COMMON ION EFFECT

- Common ion effect is the shift in equilibrium caused by the addition of an ion that takes part in the equilibrium.

- For example, consider the effect of adding HCl to a solution of acetic acid. Since HCl is a strong acid, it ionizes completely to produce H_3O^+, which then suppresses the ionization of the acetic acid due to Le Chatelier's principle:

$$HCl\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)$$

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

- The net result of adding HCl to a solution of acetic acid is to decrease the degree of ionization. This decrease can be quantified as shown below:

Examples:

1. Calculate the degree of ionization of benzoic acid, $HC_7H_5O_2$ in a 0.15 M solution to which sufficient HCl is added to make it 0.010 M. Compare the degree of ionization to that of 0.15 M benzoic acid with no HCl added (K_a of benzoic acid = 6.3×10^{-5})

Calculate the degree of ionization of benzoic acid ($HC_7H_5O_2$) with no HCl added:

	$HC_7H_5O_2$ (aq) +	H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	$C_7H_5O_2^-$ (aq)
Initial	0.15	----	0	0
Δ	–x	----	+x	+x
Equilibrium	0.15–x	-----	x	x

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = \frac{x^2}{0.15-x} \approx \frac{x^2}{0.15} = 6.3 \times 10^{-5}$$

$$x = [C_7H_5O_2^-] = 3.\underline{0}7 \times 10^{-3}$$

$$\text{Degree of Ionization \%} = \frac{[C_7H_5O_2^-]}{[HC_7H_5O_2]} \times 100 = \frac{3.\underline{0}7 \times 10^{-3}}{0.15} \times 100 = \mathbf{2.0\%}$$

Examples (cont'd):

Calculate the degree of ionization of benzoic acid ($HC_7H_5O_2$) with HCl added (0.010 M):

	$HC_7H_5O_2$ (aq) +	H_2O (l) $\rightleftharpoons$	H_3O^+(aq) +	$C_7H_5O_2^-$ (aq)
Initial	0.15	----	**0.010**	0
Δ	–x	----	+x	+x
Equilibrium	0.15–x	-----	x	x

$$K_a = \frac{[H_3O^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = \frac{(0.010 + x)\,x}{0.15 - x}$$

Assumptions: $0.010 + x \approx 0.010$ $0.15 - x \approx 0.15$

$$K_a = \frac{0.010\,x}{0.15} = 6.3\text{x}10^{-5} \qquad x = [C_7H_5O_2^-] = 9.\underline{4}5 \text{ x } 10^{-4}$$

$$\text{Degree of Ionization} = \frac{[C_7H_5O_2^-]}{[HC_7H_5O_2]} \text{ x } 100 = \frac{9.\underline{4}5 \text{ x } 10^{-4}\text{ M}}{0.15\text{ M}} \text{ x } 100 = \mathbf{0.63\ \%}$$

NOTE: **0.63 %** <<<<<<< **2.0%**
(with HCl) (without HCl)

2. Calculate the pH of a 0.10 M solution of hydrofluoric acid (HF) to which sufficient NaF is added to make the concentration of NaF 0.20 M. (K_a of HF = 6.8 x 10^{-4})

BUFFERS

- Buffers are solutions that have the ability to resist changes in pH when limited amounts of acid or bases are added to it.

- What does a buffer do? Consider the solution below:

Solution	**1 L pure water** pH = 7.00	**1L buffered solution** pH = 9.43
Addition	0.01 mol HCl pH changes to 2.00	0.01 mol HCl pH changes to 9.33
Change in pH	7.00–2.00 = **5.00**	9.43–9.33 = **0.10**

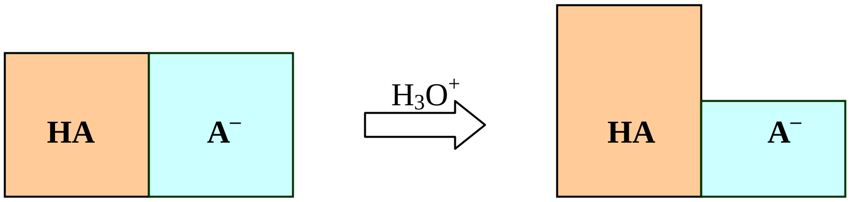
- Types of buffer solutions: There are two types of buffer solutions:

  1. Solution of a weak acid and its conjugate base ($HC_2H_3O_2$ and $NaC_2H_3O_2$)
  2. Solution of a weak base and its conjugate acid (NH_3 and NH_4Cl)

- How do buffers function?

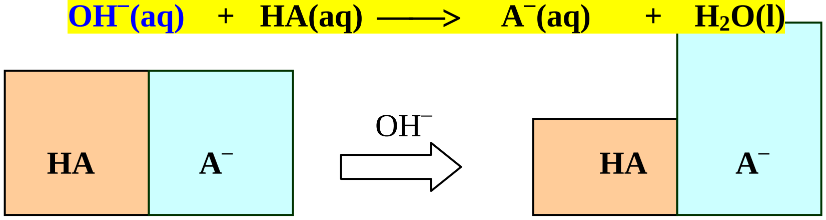
Type 1:

$$H_3O^+(aq) + A^-(aq) \longrightarrow HA(aq) + H_2O(l)$$



Results: ➢ H_3O^+ is used up ➢ little change in pH

$$OH^-(aq) + HA(aq) \longrightarrow A^-(aq) + H_2O(l)$$

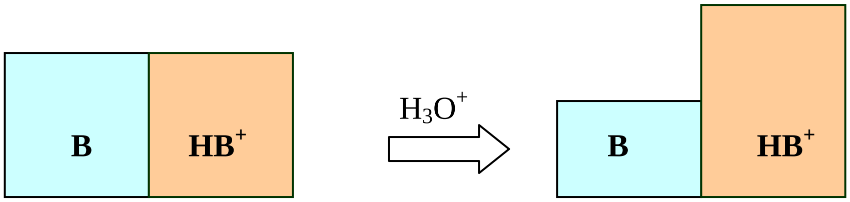


Results: ➢ OH^- is used up ➢ little change in pH

BUFFERS

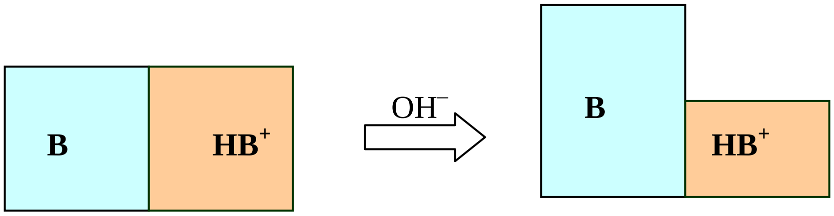
Type 2:

$$H_3O^+(aq) + B(aq) \longrightarrow HB^+(aq) + H_2O(l)$$



Results: ➢ H_3O^+ is used up ➢ little change in pH

$$OH^-(aq) + HB^+(aq) \longrightarrow B(aq) + H_2O(l)$$



Results: ➢ OH^- is used up ➢ little change in pH

SUMMARY:

- ➢ Buffers resist pH change.
- ➢ A buffer contains significant amounts of either 1) a weak acid and its conjugate base, or 2) a weak base and its conjugate acid.
- ➢ The weak acid neutralizes added base.
- ➢ The base neutralizes added acid.

Examples:

1. Which solution is a buffer?

   a) a solution that is 0.100 M HNO_2 and 0.100 M HCl

   b) a solution that is 0.100 M HNO_3 and 0.100 M $NaNO_3$

   c) a solution that is 0.100 M HNO_2 and 0.100 M NaCl

   d) a solution that is 0.100 M HNO_2 and 0.100 M $NaNO_2$

CALCULATING pH OF BUFFER SOLUTIONS

- pH of buffer of solutions can be calculated similar to the calculations done for common ions problems. Examples below demonstrated these calculations.

Examples:

1. A buffer solution is prepared to be 0.10 M acetic acid ($HC_2H_3O_2$) and 0.20 M sodium acetate ($NaC_2H_3O_2$). What is the pH of this buffer system at 25°C (K_a of acetic acid = 1.7×10^{-5})

	$HC_2H_3O_2\,(aq)$ +	$H_2O\,(l)$ $\rightleftharpoons$	$H_3O^+(aq)$ +	$C_2H_3O_2^-\,(aq)$
Initial	0.10	----	0	0.20
Δ	–x	----	+x	+x
Equilibrium	0.10–x	-----	x	0.20 + x

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x\,(0.20 + x)}{(0.10 - x)} \approx \frac{0.20\,x}{0.10} = 1.7 \times 10^{-5}$$

$x = [H_3O^+] = 8.5 \times 10^{-6}$ $\qquad$ $pH = -\log(8.5 \times 10^{-6}) = \mathbf{5.07}$

2. Calculate the pH of a buffer that is 1.00 M in NH_3 and 0.80 M in NH_4Cl. (K_b for NH_3 = 1.8×10^{-5})

Initial				
Δ				
Equilibrium				

HENDERSON – HASSELBALCH EQUATION

- In order to simplify the calculations for pH of buffer solutions, an equation can be derived that relates pH of the solution to the initial concentration of the buffer components.

- Consider a buffer containing the weak acid HA and its conjugate base A^-:

$$HA(aq) \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+(aq) \quad + \quad A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \text{rearranging,} \qquad [H_3O^+] = K_a\,\frac{[HA]}{[A^-]}$$

- Although [HA] and $[A^-]$ in the equation above are equilibrium concentrations, when ionization of the acid is small (x compared to the initial concentration), these can be nearly identical to the initial concentrations of HA and A^-.

- Therefore, the H_3O^+ concentration for a buffer solution can be calculated by multiplying the K_a with the ratio of the weak acid and the conjugate base.

- Note that when the concentrations of the weak acid (HA) and the conjugate base (A^-) are equal, $[H_3O^+]$ becomes equal to the K_a:

$$[H_3O^+] = K_a\,\frac{[HA]}{[A^-]} \qquad \text{if} \quad [HA] = [A^-], \quad \text{then} \quad [H_3O^+] = K_a$$

- Taking negative logs of both sides of the equation above:

$$\underset{\substack{\Big\downarrow \\ \text{pH}}}{-\log\,[H_3O^+]} = -\log\left[K_a \times \frac{[HA]}{[A^-]}\right] = \underset{\substack{\Big\downarrow \\ \text{p}K_a}}{-\log K_a} \; -\log\,\frac{[HA]}{[A^-]}$$

$$\boxed{\textbf{pH} = \textbf{p}K_a + \textbf{log}\,\frac{[A^-]}{[HA]}} \qquad\qquad \boxed{\textbf{pH} = \textbf{p}K_a + \textbf{log}\,\frac{[\text{base}]}{[\text{acid}]}}$$

Henderson-Hasselbalch Equation

HENDERSON – HASSELBALCH EQUATION

- The Henderson-Hasselbalch Equation can be used for both type of buffers.
- To prepare a buffer with a specific pH:
  - A weak acid and its conjugate base must be found for which the pK_a of the weak acid is close to the desired pH.
  - The pH value is fine-tuned using the acid-base ratio

Examples:

1. A buffer with a pH of 4.90 is desired. Would acetic acid/acetate be a suitable buffer system?

   $K_a(HC_2H_3O_2) = 1.8 \times 10^{-5}$

   $pK_a = -\log(1.8 \times 10^{-5}) = \mathbf{4.74}$

   This is relatively close to the desired pH (**4.74** versus **4.90**). The pH may be increased by increasing the ratio: $\dfrac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$

2. Calculate the pH of a buffer containing 0.10 M NH_3 and 0.2 M NH_4^+. (K_b for $NH_3 = 1.8 \times 10^{-5}$)

3. A buffer contains the weak acid HA and its conjugate base A^-. The weak acid has a pKa of 4.82 and the buffer has a pH of 4.25.

   a) Which statement below is correct?

   $[HA] > [A^-]$ $[HA] < [A^-]$ $[HA] = [A^-]$

   b) Which buffer component would you add to change the pH of the buffer to 4.72?

ADDITION OF ACID OR BASE TO A BUFFER

- Addition of acid or base to a buffer will cause a slight change in pH. This change in pH can be calculated by breaking the problem into two parts:

  1. ***Stoichiometry calculation*** to calculate the changes in relative amounts of acid and conjugate base after the addition.

