| Chem 131 | Name | |
|---------------------------|------|-------------------------|
| Exam 4, Ch 17, 18, 20, 24 | | December 4, 2019 |
| 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 I: Complete all of problems 1-10

- 1. What is the oxidizing agent in this reaction: $Mg(s) + Cl_2(g) \rightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$? (4 points)
 - a. Mg(s) b. $Cl_2(g)$ c. $Mg^{2+}(aq)$ d. $Cl^-(aq)$ Answer <u>b</u>
- 2. Which of these reagents will oxidize Al to Al^{3+} , but not oxidize Pb to Pb^{2+} . (4 points)

a.
$$Br_2$$
 b. Ca^{2+} c. Fe^{2+} d. Br^- Answer c

Answer ____

С

3. Consider the titration curve below. The curve represents (4 points)



b. the titration of a weak acid with a strong base.c. the titration of a weak base with a strong acid.

d. the titration of a strong base with a strong acid.

a. the titration of a strong acid with a strong base.

- 4. The equilibrium concentration of barium ion in a saturated solution of barium fluoride is found to be 7.21×10^{-3} M. What is the K_{sp} for barium fluoride? (4 points)
 - a. 7.21×10^{-3} b. 1.44×10^{-2} c. 7.50×10^{-7} d. 1.50×10^{-6} Answer _____d____
- 5. From the structures below, identify the two structures that represent the same compound. (4 points)



6. Define the following in one or two sentences each. (6 points)

a. anode: electrode at which the oxidation half reaction occurs.

- b. stereoisomer: molecules have the same molecular formula and sequence of bonded atoms, but differ in the three-dimensional orientations of their atoms in space
- c. low spin: describes a coordination compound with the maximum number of paired electrons.

| Formula of complex | trans-[Co(en) ₂ Cl ₂] ⁺ | $[Fe(ox)_3]^{3-1}$ |
|-----------------------|---|--------------------------------|
| Name of complex | trans-dichlorobis(ethylenediamine)cobalt(III) | tris(oxalato)ferrate(III) |
| Metal oxidation state | +3 | +3 |
| Coordination number | 6 | 6 |
| Sketch | Or some similar representation | Or some similar representation |

7. Complete the table below. (10 points)

8. A 0.641 g sample of a monoprotic acid is dissolved in water and titrated with 0.230 M KOH. What is the molar mass of the acid if 14.5 mL of the KOH solution is required to neutralize the sample? (10 points)

$HA + KOH \rightarrow KA + H_2O$

Answer_____192 g/mol_____

9. A galvanic (voltaic) cell consists of an electrode composed of iron immersed in a 1.0 M iron (II) ion solution and another electrode composed of silver immersed in a 1.0 M silver (I) ion solution, connected by a salt bridge. Identify the cathode and anode and calculate the standard potential for this cell at 25 C. (10 points)

$$Fe^{2+} + 2e^{-} \rightarrow Fe(s) \quad E^{0} = -0.440 \text{ V}$$

Ag⁺ + e⁻ \rightarrow Ag(s) $E^{0} = +0.800 \text{ V}$

Since the silver reaction is more positive in the galvanic cell, it will be the cathode.

 $E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = +0.800 \text{ V} - (-0.440 \text{ V}) = +1.240 \text{ V}$

Answer_____+1.240 V_____

10. The K_{sp} of PbBr₂ is 6.60×10⁻⁶. What is the molar solubility of PbBr₂ in 0.511 M sodium bromide? (10 points)

| | PbBr ₂ | 1 | Pb ²⁺ | + | 2Br⁻ |
|---|-------------------|---|------------------|---|------------|
| Ι | | | 0 | | 0.511 |
| С | - | | +x | | +2x |
| E | | | Х | | 0.511 + 2x |

$K_{sp} = [Pb^{2+}][Br^{-}]^{2}$ $K_{sp} = (x)(0.511 + 2x)^{2}$

Assume 2x << 0.511

Now $K_{sp} = (x)(0.511)^2$ x = $K_{sp}/(0.511)^2 = 6.60x10^{-6}/0.2611 = 2.53 x 10^{-5}M = [Pb^{2+}]$

Checking our assumption, $2x = 2(2.53 \times 10^{-5} \text{M}) = 5.05 \times 10^{-5} = 0.0000505$ is << 0.511, so our assumption is good

Answer_____2.53 x 10⁻⁵M _____

Part II. Answer three (3) of problems 11-14. Clearly mark the problems you do not want graded. 12 points each.

