CHEM 3600 EXAM 2 11/10/2003

Name:_____________________________

Read through the entire exam before starting. Make sure to get the easy ones done first. Remember to show all your work for full credit; there is extra room on p.4 if you need it.

Possibly useful equations and numbers

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \qquad \mathrm{pH} = 1/2(\mathrm{p}K_1 + \mathrm{p}K_2) \qquad \Delta G = -nFE$$

$$E = E^\circ - \frac{0.05916\ \mathrm{V}}{n}\log\frac{[\mathrm{B}]}{[\mathrm{A}]} \qquad E = E_+ - E_- \qquad E = \frac{0.05916\ \mathrm{V}}{n}\log K \qquad F = 9.649\times10^4\ \mathrm{C/mol\ e^-}$$

Reaction	E°
$Ag^+ + e^- \leftrightarrow Ag(s)$	0.799
$AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-$	0.222
$Au^{3+} + 2e^- \leftrightarrow Au^+$	1.41
$Au^+ + e^- \leftrightarrow Au(s)$	1.69
$H_2O + e^- \leftrightarrow ½H_2(g) + OH^-$	-0.828
$IO_3^- + 3H_2O + 6e^- \leftrightarrow I^- + 6OH^-$	0.269
$IO_4^- + 2H^+ + 2e^- \leftrightarrow IO_3^- + H^2O$	1.589
$IO_3^- + 6H^+ + 5e^- \leftrightarrow ½I_2(s) + 3H_2O$	1.210
$I_2(aq) + 2e^- \leftrightarrow 2I^-$	0.620
$I_3^- + 2e^- \leftrightarrow 3I^-$	0.535

1) (20 points) A 500 mg supplement tablet containing **only** Vitamin A ($C_{18}H_{30}O$, MW=262.43), Vitamin C ($C_6H_8O_6$, MW=176.124), and Zinc (AW=65.39) in the form of sulfite ($ZnSO_3$, MW=145.45) was analyzed by combustion for carbon and precipitation for zinc. Upon combustion, the tablet produced 1.194 g of CO_2 (MW=44.01). The residue left from the combustion was dissolved and zinc was precipitated as zinc sulfide (ZnS, MW=97.45), and weighed 16.48 mg. What is the wt % of Vitamin A, Vitamin C, and Zinc in the tablet?

$$16.48\mathrm{mg\ ZnS} \div 97.45\ \mathrm{g/mol\ ZnS} = 0.169\ \mathrm{mol\ ZnS} = \mathrm{mol\ Zn} = \mathrm{mol\ ZnSO_3} \times 145.45\ \mathrm{g/mol} = 24.60\ \mathrm{mg\ ZnSO_3}$$

$$500\mathrm{mg\ tablet} - 24.60\ \mathrm{mg\ ZnSO_3} = 475.40\ \mathrm{mg\ (Vitamin\ A + Vitamin\ C)}$$

$$x = \mathrm{mass\ Vitamin\ A;\ mass\ Vitamin\ C} = 0.47540 - x$$

$$18\left(\frac{x}{262.43}\right) + 6\left(\frac{.4754 - x}{176.124}\right) = \frac{1.194\ \mathrm{g\ CO_2}}{44.01\ \mathrm{g/mol\ CO_2}}$$

$$\frac{3170.23x}{46220.22} + \frac{748.555 - 1574.58x}{46220.22} = 0.02713\ \mathrm{mol\ CO_2} = 0.02713\ \mathrm{mol\ C}$$

$$1595.65x + 748.555 = 1253.964$$

$$x = .3167\ \mathrm{g} = \mathrm{mass\ Vitamin\ A}$$

$$\mathrm{mass\ Vitamin\ C} = .4754 - x = .1587\ \mathrm{g}$$

$$wt\%\ \mathrm{Vitamin\ A} = 0.3167/0.500*100 = 63.3\%$$

$$wt\%\ \mathrm{Vitamin\ C} = 0.1587/0.500*100 = 31.7\%$$

$$wt\%\ \mathrm{Zn} = 0.02460/0.500 \times \frac{65.39}{145.45}*100 = 2.21\%$$

2) (20 points total) A solution at equilibrium contains 0.100 M IO_3^-, 1x10^{-4} M I^-, 1x10^{-5} M OH^-, 1x10^{-3} M Au^{3+}, and 0.100 M Au^+.

a) Write a balanced net reaction that can occur between the species in this solution (5)

$Au^{3+} + 2e^- \leftrightarrow Au^+$	1.41 V
$IO_3^- + 3H_2O + 6e^- \leftrightarrow I^- + 6OH^-$	0.269 V
$3Au^{3+} + I^- + 6OH^- \leftrightarrow 3Au^+ + IO_3^- + 3H_2O$	1.14 V

b) Calculate K for the reaction (5)

$$\Delta G = -6FE = -660\text{kJ} \qquad K = 10^{6E^\circ/.05196} = 4\times10^{131}$$

Note: because I said "at equilibrium" in the problem, this is an acceptable answer:

$$K = \frac{[Au^+]^3[IO_3^-]}{[Au^{3+}]^3[I^-][OH^-]^6} = \frac{(0.100)^3(0.100)}{(1\times10^{-3})^3(1\times10^{-4})(1\times10^{-5})^6} = 1\times10^{39}$$

c) Calculate E for the conditions given (5)

Because I made the mistake of saying "at equilibrium" without giving you any numbers for temperature, etc., E would be equal to E^o

