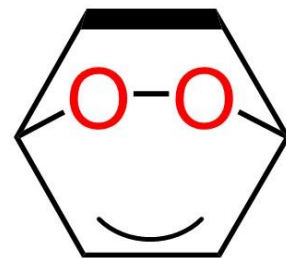# CHEM103
General Chemistry

Chapter 17: Additional Aspects of Aqueous Equilibria

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Homeworks 15-16

Homework 15
Due date: 7th Dec. (Wed)

Homework 16
Due date: 14th Dec. (Wed)

Acids
and
Bases

Review on Chapter 16

Arrhenius/Brønsted/Lewis acids & bases

Conjugate acids and bases

Amphiprotic, autoionization, ion product constant (K_w)

Acid and base strength (pH), acid dissociation constant (K_a or pK_a), base dissociation constant (K_b or pK_b), percent ionization

Polyprotic acids, binary acids, oxyacids, zwitterion

Acids
and
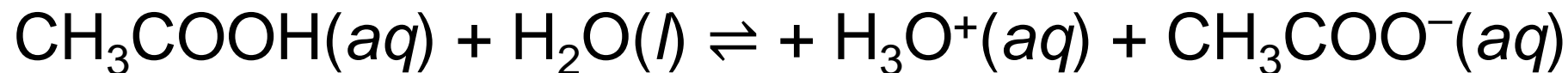Bases

Outline of Chapter 17

The common-ion effect

Buffer solution, Henderson–Hasselbalch equation

Solubility equilibria, solubility-product constant (K_{sp}), complex ion formation, amphoterism

Acids
and
Bases

The Common-Ion Effect (同离子效应)

• Acetic acid is a weak acid:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons + H_3O^+(aq) + CH_3COO^-(aq)$$

• The **addition of acetate** from a **strong electrolyte** sodium acetate in an acetic acid solution will **shift the left side** of the equilibrium, according to Le Châtelier's Principle:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons + H_3O^+(aq) + CH_3COO^-(aq)$$
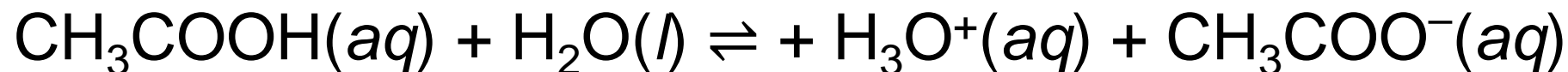
Addition of CH_3COO^- shifts equilibrium concentrations, lowering $[H^+]$

Acids and Bases

The Common-Ion Effect (同离子效应)

- *"The extent of **ionization** of a **weak electrolyte** is **decreased** by **adding** to the solution a **strong electrolyte** that has an **ion in common** with the weak electrolyte."*

- This affects acid–base **equilibria**.

- This also affects **solubility**.

Acids
and
Bases

An Acid–Base Example

• 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?

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
$$K_a = [H^+][CH_3COO^-]/[CH_3COOH] = 1.8 \times 10^{-5}$$
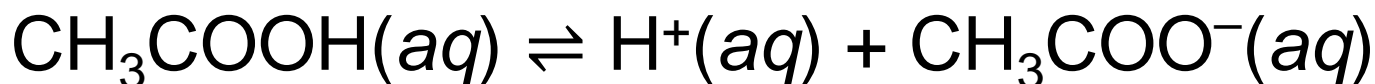
	$CH_3COOH(aq)$ $\rightleftharpoons$	$H^+(aq)$ $+$	$CH_3COO^-(aq)$
Initial (M)	0.30	0	0.30
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(0.30 - x)$	x	$(0.30 + x)$

Acids
and
Bases

$$1.8 \times 10^{-5} = (x)(0.30 + x)/(0.30 - x)$$

Assume that adding or subtracting x from 0.30 will not change 0.30 enough to matter and the equation becomes:

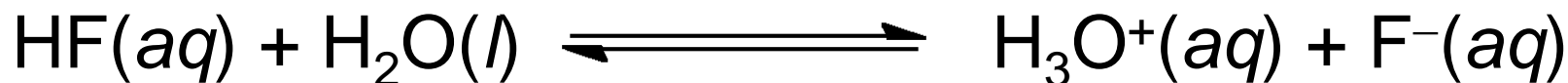$$1.8 \times 10^{-5} = (x)(0.30)/(0.30)$$

➔

$$x = 1.8 \times 10^{-5} = [H^+]$$

So,

$$pH = -log[H^+] = 4.74 \ (4.7)$$

Acids
and
Bases

Calculate the fluoride ion concentration and pH of a solution that is 0.20 *M* in HF and 0.10 *M* in HCl. (K_a for HF is 6.8×10^{-4})

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

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4}$$

	$HF(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$F^-(aq)$
Initial (*M*)	0.20		0.10		0
Change (*M*)	$-x$		$+x$		$+x$
Equilibrium (*M*)	$(0.20 - x)$		$(0.10 + x)$		x

Because HCl, a strong acid, is also present, the initial [H_3O^+] is not 0, but rather 0.10 *M*.

	HF(aq) $\rightleftharpoons$	H$^+$(aq) +	F$^-$(aq)
Initial (M)	0.20	0.10	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(0.20 - x)$	$(0.10 + x)$	x

$$6.8 \times 10^{-4} = \frac{(0.10)\,(x)}{(0.20)}$$

$$x = 1.4 \times 10^{-3}$$

$$[F^-] = x = 1.4 \times 10^{-3}$$
$$[H_3O^+] = 0.10 + x = 0.10 + 1.4 \times 10^{-3} = 0.10 \ M$$

$$pH = 1.00$$

Acids
and
Bases
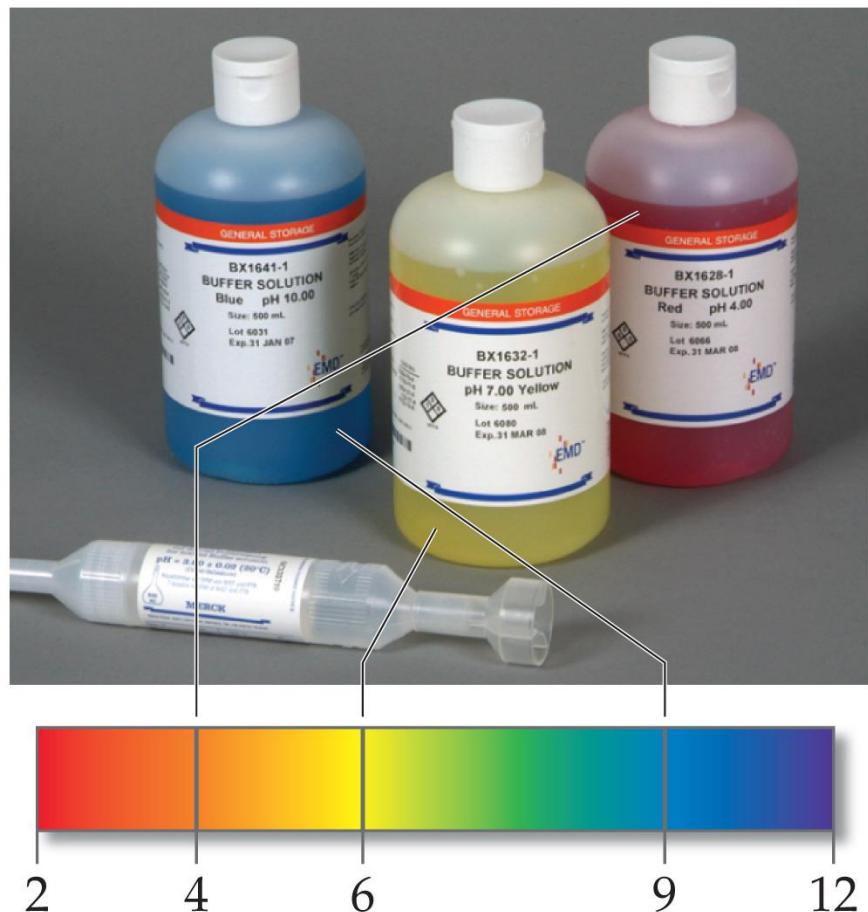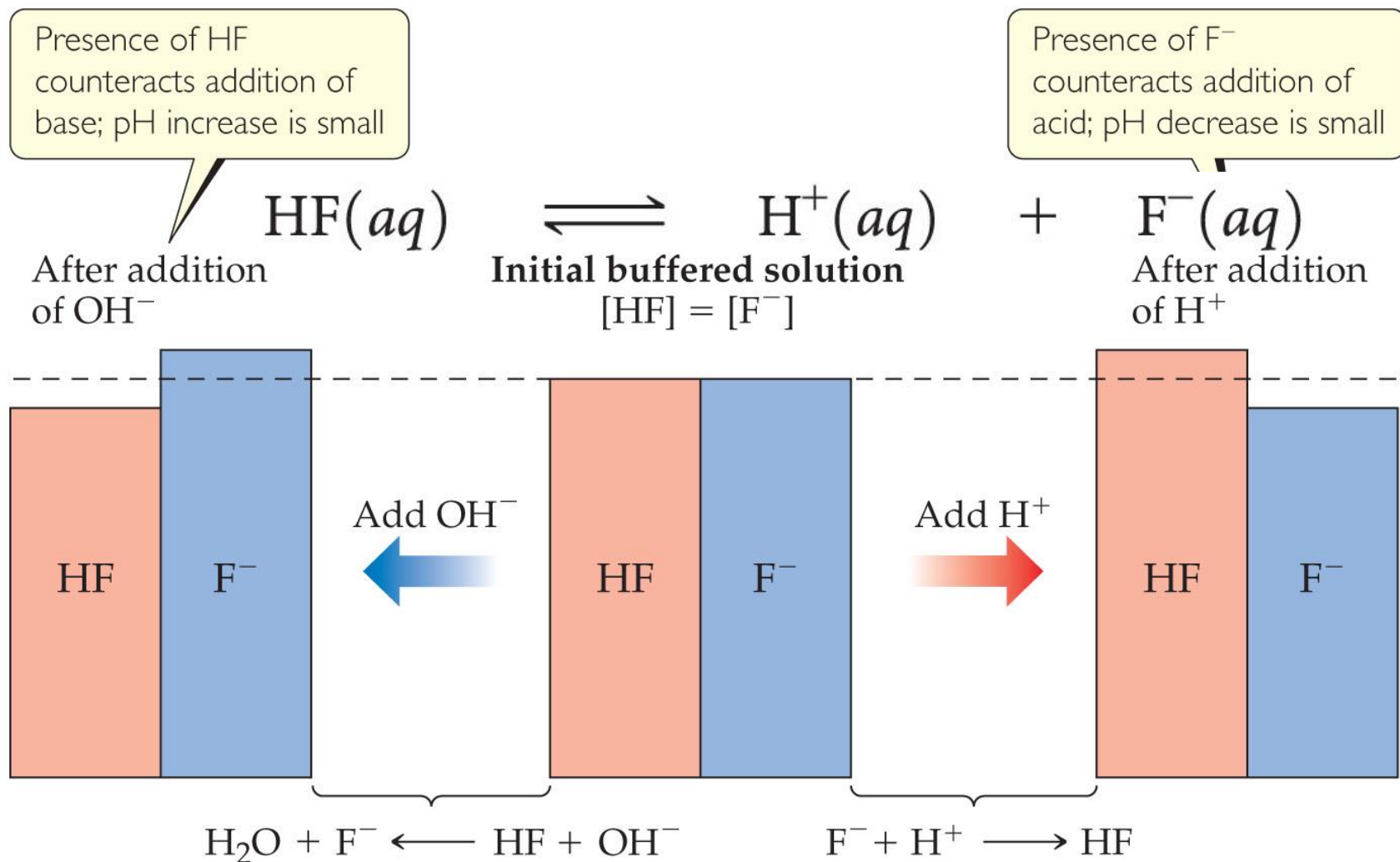
Buffers

- **Solutions of a weak conjugate acid–base pair** that resist drastic changes in pH are called **buffer solutions** (缓冲溶液).

- These solutions contain relatively **high concentrations (10^{-3} M or more) of both the acid and base**. Their concentrations are approximately equal.

Acids and Bases

How a Buffer Works

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

After addition of OH⁻

Initial buffered solution
$[HF] = [F^-]$

After addition of H⁺

HF | F⁻

Add OH⁻

HF | F⁻

Add H⁺

HF | F⁻

$$H_2O + F^- \longleftarrow HF + OH^- \qquad F^- + H^+ \longrightarrow HF$$

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

Acids and Bases

Calculating the pH of a Buffer

- For a weak acid:

$$K_a = [H^+][A^-]/[HA]$$
$$-\log K_a = -\log[H^+] + -\log([A^-]/[HA])$$

- Rearrange:

$$-\log[H^+] = -\log K_a + \log([A^-]/[HA])$$

$$pH = pK_a + \log([A^-]/[HA])$$
$$= pK_a + \log([base]/[acid])$$

- This equation is known as the **Henderson–Hasselbalch equation**.

