Chapter 17

Buffers!!

17.1 The Common-Ion Effect

- What is ”the common ion effect?
  - It’s what happens when you add more of the product ion to an acid/base reaction.

- This, like most things makes most sense with an example:

Example: What happens when you add Acetate to Acetic Acid? (1 of 2)

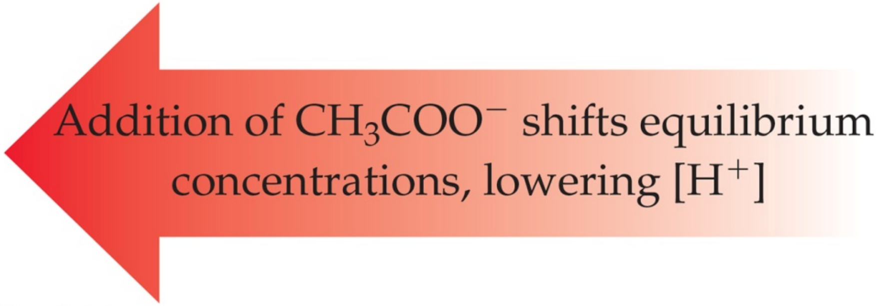
- Acetic acid is a weak acid:
  - CH3COOH(aq) + $H_2O(l) \rightleftharpoons$ CH3COO$^-$(aq) + $H_3O^+(aq)$
- Sodium acetate is a strong electrolyte:
  - $NaCH_3COO(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$
  - all of it dissociates:

    $[NaCH_3COO] = [CH_3COO^-]$
  - What does that do to the equilibrium?

Effect of Acetate on the Acetic Acid Equilibrium (2 of 2)

- Le Châtelier’s principle says:
  - Add **product** ($CH_3CO_2^-$), **shift** to **reactants**.

  - $CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^{-}(aq) + H_3O^{+}(aq)$

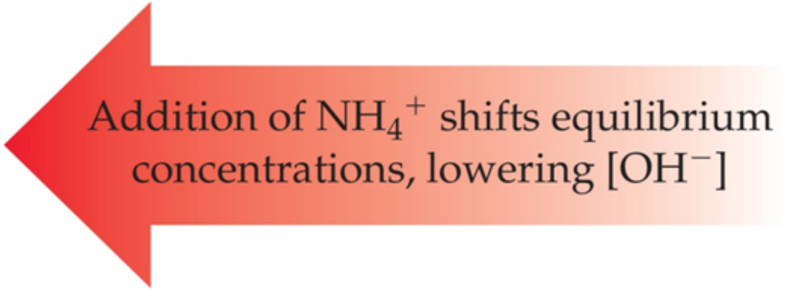


Addition of CH_3COO^- shifts equilibrium concentrations, lowering $[H^+]$

Weak Bases Work the Same Way

- Adding the a weak base will do the same thing.

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



Addition of NH_4^+ shifts equilibrium concentrations, lowering $[OH^-]$

Example: Calculating pH for a Common Ion (1 of 3)

- What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?

Example:
Calculating pH for a Common Ion (1 of 3)

- What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?
- Assume the salt dissociates 100%.
- 0.3 moles sodium acetate = 0.3 moles acetate in 1L, 0.3 M
- Focus on the acetic acid equilibrium.

1) $CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^-(aq) + H_3O^+(aq)$

2) $$K_a = 1.8 \times 10^{-5} = \frac{[H_3O]^+[CH_3COO^-]}{[CH_3OOH]}$$

Calculating pH for a Common Ion (2 of 3)

3) $CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^-(aq) + H_3O^+(aq)$

	CH_3CO_2H	H_3O^+	$CH_3CO_2^-$
Initial (*M*)			
Change (*M*)			
Equilibrium (*M*)			

Calculating pH for a Common Ion (2 of 3)

3) $CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^-(aq) + H_3O^+(aq)$

	CH_3CO_2H	H_3O^+	$CH_3CO_2^-$
Initial (*M*)	0.30	0	0.30
Change (*M*)			
Equilibrium (*M*)			

Calculating pH for a Common Ion (2 of 3)

3) $CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^-(aq) + H_3O^+(aq)$

	CH_3CO_2H	H_3O^+	$CH_3CO_2^-$
Initial (*M*)	0.30	0	0.30
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$(0.30 - x)$	x	$(0.30 + x)$

$$1.8x10^{-5} = \frac{[H_3O]^+[CH_3OO^-]}{[CH_3OOH]}$$

$$1.8x10^{-5} = \frac{x\,(0.3 + x)}{0.3 - x}$$

Can we assume that *x* is so small that:

adding or subtracting it from 0.30 will not matter?

Calculating pH for a Common Ion (3 of 3)

Yes!

$1.8x10^{-5} = \frac{x\,(0.3+x)}{0.3-x}$ becomes: $1.8 \times 10^{-5} = \frac{(x)(0.30)}{(0.30)}$

which results in: $x = 1.8 \times 10^{-5}\text{M} = \left[\text{H}^{+}\right]$

Check: $1.8x10^{-5}$ << 0.3 M

So: $\text{pH} = -\log\left[\text{H}^{+}\right] = 4.74$

Calculating pH for a Common Ion (3 of 3)

- Note!!

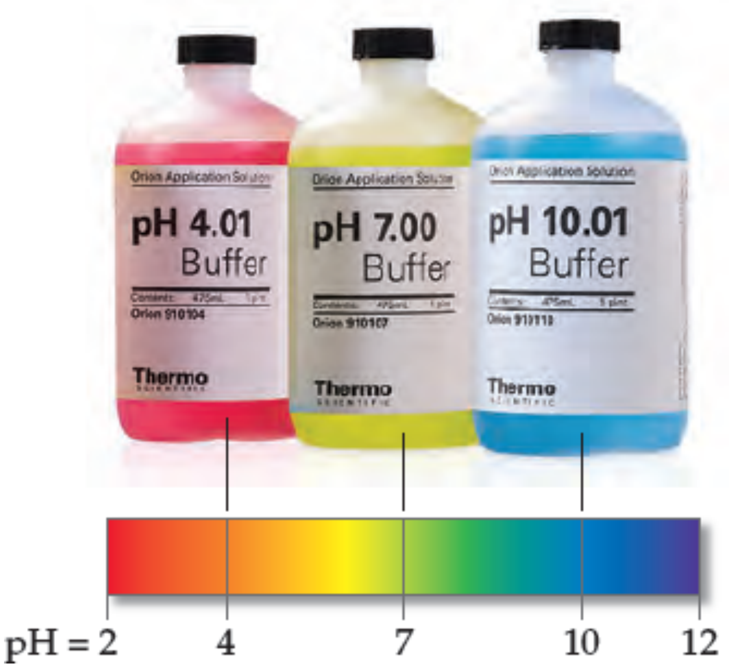
$$CH3COOH(aq) + H_2O(l) \rightleftharpoons CH3COO^{-}(aq) + H_3O^{+}(aq)$$

	CH_3CO_2H	H_3O^+	$CH_3CO_2^-$
Initial (*M*)	0.30	0	0.30
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	0.30	$1.8x10^{-5}$	0.30

Minimal apparent change

17.2 But why do we care about buffers?

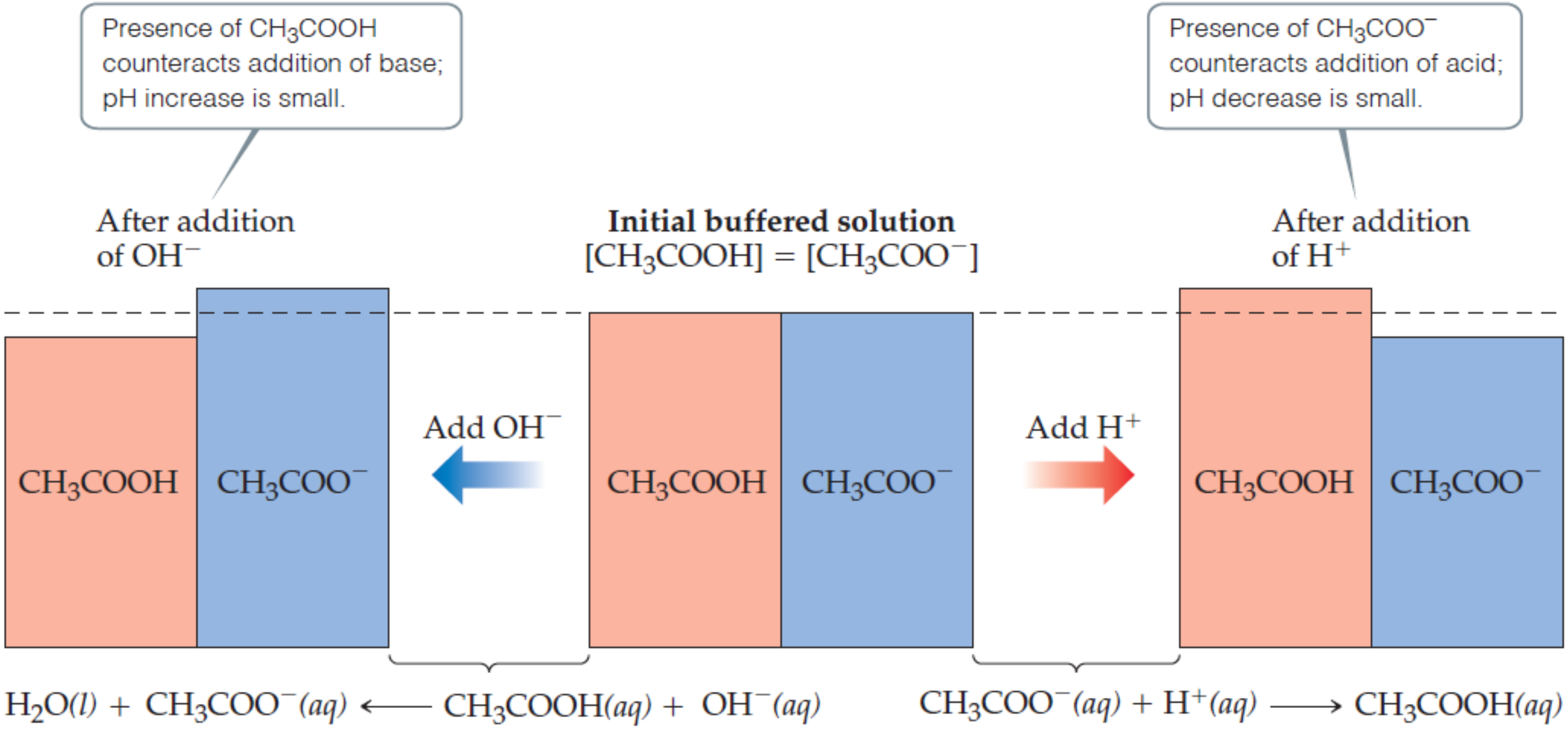
- A mixture of a weak acid and its conjugate base (salt product) **resists changes in pH.**
- But there has to be **enough** of each of them to do it.
- A reasonable buffer:
  - 10^{-3} M or more
  - of **Both AH and A^-**



Ways to Make a Buffer

1) Mix a weak acid and its conjugate base "salt"
   1) Mix HA with A^- (acetic acid and acetate).
2) Mix a weak base and its conjugate acid "salt".
   1) Mix B with HB (NH_3 and NH_4^+)
3) Add strong base to a weak acid
   1) That will make the conjugate base
   2) $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^-(aq) + H_2O$
4) Add strong acid to a weak base
   1) That will make the conjugate acid.
   2) $NH_3 + HCl \rightarrow NH_4^+(aq) + Cl^-(aq)$

How a Buffer Works



Presence of CH_3COOH counteracts addition of base; pH increase is small.

