Chapter 11

Solving Equilibrium Problems for Complex Systems

Equilibrium Calculations

Previous

\[ \text{BaC}_2\text{O}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{C}_2\text{O}_4^{2-} \]

\[ [\text{Ba}^{2+}] = [\text{C}_2\text{O}_4^{2-}] \]

But what if oxalate then reacted with H\textsubscript{2}O

\[ \text{C}_2\text{O}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HC}_2\text{O}_4^- + \text{OH}^- \]

\[ \text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 + \text{OH}^- \]

\[ [\text{Ba}^{2+}] \neq [\text{C}_2\text{O}_4^{2-}] \]

because \([\text{C}_2\text{O}_4^{2-}] = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4] \]

Systematic Treatment of Equilibrium

1. Write all pertinent reactions
2. Write the charge balance equation
3. Write the mass balance equation
4. Write the equilibrium constant for each chemical reaction (should use activities but we will ignore them)
5. Count the equations and unknowns (\# equations = \# unknowns)
6. Solve the unknowns
Charge Balance Equations

- Charge Balance Equations -
  - An algebraic statement of electroneutrality.
  - The concentration of the sum of the positive charges = the concentration of the sum of the negative charges.
  - General Form of the Equation

\[ n_1[C_1] + n_2[C_2] + \ldots = m_1[A_1] + m_2[A_2] + \ldots \]

In the equation, \( n \) and \( m \) represent the magnitude of the charge of the ion, \([C] \) and \([A] \) represent the concentration of each cation and anion respectively.

Charge Balance Examples

- Given

\[
[H^+] = 5.1 \times 10^{-12} \text{ M} \quad [K^+] = 0.0550 \text{ M} \\
[OH^-] = 0.0020 \text{ M} \quad [H_2PO_4^-] = 1.3 \times 10^{-6} \text{ M} \\
[HPO_4^{2-}] = 0.0220 \text{ M} \quad [PO_4^{3-}] = 0.0030 \text{ M}
\]

Find the solution for the Charge Balance equation.

\[
[H^+] + [K^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]
\]

Charge Balance Examples

- Write the charge balance equation for a solution containing \( \text{H}_2\text{O}, \text{H}^+, \text{OH}^-, \text{ClO}_4^-, \text{Fe(CN)}_6^{3-}, \text{CN}^-, \text{Fe}^{3+}, \text{Mg}^{2+}, \text{CH}_3\text{OH}, \text{HCN}, \text{NH}_3, \text{and NH}_4^+ \).

\[
[H^+] + 3[Fe^{3+}] + 2[Mg^{2+}] + [NH_4^+] = \\
[OH^-] + [\text{ClO}_4^-] + 3[\text{Fe(CN)}_6^{3-}] + [\text{CN}^-]
\]
Charge Balance Examples

Write a charge balance equation for aqueous solution of glycine, which reacts as follows:

\[ +\text{H}_3\text{NCH}_2\text{CO}_2^- \rightleftharpoons \text{H}_2\text{NCH}_2\text{CO}_2^- + \text{H}^+ \]
\[ +\text{H}_3\text{NCH}_2\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons +\text{H}_3\text{NCH}_2\text{CO}_2\text{H} + \text{OH}^- \]

Charge Balance Examples

Write a charge balance equation for a solution of Al(OH)₃ dissolved in 1 M KOH. Possible species are Al³⁺, Al(OH)²⁺, Al(OH)₃, Al(OH)₂⁺, and Al(OH)₄⁻.

\[ 3[\text{Al}^3^+] + 2[\text{Al(OH)}^2^+] + [\text{Al(OH)}_3^+] + [\text{H}^+] + [\text{K}^+] = [\text{Al(OH)}_4^-] + [\text{OH}^-] \]

Mass (Concentration) Balance Equation

Mass Balance (Material Balance) -
- Statement of Conservation of Matter -

The quantity of all species in a solution containing a particular atom (or group of atoms) must be equal to the amount of that atom (or group of atoms) delivered to the solution.
Mass Balance Example
(known concentrations)

^ Write the mass balance equation for the acetate group of atoms in a 0.05 M solution of acetic acid.

\[[\text{HAc}] + [\text{Ac}^-] = 0.05 \text{ M}\]

