APPLICATIONS OF AQUEOUS EQUILIBRIA

Operational Skills

- Calculating the common-ion effect on acid ionization
- Calculating the pH of a buffer from given volumes of solution
- Calculating the pH of a solution of a strong acid and a strong base
- Calculating the pH at the equivalence point in the titration of a weak acid with a strong base

Operational Skills

- **Writing solubility product expressions**
- **Calculating Ksp from the solubility, or vice versa.**
- **Calculating the solubility of a slightly soluble salt in a solution of a common ion.**
- **Predicting whether precipitation will occur**
- **Determining the qualitative effect of pH on solubility**
- **Calculating the concentration of a metal ion in equilibrium with a complex ion**
- **Predicting whether a precipitate will form in the presence of the complex ion**
- **Calculating the solubility of a slightly soluble ionic compound in a solution of the complex ion**

The Common Ion Effect

- The **common-ion effect** is the shift in an ionic equilibrium caused by the addition of a solute that provides an ion common to the equilibrium.

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

  - If we add either product (H_3O^+ or $C_2H_3O_2^-$), the equilibrium will shift to the left to form more acetic acid - the ionization of the acetic acid is repressed.

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, HCH_2O and 0.018 M in sodium formate, $NaCH_2O$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.

$$HCHO_2\,(aq) + H_2O\,(s) \rightleftharpoons H_3O^+\,(aq) + CHO_2^-\,(aq)$$

Initial	0.025
Change	-x
Equilibrium	0.025-x

0	0.018
+x	+x
x	0.018+x

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, $HCHO_2$ and 0.018 M in sodium formate, $NaCHO_2$. What is the pH of the solution. The K_a for formic acid is 1.7×10^{-4}.
  - The equilibrium constant expression is:

$$\frac{[H_3O^+][CHO_2^-]}{[HCHO_2]} = K_a$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, $HCHO_2$ and 0.018 M in sodium formate, $NaCHO_2$. What is the pH of the solution. The K_a for formic acid is 1.7 x 10^{-4}.
  - Substituting into this equation gives:

$$\frac{x(0.018+x)}{(0.025-x)} = 1.7\times10^{-4}$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, $HCHO_2$ and 0.018 M in sodium formate, $NaCHO_2$. What is the pH of the solution. The K_a for formic acid is 1.7 x 10^{-4}.
  - Assume that x is small compared with 0.018 and 0.025. Then

$$(0.018+x) \cong 0.018 \quad (C_b/K_b = 3.1 \times 10^8)$$

$$(0.025-x) \cong 0.025 \quad (C_a/K_a = 106)$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, $HCHO_2$ and 0.018 M in sodium formate, $NaCHO_2$. What is the pH of the solution. The K_a for formic acid is 1.7 x 10^{-4}.
  - The equilibrium equation becomes

$$\frac{x(0.018)}{(0.025)} \cong 1.7\times10^{-4}$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, $HCHO_2$ and 0.018 M in sodium formate, $NaCHO_2$. What is the pH of the solution. The K_a for formic acid is 1.7 x 10^{-4}.
  - Hence,

$$x \cong (1.7\times10^{-4})\times\frac{0.025}{0.018} = 2.4\times10^{-4}$$

A Problem To Consider

- An aqueous solution is 0.025 M in formic acid, $HCHO_2$ and 0.018 M in sodium formate, $NaCHO_2$. What is the pH of the solution. The K_a for formic acid is 1.7 x 10^{-4}.
  - Note that x was much smaller than 0.018 or 0.025.

$$pH = -\log(2.4\times10^{-4}) = 3.63$$

  - For comparison, the pH of 0.025 M formic acid is 2.69.

Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - Buffers contain either a **weak acid and its conjugate base** or a **weak base and its conjugate acid**.
  - Thus, a buffer contains both an acid species and a base species in equilibrium.

Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - Consider a buffer with equal molar amounts of HA and its conjugate base A^-.

    When H_3O^+ is added to the buffer it reacts with the base A^-. Added base reacts with HA.

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

A Buffered Solution

•. . . resists change in its pH when either H^+ or OH^- are added.

•1.0 L of 0.50 M H_3CCOOH

– + 0.50 M $H_3CCOONa$

•pH = 4.74

•Adding 0.010 mol solid NaOH raises the pH of the solution to 4.76, a very minor change.

