Chapter 16: Acid-Base Equilibria and Solubility Equilibria

16.1: Homogeneous Versus Heterogeneous Solution Equilibria

In acids and bases chemistry as well as solubility of ionic products, the equilibria involve are usually heterogeneous (where the phases of chemical species in the equilibrium are not in the same phases). Hence, great care is required when handling problems of these equilibria.

16.2 & 16.3: The Common Ion Effect & Buffer Solutions

Common Ion: - the ion that is present in two separate solutions as they are added together.

Common Ion Effect: - the shifting of the equilibrium, as outlined by Le Châtelier's principle, due to the addition or presence of a common ion in system.

Example 1: Identify the common ion in the following solutions.

a. 0.0250 M of carbonic acid with 0.0300 M of sodium hydrogen carbonate.

Carbonic Acid Dissociation: $H_2CO_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \mathbf{HCO_3^-}_{(aq)}$ (←)

Sodium Hydrogen Carbonate: $NaHCO_{3\,(aq)} \rightarrow Na^+ + \mathbf{HCO_3^-}_{(aq)}$

Common Ion: $HCO_3^-{}_{(aq)}$

Overall Equilibrium System: $H_2CO_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \mathbf{HCO_3^-}_{(aq)}\uparrow$ (⟸)

b. 0.500 M of methylamine with 0.450 M of CH_3NH_3Cl

Methylamine (Base) Dissociation: $CH_3NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons \mathbf{CH_3NH_3^+}_{(aq)} + OH^-_{(aq)}$ (←)

CH_3NH_3Cl: $CH_3NH_3Cl_{(aq)} \rightarrow \mathbf{CH_3NH_3^+}_{(aq)} + Cl^-_{(aq)}$

Common Ion: $CH_3NH_3^+{}_{(aq)}$

Overall Equilibrium System: $CH_3NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons \mathbf{CH_3NH_3^+}_{(aq)}\uparrow + OH^-_{(aq)}$ (⟸)

pH Calculation Involving Common Ion:

1. **Determine the Initial Concentration of ALL Major Species in the equilibrium.**
2. **Set up the ICE Box and the Equilibrium Expression Equating it to the Equilibrium Constant.**
3. **Calculate the $[H_3O^+]$ or $[OH^-]$ and the pH.**

Example 2: Calculate the pH of the solution that consists of 0.0250 M of carbonic acid ($K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 5.6 \times 10^{-11}$) with 0.0300 M of sodium hydrogen carbonate.

Carbonic Acid Dissociation: $H_2CO_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-{}_{(aq)}$

Sodium Hydrogen Carbonate: $NaHCO_{3\,(aq)} \rightarrow Na^+_{(aq)} + HCO_3^-{}_{(aq)}$

0.0300 M → **0.0300 M**

$H_2CO_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-{}_{(aq)}$

	$[H_2CO_3]$		$[H_3O^+]$	$[HCO_3^-]$
Initial	0.0250 M		0	0.0300 M
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.025 - x)$		x	$(0.03 + x)$

$$K_a = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} \qquad 4.3 \times 10^{-7} = \frac{(x)(0.03 + x)}{(0.025 - x)} \approx \frac{x(0.03)}{(0.025)}$$

$$4.3 \times 10^{-7}\,\frac{(0.025)}{(0.03)} \approx x \qquad x \approx 3.58 \times 10^{-7}$$

CAN use Approximation:

$$\frac{[H_2CO_3]_0}{K_a} = \frac{0.0250\text{ M}}{4.3 \times 10^{-7}} = 58140 \geq 1000$$

Use 0.03 in the numerator, because $(0.03 + x) \approx 0.03$ [x is so small compared to 0.03 M].

Use 0.025 in the denominator, because $(0.025 - x) \approx 0.025$ [x is so small compared to 0.025 M].

Verify that we could use Approximation:

$$\frac{[H_3O^+]}{[H_2CO_3]_0} \times 100\% = \frac{3.58 \times 10^{-7}\text{ M}}{0.0250\text{ M}} \times 100\%$$

$= 0.00143\% \leq 5\%$ **(Appropriate Approximation)**

$[H_3O^+] = 3.58 \times 10^{-7}$ mol/L

$pH = -\log [H_3O^+]$

$pH = -\log(3.58 \times 10^{-7})$ **pH = 6.45**

Buffered Solution: - a solution that **resists a change in pH** when a small amount of H_3O^+ or OH^- is added.
- consists of a pair of **weak acid/conjugate base common ion** or a pair of **weak base/conjugate acid common ion**.

Acidic Buffered Solution: $HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$

a. Small Amounts of H_3O^+ is Added: $A^-_{(aq)} + H_3O^+_{(aq)} \rightarrow H_2O_{(l)} + HA_{(aq)}$

(H^+ - Strong Acid reacts completely with A^-)

(More HA – Weak Acid: pH will only be lowered SLIGHTLY!)

b. Small Amounts of OH^- is Added: $HA_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + A^-_{(aq)}$

(OH^- - Strong Base reacts completely with HA)

(More A^- – Weak Base: pH will only be raised SLIGHTLY!)

Basic Buffered Solution: $B_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HB^+_{(aq)}$

a. Small Amounts of H_3O^+ is Added: $B_{(aq)} + H_3O^+_{(aq)} \rightarrow H_2O_{(l)} + HB^+_{(aq)}$

(H^+ - Strong Acid reacts completely with B)

(More HB^+ – Weak Acid: pH will only be lowered SLIGHTLY!)

b. Small Amounts of OH^- is Added: $B_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HB^+_{(aq)}$

(OH^- - Strong Base increases $[OH^-]$; eq shifts left)

(More B – Weak Base: pH will only be raised SLIGHTLY!)

pH Calculations Involving Buffered Solutions and any Subsequent Addition of H^+ or OH^- Amounts:

1. **Determine the initial concentration of all major species in the equilibrium.**
2. **Set up the ICE Box and the Equilibrium Expression Equating it to the Equilibrium Constant.**
3. **Calculate the $[H_3O^+]$ or $[OH^-]$ and the pH of the original buffered solution.**
4. **Write out the Complete Reaction for the ADDITION of H^+ or OH^- into the system. Because we are adding a strong acid or a strong base, we will Treat the Reaction as One-Way. Hence, we can Apply Regular Stoichiometric Principle to calculate the moles of each major species.**
5. **Again, set up the ICE Box and the Equilibrium Expression Equating it to the Equilibrium Constant.**
6. **Calculate the $[H_3O^+]$ or $[OH^-]$ and the pH of the revised buffered solution.**

Example 3: Calculate the pH of a 1.00 L buffered solution consisting of 0.500 M of methylamine (K_b = 4.38×10^{-4}) with 0.450 M of CH_3NH_3Cl when:

a. 0.0200 mol of KOH is added to it.
b. 3.00 mL of 0.750 M of $HNO_{3\,(aq)}$ is added to it.
c. Contrast the pH's of the above two additions against the same additions to 1.00 L of water.

First, we have to figure out the $[OH^-]$ and pH for the buffered solution system.

Methylamine (Base) Dissociation: $CH_2NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons CH_2NH_3^+{}_{(aq)} + OH^-_{(aq)}$

CH_3NH_3Cl: $CH_3NH_3Cl_{(aq)} \rightarrow CH_2NH_3^+{}_{(aq)} + Cl^-_{(aq)}$
0.450 M 0.450 M

$CH_2NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons CH_2NH_3^+{}_{(aq)} + OH^-_{(aq)}$

	$[CH_2NH_2]$		$[CH_2NH_3^+]$	$[OH^-]$
Initial	0.500 M		0.450 M	0
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.5 - x)$		$(0.45 + x)$	x

CAN use Approximation:

$$\frac{[CH_2NH_2]_0}{K_b} = \frac{0.500\text{ M}}{4.38\times10^{-4}} = 1142 \geq 1000$$

$$K_b = \frac{[OH^-][CH_2NH_3^+]}{[CH_2NH_2]} \qquad 4.38 \times 10^{-4} = \frac{(x)(0.45+x)}{(0.5-x)} \approx \frac{x(0.45)}{(0.5)}$$

Use 0.45 in the numerator, because $(0.45 + x) \approx 0.45$ [x is so small compared to 0.45 M].

Use 0.5 in the denominator, because $(0.5 - x) \approx 0.5$ [x is so small compared to 0.5 M].

$$4.38 \times 10^{-4}\,\frac{(0.5)}{(0.45)} \approx x$$

$$x \approx 4.87 \times 10^{-4}$$

Verify that we could use Approximation:

$$\frac{[OH^-]}{[CH_2NH_2]_0} \times 100\% = \frac{4.87\times10^{-4}\text{ M}}{0.500\text{ M}} \times 100\%$$

$$= 0.0973\% \leq 5\%$$

Therefore, approximation would be appropriate.

$$[OH^-] = 4.87 \times 10^{-4}\text{ mol/L}$$

$pOH = -\log[OH^-]$
$pOH = -\log(4.87 \times 10^{-4})$
$pOH = 3.31$

$pH = 14 - pOH$
$pH = 14 - 3.31$
$pH = 10.69$

a. 0.0200 mol of KOH is added to the buffered solution **(Complete Rxn between OH^- & $CH_2NH_3^+$).**

$$OH^-_{(aq)} + CH_2NH_3^+{}_{(aq)} \rightarrow H_2O_{(l)} + CH_2NH_{2\,(aq)}$$

	n of OH^-	*n* of $CH_2NH_3^+$		*n* of CH_2NH_2
Before	0.0200 mol (Limiting)	0.450 mol		0.500 mol
Change	− 0.0200 mol	− 0.0200 mol		+ 0.0200 mol
After	0	0.430 mol		0.520 mol

Recalculate equilibrium concentrations using **NEW** $[CH_2NH_3^+]_0$ and $[CH_2NH_2]_0$

$$CH_2NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons CH_2NH_3^+{}_{(aq)} + OH^-_{(aq)}$$

	$[CH_2NH_2]$		$[CH_2NH_3^+]$	$[OH^-]$
Initial	0.520 M		0.430 M	0
Change	$-y$		$+y$	$+y$
Equilibrium	$(0.52 - y)$		$(0.43 + y)$	y

$$K_b = \frac{[OH^-][CH_2NH_3^+]}{[CH_2NH_2]}$$

$$4.38 \times 10^{-4} = \frac{(y)(0.43 + y)}{(0.52 - y)}$$

$$4.38 \times 10^{-4} \approx \frac{y(0.43)}{(0.52)}$$

$$4.38 \times 10^{-4}\,\frac{(0.52)}{(0.43)} \approx y$$

$$y \approx 5.30 \times 10^{-4}$$

CAN use Approximation:

$$\frac{[CH_2NH_2]_0}{K_b} = \frac{0.520\text{ M}}{4.38 \times 10^{-4}} = 1187 \geq 1000$$

Use 0.43 in the numerator, because $(0.43 + y) \approx 0.43$ [y is so small compared to 0.43 M].

Use 0.52 in the denominator, because $(0.52 - y) \approx 0.52$ [y is so small compared to 0.52 M].

Verify that we could use Approximation:

$$\frac{[OH^-]}{[CH_2NH_2]_0} \times 100\% = \frac{5.30 \times 10^{-4}\text{ M}}{0.520\text{ M}} \times 100\%$$

= 0.102% ≤ 5% (Appropriate Approximation)

$$[OH^-] = 5.30 \times 10^{-4}\text{ mol/L}$$

pOH = − log $[OH^-]$
pOH = − log(5.30×10^{-4})
pOH = 3.28

pH = 14 − pOH
pH = 14 − 3.28
pH = 10.72

b. 3.00 mL of 0.750 M (0.00225 mol) of $HNO_{3\,(aq)}$ is added to the buffered solution **(Complete Reaction between H_3O^+ & CH_2NH_2).**

$$H_3O^+{}_{(aq)} + CH_2NH_{2\,(aq)} \rightarrow H_2O_{(l)} + CH_2NH_3^+{}_{(aq)}$$

	n of H_3O^+	*n* of CH_2NH_2		*n* of $CH_2NH_3^+$
Before	0.00225 mol (Limiting)	0.500 mol		0.450 mol
Change	− 0.00225 mol	− 0.00225 mol		+ 0.00225 mol
After	0	0.49775 mol		0.45225 mol

Recalculate equilibrium concentrations using **NEW** $[CH_2NH_2]_0$ and $[CH_2NH_3^+]_0$ **(neglect Δvolume)**

$$CH_2NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons CH_2NH_3^+{}_{(aq)} + OH^-_{(aq)}$$

	$[CH_2NH_2]$		$[CH_2NH_3^+]$	$[OH^-]$
Initial	0.49775 M		0.45225 M	0
Change	$-z$		$+z$	$+z$
Equilibrium	$(0.49775 - z)$		$(0.45225 + z)$	z

$$K_b = \frac{[OH^-][CH_2NH_3^+]}{[CH_2NH_2]}$$

$$4.38 \times 10^{-4} = \frac{(y)(0.45225 + z)}{(0.49775 - z)}$$

$$4.38 \times 10^{-4} \approx \frac{z(0.45225)}{(0.49775)}$$

$$4.38 \times 10^{-4}\,\frac{(0.49775)}{(0.45225)} \approx z$$

$$z \approx 4.82 \times 10^{-4}$$

CAN use Approximation:

$$\frac{[CH_2NH_2]_0}{K_b} = \frac{0.520\text{ M}}{4.38 \times 10^{-4}} = 1187 \geq 1000$$

Use 0.45225 in the numerator, because $(0.45225 + z) \approx 0.45225$ [z is so small compared to 0.45225 M].

Use 0.49775 in the denominator, because $(0.49775 - z) \approx 0.49775$ [z is so small compared to 0.49775 M].

Verify that we could use Approximation:

$$\frac{[OH^-]}{[CH_3NH_2]_0} \times 100\% = \frac{4.82\times10^{-4}\ M}{0.49775\ M} \times 100\%$$

$= 0.0968\% \leq 5\%$ **(Appropriate Approximation)**

$[OH^-] = 4.82 \times 10^{-4}$ mol/L

pOH = – log [OH⁻]
pOH = – log(4.82×10^{-4})
pOH = 3.32

pH = 14 – pOH
pH = 14 – 3.28
pH = 10.68

c. Contrast the pH's of the above two additions against the same additions to 1.00 L of water.

i. 0.0200 mol of KOH is added to 1.00 L of water

pOH = – log [OH⁻]
pOH = – log(0.0200)
pOH = 1.70

pH = 14 – pOH
pH = 14 – 1.70
pH = 12.30

Adding the 0.0200 mol of KOH to buffered solution.

pH changes from 10.69 to 10.72

ii. 3.00 mL of 0.750 M (0.00225 mol) of $HNO_{3\,(aq)}$ is added to 1.00 L of water (neglect Δvolume).

pH = – log [H_3O^+]
pH = – log(0.00225)
pH = 2.65

Adding the 0.00225 mol of HNO_3 to buffered solution.

pH changes from 10.69 to 10.68

Acid/Conjugate Base Ratio $\left(\frac{[HA]}{[A^-]}\right)$: - together with K_a, it governs the [H_3O^+] of a buffered solution.
- it can be used to adjust the pH range of the buffered solution.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \Longrightarrow [H_3O^+] = K_a\left(\frac{[HA]}{[A^-]}\right)$$

(Assumes that $[HA]_0 \approx ([HA]_{eq} - x) \approx ([HA]_{eq}$ and $[A^-]_0 \approx ([HA]_{eq} + x) \approx [A^-]_{eq}$ because K_a is usually small)

$[H_3O^+] = K_a\left(\frac{[HA]}{[A^-]}\right)$ (Relationship of Conjugate Base/Acid Ratio of Buffered Solution)

$-\log[H_3O^+] = -\log\left[K_a\left(\frac{[HA]}{[A^-]}\right)\right]$ (Log Both sides)

$-\log[H_3O^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right)$ (Apply Logarithmic Law: $\log(MN) = \log M + \log N$)

$\mathbf{pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)}$ (Apply Logarithmic Law: $\log(M^{-1}) = -\log M$)

Henderson-Hasselbalch Equation

For a Buffered Solution with small K_a, assuming $[HA]_0 \approx [HA]_{eq}$ and $[A^-]_0 \approx [A^-]_{eq}$, it has a pH of:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

(For Basic Buffered Solution $K_a = \frac{K_w}{K_b}$)

$pK_a = -\log K_a$ **$[A^-]$ = initial [Conjugate Base]** **[HA] = initial [Acid]**

Example 4: Calculate the pH of a 1.00 L buffered solution consisting of 0.650 M of nitrous acid (K_a = 4.0 × 10^{-4}) with 0.580 M of sodium nitrite solution. What is the new pH after 0.125 mol of $Ba(OH)_2$ is added to it?

