

Week 8: Aqueous Solutions and Activity Diagrams

ESS 312 Spring 2009

Due Wednesday May 27

In this lab you are going to learn about calculating activities of ions in aqueous solutions and about how to use activity diagrams as "phase diagrams for water-rock interaction". We will look at the weathering of feldspar by river water as a model system.

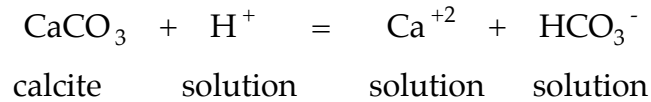
The concentrations of constituents in aqueous solutions are typically reported in units of ppm (parts per million; by weight), and mg/l (milligrams per liter). In the more modern literature, constituents may be reported in mol/l (moles/liter), mmol/l (milli-moles/liter) or $\mu\text{mol/l}$ (micro-moles/liter). As an example, the analysis listed below describes the composition of "average" river water taken from Garrels and McKenzie (the silica content has been reduced a bit to make the reaction path more interesting. It should really be about 100 times larger):

	ppm	formula wt	Molality		Units (ppm)	formula wt	Molality
Na^+	6.3	23.0		SiO_2	0.13	60.1	
K^+	2.3	39.1		Cl^-	7.8	35.5	
Mg^{+2}	4.1	24.3		NO_3^-	1.0	62.0	
Ca^{+2}	15.0	40.1		HCO_3^-	58.4	61.0	
Fe^{+2}	0.67	55.8		SO_4^{-2}	11.2	96.1	
Al^{+3}	0.01	27.0		C (org)	9.6	12	

- (1) Calculate the molality of each constituent above, and place results in the appropriate column of the Answer Sheet provided. Remember that molality (m) is moles/(kg of solvent).

Suppose we wanted to ask the question, "Is this river water saturated with the mineral calcite?" In order to answer that question we must first write a reaction between calcite and ions in solution, and then evaluate the thermodynamic properties of that reaction to determine if the free energy change is negative, zero, or positive.

For instance,



For which the free energy change is given by

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{a_{\text{Ca}^{+2}} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \right)$$

and since ΔG^0 is equal to $-RT \ln K$, where K is the equilibrium constant,

$$\Delta G = -RT \ln K + RT \ln \left(\frac{a_{\text{Ca}^{+2}} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \right) \quad (1)$$

(2) Why does a_{CaCO_3} not appear in the above equation (Equation 1)?

The free energy change of Eq (1) is zero if calcite is in equilibrium with the river water, negative if the water is undersaturated with respect to calcite, and positive if the water is supersaturated with calcite. The above reaction is an example of a *mineral dissolution reaction*. In Eq (1), the standard state free energy change is expressed in terms of the more familiar equilibrium constant (K) for the reaction. Values of K for mineral dissolution reactions can be obtained from standard thermodynamic data tables. The K for the above reaction has a value of approximately 100. In order to evaluate the free energy change using Eq (1), we need some method for computing the activities of constituents (often called species) in aqueous solution. The approximation $a = m$ turns out to be fine for neutral species in solution, but for charged species we must use $a = \gamma m$ where the activity coefficient (γ) is modeled using Debye-Huckel theory:

$$\log_{10} \gamma_i = -z_i^2 A \sqrt{I} \quad (2)$$

Note: This is a simplification, valid for dilute solutions, of the general Debye-Huckel formulation:

$$\log_{10} \gamma_i = \frac{-z_i^2 A \sqrt{I}}{1 + B a_{0,i} \sqrt{I}} \quad (2A)$$

In Eq (2), A is a function only of T and P (and is equal to 0.5092 at 25°C and 1 bar), z denotes the charge on the ion (+2 for Ca⁺², -1 for HCO₃⁻), and I refers to the ionic strength of the solution, $I = 1/2 \sum z_i^2 m_i$, where the sum is taken over all the ions in solution.

Eq (2) works reasonably well for solutions as concentrated as rain- and river water, but requires modification for more concentrated solutions, like seawater.

- (3) Determine the charge (z) of each constituent, then calculate ($z_i^2 m_i$). Place results in the appropriate columns on the Answer Sheet. Use these values to calculate the ionic strength (I) of the river water. What approximations must you make to do this calculation? List at least 2.
- (4) Using Equation (2) and your results above, calculate the activity coefficient (γ_i) and activity of each constituent. Place results in the appropriate column on the Answer Sheet.

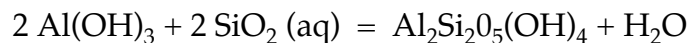
	molality	$z_i^2 m_i$	γ	activity
Na ⁺				
K ⁺				
Mg ⁺²				
Ca ⁺²				
Fe ⁺²				
Al ⁺³				
SiO ₂				
Cl ⁻				
NO ₃ ⁻				
HCO ₃ ⁻				
SO ₄ ⁻²				
C (organic)				
	$0.5 \sum z_i^2 m_i$			

- (5) **Using these results, calculate the free energy change for the calcite dissolution reaction using Equation (1). Assume a pH of 5.5. What is the saturation state of calcite with respect to this river water?**