Acids
and
Bases

Henderson–Hasselbalch Equation

What is the pH of a buffer that is 0.12 M in lactic acid, $CH_3CH(OH)COOH$, and 0.10 M in sodium lactate? K_a for lactic acid is 1.4×10^{-4}.

$$pH = pK_a + \log([A^-]/[HA])$$

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

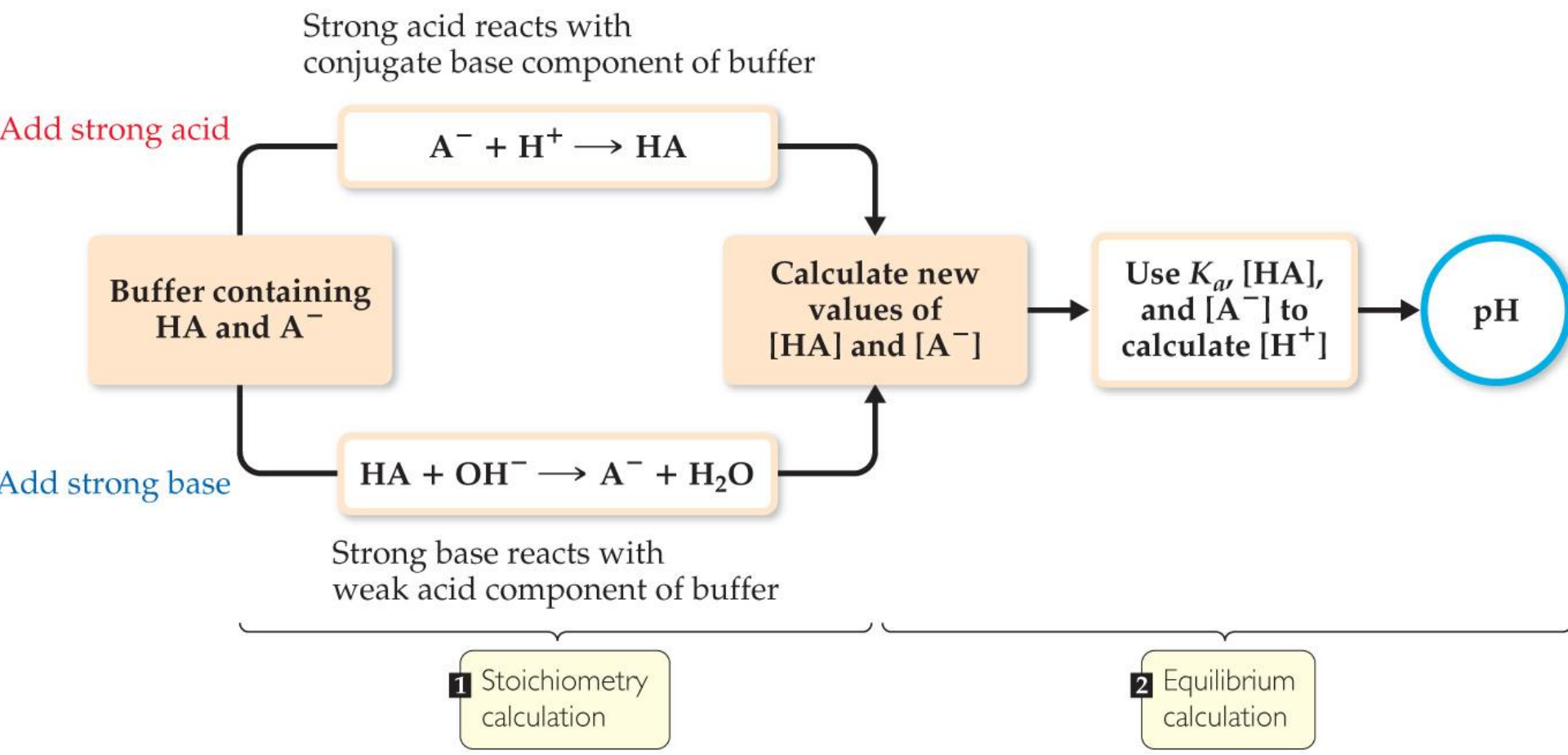$$= 3.85 + (-0.08) = 3.77$$

Acids and Bases

Buffer Capacity & pH Range

• The **amount of acid or base the buffer** can neutralize before the pH begins to **change** to an appreciable degree.

• The buffer capacity depends on the **amount of acid and base** used to prepare the buffer.

• The range of pH values over which a buffer system works effectively.

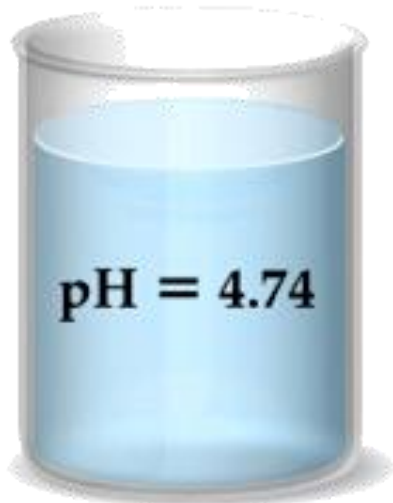• It is best to **choose an acid with a pK_a close to the desired pH**.

$$pH = pK_a + \log([base]/[acid])$$

Acids
and
Bases

Addition of a Strong Acid or Base to a Buffer
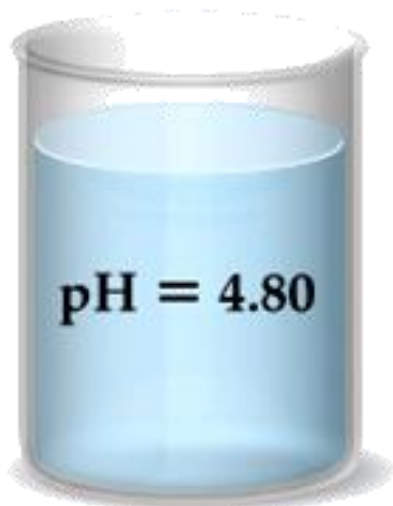
• Calculate [HA] and [A⁻] by assuming **all** of the added **strong acid or base** reacts with a buffer.

• Use the Henderson–Hasselbalch equation to determine the new pH of the solution.

Strong acid reacts with
conjugate base component of buffer

Add strong acid

$$A^- + H^+ \longrightarrow HA$$

Buffer containing
HA and A⁻

Calculate new
values of
[HA] and [A⁻]

Use K_a, [HA],
and [A⁻] to
calculate [H⁺]

pH

Add strong base

$$HA + OH^- \longrightarrow A^- + H_2O$$

Strong base reacts with
weak acid component of buffer

1 Stoichiometry
calculation

2 Equilibrium
calculation

1.000 L buffer
0.300 M CH_3COOH
0.300 M CH_3COO^-
pH = 4.74

1.000 L H_2O
pH = 7.00

Add 5.0 mL of
4.0 M NaOH(aq)

Add 5.0 mL of
4.0 M NaOH(aq)

Effect of adding a strong base to a buffered solution & to water

pH = 4.80

pH = 12.30

pH increases by
0.06 pH units

pH increases by
5.30 pH units

Acids
and
Bases

Example

A buffer is made by adding 0.300 mol $C_2H_3O_2H$ and 0.300 mol $C_2H_3O_2Na$ to enough water to make 1.00 L of solution. The pH of the buffer is 4.74. Calculate the pH after 0.020 mol of NaOH is added.

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

	CH_3COOH	OH^-	H_2O	CH_3COO^-
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

Acids and Bases

Use the Henderson–Hasselbalch equation:
$$pH = pK_a + \log([A^-]/[HA])$$

Since this is a buffer, the volume for each concentration is the same, so the ratio of molarity can be calculated using a ratio of moles.

$$pH = pK_a + \log (n_{HA}/n_{A^-})$$

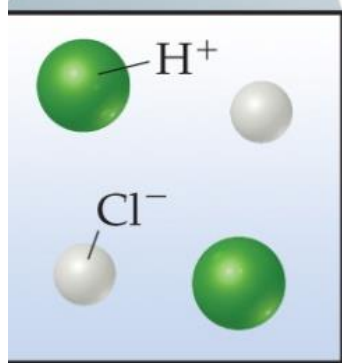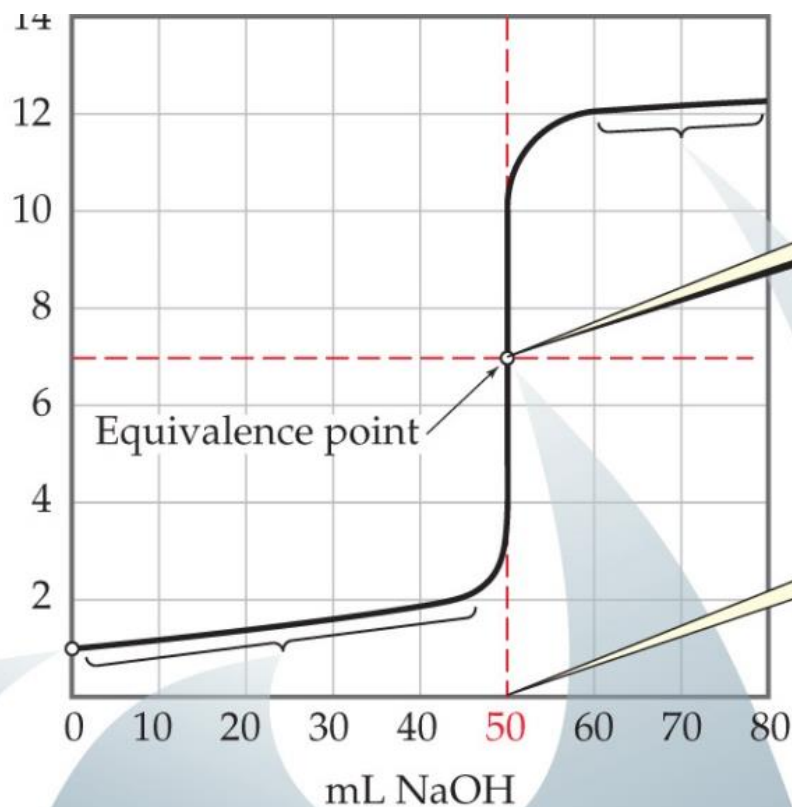$$pH = 4.74 + \log(0.320/0.280) = 4.80$$

Acids
and
Bases

Titration

• In this technique, an acid (or base) solution of known concentration is slowly added to a base (or acid) solution of unknown concentration.

• A pH meter or indicators are used to determine when the solution has reached the **equivalence point**: The amount of acid equals that of base (if 1:1 ratio).
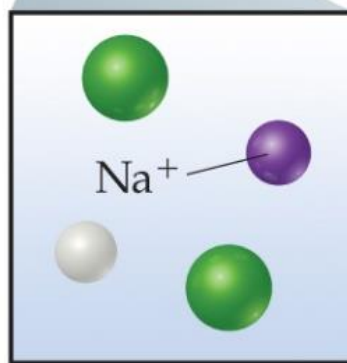
Burette containing NaOH(aq) of known concentration

pH meter

Beaker containing HCl(aq) of unknown concentration

Bases
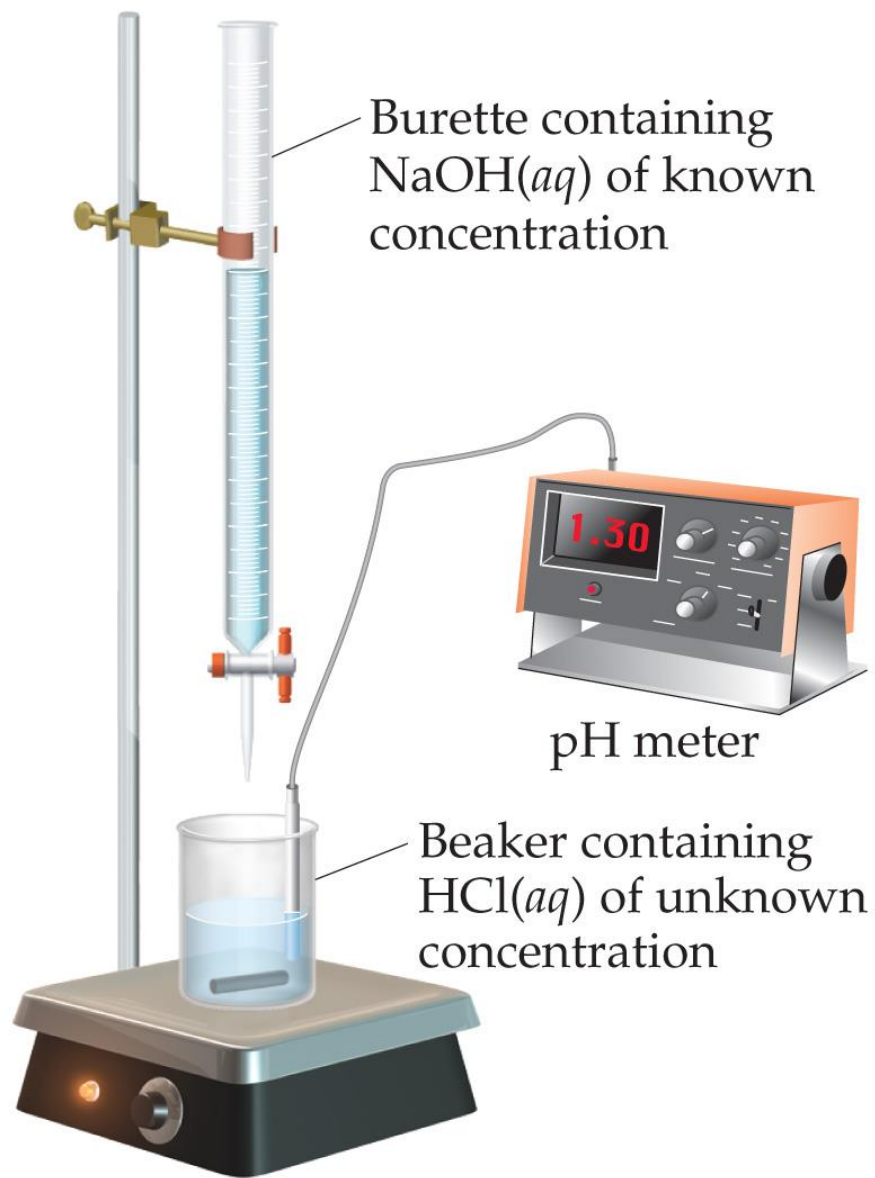
Titration of a Strong Acid with a Strong Base

• From the start to near the equivalence point, the pH goes up slowly.

