**CHEM2100J
Chemistry
Autumn 2024**

Chapter 12
Aqueous Solution Equilibrium

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Composition and pH

Sometimes we need to know how the concentrations of the ions present in a solution of a polyprotic acid vary with pH.
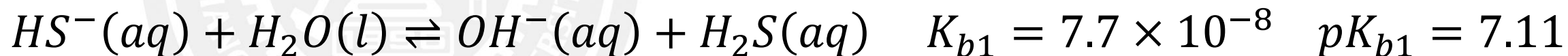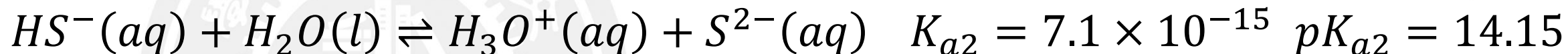
In rainwater, the amount of carbonic acid at low pH (when hydronium ions are abundant), should be dominant so we expect to see the fully protonated species H_2CO_3.

At high pH (when hydroxide ions are abundant), we expect the fully deprotonated species (CO_3^{2-}) to be dominant.

At intermediate pH, we expect the intermediate species HCO_3^- to dominate.
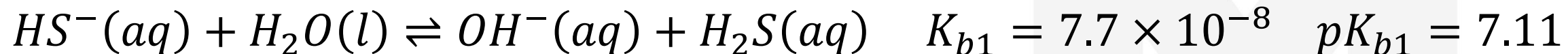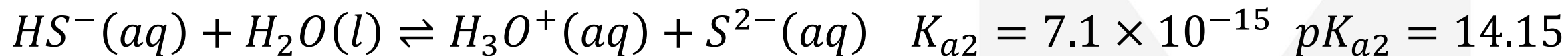
Solutions of Salts of Polyprotic Acids

Conjugate bases of polyprotic acids are **amphiprotic**: they can act as either an acid or a base, donating or accepting a proton—this is a <u>major topic in the next chapter</u>.

For example, a hydrogen sulfide ion, HS⁻, in water acts as both an acid and a base:

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 7.1 \times 10^{-15} \quad pK_{a2} = 14.15$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2S(aq) \quad K_{b1} = 7.7 \times 10^{-8} \quad pK_{b1} = 7.11$$

HS⁻ is amphiprotic, so it is not immediately apparent whether NaHS is acidic or basic.

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 7.1 \times 10^{-15} \quad pK_{a2} = 14.15$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2S(aq) \quad K_{b1} = 7.7 \times 10^{-8} \quad pK_{b1} = 7.11$$

However, we can use the pK_a and pK_b values of the HS$^-$ ion to conclude that:

- HS$^-$ is a weak acid (K_{a2}) and the basic character of S^{2-} will dominate, leading to a pH > 7.

- HS$^-$ is a weak base; again pH > 7.

As long as $[X]_{initial} \gg K_{a1}$:

$$pH = \frac{(pK_{a1} + pK_{a2})}{2}$$

Useful for determining buffer points, choose indicators, or determine where intermediate species will be present.
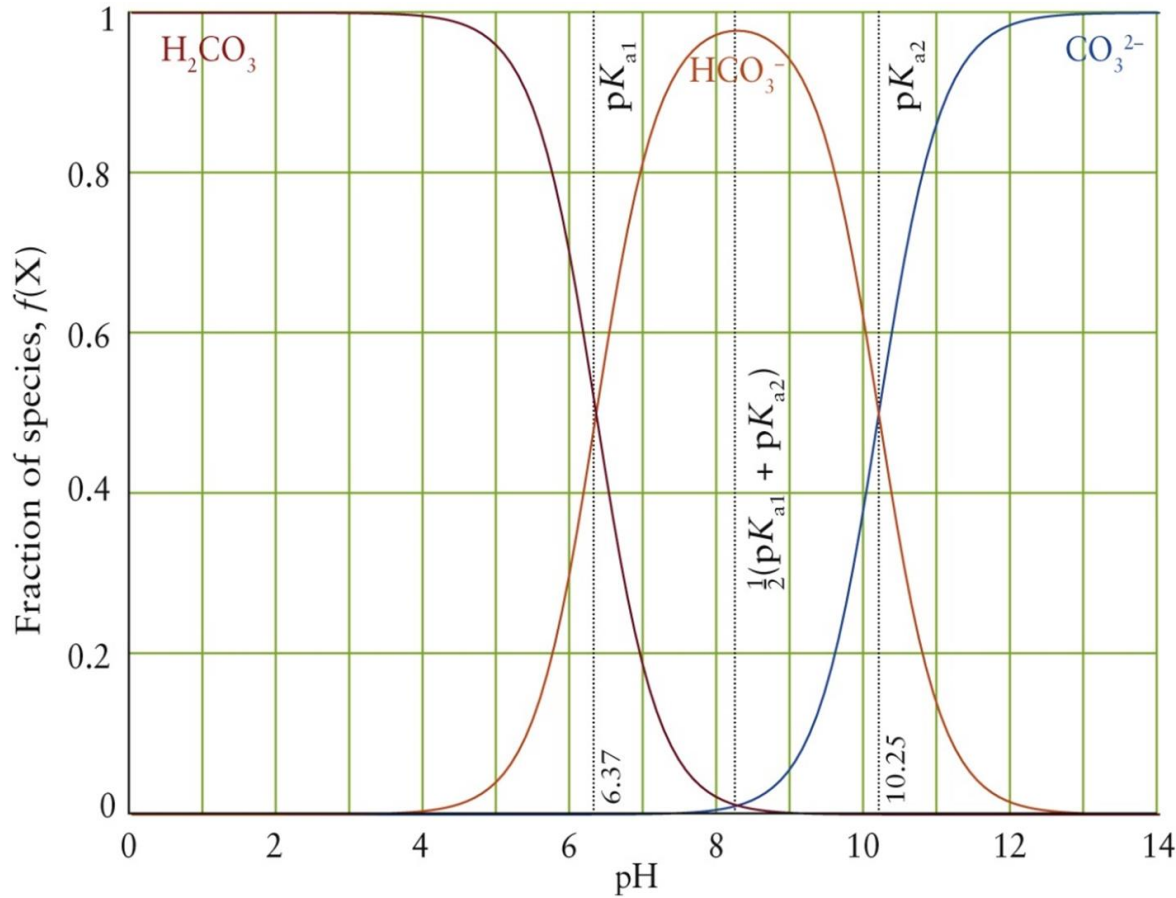
pH and Solute Concentrations

Figure 6E.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

pH variation can cause significant changes to the concentrations of other solutes
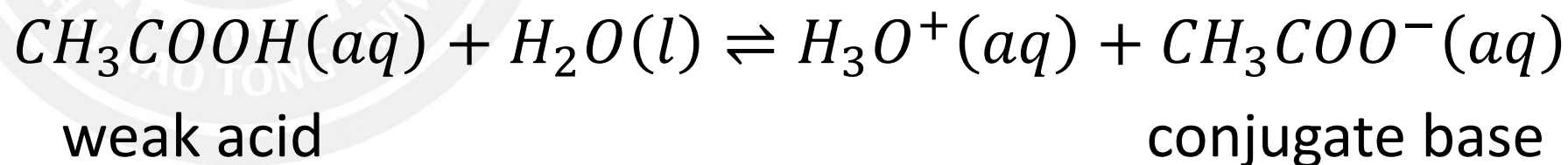
Buffer Action

A buffer is a solution that resists a change in pH when small amounts of strong acids or bases are added.

We see buffers in intravenous solutions to patients; blood plasma is buffered to a pH of 7.4 ($\pm$ 0.2); the ocean is buffered to a pH of 8.

A buffer is a **weak acid** with its **conjugate base** or a **weak base** with its **conjugate acid**.

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

weak acid   conjugate base

Buffer Action

For example, 1.0 L of water, would have a pH of 7.0.

Adding 1 mL of 1.0 M HCl solution, we can calculate the new hydronium ion concentration:

$$[H_3O^+] = \frac{[HCl] \cdot V_{HCl}}{V_{H_2O} + V_{HCl}} = \frac{1.0 \, \frac{mol}{L} \times 0.001 \, L}{1.0 \, L + 0.001 L} = 0.001 \, \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -\log(0.001) = 3.0$$

That means that $\Delta pH = 7 - 3 = 4$.

So, the effect of adding 1 mL of a strong acid to 1 L of pure water (1‰) can increase water's hydronium ion concentration [H$_3$O$^+$] by 10,000!

Buffer Action

Our **definition of a buffer** is the ability to **resist a change in pH**.

Our previous example of $\Delta pH = 7 - 3 = 4$ shows not much resistance.

Next, we look at how to design a buffer.

We will calculate our **initial buffer pH** (an acid and its conjugate base).

Suppose we want to culture bacteria, needing to maintain a pH around 4. We prepare a buffer solution that is 0.040 M $NaCH_3CO_2(aq)$ and 0.080 M $CH_3COOH(aq)$ at 25 °C. What is the pH of the buffer solution?

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq), K_a = 1.8 \times 10^{-5}$$
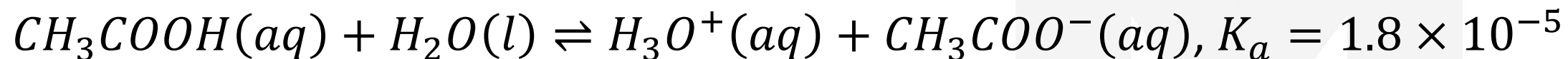
First, we build our ICE table:

	CH_3COOH	H_3O^+	CH_3COO^-
initial	0.080	0	0.040
change	-x	+x	+x
equilibrium (final)	0.080-x	x	0.040+x

Example

$K_a = 1.8 \times 10^{-5} \ll 0.040$ (the smallest of the starting concentrations), so we can ignore the changes in initial acid and base concentrations.

$$K_a = \frac{[CH_3COO^-]x}{[CH_3COOH]}$$

$$x = \frac{K_a \cdot [CH_3COOH]}{[CH_3COO^-]} = \frac{1.8 \times 10^{-5} \cdot 0.080}{0.040} = 3.6 \times 10^{-5}$$

$$[CH_3COOH] = 0.080 \, \frac{mol}{L} \quad [CH_3COO^-] = 0.040 \, \frac{mol}{L} \quad [H_3O^+] = 3.6 \times 10^{-5} \, \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -\log(3.6 \times 10^{-5}) = 4.44$$

$$degree \ of \ deprotonation = \frac{x}{[CH_3COOH]_{initial}} = \frac{3.6 \times 10^{-5}}{0.080} = 4.5 \times 10^{-4}$$
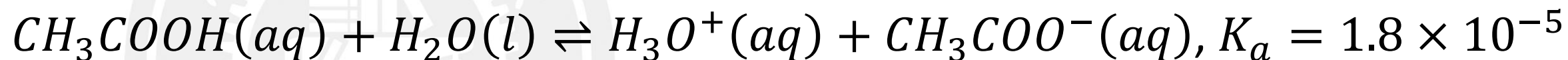
A Buffer in Action: Acid

Adding 1 mL of 1.0 M HCl solution to 1.0 L of pure water resulted in a pH of 3.0, a change in the water's hydronium ion concentration [H_3O^+] of 10,000.

Now let's buffer the 1.0 L of pure water with our previous buffer of acetic acid and the conjugate acetate ion solution:

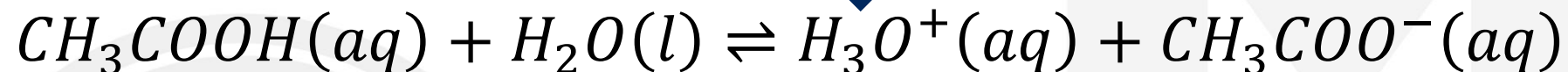$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq), K_a = 1.8 \times 10^{-5}$$

First, we'll see the **descriptive** analysis followed by a **quantitative** interpretation of what happens when 1 mL of HCl is added to a buffer, CH_3COOH/CH_3COO^- solution.
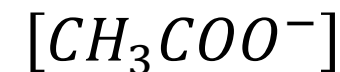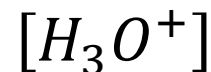
A Buffer in Action: Acid

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
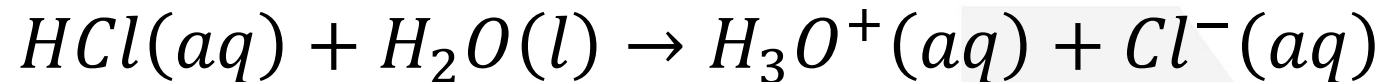
1. The strong acid reacts with the weak base

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

2. The equilibrium is shifted towards the weak acid

$[CH_3COOH]$ $[H_3O^+]$ $[CH_3COO^-]$

Buffers are an acid/conjugate base pair (and visa versa).

3. HCl is removed and replaced with CH$_3$COOH!
A strong acid has been replaced with a weak acid!

A Buffer in Action: Acid

Remember that a **strong acid** reacts **completely** with a **weak base**.

