

## Marine Chemistry 12.742

### Problem Set #4

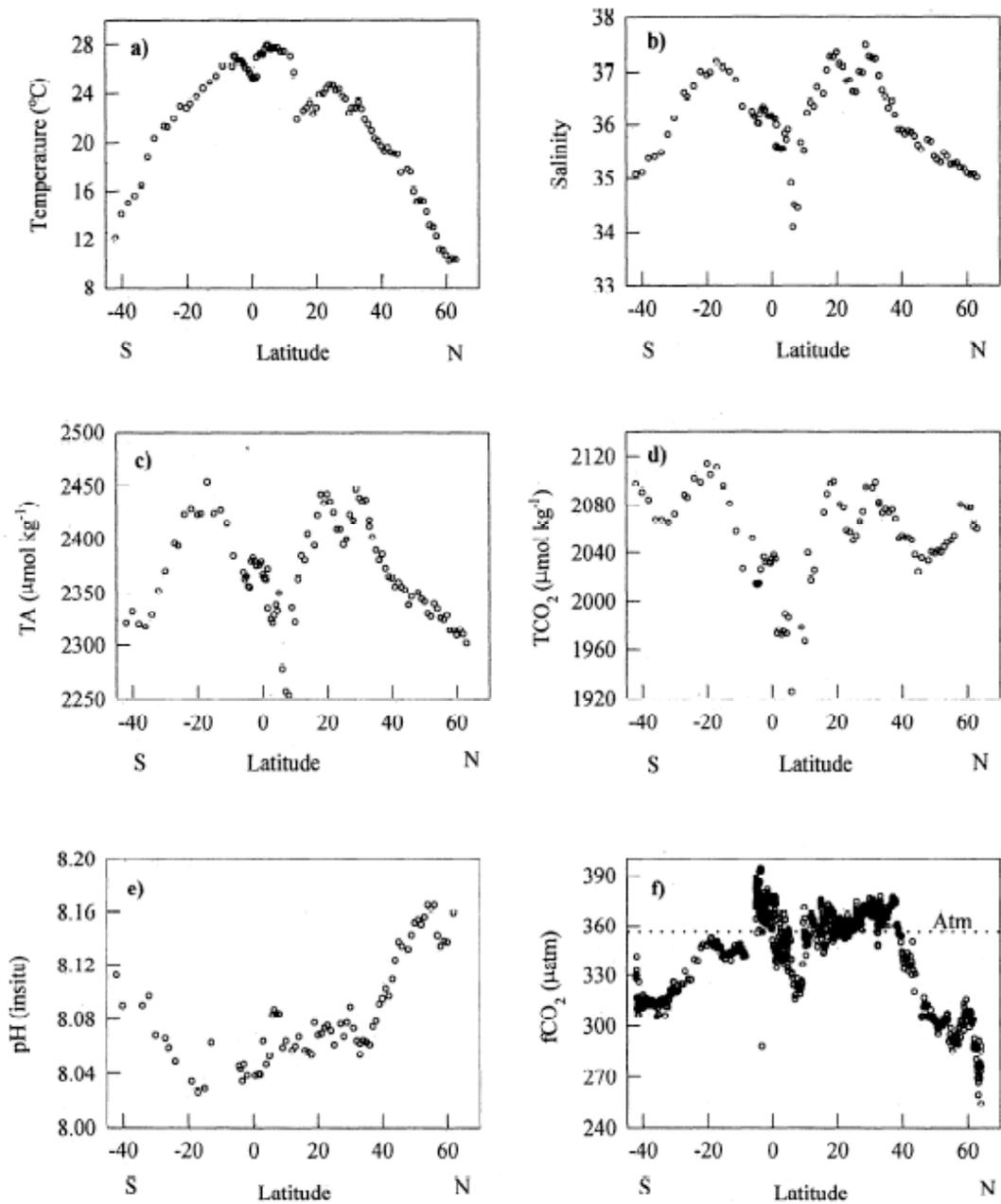
#### Problem 1:

- Using the thermodynamic data from Dickson and Goyet (1994) (Chapter 5, page 14 of 22), compute the dissociation coefficient for boric acid in a seawater solution at  $S=36$ ,  $T=25$  deg. C. Find the corresponding dissociation coefficient in the literature (e.g., CRC tables) for an idealized dilute freshwater system at the same temperature. How do these coefficients differ and why?
- Draw a diagram of the  $\log_{10}$  concentration of the different species of boron as a function of pH in seawater and freshwater.
- Describe how boron contributes to seawater titration alkalinity. Given the information above and what you know about the average seawater concentration of boron and surface and deep water pHs, estimate the magnitude and sign of the error of approximating titration alkalinity from carbonate alkalinity (versus the more complete “practical” alkalinity defined by Zeebe and in the notes).

#### Problem 2:

The figure below from Lee et al. (J. Geophys. Res. Oceans, 1997) shows surface water properties along a section in the Atlantic ocean. Use the  $S=35$ ,  $T=25$  deg. C values for the Henry's law constant for  $\text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3^*(\text{aq})$  and the carbonate found in Dickson and Goyet (1994) Chapter 5. Using the data from the figure then:

- Estimate the concentrations of  $[\text{H}_2\text{CO}_3^*]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$  at 20S and at the  $\text{TCO}_2$  minimum just north of the Equator *using two different approaches*. Why does inorganic speciation vary with latitude? (Hint: There are several different ways to do this; remember from lecture that given measurements of two parameters for the inorganic carbon system, you can calculate everything else).
- Estimate the saturation state of calcite and aragonite for the some locations (for simplicity use constant effective saturation product of  $K^*_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$  for calcite of  $43 \times 10^{-8} \text{ mol}^2 \text{ kg}^{-2}$  and for aragonite of  $67 \times 10^{-8} \text{ mol}^2 \text{ kg}^{-2}$  at  $S=35$ ,  $T=25$ ). Discuss the results.