Presence of CH_3COO^- counteracts addition of acid; pH decrease is small.

After addition of OH^-

Initial buffered solution
$[CH_3COOH] = [CH_3COO^-]$

After addition of H^+

$H_2O(l) + CH_3COO^-(aq) \longleftarrow CH_3COOH(aq) + OH^-(aq)$

$CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH(aq)$

- Adding a small amount of acid or base only slightly neutralizes one component of the buffer, so the pH doesn’t change very much.

The Henderson-Hasselback Equation : The equation of buffers

- For a weak acid: $K_a = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$
- Take $-\log$ of both sides:

$$-\log K_a = -\log[\mathrm{H}^+] + -\log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

- Rearrange:

$$-\log[\mathrm{H}^+] = -\log K_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

  - Which is:

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

Deriving the Henderson-Hasselback Equation (2 of 2)

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

- **Henderson–Hasselbalch equation**.
  - Works with any weak acid or base and their respective salts.
  - There are four variables.
    - $[H_3O^+]$
    - K_a
    - [HA]
    - [A-]

Example: Using the Henderson–Hasselback Equation to Find pH

- What is the pH of a buffer that is 0.12 *M* in lactic acid, $\mathrm{CH_3CH(OH)COOH}$, and 0.10 *M* in sodium lactate?

K_a for lactic acid is 1.4×10^{-4}.

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

$$= -\log\left(1.4 \times 10^{-4}\right) + \log\left[\frac{(0.10\,M)}{(0.12\,M)}\right]$$

$$= 3.85 + (-0.08) = 3.77$$

Buffer Concentration vs. Buffer pH

- How does the buffer **concentration** affect pH of solution?

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

- It's the ***ratio*** of acid and conjugate base that determines pH.
- **Not concentration**
- 1M/1M = .01M/.01M
- **Both** have pH=pKa

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- It's the ***ratio*** of acid and conjugate base that determines pH.
- **Not concentration**
- 1M/1M = .01M/.01M
- **Both** have pH=pKa

- **But:** If you add 0.01 M acid to 1M solution, ratio barely changes
  - **So pH barely changes**
- Add 0.01M acid to .01 M solution, ***pH changes a lot.***
- **Buffer capacity**

Buffer pH range.

- Buffers only work within certain pH ranges.
  - Why?
  - What's the range?

$$HA(aq) + B(aq) \rightleftharpoons A^{-}(aq) + BH(aq)$$

- Once all HA is gone,
- $B + H_2O \longrightarrow OH^{-} + BH$
- All the added base makes OH^{-}
- pH changes quickly!

Buffer pH range.

- Buffers only work within certain pH ranges.
  - Why?
  - What's the range?

$$HA(aq) + B(aq) \rightleftharpoons A^-(aq) + BH(aq)$$

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

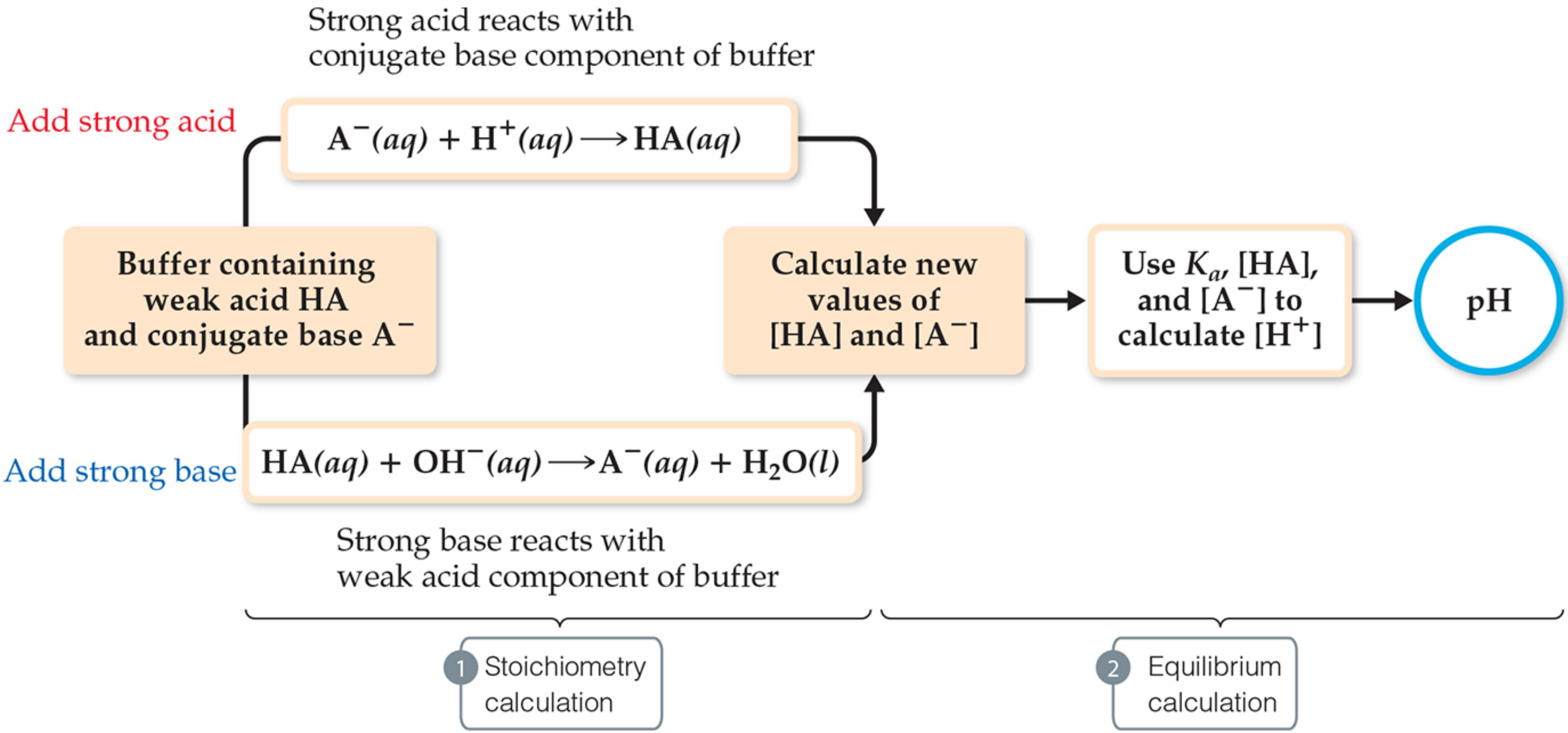
- If $[HA] > 10 \times [A^-]$
- or $[HA] < [A^-] / 10$
- Then $|\log([A^-]/[HA])| > 1$
- Buffering action is poor

Addition of a Strong Acid or a Strong Base to a Buffer (1 of 2)

Addition of the strong acid or base is a neutralization reaction.

1) Calculate like a stoichiometry problem to find $[\text{HA}]$ and $[\text{A}^-]$ when **all** of the added acid or base reacts. This is a limiting agent situation.
2) Use the Henderson–Hasselbalch equation to find pH. The equilibrium calculation is simplified by using this equation.

Addition of a Strong Acid or a Strong Base to a Buffer (2 of 2)



Strong acid reacts with conjugate base component of buffer

Add strong acid

$A^-(aq) + H^+(aq) \longrightarrow HA(aq)$

Buffer containing weak acid HA and conjugate base A^-

Calculate new values of [HA] and $[A^-]$

Use K_a, [HA], and $[A^-]$ to calculate $[H^+]$

pH

Add strong base

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

Strong base reacts with weak acid component of buffer

① Stoichiometry calculation

② Equilibrium calculation

Example of pH Calculation for Buffer after Strong Base Addition (1 of 2)

- A buffer is made by adding 0.30 mol CH_3COOH and 0.30 mol $NaCH_3COO$ to enough water to make 1.00 L. Then 0.020 mol of NaOH is added. What’s the pH?

Example of pH Calculation for Buffer after Strong Base Addition (1 of 2)

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1) Stoichiometry table – limiting reactant calculation

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

Before reaction (mol)			-	
Change (limiting reactant) (mol)			-	
After reaction (mol)				

Example of pH Calculation for Buffer after Strong Base Addition (1 of 2)

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1) Stoichiometry table – limiting reactant calculation

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

Before reaction (mol)	0.300	0.020	-	0.300
Change (limiting reactant) (mol)			-	
After reaction (mol)				

Example of pH Calculation for Buffer after Strong Base Addition (1 of 2)

- A buffer is made by adding 0.30 mol CH_3COOH and 0.30 mol $NaCH_3COO$ to enough water to make 1.00 L.. Then 0.020 mol of NaOH is added. What's the pH?

