CEE 543 Aut 2011, Midterm Exam #2 Solutions

Atomic weights of potential use are: $C = 12$, $O = 16$, $Si = 28$, $Cl = 35.5$, $Ca = 40$.

1. A treated water supply at pH 9.54 has an alkalinity of 20 mg/L as $CaCO_3$ and contains *TOT*Si at a concentration of 8 mg/L as SiO_2. The silica is present in solution primarily as H_4SiO_4 and $H_3SiO_4^-$, which are related by $pK_a = 9.84$.

   (a) (15) At the pH of the solution, the activity of H_4SiO_4 is twice the activity of $H_3SiO_4^-$. Assuming that the solution is ideal, what fraction of the alkalinity is contributed by the silica species?

   (b) (5) Explain briefly how your answer to part (a) would change, if at all, if you discovered that the ionic strength of the solution was high enough to cause the activity coefficient of $H_3SiO_3^-$ to be 0.8. Because it is neutral, the activity coefficient of H_4SiO_4 can still be assumed to be close to 1.0.

Answer. (a) The molar concentration of Si in the solution is

$$TOTSi = \frac{8 \text{ mg/L as } SiO_2}{60,000 \text{ mg } SiO_2 / \text{mol}} = 1.33x10^{-4} M$$

In an ideal solution, the molar concentrations of solutes equal their activities, so the given information indicates that the concentration of H_4SiO_4 is twice that of $H_3SiO_4^-$. Because the sum of these concentrations equals *TOT*Si, the concentration of $H_3SiO_3^-$ is

$$\left(H_3SiO_4^- \right) = \frac{TOTSi}{3} = \frac{1.33x10^{-4} M}{3} = 4.43x10^{-5} M$$

Because pK_a is 9.84, essentially all of the silica is present as H_4SiO_4 at the endpoint of the alkalinity titration (pH ~4.5), so each $H_3SiO_3^-$ ion combines with one H^+ ion during the titration, and the contribution of *TOT*Si to the alkalinity is $4.43x10^{-5}$ equiv/L. The total alkalinity of the solution is

$$Alk = \frac{20 \text{ mg/L as } CaCO_3}{50,000 \text{ mg } CaCO_3 / \text{equiv}} = 4.0x10^{-4} \text{ equiv/L}$$

Correspondingly, the fraction of the alkalinity contributed by silica species is

$$\frac{\text{Alk from } SiO_4 \text{ species}}{\text{Total Alk}} = \frac{4.43x10^{-5} \text{ equiv/L}}{4.0x10^{-4} \text{ equiv/L}} = 0.111$$

(b) At the given pH, the ratio of the activities of $H_3SiO_4^-$ and H_4SiO_4 is controlled by the pH, independent of the species' activity coefficients; thus, the activity ratio will be the same in this

solution as in the solution described in part (a). However, if the activity coefficient of $H_3SiO_3^-$ is 0.8 and that of H_4SiO_4 is 1.0, then the concentration ratio of H_4SiO_4 to $H_3SiO_4^-$ will be different from the activity ratio. The concentration ratio can be found as follows:

$$2.0 = \frac{\{H_4SiO_4\}}{\{H_3SiO_4^-\}} = \frac{\gamma_{H_4SiO_4}[H_4SiO_4]}{\gamma_{H_3SiO_4^-}[H_3SiO_4^-]} = \frac{1.0[H_4SiO_4]}{0.8[H_3SiO_4^-]}$$

$$1.6 = \frac{[H_4SiO_4]}{[H_3SiO_4^-]}$$

The fact that this ratio is 1.6 instead of 2.0 means that the concentration of $H_3SiO_4^-$ will be larger, and that of H_4SiO_4 will be smaller, than if the solutes behaved ideally. Correspondingly, because alkalinity is a concentration-based parameter, the alkalinity of the solution will be larger than that computed in part (a).

