CHEM 301
Assignment #1

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, Sept 29th, 2016
Attempt all questions.

1. In an effort to relate some fundamental concepts in aquatic chemistry to your local politician, you realize that you need to use an appropriate analogy. Given that a typical Olympic sized swimming pool holds 2500 m^3 of water, answer each of the following, showing your work and stating any assumptions;
a) The number of teaspoons of a water soluble pollutant it take to contaminate a pool to a level of 10 pptr.
b) The number of days required to flush this pollutant to a concentration of 5 pptr with a garden hose (at 25 liters per minute).

2. Refer to speciation diagrams (Figures 1.2 and 1.3, textbook) to answer each of the following.
a) Estimate the concentration of individual inorganic carbon species at pH 6.8, if the total carbonate concentration, $[\mathbf{CO_3^{2-}}]_T$ = 4.2 mM. Confirm these estimates using the acid dissociation constants for carbonic acid.
b) Estimate the fraction of mercury (II) present as $\mathbf{HgCl_3^-}$ in estuarine water (density = 1.02 g/mL) containing 3550 ppm chloride.

3. The hydroxides, carbonates and sulfides of most metals are insoluble and less likely to be mobile in the aquatic environment. Write chemical equations to describe/explain how the aqueous solubility of the following cadmium compounds will be affected;
a) the influence of pH on $\mathbf{Cd(OH)_2}$ mobility
b) the influence of pe on **CdS** mobility

4. The concentrations of the major ions (ppm) in San Pellegrino Natural Mineral Water (Case Study #1, Friday, Sept 16th) are given below. Use this information to calculate each of the following;

$\mathbf{SO_4^{2-}}$	$\mathbf{HCO_3^-}$	$\mathbf{Ca^{2+}}$	$\mathbf{Cl^-}$	$\mathbf{Mg^{2+}}$	$\mathbf{Na^+}$	$\mathbf{NO_3^-(N)}$	$\mathbf{K^+}$	$\mathbf{F^-}$
430	245	170	52.0	51.4	33.3	2.6	2.2	0.5

a) The charge balance and express as the % error = (difference/sum)*100.
b) The total dissolved solids (TDS) and the temporary hardness (ppm $\mathbf{CaCO_3}$).
c) The ionic strength (molar) and use this to estimate the activity coefficients of the most dominant cation and anion, using the appropriate model.

5. Using the appropriate equilibrium constant/s,
a) Sketch a labeled pH speciation diagram for hydrogen sulfide.
b) Calculate the fraction of $\mathbf{H_2S}$ present in a water sample at pH 8.20.
c) Calculate the molar concentration of sulfide ion ($\mathbf{S^{2-}}$), if the total reduced [**S**(-II)]T concentration has been determined to be 2.00 ppm in freshwater.
d) Calculate the concentration in ppm of sulphate ion, if this water were to become oxic (high pe).

6. A non-volatile water soluble dye is released to a lake at a rate of 6.0 kg per day. The lake has a volume of 2.8×10^6 m^3 and the average flow rate of the river feeding the lake is 6.9×10^3 m^3/day. The lake is well mixed and 10% of the lake water is lost through evaporation.

a) Draw a diagram of the system illustrating stocks and fluxes, where possible.

b) What is the *steady state* concentration of the dye in the lake?

7. In temperate regions, lake sediments often show stratified layers that vary with season - dominated by the presence of lighter coloured metal carbonates in summer and darker metal sulfides in winter. Explain using the expected seasonal changes in pH and pe. *You may find it useful to refer to the pe-pH diagrams for aqueous carbon and sulfur species.*

8. One of the parameters used to characterize water supplies to discriminate between water influenced by sea-salt ($\mathbf{Na^+}$ dominant), chemical weathering (dissolution of minerals, $\mathbf{Ca^{2+}}$ dominant) and evaporation is the weight ration of $\mathbf{Na^+}/(\mathbf{Na^+} + \mathbf{Ca^{2+}})$. Calculate the Na/Na+Ca weight ratio and the TDS for the four major rivers listed below. Plot Na/Na+Ca ($0 \rightarrow 1$) on the x-axis versus the log TDS (mg/L) on the y-axis and compare it to a similar plot appearing in *Science* **170**, 1088-1090. Characterize each of these river waters as being dominated by rainfall, chemical weathering or evaporation. (See further *An Introduction to Environmental Chemistry* (2nd Ed) by J.E. Andrews et al., Blackwell Pubs, 2004 pp.145 – 151.)

Major dissolved ion composition (mmol L^{-1}) of major rivers.

	MacKenzie (1)	**Orinoco** (2)	**Ganges** (3)	**Rio Grande** (4)
$\mathbf{Ca^{2+}}$	0.82	0.08	0.61	2.72
$\mathbf{Mg^{2+}}$	0.43	0.04	0.20	0.99
$\mathbf{Na^+}$	0.30	0.06	0.21	5.10
$\mathbf{K^+}$	0.02	0.02	0.08	0.17
$\mathbf{Cl^-}$	0.25	0.08	0.09	4.82
$\mathbf{SO_4^{2-}}$	0.38	0.03	0.09	2.48
$\mathbf{HCO_3^-}$	1.82	0.18	1.72	3.00
$\mathbf{SiO_2}$	0.05	0.19	0.21	0.50

(1) northern arctic Canada; (2) tropical northern South America; (3) southern Himalayas; (4) arid southwestern N.America

9. In a police report last summer, it was revealed that approximately 400 L of alcoholic beverages were dumped into Cowichan river. Assuming an average ethanol content of 6% (v/v), estimate the mass of dissolved oxygen that would be consumed during biodegradation. How many cubic meters of river water originally containing 10. mg $\mathbf{O_2}$/L would be completely depleted of $\mathbf{O_2}$? What factors would mitigate the loss of dissolved oxygen? Would you expect such an incident to have a greater or lesser impact in warmer waters? Explain.

10. In seawater the ions $\mathbf{CO_3^{2-}}$ and $\mathbf{HCO_3^-}$ are present in concentrations of 0.27mM and 2.3 mM, respectively. However, in seawater the most of the carbonate ions are *complexed*, such that only 10% are 'free' in solution. Similarly, 75% of the hydrogen carbonate ions are 'free' in seawater. Furthermore, the *activity coefficients* of $\mathbf{CO_3^{2-}}$ and $\mathbf{HCO_3^-}$ are 0.20 and 0.60, respectively. Use K_a for $\mathbf{HCO_3^-}$ as 3.7×10^{-11}.

a) Calculate the pH of seawater based on the molar concentrations of $\mathbf{CO_3^{2-}}$ and $\mathbf{HCO_3^-}$.

b) Repeat taking into account the effect of complexation and activity coefficients.

c) How do your results compare to the observed global average pH of seawater?