Nitrous Acid Dissociation: $HNO_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + NO_2^-{}_{(aq)}$ $K_a = 4.0 \times 10^{-4}$

Sodium Nitrite: $NaNO_{2\,(aq)} \rightarrow Na^+ + NO_2^-{}_{(aq)}$

0.580 M → **0.580 M**

For the buffered solution we can use the Henderson-Hasselbalch Equation.

$$pH = pK_a + \log\left(\frac{[NO_2^-]}{[HNO_2]}\right)$$

$$pH = -\log K_a + \log\left(\frac{[NO_2^-]}{[HNO_2]}\right) = -\log(4.0 \times 10^{-4}) + \log\left(\frac{0.580\text{ M}}{0.650\text{ M}}\right)$$

CAN use Approximation:

$$\frac{[HNO_2]_0}{K_a} = \frac{0.650\text{ M}}{4.0\times10^{-4}}$$

$$= 1625 \geq 1000$$

Buffered Solution pH = 3.35

Calculate new pH after 0.125 mol of $Ba(OH)_2$ is added to the Buffered Solution.

(Complete Reaction between OH^- & HNO_2).

Barium Hydroxide: $Ba(OH)_{2\,(aq)} \rightarrow Ba^{2+} + 2\,OH^-{}_{(aq)}$

0.125 mol → **0.250 mol**

$$OH^-{}_{(aq)} + HNO_{2\,(aq)} \rightarrow H_2O_{(l)} + NO_2^-{}_{(aq)}$$

	n of OH^-	n of HNO_2		n of NO_2^-
Before	**0.250 mol (Limiting)**	**0.650 mol**		**0.580 mol**
Change	**– 0.250 mol**	**– 0.250 mol**		**+ 0.250 mol**
After	**0**	**0.400 mol**		**0.830 mol**

CAN use Approximation:

$$\frac{[HNO_2]_0}{K_a} = \frac{0.400\text{ M}}{4.0\times10^{-4}}$$

$$= 1000 \geq 1000$$

$$[HNO_2]_{eq} \approx [HNO_2]_0 = \frac{0.400\text{ mol}}{1.00\text{ L}} = 0.400\text{ M}$$

$$[NO_2^-]_{eq} \approx [NO_2^-]_0 = \frac{0.830\text{ mol}}{1.00\text{ L}} = 0.830\text{ M}$$

For the buffered solution with $Ba(OH)_2$ added, we can again use the Henderson-Hasselbalch Equation.

$$pH = pK_a + \log\left(\frac{[NO_2^-]}{[HNO_2]}\right) = -\log K_a + \log\left(\frac{[NO_2^-]}{[HNO_2]}\right)$$

$$pH = -\log(4.0 \times 10^{-4}) + \log\left(\frac{0.830\text{ M}}{0.400\text{ M}}\right)$$

pH (Buffered Solution with $Ba(OH)_2$ added) = 3.71

Example 5: Calculate the pH of a 1.00 L buffered solution consisting of 0.0750 M of hydrazine, $H_2NNH_{2\,(aq)}$, ($K_b = 3.0 \times 10^{-6}$) with 0.0825 M of H_2NNH_3Br solution. What is the new pH after 15.0 mL of 1.00 mol/L HBr is added to it (neglect any volume changes)?

Hydrazine Dissociation: $H_2NNH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons H_2NNH_3^+{}_{(aq)} + OH^-{}_{(aq)}$ $\quad K_b = 3.0 \times 10^{-6}$

H_2NNH_3Br: $H_2NNH_3Br_{(aq)} \rightarrow H_2NNH_3^+{}_{(aq)} + Br^-{}_{(aq)}$

0.0825 M $\quad$ **0.0825 M**

We need to write the acid dissociation reaction and obtain K_a.

$$H_2NNH_3^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + H_2NNH_{2\,(aq)} \qquad K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{3.0\times10^{-6}} \qquad K_a = 3.333\times 10^{-9}$$

For the buffered solution, we can use the Henderson-Hasselbalch Equation.

$$pH = pK_a + \log\left(\frac{[H_2NNH_2]}{[H_2NNH_3^+]}\right) = -\log K_a + \log\left(\frac{[H_2NNH_2]}{[H_2NNH_3^+]}\right)$$

$$pH = -\log(3.333 \times 10^{-9}) + \log\left(\frac{0.0750\text{ M}}{0.0825\text{ M}}\right)$$

CAN use Approximation:

$$\frac{[H_2NNH_3^+]_0}{K_a} = \frac{0.0825\text{ M}}{3.333\times10^{-9}} = \mathbf{2.48 \times 10^{7} \geq 1000}$$

Buffered Solution pH = 8.44

Calculate new pH after 15.0 mL of 1.00 mol/L (0.0150 mol) HBr is added to the Buffered Solution.
(Complete Reaction between H_3O^+ & H_2NNH_2).

$$H_3O^+{}_{(aq)} + H_2NNH_{2\,(aq)} \rightarrow H_2O_{(l)} + H_2NNH_3^+{}_{(aq)}$$

	n of H_3O^+	*n* of H_2NNH_2		*n* of $H_2NNH_3^+$
Before	**0.0150 mol (Limiting)**	**0.0750 mol**		**0.0825 mol**
Change	**– 0.0150 mol**	**– 0.0150 mol**		**+ 0.0150 mol**
After	**0**	**0.0600 mol**		**0.0975 mol**

CAN use Approximation:

$$\frac{[HNO_2]_0}{K_a} = \frac{0.0975\text{ M}}{3.333\times10^{-9}} = \mathbf{2.93 \times 10^{7} \geq 1000}$$

$$[H_2NNH_3^+]_{eq} \approx [H_2NNH_3^+]_0 = \frac{0.0975\text{ mol}}{1.00\text{ L}} = 0.0975\text{ M}$$

$$[H_2NNH_2]_{eq} \approx [H_2NNH_2]_0 = \frac{0.0600\text{ mol}}{1.00\text{ L}} = 0.0600\text{ M}$$

For the buffered solution with HBr added, we can again use the Henderson-Hasselbalch Equation.

$$pH = pK_a + \log\left(\frac{[H_2NNH_2]}{[H_2NNH_3^+]}\right) = -\log K_a + \log\left(\frac{[H_2NNH_2]}{[H_2NNH_3^+]}\right)$$

$$pH = -\log(3.333 \times 10^{-9}) + \log\left(\frac{0.0600\text{ M}}{0.097500\text{ M}}\right)$$

pH (Buffered Solution with HBr added) = 8.27

Example 6: Devise a procedure to make a buffered solution using carbonic acid ($K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 5.6 \times 10^{-11}$) and sodium hydrogen carbonate that is in the range of pH = 7.50.

Carbonic Acid Dissociation: $H_2CO_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \mathbf{HCO_3^-}_{(aq)}$ $\quad K_a = 4.3 \times 10^{-7}$

Sodium Hydrogen Carbonate: $NaHCO_{3\,(aq)} \rightarrow Na^+ + \mathbf{HCO_3^-}_{(aq)}$

For the buffered solution, we can use the Henderson-Hasselbalch Equation to find $\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$.

$$\text{pH} = \text{p}K_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$\text{pH} - \text{p}K_a = \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$7.50 - [-\log(4.3 \times 10^{-7})] = \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$\log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right) = 1.133468456$$

$$10^{1.133468456} = \left(\frac{[HCO_3^-]}{[H_2CO_3]}\right) \qquad \left(\frac{[HCO_3^-]}{[H_2CO_3]}\right) = 13.59779394$$

One way to make this HCO_3^-/H_2CO_3 buffered solution (pH = 7.50) is to use 0.136 M of $NaHCO_{3\,(aq)}$ with 0.0100 M of $H_2CO_{3\,(aq)}$. The conjugate base/acid ratio would be $\frac{0.136\text{ M}}{0.0100\text{ M}} \approx 13.59779394$.

Buffering Capacity: - the amounts of H^+ or OH^- a buffered solution can handle before there is a significant change in pH.

- a large buffering capacity means it can absorbs large amount of H^+ or OH^- before there is a notable change in pH.
- **depends very much on the conjugate base/acid ratio $\left(\frac{[A^-]}{[HA]}\right)$.**
- **the optimal buffering occurs when $[A^-] = [HA]$ and they are relatively large compared to the amounts of H^+ or OH^- added.**

Optimal Buffering Capacity

For an Optimal Buffering Capacity, a Buffered Solution should have large [HA] = large [A⁻]:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right) \text{ (ratio} \rightarrow 1) \qquad \text{pH} = \text{p}K_a \quad \text{(for Best Buffering Capacity)}$$

Therefore, the desired pH for the buffered solution should be the SAME as the pK_a of the weak acid, HA.

Example 7: Calculate the pH of a 1.00 L buffered solution consisting of 0.0300 M of $NaC_2H_5COO_{(aq)}$/ $C_2H_5COOH_{(aq)}$ and another 1.00 L buffered solution consisting of 3.00 M of $NaC_2H_5COO_{(aq)}$/ $C_2H_5COOH_{(aq)}$ ($K_{a1} = 1.3 \times 10^{-5}$). What are the new pHs after 0.0150 mol of NaOH is added to them?

First, we have to figure out the $[H_3O^+]$ and pH for the 0.0300 M of $NaC_2H_5COO_{(aq)}/C_2H_5COOH_{(aq)}$ buffered system.

Propanoic Acid Dissociation: $C_2H_5COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_2H_5COO^-_{(aq)}$

Sodium Propanoate: $NaC_2H_5COO_{(aq)} \rightarrow Na^+_{(aq)} + C_2H_5COO^-_{(aq)}$

0.0300 M 0.0300 M

$C_2H_5COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_2H_5COO^-_{(aq)}$

	$[C_2H_5COOH]$		$[H_3O^+]$	$[C_2H_5COO]$
Initial	0.0300 M		0	0.0300 M
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.03 - x)$		x	$(0.03 + x)$

CAN use Approximation:

$$\frac{[C_2H_5COOH]_0}{K_a} = \frac{0.0300\text{ M}}{1.3\times10^{-5}}$$

$= 2308 \geq 1000$

Use 0.03 in the numerator, because $(0.03 + x) \approx 0.03$ [x is so small compared to 0.03 M].

Use 0.03 in the denominator, because $(0.03 - x) \approx 0.03$ [x is so small compared to 0.03 M].

$$K_a = \frac{[H_3O^+][C_2H_5COO^-]}{[C_2H_5COOH]} \qquad 1.3\times10^{-5} = \frac{(x)(0.03+x)}{(0.03-x)} \approx \frac{x(0.03)}{(0.03)}$$

$$1.3\times10^{-5}\,\frac{(0.03)}{(0.03)} \approx x \qquad K_a = [H_3O^+] = x \approx 1.3\times10^{-5}$$

Verify that we could use Approximation:

$$\frac{[H_3O^+]}{[C_2H_5COOH]_0}\times100\% = \frac{1.3\times10^{-5}\text{ M}}{0.0300\text{ M}}\times100\%$$

$= 0.0433\% \leq 5\%$ (Appropriate Approximation)

$pH = -\log[H_3O^+] = pK_a$

$pH = -\log(1.3 \times 10^{-5})$

(Buffered Solution) pH = 4.89

Next, we have to figure out the $[H_3O^+]$ and pH for the 3.00 M of $NaC_2H_5COO_{(aq)}/C_2H_5COOH_{(aq)}$ buffered system. Since 0.0300 M of buffer can use approximation, we would expect that we could also use approximation with 3.00 M of buffer solution.

$$K_a = \frac{[H_3O^+][C_2H_5COO^-]}{[C_2H_5COOH]} \qquad 1.3\times10^{-5} = \frac{(x)(3.00+x)}{(3.00-x)} \approx \frac{x(3.00)}{(3.00)}$$

$$1.3\times10^{-5}\,\frac{(3.00)}{(3.00)} \approx x \qquad K_a = [H_3O^+] = x \approx 1.3\times10^{-5}$$

$pH = -\log[H_3O^+] = pK_a$

$pH = -\log(1.3 \times 10^{-5})$

(Buffered Solution) pH = 4.89

Calculate new pH after 0.0150 mol of NaOH is added to the 0.0300 M of $NaC_2H_5COO_{(aq)}/C_2H_5COOH_{(aq)}$ Buffered Solution. **(Complete Reaction between OH^- & C_2H_5COOH).**

$OH^-_{(aq)} + C_2H_5COOH_{(aq)} \rightarrow H_2O_{(l)} + C_2H_5COO^-_{(aq)}$

	n of OH^-	n of C_2H_5COOH		n of $C_2H_5COO^-$
Before	0.0150 mol (Limiting)	0.0300 mol		0.0300 mol
Change	− 0.0150 mol	− 0.0150 mol		+ 0.0150 mol
After	0	0.0150 mol		0.0450 mol

$$[C_2H_5COOH]_{eq} \approx [C_2H_5COOH]_0 = \frac{0.0150\text{ mol}}{1.00\text{ L}} = 0.0150\text{ M}$$

$$[C_2H_5COO^-]_{eq} \approx [C_2H_5COO^-]_0 = \frac{0.0450\text{ mol}}{1.00\text{ L}} = 0.0450\text{ M}$$

CAN use Approximation:

$$\frac{[C_2H_5COOH]_0}{K_a} = \frac{0.0150\text{ M}}{1.3\times10^{-5}}$$

$$\mathbf{= 1154 \geq 1000}$$

For the buffered solution with NaOH added, we can again use the Henderson-Hasselbalch Equation.

$$pH = pK_a + \log\left(\frac{[C_2H_2COO^-]}{[C_2H_2COOH]}\right) = -\log K_a + \log\left(\frac{[C_2H_2COO^-]}{[C_2H_2COOH]}\right)$$

$$pH = -\log(1.3\times10^{-5}) + \log\left(\frac{0.0450\text{ M}}{0.0150\text{ M}}\right)$$

pH changed from 4.89 to 5.36

pH (0.0300 M Buffered Solution with NaOH added) = 5.36

Calculate new pH after 0.0150 mol of NaOH is added to the 3.00 M of $NaC_2H_5COO_{(aq)}/C_2H_5COOH_{(aq)}$ Buffered Solution. **(Complete Reaction between OH^- & C_2H_5COOH).**

$$OH^-_{(aq)} + C_2H_5COOH_{(aq)} \rightarrow H_2O_{(l)} + C_2H_5COO^-_{(aq)}$$

	***n* of OH^-**	***n* of C_2H_5COOH**		***n* of $C_2H_5COO^-$**
Before	**0.0150 mol (Limiting)**	**3.00 mol**		**3.00 mol**
Change	**− 0.0150 mol**	**− 0.0150 mol**		**+ 0.0150 mol**
After	**0**	**2.985 mol**		**3.015 mol**

$$[C_2H_5COOH]_{eq} \approx [C_2H_5COOH]_0 = \frac{2.985\text{ mol}}{1.00\text{ L}} = 2.985\text{ M}$$

$$[C_2H_5COO^-]_{eq} \approx [C_2H_5COO^-]_0 = \frac{3.015\text{ mol}}{1.00\text{ L}} = 3.015\text{ M}$$

CAN use Approximation:

$$\frac{[C_2H_5COOH]_0}{K_a} = \frac{2.985\text{ M}}{1.3\times10^{-5}}$$

$$\mathbf{= 229615 \geq 1000}$$

For the buffered solution with NaOH added, we can again use the Henderson-Hasselbalch Equation.

$$pH = pK_a + \log\left(\frac{[C_2H_2COO^-]}{[C_2H_2COOH]}\right) = -\log K_a + \log\left(\frac{[C_2H_2COO^-]}{[C_2H_2COOH]}\right)$$

$$pH = -\log(1.3\times10^{-5}) + \log\left(\frac{3.015\text{ M}}{2.985\text{ M}}\right)$$

pH stayed at 4.89 from before

pH (3.00 M Buffered Solution with NaOH added) = 4.89

Hence, when $[A^-] = [HA]$ and if both concentrations are large, then we achieve optimal buffering capacity.

Example 8: Calculate the number of moles of $HI_{(aq)}$ that must be added to 0.500 L of 2.00 mol/L of $C_5H_5NHI_{(aq)}$ (K_b of $C_5H_5N = 1.7 \times 10^{-9}$) to produce a solution buffered at pH = 4.75.

