CEE 543 Autumn 2007 Final Exam

Assume all solutes behave ideally unless the problem statement indicates otherwise. Some atomic weights that might be useful are provided below. Equilibrium constants that might be useful are included in the problem statements. Total points: 200.

Atomic Wt: H=1, C=12; O=16, F=19; Al-27; S=32; Ca=40; Zn=65

1. A solution at pH 7.5 contains 2×10^{-3} *M TOT*Ac, essentially all of which is consumed in a biological treatment process according to the following reaction:

$$C_2H_3O_2^- + 2O_2 \rightarrow 2\,HCO_3^- + H^+$$

Note that the right side of the reaction could also be written as $HCO_3^- + H_2CO_3$. pK_a for HAc is 4.76, and for H_2CO_3, p$K_{a1} = 6.35$ and p$K_{a2} = 10.33$.

(a) Determine the change in Alkalinity, if any, that occurs when the acetate undergoes the reaction shown. Express your answer in mg/L as $CaCO_3$. To simplify the calculations, assume that the solution is ideal and that the endpoint of the alkalinity titration is at pH 4.76.

(b) Consider a solution in which the ionic strength is high enough to cause the activity coefficient for species with charge of ±1 to be 0.7. What is the distribution of *TOT*Ac in the original solution between HAc and Ac^- at the endpoint of the alkalinity titration under these conditions?

(c) How would your answer to part *a* change, if at all, if the reaction occurred in the solution described in part *b*? Assume that carbonate is present entirely as H_2CO_3 at the titration endpoint, regardless of the ionic strength. Note that pH is defined as $-\log a_{H^+}$.

Answer. (a) The biological reaction destroys acetate and generates carbonate species. The change in alkalinity associated with the reaction must take into account any alkalinity that is lost when the acetate is destroyed as well as any alkalinity that is produced with the products are generated. The reactant, acetate, is present 50% as HAc and 50% as Ac^- at the endpoint of the titration, so removal of one mole of acetate removes 0.5 equiv of Alk. When one mole of acetate reacts, two moles of HCO_3^- and one mole of H^+ are produced. The two moles of HCO_3^- contribute two equiv of alkalinity, but the mole of H^+ reduces the alkalinity by one equiv, so the products of the reaction correspond to one equiv of Alk generated per mole of acetate destroyed.

Thus, in the overall reaction, when one mole of acetate reacts, 0.5 equiv of Alk is destroyed (from the disappearance of the Ac^-), and 1.0 equiv of Alk is generated (from the appearance of the products), for a net change of +0.5 equiv of Alk per mole of acetate reacting. Correspondingly, if 2×10^{-3} mol/L of Ac^- is consumed, 1×10^{-3} eq/L of Alk is generated. One mole of $CaCO_3$ corresponds to two equiv of Alk, so 1 equiv of Alk corresponds to 0.5 mole of $CaCO_3$, or 50 g, and 1 meq/L of Alk corresponds to 50 mg/L as $CaCO_3$. Thus, the alkalinity of the solution increases by 50 mg/L of Alk as $CaCO_3$.

(b) Because $\mathrm{pH} = \mathrm{p}K_a$, the activity of HAc equals that of Ac^-, but their concentrations are not equal. Rather, assuming the standard state concentrations of both species are 1.0 mol/L, the distribution of *concentration* is governed by:

$$\{\mathrm{HAc}\} = \gamma_{\mathrm{HAc}}[\mathrm{HAc}] = \{\mathrm{Ac}^-\} = \gamma_{\mathrm{Ac}^-}\left[\mathrm{Ac}^-\right]$$

$$1.0[\mathrm{HAc}] = 0.7\left[\mathrm{Ac}^-\right]$$

$$TOT\mathrm{Ac} = 2\mathrm{x}10^{-3}M = [\mathrm{HAc}] + \left[\mathrm{Ac}^-\right] = 0.7\left[\mathrm{Ac}^-\right] + \left[\mathrm{Ac}^-\right] = 1.7\left[\mathrm{Ac}^-\right]$$

$$\left[\mathrm{Ac}^-\right] = \frac{2\mathrm{x}10^{-3}M}{1.7} = 1.18\mathrm{x}10^{-3}M$$

