Final Exam

1. Gas Exchange and Net Biological Production
During our recent cruise to the Santa Barbara Basin the surface O₂ was
300 µmol kg⁻¹ and it appeared to be at steady state. The water temperature was 25°C.

a) (10) What was the magnitude of the gas exchange flux of O₂ (in mol m⁻² s⁻¹) and which
direction did it go? Show all your work and explain your steps.

Important information:
assume 1 l = 1 kg
atmospheric P₀₂ = 0.20 atm
Henry's Law constant for O₂ in seawater at 25°C = 1.26 x 10⁻³ mol l⁻¹ atm⁻¹
molecular diffusion coefficient for O₂ at 25°C = 2.0 x 10⁻⁵ cm² sec⁻¹
the stagnant boundary layer thickness = 50 µm = 5 x 10⁻³ cm

b) (10) One student exclaimed "Hey, we can calculate the net biological productivity
from this flux". What do you think he had in mind? Show how you can do this and
calculate the net productivity in the units mmol C m⁻² d⁻¹. What assumptions do you
have to make to do this calculation?
2. **Carbonate Chemistry**

Assume surface seawater has an alkalinity of $2.0 \times 10^{-3}$ and a pH = 8.1. Assume there is no borate contribution to the alkalinity.

Assume $K_1' = 10^{-6.0}, K_2' = 10^{-9.1}$ and $K_{1H} = 10^{-1.5}$

a) (10) What is the total CO$_2$ (also called DIC or C$_T$)?

b) (10) What is the PCO$_2$?

c) (10) Is the PCO$_2$ in this water in equilibrium with the atmosphere?

(PCO$_2$ = 380ppm = 10$^{-3.420}$)
3. **Radioactive Decay**
   Tritium (³H₁) decays to helium (³He₂).

   a) (5) Is this an example of alpha or beta decay? Explain.

   b) (5) Can ³He ever be in secular equilibrium with ³H? Explain.
4. (5) Where would you expect to find the highest concentration of NO₃ in the ocean. Explain your answer and be as specific as possible.

5. (5) What is preformed NO₃? Where would you expect to find the highest concentrations of preformed NO₃ in seawater? Explain.

6. Which of the following is the essential approximation made when assuming an element is at steady state in the ocean (10 pts):
   a. ocean inputs from rivers equals the particle flux out of the euphotic zone
   b. the removal flux must be first order
   c. the concentration does not change with time
   d. the river input must equal the hydrothermal sink at mid-ocean ridges.

7. (10) For the reaction below:
   \[ \text{O}_2 + \text{CH}_2\text{O} = \text{CO}_2 + \text{H}_2\text{O} \]
   a) Which are the electron acceptors (there are two)? (5 points)
   b) Which are the electron donors (there are two)? (5 points)
8. **Oxidation-Reduction**

Sometimes different oxidation states of the same element can be both oxidants and reductants. In one case the oxidized form of sulfur (SO$_4^{2-}$) can react with the reduced form (H$_2$S) to form solid elemental sulfur (S$^\circ$). Such a reaction may occur at the oxic-anoxic interface in the Black Sea.

Here are two relevant half reactions:

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

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

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

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

d) Which way will this reaction proceed at the point of reaction in the Black Sea where pH = 7.5, SO$_4^{2-}$ = 17 mM, H$_2$S = 1 µM. (10 pts)
9. Carbonate Equilibria

Water has been discovered in the present polar ice cap regions of Mars. At some time in its early history Mars had a global ocean that averaged 30m deep. Most of the water has been lost due to hydrodynamic escape to space.

Data in Science (Krasnopolsky and Feldman, 2001, Science, 294, 1914-1917) suggests that the current total atmospheric pressure on Mars is 6 mbar (e.g. $6 \times 10^{-3}$ atm) and that the atmosphere is 95% CO$_2$ (N$_2$ is only 2.7%, O$_2$ is 0.13% and H$_2$O is variable).

