Ocean 421  
Chemical Oceanography  
Spring 2000

Final Exam
(Use the back of the pages if necessary) (More than one answer may be correct.)

1. Due to the water molecule’s (H₂O) great abundance in seawater: (10 pts)
   a) Seawater has a high heat capacity
   b) The activity of H₂O is 1 in all equilibrium calculations
   c) Salts dissolve easily in seawater
   d) The activity coefficients of all dissolved constituents are equal
   e) The activity of Ca²⁺ is greater than its concentration.

2. Due to the great abundance of dissolved salts in seawater: (10 pts)
   a) sea water has a higher density than freshwater
   b) sea water has a higher molar volume than freshwater
   c) sea water has a higher boiling point than freshwater
   d) sea water has a high ionic strength
   e) sea water has a higher sound absorption than freshwater

3. Some elements in seawater are considered to be conservative.
   a) What is the definition of a conservative element? (5 pts)
      A non-reactive element whose ratio to salinity (S) is constant in the ocean.
   
   b) There are statements in the literature that uranium (U) is a conservative element in seawater. How would you design a study to show this is true or not true? (5 pts)

      measure uranium together with a conservative element or property — such as salinity (S), potential temperature (Θ) or Ca⁺, Ca²⁺ etc.

      If U is conservative it will make a linear plot versus another conservative property.
4. Both equilibrium and kinetic (dynamic) models have been proposed for the composition of seawater. What arguments can be given favoring the kinetic model relative to the equilibrium approach? (10 pts)

1. CLAYS COME FROM DETRITAL SOURCES RATHER THAN REVERSE WEATHERING.
2. LACK OF EVIDENCE FOR SUFFICIENT MINERALS OF REVERSE WEATHERING ORIGIN.
3. SW. COMPOSITION HAS CHANGED WITH TIME WHICH IS ALLOWED BY THE KINETIC MODEL BUT NOT THE EQUILIBRIUM MODEL.

5. As deep water flows from the North Atlantic to the North Pacific the carbonate alkalinity increases from 2350 µEq to 2475 µEq while total CO₂ (e.g., DIC) increases from 2200 µM to 2375 µM. Estimate the average contributions of CaCO₃ dissolution and organic carbon respiration that create this increase in DIC. (15 pts)

\[ \Delta \text{Allic} = 2475 - 2350 = 125 \text{ µEq} \]
\[ \Delta \text{DIC} = 2375 - 2200 = 175 \text{ µM} = 62.25 \]

Assume:
\[ \text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-} \]
\[ \text{DIC} = 1 \quad \text{Allic} = 2 \]
\[ \text{DIC} = 1 \quad \text{Allic} = 0 \]

\[ \frac{\Delta \text{DIC}_{\text{CaCO}_3}}{\Delta \text{DIC}_{\text{Allic}}} = \frac{112.75}{62.25} = 1.8 \]

6. CaCO₃ is added to water and it dissolves. How will the following parameters vary? (10 pts)

pH \(\uparrow\)
alkalinity \(\uparrow\)
total CO₂ \(\uparrow\)
Ca\(^{2+}\) \(\uparrow\)
PcO₂ \(\downarrow\)
7. $^{238}\text{U} (\tau_{1/2} = 4.5 \times 10^{9} \text{ yr})$ decays to $^{234}\text{Th} (\tau_{1/2} = 24.1 \text{ d})$

   a) Define, and give the conditions for, secular equilibrium (5 pts)
   
   
   DECAY ONLY
   
   $t_{1/2} \gg \tau_{1/2}$

   b) Assuming the activity of $^{234}\text{U} = 2.3 \text{ dpm kg}^{-1}$ what is the molar concentration of $^{234}\text{Th}$? (10 pts)

   $A_{^{238}\text{U}} = A_{^{234}\text{Th}} = 2.3 \frac{\text{dpm}}{\text{kg}} = \lambda N_{\text{Th}}$

   $t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} = 0.028 \text{ d}^{-1}$

   $N_{\text{Th}} = \frac{2.3 \text{ dpm kg}^{-1}}{0.028 \text{ d}^{-1}}$

   c) Assume there has been an extreme bloom period with intensive scavenging that removes most of the $^{234}\text{Th}$ from the water column in the euphotic zone. Suddenly the bloom stops. How long will it take for $^{234}\text{Th}$ to reach secular equilibrium with $^{238}\text{U}$? (5 pts)