C_5H_5NHI:

$$C_5H_5NHI_{(aq)} \rightarrow C_5H_5NH^+_{(aq)} + I^-_{(aq)}$$
$$2.00\text{ M} \qquad 2.00\text{ M}$$

$C_5H_5NH^+$ is a weak acid. Hence, we need to write the acid dissociation reaction and obtain K_a.

$$C_5H_5NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_5H_5N_{(aq)} \qquad K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.7\times10^{-9}} \qquad \boldsymbol{K_a = 5.882 \times 10^{-6}}$$

Adding HI (or H_3O^+) will <u>react completely</u> with the base C_5H_5N:

$$C_5H_5N_{(aq)} + H_3O^+_{(aq)} \rightarrow H_2O_{(l)} + C_5H_5NH^+_{(aq)}$$
$$[C_5H_5N] = [HI]$$

For the buffered solution, we can use the Henderson-Hasselbalch Equation to find $\left(\frac{[C_5H_5N]}{[C_5H_5NH^+]}\right)$.

$$pH = pK_a + \log\left(\frac{[C_5H_5N]}{[C_5H_5NH^+]}\right) \qquad pH - pK_a = \log\left(\frac{[C_5H_5N]}{[C_5H_5NH^+]}\right)$$

$$4.75 - [-\log(5.882 \times 10^{-6})] = \log\left(\frac{[C_5H_5N]}{2.00\text{ M}}\right)$$

$$\log\left(\frac{[C_5H_5N]}{2.00\text{ M}}\right) = -0.4804749798$$

$$10^{-0.484749798} = \left(\frac{[C_5H_5N]}{2.00\text{ M}}\right)$$

$$[C_5H_5N] = (2.00\text{ M})(10^{-0.484749798})$$
$$[C_5H_5N] = 0.662\text{ M}$$

Since $[C_5H_5N] = [HI]$

$[HI] = 0.662$ M ←

$n_{HI} = [HI]V =$ (0.662 mol/L)(0.500 L) **$n_{HI} = 0.331$ mol**

Example 9: From a list of the K_a below, select the buffered solution that has a pH of around 3.20. Write up a procedure that makes 1.00 L of this particular buffered solution.

Monochloracetic Acid ($HC_2H_2ClO_{2\,(aq)}$)	$K_a = 1.35 \times 10^{-3}$
Hydrofluoric Acid ($HF_{(aq)}$)	$K_a = 7.2 \times 10^{-4}$
Nitrous Acid ($HNO_{2\,(aq)}$)	$K_a = 4.0 \times 10^{-4}$
Methanoic Acid ($HCOOH_{(aq)}$)	$K_a = 1.8 \times 10^{-4}$

For Optimal Buffering Capacity, [HA] = [A⁻], which means pH = pK_a.

$pK_a = -\log K_a$
$K_a = 10^{-pK_a} = 10^{-(3.20)}$ **$K_a = 6.31 \times 10^{-4}$ (Closest Weak Acid to this K_a is $HF_{(aq)}$)**

<u>Possible Procedure to Make 2.00 M of F^-/HF Buffered Solution</u>.
(Large concentrations are needed for good buffering capacity.)
1. Obtain 1.00 L of 2.00 M of HF. (May entail dilution from stock solution.)
2. Dissolve 83.98 g of NaF ($m = nM$ = 2.00 ~~mol~~/~~L~~ × 1.00 ~~L~~ × 41.99 g/~~mol~~) into the 1.00 L of 2.00 M $HF_{(aq)}$

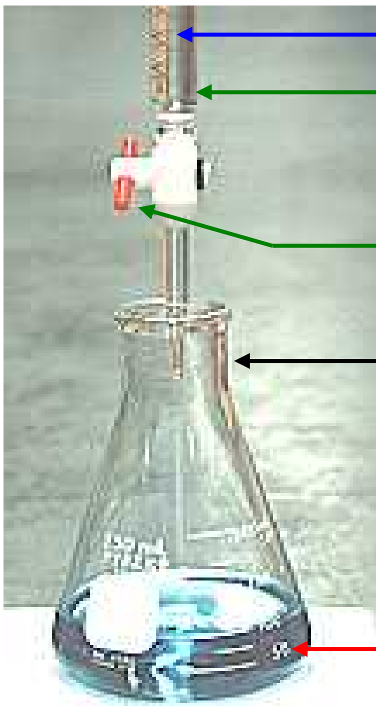
<u>Assignment</u>
16.1 & 16.2 pg. 740 #1 to 6; #7 to 20; pg. 744 #102 and 107

16.4: Acid-Base Titrations

pH Curve: - a graph that shows the how the pH changes as the titration proceeds (as titrant is to the analyzed).

Titration: - a volumetric analysis that involves measuring the volume of known concentration solution to measure a given volume of an unknown concentration solution.

Titration Set-up



Titrant: - the solution of known concentration.

Buret: - a precise apparatus to deliver the titrant.
- the volume of the titrant added is read by subtracting the final volume and the initial volume.

Buret Valve: - can be adjusted to let one drop out at a time.

Erlenmeyer Flask: - a container commonly uses to hold the analyte. (Narrow mouth prevents splash and spillage.)

Analyte: - the solution of an unknown concentration.
- the exact volume is usually delivered by a pipet.

Acid-Base Titration: - volumetric analysis that assist in determining the unknown concentration in an acid and base neutralization.

Equivalent Point (Stoichiometric Point): - a point where the number of moles of H^+ is equivalent to the number of moles of OH^-. ($n_{H^+} = n_{OH^-}$)

Endpoint: - a point where the indicator actually changes colour to indicate neutralization is completed.

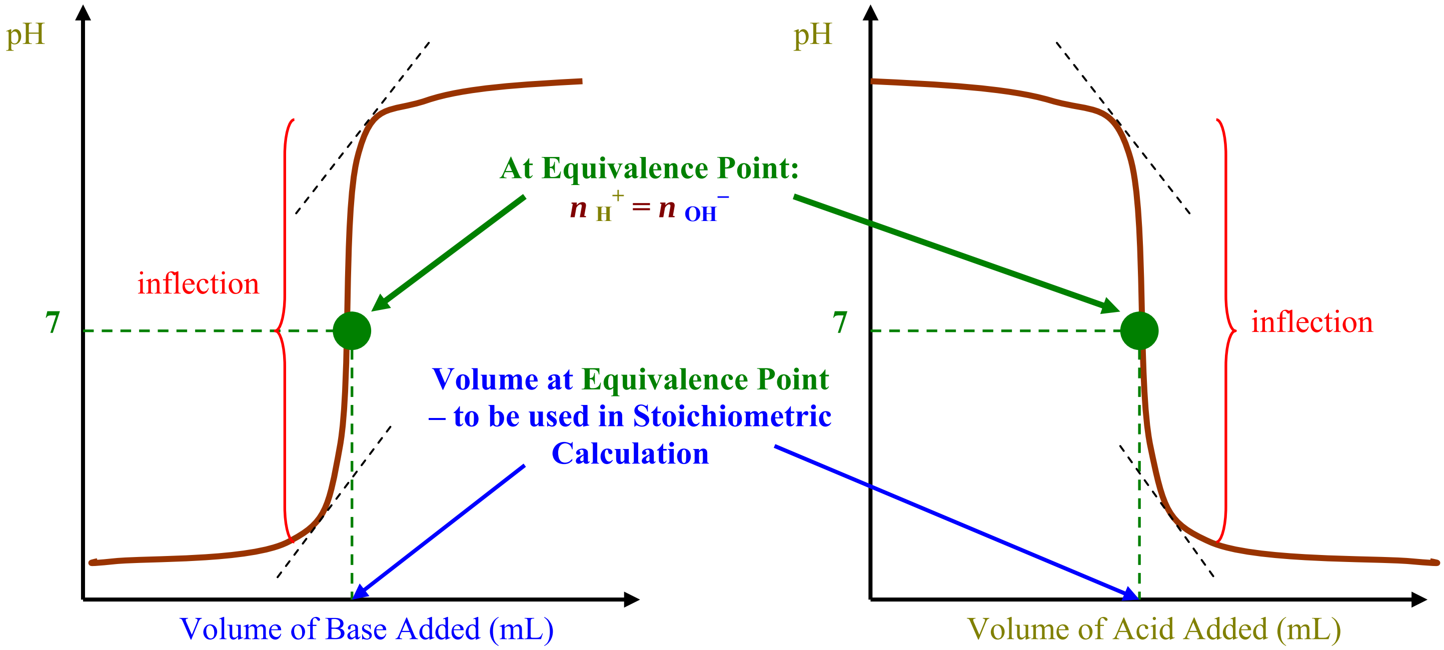
Indicator: - a chemical that changes colour due to the pH of the solution (more in the next section).

Inflection: - the part of the curve where there is a sudden rise or drop in pH.
- the midpoint of the inflection marks the equivalence point.

1. **Titration Between Strong Acids and Strong Base**: - **Equivalence Point** always occur at **pH = 7**.

Strong Acid (unknown concentration with known volume - analyte) titrated with Strong Base (known concentration - titrant)

Strong Base (unknown concentration and known volume - analyte) titrated with Strong Acid (known concentration - titrant)



Example 1: Calculate the pH when 30.0 mL of 0.100 M of $HCl_{(aq)}$ is titrated with 0.200 M of $KOH_{(aq)}$ at:

a. 0 mL of $KOH_{(aq)}$ added.
b. 5.00 mL of $KOH_{(aq)}$ added.
c. 15.00 mL of $KOH_{(aq)}$ added.
d. 20.00 mL of $KOH_{(aq)}$ added.

a. At 0 mL of $KOH_{(aq)}$ added, the pH will be solely based on the [HCl] in the flask:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

pH = –log $[H_3O^+]$ = –log(0.100) **pH = 1.00**

b. At 5.00 mL of $KOH_{(aq)}$ added: **(Before Stoichiometric Point)**

Chemical Species Present: H_3O^+ (SA), Cl^- (B), K^+, OH^- (SB), H_2O (A, B)

Net-Ionic Equation: $H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2\ H_2O_{(l)}$

	n of H_3O^+	*n* of OH^-
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(5.00 mL) = 1.00 mmol (LR)
Change	**– 1.00 mmol**	**– 1.00 mmol**
After	**2.00 mmol**	**0.00 mmol**

$$[H_3O^+] = \frac{n_{H_3O^+}}{\text{Total Volume}} = \frac{2.00\ \text{mmol}}{(30.00\ \text{mL} + 5.00\ \text{mL})} = 0.05714\ \text{mol/L}$$

pH = –log $[H_3O^+]$ = –log(0.05714) **pH = 1.24**

(pH's results from similar Calculations with other volumes before the stoichiometric point is listed on the next page.)

c. At 15.00 mL of KOH $_{(aq)}$ added: **(Stoichiometric Point)**

Chemical Species Present: H_3O^+ (SA), Cl^- (B), K^+, OH^- (SB), H_2O (A, B)

Net-Ionic Equation: $H_3O^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow 2\ H_2O_{(l)}$

	n of H_3O^+	*n* of OH^-
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(15.00 mL) = 3.00 mmol
Change	**– 3.00 mmol**	**– 3.00 mmol**
After	**0.00 mmol**	**0.00 mmol**

$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7}$ mol/L

$pH = -\log[H_3O^+] = -\log(1.00 \times 10^{-7})$ **pH = 7.00**

d. At 20.00 mL of KOH $_{(aq)}$ added: **(After Stoichiometric Point)**

Chemical Species Present: H_3O^+ (SA), Cl^- (B), K^+, OH^- (SB), H_2O (A, B)

Net-Ionic Equation: $H_3O^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow 2\ H_2O_{(l)}$

	n of H_3O^+	*n* of OH^-
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol (Limiting Reagent)	(0.200 mol/L)(20.00 mL) = 4.00 mmol
Change	**– 3.00 mmol**	**– 3.00 mmol**
After	**0.00 mmol**	**1.00 mmol**

$$[OH^-] = \frac{n_{OH^-}}{\text{Total Volume}} = \frac{1.00\ \text{mmol}}{(30.00\ \text{mL} + 20.00\ \text{mL})} = 0.0200\ \text{mol/L}$$

$pOH = -\log[OH^-] = -\log(0.0200)$ pOH = 1.70

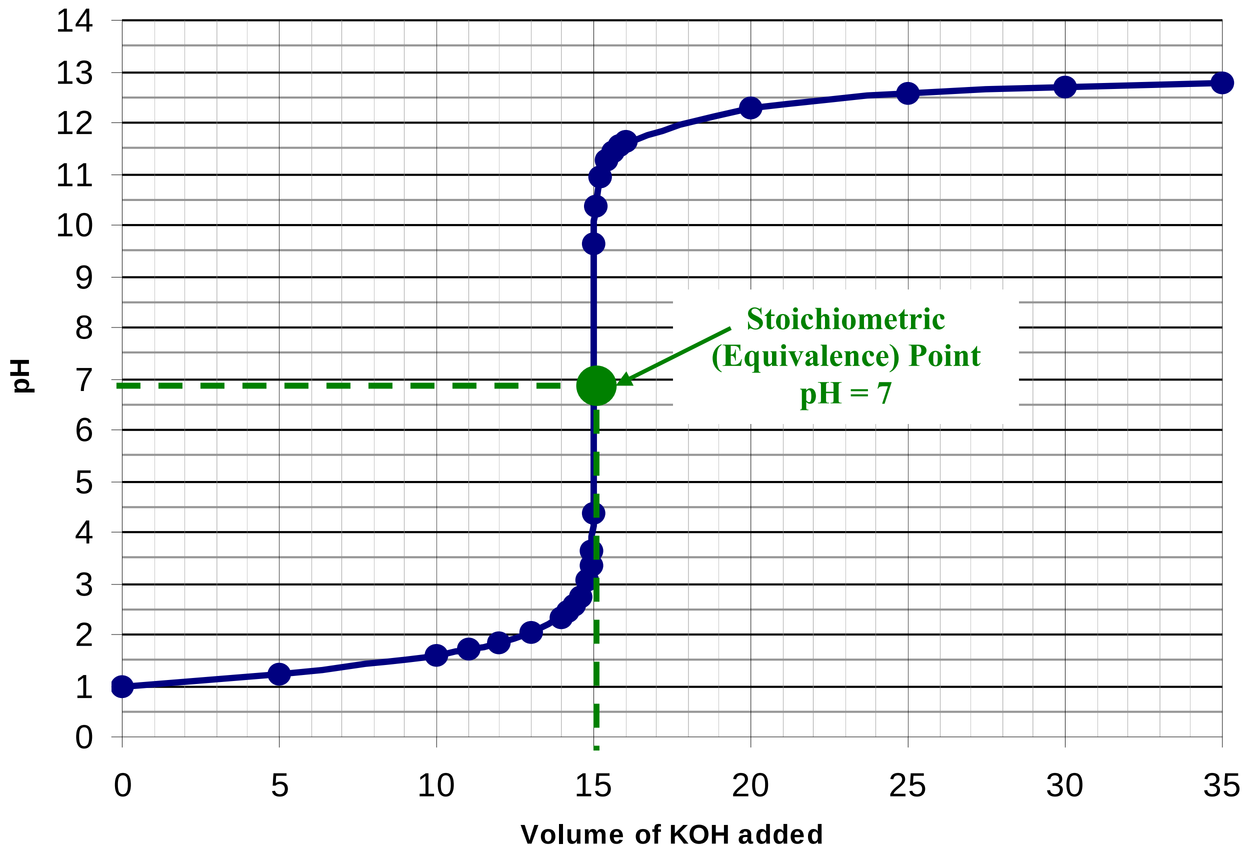
pH = 14 – pOH **pH = 12.30**

(pH's results from similar Calculations with other volumes after the stoichiometric point is listed below.)