pH

14
12
10
8
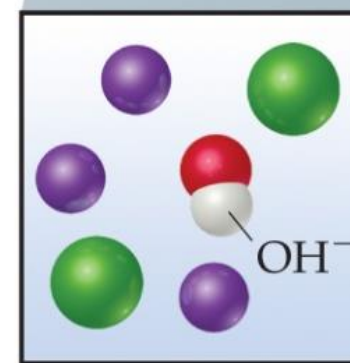6
4
2

Equivalence point

0 10 20 30 40 50 60 70 80

mL NaOH

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

Equivalence point occurs when moles base = moles acid

H⁺

Cl⁻

Na⁺

OH⁻

1 Only HCl(*aq*) present before titration

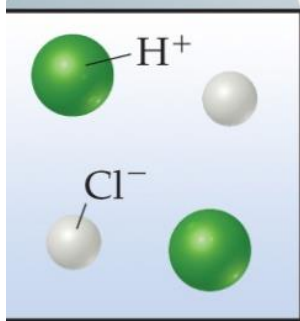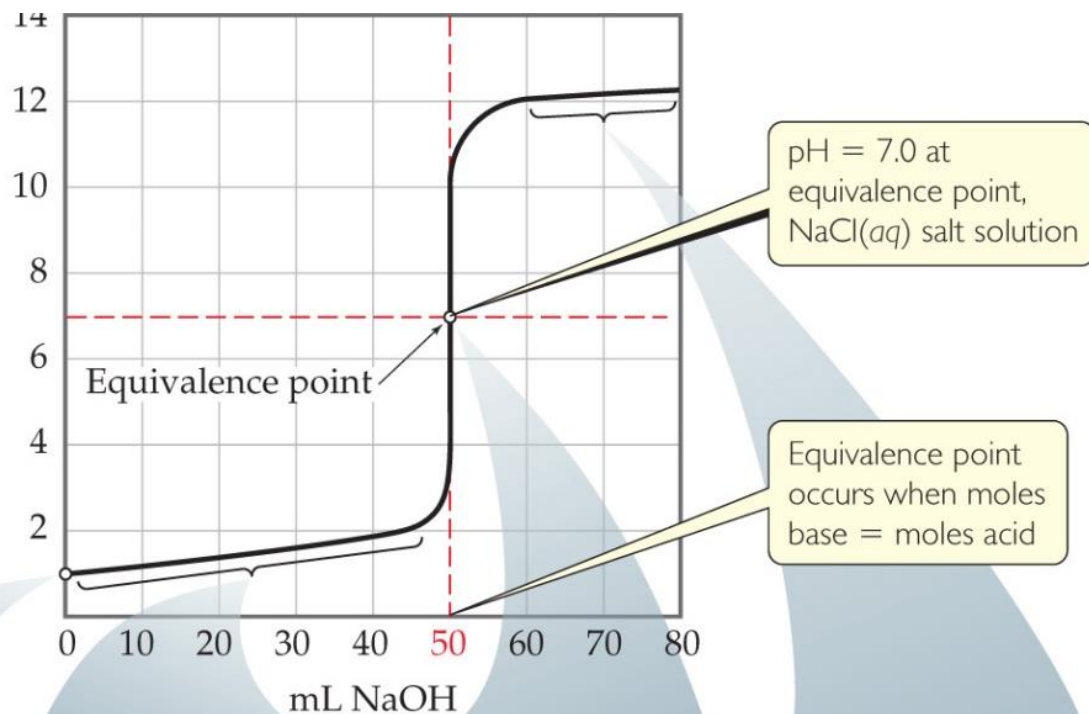**2** H⁺ consumed as OH⁻ added, forming H_2O (pH < 7.0)
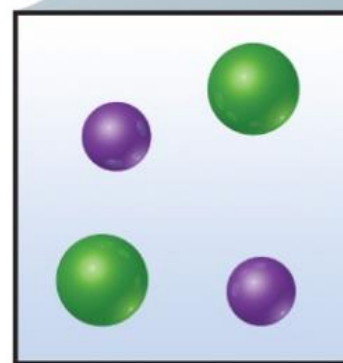
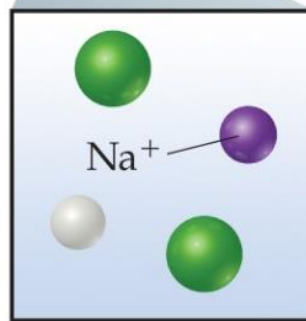**3** H⁺ completely neutralized by OH⁻ (pH = 7.0)

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

• **Just before and after** the equivalence point (**pH = 7**), **the pH rises rapidly**.

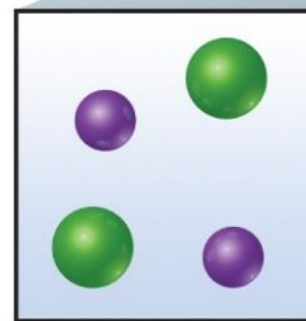• At the equivalence point, moles acid = moles base, & the solution contains only water and the salt.

• As more base is added, the pH again levels off.

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

Equivalence point

Equivalence point occurs when moles base = moles acid

pH

mL NaOH

H⁺

Cl⁻

Na⁺

OH⁻
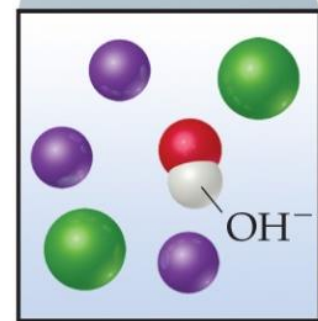
1 Only HCl(aq) present before titration

2 H⁺ consumed as OH⁻ added, forming H_2O (pH < 7.0)
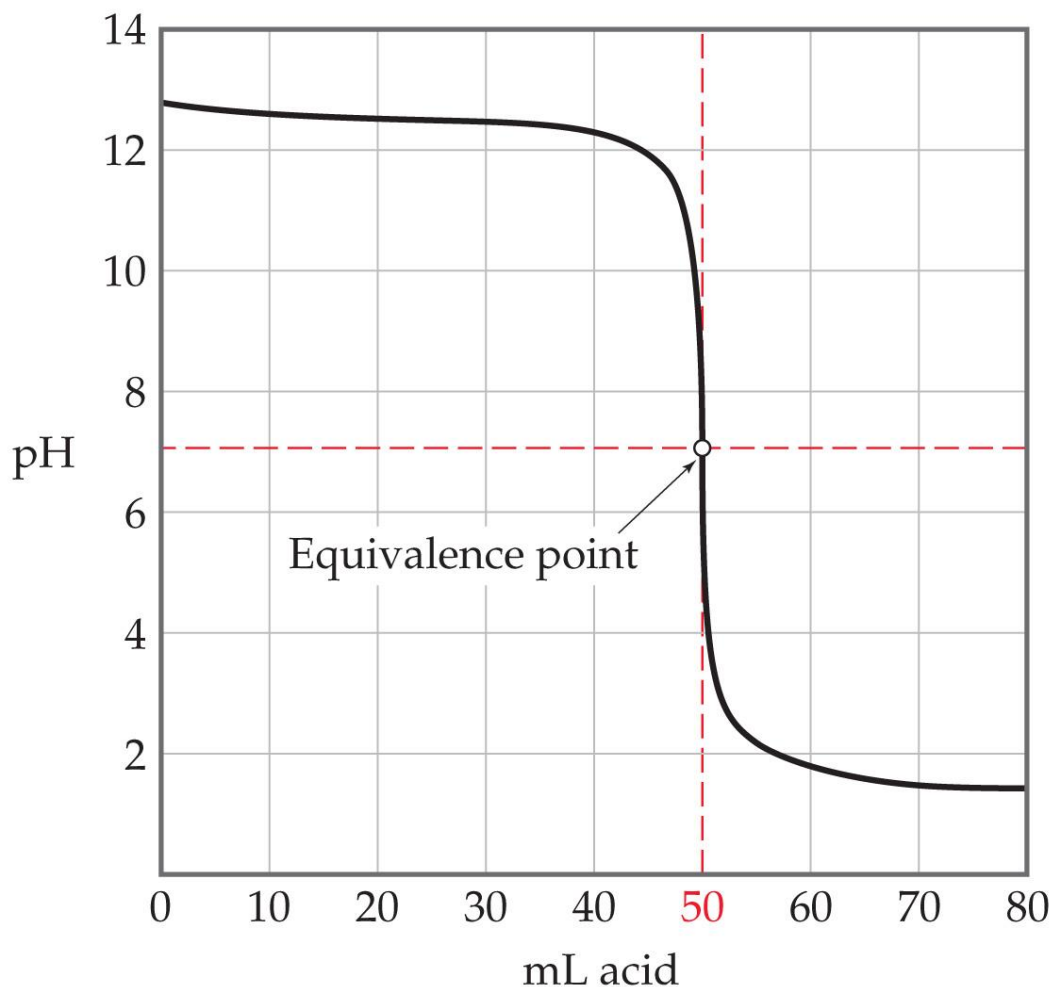
3 H⁺ completely neutralized by OH⁻ (pH = 7.0)

4 No H⁺ left to react with excess OH⁻ (pH > 7.0)
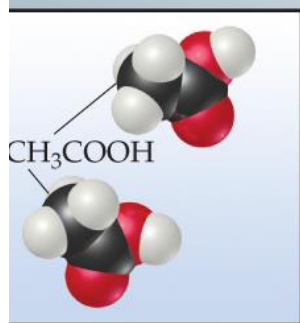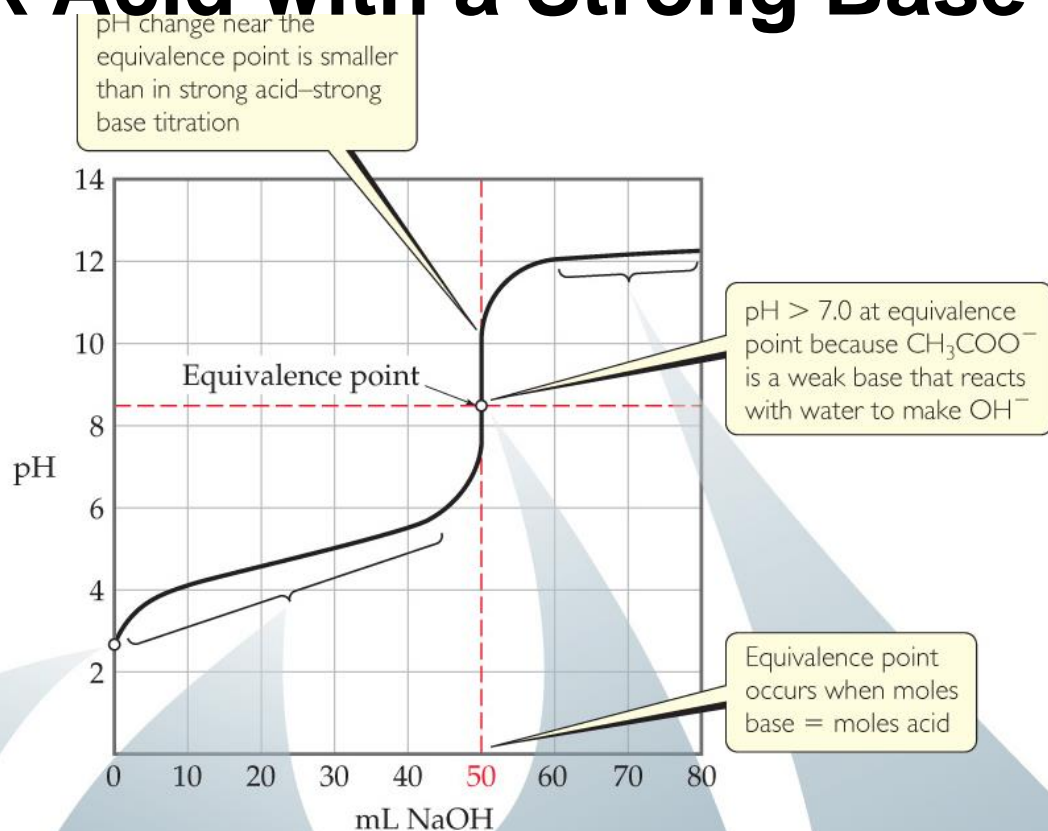
Titration of a Strong Base with a Strong Acid

• Looks like you "flipped over" the strong acid being titrated by a strong base.

• Start with a high pH (basic solution); the **pH = 7** at the equivalence point; low pH to end.

Acids
and
Bases

Titration of a Weak Acid with a Strong Base

- At the equivalence point the pH is **>7**.
- Use the conjugate base of the weak acid to determine the pH.
- As more base is added, the pH levels off. This is same as for strong acids.

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

Equivalence point occurs when moles base = moles acid

CH_3COOH

CH_3COO^-

Na^+

OH^-

1 $CH_3COOH(aq)$ solution before titration
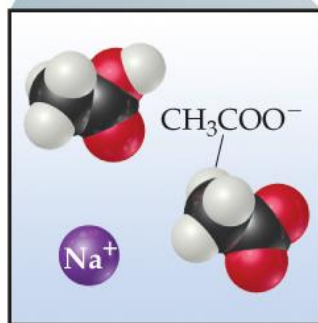
2 Added OH^- converts $CH_3COOH(aq)$ into $CH_3COO^-(aq)$, forming buffer solution
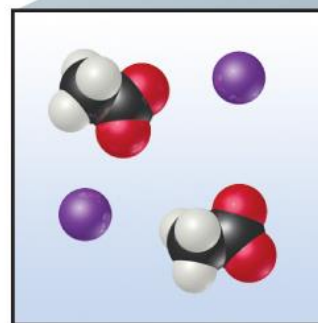
3 Acid completely neutralized by added base, $CH_3COONa(aq)$ salt solution results
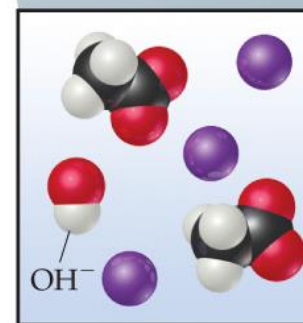
4 No acid left to react with excess OH^-

Neutralization reaction:
[HX] decreases
[X⁻] increases

| Solution containing weak acid | Add strong base | $HX + OH^- \longrightarrow X^- + H_2O$ | Calculate new values of [HX] and [X⁻] | Use K_a, [HX], and [X⁻] to calculate [H⁺] | pH |

① Stoichiometry calculation   ② Equilibrium calculation
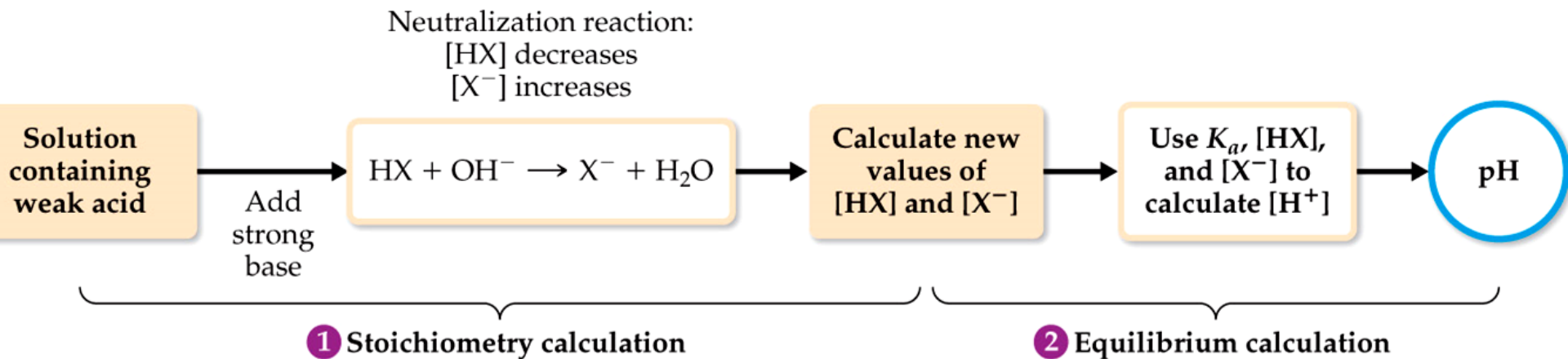
• Use K_a to find initial pH.
• Find the pH in the "buffer region" using stoichiometry followed by the Henderson–Hasselbalch equation.