   5 half lives of daughter

   $5 \times 24.1 \text{ d} = 120 \text{ d}$

8. Which of the following is a first order process? (10 pts)
   
   a) River input
   b) Downwelling
   c) Biological Production, with respect to DIC
   d) Biological Production, with respect to N, P, Fe or another biolimiting element
   e) Radioactive decay

9. The Redfield (or RKR) ratio represents (10 pts)
   
   a) C:N:P content of organic matter formed during photosynthesis
   b) C:N:P content of nutrients released during respiration
   c) C:N:P of preformed nutrients in the surface ocean
   d) C:N:P of nutrient uptake during photosynthesis
   e) C:N:P of organic matter found in sediments
10. Relative to the Atlantic, Pacific deepwater (10 pts)
   a) pH is higher
   b) Pco2 is higher
   c) Alkalinity is higher due to a larger organic C respiration: CaCO3 dissolution rate ratio
   d) Alkalinity is higher due to a smaller organic C respiration: CaCO3 dissolution rate ratio
   e) Total CO2 is higher than alkalinity

11. In which situations is it advantageous to use K', the apparent equilibrium constant (10 pts)
   a) Ion activites (but not concentrations) can be measured and free energies are known
   b) Trace metal speciation calculations
   c) At ionic strength, I=0
   d) Carbonate system equilibria in seawater
   e) When Q > K.

12. Due to the input of radionuclides during bomb testing in the 1960s, which information has been gained? (10 pts)
   a) Water mass ventilation using chlorofluorocarbon (CFC) tracers
   b) N-S mixing across the equator using 3H as a tracer
   c) Export production using 234Cp/234Th ratios
   d) Stagnant boundary layer thickness using a 14C steady state box model
   e) The rate of turbulent mixing in the bottom boundary layer.

13. The oxidation of organic matter (10 pts)
   a) produces dissolved organic carbon
   b) produces dissolved inorganic carbon
   c) consumes energy
   d) provides bacteria with energy for growth and function
   e) is not possible in the absence of oxygen

14. Trace elements with nutrient-like distributions, such as barium and copper (10 pts)
   a) show a linear relationship with salinity and [Cl-]
   b) are depleted at the surface
   c) are enriched at the surface
   d) are regenerated (i.e. increase) with depth
   e) have fixed stoichiometric ratios to P
15. CO$_2$ and climate. There is evidence that the ocean's circulation varied in a regular way during the past glacial periods. This has to do with the different sources and strengths of bottom water formation.

a) Broecker (1997) used a conservative geochemical tracer called PO$_4^*$ to determine the intensity of the northern and southern sources, where waters of southern origin are described by:

$$\text{PO}_4^* = \text{PO}_4 + \frac{\text{O}_2}{175} - 1.95 \text{ mmol kg}^{-1}$$

and waters of northern origin by:

$$\text{PO}_4^* = \text{PO}_4 + \frac{\text{O}_2}{175} + 0.73 \text{ mmol kg}^{-1}$$

Explain the origin of these equation and how it can be used for this purpose and why they are different for the norther and southern sources. (5 pts)

**THE SUM OF \( \text{PO}_4 + \frac{\text{O}_2}{175} \)** **SHOULD REMAIN CONSTANT**

**BECAUSE AS \( \text{PO}_4 + \text{O}_2 \)** **DUE TO RESPIRATION**

**THE LAST NUMBER IS THE PRE-PERIOD \( \text{PO}_4 \) WITH**

**IS DIFFERENT IN THE NORTHERN AND**

**SOUTHERN SOURCES**

**WHY? PERHAPS BECAUSE THE SOUTHERN SOURCE**

**IS UNDER THE ICE AND \( \text{PO}_4 \) IS HIGHER BECAUSE**

**THERE IS LESS BIOLOGICAL REMOVAL**

b) What were the reorganizations in ocean circulation that occurred in the past and what was their origin? (5 pts)

**NAADW WAS SHUT DOWN AT SEMI-REGULAR INTERVALS DUE TO FRESHENING OF THE N. ATLANTIC SURFACE WATER**

c) If there are ocean reorganizations in the future, will they be caused by the same mechanism? If not what will be the cause? (5 pts)