$$[\mathrm{HAc}] = 0.82\mathrm{x}10^{-3}M$$

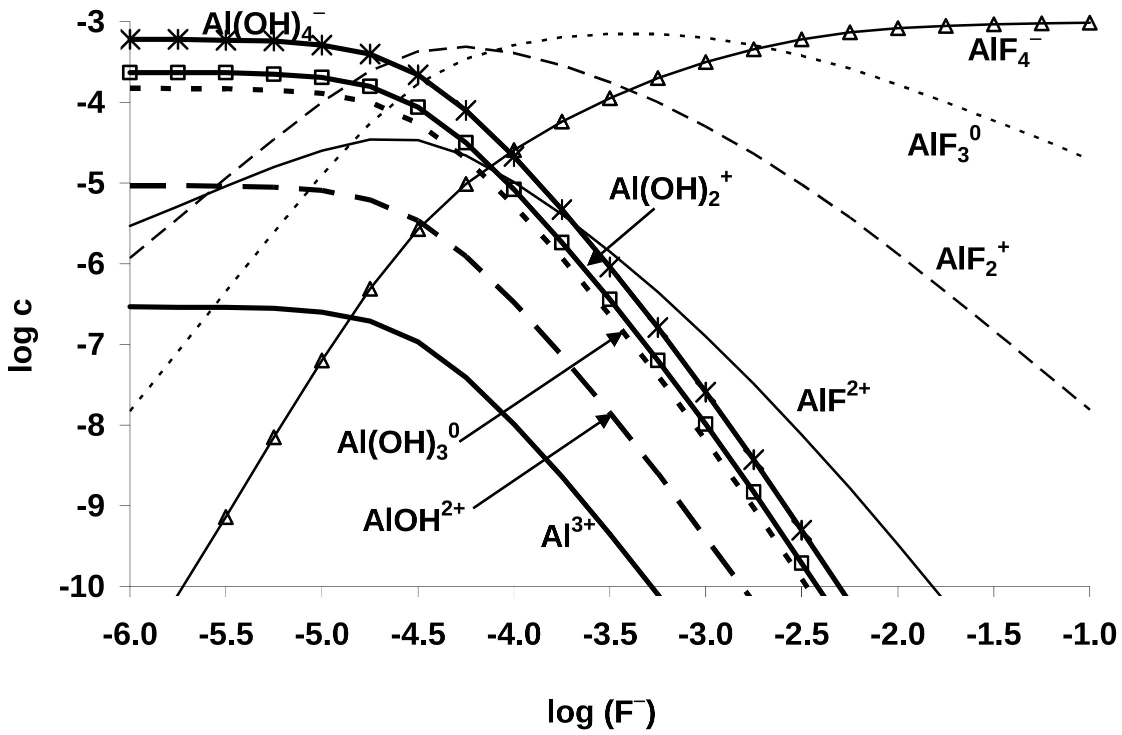
(c) The result in part *b* indicates that the 2×10^{-3} M Ac^- in the original solution is converted to 0.82×10^{-3} M HAc and 1.18×10^{-3} M Ac^- when the solution titrated to pH 4.76. Thus, the alkalinity of that solution is 0.82×10^{-3} eq/L (as opposed to 1.0×10^{-3} eq/L if the solution is ideal). Correspondingly, destruction of 2×10^{-3} M Ac^- by the biological reaction removes only 0.82×10^{-3} eq/L of Alk. The products of the reaction still contribute 1×10^{-3} eq/L of Alk, so the net effect of the reaction is to increase the alkalinity of the solution by 1.18×10^{-3} eq/L. The corresponding value as $CaCO_3$ is $(1.18 \times 10^{-3})(50)$, or 59 mg/L as $CaCO_3$.

2. Although fluoride (F^-) forms relatively weak complexes with most metals, its complexes with Al^{3+} and Fe^{3+} are fairly strong. A $\log c$ - $\log(F^-)$ diagram for a solution at pH 6.5 that contains 10^{-3} M *TOT*Al is shown below. The possibility that a solid might precipitate was not considered when the graph was prepared.

(a) What is $\log \beta_3$ for Al-F complexes?

(b) Is $Al(OH)_3(s)$ ($\log K_{s0} = -31.62$) supersaturated at any condition(s) shown on the plot? If so, what condition(s)?

(c) A solution is well buffered at pH 6.5 and contains 10^{-3} M *TOT*Al. If you concluded in part *b* that $Al(OH)_3(s)$ is supersaturated under some conditions shown on the graph, determine whether precipitation could be prevented by adding fluoride, and if so, find the value of *TOT*F that would prevent precipitation. If you concluded that $Al(OH)_3(s)$ is not supersaturated under any conditions shown, determine what *TOT*Al would have to be present to cause $Al(OH)_3(s)$ to precipitate if the F^- activity were fixed at $10^{-4.5}$.



