Exam 2 Name:
Fall 2004
Chem 311
Evans

Do any 4 of the 6 problems!!!!!!!

1. An iodometric titration was performed on a dilute solution of HOCl (a weak acid!!!!). The solution that was analyzed was first diluted by a factor of 100 with 0.5 M H_2SO_4. 25.00 ml of this diluted solution was mixed in a 250 ml Erlenmeyer flask with 50.00 ml of a 0.02564 M solution of KI in 0.5 M H_2SO_4. The I_3^- generated from the reaction was then titrated with 0.04956 M solution of thiosulfate ($S_2O_3^{2-}$), requiring 14.28 ml to reach the endpoint with the starch indictor. (HINT: Table 16-5 may be helpful)

   a) Calculate the [HOCl] of the original solution.

$$HOCl + H^+ + 3I^- \rightarrow Cl^- + I_3^- + H_2O$$

$$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$$

(0.04956 M)*(14.28 ml) *(1 mmol I_3^-/2 mmol $S_2O_3^{2-}$)*(1 mmol HOCl/1 mmol $S_2O_3^{2-}$)*(1/25.00 ml)*(100) = 1.415 M

   b) Should the starch indicator be added at the start of the titration or right before the endpoint? Explain why.

Starch irreversibly binds to I_3^-, and since I_3^- is present at the beginning of this titration, the starch must be added right before the endpoint is reached.

   c) Assuming the presence of only HOCl in the original solution, calculate the pH of the original solution.

HOCl is a weak acid. Ka = $3.0*10^{-8}$.

$3.0*10^{-8} = [H_3O^+]^2/1.418$

$[H_3O^+] = 0.000206066$ M

pH = 3.69

2. The following data was obtained from a Zn indicator electrode that was constructed using a Ag/AgCl reference electrode. Measurement of an unknown solution of zinc acetate, $Zn(Ac)_2$, a soluble salt, produced a cell voltage of -876 mV.

a. Calculate the concentration of the $[Zn^{2+}]$ in this unknown solution.

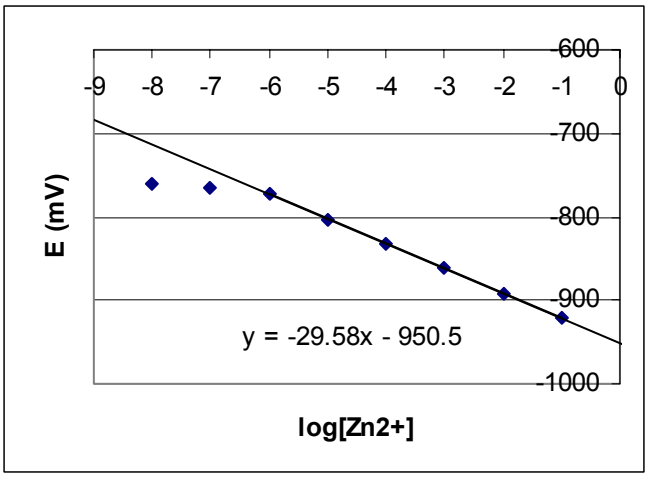
$-876 = -29.58 \log[Zn^{2+}] - 950.5$

$[Zn^{2+}] = 0.003$ M

b. Calculate the magnitude of the junction potential at the porous plug (the salt bridge that creates a second junction potential that is that is independent of the ion selective membrane; look at Figure 15-9). $-876 = -762-29.58\log[Zn^{2+}] - 197 + jp$

$Jp = 8$ mV

[Zn2+] of Stds	log[Zn2+]	cell voltage,E (mV)
1.00E-01	-1.000	-921
1.00E-02	-2.000	-891
1.00E-03	-3.000	-862
1.00E-04	-4.000	-832
1.00E-05	-5.000	-803
1.00E-06	-6.000	-773
1.00E-07	-7.000	-765
1.00E-08	-8.000	-760



c. Why do you think the cell potentials for the last two standards do not fall on the standard curve.

Diffusion of Zn^{2+} across the junction limits the detection limit.

3. 50.00 ml of a 0.500 M $Cu(NO_3)_2$ solution is mixed with 50.00 ml of a 0.500 M solution of KCl in a large beaker. A large chunk of solid silver metal is added to the solution. (HINT: Take a look at the Ag/AgCl half cell)

a) Does a reaction occur? Write down a balanced reaction describing what occurs when the silver is added.

$AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-$ $\quad E^0 = 0.222$ V

$Cu^{2+} + 2e^- \leftrightarrow Cu(s)$ $\quad E^0 = 0.339$ V

$Cu^{2+} + 2Cl^- + 2Ag(s) \leftrightarrow 2AgCl(s) + Cu(s)$

$E = (.339-.222) - (0.05916/2)\log \{1/([Cu^{2+}][Cl^-]^2)\} = 0.064$ V

b) Once equilibrium has been reached will the concentration of the $[Cl^-]$ be greater than or less than 0.0010 M. Justify your answer.

	Cu^{2+}	$+ 2Cl^-$	$+ 2Ag(s)$	$\leftrightarrow$	$2AgCl(s)$	$+$	$Cu(s)$
Initial	.25	.25					
Final	.125	.001					

$E = (.339-.222) - 0.05916/2\log \{1/((.125)(.001)^2)\} = -0.087$ V

So, equilibrium will be reached before the $[Cl^-]$ reaches 0.001 M

4. In region rich in limestone deposits, $[Ca^{2+}]$ in streams is about $1.0*10^{-5}$ M. A Ca^{2+} ion selective electrode can be used for continuous monitoring of $[Ca^{2+}]$ in streams. High levels of Mg^{2+} can interfere with this measurement. Assuming the calcium ion selective electrode used has a selectivity coefficient, $k_{Ca2+,Mg2+}$, of 0.00055, calculate the maximum $[Mg^{2+}]$ that can be tolerated to ensure less than a 10 % error in the measured $[Ca^{2+}]$.

$$E = \text{constant} + 59.16/2 \log\{[Ca^{2+}] + k_{Ca2+,Mg2+} [Mg^{2+}]\}$$

A 10 % error would occur when $k_{Ca2+,Mg2+} [Mg^{2+}] = 1.0*10^{-6}$

Solving for $[Mg^{2+}]$, $[Mg^{2+}]_{max} = 0.0018$ M

5. 50.00 ml of a 0.0250 M solution of $SnCl_2$ (soluble salt) in 1 F HCl is titrated with a 0.100 M standard solution of Cerium(IV) in 1 F HCl.

a) Calculate the volume it will take to reach the equivalence point.

$Sn^{2+} + 2Ce^{4+} \rightarrow Sn^{4+} + 2Ce^{3+}$

(50.00 ml)*(0.0250 M)*(2mmol Ce^{4+}/1 mmol Sn^{2+})*(1 ml / 0.1mmol) = 25.0 ml

b) If the course of the titration is followed potentiometrically using an SCE reference electrode, calculate the expected cell voltage at the equivalence point.

$E_+ = 0.139-(0.05916/2)\log([Sn^{2+}]/[Sn^{4+}]) = 1.47 - 0.05916\log([Ce^{3+}]/[Ce^{4+}])$

$2E_+ = 2(0.139)-(0.05916)\log([Sn^{2+}]/[Sn^{4+}])$

$3E_+ = 2(0.139)-(0.05916)\log([Sn^{2+}]/[Sn^{4+}]) + 1.47 - 0.05916\log([Ce^{3+}]/[Ce^{4+}])$

$3E_+ = 2(0.139) + 1.47 - 0.05916\log([Ce^{3+}][Sn^{2+}]/[Ce^{4+}][Sn^{4+}])$

at the equivalence point

$3E_+ = 2(0.139) + 1.47$

$E_+ = 0.58$

$E = 0.58 - .241 = 0.34$

c) If you wanted to use a redox indicator instead, which indicator from Table 16-2 would be most appropriate?

Match the E_+ to values in Table 16.2
Methylene blue 0.53 ± 0.06 V

6. Using the Appendix F and Appendix H, calculate the standard reduction potential for the following half-cell.

$CuBr_{(s)} + e^- \leftrightarrow Cu(s) + Br^-$

$CuBr(s) \leftrightarrow Cu^+ + Br^-$ $\quad Ksp = 5*10^{-9}$

$Cu^+ + e^- \leftrightarrow Cu(s)$ $\quad E^0 = 0.518$ $\quad K_b = 10^{\{0.518)(1)/(0.05916)\}} = 5.7*10^8$

$CuBr_{(s)} + e^- \leftrightarrow Cu(s) + Br^-$ $\quad K = Ksp*Kb = 2.85$

$E^0 = 0.05916\log(2.850) = 0.0269\ V = 0.0\ V$