1. Ocean carbonate system

Acidity derived from the carbonic acid system is the most important control on the pH seawater and links many key processes. When necessary use the solubility and first and second acidity constants written below.

\[
\begin{align*}
\text{CO}_2(g) + \text{H}_2\text{O} &= \text{H}_2\text{CO}_3^0 \\
\text{H}_2\text{CO}_3^0 &= \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- &= \text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

\[
\begin{align*}
\log K'_H &= -1.5 \\
\log K'_{1} &= -6.0 \\
\log K'_{2} &= -9.0 \\
\log K'_s &= -6.13 \text{ (at 25°C)}
\end{align*}
\]

A distribution diagram for the carbonate system in seawater is shown on the next page.

a) Use the graph of the carbonate species shown on the next page.
   At what pH are \([\text{H}_2\text{CO}_3]\) and \([\text{CO}_3^{2-}]\) equal? (5 pts)

b) Use the graph. What is the concentration of \([\text{CO}_3^{2-}]\) at pH = 8.0? (5 pts)

c) Calculate by hand. The DIC = 2 \times 10^{-3} M (= 10^{-2.7} M). What is the concentration of \([\text{CO}_3^{2-}]\) at pH = 8.0? (10 pts)
d) Pteropods are a swimming snail important in high latitude ecosystems. They make their shells out of a form of CaCO$_3$(s) called aragonite. The solubility reaction and solubility product at 25°C is given above. The concentration of total [Ca$^{2+}$] = 10.5 x $10^{-3}$ M. At what concentration of CO$_3^{2-}$ will aragonite be undersaturated? (10 pts)

e) Calculate by hand. At what pH value will the CO$_3^{2-}$ reach this value? You know the final answer will be close to pH 8, so neglect small terms to simplify the calculation. (10 pts)

f) If increases in atmospheric CO$_2$ continue, and pH decreases further, what would be one likely effect on pteropod abundance. How might that be reflected in the carbon to phosphorus ratio measured in sediment traps? The ratio measured in the present ocean is about C:P = 131:1. (5 pts)

2) (T/F) During organic matter respiration…(10 pts)

pH goes up  
Carbonate alkalinity goes up  
DIC goes up  
P$_{CO2}$ goes up  
CO$_3^{2-}$ goes up
Figure, Distribution of carbonate species in seawater as a function of pH
3. Match Processes (draw connecting lines)

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>regenerated production</td>
<td>after most oxygen is consumed, this process is used by bacteria to oxidize organic material</td>
</tr>
<tr>
<td>new production</td>
<td>some diatoms may use chitin, a large organic molecule composed of C and N, to grow under low N-conditions. This type of production is an example of _____</td>
</tr>
<tr>
<td>preformed nitrate</td>
<td>this value can be used to estimate new production rates, if the age of a water mass is known.</td>
</tr>
<tr>
<td>apparent oxygen utilization</td>
<td>a bloom of N₂-fixing <em>Trichodesmium</em> is an example of this type of production.</td>
</tr>
<tr>
<td>Denitrification</td>
<td>multiplying this process by the f-ratio yields new production</td>
</tr>
<tr>
<td>export production</td>
<td>this type of production would be close to new production at steady state</td>
</tr>
<tr>
<td>primary production</td>
<td>if AOU = 0, then the concentration of this should be equal to the concentration of nitrate at depth</td>
</tr>
<tr>
<td>regenerated nitrate</td>
<td>an increase in concentration usually leads to an increase in AOU.</td>
</tr>
</tbody>
</table>
4) **Jenkins (1982)** calculated an integrated oxygen consumption of 5.7 mol O$_2$ m$^{-2}$ y$^{-1}$ in the water column of the North Atlantic below the euphotic zone (integrated in the water column from 100m to $\infty$).

a) Explain how he derived this value. What information did he use and how did he do the calculation? (10 pts)

b) Convert this O$_2$ consumption to a carbon flux and explain how you did it and what parameters you used. (5 pts)

5) **Suess (1980)**

The main equation from Suess (1980) was that $C_{\text{flux}} = \frac{C_{\text{prod}}}{0.0238Z + 0.212}$, where $Z$ equals depth in meters. Rearrange this equation to solve for the ratio of $\frac{C_{\text{flux}}}{C_{\text{prod}}}$ at $Z = 100$m.

