

**FINAL EXAM**

Closed book, three pages of notes allowed.

**Answer any 3 of the 4 Questions.** Each is worth 33⅓%. Please indicate clearly which 3 questions you wish to be graded. State any important assumptions you made, and **show all work**. If you don't have time to complete a section, please describe how you would solve the problem (without using a computer program such as MINEQL).

<p><u>Miscellaneous Information:</u></p> <p><math>R = 1.987 \text{ cal/mole}^\circ\text{K} = 8.314 \text{ J/mole}^\circ\text{K}</math></p> <p>Absolute zero = <math>-273.15^\circ\text{C}</math></p> <p>1 joule = 0.239 calories</p>
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**1. Alkalinity & Buffering (33 ⅓%)**

You have been asked to prepare a 10 mM phosphate buffer designed to hold pH at 7.0 (25°C, assume  $I \approx 0$ ). The two chemicals at your disposal are  $\text{Na}_3\text{PO}_4$  and HCl.

- How much of each compound (in mM concentration) would you add to create your buffer?
- If you were to elevate the solution pH to 8.0, how much more  $\text{Na}_3\text{PO}_4$  would you need to add to the pH 7.0 buffer prepared in part A (again in mM)?

**2. Redox (33 ⅓%)**

Ferrate (iron in the +VI oxidation state) is being considered for use in potable water treatment. You have been asked to pilot a ferrate treatment system on a small community in eastern MA. You will be adding about 25  $\mu\text{M}$  of ferrate to the water in the form of the oxyanion salt ( $\text{FeO}_4^{2-}$ ). Shortly after adding the ferrate you will need to add hypochlorous acid (as NaOCl) to maintain a disinfectant residual. Your concern is that any unreacted ferrate might react with the added hypochlorous acid forming chlorite which is regulated by the EPA at 1 mg/L.

- Write a balanced equation for the oxidation of hypochlorous acid (HOCl) to chlorite ( $\text{ClO}_2^-$ ) by ferrate ( $\text{FeO}_4^{2-}$ ).
- Determine the overall standard potential ( $E_{\text{net}}^0$ ) for this reaction from the half cell potentials in the attached table.
- Determine the equilibrium constant (K) for this reaction and comment on what thermodynamics tells you about whether this is a favorable reaction in a typical drinking water distribution system.
- Consider that this water will be at near neutral pH. Under this condition what would the  $\text{Fe}^{+3}$  concentration be? Explain.
- How does this affect your judgment about the likelihood that ferrate will oxidized hypochlorous acid to chlorite under these conditions?

### 3. Solubility (33 1/3%)

Schock, Wagner and Oliphant (1996)<sup>1</sup> published a careful study of lead solubility under conditions of relevance to water treatment systems. In their model they cite the equilibria below for 25°C and zero ionic strength.

<u>Equilibria</u>	<u>Log K</u>
$\text{Pb}^{+2} + \text{H}_2\text{O} = \text{PbOH}^+ + \text{H}^+$	-7.22
$\text{Pb}^{+2} + 2\text{H}_2\text{O} = \text{Pb(OH)}_2^0 + 2\text{H}^+$	-16.91
$\text{Pb}^{+2} + 3\text{H}_2\text{O} = \text{Pb(OH)}_3^- + 3\text{H}^+$	-28.08
$\text{Pb}_5(\text{PO}_4)_3\text{OH}_{(s)} = 5\text{Pb}^{+2} + 3\text{PO}_4^{-3} + \text{H}_2\text{O}$	-62.83

- Using these equilibria, prepare a graph of log C vs pH for all soluble species over the pH range of 8 to 11. Assume there is a total phosphate concentration of 1 mg/L as P. Show the four soluble lead species as well as the total soluble lead that is in equilibrium with the lead hydroxyl phosphate solid from the table above ( $\text{Pb}_5(\text{PO}_4)_3\text{OH}_{(s)}$ ).
- Estimate the pH where the soluble lead level exceeds the EPA regulatory action level
- Explain in qualitative terms how an increase in the phosphate dose would affect soluble lead in this pH range
- Explain in qualitative terms how high levels of carbonate might impact soluble lead levels

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<sup>1</sup> Chapter 4 from: Internal Corrosion of Water Distribution System, (2<sup>nd</sup> ed) by Snoeyink, Wagner et al., 1996 (AWWARF, Denver, CO)

#### 4. Multiple Choice and True/False (33 ⅓%)

Answer all 20 of the following questions. The first 10 are multiple choice. Please indicate which of the options is the best choice.

