CE 59700 008
Practice Problems for Exam 2

Some Reactions that may be given:

Reaction	$p\varepsilon^o$	E_h^o (V)	K
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	13	+ 0.77	+ 13.0
$Fe(OH)_{3,(s)} + 3\ H^+ + e^- \leftrightarrow Fe^{2+} + 3\ H_2O$	17.9	+ 1.06	
$Fe(OH)_{3,(s)} \leftrightarrow Fe^{3+} + 3\ OH^-$			10^{-38}
$O_{2,(g)} + 4\ H^+ + 4\ e^- \leftrightarrow 2\ H_2O$	+ 20.8	+ 1.23	
$H_2O \leftrightarrow H^+ + OH^-$			10^{-14}
$H^+ + e^- \leftrightarrow ½\ H_{2,(g)}$	0.0	0.0	
$SO_4^{2-} + 9\ H^+ + 8\ e^- \leftrightarrow HS^- + 4\ H_2O$	+ 4.13	+ 0.24	
$Cu^{2+} + 2\ e^- \leftrightarrow Cu_{(s)}$	+ 5.7	+ 0.34	
$Pb^{2+} + 2\ e^- \leftrightarrow Pb_{(s)}$	-2.2	-0.13	
2 cyto-c(ox) + 2 e^- $\leftrightarrow$ 2 cyto-c(red)	+ 4.3		

Equations that will be give:

$$\Delta G^o = \left(\sum \nu_i \overline{\Delta G^o_{f,i}}\right)_{\text{products}} - \left(\sum \nu_i \overline{\Delta G^o_{f,i}}\right)_{\text{reactants}} \qquad \Delta H^o = \left(\sum \nu_i \overline{\Delta H^o_{f,i}}\right)_{\text{products}} - \left(\sum \nu_i \overline{\Delta H^o_{f,i}}\right)_{\text{reactants}}$$

$$\Delta G = \Delta G^o + RT \ln Q \qquad \Delta G^o = -RT \ln K_{eq}$$

$$\ln K_1 - \ln K_2 = \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$p\varepsilon^{O} = \left(\frac{1}{n}\right)(\log K) \qquad \frac{2.3RT}{F} = 0.059 \text{ at } 25^oC \qquad RT = 2.477 \text{ KJ / mole at } 25^oC$$

$$E_H^o = \frac{-\Delta G^o}{nF} = \frac{2.3RT}{nF}\log K = \frac{2.3RT}{F}\cdot p\varepsilon^o$$

$p\varepsilon = F\,E_H / (2.3\,R\,T) = 16.9\,E_H$ at 25^oC $\qquad E_H^O = \left(\frac{0.059}{n}\right)\log K = 0.059\,p\varepsilon^O$

$p\varepsilon^O = F\,E_H^O / (2.3\,R\,T) = 16.9\,E_H^O$ at 25^OC

R = 8.314 Joule / (mole K)

$p\varepsilon^o = -\Delta G^o / (2.3\,n\,R\,T)$ F = 96,493 coulomb / eq (or Joule / (Volt eq))

1. (a) Write and *number* all of the equations necessary to solve for the aqueous concentration of Fe^{2+} in equilibrium with $FeS_{2\,(s)}$ if the gas phase H_2S concentration and aqueous phase pH values are known accounting for only the first Fe(II)-OH complex. Recall hydrogen sulfide has 2 pK_a values
(b) List all the components, and list all the species in this problem.

2. Derive the equation for the concentration of $Fe(OH)^{2+}$ as a function of $[H^+]$, if this species ($Fe(OH)^{2+}$) is in equilibrium with solid $Fe(OH)_{3,\,(s)}$. Further, develop the equation of the line describing $p[Fe(OH)^{2+}]$ versus pH, as would appear on a pC-pH solubility diagram (Note: your final equation should have $p[Fe(OH)^{2+}]$ and pH in it!).