Answer. (a)The reaction corresponding to β_3 is: Al + 3 F^- $\leftrightarrow$ AlF_3^-. The equilibrium constant can be determined by inserting values for the activities of the three relevant species into the equilibrium constant expression. For instance, using the values at log $(F^-) = -3.3$, we find:

$$\beta_3 = \frac{\left(AlF_3^-\right)}{\left(Al^{3+}\right)\left(F^-\right)^3} = \frac{10^{-3.1}}{\left(10^{-10.0}\right)\left(10^{-3.3}\right)^3} = 10^{+16.8}$$

Thus, $\log \beta_3 = 16.8$. (The value used by Mineql+ is $\beta_3 = 10^{16.7}$.)

(b) At pH 6.5, the concentration of Al^{3+} that can exist in solution without causing $Al(OH)_3(s)$ to be supersaturated is:

$$\left(Al^{3+}\right) = \frac{K_{s0}}{\left(OH^-\right)^3} = \frac{10^{-31.62}}{\left(10^{-7.5}\right)^3} = 10^{-9.12}$$

This Al^{3+} concentration is exceeded at all values of $\log (F^-) < -3.6$, so the solid is supersaturated under conditions where $(F^-) < 10^{-3.6}$.

(c) As found in part *b*, to prevent the solid from precipitating, the activity of F^- must be $>10^{-3.6}$. At this F^- activity, assuming ideal solution behavior, the concentrations of F-containing species and *TOT*F are as follows:

$$(F^-) \approx 10^{-3.6};\ (AlF^{2+}) \approx 10^{-5.7};\ (AlF_2{}^+) \approx 10^{-3.8};\ (AlF_3{}^0) \approx 10^{-3.1};\ (AlF_4{}^-) \approx 10^{-4.0}$$

$$TOT\text{F} = \left(F^-\right) + \left(AlF^{2+}\right) + 2\left(AlF_2{}^+\right) + 3\left(AlF_3{}^0\right) + 4\left(AlF_4{}^-\right)$$

$$= 10^{-3.6} + 10^{-5.7} + 2\left(10^{-3.8}\right) + 3\left(10^{-3.1}\right) + 4\left(10^{-4.0}\right) = 3.35\text{x}10^{-3}$$

Thus, if *TOT*F is $\geq 3.35\text{x}10^{-3}$ *M*, the Al^{3+} concentration will be maintained at a low enough value to prevent precipitation of the solid.

3. A wastewater at pH 7.5 contains 45 mg/L SO_4-S, which might be reduced to sulfide (i.e., S(–II)) species under anaerobic conditions. For H_2S, $pK_{a1} = 6.99$ and $pK_{a2} = 12.92$, and the Henry's constant, *H* (not log *H*), is 9.8 atm/(mol/L).

(a) What fraction of the sulfate can be reduced to sulfide without causing the partial pressure of H_2S in equilibrium with the solution to exceed 10^{-6} atm? Assume the solution is well-buffered at pH 7.5.

(b) If the H_2S partial pressure reached 10^{-6} atm and the solution contained 0.1 mg/L *TOT*Zn, would you expect ZnS(*s*) to precipitate? K_{s0} for ZnS(*s*) is $10^{-21.97}$. Hydroxo-complexes that might form include $ZnOH^+$ ($\log K_1 = 5.04$) and $Zn(OH)_2{}^0$ ($\log \beta_2 = 11.10$). Also, the complex $Zn(HS)^0$ can form via the reaction:

$$Zn^{2+} + 2\,HS^- \leftrightarrow Zn(HS)_2{}^0 \qquad \log \beta_2 = 12.82$$

Answer. (a) Based on the Henry's constant, the concentration of dissolved H_2S in equilibrium with a gas phase that contains H_2S at a partial pressure of 10^{-6} atm is:

$$\left(H_2S(aq)\right) = \frac{\left(H_2S(g)\right)}{K_{H,H_2S}} = \frac{10^{-6}\,\text{atm}}{9.8\,\dfrac{\text{atm}}{\text{mol/L}}} = 1.02\text{x}10^{-7}\,\frac{\text{mol}}{\text{L}}$$

At pH 6.5, the S^{2-} concentration in solution is negligible, and the concentration of HS^- is:

$$\left(HS^-\right) = \frac{K_{a1,H_2S}\left(H_2S(aq)\right)}{\left(H^+\right)} = \frac{\left(10^{-6.99}\right)\left(1.02\text{x}10^{-7}\right)}{10^{-7.5}} = 3.30\text{x}10^{-7}$$

Therefore, *TOT*S(–II) is 4.32×10^{-7} mol/L. *TOT*S(VI) in the original solution is:

$$TOT\mathrm{S}\left(\mathrm{VI}\right)=\frac{45\text{ mg/L}}{32,000\text{ mg/mol}}=1.41\text{x}10^{-3}\,\frac{\text{mol}}{\text{L}}$$

Thus, only a small faction ($4.32\text{x}10^{-7}/1.41\text{x}10^{-3}$, or 0.031%) of the sulfate can be reduced if the partial pressure of H_2S is to be maintained at $<10^{-6}$ atm.