Henderson-Hasselbalch Equation

- Useful for calculating pH when the $[A^-]/[HA]$ ratios are known.

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

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

Note: When we have equal concentrations of acid and base forms then $pH = pK_a$

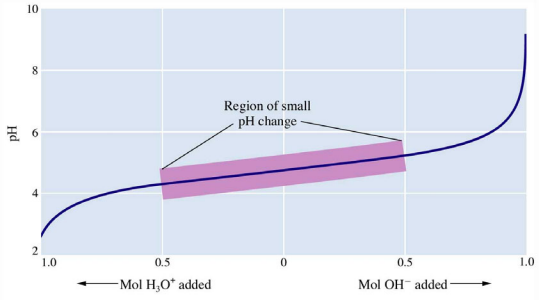
Buffered Solution Characteristics

- Buffers contain relatively large amounts of weak acid and corresponding base.
- Added H^+ reacts to completion with the weak base.
- Added OH^- reacts to completion with the weak acid.
- The pH is determined by the ratio of the concentrations of the weak acid and weak base.

Buffers

- A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it.
  - Two important characteristics of a buffer are its **buffer capacity** and its **pH**.
  - Buffer capacity depends on the **amount** of acid and conjugate base present in the solution.
  - The next example illustrates how to calculate the pH of a buffer.

Effect of added acid or base on a buffer solution.



The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - A buffer must be prepared from a conjugate acid-base pair in which the **K_a of the acid is approximately equal to the desired H_3O^+ concentration**.
  - To illustrate, consider a buffer of a weak acid HA and its conjugate base A^-.

The acid ionization equilibrium is:

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

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - The acid ionization constant is:

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

  - By rearranging, you get an equation for the H_3O^+ concentration.

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

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - Taking the negative logarithm of both sides of the equation we obtain:

$$-\log[H_3O^+] = -\log(K_a) - \log\frac{[HA]}{[A^-]}$$

  - The previous equation can be rewritten

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

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - More generally, you can write

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

  - This equation relates the pH of a buffer to the concentrations of the conjugate acid and base. It is known as the **Henderson-Hasselbalch equation.**

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - So to prepare a buffer of a given pH (for example, **pH 4.90**) we need a conjugate acid-base pair with a pK_a close to the desired pH.
  - The K_a for acetic acid is 1.7×10^{-5}, and its pK_a is 4.77.
  - You could get a buffer of pH 4.90 by increasing the ratio of [base]/[acid].

$4.90 = 4.77 + \log \{[base]/[acid]\}$ or $0.13 = \log \{[base]/[acid]\}$
And $\{[base]/[acid]\} = 1.35$ Therefore:
$[C_2H_3O_2^-] = 1.35[HC_2H_3O_2]$

TABLE 15.1 Change in $[C_2H_3O_2^-]/[HC_2H_3O_2^-]$ for Two Solutions When 0.01 mol H^+ Is Added to 1.0 L of Each

Solution	$\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{orig}$	$\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)_{new}$	Change	Percent Change
A	$\frac{1.00\ M}{1.00\ M} = 1.00$	$\frac{0.99\ M}{1.01\ M} = 0.98$	1.00 → 0.98	2.00%
B	$\frac{1.00\ M}{0.01\ M} = 100$	$\frac{0.99\ M}{0.02\ M} = 49.5$	100 → 49.5	50.5%

We can increase buffering capacity by increasing concentration of the conjugate acid/base pair. If we know that acid only will be added, then we can design a buffer with a higher conjugate base concentration to react with the expected acid influx.

Titration (pH) Curve

- A plot of pH of the solution being analyzed as a function of the amount of titrant added.
- Equivalence (stoichiometric) point: Enough titrant has been added to react exactly with the solution being analyzed.

Figure 15.1: The pH curve for the titration of 50.0 mL of 0.200 *M* HNO_3 with 0.100 *M* NaOH.

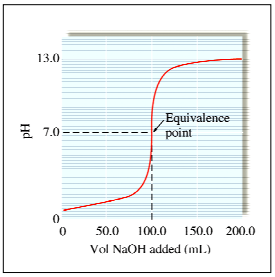
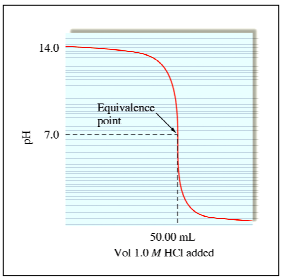


Figure 15.2: The pH curve for the titration of 100.0 mL of 0.50 *M* NaOH with 1.0 *M* HCl.

