

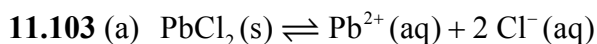$$(5.6 \times 10^{-14}) - (8.3 \times 10^{-13} x) = 1 \times 10^{-7} x + x^2$$

$$x^2 + (1 \times 10^{-7} x) - (5.6 \times 10^{-14}) = 0$$

$$x = \frac{-1 \times 10^{-7} + \sqrt{(1 \times 10^{-7})^2 + (4)(5.6 \times 10^{-14})}}{2}$$

$$x = [HSO_4^{-}] = 1.9 \times 10^{-7} mol \cdot L^{-1}$$

$$[OH^-] = (1.0 \times 10^{-7}) + (1.9 \times 10^{-7}) = 2.9 \times 10^{-7} mol \cdot L^{-1}$$

$$pOH = -\log(2.9 \times 10^{-7}) = 6.54, \ pH = 14.00 - 6.54 = 7.46$$

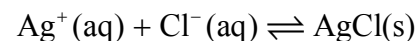**11.103** (a) $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$

$$[Pb^{2+}][Cl^-]^2 = K_{sp} = 1.6 \times 10^{-5}$$

$$[0.010][Cl^-]^2 = 1.6 \times 10^{-5}$$

$$[Cl^-]^2 = 1.6 \times 10^{-3}$$

$[Cl^-] = 4.0 \times 10^{-2} \ mol \cdot L^{-1}$; will precipitate lead (II) ion

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

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

$$[0.010][Cl^-] = 1.6 \times 10^{-10}$$

$[Cl^-] = 1.6 \times 10^{-8} \ mol \cdot L^{-1}$; will precipitate Ag^+

(b) From part (a), Ag^+ will precipitate first.

(c) $[Ag^+](4.0 \times 10^{-2}) = 1.6 \times 10^{-10}$

$$[Ag^+] = \frac{1.6 \times 10^{-10}}{4.0 \times 10^{-2}} = 4.0 \times 10^{-9} \ mol \cdot L^{-1}$$

(d) percentage Ag^+ remaining $= \dfrac{4.0 \times 10^{-9}}{0.010} \times 10^2 = 4.0 \times 10^{-5}$ %

unprecipitated; virtually 100% of the first cation (Ag^+) is precipitated

11.105 The K_{sp} value for PbF_2 obtained from Table 11.5 is 3.7×10^{-8}. Using this value, the $\Delta G°$ of the dissolution reaction can be obtained from

$\Delta G° = -RT \ln K$.

$\Delta G° = -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.2 \text{ K}) \ln (3.7 \times 10^{-8})$

$\Delta G° = +42.43 \text{ kJ} \cdot \text{mol}^{-1}$

From the Appendices we find that $\Delta G°_f (F^-, aq) = -278.79 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta G°_f (Pb^{2+}, aq) = -24.43 \text{ kJ} \cdot \text{mol}^{-1}$.
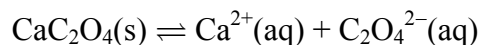
$\Delta G° = +42.43 \text{ kJ} \cdot \text{mol}^{-1} = \Delta G°_f (Pb^{2+}, aq) + \Delta G°_f (F^-, aq) - \Delta G°_f (PbF_2, s)$

$\quad +42.43 \text{ kJ} \cdot \text{mol}^{-1} = (-24.43 \text{ kJ} \cdot \text{mol}^{-1}) + (-278.79 \text{ kJ} \cdot \text{mol}^{-1})$

$- \Delta G°_f (PbF_2, s)$

$\Delta G°_f (PbF_2, s) = -345.65 \text{ kJ} \cdot \text{mol}^{-1}$

11.107 (a) The dissolution reaction for calcium oxalate is:

$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$

$K_{sp} = 10^{-pK_{sp}} = 10^{-8.59} = 2.57 \times 10^{-9}$

The concentration of each ion at equilibrium is equal to the molar solubility, s. Therefore,

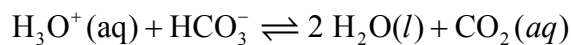$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = s \times s = 2.57 \times 10^{-9}$, and $s = 5.07 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$.

(b) Given $[Mg^{2+}] = 0.020$ M and $[C_2O_4^{2-}] = 0.035$ M:

$Q_{sp} = [Mg^{2+}][C_2O_4^{2-}] = (0.020)(0.035) = 7 \times 10^{-4}$

Q_{sp} is significantly less than K_{sp}, which is given as $10^{-4.07} = 8.51 \times 10^{-5}$, indicating that a precipitate will form.

11.109 (a) The amount of CO_2 present at equilibrium may be found using the equilibrium expression for the reaction of interest:

$$H_3O^+(aq) + HCO_3^- \rightleftharpoons 2\, H_2O(l) + CO_2(aq)$$

$$K = 7.9 \times 10^{-7} = \frac{[CO_2]}{[H_3O^+][HCO_3^-]}$$

Solving for $[CO_2]$:

$$[CO_2] = (7.9 \times 10^{-7})[H_3O^+][HCO_3^-]$$

Given: $[H_3O^+] = 10^{-6.1} = 7.9 \times 10^{-7}$ M, and $[HCO_3^-] = 5.5\ \mu mol \cdot L^{-1} = 5.5 \times 10^{-6}$ M

$$[CO_2] = (7.9 \times 10^{-7})(7.9 \times 10^{-7})(5.5 \times 10^{-6}) = 3.5 \times 10^{-18}\, mol \cdot L^{-1}$$

In 1.0 L of solution there will be 3.5×10^{-18} mol of CO_2 (aq)

(b) Adding 0.65×10^{-6} mol of H_3O^+(aq) to the equilibrium system in (a)

will give an initial $[H_3O^+]$ of 1.44×10^{-6} M. To determine the equilibrium

concentration of H_3O^+(aq) we set up the familiar problem:

Concentration

$(mol \cdot L^{-1})$	$H_3O^+(aq)$	$+$	$HCO_3^-(l)$	$\rightleftharpoons$	$2\, H_2O(l)$	$+$	$CO_2(aq)$
initial	1.44×10^{-6}		5.5×10^{-6}		—		3.45×10^{-18}
change	$-x$		$-x$		—		$+x$
equilibrium	$1.44 \times 10^{-6} - x$		$5.5 \times 10^{-6} - x$		—		$3.45 \times 10^{-18} + x$

$$K = 7.9 \times 10^{-7} = \frac{3.45 \times 10^{-18} + x}{\left(1.44 \times 10^{-6} - x\right)\left(5.5 \times 10^{-6} + x\right)}$$

Rearranging to obtain a polynomial in x:

$$2.83 \times 10^{-18} - x + 7.9 \times 10^{-7} x^2 = 0$$

Using the quadratic forumla one finds:

$$x = 2.825 \times 10^{-18}$$

Giving: $[H_3O^+] = 1.4 \times 10^{-6}$, and pH $= 5.8$. The same pH as the initial solution.