Chem 131
Exam 3, Ch 17, 18, 20, 24
100 Points

Name
April 25, 2012

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. $\mathrm{HNO}_{2}, \mathrm{~K}_{\mathrm{a}}=4.0 \times 10^{-4}$
c. $\mathrm{HClO}_{2}, \mathrm{~K}_{\mathrm{a}}=1.2 \times 10^{-2}$

Answer $\qquad$
d. $\mathrm{HOCl}, \mathrm{K}_{\mathrm{a}}=3.5 \times 10^{-8}$
e. Not enough information to tell.
2. Consider the following salts: $\mathrm{Agl}^{2}, \mathrm{Pbl}_{2}$, and $\mathrm{Col}_{3}$. If all three salts have the same $\mathrm{K}_{\mathrm{sp}}$, which of the salts has the largest solubility?
a. AgI
b. $\mathrm{Pbl}_{2}$
c. $\mathrm{Col}_{3}$

Answer $\qquad$
d. They have the same solubility.
3. Based on the data below, arrange the following in order of increasing strength as a reducing agent. Poorest reducing agent $\rightarrow$ Best reducing agent.

| $\mathrm{Fe}^{3+}+2 \mathrm{e}^{-} \rightleftarrows \mathrm{Fe}^{2+}$ | $\mathrm{E}^{\circ}=+0.77 \mathrm{~V}$ |
| :--- | :--- |
| $\mathrm{H}_{2} \mathrm{O}_{2}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightleftarrows 2 \mathrm{H}_{2} \mathrm{O}$ | $\mathrm{E}^{\circ}=+1.78 \mathrm{~V}$ |$:$| $2 \mathrm{H}^{+}+\mathrm{e}^{-} \rightleftarrows \mathrm{H}_{2}$ | $\mathrm{E}^{\circ}=+0.00 \mathrm{~V}$ |
| :--- | :--- |
| $\mathrm{ClO}_{2}+\mathrm{e}^{-} \rightleftarrows \mathrm{ClO}_{2}^{-}$ | $\mathrm{E}^{\circ}=+0.91 \mathrm{~V}$ |

a. $\mathrm{H}_{2} \mathrm{O}<\mathrm{ClO}_{2}^{-}<\mathrm{H}_{2}<\mathrm{Fe}^{2+}$
b. $\mathrm{H}_{2} \mathrm{O}<\mathrm{Fe}^{2+}<\mathrm{H}_{2}<\mathrm{ClO}_{2}^{-}$
c. $\mathrm{H}_{2}<\mathrm{ClO}_{2}^{-}<\mathrm{H}_{2} \mathrm{O}<\mathrm{Fe}^{2+}$

Answer $\qquad$
d. $\mathrm{H}_{2}<\mathrm{Fe}^{2+}<\mathrm{ClO}_{2}<\mathrm{H}_{2} \mathrm{O}$

## 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:
b. coordination number:
c. electrolytic cell:
d. bidentate:
5. $\mathrm{KI}(\mathrm{aq})$ is slowly added to a solution with $\left[\mathrm{Pb}^{2+}\right]=\left[\mathrm{Ag}^{+}\right]=0.10 \mathrm{M}$. What precipitate should form first? What $[1]$ is required for the second cation to begin to precipitate? Justify your answers with calculations. $\mathrm{K}_{\text {sp }}$ for lead iodide is $7.1 \times 10^{-9}, \mathrm{~K}_{\text {sp }}$ for silver iodide is $8.5 \times 10^{-17}$ (12 points)
6. Consider the titration of 20.0 mL of 0.200 M lactic acid $\left(\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{3}, \mathrm{pK}_{\mathrm{a}}=3.86\right)$ with 0.200 M NaOH .
a. Calculate the pH after the addition of two of the following volumes of $\mathrm{NaOH}: 0.00 \mathrm{~mL}$, $5.00 \mathrm{~mL}, 10.00 \mathrm{~mL}, 15.00 \mathrm{~mL}, 20.00 \mathrm{~mL}, 25.00 \mathrm{~mL}, 30.00 \mathrm{~mL}$ (10 points)
Volume $1=$ $\qquad$ mL

