

# Recap

- ❑ Buffer solution ( $\text{pK}_a \pm 1$ )
- ❑ Titration (strong vs. strong; strong vs. weak)
- ❑ pH curve
- ❑  $K_{a1}/K_{b1}$ ,  $K_{a2}/K_{b2}$

# Strong Acid-Weak Base and Weak Acid-Strong Base Titrations

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

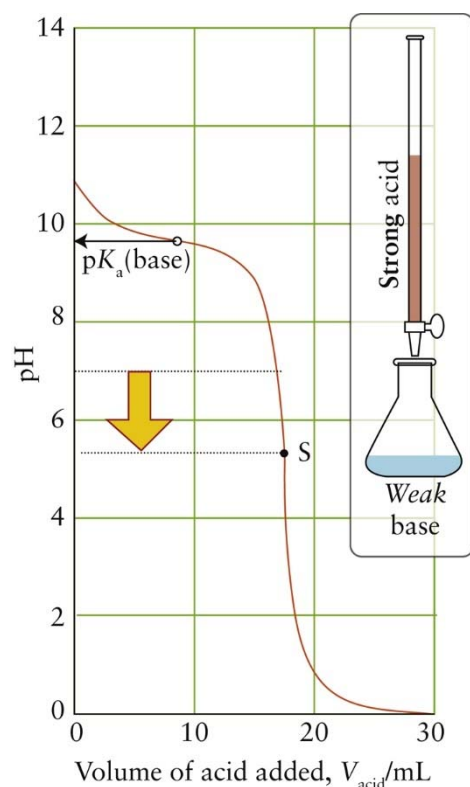


Figure 6H.4  
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The pH in this case will not be 7.

The pH depends on the conjugate salt produced.

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

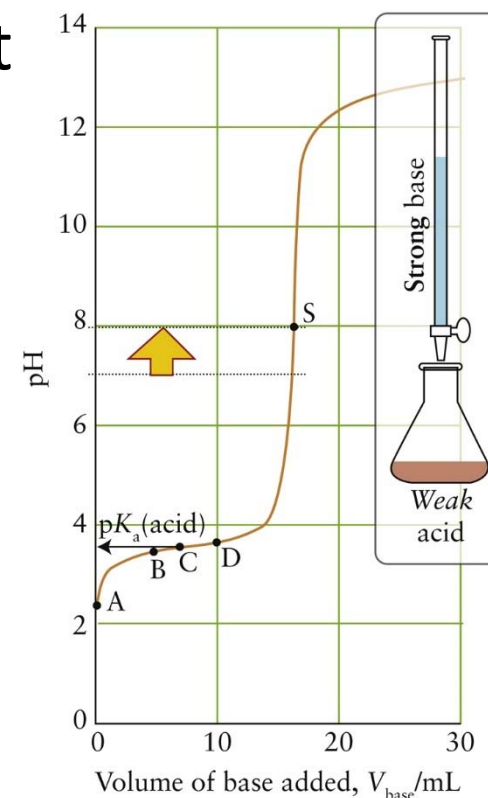
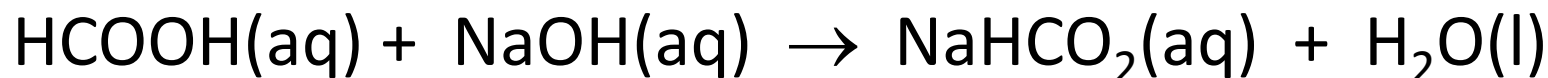


Figure 6H.3  
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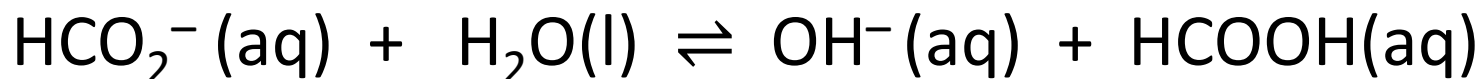
## Estimating the pH at the Stoichiometric Point of the Titration of a Weak Acid with a Strong Base

Example 13.5 Estimate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M  $\text{HCOOH(aq)}$  with 0.150 M  $\text{NaOH(aq)}$ .

The stoichiometric point only has  $\text{Na}^+ \text{(aq)}$  and  $\text{HCO}_2^- \text{(aq)}$ .  
 $\text{HCOOH(aq)} + \text{NaOH(aq)} \rightarrow \text{NaHCO}_2\text{(aq)} + \text{H}_2\text{O(l)}$

This is a two-part problem:

- First**, find the moles  $\text{HCO}_2^-$  produced and liters of  $\text{NaOH}$  needed.
- Second**, calculate the pH of the new conjugate base produced.



Example 6H.2 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).

Our reaction is  $\text{HCOOH(aq)} + \text{NaOH(aq)} \rightarrow \text{NaHCO}_2\text{(aq)} + \text{H}_2\text{O(l)}$ .

First, find the moles of HCOOH. This will help us calculate the volume of NaOH needed.

$$\text{Moles HCOOH} = \frac{0.100 \text{ mol HCOOH}}{\text{L HCOOH}} \times \frac{0.02500 \text{ L}}{1} = .002500 \text{ mol}$$

	HCOOH	OH <sup>-</sup>	HCOO <sup>-</sup>
initial	0.002500	0.002500	0
change	- 0.002500	- 0.002500	+ 0.002500
equilibrium	0	0	0.002500

$$\text{Liters NaOH needed} = \frac{1 \text{ L NaOH}}{0.150 \text{ mol NaOH}} \times \frac{0.002500 \text{ mol}}{1} = 0.0167 \text{ L}$$

Total volume is .02500 L + 0.0167 L = 0.0417 L

$$\text{Molarity of HCOO}^- = \frac{0.002500 \text{ mol}}{0.0417 \text{ L}} = 0.0600 \text{ M HCOO}^-$$

Example 6H.2 Estimate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M  $\text{HCOOH(aq)}$  with 0.150 M  $\text{NaOH(aq)}$ .

In the second step, we look at the new equilibrium of the conjugate base,  $\text{HCO}_2^- (\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{OH}^- (\text{aq}) + \text{HCOOH(aq)}$

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

	$\text{HCOO}^-$	$\text{OH}^-$	$\text{HCOOH}$
initial	0.060	0	0
change	$-x$	$+x$	$+x$
equilibrium	0.0600	$x$	$x$

Solving  $K_b = 5.6 \times 10^{-11} = \frac{x^2}{0.0600}$ ,  $x = 1.8 \times 10^{-6} = [\text{OH}^-]$

$\text{pH} = -\log [1.8 \times 10^{-6}] = 5.74$ ,  $\text{pH} = 14 - 5.74 = 8.26$

percentage deprotonation =  $\frac{1.8 \times 10^{-6}}{0.0600} \times 100 = 0.003\%$

# Calculating the pH During a Titration

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.

