

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 10 % of your overall grade broken down as described at the bottom of page 2. You have about two weeks to complete this assignment and submit it to me electronically in either MS Word or Excel format (due 2/22/18 by 3:00 PM). Please name the file using 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 5 °C, prepare a table giving the concentrations in molarity (M), molality (m) and molinity. Use a density of 1.019783 kg L<sup>-1</sup> 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 2 factors affect the density of SW in this example and cause it to be lower than what we have seen previously? (e.g. slide 12 of lecture notes posted for 1/30/18 or others).

Ion	Concentration			
	mg L <sup>-1</sup> (ppm)	mol L <sup>-1</sup> (M) (molarity)	mol kg <sup>-1</sup> (m) (molality)	mol kg <sup>-1</sup> (molinity)
Ca <sup>2+</sup>	308.9			
Mg <sup>2+</sup>	1712			
Na <sup>+</sup>	8085			
K <sup>+</sup>	299.3			
SO <sub>4</sub> <sup>2-</sup>	2034			
Cl <sup>-</sup>	14515			

2) To demonstrate the effect of Ionic Strength (I) on activity coefficients ( $\gamma$ ), use the Davies Equation to calculate  $\gamma$  for monovalent, divalent and trivalent ions at I values of 0.001, 0.01, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.9, and 1.0 mol/kg solution. Use a spreadsheet (e.g., Microsoft Excel) to calculate, display (table) and graph the data. Use the form of the Davies Equation given in class.

3) Using data for the 6 most abundant ions in seawater (Table 3.5 from Emerson & Hedges), calculate the ionic strength of seawater in moles/kg SW to the nearest 0.001. Compare this with the ionic strength calculated in the same way (i.e., 6 most abundant ions in moles/kg) for Artificial Seawater as described by Millero (2006) in Table 2.3 (see below). (Note: When selecting the 6 species, exclude carbonate, bicarbonate, fluoride and borate) What is different about carbonate, bicarbonate, fluoride and borate compared to the other ions that might make us want to leave them out of this calculation? Give as many reasons that you can think of for why these calculations are different.

**TABLE 2.3**

Preparation of 1 kg of S = 35.00 of Artificial Seawater

Salt	Grams/Kilogram	Moles/Kilogram	Molecular Weight
<i>Gravimetric Salts</i>			
NaCl	23.9849	0.41040	58.4428
Na <sub>2</sub> SO <sub>4</sub>	4.0111	0.02824	142.0372
KCl	0.6986	0.00937	74.5550
NaHCO <sub>3</sub>	0.1722	0.00205	84.0070
KBr	0.1000	0.00084	119.0060
B(OH) <sub>3</sub>	0.0254	0.00041	61.8322
NaF	0.0029	0.00007	41.9882
	28.9951		
<i>Volumetric Salts</i>			
MgCl <sub>2</sub>	5.0290	0.05282	95.211
CaCl <sub>2</sub>	1.1409	0.01028	110.986
SrCl <sub>2</sub>	0.0143	0.00009	158.526

Use 1 molar MgCl<sub>2</sub>, CaCl<sub>2</sub>, and SrCl<sub>2</sub> (standardize by AgNO<sub>3</sub> titration).  
 52.8 ml of 1 molar MgCl<sub>2</sub>, 10.3 ml of 1 molar CaCl<sub>2</sub>, and 0.1 ml of  
 1 molar SrCl<sub>2</sub> are needed. The densities of these solutions are 1.017 g/ml,  
 1.013 g/ml, and 1.131 g/ml, respectively, for MgCl<sub>2</sub>, CaCl<sub>2</sub>, and SrCl<sub>2</sub>  
 solutions at 1 molar. The grams of water in each solution are given by

$$H_2O = g_{SOLN} - g_{SALT} = ml \times density - g_{SALT}$$

*Addition of Water*

$$g_{H_2O} \text{ to add} = 1000 - g_{H_2O} \text{ from MgCl}_2, \text{ CaCl}_2, \text{ and SrCl}_2$$

- 4) Seawater contains both Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> which can react according to the following equilibrium to form an uncharged, but soluble ion pair or complex



Using seawater total concentration data for Ca and SO<sub>4</sub> as described in Problem #3 above, calculate the concentrations of free Ca<sup>2+</sup>, bound Ca (i.e., Ca in CaSO<sub>4</sub>), free SO<sub>4</sub><sup>2-</sup> and bound SO<sub>4</sub> as well as the percentage of each (i.e., free and bound Ca as a percentage of total Ca and free and bound SO<sub>4</sub> as a percentage of total SO<sub>4</sub>). 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 given above. You may assume the only equilibrium operating in this system is the CaSO<sub>4</sub> equilibrium given.

- 5) 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 °C. Prepare a table of the same form as their Table VII to summarize your results.

Point values: 1) = 1.5, 2) = 1.5, 3) = 1.5, 4) = 3.0, 5) = 2.5 Total points = 10.0