CEE 680 16 October 2012

# FIRST EXAM

Closed book, one page of notes allowed.

Answer question #1 and #4, and either #2 or #3. Please state any additional assumptions you made, and show all work. You are welcome to use a graphical method of solution if it is appropriate.

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| Miscellaneous Information: |
| R = 1.987 cal/mole°K = 8.314 J/mole°K |
| Absolute zero = -273.15°C |
| 1 joule = 0.239 calories |
| -20°C = wicked cold |

1. (50%) You've been asked to make a mixed carbon standard solution for total organic carbon (TOC) and total inorganic carbon (TIC) analysis. To do this you add 1 mM of KHP (potassium hydrogen phthalate, $C_6H_4(COOH)COO^-K^+$) to a liter of water followed by 10 mM of sodium bicarbonate.

   a. Determine the pH and concentration of all soluble species in this solution? Approximate values (±0.2 log units) will suffice.
   b. What is the TOC of this solution in mg-C/L? What is the TIC of this solution in mg-C/L?
   c. You are then asked to acidify the solution by adding 11 mM of HCl. Determine the pH and concentration of soluble species after this last step.

**Answer either question #2 or #3, but not both**

2. (40%) You have been asked to prepare a buffer at pH 6.0. The choices are an acetate buffer with a $C_T$ of 5mM and carbonate buffer with a $C_T$ of 2 mM. Which of the two will have a higher buffer intensity at the desired pH (i.e., at pH 6.0) under each of the following conditions? In answering this please show the calculated buffer intensity for both under each condition. Assume a closed system.

   a. 25°C, I = 0
   b. 25°C, I = 0.4

3. (40%) At what pH is the molar concentration of $H_3PO_4$ and $H_2PO_4^-$ equal under each of the following conditions?

a. 25°C, I = 0
b. 100°C, I = 0
c. 25°C, I = 0.25

4. (10%) True/False. Mark each one of the following statements with either a "T" or an "F".

a. ______ pH electrodes measure hydrogen ion activity rather than concentration

b. ______ The Bronsted-Lowry definition of an acid is a substance that can donate a proton

c. ______ Hardness is normally defined as the sum of all monovalent cations

d. ______ Organic forms of carbon are those not bound to an oxygen atom.

e. ______ Mass defects are directly proportional to nuclear binding energy

f. ______ The alkalinity minus the acidity is equal to one-half the $C_T$ (total carbonates)

g. ______ Water forms cage-like structures that are due to hydrogen bonding between adjacent molecules

h. ______ Increases in ionic strength have relatively minor effects on neutral species.