  2. ***Equilibrium calculation*** to calculate the pH based on the new amounts of acid and conjugate base.

Examples:

1. A 1.0 L buffer solution contains 0.100 mol of $HC_2H_3O_2$ ($K_a = 1.8\text{x}10^{-5}$) and 0.100 mol of $NaC_2H_3O_2$. Calculate the pH of this buffer solution before and after addition of 0.010 mol of solid NaOH. (Assume no volume change occurs after addition of base)

Calculate the pH of the buffer solution before addition of NaOH:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = 4.74 + \log \frac{0.100}{0.100} = 4.74$$

Calculate the pH of the buffer solution after addition of 0.010 mol NaOH:

Stoichiometry calculation:

	OH^- +	$HC_2H_3O_2$ $\longrightarrow$	$C_2H_3O_2^-$ +	H_2O
Initial	0.010 mol	0.100 mol	0.100 mol	-----
Δ	–0.010 mol	–0.010 mol	+0.010 mol	-----
End	**0.00**	**0.090 mol**	**0.110 mol**	------

pH calculation:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = 4.74 + \log \frac{0.110}{0.090} = 4.83$$

ADDITION OF ACID OR BASE TO A BUFFER

Examples (cont'd):

2. Calculate the pH of the solution in example 1 after addition of 2.5 mL of 1.00 M HCl to 275 mL of the original buffer.

Step 1: Calculate the mmol of the species involved before addition:

$$\text{mmol HCl} = 2.5\ \text{mL} \times \frac{1.00\ \text{mol}}{1\ \text{L}} = 2.5\ \text{mmol}$$

$$\text{mmol } HC_2H_3O_2 = 275\ \text{mL} \times \frac{0.100\ \text{mol}}{1\ \text{L}} = 27.5\ \text{mmol}$$

$$\text{mmol } C_2H_3O_2^- = 275\ \text{mL} \times \frac{0.100\ \text{mol}}{1\ \text{L}} = 27.5\ \text{mmol}$$

Step 2: Calculate the mmol of the species involved after addition:

All of the H_3O^+ reacts with the $C_2H_3O_2^-$ ion:

	H_3O^+ +	$C_2H_3O_2^-$ $\longrightarrow$	$HC_2H_3O_2$	+ H_2O
Initial	2.5 mmol	27.5 mmol	27.5 mmol	-----
Change (Δ)	–2.5 mmol	–2.5 mmol	+2.5 mmol	-----
End	**0**	**25.0 mmol**	**30.0 mmol**	------

Step 3: Calculate the initial concentrations of the species involved before equilibrium:

Total Volume of Solution = 275 mL buffer + 2.5 mL HCl = $27\underline{7}.5$ mL

$$[HC_2H_3O_2] = \frac{30.0\ \text{mmol}}{27\underline{7}.5\ \text{mL}} = 0.108\ \text{M} \qquad [C_2H_3O_2^-] = \frac{25.0\ \text{mmol}}{27\underline{7}.5\ \text{mL}} = 0.0901\ \text{M}$$

Step 4 : Calculate pH:

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]} = 4.74 + \log\frac{0.0901}{0.108} = 4.66$$

BUFFER EFFECTIVENESS

- A buffer is most effective (most resistant to pH change) when the concentration of acid and the conjugate base are nearly equal. For example, consider two buffers composed of HA and A^- with $pK_a = 5.00$, but differing acid to conjugate base ratios shown below:

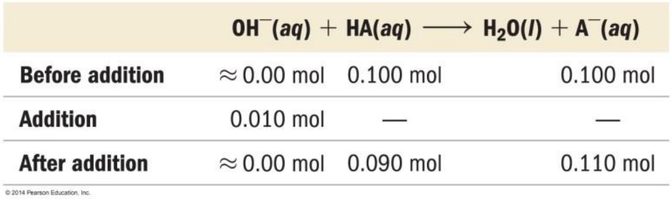
$$\text{Buffer A} \quad \frac{[A^-]}{[HA]} = \frac{0.10\text{ M}}{0.10\text{ M}} = 1$$

$$\text{Buffer B} \quad \frac{[A^-]}{[HA]} = \frac{0.02\text{ M}}{0.18\text{ M}} = 0.1$$

- If 0.010 mol NaOH is added to each of the above buffers, what would be the percent change in pH of each buffer? The initial pH of each buffer can be calculated using the Henderson–Hasselbalch equation, and determined as 5.00 for buffer A and 4.05 for buffer B.

- The change in pH of each buffer after addition of NaOH is shown below:

<u>Buffer A:</u>



	$OH^-(aq)$ +	$HA(aq)$ $\longrightarrow$	$H_2O(l)$ +	$A^-(aq)$
Before addition	≈ 0.00 mol	0.100 mol		0.100 mol
Addition	0.010 mol	—		—
After addition	≈ 0.00 mol	0.090 mol		0.110 mol

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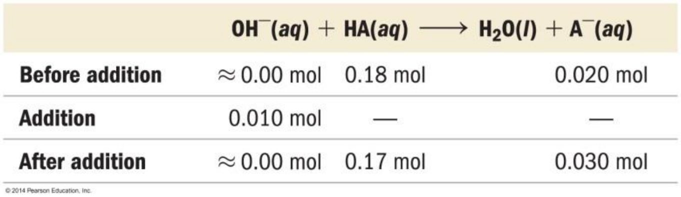
$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$= 5.00 + \log \frac{0.110}{0.090} = 5.09$$

$$\%\text{ change} = \frac{5.09\text{-}5.00}{5.00} \text{x}100 = 1.8\%$$

<u>Buffer B:</u>



	$OH^-(aq)$ +	$HA(aq)$ $\longrightarrow$	$H_2O(l)$ +	$A^-(aq)$
Before addition	≈ 0.00 mol	0.18 mol		0.020 mol
Addition	0.010 mol	—		—
After addition	≈ 0.00 mol	0.17 mol		0.030 mol

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

$$= 5.00 + \log \frac{0.030}{0.17} = 4.25$$

$$\%\text{ change} = \frac{4.25\text{-}4.05}{4.05} \text{x}100 = 5.0\%$$

- A buffer becomes less effective as the difference in relative amounts of acid and conjugate base increases. In order for a buffer to be reasonably effective, the relative concentrations of acid and conjugate base should not differ by a factor of more than 10.

BUFFER EFFECTIVENESS

- Buffer effectiveness is also affected by the absolute concentrations of the acid and conjugate base. For example, consider two buffers composed of HA and A^- with $pK_a = 5.00$, with same conjugate base to acid ration, but differing absolute concentrations shown below:

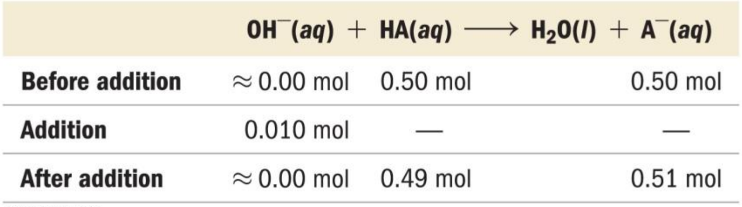
$$\text{Buffer A} \quad \frac{[A^-]}{[HA]} = \frac{0.50\ M}{0.50\ M} = 1$$

$$\text{Buffer B} \quad \frac{[A^-]}{[HA]} = \frac{0.050\ M}{0.050\ M} = 1$$

- If 0.020 mol NaOH is added to each of the above buffers, what would be the percent change in pH of each buffer? Because both solutions have equal concentrations of the acid and conjugate base, they both have initial pH of 5.00.

- The change in pH of each buffer after addition of NaOH is shown below:

Buffer A:



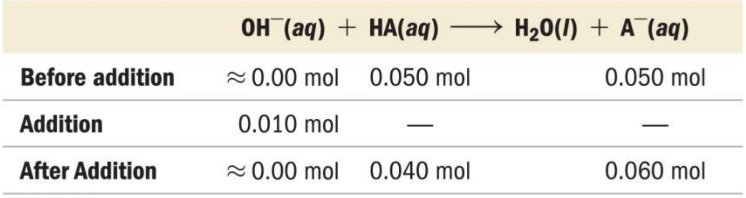
	$OH^-(aq)$	$+\ HA(aq)$	$\longrightarrow H_2O(l)$	$+\ A^-(aq)$
Before addition	≈ 0.00 mol	0.50 mol		0.50 mol
Addition	0.010 mol	—		—
After addition	≈ 0.00 mol	0.49 mol		0.51 mol

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

$$= 5.00 + \log \frac{0.51}{0.49} = 5.02$$

$$\%\ \text{change} = \frac{5.02\text{-}5.00}{5.00} x100 = 0.4\%$$

Buffer B:



	$OH^-(aq)$	$+\ HA(aq)$	$\longrightarrow H_2O(l)$	$+\ A^-(aq)$
Before addition	≈ 0.00 mol	0.050 mol		0.050 mol
Addition	0.010 mol	—		—
After Addition	≈ 0.00 mol	0.040 mol		0.060 mol

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

$$= 5.00 + \log \frac{0.060}{0.040} = 5.18$$

$$\%\ \text{change} = \frac{5.18\text{-}5.00}{5.00} x100 = 3.6\%$$

- A buffer becomes with greater amount of acid and conjugate base is more resistant to pH changes and therefore the more effective buffer. The more dilute the buffer components, the less effective the buffer.

BUFFER RANGE

- Earlier it was stated that for a buffer to be effective, the relative concentrations of the acid and conjugate base should not differ by more than a factor of 10.

- Using the Henderson-Hasselbalch, we can calculate the pH range over which a particular acid and its conjugate base can make an effective buffer. The outermost points of the effective buffer range can be calculated as follows:

  Lowest pH $\text{pH} = \text{pKa} + \log \frac{[\text{base}]}{[\text{acid}]} = \text{pKa} + \log 0.1 = \text{pKa} - 1$

  Highest pH $\text{pH} = \text{pKa} + \log \frac{[\text{base}]}{[\text{acid}]} = \text{pKa} + \log 10 = \text{pKa} + 1$

- The effective range for a buffering system is one pH unit on either side of the pKa. For example, a weak acid with a pKa of 5.0 (and its conjugate base) can be used to prepare a buffer in the range of 4.0-6.0. The relative amounts of the acid and conjugate base can be used to prepare any pH within this range.

<u>Examples:</u>

1. Which acid, from the list below, would you choose to create a buffer with a pH of 7.35. What mass of the corresponding sodium salt would you need to add to 500.0 mL of 0.10 M acid solution to prepare this buffer?

$HClO_2$	pKa = 1.95	$HCHO_2$	pKa = 3.74
HNO_2	pKa = 3.34	HClO	pKa = 7.54

2. Which solution is the most effective buffer?

   a) A solution prepared by mixing 150 mL of 0.10 M HCl and 150 mL of 0.1M NaCl.

   b) A solution prepared by mixing 100 mL of 0.10 M HF and 200 mL of 0.1M NaF.

   c) A solution prepared by mixing 150 mL of 0.10 M HF and 150 mL of 0.1M NaF.

   d) A solution prepared by mixing 200 mL of 0.10 M HF and 100 mL of 0.1M NaF.

PREPARATION OF BUFFER SOLUTIONS

- Buffer solutions can be prepared by a variety of methods in the laboratory. Shown next are several examples with different methods of preparation.

- The general method outlined below can be used to calculate the pH of these buffer solutions:

    1. Calculate the initial molarities of weak acid and conjugate base solutions after mixing.
    2. Use Henderson–Hasselbalch equation to calculate the pH of the buffer from K_a and concentrations calculated in step 1.