If the ratio $\frac{C_{\text{flux}}}{C_{\text{prod}}}$ stands for export ratio, is this value consistent with what you know about the magnitude and distribution of new production in the ocean? Should this value be constant for all ocean areas (10 pts)
6) **Impact of increasing CO₂ and global warming on ocean cycles.**
The main source of nitrogen to the ocean is by nitrogen fixation. The main sink is some combination of denitrification and anammox. Write a short analysis of how the ocean nitrogen cycle might change in response to global change. No longer than the front and back of this page. (30 pts)
7. Metal Speciation

Ligands have been observed to control the concentration of dissolved trace metals at many ocean sites. Boye and colleagues measured an increase of dissolved iron concentrations closer to the coast in the North Atlantic corresponding with increased ligand concentrations (see figure from Boye et. al, *Marine Chemistry* 2003).

Several ligands do not specifically bind a particular metal and can bind to multiple metals, i.e. iron and zinc. Boye et. al observed that even though the ligand concentration ([L]) was the same for both metals, the concentration of Zn-bound ligands were less than Fe-bound ligands. The concentrations of dissolved Zn$^{2+}$ and Fe$^{3+}$ were equal at 1.0 nM ($10^{-9}$ M). Cathodic stripping voltammetry measurements yielded the following stability constants for Fe and Zn:

\[
\begin{align*}
    \text{Fe}^{3+} + \text{L}^2_- &= \text{FeL}^+ & \log K_{\text{FeL}} &= 20 \\
    \text{Zn}^{2+} + \text{L}^2_- &= \text{ZnL} & \log K_{\text{ZnL}} &= 19
\end{align*}
\]

a) Express [FeL] and [ZnL] in terms of [Fe$^{3+}$], [Zn$^{2+}$], [L], and $K_{(\text{Fe/Zn)L}}$. (10 pts)

b) Assuming thermodynamic equilibrium, what is the ratio of complexed zinc to complexed iron? Assume the same ligand binds both iron and zinc. Why is complexed zinc ([ZnL]) less abundant than complexed iron? (10 pts)
c) Increased concentrations of Al$^{3+}$ were also observed closer to the coast during Boye’s study (not shown). Like iron, Al readily undergoes hydrolysis via the following reactions:

\[
\begin{align*}
\text{Al}{}^{3+} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}{}^{2+} + \text{H}^+ \quad \log K_1 = -5.0 \\
\text{Al(OH)}{}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}{}^{2+} + \text{H}^+ \quad \log K_2 = -5.1 \\
\text{Al(OH)}{}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}{}^3{}^0 + \text{H}^+ \quad \log K_3 = -6.8 \\
\text{Al(OH)}{}^3{}^0 + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}{}^4{}^- + \text{H}^+ \quad \log K_4 = -5.8
\end{align*}
\]

If open ocean concentrations of Al$^{3+}$ are $10^{-15}$ M, what concentration of Al(OH)$_3^0$ would you predict at thermodynamic equilibrium at pH = 8? (10 pts)
8) **Radioactive Decay**

See attached Figure of the U-Th decay schemes.

a) Some parent / daughter isotope pairs in these series are sometimes said to be at secular equilibrium. What are the criteria for secular equilibrium and what does this mean if two isotopes are in secular equilibrium? Give one example from the isotopes in the U-Th decay chains. (10 pts)

b) The concept of secular equilibrium for isotopes from the U-Th series serves as a starting point for calculating useful geochemical rates. Give and explain an example that could be used to study gas exchange. (5 pts)

c) $^{210}$Po is a very toxic isotope (about 106 times more toxic than cyanide). The main hazard is its intense alpha radiation (half-life = 138 days) which, if ingested, does serious damage to internal tissues. Imagine that you are an undercover spy and you want to poison some critic of your government by slipping some $^{210}$Po into their margarita. The maximum safe body burden of $^{210}$Po is ~1000 Bq = 16.7 dpm. To make sure your deadly poison works you want to increase the body burden by >10 times to >167 dpm.