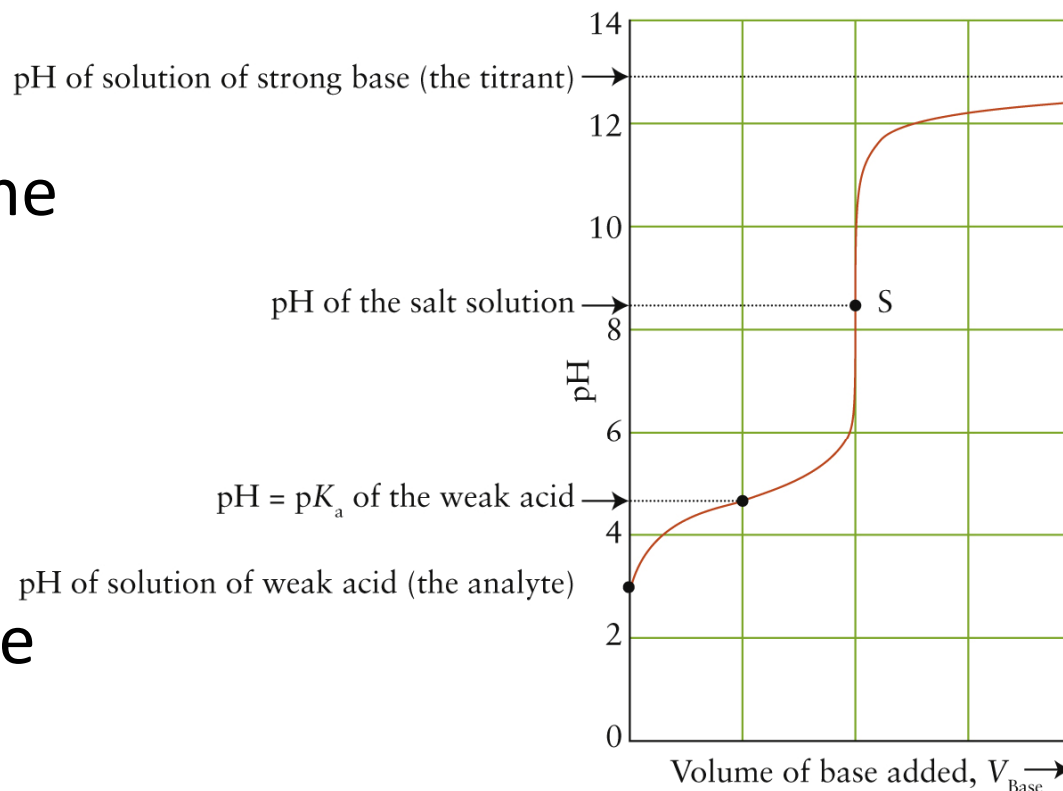


Figure 6H.5

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

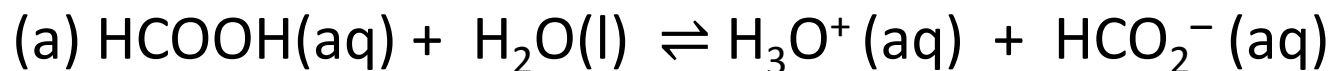
## Calculating the pH before the Stoichiometric Point in a Weak Acid-Strong Base Titration

Calculate the pH of (a) 0.100 M  $\text{HCOOH(aq)}$  and (b) the solution resulting when 5.00 mL of 0.150 M  $\text{NaOH(aq)}$  is added to 25.00 mL of the acid. Use  $K_a = 1.8 \times 10^{-4}$  for  $\text{HCOOH}$ .

In (a) we calculate the initial pH. Since  $\text{HCOOH}$  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  $\text{NaOH}$  that will react with  $\text{HCOOH}$ , which means  $\text{HCOO}^-$  is formed, so a new pH is calculated.

Example 6H.3 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.



ICE table

	HCOOH	H <sub>3</sub> O <sup>+</sup>	HCOO <sup>-</sup>
initial	0.100	0	0
change	- x	+ x	+ x
equilibrium	0.100	x	x

$$1.8 \times 10^{-4} = \frac{x^2}{0.100}, \quad x = 0.00424$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+], \quad \text{pH} = -\log 0.00424 = 2.37$$



(b) the solution resulting when 5.00 mL of 0.150 M NaOH(aq) is added to 25.00 mL of the acid.

We need to find the moles of base that react with the acid.

$$\text{Moles base, } \frac{0.150 \text{ mol OH}^-}{1 \text{ L OH}^-} \times \frac{0.0050 \text{ L}}{1} = .00075 \text{ mol OH}^-$$

$$\text{The moles of acid, } \frac{0.100 \text{ mol HCOOH}}{1 \text{ L HCOOH}} \times \frac{0.0250 \text{ L}}{1} = .0025 \text{ mol HCOOH}$$

	HCOOH	OH <sup>-</sup>	HCOO <sup>-</sup>
initial	0.0025	0.00075	0
change	-0.00075	-0.00075	+ 0.00075
equilibrium	0.00175	0	0.00075

(b) the solution resulting when 5.00 mL of 0.150 M NaOH(aq) is added to 25.00 mL of the acid.

	HCOOH	OH <sup>-</sup>	HCOO <sup>-</sup>
initial	0.0025	0.00075	0
change	- 0.00075	- 0.00075	+ 0.00075
equilibrium	0.00175	0	0.00075

New volume is 25.00 + 5.00 mL or 0.030 L

$$\text{Acid: } \frac{0.00175 \text{ mol}}{0.030 \text{ L}} = 0.0583$$

$$\text{Con. base } \frac{0.00075 \text{ mol}}{0.030 \text{ L}} = 0.025$$

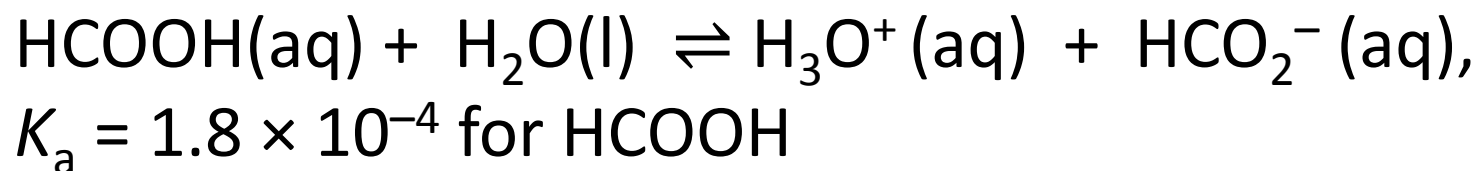
$$1.8 \times 10^{-4} = \frac{0.025 x}{0.0583}, \quad x = 0.000424$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+], \quad \text{pH} = -\log 0.00424 = 3.37$$

The previous problem is continued as a Self-test exercise in 6H.3B.

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.



$$[\text{HCOOH}] = 0.0583, [\text{HCO}_2^-] = 0.025$$

$$\text{Moles base, } \frac{0.150 \text{ mol OH}^-}{1 \text{ L OH}^-} \times \frac{0.0050 \text{ L}}{1} = .00075 \text{ mol OH}^-$$

From the table: mole HCOOH = 0.00175; moles HCOO<sup>-</sup> = 0.00075

	HCOOH	OH <sup>-</sup>	HCOO <sup>-</sup>
initial	0.00175	0.00075	0.00075
change	-0.00075	-0.00075	+ 0.00075
equilibrium	0.00100	0	0.0015

New volume is  
30.00 + 5.00 mL  
or 0.035 L

$$\text{Acid: } \frac{0.0010 \text{ mol}}{0.035 \text{ L}} = 0.0285$$

$$\text{Con. base } \frac{0.0015 \text{ mol}}{0.035 \text{ L}} = 0.0429$$

$$1.8 \times 10^{-4} = \frac{0.0429 x}{0.0285}, \quad x = 0.000120$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+], \quad \text{pH} = -\log 0.000120 = 3.92$$

## Acid-Base Indicators

A pH meter is a simple, reliable, and fast method for determining the pH of a solution. A special electrode measures  $\text{H}_3\text{O}^+$  concentration.