$Fe^{3+} + OH^- = Fe(OH)^{2+}$	$K_{s1} = 10^{11.8}\ M^{-1}$
$Fe(OH)^{2+} + OH^- = Fe(OH)_2^{+}$	$K_{s2} = 10^{10.7}\ M^{-1}$
$Fe^{3+} + 2\ OH^- = Fe(OH)^{+}$	$\beta_2 = 10^{22.5}\ M^{-2}$
$Fe(OH)_{3,(s)} = Fe^{3+} + 3\ OH^-$	$K_{sp} = 10^{-38}\ M^4$

3. Derive a set of *two* equations that, if their roots are found, solve for the aqueous phase concentrations of free Cu^{2+} and $EDTA^{4-}$ at a known pH value. Assume that only those species in the following reactions are important, and that the total concentrations of Cu and of EDTA are known, and that the K's are known values.

$Cu^{2+} + EDTA^{4-} = CuEDTA^{2-}$	K_1
$Cu^{2+} + H^+ + EDTA^{4-} = CuHEDTA^-$	K_2
$Cu^{2+} + OH^- + EDTA^{4-} = CuOHEDTA^-$	K_3

4. What is the concentration of free Ca^{2+} in aqueous solution prepared by adding $CaHPO_{4,s}$ to pure water such that excess solid $CaHPO_{4,s}$ exists in equilibrium with aqueous phase species, and the pH has been adjusted by adding NaOH to a final pH value of 8.5. Start by listing and numbering the necessary equations, and listing the unknowns. You may assume that the concentrations of all aqueous phase complexes are insignificant. (Hints: (1) solve for PO_4^{3-}. (2) H_3PO_4 is negligible- you don't have an equation for it! (3) other species may also be negligible)

$CaHPO_{4,s} = Ca^{2+} + H^+ + PO_4^{-3}$ $\quad K_{sp} = 10^{-19}$

$pK_{a,2} = 7.2$ (for $H_2PO_4^-$)

$pK_{a,3} = 12.3$ (for HPO_4^-)

5. Given the following half reaction, develop the line for a predominance diagram between the species $MnO_{2(s)}$ and Mn^{2+}, assuming a total concentration of Mn of 10^{-3} M :

$MnO_{2(s)} + 4\ H^+ + 2\ e^- \quad \_ \quad Mn^{2+} + 2\ H_2O \quad \log K = 43.6$

6. Briefly Define COD (and what does COD stand for?)

7. Balance the following half reactions:

$SO_4^{2-} \rightarrow HS^-$

$NO_3^- \rightarrow NH_4^+$

$CO_2 \rightarrow CH_3OH$

8. Solve for the relative ratio of ammonium (NH_4^+) to nitrate (NO_3^-) when (a) the oxygen concentration of water is 1 mg / L (molecular weight of molecular oxygen = 32 g/mole), and when (b) the E_H is controlled to - 0.5 Volts by other environmental factors other than oxygen.

Reaction $pe^o = \log K$

$1/8\ NO_3^- + 5/4\ H^+ + e^- \_ 1/8\ NH_4^+ + 3/8\ H_2O$ 14.9

$1/4\ O_2 + H^+ + e^- \_ 1/2\ H_20$ 20.75

9. What are common oxidation states (valences) of the following elements in nature?
Provide the molecular formula of a species that contains each element at each oxidation state.
No credit for the zero valent species.

	Common Molecule	Oxidation State on Atom

a) Sulfur (S) – list 2

b) Nitrogen (N) – list 3

c) Iron (Fe) – list 2

10. Write a balanced redox reaction for the oxidation of benzoic acid ($C_7H_6O_2$) by O_2 , with H_2O and CO_2 as the final products.

11. What is the ultimate BOD of a solution that contains 50 mg / L benzoic acid ($C_7H_6O_2$) (Recall O = 16, C = 12, H = 1). Report your answer in units of mg / L O_2.

12. What is the equilibrium constant for the following reaction at 25° C? (Hint: Fe^{3+} is very insoluble)

$Fe(OH)_{3(s)} = Fe^{3+} + 3\ OH^-$

Species	$\overline{\Delta G^o_{f,i}}$ (kJ / mol)
$Fe(OH)_{3(s)}$	-700
Fe^{3+}	-4.6
OH^-	-157.3

13. An aqueous solution contains 10^{-3} M total sulfur: Assume that it exists as only SO_4^{2-} and H_2S in equilibrium with each other. The pH = 5.5, and the pe = –1.0. Calculate the concentration of each species.

$SO_4^{2-} + 10\ H^+ + 8\ e^- \leftrightarrow H_2S_{aq} + 4\ H_2O$ $E_H° = 0.303$ Volts