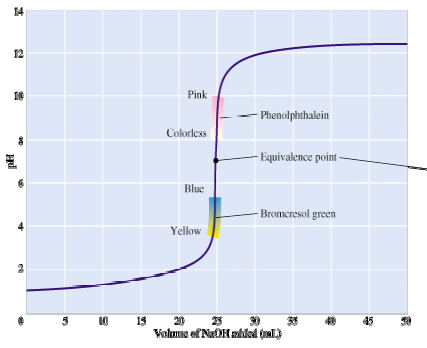


Acid-Base Indicator

•. . . marks the end point of a titration by changing color.

•The equivalence point is not necessarily the same as the end point.

Figure 17.11 Curve for the titration of a strong acid by a strong base.



Volume NaOH added (mL)	pH
0	1.00
5	1.18
10	1.37
15	1.60
20	1.95
21	2.06
22	2.20
23	2.38
24	2.69
25	7.00
26	11.29
27	11.59
28	11.75
29	11.87
30	11.96
35	12.22
40	12.36
45	12.46
50	12.52

Figure 15.6:
The acid and base forms of the indicator phenolphthalein. In the acid form (Hln), the molecule is colorless. When a proton (plus H_2O) is removed to give the base form (ln-), the color changes to pink.

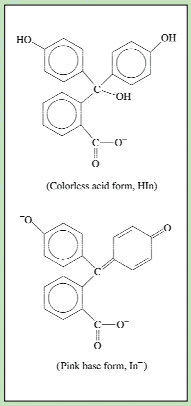
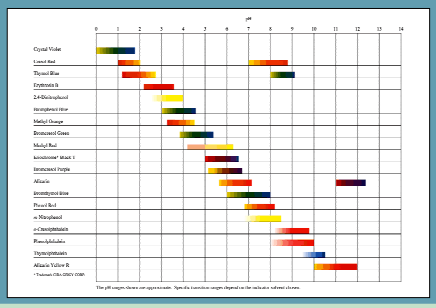


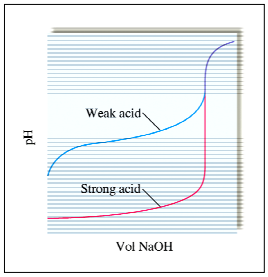
Figure 15.8: The useful pH ranges for several common indicators. Note that most indicators have a useful range of about two pH units, as predicted by the expression p*Ka* ± 1.



Weak Acid - Strong Base Titration

- Step 1 - A stoichiometry problem - reaction is assumed to run to completion - then determine remaining species.
- Step 2 - An equilibrium problem - determine position of weak acid equilibrium and calculate pH.

Comparison of strong and weak acid titration curves.



A Problem To Consider

- Calculate the pH of the solution at the equivalence point when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - At the equivalence point, equal molar amounts of acetic acid and sodium hydroxide react to give sodium acetate.

A Problem To Consider

- Calculate the pH of the solution at the equivalence point when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - First, calculate the concentration of the acetate ion.
  - In this case, 25.0 mL of 0.10 M NaOH is needed to react with 25.0 mL of 0.10 M acetic acid.

A Problem To Consider

- Calculate the pH of the solution at the equivalence point when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - The molar amount of acetate ion formed equals the initial molar amount of acetic acid.

$$25\times10^{-3}\ \text{L soln}\times\frac{0.10\ \text{mol acetate ion}}{1\ \text{L soln}}=2.5\times10^{-3}\ \text{mol acetate ion}$$

A Problem To Consider

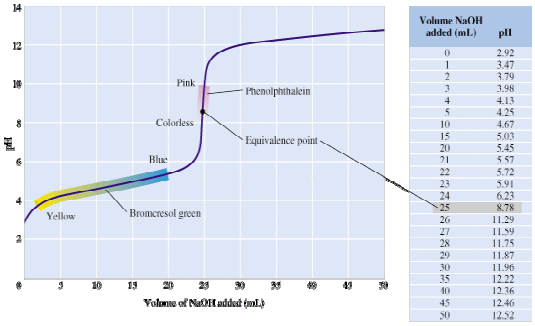
- Calculate the pH of the solution at the equivalence point when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7 x 10^{-5}.
  - The total volume of the solution is 50.0 mL. Hence,

$$\text{molar concentration} = \frac{2.5\times10^{-3}\,\text{mol}}{50\times10^{-3}\,\text{L}} = 0.050\ \text{M}$$

