forms a precipitate with one of the dissolved cations but not the others. The appropriate reagent must form compounds with both metal cations with sufficiently different $K_{sp}$ values (a difference of a factor of at least $10^3$), so that one compound will remains dissolved while the other compound significantly precipitates.

16.25    Qualitative analysis is a systematic way to determine the metal ions present in an unknown solution by the selective precipitation of the ions. The word qualitative means involving quality or kind. So qualitative analysis involves finding the kind of ions present in the solution. Quantitative analysis is concerned with quantity, or the amounts of substances in a solution or mixture.

16.26    A general qualitative analysis scheme involves separating a mixture of the common ions into five groups by sequentially adding five different precipitating agents. After each precipitating agent is added, the mixture is put into a centrifuge to separate the solid from the liquid. The liquid is decanted for the next step, and the solid is set aside for subsequent analysis. Group I removes insoluble chlorides by treating the solution with dilute HCl. Since most chlorides are soluble, the chloride ions do not form a precipitate with the majority of the cations in mixture. However, $Ag^+$, $Pb^{2+}$, and $Hg_2^{2+}$ do form insoluble chlorides and will precipitate out. The absence of a precipitate constitutes a negative test for $Ag^+$, $Pb^{2+}$, and $Hg_2^{2+}$. After the solid is separated from the liquid, the solution is ready for the next step, where Group II, acid-insoluble sulfides are removed. This is accomplished by taking the aqueous mixture containing the remaining metal cations and treating it with $H_2S$, a weak diprotic acid that dissociates to form sulfide ions, $S^{2-}$. Since the solution is acidic from the first treatment, only the acid-insoluble sulfide metals will precipitate out. These include $Hg^{2+}$, $Cd^{2+}$, $Bi^{3+}$, $Cu^{2+}$, $Sn^{4+}$, $As^{3+}$, and $Sb^{3+}$. If any of these metal cations are present, they precipitate out as sulfides. After the solid is separated from the liquid, the solution is ready for the next step. In the third step, Group III, the base-insoluble sulfides and hydroxides, are removed by taking the acidic aqueous mixture containing the remaining metal cations and treating it with a base and additional $H_2S$. The added base reacts with acid, shifting the $H_2S$ ionization equilibria to the right and creating a higher $S^{2-}$ concentration. This causes the precipitation of those sulfides that were too soluble to precipitate out in the previous step, but not soluble enough to prevent precipitation with the higher sulfide ion concentration. The ions that precipitate as sulfides at this point (if they are present) are $Co^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Ni^{2+}$, and $Fe^{2+}$. In addition, the basic solution causes $Cr^{3+}$ and $Al^{3+}$ to precipitate as hydroxides. After the solid is separated from the liquid, the solution is ready for the next step, removing the Group IV, insoluble carbonate, metal ions. At this stage, all of the cations have been precipitated except those belonging to the alkali metal family (group 1A in the periodic table) and the alkaline earth metal family (group 2A in the periodic table). The alkaline earth metal cations can be precipitated by adding sodium carbonate to the solution. The carbonate ion precipitates $Mg^{2+}$, $Ca^{2+}$, and $Ba^{2+}$ as metal carbonates, which are separated from the liquid. The only dissolved ions belong to Group V, the alkali metals and $NH_4^+$. The liquid decanted from the previous step can now contain are $Na^+$, $K^+$, and $NH_4^+$. These cations do not form insoluble compounds with any anions and cannot be precipitated from the solution. Their presence can be tested by other means. Sodium and potassium ions, for example, are usually identified through flame tests. The sodium ion produces a yellow-orange flame and the potassium ion produces a violet flame. By applying the previous procedure, nearly two dozen metal cations can be separated from a solution initially containing all of them. Each of the groups can then be further analyzed to determine the specific ions present from that group.
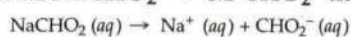
## The Common Ion Effect and Buffers

16.27    The only solution that $HNO_2$ will ionize less in is d) 0.10 M $NaNO_2$. It is the only solution that generates a common ion $NO_2^-$ with nitrous acid.

16.28    Formic acid is $HCHO_2$ which dissociates to $H^+$ and $CHO_2^-$. The only solution that generates a common ion ($CHO_2^-$) with formic acid is (c) $NaCHO_2$.

16.29    (a)    **Given:** 0.20 M $HCHO_2$ and 0.15 M $NaCHO_2$ **Find:** pH **Other:** $K_a$ ($HCHO_2$) = $1.8 \times 10^{-4}$
          **Conceptual Plan: M NaCHO$_2$ → M CHO$_2^-$ then M HCHO$_2$, M CHO$_2^-$ → [H$_3$O$^+$] → pH**
                    $NaCHO_2\ (aq) \rightarrow Na^+\ (aq) + CHO_2^-\ (aq)$                    $ICE\ Chart$      pH = $- \log [H_3O^+]$
          **Solution:** Since 1 $CHO_2^-$ ion is generated for each $NaCHO_2$, [$CHO_2^-$] = 0.15 M $CHO_2^-$.

$$HCHO_2 \,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CHO_2^-\,(aq)$$

| | $[HCHO_2]$ | $[H_3O^+]$ | $[CHO_2^-]$ |
|---|---|---|---|
| Initial | 0.20 | $\approx 0.00$ | 0.15 |
| Change | $-x$ | $+x$ | $+x$ |
| Equil | $0.20 - x$ | $+x$ | $0.15 + x$ |

$K_a = \dfrac{[H_3O^+]\,[CHO_2^-]}{[HCHO_2]} = 1.8 \times 10^{-4} = \dfrac{x(0.15 + x)}{0.20 - x}$ Assume $x$ is small ($x << 0.15 < 0.20$) so

$\dfrac{x(0.15 + x)}{0.20 - x} = 1.8 \times 10^{-4} = \dfrac{x(0.15)}{0.20}$ and $x = 2.4 \times 10^{-4}\,M = [H_3O^+]$. Confirm that the more stringent assumption is valid.
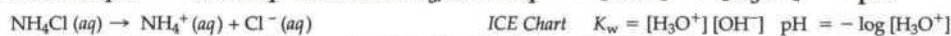
$\dfrac{2.4 \times 10^{-4}}{0.15} \times 100\% = 0.16\%$ so assumption is valid. Finally,

$pH = -\log[H_3O^+] = -\log(2.4 \times 10^{-4}) = 3.62$

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH should be greater than $-\log(0.20) = 0.70$ because this is a weak acid and there is a common ion effect.

(b)    **Given:** 0.16 M $NH_3$ and 0.22 M $NH_4Cl$ **Find:** pH **Other:** $K_b\,(NH_3) = 1.79 \times 10^{-5}$

**Conceptual Plan:** M $NH_4Cl \rightarrow$ M $NH_4^+$ then M $NH_3$, M $NH_4^+ \rightarrow [OH^-] \rightarrow [H_3O^+] \rightarrow$ pH

     $NH_4Cl\,(aq) \rightarrow NH_4^+\,(aq) + Cl^-\,(aq)$      ICE Chart    $K_w = [H_3O^+]\,[OH^-]$   pH $= -\log[H_3O^+]$

**Solution:** Since 1 $NH_4^+$ ion is generated for each $NH_4Cl$, $[NH_4^+] = 0.22$ M $NH_4^+$.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

| | $[NH_3]$ | $[NH_4^+]$ | $[OH^-]$ |
|---|---|---|---|
| Initial | 0.16 | 0.22 | $\approx 0.00$ |
| Change | $-x$ | $+x$ | $+x$ |
| Equil | $0.16 - x$ | $0.22 + x$ | $+x$ |

$K_b = \dfrac{[NH_4^+]\,[OH^-]}{[NH_3]} = 1.79 \times 10^{-5} = \dfrac{(0.22 + x)x}{0.16 - x}$

Assume $x$ is small ($x << 0.16 < 0.22$) so $\dfrac{(0.22 + x)x}{0.16 - x} = 1.79 \times 10^{-5} = \dfrac{(0.22)x}{0.16}$ and $x = 1.30182 \times 10^{-5}\,M = [OH^-]$. Confirm that the more stringent assumption is valid.

$\dfrac{1.30182 \times 10^{-5}}{0.16} \times 100\% = 8.1 \times 10^{-3}\%$ so assumption is valid.

$K_w = [H_3O^+]\,[OH^-]$ so $[H_3O^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.0 \times 10^{-14}}{1.30182 \times 10^{-5}} = 7.6816 \times 10^{-10}\,M$.

Finally, pH $= -\log[H_3O^+] = -\log(7.6816 \times 10^{-10}) = 9.11$

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH should be less than $14 + \log(0.16) = 13.2$ because this is a weak base and there is a common ion effect.

16.30    (a)    **Given:** 0.195 M $HC_2H_3O_2$ and 0.125 M $KC_2H_3O_2$ **Find:** pH

**Other:** $K_a\,(HC_2H_3O_2) = 1.8 \times 10^{-5}$

**Conceptual Plan:** M $KC_2H_3O_2 \rightarrow$ M $C_2H_3O_2^-$ then M $HC_2H_3O_2$, M $C_2H_3O_2^- \rightarrow [H_3O^+] \rightarrow$ pH

     $KC_2H_3O_2\,(aq) \rightarrow K^+\,(aq) + C_2H_3O_2^-\,(aq)$      ICE Chart    pH $= -\log[H_3O^+]$

**Solution:** Since 1 $C_2H_3O_2^-$ ion is generated for each $KC_2H_3O_2$, $[C_2H_3O_2^-] = 0.125$ M $C_2H_3O_2^-$.

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

| | $[HC_2H_3O_2]$ | $[H_3O^+]$ | $[C_2H_3O_2^-]$ |
|---|---|---|---|
| Initial | 0.195 | $\approx 0.00$ | .125 |
| Change | $-x$ | $+x$ | $+x$ |
| Equil | $0.195 - x$ | $+x$ | $0.125 + x$ |

$K_a = \dfrac{[H_3O^+]\,[HC_2H_3O_2]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5} = \dfrac{x(0.125 + x)}{0.195 - x}$ Assume $x$ is small ($x << 0.125 < 0.195$) so

$\dfrac{x(0.125 + x)}{0.195 - x} = 1.8 \times 10^{-5} = \dfrac{x(0.125)}{0.195}$ and $x = 2.808 \times 10^{-5}\,M = [H_3O^+]$. Confirm that the more stringent assumption is valid.

$$HC_7H_5O_2 \, (aq) + H_2O \, (l) \rightleftharpoons H_3O^+ \, (aq) + C_7H_5O_2^- \, (aq)$$

|          | $[HC_7H_5O_2]$ | $[H_3O^+]$ | $[C_7H_5O_2^-]$ |
|----------|----------------|------------|-----------------|
| Initial  | 0.15           | ≈0.00      | 0.10            |
| Change   | $-x$           | $+x$       | $+x$            |
| Equil    | $0.15 - x$     | $+x$       | $0.10 + x$      |

$K_a = \dfrac{[H_3O^+]\,[C_7H_5O_2^-]}{[HC_7H_5O_2]} = 6.5 \times 10^{-5} = \dfrac{x(0.10 + x)}{0.15 - x}$ Assume $x$ is small ($x \ll 0.10 < 0.15$) so

$\dfrac{x(0.10 + x)}{0.15 - x} = 6.5 \times 10^{-5} = \dfrac{x(0.10)}{0.15}$ and $x = 9.\underline{7}5 \times 10^{-5}\,M = [H_3O^+]$, then
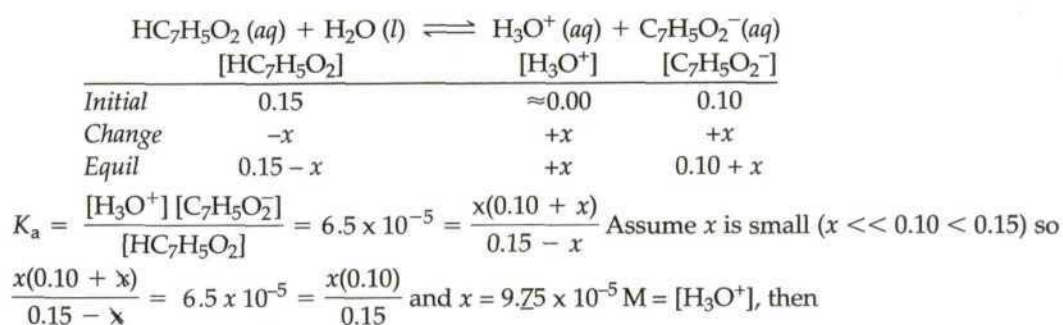
% ionization $= \dfrac{[H_3O^+]_{equil}}{[HC_7H_5O_2]_0} \times 100\% = \dfrac{9.\underline{7}5 \times 10^{-5}}{0.15} \times 100\% = 0.065\%$, which also confirms that the

assumption is valid (since it is less than 5 %). The percent ionization in the sodium benzoate solution is less than in pure water because of the common ion effect. An increase in one of the products (benzoate ion) shifts the equilibrium to the left, so less acid dissociates.

**Check:** The units (%) are correct. The magnitude of the answer makes physical sense because the acid is weak and so the percent ionization is low. With a common ion present, the percent ionization decreases.

**16.32**

**Given:** 0.13 M $HCHO_2$ in pure water and in 0.11 M $KCHO_2$ **Find:** % ionization in both solutions
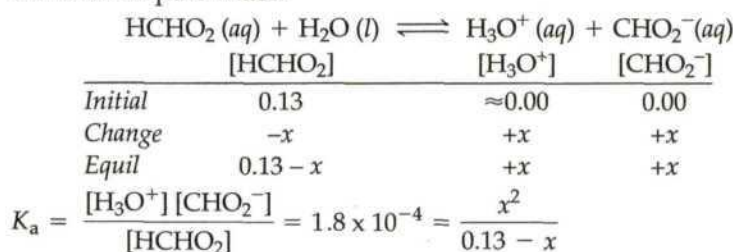**Other:** $K_a\,(HCHO_2) = 1.8 \times 10^{-4}$
**Conceptual Plan:** pure water: M $HCHO_2 \rightarrow [H_3O^+] \rightarrow$ % ionization then in $KCHO_2$ solution:

ICE Chart          % ionization $= \dfrac{[H_3O^+]_{equil}}{[HCHO_2]_0} \times 100\%$

**M $KCHO_2 \rightarrow$ M $CHO_2^-$ then M $HCHO_2$, M $CHO_2^- \rightarrow [H_3O^+] \rightarrow$ % ionization**

$KCHO_2 \, (aq) \rightarrow K^+ \, (aq) + CHO_2^- \, (aq)$          ICE Chart          % ionization $= \dfrac{[H_3O^+]_{equil}}{[HCHO_2]_0} \times 100\%$

**Solution:** in pure water:

$$HCHO_2 \, (aq) + H_2O \, (l) \rightleftharpoons H_3O^+ \, (aq) + CHO_2^- \, (aq)$$

|          | $[HCHO_2]$  | $[H_3O^+]$ | $[CHO_2^-]$ |
|----------|-------------|------------|-------------|
| Initial  | 0.13        | ≈0.00      | 0.00        |
| Change   | $-x$        | $+x$       | $+x$        |
| Equil    | $0.13 - x$  | $+x$       | $+x$        |

$K_a = \dfrac{[H_3O^+]\,[CHO_2^-]}{[HCHO_2]} = 1.8 \times 10^{-4} = \dfrac{x^2}{0.13 - x}$

Assume $x$ is small ($x \ll 0.10$) so $\dfrac{x^2}{0.13 - x} = 1.8 \times 10^{-4} = \dfrac{x^2}{0.13}$ and $x = 4.\underline{8}374 \times 10^{-3}\,M = [H_3O^+]$. Then

% ionization $= \dfrac{[H_3O^+]_{equil}}{[HCHO_2]_0} \times 100\% = \dfrac{4.\underline{8}374 \times 10^{-3}}{0.13} \times 100\% = 3.7\%$ which also confirms that the

assumption is valid (since it is less than 5%).