1. The molar ratio of carbon to nitrogen to phosphorus in algae:
  - a. is about 106:16:1
  - b. is called the Redfield Ratio
  - c. is used to predict nutrient limitation in natural waters
  - d. all of the above
  - e. none of the above
  
2. The third most prevalent gas in the atmosphere is:
  - a. argon
  - b. helium
  - c. carbon dioxide
  - d. ozone
  - e. none of the above
  
3. One Dalton is
  - a. the weight of a proton
  - b. one 12<sup>th</sup> the weight of Carbon-12
  - c. the weight of a hydrogen atom
  - d. a mass unit developed by Timothy Dalton
  - e. a mass unit developed in Dalton, MA
  
4. V-SMOW is:
  - a. a standard established by the IAEA in Vienna
  - b. associated with a precise ratio of deuterium to <sup>1</sup>H
  - c. a value that can be used to estimate the age of water
  - d. all of the above
  - e. none of the above
  
5. The law of mass action states that:
  - a. all matter can be converted to energy
  - b. all chemical processes can be reduced to a series of elementary reactions
  - c. atoms and molecules are always in motion
  - d. all of the above
  - e. none of the above
  
6. The Van't Hoff equation:
  - a. can be used to estimate ratios of base and acid in producing a buffer solution
  - b. can be used to adjust equilibrium constants to changes in temperature
  - c. is one of many models for adjusting activity for different ionic strengths
  - d. all of the above
  - e. none of the above

7. The strong acid assumption is most effectively used when:
- you've added a large amount of acid to water
  - the pKa of acid you've added is well below the pH of the water
  - the pH of your water is low
  - the solution contains several acids
  - you have not added any strong bases
8. The "f" value in a titration is:
- always equal to one
  - never exceeds one
  - the reciprocal of the "g" value
  - directly proportional to number of the base equivalents added
  - used as a direct measure of the pH, when there are no colorimetric indicators
9. The local maximum of a buffer intensity curve for a pure acid/base system occurs at:
- the very end of the titration of that system
  - the pH where this acid/base system must be used, if it is to be used as a laboratory buffer
  - the pH of the pure acid
  - a point where the acid can no longer neutralize any more base
  - the pH equal to the pKa of the acid/base system
10. Phenolphthalein
- is used whenever you don't have a pH meter
  - is one of the strongest ligands ever discovered
  - can be used to estimate hardness
  - changes color at about pH 8.3
  - precipitates at high pH

The 10 below are true/false. Mark each one of the following statements with either a "T" or an "F"

11. \_\_\_\_\_ A nanogram is  $10^{-9}$  milligrams.
12. \_\_\_\_\_ Noncarbonate hardness can be calculated from the total hardness, the total alkalinity and the pH
13. \_\_\_\_\_ There are 100,000 mg of alkalinity in one equivalent of alkalinity
14. \_\_\_\_\_ First order reactions are inherently slower than second order reactions
15. \_\_\_\_\_ When the enthalpy of a reaction is less than zero, it is called an endothermic reaction.

16. \_\_\_\_\_ Increasing temperature on a water that is saturated with respect to calcium carbonate causes it to precipitate
17. \_\_\_\_\_ Conditional equilibrium constants describe equilibria where one or more of the participating species are in molar units whereas the rest are in units of activity
18. \_\_\_\_\_ The sum of all of the alpha values for an acid system equal the number of exchangeable protons for that acid
19. \_\_\_\_\_ Buffer intensity is the reciprocal of the slope of the pH vs f curve
20. \_\_\_\_\_ Carbon in the -IV oxidation state is termed inorganic carbon.

Some important equilibrium constants:

<u>Equilibria</u>	<u>Log K</u>
$\text{Mg(OH)}_2(\text{s}) = \text{Mg}^{+2} + 2\text{OH}^-$	-11.6
$\text{Mg}^{+2} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$	-11.44
$\text{MgCO}_3(\text{s}) = \text{Mg}^{+2} + \text{CO}_3^{-2}$	-7.5
$\text{CaCO}_3(\text{s}) = \text{Ca}^{+2} + \text{CO}_3^{-2}$	-8.34
$\text{Ca(OH)}_2(\text{s}) = \text{Ca}^{+2} + 2\text{OH}^-$	-5.19
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s}) = \text{Ca}^{+2} + \text{SO}_4^{-2} + 2\text{H}_2\text{O}$	-4.62
$\text{CaOH}^+ = \text{Ca}^{+2} + \text{OH}^-$	-1.15
$\text{Fe(OH)}_3(\text{s}) = \text{Fe}^{+3} + 3\text{OH}^-$	-38.8
$\text{FeCO}_3(\text{s}) = \text{Fe}^{+2} + \text{CO}_3^{-2}$	-10.7
$\text{AlOH}^{+2} = \text{Al}^{+3} + \text{OH}^-$	-9.01
$\text{CdOH}^+ = \text{Cd}^{+2} + \text{OH}^-$	-3.92
$\text{CoOH}^+ = \text{Co}^{+2} + \text{OH}^-$	-4.80
$\text{CuOH}^+ = \text{Cu}^{+2} + \text{OH}^-$	-6.00
$\text{HgOH}^+ = \text{Hg}^{+2} + \text{OH}^-$	-10.60
$\text{NiOH}^+ = \text{Ni}^{+2} + \text{OH}^-$	-4.14
$\text{Pb}^{+2} + \text{H}_2\text{O} = \text{PbOH}^+ + \text{H}^+$	-7.22
$\text{Pb}^{+2} + 2\text{H}_2\text{O} = \text{Pb(OH)}_2^0 + 2\text{H}^+$	-16.91
$\text{Pb}^{+2} + 3\text{H}_2\text{O} = \text{Pb(OH)}_3^- + 3\text{H}^+$	-28.08
$\text{Pb}_5(\text{PO}_4)_3\text{OH}(\text{s}) = 5\text{Pb}^{+2} + 3\text{PO}_4^{-3} + \text{H}_2\text{O}$	-62.83
$\text{ZnOH}^+ = \text{Zn}^{+2} + \text{OH}^-$	-5.04
$\text{HgS}(\text{s}) = \text{Hg}^{+2} + \text{S}^{-2}$	-42.7