A Problem To Consider

- Calculate the pH of the solution at the equivalence point when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7 x 10^{-5}.
  - The hydrolysis of the acetate ion follows the method given in an earlier section of this chapter.
  - You find the K_b for the acetate ion to be 5.9 x 10^{-10} and that the concentration of the hydroxide ion is 5.4 x 10^{-6}. **The pH is 8.73**

Figure 17.12 Curve for the titration of a weak acid by a strong base.

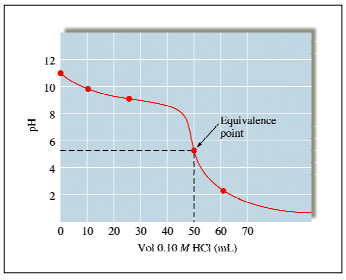


Volume NaOH added (mL)	pH
0	2.92
1	3.47
2	3.79
3	3.98
4	4.13
5	4.25
10	4.67
15	5.03
20	5.45
21	5.57
22	5.72
23	5.91
24	6.23
25	8.78
26	11.29
27	11.59
28	11.75
29	11.87
30	11.96
35	12.22
40	12.36
45	12.46
50	12.52

TABLE 15.2 Summary of Results for the Titration of 100.0 mL 0.050 *M* NH_3 with 0.10 *M* HCl

Volume of 0.10 *M* HCl Added (mL)	$[NH_3]_0$	$[NH_4^+]_0$	$[H^+]$	pH
0	0.05 *M*	0	1.1×10^{-11} *M*	10.96
10.0	$\frac{4.0\ \text{mmol}}{(100 + 10)\ \text{mL}}$	$\frac{1.0\ \text{mmol}}{(100 + 10)\ \text{mL}}$	1.4×10^{-10} *M*	9.85
25.0*	$\frac{2.5\ \text{mmol}}{(100 + 25)\ \text{mL}}$	$\frac{2.5\ \text{mmol}}{(100 + 25)\ \text{mL}}$	5.6×10^{-10} *M*	9.25
50.0†	0	$\frac{5.0\ \text{mmol}}{(100 + 50)\ \text{mL}}$	4.3×10^{-9} *M*	5.36
60.0‡	0	$\frac{5.0\ \text{mmol}}{(100 + 60)\ \text{mL}}$	$\frac{1.0\ \text{mmol}}{160\ \text{mL}} = 6.2 \times 10^{-3}$ *M*	2.21

Figure 15.5: The pH curve for the titration of 100.0 mL of 0.050 *M* NH_3 with 0.10 *M* HCl.



Solubility Equilibria

- Many natural processes depend on the precipitation or dissolving of a **slightly soluble salt**.
  - In the next section, we look at the **equilibria** of slightly soluble, or nearly insoluble, ionic compounds.
  - Their equilibrium constants can be used to answer questions regarding **solubility** and **precipitation**.

Table 4.1
Solubility Rules for Ionic Compounds

Rule	Applies to	Statement	Exceptions
1	Li^+, Na^+, K^+, NH_4^+	Group IA and ammonium compounds are soluble.	—
2	$C_2H_3O_2^-$, NO_3^-	Acetates and nitrates are soluble.	—
3	Cl^-, Br^-, I^-	Most chlorides, bromides, and iodides are soluble.	AgCl, Hg_2Cl_2, $PbCl_2$, AgBr, $HgBr_2$, Hg_2Br_2, $PbBr_2$, AgI, HgI_2, Hg_2I_2, PbI_2
4	SO_4^{2-}	Most sulfates are soluble.	$CaSO_4$, $SrSO_4$, $BaSO_4$, Ag_2SO_4, Hg_2SO_4, $PbSO_4$
5	CO_3^{2-}	Most carbonates are insoluble.	Group IA carbonates, $(NH_4)_2CO_3$
6	PO_4^{3-}	Most phosphates are insoluble.	Group IA phosphates, $(NH_4)_3PO_4$
7	S^{2-}	Most sulfides are insoluble.	Group IA sulfides, $(NH_4)_2S$
8	OH^-	Most hydroxides are insoluble.	Group IA hydroxides, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