In $KCHO_2$ Solution: Since 1 $CHO_2^-$ ion is generated for each $KCHO_2$, $[CHO_2^-] = 0.11$ M $CHO_2^-$.

$$HCHO_2 \, (aq) + H_2O \, (l) \rightleftharpoons H_3O^+ \, (aq) + CHO_2^- \, (aq)$$

|          | $[HCHO_2]$  | $[H_3O^+]$ | $[CHO_2^-]$ |
|----------|-------------|------------|-------------|
| Initial  | 0.13        | ≈0.00      | 0.11        |
| Change   | $-x$        | $+x$       | $+x$        |
| Equil    | $0.13 - x$  | $+x$       | $0.11 + x$  |

$K_a = \dfrac{[H_3O^+]\,[CHO_2^-]}{[HCHO_2]} = 1.8 \times 10^{-4} = \dfrac{x(0.11 + x)}{0.13 - x}$
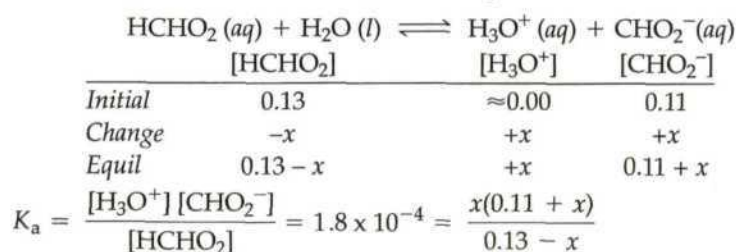
Assume $x$ is small ($x \ll 0.11 < 0.13$) so $\dfrac{x(0.11 + x)}{0.13 - x} = 1.8 \times 10^{-4} = \dfrac{x(0.11)}{0.13}$ and $x = 2.\underline{1}273 \times 10^{-4}\,M = [H_3O^+]$.

Then % ionization $= \dfrac{[H_3O^+]_{equil}}{[HCHO_2]_0} \times 100\% = \dfrac{2.\underline{1}273 \times 10^{-4}}{0.13} \times 100\% = 0.16\%$, which also confirms that the

assumption is valid (since it is less than 5%). The percent ionization in the potassium formate solution is less than in pure water because of the common ion effect. An increase in one of the products (formate ion) shifts the equilibrium to the left, so less acid dissociates.

**Check:** The units (%) are correct. The magnitude of the answer makes physical sense because the acid is weak and so the percent ionization is low. With a common ion present, the percent ionization decreases.

16.33   (a)   **Given:** 0.15 M HF   **Find:** pH   **Other:** $K_a$ (HF) = 3.5 x $10^{-4}$

**Conceptual Plan:** M HF $\rightarrow$ [$H_3O^+$] $\rightarrow$ pH

$$\text{ICE Chart} \quad \text{pH} = -\log[H_3O^+]$$

**Solution:**

$$HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-(aq)$$

|  | [HF] | [$H_3O^+$] | [$F^-$] |
|---|---|---|---|
| *Initial* | 0.15 | ≈0.00 | 0.00 |
| *Change* | $-x$ | $+x$ | $+x$ |
| *Equil* | $0.15 - x$ | $+x$ | $+x$ |

$K_a = \dfrac{[H_3O^+][F^-]}{[HF]} = 3.5 \times 10^{-4} = \dfrac{x^2}{0.15 - x}$ Assume $x$ is small ($x \ll 0.15$) so

$\dfrac{x^2}{0.15 - x} = 3.5 \times 10^{-4} = \dfrac{x^2}{0.15}$ and $x = 7.2457 \times 10^{-3}$ M = [$H_3O^+$]. Confirm that

assumption is valid $\dfrac{7.2457 \times 10^{-3}}{0.15}$ x 100% = 4.8% < 5% so assumption is valid.

Finally, pH $= -\log[H_3O^+] = -\log(7.2457 \times 10^{-3}) = 2.14$.

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH should be greater than $-\log(0.15) = 0.82$ because this is a weak acid.

  (b)   **Given:** 0.15 M NaF   **Find:** pH   **Other:** $K_a$ (HF) = 3.5 x $10^{-4}$

**Conceptual Plan:** M NaF $\rightarrow$ M F$^-$ and $K_a \rightarrow K_b$ then M F$^- \rightarrow$ [OH$^-$] $\rightarrow$ [$H_3O^+$] $\rightarrow$ pH

$$\text{NaF}\,(aq) \rightarrow \text{Na}^+\,(aq) + \text{F}^-\,(aq) \qquad K_w = K_a K_b \qquad \text{ICE Chart } K_w = [H_3O^+][OH^-] \quad \text{pH} = -\log[H_3O^+]$$

**Solution:** Since 1 F$^-$ ion is generated for each NaF, [F$^-$] = 0.15 M F$^-$. Since $K_w = K_a K_b$, rearrange to

solve for $K_b$.   $K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.8571 \times 10^{-11}$

$$F^-\,(aq) + H_2O\,(l) \rightleftharpoons HF\,(aq) + OH^-\,(aq)$$

|  | [$F^-$] | [HF] | [OH$^-$] |
|---|---|---|---|
| *Initial* | 0.15 | 0.00 | ≈0.00 |
| *Change* | $-x$ | $+x$ | $+x$ |
| *Equil* | $0.15 - x$ | $+x$ | $+x$ |

$K_b = \dfrac{[HF][OH^-]}{[F^-]} = 2.8571 \times 10^{-11} = \dfrac{x^2}{0.15 - x}$

Assume $x$ is small ($x \ll 0.15$) so $\dfrac{x^2}{0.15 - x} = 2.8571 \times 10^{-11} = \dfrac{x^2}{0.15}$ and $x = 2.0702 \times 10^{-6}$ M = [OH$^-$].

Confirm that assumption is valid $\dfrac{2.0702 \times 10^{-6}}{0.15}$ x 100% = 0.0014% < 5% so assumption is valid.

$K_w = [H_3O^+][OH^-]$ so [$H_3O^+$] $= \dfrac{K_w}{[OH^-]} = \dfrac{1.0 \times 10^{-14}}{2.0702 \times 10^{-6}} = 4.8305 \times 10^{-9}$ M.

Finally, pH $= -\log[H_3O^+] = -\log(4.8305 \times 10^{-9}) = 8.32$.

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH should be slightly basic, since the fluoride ion is a very weak base.

  (c)   **Given:** 0.15 M HF and 0.15 M NaF   **Find:** pH   **Other:** $K_a$ (HF) = 3.5 x $10^{-4}$

**Conceptual Plan:** M NaF $\rightarrow$ M F$^-$ then M HF, M F$^- \rightarrow$ [$H_3O^+$] $\rightarrow$ pH

$$\text{NaF}\,(aq) \rightarrow \text{Na}^+\,(aq) + \text{F}^-\,(aq) \qquad\qquad \text{ICE Chart} \qquad \text{pH} = -\log[H_3O^+]$$

**Solution:** Since 1 F$^-$ ion is generated for each NaF, [F$^-$] = 0.15 M F$^-$.

Confirm that assumption is valid $\dfrac{2.0226 \times 10^{-6}}{0.18} \times 100\% = 0.0012\% < 5\%$ so assumption is valid.
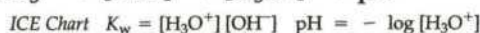
Finally, pH $= -\log [H_3O^+] = -\log (2.0226 \times 10^{-6}) = 5.69$.

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH should be slightly acidic, since the methylammonium cation is a very weak acid.

(c) **Given:** 0.18 M $CH_3NH_2$ and 0.18 M $CH_3NH_3Cl$ **Find:** pH **Other:** $K_b$ ($CH_3NH_2$) $= 4.4 \times 10^{-4}$

**Conceptual Plan: M $CH_3NH_3Cl$ $\rightarrow$ M $CH_3NH_3^+$ then**

$$CH_3NH_3Cl\ (aq) \rightarrow CH_3NH_3^+\ (aq) + Cl^-\ (aq)$$

**M $CH_3NH_2$, M $CH_3NH_3^+$ $\rightarrow$ [OH⁻] $\rightarrow$ [H$_3$O⁺] $\rightarrow$ pH**

$$ICE\ Chart\quad K_w = [H_3O^+][OH^-]\quad pH = -\log[H_3O^+]$$

**Solution:** Since 1 $CH_3NH_3^+$ ion is generated for each $CH_3NH_3Cl$, $[CH_3NH_3^+] = 0.105$ M $CH_3NH_3^+$.

$$CH_3NH_2\ (aq) + H_2O\ (l) \rightleftharpoons CH_3NH_3^+\ (aq) + OH^-(aq)$$

|  | $[CH_3NH_2]$ | $[CH_3NH_3^+]$ | $[OH^-]$ |
|---|---|---|---|
| Initial | 0.18 | 0.18 | $\approx 0.00$ |
| Change | $-x$ | $+x$ | $+x$ |
| Equil | $0.18 - x$ | $0.18 + x$ | $+x$ |

$$K_b = \dfrac{[CH_3NH_3^+]\,[OH^-]}{[CH_3NH_2]} = 4.4 \times 10^{-4} = \dfrac{(0.18 + x)x}{0.18 - x}$$

Assume $x$ is small ($x << 0.18$) so $\dfrac{(0.18 + x)x}{0.18 - x} = 4.4 \times 10^{-4} = \dfrac{(0.18)x}{0.18}$ and $x = 4.4 \times 10^{-4}$ M $= [OH^-]$.

Confirm that assumption is valid $\dfrac{4.4 \times 10^{-4}}{0.18} \times 100\% = 0.24\% < 5\%$ so assumption is valid.

$K_w = [H_3O^+][OH^-]$ so $[H_3O^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.2727 \times 10^{-11}$ M.

Finally, pH $= -\log [H_3O^+] = -\log (2.2727 \times 10^{-11}) = 10.64$

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH should be less than $14 + \log (0.18) = 13.3$ because this is a weak base and there is a common ion effect.

16.35 When an acid (such as HCl) is added it will react with the conjugate base of the buffer system as follows: $HCl + NaC_2H_3O_2 \rightarrow HC_2H_3O_2 + NaCl$. When a base (such as NaOH) is added it will react with the weak acid of the buffer system as follows: $NaOH + HC_2H_3O_2 \rightarrow H_2O + NaC_2H_3O_2$. The reaction generates the other buffer system component.

16.36 When an acid (such as HCl) is added it will react with the conjugate base of the buffer system as follows: $HCl + NH_3 \rightarrow NH_4Cl$. When a base (such as NaOH) is added it will react with the weak acid of the buffer system as follows: $NaOH + NH_4Cl \rightarrow H_2O + NH_3 + NaCl$. The reaction generates the other buffer system component.

16.37 (a) **Given:** 0.20 M $HCHO_2$ and 0.15 M $NaCHO_2$ **Find:** pH **Other:** $K_a$ ($HCHO_2$) $= 1.8 \times 10^{-4}$

**Conceptual Plan: Identify acid and base components then M $NaCHO_2$ $\rightarrow$ M $CHO_2^-$ then**

$$acid = HCHO_2\ base = CHO_2^- \qquad\qquad NaCHO_2\ (aq) \rightarrow Na^+\ (aq) + CHO_2^-\ (aq)$$

**$K_a$, M $HCHO_2$, M $CHO_2^-$ $\rightarrow$ pH.**

$$pH = pK_a + \log \dfrac{[base]}{[acid]}$$

**Solution:** Acid $= HCHO_2$, so [acid] $= [HCHO_2] = 0.20$ M. Base $= CHO_2^-$. Since 1 $CHO_2^-$ ion is generated for each $NaCHO_2$, $[CHO_2^-] = 0.15$ M $CHO_2^- = $ [base]. Then

$$pH = pK_a + \log \dfrac{[base]}{[acid]} = -\log (1.8 \times 10^{-4}) + \log \dfrac{0.15\ M}{0.20\ M} = 3.62.$$

Note that in order to use the Henderson–Hasselbalch Equation, the assumption that $x$ is small must be valid. This was confirmed in Problem 29.

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH should be less than the $pK_a$ of the acid because there is more acid than base. The answer agrees with Problem 29.

(b)  **Given:** 0.16 M $NH_3$ and 0.22 M $NH_4Cl$  **Find:** pH **Other:** $K_b$ ($NH_3$) = 1.79 x $10^{-5}$
**Conceptual Plan:** Identify acid and base components then M $NH_4Cl \rightarrow$ M $NH_4^+$ and $K_b \rightarrow pK_b \rightarrow pK_a$
$$\text{acid} = NH_4^+ \text{ base} = NH_3 \quad NH_4Cl\,(aq) \rightarrow NH_4^+\,(aq) + Cl^-\,(aq) \quad pK_b = -\log K_b \quad 14 = pK_a + pK_b$$
then $pK_a$, M $NH_3$, M $NH_4^+ \rightarrow$ **pH**.
$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$
**Solution:** Base = $NH_3$, [base] = $[NH_3]$ = 0.16 M Acid = $NH_4^+$. Since 1 $NH_4^+$ ion is generated for each
$NH_4Cl$, $[NH_4^+]$ = 0.18 M $NH_4^+$ = [acid].
Since $K_b$ ($NH_3$) = 1.79 x $10^{-5}$, $pK_b = -\log K_b = -\log (1.79 \times 10^{-5})$ = 4.75. Since $14 = pK_a + pK_b$,

$$pK_a = 14 - pK_b = 14 - 4.75 = 9.25 \text{ then } pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = 9.25 + \log \frac{0.16\text{ M}}{0.22\text{ M}} = 9.11.$$

Note that in order to use the Henderson–Hasselbalch Equation, the assumption that $x$ is small must
be valid. This was confirmed in Problem 29.
**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH
should be less than the $pK_a$ of the acid because there is more acid than base. The answer agrees with
problem 29, within the error of the value.

16.38  (a)  **Given:** 0.195 M $HC_2H_3O_2$ and 0.125 M $KC_2H_3O_2$ **Find:** pH **Other:** $K_a$ ($HC_2H_3O_2$) = 1.8 x $10^{-5}$
**Conceptual Plan:** Identify acid and base components then M $KC_2H_3O_2 \rightarrow$ M $C_2H_3O_2^-$ then
$$\text{acid} = HC_2H_3O_2 \text{ base} = C_2H_3O_2^- \qquad KC_2H_3O_2\,(aq) \rightarrow K^+\,(aq) + C_2H_3O_2^-\,(aq)$$
**M $HC_2H_3O_2$, M $C_2H_3O_2^- \rightarrow$ pH.**
$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$
**Solution:** Acid = $HC_2H_3O_2$, so [acid] = $[HC_2H_3O_2]$ = 0.195 M. Base = $C_2H_3O_2^-$. Since 1 $C_2H_3O_2^-$ ion is
generated for each $KC_2H_3O_2$, $[C_2H_3O_2^-]$ = 0.125 M $C_2H_3O_2^-$ = [base]. Then
$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = -\log (1.8 \times 10^{-5}) + \log \frac{0.125\text{ M}}{0.195\text{ M}} = 4.55.$$
Note that in order to use the Henderson–Hasselbalch Equation, the assumption that $x$ is small must
be valid. This was confirmed in Problem 30.
**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH
should be less than the $pK_a$ of the acid because there is more acid than base. The answer agrees with
Problem 30.

(b)  **Given:** 0.255 M $CH_3NH_2$ and 0.135 M $CH_3NH_3Br$ **Find:** pH **Other:** $K_b$ ($CH_3NH_2$) = 4.4 x $10^{-4}$
**Conceptual Plan:** Identify acid and base components then M $CH_3NH_3Br \rightarrow$ M $CH_3NH_3^+$ and
$$\text{acid} = CH_3NH_3^+ \text{ base} = CH_3NH_2 \qquad CH_3NH_3Br\,(aq) \rightarrow CH_3NH_3^+\,(aq) + Br^-\,(aq)$$
$K_b \rightarrow pK_b \rightarrow pK_a$ then $pK_a$, M $NH_3$, M $NH_4^+ \rightarrow$ **pH.**
$$pK_b = -\log K_b \quad 14 = pK_a + pK_b \qquad\qquad pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$
**Solution:** Base = $CH_3NH_2$, [base] = $[CH_3NH_2]$ = 0.255 M Acid = $NH_3^+$. Since 1 $CH_3NH_3^+$ ion is gen-
erated for each $CH_3NH_3Br$, $[CH_3NH_3^+]$ = 0.135 M $CH_3NH_3^+$ = [acid].
Since $K_b$ ($CH_3NH_2$) = 4.4 x $10^{-4}$, $pK_b = -\log K_b = -\log (4.4 \times 10^{-4})$ = 3.36.
Since $14 = pK_a + pK_b$, $pK_a = 14 - pK_b = 14 - 3.36 = 10.64$ then

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} = 10.64 + \log \frac{0.255\text{ M}}{0.135\text{ M}} = 10.92.$$

Note that in order to use the Henderson–Hasselbalch Equation, the assumption that $x$ is small must
be valid. This was confirmed in Problem 30.
**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH
should be greater than the $pK_a$ of the acid because there is more base than acid. The answer agrees
with Problem 30.

