CHEM 301
Assignment #4

Provide solutions to the following questions in a neat and organized manner.
Clearly state assumptions and reference sources for any constants or data used.
Due date: December 6^{th}.
Only even numbered questions will be assessed.

1. Using information provided in your textbook, calculate the value of the pe and pH for the 'triple point' between $HOCl/OCl^-/Cl^-$. Is hypochlorous acid thermodynamically stable at ambient conditions in freshwaters?

2. A drinking water treatment facility uses a one million liter flow through chlorination tank and requires a 30 min contact time (residence time) for dis-infection.
a) How many liters of water can be treated per hr using this system?
b) How much chlorine (mass in kg as Cl_2) will be used in one day, if the source water has a chlorine demand of 0.40 ppm and the finished water is to have a chlorine residual of 1.0 ppm?

3. Lead solder on copper plumbing has been suggested as a possible source of low levels of lead (II) ions in drinking water. Using the standard reduction tables and the Nernst equation, comment on the possibility of Pb^{2+} being present at or above the MAC of 10. ppb, if the water in contact with **Pb**(s) contains Cu^{2+} at 0.10 ppm (*ignore* Cu^+ *ions*).

4. Filter alum $Al_2(SO_4)_3$ is often used to remove phosphate from wastewater. A wastewater with a pH = 5.62 containing 25 ppm total phosphate is treated with alum until the equilibrium concentration of Al^{3+} is 4.0×10^{-9} mol L^{-1}. What fraction of the total phosphate is precipitated as $AlPO_4$(s)? Consider that the phosphate ion concentration is controlled by the precipitation of aluminum phosphate ($K_{sp} = 1.0 \times 10^{-21}$) and ignore the precipitation of $Al(OH_3)$.

5. The Langelier index (LI) uses the difference between the actual pH of a solution and the calculated pH of a saturated solution to predict whether or not calcite scale ($CaCO_3$(s)) will form, where LI = $pH_{actual} - pH_{saturated}$
If LI > 0, then water is supersaturated and calcite precipitation occurs. A water supply has the following reported water quality parameters. Predict the potential for scale formation based on the temperature dependence of K_{sp} (calcite) and K_{a2} (carbonic acid) given by the following empirical temperature regressions (Kelvin).

Temperature = 8 ^oC	pH = 7.89
Calcium Hardness = 178 ppm $CaCO_3$	Total Alkalinity = 120 ppm $CaCO_3$

$\log K_{sp} = -171.9065 - 0.077993(T) + 2839.32(T)^{-1} + 71.595 (\log T)$
$\log K_{a2} = -107.887 - 0.0325285(T) + 5151.79(T)^{-1} + 38.9256 (\log T) - 563713.9 (T)^{-2}$

6. One of the concerns of chlorine based dis-infection is the inadvertent oxidation of iodide to *active* iodine (and hypoiodous acid) and the subsequent reaction with dissolved organic carbon to form genotoxic iodinated dis-infection by-products. It turns out that under most natural water conditions chlorine will oxidize iodide ion to the less reactive iodate ion. However, chloramines (which are less powerful oxidants) have employed in place of chlorine (because of concerns over trichloromethane formation) will oxidize iodide ion to *active* iodine, which subsequently reacts with water to form hypoiodous acid. This active form of iodine has been observed to react further with DOC to yield iodinated trihalomethanes and haloacetic acids.
a) Use the standard reduction potentials of $\mathbf{Cl_2}$ and $\mathbf{IO_3^-}$ to confirm that the oxidation of iodide ion to iodate is spontaneous under standard conditions.
b) Write a series of chemical reactions that outline the formation of an iodinated DBP when a natural water supply containing iodide ion and DOC is treated with chloroamine.
(See further S. Krasner, The formation and control of emerging disinfection by-products of health concern, Phil. Trans. R. Soc. A (2009) 367, 4077–4095. doi:10.1098/rsta.2009.0108)

7. Calculate the maximum theoretical removal of copper from a leachate containing 145 ppm of $\mathbf{Cu^{2+}}$ with the use of zero valent iron by the 'cementation' reaction if cupric ion is the only cation present. Does your result change if the solution contains 350 ppm of $\mathbf{Fe^{2+}}$.

$$\mathbf{Cu^{2+}}(aq) \quad + \quad \mathbf{Fe}(s) \quad ==== \quad \mathbf{Cu}(s) \quad + \quad \mathbf{Fe^{2+}}(aq)$$

8. Gold ores are frequently leached with cyanide dissolving the gold according to;

$$\mathbf{Au}(s) \;+\; 2\,\mathbf{CN^-} \;+\; \tfrac{1}{4}\,\mathbf{O_2}(g) \;+\; \tfrac{1}{2}\,\mathbf{H_2O}(l) \quad ===== \quad \mathbf{Au(CN)_2^-}(aq) \;+\; \mathbf{OH^-}(aq)$$

Which has an equilibrium constant, $K = 1.2 \times 10^{17}$. In order to prevent undue environmental contamination by cyanide, you wish to operate this process under conditions such that at least 98% of the $\mathbf{CN^-}$ is converted to $\mathbf{Au(CN)_2^-}$. Your process operates at a pH 9.0 and the $\mathbf{O_2}$ pressure inside the ore body is constant at 0.032 atm. Calculate the molar concentration of $\mathbf{CN^-}$ required.

9. Iron can occur as a carbonate mineral $\mathbf{FeCO_3}$, which has a $K_{sp} = 3.1 \times 10^{-11}$. Calculate the concentration of $\mathbf{Fe^{2+}}$ (ppm) in a groundwater in equilibrium with iron (II) carbonate, given that the concentration of calcium ion in equilibrium with solid calcium carbonate ($K_{sp} = 6.0 \times 10^{-9}$) is 120 ppm.

10. A sewage treatment plant is designed to process 3.0×10^{12} L of wastewater daily.
a) What capacity (m^3) is required for the primary settling lagoon if the residence time is to be 6 hours?
b) If the influent water has a BOD of 850 ppm, what volume (m^3) of air at 15ºC is required per hour to provide the oxygen to reduce the BOD by 90%.