11. Calculate the potential for the galvanic cell below using the given conditions. You may assume a temperature of 298K.

Al(s) $| 0.234 \text{ M Al}^{3+}(aq) || 0.0115 \text{ M Sn}^{2+}(aq) || Sn(s)$ Anode: Al³⁺ + 3e⁻ \rightleftharpoons Al(s) E^o = -1.676 V Cathode: Sn²⁺ + 2e⁻ \rightleftharpoons Sn(s) E^o = -0.137 V Overall reaction: $3\text{Sn}^{2+} + 2\text{Al}(s) \rightleftharpoons 3\text{Sn}(s) + 2\text{Al}^{3+}$ E^o_{cell} = -0.137V - (-1.676V) = +1.539V E = E^o - <u>0.05916</u> log <u>[Al^{3+}]^2</u> [Sn^{2+}]^3 E = +1.539 V - <u>0.05916</u> log <u>[0.234]^2</u> [0.0115]^3 E = +1.494 V

Answer_____+1.494 V_____

- 12. Maleic acid (C₄H₄O₄, molar mass 116.1 g/mol, $pK_{a1} = 1.92$, $pK_{a2} = 6.27$) is a weak diprotic acid that is often used to increase the stability of drug compounds. Calculate the pH at *any three (3)* of the following points in the titration of 20.0 mL of 0.100 M maleic acid with 0.100 M NaOH.
 - a. Before the addition of NaOH
 - b. After the addition of 10.0 mL NaOH
 - c. After the addition of 20.0 mL NaOH
 - d. After the addition of 30.0 mL NaOH
 - e. After the addition of 50.0 mL NaOH

It is helpful to first figure out where the equivalence points are. Since the concentrations of NaOH and maleic acid (which I'll call H_2A) are the same, if we have 20.00 mL of 0.100 M H_2A , equivalence points will occur at 20 and 40 mL of NaOH added.

a. This is a solution of H_2A , which we can treat as a weak monoprotic acid.

| | H_2A | ⇒ | HA | + | H^+ |
|---|---------|---|----|---|-------|
| Ι | 0.100 M | | 0 | | 0 |
| С | -X | | +x | | +x |
| E | 0.100-x | | х | | Х |

Inserting into the K_b expression, we get:

$$K_{a1} = 10^{-1.92} = 0.0120 = [HA][OH^{-}] = x^{2}$$

[A] $0.100 - x$

Rearranging: $0 = x^2 + K_{a1}x - 0.100K_{a1}$

Solving, we get x = 0.02918 or -0.0412. Since $x = [H^+]$, the negative value doesn't make sense, so $[H^+] = 0.02918$ M and **pH = 1.53**.

Note it is tempting to try to simplify the math by assuming $x \le 0.100$ to avoid solving a quadratic, but you find that 0.02918 is not ≤ 0.100 , so the assumption is not valid.

- c. This is half way to the first equivalence point, $pH = pK_{a1} = 1.92$
- d. This is at the first equivalence point. The amphiprotic HA⁻ is the only species in solution and the pH is the average of pK_{a1} and pK_{a2}: **pH** = $\frac{1}{2}(1.92 + 6.27) = 4.10$
- e. This is half way between the first and second equivalence points, $pH = pK_{a2} = 6.27$
- f. At this point, we have added 10 mL of NaOH beyond the equivalence point. We have a number of moles of unreacted NaOH present in that 10 mL, but diluted to the total volume of 70 mL (the original 20 mL sample plus the 50 mL titrant that has been added. pH is determined by finding the concentration of unreacted NaOH:

10.0 mL NaOH x 0.100 mol NaOH x 1 = 0.0143 M NaOHL 70.0 mL

13. You have a bottle of a white solid that you believe to be either calcium hydroxide ($K_{sp} = 6.5 \times 10^{-6}$) or manganese (II) hydroxide ($K_{sp} = 1.6 \times 10^{-13}$). You prepare a saturated solution of the salt and measure the solution's pH. If the pH of the solution is 9.84, what is the identity of your unknown salt? Justify your answer with a calculation.

