Chapter 11

Solving Equilibrium Problems for Complex Systems

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Equilibrium Calculations

▲ Previous

 $BaC_2O_4(s) \Leftrightarrow Ba^{2+} + C_2O_4^{-2-}$

 $[\mathrm{Ba}^{2+}] = [\mathrm{C}_2 \mathrm{O_4}^{2-}]$

 $\begin{array}{c} \stackrel{\scriptstyle \wedge}{\xrightarrow{}} \underline{But} \hspace{0.1 cm} \text{what if oxalate then reacted with } H_2O \\ C_2O_4{}^{2-} + H_2O \Leftrightarrow HC_2O_4{}^- + OH{}^- \\ HC_2O_4{}^- + H_2O \Leftrightarrow H_2C_2O_4 + OH{}^- \end{array}$

$$\label{eq:because} \begin{split} & [Ba^{2+}] \neq [C_2O_4^{2-}] \\ & \text{because} \ [C_2O_4^{2-}]_T = [C_2O_4^{2-}] + [HC_2O_4^{-}] + [H_2C_2O_4] \end{split}$$





Charge Balance Equations

▲ Charge Balance Equations -

- An algebraic statement of electroneutrality.
- \checkmark The concentration of the sum of the positive charges = the
- concentration of the sum of the negative charges.
- ▲ General Form of the Equation

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

 n_1 and m_1 represent the magnitude of the charge of the ion $[C_1]$ and $[A_1]$ represent the concentration of each cation and anion respectively

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Charge Balance Examples

▲ Given

$$\begin{split} [\mathrm{H}^+] &= 5.1 \ \mathrm{x} \ 10^{-12} \ \mathrm{M} \qquad [\mathrm{K}^+] &= 0.0550 \ \mathrm{M} \\ [\mathrm{OH}^-] &= 0.0020 \ \mathrm{M} \qquad [\mathrm{H}_2\mathrm{PO}_4^{-1}] &= 1.3 \ \mathrm{x} \ 10^{-6} \ \mathrm{M} \\ [\mathrm{HPO}_4^{2-}] &= 0.0220 \ \mathrm{M} \qquad [\mathrm{PO}_4^{3-}] &= 0.0030 \ \mathrm{M} \end{split}$$

Find the solution for the Charge Balance equation.

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

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Charge Balance Examples

▲ Write the charge balance equation for a solution containing H₂O, H⁺, OH⁻, ClO₄⁻, Fe(CN)₆³⁻, CN⁻, Fe³⁺, Mg²⁺, CH₃OH, HCN, NH₃, and NH₄⁺.

 $[H^+] + 3[Fe^{3+}] + 2[Mg^{2+}] + [NH_4^+] =$ $[OH^-] + [CIO_4^-] + 3[Fe(CN_6^{3-}] + [CN^-]$

Charge Balance Examples

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

$$\label{eq:hardenergy} \begin{split} ^{+}\!\mathrm{H}_{3}\mathrm{NCH}_{2}\mathrm{CO}_{2}^{-} \Leftrightarrow \mathrm{H}_{2}\mathrm{NCH}_{2}\mathrm{CO}_{2}^{-} + \mathrm{H}^{+} \\ ^{+}\!\mathrm{H}_{3}\mathrm{NCH}_{2}\mathrm{CO}_{2}^{-} + \mathrm{H}_{2}\mathrm{O} \Leftrightarrow ^{+}\!\mathrm{H}_{3}\mathrm{NCH}_{2}\mathrm{CO}_{2}\mathrm{H} + \mathrm{OH}^{-} \end{split}$$

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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⁻

 $3[A1^{3+}]+2[A1OH^{2+}]+[A1(OH)_2^+]+[H^+]+[K^+] = [A1(OH)_4^-]+[OH^-]$

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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.

$[HAc] + [Ac^-] = 0.05 M$

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

 $[H_3PO_4^{0}]+[H_2PO_4^{-}]+[HPO_4^{2-}]+[PO_4^{3-}] = 0.025 M$

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Mass Balance Example

(known concentrations)

▲ Write the mass balances expression for the system formed when a 0.010 M NH₃ solution is saturated with AgBr.

