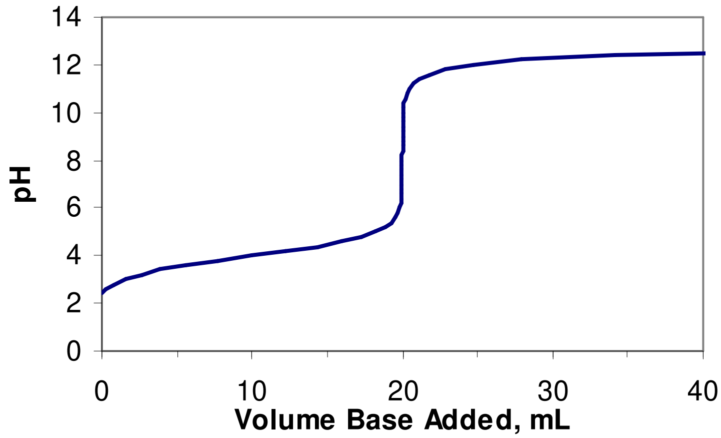
Chem 131 **Name**________________________________
Exam 3, Ch 17, 18, 20, 24 **April 25, 2012**
100 Points

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

Part 0: Warmup. 4 points each

1. The titration curve show below is for the titration of 0.10 M acid with 0.10 M NaOH. Which of the acids below must have been titrated to generate this curve?



   a. HCl
   b. HNO_2, $K_a = 4.0 \times 10^{-4}$
   c. $HClO_2$, $K_a = 1.2 \times 10^{-2}$ Answer ______b______
   d. HOCl, $K_a = 3.5 \times 10^{-8}$
   e. Not enough information to tell.

2. Consider the following salts: AgI, PbI_2, and CoI_3. If all three salts have the same K_{sp}, which of the salts has the largest solubility?
   a. AgI
   b. PbI_2
   c. CoI_3 Answer ______c______
   d. They have the same solubility.

3. Based on the data below, arrange the following in order of increasing strength as a <u>reducing agent</u>. Poorest reducing agent → Best reducing agent.

$Fe^{3+} + 2e^- \rightleftarrows Fe^{2+}$	$E^o = +0.77$ V	$2H^+ + e^- \rightleftarrows H_2$	$E^o = +0.00$ V
$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O$	$E^o = +1.78$ V	$ClO_2 + e^- \rightleftarrows ClO_2^-$	$E^o = +0.91$ V

   a. $H_2O < ClO_2^- < H_2 < Fe^{2+}$
   b. $H_2O < Fe^{2+} < H_2 < ClO_2^-$
   c. $H_2 < ClO_2^- < H_2O < Fe^{2+}$ Answer ______N/A_____
   d. $H_2 < Fe^{2+} < ClO_2^- < H_2O$

There was significant confusion on the interpretation of this question so I chose to give everyone full credit on #3.

Part I: Complete all of problems 3-7

4. Define **three** of the following in a maximum of three sentences per item: (12 points)

   a. equivalence point:
   Part of a titration when a stoichiometric amount of titrant has been added to consume all of the analyte. Neither reactant is in excess.

   b. coordination number:
   The number of positions around a central atom where ligands are attached in a complex.

   c. electrolytic cell:
   Electrochemical cell where a nonsponaneous reaction is carried out by electrolysis (supplying an external potential).

   d. bidentate:
   A ligand that has two points of attachment with the metal in a complex.

5. KI(aq) is slowly added to a solution with $[Pb^{2+}] = [Ag^{+}] = 0.10$ M. What precipitate should form first? What $[I^{-}]$ is required for the second cation to begin to precipitate? Justify your answers with calculations. K_{sp} for lead iodide is $7.1\text{x}10^{-9}$, K_{sp} for silver iodide is $8.5\text{x}10^{-17}$ (12 points)

   We need to determine the iodide concentration required to cause each salt to precipitate.