Shown is a fully-automated 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 color that depends on the pH.

The color 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.

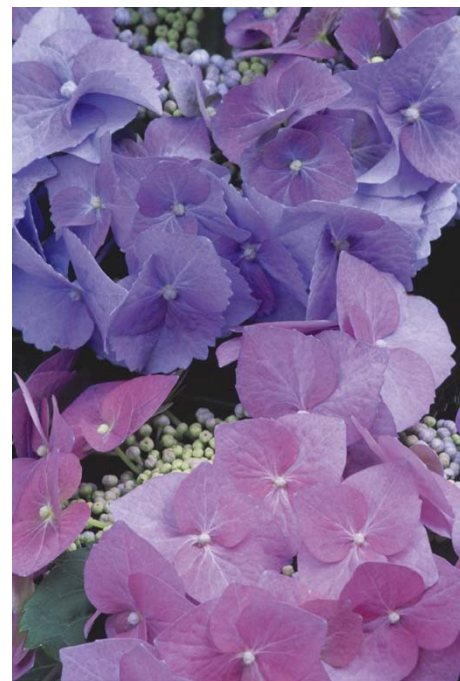


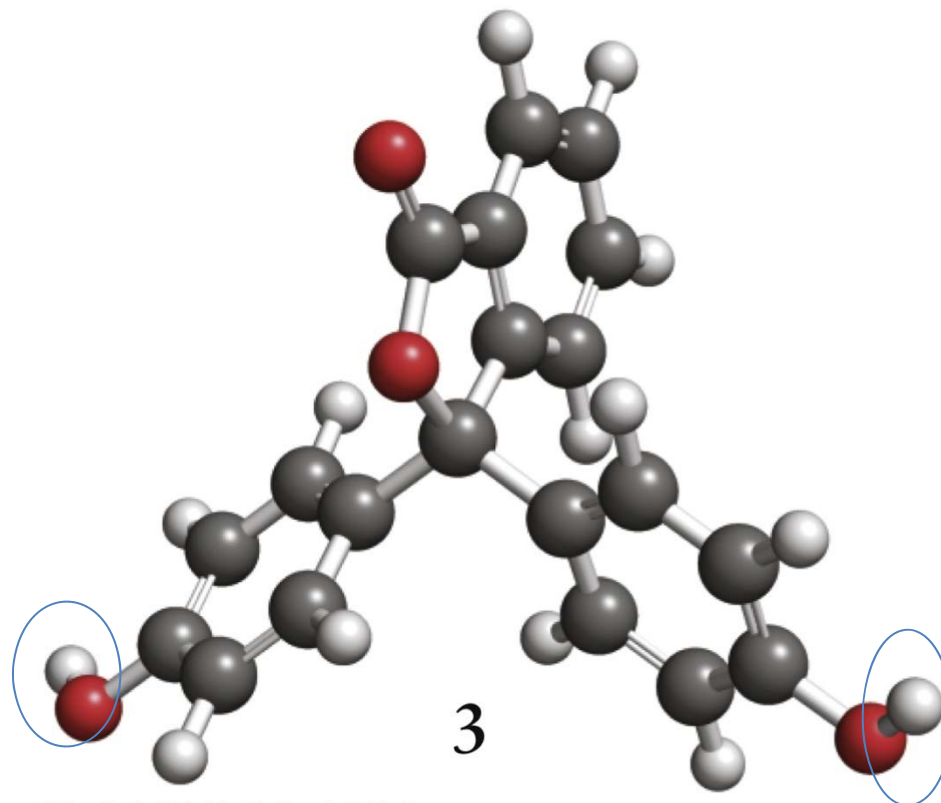
Figure 6H.8  
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Figure 6H.7  
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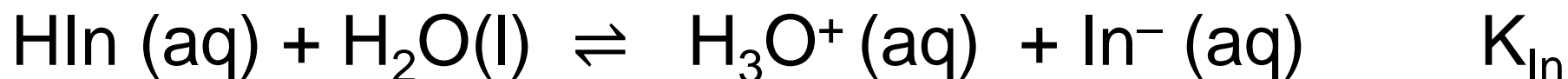
An acid-base indicator changes color with pH in its acid form ( $\text{HIn}$ , where “In” stands for indicator) and another color in its conjugate base form ( $\text{In}^-$ ).

The **color 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  $\text{In}^-$ .















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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 color.



**TABLE 6H.2** Indicator Color Changes\*

Indicator	$\text{p}K_{\text{In}}$	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.

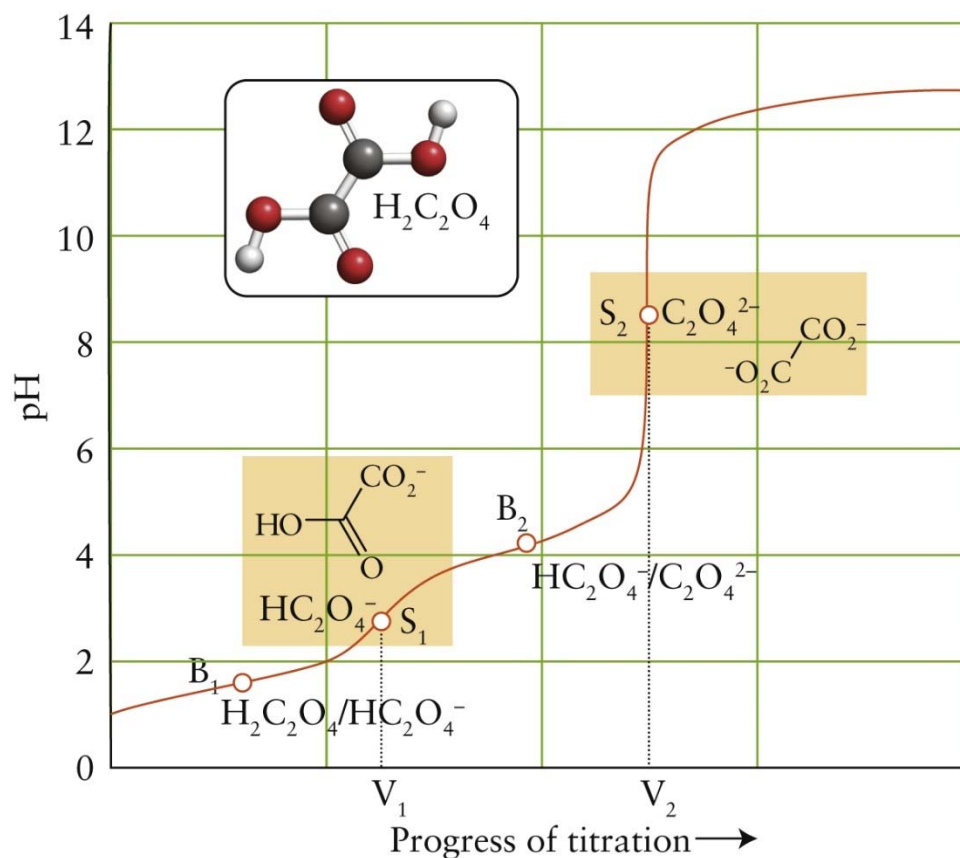
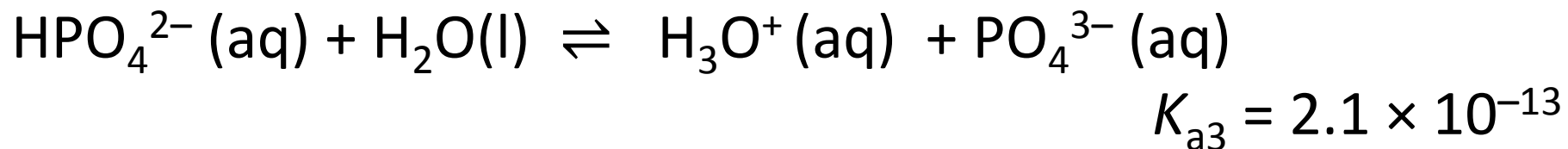
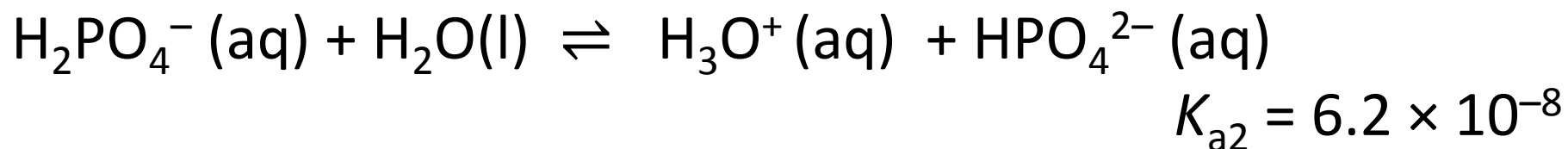
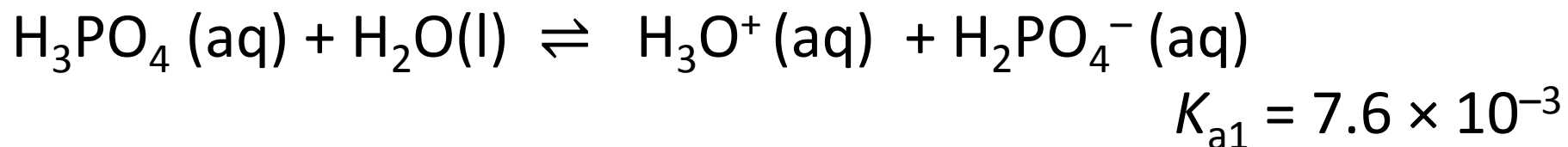