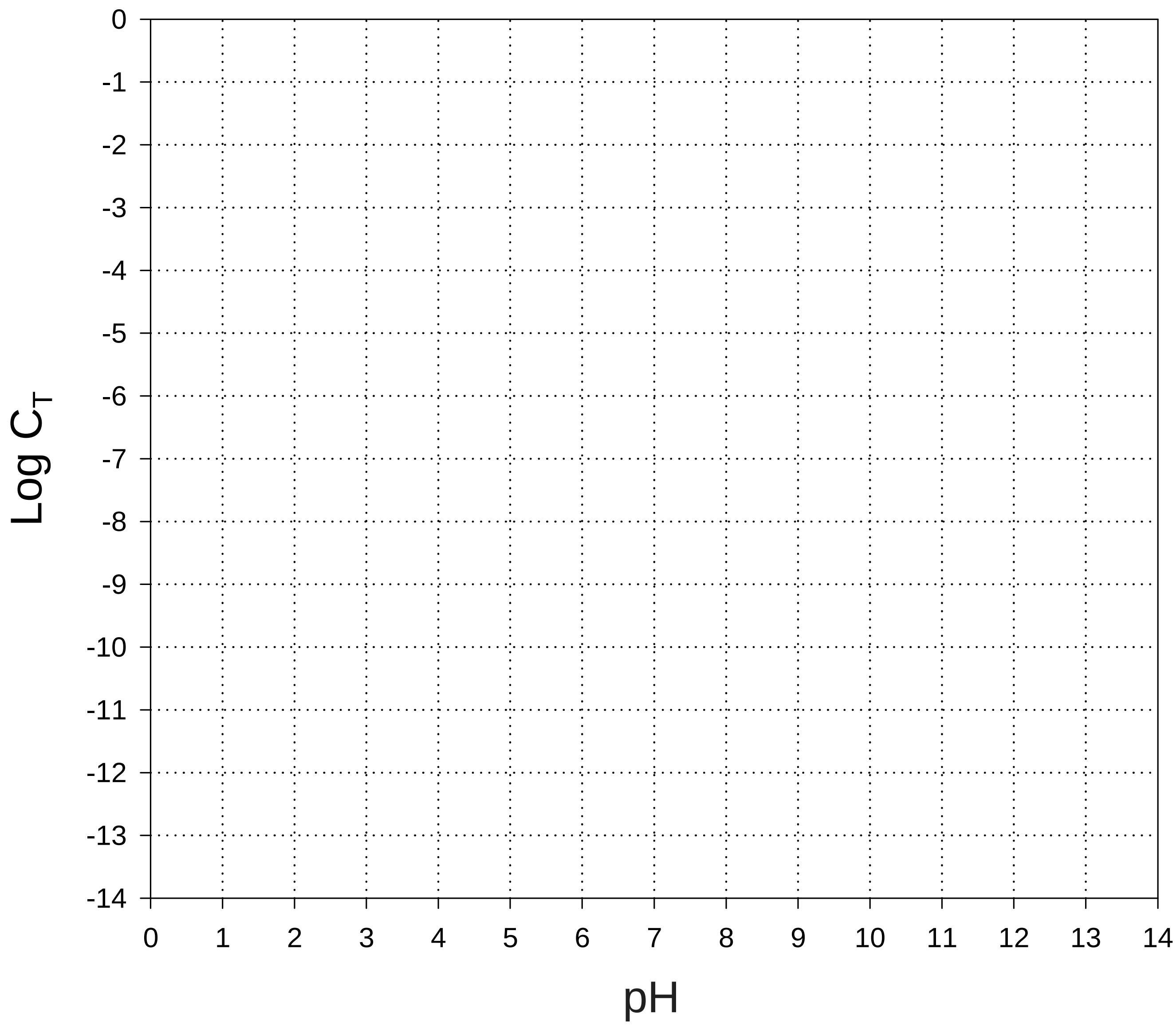
i. ______ The standard assumption used for calculating the pH of a strong acid is that [A-] >> [HA].

j. ______ The value of $\alpha_o$ plus $\alpha_1$ must never exceed unity for any acid system.

Selected Acidity Constants (Aqueous Solution, 25°C, I = 0)

| NAME | FORMULA | $pK_a$ |
|---|---|---|
| Perchloric acid | $HClO_4 = H^+ + ClO_4^-$ | -7 STRONG |
| Hydrochloric acid | $HCl = H^+ + Cl^-$ | -3 |
| Sulfuric acid | $H_2SO_4 = H^+ + HSO_4^-$ | -3 (&2) ACIDS |
| Nitric acid | $HNO_3 = H^+ + NO_3^-$ | -0 |
| Hydronium ion | $H_3O^+ = H^+ + H_2O$ | 0 |
| Trichloroacetic acid | $CCl_3COOH = H^+ + CCl_3COO^-$ | 0.70 |
| Iodic acid | $HIO_3 = H^+ + IO_3^-$ | 0.8 |
| Bisulfate ion | $HSO_4^- = H^+ + SO_4^{-2}$ | 2 |
| Phosphoric acid | $H_3PO_4 = H^+ + H_2PO_4^-$ | 2.15 (&7.2,12.3) |
| o-Phthalic acid | $C_6H_4(COOH)_2 = H^+ + C_6H_4(COOH)COO^-$ | 2.89 (&5.51) |
| Citric acid | $C_3H_5O(COOH)_3 = H^+ + C_3H_5O(COOH)_2COO^-$ | 3.14 (&4.77,6.4) |
| Hydrofluoric acid | $HF = H^+ + F^-$ | 3.2 |
| Aspartic acid | $C_2H_6N(COOH)_2 = H^+ + C_2H_6N(COOH)COO^-$ | 3.86 (&9.82) |
| m-Hydroxybenzoic acid | $C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$ | 4.06 (&9.92) |
| p-Hydroxybenzoic acid | $C_6H_4(OH)COOH = H^+ + C_6H_4(OH)COO^-$ | 4.48 (&9.32) |
| Nitrous acid | $HNO_2 = H^+ + NO_2^-$ | 4.5 |
| Acetic acid | $CH_3COOH = H^+ + CH_3COO^-$ | 4.75 |
| Propionic acid | $C_2H_5COOH = H^+ + C_2H_5COO^-$ | 4.87 |
| Carbonic acid | $H_2CO_3 = H^+ + HCO_3^-$ | 6.35 (&10.33) |
| Hydrogen sulfide | $H_2S = H^+ + HS^-$ | 7.02 (&13.9) |
| Dihydrogen phosphate | $H_2PO_4^- = H^+ + HPO_4^{-2}$ | 7.2 |
| Hypochlorous acid | $HOCl = H^+ + OCl^-$ | 7.5 |
| Boric acid | $B(OH)_3 + H_2O = H^+ + B(OH)_4^-$ | 9.2 (&12.7,13.8) |
| Ammonium ion | $NH_4^+ = H^+ + NH_3$ | 9.24 |
| Hydrocyanic acid | $HCN = H^+ + CN^-$ | 9.3 |
| p-Hydroxybenzoic acid | $C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$ | 9.32 |
| Phenol | $C_6H_5OH = H^+ + C_6H_5O^-$ | 9.9 |
| m-Hydroxybenzoic acid | $C_6H_4(OH)COO^- = H^+ + C_6H_4(O)COO^{-2}$ | 9.92 |
| Bicarbonate ion | $HCO_3^- = H^+ + CO_3^{-2}$ | 10.33 |
| Monohydrogen phosphate | $HPO_4^{-2} = H^+ + PO_4^{-3}$ | 12.3 |
| Bisulfide ion | $HS^- = H^+ + S^{-2}$ | 13.9 |
| Water | $H_2O = H^+ + OH^-$ | 14.00 |
| Ammonia | $NH_3 = H^+ + NH_2^-$ | 23 |
| Methane | $CH_4 = H^+ + CH_3^-$ | 34 |