Volume $2=$ $\qquad$ mL
b. Would methyl orange ( $\mathrm{pK}_{\mathrm{HIn}}=4.0$ ) be an appropriate indicator for this titration? Why or Why not? (4 points)

## 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?
8. The potential of the electrochemical cell below was measured to be +0.0567 V . What is the $\mathrm{K}_{\text {sp }}$ for $\mathrm{Pbl}_{2}$ ? The $\mathrm{E}^{\circ}$ for $\mathrm{Pb}^{2+}+2 \mathrm{e}^{-} \rightleftarrows \mathrm{Pb}^{\circ}$ is -0.125 V

$$
\mathrm{Pb}(\mathrm{~s}) \mid \mathrm{Pb}^{2+}\left(\text { sat'd } \mathrm{Pbl}_{2}\right) \| \mathrm{Pb}^{2+}(0.100 \mathrm{M}) \mid \mathrm{Pb}(\mathrm{~s})
$$

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

$$
\begin{array}{ll}
\mathrm{Au}^{3+}+3 \mathrm{e}^{-} \rightleftarrows \mathrm{Au}^{\circ} & \mathrm{E}^{\circ}=+1.500 \mathrm{~V} \\
\mathrm{Sn}^{2+}+2 \mathrm{e}^{-} \rightleftarrows \mathrm{Sn}^{\circ} & \mathrm{E}^{\circ}=-0.137 \mathrm{~V}
\end{array}
$$

a. Determine the spontaneous overall cell reaction and calculate $\mathrm{E}^{0}{ }_{\text {cell }}$. Indicate which electrode is behaving as the anode and which is behaving as the cathode. (5 points)
b. Calculate K for the cell reaction at $25^{\circ} \mathrm{C}$. If you did not get a result for part a, propose a reasonable value. (4 points)
c. Calculate $\mathrm{E}_{\text {cell }}$ at $25^{\circ} \mathrm{C}$ when $\left[\mathrm{Au}^{3+}\right]=0.0100 \mathrm{M}$ and $\left[\mathrm{Sn}^{2+}\right]=0.00100 \mathrm{M}$. ( 5 points)

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- $\left[\mathrm{CrCl}(\mathrm{ox})\left(\mathrm{NH}_{3}\right)_{3}\right]$ |  |
| :---: | :---: | :---: |
| Name |  | cis-diamminedichloroplatinum (II) |
| Metal <br> oxidation state |  |  |
| Coordination <br> number |  |  |
|  |  |  |
| Sketch |  |  |

11. Consider the two complexes: $\left[\mathrm{MnCl}_{6}\right]^{4-}$ and $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{4}$. What leads to crystal-field splitting in these complex ions? Given that $\mathrm{CN}^{-}$is a strong-field ligand and $\mathrm{Cl}^{-}$is a weak-field ligand, sketch the orbital-energy level diagram for each ion. How many unpaired electrons are in each ion?
12. Briefly compare and contrast each of the terms in the following pairs:
a. weak-field ligand vs. strong field ligand
b. low-spin complex vs. high-spin complex

Possibly Useful Information

| $R=8.31441 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ | ${ }^{\circ} \mathrm{C}=\mathrm{K}-273.15$ |
| :---: | :---: |
| $\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$ | $\Delta \mathrm{G}=\Delta \mathrm{G}^{\circ}-\mathrm{RTInQ}$ |
| $\Delta \mathrm{G}^{\circ}=-\mathrm{nFE} \mathrm{E}^{\circ}=-\mathrm{RTInK}$ | $\mathrm{K}_{\mathrm{a}} \mathrm{K}_{\mathrm{b}}=\mathrm{K}_{\mathrm{w}=1} 1.00 \times 10^{-14}$ |
| $\mathrm{x}=\frac{-\mathrm{b} \pm \sqrt{\mathrm{b}^{2}-4 \mathrm{ac}}}{2 \mathrm{a}}$ | $\mathrm{pi}=3.14159$ |
| $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \left(\frac{[\text { conjugatebase }]}{[\text { weakacid }]}\right)$ | $\mathrm{pH}+\mathrm{pOH}=14$ |
| $\mathrm{E}=\mathrm{E}^{\circ}-\frac{\mathrm{RT}}{\mathrm{nF}} \ln \mathrm{Q}$ | $\mathrm{E}=\mathrm{E}^{\circ}-\frac{0.0591}{\mathrm{n}} \log \mathrm{Q}$ at $25^{\circ} \mathrm{C}$ |
| $1 \mathrm{~A}=1 \mathrm{C} / \mathrm{s}$ | $\mathrm{F}=96485 \mathrm{C} / \mathrm{mol} \mathrm{e}$ |