**AS \( \text{CO}_2 \) SET \( \uparrow \) SO NAADW MAY BE SHUT OF BUT BECAUSE OF WARMING RATHER THAN FRESHENING.**
16. Acantharian protozoa use strontium to form celestite, SrSO_4(s) skeletons. Is the formation of celestite thermodynamically favorable in seawater? The solubility of celestite is written as:

\[ \text{SrSO}_4(s) = \text{Sr}^{2+} + \text{SO}_4^{2-} \]

a) Calculate the equilibrium constant for this reaction at 25°C given the following free energies of formation (\(\Delta G_f^o\)) and using (\(\Delta G_f^o\)-2.3RT log K=-5.708 log K at 25°C)

<table>
<thead>
<tr>
<th>Species</th>
<th>(\Delta G_f^o (kJ , \text{mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrSO_4(s)</td>
<td>-1340.9</td>
</tr>
<tr>
<td>Sr^{2+}(aq)</td>
<td>-563.83</td>
</tr>
<tr>
<td>SO_4^{2-}(aq)</td>
<td>-744.53</td>
</tr>
</tbody>
</table>

\[ \Delta G_f^o = -563.83 + 744.53 - 1340.9 = -1204.26 \quad \text{kJ mol}^{-1} \]

\[ \log K = \frac{\Delta G_f^o}{-RT} = \frac{-5.708}{-5.34} = 1.07 \]

\[ K = 10^{-1.07} \]

b) What is the equilibrium expression? (\(\text{S}+\text{H}_2\text{O}\))

\[ K_c = \frac{([\text{Sr}^{2+}] [\text{SO}_4^{2-}])}{([\text{SrSO}_4(s)])} \]

c) If seawater has [Sr^{2+}]=0.0928 mmol/L and [SO_4^{2-}]=28.93 mmol/L and the total activity coefficients are \(\gamma_{\text{Sr}}=0.25\) and \(\gamma_{\text{SO}_4}=0.065\), what is \(\Delta G_f\)? Is the formation of celestite thermodynamically favorable in seawater? (\(\text{S}+\text{H}_2\text{O}\))

\[ Q = [\text{Sr}^{2+}] [\text{SO}_4^{2-}] \gamma_{\text{Sr}} \gamma_{\text{SO}_4} \]

\[ = (9.28 \times 10^{-5} \text{ M})(0.25)(28.93 \times 10^{-3} \text{ M})(0.065) \]

\[ = 4.136 \times 10^{-8} \]

\[ \Delta G_f = \Delta G_f^o + 2.3RT \log Q \]

\[ = -5.708 + (5.708)(-7.36) \]

\[ = 37.54 - 42.01 \]

\[ = -4.47 \quad \text{kJ mol}^{-1} \]

\[ \text{Rxn TO RIGHT} \]

\[ \text{(in seawater)} \]

The average partial pressure of N₂O in the atmosphere over the Arabian Sea was 313 ppbv or \(10^{-6.50}\) atm. The Henry's Law constant for N₂O solubility at 25°C is \(K_H = 10^{-1.39}\) mol l⁻¹ atm⁻¹.

\[ [N_2O] = K_H P_{N_2O} = 10^{-1.54} \times 10^{-6.50} = 10^{-8.04} \times 10^{-9} = 8.12 \times 10^{-9} \text{ M} \]

a. What was the mean saturated concentration of N₂O in surface water in mol l⁻¹. (5 points)

b. The average degree of supersaturation was 130% and the average piston velocity for the average wind speed was 22.7 cm hr⁻¹. Calculate the average gas exchange flux in mol cm⁻² d⁻¹ using the stagnant boundary layer model. (10 points)

\[
\text{Flux} = \frac{D}{\tau_{\text{film}}} (C - C_{\text{sat}})
\]
\[
= \frac{D}{\tau_{\text{film}}} (1.30 \times 10^{-8.09} - 10^{-8.09})
\]
\[
= 22.7 \text{ cm} / \text{m} \left( 10^{-8.09} - 8.12 \times 10^{-9} \right)
\]
\[
= 22.7 \text{ cm} / \text{m} \left( 2.13 \times 10^{-9} \text{ mol} / \text{m}^3 \right) \frac{1}{10^3 \text{ cm}^3}
\]
\[
= (22.7 \text{ cm} / \text{m}) \left( 2.13 \times 10^{-12} \text{ mol} / \text{cm}^3 \right)
\]
\[
= 53.7 \times 10^{-12} \frac{\text{mol}}{\text{cm}^2 \text{m}} \times 2.4 \frac{\text{hr}}{\text{d}}
\]
\[
= 1.289 \times 10^{-12} \frac{\text{mol}}{\text{cm}^2 \text{d}}
\]

= 1.289 \times 10^{-9} \frac{\text{mol}}{\text{cm}^2 \text{d}}
18. Sometimes different oxidation states of the same element can be both oxidants and reductants. In one case the oxidized form of sulfur (SO₄²⁻) can react with the reduced form (H₂S) to form solid elemental sulfur (S⁰). Such as reaction may occur at the oxic-anoxic interface in the Black Sea.