Figure 6H.11  
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We keep track of **each major species** in solution.

## Stoichiometry of Polyprotic Acid Titrations

For a triprotic acid like  $\text{H}_3\text{PO}_4$ , there are three equilibria.



Adding a strong base like NaOH will remove protons from  $\text{H}_3\text{PO}_4$ .

# Stoichiometry of Polyprotic Acid Titrations

At point  $B_1$ , equal  $H_2C_2O_4$  and  $HC_2O_4^-$  therefore the  $pH = pK_{a1}$ .

At point  $B_2$ , equal  $HC_2O_4^-/C_2O_4^{2-}$ , so the  $pH = pK_{a2}$ .

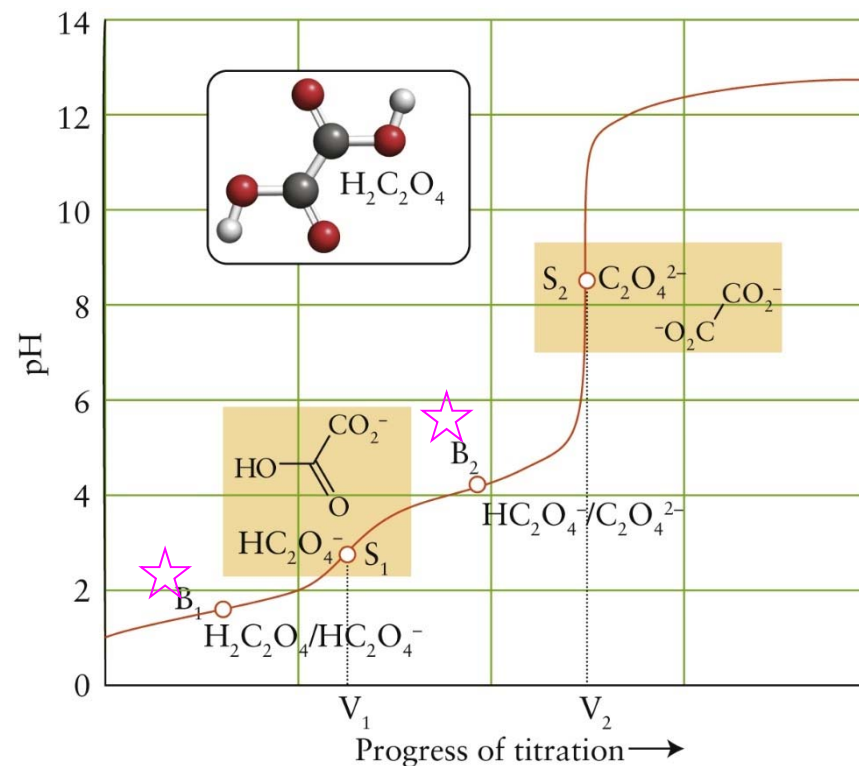


Figure 6H.11  
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# Stoichiometry of Polyprotic Acid Titrations

**We assume** that the first stoichiometric amount of NaOH added reacts only with  $\text{H}_2\text{C}_2\text{O}_4$  because of the **large**  $K_{a1}$ .

$$K_{a1} \gg \gg K_{a2}$$

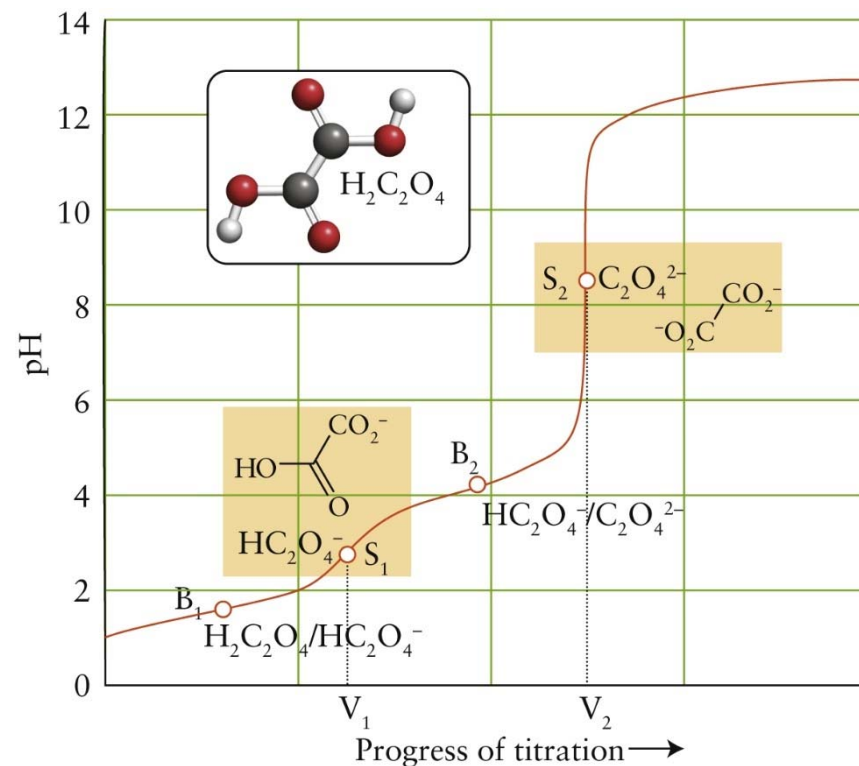
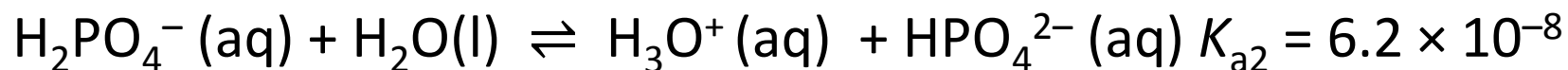
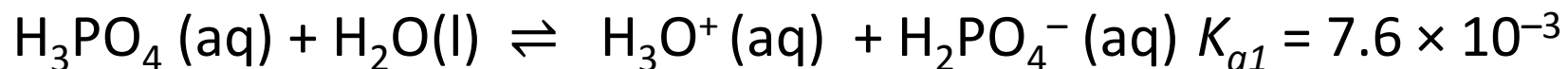