Examples:

1. What is the pH of a buffer made by mixing 3.00 L of 0.020 M benzoic acid ($HC_7H_5O_2$) with 1.00 L of 0.050 M sodium benzoate ($NaC_7H_5O_2$) ? K_a of benzoic acid = 6.3 x 10^{-5}

Step 1: Calculate the initial molarities of solutions:

$$\text{Initial molarity } HC_7H_5O_2 = 3.00\text{ L} \times \frac{0.020\text{ mol}}{1.00\text{ L}} \times \frac{1}{4.00\text{ L}} = 0.015\text{ M}$$

$$\text{Initial molarity of } NaC_7H_5O_2 = 1.00\text{ L} \times \frac{0.050\text{ mol}}{1.00\text{ L}} \times \frac{1}{4.00\text{ L}} = 0.0\underline{2}5\text{ M}$$

Step 2: Calculate pH from K_a:

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = 4.20 + \log\frac{0.01\underline{2}5}{0.015} = 4.12$$

2. A buffer is prepared by adding 115 mL of 0.30 M NH_3 to 145 mL of 0.15 M NH_4NO_3. What is the pH of the final solution? (K_b of ammonia = 1.8 x 10^{-5})

Examples (cont'd):

3. Calculate the pH of a solution prepared by mixing 400. mL of a 0.200 M acetic acid solution and 100. mL of a 0.300 M sodium hydroxide solution. (K_a acetic acid = $1.8\text{x}10^{-5}$)

Note: NaOH is a strong base, and reacts with acetic acid to form sodium acetate. If an appreciable amount of excess acetic acid is still present after the NaOH has reacted, the excess acetic acid and the newly formed sodium acetate form a buffer solution.

$$HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O$$

Step 1: Calculate the amount of acetic acid neutralized:

$$\text{mmol of acetic acid} = 400.\text{ mL x } \frac{0.200\text{ mol}}{1.00\text{ L}} = 80.0\text{ mmol}$$

$$\text{mmol of NaOH} = 100.\text{ mL x } \frac{0.300\text{ mol}}{1.00\text{ L}} = 30.0\text{ mmol}$$

	$HC_2H_3O_2$ +	NaOH ⟶	$NaC_2H_3O_2$ +	H_2O
Initial	80.0	30.0	0	----
Δ				----
End				----

Step 2: Calculate the concentration of species present after neutralization:

$$\text{Conc. of } HC_2H_3O_2 = \frac{\text{mmol } HC_2H_3O_2}{\text{mL solution}} =$$

$$\text{Conc. of } NaC_2H_3O_2 = \frac{\text{mmol } NaC_2H_3O_2}{\text{mL solution}} =$$

Step 3: Calculate pH from K_a:

Examples (cont'd):

4. Which solution is the most effective buffer?

    a) A solution prepared by mixing 150 mL of 0.10 M HCl and 150 mL of 0.10 M NaOH.

    b) A solution prepared by mixing 200 mL of 0.10 M HF and 100 mL of 0.10 M NaOH.

    c) A solution prepared by mixing 150 mL of 0.10 M HF and 100 mL of 0.10 M NaOH.

    d) A solution prepared by mixing 100 mL of 0.10 M HF and 200 mL of 0.10 M NaOH.

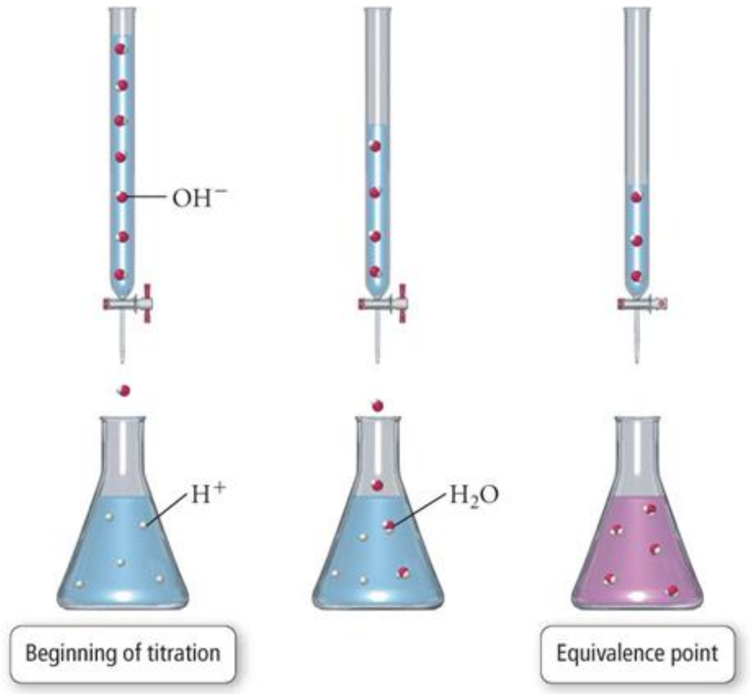
5. A buffer is prepared by dissolving $(CH_3)_2NH$ and $(CH_3)_2NH_2Cl$ in enough water to make 200.0 mL of solution. How many grams of $(CH_3)_2NH_2Cl$ must be added to 4.2 g of $(CH_3)_2NH$ to prepare this buffer with pH= 10.43? (K_b for $(CH_3)_2NH = 5.0\text{x}10^{-4}$)

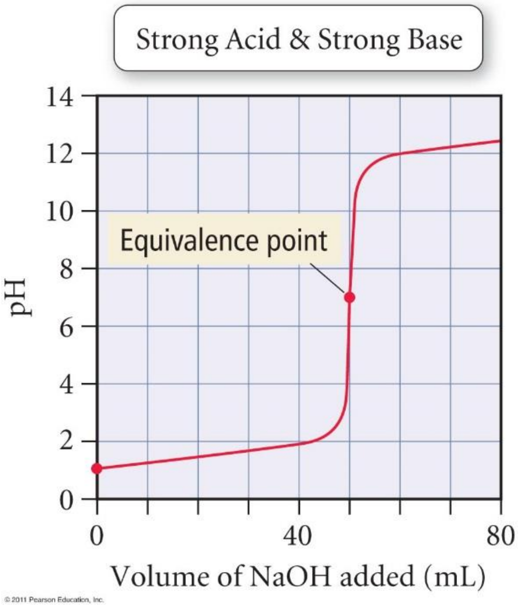
6. You are instructed to prepare 100.0 mL of a buffer solution with a pH of 7.40. You have available 75 mL of 3.0 M stock solution of KH_2PO_4 and 5.0 g of K_2HPO_4. Develop a plan to prepare this buffer solution from the given materials. (Ka for $H_2PO_4^- = 6.3\text{x}10^{-8}$)

ACID–BASE TITRATION CURVES

- Titration is a procedure for determining the amount of acid (or base) in a solution by determining the volume of base (or acid) of known concentration that will completely react with it.

- In titration, the known solution is slowly added to the unknown one, while the pH is monitored with either a pH meter or an indicator. As the acid and base combine, they neutralize each other. At the ***equivalence*** point–the point when the number of moles of base is stoichiometrically equivalent to the number of moles of acid–the titration is complete.





- Acid–base titration curve is a plot of the pH of a solution of acid (or base) against the volume of added base (or acid).

- In the next few sections we will examine the specifics of titration for the following 3 cases:

    1. Titration of strong acid with strong base

    2. Titration of weak acid with strong base

    3. Titration of weak base with strong acid

TITRATION OF A STRONG ACID BY A STRONG BASE

- Consider the titration of 25.0 mL of 0.100 M HCl with 0.100 M NaOH. We begin by calculating the volume of base required to reach equivalence point, and evaluate the pH at several points during the titration.

$$\underset{\substack{0.100\text{ M}\\25.0\text{ mL}}}{\text{HCl (aq)}} \quad + \quad \underset{\substack{0.100\text{ M}\\?\text{ mL}}}{\text{NaOH (aq)}} \longrightarrow \text{NaCl (aq)} \quad + \quad H_2O\text{ (aq)}$$

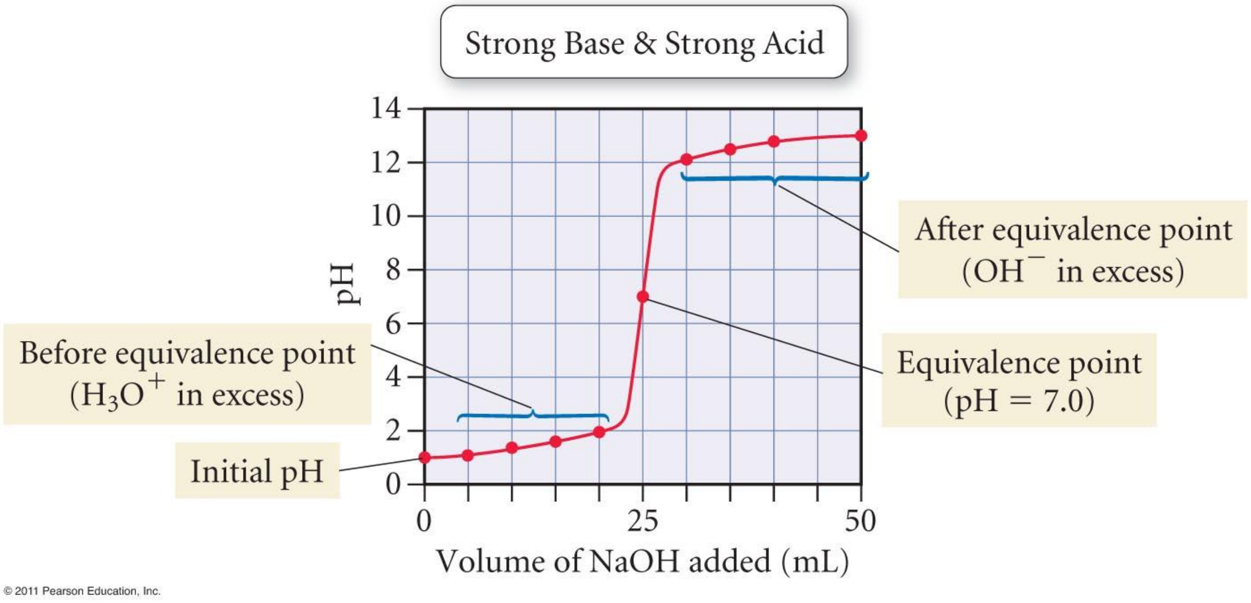
- Volume of NaOH needed to reach equivalence point can be calculated as shown below:

$$\text{mmol of HCl} = 25.0\text{ mL x } \frac{0.100\text{ mol}}{1\text{L}} = 2.50\text{ mmol}$$

$$\text{mmol of NaOH} = \text{mmol of HCl} = 2.50$$

$$\text{mL of NaOH} = 2.50\text{ mmol x } \frac{1\text{ L}}{0.100\text{ mol}} = 25.0\text{ mL}$$

- The titration curve for this titration is shown below. Note that the pH changes slowly initially as base is added, and changes rapidly as equivalence point is approached.



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TITRATION OF A STRONG ACID BY A STRONG BASE

Summary:

- The initial pH is the pH of the strong acid being titrated.
- Before equivalence point, H_3O^+ is in excess. The $[H_3O^+]$ at any of these points can be calculated by subtracting moles of OH^- added from initial mole of H_3O^+ present, and dividing by total volume.
- At equivalence point, only salt is present. Since conjugate salt of a strong acid and a strong base is pH neutral, the pH at this point is 7.00.
- Beyond equivalence point, OH^- is in excess and pH is determined by amount of excess OH^- present after neutralization of all the acid.

Examples:

1. A 50.0 mL sample of 0.200 M NaOH is titrated with 0.200 M HNO_3. Calculate the pH:
   a) after adding 30.0 mL of HNO_3

   b) at equivalence point.

2. A 30.0 mL sample of 0.100 M HCl is titrated with 0.120 M NaOH. Calculate the pH after addition of 20.0 mL of NaOH.

TITRATION OF A WEAK ACID BY A STRONG BASE

- Consider the titration of 25.0 mL of 0.100 M $HC_2H_3O_2$ with 0.100 M NaOH. We begin by calculating the volume of base required to reach equivalence point, and evaluate the pH at several points during the titration.