(b) For the solution composition determined in part *a*, the concentration of S^{2-} is:

$$\left(\mathrm{S}^{2-}\right)=\frac{K_{a1,\mathrm{H_2S}}\left(\mathrm{HS}^-\right)}{\left(\mathrm{H}^+\right)}=\frac{\left(10^{-12.92}\right)\left(3.30\text{x}10^{-8}\right)}{10^{-7.50}}=1.25\text{x}10^{-13}$$

For this concentration of sulfide ion, the concentrations of dissolved Zn species in equilibrium with ZnS(*s*) are:

$$\left(\mathrm{Zn}^{2+}\right)=\frac{K_{s0,\mathrm{ZnS}(s)}}{\left(\mathrm{S}^{2-}\right)}=\frac{10^{-21.97}}{1.25\text{x}10^{-13}}=8.57\text{x}10^{-10}$$

$$\left(\mathrm{ZnOH}^+\right)=K_{1,\text{Zn-OH}}\left(\mathrm{Zn}^{2+}\right)\left(\mathrm{OH}^-\right)=10^{5.04}\left(8.57\text{x}10^{-10}\right)\left(10^{-6.5}\right)=2.97\text{x}10^{-11}$$

$$\left(\mathrm{Zn}\left(\mathrm{OH}\right)_2^{\,0}\right)=\beta_{2,\text{Zn-OH}}\left(\mathrm{Zn}^{2+}\right)\left(\mathrm{OH}^-\right)^2=10^{11.10}\left(8.57\text{x}10^{-10}\right)\left(10^{-6.5}\right)^2=1.08\text{x}10^{-11}$$

$$\left(\mathrm{Zn}\left(\mathrm{HS}\right)_2^{\,0}\right)=\beta_{2,\text{Zn-S}}\left(\mathrm{Zn}^{2+}\right)\left(\mathrm{HS}^-\right)^2=10^{12.82}\left(8.57\text{x}10^{-10}\right)\left(3.30\text{x}10^{-7}\right)^2=6.17\text{x}10^{-10}$$

The total dissolved Zn in equilibrium with the solid for the given partial pressure of H_2S is the sum of the preceding four values, or $1.51\text{x}10^{-9}$ *M*, most of which is present as Zn^{2+} and the $Zn(HS)_2^0$ complex. The total Zn in the original solution is:

$$\frac{0.1\text{ mg/L}}{65,000\text{ mg/mol}}=1.54\text{x}10^{-6}\,\frac{\text{mol}}{\text{L}}$$

Thus, the total Zn present is approximately 1000 times the amount needed to cause the solid to precipitate, so the solid will form.

4. A solution is at pH 8.35 and has reached equilibrium with the atmosphere. You wish to determine how much H_2SO_4 (mol/L) must be added to lower the pH to 6.0, if no gas/liquid exchange occurs, and also how much is needed if the solution remains in equilibrium with the atmosphere as the acid is added. Describe how you would use Mineql+ to get the values you want. In your response, describe the input information and also how you would manipulate the output to get the values of interest.

> **Answer.** To carry out the analysis, we first need to determine the composition of the original solution, at pH 8.35. To do that, we input a fixed pH of 8.35 and a fixed partial pressure of CO_2 at the default value of 3.5×10^{-4} atm. The result indicates the values of *TOT*CO_3 and *TOT*H needed to generate the original solution.
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> To determine the amount of H_2SO_4 that must be added to lower the pH to 6.0 in a closed system, we can input the values of *TOT*CO_3 and *TOT*H found in the first run, but change the constraint on the carbonate to specify that we are simulating a closed system, and change the fixed pH to 6.0. *TOT*H will be larger for this simulation. One-half of the difference in *TOT*H between the two simulations indicates the molar amount of H_2SO_4 that must be added. Alternatively, we can carry out a titration, increasing *TOT*H and *TOT*SO4 in a 2:1 ratio, until the pH declines to 6.0, and interpret *TOT*SO4 as the amount of H_2SO_4 added.
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> To determine the amount of H_2SO_4 that must be added to lower the pH to 6.0 while the solution remains in equilibrium with the atmosphere, we can again specify the inputs as determined in the initial run. We then carry out a titration, incrementing *TOT*H and *TOT*SO4 in a 2:1 ratio as in the second run, but this time with the system remaining open, so that CO_2 can exchange between the solution and the gas phase. Again, the *TOT*SO_4 when the solution pH is 6.0 indicates the dose of H_2SO_4 required.