Figure 6H.11  
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6H.4B In a titration of 30.00 mL of 0.010 M  $\text{H}_3\text{PO}_4(\text{aq})$  with NaOH, what volume of 0.020 M  $\text{NaOH}(\text{aq})$  is required to reach (a) the first stoichiometric point and (b) the second stoichiometric point in



We need a stoichiometric amount of NaOH to remove the first proton, and a second stoichiometric amount of NaOH to remove the second proton.

$$\text{Moles of } \text{H}_3\text{PO}_4 = \frac{0.010 \text{ mol } \text{H}_3\text{PO}_4}{1 \text{ L } \text{H}_3\text{PO}_4} \times \frac{0.03000 \text{ L}}{1} = 0.00030 \text{ mol } \text{H}_3\text{PO}_4$$

Meaning, we need 0.00030 mol NaOH.

$$\text{Volume of NaOH} = \frac{1 \text{ L NaOH}}{0.020 \text{ mol NaOH}} \times \frac{0.00030 \text{ mol}}{1} = 0.015 \text{ L NaOH, } 15 \text{ mL}$$

For (b), we need a second stoichiometric or  $15 \text{ mL} \times 2 = 30. \text{ mL NaOH}$

# 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 analyze 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,  $\text{Bi}_2\text{S}_3$ , is defined as  
$$\text{Bi}_2\text{S}_3(\text{s}) \rightleftharpoons 2 \text{Bi}^{3+}(\text{aq}) + 3 \text{S}^{2-}(\text{aq}) \quad K_{sp} = (a_{\text{Bi}^{3+}})^2(a_{\text{S}^{2-}})^3$$

The concentrations of ions in a sparingly soluble salt solution are low, so we assume that we can approximate  $K_{sp}$  by

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

Solid  $\text{Bi}_2\text{S}_3$  does not appear in the expression for  $K_{sp}$  because it is a pure solid and its activity is 1 (Section 10.2).



## 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 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

**TABLE 6I.1 Solubility Products at 25 °C**

Compound	Formula	$K_{sp}$
aluminum hydroxide	$\text{Al}(\text{OH})_3$	$1.0 \times 10^{-33}$
antimony sulfide	$\text{Sb}_2\text{S}_3$	$1.7 \times 10^{-93}$
barium carbonate	$\text{BaCO}_3$	$8.1 \times 10^{-9}$
fluoride	$\text{BaF}_2$	$1.7 \times 10^{-6}$
sulfate	$\text{BaSO}_4$	$1.1 \times 10^{-10}$
bismuth sulfide	$\text{Bi}_2\text{S}_3$	$1.0 \times 10^{-97}$
calcium carbonate	$\text{CaCO}_3$	$8.7 \times 10^{-9}$
fluoride	$\text{CaF}_2$	$4.0 \times 10^{-11}$
hydroxide	$\text{Ca}(\text{OH})_2$	$5.5 \times 10^{-6}$
sulfate	$\text{CaSO}_4$	$2.4 \times 10^{-5}$
chromium(III) iodate	$\text{Cr}(\text{IO}_3)_3$	$5.0 \times 10^{-6}$
copper(I) bromide	$\text{CuBr}$	$4.2 \times 10^{-8}$
chloride	$\text{CuCl}$	$1.0 \times 10^{-6}$

## Example 6I.1 Determining the Solubility Product

The molar solubility of silver chromate,  $\text{Ag}_2\text{CrO}_4$ , is  $6.5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ . Determine the value of  $K_{\text{sp}}$  for silver chromate.

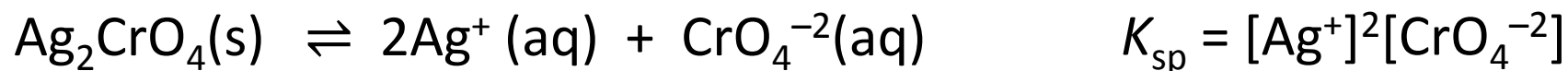
First, we write the equilibrium expression for the solubility product.



Write the expression for the solubility product.

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

The molar solubility of silver chromate,  $\text{Ag}_2\text{CrO}_4$ , is  $6.5 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ . Determine the value of  $K_{\text{sp}}$  for silver chromate.



$$\begin{aligned} 2 \text{ mol Ag}^+ &\simeq 1 \text{ mol CrO}_4^{2-}, [\text{Ag}^+] = 2s = 2(6.5 \times 10^{-5}) \\ 1 \text{ mol CrO}_4^{2-} &\simeq 1 \text{ mol Ag}_2\text{CrO}_4, [\text{CrO}_4^{2-}] = s = 6.5 \times 10^{-5} \end{aligned}$$

$$\text{From } K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}], K_{\text{sp}} = (2s)^2(s) = 4s^3$$

$$\text{Therefore, } K_{\text{sp}} = 4(6.5 \times 10^{-5})^3 = 1.1 \times 10^{-12}$$

## Example 6I.2 Estimating the molar solubility from the solubility product constant.

According to Table 6I.1,  $K_{sp} = 5.0 \times 10^{-6}$  for chromium(III) iodate in water. Estimate the molar solubility of the compound.

First, we write the equilibrium expression for the solubility product.

$$\text{Cr}(\text{IO}_3)_3(\text{s}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3 \text{IO}_3^{-}(\text{aq})$$

Write the expression for the solubility product.

$$K_{sp} = [\text{Cr}^{3+}][\text{IO}_3^{-}]^3$$

According to Table 6I.1,  $K_{sp} = 5.0 \times 10^{-6}$  for chromium(III) iodate in water. Estimate the molar solubility of the compound.

$$K_{sp} = [\text{Cr}^{3+}][\text{IO}_3^-]^3$$

Using the **first** method, based on the mole ratios we solve for  $K_{sp}$ ,  
 $K_{sp} = [\text{Cr}^{3+}][\text{IO}_3^-]^3$ ,  $[\text{Cr}^{3+}] = s$ , and  $[\text{IO}_3^-] = 3s$ ,  $K_{sp} = s(3s)^3 = 27s^4$

$$K_{sp} = 5.0 \times 10^{-6} = 27s^4, \text{ solving for } s, s = \sqrt[4]{\frac{5.0 \times 10^{-6}}{27}} = 0.021 \text{ M}$$

The **second** method using an ICE table; this might help see the equilibrium values.

	$\text{Cr}(\text{IO}_3)_3$	$\text{Cr}^{3+}$	$\text{IO}_3^-$
initial	N/A	0	0
change		+ $s$	+ $3s$
equilibrium		$s$	$3s$

Then solve for  $K_{sp}$  above,  $K_{sp} = s(3s)^3 = 27s^4$ .