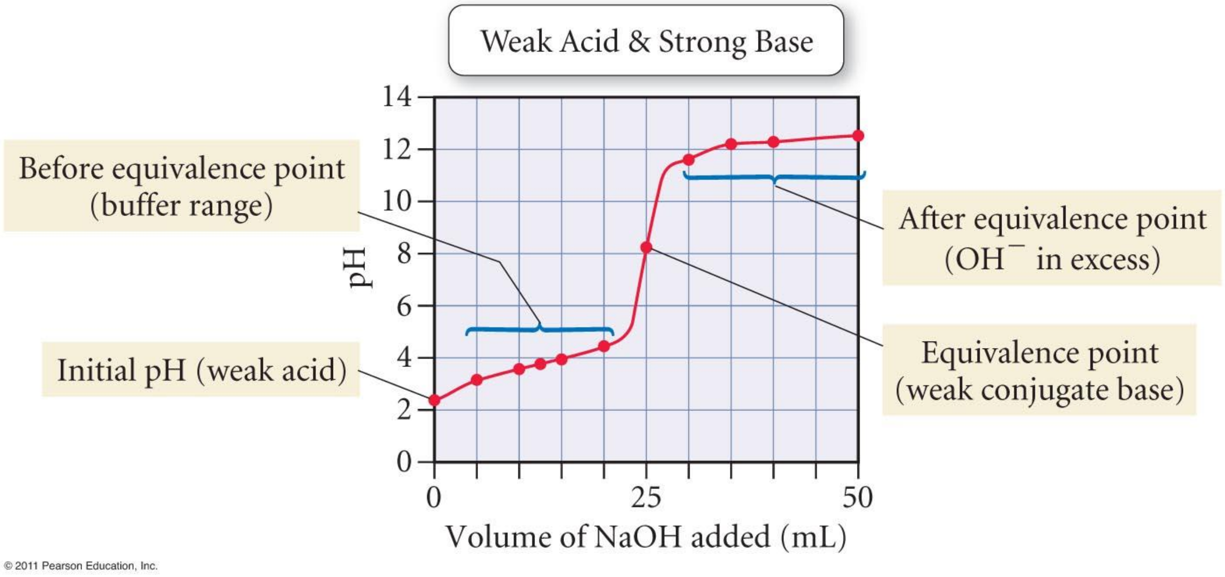
$$\underset{\substack{0.100\text{ M}\\25.0\text{ mL}}}{HC_2H_3O_2\,(aq)} \quad + \quad \underset{\substack{0.100\text{ M}\\?\text{ mL}}}{NaOH\,(aq)} \quad \longrightarrow \quad NaCl\,(aq) \quad + \quad H_2O\,(aq)$$

- Volume of NaOH needed to reach equivalence point can be calculated as shown below:

$$\text{mL of NaOH} = 25.0\text{ mL HA} \times \frac{0.100\text{ mol}}{1\text{L}} \times \frac{1\text{ mol NaOH}}{1\text{ mol HA}} \times \frac{1\text{ L}}{0.100\text{ mol}} = 25.0\text{ mL}$$

- The titration curve for this titration is shown below. Note that the initial pH of this titration is higher compared to the strong acid since weak acids ionize less. The pH changes slowly as base is added (buffer range) , and changes rapidly as equivalence point is approached.

- At equivalence point only salt is present. However, since the salt is composed of the conjugate base of a weak acid, it hydrolyzes to a basic solution and therefore the pH at equivalence point is slightly above 7.00



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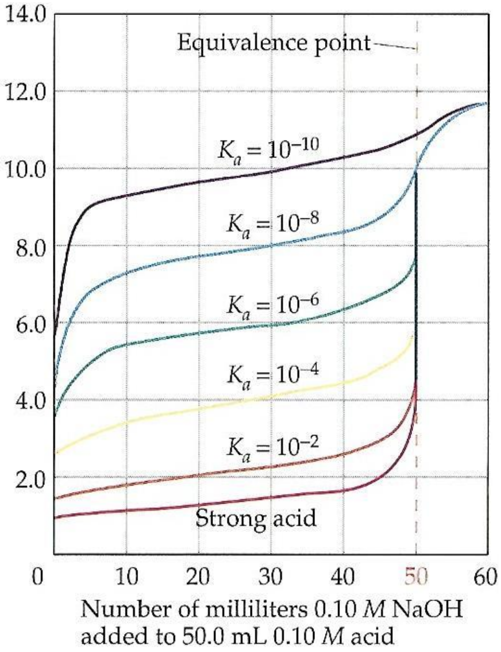
TITRATION OF A WEAK ACID BY A STRONG BASE

- To further illustrate the differences between titration of strong and weak acids by a strong base, consider the family of titration curves shown below. These differences can be summarized as:
  - The initial pH of the weak-acid solution is always higher than that of the strong acid solution of the same concentration.
  - The pH changes near the equivalence point become less marked as the acid becomes weaker (K_a decreases).
  - The pH at equivalence point steadily increases as the acid becomes weaker (due to hydrolysis of the conjugate base).



Summary:

- The initial pH is that of a weak acid and is calculated by working an equilibrium problem for ionization of a weak acid.
- Between the initial pH and the equivalence point, the solution becomes a buffer. pH can be calculated by using the reaction stoichiometry to calculate concentrations of the buffer component and using the Henderson–Hasslebalch equation.
- At equivalence point, only salt is present. pH can be calculated by first using reaction stoichiometry to determine concentration of salt anion present in solution, and then an equilibrium problem for the hydrolysis of the anion.
- Past equivalence point, excess strong base is present and pH is determined by amount of OH^- ions present after neutralization of all the acid.

Examples:

1. A 40.0 mL sample of 0.100 M HNO_2 ($K_a = 4.6x10^{-4}$) is titrated with 0.200 M KOH. Determine the pH after addition of
   a) 5.00 mL of KOH.

   b) at equivalence point.

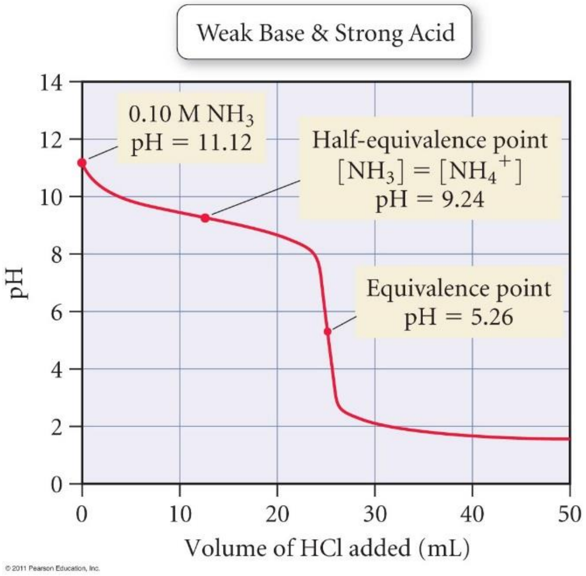
2. 60.0 mL of 0.100 M acetic acid ($K_a = 1.8x10^{-5}$) is titrated with 0.150 M NaOH. Determine the pH of solution after addition of (a) 20.0 mL of base, and (b) at equivalence point.

TITRATION OF A WEAK BASE BY A STRONG ACID

- The curve for the titration of a weak base by a strong acid is shown below. Calculations for pH for this titration are very similar to that of a weak acid by as strong base.

- The main differences are that the pH starts at a high value (solution is basic at start) and the solution is acidic at equivalence point (conjugate acid of a weak base will hydrolyze to produce an acidic solution).

- Also note that the point at which all the strong acid reacts with half of the initial base (1/2 equivalence point) at which the pH is equal to the pK_a.

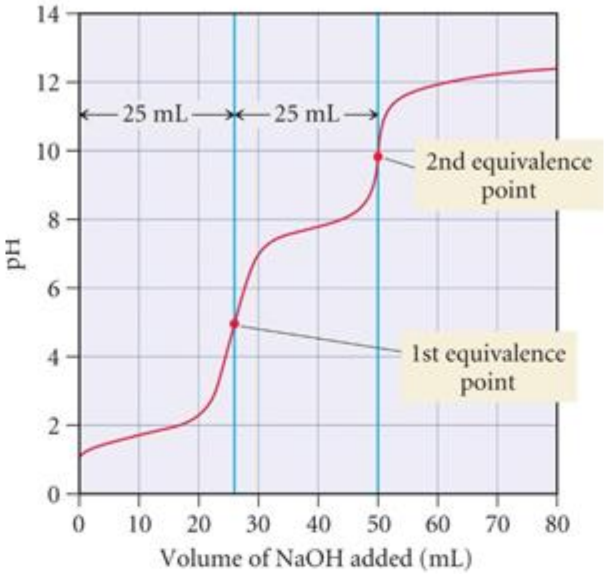


Examples:

1. What is the pH at the equivalence point when 35 mL of 0.20 M ammonia is titrated by 0.12 M HCl? (K_b for NH_3 is 1.8×10^{-5})

TITRATION OF A POLYPROTIC ACID

- When a weak diprotic acid is titrated with a strong base, if K_{a1} and K_{a2} are sufficiently different, the titration curve will have two equivalence points. For example, the curve below shows the titration of H_2SO_3 with NaOH.
- Note that the volume of base required to reach the first equivalence point is equal to the volume required to reach the second equivalence point. This is so, because the number of moles of H_2SO_3 in the first ionization determines the number of moles of HSO_3^- in the second ionization.



$$H_2SO_3\,(aq) \rightleftharpoons H^+\,(aq) + HSO_3^-\,(aq) \qquad K_{a1} = 1.6\text{x}10^{-2}$$

$$HSO_3^-\,(aq) \rightleftharpoons H^+\,(aq) + SO_3^{2-}\,(aq) \qquad K_{a2} = 6.4\text{x}10^{-8}$$

Examples:

1. Consider the three titrations below:

(A) Titration of 25.0 mL of a 0.100 M monoprotic weak acid with 0.100 M NaOH

(B) Titration of 25.0 mL of a 0.100 M diprotic weak acid with 0.100 M NaOH

(C) Titration of 25.0 mL of a 0.100 M strong acid with 0.100 M NaOH

Which statement below is most likely to be true?

a) All three titrations have the same initial pH.

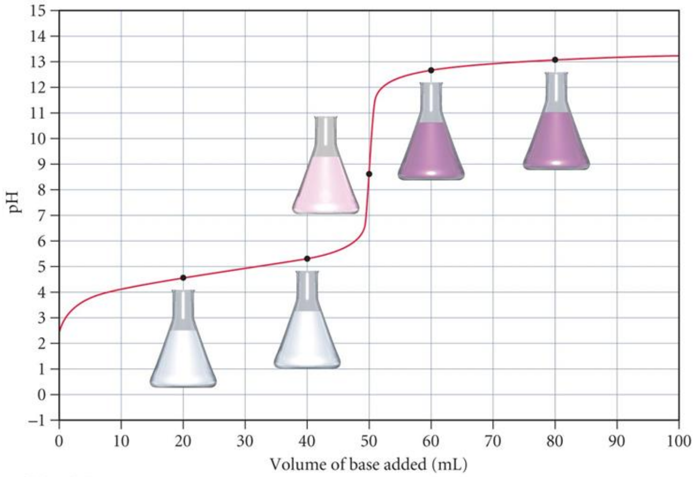
b) All three titrations have the same pH at their first equivalence point.

c) All three titrations require the same volume of NaOH to reach their first equivalence point.

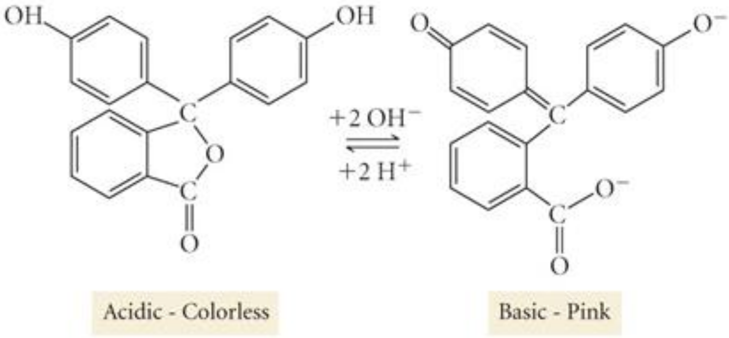
INDICATORS

- The pH changes in a titration can be monitored by a pH meter or an indicator. When choosing and using an indicator, a change in color (called ***endpoint***) should occur at the ***equivalence point***.

- The diagram below shows such change for titration of 0.100 M acetic acid with 0.100 M NaOH using phenolphthalein as an indicator.



- An indicator itself is a weak organic acid that is a different color than its conjugate base. For example, phenolphthalein is a common indicator whose acid form is colorless and conjugate base form is pink.