**Figure 4.** Distributions of sea surface properties: (a) temperature in degrees Celsius, (b) salinity, (c) TA in micromoles per kilogram, (d)  $\text{TCO}_2$  in micromoles per kilogram, (e) in situ pH, and (f) underway  $f\text{CO}_2$  in microatmosphere along the cruise track. The data from 5° to 40°S were obtained from NOAA's South Atlantic cruise during the austral winter in 1991 [Forde *et al.*, 1994]. Surface water values of alkalinity in the eastern Atlantic obtained from TTO/NAS were combined with the values obtained from the OACES 93 cruise.

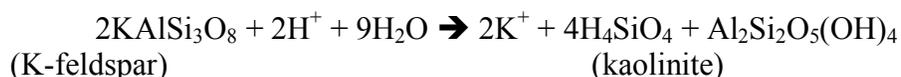
**Problem 3:**

	K <sup>+</sup> (mg l <sup>-1</sup> )	K flux for rivers/vents
Atlantic rivers	1.4	
Indian rivers	2.5	
Arctic rivers	1.2	
Pacific rivers	1.2	
River average	1.5	7.4 x 10 <sup>13</sup> g/yr
Seawater	405	
EPR 21N vent fluid	964	
EPR 9N (1991) vent fluid	46	
EPR 9N (1994) vent fluid	1665	
TAG vent fluid	687	
“Average” MOR vent fluid	964	2.5 x 10 <sup>13</sup> g/yr
Estimated ridge flank flux		-1.5 x 10 <sup>13</sup> g/yr

The main sources and sinks for potassium in the ocean include river input and on-axis and off-axis hydrothermal activity. The table above shows concentrations of K<sup>+</sup> in river waters, vent fluids, and seawater, as well as estimated fluxes of K<sup>+</sup> into or out of the ocean.

a) Using data in the table, calculate the volumes of river water and on-axis mid-ocean ridge vent fluid that enter the ocean each year.

b) The reaction



is one process that controls the riverine flux of K<sup>+</sup> to the oceans.

i. Is this weathering reaction an example of congruent or incongruent dissolution? (Provide a 1 sentence explanation for your answer).

ii. List 2 factors that can affect the ion composition of rivers and that may explain the different K<sup>+</sup> concentrations shown in the table above.

c) Why are K<sup>+</sup> concentrations in vent fluids so much higher than those in river waters?

d) What information was used to estimate the ridge flank flux of K<sup>+</sup>, and why is hydrothermal activity on ridge flanks a sink instead of a source for K as it is at the ridge axis? (Hint: very few ridge flank vents have been discovered and sampled).

**Problem 4:**

a) Given the following information:

- Salinity of coastal water ( $S_{cw}$ ): 33 permil
- Salinity of open ocean water ( $S_{sw}$ ): 35 permil
- River flow into coastal water ( $F_{rw}$ ): 1 (arbitrary unit)
- Concentration of tracer T in coastal water ( $T_{cw}$ ): 1 (arbitrary unit)
- Concentration of tracer T in open ocean water ( $T_{sw}$ ): 0.5
- Concentration of tracer T in river water ( $T_{rw}$ ): 0.0
- Concentration of tracer T in groundwater ( $T_{gw}$ ): 100

What is the steady state flow of groundwater relative to river flow into the coastal zone?

b) Would you reconsider your estimate if you were told that the river concentration estimate was only for the dissolved fraction of tracer T and that the measurements were done upstream of the estuary?

What additional information would you want to know in order to make a better estimate of the riverine and groundwater fluxes of dissolved T into the coastal ocean?

**Problem 5:**

Consider a gas exchange experiment where an inert dye,  $^3\text{He}$ , and  $\text{SF}_6$  have been injected into the surface ocean. Assume that the mixed layer is uniformly 40m deep, temperature is 20 °C and wind speed is 8.5 m/s. Some constants that might be useful are:

- viscosity of seawater at 20°C =  $1.0 \times 10^{-2} \text{ cm}^2/\text{s}$
- diffusivity of  $^3\text{He}$  at 20°C =  $6.5 \times 10^{-5} \text{ cm}^2/\text{s}$
- diffusivity of  $\text{SF}_6$  at 20°C =  $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$

a) Using the Wanninkhof, 1992 parameterization of gas transfer velocity as a function of wind speed:

$$k = 0.31 U^2 (Sc/660)^{-0.5}$$

compute the gas exchange time-scales for  $^3\text{He}$  and  $\text{SF}_6$ .

b) Write the differential equation and solution for the time rate of change of the  $\text{SF}_6$  as a function of time due just to gas exchange. If you knew the exponent (n), in the generalized gas exchange parameterization, show how you could compute k from supersaturation of  $\text{SF}_6$  at two time points  $T_0$  and  $T_1$ .

c) If you could estimate dilution from the dye, how would you modify the differential equation for  $\text{SF}_6$ ?

c) With information from both He-3 and  $\text{SF}_6$  tracers at  $T_0$  and  $T_1$ , show how you could also compute n. Assuming an initial supersaturation of 5% for both gases and a measurement error of 0.5%, how long would you need to wait to remeasure the supersaturations following the initial injection (i.e.,  $T_1 - T_0$ ) to decide whether n should be 0.5 or 1.0?