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$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

Before reaction (mol)	0.300	0.020	-	0.300
Change (limiting reactant) (mol)	–0.020	–0.020	-	+0.020
After reaction (mol)	0.280	0	-	0.320

Example of pH Calculation for Buffer after Strong Base Addition (2 of 2)

2) Henderson–Hasselbalch equation:

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

HA and A^- are in the same solution,

volume for each is the same

molarity ratio = moles ratio

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{n_{HA}}{n_{A^-}}\right) \qquad \mathrm{pH} = 4.74 + \log\left(\frac{0.320}{0.280}\right) = 4.80$$

Contrast Base Addition on pH for Buffer versus Water

Add 5.00 mL of 4.0 M NaOH to a) or b) below

a) 1.000 L of a buffer that is 0.30 M acetate/0.30 M acetic acid.

b) 1.000 L of water

Contrast Base Addition on pH for Buffer versus Water

Add 5.00 mL of 4.0 M NaOH to a)

a) 1.000 L of a buffer that is 0.30 M acetate/0.30 M acetic acid.

b) 1.000 L of water

a)

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

Before reaction (mol)	0.300	0.020	-	0.300
Change (limiting reactant) (mol)	–0.020	–0.020	-	+0.020
After reaction (mol)	0.280	0	-	0.320

$$\text{pH} = 4.74 + \log\left(\frac{0.320}{0.280}\right) = 4.80$$

Contrast Base Addition on pH for Water versus Buffer

b) Pure water

$$(4.0\,\text{mol/L}) \times 5.00 \times 10 - 3\text{L} = 2.0 \times 10^{-2}\,\text{mol}$$

$$2.0 \times 10^{-2}\,\text{mol} / 1.005\text{L} = 0.0199\text{ M}$$

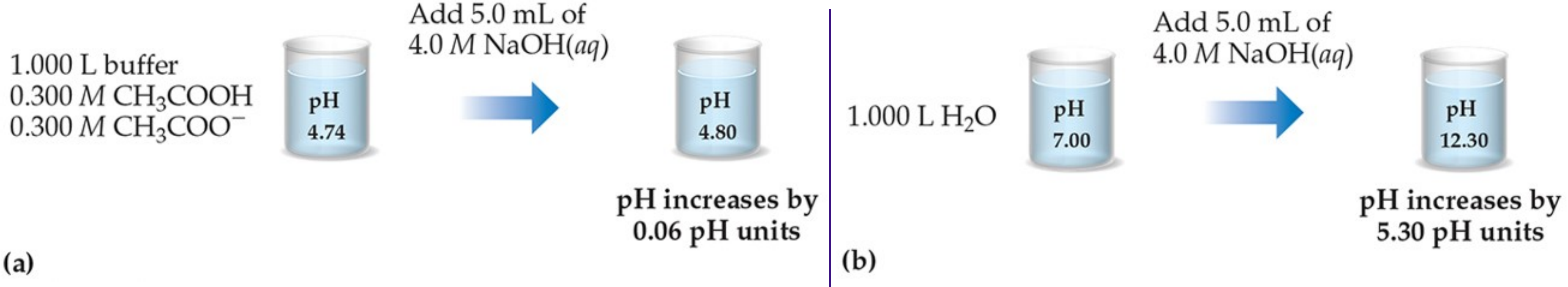
$$\text{pOH} = -\log\left[\text{OH}^-\right] = -\log\,(0.0199) = 2.70$$

$$\text{pH} = 14.00 - 1.70 = \mathbf{12.30}$$

pH change minimized using buffer:

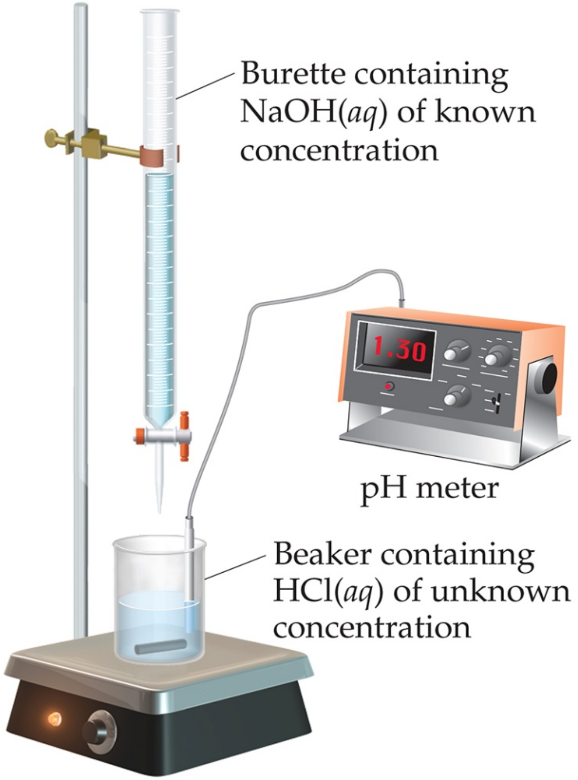
Adding base to buffer: 4.74 to 4.80 **is 0.06 units**

Adding base to water: 7.00 to 12.30 is **5.30 units**



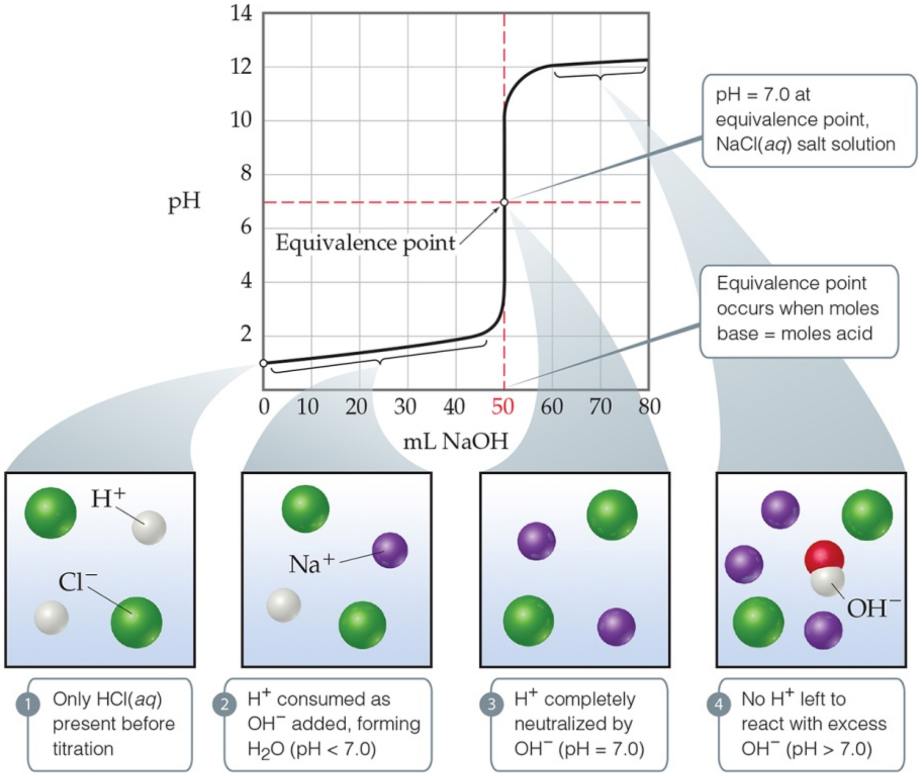
17.3 Acid–Base Titrations

- An acid (or base) solution of **known** concentration
- is slowly added to a base (or acid) solution of **unknown** concentration.
- Addition until the **equivalence point** is reached.
  - amount of acid =amount base.
- Equivalence point seen by monitoring pH change.



Titration of a Strong Acid with a Strong Base

- Plot pH versus mL of strong base.
- From the start to near the equivalence point, the *pH goes up slowly.*
- Just before (and after) the equivalence point, *the pH rises rapidly.*
- At the equivalence point, pH = 7.
- As more base is added, the pH again levels off.



pH = 7.0 at equivalence point, NaCl(*aq*) salt solution

Equivalence point occurs when moles base = moles acid

① Only HCl(*aq*) present before titration

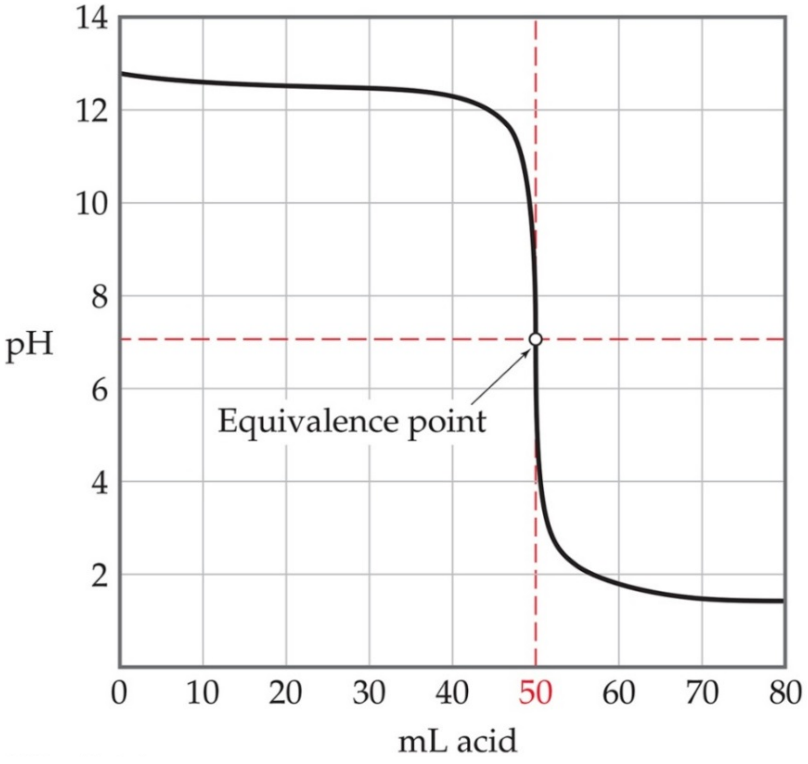
② H^+ consumed as OH^- added, forming H_2O (pH < 7.0)

③ H^+ completely neutralized by OH^- (pH = 7.0)

④ No H^+ left to react with excess OH^- (pH > 7.0)

Titration of a Strong Base with a Strong Acid

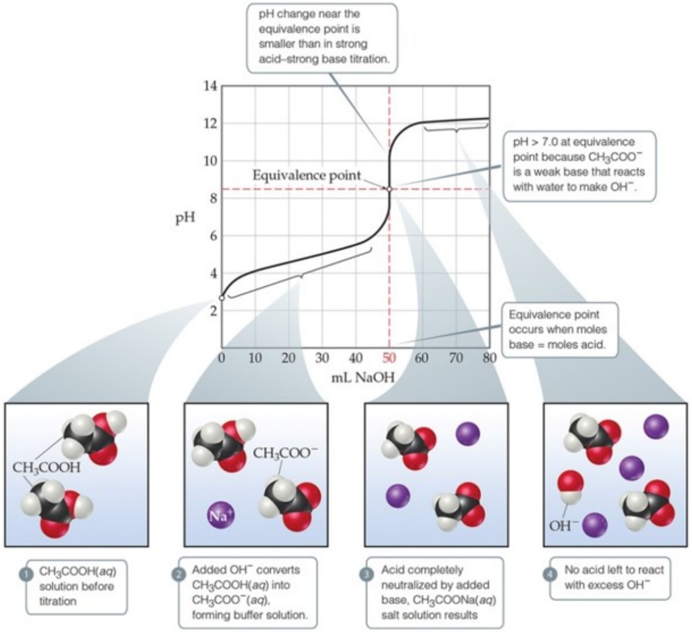
- Start with a high pH (basic solution).
- pH = 7 at the equivalence point.
- Adding more acid, pH levels off.