^ Write the mass balance equation for the phosphate group of atoms in a 0.025 M solution of phosphoric acid.

\[[\text{H}_3\text{PO}_4^+] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = 0.025 \text{ M}\]

Mass Balance Example
(known concentrations)

^ Write the mass balances expression for the system formed when a 0.010 M \(\text{NH}_3\) solution is saturated with \(\text{AgBr}\).

\[
\begin{align*}
\text{AgBr} &\rightleftharpoons \text{Ag}^+ + \text{Br}^- \\
\text{Ag}^+ + \text{NH}_3 &\rightleftharpoons \text{Ag(NH}_3)^+ \\
\text{Ag(NH}_3)^+ + \text{NH}_3 &\rightleftharpoons \text{Ag(NH}_4)^+ \\
\text{NH}_3 + \text{H}_2\text{O} &\rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\
2\text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \\
\end{align*}
\]

\[
[\text{Ag}^+] + [\text{Ag(NH}_3)^+] + [\text{Ag(NH}_4)^+] + [\text{Br}^-] + [\text{NH}_3] + [\text{NH}_4^+] + [\text{NH}_2^-] + c_{\text{min}} = 0.010 \text{M} \\
[\text{OH}^-] + [\text{NH}_2^-] = [\text{H}_3\text{O}^+] \\
\]

Which of the following is the correct answer of the charge balance and mass balance for a system containing saturated \(\text{CaF}_2\) in a pH 4.00 buffer?

(A) \(2[\text{Ca}^{2+}] = 2[\text{F}^-]\)

(B) \(2[\text{Ca}^{2+}] + [\text{H}_2\text{O}] = [\text{OH}^-] + [\text{F}^-]\)

(C) \(2[\text{Ca}^{2+}] = 2[\text{F}^-] + 2[\text{HF}]\)

(D) \(2[\text{Ca}^{2+}] = [\text{F}^-] + [\text{HF}]\)
Calculation of Solubility's by Systematic Method

**EXAMPLE 11-5**
Calculate the molar solubility of Mg(OH)₂ in water.

**Step 1. Write Equations for the Pertinent Equilibria**
Two equilibria that need to be considered are:

\[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^- \]
\[ 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]

**Step 2. Define the Unknown**
Since 1 mol of Mg²⁺ is formed for each mole of Mg(OH)₂ dissolved, the solubility Mg(OH)₂ = [Mg²⁺].

**Step 3. Write All Equilibrium-Constant Expressions**

\[ [\text{Mg}^{2+}][\text{OH}^-]^2 = 7.1 \times 10^{-12} \quad (11-5) \]
\[ [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (11-6) \]

**Step 4. Write Mass-Balance Expressions**
As shown by the two equilibrium equations, there are two sources of hydronium ions: Mg(OH)₂ and H₂O. The hydronium ion concentration resulting from dissociation of Mg(OH)₂ is twice the magnesium ion concentration, and the hydronium ion concentration from the dissociation of water is equal to the hydronium ion concentration. Thus:

\[ [\text{OH}^-] = 2[Mg^{2+}] + [\text{H}_3\text{O}^+] \quad (11-7) \]

**Step 5. Write the Charge-Balance Expression**

\[ [\text{OH}^-] = 2[Mg^{2+}] + [\text{H}_3\text{O}^+] \]

Note that this equation is identical to Equation 11-7. Often, a mass-balance and a charge-balance equation are the same.

**Step 6. Count the Number of Independent Equations and Unknowns**
We have developed three independent algebraic equations (Equations 11-5, 11-6, and 11-7) and have three unknowns ([Mg²⁺], [OH⁻], and [H₃O⁺]). Therefore, the problem can be solved rigorously.

