## CEE 543 Aut 2012 HW\#6

1. a. How much does the alkalinity of a water sample change upon addition of $10^{-4} \mathrm{M}$ of the following chemicals? Assume alkalinity is determined by titration to pH 4.7 , that the solutions are ideal, and that the water is initially at pH 7.5 due to the presence of an unknown mixture of weak acids and bases. Briefly explain your reasoning.

> i. HCl
> ii. NaOH
> iii. $\mathrm{Na}_{2} \mathrm{CO}_{3}$
> iv. $\mathrm{NaHCO}_{3}$
> v. $\mathrm{CO}_{2}$
> vi. $\mathrm{NaH}_{2} \mathrm{Cit}$
b. How would your answers to part $a$ be different if the solutions were initially at pH 8.5 ? You need not do any calculations; just explain the reasoning that leads you to conclude whether the change in the alkalinity would be larger, smaller, or the same. (Hint: you only need to give one explanation, because the answer is the same for all six additives.)
2. Two waters at $25^{\circ} \mathrm{C}$ are in equilibrium with air, one at pH 9.5 and one at pH 7.3 . These waters are mixed in proportions ranging from $0.1: 1$ to $10: 1$. Assuming that carbonate species dominate the acid/base behavior of both solutions and that no gas transfer occurs when they are mixed, determine the alkalinity and pH of the mixture as a function of the mixing ratio. For each ratio considered, determine whether the mixture will be undersaturated, supersaturated, or in equilibrium with atmospheric $\mathrm{CO}_{2}$. For the $1: 1$ mixture, how much $\mathrm{CO}_{2}$ will dissolve into or volatilize out of solution? Express your answer in moles $\mathrm{CO}_{2}$ per liter of solution.
3. The raw water supply for a community is at pH 7.5 and has $\mathrm{Alk}=40 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$. Essentially all the alkalinity is attributable to the carbonate acid/base system. The water is treated by addition of alum, causing $\mathrm{Al}(\mathrm{OH})_{3}(\mathrm{~s})$ to precipitate and aiding in the removal of colloidal matter from suspension. The precipitation of the alum generates acid by the reaction shown below:

$$
\mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3} \bullet 14 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{Al}(\mathrm{OH})_{3}(\mathrm{~s})+3 \mathrm{SO}_{4}^{2-}+6 \mathrm{H}^{+}+8 \mathrm{H}_{2} \mathrm{O}
$$

(a) Prepare a titration curve showing the pH as a function of alum added, for alum additions of 0 to $200 \mathrm{mg} / \mathrm{L}$.
(b) It is determined that the optimal alum dose for coagulation is $60 \mathrm{mg} / \mathrm{L}$. In addition, to minimize corrosion, it is desired to maintain $\mathrm{pH} \geq 6.5$ in the treated water. Will chemical (base) addition be necessary when the alum is added? If so, how much? Assume that gas exchange during the various treatment steps is slow enough that the solution can be treated as a closed system.
(c) If no base is added to the solution, will it be possible to reach the target pH by bubbling the treated water with air? How much $\mathrm{CO}_{2}$ must be stripped out of solution to reach the
target pH ? (Hint: recall what happens to alkalinity when $\mathrm{CO}_{2}$ is added to or removed from a solution.)