   Solve two K_{sp} systems:

$$PbI_2 \rightleftarrows Pb^{2+} + 2I^{-} \qquad K_{sp} = [Pb^{2+}][I^{-}]^2$$

   So, $K_{sp} = [0.10][I^{-}]^2$ and $[I^{-}] = (K_{sp}/0.10)^{1/2} = (7.1\text{x}10^{-8})^{1/2} = 2.66 \text{ x } 10^{-4}$ M

$$AgI \rightleftarrows Ag^{+} + I^{-} \qquad K_{sp} = [Ag^{+}][I^{-}]$$

   So, $K_{sp} = [0.10][I^{-}]$ and $[I^{-}] = (K_{sp}/0.10) = 8.5 \text{ x } 10^{-16}$ M

   So, AgI will precipitate first because it requires less iodide to satisfy the K_{sp} expression. Lead iodide will begin to precipitate when the iodide concentration reached 0.000266 M.

6. Consider the titration of 20.0 mL of 0.200 M lactic acid ($HC_3H_5O_3$, $pK_a = 3.86$) with 0.200 M NaOH.
   a. Calculate the pH after the addition of **two** of the following volumes of NaOH: 0.00 mL, 5.00 mL, 10.00 mL, 15.00 mL, 20.00 mL, 25.00 mL, 30.00.mL (10 points)

   Depending on the volumes you choose, your approach to a pH will differ. At 0 mL, you have only HA and can use an ICE table to find $[H^+]$. At 5, 10, and 15 mL, you have a buffer solution and can use the Henderson-Hasslebach equation or an ICE table. At 20 mL, you have a solution of the weak base, A^-, and can use an ICE table to find $[OH^-]$, At 25 and 30 mL, you have excess NaOH present.

   You must remember that as NaOH is added, the HA must be consumed as the weak acid is converted to its conjugate base.

Volume (mL)	mmol HA	mmol A^-	mmol OH^- excess	Total volume (mL)	Approach	pH
0.00	4.00	0	0	20.00	ICE table for HA	2.28
5.00	3.00	1.00	0	25.00	Buffer or ICE table	3.38
10.00	2.00	2.00	0	30.00	$pH = pK_a$	3.86
15.00	1.00	3.00	0	35.00	Buffer or ICE table	4.33
20.00 (eq pt.)	0.00	4.00	0	40.00	ICE table for HA	8.43
25.00	0.00	4.00	1.00	45.00	Excess OH^-	12.35
30.00	0.00	4.00	1.00	50.00	Excess OH^-	12.60

   b. Would methyl orange ($pK_{HIn} = 4.0$) be an appropriate indicator for this titration? Why or Why not? (4 points)

   Since this is a titration of a weak acid with a strong base, the pH at the equivalence point will be slightly basic and we need an indicator whose transition range (near the pK_{HIn}) occurs at a slightly basic pH. Since methyl orange has a pK_{HIn} of 4.0, it will change color prior to the solution becoming basic, therefore it is not a suitable indicator.

Part II. Electrochemistry. Answer two (2) of problems 7-9. Clearly mark the problem you do not want graded. 14 points each.

7. In electrorefining, impure metals, such as copper and gold are purified via electrolysis. For copper, an impure piece of copper ore is used as the anode and pure copper as the cathode. Both electrodes are immersed in a solution of copper (II) sulfate and a current is passed through the cell, resulting in deposition of pure copper on the cathode. If a current of 1.75 A is passed for 1 hour and 45 minutes, what mass of copper should deposit?

$$Cu^{2+} + 2e^- \rightarrow Cu^o$$

$$\frac{1.75\ C}{s} \times \frac{105\ min}{} \times \frac{60\ sec}{1\ min} \times \frac{1\ mol\ e^-}{96485\ C} \times \frac{1\ mol\ Cu}{2\ mol\ e^-} \times \frac{63.546\ g}{1\ mol\ Cu} = \mathbf{3.63\ g\ Cu}$$

8. The potential of the electrochemical cell below was measured to be +0.0567 V. What is the K_{sp} for PbI_2? The E^o for $Pb^{2+} + 2\ e^- \rightleftarrows Pb^o$ is -0.125 V

$$Pb(s)\ |\ Pb^{2+}\ (sat'd\ PbI_2)\ \|\ Pb^{2+}\ (0.100\ M)\ |\ Pb(s)$$

The overall cell reaction is:

$$Pb^o_a + Pb^{2+}_c \rightleftarrows Pb^o_c + Pb^{2+}_a$$

Where the c and a subscripts refer to the cathode and anode compartments.