Titration of a Weak Acid with a Strong Base

- four distinct regions:

1. Initial pH uses K_a calculation.
2. Between initial pH and equivalence point (excess acid) uses limiting reactant then Henderson-Hasselback.
3. At the equivalence point.
4. After the equivalence point (excess strong base).



pH change near the equivalence point is smaller than in strong acid–strong base titration.

pH > 7.0 at equivalence point because CH_3COO^- is a weak base that reacts with water to make OH^-.

Equivalence point occurs when moles base = moles acid.

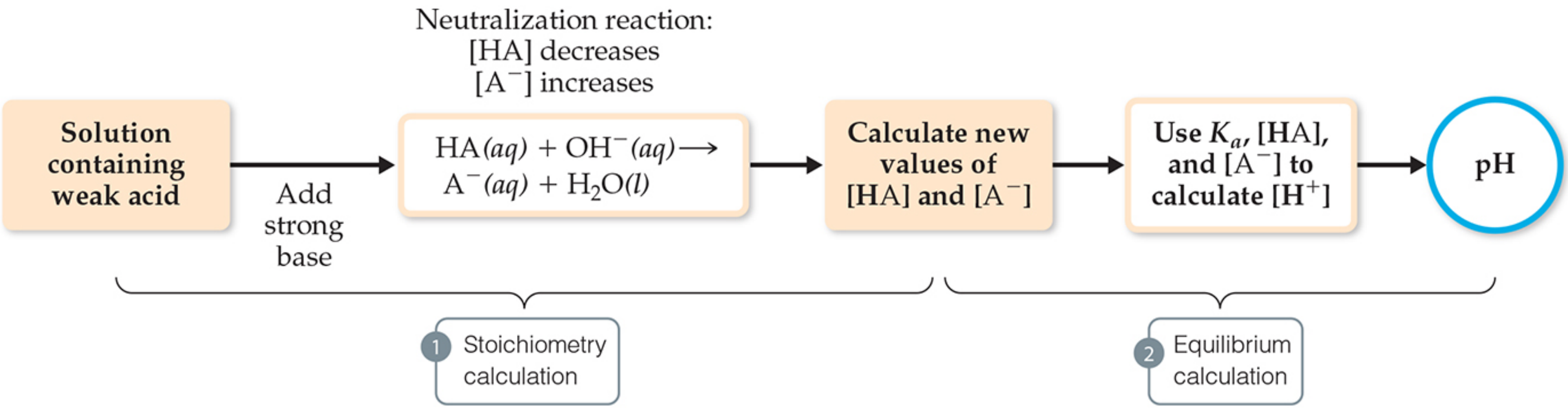
① $CH_3COOH(aq)$ solution before titration

② Added OH^- converts $CH_3COOH(aq)$ into $CH_3COO^-(aq)$, forming buffer solution.

③ Acid completely neutralized by added base, $CH_3COONa(aq)$ salt solution results

④ No acid left to react with excess OH^-

Calculating pH When a Weak Acid is Neutralized—Excess Acid



Neutralization reaction:
[HA] decreases
$[A^-]$ increases

Solution containing weak acid

Add strong base

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

Calculate new values of [HA] and $[A^-]$

Use K_a, [HA], and $[A^-]$ to calculate $[H^+]$

pH

① Stoichiometry calculation

② Equilibrium calculation

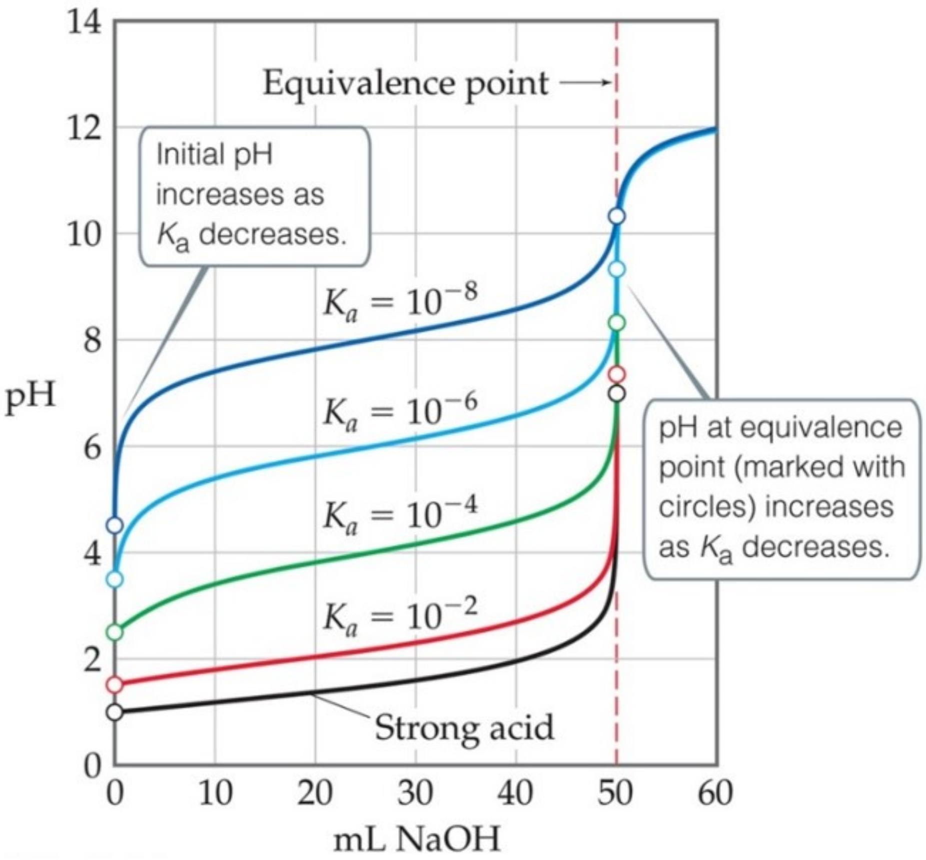
- Calculate the moles of weak acid and strong base.
- Write the neutralization reaction.
- Track limiting reactant change using the table. Gives you moles of remaining acid and the moles of anion formed.
- Substitute into the Henderson-Hasselbalch equation to find pH.

Calculating pH for titrating a Weak Acid With a Strong Base

- The pH is **Not 7.00** at the equivalence point.
- Calculate the moles of weak acid and strong base.
- Write the neutralization equation.
- Substitute into table.
- **Titration point:** moles strong base = moles weak acid.
  - No more HA, only A^-
- Find molarity of weak acid using the new volume.
- Use the equations of either the K_b of the anion or the K_a of the weak acid to determine the pH (like in Chapter 16).

Ways That a Weak Acid Titration Differs from a Strong Acid Titration

1) A solution of **weak** acid has a **higher** initial pH than a **strong** acid.
2) The pH change is smaller
3) The pH midway to equivalence point = pK_a
4) pH at the equivalence point is **greater than 7** for a weak acid.

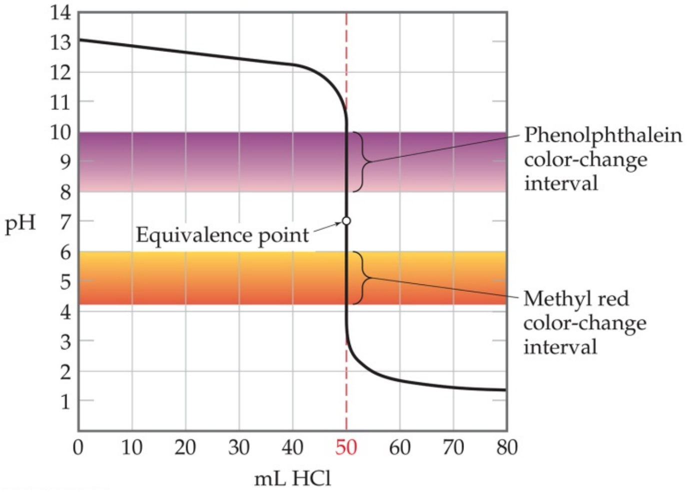


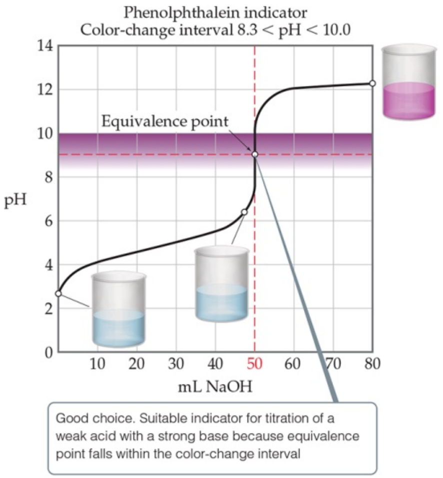
Initial pH increases as K_a decreases.

pH at equivalence point (marked with circles) increases as K_a decreases.

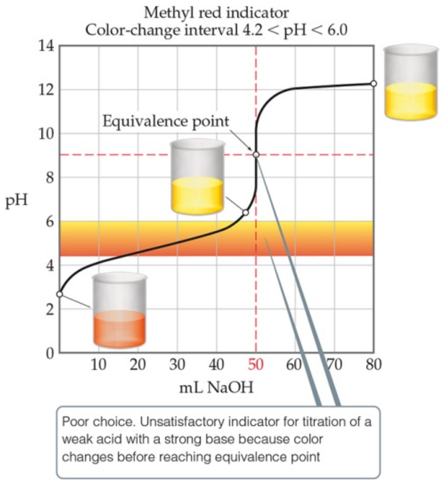
Titrations with an Acid–Base Indicator

- Indicators are weak acids that have a different color than their conjugate base form.
  - Each indicator has its own pH range over which it changes color.
  - Can be used to determine the equivalence point in a titration as long as it changes color at the pH of the equivalence point.





Good choice. Suitable indicator for titration of a weak acid with a strong base because equivalence point falls within the color-change interval



Poor choice. Unsatisfactory indicator for titration of a weak acid with a strong base because color changes before reaching equivalence point

Let’s calculate the pH at the equivalence point for a weak acid/strong base titration.

- Calculate the pH at the equivalence point in the titration of 50 mL of 0.1 M acetic acid with 0.1 M NaOH.

Let’s calculate the pH at the equivalence point for a weak acid/strong base titration.

- Calculate the pH at the equivalence point in the titration of 50 mL of 0.1 M acetic acid with 0.1 M NaOH.
- $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COO^-(aq) + H_2O + Na^+(aq)$
- 50 mL 0.1M. 0.1 M
- 0.05L x (0.1mole/L)= 0.005 moles

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- 50 mL 0.1M. 0.1 M
- 0.05L x (0.1mole/L)= 0.005 moles

Initial:	0.005 moles HA	0.005 moles OH-	0 A^-
Change:	-0.005 moles	-0.005 moles	+0.005
Equil.:	0	0	**0.005** moles

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- 50 mL 0.1M. 0.1 M
- 0.05L x (0.1mole/L)= 0.005 moles
- Initial: 0.005 moles HA 0.005 moles OH- 0 A^-
- Change: -0.005 moles -0.005 moles +0.005
- Equil.: 0 0 **0.005**

- Important!!! Now convert “**moles**” into ”**<u>Molarity</u>**” for next step
- Total volume of solution at equivalence point: 100 mL = 0.1 L
- **0.005 moles** CH_3COO^- in **0.1 L** solution = **0.05 M**

Let’s calculate the pH at the equivalence point for a weak acid/strong base titration.