 $\begin{array}{l} AgBr \mathop{\longrightarrow}\limits_{\longleftrightarrow} Ag^{+} + Br^{-} \\ Ag^{+} + NH_{3} \rightleftharpoons Ag(NH_{3})^{+} \\ Ag(NH_{3})^{+} + NH_{3} \rightleftharpoons Ag(NH_{3})_{2}^{+} \\ NH_{3} + H_{2}O \rightleftharpoons NH_{4}^{+} + OH^{-} \\ 2H_{2}O \rightleftharpoons H_{3}O^{+} + OH^{-} \end{array}$

$$\begin{split} & [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] = [Br^-] \\ & [NH_3] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] + [NH_4^+] = c_{NH_3} = 0.010M \\ & [OH^-] = [NH_4^+] + [H_3O^+] \end{split}$$

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Which of the following is the correct answer of the charge balance and mass balance for a system containing saturated CaF_2 in a pH 4.00 buffer?

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

(**B**) $2[Ca^{2+}] + [H_3O^+] = [OH^-] + [F^-]$

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

(**D**) $2[Ca^{2+}] = [F^-] + [HF]$

Calculation of Solubility's by Systematic Method

EXAMPLE 11-5

Calculate the molar solubility of Mg(OH)₂ in water.

Solution

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

 $Mg(OH)_{2}(s) \rightleftharpoons Mg^{2+} + 2OH^{-}$ $2H_{2}O \rightleftharpoons H_{3}O^{+} + OH^{-}$

Step 2. Define the Unknown Since 1 mol of Mg^{2+} is formed for each mole of $Mg(OH)_2$ dissolved,

solubility $Mg(OH)_2 = [Mg^{2+}]$

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Step 3. Write Al	Equilibrium-Constant Expressions	
	$K_{\rm sp} = [{\rm Mg}^{2+}][{\rm OH}^{-}]^2 = 7.1 \times 10^{-12}$	(11-5)
	$K_{\rm w} = [{\rm H}_3{\rm O}^+][{\rm O}{\rm H}^-] = 1.00 \times 10^{-14}$	(11-6)
Step 4. Write M	ass-Balance Expressions As shown by the two equil	ibrium equa-

tions, there are two sources of hydroxide ions: $Mg(OH)_2$ and H_2O . The hydroxide ion concentration resulting from dissociation of $Mg(OH)_2$ is twice the magnesium ion concentration, and the hydroxide ion concentration from the dissociation of water is equal to the hydronium ion concentration. Thus,

 $[OH^{-}] = 2[Mg^{2+}] + [H_{3}O^{+}]$ (11-7)

Step 5. Write the Charge-Balance Expression

 $[OH^{-}] = 2[Mg^{2+}] + [H_{3}O^{+}]$ (11-8)

Note that this equation is identical to Equation 11-7. Often, a mass-balance equation for a system is identical to the charge-balance equation.

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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 $[H_3O^+] \ll [OH^-]$. Equation 11-7 then simplifies to

 $2[\mathrm{Mg}^{2+}]\approx [\mathrm{OH}^{-}]$

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

$$\begin{split} [Mg^{2+}](2[Mg^{2+}])^2 &= 7.1 \times 10^{-12} \\ [Mg^{2+}]^3 &= \frac{7.1 \times 10^{-12}}{4} = 1.78 \times 10^{-12} \end{split}$$

 $[Mg^{2+}] = solubility = (1.78 \times 10^{-12})^{1/3} = 1.21 \times 10^{-4} \text{ or } 1.2 \times 10^{-4} \text{ M}$

Step 9. Check the Assumptions Substitution into Equation 11-8 yields

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

and, from Equation 11-6,

$$[H_{3}O^{+}] = \frac{1.00 \times 10^{-14}}{2.42 \times 10^{-4}} = 4.1 \times 10^{-11} M$$

Thus, our assumption that $[{\rm H_3O^+}] \ll [{\rm OH^-}]$ is certainly valid.