• At each point below the equivalence point, the pH of the solution during titration is determined from the amounts of the acid and its conjugate base present at that particular time.

• Phenolphthalein is commonly used as an indicator in these titrations.

Acids
and
Bases

1) A solution of weak acid has a higher initial pH than a strong acid.
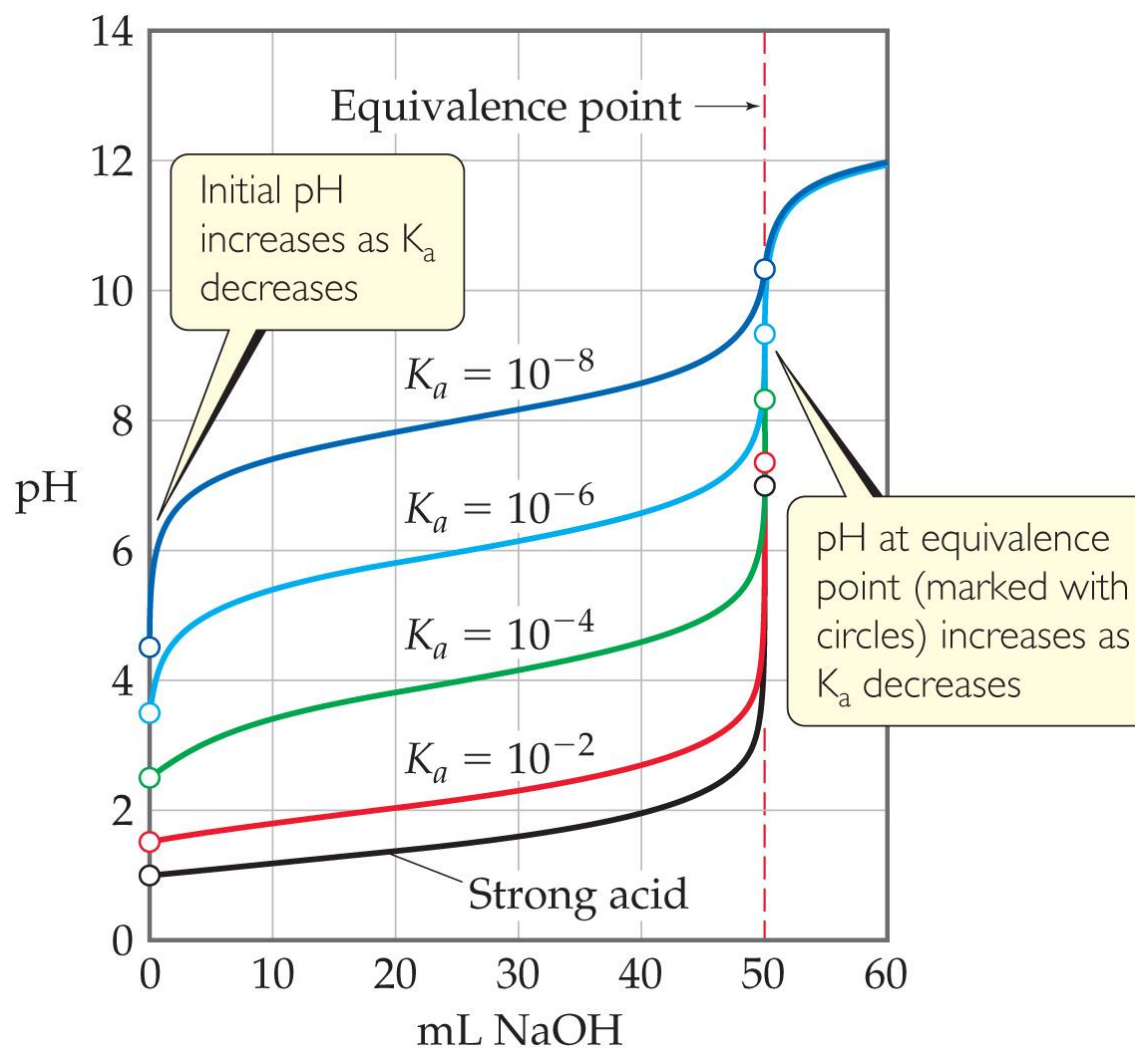2) The **pH change** near the equivalence point is **smaller for a weak acid** (at least partly due to the buffer region).
3) The pH at the equivalence point is **greater than 7 for a weak acid**.

Equivalence point →

Initial pH increases as K_a decreases

$K_a = 10^{-8}$

$K_a = 10^{-6}$

$K_a = 10^{-4}$

$K_a = 10^{-2}$

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

pH

Strong acid

mL NaOH

Acids and Bases

Use of Indicators

• **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.

• An indicator can be used to find the equivalence point in a titration **as long as it changes color in the small volume change region** where the pH rapidly changes.

Phenolphthalein color-change interval

Equivalence point

Methyl red color-change interval

pH

mL HCl

Acids and Bases
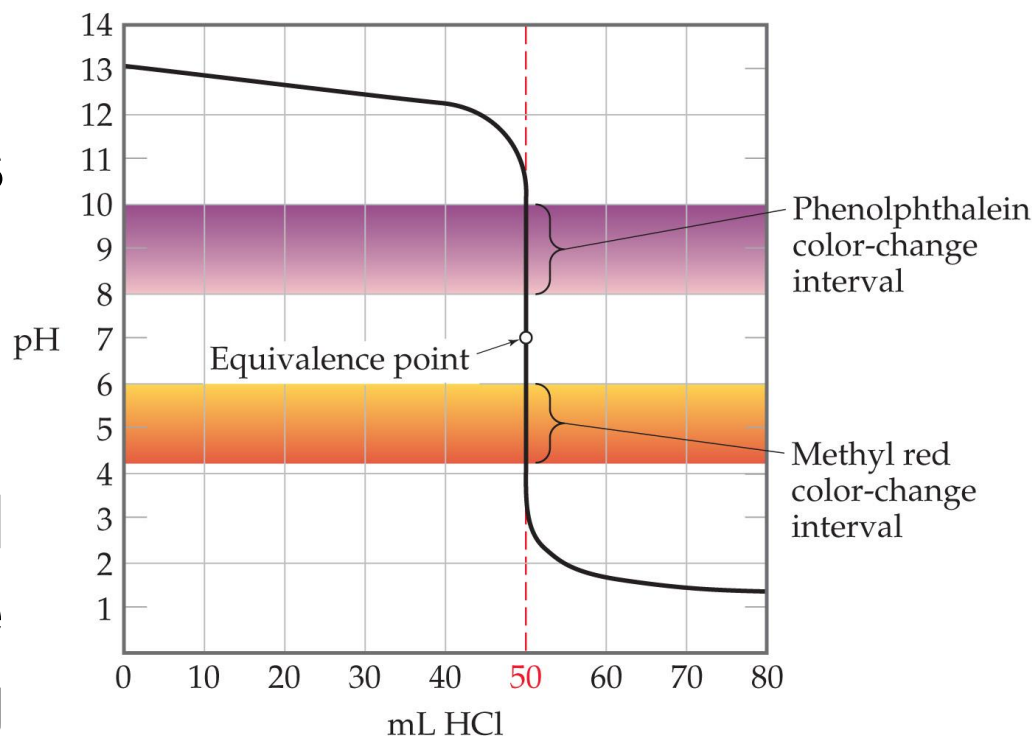
Indicator Choice Can Be Critical!

Phenolphthalein indicator
Color-change interval 8.3 < pH < 10.0

Methyl red indicator
Color-change interval 4.2 < pH < 6.0

pH

mL HCl
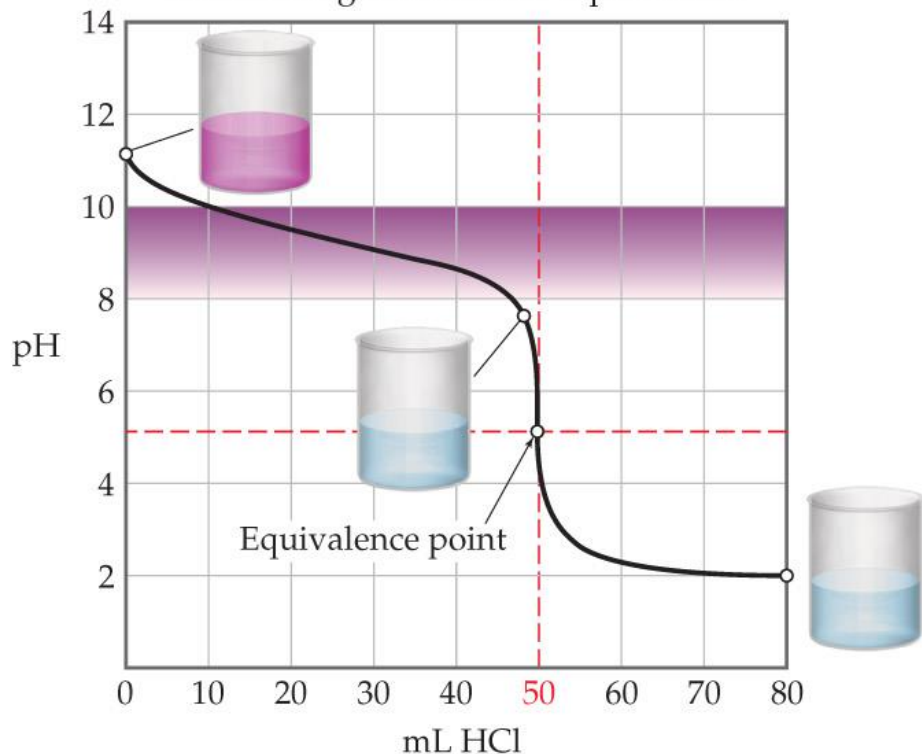
Equivalence point

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

pH

mL HCl
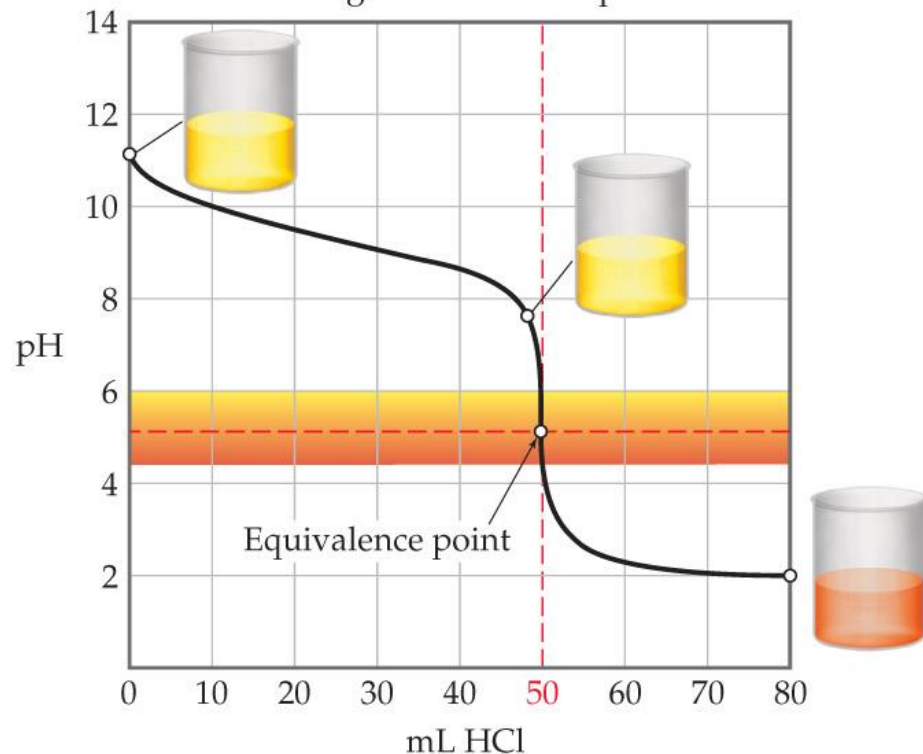
Equivalence point

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

- The pH at the equivalence point in these titrations is <7, so using phenolphthalein would not be a good idea.
- Methyl red is the indicator of choice.

Acids and Bases

Titrations of Polyprotic Acids

• When a **polyprotic acid** is titrated with a base, there is **an equivalence point for each dissociation**.