An activity diagram is a kind of phase diagram that relates solution composition to mineral phases coexisting with the solution. An example of an activity diagram for the system $K_2O-Al_2O_3-SiO_2-H_2O$ is attached to this handout. These diagrams are called activity diagrams because the axes correspond to \log_{10} activity of some neutral species in solution (like $\log_{10} a_{SiO_2}$) or alternatively, the \log_{10} activity ratio or product of some charged species and the hydrogen ion [like

$$\log_{10} \left(\frac{a_{K^+}}{a_{H^+}} \right) \text{ or } \log_{10} \left(a_{HCO_3^-} \cdot a_{H^+} \right)] .$$

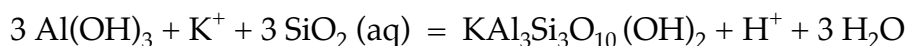
Mineral stability fields on the diagram correspond to solution compositions in equilibrium with that mineral. Boundaries between mineral fields give solution compositions that correspond to equilibrium conditions with respect to both minerals - only along these boundaries can both mineral phases coexist with solution at equilibrium. The slopes of the boundaries between mineral fields are derived by writing a balanced chemical reaction between the two minerals and any necessary components in aqueous solution. By convention, these reactions are always written conserving aluminum to the solid phase. For instance, the reaction between gibbsite $[Al(OH)_3]$ and kaolinite $[Al_2Si_2O_5(OH)_4]$ is written:



where aluminum is conserved by transforming 2 gibbsite molecules to form 1 kaolinite molecule. This reaction consumes silica in solution and releases water to solution. If gibbsite and kaolinite coexist, they can only do so in equilibrium at a specific activity of silica. Note that the coexistence of these phases is independent of the activity ratio of K^+ to H^+ in solution.

- (6) **Would you expect to find secondary silica precipitating from water percolating through a soil profile that contains gibbsite + kaolinite? Explain.** (In this example, the large excess of the solid minerals relative to the amount of water in the soil is said to "buffer" the silica activity).

Alternatively, if we consider the reaction of gibbsite to muscovite $[\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2]$:



which is written to conserve aluminum to the solid phases, we see that K^+ and SiO_2 must vary in a coordinated fashion at equilibrium in order to keep the reaction from proceeding to the right or to the left. The boundary line between the muscovite and gibbsite fields on the attached activity diagram reflects the three to-one slope that embodies this dependence. All the remaining boundary lines between mineral fields on this activity diagram may be described with similar mineral-mineral reactions balanced on aluminum.

The activity diagram for the $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ system also includes information on solution compositions corresponding to equilibrium with mineral phases that do not contain aluminum. These "solubility relations" are denoted by dashed lines. That labeled "quartz", for example, denotes the activity of silica in solution that corresponds to equilibrium with quartz. A solution is in equilibrium with quartz only along that dashed line. Lower silica activities refer to quartz undersaturated conditions, higher silica activities, quartz supersaturated conditions.

Now that you know how to read the diagram, we'll use it to describe the reaction of potassium feldspar (Ksp) with a finite amount of river water.

- (7) **Plot the composition of the river water you worked with earlier in this lab exercise on the attached $\log_{10}(a_{\text{K}^+}/a_{\text{H}^+})$ vs $\log_{10} a_{\text{SiO}_2}$ diagram. Assume a pH of 5.5.**
- (8) **Let us assume that K-feldspar (KAlSi_3O_8) reacts initially with river water to form gibbsite. Write a balanced equation for this reaction (aluminum is conserved).**
- (9) **The balanced reaction from (8) above tells you that K^+ , H^+ and $\text{SiO}_2(\text{aq})$ are consumed or released as K-feldspar dissolves. From the stoichiometry of the reaction, sketch qualitatively the path the solution will follow across the $\log_{10}(a_{\text{K}^+}/a_{\text{H}^+})$ vs $\log_{10} a_{\text{SiO}_2}$ diagram as K-feldspar reacts to form gibbsite.**

Hints: (i) Assume the pH of the solution is buffered, i.e. activity of H^+ is fixed at $10^{-5.5}$ by some other reaction. (ii) The initial slope is close to horizontal - indicate by your sketched

line whether K^+ and silica activity are both increasing, both decreasing or if one is increasing and the other decreasing.

As the reaction of K-feldspar with water proceeds, the solution composition will eventually evolve across the diagram until it intersects the gibbsite-kaolinite boundary.

(10) Write a balanced chemical reaction that conserves aluminum to the solid phases and describes the reaction of K-feldspar with solution to form kaolinite. Remember that gibbsite may be involved in this reaction as a product or as a reactant. [This is a bit tricky. Check with an instructor before moving to the next question.]

(11) At this point, what path does the solution take as feldspar continues to react with solution? Explain in words.

Hint: Pay attention to the products of the reaction you wrote in answer to (10).

(12) Assuming gibbsite in the previous reaction is a reactant, what happens when the amount of gibbsite produced during the initial dissolution of K-feldspar in this solution is exhausted? Explain in words.

(13) Assume that the reaction of K-feldspar with solution continues until the solution eventually comes to equilibrium with K-feldspar. Trace the reaction path of the solution across the activity diagram and write balanced chemical reactions for each leg of the path. You should assume that solid quartz precipitates if $a_{\text{SiO}_2(\text{aq})}$ reaches 10^{-4} (i.e. if your reaction path reaches the quartz saturation line on the diagram). Note and discuss any other assumptions you must make in determining this path.

Hint: You should end up with 4 reactions.

25°C

