EQUILIBRIUM CALCULATIONS

I. Introduction

A. Equilibria in aqueous solutions are usually more complicated than the "simple" cases we have discussed so far.

B. Multiple equilibria usually exist. For example, consider sodium bicarbonate dissolved in water. At least three different equilibria are involved:

$$NaHCO_3 + H_2O \rightarrow Na^+ + HCO_3^- \quad (100\% ionization)$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+ \quad K_a = \frac{[CO_3^{2-}][H_3O^+]}{HCO_3^-}$$

$$HCO_3^- + H_2O \Leftrightarrow H_2CO_3 + OH^- \quad K_b = \frac{[H_2CO_3][OH^-]}{HCO_3^-}$$

$$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^- \quad K_w = [H_3O^+][OH^-]$$

Note that:

1. The form and validity of each equilibrium constant are unaffected by the other equilibria.

   a. This doesn't mean that concentrations won't change when new species are added/subtracted.
   b. This means the algebraic expression of "K_{eq}" is the same.

2. To calculate the concentration of the species in these multiple equilibria, you must generate a number of independent algebraic expressions equal to (or greater than) the number of species present. Then you must solve the set of algebraic expressions simultaneously.

II. Algebraic Expressions for Multiple Equilibria.

A. Three types of algebraic expressions are commonly derived/used in solving multiple equilibria. These include:

1. Equilibrium constant expressions (K_{eq}, K_a, K_b, K_{sp}, K_f, K_d, etc.).
2. Mass-balance equations.
3. Charge-balance equations.

B. Mass-balance equations are equations that relate the equilibrium concentrations of species in a solution to each other and the formal concentrations of the solutes. Thus, you must known the equilibria involved!! For example:

1. Write a mass-balance expression for a 0.10 F Na_2HPO_4 solution. Note the complex equilibria involved:

$Na_2HPO_4 \Leftrightarrow 2\ Na^+ + HPO_4^{2-}$

$HPO_4^{2-} \Leftrightarrow PO_4^{3-} + H_3O^+$

$HPO_4^{2-} \Leftrightarrow H_2PO_4^- + OH^-$

$H_2PO_4^- \Leftrightarrow H_3PO_4 + OH^-$

$(2H_2O \Leftrightarrow H_3O^+ + OH^-)$

Ignoring the K_w relationship, the mass-balance is:

$1/2\ [Na^+] = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = 0.10\ M$

$[Na^+] = 2(0.10) = 0.20\ M$

2. Write mass-balance expressions for each of the following:

a. AgCl solution:

$AgCl \Leftrightarrow Ag^+ + Cl^-$

Mass-balance: $[Ag^+] = [Cl^-]$

b. PbI_2 solution:

$PbI_2 \Leftrightarrow Pb^{2+} + 2\ I^-$

Mass-balance: $2\ [Pb^{2+}] = [I^-]$

c. Ag_2S solution:

$Ag_2S \Leftrightarrow 2\ Ag^+ + S^{2-}$

$S^{2-} \Leftrightarrow HS^- + OH^-$

$HS^{2-} \Leftrightarrow H_2S + OH^-$

$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^-$

Mass-balance (***ignoring*** the water equilibrium):

$1/2\ [Ag^+] = [S^{2-}] + [HS^-] + [H_2S]$

Note that if you consider the water equilibrium, an addition relationship is evident:

$[OH^-] = [H_3O^+] + [H_2S] + [HS^-]$

C. Charge-balance equations are equations that express the electrical neutrality of a solution by equating the molar concentrations of the positive and negative charges.

moles positive charge/liter = # moles negative charge/liter

1. For example, write a charge-balance equation for 0.10 F Na_2HPO_4.

For the positive charges:

$[Na^+] + [H_3O^+] = \#$ moles positive charges/liter

For the negative charges:

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

Equating the two:

$[Na^+] + [H_3O^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-]$

III. Steps in Solving Problems of Multiple Equilibria.

A. Write balanced equations for all equilibria.

B. Develop an equation for the unknown in terms of the equilibrium concentrations of the other species involved.

C. Write out all equilibrium constants and obtain their values from the tables in the back of the textbook, the CRC Handbook, or other sources.

D. Write out as many mass-balance equations as possible.

E. Write out as many charge-balance equations as possible.

F. Count the number of unknown species in the equilibrium system and count the number of independent algebraic relationships available in the mass-balance equations, charge balance equations, and equilibrium constant expressions.

1. If the number of independent equations $\geq$ the number of unknowns, a solution ***is*** possible.

2. If the number of independent equations $\leq$ the number of unknowns, a solution ***is not*** possible.

G. Solve the system of simultaneous equations.

1. Make any assumptions that seem appropriate in solving the equations.

2. ***All assumptions must be checked before a solution is accepted***.

IV. Sample Calculations Involving Multiple Equilibria.

Solubility calculations: Calculate the molar solubility of Ag_2CO_3 in a solution buffered at pH 6.000.