Here are two relevant half reactions:

\[
\begin{align*}
1/6 \text{SO}_4^{2-} + 8/6 \text{H}^+ + e^- &= 1/6 \text{S}^0 + 4/6 \text{H}_2\text{O} & \log K = 6.03 \\
1/8 \text{SO}_4^{2-} + 10/8 \text{H}^+ + e^- &= 1/8 \text{H}_2\text{S} + 4/8 \text{H}_2\text{O} & \log K = 5.12
\end{align*}
\]

a) write the balanced oxidation-reduction reaction (10 pts)

\[
\begin{align*}
1/6 \text{SO}_4^{2-} + 8/6 \text{H}^+ + e^- + 1/6 \text{S}^0 + 4/6 \text{H}_2\text{O} &= 1/8 \text{H}_2\text{S} + 4/8 \text{H}_2\text{O} \\
1/6 \text{SO}_4^{2-} + 1/8 \text{H}_2\text{S} + 8/6 \text{H}^+ + 4/6 \text{H}_2\text{O} &= 1/6 \text{S}^0 + 1/8 \text{SO}_4^{2-} + 10/6 \text{H}^+ + 10/6 \text{H}_2\text{O}
\end{align*}
\]

b) which compounds are oxidants in this reaction (note that there are two oxidants) (5 pts)

\[
\text{SO}_4^{2-} \text{ and } \text{H}_2\text{S}
\]

(5 pts)

\[
\text{SO}_4^{2-} \text{ and } \text{H}_2\text{O}
\]

\[
\text{K} = \frac{[\text{S}^0]^1 [\text{H}_2\text{O}]^4}{[\text{SO}_4^{2-}]^1 [\text{H}_2\text{S}]^1 [\text{H}^+]^4}
\]

\[
\text{K} = \frac{1}{\left(\frac{[\text{SO}_4^{2-}]}{[\text{S}^0]^1 [\text{H}_2\text{O}]^4}\right)^{1/10}}
\]

c) what is the equilibrium constant for this reaction (5pts)

\[
\text{K} = 10^{2.184}
\]

d) Is S⁰ stable with regard to this reaction at the point of reaction in the Black Sea where pH = 7.5, SO₄²⁻ = 17 mM, H₂S = 1 μM. Assume for this calculation that concentrations and activities are equal. (10 pts)

\[
\Omega = \frac{(17 \times 10^{-3})^2 (1 \times 10^{-6})^6 (10^{-2.184})^4}{(289 \times 10^{-6}) (10^{-36}) (10^{-30})}
\]

\[
\Omega = \frac{(10^{-3.25}) (10^{-2.6}) (10^{-30})}{10^{-69.5}}
\]

\[
\Omega = 10^{69.5}
\]

\[
\Omega / K = 10^{25.8} > 1
\]

so reaction to left, S⁰ NOT stable!
19. Fossil fuel CO₂ is on its way up from the pre-industrial value of about \( P_{CO_2} = 300 \mu atm \) to about 600 \( \mu atm \). By one scenario we can assume that alkalinity will stay constant at 2100 \( \mu Eq \).

Remember that the equilibrium constants for CO₂ and carbonic acid are:

\[
K_{H} = \frac{[H_2CO_3^\ast]}{P_{CO_2}} = 10^{1.5} \\
K_{i} = \frac{[HCO_3^-][H^\ast]}{[H_2CO_3]} = 10^{-6.0} \\
K_{2} = \frac{[CO_3^{2\ast}][H^\ast]}{[HCO_3^-]} = 10^{-9.0}
\]

a) Calculate the \([H_2CO_3^\ast]\) in equilibrium with an atmospheric \( P_{CO_2} = 300 \mu atm \). (10 pts)

\[
[\text{H}_2\text{CO}_3^\ast] = K_H \rho \omega_2 = 10^{-1.5} \times 10^{-3.5} = 10^{-5.0} 
\]

b) Calculate pH for this open carbonate system when \( P_{CO_2} \) has doubled to 600 \( \mu atm \). (10 pts)