H_3PO_3 is the dominant species

$H_2PO_3^-$ is the dominant species

HPO_3^{2-} is the dominant species

pH

mL NaOH
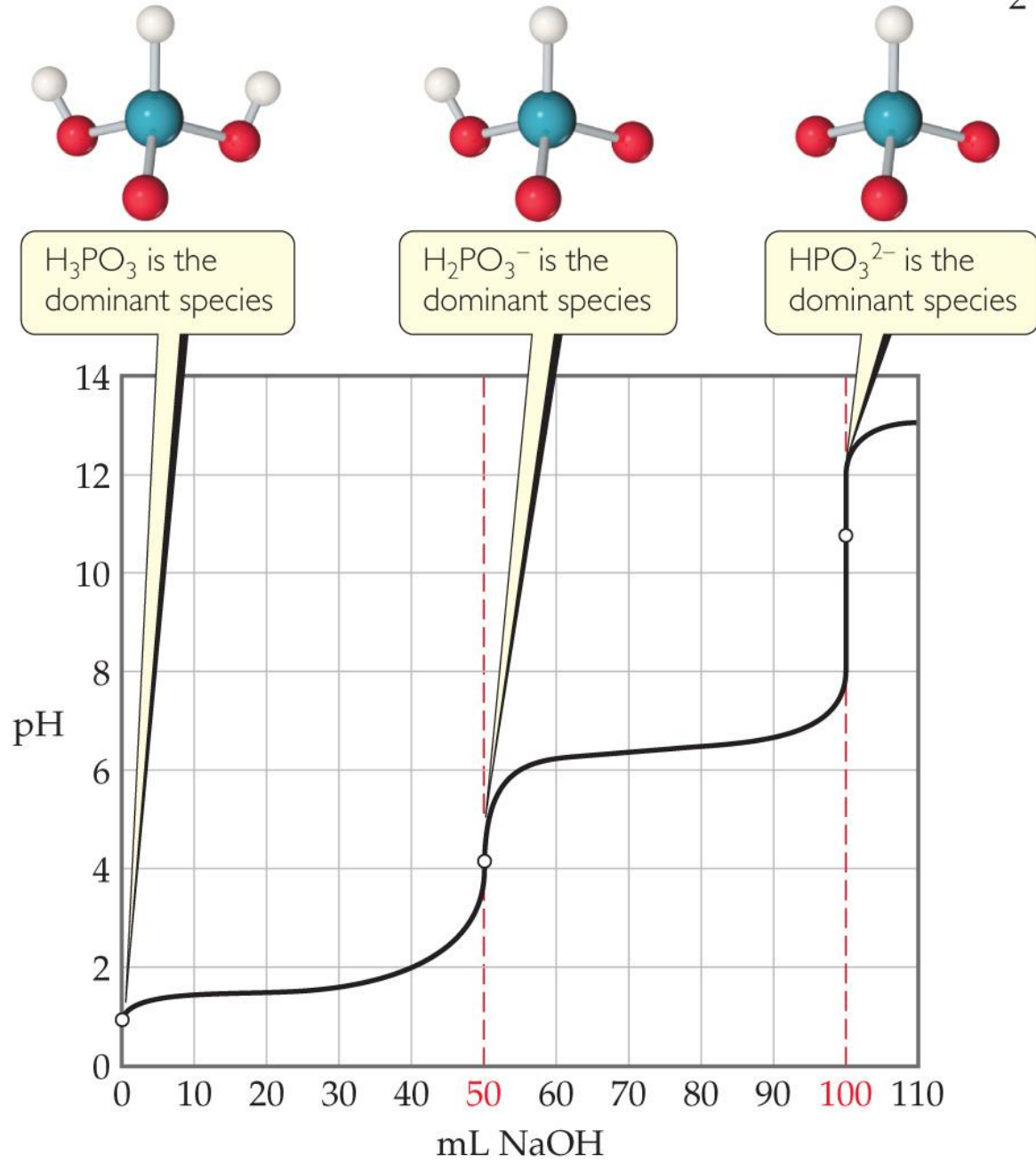
If solutions of $NH_4Cl(aq)$ and $NH_3(aq)$ are mixed, which ions in the resulting solution are spectator ions in any acid–base chemistry occurring in the solution? What equilibrium reaction determines [OH⁻] and, therefore, the pH of the solution?

(a)

A. There are no spectator ions.

B. Cl^-

C. Both NH_4^+ and Cl^-

D. NH_4^+

(b)

A. $NH_3(aq) + H_2O(l) \Leftrightarrow NH_4^+(aq) + OH^-(aq)$

B. $NH_4^+(aq) + Cl^-(aq) \Leftrightarrow NH_3(aq) + HCl(l)$

C. $H_3O^+(aq) + OH^-(aq) \Leftrightarrow 2H_2O(l)$

D. $NH_4^+(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + NH_3(aq)$

Acids
and
Bases

Which of these conjugate acid–base pairs will *not* function as a buffer: C_2H_5COOH and $C_2H_5COO^-$, HCO_3^- and CO_3^{2-}, or HNO_3 and NO_3^-? Explain.

A. All listed pairs will not function as buffers.

B. $HCHO_2$ and CHO_2^- will not work as a buffer because $HCHO_2$ is a weak acid and CHO_2^- is a spectator ion.

C. HCO_3^- and CO_3^{2-} will not work as a buffer because HCO_3^- is a weak acid and HCO_3^- is a spectator ion.

D. HNO_3 and NO_3^- will not work as a buffer because HNO_3 is a strong acid and NO_3^- is a spectator ion.

a. What happens when NaOH is added to a buffer composed of CH_3COOH and CH_3COO^-?

b. What happens when HCl is added to this buffer?

(a)

A. There is no reaction because $C_2H_3O_2^-$ and $C_2H_3O_2H$ form a buffer.

B. The NaOH reacts with $C_2H_3O_2^-$ converting some of it into $C_2H_3O_2H$.

C. The NaOH reacts with $C_2H_3O_2H$ converting some of it into $C_2H_3O_2^-$.

D. The NaOH is neutralized and all concentrations ($C_2H_3O_2H$ and $C_2H_3O_2^-$) remain unchanged.

Acids
and
Bases

a. What happens when NaOH is added to a buffer composed of CH_3COOH and CH_3COO^-?

b. What happens when HCl is added to this buffer?

(b)

A. There is no reaction because $C_2H_3O_2^-$ and $C_2H_3O_2H$ form a buffer.

B. The HCl reacts with $C_2H_3O_2^-$ converting some of it into $C_2H_3O_2H$.

C. The HCl is neutralized and all concentrations ($C_2H_3O_2H$ and $C_2H_3O_2^-$) remain unchanged.

D. The HCl reacts with $C_2H_3O_2H$ converting some of it into $C_2H_3O_2^-$.

Acids
and
Bases

The K_a values for nitrous acid (HNO_2) and hypochlorous (HClO) acid are 4.5×10^{-4} and 3.0×10^{-8}, respectively. Which one would be more suitable for use in a solution buffered at pH = 7.0? What other substance would be needed to make the buffer?

A. HClO because it is a stronger weak acid. A salt containing ClO^- is also needed.

B. HNO_2 because it is a stronger weak acid. A salt containing NO_2^- is also needed.

C. HClO because its pK_a is closer to pH = 7.0. A salt containing ClO^- is also needed.

D. HNO_2 because its pK_a is closer to pH = 7.0. A salt containing NO_2^- is also needed.

Acids
and
Bases

How many moles of NH_4Cl must be added to 2.0 L of 0.10 M NH_3 to form a buffer whose pH is 9.00? (Assume that the addition of NH_4Cl does not change the volume of the solution.)

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$
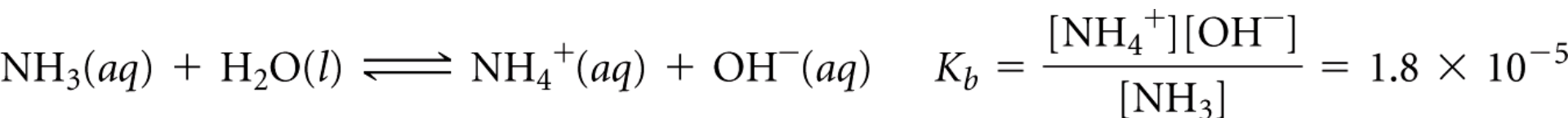
pOH = 14.00 − pH = 14.00 − 9.00 = 5.00
$[OH^-]$ = 1.0 × 10⁻⁵ M
$[NH_3]_{initial}$ = 0.10 M ~ $[NH_3]_{eq.}$

$$[NH_4^+] = K_b \frac{[NH_3]}{[OH^-]} = (1.8 \times 10^{-5}) \frac{(0.10\ M)}{(1.0 \times 10^{-5}\ M)} = 0.18\ M$$

(2.0 L)(0.18 mol NH_4Cl/L) = 0.36 mol NH_4Cl

What is the pH at the equivalence point when 0.10 M HNO_3 is used to titrate a volume of solution containing 0.30 g of KOH?

A. pH = 4.2

B. pH = 7.0

C. pH = 8.2

D. pH = 9.8

If the acetic acid being titrated here were replaced by hydrochloric acid, would the amount of base needed to reach the equivalence point change? Would the pH at the equivalence point change?

A. The volume of base does not change but the equivalence point pH increases.

B. The volume of base increases but the equivalence point pH does not change.

C. The volume of base decreases and the equivalence point pH does not change.

D. The volume of base does not change but the equivalence point pH decreases.

Acids
and
Bases

Why is the choice of indicator more crucial for a weak acid–strong base titration than for a strong acid–strong base titration?

A. The nearly vertical equivalence point portion of the titration curve is large for a weak acid-strong base titration, and fewer indicators undergo their color change so quickly because the change is difficult to monitor.

B. The nearly vertical equivalence point portion of the titration curve is smaller for a weak acid-strong base titration, and fewer indicators undergo their color change within this narrow range.

C. Many indicators do not change colors at the equivalence points of weak acid-strong base titrations.

D. Equivalence points at pH's other than 7.00 are difficult to determine.

Acids and Bases

Calculate the pH of the solution formed when 45.0 mL of 0.100 M NaOH is added to 50.0 mL of 0.100 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$).

$$(0.0500 \text{ L soln})\left(\frac{0.100 \text{ mol } CH_3COOH}{1 \text{ L soln}}\right) = 5.00 \times 10^{-3} \text{ mol } CH_3COOH$$

$$(0.0450 \text{ L soln})\left(\frac{0.100 \text{ mol NaOH}}{1 \text{ L soln}}\right) = 4.50 \times 10^{-3} \text{ mol NaOH}$$

4.50×10^{-3} of NaOH consumes 4.50×10^{-3} of CH_3CO_2H
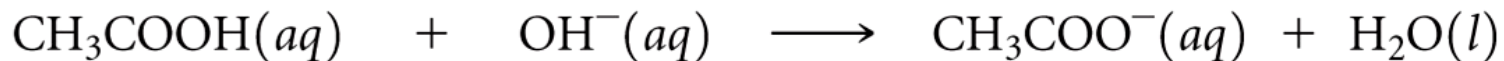
	$CH_3COOH(aq)$	+	$OH^-(aq)$	$\longrightarrow$	$CH_3COO^-(aq)$	+	$H_2O(l)$
Before addition	5.00×10^{-3} mol		0		0		—
Addition			4.50×10^{-3} mol				
After addition	0.50×10^{-3} mol		0		4.50×10^{-3} mol		—

The total volume of the solution is 45.0 mL + 50.0 mL = 95.0 mL = 0.0950 L
The resulting molarities of CH_3COOH and CH_3COO^-:

$$[CH_3COOH] = \frac{0.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0053 \, M$$

$$[CH_3COO^-] = \frac{4.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0474 \, M$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$[H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} = (1.8 \times 10^{-5}) \times \left(\frac{0.0053}{0.0474}\right) = 2.0 \times 10^{-6} \, M$$

$$pH = -\log(2.0 \times 10^{-6}) = 5.70$$

For HCN, $K_a = 4.9 \times 10^{-10}$. What is the pH of a buffer solution in which [HCN] = 0.100 M = [KCN] ?

a. 4.7

b. 7.0

c. 9.3

d. 14.0

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

For HCN, $K_a = 4.9 \times 10^{-10}$. [HCN] = 0.100 M, [KCN] = 0.200 M, pH of buffer solution = _____.

a. 7.0

b. 9.0

c. 9.3

d. 9.6

Acids
and
Bases

For HCN, $K_a = 4.9 \times 10^{-10}$. [HCN] = 1.00 M, [KCN] = 0.100 M, pH of buffer solution = _____.

a. 7.0
b. 8.3
c. 9.0
d. 9.3

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

When titrating a weak base with a strong acid, a good indicator to use would be

a. methyl red (color change at pH = 5).
b. bromothymol blue (change at pH = 7).
c. phenolphthalein (change at pH = 9).
d. None of the above

Acids
and
Bases

When titrating a weak acid with a strong base, a good indicator to use would be

a. methyl red (color change at pH = 5).
b. bromothymol blue (change at pH = 7).
c. phenolphthalein (change at pH = 9).
d. None of the above

Which of the following mixtures could be used to prepare an effective buffer solution?

a. HCl and KCl
b. HNO_3 and KNO_3
c. HCl and NH_4Cl
d. NH_3 and NH_4Cl

Acids
and
Bases

Solubility Equilibria

• Consider the equilibrium in **a saturated solution** of $BaSO_4$ in water. An equilibrium equation can be expressed (**ions in solution: the products**):

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

• The equilibrium constant expression is called the **solubility-product constant**. It is represented as K_{sp}.

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

➢ Another example:

$$Ba_3(PO_4)_2(s) \rightleftharpoons 3\ Ba^{2+}(aq) + 2\ PO_4^{3-}(aq)$$
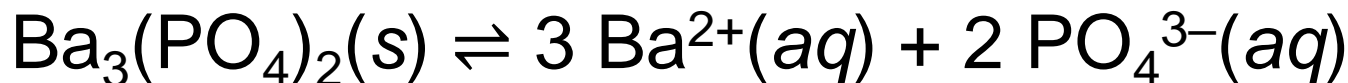
➢ The equilibrium constant expression is

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

Acids and Bases

Solubility vs. Solubility Product

- *K_{sp}* is **NOT the same as solubility**.
- **Solubility** is the **quantity** of a *substance that dissolves to form a saturated solution* and is generally expressed as the mass of solute dissolved in 1 L (g/L) or 100 mL (g/mL) of solution, or in mol/L (**M**).