**Step 7a. Make Approximations**
We can make approximations only in Equation 11-7. Since the solubility-product constant for Mg(OH)₂ is relatively large, the solution will be somewhat basic. Therefore, it is reasonable to assume that [H₃O⁺] ≪ [OH⁻]. Equation 11-7 then simplifies to:

\[ 2[Mg^{2+}] = [\text{OH}^-] \quad (11-8) \]

**Step 8. Solve the Equations**
Substitution of Equation 11-8 into Equation 11-5 gives:

\[ [\text{Mg}^{2+}]^2[\text{Mg}^{2+}]^2 = 7.1 \times 10^{-12} \]
\[ [\text{Mg}^{2+}]^2 = \frac{7.1 \times 10^{-12}}{4} = 1.78 \times 10^{-12} \]
\[ [\text{Mg}^{2+}] = \text{solubility} = (1.78 \times 10^{-12})^{1/2} = 1.21 \times 10^{-6} \text{ or } 1.2 \times 10^{-4} \text{ M} \]
Step 9. Check the Assumptions. Substitution into Equation 11-8 yields

\[ [\text{OH}^-] = 2 \times 1.21 \times 10^{-4} = 2.42 \times 10^{-4} \text{ M} \]

And from Equation 11-6,

\[ [\text{H}_2\text{O}^+] = \frac{1.00 \times 10^{-14}}{2.42 \times 10^{-4}} = 4.1 \times 10^{-11} \text{ M} \]

Thus, our assumption that \([\text{H}_2\text{O}^+] \ll [\text{OH}^-]\) is certainly valid.

EXAMPLE 11-6

Calculate the solubility of \(\text{Fe(OH)}_3\) in water. Proceeding by the systematic approach used in Example 11-5, we write.

Step 1. Write Equations for the Pertinent Equilibrium

\(\text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-\)

\(2\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}^+ + \text{OH}^-\)

Step 2. Define the Unknown

solubility = \([\text{Fe}^{3+}]\)

Step 5. Write All the Equilibrium-Constant Expressions

\([\text{Fe}^{3+}][\text{OH}^-]^3 = 2 \times 10^{-39}\)

\([\text{H}_2\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}\)

Step 6 and 5. Write Mass-Balance and Charge-Balance Equations. As in Example 11-5, the mass-balance equation and the charge-balance equation are identical. That is,

\([\text{OH}^-] = 3[\text{Fe}^{3+}] + [\text{H}_2\text{O}^+]\)

Step 6. Count the Number of Independent Equations and Unknowns. We see that we have enough equations to calculate the three unknowns.

Step 7. Make Approximations. As in Example 11-5, assume that \([\text{H}_2\text{O}^+]\) is very small, so that \([\text{H}_2\text{O}^+] \ll [\text{Fe}^{3+}]\), and

\(3[\text{Fe}^{3+}] = [\text{OH}^-]\)

Step 8. Solve the Equations. Substituting \([\text{OH}^-] = 3[\text{Fe}^{3+}]\) into the solubility-product expression gives

\([\text{Fe}^{3+}][\text{Fe}^{3+}][\text{OH}^-]^3 = 2 \times 10^{-39}\)

\([\text{Fe}^{3+}] = \left( \frac{2 \times 10^{-39}}{3^3} \right)^{1/3} = 9 \times 10^{-13} \text{ M}\)

Solubility = \([\text{Fe}^{3+}] = 9 \times 10^{-13} \text{ M}\)
When $K_{sp}$ is very small, the dissolution of hydroxide precipitate has insignificant effect on solution pH, i.e., $pH = 7$.

Note: if $x(3x)^3 = K_{sp}$ is used, $x = 9.2 \times 10^{-11}$ M.

Solubility calculation when the pH is Variable

Class Practice: Write the expressions needed to calculate the solubility of CaC$_2$O$_4$ in water, and CB and MB equations.
Effect of pH on Solubility in Buffer

Example 11-7

Calculate the molar solubility of calcium oxalate in a solution that has been buffered so that its pH is constant and equal to 4.00.

Step 1: Write Pertinent Equilibria

CaC₂O₄(s) ⇌ Ca²⁺ + C₂O₄²⁻ [11-8]

Oxalate ions react with water to form H₂C₂O₄⁻ and H₂C₂O₄. Thus, there are three other equilibria present in this solution:

H₂C₂O₄⁻ + H₂O ⇌ H₂C₂O₄ + H₂O⁺ [11-10]
H₂C₂O₄ → H⁺ + H₂C₂O₄⁻ [11-11]
2H₂C₂O₄⁻ → H₂₂C₂O₄⁻ + H₂O + OH⁻ [11-12]

Step 2: Define the Unknown

Calcium oxalate is a strong electrolyte, so that its molar concentration is equal to the equilibrium calcium ion concentration. That is,

solubility = [Ca²⁺] [11-13]