pH of 30.0 mL of 0.100 M HCl $_{(aq)}$ titrated by 0.200 M of KOH $_{(aq)}$

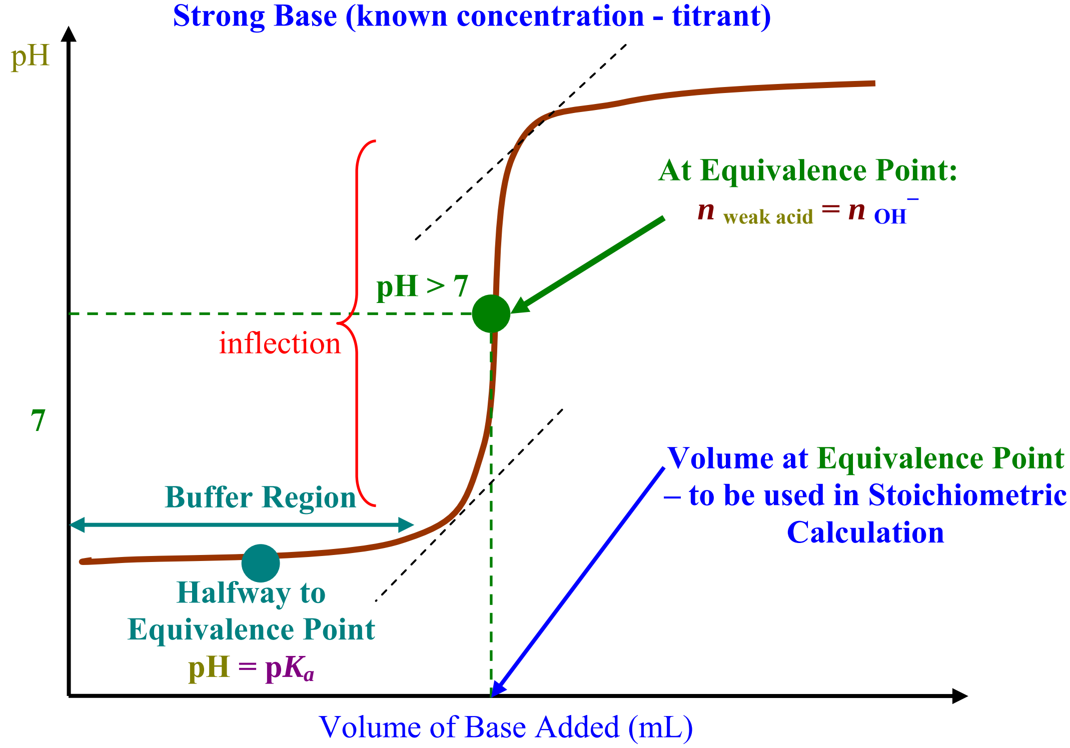
Volume of KOH added	pH	Volume of KOH added	pH	Volume of KOH added	pH
0.00 mL	1.00	14.60 mL	2.75	15.40 mL	11.25
5.00 mL	1.24	14.80 mL	3.05	15.60 mL	11.42
10.00 mL	1.60	14.90 mL	3.35	15.80 mL	11.54
11.00 mL	1.71	14.95 mL	3.65	16.00 mL	11.64
12.00 mL	1.85	14.99 mL	4.35	20.00 mL	12.30
13.00 mL	2.03	**15.00 mL (Equivalence)**	**7.00**	25.00 mL	12.56
14.00 mL	2.34	15.01 mL	9.65	30.00 mL	12.70
14.20 mL	2.44	15.05 mL	10.35	35.00 mL	12.79
14.40 mL	2.57	15.20 mL	10.95		

pH of 30.0 mL of 0.100 M HCl titrated by 0.200 M of KOH



2. **Titration Between Weak Acids and Strong Base**: - **Equivalence Point** always occur at **pH > 7**.

Weak Acid (unknown concentration with known volume - analyte) titrated with Strong Base (known concentration - titrant)



Example 2: Calculate the pH when 30.0 mL of 0.100 M of HCOOH $_{(aq)}$ ($K_a = 1.8 \times 10^{-4}$) is titrated with 0.200 mol/L of KOH $_{(aq)}$ at:

a. 0 mL of KOH $_{(aq)}$ added.
b. 7.50 mL of KOH $_{(aq)}$ added.
c. 15.00 mL of KOH $_{(aq)}$ added.
d. 20.00 mL of KOH $_{(aq)}$ added.

a. At 0 mL of KOH $_{(aq)}$ added, the pH will be calculated the weak acid dissociation in the flask:

$$HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

	$[HCOOH]$		$[H_3O^+]$	$[HCOO^-]$
Initial	**0.100 M**		0	**0 M**
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.1 - x)$		x	x

CANNOT use Approximation:

$$\frac{[HCOOH]_0}{K_a} = \frac{0.100\text{ M}}{1.8 \times 10^{-4}} = 555.6 < 1000$$

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} \qquad 1.8 \times 10^{-4} = \frac{(x)(x)}{(0.1 - x)} = \frac{x^2}{(0.1 - x)}$$

```
solve(X²/(.1-X)-
1.8E-4,X,0,{0,0.
1})
       .0041535952
```

$[H_3O^+] = x = 0.0042$ mol/L

pH = $-\log [H_3O^+] = -\log(0.042)$

pH = 2.38

b. At 7.50 mL of KOH $_{(aq)}$ added: **(Before Stoichiometric Point: at Halfway to Equivalence Point)**

Chemical Species Present: HCOOH, K^+, OH^-, H_2O
(SA: HCOOH; SB: OH^-; A/B: H_2O)

Net-Ionic Equation: $HCOOH_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + HCOO^-_{(aq)}$

	n of HCOOH	*n* of OH^-		*n* of $HCOO^-$
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(7.50 mL) = 1.50 mmol (LR)		0 mmol
Change	**− 1.50 mmol**	**− 1.50 mmol**		**+ 1.50 mmol**
After	**1.50 mmol**	**0 mmol**		**1.50 mmol**

$$[HCOOH] = \frac{n_{HCOOH}}{\text{Total Volume}} = \frac{1.50\text{ mmol}}{(30.00\text{ mL} + 7.50\text{ mL})} = 0.0400\text{ mol/L}$$

$$[HCOO^-] = \frac{n_{HCOO^-}}{\text{Total Volume}} = \frac{1.50\text{ mmol}}{(30.00\text{ mL} + 7.50\text{ mL})} = 0.0400\text{ mol/L}$$

$[HCOOH] = [HCOO^-]$
pH ≈ pK_a
(Max Buffer Capacity)

After all the OH^- is used up, the resulting solution follows the regular weak acid dissociation.

$$HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$$

	$[HCOOH]$		$[H_3O^+]$	$[HCOO^-]$
Initial	**0.0400 M**		0	**0.0400 M**
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.04 - x)$		x	$(0.04 + x)$

CANNOT use Approximation:

$$\frac{[HCOOH]_0}{K_a} = \frac{0.0400\text{ M}}{1.8 \times 10^{-4}} = 222.22 < 1000$$

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} \qquad 1.8 \times 10^{-4} = \frac{(x)(0.04 + x)}{(0.04 - x)}$$

```
solve(X(0.04+X)/
(0.04-X)-1.8E-4,
X,0,{0,0.04})
   1.784015157E-4
```

$[H_3O^+] = x = 1.8 \times 10^{-4}$ mol/L   pH = pK_a = $-\log(1.8 \times 10^{-4})$

(pH's results from similar Calculations with other volumes before the stoichiometric point is listed on page 306.)

pH = 3.75

c. At 15.00 mL of KOH $_{(aq)}$ added: **(Stoichiometric Point)**

Chemical Species Present: **HCOOH,** K^+, **OH^-,** H_2O
SA SB A/B

Net-Ionic Equation: $HCOOH_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + HCOO^-_{(aq)}$

	n of HCOOH	*n* of OH^-		*n* of $HCOO^-$
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(15.00 mL) = 3.00 mmol		0 mmol
Change	**– 3.00 mmol**	**– 3.00 mmol**		**+ 3.00 mmol**
After	**0 mmol**	**0 mmol**		**3.00 mmol**

$$[HCOO^-] = \frac{n_{HCOO^-}}{\text{Total Volume}} = \frac{3.00\ \text{mmol}}{(30.00\ \text{mL} + 15.00\ \text{mL})} = 0.0667\ \text{mol/L}$$

At Stoichiometric Point, after all the OH^- and HCOOH are used up, the resulting solution follows the regular weak base dissociation.

$HCOO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCOOH_{(aq)} + OH^-_{(aq)}$

	$[HCOO^-]$		[HCOOH]	$[OH^-]$
Initial	**0.0667 M**		0	**0 M**
Change	**$-x$**		$+x$	$+x$
Equilibrium	**$(0.0667 - x)$**		x	x

CAN use Approximation:

$$\frac{[HCOO^-]_0}{K_b} = \frac{0.0667\ \text{M}}{5.556\times10^{-11}}$$

$= 1.2 \times 10^9 \geq 1000$

Use 0.0667 in the denominator, because $(0.0667 - x) \approx 0.03667$ [x is so small compared to 0.0667 M].

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.8\times10^{-4}} \qquad K_b = 5.556 \times 10^{-11} = \frac{[HCOOH][OH^-]}{[HCOO^-]}$$

$$5.556 \times 10^{-11} = \frac{(x)(x)}{(0.0667 - x)} \approx \frac{x^2}{0.0667}$$

$[OH^-] = x = 1.92 \times 10^{-6}$ mol/L

$pOH = -\log(1.92 \times 10^{-6}) = 5.72$

$pH = 14 - pOH = 14 - 5.72$

pH = 8.28

d. At 20.00 mL of KOH $_{(aq)}$ added: **(After Stoichiometric Point)**

Chemical Species Present: **HCOOH,** K^+, **OH^-,** H_2O
SA SB A/B

Net-Ionic Equation: $HCOOH_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + HCOO^-_{(aq)}$

	n of HCOOH	*n* of OH^-
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol (LR)	(0.200 mol/L)(20.00 mL) = 4.00 mmol
Change	**– 3.00 mmol**	**– 3.00 mmol**
After	**0 mmol**	**1.00 mmol**

After all the HCOOH is used up, the resulting solution has the following major species.

Chemical Species Present: K^+, **OH^-,** H_2O
SB A/B

$$[OH^-] = \frac{n_{OH^-}}{\text{Total Volume}} = \frac{1.00\ \text{mmol}}{(30.00\ \text{mL} + 20.00\ \text{mL})} = 0.0200\ \text{mol/L}$$

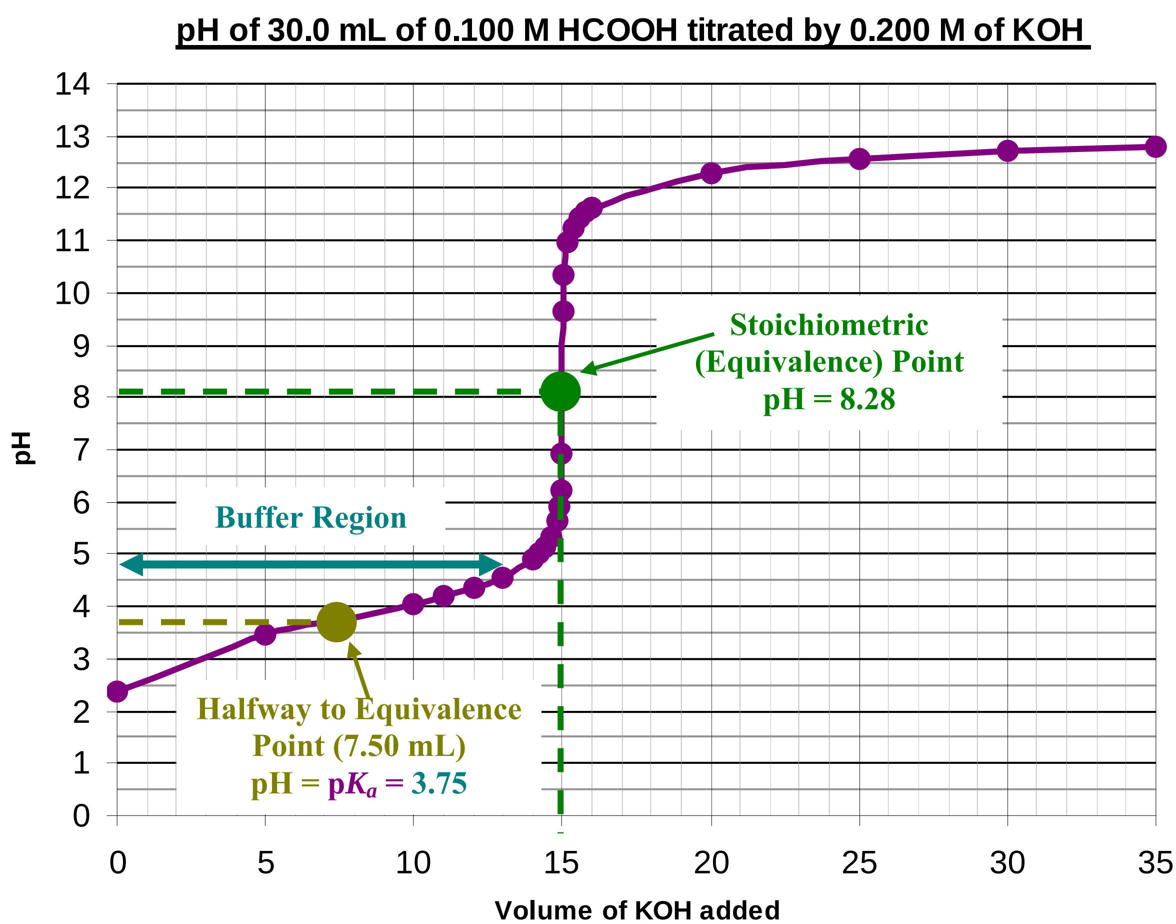
$pOH = -\log(0.0200) = 1.70$

$pH = 14 - pOH = 14 - 1.70$ **pH = 12.30**

(pH's results from similar Calculations with other volumes after the stoichiometric point is listed on the next page.)

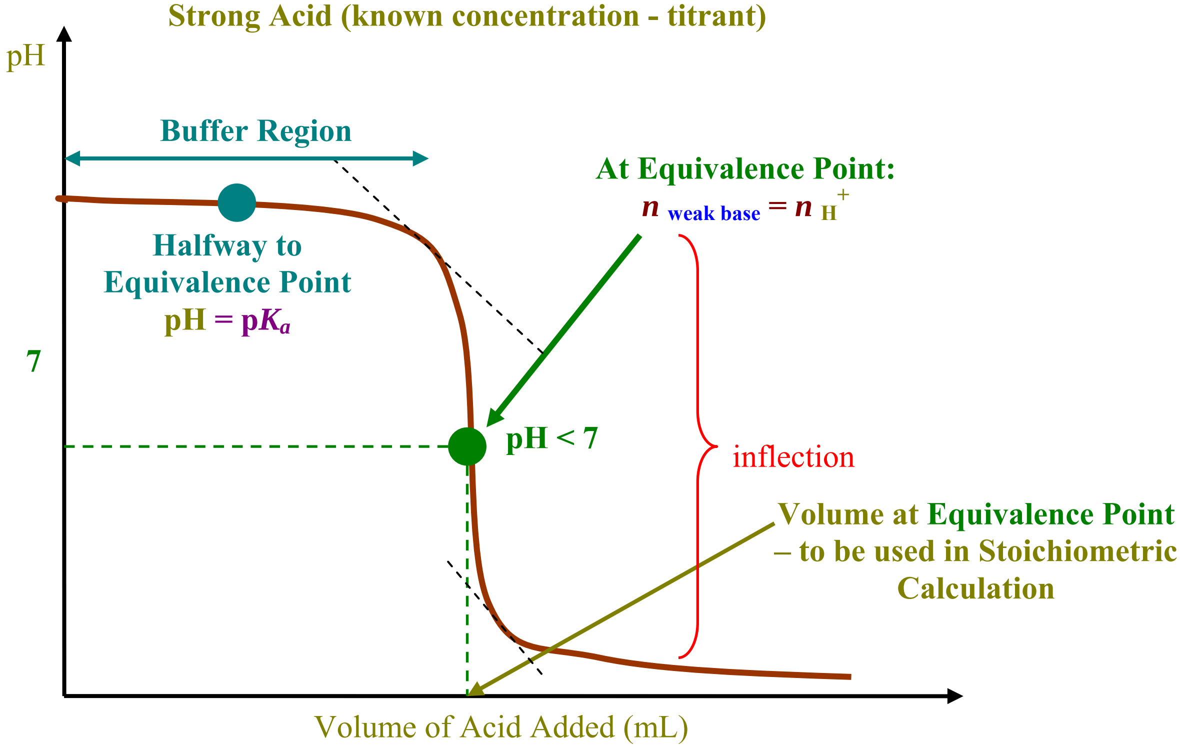
pH of 30.0 mL of 0.100 M $HCOOH_{(aq)}$ titrated by 0.200 M of $KOH_{(aq)}$

Volume of KOH added	pH	Volume of KOH added	pH	Volume of KOH added	pH
0.00 mL	2.38	14.40 mL	5.13	15.20 mL	10.95
5.00 mL	3.45	14.60 mL	5.31	15.40 mL	11.25
7.50 mL (Halfway to Equivalence)	3.75	14.80 mL	5.62	15.60 mL	11.42
10.00 mL	4.05	14.90 mL	5.91	15.80 mL	11.54
11.00 mL	4.19	14.95 mL	6.22	16.00 mL	11.64
12.00 mL	4.35	14.99 mL	6.92	20.00 mL	12.30
13.00 mL	4.56	**15.00 mL (Equivalence)**	**8.28**	25.00 mL	12.56
14.00 mL	4.89	15.01 mL	9.65	30.00 mL	12.70
14.20 mL	5.00	15.05 mL	10.35	35.00 mL	12.79



3. **Titration Between Weak Bases and Strong Acid**: - **Equivalence Point** always occur at **pH < 7**.

