OCN400 - Problem Set #1 **Jim Murray**
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1. The boiling point of seawater is elevated relative to that of distilled water. Give a brief explanation in terms of the structure of water and ionic solutions.

2. One way we can get the equilibrium constant for a reaction we are interested in is to combine other reactions for which we know the constants. Show how this is done by deriving the equilibrium constant for the reaction of calcite with Mg^{2+} to form the CaMg carbonate mineral called dolomite as written below:

$2CaCO_3(s)(calcite) + Mg^{2+} = CaMg(CO_3)_2(s)(dolomite) + Ca^{2+}$ $K_{eq} = ?$

This is an important reaction used to describe the conversion of limestone in dolomite rock over geological time frames.

a. Combine (by addition or subtraction as necessary) the Keq values for the following reactions (for 25°C) to get the Keq (at 25°C) for the reaction of $CaCO_3$ with Mg^{2+} given above.

$CaCO_3(s) = Ca^{2+} + CO_3^{2-}$ $\log K_{so} = -8.48$
$CaMg(CO_3)_2(s) = Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$ log Kso = -16.70

b. Derive an equation that expresses Keq in terms of the Kso listed above.

c. The ratio of the concentration of Ca to Mg measured in Florida ground waters is 0.8 $\pm$ 0.1. Could these ground waters be in equilibrium with both calcite and dolomite phases simulatneously.

3. The equilibrium constant for this reaction can also be calculated from the values of free energy of formation. From thermodynamic data tables (e.g. Stumm and Morgan, 1981; Drever, 1997) we obtain the following standard free energies of formation at 25°C.

a) Calculate the standard free energy of reaction (ΔG_r^o)

b) Calculate the equilibrium constant Keq at 25°C.

c) Is this the same value as obtained in Problem 2? Comment.

Substance	ΔG_f^o (kJ mol^{-1})
$CaCO_3$(calcite)	-1128.8
$CaMg(CO_3)_2$ (dolomite)	-2161.7
Ca^{2+}	-553.54
Mg^{2+}	-454.8

4. Calculate to show whether calcite and dolomite are at equilibrium in surface seawater with S = 35.000 at 25°C.

Use the equilibrium constant from Problem 2.
Use total concentrations and activity corrections for Ca and Mg from the class notes or readings. Reference your values to where you got them.

5. The breakdown of the silicate mineral called Ca-feldspar (also called anorthite) to form kaolinite clay is an important weathering reaction, particularly in humid climate soils. The reaction may be written:

$CaAlSi_2O_8 + 2H^+ + H_2O(l) = Al_2Si_2O_5(OH)_4 + Ca^{2+}$
Ca-feldspar kaolinite

a). Calculate the equilibrium constant for this reaction given the following free energies of formation.

Substance	ΔG_f^o
Ca-feldspar	-4001.4 kJ/mol
H^+	0
$H_2O(l)$	-237.14 kJ/mol
kaolinite	-3799.4 kJ/mol
Ca^{2+}	-553.54 kJ/mol

b) Write the corresponding equilibrium constant expression.

c) Assuming that soil moisture contains concentrations of $[Ca^{2+}] = 2 \times 10^{-4}$ mol/l, and behaves as an ideal solution (no activity corrections), at what pH would anorthite be in equilibrium with the kaolinite and, therefore not weather?

d) Assume that you are now in typical marine red clay sediments with $[Ca^{2+}] = 10.3 \times 10^{-3}$ mol/l and pH = 7.5. This is no longer an ideal solution. Calculate the free energy of reaction (ΔG_r) for these conditions. Which direction will this reaction tend to go for this set of conditions?