16.39  (a)  **Given:** 0.135 M HClO and 0.155 M KClO  **Find:** pH **Other:** $K_a$ (HClO) = 2.9 x $10^{-8}$
**Conceptual Plan:** Identify acid and base components then M KClO $\rightarrow$ M ClO$^-$ then
$$\text{acid} = HClO \text{ base} = ClO^- \qquad KClO\,(aq) \rightarrow K^+\,(aq) + ClO^-\,(aq)$$
**M HClO, M ClO$^- \rightarrow$ pH.**
$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$[NH_4Cl] = 0.0776841$ M. Convert to moles using $M = \frac{mol}{L}$.

$$\frac{0.0776841 \text{ mol NH}_4\text{Cl}}{1 \text{ L}} \times 2.55 \text{ L} = 0.198094 \text{ mol NH}_4\text{Cl} \times \frac{53.49 \text{ g NH}_4\text{Cl}}{1 \text{ mol NH}_4\text{Cl}} = 10.6 \text{ g NH}_4\text{Cl}.$$

**Check:** The units (g) are correct. The magnitude of the answer makes physical sense because the volume of solution is large and the concentration is low, so less than a mole is needed.

**16.47** (a) **Given:** 250.0 mL buffer 0.250 M $HC_2H_3O_2$ and 0.250 M $NaC_2H_3O_2$  **Find:** initial pH
**Other:** $K_a$ ($HC_2H_3O_2$) = 1.8 x 10$^{-5}$
**Conceptual Plan: Identify acid and base components then M $NaC_2H_3O_2$ → M $C_2H_3O_2^-$ then**

acid = $HC_2H_3O_2$ base = $C_2H_3O_2^-$ $\qquad\qquad$ $NaC_2H_3O_2$ (aq) → Na$^+$ (aq) + $C_2H_3O_2^-$ (aq)
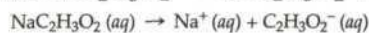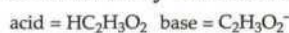
**M $HC_2H_3O_2$, M $C_2H_3O_2^-$ → pH.**

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

**Solution:** Acid = $HC_2H_3O_2$, so [acid] = [$HC_2H_3O_2$] = 0.250 M. Base = $C_2H_3O_2^-$. Since 1 $C_2H_3O_2^-$ ion is generated for each $NaC_2H_3O_2$, [$C_2H_3O_2^-$] = 0.250 M $C_2H_3O_2^-$ = [base]. Then

$$pH = pK_a + \log\frac{[base]}{[acid]} = -\log(1.8 \times 10^{-5}) + \log\frac{0.250 \text{ M}}{0.250 \text{ M}} = 4.74.$$

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH is equal to the p$K_a$ of the acid because there are equal amounts of acid and base.

(b) **Given:** 250.0 mL buffer 0.250 M $HC_2H_3O_2$ and 0.250 M $NaC_2H_3O_2$, add 0.0050 mol HCl  **Find:** pH
**Other:** $K_a$ ($HC_2H_3O_2$) = 1.8 x 10$^{-5}$
**Conceptual Plan: Part I: Stoichiometry:**
**mL → L then [$NaC_2H_3O_2$], L → mol $NaC_2H_3O_2$ and [$HC_2H_3O_2$], L → mol $HC_2H_3O_2$**

$\frac{1 \text{ L}}{1000 \text{ mL}}$ $\qquad\qquad$ $M = \frac{mol}{L}$ $\qquad\qquad\qquad\qquad$ $M = \frac{mol}{L}$

**write balanced equation then**

HCl + $NaC_2H_3O_2$ → $HC_2H_3O_2$ + NaCl

**mol $NaC_2H_3O_2$, mol $HC_2H_3O_2$, mol HCl → mol $NaC_2H_3O_2$, mol $HC_2H_3O_2$ then**

*set up stoichiometry table*

**Part II: Equilibrium:**
**mol $NaC_2H_3O_2$, mol $HC_2H_3O_2$, L, $K_a$ → pH**

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

**Solution:** $250.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.2500$ L then

$$\frac{0.250 \text{ mol HC}_2\text{H}_3\text{O}_2}{1 \text{ L}} \times 0.250 \text{ L} = 0.0625 \text{ mol HC}_2\text{H}_3\text{O}_2 \text{ and}$$

$$\frac{0.250 \text{ mol NaC}_2\text{H}_3\text{O}_2}{1 \text{ L}} \times 0.250 \text{ L} = 0.0625 \text{ mol NaC}_2\text{H}_3\text{O}_2.$$ Set up a table to track changes:

|  | HCl (aq) | + $NaC_2H_3O_2$ (aq) | → $HC_2H_3O_2$ (aq) | + NaCl (aq) |
|---|---|---|---|---|
| Before addition | ≈ 0.00 mol | 0.0625 mol | 0.0625 mol | 0.00 mol |
| Addition | 0.0050 mol | — | — | — |
| After addition | ≈ 0.00 mol | 0.0575 mol | 0.0675 mol | 0.0050 mol |

Since the amount of HCl is small, there are still significant amounts of both buffer components, so the Henderson–Hasselbalch equation can be used to calculate the new pH.

$$pH = pK_a + \log\frac{[base]}{[acid]} = -\log(1.8 \times 10^{-5}) + \log\frac{\frac{0.0575 \text{ mol}}{0.250 \text{ L}}}{\frac{0.0675 \text{ mol}}{0.250 \text{ L}}} = 4.68.$$

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because the pH dropped slightly when acid was added.

(c) **Given:** 250.0 mL buffer 0.250 M $HC_2H_3O_2$ and 0.250 M $NaC_2H_3O_2$, add 0.0050 mol NaOH
**Find:** pH  **Other:** $K_a$ ($HC_2H_3O_2$) = 1.8 x 10$^{-5}$

**Conceptual Plan: Part I: Stoichiometry:**

mL → L then $[NaC_2H_3O_2]$, L → mol $NaC_2H_3O_2$ and $[HC_2H_3O_2]$, L → mol $HC_2H_3O_2$

$\dfrac{1\,L}{1000\,mL}$          $M = \dfrac{mol}{L}$                    $M = \dfrac{mol}{L}$

**write balanced equation then**

$NaOH + HC_2H_3O_2 \rightarrow H_2O + NaC_2H_3O_2$

mol $NaC_2H_3O_2$, mol $HC_2H_3O_2$, mol NaOH → mol $NaC_2H_3O_2$, mol $HC_2H_3O_2$ then

*set up stoichiometry table*

**Part II: Equilibrium:**

mol $NaC_2H_3O_2$, mol $HC_2H_3O_2$, L, $K_a$ → pH

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

**Solution:** $250.0\ \cancel{mL} \times \dfrac{1\,L}{1000\ \cancel{mL}} = 0.2500\ L$ then

$\dfrac{0.250\ mol\ HC_2H_3O_2}{1\ \cancel{L}} \times 0.2500\ \cancel{L} = 0.0625\ mol\ HC_2H_3O_2$ and

$\dfrac{0.250\ mol\ NaC_2H_3O_2}{1\ \cancel{L}} \times 0.2500\ \cancel{L} = 0.0625\ mol\ NaC_2H_3O_2$ set up a table to track changes:

$$NaOH\ (aq)\ +\ HC_2H_3O_2\ (aq)\ \rightarrow\ NaC_2H_3O_2\ (aq)\ +\ H_2O\ (l)$$

| | NaOH (aq) | HC₂H₃O₂ (aq) | NaC₂H₃O₂ (aq) | H₂O (l) |
|---|---|---|---|---|
| Before addition | ≈ 0.00 mol | 0.0625 mol | 0.0625 mol | — |
| Addition | 0.0050 mol | — | — | — |
| After addition | ≈ 0.00 mol | 0.0575 mol | 0.0675 mol | — |

Since the amount of NaOH is small, there are still significant amounts of both buffer components, so the Henderson–Hasselbalch equation can be used to calculate the new pH.

$$pH = pK_a + \log\frac{[base]}{[acid]} = -\log(1.8 \times 10^{-5}) + \log\frac{\dfrac{0.0675\ \cancel{mol}}{\cancel{0.2500\ L}}}{\dfrac{0.0575\ \cancel{mol}}{\cancel{0.2500\ L}}} = 4.81.$$
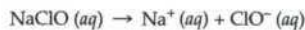
**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because the pH rose slightly when base was added.

16.48   (a)   **Given:** 100.0 mL buffer 0.175 M HClO and 0.150 M NaClO  **Find:** initial pH
**Other:** $K_a$ (HClO) = 2.9 x 10⁻⁸

**Conceptual Plan: Identify acid and base components then M NaClO → M ClO⁻ then**

acid = HClO   base = ClO⁻                        $NaClO\ (aq) \rightarrow Na^+\ (aq) + ClO^-\ (aq)$

**M HClO, M ClO⁻ → pH.**

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

**Solution:** Acid = HClO, so [acid] = [HClO] = 0.175 M. Base = ClO⁻. Since 1 ClO⁻ ion is generated for each NaClO, [ClO⁻] = 0.150 M ClO⁻ = [base].

Then $pH = pK_a + \log\dfrac{[base]}{[acid]} = -\log(2.9 \times 10^{-8}) + \log\dfrac{0.150\ M}{0.175\ M} = 7.47.$

**Check:** The units (none) are correct. The magnitude of the answer makes physical sense because pH is less than the $pK_a$ of the acid because there is more acid than base.

(b)   **Given:** 100.0 mL buffer 0.175 M HClO and 0.150 M NaClO, add 150.0 mg HBr  **Find:** pH
**Other:** $K_a$ (HClO) = 2.9 x 10⁻⁸

**Conceptual Plan: Part I: Stoichiometry:**

mL → L then [NaClO], L → mol NaClO and [HClO], L → mol HClO and

$\dfrac{1\,L}{1000\,mL}$          $M = \dfrac{mol}{L}$                    $M = \dfrac{mol}{L}$

mg HBr → g HBr → mol HBr write balanced equation then

$\dfrac{1\ g\ HBr}{1000\ mg\ HBr}\quad \dfrac{1\ mol\ HBr}{71.91\ g\ HBr}$   $HBr + NaClO \rightarrow HClO + NaBr$
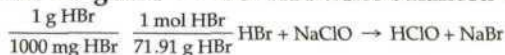
mol NaClO, mol HClO, mol HBr → mol NaClO, mol HClO then

*set up stoichiometry table*

(c)    For HI: $1.5 \, \text{g HI} \times \dfrac{1 \, \text{mol HI}}{127.91 \, \text{g HI}} = 0.011727$ mol HI. Since HI is a strong acid, [HI] = [H$^+$], and

set up a table to track changes:

$$H^+ \, (aq) \; + \; NO_2^- \, (aq) \; \rightarrow \; HNO_2 \, (aq)$$

| | | | |
|---|---|---|---|
| Before addition | ≈ 0.00 mol | 0.145 mol | 0.125 mol |
| Addition | 0.011727 mol | — | — |
| After addition | ≈ 0.00 mol | 0.133 mol | 0.137 mol |

Because the concentrations of the acid and base components have not changed much, the buffer is still able to do its job. Finally, since there is 1.0 L of solution, [HNO$_2$] = 0.14 M and [NaNO$_2$] = 0.13 M. **Check:** The units (M) are correct. Since the number of moles added is small compared to the buffer components, the buffer still remains active. Adding acid increases the amount of the conjugate base. Adding base increases the amount of the weak acid.

## Titrations, pH Curves, and Indicators

16.61  (i)    The equivalence point of a titration is where the pH rises sharply as base is added. The pH at the equivalence point is the midpoint of the sharp rise at ~ 50 mL added base. For (a) the pH = ~ 8 and for (b) the pH = ~ 7.

(ii)   Graph (a) represents a weak acid and graph (b) represents a strong acid. A strong acid titration starts at a lower pH, has a flatter initial region and a sharper rise at the equivalence point than a weak acid. The pH at the equivalence point of a strong acid is neutral, while the pH at the equivalence point of a weak acid is basic.

16.62  **Given:** 25.0 mL 0.100 M HCl and 0.100 M HF titrated with 0.200 M KOH

(a)    **Find:** volume of base to reach equivalence point
       **Conceptual Plan: The answer for both titrations will be the same since the initial concentration and volumes of the acids are the same and both acids are monoprotic. Write balanced equation**

$$HCl + KOH \rightarrow KCl + H_2O \text{ and } HF + KOH \rightarrow KF + H_2O$$

**then mL $\rightarrow$ L then [acid], L $\rightarrow$ mol acid then set mol acid = mol base and**

$$\dfrac{1 \, L}{1000 \, mL} \qquad\qquad M = \dfrac{mol}{L} \qquad\qquad \textit{balanced equation has 1:1 stoichiometry}$$

**[KOH], mol KOH $\rightarrow$ L KOH $\rightarrow$ mL KOH**

$$M = \dfrac{mol}{L} \qquad \dfrac{1000 \, mL}{1 \, L}$$

**Solution:** $25.0 \, \text{mL acid} \times \dfrac{1 \, L}{1000 \, \text{mL}} = 0.0250$ L acid then

$\dfrac{0.100 \, \text{mol acid}}{1 \, L} \times 0.0250 \, \text{L} = 0.00250$ mol acid. So mol acid = 0.00250 mol = mol KOH then

$0.00250 \, \text{mol KOH} \times \dfrac{1 \, L \, KOH}{0.200 \, \text{mol KOH}} = 0.0125 \, \text{L KOH} \times \dfrac{1000 \, mL}{1 \, L} = 12.5$ mL KOH for both titrations.

**Check:** The units (mL) are correct. The volume of base is half the volume of acids because the concentration of the base is twice that of the acids. The answer for both titrations is the same because the stoichiometry is the same for both titration reactions.

(b)    The pH at the equivalence point will be neutral for HCl (since it is a strong acid) and it will be basic for HF (since it is a weak acid).

(c)    The initial pH will be lower for HCl (since it is a strong acid) and so it dissociates completely. The HF (since it is a weak acid) will only partially dissociate and not drop the pH as low as HCl at the same acid concentration.

(d)     The titration curves will look like the following:

HCl:



HF:
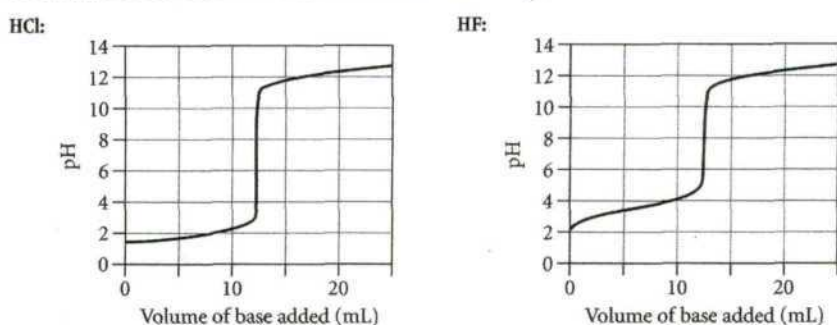


Important features to include are a low initial pH (if strong acid pH is 1 and higher for a weak acid), flat initial region (very flat for strong acid, not as flat for weak acid where pH halfway to equivalence point is the $pK_a$ of the acid), sharp rise at equivalence point, pH at equivalence point (neutral for strong acid and higher for weak acid), and then flatten out at high pH.

16.63     **Given:** 20.0 mL 0.200 M KOH and 0.200 M $CH_3NH_2$ titrated with 0.100 M HI

(a)     **Find:** volume of base to reach equivalence point
        **Conceptual Plan: The answer for both titrations will be the same since the initial concentration and volumes of the bases are the same. Write balanced equation then mL $\rightarrow$ L then**

$$HI + KOH \rightarrow KI + H_2O \text{ and } HI + KOH \rightarrow CH_3NH_3I$$

$$\frac{1\ L}{1000\ mL}$$

**[base], L $\rightarrow$ mol base then set mol base = mol acid and [HI], mol HI $\rightarrow$ L HI $\rightarrow$ mL HI**

$$M = \frac{mol}{L} \qquad \textit{balanced equation has 1:1 stoichiometry} \qquad M = \frac{mol}{L} \qquad \frac{1000\ mL}{1\ L}$$

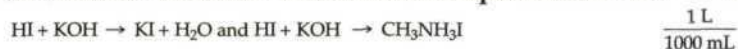**Solution:** $20.0\ \overline{mL\ base} \times \dfrac{1\ L}{1000\ \overline{mL}} = 0.0200$ L base then

$\dfrac{0.200\ mol\ base}{1\ \overline{L}} \times 0.0200\ \overline{L} = 0.00400$ mol base. So mol base = 0.00400 mol = mol HI then

$0.00400\ \overline{mol\ HI} \times \dfrac{1\ L\ HI}{0.100\ \overline{mol\ HI}} = 0.0400\ \overline{L\ HI} \times \dfrac{1000\ mL}{1\ \overline{L}} = 40.0$ mL HI for both titrations.