Adding 1 mL of 1.0 M HCl solution to a 1.0 L buffer solution of 0.040 M NaCH$_3$CO$_2$(aq) and 0.080 M CH$_3$COOH(aq)

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq), K_a = 1.8 \times 10^{-5}$$
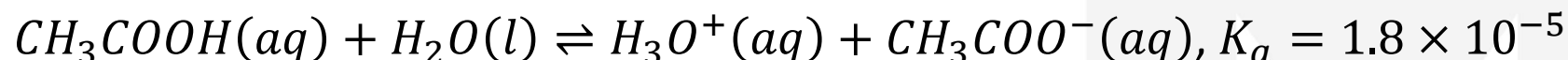
H$_3$O$^+$ and CH$_3$COO$^-$ react first. We need to find which amount of H$_3$O$^+$ will be introduced and which amount of CH$_3$COO$^-$ will remain afterwards.

$$n_{CH_3COOH,initial} = [CH_3COO] \cdot V_{buffer} = 0.080 \, \frac{mol}{L} \times 1.0 \, L = 0.080 \text{ mol}$$

$$n_{H_3O^+,initial} = [HCl] \cdot V_{HCl} = 1.0 \, \frac{mol}{L} \times 0.001 \, L = 0.001 \text{ mol}$$

$$n_{CH_3COO^-,initial} = [CH_3COO^-] \cdot V_{buffer} = 0.040 \, \frac{mol}{L} \times 1.0 \, L = 0.040 \text{ mol}$$

Now we let the reaction between H$_3$O$^+$ and CH$_3$COO$^-$ occur:

$$n_{CH_3COOH} = n_{CH_3COOH,initial} + n_{H_3O^+,initial} = 0.080 \text{ mol} + 0.001 \text{ mol} = 0.081 \text{ mol}$$

$$n_{H_3O^+} = n_{H_3O^+,initial} - n_{CH_3COO^-,initial} = 0.001 \text{ mol} - 0.040 \text{ mol} \rightarrow 0 \text{ mol}$$

$$n_{CH_3COO^-} = n_{CH_3COO^-,initial} - n_{H_3O^+,initial} = 0.040 \text{ mol} - 0.001 \text{ mol} = 0.039 \text{ mol}$$

A Buffer in Action: Acid

To find out the pH of the buffer after the HCl was added, we first need to convert our amounts into concentrations again:

$$[CH_3COOH] = \frac{n_{CH_3COOH}}{V_{total}} = \frac{n_{CH_3COOH}}{V_{buffer} + V_{HCl}} = \frac{0.081 \text{ mol}}{1.001 \text{ L}} = 0.081 \frac{\text{mol}}{\text{L}}$$

$$[H_3O^+] = \frac{n_{H_3O^+}}{V_{total}} = \frac{n_{H_3O^+}}{V_{buffer} + V_{HCl}} = \frac{0 \text{ mol}}{1.001 \text{ L}} = 0 \frac{\text{mol}}{\text{L}}$$

$$[CH_3COO^-] = \frac{n_{CH_3COO^-}}{V_{total}} = \frac{n_{CH_3COO^-}}{V_{buffer} + V_{HCl}} = \frac{0.039 \text{ mol}}{1.001 \text{ L}} = 0.039 \frac{\text{mol}}{\text{L}}$$

But now we realize, that CH_3COOH and CH_3COO^- will re-establish an equilibrium, creating new hydronium ions. So, we need to use our ICE table to find the concentrations in this new equilibrium.

	CH_3COOH	H_3O^+	CH_3COO^-
initial	0.081	0	0.039
change	-x	+x	+x
equilibrium (final)	0.081-x	x	0.039+x

A Buffer in Action: Acid

$K_a = 1.8 \times 10^{-5} \ll 0.039$ (the smallest of the starting concentrations), so we can ignore the changes in initial acid and base concentrations.

$$K_a = \frac{[CH_3COO^-]x}{[CH_3COOH]}$$

$$x = \frac{K_a \cdot [CH_3COOH]}{[CH_3COO^-]} = \frac{1.8 \times 10^{-5} \times 0.081}{0.039} = 3.7 \times 10^{-5}$$

$$[CH_3COOH] = 0.081 \frac{mol}{L} \qquad [CH_3COO^-] = 0.039 \frac{mol}{L} \qquad [H_3O^+] = 3.7 \times 10^{-5} \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -\log(3.7 \times 10^{-5}) = 4.43$$

We remember that the initial pH of our buffer solution was 4.44. Therefore, $\Delta pH = 4.44 - 4.43 = 0.01$. This is a lot **less dramatic** than the increase in $[H_3O^+]$ by a factor of 10,000 we saw for pure water. Also, note that the **strong acid** HCl is gone and has been **replaced** with the **weak acid** CH$_3$COOH.

A Buffer in Action: Base

Adding 1.2 g NaOH (0.030 mol) to 500. mL of a buffer solution that is 0.040 M $NaCH_3CO_2(aq)$ and 0.080 M $CH_3COOH(aq)$:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq), K_a = 1.8 \times 10^{-5}$$
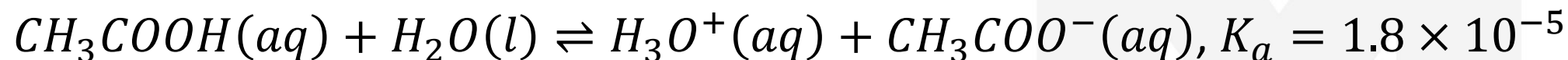
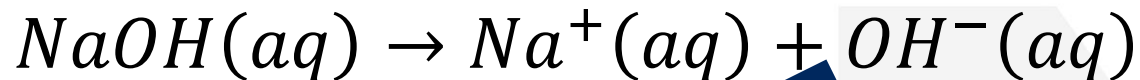From our previous calculations we know that pH = 4.44.

This time we're adding a base to the buffer. The key point now is to remember that a **strong base** reacts **completely** with a **weak acid**.
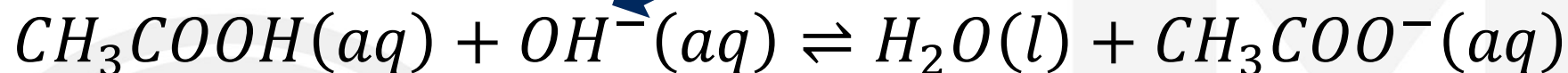
In pure water, adding 1.2 g NaOH produces 0.030 mol OH⁻:

$$[OH^-] = \frac{n_{OH^-}}{V_{H_2O}} = \frac{0.030 \text{ mol}}{0.500 \text{ L}} = 0.060 \, \frac{\text{mol}}{\text{L}}$$

$$pH = 14 - pOH = 14 - (-\log([OH^-])) = 14 - (-\log([0.060])) = 14 - 1.22 = 12.78$$

A Buffer in Action: Base
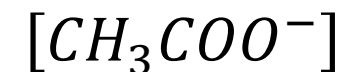
$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

1. The strong base reacts with the weak acid

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

2. The equilibrium is shifted towards the weak base

$[CH_3COOH]$ $[OH^-]$ $[CH_3COO^-]$

Buffers are a base/conjugate acid pair (and visa versa).
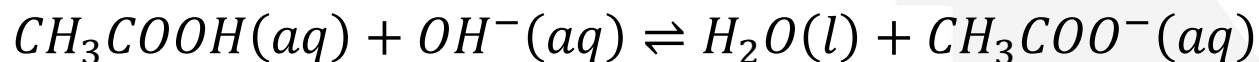
3. NaOH is removed and replaced with CH_3COO^-!
A strong base has been replaced with a weak base!

A Buffer in Action: Base

Now adding a base reacts with the acid in our buffer.

Adding 1.2 g NaOH (0.030 mol) to 500. mL of a buffer solution, we realize that OH^- and CH_3COOH react first.
$$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + CH_3COO^-(aq)$$

We need to find which amount of H_3O^+ will be introduced and which amount of CH_3COO^- will remain afterwards.

$$n_{CH_3COOH,initial} = [CH_3COOH] \cdot V_{buffer} = 0.080 \frac{mol}{L} \times 0.500 \text{ L} = 0.040 \text{ mol}$$

$$n_{OH^-,initial} = \frac{m_{NaOH}}{M_{NaOH}} = \frac{1.2 \text{ g}}{40.00 \frac{g}{mol}} = 0.030 \text{ mol}$$

$$n_{CH_3COO^-,initial} = [CH_3COO^-] \cdot V_{buffer} = 0.040 \frac{mol}{L} \times 0.500 \text{ L} = 0.020 \text{ mol}$$

Now we let the reaction between OH^- and CH_3COOH occur:

$$n_{CH_3COOH} = n_{CH_3COOH,initial} - n_{OH^-,initial} = 0.040 \text{ mol} - 0.030 \text{ mol} = 0.010 \text{ mol}$$

$$n_{OH^-} = n_{OH^-,initial} - n_{CH_3COOH,initial} = 0.030 \text{ mol} - 0.040 \text{ mol} \rightarrow 0 \text{ mol}$$

$$n_{CH_3COO^-} = n_{CH_3COO^-,initial} + n_{OH^-,initial} = 0.020 \text{ mol} + 0.030 \text{ mol} = 0.050 \text{ mol}$$

A Buffer in Action: Acid

To find out the pH of the buffer after the NaOH was added, we first need to convert our amounts into concentrations again:

$$[CH_3COOH] = \frac{n_{CH_3COOH}}{V_{total}} = \frac{n_{CH_3COOH}}{V_{buffer}} = \frac{0.010 \text{ mol}}{0.500 \text{ L}} = 0.020 \frac{mol}{L}$$

$$[OH^-] = \frac{n_{OH^-}}{V_{total}} = \frac{n_{OH^-}}{V_{buffer}} = \frac{0 \text{ mol}}{0.500 \text{ L}} = 0 \frac{mol}{L}$$

$$[CH_3COO^-] = \frac{n_{CH_3COO^-}}{V_{total}} = \frac{n_{CH_3COO^-}}{V_{buffer}} = \frac{0.050 \text{ mol}}{0.500 \text{ L}} = 0.100 \frac{mol}{L}$$

But now we realize, that CH$_3$COOH and CH$_3$COO$^-$ will re-establish an equilibrium, creating new hydronium ions. So, we need to use our ICE table to find the concentrations in this new equilibrium.

	CH$_3$COOH	H$_3$O$^+$	CH$_3$COO$^-$
initial	0.020	0	0.100
change	-x	+x	+x
equilibrium (final)	0.020-x	x	0.100+x

$K_a = 1.8 \times 10^{-5} \ll 0.020$ (the smallest of the starting concentrations), so we can ignore the changes in initial acid and base concentrations.

$$K_a = \frac{[CH_3COO^-]x}{[CH_3COOH]}$$

$$x = \frac{K_a \cdot [CH_3COOH]}{[CH_3COO^-]} = \frac{1.8 \times 10^{-5} \times 0.020}{0.100} = 3.6 \times 10^{-6}$$

$$[CH_3COOH] = 0.020 \, \frac{mol}{L} \qquad [CH_3COO^-] = 0.100 \, \frac{mol}{L} \qquad [H_3O^+] = 3.6 \times 10^{-6} \, \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -\log(3.6 \times 10^{-6}) = 5.44$$

We remember that the initial pH of our buffer solution was 4.44. Therefore, $\Delta pH = 5.44 - 4.44 = 1$. This is a lot **less dramatic** than the increase in $[H_3O^+]$ for pure water ($\Delta pH = 12.78 - 7 = 5.78$). Also, note that the **strong base** NaOH is gone and has been **replaced** with the **weak base** CH₃COO⁻.

Preparation of a Buffer

Typically, a buffer is made of equal concentrations of both the conjugate acid and base, this is called **equimolar**.

Since $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$, being equimolar means $[HA] = [A^-]$.

This also means that $K_a = \dfrac{[H_3O^+][A^-]}{[HA]} = [H_3O^+]$, so that $pH = pK_a$.

For example, if you wanted a buffer solution close to a pH of 5, you would choose the acetic acid/acetate buffer ($pK_a = 4.75$).

| Acid Buffer	pK_a
CH_3COOH/CH_3COO^-	4.75
HNO_2/NO_2^-	3.37
$HClO_2/ClO_2^-$	2.00

To prepare a buffer, match the pH to the pK_a or pOH to the pK_b.

Henderson-Hasselbalch

The Henderson-Hasselbalch equation allows for a quick approximation of pH calculations for buffer solutions. It assumes K_a is sufficiently small compared to the initial concentrations of acid and base.

For any weak acid:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
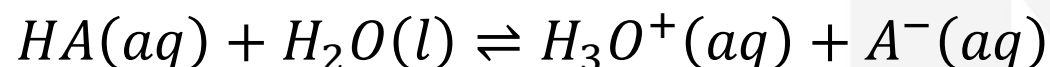
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$[H_3O^+] = K_a \cdot \frac{[HA]}{[A^-]}$$

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

Note: The "+" sign requires the fraction to be turned around, as $pX = -\log(X)$.

Calculate the ratio of the molarities of CO_3^{2-} and HCO_3^- ions required to achieve buffering at pH = 9.50. The pK_{a2} of H_2CO_3 is 10.25.

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

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = 10^{pH-pK_a} = 10^{9.50-10.25} = 0.18 = \frac{0.18}{1}$$

For example:

$$[CO_3^{2-}] = 0.18\ \frac{\text{mol}}{\text{L}} \qquad [HCO_3^-] = 1.00\ \frac{\text{mol}}{\text{L}}$$

Buffer Capacity

Just as a sponge can hold only so much water, a buffer can neutralize only so many hydronium ions.

Buffer capacity is the maximum amount of acid or base that can be added before the buffer loses its ability to resist large changes in pH.

Adding excess acid will overwhelm the conjugate base, or adding to much excess base will overwhelm the conjugate acid.

Buffer Capacity

Broadly speaking, a buffer is found experimentally to have a high capacity for acid when the amount of base present is at least 10% of the amount of acid; similarly for a base.