Weak Base (unknown concentration with known volume - analyte) titrated with Strong Acid (known concentration - titrant)



Example 3: Calculate the pH when 30.0 mL of 0.100 M of $CH_3NH_{2\,(aq)}$ ($K_b = 4.38 \times 10^{-4}$) is titrated with 0.200 mol/L of $HCl_{(aq)}$ at:

a. 0 mL of $HCl_{(aq)}$ added.
b. 7.50 mL of $HCl_{(aq)}$ added.
c. 15.00 mL of $HCl_{(aq)}$ added.
d. 20.00 mL of $HCl_{(aq)}$ added.

a. At 0 mL of $HCl_{(aq)}$ added, the pH will be calculated the weak base dissociation in the flask:

$$CH_3NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons CH_3NH_3^+{}_{(aq)} + OH^-{}_{(aq)}$$

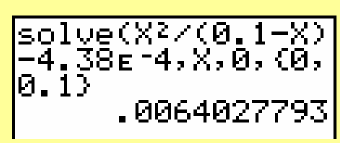
	$[CH_3NH_2]$		$[CH_3NH_3^+]$	$[OH^-]$
Initial	**0.100 M**		**0**	**0 M**
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.1 - x)$		x	x

CANNOT use Approximation:

$$\frac{[CH_3NH_2]_0}{K_b} = \frac{0.100\text{ M}}{4.38 \times 10^{-4}}$$

$= 228.3 < 1000$

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} \qquad 4.38 \times 10^{-4} = \frac{(x)(x)}{(0.1-x)} = \frac{x^2}{(0.1-x)}$$



$[OH^-] = x = 0.00640$ mol/L

$pOH = -\log[OH^-] = -\log(0.00640) = 2.19$

$pH = 14 - pOH = 14 - 2.19$ **pH = 11.81**

b. At 7.50 mL of HCl $_{(aq)}$ added: **(Before Stoichiometric Point: at Halfway to Equivalence Point)**

Chemical Species Present: **CH_3NH_3, H_3O^+,** Cl^-, H_2O
SB **SA** A/B

Net-Ionic Equation: $CH_3NH_{2\,(aq)} + H_3O^+_{(aq)} \rightarrow H_2O_{(l)} + CH_3NH_3^+{}_{(aq)}$

	n of CH_3NH_2	*n* of H_3O^+		*n* of $CH_3NH_3^+$
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(7.50 mL) = 1.50 mmol (LR)		0 mmol
Change	**– 1.50 mmol**	**– 1.50 mmol**		**+ 1.50 mmol**
After	**1.50 mmol**	**0 mmol**		**1.50 mmol**

$$[CH_3NH_2] = \frac{n_{CH_3NH_2}}{\text{Total Volume}} = \frac{1.50 \text{ mmol}}{(30.00 \text{ mL} + 7.50 \text{ mL})} = 0.0400 \text{ mol/L}$$

$$[CH_3NH_3^+] = \frac{n_{CH_3NH_3^+}}{\text{Total Volume}} = \frac{1.50 \text{ mmol}}{(30.00 \text{ mL} + 7.50 \text{ mL})} = 0.0400 \text{ mol/L}$$

$[CH_3NH_3^+] = [CH_2NH_2]$
pH ≈ pK_a
(Max Buffer Capacity)

After all the H_3O^+ is used up, the resulting solution follows the regular weak base dissociation.

$$CH_3NH_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons CH_3NH_3^+{}_{(aq)} + OH^-{}_{(aq)}$$

	$[CH_3NH_2]$		$[CH_3NH_3^+]$	$[OH^-]$
Initial	**0.0400 M**		**0**	**0.0400 M**
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.04 - x)$		x	$(0.04 + x)$

CANNOT use Approximation:

$$\frac{[CH_3NH_2]_0}{K_b} = \frac{0.0400 \text{ M}}{4.38 \times 10^{-4}} = 91.3 < 1000$$

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} \qquad 4.38 \times 10^{-4} = \frac{(x)(0.04 + x)}{(0.04 - x)}$$

```
solve(X(0.04+X)/
(0.04-X)-4.38E-4
,X,0,{0,0.04})
   4.287107932E-4
```

$[OH^-] = x = 4.29 \times 10^{-4}$ mol/L

pOH = –log $[OH^-]$ = –log(4.29×10^{-4}) = 3.37

pH = 14 – pOH = 14 – 3.37

pH = 10.63

(pH's results from similar Calculations with other volumes before the stoichiometric point is listed on the next page.)

c. At 15.00 mL of HCl $_{(aq)}$ added: **(Stoichiometric Point)**

Chemical Species Present: **CH_3NH_2, H_3O^+,** Cl^-, H_2O
SB **SA** A/B

Net-Ionic Equation: $CH_3NH_{2\,(aq)} + H_3O^+_{(aq)} \rightarrow H_2O_{(l)} + CH_3NH_3^+{}_{(aq)}$

	n of CH_3NH_2	*n* of H_3O^+		*n* of $CH_3NH_3^+$
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(15.00 mL) = 3.00 mmol		0 mmol
Change	**– 3.00 mmol**	**– 3.00 mmol**		**+ 3.00 mmol**
After	**0 mmol**	**0 mmol**		**3.00 mmol**

$$[CH_3NH_3^+] = \frac{n_{CH_3NH_3^+}}{\text{Total Volume}} = \frac{3.00 \text{ mmol}}{(30.00 \text{ mL} + 15.00 \text{ mL})} = 0.0667 \text{ mol/L}$$

At Stoichiometric Point, after all the H_3O^+ and CH_3NH_2 are used up, the resulting solution follows the regular weak acid dissociation.

$$CH_3NH_3^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3NH_2{}_{(aq)} + H_3O^+{}_{(aq)}$$

	$[CH_3NH_3^+]$		$[CH_3NH_2]$	$[H_3O^+]$
Initial	**0.0667 M**		**0**	**0 M**
Change	$-x$		$+x$	$+x$
Equilibrium	$(0.0667 - x)$		x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{4.38\times10^{-4}} \qquad K_a = 2.28\times10^{-11} = \frac{[CH_2NH_2][H_3O^+]}{[CH_3NH_3]}$$

$$2.28\times10^{-11} = \frac{(x)(x)}{(0.0667 - x)} \approx \frac{x^2}{0.0667}$$

CAN use Approximation:

$$\frac{[CH_3NH_3^+]_0}{K_a} = \frac{0.0667\text{ M}}{2.28\times10^{-11}}$$

$$= 2.9\times10^9 \geq 1000$$

Use 0.0667 in the denominator, because $(0.0667 - x) \approx 0.03667$ [x is so small compared to 0.0667 M].

$[H_3O^+] = x = 1.23\times10^{-6}$ **mol/L** $\quad pH = -\log[H_3O^+] = -\log(1.23\times10^{-6})$ $\quad$ **pH = 5.91**

d. At 20.00 mL of $HCl_{(aq)}$ added: **(After Stoichiometric Point)**

Chemical Species Present: CH_3NH_2, H_3O^+, Cl^-, H_2O
(SB: CH_3NH_2; SA: H_3O^+; A/B: H_2O)

Net-Ionic Equation: $CH_3NH_2{}_{(aq)} + H_3O^+{}_{(aq)} \rightarrow H_2O_{(l)} + CH_3NH_3^+{}_{(aq)}$

	***n* of CH_3NH_2**	***n* of H_3O^+**
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol (LR)	(0.200 mol/L)(20.00 mL) = 4.00 mmol
Change	**– 3.00 mmol**	**– 3.00 mmol**
After	**0 mmol**	**1.00 mmol**

After all the CH_3NH_2 is used up, the resulting solution has the following major species.

Chemical Species Present: Cl^-, H_3O^+, H_2O
(SA: H_3O^+; A/B: H_2O)

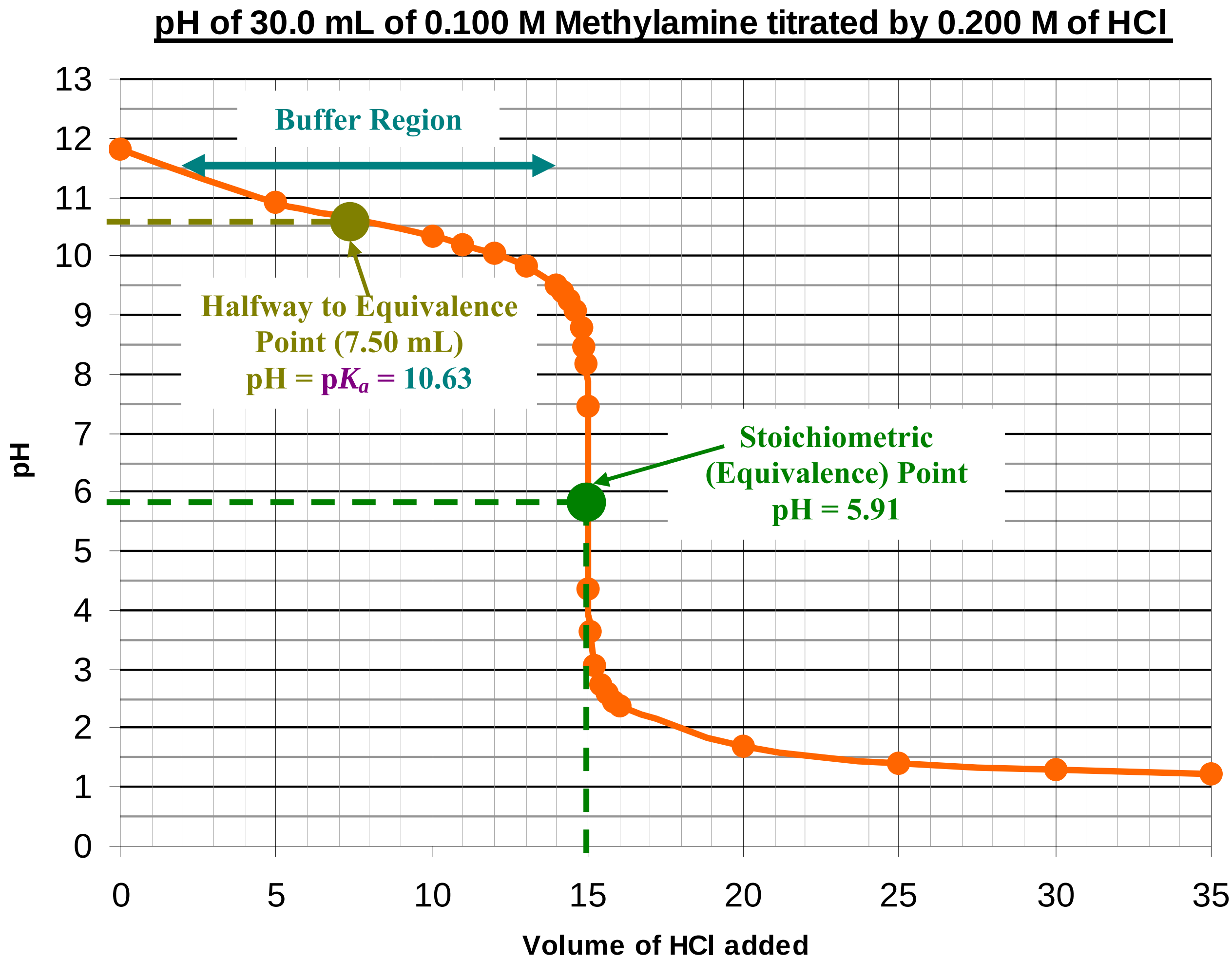
$$[H_3O^+] = \frac{n_{H_3O^+}}{\text{Total Volume}} = \frac{1.00\text{ mmol}}{(30.00\text{ mL} + 20.00\text{ mL})} = 0.0200\text{ mol/L}$$

$pH = -\log[H_3O^+] = -\log(0.0200)$ $\quad$ **pH = 1.70**

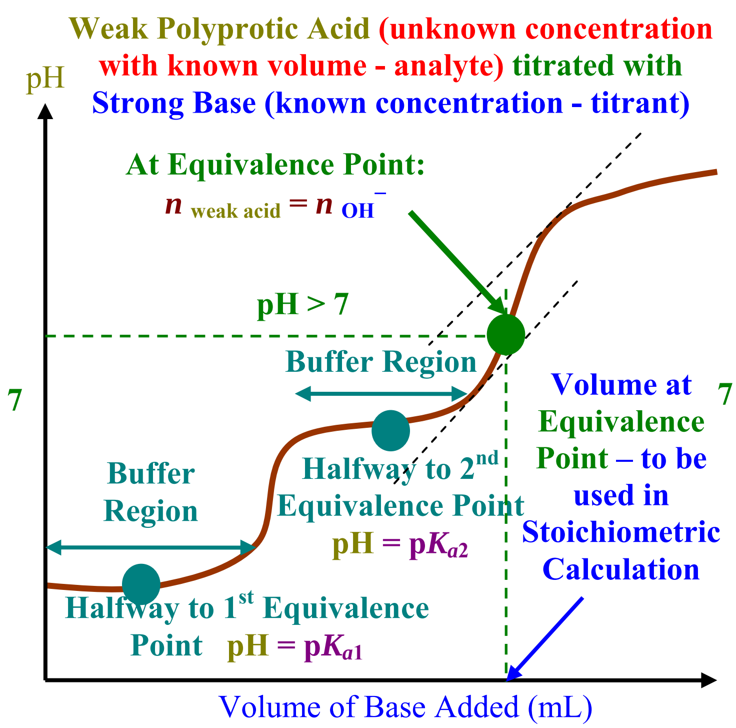
(pH's results from similar Calculations with other volumes after the stoichiometric point is listed below.)

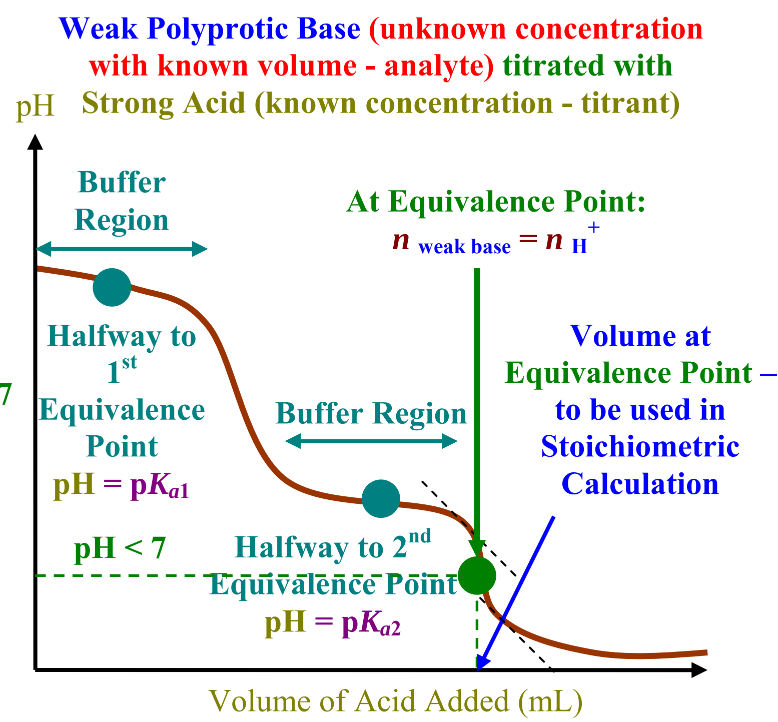
pH of 30.0 mL of 0.100 M $CH_3NH_2{}_{(aq)}$ titrated by 0.200 M of $HCl_{(aq)}$

Volume of HCl added	pH	Volume of HCl added	pH	Volume of HCl added	pH
0.00 mL	11.81	14.40 mL	9.26	15.20 mL	3.05
5.00 mL	10.92	14.60 mL	9.08	15.40 mL	2.75
7.50 mL (Halfway to Equivalence)	10.63	14.80 mL	8.77	15.60 mL	2.58
10.00 mL	10.33	14.90 mL	8.47	15.80 mL	2.46
11.00 mL	10.20	14.95 mL	8.16	16.00 mL	2.36
12.00 mL	10.03	14.99 mL	7.46	20.00 mL	1.70
13.00 mL	9.82	**15.00 mL (Equivalence)**	**5.91**	25.00 mL	1.40
14.00 mL	9.49	15.01 mL	4.35	30.00 mL	1.30
14.20 mL	9.39	15.05 mL	3.65	35.00 mL	1.21



4. **Titration Between Strong Acid/Bases and Polyprotic Acid/Base**: - there are multiple equivalence points.
- the last equivalence point indicates the stoichiometric volume.