**Check:** The units (mL) are correct. The volume of acid is twice the volume of bases because the concentration of the base is twice that of the acid in each case. The answer for both titrations is the same because the stoichiometry is the same for both titration reactions.

(b)     The pH at the equivalence point will be neutral for KOH (since it is a strong base) and it will be acidic for $CH_3NH_2$ (since it is a weak base).

(c)     The initial pH will be lower for $CH_3NH_2$ (since it is a weak base and will only partially dissociate and not raise the pH as high as KOH (since it is a strong base and so it dissociates completely) at the same base concentration.

(d)     The titration curves will look like the following:

KOH:



$CH_3NH_2$:
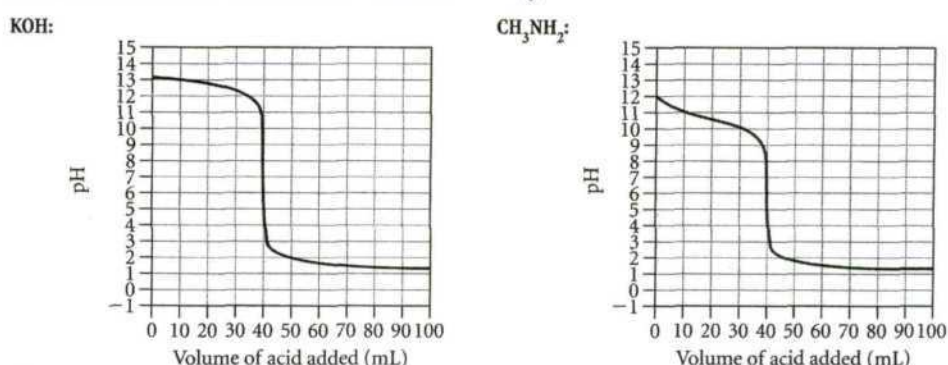


Important features to include are a high initial pH (if strong base pH is over 13 and lower for a weak base), flat initial region (very flat for strong base, not as flat for weak base where pH halfway to

equivalence point is the $pK_b$ of the base), sharp drop at equivalence point, pH at equivalence point (neutral for strong base and lower for weak base), and then flatten out at low pH.

16.64   (i)   The equivalence point of a titration is where the pH drops sharply as acid is added. The pH at the equivalence point is the midpoint of the sharp drop at ~ 25 mL added acid. For (a) the pH = ~ 7 and for (b) the pH = ~ 5.

   (ii)   Graph (a) represents a strong base and graph (b) represents a weak base. A strong base titration starts at a higher pH, has a flatter initial region and a sharper drop at the equivalence point than a weak base. The pH at the equivalence point of a strong base is neutral, while the pH at the equivalence point of a weak base is acidic.

16.65   (a)   The equivalence point of a titration is where the pH rises sharply as base is added. The volume at the equivalence point is ~ 30 mL. The pH as the equivalence point is the midpoint of the sharp rise at ~ 30 mL added base, which is a pH = ~ 9.

   (b)   At 0 mL the pH is calculated by doing an equilibrium calculation of a weak acid in water (as done in Chapter 15).

   (c)   The pH one-half way to the equivalence point is equal to the $pK_a$ of the acid, or ~ 15 mL.

   (d)   The pH at the equivalence point, or ~ 30 mL, is calculated by doing an equilibrium problem with the $K_b$ of the acid. At the equivalence point, all of the acid has been converted to its conjugate base.

   (e)   Beyond the equivalence point (30 mL) there is excess base. All of the acid has been converted to its conjugate base and so the pH is calculated by focusing on this excess base concentration.

16.66   (a)   The equivalence point of a titration is where the pH drops sharply as acid is added. The volume at the equivalence point is ~ 25 mL. The pH at the equivalence point is the midpoint of the sharp drop at ~ 25 mL added acid, which is a pH = ~ 5.

   (b)   At 0 mL the pH is calculated by doing an equilibrium calculation of a weak base in water (as done in Chapter 15).

   (c)   The pH one-half way to the equivalence point is equal to the $14 - pK_b = pK_a$ of the base, or ~ 12 mL.

   (d)   The pH at the equivalence point, or ~ 25 mL, is calculated by doing an equilibrium problem with the $K_a$ of the base. At the equivalence point, all of the base has been converted to its conjugate acid.

   (e)   Beyond the equivalence point (25 mL) there is excess acid. All of the base has been converted to its conjugate acid and so the pH is calculated by focusing on this excess acid concentration.

16.67   **Given:** 35.0 mL of 0.175 M HBr titrated with 0.200 M KOH

   (a)   **Find:** initial pH
**Conceptual Plan: Since HBr is a strong acid, it will dissociate completely, so initial pH $= -\log [H_3O^+] = -\log [HBr]$.**
**Solution:** $pH = -\log [HBr] = -\log 0.175 = 0.757$
**Check:** The units (none) are correct. The pH is reasonable since the concentration is greater than 0.1 M and the acid dissociates completely, the pH is less than 1.

   (b)   **Find:** volume of base to reach equivalence point
**Conceptual Plan: Write balanced equation then mL $\rightarrow$ L then [HBr], L $\rightarrow$ mol HBr then**
$$HBr + KOH \rightarrow KBr + H_2O \qquad \frac{1 \text{ L}}{1000 \text{ mL}} \qquad M = \frac{mol}{L}$$
**set mol acid (HBr) = mol base (KOH) and [KOH], mol KOH $\rightarrow$ L KOH $\rightarrow$ mL KOH.**
$$\textit{balanced equation has 1:1 stoichiometry} \qquad M = \frac{mol}{L} \qquad \frac{1000 \text{ mL}}{1 \text{ L}}$$
**Solution:** $35.0 \text{ mL HBr} \times \dfrac{1 \text{ L}}{1000 \text{ mL}} = 0.0350 \text{ L HBr}$ then
$\dfrac{0.175 \text{ mol HBr}}{1 \text{ L}} \times 0.0350 \text{ L} = 0.006125 \text{ mol HBr}.$

So mol acid = mol HBr = 0.006125 mol = mol KOH then

$$0.006125 \ \text{mol KOH} \times \frac{1 \ \text{L}}{0.200 \ \text{mol KOH}} = 0.030625 \ \text{L KOH} \times \frac{1000 \ \text{mL}}{1 \ \text{L}} = 30.6 \ \text{mL KOH}.$$

**Check:** The units (mL) are correct. The volume of base is a little less than the volume of acid because the concentration of the base is a little greater than that of the acid.

(c) **Find:** pH after adding 10.0 mL of base

**Conceptual Plan:** Use calculations from part b. Then mL $\rightarrow$ L then [KOH], L $\rightarrow$ mol KOH then

$$\frac{1 \ \text{L}}{1000 \ \text{mL}} \qquad\qquad M = \frac{\text{mol}}{\text{L}}$$

mol HBr, mol KOH $\rightarrow$ mol excess HBr and L HBr, L KOH $\rightarrow$ total L then

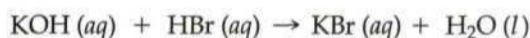$$\textit{set up stoichiometry table} \qquad\qquad \text{L HBr} + \text{L KOH} = \text{total L}$$

mol excess HBr, L $\rightarrow$ [HBr] $\rightarrow$ pH.

$$M = \frac{\text{mol}}{\text{L}} \quad pH = -\log[\text{HBr}]$$

**Solution:** $10.0 \ \text{mL KOH} \times \dfrac{1 \ \text{L}}{1000 \ \text{mL}} = 0.0100 \ \text{L KOH}$ then

$$\frac{0.200 \ \text{mol KOH}}{1 \ \text{L}} \times 0.0100 \ \text{L} = 0.00200 \ \text{mol KOH}.$$

Since KOH is a strong base, [KOH] = [OH$^-$], and set up a table to track changes:

$$\text{KOH} \ (aq) \ + \ \text{HBr} \ (aq) \ \rightarrow \ \text{KBr} \ (aq) \ + \ \text{H}_2\text{O} \ (l)$$

| | | | | |
|---|---|---|---|---|
| Before addition | $\approx 0.00$ mol | 0.006125 mol | 0.00 mol | — |
| Addition | 0.00200 mol | — | — | — |
| After addition | $\approx 0.00$ mol | 0.004125 mol | 0.00200 mol | — |

Then 0.0350 L HBr + 0.0100 L KOH = 0.0450 L total volume.

So mol excess acid = mol HBr = 0.004125 mol in 0.0450 L so

$$[\text{HBr}] = \frac{0.004125 \ \text{mol HBr}}{0.0450 \ \text{L}} = 0.0916667 \ \text{M and}$$

$$pH = -\log[\text{HBr}] = -\log 0.0916667 = 1.038.$$

**Check:** The units (none) are correct. The pH is a little higher than the initial pH, which is expected since this is a strong acid.

(d) **Find:** pH at equivalence point

**Solution:** Since this is a strong acid–strong base titration, the pH at the equivalence point is neutral or 7.

(e) **Find:** pH after adding 5.0 mL of base beyond the equivalence point

**Conceptual Plan:** Use calculations from parts b & c. Then the pH is only dependent on the amount of excess base and the total solution volumes.

mL excess $\rightarrow$ L excess then [KOH], L excess $\rightarrow$ mol KOH excess

$$\frac{1 \ \text{L}}{1000 \ \text{mL}} \qquad\qquad M = \frac{\text{mol}}{\text{L}}$$

then L HBr, L KOH to equivalence point, L KOH excess $\rightarrow$ total L then

$$\text{L HBr} + \text{L KOH to equivalence point} + \text{L KOH excess} = \text{total L}$$

mol excess KOH, total L $\rightarrow$ [KOH] = [OH$^-$] $\rightarrow$ [H$_3$O$^+$] $\rightarrow$ pH

$$M = \frac{\text{mol}}{\text{L}} \qquad K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad pH = -\log[\text{H}_3\text{O}^+]$$

**Solution:** $5.0 \ \text{mL KOH} \times \dfrac{1 \ \text{L}}{1000 \ \text{mL}} = 0.0050 \ \text{L KOH excess}$ then

$$\frac{0.200 \ \text{mol KOH}}{1 \ \text{L}} \times 0.0050 \ \text{L} = 0.0010 \ \text{mol KOH excess.}$$ Then 0.0350 L HBr + 0.0306 L KOH + 0.0050 L

KOH = 0.0706 L total volume. $[\text{KOH excess}] = \dfrac{0.0010 \ \text{mol KOH excess}}{0.0706 \ \text{L}} = 0.014164 \ \text{M KOH excess}$

Since KOH is a strong base, [KOH] excess = [OH$^-$]. $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ so

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.014164} = 7.06 \times 10^{-13} \ \text{M. Finally,}$$

$$pH = -\log[\text{H}_3\text{O}^+] = -\log(7.06 \times 10^{-13}) = 12.15.$$

Check: The units (none) are correct. The pH is rising sharply at the equivalence point, so the pH after 5 mL past the equivalence point should be quite basic.

16.68      Given: 20.0 mL of 0.125 M $HNO_3$ titrated with 0.150 M NaOH
Find: pH at five different points and plot titration curve
Conceptual Plan: Choose points to calculate: (i) initial pH, (ii) pH after 5.0 mL, (iii) pH after 10.0 mL, (iv) pH at equivalence point, and (v) pH at 25.0 mL. Points should be on both sides of the equivalence point.

(i)        Since $HNO_3$ is a strong acid, it will dissociate completely, so initial pH $= -\log [H_3O^+] = -\log [HNO_3]$.
Solution: $pH = -\log [HNO_3] = -\log 0.125 = 0.903$
Check: The units (none) are correct. The pH is reasonable since the concentration is greater than 0.1 M and the acid dissociates completely, the pH is less than 1.

(ii)       Find: pH after adding 5.0 mL of base
Conceptual Plan: Write balanced equation then mL $\rightarrow$ L then $[HNO_3]$, L $\rightarrow$ mol $HNO_3$ then

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O \qquad \frac{1\,L}{1000\,mL} \qquad M = \frac{mol}{L}$$

mL $\rightarrow$ L then $[NaOH]$, L $\rightarrow$ mol NaOH then mol $HNO_3$, mol NaOH $\rightarrow$ mol excess $HNO_3$

$$\frac{1\,L}{1000\,mL} \qquad M = \frac{mol}{L} \qquad \qquad set\ up\ stoichiometry\ table$$
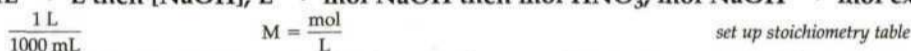
and L $HNO_3$, L NaOH $\rightarrow$ total L then mol excess $HNO_3$, L $\rightarrow$ $[HNO_3]$ $\rightarrow$ pH.

$$L\,HNO_3 + L\,NaOH = total\,L \qquad\qquad M = \frac{mol}{L} \quad pH = -\log [HNO_3]$$

Solution: $20.0\ \overline{mL\ HNO_3} \times \dfrac{1\,L}{1000\ \overline{mL}} = 0.0200\ L\ HNO_3$ then

$\dfrac{0.125\ mol\ HNO_3}{1\ \cancel{L}} \times 0.0200\ \cancel{L} = 0.00250\ mol\ HNO_3$ and $5.0\ \overline{mL\ NaOH} \times \dfrac{1\,L}{1000\ \overline{mL}} = 0.0050\ L\ NaOH$

then $\dfrac{0.150\ mol\ NaOH}{1\ \cancel{L}} \times 0.0050\ \cancel{L} = 0.00075\ mol\ NaOH$.

This is a strong acid–strong base titration, so set up a table to track changes:

$$NaOH\ (aq) + HNO_3\ (aq) \rightarrow NaNO_3\ (aq) + H_2O\ (l)$$
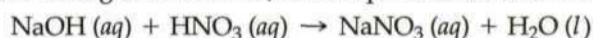
| | | | |
|---|---|---|---|
| Before addition | 0.00 mol | 0.00250 mol | 0.00 mol | — |
| Addition | 0.00075 mol | — | — | — |
| After addition | ≈ 0.00 mol | 0.00175 mol | 0.00075 mol | — |

Then 0.0200 L $HNO_3$ + 0.0050 L NaOH = 0.0250 L total volume. So mol excess acid = mol $HNO_3$ =
0.00175 mol in 0.0250 L, so $[HNO_3] = \dfrac{0.00175\ mol\ HNO_3}{0.0250\ L} = 0.0700\ M$ and
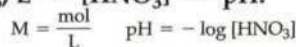
$pH = -\log [HNO_3] = -\log 0.0700 = 1.155$.
Check: The units (none) are correct. The pH remains very low in a strong acid–strong base titration before the equivalence point.

(iii)      Find: pH after adding 10.0 mL of base
Conceptual Plan: Use calculations for point (ii) then mL $\rightarrow$ L then $[NaOH]$, L $\rightarrow$ mol NaOH then

$$\frac{1\,L}{1000\,mL} \qquad M = \frac{mol}{L}$$

mol $HNO_3$, mol NaOH $\rightarrow$ mol excess $HNO_3$ and L $HNO_3$, L NaOH $\rightarrow$ total L then

$$set\ up\ stoichiometry\ table \qquad\qquad L\,HNO_3 + L\,NaOH = total\,L$$

mol excess $HNO_3$, L $\rightarrow$ $[HNO_3]$ $\rightarrow$ pH.

$$M = \frac{mol}{L} \qquad pH = -\log [HNO_3]$$

Solution: $10.0\ \overline{mL\ NaOH} \times \dfrac{1\,L}{1000\ \overline{mL}} = 0.0100\ L\ NaOH$ then

$\dfrac{0.150\ mol\ NaOH}{1\ \cancel{L}} \times 0.0100\ \cancel{L} = 0.00150\ mol\ NaOH$. Set up a table to track changes:

$$NaOH\ (aq) + HNO_3\ (aq) \rightarrow NaNO_3\ (aq) + H_2O\ (l)$$
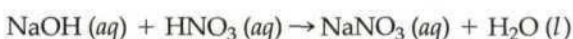
| | | | |
|---|---|---|---|
| Before addition | 0.00 mol | 0.00250 mol | 0.00 mol | — |
| Addition | 0.00150 mol | — | — | — |
| After addition | ≈ 0.00 mol | 0.00100 mol | 0.00150 mol | — |

Then 0.0200 L $HNO_3$ + 0.0100 L NaOH = 0.0300 L total volume. So mol excess acid = mol $HNO_3$ =
0.00100 mol in 0.0300 L, so $[HNO_3] = \dfrac{0.00100\ mol\ HNO_3}{0.0300\ L} = 0.0333333\ M$ and

(a)    For HF, the $K_a = 3.5 \times 10^{-4}$ and so the above equation approximates the pH at the equivalence point of ~ 8.0. Looking at Table 16.1, phenol red or $m$-nitrophenol will change at the appropriate pH range.

