Chemical Oceanography | Problem Set #1 Spring 2021
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 below. You have more than a week to complete this assignment and submit it to me electronically in either MS Word or Excel format (due 2/18/21 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 (this is big, so don't be late). Please email me concerning any specific questions so as not to use valuable class time on homework.

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

1) Hypothetically speaking, let's say you want to make artificial seawater in the laboratory in order to do some experiments under controlled conditions. Real seawater has lots of creepy and slimy things in it as well as pollutants so using nice clean laboratory reagents seems like a good idea. You have a balance to weigh out the ingredients and on the shelf you have NaCl, KOH, $MgSO_4$, $CaCl_2$, $Mg(OH)_2$ and HCl. Let's assume you will make up exactly 1.00 L of artificial seawater by adding appropriate amounts of each reagent above to produce the concentrations given in Table 3.5 of our text by Emerson and Hedges (2010). Only concern yourself with the 6 major species excluding carbonate and bicarbonate.

a) What is the weight, in grams, of each reagent needed?

b) If we use 993 g of H_2O to get 1 liter of solution, what is the density of the solution?

c) Why might the pH of this solution be near the neutral pH of 7.0?

d) List the concentration of each of the 6 species in mol/L (M), mmol/L (mM) & mg/L (ppm) as well as mol/kg and mmol/kg (make a table with the 5 concentration units across the top & a row for each species.

e) Calculate the ionic strength of the solution of artificial seawater in mol/L (You will need this in question #3 below).

Note: Results for parts d and e, and possibly parts a and b, should be displayed in tabular form (e.g. a spreadsheet). 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).

2) To demonstrate the effect of Ionic Strength (I) on activity coefficients (γ), use the Davies Equation to calculate γ 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 below in #4.

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
Gravimetric Salts			
NaCl	23.9849	0.41040	58.4428
Na_2SO_4	4.0111	0.02824	142.0372
KCl	0.6986	0.00937	74.5550
$NaHCO_3$	0.1722	0.00205	84.0070
KBr	0.1000	0.00084	119.0060
$B(OH)_3$	0.0254	0.00041	61.8322
NaF	0.0029	0.00007	41.9882
	28.9951		
Volumetric Salts			
$MgCl_2$	5.0290	0.05282	95.211
$CaCl_2$	1.1409	0.01028	110.986
$SrCl_2$	0.0143	0.00009	158.526

Use 1 molar $MgCl_2$, $CaCl_2$, and $SrCl_2$ (standardize by $AgNO_3$ titration). 52.8 ml of 1 molar $MgCl_2$, 10.3 ml of 1 molar $CaCl_2$, and 0.1 ml of 1 molar $SrCl_2$ are needed. The densities of these solutions are 1.017 g/ml, 1.013 g/ml, and 1.131 g/ml, respectively, for $MgCl_2$, $CaCl_2$, and $SrCl_2$ solutions at 1 molar. The grams of water in each solution are given by

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

Addition of Water

g_{H_2O} to add = 1000 − g_{H_2O} from $MgCl_2$, $CaCl_2$, and $SrCl_2$

4) Seawater contains both Ca^{2+} and SO_4^{2-} which can react according to the following equilibrium to form an uncharged, but soluble ion pair or complex

$$Ca^{2+} + SO_4^{2-} \longleftrightarrow CaSO_4 \qquad K_f = 10^{2.31} = 2.0 \times 10^2$$

Using seawater total concentration data for Ca and SO_4 as described in Problem #3 above (E&H Table 3.5), calculate the concentrations of free Ca^{2+}, bound Ca (i.e., Ca in $CaSO_4$), free SO_4^{2-} and bound SO_4 as well as the percentage of each (i.e., free and bound Ca as a percentage of total Ca 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 given below. You may assume the only equilibrium operating in this system is the $CaSO_4$ equilibrium given. $\mathbf{\ln \gamma = - A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]}$

5) Using total concentration data from the paper by Motekaitis and Martell (Mar. Chem. 21 (1987) 101-106; posted on the website for class 6, 2/9/21) 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. Do not include mercury (Hg) because it tends to crash the program. You may need to try different values of CO_2 partial pressure to get a reasonable result. Prepare a table in the same form as their Table VII to summarize your results. Why would your computer calculated results differ from the manual calculation you did in question #4 above?