- $CH_3COO^-(aq) + H_2O \longrightarrow CH_3COOH(aq) + OH^-$
- I: **0.05 M** 0 0
- C: -x x x
- E: 0.05-x x x

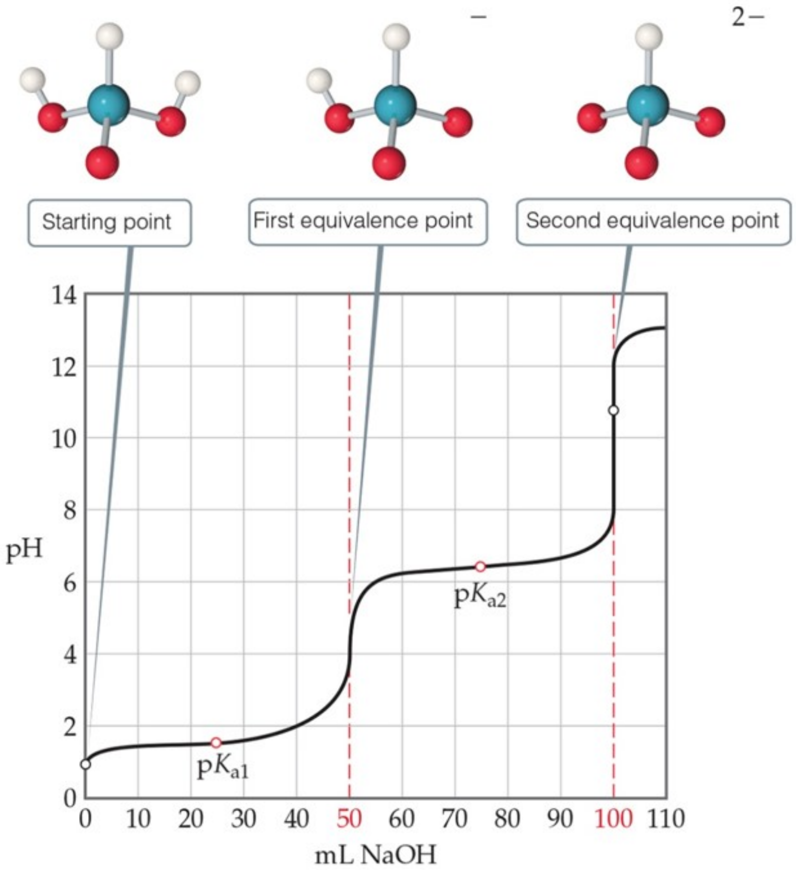
$$K_b = K_w / K_a = \left(1.0 \times 10^{-14}\right) / \left(1.8 \times 10^{-5}\right) = 5.6 \times 10^{-10}.$$

$$K_b = \frac{\left[CH_3COOH\right]\left[OH^-\right]}{\left[CH_3COO^-\right]} = \frac{(x)(x)}{0.0500 - x} = 5.6 \times 10^{-10}$$

$x = \left[OH^-\right] = 5.3 \times 10^{-6}\ M,$ which gives pOH = 5.28 and pH = 8.72

Titrations of Polyprotic Acids

- There are multiple equivalence points.
- Treat each step separately with their corresponding polyanions and K_a.
- The halfway to each equivalence point gives the pK_a
- The concentration of the dianion is always equal to K_{a2}.



17.4 Solubility Equilibria

- Many Ionic compounds are not very soluble in water.

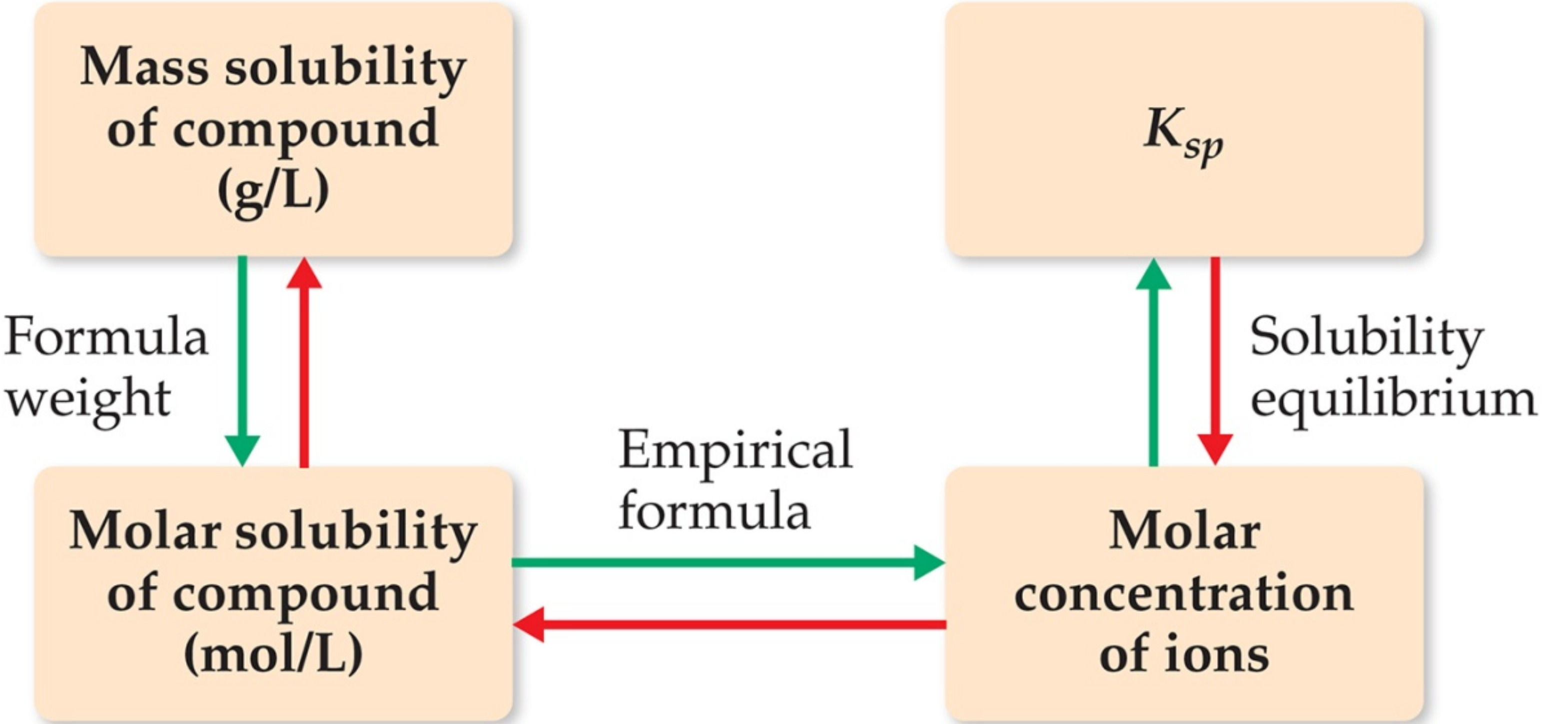
- The equilibrium constant expression is called the **solubility-product constant**. It is represented as
- K_{sp}
- $Ba_3(PO_4)(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4^{-3}(aq)$

$$K_{sp} = \left[Ba^{2+}\right]^3 \left[PO_4^{3-}\right]^2$$

Solubility and K_{sp} (1 of 2)

- K_{sp} is **not** the same as solubility.
- **Solubility:** *Maximum amount* that can dissolve.
- Common units for solubility:
  - Grams per liter $\left(\text{g/L}\right)$
  - Moles per liter $\left(\text{mol/L}\right)$

Solubility and K_{sp} (2 of 2)



Mass solubility of compound (g/L)

Formula weight

Molar solubility of compound (mol/L)

Empirical formula

Molar concentration of ions

Solubility equilibrium

K_{sp}

Calculating Solubility from K_{sp} (1 of 2)

- The K_{sp} for CaF_2 is 3.9×10^{-11} at 25 °C. What is its molar solubility?
  1) $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^{-}(aq)$
  2) $K_{sp} = \left[Ca^{2+}\right]\left[F^{-}\right]^2 = 3.9 \times 10^{-11}$
  3)

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

Initial concentration (*M*)	-	0	0
Change (*M*)	-	$+x$	$+2x$
Equilibrium concentration (*M*)	-	X	$2x$

Calculating Solubility from K_{sp} (2 of 2)

- Substitute the equilibrium concentration values from the table into the solubility-product equation:

$$3.9 \times 10^{-11} = (x)(2x)^2 = 4x^3$$

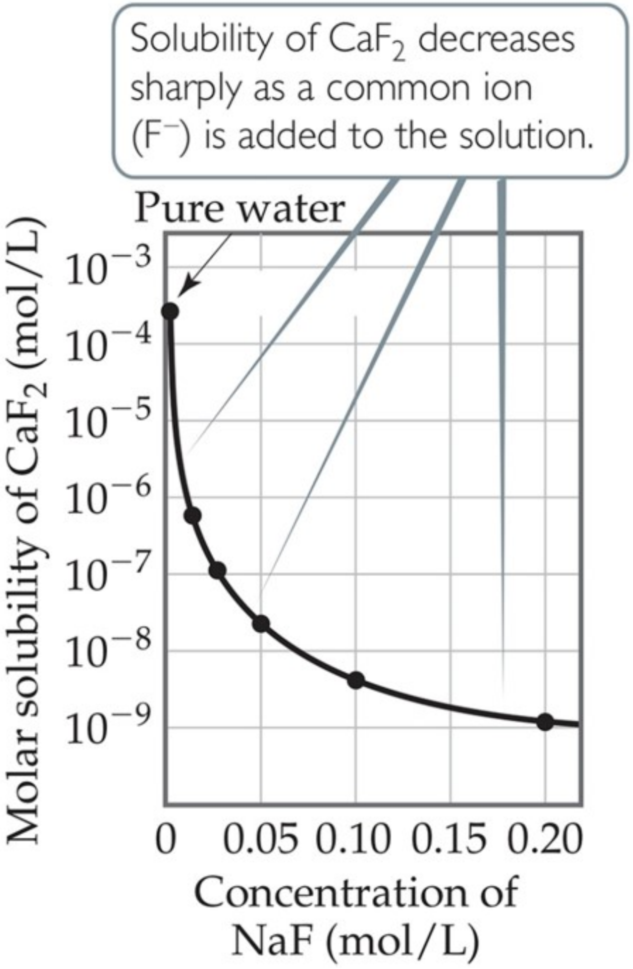
$$x = 2.1 \times 10^{-4}\ M$$

For Mass solubility in g/mol: Multiply by molar mass.

