Chapter 8 – Activity continued

$$a\,A + b\,B = c\,C + d\,D$$

Reactants **Products**

$$K = [C]^c[D]^d / [A]^a[B]^b$$

BUT REALLY….

$$K = \mathcal{A}_c^{\,c}\ \mathcal{A}_d^{\,d} / \mathcal{A}_a^{\,a}\ \mathcal{A}_b^{\,b}$$

or

$$K = [C]^c \gamma_c^{\,c}\ [D]^d \gamma_d^{\,d} / [A]^a \gamma_a^{\,a}\ [B]^b \gamma_b^{\,b}$$

Activity: $\mathcal{A} = [X]^x \gamma_x^x$

We know [X] is the molar concentration (moles/L).

γ_x is the activity coefficient for species X.

$$\log \gamma_x = \frac{-0.51\, z^2 \sqrt{\mu}}{1 + (\alpha\sqrt{\mu}/305)}$$

Where: $\mu = 0.5 \Sigma c_i z_i^2$ (ionic strength)

(c_i = molarity of ith ion and z_i = charge on ith ion)

z = charge of species x

α = ionic size (pm)

Table 8-1

Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (α, pm)	Ionic strength (μ, M)				
		0.001	0.005	0.01	0.05	0.1
Charge = ±1						
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75

a. Lanthanides are elements 57–71 in the periodic table.

SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, *59*, 1675.

Points concerning Activity ($\mathcal{A}$):

- Concentration of ions (ionic strength, μ) is important.
- Charge on ions (z) is important.
- Size of ions (α) is important.
- "Activity" ($\mathcal{A}$) should be used for exact work.
- The activity coefficient (γ_x)of a species is a measure of the effectiveness with which that species influences an equilibrium.
- In very dilute solutions ($\mu$is small), this effectiveness becomes constant and the activity coefficient is unity. The activity and molar conc. of the species is equal.

Problem 1 – Ionic Strength Calculation

Assuming complete dissociation of the salts, calculate the ionic strength, μ, of the following:

a) 0.2 mM KNO_3

b) 0.2 mM Cs_2CrO_4

Problem 2 – Activity coefficient calculation

What is the activity coefficient, γ, for the following:

a) Al^{3+} when $\mu = 0.05$ M.

b) Al^{3+} when $\mu = 0.003$ M.

Problem 3 – Using activities for solubility problems.

Using activities, find the solubility of AgSCN (moles of Ag^+ / L in the following:

a) In a solution of 0.060 M KNO_3.

b) In a solution of 0.060 M KSCN.

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 CO_2 in water

$CO_2 + H_2O \Leftrightarrow H_2CO_3$ $\quad K = 2 \times 10^{-3}$

$H_2CO_3 \Leftrightarrow HCO_3^- + H^+$ $\quad K_{a1} = 4.45 \times 10^{-7}$

$HCO_3^- \Leftrightarrow CO_3^{-2} + H^+$ $\quad K_{a2} = 4.69 \times 10^{-11}$

$H_2O \Leftrightarrow H^+ + OH^-$ $\quad K_w = 1 \times 10^{-14}$

Step 2 - Write charge balance equation.

Pertinent Reactions:

$CO_2 + H_2O \Leftrightarrow H_2CO_3$

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

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

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

Charge balance equation:

$$[H^+] = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-]$$

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:

$CO_2 + H_2O \Leftrightarrow H_2CO_3$

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

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

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

Mass balance equation:

$$[CO_2] = [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}] + [CO_2]$$

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:

$CO_2 + H_2O \Leftrightarrow H_2CO_3$ $\qquad$ $HCO_3^- \Leftrightarrow CO_3^{-2} + H^+$

$H_2CO_3 \Leftrightarrow HCO_3^- + H^+$ $\qquad$ $H_2O \Leftrightarrow H^+ + OH^-$

$$K = [H_2CO_3] / [CO_2] = 2 \text{ x } 10^{-3}$$

$$K_{a1} = [HCO_3^-] [H^+] / [H_2CO_3] = 4.45 \text{ x } 10^{-7}$$

$$K_{a2} = [CO_3^{-2}] [H^+] / [HCO_3^-] = 4.69 \text{ x } 10\text{-}11$$

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

Step 5. Count equations and unknowns.

Pertinent Reactions:

$CO_2 + H_2O \Leftrightarrow H_2CO_3$ $\quad$ $HCO_3^- \Leftrightarrow CO_3^{-2} + H^+$

$H_2CO_3 \Leftrightarrow HCO_3^- + H^+$ $\quad$ $H_2O \Leftrightarrow H^+ + OH^-$

Unknowns: $[CO_2]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{-2}]$, $[H^+]$, $[OH^-]$

Equations:

$[H^+] = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-]$

$[CO_2] = [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}] + [CO_2]$

$K = [H_2CO_3] / [CO_2] = 2 \times 10^{-3}$

$K_{a1} = [HCO_3^-] [H^+] / [H_2CO_3] = 4.45 \times 10^{-7}$

$K_{a2} = [CO_3^{-2}] [H^+] / [HCO_3^-] = 4.69 \times 10-11$

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

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.

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^+.

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 $CaCl^+$.