Weak Field $\mathrm{I}^{-}<\mathrm{Br}^{-}<\mathrm{Cl}^{-}<\mathrm{F}^{-}<\mathrm{OH}^{-}<\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-} \approx \mathrm{H}_{2} \mathrm{O}<\mathrm{NH}_{3}<\mathrm{en}<\mathrm{NO}_{2}^{-}<\mathrm{CN}^{-}$Strong Field

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


| *Lanthanide series | $\begin{gathered} 58 \\ \mathrm{Ce} \\ 140.115 \end{gathered}$ | $\begin{gathered} 59 \\ \mathrm{Pr} \\ 140.908 \end{gathered}$ | $\begin{gathered} 60 \\ \mathrm{Nd} \\ 144.24 \end{gathered}$ | $\begin{gathered} 61 \\ \text { Pm } \\ \text { (145) } \end{gathered}$ | $\begin{gathered} 62 \\ \mathrm{Sm} \\ 150.36 \end{gathered}$ | $\begin{gathered} 63 \\ \text { Eu } \\ 151.965 \end{gathered}$ | $\begin{gathered} 64 \\ \text { Gd } \\ 157.25 \end{gathered}$ | $\begin{gathered} 65 \\ \mathrm{~Tb} \\ 158.925 \end{gathered}$ | $\begin{gathered} 66 \\ \text { Dy } \\ \text { 162.50 } \end{gathered}$ | $\begin{gathered} 67 \\ \text { Ho } \\ 164.930 \end{gathered}$ | $\begin{gathered} 68 \\ \mathrm{Er} \\ 167.26 \end{gathered}$ | $\begin{gathered} 69 \\ \mathrm{Tm} \\ 168.934 \end{gathered}$ | $\begin{gathered} 70 \\ \mathbf{Y b} \\ 173.04 \end{gathered}$ | $\begin{gathered} 71 \\ \mathrm{Lu} \\ 174.967 \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{\dagger}$ Actinide series | $\begin{gathered} \hline 90 \\ \text { Th } \\ 232.038 \end{gathered}$ | $\begin{gathered} 91 \\ \mathrm{~Pa} \\ 231.036 \end{gathered}$ | $\begin{gathered} 92 \\ \mathbf{U} \\ 238.029 \end{gathered}$ | $\begin{gathered} 93 \\ \mathbf{N p}_{237.048} \end{gathered}$ | $\begin{gathered} 94 \\ \mathrm{Pu} \\ (244) \end{gathered}$ | $\begin{aligned} & \hline 95 \\ & \mathrm{Am} \\ & (243) \end{aligned}$ | $\begin{aligned} & 96 \\ & \mathrm{Cm} \\ & (247) \end{aligned}$ | $\begin{gathered} 97 \\ \text { Bk } \\ (247) \\ \hline \end{gathered}$ | $\begin{gathered} 98 \\ \text { Cf } \\ \text { (251) } \end{gathered}$ | $\begin{gathered} \hline 99 \\ \text { Es } \\ (252) \end{gathered}$ | $\begin{aligned} & 100 \\ & \text { Fm } \\ & (257) \end{aligned}$ | $\begin{aligned} & 101 \\ & \mathrm{Md} \\ & (258) \end{aligned}$ | $\begin{aligned} & 102 \\ & \text { No } \\ & \text { (259) } \end{aligned}$ | $\begin{gathered} 103 \\ \mathrm{Lr} \\ (262) \end{gathered}$ |

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