Example 4: Calculate the concentration of 10.00 mL of $Na_2S_{(aq)}$ is titrated with 0.0350 M of $HBr_{(aq)}$ when the first and second equivalence points are at 13.34 mL and 27.88 mL respectively.

For Acid-Base Stoichiometry, do NOT write the Net-Ionic Equation. Write the Molecular Equation to do Stoichiometry. We use the second equivalence point because Na_2S can accept two protons.

$2\ HBr_{(aq)}$	+	$Na_2S_{(aq)}$	→	$H_2S_{(aq)}$	+	$2\ NaBr_{(aq)}$
27.88 mL		10.0 mL				
0.0350 mol/L		? mol/L				

① $n_{HBr} = CV = (0.0350\ \text{mol/}\cancel{\text{L}})(27.88\ \text{m}\cancel{\text{L}}) = 0.9758\ \text{mmol}$

② $n_{Na_2S} = 0.9758\ \text{m}\cancel{\text{mol HBr}} \times \dfrac{1\ \text{mol}\ Na_2S}{2\ \cancel{\text{mol HBr}}} = 0.4879\ \text{mmol}\ Na_2S$

③ $[Na_2S] = \dfrac{n}{V} = \dfrac{0.4879\ \cancel{\text{m}}\text{mol}}{10.0\ \cancel{\text{m}}\text{L}} = 0.04879\ \text{mol/L}$

$[Na_2S]$ = 0.0488 mol/L

16.5: Acid-Base Indicators

Acid-Base Indicators:
- chemicals that change colours at a specific pH range.
- they are themselves organic acids. Since they are usually very big structurally, we usually use abbreviations to describe them in chemical equations.
- this is due to the acidic form of the indictor (HIn) has a different colour than its basic form (In^-).
- the colour change occurs when $\dfrac{[In^-]}{[HIn]} = \dfrac{1}{10}$ (titrating an acid with a base) or when $\dfrac{[In^-]}{[HIn]} = \dfrac{10}{1}$ (titrating a base with an acid).

Using the Henderson-Hasselbach Equation to determine pH Range for Indictors to Change Colour:

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right)$$ (Substitute observable Colour Change Ratio $\dfrac{[In^-]}{[HIn]} = \dfrac{1}{10}$ or $\dfrac{10}{1}$)

$pH = pK_a + \log\left(\dfrac{1}{10}\right)$ or $pH = pK_a + \log\left(\dfrac{10}{1}\right)$

$pH = pK_a - 1$ or $pH = pK_a + 1$

pH Range for Indictors to Change Colour

$$HIn_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}$$

$$\mathbf{pH = pK_a \pm 1}$$

$pH \leq (pK_a - 1) \rightarrow$ Colour of $HIn_{(aq)}$
$pH \geq (pK_a + 1) \rightarrow$ Colour of $In^-_{(aq)}$
$pH = pK_a \rightarrow$ Mixed Colours of $HIn_{(aq)} + In^-_{(aq)}$

Example: Phenolphthalein (HPh $_{(aq)}$ /Ph^{-}$_{(aq)}$) changes colours from colourless to pink at a pH range of 8.0 to 10.0. At its **mid-range (9.0 – average of 8.0 and 10.0)**, the colour would be **light pink (colourless + pink)**.

HPh $_{(aq)}$ + $H_2O_{(l)}$ ⇌ $H_3O^+_{(aq)}$ + **Ph^{-}** $_{(aq)}$ (Colourless) (Pink) $K_a = 1.0 \times 10^{-9}$ $pK_a = 9$ Colour Change = 9 ± 1

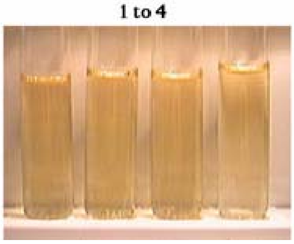
At pH ≤ 9, phenolphthalein is colourless.   At pH ≥ 10, phenolphthalein is pink.

Example: Bromothymol Blue (HBb $_{(aq)}$ /Bb^{-}$_{(aq)}$) changes colours from yellow to blue at a pH range of 6.0 to 8.0. At its **mid-range (7.0 – average of 6.0 and 8.0)**, the colour would be **green (yellow + blue)**.

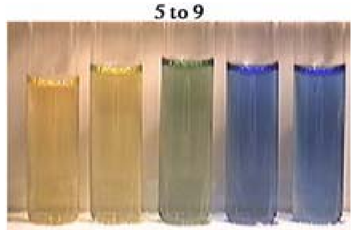
HBb $_{(aq)}$ + $H_2O_{(l)}$ ⇌ $H_3O^+_{(aq)}$ + **Bb^{-}** $_{(aq)}$ **(Yellow)** **(Blue)** $K_a = 1.0 \times 10^{-7}$ $pK_a = 7$ Colour Change = 7 ± 1

At pH ≤ 6, bromothymol blue is yellow.   At pH ≥ 8, bromothymol blue is blue.

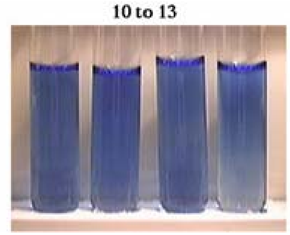
1 to 4



5 to 9



10 to 13



Example 1: The pH curve of methylamine with HCl has an equivalence point at pH = 5.91. Using the following information below, decide on an indicator to use in this titration and state what colour change the experimenter should be looking for.

Indicators	Colour Change	K_a
methyl orange	red to yellow	1.6×10^{-4}
methyl red	red to yellow	1.0×10^{-5}
bromocresol purple	yellow to purple	2.0×10^{-6}
bromothymol blue	yellow to blue	1.0×10^{-7}

First, we need to decide on the pH range that these indicators will change colors.

Indicators	Colour Change	K_a	pH range (pK_a ± 1)
methyl orange	red to yellow	1.6×10^{-4}	3.8 ± 1 (2.8 to 4.8)
methyl red	red to yellow	1.0×10^{-5}	5.0 ± 1 (4.0 to 6.0)
bromocresol purple	yellow to purple	2.0×10^{-6}	5.7 ± 1 (4.7 to 6.7)
bromothymol blue	yellow to blue	1.0×10^{-7}	7.0 ± 1 (6.0 to 8.0)

We can see that pH = 5.91 is well within the color change of **bromocresol purple** (for methyl red, it is too close to the boundary point). **The color where the experimenter will stop is brown** (yellow + purple) with the **pH = 5.7 (end-point).**

Assignment

16.4 pg. 741 #22 to 32; pg. 734−744 #88 and 106

16.5 pg. 741 #33 to 38; pg. 744 #100

16.6: Solubility Equilibria

Solubility Product (K_{sp}): - the equilibrium constant as a salt dissolves into its aqueous ions.
- sometimes refer to as **solubility product constant**.
- like equilibrium constant, **K_{sp} is unitless**.

Molar Solubility: - the equilibrium position of the solvation equilibrium.
- the maximum amount of salts in moles dissolved per Litre of solvent.

Solubility: - the maximum mass of salts in moles dissolved per Litre of solvent.

$$A_xB_{y\,(s)} \rightleftharpoons xA^{y+}_{(aq)} + yB^{x-}_{(aq)}$$

$K_{sp} = [A^{y+}]^x[B^{x-}]^y$ **Molar Solubility = $[A_xB_y]$** **Solubility = $[A_xB_y]$ × Molar Mass**

Example 1: The molar solubility of $Ba(OH)_{2\,(s)}$ is 0.108 mol/L. Determine the molar concentration of each ion and the solubility product of $Ba(OH)_{2\,(s)}$.

$$Ba(OH)_{2\,(s)} \rightleftharpoons Ba^{2+}_{(aq)} + 2\,OH^-_{(aq)}$$

0.108 M 0.108 M 0.216 M

$K_{sp} = [Ba^{2+}][OH^-]^2 = (0.108)(0.216)^2$ **$K_{sp} = 5.04 \times 10^{-3}$**

Example 2: The K_{sp} for lead (II) chloride is 1.6×10^{-5}. Calculate the molar concentrations of each ions and the molar solubility and the solubility of solid lead (II) chloride.

$$PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\,Cl^-_{(aq)}$$

	$[PbCl_2]$		$[Pb^{2+}]$	$[Cl^-]$
Initial	----		0	0
Change	----		$+x$	$+2x$
Equilibrium	----		x	$2x$

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$1.6 \times 10^{-5} = (x)(2x)^2$

$1.6 \times 10^{-5} = 4x^3$

$x = \sqrt[3]{\left(\frac{1.6\times10^{-5}}{4}\right)}$

$x = 0.016$ M

Solubility = (0.016 mol/L)(278.1 g/mol)

Molar Solubility of $PbCl_2$ = 0.016 M
$[Pb^{2+}]$ = 0.016 M; $[Cl^-]$ = 0.032 M
Solubility = 4.41 g /L

Relative Solubility: - how the solubilities of various salts compare.
- **the solubilities of salts can only be compared directly from K_{sp} values when the salts produce the same number of ions**. (In general, **the bigger the K_{sp}, the higher the solubility**.)
- **the solubilities of salts that produce Different Number of Ions CANNOT be compared directly from K_{sp}**. They must be calculated individually before comparison can be made.

Example 3: Compare the solubilities of $CaCO_3$, $BaCO_3$ and $SrCO_3$ with the K_{sp} values as 8.7×10^{-9}, 1.6×10^{-9}, and 7×10^{-10} respectively.

Since all salts listed here have the same number of ions, the general solution for the solubility is as follows:

$K_{sp} = [M^{2+}][CO_3^{2-}]$ (Let $x = [M^{2+}] = [CO_3^{2-}]$ = Solubility) $x = \sqrt{K_{sp}}$

$CaCO_{3\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = 8.7 \times 10^{-9}$ **$CaCO_3$ Solubility = 9.3×10^{-5} M**

$BaCO_{3\,(s)} \rightleftharpoons Ba^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = 1.6 \times 10^{-9}$ **$BaCO_3$ Solubility = 4.0×10^{-5} M**

$SrCO_{3\,(s)} \rightleftharpoons Sr^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $K_{sp} = 7 \times 10^{-10}$ **$SrCO_3$ Solubility = 3×10^{-5} M**

The Solubility increases from $SrCO_3$ < $BaCO_3$ < $CaCO_3$. (Since $CaCO_3$ has the largest K_{sp} and all salts have the same number of ions dissociated, $CaCO_3$ has the highest solubility.)

Example 4: Compare the solubilities of AgCl, Ag_2CO_3, and Ag_3PO_4 with the K_{sp} values as 1.6×10^{-10}, 8.1×10^{-12}, 1.8×10^{-18} respectively.

Since all salts listed here have different number of ions, the solubility of each salt has to be calculated separately.

$AgCl_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

	[AgCl]		[Ag^+]	[Cl^-]
Initial	----		**0**	**0**
Change	----		**+*x***	**+*x***
Equilibrium	----		***x***	***x***

$K_{sp} = [Ag^+][Cl^-]$

$1.6 \times 10^{-10} = (x)(x)$

$1.6 \times 10^{-10} = x^2$

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

$x = 1.3 \times 10^{-5}$ M

Solubility of AgCl = 1.3×10^{-5} M

$Ag_2CO_{3\,(s)} \rightleftharpoons 2\,Ag^{+}_{(aq)} + CO_3^{2-}{}_{(aq)}$

	[Ag_2CO_3]		[Ag^+]	[CO_3^{2-}]
Initial	----		**0**	**0**
Change	----		**+2*x***	**+*x***
Equilibrium	----		**2*x***	***x***

$K_{sp} = [Ag^+]^2[CO_3^{2-}]$

$8.1 \times 10^{-12} = (2x)^2(x)$

$8.1 \times 10^{-12} = 4x^3$

$x = \sqrt[3]{\left(\frac{8.1 \times 10^{-12}}{4}\right)} = 1.3 \times 10^{-4}$ M

Solubility of Ag_2CO_3 = 1.3×10^{-4} M

$Ag_3PO_{4\,(s)} \rightleftharpoons 3\,Ag^{+}_{(aq)} + PO_4^{-}{}_{(aq)}$

	[Ag_3PO_4]		[Ag^+]	[Cl^-]
Initial	----		**0**	**0**
Change	----		**+3*x***	**+*x***
Equilibrium	----		**3*x***	***x***

$K_{sp} = [Ag^+]^3[PO_4^{3-}]$

$1.8 \times 10^{-18} = (3x)^3(x)$

$1.8 \times 10^{-18} = 27x^4$

$x = \sqrt[4]{\left(\frac{1.8 \times 10^{-18}}{27}\right)} = 1.6 \times 10^{-5}$ M

Solubility of Ag_3PO_4 = 1.6×10^{-5} M

The Solubility increases from AgCl < Ag_3PO_4 < Ag_2CO_3. Again we can see here because these salts do not dissociate the same number of ions, we cannot compare their solubilities directly from their K_{sp} values.

16.7: Separation of Ions by Fractional Precipitation

Ion Product (*Q*): - similar to reaction quotient, its measures the initial ion concentrations and compares it with K_{sp}.

$$Q = [A^{y+}]_0^{\,x}[B^{x-}]_0^{\,y}$$

a. **When $Q > K_{sp}$, the system will shifts to the solid salt (reactant)**. ***In this condition, Q indicates that there are too much ions (products)***. Therefore, the system has to **Shift back to the Left and Precipitation occurs**.

b. **When $Q < K_{sp}$, the system will shifts to the ions (product)**. ***In this condition, Q indicates that there are too little ions (products)***. Therefore, the system has to **Shift to the Right and there will be NO Precipitation**.

Calculations involving Ion Product and Final Ion Concentrations:

1. Determine the **Initial Concentrations** of the ions that will likely form a precipitate. (Remember to divide the moles by the total volume.)
2. Calculate the **Ion product**.
3. **Compare it to the K_{sp} value** of the solid and decide whether precipitation will form.
4. If precipitation occurs **($Q > K_{sp}$)**, then **write the net ionic equation for the precipitation**.
5. **Using regular stoichiometry**, run the reaction to completion and **determine the concentration of the excess ion**.
6. **Redo the equilibrium for dissolving**. Using K_{sp} and the excess ion concentration as initial concentration to find the **final concentrations of both ions**.

Example 1: 200 mL of 0.0500 M of calcium chloride is reacted with 150 mL of 0.0600 M of ammonium phosphate. Determine whether $Ca_3(PO_4)_2$ will precipitate and calculate the concentrations of Ca^{2+} and PO_4^{3-} in the final solution. The K_{sp} value of $Ca_3(PO_4)_2$ is 1.3×10^{-32}.