Solubility Product

- For solids dissolving to form aqueous solutions.

$$Bi_2S_3(s) \leftrightarrow 2Bi^{3+}(aq) + 3S^{2-}(aq)$$

- K_{sp} = solubility product constant and
  - $K_{sp} = [Bi^{3+}]^2[S^{2-}]^3$

Solubility Product

- "Solubility" = s = concentration of Bi_2S_3 that dissolves, which equals $1/2[Bi^{3+}]$ and $1/3[S^{2-}]$.
- Note: K_{sp} is constant (at a given temperature)
- s is variable (especially with a common ion present)
  - Bi_2S_3 (s) ⇌ 2 Bi^{3+} (aq) + 3 S^{2-} (aq)
    1 mole 2 moles 3 moles

Calculating K_{sp} from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4, contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.
  - We must first convert the solubility of calcium oxalate from 0.0061 g/liter to moles per liter.

$$M\,CaC_2O_4 = (0.0061\ g\ CaC_2O_4 / L) \times \frac{1\ mol\ CaC_2O_4}{128 g\ CaC_2O_4}$$

$$= 4.8 \times 10^{-5}\ mol\ CaC_2O_4 / L$$

Calculating K_{sp} from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4, contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.
  - When 4.8×10^{-5} mol of solid dissolve it forms 4.8×10^{-5} mol of each ion.

$$CaC_2O_4(s) \xrightleftharpoons{H_2O} Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

Initial	0	0
Change	$+4.8 \times 10^{-5}$	$+4.8 \times 10^{-5}$
Equilibrium	4.8×10^{-5}	4.8×10^{-5}

Calculating K_{sp} from the Solubility

- A 1.0-L sample of a saturated calcium oxalate solution, CaC_2O_4, contains 0.0061-g of the salt at 25 °C. Calculate the K_{sp} for this salt at 25 °C.
  - You can now substitute into the equilibrium-constant expression.

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

$$K_{sp} = (4.8 \times 10^{-5})(4.8 \times 10^{-5})$$

$$K_{sp} = 2.3 \times 10^{-9}$$

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2 x 10^{-3} mol of lead(II) iodide, PbI_2, dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
  - Note that in this example, you find that 1.2 x 10^{-3} mol of the solid dissolves to give 1.2 x 10^{-3} mol Pb^{2+} and 2 x (1.2 x 10^{-3}) mol of I^-.

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2 x 10^{-3} mol of lead(II) iodide, PbI_2, dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
  - The following table summarizes.

$$PbI_2(s) \overset{H_2O}{\rightleftharpoons} Pb^{2+}(aq) + 2I^-(aq)$$

Initial	0	0
Change	+1.2 x 10^{-3}	+2 x (1.2 x 10^{-3})
Equilibrium	1.2 x 10^{-3}	2 x (1.2 x 10^{-3})

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2 x 10^{-3} mol of lead(II) iodide, PbI_2, dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
  - Substituting into the equilibrium-constant expression:

$$K_{sp} = [Pb^{2+}][I^-]^2$$

$$K_{sp} = (1.2\times10^{-3})(2\times(1.2\times10^{-3}))^2$$

$$K_{sp} = 6.9\times10^{-9}$$

Calculating K_{sp} from the Solubility

- By experiment, it is found that 1.2 x 10^{-3} mol of lead(II) iodide, PbI_2, dissolves in 1.0 L of water at 25 °C. What is the K_{sp} at this temperature?
  - Table 15.4 lists the solubility product constants for various ionic compounds.
  - If the solubility product constant is known, the solubility of the compound can be calculated.