Experimentally, a buffer works best when it is initially within ± 1 pH of the pK_a of the buffer solution.
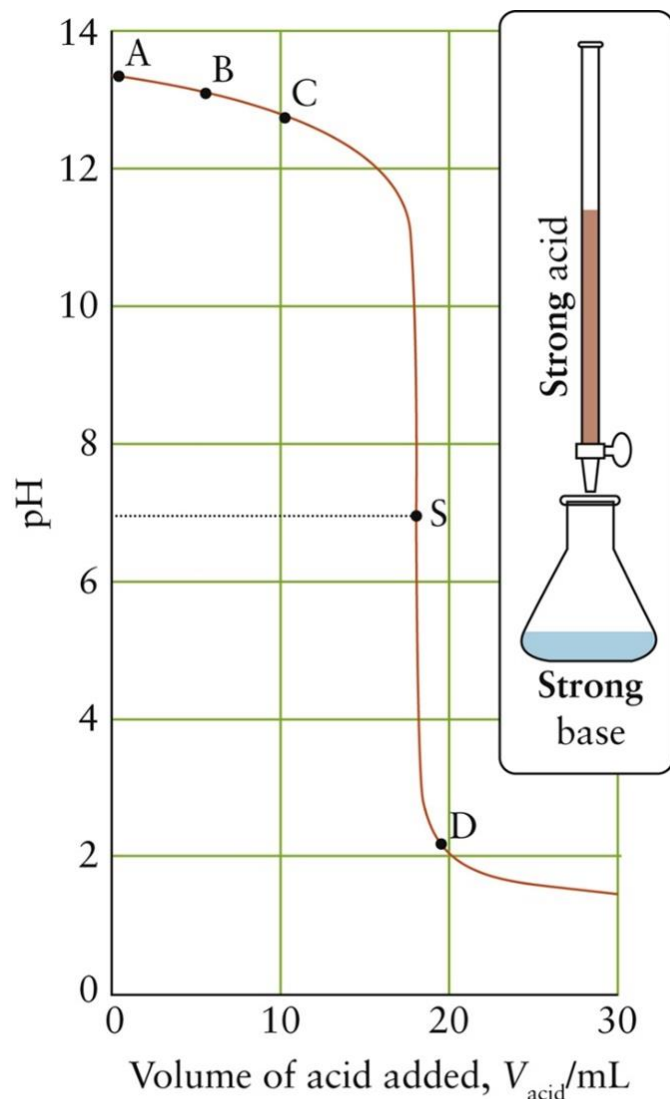
Titrations

We encountered titration in Fundamentals, involving adding a solution, called the titrant, from a burette to a flask containing the sample, called the analyte.

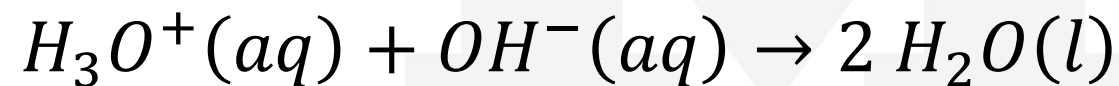Upon reaching the stoichiometric point, $[H_3O^+] = [OH^-]$, the indicator changes colour.

We continue using this technique to determine the pH and to select the appropriate indicator.

Strong Acid-Strong Base Titrations

Figure 6H.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

In a neutralization reaction, a strong acid mixes with a strong base:

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2\,H_2O(l)$$

Plotting the pH against the volume of titrant added during a titration is yields a **pH curve**.

A strong acid-strong base titration shows a sudden change in pH at the stoichiometric point near pH 7.
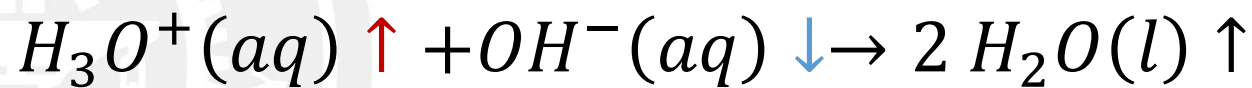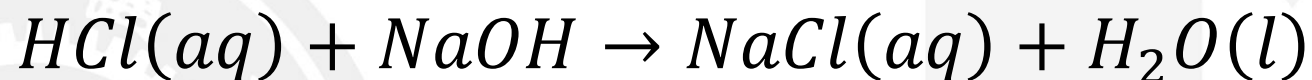
Write the neutralization reaction.

Determine the **amount (in moles)** of acid or base present in the analyte and titrant.

Calculate the **final concentration** by taking the **amount** calculated divided by the **total volume**.

Suppose we are carrying out a titration in which the analyte initially consists of 25.00 mL of 0.250 M NaOH(aq), and the titrant is 0.340 M HCl(aq). After the addition of 5.00 mL of the acid titrant, we can expect the pH to decrease slightly from its initial value. Calculate the new pH.

$$HCl(aq) + NaOH \rightarrow NaCl(aq) + H_2O(l)$$

$$H_3O^+(aq) \uparrow + OH^-(aq) \downarrow \rightarrow 2\,H_2O(l) \uparrow$$

Le Chatelier's principle says an **increase** in acid will cause a **shift** to the product side, thereby **removing** base, so the pH will decrease.

$$pH_{initial} = 14 - pOH = 14 - (-\log([OH^-]_{initial})) = 14 - (-\log(0.250)) = 14 - 0.0602 = 13.40$$

Example

Suppose we are carrying out a titration in which the analyte initially consists of 25.00 mL of 0.250 M NaOH(aq), and the titrant is 0.340 M HCl(aq). After the addition of 5.00 mL of the acid titrant, we can expect the pH to decrease slightly from its initial value. Calculate the new pH.

$$n_{OH^-,initial} = [NaOH] \cdot V_{analyte} = 0.250 \; \frac{mol}{L} \times 0.025 \; L = 0.0063 \; mol$$

$$n_{H_3O^+} = [HCl] \cdot V_{titrant} = 0.340 \; \frac{mol}{L} \times 0.005 \; L = 0.0017 \; mol$$

As a strong acid will react completely with a strong base, we can easily calculate how much OH⁻ remains:

$$n_{OH^-} = n_{OH^-,initial} - n_{H_3O^+} = 0.0063 \; mol - 0.0017 \; mol = 0.0046 \; mol$$

$$[OH^-] = \frac{n_{OH^-}}{V_{total}} = \frac{n_{OH^-}}{V_{analyte} + V_{titrant}} = \frac{0.0046 \; mol}{0.025 \; L + 0.005 \; L} = 0.152 \; \frac{mol}{L}$$

$$pH = 14 - pOH = 14 - (-\log([OH^-])) = 14 - (-\log(0.152)) = 14 - 0.8181 = 13.18$$

$$\Delta pH = 13.40 - 13.18 = 0.22$$

In the titration of a strong acid with a strong base, the pH changes slowly, then rapidly through the stoichiometric point at $pH = 7$, and then slowly again.

At the stoichiometric point:
$$[H_3O^+] = [OH^-]$$

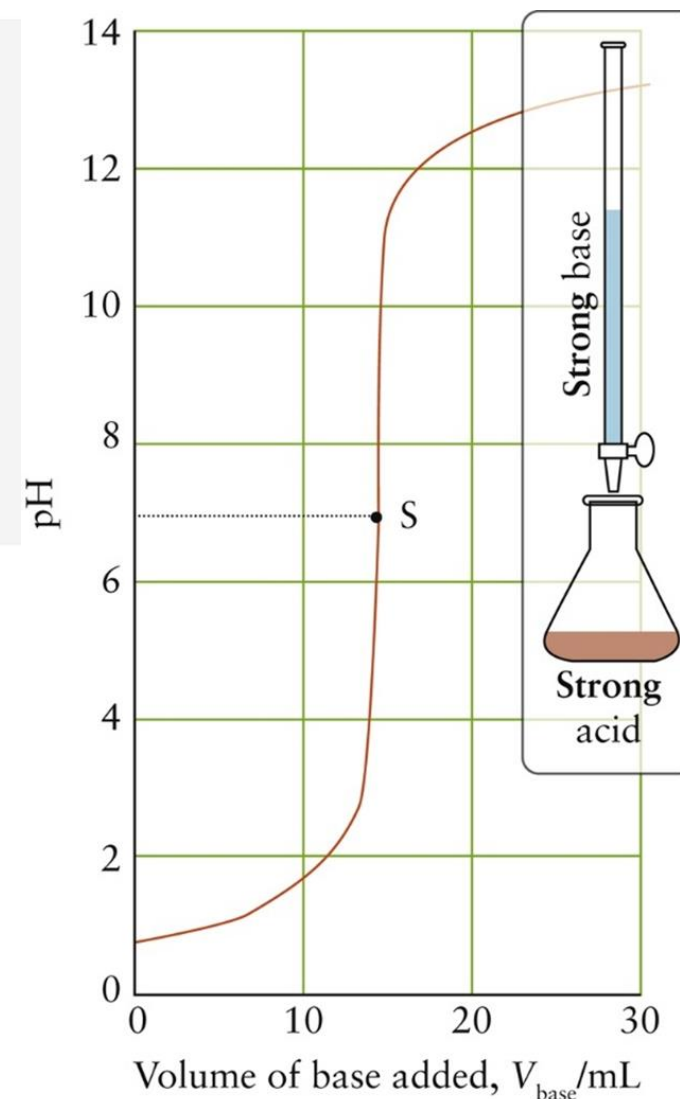A final pH of 7 is reached for all strong acid-strong base titrations.

Figure 6H.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
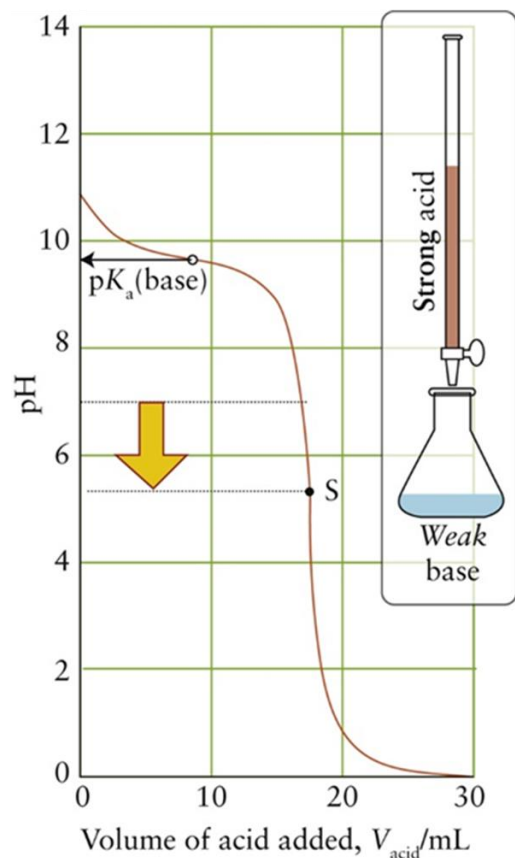W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Figure 6H.4
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman
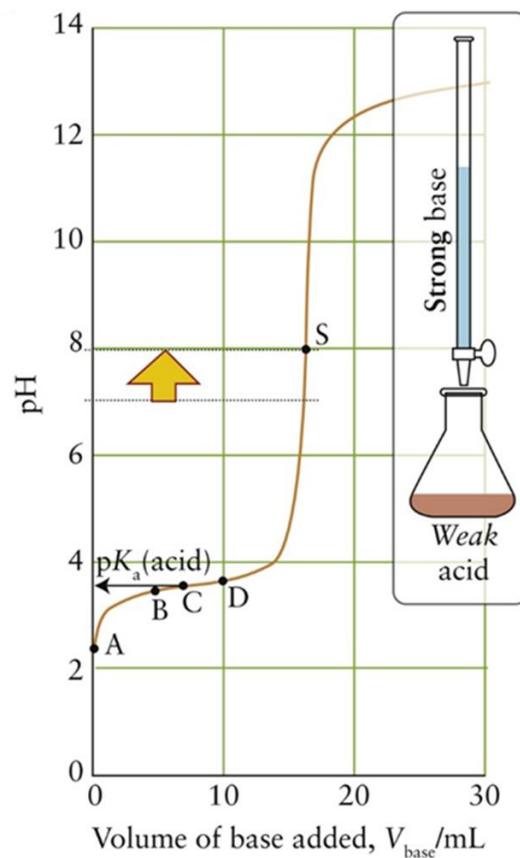
Figure 6H.3
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

A more common titration is between a **weak** acid or base and a **strong** base or acid.

The final pH in this case will not be 7.

The final pH depends on the conjugate salt produced.

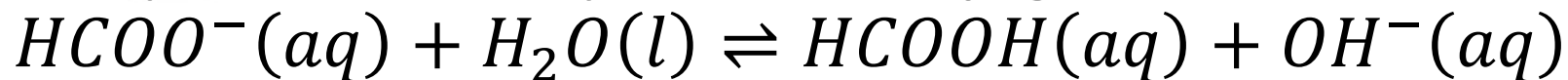In the next example, we calculate the pH of this solution.

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOO^-(aq) + Na^+(aq) + H_2O(l)$$

Example

Estimate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M HCOOH(*aq*) with 0.150 M NaOH(*aq*).

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOO^-(aq) + Na^+(aq) + H_2O(l)$$

At the stoichiometric point only Na$^+$(*aq*) and HCOO$^-$(*aq*) will be present in the solution, as all OH$^-$ has been neutralised by the HCOOH.