- The equation below shows the equilibrium present for a generic indicator whose acid form is HIn and its conjugate base form is In^-:

$$\underset{\text{color 1}}{\text{HIn (aq)}} + H_2O\text{ (l)} \rightleftharpoons H_3O^+\text{ (aq)} + \underset{\text{color 2}}{In^-\text{ (aq)}}$$

INDICATORS

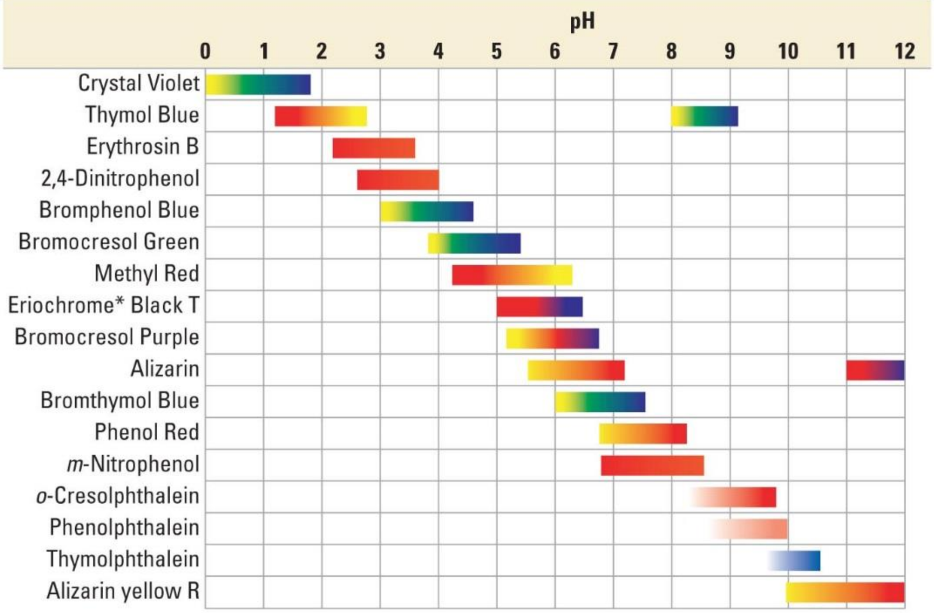
- As titration proceeds, the [H_3O^+] decreases, shifting the equilibrium to the right. Since pH change is large near the equivalence point of the titration, there is a large change in [H_3O^+] near the equivalence point. If the indicator is chosen properly, there should also be a correspondingly significant change in color.

- The color of the solution containing the indicator is dependent upon the relative concentrations of HIn and In^-. Listed below are three cases with pH relative to pK_a and color of the indicator solution:

pH (relative to pK_a)	$[In^-]/[HIn]$ ratio	Color of Indicator Solution
$pH = pK_a$	$\frac{[In^-]}{[HIn]} = 10^0 = 1$	Intermediate color
$pH = pK_a + 1$	$\frac{[In^-]}{[HIn]} = 10^1 = 10$	Color of In^-
$pH = pK_a - 1$	$\frac{[In^-]}{[HIn]} = 10^{-1} = 0.10$	Color of HIn

- The table below shows various indicators and their colors as a function of pH:

TABLE 16.1 Ranges of Color Changes for Several Acid–Base Indicators



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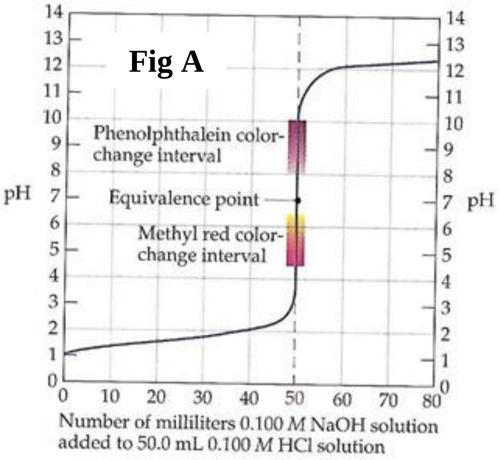
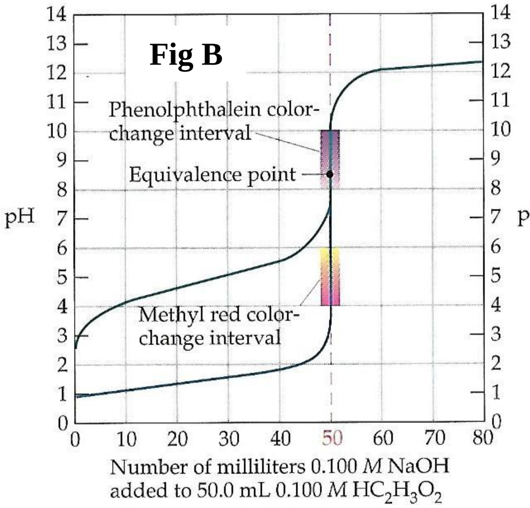
INDICATORS

- When choosing an indicator for a titration, it is important to select one that changes color in the range of pH of solution at equivalence point.

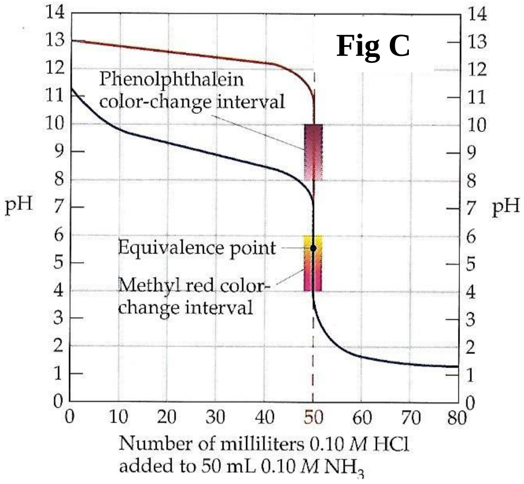
- For example, for the titration of a strong acid with a strong base, since there is a very large increase in the pH of solution at equivalence point, either phenolphthalein or methyl red can be used as an indicator (Fig A).



- On the other hand, when titrating a weak acid (acetic acid) with a strong base (NaOH), the pH of solution at equivalence point is above 7 (≈8.5) due to the hydrolysis of the anion. As a result, while phenolphthalein can be used as an indicator, methyl red is not a suitable indicator (Fig. B).



- Similarly, when titrating a weak base (ammonia) with a strong acid (HCl), the pH of the solution at equivalence point is 5.3, making methyl red an ideal candidate while phenolphthalein is not a suitable choice (Fig C).



Examples:

1. A sample of rainwater gives a yellow color with methyl red indicator.
   a) What is the approximate pH of this rainwater?

   b) If bromothymol blue indicator was used as an indicator, what color would be observed?

2. Propionic acid is a weak organic acid with $K_a = 1.34\text{x}10^{-5}$. Which of the indicators listed below is the best choice for titration of propionic acid with KOH?

   a) methyl red

   b) bromothymol blue

   c) thymol blue

   d) alizarin yellow

3. Using the table of indicators on the previous page, choose a suitable indicator for use in the titration of each of the following acids with a strong base:

   a) HF ($K_a = 3.5\text{x}10^{-4}$)

   b) HCN ($K_a = 4.9\text{x}10^{-10}$)

SOLUBILITY EQUILIBRIA & SOLUBILITY PRODUCT CONSTANT (K_{sp})

- We learned earlier that a compound is considered soluble if it dissolves in water and insoluble if it does not. As a result, we used the solubility rules to classify ionic compounds as soluble or insoluble.

- The solubility of an ionic compound could be better understood by applying the principles of equilibrium to the process of dissolution. For example, the dissolution of calcium fluoride can be represented as:

$$CaF_2\ (s) \underset{\textbf{precipitation}}{\overset{\textbf{dissolution}}{\rightleftharpoons}} Ca^{2+}\ (aq) + 2\ F^-\ (aq)$$

- This equilibrium views solubility as reversible processes of dissolution and precipitation, and represents the extent of solubility.

- The equilibrium constant for the equilibrium shown above is called the ***solubility product constant (K_{sp})*** and has the following form:

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

- Note that solids are omitted from this expression since concentration of solids is constant.

- The value of K_{sp} is a measure of the degree of solubility of the compound. The table below lists the value of K_{sp} for a number of ionic compounds.

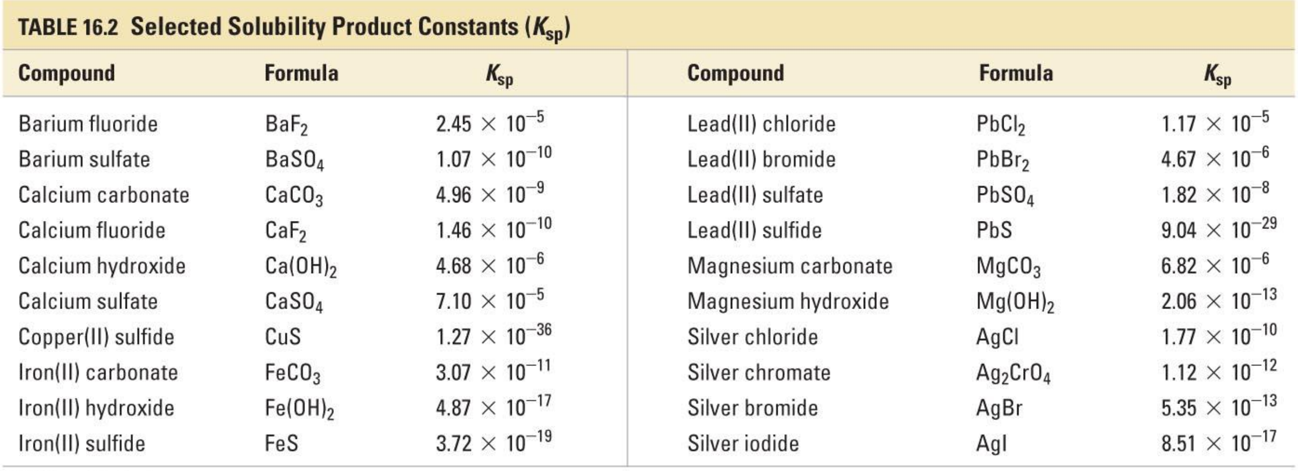


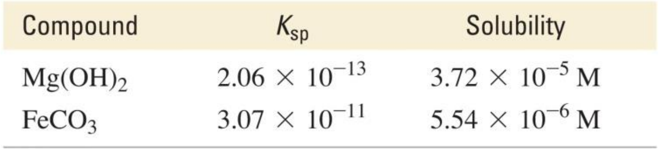
TABLE 16.2 Selected Solubility Product Constants (K_{sp})

Compound	Formula	K_{sp}	Compound	Formula	K_{sp}
Barium fluoride	BaF_2	2.45×10^{-5}	Lead(II) chloride	$PbCl_2$	1.17×10^{-5}
Barium sulfate	$BaSO_4$	1.07×10^{-10}	Lead(II) bromide	$PbBr_2$	4.67×10^{-6}
Calcium carbonate	$CaCO_3$	4.96×10^{-9}	Lead(II) sulfate	$PbSO_4$	1.82×10^{-8}
Calcium fluoride	CaF_2	1.46×10^{-10}	Lead(II) sulfide	PbS	9.04×10^{-29}
Calcium hydroxide	$Ca(OH)_2$	4.68×10^{-6}	Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Calcium sulfate	$CaSO_4$	7.10×10^{-5}	Magnesium hydroxide	$Mg(OH)_2$	2.06×10^{-13}
Copper(II) sulfide	CuS	1.27×10^{-36}	Silver chloride	$AgCl$	1.77×10^{-10}
Iron(II) carbonate	$FeCO_3$	3.07×10^{-11}	Silver chromate	Ag_2CrO_4	1.12×10^{-12}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}	Silver bromide	$AgBr$	5.35×10^{-13}
Iron(II) sulfide	FeS	3.72×10^{-19}	Silver iodide	AgI	8.51×10^{-17}

K_{sp} AND RELATIVE SOLUBILITY

- Molar solubility and K_{sp} are related and each can be calculated from the other. However, the K_{sp} of two different compounds cannot be generally used to compare their molar solubility.