TABLE 15.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)
Fluorides		Hg_2CrO_4*	2×10^{-9}	$Co(OH)_2$	2.5×10^{-16}
BaF_2	2.4×10^{-5}	$BaCrO_4$	8.5×10^{-11}	$Ni(OH)_2$	1.6×10^{-16}
MgF_2	6.4×10^{-9}	Ag_2CrO_4	9.0×10^{-12}	$Zn(OH)_2$	4.5×10^{-17}
PbF_2	4×10^{-8}	$PbCrO_4$	2×10^{-16}	$Cu(OH)_2$	1.6×10^{-19}
SrF_2	7.9×10^{-10}			$Hg(OH)_2$	3×10^{-26}
CaF_2	4.0×10^{-11}	**Carbonates**		$Sn(OH)_2$	3×10^{-27}
		$NiCO_3$	1.4×10^{-7}	$Cr(OH)_3$	6.7×10^{-31}
Chlorides		$CaCO_3$	8.7×10^{-9}	$Al(OH)_3$	2×10^{-32}
$PbCl_2$	1.6×10^{-5}	$BaCO_3$	1.6×10^{-9}	$Fe(OH)_3$	4×10^{-38}
$AgCl$	1.6×10^{-10}	$SrCO_3$	7×10^{-10}	$Co(OH)_3$	2.5×10^{-43}
Hg_2Cl_2*	1.1×10^{-18}	$CuCO_3$	2.5×10^{-10}		
		$ZnCO_3$	2×10^{-10}	**Sulfides**	
Bromides		$MnCO_3$	8.8×10^{-11}	MnS	2.3×10^{-13}
$PbBr_2$	4.6×10^{-6}	$FeCO_3$	2.1×10^{-11}	FeS	3.7×10^{-19}
$AgBr$	5.0×10^{-13}	Ag_2CO_3	8.1×10^{-12}	NiS	3×10^{-21}
Hg_2Br_2*	1.3×10^{-22}	$CdCO_3$	5.2×10^{-12}	CoS	5×10^{-22}
		$PbCO_3$	1.5×10^{-15}	ZnS	2.5×10^{-22}
Iodides		$MgCO_3$	6.8×10^{-6}	SnS	1×10^{-26}
PbI_2	1.4×10^{-8}	Hg_2CO_3*	9.0×10^{-15}	CdS	1.0×10^{-28}
AgI	1.5×10^{-16}			PbS	7×10^{-29}
Hg_2I_2*	4.5×10^{-29}	**Hydroxides**		CuS	8.5×10^{-45}
		$Ba(OH)_2$	5.0×10^{-3}	Ag_2S	1.6×10^{-49}
Sulfates		$Sr(OH)_2$	3.2×10^{-4}	HgS	1.6×10^{-54}
$CaSO_4$	6.1×10^{-5}	$Ca(OH)_2$	1.3×10^{-6}		
Ag_2SO_4	1.2×10^{-5}	$AgOH$	2.0×10^{-8}	**Phosphates**	
$SrSO_4$	3.2×10^{-7}	$Mg(OH)_2$	8.9×10^{-12}	Ag_3PO_4	1.8×10^{-18}
$PbSO_4$	1.3×10^{-8}	$Mn(OH)_2$	2×10^{-13}	$Sr_3(PO_4)_2$	1×10^{-31}
$BaSO_4$	1.5×10^{-9}	$Cd(OH)_2$	5.9×10^{-15}	$Ca_3(PO_4)_2$	1.3×10^{-32}
		$Pb(OH)_2$	1.2×10^{-15}	$Ba_3(PO_4)_2$	6×10^{-39}
Chromates		$Fe(OH)_2$	1.8×10^{-15}	$Pb_3(PO_4)_2$	1×10^{-54}
$SrCrO_4$	3.6×10^{-5}				

Calculating the Solubility from K_{sp}

- The mineral fluorite is calcium fluoride, CaF_2. Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4 x 10^{-11})
  - Let x be the molar solubility of CaF_2.

$$CaF_2(s) \overset{H_2O}{\rightleftharpoons} Ca^{2+}(aq) + 2F^-(aq)$$

Initial	0	0
Change	+x	+2x
Equilibrium	x	2x

Calculating the Solubility from K_{sp}

- The mineral flu0orite is calcium fluoride, CaF_2. Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})
  - You substitute into the equilibrium-constant equation

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

$$(x)(2x)^2 = 3.4\times10^{-11}$$

$$4x^3 = 3.4\times10^{-11}$$

Calculating the Solubility from K_{sp}

- The mineral fluorite is calcium fluoride, CaF_2. Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})
  - You now solve for x.

$$x = \sqrt[3]{\frac{3.4\times10^{-11}}{4}} = 2.0\times10^{-4}$$

Calculating the Solubility from K_{sp}

- The mineral fluorite is calcium fluoride, CaF_2. Calculate the solubility (in grams per liter) of calcium fluoride in water from the K_{sp} (3.4×10^{-11})
  - Convert to g/L (CaF_2 78.1 g/mol).

$$\text{solubility} = 2.0\times10^{-4}\,\text{mol/L}\times\frac{78.1\,\text{g CaF}_2}{1\,\text{mol CaF}_2}$$

$$= 1.6\times10^{-2}\,\text{g CaF}_2\,\text{/ L}$$

Common Ion Effect

•The shift in equilibrium that occurs because of the addition of an ion already involved in the equilibrium reaction.