The solution of this problem requires two parts:

1. Find the amount of HCOO$^-$ produced and the volume of titrant (NaOH) required.

2. Calculate the pH of the newly formed conjugate base:
$$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$$

Example

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOO^-(aq) + Na^+(aq) + H_2O(l)$$

First, we need the amount of HCOOH to determine the amount of HCOO⁻ at the stoichiometric point and the volume of titrant (NaOH) required.

$$n_{HCOOH,initial} = [HCOOH] \cdot V_{analyte} = 0.100 \ \frac{mol}{L} \times 0.02500 \ L = 0.002500 \ mol$$

At the stoichiometric point, only Na⁺ and HCOO⁻ are present, therefore:

$$n_{HCOO^-} = n_{HCOOH,initial} = 0.002500 \ mol$$

The volume of titrant required to deprotonate HCOOH to HCOO⁻:

$$V_{titrant} = \frac{n_{HCOO^-}}{[NaOH]} = \frac{0.002500 \ mol}{0.150 \ \frac{mol}{L}} = 0.0167 \ L$$
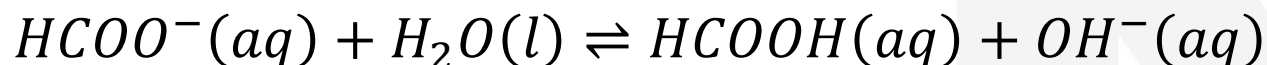
The concentration of HCOO⁻ at the stoichiometric point:

$$[HCOO^-] = \frac{n_{HCOO^-}}{V_{total}} = \frac{n_{HCOO^-}}{V_{analyte} + V_{titrant}} = \frac{0.002500 \ mol}{0.02500 \ L + 0.0167 \ L} = 0.0600 \ \frac{mol}{L}$$

Now that the stoichiometric point has been reached and all initial HCOOH has been neutralised, we need to look at the new equilibrium of the conjugate base HCOO⁻:

$$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

$$[HCOO^-] = \frac{n_{HCOO^-}}{V_{total}} = \frac{n_{HCOO^-}}{V_{analyte} + V_{titrant}} = \frac{0.002500 \text{ mol}}{0.02500 \text{ L} + 0.0167 \text{ L}} = 0.0600 \frac{\text{mol}}{\text{L}}$$

	HCOO⁻	OH⁻	HCOO^H
initial	0.0600	0	0
change	-x	+x	+x
equilibrium (final)	0.060-x	x	x

$K_b = 5.6 \times 10^{-11} \ll 0.060$, so we can ignore the change in initial base concentration.

$$K_b = \frac{x^2}{[HCOO^-]}$$

$$x = \sqrt{K_b \cdot [HCOO^-]} = \sqrt{5.6 \times 10^{-11} \times 0.0600} = 1.8 \times 10^{-6}$$

$$[HCOO^-] = 0.0600 \, \frac{\text{mol}}{\text{L}} \qquad [HCOOH] = [OH^-] = 1.8 \times 10^{-6} \, \frac{\text{mol}}{\text{L}}$$

$$pH = 14 - pOH = 14 - (-\log([OH^-])) = 14 - (-\log(1.8 \times 10^{-6})) = 14 - 5.74 = 8.26$$

$$degree \ of \ protonation = \frac{x}{[HCOO^-]_{initial}} = \frac{1.8 \times 10^{-6}}{0.0600} = 3.0 \times 10^{-5}$$

pH of solution of strong base (the titrant) →

pH of the salt solution → ● S

pH = pK_a of the weak acid →

pH of solution of weak acid (the analyte)

14
12
10
8
6
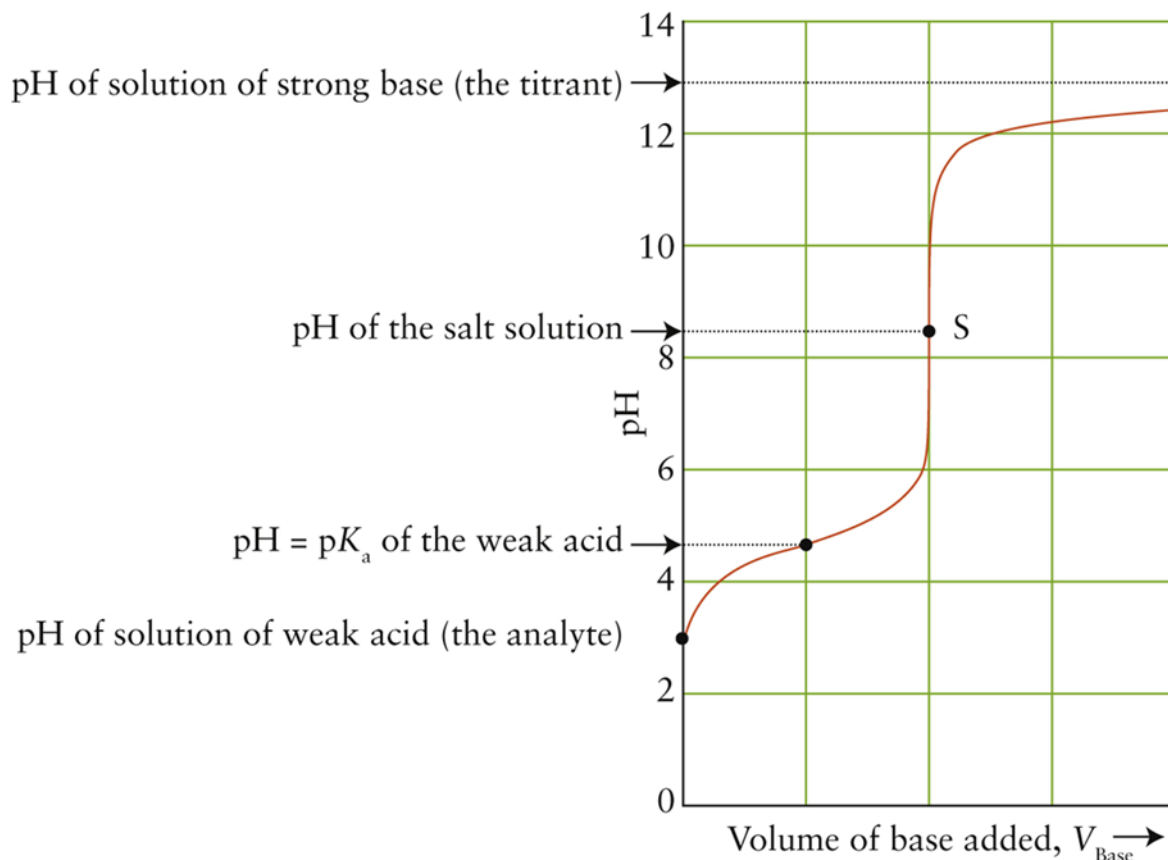4
2
0

pH

Volume of base added, V_{Base} →

Figure 6H.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

At the halfway point of the titration, $[HA] = [A^-]$ and $pH = pK_a$. The flatness of the curve near $pH = pK_a$ illustrates the ability of a buffer solution to stabilize the pH of the solution.

The slow change in pH about halfway to the stoichiometric point indicates that the solution acts as a buffer in that region.

At the stoichiometric point:
$$[H_3O^+] = [OH^-]$$

Example

Calculating the pH before the Stoichiometric Point in a Weak Acid-Strong Base Titration

Calculate the pH of (a) 0.100 M HCOOH(*aq*) and (b) the solution resulting when 5.00 mL of 0.150 M NaOH(*aq*) is added to 25.00 mL of the acid.

Use K_a = 1.8×10^{-4} for HCOOH.

In (a) we calculate the initial pH. Since HCOOH is a weak acid, there will be both the acid and its conjugate base, so we make an ICE table to find pH.

In (b) we need to find the moles of NaOH that will react with HCOOH, which means HCOO$^-$ is formed, so a new pH is calculated.
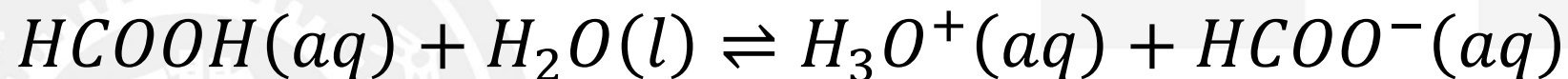
Calculate the pH of (a) 0.100 M HCOOH(aq) and (b) the solution resulting when 5.00 mL of 0.150 M NaOH(aq) is added to 25.00 mL of the acid.

Use $K_a = 1.8 \times 10^{-4}$ for HCOOH.

a)

$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

	HCOOH	H_3O^+	HCOO$^-$
initial	0.100	0	0
change	-x	+x	+x
equilibrium (final)	0.100-x	x	x

$K_a = 1.8 \times 10^{-4} \ll 0.100$, so we can ignore the change in initial acid concentration.

$$K_a = \frac{x^2}{[HCOOH]}$$

$$x = \sqrt{K_a \cdot [HCOOH]} = \sqrt{1.8 \times 10^{-4} \times 0.100} = 0.00424$$

$$[HCOOH] = 0.100 \frac{\text{mol}}{\text{L}} \quad [HCOO^-] = [H_3O^+] = 0.00424 \frac{\text{mol}}{\text{L}}$$

$$pH = -\log([H_3O^+]) = -\log(0.00424) = \mathbf{2.37}$$

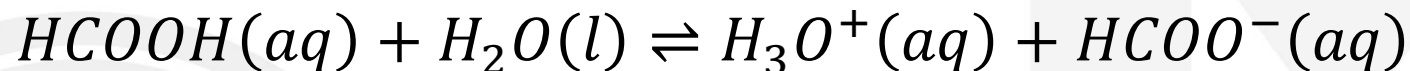$$degree\ of\ deprotonation = \frac{x}{[HCOOH]_{initial}} = \frac{0.00424}{0.100} = 0.0424$$

Example

Calculate the pH of (a) 0.100 M HCOOH(aq) and (b) the solution resulting when 5.00 mL of 0.150 M NaOH(aq) is added to 25.00 mL of the acid.

Use K_a = 1.8 × 10^{-4} for HCOOH.

b)

$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

We first need to find out the amount (in moles) of acid and base added.

$$n_{HCOOH,initial} = [HCOOH] \cdot V_{analyte} = 0.100\ \frac{mol}{L} \times 0.02500\ L = 0.0025\ mol$$

$$n_{OH^-,initial} = [NaOH] \cdot V_{titrant} = 0.150\ \frac{mol}{L} \times 0.00500\ L = 0.00075\ mol$$

Now we let the reaction between OH$^-$ and HCOOH occur:

$$n_{HCOOH} = n_{HCOOH,initial} - n_{OH^-,initial} = 0.0025\ mol - 0.00075\ mol = 0.00175\ mol$$

$$n_{OH^-} = n_{OH^-,initial} - n_{HCOOH,initial} = 0.00075\ mol - 0.0025\ mol \rightarrow 0\ mol$$

$$n_{HCOO^-} = n_{HCOO^-,initial} + n_{OH^-,initial} = 0\ mol + 0.00075\ mol = 0.00075\ mol$$

Example

To find out the pH of the solution after the NaOH was added, we first need to convert our amounts into concentrations again:

$$[HCOOH] = \frac{n_{CH_3COOH}}{V_{total}} = \frac{n_{HCOOH}}{V_{analyte} + V_{titrant}} = \frac{0.00175 \text{ mol}}{0.02500 \text{ L} + 0.000500 \text{ L}} = 0.0583 \frac{\text{mol}}{\text{L}}$$

$$[OH^-] = \frac{n_{OH^-}}{V_{total}} = \frac{n_{OH^-}}{V_{analyte} + V_{titrant}} = \frac{0 \text{ mol}}{0.02500 \text{ L} + 0.000500 \text{ L}} = 0 \frac{\text{mol}}{\text{L}}$$

$$[HCOO^-] = \frac{n_{CH_3COO^-}}{V_{total}} = \frac{n_{HCOO^-}}{V_{analyte} + V_{titrant}} = \frac{0.00075 \text{ mol}}{0.02500 \text{ L} + 0.000500 \text{ L}} = 0.0250 \frac{\text{mol}}{\text{L}}$$

But now we realize, that HCOOH and HCOO⁻ will re-establish an equilibrium, creating new hydronium ions. So, we need to use our ICE table to find the concentrations in this new equilibrium.

	HCOOH	H_3O^+	HCOO⁻
initial	0.0583	0	0.025
change	-x	+x	+x
equilibrium (final)	0.0583-x	x	0.0250+x

Example

$K_a = 1.8 \times 10^{-4} \ll 0.025$ (the smallest of the starting concentrations), so we can ignore the changes in initial acid and base concentrations.

$$K_a = \frac{[HCOO^-]x}{[HCOOH]}$$

$$x = \frac{K_a \cdot [HCOOH]}{[HCOO^-]} = \frac{1.8 \times 10^{-4} \times 0.0583}{0.025} = 0.00042$$

$$[HCOOH] = 0.0583 \frac{mol}{L} \qquad [HCOO^-] = 0.0250 \frac{mol}{L} \qquad [H_3O^+] = 0.00042 \frac{mol}{L}$$

$$pH = -\log([H_3O^+]) = -\log(0.00042) = \mathbf{3.38}$$

$$degree\ of\ deprotonation = \frac{x}{[HCOOH]_{initial}} = \frac{0.00042}{0.0583} = 0.0072$$

Example

Calculate the pH of the solution after the addition of another 5.00 mL of 0.150 M NaOH(*aq*). Use the data from the previous problem.