2. A log c - pH diagram for a solution containing $7 \times 10^{-3}\, M$ of a triprotic acid H_3A is shown below. The diagram was prepared assuming ideal solution behavior. Note that HA^{2-} is never a significant species compared to the other forms of the acid.

    a. (10) What are the pK_a values of the acid?

    b. (15) A solution at pH 6.8 containing an unknown amount of $TOTA$ is titrated with strong base to pH 12.0, yielding the titration curve shown below the $\log c - $ pH diagram. What is $TOTA$ in the system being titrated?

    c. (15) Hydrochloric acid (HCl) is gradually added to the solution that has been titrated to pH 12.0 until the pH decreases to 4.5. On the graph, sketch a plot of pH vs. HCl added, starting at the point where the previous titration ended, i.e., at (0.025, 12.0). The amount of acid added can be represented as negative additions of base. You need not do detailed calculations, but the curve should have the correct shape and should be fairly accurate as it passes through points near any pK_a values and at the end of the titration.
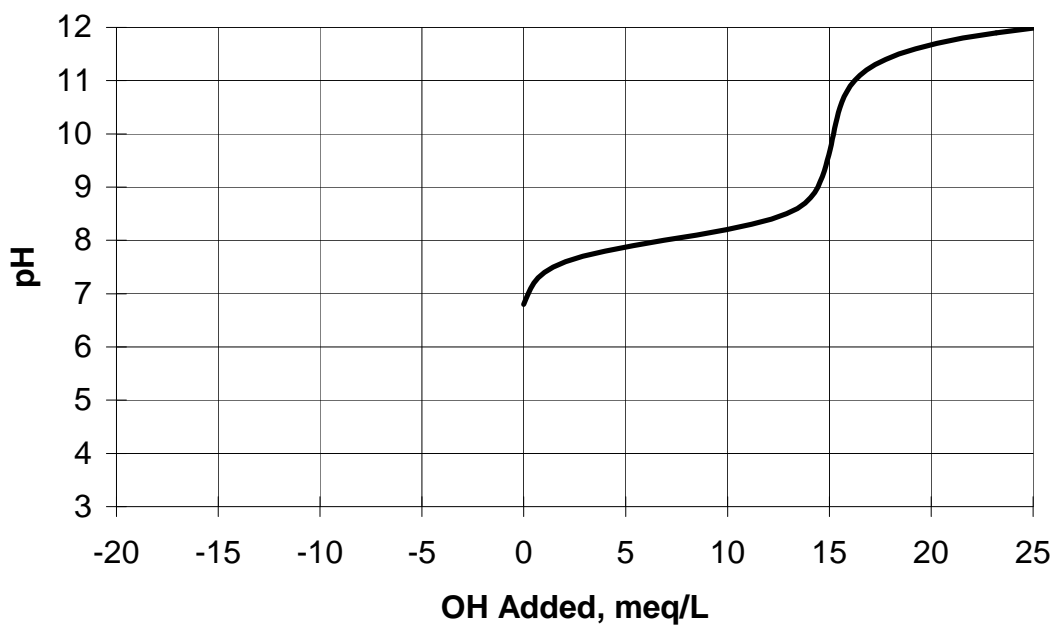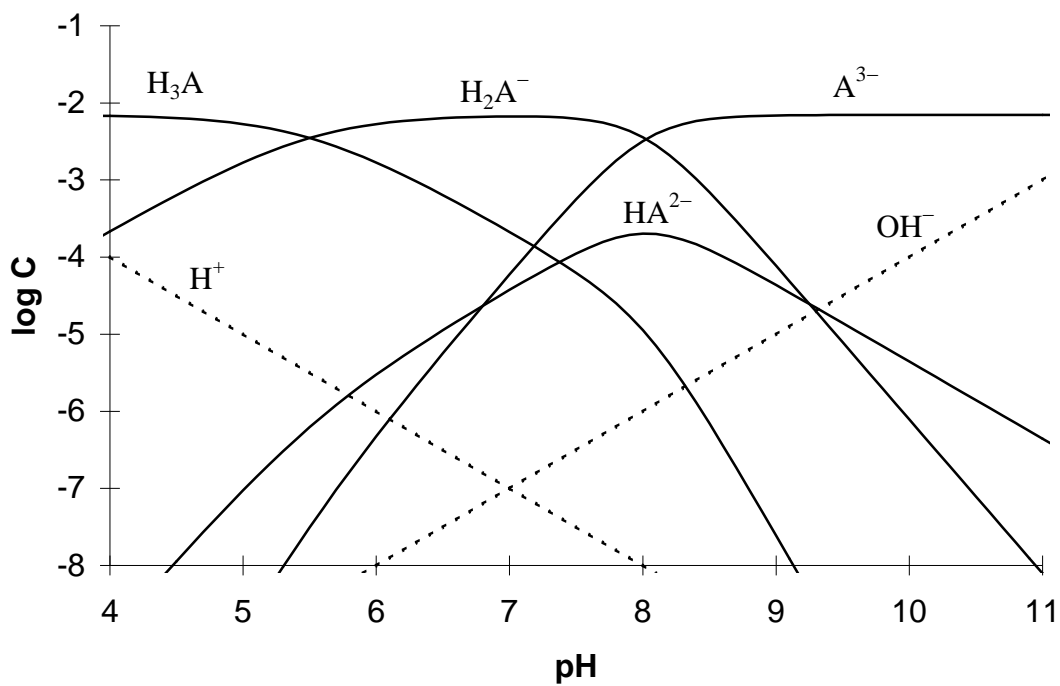
Answer. (a) The pK_a values correspond to the pH's where the concentration of each acid equals that of its conjugate base. These values are 5.5, 9.3, and 6.8 for pK_{a1}, pK_{a2}, and pK_{a3}, respectively.