$2.1\text{x}10^{-4}$ mol/L (78.1g/mol) = 0.0164 g/L

17.5 Factors That Affect Solubility

- **The common-ion effect**:
  - If one of the ions is added
    - ***Independently***
  - ***The salt will be even less soluble.***
  - For CaF_2,
    - Add either Ca^{2+} or F^-
    - CaF_2 less soluble.



Solubility of CaF_2 decreases sharply as a common ion (F^-) is added to the solution.

Calculating Solubility with a Common Ion (1 of 2)

- What is the molar solubility CaF_2 in $0.010\ M\ Ca(NO_3)_2$?

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

2) $K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$

3)

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

Initial concentration (*M*)	-	0.010	0
Change (*M*)	-	$+x$	$+2x$
Equilibrium concentration (*M*)	-	$(0.010 + x)$	$2x$

Calculating Solubility with a Common Ion (2 of 2)

4) Substitute the equilibrium concentration values from the table into the solubility-product equation:

$$3.9 \times 10^{-11} = (0.010 + x)(2x)^2$$

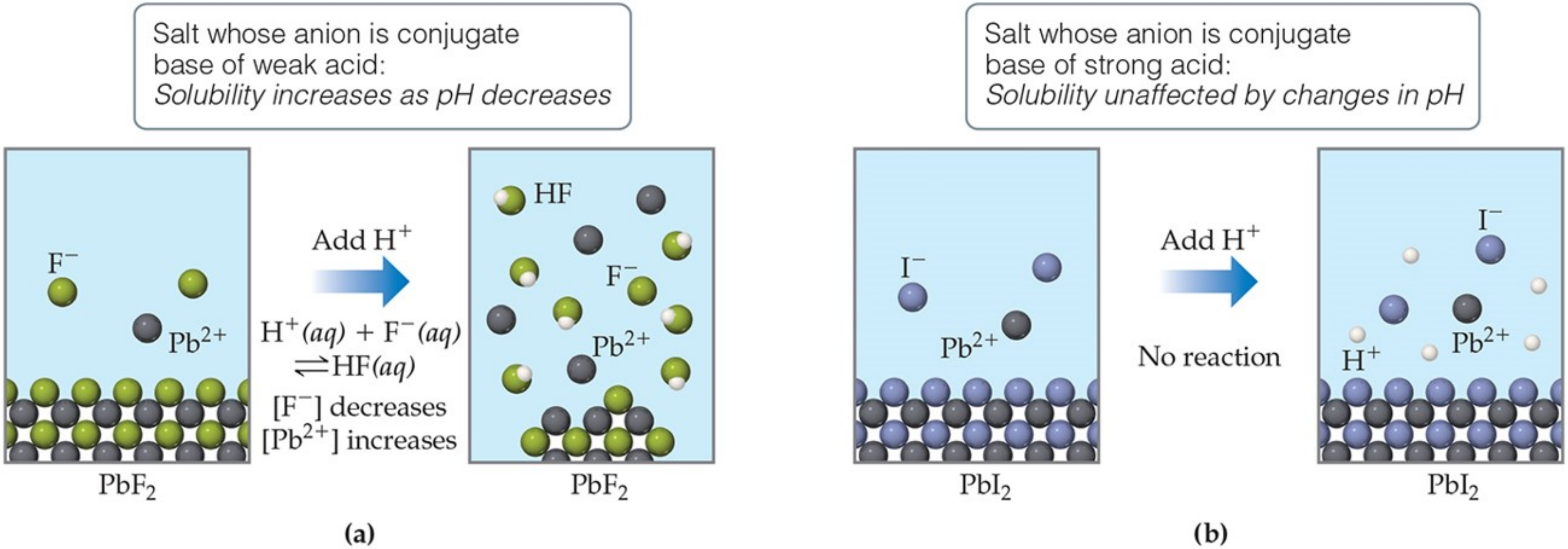
(We assume that $x << 0.010,$ so that $0.010 + x = 0.010!$)

$$3.9 \times 10^{-11} = (0.010)(2x)^2$$

$$x = 3.1 \times 10^{-5}\,M$$

Solubility can be effected by pH

- When?
  - When the **anion** is a weak base…(conj. of weak acid)
    - Adding acid reduces anion.
    - $F^- + HA \rightleftharpoons HF + A^-$



Sample Exercise 17.15 Predicting the Effect of Acid on Solubility (1 of 4)

Which of these substances are more soluble in acidic solution than in basic solution? **(a)** $Ni(OH)_2(s)$ **(b)** $CaCO_3(s)$ **(c)** $BaF_2(s)$ **(d)** $AgCl(s)$

(**a**) $Ni(OH)_2(s)$ is more soluble in acidic solution because of the basicity of OH^-; the H^+ reacts with the OH^- ion, forming water:

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

$$\underline{2OH^- + 2HA \rightleftharpoons 2H_2O(l) + 2A^-(aq)}$$

$$Ni(OH)_2(s) + 2HA(aq) \rightleftharpoons Ni^{2+} + 2H_2O(l) + 2A^-(aq)$$

Sample Exercise 17.15 Predicting the Effect of Acid on Solubility (1 of 4)

(**b**) $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

$CO_3^{2-}(aq) + 2H^+ \rightleftharpoons H_2CO_3$

$H_2CO_3(aq) \rightleftharpoons CO_2(g) + H_2O(l)$

$CaCO_3(s) + 2H^+(aq) \qquad CO_2(g) + H_2O(l) + Ca^{2+}(aq)$

(c) $BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$

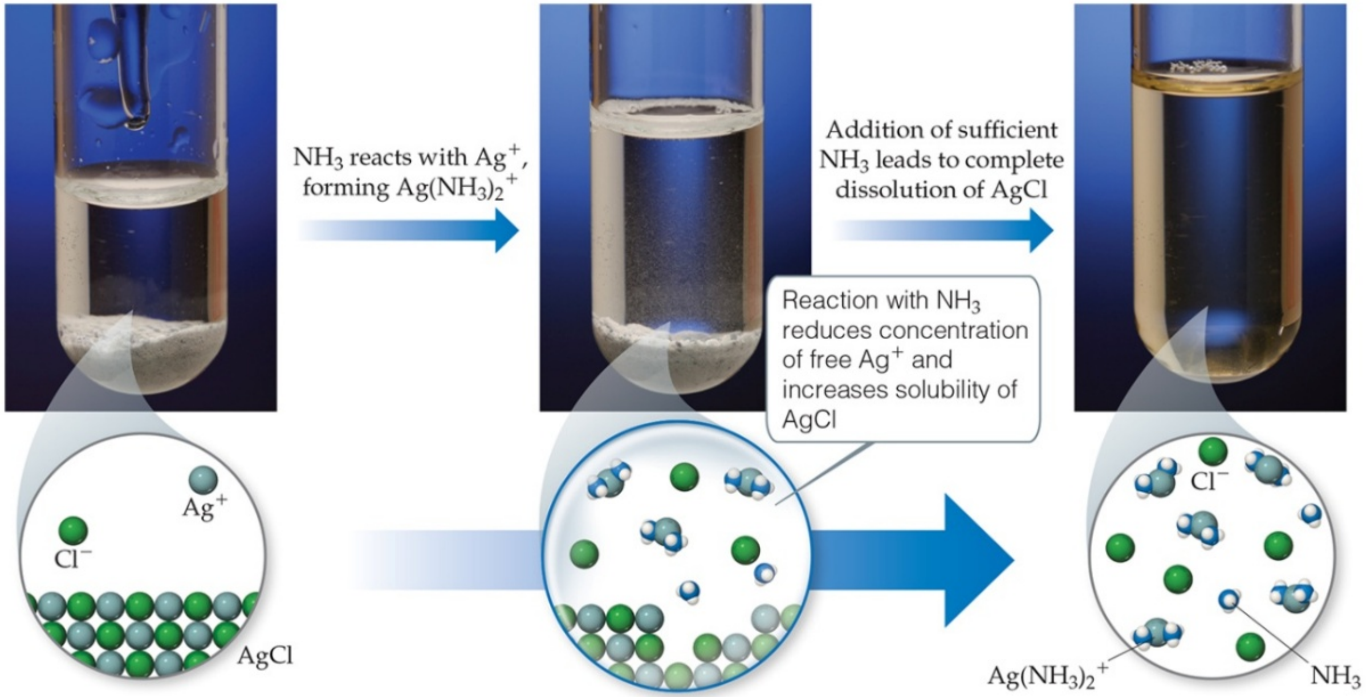
$2F^-(aq) + 2H^+ + 2A^- \rightleftharpoons 2HF + 2A^-(aq)$

$BaF_2(s) + 2HA \rightleftharpoons 2HF + Ba^{2+}(aq) + 2A^-(aq)$

(d) $Cl^-(aq) + H^+(aq) \rightleftharpoons Cl^-(aq) + H^+(aq)$: ***acid does nothing.***

Complex Ion Formation (1 of 4)

- Metal ions can act as Lewis acids and form **complex ions** with Lewis bases in the solvent.
- The formation of these complex ions can increase the solubility of these salts.