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

$\leftarrow$ adding $NaCl(aq)$ shifts equilibrium position

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - Note that before the calcium oxalate dissolves, there is already 0.15 M Ca^{2+} in the solution.

$$CaC_2O_4(s) \overset{H_2O}{\rightleftharpoons} Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

Initial	0.15	0
Change	+x	+x
Equilibrium	0.15+x	x

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - You substitute into the equilibrium-constant equation

$$[Ca^{2+}][C_2O_4^{2-}] = K_{sp}$$

$$(0.15 + x)(x) = 2.3\times10^{-9}$$

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - Now rearrange this equation to give

$$x = \frac{2.3\times10^{-9}}{0.15+x} \cong \frac{2.3\times10^{-9}}{0.15}$$

  - We expect x to be negligible compared to 0.15.

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - Now rearrange this equation to give

$$x = \frac{2.3\times10^{-9}}{0.15+x} \cong \frac{2.3\times10^{-9}}{0.15}$$

$$x = 1.5\times10^{-8}$$

A Problem To Consider

- What is the molar solubility of calcium oxalate in 0.15 M calcium chloride? The K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - Therefore, the molar solubility of calcium oxalate in 0.15 M $CaCl_2$ is 1.5×10^{-8} M.
  - In pure water, the molarity was 4.8×10^{-5} M, which is over **3000 times greater**.

Precipitation Calculations

- Precipitation is merely another way of looking at solubility equilibrium.
  - Rather than considering how much of a substance will dissolve, we ask: **Will precipitation occur for a given starting ion concentration?**

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c**.
  - To predict the direction of reaction, you compare Q_c with K_c (Chapter 13).
  - The reaction quotient has the same form as the K_{sp} expression, but the concentrations of products are starting values.

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c**.
  - Consider the following equilibrium.

$$PbCl_2(s) \overset{H_2O}{\rightleftharpoons} Pb^{2+}(aq) + 2Cl^-(aq)$$

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c**.
  - The Q_c expression is

$$Q_c = [Pb^{2+}]_i[Cl^-]_i^2$$

where initial concentration is denoted by *i*.

Criteria for Precipitation

- To determine whether an equilibrium system will go in the forward or reverse direction requires that we evaluate the **reaction quotient, Q_c**.
  - If Q_c exceeds the K_{sp}, precipitation occurs.
  - If Q_c is less than K_{sp}, more solute can dissolve.
  - If Q_c equals the K_{sp}, the solution is saturated.

Predicting Whether Precipitation Will Occur

- The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is 1.0×10^{-7} M, do you expect calcium oxalate to precipitate? K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - The ion product quotient, Q_c, is:

$$Q_c = [Ca^{2+}]_i[C_2O_4^{2-}]_i$$
$$Q_c = (0.0025) \times (1.0 \times 10^{-7})$$
$$Q_c = 2.5 \times 10^{-10}$$

Predicting Whether Precipitation Will Occur

- The concentration of calcium ion in blood plasma is 0.0025 M. If the concentration of oxalate ion is 1.0×10^{-7} M, do you expect calcium oxalate to precipitate? K_{sp} for calcium oxalate is 2.3×10^{-9}.
  - This value is smaller than the Ksp, so **you do not expect precipitation to occur**.

$$Q_c = 2.5 \times 10^{-10} < K_{sp}$$

Fractional Precipitation

- **Fractional precipitation** is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.
  - For example, when you slowly add potassium chromate, K_2CrO_4, to a solution containing Ba^{2+} and Sr^{2+}, **barium chromate precipitates first**.

$K_{sp} = 1.2 \times 10^{-10}$ for $BaCrO_4$
$K_{sp} = 3.5 \times 10^{-5}$ for $SrCrO_4$

Fractional Precipitation

- **Fractional precipitation** is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.
  - After most of the Ba^{2+} ion has precipitated, strontium chromate begins to precipitate.
  - It is therefore possible to separate Ba^{2+} from Sr^{2+} by **fractional precipitation** using K_2CrO_4 because strontium chromate is more soluble.