(b) At pH 6.8, essentially all of the *TOT*A is present as H_2A^-, and at pH 12 it is present as A^{3-}. We also know that, at pH 12, the concentration of free OH^- ion is 0.01 M. The titration curve indicates that 0.025 M OH^- must be added to the initial solution to bring it to pH 12. Subtracting the 0.01 M OH^- that remains in that form at pH 12, we infer that 0.015 M OH^- that was added during the titration was neutralized by H^+. The only source of this H^+ is dissociation of the H_nA species. Because essentially every A-containing molecule releases two H^+ ions during the titration, the concentration of *TOT*A in the initial solution must be one-half of 0.015 M, or 0.0075 M.

(c) When acid is added to the solution at pH 12, it essentially reverses the titration described in part (b), so the titration curve follows exactly along the original curve back to pH 6.8. The next region of significant buffering is near the transition in dominant species from H_2A^- to H_3A, around pH 5.5 (i.e., pK_{a1}). Because this is a one-proton conversion, the "extra" H^+ required (compared to titration of a blank) is *TOT*A, which is only one-half as much as the extra H^+ required near pH 8.1 (where the change in dominant species involves transfer of two protons). Also, because only one-half as much H^+ is required to carry out the conversion, the buffer intensity is less, and the titration curve is therefore steeper, than near pH 8.1. The correct titration curve is shown below.
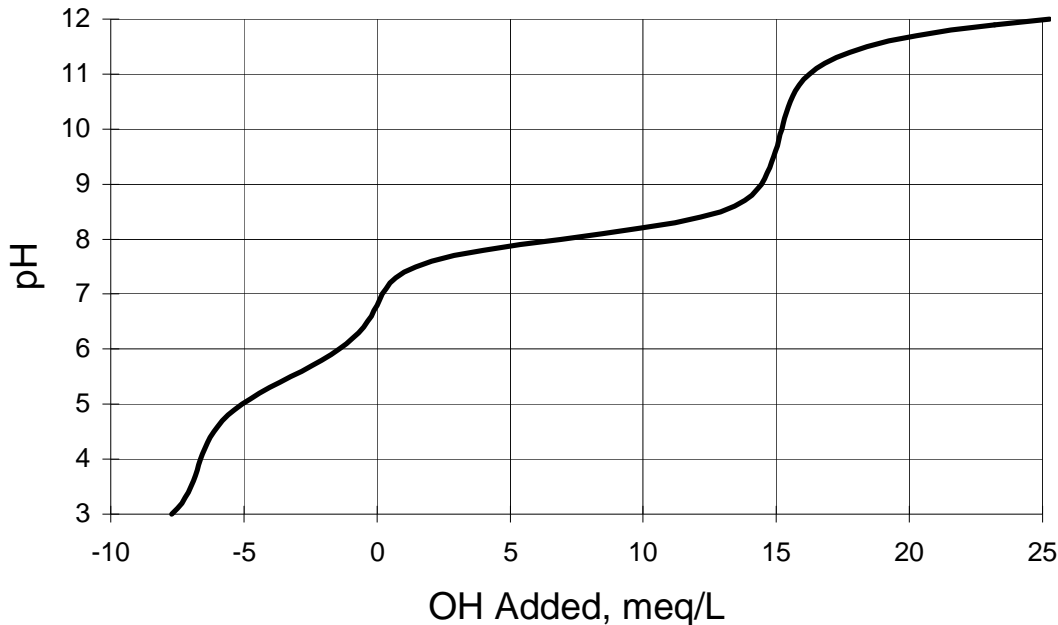
3. (20) After water has been 'softened' to remove hardness ions like Ca^{2+} and Mg^{2+}, it is typically at high pH, and must be partially neutralized before being distributed. The neutralization is sometimes carried out by bubbling the solution with air.