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EXAMPLE 11-6
Calculate the solubility of Fe(OH) ₃ in water.
Solution
Proceeding by the systematic approach used in Example 11-5, we write
Step 1. Write the Equations for the Pertinent Equilibria
$Fe(OH)_3(s) \rightleftharpoons Fe^{3+} + 3OH^-$
$2H_2O \rightleftharpoons H_3O^+ + OH^-$
Step 2. Define the Unknown
solubility = $[Fe^{3+}]$
Step 3. Write All the Equilibrium-Constant Expressions

 $K_{\rm sp} = [{\rm Fe}^{3+}][{\rm OH}^-]^3 = 2 \times 10^{-39}$ $K_{\rm w} = [{\rm H}_3{\rm O}^+][{\rm OH}^-] = 1.00 \times 10^{-14}$ te.

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Step 4 and 5. Write Mass-Balance and Charge-Balance Equations As in Example 11-5, the mass-balance equation and the charge-balance equations are identical, that is,

 $[OH^{-}] = 3[Fe^{3+}] + [H_{3}O^{+}]$

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

Step 7a. Make Approximations As in Example 11-5, assume that $[\rm H_3O^+]$ is very small so that $[\rm H_3O^+]\ll 3[Fe^{3+}]$ and

 $3[\text{Fe}^{3+}] \approx [\text{OH}^{-}]$

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

$$[Fe^{3+}](3[Fe^{3+}])^3 = 2 \times 10^{-39}$$
$$[Fe^{3+}] = \left(\frac{2 \times 10^{-39}}{27}\right)^{1/4} = 9 \times 10^{-11}$$

Step 9. Check the Assumption From the assumption made in Step 7, we can calculate a provisional value of $[OH^-]$:

$$[OH^{-}] \approx 3[Fe^{3+}] = 3 \times 9 \times 10^{-11} = 3 \times 10^{-10} M$$

Using this value of $[\mathrm{OH}^-]$ to compute a provisional value for $[\mathrm{H_3O}^+],$ we have

$$[H_3O^+] = \frac{1.00 \times 10^{-14}}{3 \times 10^{-10}} = 3 \times 10^{-5} \,\mathrm{M}$$

But 3×10^{-5} is not much smaller than three times our provisional value of $[Fe^{3+}]$. This discrepancy means that our assumption was invalid and the provisional values for $[Fe^{3+}]$, $[OH^-]$, and $[H_3O^+]$ are all significantly in error. Therefore, go back to Step 7a and assume that

 $3[Fe^{3^+}] <\!\!< [H_3O^+]$

Now, the mass-balance expression becomes

 $[H_3O^+] = [OH^-]$

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Substituting this equality into the expression for K_w gives

$$[H_3O^+] = [OH^-] = 1.00 \times 10^{-7} M$$

Substituting this number into the solubility-product expression developed in Step 3 gives

$$[Fe^{3^+}] = \frac{2 \times 10^{-39}}{(1.00 \times 10^{-7})^3} = 2 \times 10^{-18} \,\mathrm{M}$$

Since $[H_3O^+] = [OH^-]$, our assumption is that $3[Fe^{3+}] \ll [H_3O^+]$ or $3 \times 2 \times 10^{-18} \ll 10^{-7}$. Thus, our assumption is valid, and we may write

solubility = 2×10^{-18} M

Note the very large error (-8 orders of magnitude!) introduced by the invalid assumption.

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 = 9.2e-11 M.

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Class Practice:

Write the expressions needed to calculate the solubility of CaC_2O_4 in water, and CB and MB equations.

 $CaC_{2}O_{4}(s) \rightleftharpoons Ca^{2+}+C_{2}O_{4}^{2-}$ $C_{2}O_{4}^{2-}+H_{2}O \rightleftharpoons HC_{2}O_{4}^{-}+OH^{-}$ $HC_{2}O_{4}^{-}+H_{2}O \rightleftharpoons H_{2}C_{2}O_{4}^{-}+OH^{-}$ $H_{2}O \rightleftharpoons H^{+}+OH^{-}$