Effect of pH on Solubility

- Sometimes it is necessary to account for **other reactions** aqueous ions might undergo.
  - For example, if the anion is the **conjugate base of a weak acid**, it will react with H_3O^+.
  - You should expect the solubility to be affected by pH if the anion in the salt is weak base (i.e., F^- or CN^-)

Effect of pH on Solubility

- Sometimes it is necessary to account for **other reactions** aqueous ions might undergo.
  - Consider the following equilibrium.

$$CaC_2O_4(s) \overset{H_2O}{\rightleftharpoons} Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

  - Because the oxalate ion is conjugate to a weak acid ($HC_2O_4^-$), it will react with H_3O^+.

$$C_2O_4^{2-}(aq) + H_3O^+(aq) \overset{H_2O}{\rightleftharpoons} HC_2O_4^-(aq) + H_2O(l)$$

Effect of pH on Solubility

- Sometimes it is necessary to account for **other reactions** aqueous ions might undergo.
  - According to Le Chatelier's principle, as $C_2O_4^{2-}$ ion is removed by the reaction with H_3O^+, more calcium oxalate dissolves.
  - Therefore, you expect calcium oxalate to be **more soluble in acidic solution (low pH) than in pure water**.

Separation of Metal Ions by Sulfide Precipitation

- Many metal sulfides are insoluble in water but dissolve in acidic solution.
  - **Qualitative analysis** uses this change in solubility of the metal sulfides with pH to separate a mixture of metal ions.
  - By adjusting the pH in an aqueous solution of H_2S, you adjust the sulfide concentration to precipitate the least soluble metal sulfide first.
  - **Qualitative analysis** is covered in pp 764-766.

Figure 15.11: The separation of Cu^{2+} and Hg^{2+} from Ni^{2+} and Mn^{2+} using H_2S.

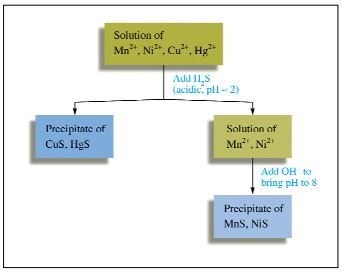
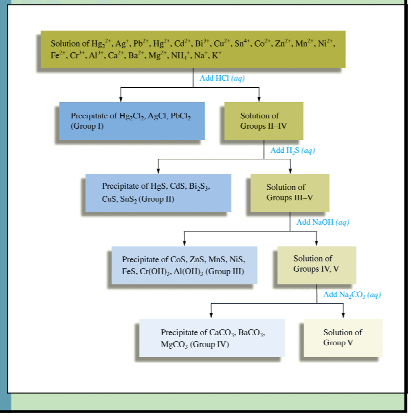


TABLE 15.5 Calculated Solubilities for CuS, Ag_2S, and Bi_2S_3 at 25°C

Salt	K_{sp}	Calculated Solubility (mol/L)
CuS	8.5×10^{-45}	9.2×10^{-23}
Ag_2S	1.6×10^{-49}	3.4×10^{-17}
Bi_2S_3	1.1×10^{-73}	1.0×10^{-15}

Figure 15.12: A schematic diagram of the classic method for separating the common cations by selective precipitation.



From left to right, cadmium sulfide, chromium(III) hydroxide, aluminum hydroxide, and nickel(II) hydroxide.

(left) Aqueous ammonia is added to silver chloride (white). (right) Silver chloride, insoluble in water, dissolves to form $Ag(NH_3)_2^+(aq)$ and $Cl^-(aq)$.

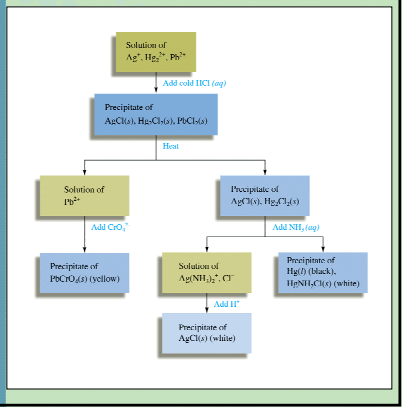



Figure 15.13: The separation of the Group I ions in the classic scheme of qualitative analysis.