Some important half-cell reactions

<u>Half Cell Reaction</u>	<u><math>\Delta E^\circ</math> (Volts)</u>
$\text{O}_2(\text{aq}) + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	+1.23
$\text{Mn}^{+3} + \text{e}^- = \text{Mn}^{+2}$	+1.51
$\text{Mn}^{+4} + \text{e}^- = \text{Mn}^{+3}$	+1.65
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- = \text{Mn}^{+2} + 4\text{H}_2\text{O}$	+1.49
$\frac{1}{3}\text{FeO}_4^{-2} + 2\frac{2}{3}\text{H}^+ + \text{e}^- = \frac{1}{3}\text{Fe}^{+3} + 1\frac{1}{3}\text{H}_2\text{O}$	+2.20
$\text{Fe}^{+3} + \text{e}^- = \text{Fe}^{+2}$	+0.77
$\text{Cu}^{+2} + \text{e}^- = \text{Cu}^+$	+0.16
$\frac{1}{2}\text{HOBr} + \frac{1}{2}\text{H}^+ + \text{e}^- = \frac{1}{2}\text{Br}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.33
$\text{O}_3(\text{g}) + 2\text{H}^+ + 2\text{e}^- = \text{O}_2(\text{g}) + \text{H}_2\text{O}$	+2.07
$\text{Al}^{+3} + 3\text{e}^- = \text{Al}(\text{s})$	-1.68
$\frac{1}{2}\text{HOCl} + \frac{1}{2}\text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.48
$\frac{1}{4}\text{ClO}_2^- + \text{H}^+ + \text{e}^- = \frac{1}{4}\text{Cl}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.61
$\frac{1}{2}\text{OCl}^- + \text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{H}_2\text{O}$	+1.64
$\text{BrO}_3^- + 5\text{H}^+ + 4\text{e}^- = \text{HOBr} + 2\text{H}_2\text{O}$	+1.45

$\frac{1}{2}\text{NH}_2\text{Cl} + \text{H}^+ + \text{e}^- = \frac{1}{2}\text{Cl}^- + \frac{1}{2}\text{NH}_4^+$	+1.40
$\text{Fe}(\text{OH})_{3(\text{am})} + 3\text{H}^+ + \text{e}^- = \text{Fe}^{+2} + 3\text{H}_2\text{O}$	+0.95
$\text{SO}_4^{-2} + 9\text{H}^+ + 8\text{e}^- = \text{HS}^- + 4\text{H}_2\text{O}$	+0.25
$\text{S}_{(\text{s})} + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{S}_{(\text{g})}$	+0.17
$\text{Zn}^{+2} + 2\text{e}^- = \text{Zn}(\text{s})$	-0.76
$\text{Ni}^{+2} + 2\text{e}^- = \text{Ni}(\text{s})$	-0.24
$\text{Pb}^{+2} + 2\text{e}^- = \text{Pb}(\text{s})$	-0.126
$\text{ClO}_2 + \text{e}^- = \text{ClO}_2^-$	+0.95
$\text{PbO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- = \text{Pb}^{+2} + 2\text{H}_2\text{O}$	+1.451