**Hint:** 1 Becquerel (Bq) = 1 dps = 0.016 dpm

i) Your chemical lab knows how to separate $^{210}$Po from $^{210}$Pb. You just have to get them the material. You have 200 dps of pure $^{210}$Pb. How long do you have to let the $^{210}$Pb decay so that you have almost 200 dps of $^{210}$Po? (10 pts)

ii) Your lab chemists do their job well and now you have a sugar cube containing 200 dps of $^{210}$Po. You get ready to meet your victim in a bar in Fremont but suddenly he is out of the country (gone to Britain) for 138 days. Finally you meet and while his back is turned you slip the sugar cube into his drink. Will your poison work?? (10 pts)
<table>
<thead>
<tr>
<th>Element</th>
<th>U-238 Series</th>
<th>Th-232 Series</th>
<th>U-235 Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neptunium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uranium</td>
<td>U-238</td>
<td>U-234</td>
<td>U-235</td>
</tr>
<tr>
<td></td>
<td>4.47 x 10^8</td>
<td>3.6 x 10^9</td>
<td>2.49 x 10^7</td>
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<tr>
<td>Protactinium</td>
<td>Pa-234</td>
<td></td>
<td>Pa-233</td>
</tr>
<tr>
<td></td>
<td>2.68 x 10^5</td>
<td></td>
<td>2.15 x 10^7</td>
</tr>
<tr>
<td>Thorium</td>
<td>Th-238</td>
<td>Th-230</td>
<td>Th-231</td>
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<tr>
<td></td>
<td>24.1</td>
<td>7.09 x 10^6</td>
<td>1.49 x 10^7</td>
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<td>Astatium</td>
<td>Fr-230</td>
<td>Ae-226</td>
<td>Ae-227</td>
</tr>
<tr>
<td></td>
<td>8.01</td>
<td>6.15</td>
<td>29.8</td>
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<td>Radon</td>
<td>Ra-226</td>
<td>Ra-228</td>
<td>Ra-223</td>
</tr>
<tr>
<td></td>
<td>1.82 x 10^5</td>
<td>1.73</td>
<td>11.4</td>
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<tr>
<td>Francium</td>
<td>Rn-222</td>
<td>Rn-220</td>
<td>Rn-219</td>
</tr>
<tr>
<td></td>
<td>2.83</td>
<td>55.2</td>
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<tr>
<td>Polonium</td>
<td>Po-210</td>
<td>Po-212</td>
<td>Po-218</td>
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<td></td>
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<td>22.3</td>
<td>24.1</td>
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<td>Tl-205</td>
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<tr>
<td></td>
<td>3.09</td>
<td></td>
<td>1.4</td>
</tr>
</tbody>
</table>
9) What controls the composition of seawater? Why is seawater salty? (15 pts)

10) **Sabine et al**
You measure a profile of DIC in the ocean. How can you distinguish anthropogenic DIC from DIC derived from other sources? What information do you need? (10 pts)
11) Anammox is one of the new and exciting areas of biogeochemical oceanography.

The half reactions for the reduction of $\text{NO}_3^-$ to $\text{N}_2$ and reduction of $\text{N}_2$ to $\text{NH}_4^+$ are given below.

a) Write a balanced reaction of $\text{NO}_3^-$ plus $\text{NH}_4^+$ to produce $\text{N}_2$ and give the equilibrium constant. (10 pts)

\[
\frac{1}{5} \text{NO}_3^- + \frac{6}{5} \text{H}^+ + \text{e}^- = \frac{1}{10} \text{N}_2(g) + \frac{3}{5} \text{H}_2\text{O} \quad \log K = +21.05
\]
\[
\frac{1}{6} \text{N}_2(g) + \frac{4}{3} \text{H}^+ + \text{e}^- = \frac{1}{3} \text{NH}_4^+ \quad \log K = +4.68
\]

b) Will anammox proceed if the concentrations of $\text{NO}_3^-$ = $10^{-6}$, $\text{NH}_4^+$ = $10^{-6}$ and $P_{\text{N}_2}$ = 0.8 atm? Use pH = 8.0 (10 pts)