Step 5. Write All the Equilibrium- Constant Expressions

[Ca²⁺][C₂O₄²⁻] = Kₛₛ = 1.7 × 10⁻⁹ [11-13]

[H₂C₂O₄⁻][H₂C₂O₄] = Kₛₖ = 5.60 × 10⁻² [11-14]

[H₂C₂O₄⁻][C₂O₄²⁻] = Kₛ₅ = 5.42 × 10⁻⁵ [11-15]

[H₂C₂O₄⁻][OH⁻] = K₆ = 1.0 × 10⁻¹⁴

Step 6. Mass-Balance Expression

Because CaC₂O₄ is the only source of Ca²⁺ and the three oxalate species,

[Ca²⁺] = [C₂O₄²⁻] + [H₂C₂O₄⁻] + [H₂C₂O₄] = solubility [11-16]

Moreover, the problem states that the pH is 4.00. Thus,

[H₂O⁺] = 1.0 × 10⁻⁴ and [OH⁻] = K₆/H₂O⁺ = 1.00 × 10⁻¹⁰

Step 5. Write Charge-Balance Expression

A buffer is required to maintain the pH at 4.00. The buffer most likely consists of some weak acid HA and its conjugate base, A⁻. The nature of the three species and their concentrations have not been specified, however, so we do not have enough information to write a charge-balance equation.

Step 6. Count the Number of Independent Equations and Unknowns

We have four unknowns ([Ca²⁺], [C₂O₄²⁻], [H₂C₂O₄⁻], and [H₂C₂O₄]), as well as four independent algebraic relationships (Equations 11-13, 11-14, 11-15, and 11-16). Therefore, an exact solution can be obtained, and the problem becomes one of algebra.

Step 7a. Make Approximations

An exact solution is more readily obtained in this case that we will not bother with approximations.
Step 8. Solve the Equations. A convenient way to solve the problem is to substitute Equations 11-14 and 11-15 into 11-16 in such a way as to develop a relationship between [Ca^{2+}], [Ca(OH)_2], and [H_3O^+]. Thus, we rearrange Equation 11-13 to give

\[ [HC_2O_4^-] = \frac{[H_2O^+] [C_2O_4^{2-}]}{K_1} \]

Substituting numerical values for [H_2O^+] and K_1 gives

\[ [HC_2O_4^-] = \frac{1.00 \times 10^{-4} [C_2O_4^{2-}]}{5.42 \times 10^{-3}} = 1.85 [C_2O_4^{2-}] \]

Substituting this relationship into Equation 11-14 and rearranging gives

\[ [H_2C_2O_4] = \frac{[H_2O^+] [C_2O_4^{2-}] \times 1.85}{K_1} \]

Substituting numerical values for [H_2O^+] and K_1 yields

\[ [H_2C_2O_4] = \frac{1.85 \times 10^{-4} [C_2O_4^{2-}]}{5.60 \times 10^{-3}} = 3.30 \times 10^{-3} [C_2O_4^{2-}] \]

Substituting these expressions for [HC_2O_4^-] and [H_2C_2O_4] into Equation 11-16 gives

\[ [Ca^{2+}] = [C_2O_4^{2-}] + 1.85 [C_2O_4^{2-}] + 3.30 \times 10^{-3} [C_2O_4^{2-}] \]

or

\[ [C_2O_4^{2-}] = [Ca^{2+}] / 2.85 \]

Substituting into Equation 11-13 gives

\[ \frac{[Ca^{2+}] [Ca^{2+}]}{2.85} = 1.7 \times 10^{-9} \]

\[ [Ca^{2+}] = \text{solubility} = \sqrt{2.85 \times 1.7 \times 10^{-9}} = 7.0 \times 10^{-5} \text{M} \]

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**Solubility of Precipitates In the Presence of Complexing Agents**

\[ \text{Al(OH)}_3(s) \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^- \]

+ 6F^-  ↓↑

\[ \text{AlF}_6^{3-} \]

Stable complex
AgCl(s) ⇌ AgCl(aq)
AgCl(aq) ⇌ Ag⁺ + Cl⁻
AgCl(s) + Cl⁻ ⇌ AgCl₂⁻
AgCl₂⁻ + Cl⁻ ⇌ AgCl₃²⁻

Effect of chloride ion concentration on the solubility of AgCl