Imagine such a water that is at pH 11.33 and contains $10^{-4}\,M$ each of TOTCa and TOTMg, and $2\times10^{-4}\,M\ TOT$CO$_3$. Assume that, at the initial pH, the Ca is distributed as 95% Ca^{2+} and 5% $CaOH^+$, and that Mg is present entirely as Mg^{2+}. Also assume that the H_2CO_3 concentration is negligible compared to HCO_3^- and CO_3^{2-}, and that the solution behaves ideally. Prepare the system tableau and write out a the corresponding TOTH equation that can be used to determine the pH of the solution after it equilibrates with air. You need not determine the equilibrium pH. The Henry's constant for $CO_2(g)$ is 29.4 atm/(mol/L). pK_{a1} and pK_{a2} for H_2CO_3 are 6.35 and 10.33, respectively.

Answer. Because the amount of CO_2 that dissolves is unknown, we must choose H_2CO_3 as a component; otherwise, it will be impossible to quantify TOTH$_{in}$. The choices for the other components are somewhat arbitrary, but the obvious choices are H^+, Ca^{2+}, and Mg^2. The "inputs" that are included in the lower portion of the tableau must account for everything that has entered the solution. We can account for all these inputs by including the complete speciation of the solution before it equilibrates with air, and then adding the CO_2 that enters by dissolution from the air; we can represent this input as addition of H_2CO_3. (An equivalent approach would be to represent each mole of CO_2 entering as a combination of 1 mol of H_2CO_3 and -1 mol of H_2O; either approach yields the same result.) The tableau and TOTH equation are as follows.

	Stoichiometric Coefficient					
	H_2O	H^+	H_2CO_3	Ca^{2+}	Mg^{2+}	Conc'n
Species						
H^+	0	1	0	0	0	
H_2CO_3	0	0	1	0	0	
Ca^{2+}	0	0	0	1	0	
Mg^{2+}	0	0	0	0	1	
OH^-	1	−1	0	0	0	
$CaOH^+$	1	−1	0	1	0	
HCO_3^-	0	−1	1	0	0	
CO_3^{2-}	0	−2	1	0	0	

Inputs				0			
Ca^{2+}	0	0	0	1	0	9.5×10^{-5}
$CaOH^+$	1	−1	0	1	0	5.0×10^{-6}
Mg^{2+}	0	0	0	0	1	1.0×10^{-4}
H^+	0	1	0	0	0	$10^{-11.33}$
OH^-	1	−1	0	0	0	$10^{-2.67}$
H_2CO_3	0	0	1	0	0	??
HCO_3^-	0	−1	1	0	0	1.8×10^{-5}
CO_3^{2-}	0	−2	1	0	0	1.8×10^{-4}

$$TOTH_{in} = (-1)(5.0 \times 10^{-6}) + (1)(10^{-11.33}) + (-1)(10^{-2.67}) + (-1)(1.8 \times 10^{-5}) + (-2)(1.8 \times 10^{-4})$$

$$= -2.52 \times 10^{-3}$$

$$TOTH_{eq} = (H^+) - (OH^-) - (CaOH^+) - (HCO_3^-) - 2(CO_3^{2-})$$

$TOTH$ equation: $\qquad -2.52 \times 10^{-3} = (H^+) - (OH^-) - (CaOH^+) - (HCO_3^-) - 2(CO_3^{2-})$

4. (20) The tableau generated by Visual Minteq for a solution containing mercuric ions (Hg^{2+}) and ammonium (NH_4^+) ions is shown below. Note that the default component for mercury species is $Hg(OH)_2^0$.