If I had not said that, the answer would be this:

$$E = \left(1.41 - \frac{0.05916}{6}\log\frac{[Au^+]^3}{[Au^{3+}]^3}\right) - \left(0.269 - \frac{0.05196}{6}\log\frac{[IO_3^-]}{[I^-][OH^-]^6}\right) = 1.37\text{ V}$$

d) Write the line notation for the cell that can be made with two Pt electrodes and the two half-reactions here (5)

$$\text{Pt}(s)\,|\,Au^{3+}, Au^+ \,||\, I^-, OH^-, IO_3^- \,|\, \text{Pt}(s)$$

3) (20 points total)

a) Find the pH of a solution prepared by dissolving 27.75 g of ethylamine ($CH_3CH_2NH_2$, MW=45.0837) and 16.73 g of ethylammonium chloride ($CH_3CH_2NH_3^+Cl^-$,MW=81.5444) in 1.50 L of water. The pK_a for ethylammonium is 10.636. (10)

$$27.75\text{ g EtAm} \div 45.0837\text{ g/mol EtAm} = 0.6155\text{ mol EtAm}$$

$$16.73\text{ g EtAm}^+ \div 81.5444\text{ g/mol EtAm}^+ = 0.2052\text{ mol EtAm}^+$$

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]} = 10.636 + \log\frac{0.6155}{0.2052} = 11.11$$

b) If you added 15.72 mL of 1.000 M $HClO_4$ is added to the solution, what is the pH? (10)

$$0.01572\text{ L HClO}_4 \times 1.00\text{ M} = 0.01572\text{ mol HClO}_4 = 0.01572\text{ mol H}^+$$

$$\text{mol EtAm} = 0.6155\text{ mol} - 0.01572\text{ mol} = 0.5998\text{ mol EtAm}$$

$$\text{mol EtAm}^+ = 0.2052 + 0.01572\text{ mol} = 0.2209\text{ mol EtAm}^+$$

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]} = 10.636 + \log\frac{0.5998}{0.2209} = 11.07$$

4) (30 points total) A chemist dissolves barium oxalate (BaC_2O_4) in water. In solution, oxalate acts as a base and can accept two protons to form oxalic acid. In addition, barium can form a complex neutral species in solution with oxalate as well as one complex ion in solution with hydroxide. Use the systematic approach to setup equations to evaluate this system.

a) Write the chemical reactions involved in this system (10)

$$BaC_2O_4(s) \leftrightarrow Ba^{2+}(aq) + C_2O_4^{2-}(aq)$$
$$C_2O_4^{2-}(aq) + H_2O \leftrightarrow HC_2O_4^{-}(aq) + OH^{-}(aq)$$
$$HC_2O_4^{-}(aq) + H_2O \leftrightarrow H_2C_2O_4(aq) + OH^{-}(aq)$$
$$Ba^{2+}(aq) + C_2O_4^{2-}(aq) \leftrightarrow BaC_2O_4(aq)$$
$$Ba^{2+}(aq) + OH^{-}(aq) \leftrightarrow BaOH^{+}(aq)$$
$$H_2O \leftrightarrow H^{+}(aq) + OH^{-}(aq)$$

b) Write the charge balance equation for this system (5)

$$2[Ba^{2+}] + [BaOH^{+}] + [H^{+}] = 2[C_2O_4^{2-}] + [HC_2O_4^{-}] + [OH^{-}]$$

c) Write the mass balance equation(s) for this system (5)

$$[Ba^{2+}] + [BaOH^{+}] = [C_2O_4^{2-}] + [HC_2O_4^{-}] + [H_2C_2O_4]$$

([BaC_2O_4]*(aq)* cancels as it's on both sides of the equation)

d) Setup the equilibrium expressions for this solution (5)

$$K_{sp} = [Ba^{2+}][C_2O_4^{2-}] \qquad K_{b1} = \frac{[HC_2O_4^{-}][OH^{-}]}{[C_2O_4^{2-}]} \qquad K_{b2} = \frac{[H_2C_2O_4][OH^{-}]}{[HC_2O_4^{-}]}$$

$$\beta_{1(BaC_2O_4)} = \frac{[BaC_2O_4]}{[Ba^{2+}][C_2O_4^{2-}]} \qquad \beta_{1(BaOH^{+})} = \frac{[BaOH^{+}]}{[Ba^{2+}][OH^{-}]} \qquad K_W = [H^{+}][OH^{-}]$$

e) Count the equations and species. Can we solve for the concentrations of all species? (5)

We have 8 unknowns ([Ba^{2+}], [$C_2O_4^{2-}$], [$HC_2O_4^{-}$], [$H_2C_2O_4$], [BaC_2O_4]*(aq)*, [$BaOH^{+}$], [H^{+}], and [OH^{-}]) and 8 equations (6 equilibria, charge balance, mass balance) so yes we can solve it!

5) (10 points total) Define/explain the following terms:

a) Chelating ligand
   A ligand that can bind to an atom through more than atom
   (or a multidentate ligand)

b) Buffer
   A solution made from weak acid and conjugate weak base that is resistant to change in pH

c) Galvanic cell
   A voltaic cell (redox reaction) that uses a spontaneous chemical reaction to generate electricity

d) Ion-selective electrode
   Electrodes which respond selectively to one ion by using a thin membrane which allows only that ion to pass between two reference electrodes based on the same reaction

e) S.C.E.
   Saturated calomel electrode; A reference electrode based on the mercury-mercury chloride redox reaction