\[
\begin{align*}
\Delta \text{HCO}_3^- & = \text{H}_2\text{O}_2 + 2\text{CO}_3^\ast \\
& = K_i \left( \chi_1 + 2\chi_2 \right) \\
& = K_{iH} \rho \omega_2 \left( \chi_1 + 2\chi_2 \right) \\
\Delta \text{HCO}_3^- & = K_{iH} \rho \omega_2 \left( \frac{HK_1 + 2K_{iC_2}}{H_2} \right) \\
2100 \times 10^{-6} & = 10^{-1.5} \times 10^{-3.22} \left( \frac{1 + 10^{-6} + 2 \times 10^{-6} 10^{-9}}{1 + 2} \right) \\
2.1 \times 10^{-3} & = 10^{-4.72} \left( \frac{1 + 10^{-6} + 2 \times 10^{-1.5}}{1 + 2} \right) \\
10^{-2.67} & = 10^{-10.72} \text{H} = 10^{-19.47} \\
10^{-2.67} & = 10^{-10.72} \text{H} + 10^{-19.47} = 0 \\
\text{H}^\ast & = 10^{-7.97} \\
\rho \text{H} & = 7.97
\end{align*}
\]
20. Nitrogen fixation has become the latest "hot topic". Let's assess its importance. A
construct a two-box ocean model for fixed nitrogen as nitrate. Include river inflow,
 atmospheric input to the surface box, nitrification input to the surface box at the air-sea
 surface, upwelling, downwelling, denitrification in the deep box and a biological flux of
 organic N (B). The removal rate to the sediments (S) is expressed as \( S = f \times B \).

From the literature, we find so information that we may (or may not) need:
\[
\begin{align*}
Q_{o_e} & = 175 \text{TgN y}^{-1} & f & = 0.01 \\
Q_R & = 76 \text{TgN y}^{-1} & \text{Area} & = 3.61 \times 10^8 \text{km}^2 \\
Q_{A_{at}} & = 30 \text{TgN y}^{-1} & \text{Volume} & = 2.61 \times 10^{18} \text{cm}^3 \\
Q_S & = 25 \text{TgN y}^{-1}. \\
Q_u & = \text{Upwelling rate } V = 300 \text{ cm y}^{-1}
\end{align*}
\]

a) Draw the two-box model for this problem and label the fluxes. (5 pts)

b) Write the mass balance equations for the surface and deep boxes. (10 pts)

Assume steady state.

Surface
\[
\begin{align*}
0 & = Q_R + Q_{nitr} + VmC_D - VmC_s - B \\
V & = VmC_s - Q_{denitr} + B - fB - VmC_D
\end{align*}
\]

Deep
\[
\begin{align*}
0 & = Q_{o_e} + Q_{nitr} + VmC_D - B \\
B & = B - Q_{denitr} - fB - VmC_D \\
& = (1-f)B - Q_{denitr} - VmC_D \\
& = (1-f)(Q_R + Q_{nitr} + VmC_D) - Q_{denitr} - VmC_D \\
0 & = (1-f)Q_{o_e} + (1-f)Q_{nitr} + (1-f)VmC_D - Q_{denitr} - VmC_D \\
0.99Q_{nitr} & = (Q_{o_e} + VmC_D - (1-f)VmC_D) - (1-f)Q_R \\
Q_{nitr} & = 1.75 + 0.01(300 \text{ cm y}^{-1})3 \times 10^{-2} \text{ m}^3 / \text{day}^2 \times A_{ocean} - 0.99(96) \\
& = 2.75 + 4.5 = 76 \text{Tg N y}^{-1}
\end{align*}
\]

d) What is its importance relative to river, atmospheric and upwelling input? (5 pts)

\[
Q_{nitr} = 104 \text{Tg N y}^{-1}
\]

\( Q_{nitr} \) larger than river & much larger than upwelling, larger than atmospheric input.
Oceanography is the study of the sea integrating all knowledge of the physics, chemistry, geology and biology of the sea. Any questions?

Scribble! Scribble! Scribble!

Of course not. You're too busy getting it all down.

Let me add that personally I believe that oceanography is a useless science for it attempts to seek answers beyond man's reach. Any comments?

Scribble! Scribble! Scribble!

No, scratch that! Stay away from oceanography since it can destroy you! What do you think of that?

Scratch! Scratch! Scratch!

Jefferson was the Antichrist! Democracy is fascism! Black is white! Night is day!

Scribble! Scribble! Scribble! Scribble!

Teaching is dead.

Boy, this course is really getting interesting. You said it. I didn't know half this stuff.