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = -0.125\ V - (-0.125\ V) = 0.000V$$

$$E_{cell} = E^o_{cell} - \frac{0.05916}{2} \log \frac{[Pb^{2+}]_a}{[Pb^{2+}]_c} = 0.000V - \frac{0.05916}{2} \log \frac{[Pb^{2+}]_a}{1\ M}$$

So

$$+0.0567\ V = -\frac{0.05916}{2} \log \frac{[Pb^{2+}]_a}{1\ M}$$

Solving for $[Pb^{2+}]$: $[Pb^{2+}] = 10^{2x0.0567V/0.05916V} = 0.01214$ M

Our only source of Pb^{2+} is the dissociation of PbI_2, so: $Pb^{2+} = 0.01214$ M and $[I^-] = 2[Pb^{2+}] =$ 0.02428 M. and

$$K_{sp} = [Pb^{2+}][I^-]^2 = [0.01214][0.02428]^2 = \mathbf{1.79x10^{-6}}$$

9. Consider a galvanic cell consisting of one half cell with a gold wire dipped in a solution containing Au^{3+}, and a second half cell containing a tin wire immersed in Sn^{2+}. The standard reduction potentials are given below.

$Au^{3+} + 3e^- \rightleftarrows Au^o$ $E^o = +1.500$ V
$Sn^{2+} + 2e^- \rightleftarrows Sn^o$ $E^o = -0.137$ V

a. Determine the spontaneous overall cell reaction and calculate E^o_{cell}. Indicate which electrode is behaving as the anode and which is behaving as the cathode. (5 points)

$Au^{3+} + 3e^- \rightleftarrows Au^o$ $E^o = +1.500$ V **Cathode**
$Sn^{2+} + 2e^- \rightleftarrows Sn^o$ $E^o = -0.137$ V **Anode**

$$2Au^{3+} + 3Sn^o \rightleftarrows 2Au^o + 3Sn^{2+}$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = +1.500-(-0.137)\text{V} = \mathbf{+1.637V}$$

b. Calculate K for the cell reaction at 25°C. If you did not get a result for part a, propose a reasonable value. (4 points)

$$-nFE^o = -RT\ln K$$
$$-nFE^o/(-RT) = \ln K$$
$$\ln K = -(6 \text{ mol e- x } 96485 \text{ C/mol e x } +1.673\text{V})/(8.31441 \text{ J/molK x } 298\text{K}) = 382.5$$
$$K = e^{382.5} = 1.31\text{x}10^{166} \text{ (HUGE)}$$

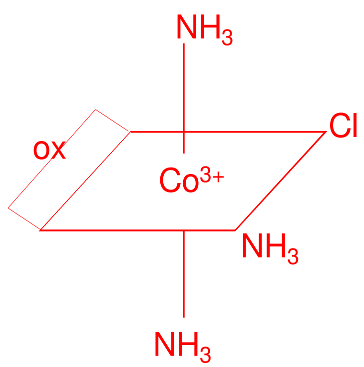
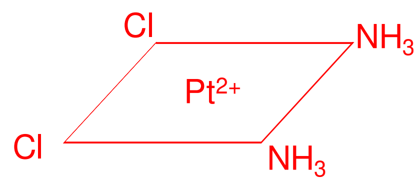
Note: this number may make your calculator unhappy! Getting to the point of $K = e^{382.5}$ will earn you full credit.

c. Calculate E_{cell} at 25°C when $[Au^{3+}] = 0.0100$ M and $[Sn^{2+}] = 0.00100$ M. (5 points)

$$E = E^o - \frac{0.05916\log}{n}\frac{[Sn^{2+}]^3}{[Au^{3+}]^2} = +1.637\text{V} - \frac{0.05916\log}{6}\frac{[0.0010\text{M}]^3}{[0.010\text{M}]^2} = \mathbf{+1.686\ V}$$