The mass-balance equation is

 $[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^{--}] + [H_2C_2O_4]$

The charge-balance equation is

 $2[Ca^{2+}] + [H_3O^+] = 2[C_2O_4^{2-}] + [HC_2O_4^{--}] + [OH^-]$



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analytical concen	tration is equal to the equilibrium calcium ion concentrat	tion, that is,
	solubility = $[Ca^{2+}]$	(11-12)
Step 3. Write Al	l the Equilibrium-Constant Expressions	
	$[Ca^{2+}][C_2O_4^{-2-}] = K_{sp} = 1.7 \times 10^{-9}$	(11-13)
	$\frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{H}\mathrm{C}_{2}\mathrm{O}_{4}^{-}]}{[\mathrm{H}_{2}\mathrm{C}_{2}\mathrm{O}_{4}]} = K_{1} = 5.60 \times 10^{-2}$	(11-14)
	$\frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{C}_{2}\mathrm{O}_{4}^{2^{-}}]}{[\mathrm{H}\mathrm{C}_{2}\mathrm{O}_{4}^{-}]} = K_{2} = 5.42 \times 10^{-5}$	(11-15)
	$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$	
Step 4. Mass-Be the three oxalate	alance Expressions Because CaC ₂ O ₄ is the only source of species.	of Ca ²⁺ and
[Ca ²⁺]	$= [C_2O_4^{2-}] + [HC_2O_4^{-}] + [H_2C_2O_4] = solubility$	(11-16)



Since the problem states that the pH is 4.00, we can also write that

 $[H_3O^+] = 1.00 \times 10^{-4} and [OH^-] = K_w/[H_3O^+] = 1.00 \times 10^{-10}$

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 ($[Ca^{2+}]$, $[C_2O_4^{2-}]$, $[HC_2O_4^{-}]$, and $[H_2C_2O_4]$) 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 It is relatively easy to solve the system of equations exactly in this case, so we will not bother with approximations.

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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 $[Ca^{2+}]$, $[C_2O_4^{2-}]$, and $[H_3O^+]$. Thus, we rearrange Equation 11-15 to give

$$[HC_2O_4^{-}] = \frac{[H_3O^+][C_2O_4^{2-}]}{K_2}$$

Substituting numerical values for $\rm [H_3O^+]$ and $\rm \textit{K}_2$ gives

$$[HC_{2}O_{4}^{-}] = \frac{1.00 \times 10^{-4} [C_{2}O_{4}^{2-}]}{5.42 \times 10^{-5}} = 1.85 [C_{2}O_{4}^{2-}]$$

Substituting this relationship into Equation 11-14 and rearranging gives

$$[\mathrm{H}_{2}\mathrm{C}_{2}\mathrm{O}_{4}] = \frac{[\mathrm{H}_{3}\mathrm{O}^{+}][\mathrm{C}_{2}\mathrm{O}_{4}^{2^{-}}] \times 1.85}{K_{1}}$$

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Substituting numerical values for
$$[H_3O^+]$$
 and K_1 yields

$$[H_3C_2O_4] = \frac{1.85 \times 10^{-4}[C_2O_4^{2^-}]}{5.60 \times 10^{-2}} = 3.30 \times 10^{-3}[C_2O_4^{2^-}]$$
Substituting these expressions for $[HC_2O_4^-]$ and $[H_2C_2O_4]$ into Equation 11-16 give

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

$$= 2.85[C_2O_4^{2^-}]$$
or $[C_2O_4^{2^-}] = [Ca^{2^+}]/2.85$
Substituting into Equation 11-13 gives

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

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



 $AgCl(s) \rightleftharpoons AgCl(aq)$ $AgCl(aq) \rightleftharpoons Ag^{+} + Cl^{-}$ $AgCl(s) + Cl^{-} \rightleftharpoons AgCl_{2}^{-}$ $AgCl_{2}^{-} + Cl^{-} \rightleftharpoons AgCl_{3}^{-2}$





Chapter 11 Summary

- Systematic method for complex equilibria
- Mass-balance and charge-balance expressions
- Steps for problems with several equilibria
- Making approximations to solve equilibrium problems
- Calculating solubilities under various conditions
- Separations by control of precipitating agent
 Important Equations

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\label{eq:hassbalance for} \begin{split} &HA+H_2O\rightleftharpoons H_3O^++A^- \qquad \rho_{HA}=[HA]+[A^-]\\ &Charge balance\\ &no.\ moles/L\ positive\ charge=no.\ moles/L\ negative\ charge\\ &Mass balance\ for\ saturated\ H_2S\ solution\\ &[S^2^-]+[HS^-]+[H_2S]=0.1 \end{split}
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