It has been proposed that an iron carbonate phase called siderite (FeCO$_3$(s)) controls atmospheric CO$_2$ on Mars. The solubility of siderite can be written as:

$$\text{FeCO}_3(\text{s}) = \text{Fe}^{2+} + \text{CO}_3^{2-} \quad \log K = -10.4 \quad (1)$$

We also know the following reactions and apparent constants for sea water conditions.

$$\text{CO}_2(\text{g}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 \quad K'_1 = 10^{-1.5} \quad (2)$$
$$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^- \quad K'_1 = 10^{-6.0} \quad (3)$$
$$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \quad K'_2 = 10^{-10.1} \quad (4)$$

a) Write the siderite solubility reaction in terms of P$_{\text{CO}_2}$ and H$^+$ by combining reactions 1 to 4. (10 pts)

c) What is the value of the equilibrium constant for the reaction in part a, calculated from the equilibrium constants (1 to 4) given above? (5 pts)

d) Write the corresponding equilibrium constant expression in terms of P$_{\text{CO}_2}$, e.g. $K = ?$ (5 pts)

e) If pH = 7.0 and Fe$^{2+} = 10^{-3}$M in this Martian ocean, what value would you predict for atmospheric P$_{\text{CO}_2}$? (10 pts)
10. Many of the Lakes in New England have become acidified due to industrial emissions. The pH of one such lake is 5.2. In descending order of concentration, the inorganic carbon speciation in this lake would be (5 pts)

   a. $H_2CO_3, HCO_3^-, CO_3^{2-}$
   b. $HCO_3^-, CO_3^{2-}, H_2CO_3$
   c. $CO_3^{2-}, HCO_3^-, H_2CO_3$
   d. $HCO_3^-, H_2CO_3, CO_3^{2-}$

11. As a result of CaCO₃ precipitation (8 pts):

   a. $P_{CO_2}$ goes down
   b. pH goes up
   c. DIC goes down
   d. Alkalinity stays constant

12. Profiles of PO₄ and O₂ (8 pts):

   a. are mirror images of each other
   b. show that both are conservative in the deep ocean
   c. are both positively correlated with $\Sigma CO_2$
   d. are both highest in the deep Pacific
13. Box Models of Nitrogen Cycling

Nitrogen fixation has become the latest "hot topic". Let's assess its importance. A two-box ocean model for fixed nitrogen as nitrate. Include river inflow, atmospheric deposition of NO₃, nitrogen fixation, 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 x B.

From the literature we find some information that we may (or may not) need:
- Global denitrification = 175 TgN y⁻¹  \( f = 0.01 \)
- River Input = 76 TgN y⁻¹  \( \text{Area} = 3.61 \times 10^8 \text{km}^2 \)
- Atmospheric Deposition = 30 TgN y⁻¹
- Sediment Burial = 25 TgN y⁻¹
- Upwelling rate \( V = 300 \text{ cm y}^{-1} \)

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)

c) If the average concentration of nitrate in the deep box is \( C_D = 30 \mu\text{M} \), and the surface box is \( C_S = 0 \mu\text{M} \), what is the rate of nitrogen fixation required for a steady state balance? (10 pts)

d) What is its magnitude relative to river, atmospheric and upwelling input? (5 pts)
14. Speciation

Mg$^{2+}$ and SO$_4^{2-}$ are major ions in seawater. They react to form a neutral ion pair – MgSO$_4^o$. The Navy is very interested in this species as it is a major absorber of sound in the ocean. What is the concentration of MgSO$_4^o$ in seawater given the following? (10 pts)

**Set up the equations but don’t solve them!**

The reaction and equilibrium constant for formation of MgSO$_4^o$ are:

\[
\begin{align*}
\text{Mg}^{2+} + \text{SO}_4^{2-} &= \text{MgSO}_4^o & \log K &= 2.4 \\
\text{Mg}_T &= \text{Mg}^{2+} + \text{MgSO}_4^o &= 54 \times 10^{-3} \text{ M} \\
\text{SO}_4_T &= \text{SO}_4^{2-} + \text{MgSO}_4^o &= 28 \times 10^{-3} \text{ M}
\end{align*}
\]