- For example, consider the K_{sp} and molar solubilities of the two compounds shown below:



Compound	K_{sp}	Solubility
$Mg(OH)_2$	2.06×10^{-13}	3.72×10^{-5} M
$FeCO_3$	3.07×10^{-11}	5.54×10^{-6} M

- Magnesium hydroxide has a smaller K_{sp} than iron(II) carbonate, but a higher molar solubility.

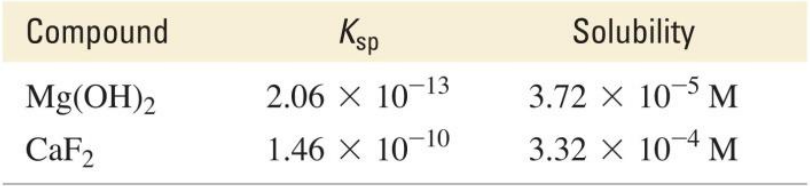
- The relationship between K_{sp} and molar solubility depends on the stoichiometery of the dissociation reaction.

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2\ OH^-$$

$$FeCO_3 \rightarrow Fe^{2+} + CO_3^{2-}$$

- Consequently, any direct comparison of the K_{sp} and molar solubility of compounds can only be made if their dissociation reaction has the same stoichiometry.

- For example, when considering the K_{sp} and molar solubilities shown below:



Compound	K_{sp}	Solubility
$Mg(OH)_2$	2.06×10^{-13}	3.72×10^{-5} M
CaF_2	1.46×10^{-10}	3.32×10^{-4} M

- Since both compounds have the same stoichiometry in their dissociation reaction, it would be appropriate to relate the lower K_{sp} of magnesium hydroxide as indication of lower solubility.

Examples:

Write the solubility product constant expressions for the following compounds:

1) $Mg(OH)_2$

2) $Ca_3(PO_4)_2$

3) Ag_2S

4) Which has the greater solubility: BaF_2 or CaF_2?

CALCULATING MOLAR SOLUBILITY FROM K_{SP}

- ***Molar Solubility*** is defined as moles of compound that dissolve in 1 L of water to give a saturated solution, and is related to the K_{sp} value for the compound.

- The examples below show the relationship between K_{sp} and molar solubility and variations of problems in the calculations for each.

Examples:

1. The solubility of silver chromate, Ag_2CrO_4 , in water is 0.022 g/L. Calculate K_{sp} for Ag_2CrO_4

Step 1: Calculate the molar solubility:

Step 2: Set up the solubility equilibrium:

	Ag_2CrO_4 (s) $\rightleftharpoons$	2 Ag^+ (aq) +	CrO_4^{2-} (aq)
Initial			
Δ			
Equilibrium			

Step 3: Write K_{sp} expression and solve using equilibrium concentrations above:

Examples (cont'd):

2. What is the molar solubility of MgF_2 in water? ($K_{sp} = 7.4 \times 10^{-11}$)

Let x = the molar solubility of MgF_2

	$MgF_2 (s) \rightleftharpoons$	$Mg^{2+} (aq)$ +	$2 F^- (aq)$
Initial	-----	0	0
Δ	-----	+ x	+ 2 x
Equilibrium	-----	+ x	+ 2 x

Substitute from the table into the equilibrium-constant expression:

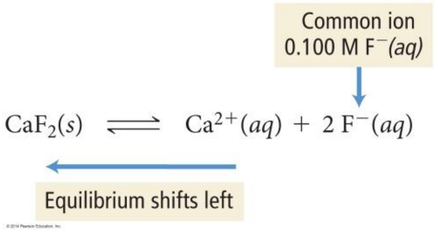
$$K_{sp} = [Mg^{2+}]\,[F^-]^2$$

3. The Ksp of magnesium carbonate is 1.0×10^{-5}. Calculate the solubility of magnesium carbonate in grams per liter of water.

SOLUBILITY AND THE COMMON ION EFFECT

- How is the solubility of an ionic compound affected by presence of a common ion? For example, what is the solubility of CaF_2 in a solution that is 0.100 M NaF?

- The effect on solubility can be determined by considering the common ion effect studied earlier in this chapter. Based on Le Chaterlier's principle, the presence of F^- in solution causes the equilibrium to shift to the left, decreasing solubility:



- In general, the solubility of an ionic compound is lower in a solution containing a common ion than in pure water.

Example:

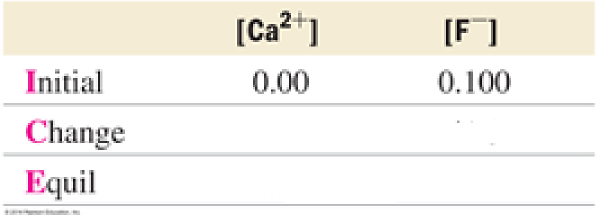
1. In which solution is $BaSO_4$ is most soluble?

   a) In a solution that is 0.10 M $BaNO_3$

   b) In a solution that is 0.10 M Na_2SO_4

   c) In a solution that is 0.10 M $NaNO_3$

2. What is the molar solubility of CaF_2 in a solution containing 0.100 M NaF?



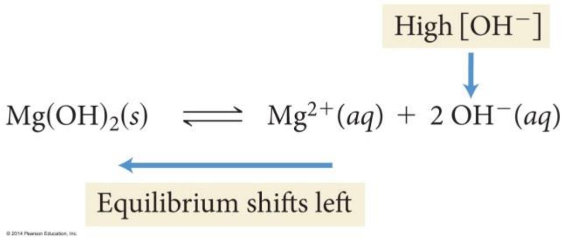
	$[Ca^{2+}]$	$[F^-]$
Initial	0.00	0.100
Change		
Equil		

EFFECT OF pH ON SOLUBILITY

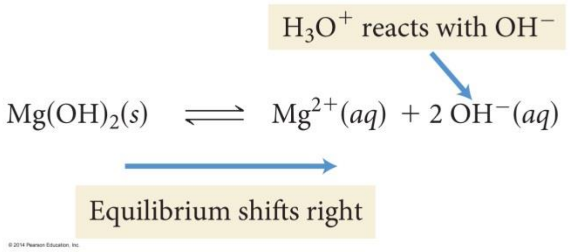
- The pH of a solution can affect the solubility of a compound in that solution. For example, consider the solubility of $Mg(OH)_2$:

$$Mg(OH)_2 \, (s) \rightleftharpoons Mg^{2+} \, (aq) + 2 \, OH^- \, (aq)$$

- The solubility of this compound is highly dependent on the pH of the solution in which it dissolves. If pH is high, the high $[OH^-]$ shifts the equilibrium to the left in accordance with the common ion effect.

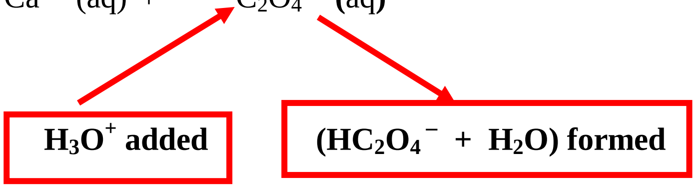


- If the pH is low, then the $[H_3O^+]$ is high. As the magnesium hydroxide dissolves, the H_3O^+ react with newly formed OH^-, driving the reaction to the right.



- Similarly, consider the effect of lowering pH on the solubility of calcium oxalate (CaC_2O_4). Since oxalate anion ($C_2O_4^-$) is the conjugate based of a weak acid, it can react with the additional H_3O^+ in solution, shifting the equilibrium to the right and increasing the solubility of the salt.

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



- ***In general, the solubility of an ionic compound with a strongly basic or weakly basic anion increases with increasing acidity (decreasing pH).***

<u>Example</u>:

1. Determine whether each compound below is more soluble in an acidic solution than in pure water:

a) BaF_2 b) AgI c) $CaCO_3$

PRECIPITATION

- We learned earlier that a precipitation occurs when the ions of a slightly soluble salt come in contact with one another. Now we can ask the question: What concentration of ions will cause a substance to precipitate?

- We can answer this question by revisiting the concept of reaction quotient (Q) discussed earlier in Chapter 14. ***The reaction quotient for solubility equilibria (Q_{sp})*** is defined as the product of the concentration of the ionic components raised to their stoichiometric coefficients.

- For example, for the dissolution of CaF_2, the Q_{sp} can be written as shown below:

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

$$Q_{sp} = [Ca^{2+}]\,[F^-]^2$$

- Note that the difference between K_{sp} and Q_{sp} are that K_{sp} is the value of this product as equilibrium concentrations, whereas Q_{sp} is the value of the product as any concentration.

- Comparing the Q_{sp} and K_{sp} values, we can generalize the following situations:

$Q_{sp} < K_{sp}$	$Q_{sp} = K_{sp}$	$Q_{sp} > K_{sp}$
• Solution is unsaturated • Compound remains dissolved in solution • Additional solid will dissolve in solution	• Solution is saturated • Compound remains dissolved in solution • Additional solid will not dissolve in solution	• Solution is supersaturated • Under most circumstances excess solid precipitates out of solution

Examples:

1. A solution containing $Pb(NO_3)_2$ is mixed with one containing NaBr. After mixing the concentration of $Pb(NO_3)_2$ is 0.0150 M and that of NaBr is 0.00350 M. Will a precipitate form in the mixture? (K_{sp} of $PbBr_2 = 4.67 \times 10^{-6}$)

$$Pb^{2+}\,(aq) \quad + \quad 2\,Br^{-}\,(aq) \rightleftharpoons PbBr_2\,(s)$$

2. In example 1, what is the minimum concentration of NaBr that will precipitate $PbBr_2$?

3. Exactly 0.400 L of 0.50 M $Pb(NO_3)_2$ and 1.60 L of 2.50×10^{-2} M NaCl are mixed together. Predict whether $PbCl_2$ will precipitate from this solution after mixing.
(K_{sp} of $PbCl_2 = 1.17 \times 10^{-5}$)

SELECTIVE PRECIPITATION

- The technique of separating two or more ions from a solution by adding a reagent that precipitates first one ion, then another, is called **selective precipitation**.

- For example, consider a solution containing 0.10 M Ba^{2+} and 0.10 M Sr^{2+} . To this solution is added dropwise K_2CrO_4. Both cations can form precipitates with CrO_4^{2-} with K_{sp} values listed below:

  Ksp ($BaCrO_4$) = 1.2×10^{-10} and Ksp ($SrCrO_4$) = 3.5×10^{-5}

- Which cation will precipitate first? Why?

- Shown below are the calculations to determine the minimum concentration of CrO_4^{2-} to form each precipitate.

0.10 M Ba^{2+}
+
0.10 M Sr^{2+}
+
small amt. of K_2CrO_4

$BaCrO_4$

$[Ba^{2+}]\,[CrO_4^{2-}]$ = Ksp (for $BaCrO_4$) = 1.2×10^{-10}

$[0.10\text{ M}]\,[CrO_4^{2-}] = 1.2 \times 10^{-10}$ **$[CrO_4^{2-}] = 1.2 \times 10^{-9}$ M**

$SrCrO_4$

$[Sr^{2+}]\,[CrO_4^{2-}]$ = Ksp (for $SrCrO_4$) = 3.5×10^{-5}

$[0.10\text{ M}]\,[CrO_4^{2-}] = 3.5 \times 10^{-5}$ **$[CrO_4^{2-}] = 3.5 \times 10^{-4}$ M**

Note: $[CrO_4^{2-}]$ to precipitate Ba^{2+} < $[CrO_4^{2-}]$ to precipitate Sr^{2+}

1.2×10^{-9} M < 3.5×10^{-4} M

Examples:

1. The magnesium and calcium ions present in seawater ($[Mg^{2+}]$= 0.059M and $[Ca^{2+}]$= 0.011 M) can be separated by addition of KOH to precipitate the insoluble hydroxides.
   (a) Based on the K_{sp} values given below, which ion precipitates first?

   K_{sp} for $Mg(OH)_2 = 2.06\text{x}10^{-13}$ K_{sp} for $Ca(OH)_2 = 4.68\text{x}10^{-6}$

   (b) What is the minimum $[OH^{-}]$ that is required for the first ion to precipitate?

   (c) When Ca^{2+} first begins to precipitate, what is the Mg^{2+} concentration?