K_a = 1.8 × 10^{-4} for HCOOH

$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$
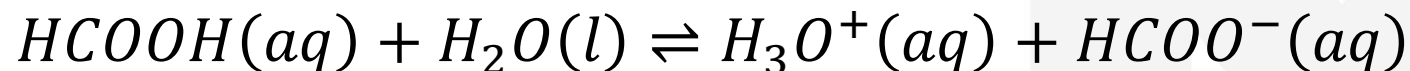
Again, we first need to determine the amount of acid in the analyte and the amount of base added. We can use the results from our **previous calculations**:

$$\boldsymbol{n_{HCOOH,initial} = 0.00175 \text{ mol}}$$

$$n_{OH^-,initial} = [NaOH] \cdot V_{titrant} = 0.150 \ \frac{\text{mol}}{\text{L}} \times 0.00500 \text{ L} = 0.00075 \text{ mol}$$

$$\boldsymbol{n_{HCOO^-,initial} = 0.00075 \text{ mol}}$$

Now we let the reaction between OH⁻ and HCOOH occur:

$$n_{HCOOH} = n_{CH_3COOH,initial} - n_{OH^-,initial} = 0.00175 \text{ mol} - 0.00075 \text{ mol} = 0.00100 \text{ mol}$$

$$n_{OH^-} = n_{OH^-,initial} - n_{HCOOH,initial} = 0.00075 \text{ mol} - 0.00175 \text{ mol} \rightarrow 0 \text{ mol}$$

$$n_{HCOO^-} = n_{HCOO^-,initial} + n_{OH^-,initial} = 0.00075 \text{ mol} + 0.00075 \text{ mol} = 0.00150 \text{ mol}$$

Example

To find out the pH of the solution after the NaOH was added, we first need to convert our amounts into concentrations again:

$$[HCOOH] = \frac{n_{CH_3COOH}}{V_{total}} = \frac{n_{HCOOH}}{V_{analyte} + V_{titrant}} = \frac{0.00100 \text{ mol}}{\mathbf{0.03000 \text{ L}} + 0.000500 \text{ L}} = 0.0286 \frac{\text{mol}}{\text{L}}$$

$$[OH^-] = \frac{n_{OH^-}}{V_{total}} = \frac{n_{OH^-}}{V_{analyte} + V_{titrant}} = \frac{0 \text{ mol}}{\mathbf{0.03000 \text{ L}} + 0.000500 \text{ L}} = 0 \frac{\text{mol}}{\text{L}}$$

$$[HCOO^-] = \frac{n_{CH_3COO^-}}{V_{total}} = \frac{n_{HCOO^-}}{V_{analyte} + V_{titrant}} = \frac{0.00150 \text{ mol}}{\mathbf{0.03000 \text{ L}} + 0.000500 \text{ L}} = 0.0429 \frac{\text{mol}}{\text{L}}$$

But now we realize, that HCOOH and HCOO$^-$ will re-establish an equilibrium, creating new hydronium ions. So, we need to use our ICE table to find the concentrations in this new equilibrium.

	HCOOH	H$_3$O$^+$	HCOO$^-$
initial	0.0286	0	0.0429
change	-x	+x	+x
equilibrium (final)	0.0286-x	x	0.0429+x

Example

$K_a = 1.8 \times 10^{-4} \ll 0.0286$ (the smallest of the starting concentrations), so we can ignore the changes in initial acid and base concentrations.

$$K_a = \frac{[HCOO^-]x}{[HCOOH]}$$

$$x = \frac{K_a \cdot [HCOOH]}{[HCOO^-]} = \frac{1.8 \times 10^{-4} \times 0.0286}{0.0429} = 0.00012$$

$$[HCOOH] = 0.0286 \frac{\text{mol}}{\text{L}} \qquad [HCOO^-] = 0.0429 \frac{\text{mol}}{\text{L}} \qquad [H_3O^+] = 0.00012 \frac{\text{mol}}{\text{L}}$$

$$pH = -\log([H_3O^+]) = -\log(0.00012) = \mathbf{3.92}$$

$$\textit{degree of deprotonation} = \frac{x}{[HCOOH]_{initial}} = \frac{0.00012}{0.0286} = 0.0042$$

Acid-Base Indicators

A pH meter is a simple, reliable, and fast method for determining the pH of a solution. A special electrode measures H_3O^+ concentration.

Shown is a fully-automated titrator with integrated pH meter.

Figure 6H.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
Courtesy Mettler Toledo.

Acid-Base Indicators

An acid-base indicator is a water soluble dye with a colour that depends on the pH.

The colour of these hydrangeas depends on the acidity of the soil in which they are growing: acid soil results in blue flowers, and alkaline soil results in pink flowers.

Figure 6H.8
Atkins, *Chemical Principles: The Quest for Insight*, 7e
© Darrell Gulin/Corbis.

Figure 6H.7
Atkins, *Chemical Principles: The Quest for Insight*, 7e
©1991 Chip Clark–Fundamental Photographs.

An acid-base indicator changes colour with pH in its acid form (HIn, where "In" stands for indicator) and another colour in its conjugate base form (In⁻).
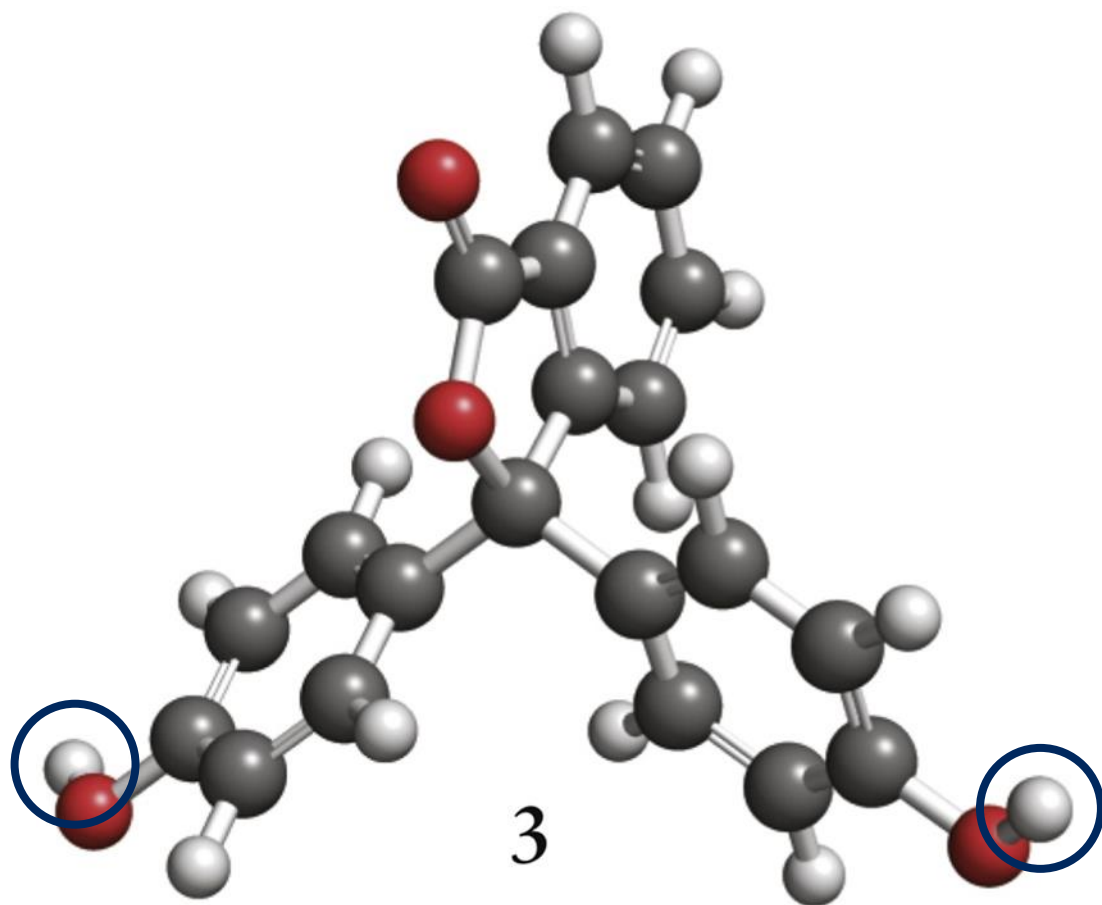
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Phenolphthalein

The **colour change** results because the **proton in HIn changes the structure** of the molecule in such a way that the **light absorption characteristics** of HIn are different from those of In⁻.

Electrons are delocalized across all three of the benzenelike rings of carbon atoms and this delocalization is part of the reason for the change in colour.

Acid-Base Indicators

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$
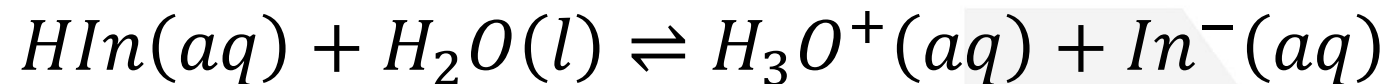
TABLE 6H.2   Indicator Color Changes*

Indicator	pK_{In}	pH range of color change	Color of acid form		Color of base form
thymol blue	1.7	1.2 to 2.8	red		yellow
methyl orange	3.4	3.2 to 4.4	red		yellow
bromophenol blue	3.9	3.0 to 4.6	yellow		blue
bromocresol green	4.7	3.8 to 5.4	yellow		blue
methyl red	5.0	4.8 to 6.0	red		yellow
litmus	6.5	5.0 to 8.0	red		blue
bromothymol blue	7.1	6.0 to 7.6	yellow		blue
phenol red	7.9	6.6 to 8.0	yellow		red
thymol blue	8.9	8.0 to 9.6	yellow		blue
phenolphthalein	9.4	8.2 to 10.0	colorless		pink
alizarin yellow R	11.2	10.1 to 12.0	yellow		red
alizarin	11.7	11.0 to 12.4	red		purple

*The colors of the acid and base forms are only a symbolic representation of the actual colors.

Stoichiometry of Polyprotic Acid Titrations

Many **biological systems** use **polyprotic acids** and their anions to control pH.

The titration of a polyprotic acid proceeds in the same way as a monoprotic acid, except there are many stoichiometric equivalency points since there are many acidic hydrogen atoms.

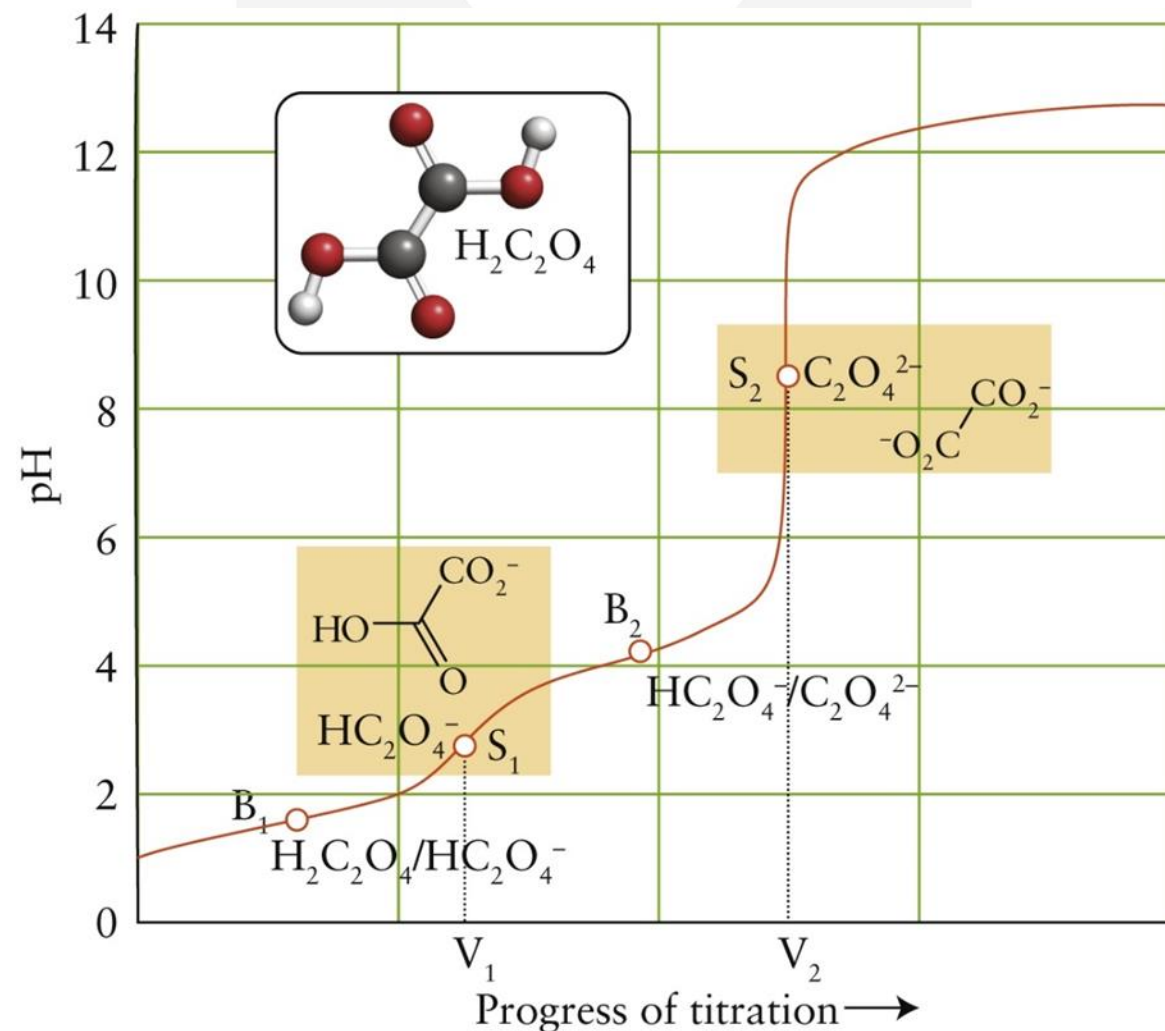We keep track of **each major species** in solution.