Part III. Transition Metals and Coordination Chemistry. Complete two (2) of problems 10-12. Clearly mark the problem you do not want graded. (14 points each)

10. Complete the table below.

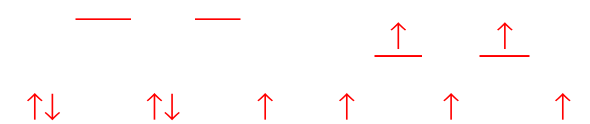
Formula	*mer*-$[CrCl(ox)(NH_3)_3]$	*cis*-$[PtCl_2(NH_3)_2]$
Name	*mer*-triamminechloroxalatochromium (III)	*cis*-diamminedichloroplatinum (II)
Metal oxidation state	+3	+2
Coordination number	6	4
Sketch		

11. Consider the two complexes: $[MnCl_6]^{4-}$ and $[Mn(CN)_6]^{4-}$. What leads to crystal-field splitting in these complex ions? Given that CN^- is a strong-field ligand and Cl^- is a weak-field ligand, sketch the orbital-energy level diagram for each ion. How many unpaired electrons are in each ion?

Crystal field splitting is a separation in energy of the d orbitals due to a repulsive interaction of the ligand electrons and the d-orbitals. Orbitals with electron density along the axis of approach of the ligands are raised in energy because of this repulsion. The magnitude of this separation depends on the identity of the ligand.

In both complexes, Mn is in the +2 oxidation state, with e^- configuration of $[Ar]3d^5$. So we have 5 d-electrons to work with,

$[Mn(CN)_6]^{4-}$	$[MnCl_6]^{4-}$
(large Δ, low spin)	(small Δ, high spin)



So, the cyanide complex has one unpaired electron, while the chloride complex has five.

12. Briefly compare and contrast each of the terms in the following pairs:

a. weak-field ligand vs. strong field ligand

Weak-field ligands have a small influence on the difference in energy between metal d-orbitals in a complex, while strong-field ligands have a larger influence and tend to lead to complexes where the is greater crystal-field splitting. Complexes with weak-field ligands generally half-fill all of the d-orbitals first before pairing electrons, while complexes with strong-field ligands fill the lower energy d-orbitals completely first.

NOTE: Ligands to not "have" a strong or weak field! Whether a complex is paramagnetic or diamagnetic depends on the number of d-electrons, the geometry of the complex, and the ligand-field splitting, not only on the ligand!

b. low-spin complex vs. high-spin complex

This is a result of the size of the crystal-field splitting. If Δ is large enough (strong field), electrons will tend to completely fill the lower energy d-orbitals first, maximizing the number of paired electrons (low-spin). If Δ is small enough (weak-field), all of the d-orbitals can be half-filled, maximizing the number of unpaired electrons (high-spin).

NOTE: Ligands do not have high or low spin, the magnitude of the crystal field splitting is influenced by the ligands. This splitting determines the number of unpaired electrons and whether the complex is high or low spin,

Possibly Useful Information

$R = 8.31441\ J\ mol^{-1}\ K^{-1}$	$^oC = K - 273.15$
$\Delta G = \Delta H - T\Delta S$	$\Delta G = \Delta G^o - RTlnQ$
$\Delta G^o = -nFE^o = -RTlnK$	$K_aK_b = K_w = 1.00 \times 10^{-14}$
$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$	pi = 3.14159
$pH = pK_a + \log\left(\frac{[conjugatebase]}{[weak\,acid]}\right)$	pH + pOH = 14
$E = E^o - \frac{RT}{nF}\ln Q$	$E = E^o - \frac{0.0591}{n}\log Q$ at 25°C
1 A = 1 C/s	F = 96485 C/mol e^-

Weak Field $I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \approx H_2O < NH_3 <$ en $< NO_2^- < CN^-$ **Strong Field**

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.9381	26 Fe 55.847	27 Co 58.9332	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)							

*Lanthanide series	58 Ce 140.115	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)