Mass solubility of compound (g/L)		K_{sp}
Formula weight		Solubility equilibrium
Molar solubility of compound (mol/L)	Empirical formula	Molar concentration of ions
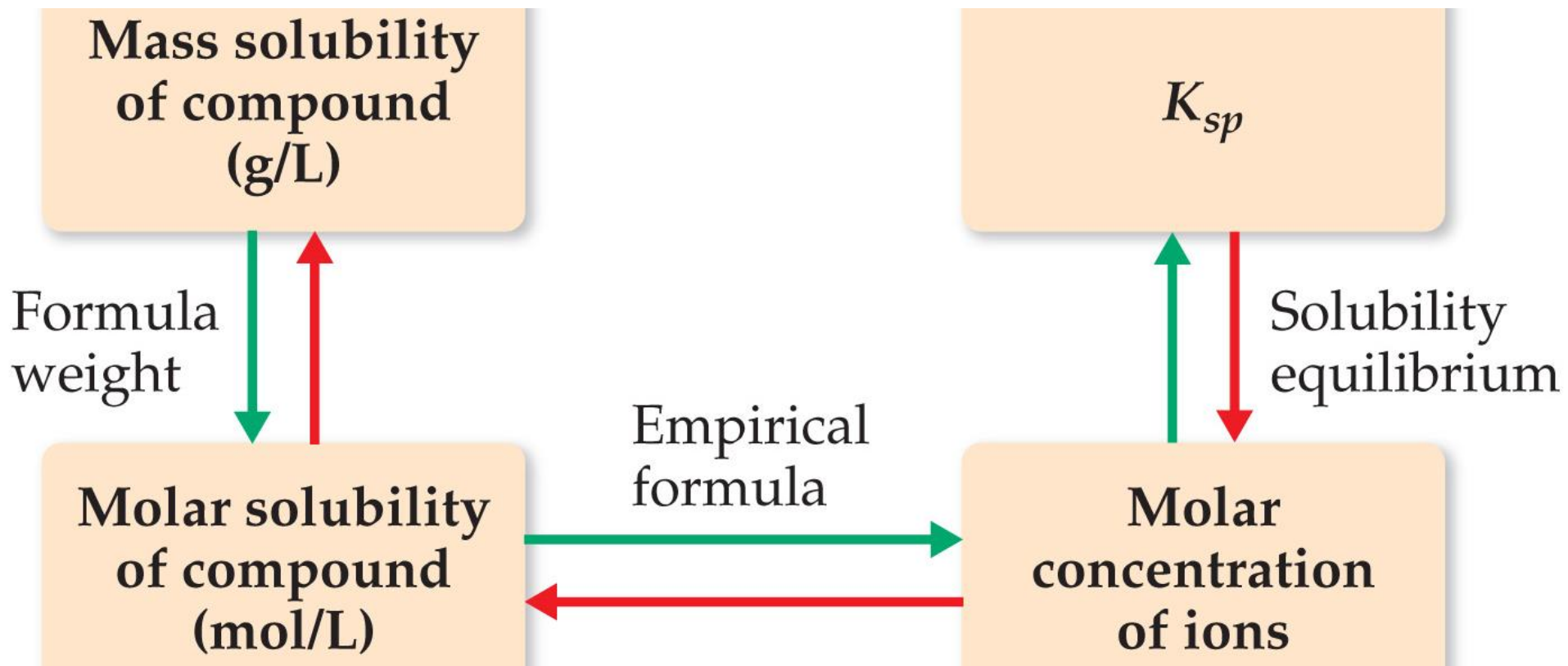
Factors Affecting Solubility

• The **Common-Ion Effect**:

1) If one of the ions in a solution equilibrium is already dissolved in the solution, the **solubility of the salt** will **decrease**.

2) If either calcium ions or fluoride ions are present, then calcium fluoride will be less soluble.
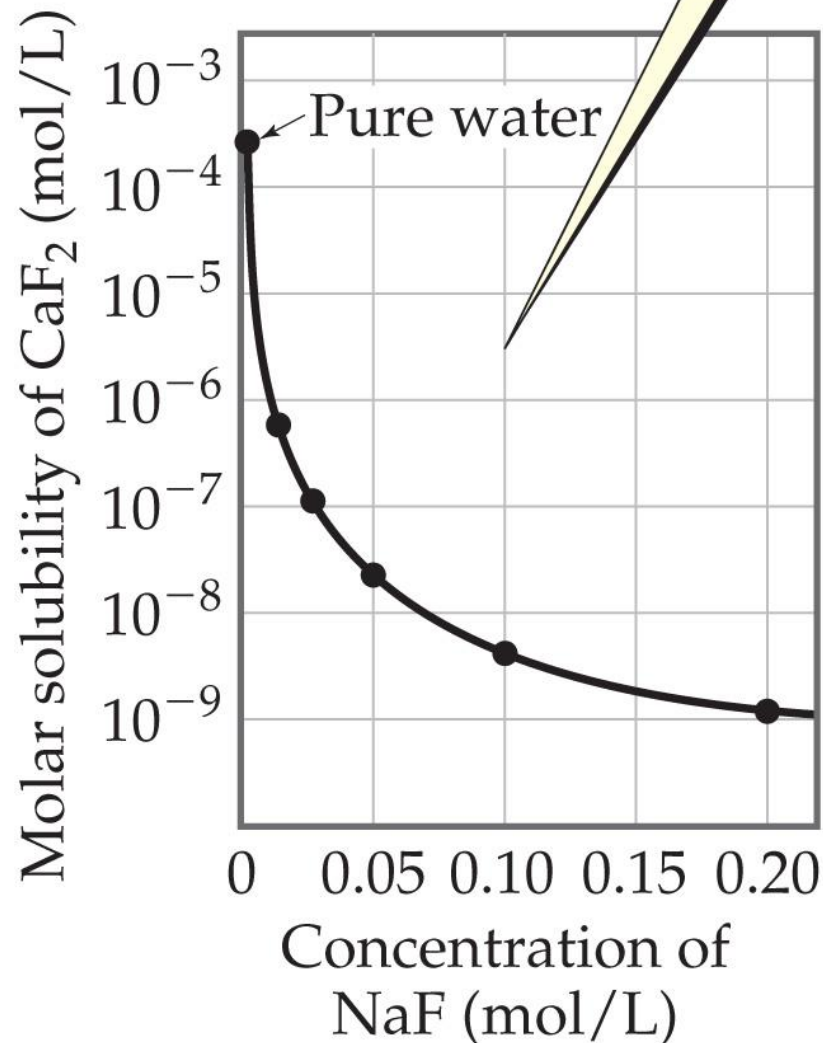
Solubility of CaF_2 decreases sharply as a common ion (F^-) is added to the solution

Calculating Solubility from K_{sp}

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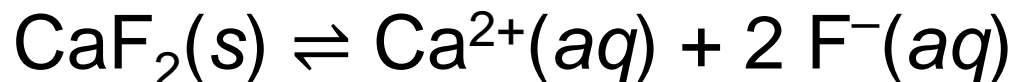
$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$
$$K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$$

	$CaF_2(s) \rightleftharpoons$	$Ca^{2+}(aq)$ +	$2\,F^-(aq)$
Initial concentration (M)	—	0	0
Change (M)	—	$+x$	$+2x$
Equilibrium concentration (M)	—	x	$2x$

$$3.9 \times 10^{-11} = (x)(2x)^2 = 4x^3$$
$$x = 2.1 \times 10^{-4}\ M$$

(If you want the answer in g/L, multiply by molar mass; this would give 0.016 g/L)

Acids and Bases

Calculating Solubility with a Common Ion

What is the molar solubility of CaF_2 in 0.010 M $Ca(NO_3)_2$?
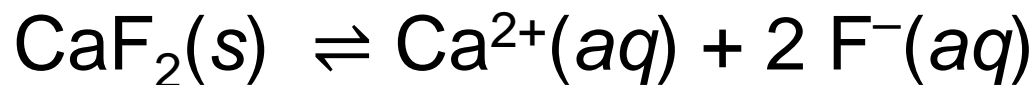
$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$
$$K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$$
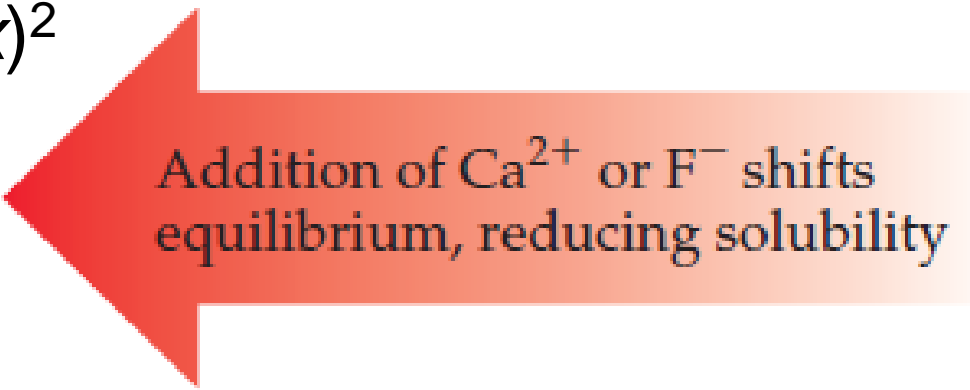
	$CaF_2(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	$+$	$2\,F^-(aq)$
Initial Concentration (M)	—		0.010		0
Change (M)	—		$+x$		$+2x$
Equilibrium Concentration (M)	—		$(0.010 + x)$		$2x$

$3.9 \times 10^{-11} = (0.010 + x)(2x)^2$
Assuming $x \ll 0.010$,
$3.9 \times 10^{-11} = (0.010)(2x)^2$
$x = 3.1 \times 10^{-5}\ M$

Addition of Ca^{2+} or F^- shifts equilibrium, reducing solubility

Factors Affecting Solubility

• **pH**: If a **substance** has a **basic** anion, it will be more **soluble** in an **acidic solution**.

• Remember that buffers control pH. When a buffer is used, there is *no change* in concentration of hydroxide ion!

Salt whose anion is conjugate base of weak acid: *Solubility increases as pH decreases*
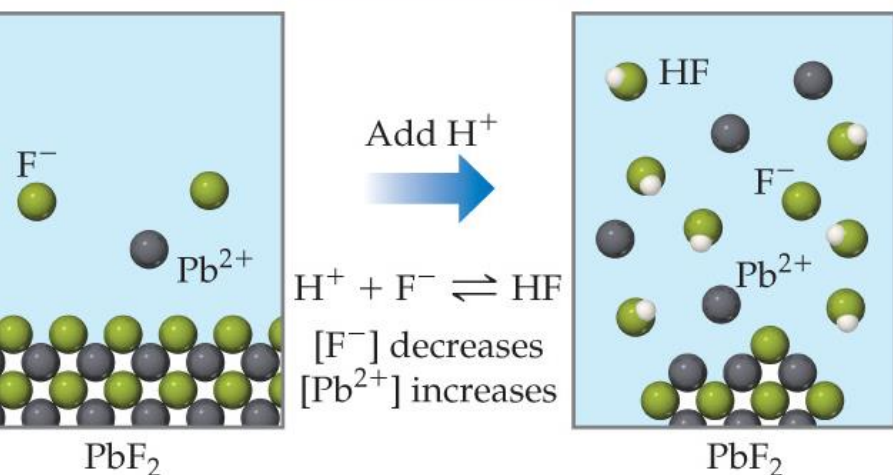
Salt whose anion is conjugate base of strong acid: *Solubility unaffected by changes in pH*

$H^+ + F^- \rightleftharpoons HF$

$[F^-]$ decreases
$[Pb^{2+}]$ increases

(a)
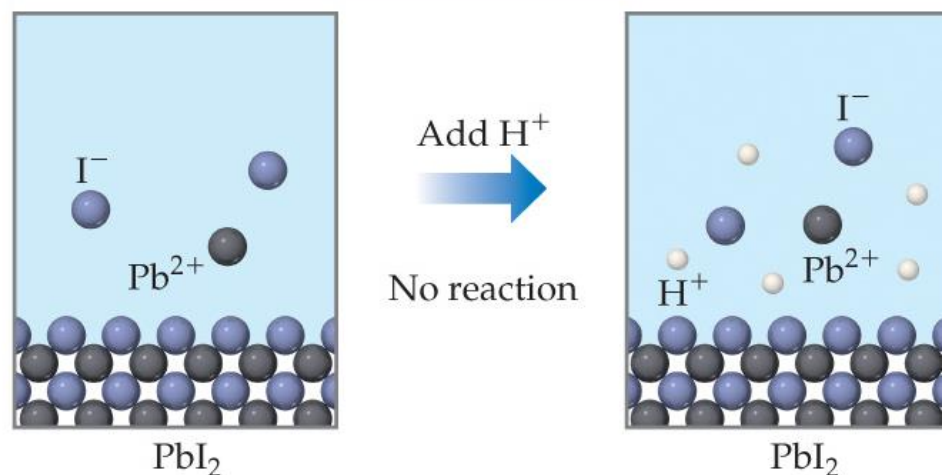
(b)

• **Complex Ion Formation**: Metal ions can act as Lewis acids and form **complex ions** (络离子) with Lewis bases in the solvent.

• The **formation** of these **complex ions** increases 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

Cl^-
Ag^+
AgCl

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

$Ag(NH_3)_2^+$
Cl^-
NH_3

Acids and Bases

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

NH₃ reacts with Ag⁺, forming Ag(NH₃)₂⁺

Addition of sufficient NH₃ leads to complete dissolution of AgCl

Cl⁻
Ag⁺
AgCl

Reaction with NH₃ reduces concentration of free Ag⁺ and increases solubility of AgCl