Figure 6H.11
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

At point B_1:
$$[H_2C_2O_4] = [HC_2O_4^-]$$

$$pH = pK_{a1}$$

At point B_2:
$$[HC_2O_4^-] = [C_2O_4^{2-}]$$

$$pH = pK_{a2}$$

Figure 6H.11
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Stoichiometry of Polyprotic Acid Titrations

We assume that the first stoichiometric amount of NaOH added <u>reacts only with</u> $H_2C_2O_4$ because of the **large K_{a1}**.
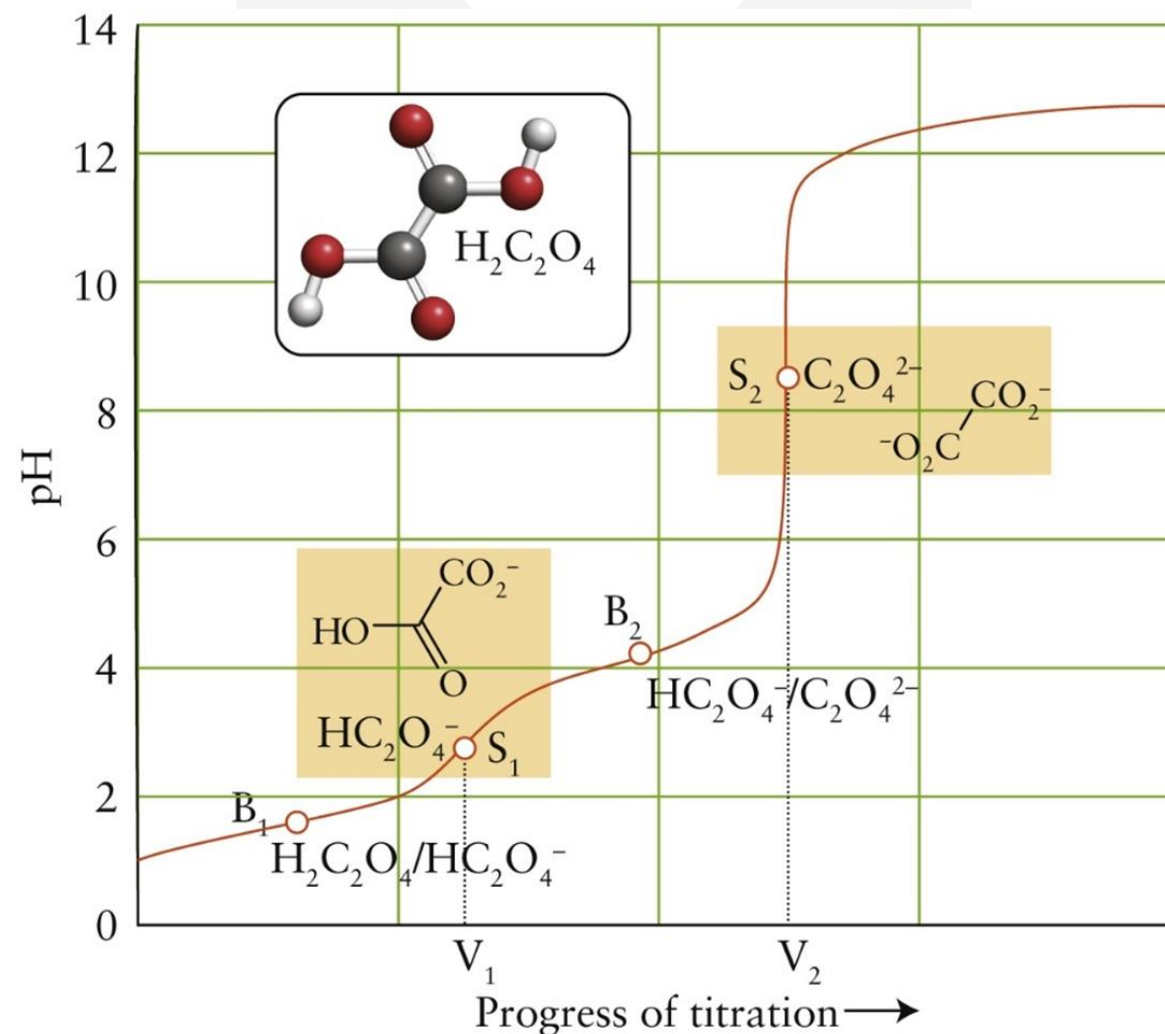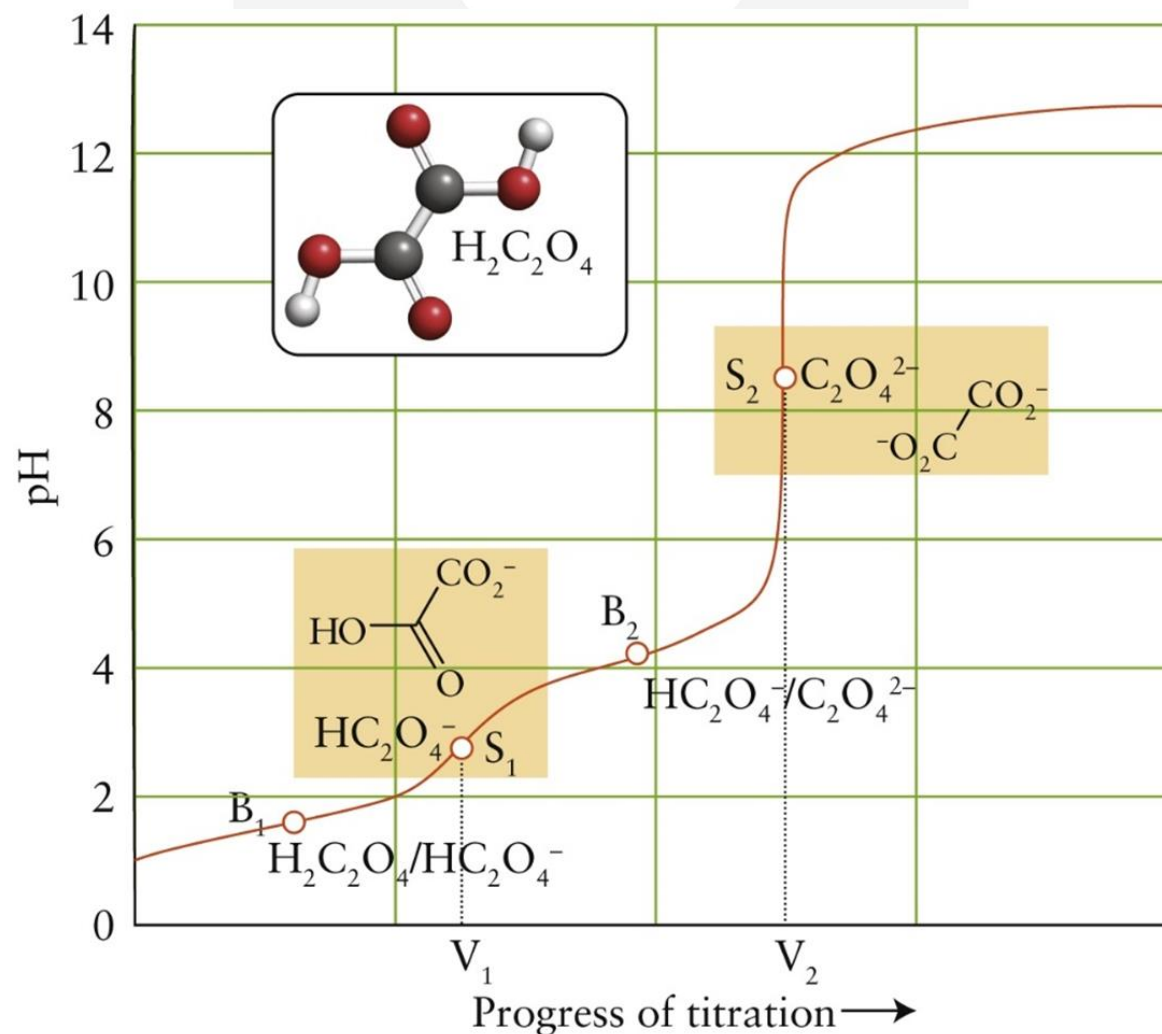
$$K_{a1} \gg K_{a2}$$

Figure 6H.11
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

For a triprotic acid like H_3PO_4, there are three equilibra:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \qquad K_{a1} = 7.6 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = 2.1 \times 10^{-13}$$
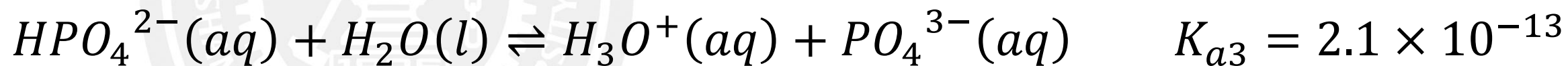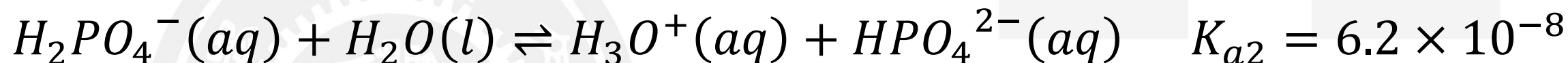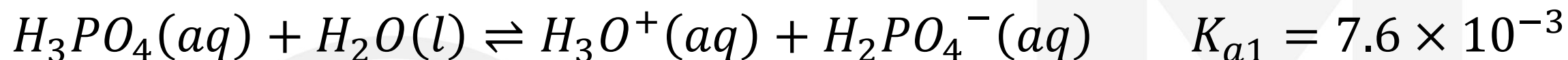
Adding a strong base like NaOH will remove protons from H_3PO_4 first.

Example

In a titration of 30.00 mL of 0.010 M $H_3PO_4(aq)$ with NaOH, what volume of 0.020 M NaOH(aq) is required to reach (a) the first stoichiometric point and (b) the second stoichiometric point?

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq) \qquad K_{a1} = 7.6 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$
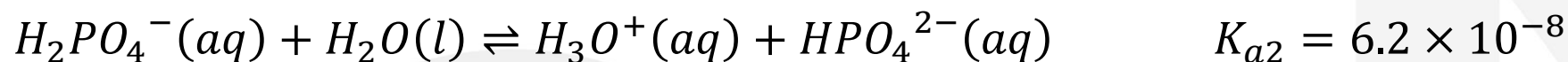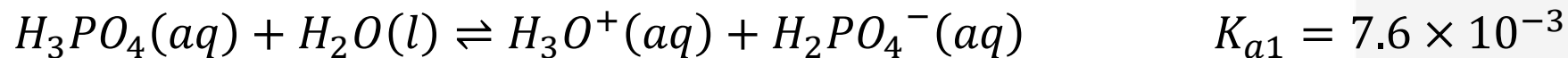
a) We need a stoichiometric amount of NaOH to remove the first proton from H_3PO_4:

$$V_{NaOH} = \frac{n_{NaOH}}{[NaOH]} = \frac{n_{H_3PO_4}}{[NaOH]} = \frac{[H_3PO_4] \cdot V_{H_3PO_4}}{[NaOH]} = \frac{0.01 \frac{mol}{L} \times 0.03000 \text{ L}}{0.020 \frac{mol}{L}} = 0.015 \text{ L}$$

b) For the second stoichiometric point, we need to remove the second proton from $H_2PO_4^-$, we need a second stoichiometric amount. Therefore, we need in total:

$$V_{NaOH} = \frac{n_{NaOH}}{[NaOH]} = \frac{n_{H_3PO_4} + n_{H_2PO_4^-}}{[NaOH]} = \frac{2 \cdot ([H_3PO_4] \cdot V_{H_3PO_4})}{[NaOH]} = \frac{2 \times \left(0.01 \frac{mol}{L} \times 0.03000 \text{ L}\right)}{0.020 \frac{mol}{L}} = 0.030 \text{ L}$$

Solubility Equilibria Precipitation/Dissolution

Solubility Equilibria

We've just seen proton transfer in equilibria.

Now we look at the equilibria of solid and salt solutions.

Our **goal** is to control the formation of precipitates.

These common methods are used in the laboratory to separate and analyse mixtures of salts. They also have important practical applications in municipal **wastewater treatment**, the **extraction of minerals from seawater**, the **formation and loss of bones and teeth**, and the **global carbon cycle**.

The Solubility Product

The equilibrium constant for the solubility equilibrium is called the **solubility product**, K_{sp}.

The solubility product for bismuth sulfide, Bi_2S_3, is defined as:

$$Bi_2S_3(s) \rightleftharpoons 2\,Bi^{3+}(aq) + 3\,S^{2-}(aq)$$
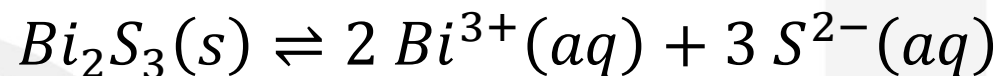
$$K_{sp} = (a_{Bi^{3+}})^2(a_{S^{2-}})^3$$

The concentrations of ions in a sparingly soluble salt solution are low, so we assume that we have an ideal, very dilute solution and can approximate K_{sp} by:

$$K_{sp} = [Bi^{3+}]^2[S^{2-}]^3$$

Solid Bi_2S_3 does not appear in the expression for K_{sp} because it is a pure solid and its activity is 1.