COMPLEX-ION EQUILIBRIA

- Another type of equilibria that primarily involves transition metals is called ***complex-ion equilibria***. In aqueous solutions, water molecules act as Lewis base to donate electrons to the transition metal (good Lewis acids), and form hydrates.

- For example, silver ions are hydrated by water to form $Ag(H_2O)_2^+$. We often write Ag^+ as a shorthand notation for this species, but the bare ions do not exist by themselves in solution.

- Species such as $Ag(H_2O)_2^+$ are known as complex ions. A ***complex ion*** is contains a central metal ion bound to one or more ligands. A ***ligand*** is a neutral molecule or ion that acts as a Lewis base with the metal ion.

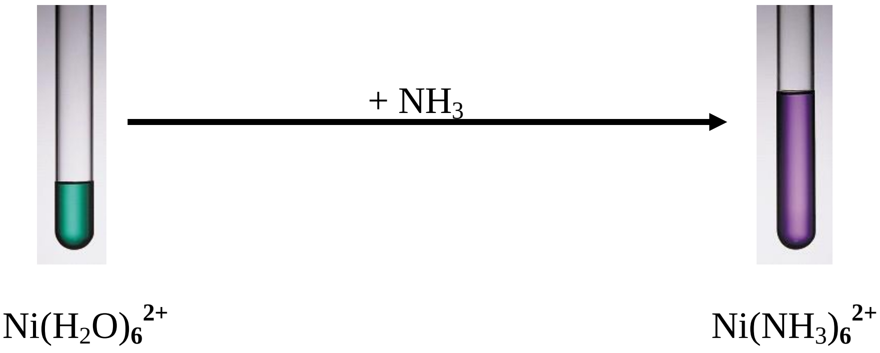
- If a stronger Lewis base such as NH_3 is added to the solution containing the $Ag(H_2O)_2^+$, it displaces water molecules by the following reaction:

$$Ag(H_2O)_2^+ \text{ (aq)} + 2\ NH_3 \text{ (aq)} \rightleftharpoons Ag(NH_3)_2^+ \text{ (aq)} + 2\ H_2O \text{ (l)}$$

- For simplification, the water molecules are often not included in the equation:

$$\underset{\text{Lewis acid}}{Ag^+ \text{ (aq)}} \quad + \quad \underset{\text{Lewis base}}{2\ NH_3 \text{ (aq)}} \rightleftharpoons \underset{\text{complex ion}}{Ag(NH_3)_2^+ \text{ (aq)}}$$

- Different ligands usually impart different colors to the complex ion formed, and are useful in qualitative analysis involving the metal ions. For example:



COMPLEX-ION EQUILIBRIA

- The equilibrium constant associated with the equilibrium for the formation of a complex ions is called the ***formation constant (K_f).*** For $Ag(NH_3)_2^+$, the expression for K_f is:

$$\mathbf{K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}}$$

- The table below lists the formation constant for a number of common complex ions. Note that most K_f values are very large, indicating the formation of the complex ion is highly favored. The examples on the next pages illustrate some of the calculations using K_f and complex-ion equilibria.

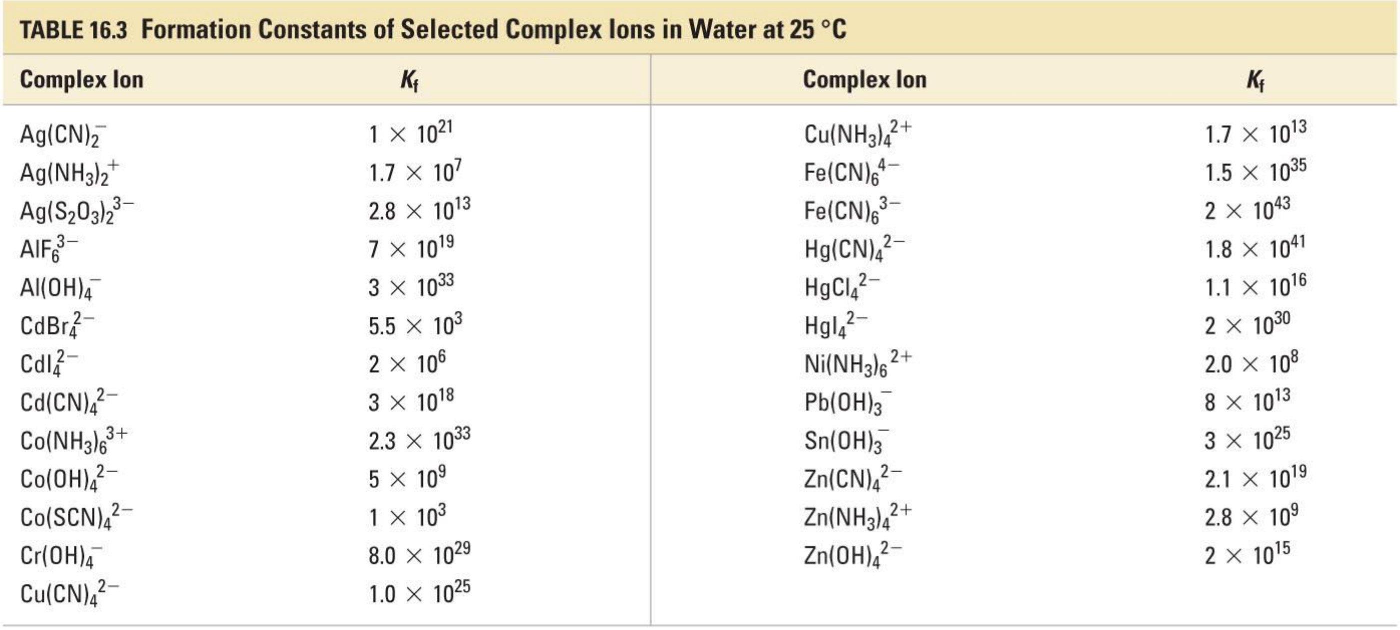


TABLE 16.3 Formation Constants of Selected Complex Ions in Water at 25 °C

Complex Ion	K_f	Complex Ion	K_f
$Ag(CN)_2^-$	1×10^{21}	$Cu(NH_3)_4^{2+}$	1.7×10^{13}
$Ag(NH_3)_2^+$	1.7×10^{7}	$Fe(CN)_6^{4-}$	1.5×10^{35}
$Ag(S_2O_3)_2^{3-}$	2.8×10^{13}	$Fe(CN)_6^{3-}$	2×10^{43}
AlF_6^{3-}	7×10^{19}	$Hg(CN)_4^{2-}$	1.8×10^{41}
$Al(OH)_4^-$	3×10^{33}	$HgCl_4^{2-}$	1.1×10^{16}
$CdBr_4^{2-}$	5.5×10^{3}	HgI_4^{2-}	2×10^{30}
CdI_4^{2-}	2×10^{6}	$Ni(NH_3)_6^{2+}$	2.0×10^{8}
$Cd(CN)_4^{2-}$	3×10^{18}	$Pb(OH)_3^-$	8×10^{13}
$Co(NH_3)_6^{3+}$	2.3×10^{33}	$Sn(OH)_3^-$	3×10^{25}
$Co(OH)_4^{2-}$	5×10^{9}	$Zn(CN)_4^{2-}$	2.1×10^{19}
$Co(SCN)_4^{2-}$	1×10^{3}	$Zn(NH_3)_4^{2+}$	2.8×10^{9}
$Cr(OH)_4^-$	8.0×10^{29}	$Zn(OH)_4^{2-}$	2×10^{15}
$Cu(CN)_4^{2-}$	1.0×10^{25}		

Examples:

1. What is the concentration of $Cu^{2+}(aq)$ in a solution that was originally 0.015 M $Cu(NO_3)_2$ and 0.100 M NH_3 ? The Cu^{2+} ion forms the complex ion $Cu(NH_3)_4^{2+}$ with $K_f = 1.7 \times 10^{13}$.

Step 1: Stoichiometry Calculation:

	$Cu^{2+}(aq)$ +	$4\ NH_3(aq)$ $\longrightarrow$	$Cu(NH_3)_4^{2+}(aq)$
Initial	0.015 M	0.100 M	0
Change	0.015 M	0.060 M	0
End	0.00	0.040	0.015

Step 2: Equilibrium Calculation:

	$Cu^{2+}(aq)$ +	$4\ NH_3(aq)$ $\rightleftharpoons$	$Cu(NH_3)_4^{2+}(aq)$
Initial	0.00	0.040	0.015
Change	+ x	+4 x	– x
Equilibrium	x	0.040 + x	0.015 – x

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{(0.015 - x)}{x\,(0.040 + 4x)^4} = 1.7 \times 10^{13}$$

Since x is small compared to the other concentrations,

$$K_f = \frac{(0.015)}{x\,(0.040)^4} = 1.7 \times 10^{13} \qquad x = [Cu^{2+}] = 3.4 \times 10^{-10}\ M$$

Examples (cont'd):

2. The formation constant for the complex HgI_4^{2-} is $1.0\text{x}10^{30}$. What is the $[Hg^{2+}]$ after complexation, in a solution that was originally 0.010 M Hg^{2+} and 0.78 M I^-.

3. In the presence of CN^-, Fe^{3+} forms the complex ion $Fe(CN)_6^{3-}$. The equilibrium concentrations of Fe^{3+} and $Fe(CN)_6^{3-}$ are $8.5\text{x}10^{-40}$ M and $1.5\text{x}10^{-3}$ M, respectively, in a 0.11 M KCN solution. Calculate the value of the formation constant (K_f) for this complex.

COMPLEX IONS AND SOLUBILITY

- The formation of a complex ion reduces the concentration of the metallic ion in solution. Therefore, the solubility of an ionic compound containing a cation that forms a complex ion increases in presence of Lewis bases that form complex with the cation.

- The most common Lewis bases that increase the solubility of metal cations are NH_3, CN^-, and OH^-. For example, silver chloride is only slightly soluble in pure water:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq) \qquad K_{sp} = 1.77\text{x}10^{-10}$$

- However, adding NH_3 increases the solubility dramatically, because ammonia forms a complex with silver cation:

$$Ag^+\,(aq) + 2\,NH_3\,(aq) \rightleftharpoons Ag(NH_3)_2^+\,(aq) \qquad K_f = 1.7\text{x}10^7$$

- The large value of K_f significantly lowers the concentration of Ag^+ in solution, and therefore drives the dissolution of AgCl. The two reactions above can be added together:

$$\begin{array}{rcll} AgCl\,(s) & \rightleftharpoons & Ag^+\,(aq) + Cl^-\,(aq) & K_{sp} = 1.77\text{x}10^{-10} \\ Ag^+\,(aq) + 2\,NH_3\,(aq) & \rightleftharpoons & Ag(NH_3)_2^+\,(aq) & K_f = 1.7\text{x}10^7 \\ \hline AgCl\,(s) + 2\,NH_3\,(aq) & \rightleftharpoons & Ag(NH_3)_2^+\,(aq) + Cl^-\,(aq) & K = K_{sp} \text{ x } K_f = 3.0\text{x}10^{-3} \end{array}$$

- As a result, normally insoluble AgCl is made soluble by addition of NH_3. In general, a slightly soluble salt that would precipitate in an aqueous solution, might not precipitate in a solution that provides ligands for complexation.

- This can be advantageous when identifying ions during qualitative analysis. For example, when separating Ag^+, Pb^{2+}, and Hg^{2+} ions in an unknown sample, the chlorides of each are first precipitated by adding dilute HCl. Once the mixed precipitate is separated, it must be redissolved in order to identify the cation individually. This can be done by addition of a complexing agent as discussed above.