## The Common-Ion Effect

Making precipitates of sparingly soluble salt, like heavy metal ions such as **lead** and **mercury**, can be removed 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 a “common ion” to the original solution, it will cause the equilibrium to shift away from the ion added.

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

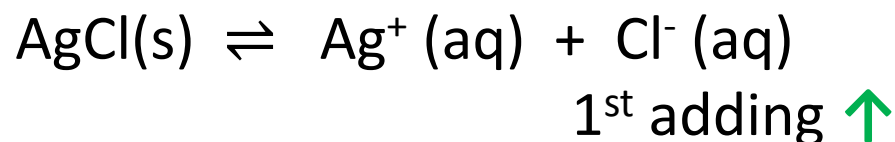
## The Common-Ion Effect

A quantitative understanding of the common-ion effect follows with  $\text{AgCl(s)}$ .



The molar solubility of  $\text{AgCl}$  in water is  $1.3 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ .

According to Le Chatelier's principle, adding a common ion  $\text{Cl}^-$  to this reaction, in the form of  $\text{NaCl}$ , will have the effect of forming more  $\text{AgCl(s)}$ .



  
2<sup>nd</sup> will cause an equilibrium shift

This will produce more  $\uparrow \text{AgCl(s)}$ .



Example 6I.3 Estimating the effect of a common ion on the solubility of silver chloride in  $1.0 \times 10^{-4} \text{ M NaCl(aq)}$ .

$$K_{\text{sp}} = 1.6 \times 10^{-10}.$$

$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$ , the molar solubility of AgCl in water is before adding NaCl is  $1.3 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ .

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.6 \times 10^{-10}}{1.0 \times 10^{-4}} = 1.6 \times 10^{-6} \text{ which is 10 times less than "s" in pure water.}$$

## Predicting Precipitation

In a multi-ion solution, it is important to precipitate one ion at a time.

It's an analytical idea, that is, removing one ion at a time.

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  $Q_{sp}$  is **greater** than  $K_{sp}$ .

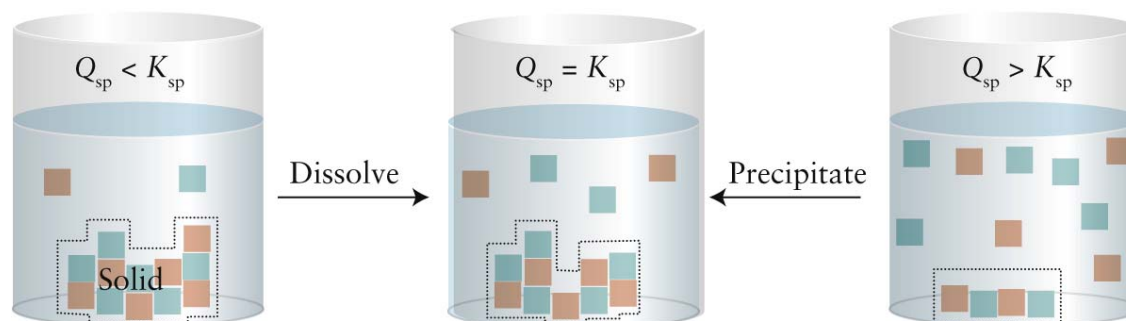


Figure 6J.1

Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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## Example 6J.1 Predicting whether a precipitate will form when two solutions are mixed.

Suppose we mix equal volumes of 0.2 M  $\text{Pb}(\text{NO}_3)_2(\text{aq})$  and  $\text{KI}(\text{aq})$ . Will lead(II) iodide precipitate?  $K_{\text{sp}} = 1.4 \times 10^{-8}$ ,

The concentrations of the  $\text{Pb}^{2+}$  and  $\text{I}^-$  ions are high, and we can expect that precipitation will be spontaneous.

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

A few drops of KI precipitates out the  $\text{Pb}^{2+}$  as  $\text{PbI}_2$ .



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

## Example 6J.1 Predicting whether a precipitate will form when two solutions are mixed.

Suppose we mix equal volumes of 0.2 M  $\text{Pb}(\text{NO}_3)_2(\text{aq})$  and  $\text{KI}(\text{aq})$ . Will lead(II) iodide precipitate?  $K_{\text{sp}} = 1.4 \times 10^{-8}$

Adding two solutions together means our volumes are changing, which means the concentrations are changing. Assuming we have 1 liter of each solution, with a total volume of 2 liters, we can use our dilution formula  $M_1V_1 = M_2V_2$ .

$$[\text{Pb}^{+2}] = \frac{0.2 \text{ M} \times 1 \text{ L}}{2 \text{ L}} = 0.1 \text{ mol} \cdot \text{L}^{-1} \quad [\text{I}^-] = \frac{0.2 \text{ M} \times 1 \text{ L}}{2 \text{ L}} = 0.1 \text{ mol} \cdot \text{L}^{-1}$$

$$Q_{\text{sp}} = [\text{Pb}^{+2}][\text{I}^-]^2 = (0.1)(0.1)^2 = 1.0 \times 10^{-3} \gg K_{\text{sp}} \text{ so it will precipitate.}$$

## Selective Precipitation

Knowing when  $Q_{sp} \gg K_{sp}$ , we can apply this strategy to common industrial problems.

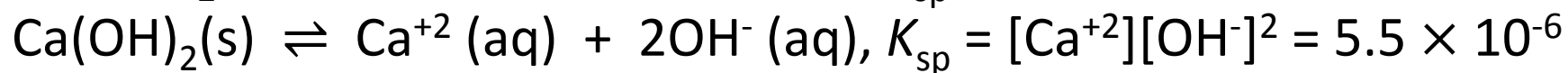
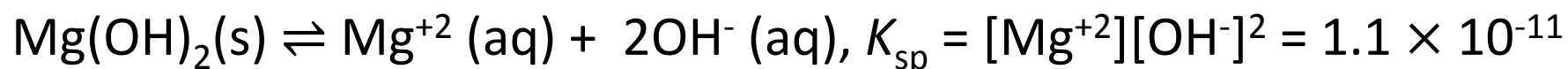
Seawater is a mixture of many different ions. It is possible to precipitate magnesium ions from seawater by adding hydroxide ions.

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 all the  $K_{sp}$  of all ions, we can predict the order of precipitation.

## Example 6J.2 Predicting the order of precipitation.

A sample of seawater contains, among other solutes, the following concentrations of soluble cations:  $0.050 \text{ mol}\cdot\text{L}^{-1} \text{ Mg}^{2+} (\text{aq})$  and  $0.010 \text{ mol}\cdot\text{L}^{-1} \text{ Ca}^{2+} (\text{aq})$ . (a) Determine the order in which each ion precipitates as solid NaOH is added, and give the concentration of  $\text{OH}^-$  when precipitation of each 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.



We do notice that the  $K_{\text{sp}} \text{ Mg}(\text{OH})_2 \lll K_{\text{sp}} \text{ Ca}(\text{OH})_2$  which does give us a general idea of what to expect.

(a)  $0.050 \text{ mol}\cdot\text{L}^{-1} \text{Mg}^{2+} (\text{aq})$  and  $0.010 \text{ mol}\cdot\text{L}^{-1} \text{Ca}^{2+} (\text{aq})$ .

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

for  $\text{Mg}(\text{OH})_2$ .

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

for  $\text{Ca}(\text{OH})_2$ .

So, once the concentration of  $[\text{OH}^{-}]$  is  $1.5 \times 10^{-5} \ll 0.023$ ,  $\text{Mg}(\text{OH})_2$  will begin to precipitate out of solution first.