The Solubility Product: Only Approximations

Two factors complicate K_{sp} calculations:

The first complication is ion-ion interactions. These are more noticeable at high ion concentrations; therefore, dilute solutions are better.

The second is that insoluble salts do not dissociate completely and instead form ion clusters. For instance, in a solution of PbI_2, there will be a substantial number of both $Pb^{2+}I^-$ and $Pb^{2+}(I^-)_2$ clusters; this is common for cations with charges greater than +1.

The Solubility Product

| Compound	Formula	K_{sp} (@25 °C)
Aluminium hydroxide	$Al(OH)_3$	1.0×10^{-33}
Antimony sulfide	Sb_2S_3	1.7×10^{-93}
Barium carbonate	$BaCO_3$	8.1×10^{-9}
Barium fluoride	BaF_2	1.7×10^{-6}
Barium sulfate	$BaSO_4$	1.1×10^{-10}
Bismuth sulfide	Bi_2S_3	1.0×10^{-97}
Calcium carbonate	$CaCO_3$	8.7×10^{-9}
Calcium fluoride	CaF_2	4.0×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	5.5×10^{-6}
Calcium sulfate	$CaSO_4$	2.4×10^{-5}
Chromium(III) iodate	$Cr(IO_3)_3$	5.0×10^{-6}
Copper(I) bromide	$CuBr$	4.2×10^{-8}
Copper(I) chloride	$CuCl$	1.0×10^{-6}

What does a small K_{sp} mean?

How to think of them in terms of chemical equilibria?

The molar solubility of silver chromate, Ag_2CrO_4, is 6.5×10^{-5} mol·L^{-1}. Determine the value of K_{sp} for silver chromate.

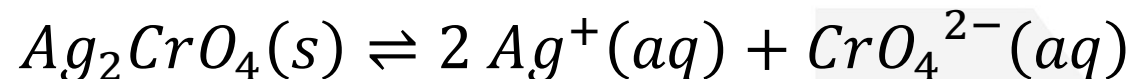First, we write the reaction equation:
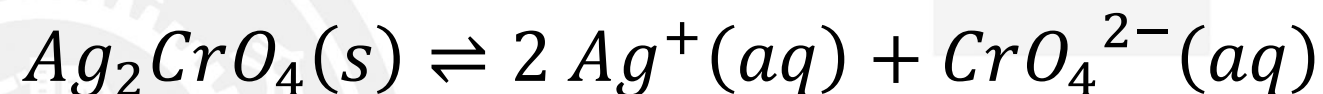
$$Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4{}^{2-}(aq)$$

Then, we write the expression for the solubility product:

$$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$$

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

As every mole of Ag_2CrO_4 releases 2 moles of Ag^+ and 1 mole of $CrO_4{}^{2-}$:

$$[Ag^+] = 2s = 2 \times (6.5 \times 10^{-5})\,\frac{\text{mol}}{\text{L}}$$

$$[CrO_4{}^{2-}] = s = 6.5 \times 10^{-5}\,\frac{\text{mol}}{\text{L}}$$

Substituting into the expression for the solubility product:

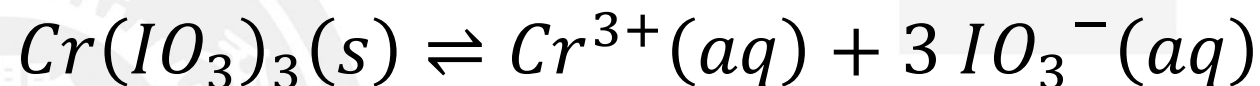$$K_{sp} = [Ag^+]^2[CrO_4{}^{2-}] = (2s)^2 \cdot s = 4s^3$$

$$K_{sp} = (6.5 \times 10^{-5})^3 = 1.1 \times 10^{-12}$$

Estimating the Molar Solubility

For chromium(III) iodate $(Cr(IO_3)_3)$ in water, K_{sp} = 5.0×10⁻⁶. Estimate the molar solubility of the compound.

First, we write the reaction equation:

$$Cr(IO_3)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3\,IO_3^-(aq)$$

Then, we write the expression for the solubility product:

$$K_{sp} = [Cr^{3+}][IO_3^-]^3$$

Estimating the Molar Solubility

$$K_{sp} = [Cr^{3+}][IO_3^-]^3$$

As every mole of Cr(IO$_3$)$_3$ releases 1 mole of Cr^{3+} and 3 mole of IO$_3^-$:

$$[Cr^{3+}] = s \qquad [IO_3^-] = 3s$$

Substituting into the expression for the solubility product:

$$K_{sp} = [Cr^{3+}][IO_3^-]^3 = s \cdot (3s)^3 = 27s^4 = 5.0 \times 10^{-6}$$

$$s = \sqrt[4]{\frac{5.0 \times 10^{-6}}{27}} = 0.021 \, \frac{\text{mol}}{\text{L}}$$

The Common-Ion Effect

Making precipitates of sparingly soluble salt, like heavy metal ions such as **lead** and **mercury**, can remove them from municipal waste water by precipitating them as a **hydroxide** salt.

How can we remove these heavy metal ions from solution?

Le Chatelier's principle tells us that, if we add a second salt or an acid, which has an ion in common with the original solution ("common-ion"), it will cause the equilibrium to shift away from the ion added.

We can precipitate unwanted ions using the **common-ion effect**.

The Common-Ion Effect

A quantitative understanding of the common-ion effect follows with AgCl(*s*).

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq), K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$
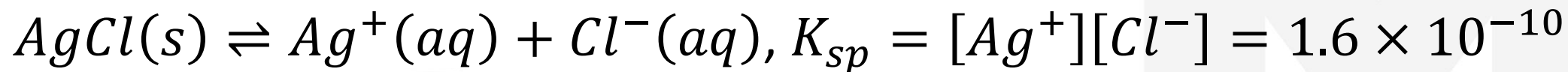
According to Le Chatelier's principle, adding the common ion **Cl⁻**, in the form of **NaCl**, to this reaction will have the effect of forming more **AgCl**(*s*).

3. Forming more AgCl   3. Consuming Ag⁺   1. Adding Cl⁻
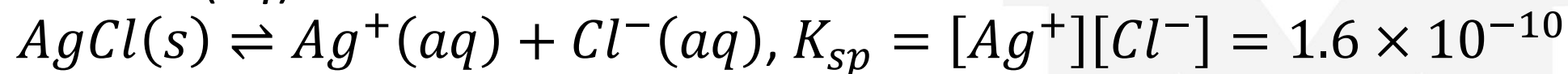
$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
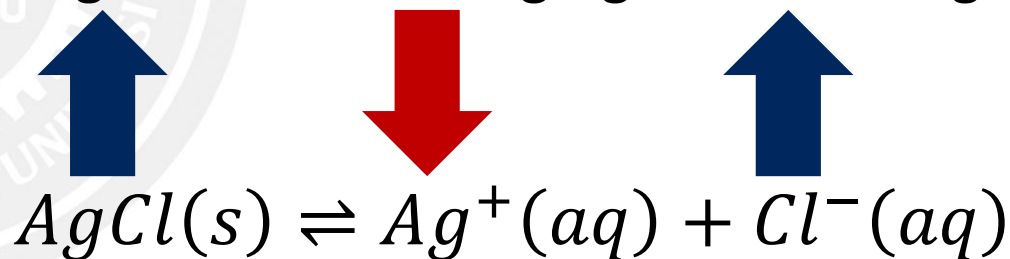
2. Shifting the equilibrium

Example

Estimating the effect of a common ion on the solubility of silver chloride in 1.0×10^{-2} M NaCl(aq).
$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq), K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$

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

As $[Ag^+] = [Cl^-]$ in pure water:
$$[Ag^+] = \frac{K_{sp}}{[Ag^+]} = \sqrt{K_{sp}} = \sqrt{1.6 \times 10^{-10}} = 1.3 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

In 1.0×10^{-2} mol·L^{-1} NaCl solution:
$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.6 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.6 \times 10^{-8}$$

About 1000 times lower than in pure water!

Predicting Precipitation

In a multi-ion solution, it is important to precipitate one ion at time. This is used extensively in elemental analysis, for example.

We gain insight as to how this works by calculating and comparing Q, the reaction quotient, to K, the equilibrium constant.

Here, the equilibrium constant is the solubility product, K_{sp}, and the reaction quotient is denoted Q_{sp}.

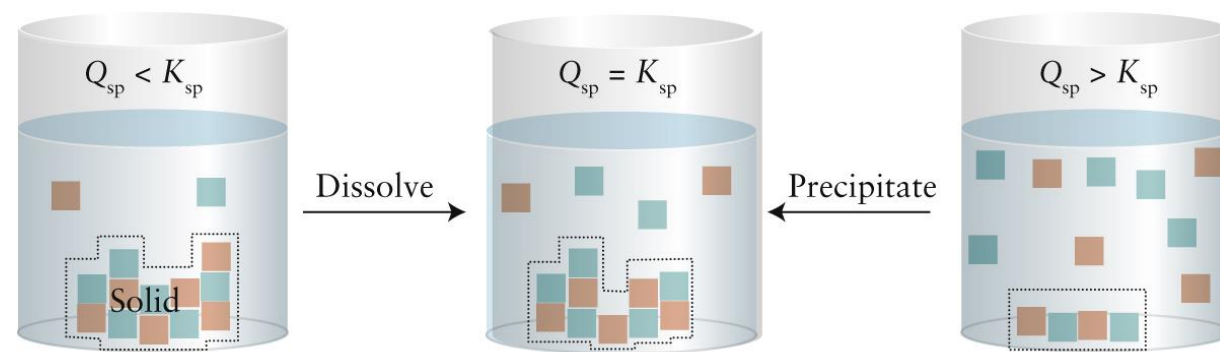Precipitation occurs when $Q_{sp} > K_{sp}$.

Figure 6J.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

Figure 6J.2
Atkins, *Chemical Principles: The Quest for Insight*, 7e
©1989 Chip Clark–Fundamental Photographs.

Suppose we mix equal volumes of 0.2 M $Pb(NO_3)_2(aq)$ and $KI(aq)$. Will lead(II) iodide precipitate? $K_{sp} = 1.4 \times 10^{-8}$

We will calculate a Q_{sp}, and if $Q_{sp} > K_{sp}$ we know it will precipitate.

A few drops of KI precipitates out the Pb^{2+} as PbI_2.

Suppose we mix equal volumes of 0.2 M $Pb(NO_3)_2(aq)$ and $KI(aq)$. Will lead(II) iodide precipitate?

K_{sp} = 1.4×10^{-8}

$$[Pb^{2+}] = \frac{[Pb(NO_3)_2] \cdot V_{Pb(NO_3)_2}}{V_{Pb(NO_3)_2} + V_{KI}}$$

As $V_{Pb(NO_3)_2} = V_{KI}$:

$$[Pb^{2+}] = \frac{[Pb(NO_3)_2] \cdot V_{Pb(NO_3)_2}}{V_{Pb(NO_3)_2} + V_{Pb(NO_3)_2}} = \frac{[Pb(NO_3)_2]}{2} = \frac{0.2 \frac{mol}{L}}{2} = 0.1 \frac{mol}{L}$$

The same applies for $[I^-]$:

$$[I^-] = \frac{[KI] \cdot V_{KI}}{V_{KI} + V_{KI}} = \frac{[KI]}{2} = \frac{0.2 \frac{mol}{L}}{2} = 0.1 \frac{mol}{L}$$

$$Q_{sp} = [Pb^{2+}][I^-]^2 = 0.1 \times (0.1)^2 = 1.0 \times 10^{-3} \gg 1.4 \times 10^{-8} = K_{sp}$$

As $Q_{sp} > K_{sp}$, PbI_2 will precipitate.

Selective Precipitation

We can apply this strategy to common industrial problems by knowing when $Q_{sp} \gg K_{sp}$.

Seawater is a mixture of many different ions. It is possible to precipitate magnesium ions from seawater by adding hydroxide ions.

However, other cations are also present in seawater. Their individual concentrations and the relative solubilities of their hydroxides determine which will precipitate first if a certain amount of hydroxide is added.
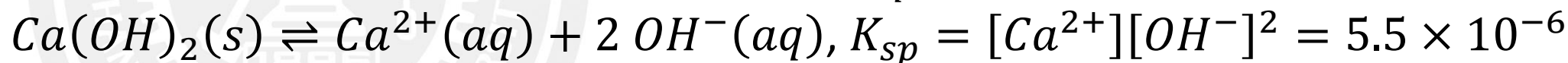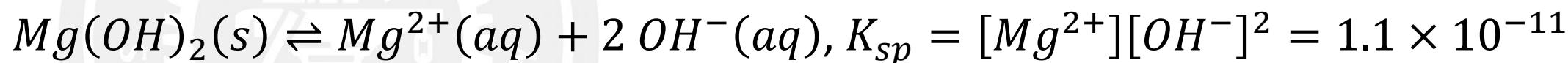
Knowing the K_{sp} of all ions, we can predict the **order** of precipitation.

Predicting the Order of Precipitation

A sample of seawater contains, among other solutes, the following concentrations of soluble cations: 0.050 mol·L^{-1} Mg^{2+}(aq) and 0.010 mol·L^{-1} Ca^{2+}(aq).

a) Determine the order in which each ion precipitates as solid NaOH is added and give the concentration of OH$^-$ when precipitation of each cation begins. Assume no volume change on addition of the NaOH.

b) Calculate the concentration of the first ion to precipitate that remains in solution when the second ion precipitates.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq), K_{sp} = [Mg^{2+}][OH^-]^2 = 1.1 \times 10^{-11}$$
$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq), K_{sp} = [Ca^{2+}][OH^-]^2 = 5.5 \times 10^{-6}$$

We notice that $K_{sp,Mg(OH)_2} \ll K_{sp,Ca(OH)_2}$, which gives us an indication of what to expect in terms of precipitation.