Properties of Selected Elements

Element	Symbol	Atomic #	Atomic Wt.	Valence	Electronegativity
Aluminum	Al	13	26.98	3	1.47
Bromine	Br	35	79.904	1,3,5,7	2.74
Calcium	Ca	20	40.08	2	1.04
Carbon	C	6	12.01	2,4	2.50
Chlorine	Cl	17	35.453	1,3,5,7	2.83
Copper	Cu	29	63.54	1,2	1.75
Hydrogen	H	1	1.01	1	2.20
Iron	Fe	26	55.845	0,2,3	1.83
Magnesium	Mg	12	24.31	2	1.23
Manganese	Mn	25	54.94	2,3,4,6,7	1.60
Nitrogen	N	7	14.0047	3,5	3.07
Oxygen	O	8	16.00	2	3.50
Phosphorus	P	15	30.97		
Potassium	K	19	39.10	1	0.91
Sodium	Na	11	22.99	1	1.01
Strontium	Sr	38	87.62	2	0.99
Sulfur	S	16	32.06	2,4,6	2.44
Zinc	Zn	30	65.39	2	1.65
Lead	Pb	82	207.19	2,4	

Atmospheric Gases

Gas	Atmospheric Abundance	Henry's Law Const <sup>2</sup>
<a href="#">Nitrogen</a> (N <sub>2</sub> )	780,840 ppmv (78.084%)	6.1 x 10 <sup>-4</sup>
<a href="#">Oxygen</a> (O <sub>2</sub> )	209,460 ppmv (20.946%)	1.3 x 10 <sup>-3</sup>
<a href="#">Argon</a> (Ar)	9,340 ppmv (0.9340%)	1.4 x 10 <sup>-3</sup>
<a href="#">Carbon dioxide</a> (CO <sub>2</sub> )	387 ppmv (0.0387%)	3.4 x 10 <sup>-2</sup>
<a href="#">Neon</a> (Ne)	18.18 ppmv (0.001818%)	4.5 x 10 <sup>-4</sup>
<a href="#">Helium</a> (He)	5.24 ppmv (0.000524%)	3.7 x 10 <sup>-4</sup>
<a href="#">Methane</a> (CH <sub>4</sub> )	1.79 ppmv (0.000179%)	
<a href="#">Krypton</a> (Kr)	1.14 ppmv (0.000114%)	
<a href="#">Hydrogen</a> (H <sub>2</sub> )	0.55 ppmv (0.000055%)	7.8 x 10 <sup>-4</sup>
<a href="#">Nitrous oxide</a> (N <sub>2</sub> O)	0.3 ppmv (0.00003%)	
<a href="#">Xenon</a> (Xe)	0.09 ppmv (9x10 <sup>-6</sup> %)	

<sup>2</sup> In: moles/L/atm



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

NAME	FORMULA	pK <sub>a</sub>
Perchloric acid	$\text{HClO}_4 = \text{H}^+ + \text{ClO}_4^-$	-7
Hydrochloric acid	$\text{HCl} = \text{H}^+ + \text{Cl}^-$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$	-3
Nitric acid	$\text{HNO}_3 = \text{H}^+ + \text{NO}_3^-$	0
Bisulfate ion	$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$	2
Phosphoric acid	$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.15
o-Phthalic acid	$\text{C}_6\text{H}_4(\text{COOH})_2 = \text{H}^+ + \text{C}_6\text{H}_4(\text{COOH})\text{COO}^-$	2.89
p-Hydroxybenzoic acid	$\text{C}_6\text{H}_4(\text{OH})\text{COOH} = \text{H}^+ + \text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	4.48
Nitrous acid	$\text{HNO}_2 = \text{H}^+ + \text{NO}_2^-$	4.5
Acetic acid	$\text{CH}_3\text{COOH} = \text{H}^+ + \text{CH}_3\text{COO}^-$	4.75
Aluminum ion	$\text{Al}(\text{H}_2\text{O})_6^{+3} = \text{H}^+ + \text{Al}(\text{OH})(\text{H}_2\text{O})_5^{+2}$	4.8
Carbonic acid	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	6.35
Hydrogen sulfide	$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	7.02
Dihydrogen phosphate	$\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$	7.2
Hypochlorous acid	$\text{HOCl} = \text{H}^+ + \text{OCl}^-$	7.5
Hypobromous acid	$\text{HOBr} = \text{H}^+ + \text{OBr}^-$	8.71
Ammonium ion	$\text{NH}_4^+ = \text{H}^+ + \text{NH}_3$	9.24
Bicarbonate ion	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	10.33
Monohydrogen phosphate	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	12.3
Sulfide	$\text{HS}^- = \text{H}^+ + \text{S}^{2-}$	13.9

$\alpha_2$  for a diprotic acid:

$$\alpha_2 = \frac{1}{\frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2} + 1}$$

$\alpha_3$  for a triprotic acid:

$$\alpha_3 = \frac{1}{\frac{[\text{H}^+]^3}{K_1 K_2 K_3} + \frac{[\text{H}^+]^2}{K_2 K_3} + \frac{[\text{H}^+]}{K_3} + 1}$$