Both $CaCl_2$ and $(NH_4)_3PO_4$ dissociates completely in water.

$$CaCl_{2\,(aq)} \rightarrow Ca^{2+}_{(aq)} + 2\,Cl^-_{(aq)}$$

$n_{CaCl_2} = (0.0500\text{ mol/L})(200\text{ mL})$ $n_{Ca^{2+}} = 10.0\text{ mmol}$

$n_{CaCl_2} = 10.0\text{ mmol}$ $[Ca^{2+}]_0 = \dfrac{10.0\text{ mmol}}{350\text{ mL}} = 0.0285714286\text{ M}$

$$(NH_4)_3PO_{4\,(aq)} \rightarrow 3\,NH_4^+{}_{(aq)} + PO_4^{3-}{}_{(aq)}$$

$n_{(NH_4)_3PO_4} = (0.0600\text{ mol/L})(150\text{ mL})$ $n_{PO_4^{3-}} = 9.00\text{ mmol}$

$n_{(NH_4)_3PO_4} = 9.00\text{ mmol}$ $[PO_4^{3-}]_0 = \dfrac{9.00\text{ mmol}}{350\text{ mL}} = 0.0257142857\text{ M}$

$$Ca_3(PO_4)_{2\,(s)} \rightleftharpoons 3\,Ca^{2+}_{(aq)} + 2\,PO_4^{3-}{}_{(aq)} \qquad K_{sp} = 1.3 \times 10^{-32}$$

Calculating Ion Product: $Q = [Ca^{2+}]_0^{\,3}[PO_4^{3-}]_0^{\,2} = (0.0285714286)^3(0.0257142857)^2$

$Q = 1.5 \times 10^{-8}$

Q (1.5×10^{-8}) > K_{sp} (1.3×10^{-32}) Precipitation Occurs

Running the precipitation reaction to completion and using regular stoichiometry,

$$3\,Ca^{2+}_{(aq)} + 2\,PO_4^{-}{}_{(aq)} \rightarrow Ca_3(PO_4)_{2\,(s)}$$

	***n* of Ca^{2+}**	***n* of PO_4^{3-}**
Before	10.0 mmol (LR)	9.00 mmol
Change	**– 10.00 mmol**	$-\left(\frac{2}{3}\right)$**(10.0 mmol)**
After	**0 mmol**	**2.33333333 mmol**

$$\text{New }[PO_4^{3-}]_0 = \frac{2.3333333\ \text{mmol}}{350\ \text{mL}}$$

New $[PO_4^{3-}]_0$ = 0.019047619 M

Finally, using K_{sp} and the new $[PO_4^{3-}]_0$,

$$Ca_3(PO_4)_{2\,(s)} \rightleftharpoons 3\,Ca^{2+}_{(aq)} + 2\,PO_4^{3-}{}_{(aq)}$$

	$[Ca_3(PO_4)_2]$		$[Ca^{2+}]$	$[PO_4^{3-}]$
Initial	----		**0**	0.019047619 M
Change	----		**+3*x***	**+2*x***
Equilibrium	----		**3*x***	**0.019047619 + 2*x***

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

$$1.3 \times 10^{-32} = (3x)^3(0.019047619 + 2x)^2$$

$$1.3 \times 10^{-32} \approx (3x)^3(0.019047619)^2$$

$$x^3 \approx \frac{1.3\times10^{-32}}{(3)^3(0.019047619)^2}$$

$$x \approx \sqrt[3]{\frac{1.3\times10^{-32}}{(3)^3(0.019047619)^2}} \approx 1.0989 \times 10^{-10}$$

CAN use Approximation:

$$\frac{[PO_4^{3-}]_0^2}{K_{sp}} = \frac{(0.019047619\ \text{M})^2}{1.3\times10^{-32}}$$

$$= \mathbf{2.8 \times 10^{28} >> 1000}$$

Because in the K_{sp} expression, PO_4^{3-} is squared, the rule of thumb must reflect this operation.

Use 0.019047619 in the denominator, because (0.019047619 + 2*x*) ≈ 0.019047619 [2*x* is so small compared to 0.019047619 M].

$[Ca^{2+}] = 3(1.0989 \times 10^{-10}\ \text{M})$

$\mathbf{[Ca^{2+}] = 3.3 \times 10^{-10}\ M}$

$[PO_4^{3-}] = 0.019047619\ \text{M} + 2(1.0989 \times 10^{-10}\ \text{M})$

$\mathbf{[PO_4^{3-}] = 0.019\ M}$

Assignment

16.6 pg. 741−744 #39 to 54, 92, 94, 99, 109, 112, 113, 116
16.7 pg. 742−744 #55, 56, 93, 110

16.8: Common Ion Effect and Solubility

Common-Ion Effect and Solubility: - when a solution containing a common ion of a salt is used as a solvent, the **solubility of the salt will lower** as a result.
- set up equilibrium ICE Box to assist in calculation.

Example 1: A 0.0150 M of KBr $_{(aq)}$ is used as a solvent for solid $PbBr_2$. Calculate the final concentrations for both ions and the molar solubility of $PbBr_{2\,(s)}$ given that K_{sp} for $PbBr_2$ is 4.6×10^{-6}.

KBr dissociates completely in water.

$KBr_{(aq)} \rightarrow K^+_{(aq)} + Br^-_{(aq)}$
0.0150 M 0.0150 M

$PbBr_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2\,Br^-_{(aq)}$

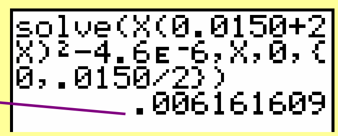
	$[PbBr_2]$		$[Pb^{2+}]$	$[Br^-]$
Initial	----		0	0.0150 M
Change	----		$+x$	$+2x$
Equilibrium	----		x	$0.0150 + 2x$

CANNOT use Approximation:

$$\frac{[Br^-]_0^2}{K_{sp}} = \frac{(0.0150\text{ M})^2}{4.6\times10^{-6}} = 48.9 < 1000$$

Because in the K_{sp} expression, Br^- is squared, the rule of thumb must reflect this operation.

$K_{sp} = [Pb^{2+}][Br^-]^2$
$4.6 \times 10^{-6} = (x)(0.0150 + 2x)^2$
$x = 0.0062$ M



$[Br^-] = 0.0150\text{ M} + 2(0.0062\text{ M})$

Solubility of $PbBr_2$ in 0.0150 M of $KBr_{(aq)}$ = 0.0062 M
$[Pb^{2+}] = 0.0062$ M; $[Br^-] = 0.027$ M

Note: If there was no common ion, the solubility of $PbBr_2$ would be 0.010 M. Hence, **with the presence of a common ion, the solubility of a salt is lowered**.

Example 2: Determine the final concentrations for both ions of $Cu(OH)_{2\,(s)}$ in neutral water given that K_{sp} for $Cu(OH)_2$ is 2.2×10^{-20}.

We have to consider the $[OH^-]$ in water.

$H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$
1×10^{-7} M (at pH = 7)

$Cu(OH)_{2\,(s)} \rightleftharpoons Cu^{2+}_{(aq)} + 2\,OH^-_{(aq)}$

	$[Cu(OH)_2]$		$[Pb^{2+}]$	$[OH^-]$
Initial	----		0	1×10^{-7} M
Change	----		$+x$	$+2x$
Equilibrium	----		x	$(1 \times 10^{-7}) + 2x$

CAN use Approximation:

$$\frac{[OH^-]_0^2}{K_{sp}} = \frac{(1\times10^{-7}\text{ M})^2}{2.2\times10^{-20}} = 4.5 \times 10^5 < 1000$$

Because in the K_{sp} expression, OH^- is squared, the rule of thumb must reflect this operation.

Use 1×10^{-7} as $[OH^-]$, because $(1 \times 10^{-7} + 2x) \approx 1 \times 10^{-7}$ [x is so small compared to 1×10^{-7} M].

$K_{sp} = [Cu^{2+}][OH^-]^2$
$2.2 \times 10^{-20} = (x)(1 \times 10^{-7} + 2x)^2$
$2.2 \times 10^{-20} \approx (x)(1 \times 10^{-7})^2$
$x \approx 2.2 \times 10^{-6}$ M

$[OH^-] = 1 \times 10^{-7}\text{ M} + 2(2.2 \times 10^{-6}\text{ M}) \approx 1.0 \times 10^{-7}$ M

$[Cu^{2+}] = 2.2 \times 10^{-6}$ M; $[OH^-] = 1 \times 10^{-7}$ M

Selective Precipitation: - by using a chemical reagent with an anion that will form precipitates with metal ions in a solution, the salts of each of these metal ions can be separated because one will precipitate first.
- when two or more precipitates is likely to form, **the solid with the lowest anion concentration at its K_{sp} will precipitate first.**
- recall that **we can only use K_{sp} to compare solubilities if and only if the solids can produce the same number of ions**. Otherwise, we have to calculate the anion concentration needed of each salt individually.

Example 3: A chemical reagent consisting of $SO_4^{2-}{}_{(aq)}$ is slowly poured into a solution containing 3.00×10^{-3} mol/L of $Ag^+{}_{(aq)}$ and 1.50×10^{-4} mol/L of $Pb^{2+}{}_{(aq)}$. The K_{sp} values of Ag_2SO_4 and $PbSO_4$ are 1.2×10^{-5} and 1.3×10^{-8} respectively. Determine which of the above solids will precipitate first by calculating the $[SO_4^{2-}]$ require for each solid.

$$Ag_2SO_{4\,(s)} \rightleftharpoons 2\,Ag^+{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

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

$$1.2 \times 10^{-5} = (3.00 \times 10^{-3})^2[SO_4^{2-}]$$

$$[SO_4^{2-}] = \frac{1.2\times10^{-5}}{\left(3.00\times10^{-3}\right)^2}$$

$[SO_4^{2-}]$ = 1.3 M is needed for $Ag_2SO_{4\,(s)}$ to form

$$PbSO_{4\,(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

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

$$1.3 \times 10^{-8} = (1.50 \times 10^{-3})[SO_4^{2-}]$$

$$[SO_4^{2-}] = \frac{1.3\times10^{-8}}{1.50\times10^{-4}}$$

$[SO_4^{2-}]$ = 8.7×10^{-5} M is needed for $PbSO_{4\,(s)}$ to form

Since $[SO_4^{2-}]$ is less for $PbSO_{4\,(s)}$ to form, lead (II) sulfate will precipitate first as $SO_4^{2-}{}_{(aq)}$ is slowly added to the solution. $PbSO_4$ can then be separated leaving the $Ag^+{}_{(aq)}$ in the filtrate.

Assignment
16.8 pg. 742−744 #57 to 62, 97, 111

16.9: pH and Solubility

pH and Solubility: - when salts containing effective bases of weak acids (OH^-, S^{2-}, CO_3^{2-}, CH_3COO^-, and CrO_4^{2-}) are dissolved in acids, their solubilities increases.
- conversely, if these effective bases salts are dissolved in bases, their solubilities decreases.

Example: Calcium carbonate is dissolved in acidic solution.

(Solubility ↑) (equilibrium shifts →)

$$CaCO_{3\,(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \downarrow$$

(Because $H_3O^+{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow HCO_3^-{}_{(aq)} + H_2O_{(l)}$)

Example: Silver hydroxide is dissolved in basic solution.

(Solubility ↓) (equilibrium shifts ←)

$$AgOH_{(s)} \rightleftharpoons Ag^+{}_{(aq)} + OH^-{}_{(aq)}$$

(Because solvent is already basic)

Example 1: Determine the minimum concentration of ammonia needed to start the precipitation of $Mg(OH)_{2\,(s)}$ from a 0.00450 M of $MgCl_{2\,(aq)}$ solution. (K_b of $NH_{3\,(aq)} = 1.79 \times 10^{-5}$ and K_{sp} of $Mg(OH)_{2\,(s)} = 1.2 \times 10^{-11}$)

$MgCl_2$ is very soluble and completely dissociates in water.

$$\underset{0.00450\text{ M}}{MgCl_{2\,(s)}} \rightarrow \underset{\mathbf{0.00450\text{ M}}}{\mathbf{Mg^{2+}_{(aq)}}} + 2\,Cl^-_{(aq)}$$

$NH_{3\,(aq)}$ is a weak base and provides the $OH^-_{(aq)}$ (after the Brønsted-Lowry dissociation) for the formation of $Mg(OH)_{2\,(s)}$.

$$NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)} \qquad K_b = 1.79 \times 10^{-5}$$

$$Mg^{2+}_{(aq)} + 2\,OH^-_{(aq)} \rightarrow Mg(OH)_{2\,(s)}$$

After $Mg(OH)_{2\,(s)}$ precipitated, some of it would dissociate back into ions according to K_{sp}.

$$Mg(OH)_{2\,(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2\,OH^-_{(aq)} \qquad K_{sp} = 1.2 \times 10^{-11}$$

Hence, we need to calculate the $[OH^-]$ first from the K_{sp} of $Mg(OH)_{2\,(s)}$. Then, we can use this $[OH^-]$ to find the original $[NH_3]$ required to initiate this precipitation.

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$1.2 \times 10^{-11} = (0.00450)[OH^-]^2$$

$$[OH^-] = \sqrt{\frac{1.2\times10^{-11}}{(0.00450)}} = 5.163977795 \times 10^{-5}\text{ M}$$

$[OH^-] = 5.16 \times 10^{-5}$ M is needed for $Mg(OH)_{2\,(s)}$ to form.

Next, we can work backwards using the ICE box and K_b to find the $[NH_3]_0$.

$$NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

	$[NH_3]$		$[NH_4^+]$	$[OH^-]$
Initial	**x M**		**0 M**	**0 M**
Change	**$- 5.163977795 \times 10^{-5}$ M**		**$+ 5.163977795 \times 10^{-5}$ M**	**$+ 5.163977795 \times 10^{-5}$ M**
Equilibrium	**$(x - 5.163977795 \times 10^{-5})$**		**$5.163977795 \times 10^{-5}$ M**	**$5.163977795 \times 10^{-5}$ M**

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad 1.79 \times 10^{-5} = \frac{(5.163977795\times10^{-5})^2}{(x - 5.163977795\times10^{-5})}$$

$$1.79 \times 10^{-5}(x - 5.163977795 \times 10^{-5}) = 2.666666667 \times 10^{-9}$$

$$1.79 \times 10^{-5}x - 9.24352025 \times 10^{-10} = 2.666666667 \times 10^{-9}$$

$$1.79 \times 10^{-5}x = 2.666666667 \times 10^{-9} + 9.24352025 \times 10^{-10}$$

$$x = \frac{3.591018692\times10^{-9}}{1.79\times10^{-5}} = 2.006155694 \times 10^{-4}\text{ M}$$

Minimum $[NH_3]_0 = x = 2.00 \times 10^{-4}$ mol/L

Assignment

16.9 pg. 742 #63 to 68; pg. 745 #118

16.10: Complex Ion Equilibria and Solubility

Complex Ion: - metal ion that is surrounding by Lewis Base (species with electron lone-pairs to donate).
- the resulting bonds between the metal ion and these Lewis Bases are called **ligands**.

Coordination Number: - the number of ligands that is attached to the metal ion.

Metal Ions and Coordination Numbers

Coordination Number	Metal Ions	Complex Ion Geometry
2	Cu^+, Ag^+, and Au^+	Linear
4	Al^{3+}, Cu^+, Au^+, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Au^{3+}	Tetrahedral or Square Planar
6	Al^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sc^{3+}, Cr^{3+}, Pt^{3+} and Co^{3+}	Octahedral

Example 1: Write the net ionic equations of the following.

a. A silver nitrate solution is mixed with an ammonia solution.

Complete Dissociation of Silver Nitrate: $AgNO_{3\,(s)} \rightarrow Ag^+_{(aq)} + NO_3^-{}_{(aq)}$

Net Ionic Equation: $Ag^+_{(aq)} + 2\ NH_{3\,(aq)} \rightarrow Ag(NH_3)_2^+$ **(Ag^+ has coordinate number 2)**

b. A cobalt (II) chloride solution is mixed with concentrated hydrochloric acid.

Complete Dissociation of Cobalt (II) Chloride: $CoCl_{2\,(s)} \rightarrow Co^{2+}_{(aq)} + 2\ Cl^-_{(aq)}$

Hydrochloric Acid is a Strong Acid: $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Net Ionic Equation(s): (Co^{2+} has coordinate numbers 4 or 6)

$$Co^{2+}_{(aq)} + 4\ Cl^-_{(aq)}\ (\text{or } 6\ Cl^-_{(aq)}) \rightarrow CoCl_4^{2-}\ (\text{or } CoCl_6^{4-})$$
$$Co^{2+}_{(aq)} + 4\ H_2O_{(l)}\ (\text{or } 6\ H_2O_{(l)}) \rightarrow Co(H_2O)_4^{2+}\ (\text{or } Co(H_2O)_6^{2+})$$

Naming Complex Ions: - when naming a complex ion, first give the name(s) of the ligand(s), in alphabetical order, followed by the name of the metal.

