

Chapter 9 - Systematic Treatment of Equilibrium

Homework: Due Wednesday, February 22

Problems 9-2, 9-5, 9-8, 9-12, 9-14, 9-17

Extra Credit: 9-25 (5 pts)

Common reactions in aqueous solutions

- Precipitation
- Acid-base
- Complex formation
- Oxidation-reduction
- Partitioning between phases

One, a few, or all of these reactions may occur in any given sample.

Systematic approach to solving equilibrium problems

Step 1. Write all pertinent chemical reactions.

Step 2. Write charge balance equation.

Step 3. Write mass balance equations.

Step 4. Write all equilibrium expressions. Use activities if known.

Step 5. Count equations and unknowns. There must be as many or more equations than unknowns or else the problem cannot be solved.

Step 6. Use algebraic expressions to solve for species concentrations.

<http://www.chem.usu.edu/faculty/sbialkow/Classes/3600/Overheads/systematic.html>

http://mason.gmu.edu/~gfoster/Chem_321/systematic_ho/systematic_treatment.html

Step 1 – Write all pertinent chemical reactions.

What are “pertinent chemical reactions”?

Example: Dissolving CO₂ in water



Step 2 - Write charge balance equation.

Pertinent Reactions:



Charge balance equation:

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

Note: coefficient in front of the species is equal to the magnitude of the charge (so -2 has a coeff. of 2)

Step 3. Write mass balance equations.

Pertinent Reactions:



Mass balance equation:

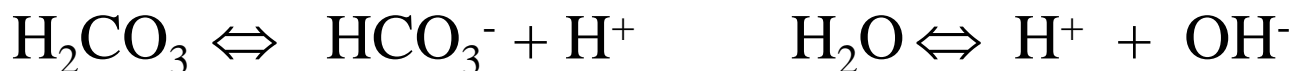
$$[\text{CO}_2] = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2]$$

Note: Mass balance is really a conservation of atoms (i.e., account for all the atoms put into solution).

Step 4. Write all equilibrium expressions.

Use activities if known.

Pertinent Reactions:



$$K = [\text{H}_2\text{CO}_3] / [\text{CO}_2] = 2 \times 10^{-3}$$

$$K_{a1} = [\text{HCO}_3^-] [\text{H}^+] / [\text{H}_2\text{CO}_3] = 4.45 \times 10^{-7}$$

$$K_{a2} = [\text{CO}_3^{2-}] [\text{H}^+] / [\text{HCO}_3^-] = 4.69 \times 10^{-11}$$

$$K_w = [\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

Step 5. Count equations and unknowns.

Pertinent Reactions:



Unknowns: $[\text{CO}_2]$, $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, $[\text{H}^+]$, $[\text{OH}^-]$

Equations:

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$$

$$[\text{CO}_2] = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2]$$

$$K = [\text{H}_2\text{CO}_3] / [\text{CO}_2] = 2 \times 10^{-3}$$

$$K_{a1} = [\text{HCO}_3^-] [\text{H}^+] / [\text{H}_2\text{CO}_3] = 4.45 \times 10^{-7}$$

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***6 unknowns
and
6 equations***

If there are as many or more equations than unknowns, then we can move to Step 6. If there are more unknowns than equations, then some assumptions must be made to simplify the system. (You cannot solve for more unknowns than there are equations.)

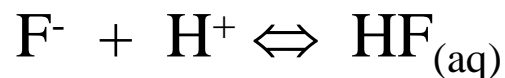
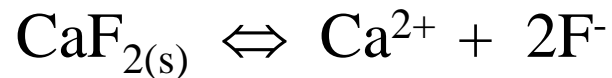
Step 6. Use algebraic expressions to solve for species concentrations.

*This step is many times easier said than done.
It is very useful to use a spreadsheet.*

Problem 9-A Write the charge balance for a solution prepared by dissolving CaF_2 in H_2O . Consider that the CaF_2 can give Ca^{2+} , F^- , and CaF^+ .

Problem 9-B a) Write the mass balance for CaCl_2 in H_2O if the aqueous species are Ca^{2+} and Cl^- . b) Write the mass balance if the species are Ca^{2+} , Cl^- , and CaCl^+ .

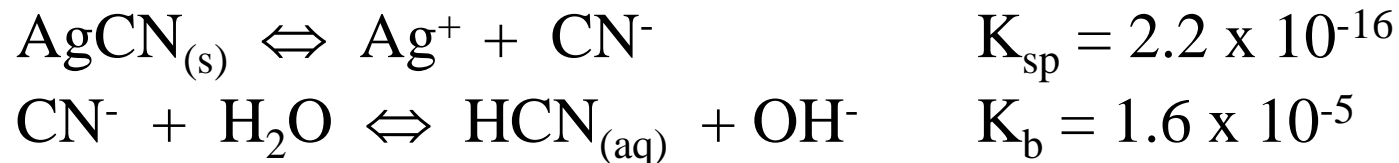
Problem 9-C a) Write the mass balance for CaF_2 in H_2O if the Rx's are:



b) Write a mass balance for CaF_2 in water if, in addition to the previous reactions, the following reaction occurs:



Problem 9-E Find the concentrations of Ag^+ , CN^- , and HCN in a saturated solution of AgCN whose pH is somehow fixed at 9.00. Consider the following equilibria:



Problem 9-F Calculate the solubility of ZnC_2O_4 (g/L) in a solution held at pH 3.00. Consider the equilibria:

