CHEM 301
Assignment #3

Provide solutions to the following questions in a neat and well organized manner.
Clearly state assumptions and reference sources for any constants used.
Due date: November 22nd.
Attempt all questions. Only even numbers will be graded.

1. Calculate the mass of carbohydrate with the generic formula {$\mathbf{CH_2O}$} required to consume the dissolved oxygen from 1.0 L of water initially in equilibrium with the atmosphere at 12 ^oC, to hypoxic conditions (< 2.0 mg/L). Will your result change markedly using the formula for dissolved humic material (Fig 12.3, textbook)? Will a water sample with this mass of carbohydrate necessarily become hypoxic? What other factors influence the oxygen status of the water?

2. A water sample is known to have a pH of 8.44, calcium hardness of 165 ppm $\mathbf{CaCO_3}$ and a total alkalinity of 168 ppm as $\mathbf{CaCO_3}$.
a) Calculate the total inorganic carbon and report concentration of the carbonate ion [$\mathbf{CO_3^{2-}}$].
b) Calculate the pH at which this sample is saturated with respect to calcite and determine the saturation state with respect to calcite for this sample.
$K_{sp(calcite)} = 3.36 \times 10^{-9}$

3. Derive an expression for [$\mathbf{H^+}$] for a water sample in equilibrium with atmospheric carbon dioxide and lithospheric calcium carbonate in terms of the appropriate equilibrium constants and the partial pressure of $\mathbf{CO_2}$. Show your work and annotate your derivation indicating your what you are doing.

4. Methane and carbon dioxide are produced under anaerobic conditions by the fermentation of organic matter, approximated by the following equation

$$2\ \{\mathbf{CH_2O}\} \rightarrow \mathbf{CH_4} + \mathbf{CO_2}$$

As gas bubbles evolve at the sediment interface at a depth of 50 meters and remain in contact with water at the sediment surface long enough so that equilibrium is attained, calculate the aqueous molar concentration of methane in the interstitial sediment pore water. Assume a total pressure at this depth of 0.61 MPa and a temperature of 5^oC.

5. A pollutant is dumped into a clean lake at a constant rate starting on July 1, 2018. When the pollutant's concentration reaches 90% of its steady state value, the flow of pollutant is stopped. On what date will the concentration of pollutant fall to 1% of its maximum concentration? Assume the rate constants of the increase and decrease are both 0.35 $year^{-1}$.

6. A natural water from a northern Ontario bog with a pH = 6.15 has a TOC determined to be 7.5 mg/L of **C**. The charge imbalance [Σ(-ve) - Σ(+ve)] = 52 μmol/L. Estimate the concentration of DOM (mg/L) and the number of carboxyl groups per gram of DOM (μmol/g).

7. Calculate the percent of fulvic acid bound to calcium in a lake sample containing 36 mg/L of calcium and 12 μg/L of DOM (as fulvic acid). Use the conditional stability constants in Table 13.3 and assume $\mathbf{Ca^{2+}}$ is the only metal present in significant concentration and a pH of 5.

8. The stepwise formation constants for $\mathbf{Pb(OH)^+}$ and $\mathbf{PbCO_3}$ are given below. For a solution containing 10^{-6} M $\mathbf{Pb}_T$, calculate the pH of the speciation boundary between $\mathbf{Pb^{2+}}$ and

a) $\mathbf{PbOH^+}$ in pure water

b) $\mathbf{PbCO_3}$ for a solution containing 10^{-3} M $\mathbf{CO_3^{2-}}_T$

$\mathbf{Pb^{2+}} + \mathbf{OH^-} \;===\; \mathbf{Pb(OH)^+}$ $\quad K_{fl} = 2.0 \times 10^6$

$\mathbf{Pb^{2+}} + \mathbf{CO_3^{2-}} \;===\; \mathbf{PbCO_3}(s)$ $\quad K_f = 1.3 \times 10^{13}$

9. Using the CO2Sys_v2.3 software, calculate the pH, the P_{CO2} , inorganic carbon concentrations, and the aragonite saturation (Ω_{Ar}) at output conditions of 4 ^oC, total pressure of 1000 dbars of pressure (~1000 m depth), for a water sample with a measured total alkalinity of 1400 umol/kg(sw), and total carbonate of 1275 umol/kg(sw) at input conditions of 20 ^oC, 0 dbar pressure (surface), 0.3 umol/kg(sw) total P and 1 umol/kg(sw) Si, and a salinity of 30. Use this program to estimate the saturation horizon depth under these conditions. Specify the choice of constants used and any other assumptions.
http://cdiac.ess-dive.lbl.gov/ftp/oceans/co2sys/CO2SYS_calc_XLS_v2.3/

10. Determine the fraction of $\mathbf{Zn^{2+}}$ and T^{3-} (from nitrilotriacetate) in water at pH 8.50 from the corresponding acid dissociation constants. Estimate the ratio of Zn-complexed NTA to total NTA in a wastewater sample with a total NTA concentration of 100. μg L^{-1} containing 2.0 ppm of zinc.

$$\log K_f\,(\mathbf{ZnT^-}) = 10.66$$