(b)    For HCl, the pH at the equivalence point is 7, since HCl is a strong acid. Looking at Table 16.1, alizarin, bromthymol blue, or phenol red will change at the appropriate pH range.

(c)    For HCN, the $K_a = 4.9 \times 10^{-10}$ and so the above equation approximates the pH at the equivalence point of ~ 11.0. Looking at Table 16.1, alizarin yellow R will change at the appropriate pH range.

16.84    Since the exact conditions of the titration are not given, a rough calculation will suffice. Looking at the pattern of earlier problems, the pH at the equivalence point of a titration of a weak base and a strong acid is the hydrolysis of the conjugate acid of the weak base that has been diluted by a factor of roughly 2 with acid. If it is assumed that the initial concentration of the weak base is ~ 0.1 M, then the conjugate acid concentration will be ~ 0.05 M. From earlier calculations it can be seen that the $K_a = \dfrac{K_w}{K_b} = \dfrac{[H_3O^+]^2}{0.05}$ thus $[H_3O^+] = \sqrt{\dfrac{0.05 \, K_w}{K_b}} = \sqrt{\dfrac{5 \times 10^{-16}}{K_b}}$ and the pH $= -\log \sqrt{\dfrac{5 \times 10^{-16}}{K_b}}$.

(a)    For $CH_3NH_2$, the $K_b = 4.4 \times 10^{-4}$ and so the above equation approximates the pH at the equivalence point of ~ 6.0. Looking at Table 16.1, methyl red, Eriochrome Black T, bromocresol purple, alizarin or bromthymol blue will change at the appropriate pH range.

(b)    For NaOH, the pH at the equivalence point is 7, since NaOH is a strong base. Looking at Table 16.1, alizarin, bromthymol blue, or phenol red will change at the appropriate pH range.

(c)    For $C_6H_5NH_2$, the $K_b = 3.9 \times 10^{-10}$ and so the above equation approximates the pH at the equivalence point of ~ 2.9. Looking at Table 16.1, erythrosin B or 2,4-dinitrophenol will change at the appropriate pH range.

## Solubility Equilibria

16.85    For the dissolution reaction, start with the ionic compound as a solid and put it in equilibrium with the appropriate cation and anion, making sure to include the appropriate stoichiometric coefficients. The $K_{sp}$ expression is the product of the concentrations of the cation and anion concentrations raised to their stoichiometric coefficients.

(a)    $BaSO_4 \, (s) \rightleftharpoons Ba^{2+} \, (aq) + SO_4^{2-} \, (aq)$ and $K_{sp} = [Ba^{2+}] \, [SO_4^{2-}]$.

(b)    $PbBr_2 \, (s) \rightleftharpoons Pb^{2+} \, (aq) + 2 \, Br^- \, (aq)$ and $K_{sp} = [Pb^{2+}] \, [Br^-]^2$.

(c)    $Ag_2CrO_4 \, (s) \rightleftharpoons 2 \, Ag^+ \, (aq) + CrO_4^{2-} \, (aq)$ and $K_{sp} = [Ag^+]^2 \, [CrO_4^{2-}]$.

16.86    For the dissolution reaction, start with the ionic compound as a solid and put it in equilibrium with the appropriate cation and anion, making sure to include the appropriate stoichiometric coefficients. The $K_{sp}$ expression is the product of the concentrations of the cation and anion concentrations raised to their stoichiometric coefficients.

(a)    $CaCO_3 \, (s) \rightleftharpoons Ca^{2+} \, (aq) + CO_3^{2-} \, (aq)$ and $K_{sp} = [Ca^{2+}] \, [CO_3^{2-}]$.

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

(c)    $AgI \, (s) \rightleftharpoons Ag^+ \, (aq) + I^- \, (aq)$ and $K_{sp} = [Ag^+] \, [I^-]$.

16.87    **Given:** ionic compound formula and Table 16.2 of $K_{sp}$ values **Find:** molar solubility $(S)$
**Conceptual Plan: The expression of the solubility product constant of $A_mX_n$ is $K_{sp} = [A^{n+}]^m \, [X^{m-}]^n$.**
**The molar solubility of a compound, $A_mX_n$, can be computed directly from $K_{sp}$ by solving for $S$ in the expression $K_{sp} = (mS)^m \, (nS)^n = m^m \, n^n \, S^{m+n}$.**
**Solution:**

(a)    For AgBr, $K_{sp} = 5.35 \times 10^{-13}$, A $= Ag^+$, $m = 1$, X $= Br^-$, and $n = 1$ so $K_{sp} = 5.35 \times 10^{-13} = S^2$. Rearrange to solve for $S$. $S = \sqrt{5.35 \times 10^{-13}} = 7.31 \times 10^{-7}$ M.

(b)    For $Mg(OH)_2$, $K_{sp} = 2.06 \times 10^{-13}$, $A = Mg^{2+}$, $m = 1$, $X = OH^-$, and $n = 2$ so $K_{sp} = 2.06 \times 10^{-13} = 2^2 S^3$.
Rearrange to solve for $S$.   $S = \sqrt[3]{\dfrac{2.06 \times 10^{-13}}{4}} = 3.72 \times 10^{-5}$ M.

(c)    For $CaF_2$, $K_{sp} = 1.46 \times 10^{-10}$, $A = Ca^{2+}$, $m = 1$, $X = F^-$, and $n = 2$ so $K_{sp} = 1.46 \times 10^{-10} = 2^2 S^3$. Rearrange
to solve for $S$.   $S = \sqrt[3]{\dfrac{1.46 \times 10^{-10}}{4}} = 3.32 \times 10^{-4}$ M.

**Check:** The units (M) are correct. The molar solubilities are much less than one and dependent not only on
the value of the $K_{sp}$, but also the stoichiometry of the ionic compound. The more ions that are generated, the
greater the molar solubility for the same value of the $K_{sp}$.

**16.88**   **Given:** ionic compound formula and Table 16.2 of $K_{sp}$ values  **Find:** molar solubility (S)
**Conceptual Plan: The expression of the solubility product constant of $A_mX_n$ is $K_{sp} = [A^{n+}]^m [X^{m-}]^n$.
The molar solubility of a compound, $A_mX_n$, can be computed directly from $K_{sp}$ by solving for S in the
expression $K_{sp} = (mS)^m (nS)^n = m^m n^n S^{m+n}$.**
**Solution:**

(a)    For MX, $K_{sp} = 1.27 \times 10^{-36}$, $A = M^+$, $m = 1$, $X = X^-$, and $n = 1$ so $K_{sp} = 1.27 \times 10^{-36} = S^2$. Rearrange
to solve for $S$.   $S = \sqrt{1.27 \times 10^{-36}} = 1.13 \times 10^{-18}$ M.

(b)    For $Ag_2CrO_4$, $K_{sp} = 1.12 \times 10^{-12}$, $A = Ag^+$, $m = 2$, $X = CrO_4^{2-}$, and $n = 1$ so $K_{sp} = 1.12 \times 10^{-12} = 2^2 S^3$.
Rearrange to solve for $S$.   $S = \sqrt[3]{\dfrac{1.12 \times 10^{-12}}{4}} = 6.54 \times 10^{-5}$ M.

(c)    For $Ca(OH)_2$, $K_{sp} = 4.68 \times 10^{-6}$, $A = Ca^{2+}$, $m = 1$, $X = OH^-$, and $n = 2$ so $K_{sp} = 4.68 \times 10^{-6} = 2^2 S^3$.
Rearrange to solve for $S$.   $S = \sqrt[3]{\dfrac{4.68 \times 10^{-6}}{4}} = 1.05 \times 10^{-2}$ M.

**Check:** The units (M) are correct. The molar solubilities are much less than one and dependent not only on
the value of the $K_{sp}$, but also the stoichiometry of the ionic compound. The more ions that are generated, the
greater the molar solubility for the same value of the $K_{sp}$.

**16.89**   **Given:** ionic compound formula and molar solubility (S)  **Find:** $K_{sp}$
**Conceptual Plan: The expression of the solubility product constant of $A_mX_n$ is $K_{sp} = [A^{n+}]^m [X^{m-}]^n$.
The molar solubility of a compound, $A_mX_n$, can be computed directly from $K_{sp}$ by solving for S in the
expression $K_{sp} = (mS)^m (nS)^n = m^m n^n S^{m+n}$.**
**Solution:**

(a)    For MX, $S = 3.27 \times 10^{-11}$ M, $A = M^+$, $m = 1$, $X = X^-$, and $n = 1$ so $K_{sp} = S^2 = (3.27 \times 10^{-11})^2 = 1.07 \times 10^{-21}$.

(b)    For $PbF_2$, $S = 5.63 \times 10^{-3}$ M, $A = Pb^{2+}$, $m = 1$, $X = F^-$, and $n = 2$ so $K_{sp} = 2^2 S^3 = 2^2 (5.63 \times 10^{-3})^3 = 7.14 \times 10^{-7}$.

(c)    For $MgF_2$, $S = 2.65 \times 10^{-4}$ M, $A = Mg^{2+}$, $m = 1$, $X = F^-$, and $n = 2$ so $K_{sp} = 2^2 S^3 = 2^2 (2.65 \times 10^{-4})^3 = 7.44 \times 10^{-11}$.

**Check:** The units (none) are correct. The $K_{sp}$ values are much less than one and dependent not only on the
value of the solubility, but also the stoichiometry of the ionic compound. The more ions that are generated,
the smaller the $K_{sp}$ for the same value of the S.

**16.90**   **Given:** ionic compound formula and molar solubility (S)  **Find:** $K_{sp}$
**Conceptual Plan: The expression of the solubility product constant of $A_mX_n$ is $K_{sp} = [A^{n+}]^m [X^{m-}]^n$.
The molar solubility of a compound, $A_mX_n$, can be computed directly from $K_{sp}$ by solving for S in the
expression $K_{sp} = (mS)^m (nS)^n = m^m n^n S^{m+n}$.**
**Solution:**

(a)    For $BaCrO_4$, $S = 1.08 \times 10^{-5}$ M, $A = Ba^{2+}$, $m = 1$, $X = CrO_4^{2-}$, and $n = 1$ so $K_{sp} = S^2 = (1.08 \times 10^{-5})^2 = 1.17 \times 10^{-10}$.

The molar solubility of a compound, $A_mX_n$, can be computed directly from $K_{sp}$ by solving for $S$ in the expression $K_{sp} = (mS)^m (nS)^n = m^m n^n S^{m+n}$.
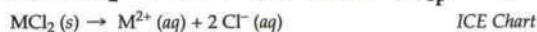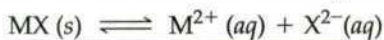
Solution: MX, $K_{sp} = 1.27 \times 10^{-36}$, $A = M^{2+}$, $m = 1$, $X = X^{2-}$, and $n = 1$. There is a 1:1 ratio of the cation:anion, so $K_{sp} = 1.27 \times 10^{-36} = S^2$. Rearrange to solve for $S$. $S = 1.13 \times 10^{-18}$ M.

(b)    **Given:** MX  **Find:** molar solubility ($S$) in 0.25 M $MCl_2$  **Other:** $K_{sp}$ (MX) $= 1.27 \times 10^{-36}$
**Conceptual Plan: M $MCl_2$ $\rightarrow$ M $M^{2+}$ then M $M^{2+}$, $K_{sp}$ $\rightarrow$ S**
$$MCl_2 (s) \rightarrow M^{2+} (aq) + 2\,Cl^- (aq) \qquad\qquad ICE\ Chart$$
**Solution:** Since 1 $M^{2+}$ ion is generated for each $MCl_2$, $[M^{2+}] = 0.25$ M.

| MX (s) $\rightleftharpoons$ | $M^{2+}$ (aq) + | $X^{2-}$(aq) |
|---|---|---|
| Initial | 0.25 | 0.00 |
| Change | S | S |
| Equil | 0.25 + S | S |

$K_{sp}$ (MX) $= [M^{2+}] [X^{2-}] = 1.27 \times 10^{-36} = (0.25 + S) S$.

Assume $S \ll 0.25$, $1.27 \times 10^{-36} = (0.25) S$, and $S = 5.08 \times 10^{-36}$ M. Confirm that the assumption is valid.

$\dfrac{5.08 \times 10^{-36}}{0.25} \times 100\% = 2.0 \times 10^{-33}\% \ll 5\%$ so the assumption is valid.

(c)    **Given:** MX  **Find:** molar solubility ($S$) in 0.20 M $Na_2S$  **Other:** $K_{sp}$ (MX) $= 1.27 \times 10^{-36}$
**Conceptual Plan: M $Na_2X$ $\rightarrow$ M $X^{2-}$ then M $X^{2-}$, $K_{sp}$ $\rightarrow$ S**
$$Na_2X (s) \rightarrow 2\,Na^+ (aq) + X^{2-} (aq) \qquad\qquad ICE\ Chart$$
**Solution:** Since 1 $X^{2-}$ ion is generated for each $Na_2X$, $[X^{2-}] = 0.20$ M.
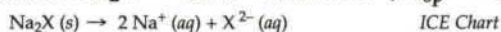
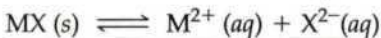| MX (s) $\rightleftharpoons$ | $M^{2+}$ (aq) + | $X^{2-}$(aq) |
|---|---|---|
| Initial | 0.00 | 0.20 |
| Change | S | S |
| Equil | S | 0.20 + S |

$K_{sp}$ (MX) $= [M^{2+}] [X^{2-}] = 1.27 \times 10^{-36} = (S)(0.20 + S)$.

Since $S \ll 0.20$, $1.27 \times 10^{-36} = (S)(0.20)$, and $S = 6.35 \times 10^{-36}$ M. Confirm that the assumption is valid.

$\dfrac{6.35 \times 10^{-36}}{0.20} \times 100\% = 3.2 \times 10^{-33}\% \ll 5\%$ so the assumption is valid.

**Check:** The units (M) are correct. The solubility of the MX decreases in the presence of a common ion.

**16.97**    **Given:** $Ca(OH)_2$  **Find:** molar solubility ($S$) in buffers at a) pH = 4, b) pH = 7, and c) pH = 9
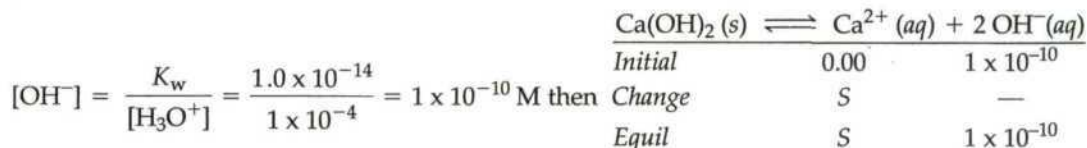**Other:** $K_{sp}$ ($Ca(OH)_2$) $= 4.68 \times 10^{-6}$
**Conceptual Plan: pH $\rightarrow$ $[H_3O^+]$ $\rightarrow$ $[OH^-]$ then M $OH^-$, $K_{sp}$ $\rightarrow$ S**
$$[H_3O^+] = 10^{-pH} \quad K_w = [H_3O^+][OH^-] \qquad\qquad set\ up\ ICE\ table$$
**Solution:**

(a)    pH = 4, so $[H_3O^+] = 10^{-pH} = 10^{-4} = 1 \times 10^{-4}$ M then $K_w = [H_3O^+][OH^-]$ so

| | | $Ca(OH)_2$ (s) $\rightleftharpoons$ | $Ca^{2+}$ (aq) + | $2\,OH^-$(aq) |
|---|---|---|---|---|
| | | Initial | 0.00 | $1 \times 10^{-10}$ |
| $[OH^-] = \dfrac{K_w}{[H_3O^+]} = \dfrac{1.0 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10}$ M then | | Change | S | — |
| | | Equil | S | $1 \times 10^{-10}$ |

$K_{sp}$ ($Ca(OH)_2$) $= [Ca^{2+}] [OH^-]^2 = 4.68 \times 10^{-6} = S (1 \times 10^{-10})^2$ and $S = 5 \times 10^{14}$ M.