| Species | $\Delta \overline{H}^o_f$ kcal/mole | $\Delta \overline{G}^o_f$ kcal/mole |
|---|---|---|
| $Ca^{+2}$(aq) | -129.77 | -132.18 |
| $CaCO_3$(s), calcite | -288.45 | -269.78 |
| CaO (s) | -151.9 | -144.4 |
| C(s), graphite | 0 | 0 |
| $CO_2$(g) | -94.05 | -94.26 |
| $CO_2$(aq) | -98.69 | -92.31 |
| $CH_4$ (g) | -17.889 | -12.140 |
| $H_2CO_3$ (aq) | -167.0 | -149.00 |
| $HCO_3^-$ (aq) | -165.18 | -140.31 |
| $CO_3^{-2}$ (aq) | -161.63 | -126.22 |
| $CH_3COOH$ | -116.79 | -95.5 |
| $CH_3COO^-$, acetate | -116.84 | -89.0 |
| $H^+$ (aq) | 0 | 0 |
| $H_2$ (g) | 0 | 0 |
| HF (aq) | -77.23 | -71.63 |
| $F^-$ (aq) | -80.15 | -67.28 |
| $Fe^{+2}$ (aq) | -21.0 | -20.30 |
| $Fe^{+3}$ (aq) | -11.4 | -2.52 |
| $Fe(OH)_3$ (s) | -197.0 | -166.0 |
| $NO_3^-$ (aq) | -49.372 | -26.43 |
| $NH_3$ (g) | -11.04 | -3.976 |
| $NH_3$ (aq) | -19.32 | -6.37 |
| $NH_4^+$ (aq) | -31.74 | -19.00 |
| $HNO_3$ (aq) | -49.372 | -26.41 |
| $O_2$ (aq) | -3.9 | 3.93 |
| $O_2$ (g) | 0 | 0 |
| $OH^-$ (aq) | -54.957 | -37.595 |
| $H_2O$ (g) | -57.7979 | -54.6357 |
| $H_2O$ (l) | -68.3174 | -56.690 |
| $PO_4^{-3}$ (aq) | -305.30 | -243.50 |
| $HPO_4^{-2}$ (aq) | -308.81 | -260.34 |
| $H_2PO_4^-$ (aq) | -309.82 | -270.17 |
| $H_3PO_4$ (aq) | -307.90 | -273.08 |
| $SO_4^{-2}$ | -216.90 | -177.34 |
| $HS^-$ (aq) | -4.22 | 3.01 |
| $H_2S$(g) | -4.815 | -7.892 |
| $H_2S$(aq) | -9.4 | -6.54 |


Log C_T
pH
0
-1
-2
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0 1 2 3 4 5 6 7 8 9 10 11 12 13 14