CHEM 301
Assignment #3

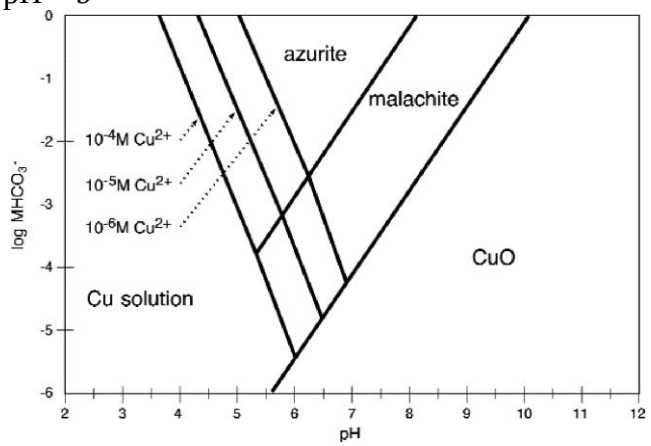
Provide solutions to the following questions in a neat and organized manner.
Clearly state assumptions and reference sources for any constants used.
Due date: November 15th.
Only even numbered questions will be assessed.

1. The diagram below depicts the dominant chemical speciation for **Cu**(II) as a function of log [$\mathbf{HCO_3^-}$] (M) and pH. *Note*: 'azurite' = $\mathbf{Cu_3(CO_3)_2(OH)_{2\,(s)}}$ and 'malachite' = $\mathbf{Cu_2CO_3(OH)_{2\,(s)}}$.

a) Predict the dominant form of **Cu**(II) in seawater.

b) Explain why the $\mathbf{Cu^{2+}}$/azurite boundary depends on the copper ion concentration.

c) Derive an expression for the log [$\mathbf{HCO_3^-}$] as a function of pH in the form of
log [$\mathbf{HCO_3^-}$] = *m* pH + *b*



2. A water sample has calcium hardness of 65.0 ppm $\mathbf{CaCO_3}$ and a total alkalinity of 120. ppm $\mathbf{CaCO_3}$. Calculate the pH at which the sample is saturated with respect to calcite ($K_{sp(calcite)} = 3.36 \times 10^{-9}$).

3. The effect of increasing atmospheric concentrations on the aqueous solubility of calcite and aragonite forms of calcium carbonate have significant environmental consequence. The saturation index is defined as the ratio of the actual solubility product activities over those at equilibrium as follows.

$$\mathbf{\Omega = Q_{sp}/K_{sp}}$$

a) What does it mean if $\Omega < 1$?

b) Which mineral form calcite or aragonite is more susceptible to aqueous dissolution and why?

c) Use the formulas derived in class for the $\mathbf{CO_2\text{-}CaCO_3\text{-}H_2O}$ system (or the *PHREEQC* program described on pg261 of your textbook) to calculate the solubility of $\mathbf{CaCO_3}$ at pre-industrial $\mathbf{CO_2}$ levels of 280 ppm_v versus present day levels of 400 ppm_v.

4. Methyl-t-butyl ether (MTBE) is a common gasoline additive used to improve the combustion characteristics. Careless use over the years has resulted in groundwater contamination. Using a reported value for K_H of MTBE of 5.8×10^{-4} atm m^3 mol^{-1}, calculate the partial pressure of MTBE in adjacent air-filled pores in the soil if the groundwater contains 175 ppm of MTBE.

5. Using the pK_a values below for the aluminum aquo complexes, plot a pH speciation diagram for the $\mathbf{Al^{3+}}$ **-** $\mathbf{Al(OH)^{2+}}$ **-** $\mathbf{Al(OH)_2^{+}}$ **-** $\mathbf{Al(OH)_3}$ **–** $\mathbf{Al(OH)_4^{-}}$ system over the pH range of 0 to 14, using Excel for repetitive calculations. Calculate the fractional abundance of aluminum species at pH 5?

$pK_{a1} = 5.00$ $pK_{a2} = 5.10$ $pK_{a3} = 6.80$ $pK_{a4} = 5.80$

6. A pollutant is dumped into a clean lake at a constant rate starting on July 1, 2000. 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 $year^{-1}$.

7. Consider dissolved organic matter to have a generic formula {$\mathbf{CH_2O}$}. For a water body containing 1.0 mg/L of DOC, calculate the mass in mg of dissolved oxygen in the same volume of water required to oxidize it completely. Use this calculation to establish a numerical relationship between COD and DOC. Will your result change markedly using the generic formula for dissolved humic material (Fig 12.3, textbook)?

8. Given the equilbria below, what fraction of lead species is present as $\mathbf{Pb^{2+}}$ at pH 7.

$\mathbf{Pb^{2+}} + \mathbf{OH^{-}} \text{ ====== } \mathbf{PbOH^{+}}$ $K = 2.0 \times 10^6$

$\mathbf{PbOH^{+}} + \mathbf{OH^{-}} \text{ ====== } \mathbf{Pb(OH)_2}$ $K = 4.0 \times 10^4$

9. What fraction of NTA is uncomplexed after $\mathbf{H_2T^{-}}$ has been brought to equilibrium with solid $\mathbf{PbCO_3}$ at pH 7 in aqueous solution with $[\mathbf{HCO_3^{-}}] = 1.25 \times 10^{-3}$ M.

$\mathbf{PbCO_3(s)} + \mathbf{HT^{2-}} \text{ ====== } \mathbf{PbT^{-}} + \mathbf{HCO_3^{-}}$

$\log K_{sp}$ ($\mathbf{PbCO_3}$) = -13.13 $\log K_f$ ($\mathbf{PbT^{-}}$) = 11.34

10. A woodwaste leachate sample has a **Fe**(II) concentration of 20 mg/L and a dissolved organic matter concentration of 50 mg/L. Using a typical value for the concentration of carboxylate ions of per gram of DOM given in the textbook and the conditional formation constant between $\mathbf{Fe^{2+}}$ and fulvic acid of 5×10^3 at pH 5, calculate the fraction of iron (II) complexed to the dissolved organic matter at pH 5. How would you expect your answer to change if the actual pH of the leachate were 7 rather than 5? Explain.