(b)    pH = 7, so $[H_3O^+] = 10^{-pH} = 10^{-7} = 1 \times 10^{-7}$ M then $K_w = [H_3O^+][OH^-]$ so

$[OH^-] = \dfrac{K_w}{[H_3O^+]} = \dfrac{1.0 \times 10^{-14}}{1 \times 10^{-7}} = 1 \times 10^{-7}$ M then

| $Ca(OH)_2$ (s) $\rightleftharpoons$ | $Ca^{2+}$ (aq) + | $2\,OH^-$(aq) |
|---|---|---|
| Initial | 0.00 | $1 \times 10^{-7}$ |
| Change | S | — |
| Equil | S | $1 \times 10^{-7}$ |

$K_{sp}$ ($Ca(OH)_2$) $= [Ca^{2+}] [OH^-]^2 = 4.68 \times 10^{-6} = S (1 \times 10^{-7})^2$ and $S = 5 \times 10^{8}$ M.

(c)   pH = 9, so $[H_3O^+] = 10^{-pH} = 10^{-9} = 1 \times 10^{-9}$ M then $K_w = [H_3O^+][OH^-]$ so

| | $Ca(OH)_2 (s) \rightleftharpoons$ | $Ca^{2+} (aq)$ | $+ 2 OH^- (aq)$ |
|---|---|---|---|
| Initial | | 0.00 | $1 \times 10^{-5}$ |
| Change | | $S$ | — |
| Equil | | $S$ | $1 \times 10^{-5}$ |

$[OH^-] = \dfrac{K_w}{[H_3O^+]} = \dfrac{1.0 \times 10^{-14}}{1 \times 10^{-9}} = 1 \times 10^{-5}$ M then
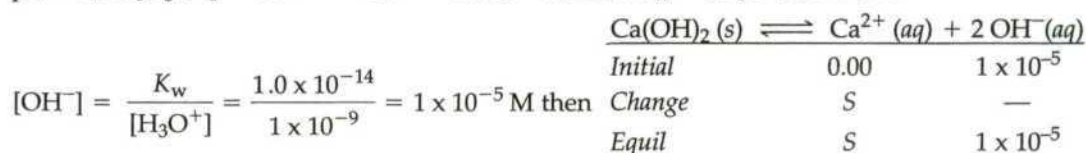
$K_{sp} (Ca(OH)_2) = [Ca^{2+}][OH^-]^2 = 4.68 \times 10^{-6} = S (1 \times 10^{-5})^2$. and $S = 5 \times 10^4$ M.

**Check:** The units (M) are correct. The solubility of the $Ca(OH)_2$ decreases as the pH increases (and the hydroxide ion concentration increases). Realize that these molar solubilities are not achievable because the saturation point of pure $Ca(OH)_2$ is ~ 30 M. The bottom line is that as long as the hydroxide concentration can be controlled with a buffer, the $Ca(OH)_2$ will be very soluble.

16.98   **Given:** $Mg(OH)_2$ in $1.00 \times 10^2$ mL solution   **Find:** grams of $Mg(OH)_2$ in pure water and buffer at pH = 10
**Other:** $K_{sp} (Mg(OH)_2) = 2.06 \times 10^{-13}$
**Conceptual Plan:** For pure water:
The expression of the solubility product constant of $A_mX_n$ is $K_{sp} = [A^{n+}]^m [X^{m-}]^n$. The molar solubility of a compound, $A_mX_n$, can be computed directly from $K_{sp}$ by solving for $S$ in the expression $K_{sp} = (mS)^m (nS)^n = m^m n^n S^{m+n}$. Then mL $\rightarrow$ L then $S, L \rightarrow$ mol $Mg(OH)_2 \rightarrow$ g $Mg(OH)_2$.

$$\frac{1 L}{1000 mL} \qquad M = \frac{mol}{L} \qquad \frac{58.33 \text{ g } Mg(OH)_2}{1 \text{ mol } Mg(OH)_2}$$

**For buffer Solution:** pH $\rightarrow [H_3O^+] \rightarrow [OH^-]$ then

$$[H_3O^+] = 10^{-pH} \qquad K_w = [H_3O^+][OH^-]$$

$M\, OH^-, K_{sp} \rightarrow S$ then $S, L \rightarrow$ mol $Mg(OH)_2 \rightarrow$ g $Mg(OH)_2$.

$$\text{set up ICE table} \qquad M = \frac{mol}{L} \qquad \frac{58.33 \text{ g } Mg(OH)_2}{1 \text{ mol } Mg(OH)_2}$$

**Solution:** For pure water, $K_{sp} = 2.06 \times 10^{-13}$, $A = Mg^{2+}$, $m = 1$, $X = OH^-$, and $n = 2$ so $K_{sp} = 2.06 \times 10^{-13} = 2^2 S^3$.
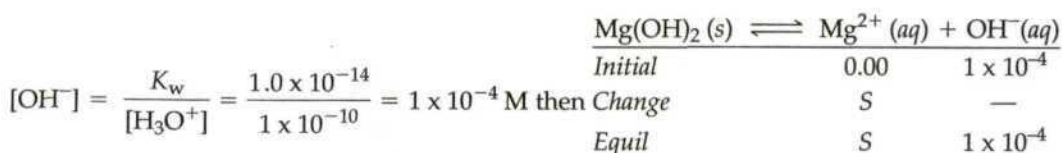
Rearrange to solve for $S$. $S = \sqrt[3]{\dfrac{2.06 \times 10^{-13}}{4}} = 3.72051 \times 10^{-5}$ M. Then

$1.00 \times 10^2 \text{ mL} \times \dfrac{1 L}{1000 \text{ mL}} = 0.100$ L then

$\dfrac{3.72051 \times 10^{-5} \text{ mol } Mg(OH)_2}{1 L} \times 0.100 \text{ L} = 3.72051 \times 10^{-6} \text{ mol } Mg(OH)_2 \times \dfrac{58.33 \text{ g } Mg(OH)_2}{1 \text{ mol } Mg(OH)_2} =$

$2.17 \times 10^{-4}$ g $Mg(OH)_2$

for pH = 10, so $[H_3O^+] = 10^{-pH} = 10^{-10} = 1 \times 10^{-10}$ M then $K_w = [H_3O^+][OH^-]$ so

| | $Mg(OH)_2 (s) \rightleftharpoons$ | $Mg^{2+} (aq)$ | $+ OH^- (aq)$ |
|---|---|---|---|
| Initial | | 0.00 | $1 \times 10^{-4}$ |
| Change | | $S$ | — |
| Equil | | $S$ | $1 \times 10^{-4}$ |

$[OH^-] = \dfrac{K_w}{[H_3O^+]} = \dfrac{1.0 \times 10^{-14}}{1 \times 10^{-10}} = 1 \times 10^{-4}$ M then

$K_{sp} (Mg(OH)_2) = [Mg^{2+}][OH^-]^2 = 2.06 \times 10^{-13} = S (1 \times 10^{-4})^2$ and $S = 2.06 \times 10^{-5}$ M. Then

$\dfrac{2.06 \times 10^{-5} \text{ mol } Mg(OH)_2}{1 L} \times 0.100 \text{ L} = 2.06 \times 10^{-6} \text{ mol } Mg(OH)_2 \times \dfrac{58.33 \text{ g } Mg(OH)_2}{1 \text{ mol } Mg(OH)_2} = 1 \times 10^{-4}$ g $Mg(OH)_2$.

**Check:** The units (M) are correct. The solubility of the $Mg(OH)_2$ decreases as the pH increases (and the hydroxide ion concentration increases).

16.99   (a)   $BaCO_3$ will be more soluble in acidic solutions because $CO_3^{2-}$ is basic. In acidic solutions it can be converted to $HCO_3^-$ and $H_2CO_3^{2-}$. These species are not $CO_3^{2-}$ so they do not appear in the $K_{sp}$ expression.

(b)   $CuS$ will be more soluble in acidic solutions because $S^{2-}$ is basic. In acidic solutions it can be converted to $HS^-$ and $H_2S^{2-}$. These species are not $S^{2-}$ so they do not appear in the $K_{sp}$ expression.

(c)   $AgCl$ will not be more soluble in acidic solutions because $Cl^-$ will not react with acidic solutions, because $HCl$ is a strong acid.

(d) $PbI_2$ will not be more soluble in acidic solutions because $I^-$ will not react with acidic solutions, because HI is a strong acid.

16.100 (a) $Hg_2Br_2$ will not be more soluble in acidic solutions because $Br^-$ will not react with acidic solutions, because HBr is a strong acid.

(b) $Mg(OH)_2$ will be more soluble in acidic solutions because $OH^-$ is basic. In acidic solutions it can be converted to $H_2O$. This species is not $OH^-$ and so it does not appear in the $K_{sp}$ expression.

(c) $CaCO_3$ will be more soluble in acidic solutions because $CO_3^{2-}$ is basic. In acidic solutions it can be converted to $HCO_3^-$ and $H_2CO_3^{2-}$. These species are not $CO_3^{2-}$ so they do not appear in the $K_{sp}$ expression.

(d) AgI will not be more soluble in acidic solutions because $I^-$ will not react with acidic solutions, because HI is a strong acid.

## Precipitation and Qualitative Analysis

16.101 **Given:** 0.015 M NaF and 0.010 M $Ca(NO_3)_2$ **Find:** Will a precipitate form? If so, identify it.
**Other:** $K_{sp}$ $(CaF_2) = 1.46 \times 10^{-10}$
**Conceptual Plan: Look at all possible combinations and consider the solubility rules from Chapter 4. Salts of alkali metals (Na) are very soluble, so NaF and $NaNO_3$ will be very soluble. Nitrate compounds are very soluble so $NaNO_3$ will be very soluble. The only possibility for a precipitate is $CaF_2$. Determine if a precipitate will form by determining the concentration of the $Ca^{2+}$ and $F^-$ in solution. Then compute the reaction quotient, $Q$. If $Q > K_{sp}$ then a precipitate will form.**
**Solution:** Since the only possible precipitate is $CaF_2$, calculate the concentrations of $Ca^{2+}$ and $F^-$. NaF $(s) \rightarrow$ $Na^+$ $(aq) + F^-$ $(aq)$. Since 1 $F^-$ ion is generated for each NaF, $[F^-] = 0.015$ M.
$Ca(NO_3)_2$ $(s) \rightarrow Ca^{2+}$ $(aq) + 2 NO_3^-$ $(aq)$. Since 1 $Ca^{2+}$ ion is generated for each $Ca(NO_3)_2$, $[Ca^{2+}] = 0.010$ M. Then calculate $Q$ $(CaF_2)$, $A = Ca^{2+}$, $m = 1$, $X = F^-$, and $n = 2$. Since $Q = [A^{n+}]^m [X^{m-}]^n$, then
$Q$ $(CaF_2) = [Ca^{2+}] [F^-]^2 = (0.010) (0.015)^2 = 2.3 \times 10^{-6} > 1.46 \times 10^{-10} = K_{sp}$ $(CaF_2)$, so a precipitate will form.
**Check:** The units (none) are correct. The solubility of the $CaF_2$ is low, and the concentration of ions are extremely large compared to the $K_{sp}$, so a precipitate will form.

16.102 **Given:** 0.013 M KBr and 0.0035 M $Pb(C_2H_3O_2)_2$ **Find:** Will a precipitate form? If so, identify it.
**Other:** $K_{sp}$ $(PbBr_2) = 4.67 \times 10^{-6}$
**Conceptual Plan: Look at all possible combinations and consider the solubility rules from Chapter 4. Salts of alkali metals (K) are very soluble, so KBr and $KC_2H_3O_2$ will be very soluble. Acetate compounds are very soluble so $Pb(C_2H_3O_2)_2$ and $KC_2H_3O_2$ will be very soluble. The only possibility for a precipitate is $PbBr_2$. Determine if a precipitate will form by determining the concentration of the $Pb^{2+}$ and $Br^-$ in solution. Then compute the reaction quotient, $Q$. If $Q > K_{sp}$ then a precipitate will form.**
**Solution:** Since the only possible precipitate is $PbBr_2$, calculate the concentrations of $Pb^{2+}$ and $Br^-$.
KBr $(s) \rightarrow K^+$ $(aq) + Br^-$ $(aq)$. Since 1 $Br^-$ ion is generated for each KBr, $[Br^-] = 0.013$ M. $Pb(C_2H_3O_2)_2$ $(s) \rightarrow$ $Pb^{2+}$ $(aq) + 2 C_2H_3O_2^-$ $(aq)$. Since 1 $Pb^{2+}$ ion is generated for each $Pb(C_2H_3O_2)_2$, $[Pb^+] = 0.0035$ M. Then calculate $Q$ $(PbBr_2)$, $A = Pb^{2+}$, $m = 1$, $X = Br^-$, and $n = 2$ Since $Q = [A^{n+}]^m [X^{m-}]^n$, then $Q$ $(PbBr_2) =$
$[Pb^{2+}] [Br^-]^2 = (0.0035) (0.013)^2 = 6.0 \times 10^{-7} < 4.67 \times 10^{-6} = K_{sp}$ $(PbBr_2)$, so a precipitate will not form.
**Check:** The units (none) are correct. The $K_{sp}$ of the $PbBr_2$ is not too low compared to the solution ion concentrations, so a precipitate will not form.

16.103 **Given:** 75.0 mL of NaOH with pOH = 2.58 and 125.0 mL of 0.0018 M $MgCl_2$ **Find:** Will a precipitate form? If so, identify it. **Other:** $K_{sp}$ $(Mg(OH)_2) = 2.06 \times 10^{-13}$
**Conceptual Plan: Look at all possible combinations and consider the solubility rules from Chapter 4. Salts of alkali metals (Na) are very soluble, so NaOH and NaCl will be very soluble. Chloride compounds are generally very soluble so $MgCl_2$ and NaCl will be very soluble. The only possibility for a precipitate is $Mg(OH)_2$. Determine if a precipitate will form by determining the concentration of the $Mg^{2+}$ and $OH^-$ in solution. Since pH, not NaOH concentration, is given pOH $\rightarrow$ $[OH^-]$ then**

$$[OH^-] = 10^{-pOH}$$

mix solutions and calculate diluted concentrations mL NaOH, mL $MgCl_2$ $\rightarrow$ mL total then

$$mL\ NaOH + mL\ MgCl_2 = total\ mL$$

mL, initial M $\rightarrow$ final M then compute the reaction quotient, $Q$.

$$M_1 V_1 = M_2 V_2$$

If $Q > K_{sp}$ then a precipitate will form.

**Solution:** Since the only possible precipitate is $Mg(OH)_2$, calculate the concentrations of $Mg^{2+}$ and $OH^-$.
For NaOH at pOH = 2.58, so $[OH^-] = 10^{-pOH} = 10^{-2.58} = 2.63027 \times 10^{-3}$ M and
$MgCl_2 (s) \rightarrow Mg^{2+} (aq) + 2\ Cl^- (aq)$. Since 1 $Mg^{2+}$ ion is generated for each $MgCl_2$, $[Mg^{2+}] = 0.0018$ M.
Then total mL = mL NaOH + mL $MgCl_2$ = 75.0 mL + 125.0 mL = 200.0 mL. Then $M_1 V_1 = M_2 V_2$,

rearrange to solve for $M_2$. $M_2 = M_1 \dfrac{V_1}{V_2} = 2.63027 \times 10^{-3}$ M $OH^- \times \dfrac{75.0\ mL}{200.0\ mL} = 9.8635 \times 10^{-4}$ M $OH^-$ and

$M_2 = M_1 \dfrac{V_1}{V_2} = 0.0018$ M $Mg^+ \times \dfrac{125.0\ mL}{200.0\ mL} = 1.125 \times 10^{-3}$ M $Mg^{2+}$. Calculate $Q$ $(Mg(OH)_2)$, A = $Mg^{2+}$,

m = 1, X = $OH^-$, and n = 2. Since $Q = [A^{n+}]^m [X^{m-}]^n$, then $Q$ $(Mg(OH)_2) = [Mg^{2+}] [OH^-]^2 =$
$(1.125 \times 10^{-3})(9.8635 \times 10^{-4})^2 = 1.1 \times 10^{-9} > 2.06 \times 10^{-13} = K_{sp}$ $(Mg(OH)_2)$, so a precipitate will form.

**Check:** The units (none) are correct. The solubility of the $Mg(OH)_2$ is low, and the NaOH (a base) is high enough that the product of the concentration of ions are large compared to the $K_{sp}$, so a precipitate will form.