(b) Just as the  $\text{Ca}(\text{OH})_2$  begins to precipitate out at  $0.023 \text{ M}$ , the

$$[\text{Mg}^{+2}] = \frac{1.1 \times 10^{-11}}{(0.023)^2} = 2.8 \times 10^{-8} \text{ M. This is the amount of } [\text{Mg}^{+2}] \text{ as}$$

$\text{Ca}(\text{OH})_2(\text{s})$  forms, which is a huge reduction in the amount of  $[\text{Mg}^{+2}]$ .

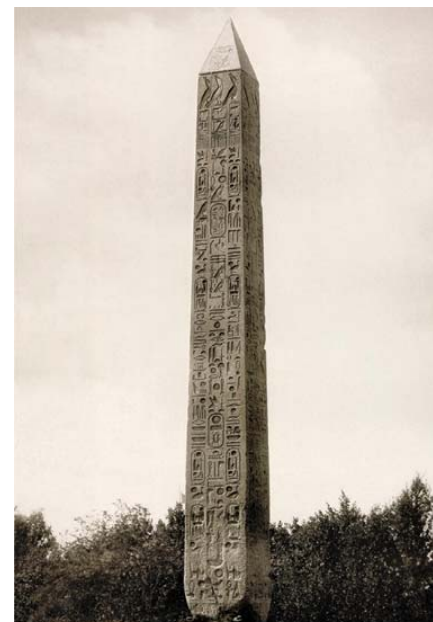
## Dissolving Precipitates

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

Many carbonates dissolve by addition of acid,  
$$\text{ZnCO}_3(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$$

The  $\text{CO}_3^{2-}$  ions react with acid to form  $\text{CO}_2$  :  
$$\text{CO}_3^{2-}(\text{aq}) + 2 \text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$$

The dissolution of carbonates by acid is an undesired result of acid rain, which has damaged the appearance of many historic marble and limestone monuments.



(a)



(b)

**Figure 6J.3**  
Atkins, *Chemical Principles: The Quest for*  
Photo (a) © CSDP / The Image Works. Photo

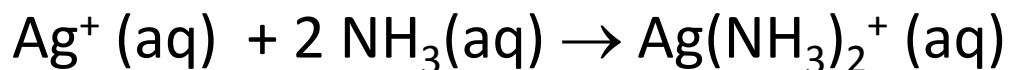


## Complex Ion Formation

Many metal cations are Lewis acids (Focus 5).

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  $\text{Ag}(\text{NH}_3)^+$  .



It is possible to add enough Lewis base ammonia to dissolve a silver-halide solid.

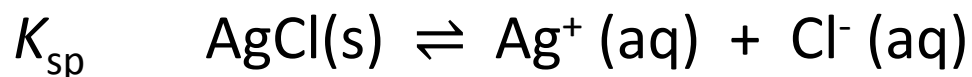
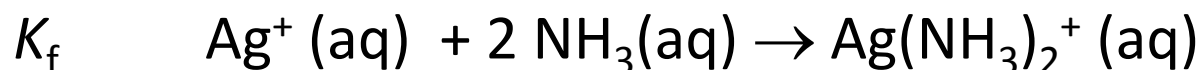
Quantitatively, a formation is called a formation constant,  $K_f$ .

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]} = 1.6 \times 10^7, \text{ a product-favored reaction.}$$

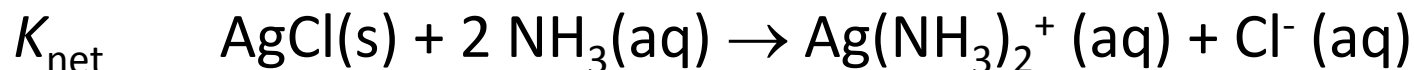
## Example 6I.4 Calculating molar solubility in the presence of complex formation

Calculate the molar solubility of silver chloride in 0.10 M  $\text{NH}_3(\text{aq})$ , given that  $K_{\text{sp}} = 1.6 \times 10^{-10}$  for silver chloride and  $K_{\text{f}} = 1.6 \times 10^7$  for the ammonia complex of  $\text{Ag}^+$  ions,  $\text{Ag}(\text{NH}_3)_2^+$ .

We have two reactions, and both are competing with each other:



We combine these, noting  $\text{Ag}^+$  is a spectator ion.



$$K_{\text{f}} \cdot K_{\text{sp}} = K_{\text{net}} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$

Knowing  $K_{\text{net}}$   $2 \text{ NH}_3(\text{aq}) \rightarrow \text{Ag}(\text{NH}_3)_2^+ (\text{aq}) + \text{Cl}^- (\text{aq})$  we set up an ICE table since we start with an initial concentration of  $\text{NH}_3$ .

	$\text{NH}_3$	$\text{Ag}(\text{NH}_3)_2^+$	$\text{Cl}^-$
initial	0.10	0	0
change	- 2x	+ x	+ x
equilibrium	$0.10 - 2x$	x	x

$$K_f \cdot K_{\text{sp}} = K_{\text{net}} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2},$$

$$(1.6 \times 10^7)(1.6 \times 10^{-10}) = \frac{x^2}{(0.10 - 2x)^2} \text{ taking the square root of both sides and solving for } x, x = 4.6 \times 10^{-3} \text{ M.}$$

$4.6 \times 10^{-3} \text{ M}$  is the new  $K$  for  $K_f$  and  $K_{\text{sp}}$ , the formation of both  $\text{Ag}(\text{NH}_3)_2^+ (\text{aq})$  and  $\text{AgCl}(\text{s})$ . This is the molar solubility for  $\text{AgCl}(\text{s})$ .

# Qualitative Analysis

Qualitative analysis uses all the methods described in this chapter

- Control of pH;
- Selective precipitation;
- Complex ion formation.

Here is an example of identifying and isolating five cations;  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ .

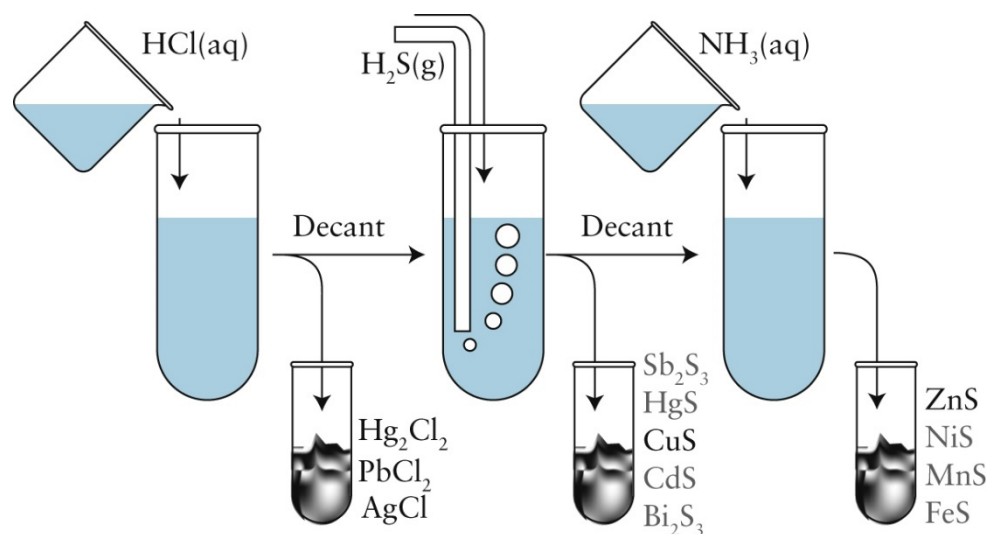
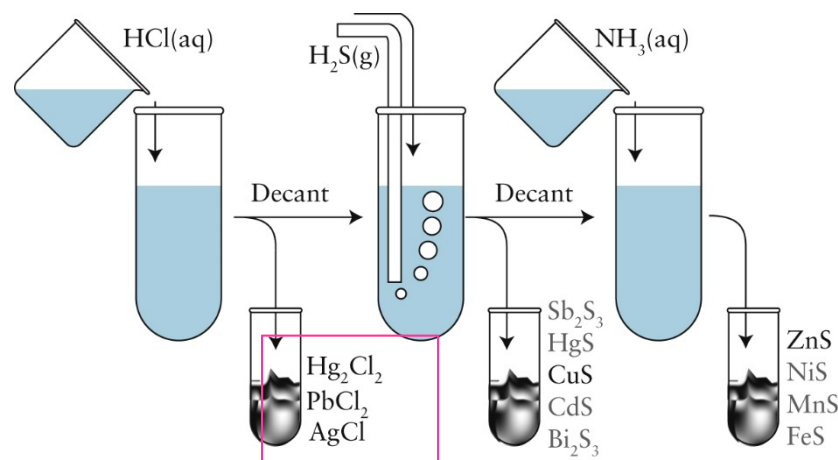