Cl⁻
Ag(NH₃)₂⁺
NH₃

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

- 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 complex ions with NH₃.**

Acids
and
Bases

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

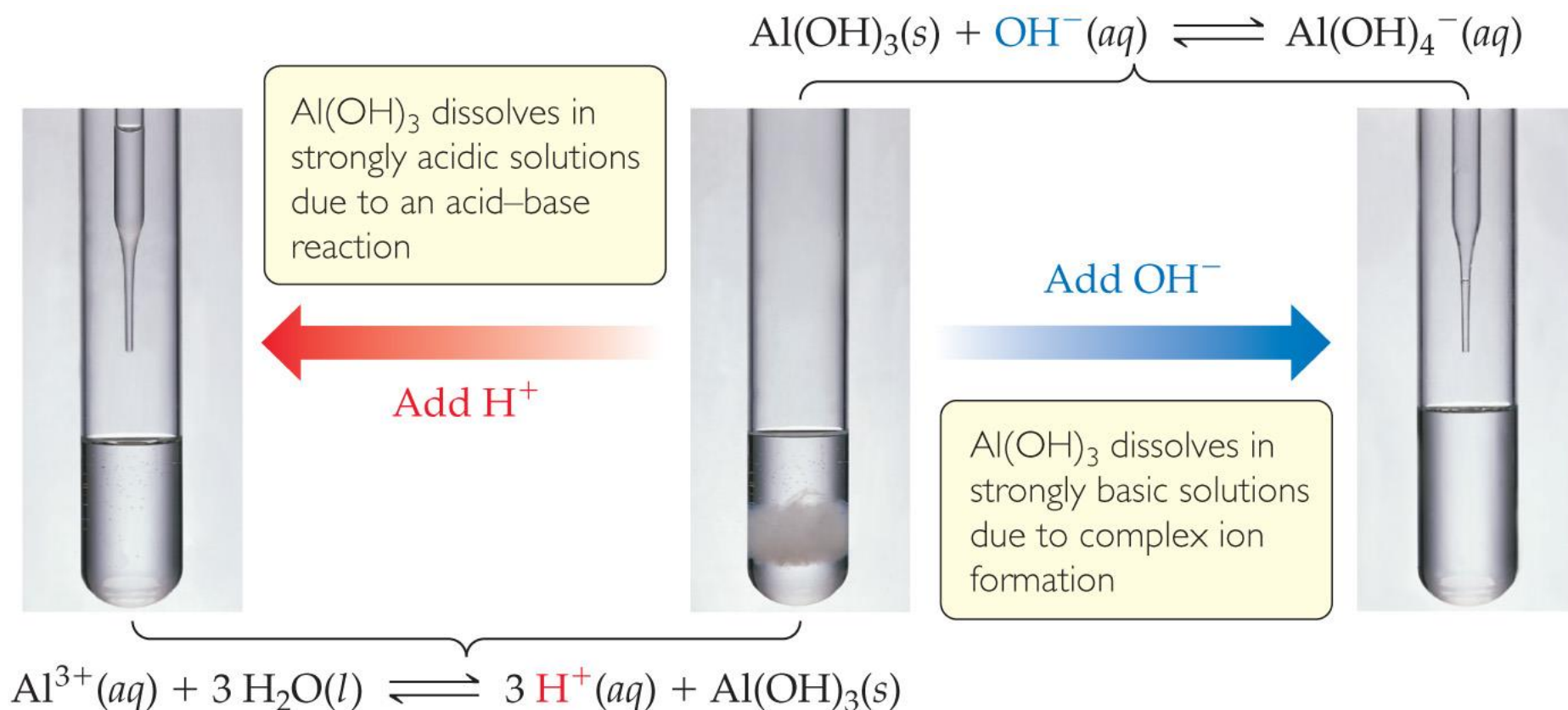| Complex Ion	K_f	Equilibrium Equation
$Ag(NH_3)_2^+$	1.7×10^7	$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
$Ag(CN)_2^-$	1×10^{21}	$Ag^+(aq) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	$Ag^+(aq) + 2\,S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$
$CdBr_4^{2-}$	5×10^3	$Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$
$Cr(OH)_4^-$	8×10^{29}	$Cr^{3+}(aq) + 4\,OH^-(aq) \rightleftharpoons Cr(OH)_4^-(aq)$
$Co(SCN)_4^{2-}$	1×10^3	$Co^{2+}(aq) + 4\,SCN^-(aq) \rightleftharpoons Co(SCN)_4^{2-}(aq)$
$Cu(NH_3)_4^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$
$Cu(CN)_4^{2-}$	1×10^{25}	$Cu^{2+}(aq) + 4\,CN^-(aq) \rightleftharpoons Cu(CN)_4^{2+}(aq)$
$Ni(NH_3)_6^{2+}$	1.2×10^9	$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$
$Fe(CN)_6^{4-}$	1×10^{35}	$Fe^{2+}(aq) + 6\,CN^-(aq) \rightleftharpoons Fe(CN_3)_6^{4-}(aq)$
$Fe(CN)_6^{3-}$	1×10^{42}	$Fe^{3+}(aq) + 6\,CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-}(aq)$

Bases

• **Amphoterism** (酸碱两性现象): **Amphoteric oxides and hydroxides** are **soluble in strong acids or base**, because they can act either as acids or bases.

• Examples are **oxides and hydroxides** of **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

Add H$^+$

Add OH$^-$

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

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

Will a Precipitate Form?

• To decide, we calculate the reaction quotient, Q, and compare it to the solubility product constant, K_{sp}.

➢ If **$Q = K_{sp}$**, the system is **at equilibrium** and the **solution is saturated**.

➢ If **$Q < K_{sp}$**, **more solid can dissolve**, so **no precipitate** forms.

➢ If **$Q > K_{sp}$**, a **precipitate will form**.

Acids
and
Bases

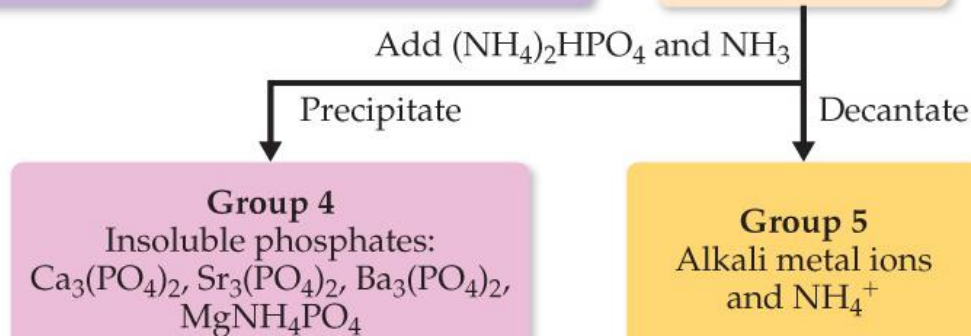# Selective Precipitation of Ions

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:
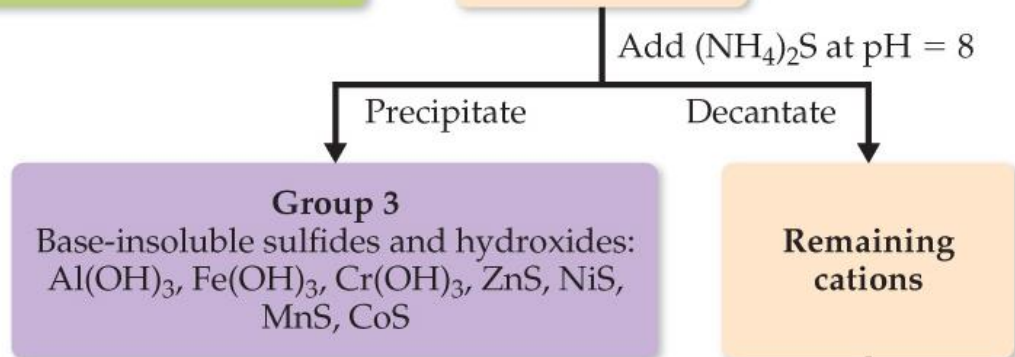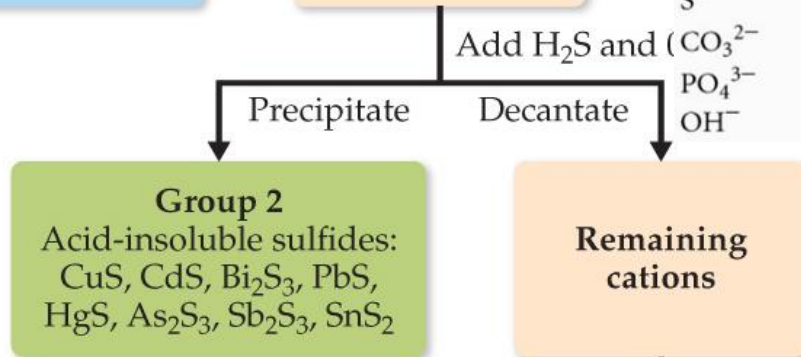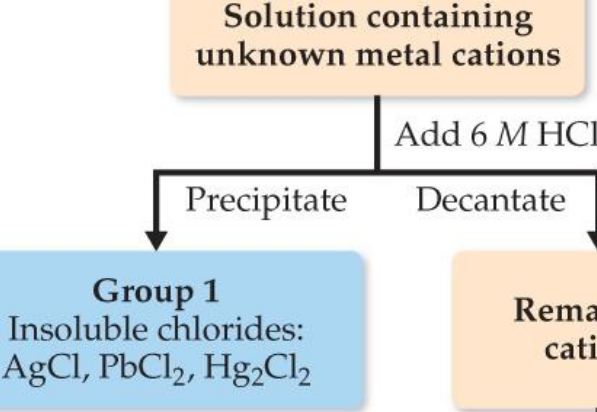$Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ba_3(PO_4)_2$,
$MgNH_4PO_4$

Group 5
Alkali metal ions
and NH_4^+

- 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.

Acids and Bases

Solution containing unknown metal cations

Add 6 M HCl

Precipitate → **Group 1** — Insoluble chlorides: AgCl, PbCl$_2$, Hg$_2$Cl$_2$

Decantate → **Remaining cations**

Add H$_2$S and (CO$_3^{2-}$ ...)

Precipitate → **Group 2** — Acid-insoluble sulfides: CuS, CdS, Bi$_2$S$_3$, PbS, HgS, As$_2$S$_3$, Sb$_2$S$_3$, SnS$_2$

Decantate → **Remaining cations**

Add (NH$_4$)$_2$S at pH = 8

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

Decantate → **Remaining cations**

Add (NH$_4$)$_2$HPO$_4$ and NH$_3$

Precipitate → **Group 4** — Insoluble phosphates: Ca$_3$(PO$_4$)$_2$, Sr$_3$(PO$_4$)$_2$, Ba$_3$(PO$_4$)$_2$, MgNH$_4$PO$_4$

Decantate → **Group 5** — Alkali metal ions and NH$_4^+$

Soluble

	Important Exceptions
NO$_3^-$	None
CH$_3$COO$^-$	None
Cl$^-$	Compounds of Ag$^+$, Hg$_2^{2+}$, and Pb^{2+}
Br$^-$	Compounds of Ag$^+$, Hg$_2^{2+}$, and Pb^{2+}
I$^-$	Compounds of Ag$^+$, Hg$_2^{2+}$, and Pb^{2+}
SO$_4^{2-}$	Compounds of Sr^{2+}, Ba^{2+}, Hg$_2^{2+}$, and Pb^{2+}

Insoluble

	Important Exceptions
S^{2-}	Compounds of NH$_4^+$, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}
CO$_3^{2-}$	Compounds of NH$_4^+$ and the alkali metal cations
PO$_4^{3-}$	Compounds of NH$_4^+$ and the alkali metal cations
OH$^-$	Compounds of NH$_4^+$, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}

(From Chapter 4)

Acids and Bases

Mixture of cations A,B,C — Add 1st precipitating agent — Cation A removed — Decant liquid — Cations B,C — Add 2nd precipitating agent — Cation B removed — Decant liquid — Cation C
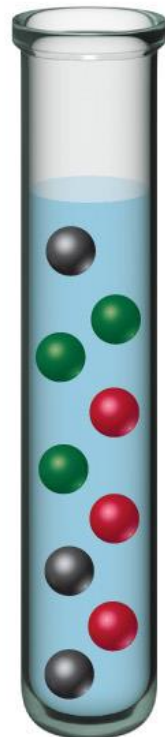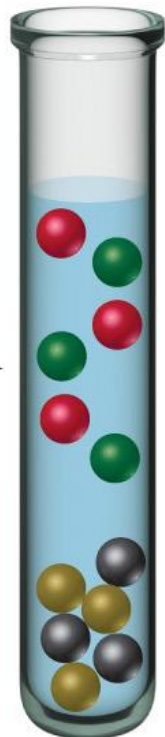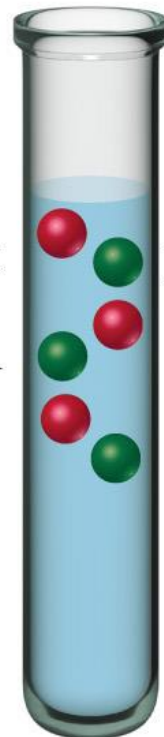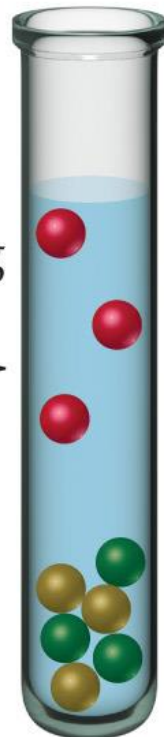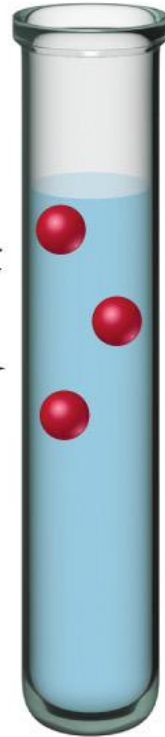
Cation A ⚫   Cation B 🟢   Cation C 🔴

Acids and Bases

Add H₂S

Remove CuS and increase pH

pH ≈ 1

pH ≈ 1

pH ≈ 8

Cu²⁺

Zn²⁺

H⁺

H₂S

HS⁻

CuS(s)

ZnS(s)
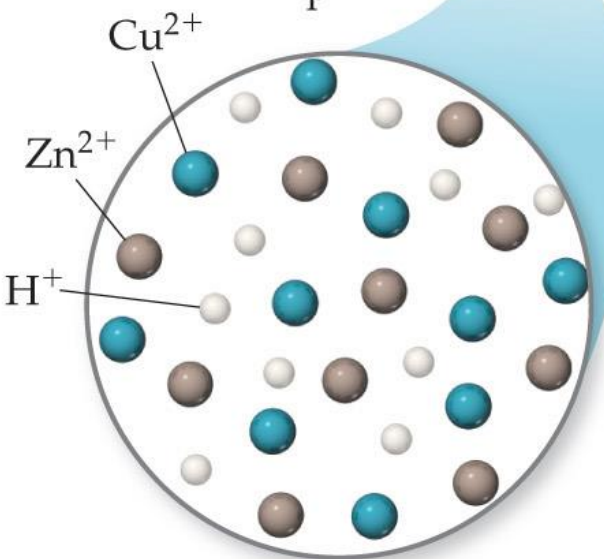
Solution containing $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$
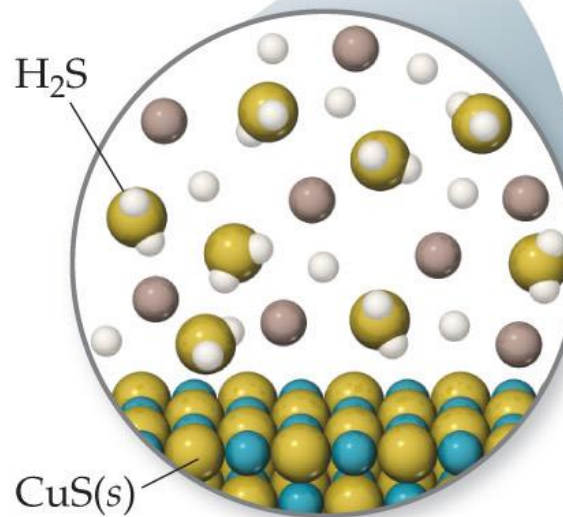
When H₂S is added to a solution whose pH exceeds 0.6, CuS precipitates
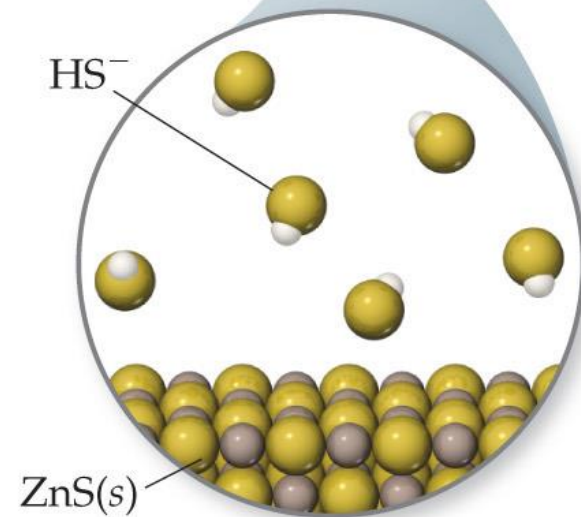
After CuS is removed, the pH is increased, allowing ZnS to precipitate

Without doing a calculation, predict which of these compounds has the greatest molar solubility in water: AgCl (K_{sp} = 1.8 × 10^{-10}), AgBr (K_{sp} = 5.0 × 10^{-13}), or AgI (K_{sp} = 8.3 × 10^{-17}).

