Chemical Oceanography | Problem Set #1 Fall 2019
Professor Ryan | David_Ryan@uml.edu

This problem set is designed to be open book and open notes, but you are expected to work individually to obtain your answers. You should show all your work and clearly delineate how you derived your results. This constitutes approximately 10 % of your overall grade broken down as described at the bottom of page 2. You have about a week to complete this assignment and submit it to me electronically in either MS Word or Excel format (due 10/3/19 by 12:00 PM). Please name the files you send with the following system Lastname, Firstname – PS1.(doc, docx, xls, or xlsx). I will confirm receipt of your assignment by return email. Late submission will result in the loss of one point per day from the 10 point total. Please email me concerning any specific questions so as not to use valuable class time on homework.

1) Given the list below of the six major ions in seawater (SW) and the concentration of each measured in an estuarine sample at 20 ºC, prepare a table giving the concentrations in molarity (M), molality (m) and molinity. Express your answers in scientific notation with the same number of significant figures given for each species in the table. Use a density of 1.017154 kg L^{-1} for seawater. Use the periodic table at the following link to obtain the needed atomic weight data http://www.mbari.org/chemsensor/pteo.htm.

What two very obvious environmental factors affect the density of SW in this example and cause it to be lower than what we have seen previously? (e.g. slide presented in class).

	Concentration			
Ion	mg L^{-1} (ppm)	mol L^{-1} (M) (molarity)	mol kg^{-1} (m) (molality)	mol kg^{-1} (molinity)
Ca^{2+}	308.9			
Mg^{2+}	963.0			
Na^{+}	8085			
K^{+}	299.3			
SO_4^{2-}	2034			
Cl^{-}	14515			

2) Calculate the freezing point depression and boiling point elevation of a 0.7 m NaCl solution, a 0.7 m $CaSO_4$ solution and a 0.7 m $CaCl_2$ solution (i.e. pure water freezes at 0 ºC, at what temperature do these solutions freeze/boil?). Use the equations and constants from class

$$\Delta T_f = - \nu K_f m \qquad \Delta T_b = \nu K_b m$$

Normally the quantity '**ν m**' would be 2 x molal concentration for NaCl or 3 x m for $CaCl_2$. How would you use the data for seawater in these equations if, for example, you had to do the calculation for the sample in problem #1?

3) Seawater contains both Na^+ and SO_4^{2-} which can react according to the following equilibrium to form a singly charged soluble ion pair or complex

$$Na^+ + SO_4^{2-} \longleftrightarrow NaSO_4^- \qquad K_f = 10^{0.33} = 2.14$$

Using seawater total concentration data of 0.480 M for Na^+ and 0.0289 M for SO_4^{2-}, calculate the concentrations of free Na^+, bound Na (i.e., Na in $NaSO_4$), free SO_4^{2-} and bound SO_4 as well as the percentage of each (i.e., free and bound Na as a percentage of total Na and free and bound SO_4 as a percentage of total SO_4). Do the calculation first without making any correction for ionic strength, then recalculate all values at an ionic strength of 0.5 using the Davies Equation. You may assume the only equilibrium operating in this system is the $NaSO_4^-$ equilibrium given.

4) Using total concentration data from the paper by Motekaitis and Martell (Mar. Chem. 21 (1987) 101-106) for the 18 components given in their Table I, calculate with MINEQL+ all species formed in seawater at pH 8.2 and an ionic strength of 0.5 at 25 ºC. Do not include mercury (Hg) because it tends to crash the program. You may need to try different values of CO2 partial pressure to get a reasonable result. Prepare a table of the same form as their Table VII to summarize your results. Why would your computer calculated results differ from the calculation in question #4 above?

5) Typically, the ratio of dissolved gases are measured more precisely than their concentrations. For assessing biological productivity in the ocean, the ratio of photosynthetically produced O_2 to inert Ar has been used in this respect. First, plot the concentrations of O_2 and Ar in seawater (salinity 35) in equilibrium with air for a 5 to 25°C range in temperature, every 0.5°. Use vertical scales sufficient to see any change in concentration and briefly explain why they occur. Calculate the ratio of O_2 to Ar for the same temperature range and plot separately. Compare and contrast any variations with temperature in the O_2/Ar ratio with how O_2 and Ar concentrations vary with temperature. Last, explain why the O_2/Ar ratio is a better indicator of biological production than O_2 concentration and how it would vary with increasing contributions of O_2 from photosynthesis.

Point values: 1) = 1.5, 2) = 1.5, 3) = 2.5, 4) = 2.5, 5) = 2.0 Total points = 10.0