NH_3 reacts with Ag^+, forming $Ag(NH_3)_2{}^+$

Addition of sufficient NH_3 leads to complete dissolution of AgCl

Reaction with NH_3 reduces concentration of free Ag^+ and increases solubility of AgCl

$$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq) + Cl^-(aq)$$

Complex Ion Formation (2 of 4)

- Silver chloride is insoluble. It has a K_{sp} of 1.6×10^{-10}.
- In the presence of NH_3, the solubility greatly increases because Ag^+ will form a complex ion with NH_3.

$$K_f = 1.7 \times 10^7$$

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

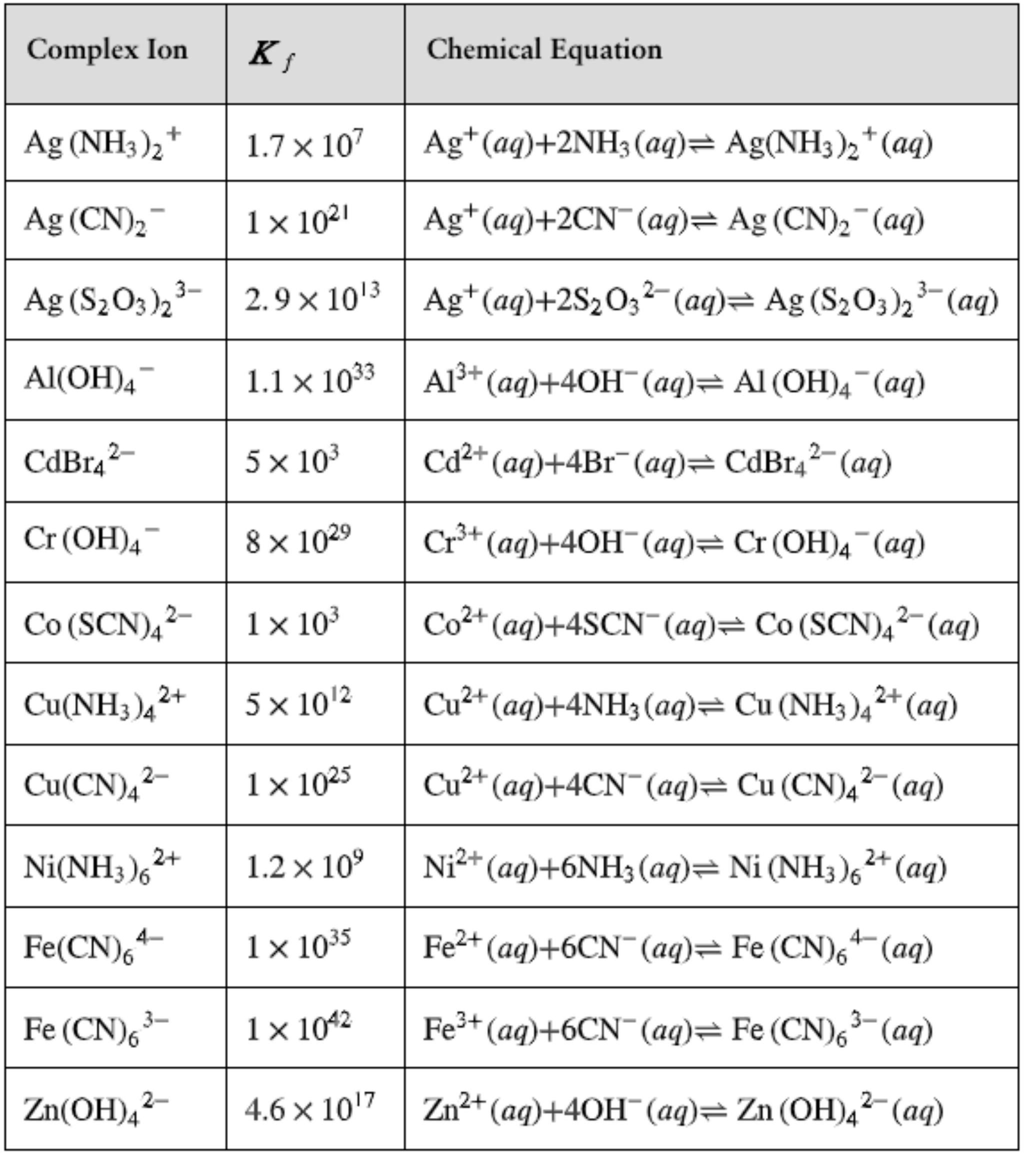
$$\underline{Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)}$$

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

$$K_f\left(Ag(NH_3)_2^+\right) = \frac{\left[Ag(NH_3)_2\right]^+}{\left[Ag^+\right][NH_3]^2} = 1.7 \times 10^7$$

Complex Ion Formation (3 of 4)

Table 17.1 Formation Constants for Some Metal Complex Ions in Water at 25 °C



Complex Ion	K_f	Chemical Equation
$Ag(NH_3)_2^+$	1.7×10^7	$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
$Ag(CN)_2^-$	1×10^{21}	$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$
$Al(OH)_4^-$	1.1×10^{33}	$Al^{3+}(aq) + 4OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$
$CdBr_4^{2-}$	5×10^3	$Cd^{2+}(aq) + 4Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$
$Cr(OH)_4^-$	8×10^{29}	$Cr^{3+}(aq) + 4OH^-(aq) \rightleftharpoons Cr(OH)_4^-(aq)$
$Co(SCN)_4^{2-}$	1×10^3	$Co^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons Co(SCN)_4^{2-}(aq)$
$Cu(NH_3)_4^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$
$Cu(CN)_4^{2-}$	1×10^{25}	$Cu^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq)$
$Ni(NH_3)_6^{2+}$	1.2×10^9	$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$
$Fe(CN)_6^{4-}$	1×10^{35}	$Fe^{2+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq)$
$Fe(CN)_6^{3-}$	1×10^{42}	$Fe^{3+}(aq) + 6CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-}(aq)$
$Zn(OH)_4^{2-}$	4.6×10^{17}	$Zn^{2+}(aq) + 4OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$

Sample Exercise 17.16 Evaluating an Equilibrium Involving a Complex Ion (1 of 5)

Calculate the equilibrium concentration of Ag^+ when concentrated NH_3 is added to 0.01 M $AgNO_3$ solution to give equilibrium concentration $[NH_3]=0.20$ M

$Ag^+ + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$ $K = (1.7x10^7)$

$Ag(NH_3)_2^+(aq) \rightleftharpoons Ag^+ + 2NH_3(aq)$ $K = 1/(1.7x10^7)= 5.9x10^{-8}$

Sample Exercise 17.16 Evaluating an Equilibrium Involving a Complex Ion (1 of 5)

Calculate the equilibrium concentration of Ag^+ when concentrated NH_3 is added to 0.01 M $AgNO_3$ solution to give equilibrium concentration $[NH_3]=0.20$ M

$$Ag^+ + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K = (1.7x10^7)$$

$$Ag(NH_3)_2^+(aq) \rightleftharpoons Ag^+ + 2NH_3(aq) \qquad K = 1/(1.7x10^7)= 5.9x10^{-8}$$

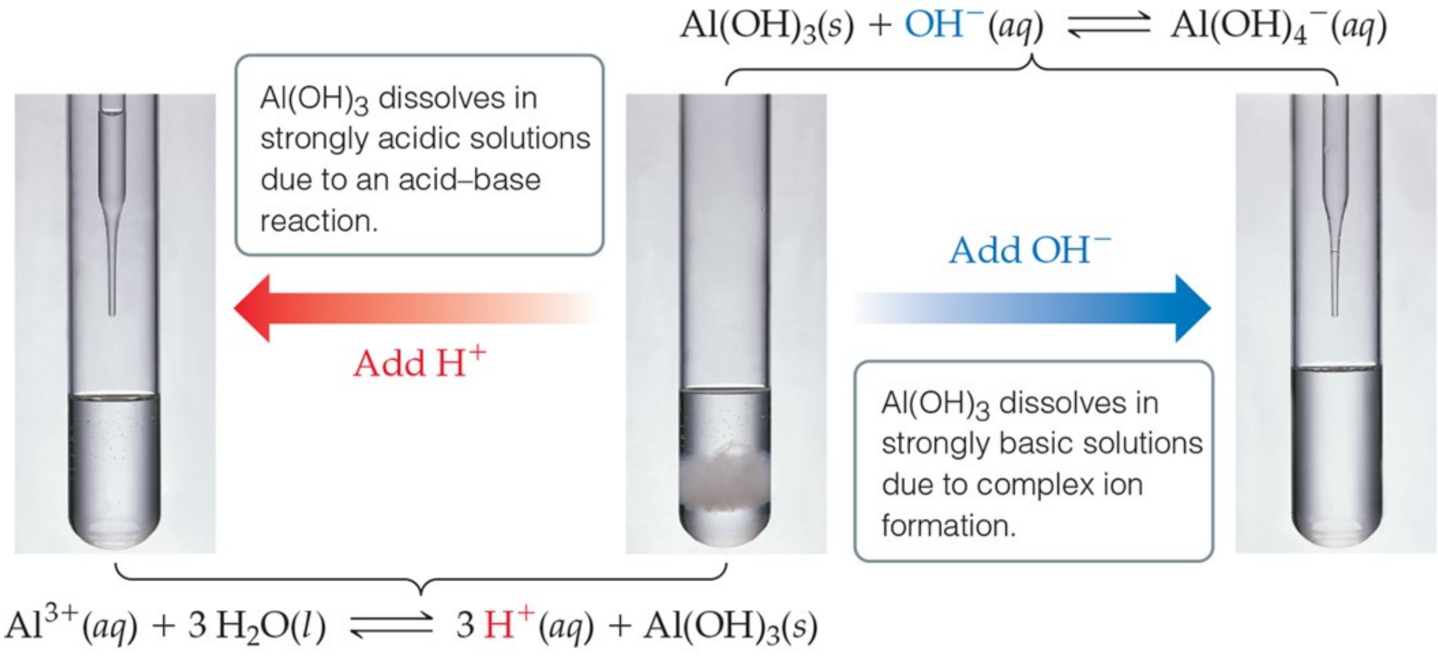
	$AgNH_3^+(aq)$	$Ag^+(aq)$ +	$NH_3(aq)$
Initial (*M*)	0.010	0	---
Change (*M*)	-*x*	+*x*	---
Equilibrium (*M*)	0.010-x	*x*	0.20

$$\frac{\left[Ag^+\right][NH_3]^2}{\left[Ag(NH_3)_2^+\right]} = \frac{(x)(0.20)^2}{0.010} = 5.9\times10^{-8}$$

$$x = 1.5\times10^{-8}\ M = \left[Ag^+\right]$$

Amphoterism

- **Amphoteric oxides and hydroxides**
  - Insoluble in water, but soluble in strong acids or base, because they can act either as acids or bases.
- Examples: Al^{3+}, Cr^{3+}, Zn^{2+}, and Sn^{2+}.



$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$$

Al(OH)$_3$ dissolves in strongly acidic solutions due to an acid–base reaction.

Al(OH)$_3$ dissolves in strongly basic solutions due to complex ion formation.

$$Al^{3+}(aq) + 3\,H_2O(l) \rightleftharpoons 3\,H^+(aq) + Al(OH)_3(s)$$

17.6 Precipitation and Ion Separation

- To decide if precipitation will occur, calculate the reaction quotient, *Q*, and compare it to K_{sp}.
- *Q* uses the given conditions and has the same form as the *K* expression.
  - If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated.
  - If $Q < K_{sp}$, more solid can dissolve, no precipitate forms.
  - If $Q > K_{sp}$, a precipitate will form.

Sample Exercise 17.17 Predicting Whether a Precipitate Forms (1 of 3)

Does a precipitate form when 0.10 L of $8.0 \times 10^{-3}\ M\ \mathrm{Pb(NO_3)_2}$ is added to 0.40 L of $5.0 \times 10^{-3}\ M\ \mathrm{Na_2SO_4}$?

$NaNO_3$ is soluble.