Figure 6J.4  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

When devising a scheme to isolate each ion, we base our decisions on pH,  $K_{\text{sp}}$  (solubility) and  $K_{\text{f}}$ . We notice in the first step that not all metal halides are equally soluble. In the second step,  $\text{H}_2\text{S(g)}$  precipitates out more and in the third step,  $\text{NH}_3$  is added.

# Qualitative Analysis



Decanted supernate

All five ions

Figure 6J.4  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
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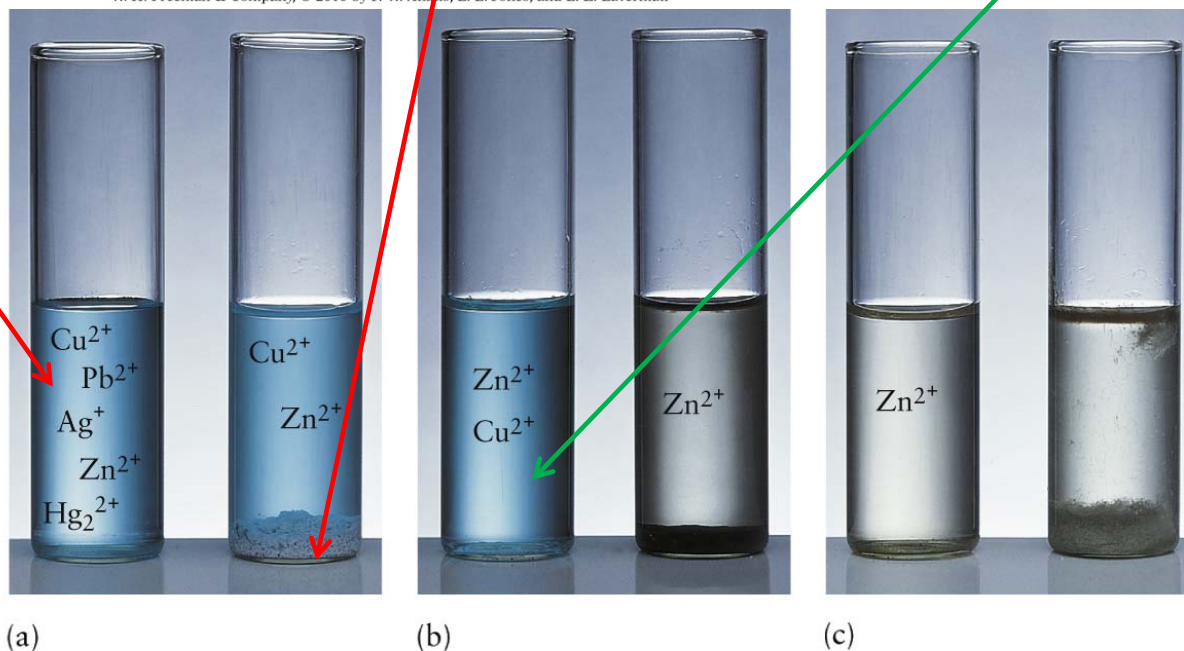


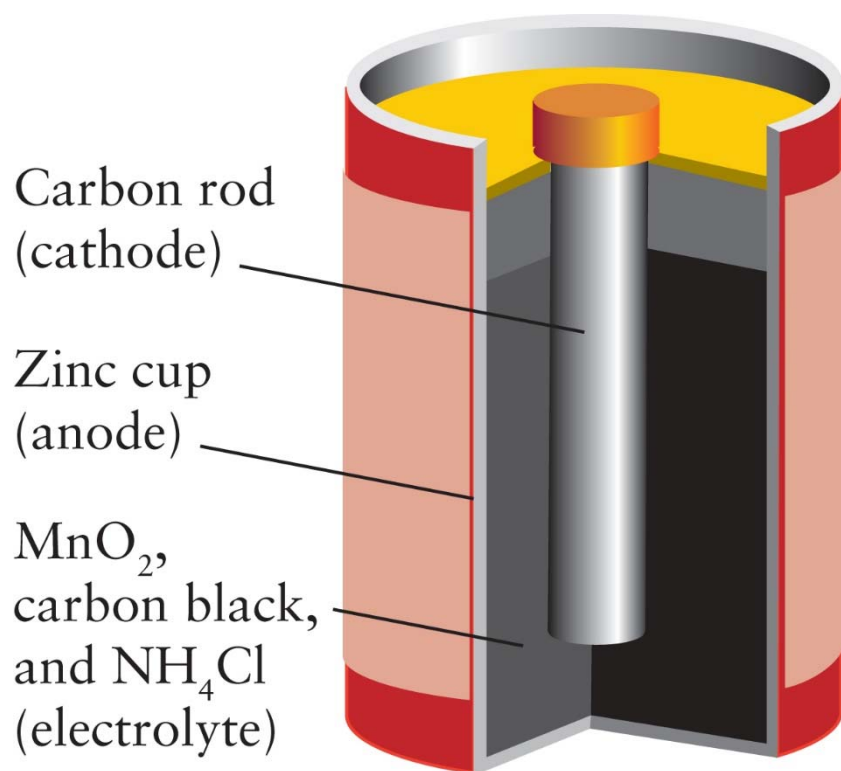
Figure 6J.5  
Atkins, *Chemical Principles: The Quest for Insight*, 7e  
W. H. Freeman photos by Ken Karp.

# Electrochemistry

## In this section

- We explore how to control electrons in chemical reactions, to create useful energy in batteries, and how to refine metal ore into metal.
- We discuss the connectivity of thermodynamic and equilibrium variables in this field of chemistry called electrochemistry.

Lightning is uncontrollable electrons, unpredictably moving between clouds and the ground. It is like getting a shock after walking on carpet and touching a door knob.



Controlling the flow of electrons from chemical reactions is the study of oxidation-reduction reactions.



# The first battery

Long time ago...

~200 years ago



Luigi Galvani  
1734-1798

Physician, Physicist, Biologist,  
Philosopher

University of Bologna, Italy

- Overturned Balloonist theory
- Father of “animal electricity”