Mg(OH)$_2$ is expected to precipitate first, as it has a lower solubility product.

a)

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq), K_{sp} = [Mg^{2+}][OH^-]^2 = 1.1 \times 10^{-11}$$
$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq), K_{sp} = [Ca^{2+}][OH^-]^2 = 5.5 \times 10^{-6}$$
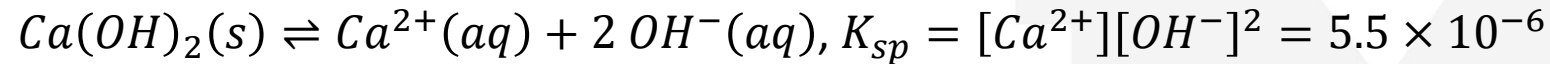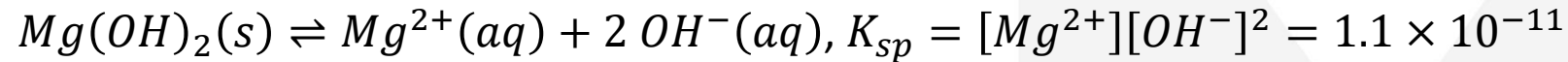
Determining the precipitation concentration of OH⁻ for Mg(OH)$_2$:

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1.1 \times 10^{-11}}{0.050}} = 1.5 \times 10^{-5}\,\frac{mol}{L}$$

Determining the precipitation concentration of OH⁻ for Ca(OH)$_2$:

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]}} = \sqrt{\frac{5.5 \times 10^{-6}}{0.010}} = 0.023\,\frac{mol}{L}$$

Therefore, as soon as $[OH^-] = 1.5 \times 10^{-5}\,\frac{mol}{L}$, Mg(OH)$_2$ will precipitate, which is far from the necessary concentration of $[OH^-] = 0.023\,\frac{mol}{L}$ required for the precipitation of Ca(OH)$_2$.

b)

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq), K_{sp} = [Mg^{2+}][OH^-]^2 = 1.1 \times 10^{-11}$$
$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq), K_{sp} = [Ca^{2+}][OH^-]^2 = 5.5 \times 10^{-6}$$
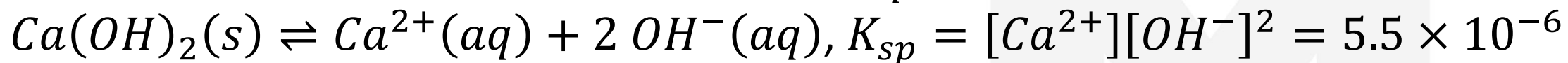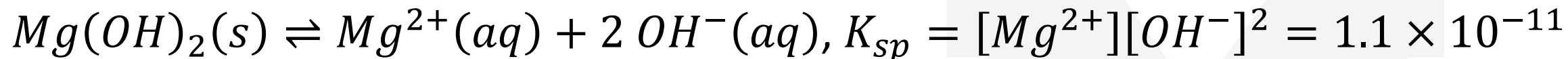
The precipitation of Ca(OH)$_2$ begins at $[OH^-] = 0.023 \frac{\text{mol}}{\text{L}}$. The concentration of $[Mg^{2+}]$ at this concentration is:

$$[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.1 \times 10^{-11}}{(0.023)^2} = 2.08 \times 10^{-8} \frac{\text{mol}}{\text{L}}$$

This means that at the moment when Ca(OH)$_2(s)$ begins to form, there are still 2.08×10^{-8} mol·L^{-1} Mg^{2+} cations in the solution. This is a huge reduction compared to the initial Mg^{2+} ion concentration of 0.050 mol·L^{-1}.

Dissolving Precipitates
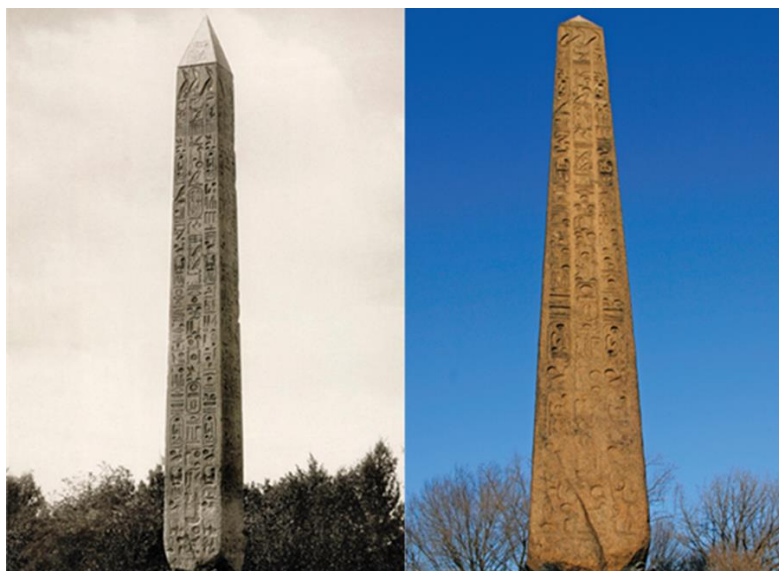
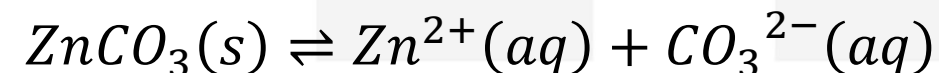The state of the carving on Cleopatra's Needle has deteriorated as a result of the action of acid rain: (left) after 3500 years in the Egyptian desert; (right) after a further 100 years in Central Park, New York City.

Many carbonates dissolve by addition of acid:
$$ZnCO_3(s) \rightleftharpoons Zn^{2+}(aq) + CO_3{}^{2-}(aq)$$

The $CO_3{}^{2-}$ ions react with acid to form CO_2:
$$CO_3{}^{2-}(aq) + 2\,H_3O^+(aq) \rightarrow CO_2(g) + 3\,H_2O(l)$$
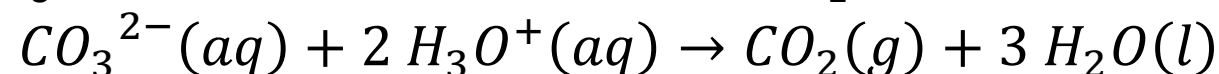
The dissolution of carbonates is an undesired result of acid rain, which has damaged the appearance of many historic marble and limestone monuments.

Complex Ion Formation

Many metal cations are Lewis acids (see Chapter 11). When a Lewis acid and a Lewis base react, they form a coordinate covalent bond. The product is called a **coordination complex**.

An example is the formation of $Ag(NH_3)_2{}^+$:

$$Ag^+(aq) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2{}^+(aq)$$
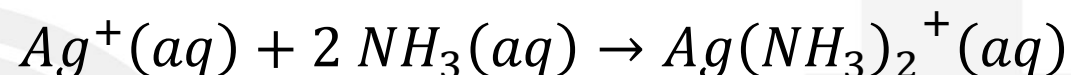
It is possible to add enough Lewis base ammonia to dissolve a silver-halide solid.

Quantitatively, a formation is expressed by a formation constant, K_f.

$$K_f = \frac{\left[Ag(NH_3)_2{}^+\right]}{[Ag^+][NH_3]^2} = 1.6 \times 10^7$$

As K_f is very large, this is a product favouring reaction.

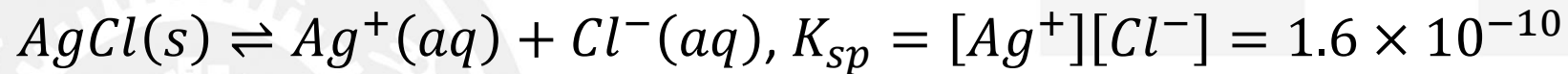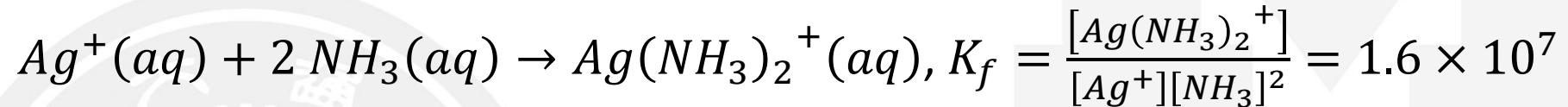# Molar Solubility in Presence of Complex Formation

Calculate the molar solubility of silver chloride in 0.10 M $NH_3(aq)$, given that $K_{sp} = 1.6\times10^{-10}$ for silver chloride and $K_f = 1.6\times10^7$ for the ammonia complex of Ag^+ ions, $Ag(NH_3)_2^+$.

We have two competing reactions:

$$Ag^+(aq) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq),\ K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.6\times10^7$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq),\ K_{sp} = [Ag^+][Cl^-] = 1.6\times10^{-10}$$

Combining these, we note that Ag^+ is a spectator ion (reactant and product):

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

$$K_{net} = K_f \cdot K_{sp} = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} \cdot [Ag^+][Cl^-] = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

Molar Solubility in Presence of Complex Formation

$$AgCl(s) + 2\,NH_3(aq) \rightarrow Ag(NH_3)_2{}^+(aq) + Cl^-(aq)$$
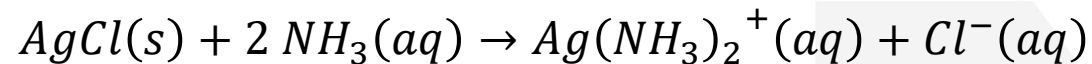
As we start with an initial concentration of NH_3, we can set up an ICE table:

	NH_3	$Ag(NH_3)_2{}^+$	Cl^-
initial	0.10	0	0
change	$-2x$	$+x$	$+x$
equilibrium (final)	$0.10-2x$	x	X

$$K_{net} = K_f \cdot K_{sp} = \frac{[Ag(NH_3)_2{}^+][Cl^-]}{[NH_3]^2} = 1.6 \times 10^7 \times 1.6 \times 10^{-10} = \frac{x^2}{(0.10 - 2x)^2}$$

Solving for x:

$$x = 4.6 \times 10^{-3}\ \frac{\text{mol}}{\text{L}}$$

Therefore, the molar solubility for AgCl(s) is 4.6×10^{-3} mol·L^{-1}.

Qualitative Analysis

Qualitative analysis uses all the methods described in this chapter

- Control of pH;

- Selective precipitation;

- Complex ion formation.

When devising a scheme to isolate each ion, we base our decisions on pH, K_{sp}(solubility) and K_f. We notice in the first step that not all metal halides are equally soluble. In the second step, $H_2S(g)$ precipitates out more and in the third step, NH_3 is added.

HCl(aq) $H_2S(g)$ NH_3(aq)

Decant   Decant

Hg_2Cl_2 Sb_2S_3 ZnS
$PbCl_2$ HgS   NiS
AgCl   CuS   MnS
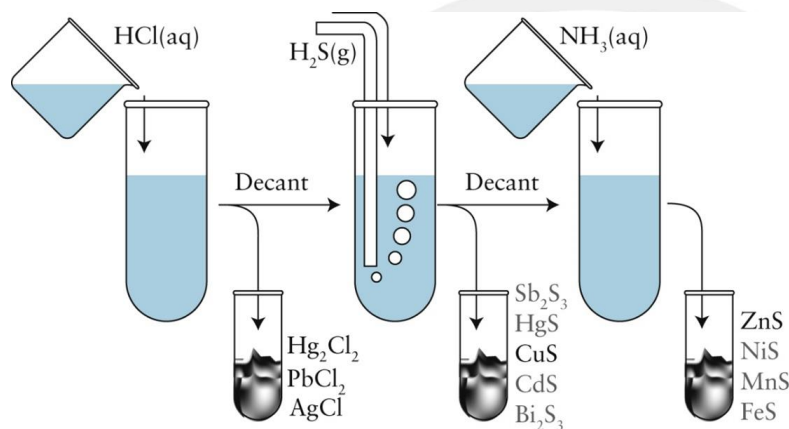   CdS   FeS
    Bi_2S_3

Figure 6J.4
Atkins, *Chemical Principles: The Quest for Insight*, 7e
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Here is an example of identifying and isolating five cations: Pb^{2+}, Hg_2^{2+}, Ag^+, Cu^{2+}, and Zn^{2+}.

Qualitative Analysis

All five ions

Here is an example of identifying and isolating five cations:
Pb^{2+}, Hg_2^{2+}, Ag^+, Cu^{2+}, and Zn^{2+}.

HCl(aq)   H$_2$S(g)   NH$_3$(aq)

Decant   Decant

Hg$_2$Cl$_2$ Sb$_2$S$_3$ ZnS
PbCl$_2$ HgS   NiS
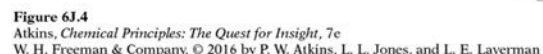AgCl   CuS   MnS
    Bi$_2$S$_3$ FeS

Figure 6J.4
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Cu^{2+}
Pb^{2+}
Ag^+
Zn^{2+}
Hg_2^{2+}

Cu^{2+}

Zn^{2+}

Zn^{2+}
Cu^{2+}

Zn^{2+}

Zn^{2+}

(a)   (b)   (c)

Figure 6J.5
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman photos by Ken Karp.

Decanted supernate