$PbSO_4$ has $K_{sp} = 6.3 \times 10^{-7}$ So, we need to find out

Sample Exercise 17.17 Predicting Whether a Precipitate Forms (2 of 3)

Solve

When the two solutions are mixed, the volume is 0.10 L + 0.40 L = 0.50 L. The number of moles of Pb^{2+} in 0.10 L of $8.0 \times 10^{-3}\ M\ \text{Pb(NO}_3\text{)}_2$ is:

$$(0.10\ \cancel{\text{L}})\left(\frac{8.0 \times 10^{-3}\ \text{mol}}{\cancel{\text{L}}}\right) = 8.0 \times 10^{-4}\ \text{mol}$$

The concentration of Pb^{2+} in the 0.50-L mixture is therefore:

$$\left[\text{Pb}^{2+}\right] = \frac{8.0 \times 10^{-4}\ \text{mol}}{0.50\ \text{L}} = 1.6 \times 10^{-3}\ M$$

The number of moles of $\text{SO}_4{}^{2-}$ in 0.40 L of $5.0 \times 10^{-3}\ M\ \text{Na}_2\text{SO}_4$ is:

$$(0.40\ \cancel{\text{L}})\left(\frac{5.0 \times 10^{-3}\ \text{mol}}{\cancel{\text{L}}}\right) = 2.0 \times 10^{-3}\ \text{mol}$$

Sample Exercise 17.17 Predicting Whether a Precipitate Forms (3 of 3)

Therefore: $\left[SO_4^{2-}\right] = \dfrac{2.0 \times 10^{-3}\ \text{mol}}{0.50\ \text{L}} = 4.0 \times 10^{-3}\ M$

and: $Q = \left[Pb^{2+}\right]\left[SO_4{}^{2-}\right] = \left(1.6 \times 10^{-3}\right)\left(4.0 \times 10^{-3}\right) = 6.4 \times 10^{-6}$

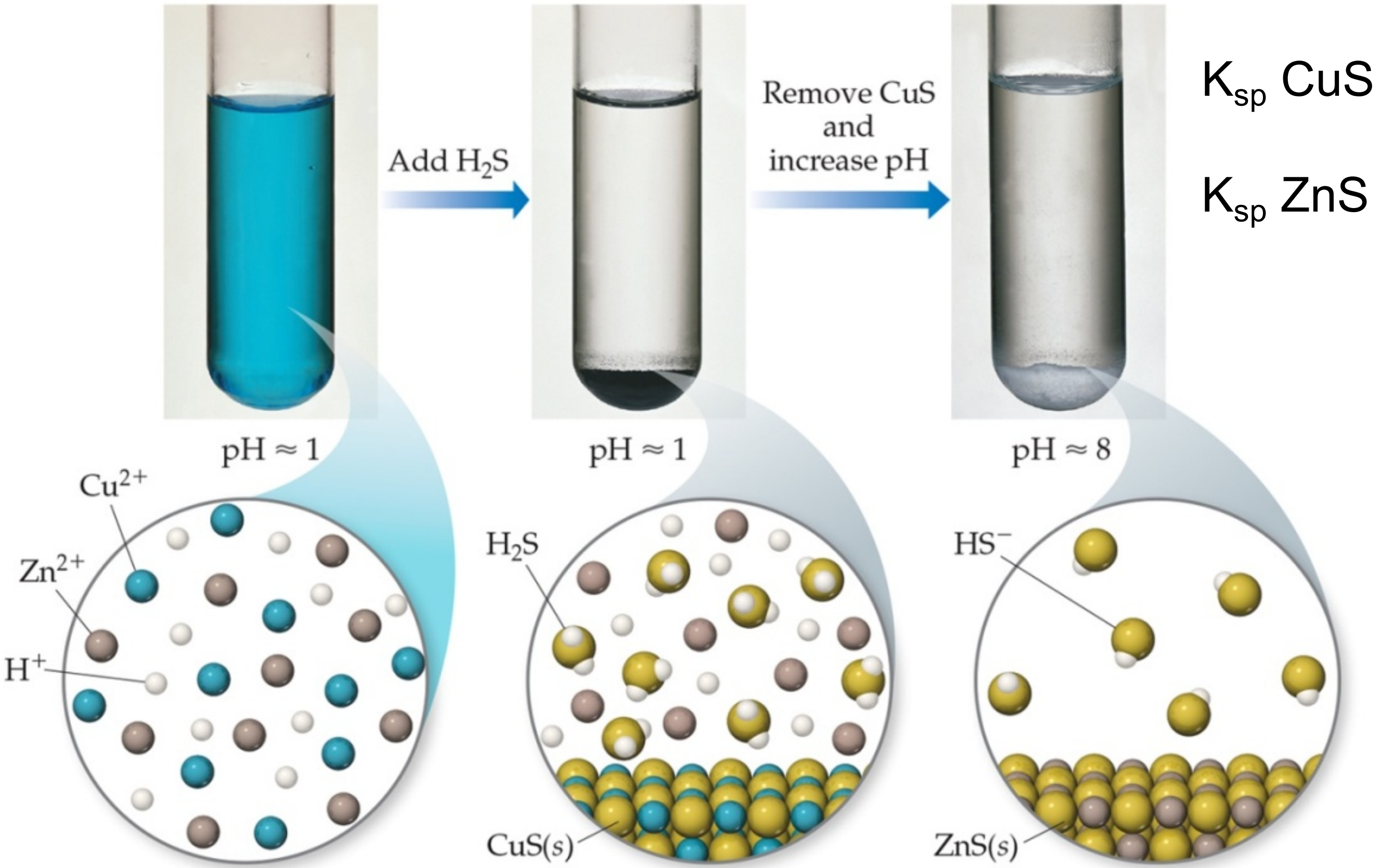
Because $Q > K_{sp}$, $PbSO_4$ precipitates.

Practice Exercise

Does a precipitate form when 0.050 L of $2.0 \times 10^{-2} M$ NaF is mixed with 0.010 L of $1.0 \times 10^{-2}\ M\ Ca(NO_3)_2$?

Selective Precipitation of Ions

- Ions can be separated from solution based on their solubilities in the presence of different ions.



Solution containing $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$

When H_2S is added to a solution whose pH exceeds 0.6, CuS precipitates

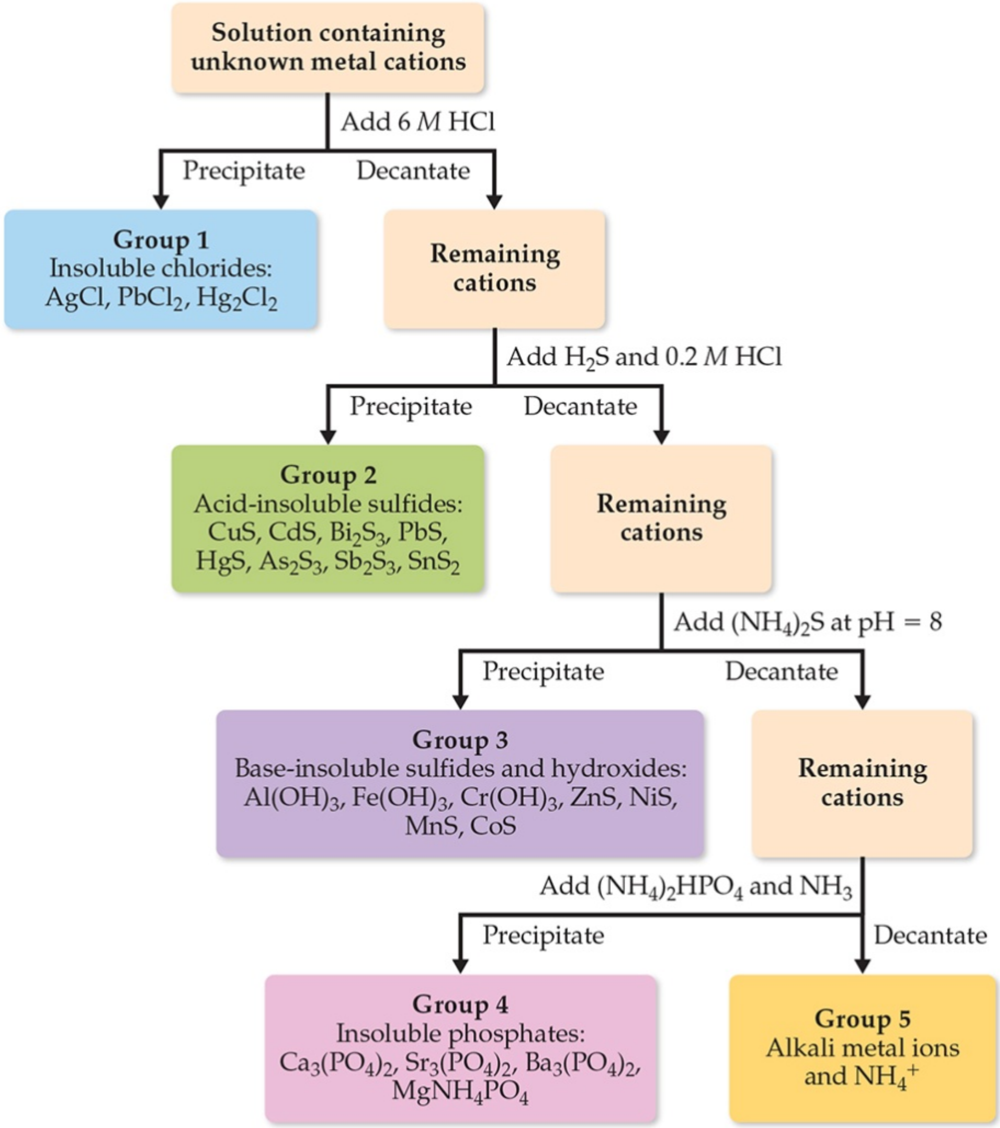
After CuS is removed, the pH is increased, allowing ZnS to precipitate

K_{sp} CuS = 6 x 10^{-37}

K_{sp} ZnS = s x 10^{-25}

17.7 Qualitative Analysis of Ions

One can use differences in solubilities of salts to separate ions in a mixture. This has been used for qualitative analysis of the presence of ions in a solution. A new application is recovery of metal ions from batteries used in electric vehicles.



Solution containing unknown metal cations

Add 6 *M* HCl

Precipitate

Decantate

Group 1
Insoluble chlorides:
$AgCl$, $PbCl_2$, Hg_2Cl_2

Remaining cations

Add H_2S and 0.2 *M* HCl

Precipitate

Decantate

Group 2
Acid-insoluble sulfides:
CuS, CdS, Bi_2S_3, PbS, HgS, As_2S_3, Sb_2S_3, SnS_2

Remaining cations

Add $(NH_4)_2S$ at pH = 8

Precipitate

Decantate

Group 3
Base-insoluble sulfides and hydroxides:
$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, ZnS, NiS, MnS, CoS

Remaining cations

Add $(NH_4)_2HPO_4$ and NH_3

Precipitate

Decantate

Group 4
Insoluble phosphates:
$Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ba_3(PO_4)_2$, $MgNH_4PO_4$

Group 5
Alkali metal ions and NH_4^+