Examples:

1. Which compound, when added to water, would most likely increase the solubility of CuS?

   a) NaCl b) KNO_3 c) NaCN d) $MgBr_2$

Examples (cont'd):

2. Using the K_{sp} value for $Cu(OH)_2$ ($1.6x10^{-19}$) and the K_f value for the complex $Cu(NH_3)_4^{2+}$ ($1.0x10^{13}$), calculate the value for the equilibrium constant for the reaction shown below:

$$Cu(OH)_2\ (s)\ +\ 4\ NH_3\ (aq) \rightleftharpoons Cu(NH_3)_4^{2+}\ (aq)\ +\ 2\ OH^-\qquad K = ???$$

3. Nanotechnology has become an important field, with many applications. One common building block of nanostructures is manganese oxide nanoparticles. These particles can be formed from manganese oxide nanorods, the formation of which is shown below:

$$Mn^{2+}\ (aq)\ +\ C_2O_4^{2-}\ (aq) \rightleftharpoons MnC_2O_4\ (aq)\qquad K_1 = 7.9x10^3$$

$$MnC_2O_4\ (aq) + C_2O_4^{2-}\ (aq) \rightleftharpoons Mn(C_2O_4)_2^{2-}\ (aq)\qquad K_2 = 7.9x10^1$$

Calculate the formation constant (K_f) for $Mn(C_2O_4)^{2-}$.

SOLUBILITY OF AMPHOTERIC HYDROXIDES

- Many metal hydroxides are insoluble or only slightly soluble in pH-neutral water. For example, $Al(OH)_3$ has $K_{sp} = 2 \times 10^{-32}$. All metal hydroxides, however, have a basic anion (OH^-), and therefore become more soluble in acidic solutions.

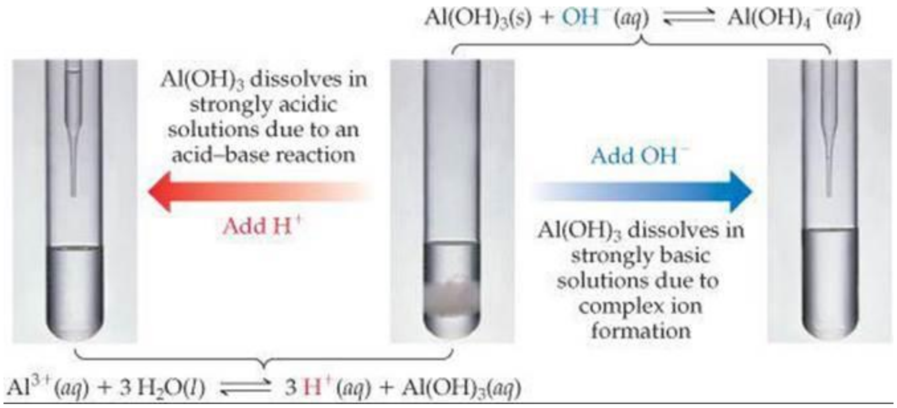
- Metal hydroxides become more soluble in acidic solutions, because they react with H_3O^+. For example, $Al(OH)_3$ dissolves in acid as shown below:

$$Al(OH)_3\,(s) + 3\,H_3O^+\,(aq) \rightarrow Al^{3+}\,(aq) + 6\,H_2O\,(l) \qquad \textbf{\textit{Al(OH)}}_{\textbf{\textit{3}}}\textbf{\textit{ acts as a base}}$$

- Some metal hydroxides also act as an acid–they are amphoteric. Therefore, these hydroxides also increase their solubility in presence of bases. For example, $Al(OH)_3$ dissolves in basic solution as shown below:

$$Al(OH)_3\,(s) + OH^-\,(aq) \rightarrow Al(OH)_4^-\,(aq) \qquad \textbf{\textit{Al(OH)}}_{\textbf{\textit{3}}}\textbf{\textit{ acts as an acid}}$$

- As a result, $Al(OH)_3$ is soluble at high pH and soluble at low pH, but insoluble in a pH-neutral solution.



$Al(H_2O)_6^{3+}$ (aq) **$Al(OH)_3$ (s)** **$Al(OH)_4^-$ (aq)**

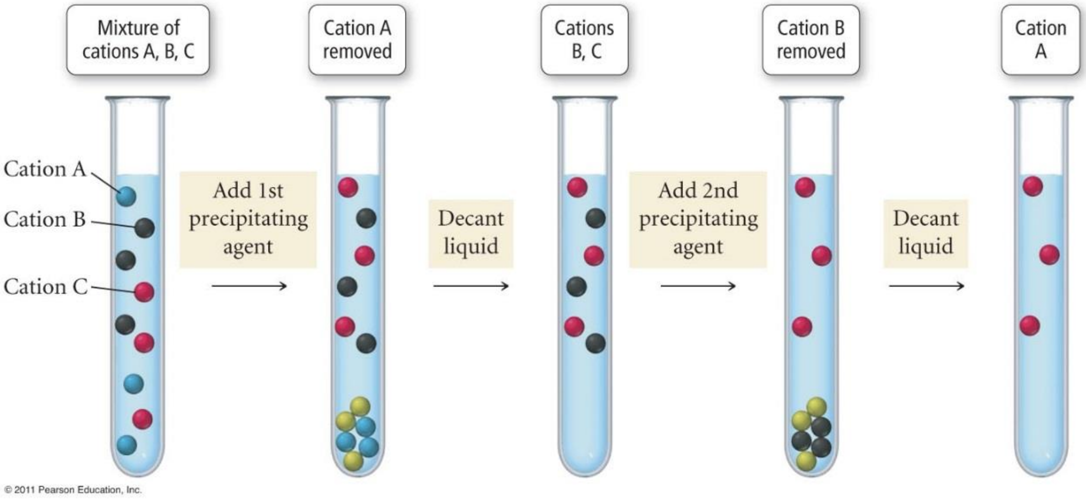
- In addition to Al^{3+}, other cations that can form amphoteric hydroxides are Cr^{3+}, Zn^{2+}, Pb^{2+} and Sn^{2+}. Other metal hydroxides, such as those of Ca^{2+}, Fe^{2+} and Fe^{3+} are not amphoteric–they become soluble in acidic solutions, but remain insoluble in basic solutions.

QUALITATIVE ANALYSIS OF METAL IONS

- ***Qualitative analysis*** is the systematic determination of the presence of a metallic ion in a mixture through its selective precipitation. In the past, qualitative analysis was used extensively to determine identity of metals in an unknown mixture.

- Although this technique has been replaced by the more precise and less time-intensive modern instrumental techniques, it is still valuable to study because of the importance of the principles involved.

- Based on this technique, the cations are divided into 5 groups and the unknown mixture is subjected to addition of several precipitating agents. After each step, precipitate formed by the cation in a group is filtered and separated from the mixture. The figure below shows the schematics for this technique:

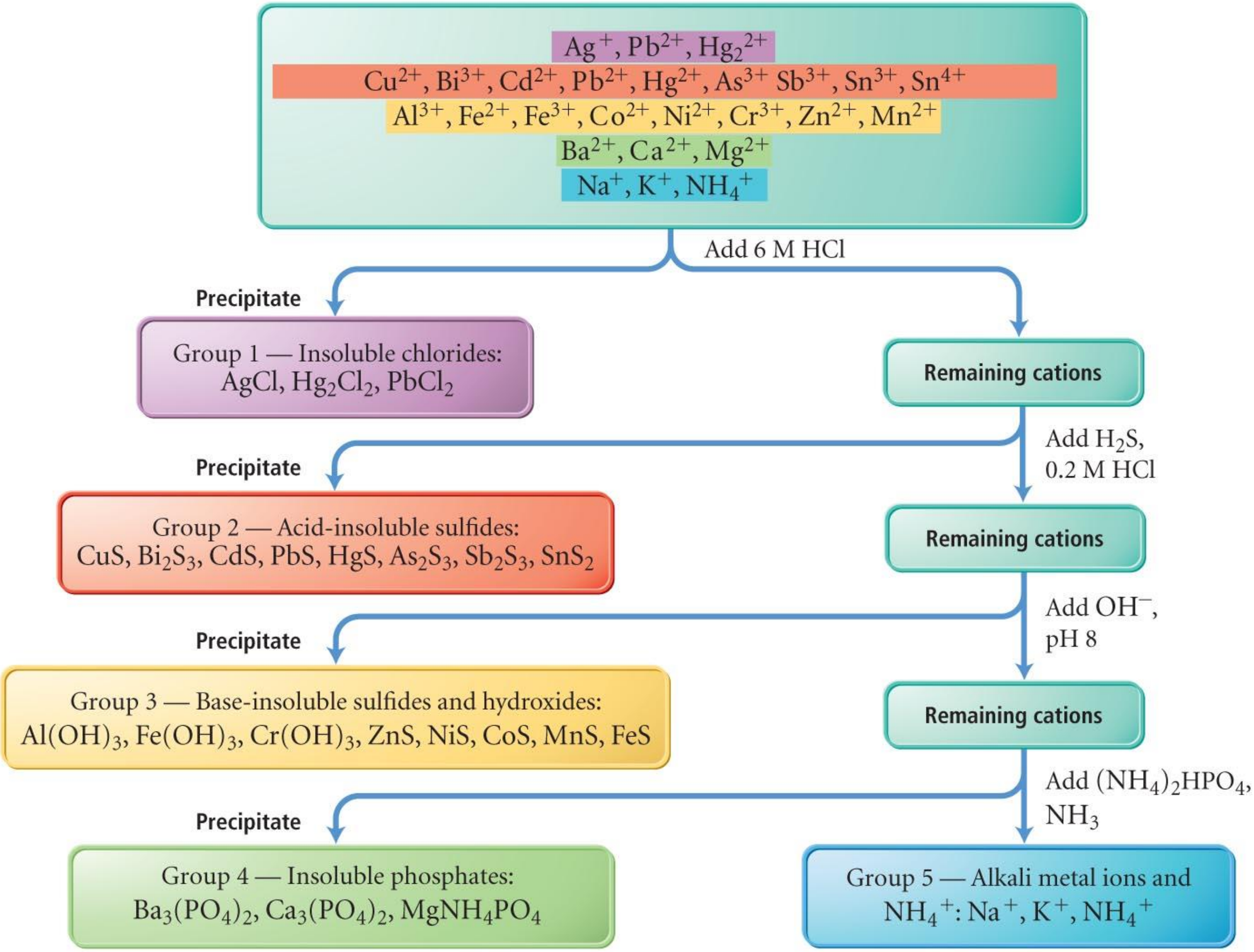


- The five cation groups are listed below:

Group 1: Insoluble chlorides
Group 2: Acid-insoluble sulfides
Group 3: Base-insoluble sulfides and hydroxides
Group 4: Insoluble phosphates
Group 5: Alkali metals and NH_4^+

- The general qualitative analysis scheme is summarize on the next page.

QUALITATIVE ANALYSIS OF METAL IONS



ANSWERS TO IN-CHAPTER PROBLEMS:

Page	***Example No.***	***Answer***
2	2	pH = 3.47
4	1	d
5	2	pH = 9.35
7	2	8.95
	3	a) [HA] > $[A^-]$ b) A^- must be added
12	1	HClO
	2	c
13	2	pH = 9.45
14	3	pH = 4.52
15	4	b
	5	14 g
	6	Dilute 4.8 mL of KH_2PO_4 stock solution to 100 mL, and add 4.0 g of K_2HPO_4.
18	1	a) pH = 12.70 b) pH = 7.00
	2	pH = 1.92
21	1	a) pH = 2.86 b) 8.08
	2	a) pH = 4.74 b) pH = 8.76
22	1	pH = 5.19
23	1	c
27	1	a) pH = 6 b) yellow
	2	c
	3	a) phenol red or m-nitrophenol b) alizarin yellow R
30	1	$K_{sp} = [Mg^{2+}][OH^-]^2$
	2	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]_2$
	3	$K_{sp} = [Ag^+]^2[S^{2-}]$
	4	BaF_2

Page	***Example No.***	***Answer***
31	1	$K_{sp} = 1.2x10^{-12}$
32	2	$2.6x10^{-4}$ M
	3	0.27 g/L
33	1	c
	2	$1.46x10^{-8}$ M
34	1	a) greater in acidic solution b) not greater in acidic solution c) greater in acidic solution
36	1	no precipitation will occur
	2	$[Br^{-}] = 0.0176$ M
	3	precipitation will occur
38	1	a) Mg^{2+} b) $[OH^{-}] = 1.9x10^{-6}$ M for Mg^{2+} to precipitate c) $[Mg^{2+}] = 4.9x10^{-10}$ M when Ca^{2+} begins to precipitate
42	2	$[Hg^{2+}] = 3.3x10^{-32}$
	3	$K_f = 1.0x10^{42}$
43	1	c
44	2	$K = 1.6x10^{-6}$
	3	$K_f = 6.2x10^{5}$