ADVANCED GEOCHEMISTRY OF NATURAL WATERS

GEOL 578

MIDTERM EXAM

MARCH 2008

Show all work, and state any assumptions and the source(s) of any thermodynamic data you use. You may use any books, notes, past problem sets or any material on the course web site in conjunction with this exam. However, you **may not** communicate with each other or any other person outside of class regarding this exam, either in person, by telephone, via the internet, or any other method. All the work must be your own. Assume 25 °C, 1 bar and infinite dilution (activity coefficients are unity) for all problems.

Problem 1 (55 points):

a) Write expressions for sulfide alkalinity both in terms of: 1) the concentrations of acid and base species present; and also 2) the ionization fractions and total sulfide concentration (S_T). Assume that the system does not contain any weak acids or bases other than H_2S and its dissociation products. Hint: sulfide alkalinity is [ANC] relative to f = 0, i.e., H_2S^0. (10 points)

b) Calculate the sulfide alkalinity of a water with a pH of 8.7 and $p_{H_2S} = 10^{-2.5}$ atm. Use pK_1 = 7.1 and pK_2 = -17. (5 points)

c) Calculate the buffer intensity of the solution in b). (10 points)

d) Sketch a speciation diagram for a closed H_2S system with $S_T = 10^{-3}$ M as a function of pH. (10 points)

e) Calculate and quantitatively sketch a titration curve for the titration of 10^{-3} M H_2S with 5×10^{-4} M NaOH. Account for dilution (15 points)

f) In what proportions do H_2S^0 and HS^- need to be mixed in order to obtain a buffer solution at pH = 8.1? (5 points)

Problem 2 (15 points):

A water with [alk] = 3 meq/L and pH = 11.2 is mixed with a water with [alk] = 0.5 meq/L and pH = 6.3. The waters are mixed in the proportion 4 parts (pH = 11.2) to 7 parts (pH = 6.3). What is the final pH of the solution? How much CO_2 would have to be added to change the pH of the mixture back to 6.3?

Problem 3 (15 points):

Calculate the pH and concentrations of all species in a solution containing 0.1 M lactic acid, for which $K_a = 1.74 \times 10^{-4}$.

Problem 4 (15 points):

Compute the pH variation resulting from isothermal (constant temperature - 25°C) ***dilution*** by deionized water of an initially 10^{-1} M $NaHCO_3$ solution that remains in equilibrium with a partial pressure of CO_2 of 2 x 10^{-3} atm. Carry out your calculations up to dilution factor of 10,000.