Chemical Oceanography | Problem Set 1-2017
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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 on page 2. You have about 1.5 weeks to complete this assignment and submit it to me electronically in either MS Word or Excel format (due 2/14/17 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) Hypothetically speaking, let's say you want to make artificial seawater in the laboratory in order to do some experiments. 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.

e) Calculate the ionic strength of the solution of artificial seawater in mol/L.

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.

2) a) Calculate the freezing point depression (ΔT_f) and boiling point elevation (ΔT_b) for 31.65 g of NaCl added to 220.0 mL of water at 35 °C. The density of water at 35 °C is 0.994 g/mL. Use the equations and constants from class.

b) What would be the ΔT_f and ΔT_b if 31.65 g of $CaSO_4$ were used?

c) What about for 31.65 g of Na_2SO_4?

d) 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) Using the values of K^*_{sp} from the table below (where $K^*_{sp} = [Ca^{2+} (aq)] [CO_3^{2-} (aq)]$) calculate the solubility of calcite and aragonite in mol/kg at S = 35 and T = 20. The data in the table has already been corrected for ionic strength so you do not have to make an activity correction.

Table G.1 *Solubility product constants for calcite and aragonite in seawater* from Pilson, 1998

	Salinity (‰)														
T (°C)	*0*	*5*	*10*	*15*	*20*	*25*	*30*	*32*	*33*	*34*	*35*	*36*	*37*	*38*	*40*
							Calcite								
0	0.416	5.47	10.98	16.89	23.03	29.35	35.94	38.67	40.06	41.47	42.91	44.36	45.84	47.35	50.45
5	0.403	5.37	10.85	16.77	22.93	29.32	36.00	38.78	40.19	41.63	43.09	44.57	46.08	47.62	50.78
10	0.389	5.25	10.68	16.57	22.76	29.20	35.96	38.79	40.23	41.69	43.17	44.69	46.22	47.79	51.02
15	0.371	5.11	10.45	16.31	22.50	28.98	35.82	38.69	40.15	41.64	43.15	44.69	46.25	47.85	51.14
18	0.360	5.01	10.29	16.12	22.30	28.80	35.68	38.57	40.05	41.55	43.07	44.63	46.21	47.83	51.16
20	0.352	4.93	10.17	15.98	22.15	28.66	35.57	38.47	39.95	41.46	43.00	44.57	46.16	47.79	51.14
25	0.331	4.74	9.86	15.58	21.72	28.24	35.20	38.13	39.63	41.16	42.72	44.31	45.93	47.59	51.01
30	0.309	4.52	9.50	15.11	21.20	27.71	34.70	37.66	39.18	40.73	42.31	43.92	45.57	47.25	50.72
35	0.286	4.29	9.10	14.59	20.60	27.08	34.09	37.07	38.61	40.17	41.76	43.39	45.06	46.76	50.28
40	0.263	4.05	8.67	14.02	19.93	26.36	33.36	36.36	37.90	39.47	41.08	42.72	44.40	46.12	49.69
							Aragonite								
0	0.652	10.08	19.80	29.46	38.87	48.23	57.88	61.92	64.00	66.12	68.28	70.49	72.76	75.09	79.95
5	0.627	9.84	19.44	29.05	38.48	47.91	57.68	61.79	63.89	66.04	68.24	70.50	72.80	75.18	80.13
10	0.598	9.54	18.97	28.49	37.89	47.35	57.20	61.35	63.48	65.65	67.88	70.16	72.50	74.91	79.93
15	0.567	9.18	18.39	27.77	37.11	46.55	56.43	60.60	62.75	64.94	67.19	69.49	71.85	74.28	79.35
18	0.547	8.95	18.00	27.27	36.54	45.96	55.83	60.01	62.16	64.36	66.61	68.92	71.29	73.73	78.82
20	0.533	8.79	17.72	26.91	36.13	45.51	55.38	59.56	61.71	63.91	66.16	68.47	70.85	73.29	78.39
25	0.497	8.35	16.97	25.92	34.97	44.25	54.06	58.22	60.37	62.57	64.82	67.13	69.50	71.95	77.06
30	0.460	7.88	16.15	24.82	33.66	42.78	52.48	56.61	58.74	60.93	63.17	65.47	67.83	70.27	75.36
35	0.423	7.39	15.27	23.62	32.20	41.13	50.67	54.75	56.86	59.02	61.23	63.51	65.85	68.27	73.33
40	0.386	6.88	14.35	22.34	30.63	39.32	48.66	52.66	54.73	56.86	59.04	61.28	63.59	65.97	70.97

The values of K^*_{sp} were calculated with Eqn. (G.6), the algorithm derived by Mucci (1983), and are expressed as $K^*_{sp} = [Ca^{++}][CO_3^{=}]$, ($mol^2\ kg^{-2}$). The concentrations are expressed in mol/kg of seawater. All values are to be multiplied by 10^{-8}.

4) 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

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

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.

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 (excluding Hg), calculate with MINEQL+ all species formed in seawater at pH 8.1 and an ionic strength of 0.5 at 20 ^oC. Prepare a table of the same form as their Table VII to summarize your results.

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