If the pH = 6.000, then the $[H^+] = 10^{-6.000} = 1.00 \times 10^{-6}$ M H^+

Following the steps given above:

Step 1: Write out the equilibria involved.

$Ag_2CO_3 \Leftrightarrow 2\ Ag^+ + CO_3^{2-}$

$CO_3^{2-} \Leftrightarrow HCO_3^- + OH^-$

$HCO_3^- \Leftrightarrow H_2CO_3 + OH^-$

$H_2O + H_2O \Leftrightarrow H_3O^+ + OH^-$

(Note: the water equilibrium is ***irrelevant*** in this system, since the solution is buffered at pH 6.000, ***fixing*** the hydrogen ion and hydroxide ion concentrations.)

Step 2: Define the unknown's equation.

$\mathbf{S_{silver\ carbonate} = 1/2\ [Ag^+]}$

(Note: often the equation expression the unknown to be solved is the most difficult to come up with.)

Step 3: Write out all the relevant equilibrium expressions.

$$K_{sp} = [Ag^+]^2[CO_3^{2-}] = 8.1 \cdot 10^{-12} = (2x)^2(x) = 4x^3$$

$$K_{b1} = \frac{[H_2CO_3][OH^-]}{HCO_3^-} = \frac{K_w}{K_{a1}} = \frac{1.00 \cdot 10^{-14}}{4.45 \cdot 10^{-7}} = 2.25 \cdot 10^{-8}$$

$$K_{b2} = \frac{[HCO_3^-][OH^-]}{CO_3^{2-}} = \frac{K_w}{K_{a2}} = \frac{1.00 \cdot 10^{-14}}{4.70 \cdot 10^{-11}} = 2.13 \cdot 10^{-8}$$

$$K_w = [H_3O^+][OH^-] = 1.00\,10^{-14}$$

Step 4: Write the mass-balance relationships.

$[H_3O^+] = 1.00 \times 10^{-6}$, $[OH^-] = 1.00 \times 10^{-8}$

$[Ag^+] = 2([CO_3^{2-}] + [HCO_3^-] + [H_2CO_3])$

Step 5: Write out the charge-balance relationships:

Note that you *cannot* write charge-balance relationships since you do not know what the buffering species are!!!

Step 6: Count the number of unknown species and independent equations. Verify that a solution is possible.

Unknowns: $[Ag^+]$, $[CO_3^{2-}]$, $[HCO_3^-]$, $[H_2CO_3]$

\# Independent Equations: K_{sp}, K_{b1}, K_{b2} and two mass balance equations

Thus, 4 unknowns < 5 equations...a solution ***is*** possible.

Step 7: Solve the system of simultaneous equations. This problem can be solved in a manner typical of such equilibria, by substituting into the mass-balance equation.

(Note that no assumptions were necessary to solve this problem!)

By rearrangement of expressions for K_{b1} and K_{b2} we have:

$$[HCO_3^-] = K_{b2} \cdot \frac{[CO_3^{2-}]}{[OH^-]}$$

$$[H_2CO_3] = K_{b1} \cdot \frac{[HCO_3^-]}{[OH^-]} = \frac{K_{b1}}{[OH^-]} \cdot \frac{K_{b2}[CO_3^{2-}]}{[OH^-]} = \frac{K_{b1}K_{b2}}{[OH^-]^2}[CO_3^{2-}]$$

Mass balance equation for the Ag^+ is:

$$[Ag^+] = 2\left([CO_3^{2-}] + \frac{K_{b2}}{[OH^-]}[CO_3^{2-}] + \frac{K_{b1}K_{b2}}{[OH^-]^2}[CO_3^{2-}]\right) = 2[CO_3^{2-}]\left(1 + \frac{K_{b2}}{[OH^-]} + \frac{K_{b1}K_{b2}}{[OH^-]^2}\right)$$

$$[Ag^+] = 1.38 \cdot 10^5 [CO_3^{2-}]$$

$$[CO_3^{2-}] = \frac{[Ag^+]}{1.38 \cdot 10^5} = 7.22 \cdot 10^{-6}[Ag^+]$$

By substitution of the last into the expression for the solubility product we have:

$$K_{sp} = [Ag^+]^2[CO_3^{2-}] = 7.22 \cdot 10^{-6}[Ag^+]^3 = 8.1 \cdot 10^{-12}$$

By rearrangement we have an expression for the Ag^+:

$$[Ag^+] = \sqrt[3]{\frac{8.1 \cdot 10^{-12}}{7.22 \cdot 10^{-6}}} = 1.04 \cdot 10^{-2} M$$

Solubility of the Ag_2CO_3 is:

$$\frac{1}{2}[Ag^+] = \frac{1.04 \cdot 10^{-2}}{2} = 5.2 \cdot 10^{-3} M$$