A. AgI is the most soluble of the three.

B. AgBr is the most soluble of the three.

C. AgCl is the most soluble of the three.

D. All of the compounds are totally insoluble based on their small K_{sp} values.

Calculate the concentration of Ag^+ present in solution at equilibrium when concentrated ammonia is added to a 0.010 *M* solution of $AgNO_3$ to give an equilibrium concentration of $[NH_3]$ = 0.20 *M*. Neglect the small volume change that occurs when NH_3 is added.

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

$$Ag(NH_3)_2^+(aq) \rightleftharpoons Ag^+(aq) + 2\,NH_3(aq)$$

$$\frac{1}{K_f} = \frac{1}{1.7 \times 10^7} = 5.9 \times 10^{-8}$$
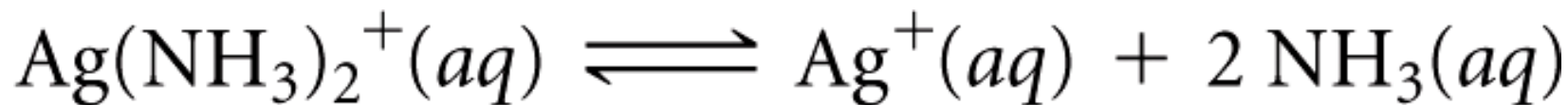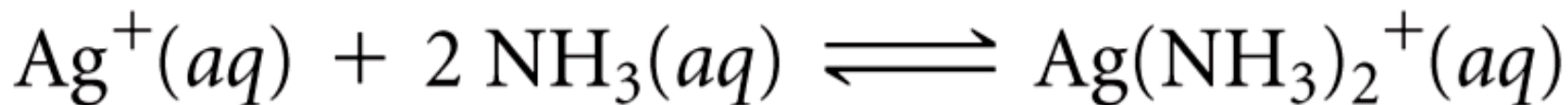
	$Ag(NH_3)_2^+(aq)$	$\rightleftharpoons$	$Ag^+(aq)$	+	$2\,NH_3(aq)$
Initial	0.010 *M*		0 *M*		
Change	$-x$ *M*		$+x$ *M*		
Equilibrium	$0.010-x$ *M*		x *M*		0.20 *M*

Because [Ag⁺] is very small,

$$0.010 - x \simeq 0.010\ M$$

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2{}^+]} = \frac{(x)(0.20)^2}{0.010} = 5.9 \times 10^{-8}$$

$$x = 1.5 \times 10^{-8}\ M = [Ag^+]$$

What is the difference between an amphoteric substance and an amphiprotic substance?

A. Amphoteric substances are acids whereas amphiprotic substances are acids.

B. Amphoteric substances are bases whereas amphiprotic substances are acids.

C. Amphoteric substances can act both as an acid and a base whereas amphiprotic substances are acids.

D. Amphoteric substances can act both as an acid and a base whereas amphiprotic substances can accept or donate a proton.

Acids and Bases

Does a precipitate form when 0.10 L of 8.0×10^{-3} M $Pb(NO_3)_2$ is added to 0.40 L of 5.0×10^{-3} M Na_2SO_4? $PbSO_4$ has a K_{sp} of 6.3×10^{-7}

The total volume is 0.10 L + 0.40 L = 0.50 L. The number of moles of Pb^{2+} in 0.10 L of 8.0×10^{-3} M $Pb(NO_3)_2$ is

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

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

The number of moles of SO_4^{2-} in 0.40 L of 5.0×10^{-3} M Na_2SO_4 is

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

$$[SO_4^{2-}] = \frac{2.0 \times 10^{-3} \text{ mol}}{0.50 \text{ L}} = 4.0 \times 10^{-3} \text{ } M$$

$Q = [Pb^{2+}][SO_4^{2-}] = (1.6 \times 10^{-3})(4.0 \times 10^{-3}) = 6.4 \times 10^{-6}$
Because $Q > K_{sp}$, $PbSO_4$ precipitates.

If a solution contained a mixture of Cu^{2+} and Zn^{2+} ions, would this separation scheme work? After which step would the first precipitate be observed?

A. No, both would precipitate in step 1 and subsequently are not easily separated.

B. No, both would precipitate in step 2 and subsequently are not easily separated.

C. Yes, ZnS precipitates in step 1 and CuS in step 4.

D. Yes, CuS precipitates in step 2 and Zn^{2+} remains in solution.

Acids
and
Bases

If a precipitate forms when HCl is added to an aqueous solution, what conclusions can you draw about the contents of the solution?

A. The solution definitely contains either Pb^{2+} or Hg_2^{2+} cation.

B. The solution definitely contains the Ag^+ cation.

C. The solution must contain one or more of the following cations: Cu^{2+}, Bi^{3+}, or Cd^{2+}.

D. The solution must contain one or more of the following cations: Ag^+, Pb^{2+} or Hg_2^{2+}.

Acids
and
Bases

Adding bromide ion to a saturated aqueous solution of _____ decreases its solubility in water.

  a. $BaSO_4$
  b. Li_2CO_3
  c. PbS
  d. AgBr

For $BaCO_3$, $K_{sp} = 5.0 \times 10^{-9}$. What is $[Ba^{2+}]$ in a saturated aqueous solution of $BaCO_3$?

  a. 7.1×10^{-5} M
  b. 1.0×10^{-8} M
  c. 2.5×10^{-9} M
  d. 5.0×10^{-9} M

Acids and Bases

For BaF_2, $K_{sp} = 1.7 \times 10^{-6}$. What is $[Ba^{2+}]$ in a saturated aqueous solution of BaF_2?

a. 1.7×10^{-6} M
b. 3.4×10^{-6} M
c. 7.6×10^{-3} M
d. 1.5×10^{-2} M

For BaF_2, $K_{sp} = 1.7 \times 10^{-6}$. What is $[F^{1-}]$ in a saturated aqueous solution of BaF_2?

a. 1.7×10^{-6} M
b. 5.7×10^{-5} M
c. 7.6×10^{-3} M
d. 1.5×10^{-2} M

Acids
and
Bases

For BaF_2, $K_{sp} = 1.7 \times 10^{-6}$. If KF is added to a saturated solution so that $[F^{1-}] = 0.10$ M, what is $[Ba^{2+}]$?
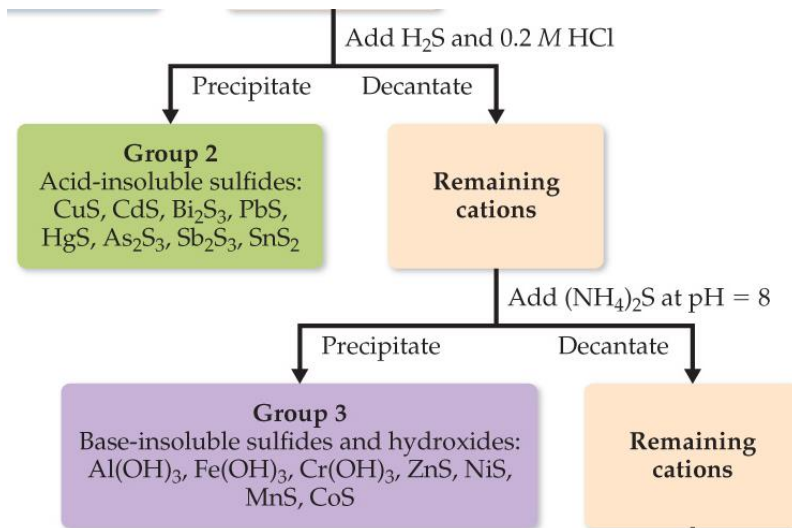
a. 1.7×10^{-6} M
b. 1.7×10^{-5} M
c. 1.7×10^{-4} M
d. 1.7×10^{-3} M

Silver bromide is insoluble in water, but dissolves in aqueous ammonia, due to the formation of _____.

a. $Ag(NH_3)_2^{1+}$
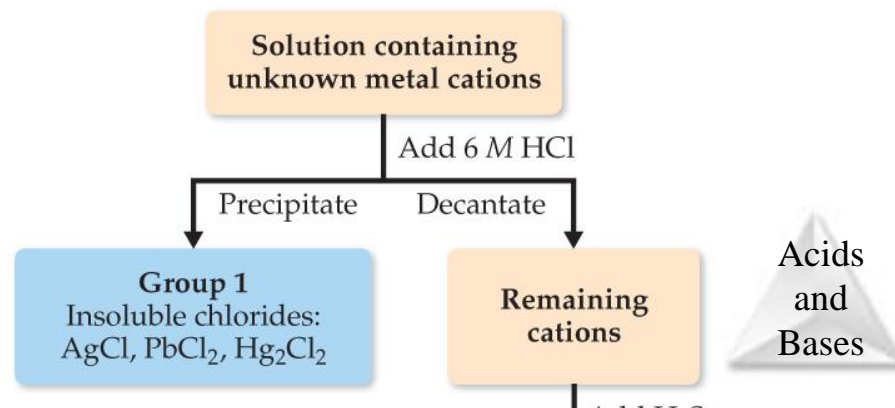b. $Ag(NH_3)^{2+}$
c. NH_3Br^{1-}
d. NH_4Br

Acids
and
Bases

Which ion will precipitate first when sulfide ion is added to a solution containing all of the ions below?
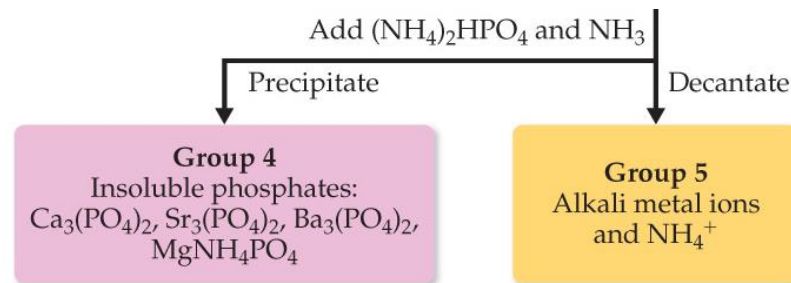
a. Hg^{2+}

b. Ni^{2+}

c. Zn^{2+}

d. Co^{2+}

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

Which ion will precipitate when HCl is added to a solution containing all of the ions below?

a. Zn^{2+}

b. Pb^{2+}

c. Al^{3+}

d. Ba^{2+}

Solution containing unknown metal cations

Add $6\ M$ HCl

Precipitate   Decantate

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

Remaining cations

Acids and Bases

Which ion will precipitate when phosphate ion is added to a solution containing all of the ions below?

a. K^{1+}

b. Ba^{2+}

c. Na^{1+}

d. NH_4^{1+}

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
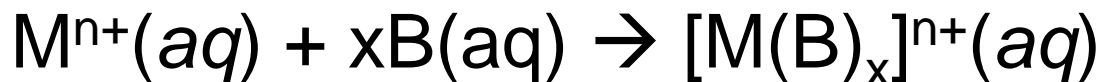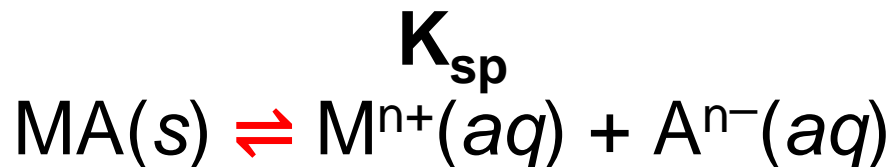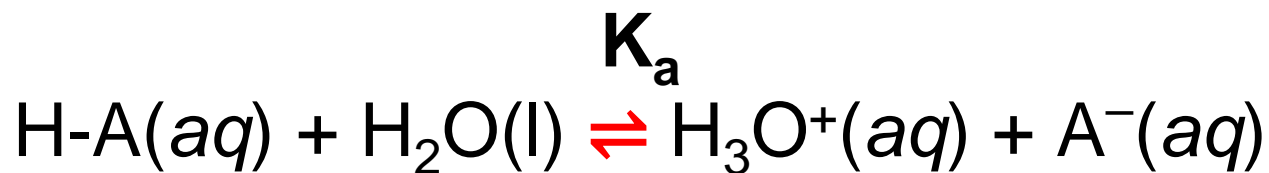and NH_4^+

Acids
and
Bases

Summary of Chapter 17

The common-ion effect

Buffer solution, Henderson–Hasselbalch equation

Solubility equilibria, solubility-product constant (K_{sp}), Complex ion formation, amphoterism

$$\text{H-A}(aq) + \text{H}_2\text{O}(l) \overset{\textbf{K}_\textbf{a}}{\rightleftharpoons} \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$$

$$\text{MA}(s) \overset{\textbf{K}_\textbf{sp}}{\rightleftharpoons} \text{M}^{n+}(aq) + \text{A}^{n-}(aq)$$

$$\text{M}^{n+}(aq) + x\text{B}(aq) \rightarrow [\text{M(B)}_x]^{n+}(aq)$$

Acids
and
Bases

Thank You for Your Attention!
Any Questions?

Acids and Bases