**16.104** **Given:** 175.0 mL of 0.0055 M KCl and 145.0 mL of 0.0015 M $AgNO_3$
**Find:** Will a precipitate form? If so, identify it. **Other:** $K_{sp}$ (AgCl) = $1.77 \times 10^{-10}$
**Conceptual Plan:** Look at all possible combinations and consider the solubility rules from Chapter 4. Salts of alkali metals (K) are very soluble, so KCl and $KNO_3$ will be very soluble. Nitrate compounds are very soluble so $KNO_3$ and Ag $NO_3$ will be very soluble. The only possibility for a precipitate is AgCl. Determine if a precipitate will form by determining the concentration of the $Ag^+$ and $Cl^-$ in solution. Mix solutions and calculate diluted concentrations mL KCl, mL $AgNO_3$ $\rightarrow$ mL total then

$$mL\ KCl + mL\ AgNO_3 = total\ mL$$

mL, initial M $\rightarrow$ final M then compute the reaction quotient, $Q$. If $Q > K_{sp}$ then a precipitate will form.

$$M_1 V_1 = M_2 V_2$$

**Solution:** Since the only possible precipitate is AgCl, calculate the concentrations of $Ag^+$ and $Cl^-$.
KCl (s) $\rightarrow$ $K^+$ (aq) + $Cl^-$ (aq). Since 1 $Cl^-$ ion is generated for each AgCl, $[Cl^-] = 0.0055$ M and $AgNO_3$ (s) $\rightarrow$
$Ag^+$ (aq) + $NO_3^-$ (aq). Since 1 $Ag^+$ ion is generated for each $AgNO_3$, $[Ag^+] = 0.0015$ M. Then total mL = mL
KCl + mL $AgNO_3$ = 175.0 mL + 145.0 mL = 320.0. Then $M_1 V_1 = M_2 V_2$, rearrange to solve for $M_2$.

$M_2 = M_1 \dfrac{V_1}{V_2} = 0.0055$ M $Cl^- \times \dfrac{175.0\ mL}{320.0\ mL} = 0.00300781$ M $Cl^-$ and

$M_2 = M_1 \dfrac{V_1}{V_2} = 0.0015$ M $Ag^+ \times \dfrac{145.0\ mL}{320.0\ mL} = 0.00067969$ M $Ag^+$. Calculate $Q$ (AgCl), A = $Ag^+$, m = 1,

X = $Cl^-$, and $n = 1$. Since $Q = [A^{n+}]^m [X^{m-}]^n$, then $Q$ (AgCl) = $[Ag^+] [Cl^-] =$
$(0.00067969)(0.00300781) = 2.0 \times 10^{-6} > 1.77 \times 10^{-10} = K_{sp}$ (AgCl), so a precipitate will form.

**Check:** The units (none) are correct. The solubility of the AgCl is low, and the concentrations of the ions are high enough that the product of the concentration of ions is very large compared to the $K_{sp}$, so a precipitate will form.

**16.105** **Given:** KOH as precipitation agent in a) 0.015 M $CaCl_2$, b) 0.0025 M $Fe(NO_3)_2$, and c) 0.0018 M $MgBr_2$
**Find:** concentration of KOH necessary to form a precipitate
**Other:** $K_{sp}$ $(Ca(OH)_2) = 4.68 \times 10^{-6}$, $K_{sp}$ $(Fe(OH)_2) = 4.87 \times 10^{-17}$, $K_{sp}$ $(Mg(OH)_2) = 2.06 \times 10^{-13}$
**Conceptual Plan:** The solubility rules from Chapter 4 state that most hydroxides are insoluble, so all precipitates will be hydroxides. Determine the concentration of the cation in solution. Since all metals have

an oxidation state of +2 and $[OH^-] = [KOH]$, all of the $K_{sp}$ = [cation] $[KOH]^2$ and so $[KOH] = \sqrt{\dfrac{K_{sp}}{[cation]}}$.

**Solution:**

(a) $CaCl_2$ (s) $\rightarrow$ $Ca^{2+}$ (aq) + 2 $Cl^-$ (aq). Since 1 $Ca^{2+}$ ion is generated for each $CaCl_2$, $[Ca^{2+}] = 0.015$ M.

Then $[KOH] = \sqrt{\dfrac{K_{sp}}{[cation]}} = \sqrt{\dfrac{4.68 \times 10^{-6}}{0.015}} = 0.018$ M KOH.

(b)  $Fe(NO_3)_2 (s) \rightarrow Fe^{2+} (aq) + 2 NO_3^- (aq)$. Since 1 $Fe^{2+}$ ion is generated for each $Fe(NO_3)_2$, $[Fe^{2+}] = 0.0025$ M.

Then $[KOH] = \sqrt{\dfrac{K_{sp}}{[\text{cation}]}} = \sqrt{\dfrac{4.87 \times 10^{-17}}{0.0025}} = 1.4 \times 10^{-7}$ M KOH.

(c)  $MgBr_2 (s) \rightarrow Mg^{2+} (aq) + 2 Br^- (aq)$. Since 1 $Mg^{2+}$ ion is generated for each $MgBr_2$, $[Mg^{2+}] = 0.0018$ M.

Then $[KOH] = \sqrt{\dfrac{K_{sp}}{[\text{cation}]}} = \sqrt{\dfrac{2.06 \times 10^{-13}}{0.0018}} = 1.1 \times 10^{-5}$ M KOH.
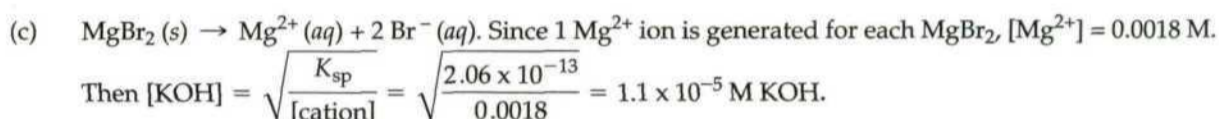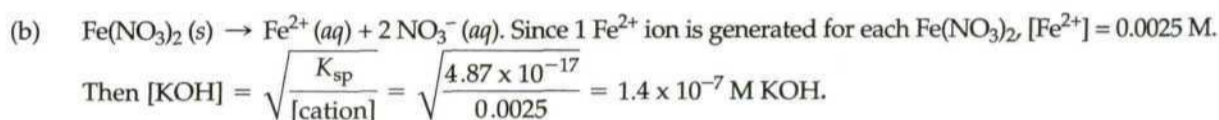
**Check:** The units (none) are correct. Since all cations have an oxidation state of +2, it can be seen that the $[KOH]$ needed to precipitate the hydroxide is lower the smaller the $K_{sp}$.

16.106   **Given:** solution and precipitation agent pairs a) 0.035 M $Ba(NO_3)_2$: NaF, b) 0.085 M $CaI_2$ : $K_2SO_4$, and c) 0.0018 M $AgNO_3$ :RbCl **Find:** concentration of precipitation agent necessary to form a precipitate.
**Other:** $K_{sp} (BaF_2) = 2.45 \times 10^{-5}$, $K_{sp} (CaSO_4) = 7.10 \times 10^{-5}$, $K_{sp} (AgCl) = 1.77 \times 10^{-10}$
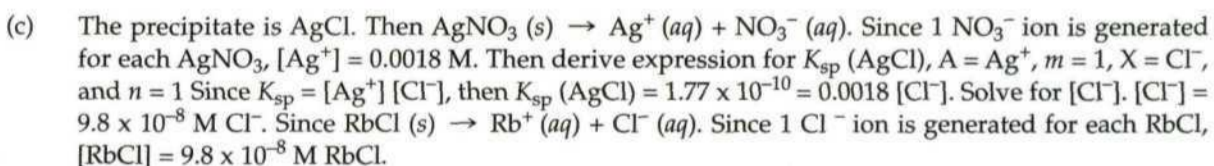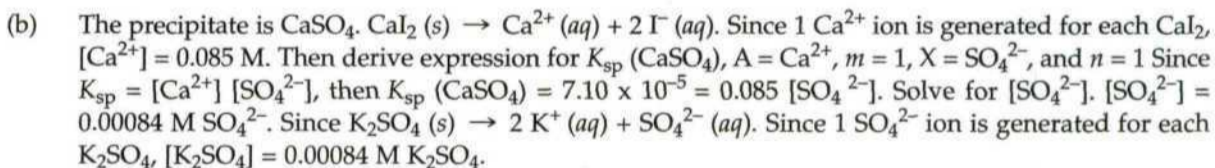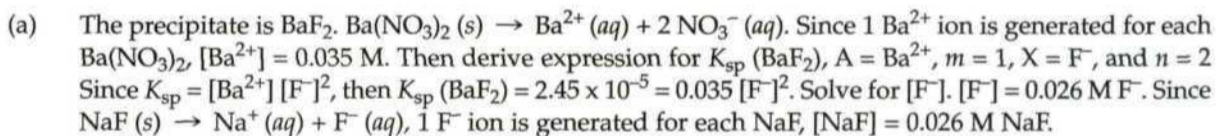**Conceptual Plan: Determine the concentration of the cation in solution. The solubility product constant ($K_{sp}$) is the equilibrium expression for a chemical equation representing the dissolution of an ionic compound. The expression of the solubility product constant of $A_mX_n$ is $K_{sp} = [A^{n+}]^m [X^{m-}]^n$. Substitute in concentration of cation and solve for concentration of anion.**
**Solution:**

(a)  The precipitate is $BaF_2$. $Ba(NO_3)_2 (s) \rightarrow Ba^{2+} (aq) + 2 NO_3^- (aq)$. Since 1 $Ba^{2+}$ ion is generated for each $Ba(NO_3)_2$, $[Ba^{2+}] = 0.035$ M. Then derive expression for $K_{sp} (BaF_2)$, $A = Ba^{2+}$, $m = 1$, $X = F^-$, and $n = 2$ Since $K_{sp} = [Ba^{2+}] [F^-]^2$, then $K_{sp} (BaF_2) = 2.45 \times 10^{-5} = 0.035 [F^-]^2$. Solve for $[F^-]$. $[F^-] = 0.026$ M $F^-$. Since $NaF (s) \rightarrow Na^+ (aq) + F^- (aq)$, 1 $F^-$ ion is generated for each NaF, $[NaF] = 0.026$ M NaF.

(b)  The precipitate is $CaSO_4$. $CaI_2 (s) \rightarrow Ca^{2+} (aq) + 2 I^- (aq)$. Since 1 $Ca^{2+}$ ion is generated for each $CaI_2$, $[Ca^{2+}] = 0.085$ M. Then derive expression for $K_{sp} (CaSO_4)$, $A = Ca^{2+}$, $m = 1$, $X = SO_4^{2-}$, and $n = 1$ Since $K_{sp} = [Ca^{2+}] [SO_4^{2-}]$, then $K_{sp} (CaSO_4) = 7.10 \times 10^{-5} = 0.085 [SO_4^{2-}]$. Solve for $[SO_4^{2-}]$. $[SO_4^{2-}] = 0.00084$ M $SO_4^{2-}$. Since $K_2SO_4 (s) \rightarrow 2 K^+ (aq) + SO_4^{2-} (aq)$. Since 1 $SO_4^{2-}$ ion is generated for each $K_2SO_4$, $[K_2SO_4] = 0.00084$ M $K_2SO_4$.

(c)  The precipitate is AgCl. Then $AgNO_3 (s) \rightarrow Ag^+ (aq) + NO_3^- (aq)$. Since 1 $NO_3^-$ ion is generated for each $AgNO_3$, $[Ag^+] = 0.0018$ M. Then derive expression for $K_{sp} (AgCl)$, $A = Ag^+$, $m = 1$, $X = Cl^-$, and $n = 1$ Since $K_{sp} = [Ag^+] [Cl^-]$, then $K_{sp} (AgCl) = 1.77 \times 10^{-10} = 0.0018 [Cl^-]$. Solve for $[Cl^-]$. $[Cl^-] = 9.8 \times 10^{-8}$ M $Cl^-$. Since $RbCl (s) \rightarrow Rb^+ (aq) + Cl^- (aq)$. Since 1 $Cl^-$ ion is generated for each RbCl, $[RbCl] = 9.8 \times 10^{-8}$ M RbCl.

**Check:** The units (M) are correct. Comparing part (a) and part (b) the effect of the stoichiometry of the precipitate is seen and the concentration of the precipitation agent is much lower. Looking at part (c) the concentration of the precipitation agent is so low because the $K_{sp}$ is so small.

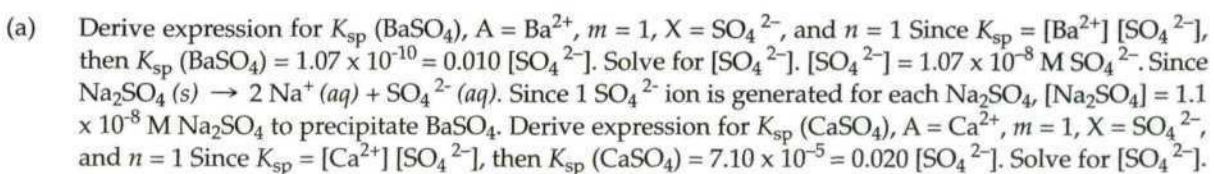16.107   **Given:** solution with 0.010 M $Ba^{2+}$ and 0.020 M $Ca^{2+}$ add $Na_2SO_4$ to form precipitates
**Find:** (a) which ion precipitates first and minimum $[Na_2SO_4]$ needed; and (b) [first cation] when second cation precipitates **Other:** $K_{sp} (BaSO_4) = 1.07 \times 10^{-10}$, $K_{sp} (CaSO_4) = 7.10 \times 10^{-5}$
**Conceptual Plan: (a) The precipitates that will form are $BaSO_4$ and $CaSO_4$.**
**Use the equation derived in Problem 19 to define $K_{sp}$. Substitute in concentration of cation and solve for**
for ionic compound, $A_mX_n$, $K_{sp} = [A^{n+}]^m [X^{m-}]^n$
**concentration of anion to form precipitate. The cation with the lower anion concentration will precipitate first.**

(b)  **Substitute the higher anion concentration into the $K_{sp}$ expression for the first cation to precipitate and calculate the amount of this first cation to remain in solution.**
**Solution:**

(a)  Derive expression for $K_{sp} (BaSO_4)$, $A = Ba^{2+}$, $m = 1$, $X = SO_4^{2-}$, and $n = 1$ Since $K_{sp} = [Ba^{2+}] [SO_4^{2-}]$, then $K_{sp} (BaSO_4) = 1.07 \times 10^{-10} = 0.010 [SO_4^{2-}]$. Solve for $[SO_4^{2-}]$. $[SO_4^{2-}] = 1.07 \times 10^{-8}$ M $SO_4^{2-}$. Since $Na_2SO_4 (s) \rightarrow 2 Na^+ (aq) + SO_4^{2-} (aq)$. Since 1 $SO_4^{2-}$ ion is generated for each $Na_2SO_4$, $[Na_2SO_4] = 1.1 \times 10^{-8}$ M $Na_2SO_4$ to precipitate $BaSO_4$. Derive expression for $K_{sp} (CaSO_4)$, $A = Ca^{2+}$, $m = 1$, $X = SO_4^{2-}$, and $n = 1$ Since $K_{sp} = [Ca^{2+}] [SO_4^{2-}]$, then $K_{sp} (CaSO_4) = 7.10 \times 10^{-5} = 0.020 [SO_4^{2-}]$. Solve for $[SO_4^{2-}]$.

$[SO_4{}^{2-}] = 0.0036$ M $SO_4{}^{2-} = 0.0036$ M $Na_2SO_4 = [Na_2SO_4]$ to precipitate $CaSO_4$. Since $1.1 \times 10^{-8}$ M $Na_2SO_4 \ll 0.0036$ M $Na_2SO_4$, the $Ba^{2+}$ will precipitate first.

(b)    Since $Ca^{2+}$ will not precipitate until $[Na_2SO_4] = 0.00355$ M $Na_2SO_4$, substitute this value into the $K_{sp}$ expression for $BaSO_4$. So $K_{sp}$ ($BaSO_4$) = $[Ba^{2+}] [SO_4{}^{2-}] = 1.07 \times 10^{-10} = [Ba^{2+}] 0.0035$. Solve for $[Ba^{2+}]$ = $3.0 \times 10^{-8}$ M $Ba^{2+}$.

Check: The units (none, M, and M) are correct. Comparing the two $K_{sp}$ values, it can be seen that the $Ba^{2+}$ will precipitate first since the solubility product is so much lower. Since the $K_{sp}$ value is so low, the concentration of precipitating agent is very low. Since the $CaSO_4$ $K_{sp}$ value is so much higher, the higher $[SO_4{}^{2-}]$ to precipitate Ca will force the concentration of $Ba^{2+}$ to very low levels.