What is the equilibrium value of P_{NH_3} under conditions where the activity of $Hg(NH_3)_2^{2+}$ is 100 times that of Hg^{2+} in a solution at pH 7.0? The Henry's constant for NH_3 at 25°C is 0.017 atm/(mol/L).

	log K	delta Hr (kJ/mol)	H+1	H2O	Hg(OH)2	NH4+1
Hg(NH3)2+2	5.47	-38.7	0	-2	1	2
Hg(NH3)4+2	-11.52	36.3	-2	-2	1	4
Hg+2	6.164	-39.72	2	-2	1	0
Hg2OH+3	9.031	-65.39	3	-3	2	0
Hg3(OH)3+3	12.101	0	3	-3	3	0
HgOH+	2.767	-18.89	1	-1	1	0
NH3 (aq)	-9.244	52	-1	0	0	1
OH-	-13.997	55.81	-1	1	0	0

Answer. The tableau provides information about the stoichiometry and $\log K$ value for reactions that generate the various species from the specified components. Based on information in the tableau, the reactions for formation of Hg^{2+} and $Hg(NH_3)_2^{2+}$ can be written in conventional form as follows:

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$$2H^+ + Hg(OH)_2^0 \leftrightarrow Hg^{2+} + 2H_2O \qquad\qquad \log K = 6.164$$

$$2NH_4^+ + Hg(OH)_2^0 \leftrightarrow Hg(NH_3)_2^{2+} + 2H_2O \quad \log K = 5.47$$

If we subtract the second of these reactions from the first, we obtain an overall reaction that directly relates the two species of interest:

$$Hg(NH_3)_2^{2+} + 2H^+ \leftrightarrow Hg^{2+} + 2NH_4^+ \qquad\qquad \log K = 6.164 - 5.47 = 0.694$$
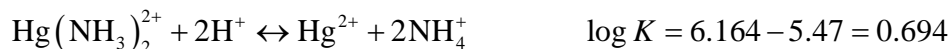
Writing out the equilibrium constant expression for this reaction, we can identify the conditions under which the di-ammonia complex of mercury is 100 times as concentrated as mercuric ion as follows:

$$\frac{\left(Hg^{2+}\right)\left(NH_4^+\right)^2}{\left(Hg(NH_3)_2^{2+}\right)\left(H^+\right)^2} = 10^{0.694}$$

$$\frac{\left(NH_4^+\right)^2}{\left(H^+\right)^2} = 10^{0.694}\frac{\left(Hg(NH_3)_2^{2+}\right)}{\left(Hg^{2+}\right)} = 10^{0.694}(100) = 10^{2.694}$$

$$\frac{\left(NH_4^+\right)}{\left(H^+\right)} = 10^{1.347}$$

We can then multiply this expression by K_a for NH_4^+ to find the equilibrium concentration of NH_3 in the solution.

$$\frac{\left(NH_4^+\right)}{\left(H^+\right)}\frac{\left(NH_3(aq)\right)\left(H^+\right)}{\left(NH_4^+\right)} = \left(10^{1.347}\right)\left(10^{-9.24}\right)$$

$$\left(NH_3(aq)\right) = 10^{-7.893}$$

Finally, we can use the Henry's constant for NH_3 to find the partial pressure of ammonia that would be in equilibrium with this dissolved concentration:

$$P_{NH_3} = H_{NH_3}\left(NH_3(aq)\right) = \left(0.017\frac{atm}{mol/L}\right)\left(10^{-7.893}\frac{mol}{L}\right) = 2.17 \times 10^{-10}\,atm$$