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: Tuesday, Oct 18th, 2018

1. Hydrogen sulfide (**H$_2$S**) is considerably more toxic to fish than either **HS$^-$** or **S^{2-}**. If hydrogen sulfide concentrations greater than 0.15 mg/L (as **S**) are harmful to fish health, calculate the minimum safe pH, if the total sulfide concentration is determined to be 20 μM.

2. Phosphoric acid is a triprotic acid (**H$_3$PO$_4$**); pK$_{a1}$ = 2.15, pK$_{a2}$ = 7.20 & pK$_{a3}$ = 12.38. What is the molar concentration of the **PO$_4$$^{3-}$** ion if the total orthophosphate ([**PO$_4$$^{3-}$**]$_T$) concentration is reported to be 10. mg/L of **PO$_4$$^{3-}$ -P**? at a pH of 9.50.

3. A small pond in an area affected by acid mine drainage is observed to have freshly precipitated **Fe(OH)$_3$**(s) at pH 4.
a) What is the chemical relationship between **Fe(OH)$_3$**, **FeO(OH)** and **Fe$_2$O$_3$**?
b) An ORP measurement of 190 mV (versus an internal silver/silver chloride reference electrode) was recorded. Is this consistent with the p*e* of air saturated surface water at this pH in redox equilibrium with the atmosphere?
c) Predict the dominant chemical speciation of carbon, sulfur and nitrogen under these conditions. Justify your answer.
d) What additional information would be useful in choosing the appropriate pe-pH (Pourbaix) diagram for copper, lead and zinc?

4. A treated wastewater sample has been analyzed to contain the following species.
[**HCN**]$_T$ = 2.0 x 10^{-5} M
[**NH$_3$**]$_T$ = 7.9 x 10^{-4} M
Using the corresponding pK$_a$ values, sketch a plot of log Conc (M) vs pH for the relevant chemical speciation (protonation states) between pH 4 and 10. Compare this with an overlay plot constructed using Excel.

5. A speciation diagram for thallium (III) as a function of pH and chloride concentration is attached. Estimate the value of the formation constants (β$_1$ – β$_4$) and the acidity constants (K$_{a1}$-K$_{a4}$). Justify your answers.

6. Determine the concentration of cadmium ion in equilibrium with cadmium carbonate in a water sample buffered at a pH of 8.10 with a total alkalinity of 32 mg/L as $CaCO_3$. The pK_{sp} of $CdCO_3$ is 13.74.

7. Lake Phillip is well mixed and has a volume of 10^8 m^3. A single river flowing at 5 x 10^5 m^3 day^{-1} feeds it. Water exits Lake Phillip via the Andrew River and evaporation is negligible. For several years, a local industry has been dumping 40 kg day^{-1} of a pollutant DCTA into the lake. DCTA disappears from the lake via two processes: it flows out of the lake in the Andrew River and it chemically degrades with a half-life of 48 days. What is the steady state concentration of DCTA in Lake Phillip?

8. For each of the following, derive an equation of the line for the redox boundary in the form of pe = m pH + b (See further Appendix B.4 and B.5 of the textbook).
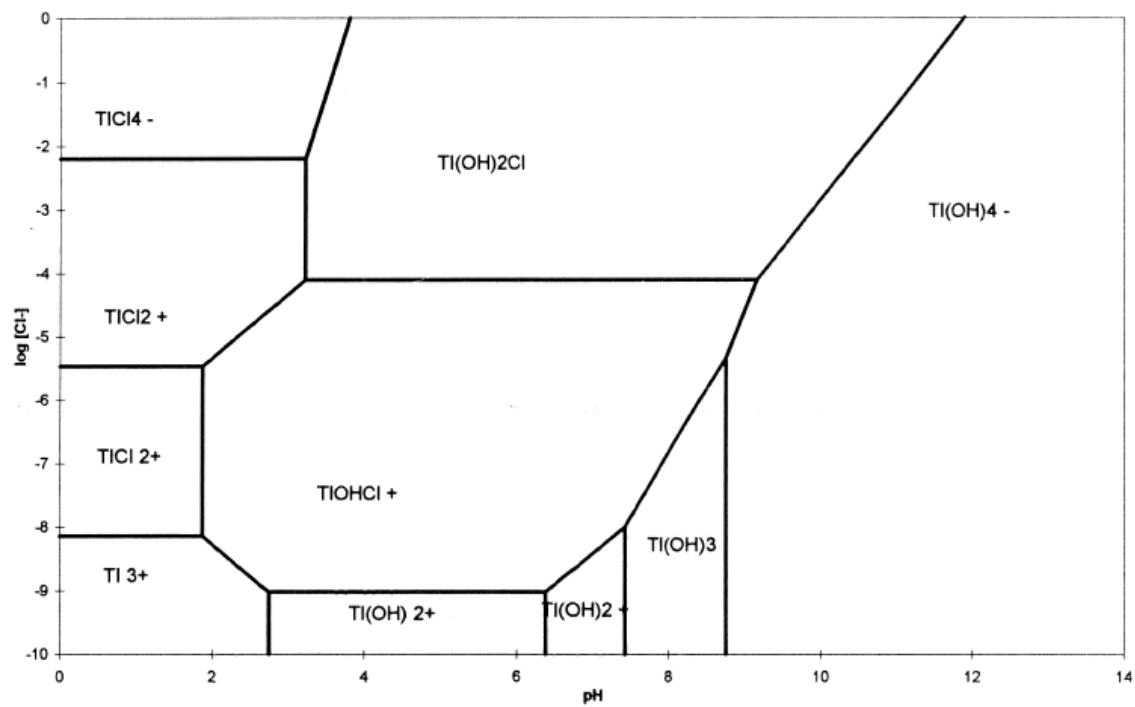a) CO_2 and $\{CH_2O\}$
b) SO_4^{2-} and H_2S
c) $HOCl$ and Cl^-
d) MnO_2(s) and Mn^{2+} in a solution containing manganese (II) ion at an activity of 10^{-5}

9. A water sample with a pH 6.0 was analyzed and found to contain 0.5 mmol/L nitrate ion and 5 µmol/L of ammonium ion. Calculate the pe of this water and predict the ratio of $[Cr_2O_7^{2-}]$ to $[Cr^{3+}]$ in the same sample.

Chemical speciation diagram for Thallium (III) species as a function of pH and pChloride.