16.108    **Given:** solution with 0.022 M $Fe^{2+}$ and 0.014 M $Mg^{2+}$ add $K_2CO_3$ to form precipitates
**Find:** (a) which ion precipitates first and minimum $[K_2CO_3]$ needed; and (b) [first cation] when second cation precipitates    **Other:** $K_{sp}$ ($FeCO_3$) = $3.07 \times 10^{-11}$, $K_{sp}$ ($MgCO_3$) = $6.82 \times 10^{-6}$
**Conceptual Plan: (a) The precipitates that will form are $FeCO_3$ and $MgCO_3$.**
**Use the equation derived in Problem 19 to define $K_{sp}$. Substitute in concentration of cation and solve for**
     for ionic compound, $A_mX_n$, $K_{sp} = [A^{n+}]^m [X^{m-}]^n$
**concentration of anion to form precipitate. The cation with the lower anion concentration will precipitate first.**
**(b)    Substitute the higher anion concentration into the $K_{sp}$ expression for the first cation to precipitate and calculate the amount of this first cation to remain in solution.**
**Solution:**

(a)    Derive expression for $K_{sp}$ ($FeCO_3$), A = $Fe^{2+}$, $m = 1$, X = $CO_3{}^{2-}$, and $n = 1$. Since $K_{sp} = [Fe^{2+}] [CO_3{}^{2-}]$, then $K_{sp}$ ($FeCO_3$) = $3.07 \times 10^{-11} = 0.022 [CO_3{}^{2-}]$. Solve for $[CO_3{}^{2-}]$. $[CO_3{}^{2-}] = 1.4 \times 10^{-9}$ M $CO_3{}^{2-}$. Since $K_2CO_3$ $(s) \rightarrow 2 K^+ (aq) + CO_3{}^{2-} (aq)$. Since 1 $CO_3{}^{2-}$ ion is generated for each $K_2CO_3$, $[K_2CO_3] = 1.4 \times 10^{-9}$ M $K_2CO_3$ to precipitate $FeCO_3$. Derive expression for $K_{sp}$ ($MgCO_3$), A = $Mg^{2+}$, $m = 1$, X = $CO_3{}^{2-}$, and $n = 1$. Since $K_{sp} = [Mg^{2+}] [CO_3{}^{2-}]$, then $K_{sp}$ ($MgCO_3$) = $6.82 \times 10^{-6} = 0.014 [CO_3{}^{2-}]$. Solve for $[CO_3{}^{2-}]$. $[CO_3{}^{2-}] = 4.9 \times 10^{-4}$ M $CO_3{}^{2-} = 4.9 \times 10^{-4}$ M $K_2CO_3 = [K_2CO_3]$ to precipitate $MgCO_3$. Since $1.4 \times 10^{-9}$ M $K_2CO_3 < 4.9 \times 10^{-4}$ M $K_2CO_3$, the $Fe^{2+}$ will precipitate first.

(b)    Since $Mg^{2+}$ will not precipitate until $[K_2CO_3] = 4.9 \times 10^{-4}$ M $K_2CO_3$, substitute this value into the $K_{sp}$ expression for $FeCO_3$. So $K_{sp}$ ($FeCO_3$) = $[Fe^{2+}] [CO_3{}^{2-}] = 3.07 \times 10^{-11} = [Fe^{2+}] 4.9 \times 10^{-4}$. Solve for $[Fe^{2+}]$ = $6.3 \times 10^{-8}$ M $Fe^{2+}$.

Check: The units (none, M, and M) are correct. Comparing the two $K_{sp}$ values, it can be seen that the $Fe^{2+}$ will precipitate first since the solubility product is so much lower. Since the $K_{sp}$ value is so low, the concentration of precipitating agent is very low. Since the $MgCO_3$ $K_{sp}$ value is so much higher, the higher $[CO_3{}^{2-}]$ to precipitate Mg will force the concentration of $Fe^{2+}$ to very low levels.

## Complex Ion Equilbria

16.109    **Given:** solution with $1.1 \times 10^{-3}$ M $Zn(NO_3)_2$ and 0.150 M $NH_3$    **Find:** $[Zn^{2+}]$ at equilibrium
**Other:** $K_f$ ($Zn(NH_3)_4{}^{2+}$) = $2.8 \times 10^9$
**Conceptual Plan: Write a balanced equation and expression for $K_f$. Use initial concentrations to set up an ICE table. Since the $K_f$ is so large, assume that reaction essentially goes to completion. Solve for $[Zn^{2+}]$ at equilibrium.**
**Solution:** $Zn(NO_3)_2$ $(s) \rightarrow Zn^{2+} (aq) + 2 NO_3{}^- (aq)$. Since 1 $Zn^{2+}$ ion is generated for each $Zn(NO_3)_2$, $[Zn^{2+}] = 1.1 \times 10^{-3}$ M. Balanced equation is:

| | $Zn^{2+}$ (aq) + 4 NH$_3$ (aq) $\rightleftharpoons$ Zn(NH$_3$)$_4^{2+}$ (aq) | | | Set up an ICE table with initial concentrations. |
|---|---|---|---|---|
| | $[Zn^{2+}]$ | $[NH_3]$ | $[Zn(NH_3)_4{}^{2+}]$ | Since $K_f$ is so large and since initially |
| Initial | $1.1 \times 10^{-3}$ | 0.150 | 0.00 | $[NH_3] > 4 [Zn^{2+}]$ the reaction essentially goes to |
| Change | $\approx 1.1 \times 10^{-3}$ | $\approx -4(1.1 \times 10^{-3})$ | $\approx 1.1 \times 10^{-3}$ | completion then write equilibrium expression |
| Equil | $x$ | 0.14$\underline{5}$6 | $1.1 \times 10^{-3}$ | and solve for $x$. |

$$K_f = \frac{[Zn(NH_3)_4{}^{2+}]}{[Zn^{2+}][NH_3]^4} = 2.8 \times 10^9 = \frac{1.1 \times 10^{-3}}{x\,(0.1456)^4}$$ So $x = 8.7 \times 10^{-10}$ M $Zn^{2+}$. Since $x$ is insignificant compared to the initial concentration, the assumption is valid.

**Check:** The units (M) are correct. Since $K_f$ is so large, the reaction essentially goes to completion and $[Zn^{2+}]$ is extremely small.

16.110    **Given:** 120.0 mL of $2.8 \times 10^{-3}$ M $AgNO_3$ mixed with 225.0 mL of 0.10 M NaCN   **Find:** $[Ag^+]$ at equilibrium
**Other:** $K_f\,(Ag(CN)_2{}^-) = 1 \times 10^{21}$
**Conceptual Plan: Mix solutions and calculate diluted concentrations mL $AgNO_3$, mL NaCN $\rightarrow$ mL total**

$$\text{mL } AgNO_3 + \text{mL NaCN} = \text{total mL}$$

**then mL, initial M $\rightarrow$ final M then write balanced equation and expression for $K_f$.**

$$M_1 V_1 = M_2 V_2$$

**Use initial concentrations to set up an ICE table. Since the $K_f$ is so large, assume that reaction essentially goes to completion. Solve for $[Ag^+]$ at equilibrium.**

**Solution:** $AgNO_3\,(s) \rightarrow Ag^+\,(aq) + NO_3{}^-\,(aq)$. Since 1 $Ag^+$ ion is generated for each $AgNO_3$, $[Ag^+] = 2.8 \times 10^{-3}$ M and NaCN $(s) \rightarrow Na^+\,(aq) + CN^-\,(aq)$. Since 1 $CN^-$ ion is generated for each NaCN, $[CN^-] = 0.10$ M. Then total mL = mL $AgNO_3$ + mL NaCN = 120.0 mL + 225.0 mL = 345.0 mL. Then $M_1 V_1 = M_2 V_2$. Rearrange to solve for $M_2$. $M_2 = M_1 \dfrac{V_1}{V_2} = 2.8 \times 10^{-3}$ M $Ag^+ \times \dfrac{120.0 \text{ mL}}{345.0 \text{ mL}} = 0.00097391$ M $Ag^+$ and

$M_2 = M_1 \dfrac{V_1}{V_2} = 0.10$ M $CN^- \times \dfrac{225.0 \text{ mL}}{345.0 \text{ mL}} = 0.065217$ M $CN^-$. The balanced equation is as follows:

|   | $Ag^+\,(aq)$ | $+\ 2\,CN^-\,(aq)$ | $\rightleftharpoons$ | $Ag(CN)_2{}^-\,(aq)$ |
|---|---|---|---|---|
|   | $[Ag^+]$ | $[CN^-]$ | | $[Ag(CN)_2{}^-]$ |
| *Initial* | 0.00097391 | 0.065217 | | 0.00 |
| *Change* | $\approx 0.00097391$ | $\approx -2(0.00097391)$ | | $\approx 0.00097391$ |
| *Equil* | x | 0.063270 | | 0.00097391 |

Set up an ICE table with initial concentrations. Since $K_f$ is so large and since initially $[CN^-] > 2\,[Ag^+]$ the reaction essentially goes to completion then write equilibrium expression and solve for $x$.

$$K_f = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = 1 \times 10^{21} = \frac{0.00097391}{x\,(0.063270)^2}$$ So $x = 2 \times 10^{-22}$ M $Ag^+$. Since $x$ is insignificant compared to the initial concentration, the assumption is valid.
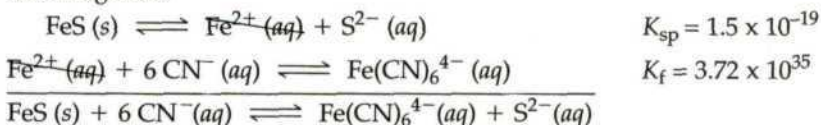
**Check:** The units (M) are correct. Since $K_f$ is so large, the reaction essentially goes to completion and $[Ag^+]$ is extremely small.

16.111    **Given:** $FeS\,(s) + 6\,CN^-\,(aq) \rightleftharpoons Fe(CN)_6{}^{4-}\,(aq) + S^{2-}\,(aq)$ use $K_{sp}$ and $K_f$ values   **Find:** $K$
**Other:** $K_f\,(Fe(CN)_6{}^{4-}) = 1.5 \times 10^{35}$, $K_{sp}\,(FeS) = 3.72 \times 10^{-19}$
**Conceptual Plan: Identify the appropriate solid and complex ion. Write balanced equations for dissolving the solid and forming the complex ion. Add these two reactions to get the desired overall reaction. Using the rules from Chapter 14, multiply the individual reaction $K$s to get the overall $K$ for the sum of these reactions.**
**Solution:** Identify the solid as FeS and the complex ion as $Fe(CN)_6{}^{4-}$. Write the individual reactions and add them together.

| | |
|---|---|
| $FeS\,(s) \rightleftharpoons Fe^{2+}\,(aq) + S^{2-}\,(aq)$ | $K_{sp} = 1.5 \times 10^{-19}$ |
| $Fe^{2+}\,(aq) + 6\,CN^-\,(aq) \rightleftharpoons Fe(CN)_6{}^{4-}\,(aq)$ | $K_f = 3.72 \times 10^{35}$ |
| $FeS\,(s) + 6\,CN^-\,(aq) \rightleftharpoons Fe(CN)_6{}^{4-}\,(aq) + S^{2-}\,(aq)$ | |

Since the overall reaction is the simple sum of the two reactions, the overall reaction $K = K_f \times K_{sp} = (1.5 \times 10^{35}) \times (3.72 \times 10^{-19}) = 5.6 \times 10^{16}$.
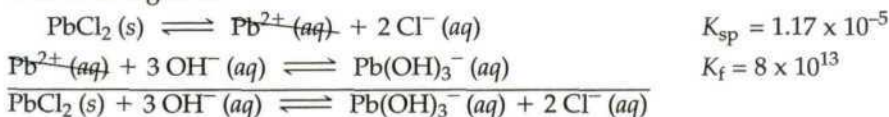**Check:** The units (none) are correct. Since $K_f$ is so large, it overwhelms the $K_{sp}$ and the overall reaction is very spontaneous.

16.112    **Given:** $PbCl_2\,(s) + 3\,OH^-\,(aq) \rightleftharpoons Pb(OH)_3{}^-\,(aq) + 2\,Cl^-\,(aq)$ use $K_{sp}$ and $K_f$ values   **Find:** $K$
**Other:** $K_f\,(Pb(OH)_3{}^-) = 8 \times 10^{13}$, $K_{sp}\,(PbCl_2) = 1.17 \times 10^{-5}$

Conceptual Plan: Identify the appropriate solid and complex ion. Write balanced equations for dissolving the solid and forming the complex ion. Add these two reactions to get the desired overall reaction. Using the rules from Chapter 14, multiply the individual reaction $K$s to get the overall $K$ for the sum of these reactions.

Solution: Identify the solid as $PbCl_2$ and the complex ion as $Pb(OH)_3^-$. Write the individual reactions and add them together.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq) \qquad\qquad K_{sp} = 1.17 \times 10^{-5}$$

$$\underline{Pb^{2+}(aq) + 3\,OH^-(aq) \rightleftharpoons Pb(OH)_3^-(aq) \qquad\qquad K_f = 8 \times 10^{13}}$$

$$PbCl_2(s) + 3\,OH^-(aq) \rightleftharpoons Pb(OH)_3^-(aq) + 2\,Cl^-(aq)$$

Since the overall reaction is the simple sum of the two reactions, the overall reaction $K = K_f \times K_{sp} = (8 \times 10^{13}) \times (1.17 \times 10^{-5}) = 9 \times 10^8$.

Check: The units (none) are correct. Since $K_f$ is so large, it overwhelms the $K_{sp}$ and the overall reaction is very spontaneous.

## Cumulative Problems

16.113    Given: 150.0 mL solution of 2.05 g sodium benzoate and 2.47 g benzoic acid  Find: pH
Other: $K_a$ ($HC_7H_5O_2$) = $6.5 \times 10^{-5}$
Conceptual Plan: g $NaC_7H_5O_2$ → mol $NaC_7H_5O_2$ and g $HC_7H_5O_2$ → mol $HC_7H_5O_2$

$$\frac{1\ mol\ NaC_7H_5O_2}{144.11\ g\ NaC_7H_5O_2} \qquad\qquad \frac{1\ mol\ HC_7H_5O_2}{122.13\ g\ HC_7H_5O_2}$$

Since the two components are in the same solution, the ratio of [base]/[acid] = (mol base)/(mol acid). Then $K_a$, mol $NaC_7H_5O_2$, mol $HC_7H_5O_2$ → pH.

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

Solution: $2.05\ \overline{g\ NaC_7H_5O_2} \times \dfrac{1\ mol\ NaC_7H_5O_2}{144.11\ \overline{g\ NaC_7H_5O_2}} = 0.0142252\ mol\ NaC_7H_5O_2$ and

$2.47\ \overline{g\ HC_7H_5O_2} \times \dfrac{1\ mol\ HC_7H_5O_2}{122.13\ \overline{g\ HC_7H_5O_2}} = 0.0202244\ mol\ HC_7H_5O_2$ then

$$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{mol\ base}{mol\ acid} = -\log(6.5 \times 10^{-5}) + \log\frac{0.0142252\ \overline{mol}}{0.0202244\ \overline{mol}} = 4.03.$$

Check: The units (none) are correct. The magnitude of the answer makes physical sense because the pH is a little lower than the $pK_a$ of the acid because there is more acid than base in the buffer solution.

16.114    Given: 10.0 mL of 17.5 M acetic acid and 5.54 g sodium acetate diluted to 1.50 L  Find: pH
Other: $K_a$ ($HC_2H_3O_2$) = $1.8 \times 10^{-5}$
Conceptual Plan: mL → L then L, initial $HC_2H_3O_2$ M → mol $HC_2H_3O_2$ then

$$\frac{1\ L}{1000\ mL} \qquad\qquad M = \frac{mol}{L}$$

g $NaC_2H_3O_2$ → mol $NaC_2H_3O_2$ then since the two components are in the same solution,

$$\frac{1\ mol\ NaC_2H_3O_2}{83.04\ g\ NaC_2H_3O_2}$$

the ratio of [base]/[acid] = (mol base)/(mol acid). Then $K_a$, mol $NaC_2H_3O_2$, mol $HC_2H_3O_2$ → pH.

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

Solution: $10.0\ \overline{mL} \times \dfrac{1\ L}{1000\ \overline{mL}} = 0.0100\ L$ then

$0.0100\ \overline{L\ HC_2H_3O_2} \times \dfrac{17.5\ mol\ HC_2H_3O_2}{1\ \overline{L\ HC_2H_3O_2}} = 0.175\ mol\ HC_2H_3O_2$ then

$5.54\ \overline{g\ NaC_2H_3O_2} \times \dfrac{1\ mol\ NaC_2H_3O_2}{82.04\ \overline{g\ NaC_2H_3O_2}} = 0.06752803\ mol\ NaC_2H_3O_2$ then

$$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{mol\ base}{mol\ acid} = -\log(1.8 \times 10^{-5}) + \log\frac{0.06752803\ \overline{mol}}{0.175\ \overline{mol}} = 4.33.$$