CHEM 301
Assignment #2
Provide solutions to the following questions in a neat and well-organized manner.
Reference data sources for any constants and state assumptions, if any.
Due date: Thursday, Oct 20th, 2016
Attempt all questions. Only even numbers will be assessed.

1. A pond in an area affected by acid mine drainage is observed to have freshly precipitated **Fe(OH)$_3$**(s) at pH 4. What is the minimum value of pe in this water? Use the appropriate pe-pH speciation diagram to predict the dominant chemical speciation of carbon, sulfur and copper under these conditions.

2. The solubility of **FeS**(s) in marine sediments is expected to be affected by the pH and the [**H$_2$S**(aq)] in the surrounding pore water? Calculate the equilibrium concentration of **Fe^{2+}** (ppb) at pH 5 and pH 8, assuming the **H$_2$S** is 1.0×10^{-3} M.
pK_{sp}(**FeS**) = 16.84.

$$\textbf{FeS}(s) \quad + \quad 2\,\textbf{H}^+(aq) \quad ==== \quad \textbf{Fe}^{2+}(aq) \quad + \quad \textbf{H}_2\textbf{S}$$
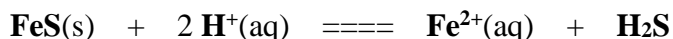
3. Boric acid is a triprotic acid (**H$_3$BO$_3$**); pK_{a1} = 9.24, pK_{a2} = 12.74 and pK_{a3} = 13.80.
   a) Derive an expression for the fractional abundance of **H$_3$BO$_3$** as a function of pH
   b) Construct a fully labeled pH speciation diagram for boric acid over the pH range of 0 to 14 using Excel spreadsheet at a 0.2 pH unit interval.

4. At p**Cl$^-$** = 2.0, **Cd^{2+}** and **CdCl$^+$** are the only dominant cadmium chloride species with a 50% fractional abundance of each.
a) Calculate the equilibrium constant for the formation of **CdCl$^+$** (β_1).
b) Derive an expression for the fractional abundance of **CdCl$^+$** as a function of [**Cl$^-$**] and $\beta_1 - \beta_4$ for cadmium chloro species.
c) Calculate the fractional abundance of **CdCl$^+$** species at [**Cl$^-$**]$_{seawater}$.

5. To measure the volume of a small lake, you add 5.0L of a 2.0M solution of a non-toxic dye which degrades by first order processes with a half-life of 3.0 days. After one week, in which the lake becomes well mixed, you take a 100. mL lake sample. The dye concentration in this sample is 2.9×10^{-6} M. Estimate the lake volume.

6. Lime (calcium hydroxide) is sometimes added to wastewater to reduce the phosphate concentration to acceptable levels. In a pilot study, 10.0 g of **Ca(OH)$_2$** was dissolved in a 100. L distilled water. Calculate the maximum total phosphate concentration [**PO$_4^{3-}$**]$_T$ that this test solution could contain assuming that the concentration of **PO$_4^{3-}$** is controlled by precipitation of calcium phosphate, $K_{sp} = 1.3 \times 10^{-32}$.

7. Water from the hypolimion of Maynard Lake has a measured pH of 5.81 and an ORP = -290 mV using an ORP probe with an internal silver/silver chloride reference electrode. Standard E_h values are referenced to a standard saturated hydrogen electrode (SHE). Look up the standard reduction potential for the **AgCl**(s) + e- → **Ag**(s) + **Cl⁻** half reaction and correct the field ORP reading to E_h (mV).
   a) Report the pe value of the sample.
   b) Predict the dominant forms of chromium, iron and selenium using the appropriate Eh-pH (Pourbaix) diagrams (attached).


8. a) Calculate the p*e* of air saturated surface water at pH 8.1 in redox equilibrium with a dry atmosphere at sea level.
b) A solution at pH = 7.0 contains **Mn²⁺** at an activity of 10^{-5}, as well as some **MnO₂**(s). The redox half-cell reaction for the **MnO₂**(s)/ **Mn²⁺** reaction is shown below. What is the pe of the solution, assuming the system is at redox equilibrium?

$$\text{MnO}_2(s) \;+\; 4\,\text{H}^+ \;+\; 2\,e^- \;\longrightarrow\; \text{Mn}^{2+} \;+\; 2\,\text{H}_2\text{O} \qquad pe^\circ = 20.8$$

c) Determine the p*e* of redox boundary between **Fe(OH)₃/Fe²⁺** as a function of pH at 25°C and a total $C_{Fe} = 0.010$ mM.

9. The potentially fatal effects of acute arsenic exposure are well known, but in recent years the effects of long term low level (chronic) exposures has been hotly debated. As a consequence, the US EPA has recommended lowering the maximum contaminant level (MCL) from 50 ppb As to 5 ppb. Arsenic occurs naturally in two oxidation states: **As** (III) and **As** (V). It is acidic in both oxidation states, but much more so as **As**(V), in which case it is chemically similar to phosphoric acid [i.e., **P**(V)]. The pK_a values of arsenous acid, **H₃AsO₃** and arsenic acid, **H₃AsO₄** are shown below and indicate that most of the **H₃AsO₃** remains fully protonated at pH 7, whereas **H₃AsO₄** is extensively deprotonated. Because of this difference in ionic charge on the dominant species, it is easier to remove **As** (V) than **As** (III) from solution by adsorption and ion-exchange processes that might be employed at a water treatment plant.

$$\text{AsO}_4^{3-} \;+\; 2\,\text{H}^+ \;+\; 2\,e^- \;\rightarrow\; \text{AsO}_3^{3-} \;+\; \text{H}_2\text{O} \qquad pe^\circ = 2.64$$
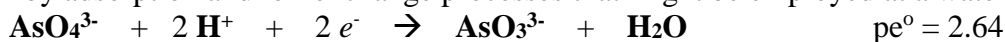
	pK_{a1}	pK_{a2}	pK_{a3}
H₃AsO₃	9.23	12.10	13.41
H₃AsO₄	2.24	6.76	11.60

Workers at a water treatment plant want to ensure that > 99% of the total arsenic $[As]_T$ in the water is in the oxidized form prior to feeding it to an ion-exchange process. If the pH of the water is 7.6, what is the minimum p*e* required for the treatment process to work?

10. A pollutant enters a thermally stratified lake by two distinct pathways. A river delivers the pollutant into the epilimnion at a rate of 35 kg/yr, whereas groundwater seepage delivers the pollutant to the hypoliminion at 4 kg/yr. Because of sedimentation, the residence time of the pollutant in the lower layer is 1.5 yrs. The average concentration in the whole lake is 80 ng/L, the total volume is 10^9 m³ and everything is at steady state.
a) Draw a diagram of the system illustrating stocks and fluxes, where possible.
b) What is the total amount of pollutant in the lake?
c) Set up equations relating stocks, flows and residence times.
d) Solve for the residence time of the pollutant in the epilimnion (upper layer)?