Ligand (Lewis Base)	Name of Ligands	Metal Ions	Metal Name for Complex *Anion*
Water (H_2O)	Aqua	Iron (Fe)	Ferrate
Ammonia (NH_3)	Ammine	Copper (Cu)	Cuprate
Methylamine (CH_3NH_2)	Methylamine	Lead (Pb)	Plumbate
Carbon Monoxide (CO)	Carbonyl	Silver (Ag)	Argentate
Nitrogen Monoxide (NO)	Nitrosyl	Gold (Au)	Aurate
Hydroxide (OH^-)	Hydroxo	Tin (Sn)	Stannate
Cyanide (CN^-)	Cyano	Platinum (Pt)	Platinate
Thiocyanide (SCN^-)	Thiocyano	Cobalt (Co)	Cobaltate
Fluoride (F^-)	Fluoro	Aluminium (Al)	Aluminiate
Chloride (Cl^-)	Chloro	Zinc (Zn)	Zincate
Bromide (Br^-)	Bromo	Nickel (Ni)	Nickelate
Iodide (I^-)	Iodo	Chromium (Cr)	Chrominate
Sulfate (SO_4^{2-})	Sulfato	Scandium (Sc)	Scandiate
Sulfite (SO_3^{2-})	Sulfito	Cadmium (Cd)	Cadminate
Nitrate (NO_3^-)	Nitrato		
Nitrite (NO_3^-)	Nitrito		

***Special Notes on Naming Complex Ions*:**

- If a ligand is an anion whose name ends in ***-ite*** or ***-ate***, the **final *e*** is changed to ***o***.
(**Example**: change sulf***ate*** to sulfat***o*** and change nitr***ite*** to nitrit***o***)
- If the ligand is an anion whose name ends in ***-ide***, the ***entire suffix ending*** is changed to ***o***.
(**Example**. change chlor***ide*** to chlor***o*** and cyan***ide*** to cyan***o***)
- If the ligand is a neutral molecule, its common name is used. The important exceptions to this, however, are that ***water (H_2O) is called aqua***, ***ammonia (NH_3) is called ammine***, and ***carbon mononxide (CO) is called carbonyl***.
- When there is ***more than one of a particular ligand***, the number of ligands is designated by the appropriate ***Greek prefix: di-, tri-, tetra-, penta-, hexa-, hepta-, etc***.
- If the ***complex ion is an anion***, the **suffix *-ate* is added to the metal name**. The Latin name is often used for the metal in this case. For example, ferro rather than iron and cupro rather than copper.
- Following the name of the metal, the ***oxidation number or original charge of the metal*** is given using ***Roman Numerals***.

Examples: $Fe(CN)_6^{3-}$ - hexacyanoferrate (III)
$Al(H_2O)_6^{3+}$ - hexaaquaaluminium (III)
$Pt[(SO_4)_5Cl]^{3+}$ - pentasulfatochloroplatinum (III)
$CoCl_4^{2-}$ - tetrachlorocobaltate (II)
$Ni(SCN)_6^{4-}$ - hexathiocyanonickelate (II)
$Zn[(NO_2)_2(H_2O)_2]$ diaquadinitritozincate (II)

Formation Constants (*K*): - the equilibrium constant of the formation of complex ions from the metal ions and their Lewis bases.
- also refer to as **Stability Constants**.
- for a particular coordination number of a complex ion, there are equal number of formation constants.
- the values of most formation constants are relatively large ($K_n >> 1$). Therefore, we can **assume the formation of complex ions goes to completion**.

$$M^{n+}_{(aq)} + LB_{(aq)} \rightleftharpoons M(LB)^{n+}_{(aq)} \qquad K_1 = \frac{[M(LB)^{n+}]}{[M^{n+}][LB]}$$

$$M(LB)^{n+}_{(aq)} + LB_{(aq)} \rightleftharpoons M(LB)_2^{n+}_{(aq)} \qquad K_2 = \frac{[M(LB)_2^{n+}]}{[M(LB)^{n+}][LB]}$$

$$M^{n+}_{(aq)} + 2\,LB_{(aq)} \rightleftharpoons M(LB)_2^{n+}_{(aq)} \qquad K = \frac{[M(LB)_2^{n+}]}{[M^{n+}][LB]^2} = K_1 \times K_2 = \frac{\cancel{[M(LB)^{n+}]}}{[M^{n+}][LB]} \times \frac{[M(LB)_2^{n+}]}{\cancel{[M(LB)^{n+}]}[LB]}$$

Overall Formation Constant

$$M^{n+}_{(aq)} + x\,LB_{(aq)} \rightleftharpoons M(LB)_x^{n+}_{(aq)}$$

$$K = K_1 \times K_2 \times K_3 \times \ldots \times K_x$$

Example 2: Write the stepwise formation equilibrium equations for $Fe(SCN)_2^+{}_{(aq)}$ and calculate its overall formation constant given that $K_1 = 890$ and $K_2 = 2.6$. Determine the final concentrations of Fe^{3+}, $Fe(SCN)^{2+}$, and $Fe(SCN)_2^+$ when 200 mL of 0.0500 M of $Fe(NO)_{3\,(aq)}$ is reacted with 150 mL of 0.600 M of $NaSCN_{(aq)}$.

Both $Fe(NO)_3$ and NaSCN dissociates completely in water.

$Fe(NO_3)_{3\,(aq)} \rightarrow Fe^{3+}{}_{(aq)} + 3\,NO_3^-{}_{(aq)}$ $NaSCN_{(aq)} \rightarrow Na^+{}_{(aq)} + SCN^-{}_{(aq)}$

$$Fe^{3+}{}_{(aq)} + SCN^-{}_{(aq)} \rightleftharpoons Fe(SCN)^{2+}{}_{(aq)} \qquad K_1 = 890$$

$$Fe(SCN)^{2+}{}_{(aq)} + SCN^-{}_{(aq)} \rightleftharpoons Fe(SCN)_2^+{}_{(aq)} \qquad K_2 = 2.6$$

$$K = K_1 \times K_2 = 890 \times 2.6$$

$$Fe^{3+}{}_{(aq)} + 2\,SCN^-{}_{(aq)} \rightleftharpoons Fe(SCN)_2^+{}_{(aq)} \qquad K = 2314$$

$Fe(NO_3)_{3\,(aq)} \rightarrow Fe^{3+}{}_{(aq)} + 3\,NO_3^-{}_{(aq)}$

$n_{Fe(NO_3)_3} = (0.0500\ \text{mol/L})(200\ \text{mL})$ $n_{Fe^{3+}} = 10.0$ mmol

$n_{Fe(NO_3)_3} = 10.0$ mmol $[Fe^{3+}]_0 = \dfrac{10.0\ \text{mmol}}{350\ \text{mL}} = 0.0285714286$ M

$NaSCN_{(aq)} \rightarrow Na^+{}_{(aq)} + SCN^-{}_{(aq)}$

$n_{NaSCN} = (0.600\ \text{mol/L})(150\ \text{mL})$ $n_{SCN^-} = 90.0$ mmol

$n_{NaSCN} = 90.0$ mmol $[SCN^-]_0 = \dfrac{90.0\ \text{mmol}}{350\ \text{mL}} = 0.257142857$ M

	$Fe^{3+}{}_{(aq)}$ +	$2\,SCN^-{}_{(aq)}$ →	$Fe(SCN)_2^+{}_{(aq)}$
	$[Fe^{3+}]$	**$[SCN^-]$**	**$[Fe(SCN)_2^+]$**
Before	0.0285714286 M (LR)	0.257142857 M	0
Change	− 0.0285714286 M	0.257142857 M −2(0.0285714286 M)	+ 0.0285714286 M
After	**≈ 0 M**	**≈ 0.200 M**	**≈ 0.0285714286 M**

Using the equilibrium expression for the second dissociation and K_2, we can find $[Fe(SCN)^{2+}]$.

$$K_2 = \frac{[Fe(SCN)_2^+]}{[Fe(SCN)^{2+}][SCN^-]}$$

$$2.6 = \frac{(0.0285714286)}{[Fe(SCN)^{2+}](0.200)}$$

$$[Fe(SCN)^{2+}] = \frac{(0.0285714286)}{(2.6)(0.200)} = 0.054945055\ \text{M}$$

$[Fe^{3+}] \approx 0$ M
$[Fe(SCN)^{2+}] = 0.055$ M
$[Fe(SCN)_2^+] = 0.0286$ M

Complex Ion and Solubility: - solubility of insoluble salts can be **"re-dissolved"** when mixed with sufficient Lewis base.

Example 3: A NaOH solution is added to $Ni(NO_3)_{2\,(aq)}$ and a precipitate forms ($K_{sp} = 1.6 \times 10^{-16}$). Addition of 6.00 M of $NH_{3\,(aq)}$ re-dissolved the precipitate into a complex ion with 6 as its coordination number.

a. Identify the precipitate and the resulting complex ion.

b. Calculate the solubility of the precipitate in $NH_{3\,(aq)}$ if the overall formation constant is 5.5×10^8. Neglect the volume of the NaOH and $Ni(NO_3)_2$ solutions.

a. Both $Ni(NO_3)_2$ and NaOH dissociates completely in water.

$$Ni(NO_3)_{2\,(aq)} \rightarrow Ni^{2+}_{(aq)} + 2\,NO_3^-{}_{(aq)} \qquad NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$Ni^{2+}_{(aq)} + 2\,OH^-_{(aq)} \rightarrow Ni(OH)_{2\,(s)}$$

Precipitate is $Ni(OH)_2$

b. We need to calculate the overall formation constant for the complex ion from $Ni(OH)_{2\,(s)}$.

$$Ni(OH)_{2\,(s)} \rightleftharpoons Ni^{2+}_{(aq)} + 2\,OH^-_{(aq)} \qquad K_{sp} = 1.6 \times 10^{-16}$$

$$Ni^{2+}_{(aq)} + 6\,NH_{3\,(aq)} \rightleftharpoons Ni(NH_3)_6^{2+}{}_{(aq)} \qquad K_{formation} = 5.5 \times 10^8$$

$$Ni(OH)_{2\,(s)} + 6\,NH_{3\,(aq)} \rightleftharpoons Ni(NH_3)_6^{2+}{}_{(aq)} + 2\,OH^-_{(aq)} \qquad K = K_{sp} \times K_{formation} = 8.8 \times 10^{-8}$$

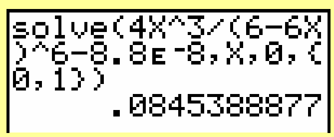
	$[Ni(OH)_2]$	$[NH_3]$		$[Ni(NH_3)_6^{2+}]$	$[OH^-]$
Initial	----	**6.00 M**		**0 M**	≈ 0 M
Change	----	**– 6*x***		+*x*	**+ 2*x***
Equilibrium	----	**6 – 6*x***		*x*	**≈ 2*x***

We can assume $[OH]_0 \approx 0$ M because of the small value of K_{sp}

$$K = \frac{[Ni(NH_3)_6^{2+}][OH^-]^2}{[NH_3]^6}$$

$$8.8 \times 10^{-8} = \frac{(x)(2x)^2}{(6-6x)^6} = \frac{4x^3}{(6-6x)^6}$$

$x = 0.085$



Solubility of $Ni(OH)_2$ in 6.00 M of $NH_{3\,(aq)}$ = 0.085 M

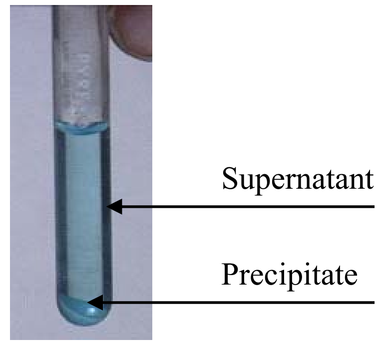
Assignment
16.10 pg. 742–743 #69 to 76, 89, 91, 98

16.10: Application of the Solubility Product to Qualitative Analysis

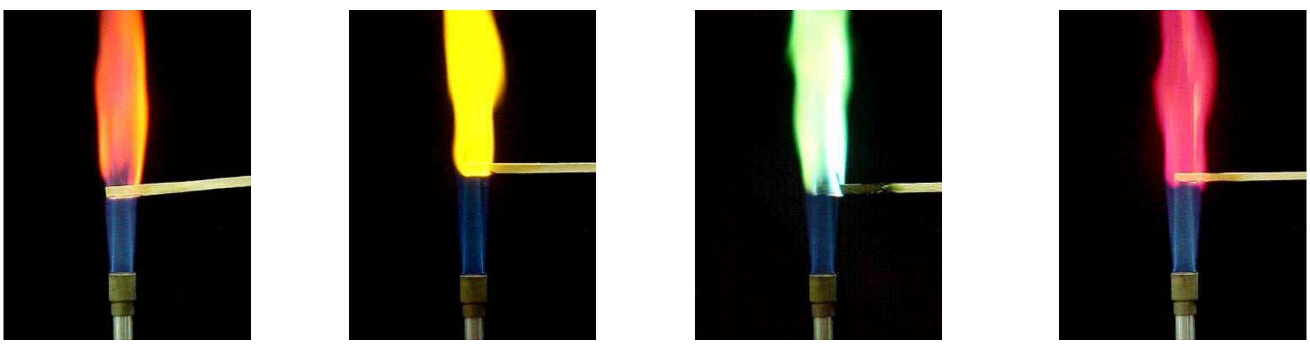
Centrifuge: - a device that speeds up the precipitation process by the use of centrifugal force (spinning the test tubes really fast).

Supernatant: - the liquid that remained after the precipitate is collected at the bottom of a test tube from the centrifuge process.

A typical laboratory centrifuge. Test tubes are placed inside the wells and the spinning will pull the precipitate down to the bottom.



Flame Test: - a test performed on a salt to detect the identity of a metal ion by the colour of the flame emitted as it is placed over a lighted Bunsen-burner.
- the principle of a metal ion emitting a certain visible colour is due to the electrons are excited to jump into higher orbitals as it is placed in a flame. As they come down to the lower orbital, a unique frequency is given in the visible spectrum producing a specific colour.



From left to right: LiCl, NaCl, $CuCl_2$, and $SrCl_2$ produce different colors during the flame tests

Qualitative Analysis: - testing for the identities of metal ions by using selective precipitation or flame tests.
- usually both tests are used to identify the exact metal ions in the solution.

Developing a Qualitative Analysis Scheme for Cations:

1. **HCl is used to precipitate with Pb^{2+}, Hg^+, Ag^+, Tl^+, and Cu^+** because their K_{sp} with Cl^- are small.
2. **Sulfide ion (S^{2-}) in acidic solution such as $H_2S_{(aq)}$ is commonly used to precipitate out the most insoluble salts such as (HgS, CuS, CdS, Bi_2S_3, As_2S_3, Sb_2S_3, and SnS_2).** At low pH (high $[H^+]$), the concentration of S^{2-} is small. ($H_2S_{(aq)} \rightleftharpoons H^+_{(aq)} + HS^-_{(aq)}$ and $HS^-_{(aq)} \rightleftharpoons H^+_{(aq)} + S^{2-}_{(aq)}$) Therefore, metal-sulfide salts with higher K_{sp} values will remain in the solution as metal ions.

3. **Increasing the pH by adding NaOH will make the metal-sulfide salts with higher K_{sp} values to precipitate out (Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, and Cr^{3+}).** This is because a decrease in the $[H^+]$ will drive both acid dissociation reactions forward, increasing the $[S^{2-}]$.
4. Finally, **CO_3^{2-} is added to precipitate the alkaline-earth ions such as Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}.**
5. **At each stage of the analysis, the residual (precipitate) can be filtered out and be subject to a flame test** for more accurate identification. Since alkali-metal ions are soluble with all anions, we will run a flame test on the filtrate or supernatant from step 4 to determine the identity of the remaining metal ions.

A Common Qualitative Analysis Scheme for most Metal Ions

Group Number	Solution Tested	Precipitating Reagent	Solids Precipitated	Metal Ions Detected	Flame Tests
1	Unknown	0.1 M HCl	$PbCl_2$, Hg_2Cl_2, AgCl, TlCl, and CuCl	Pb^{2+}, Hg^+, Ag^+, Tl^+, and Cu^+	Pb^{2+} - light blue; Hg^+ - white; Ag^+ - gray; Tl^+ - green; Cu^+ - blue green
2	Filtrate or Supernatant from Group 1	H_2S at pH 1	HgS, CuS, CdS, Bi_2S_3, As_2S_3, Sb_2S_3, SnS_2	Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, As^{3+}, Sb^{3+}, and Sn^{4+}	Hg^{2+} - white; Cu^{2+} - blue green; Cd^{2+} - colourless; As^{3+} - light blue; Bi^{3+} - yellow brownish; Sb^{3+} - green; Sn^{4+} - colourless
3	Filtrate or Supernatant from Group 2	NaOH at pH 10	MnS, FeS, NiS, CoS, ZnS, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$	Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, and Cr^{3+}	Mn^{2+} - violet; Fe^{2+} & Fe^{3+} - yellow brownish red; Ni^{2+} - brown; Co^{2+} - blue; Zn^{2+} - whitish green; Al^{3+} - colourless; Cr^{3+} - green
4	Filtrate or Supernatant from Group 3	Na_2CO_3 at pH 10	$MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$	Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}	Mg^{2+} - white; Ca^{2+} - yellowish red; Sr^{2+} - scarlet red; Ba^{2+} - yellow green
5	Filtrate or Supernatant from Group 4	None	Soluble Ions	Li, Na^+, K^+, and NH_4^+	Li^+ - red; Na^+ - yellow; K^+ - violet; NH_4^+ - green

Assignment
16.10 pg. 743 #77, 79 to 82