There are at least two approaches to solving this problem.

One approach may be to calculate the K_{sp} that corresponds to producing enough OH⁻ to raise the pH to 9.84. Both Ca(OH)₂ and Mn(OH)₂ have the same stoichiometry (A(OH)₂ \rightleftharpoons A²⁺ + 2OH⁻) and the same form for the $K_{sp} = [A^{2+}][OH^{-}]^2$.

If pH = 9.84, pOH = 14.00-9.84 = 4.16 and $[OH^-] = 10^{-4.16} = 6.92 \times 10^{-5} M$.

The stoichiometry of the reaction indicates that $[A^{2+}] = \frac{1}{2}[OH^{-}] = 3.46 \times 10^{-5} M.$

Therefore, the $K_{sp} = (3.46 \times 10^{-5})(6.92 \times 10^{-5} \text{M})^2 = 1.66 \times 10^{-13}$ which corresponds to **Mn(OH)**₂

An alternate approach would be to calculate the pH of a saturated solution of each of the salts using an ICE table:

| | Ca(OH) ₂ | 4 | Ca ²⁺ | + | 20H ⁻ |
|---|---------------------|---|------------------|---|------------------|
| Ι | | | 0 | | 0 |
| С | | | +x | | +2x |
| E | | | Х | | 2x |

$$\begin{split} K_{sp} &= [Ca^{2+}][OH^{-}]^2\\ 6.5x10^{-6} &= (x)(2x)^2\\ x &= (6.5x10^{-6}/4)^{1/3} = 0.0253 \text{ M} = [Ca^{2+}]\\ [OH^{-}] &= 2(0.0253\text{ M}) = 0.0506\text{ M}, \text{ pOH} = 1.30, \text{ pH} = 12.70 \end{split}$$

Repeating for Mn(OH)₂

| | Mn(OH) ₂ | 1 | Mn ²⁺ | + | 20H- |
|---|---------------------|---|------------------|---|------|
| Ι | | | 0 | | 0 |
| С | | | +x | | +2x |
| E | | | Х | | 2x |

$$\begin{split} K_{sp} &= [Mn^{2+}][OH^{-}]^{2} \\ &1.6x10^{-13} = (x)(2x)^{2} \\ x &= (1.6x10^{-13} / 4)^{1/3} = 3.42x10^{-5} \text{ M} = [Mn^{2+}] \\ [OH^{-}] &= 2(3.42x10^{-5}\text{M}) = 6.84x10^{-5}\text{M}, \text{ pOH} = 4.16, \text{ pH} = 9.84 \\ \text{Again, this corresponds to } Mn(OH)_{2} \text{ being the identity of the unknown salt.} \end{split}$$

Answer_____ Mn(OH)₂_____

14. Cobalt (III) forms octahedral complexes with fluoride ion and ammonia with the formulae [CoF₆]³⁻ and [Co(NH₃)₆]³⁺, respectively. Below are two possible orbital energy diagrams for these species. Which of the diagrams corresponds to the fluoride complex and which one corresponds to the ammonia complex? Clearly explain your reasoning.



In diagram A, all of the electrons are paired, producing a low-spin complex, while in diagram B, there are more unpaired electrons, indicating a high-spin complex.

Low-spin complexes result from large crystal field splitting energies (Δ), which are produced by strong-field ligand. It is more energetically favorable to pair all of the electrons in the lower energy d orbitals than to populate the higher energy orbitals. The opposite is true for high-spin complexes. They are produced by weak-field ligands and have smaller Δ , making it less energetically costly to populate the higher energy d orbitals, compared to pairing electrons.

Looking at the ligand tendencies:

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

Ammonia is a strong field ligand, which would produce the electron distribution in diagram A, while fluoride is a weak field ligand, which would produce the distribution in diagram B.

Possibly Useful Information

| $R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$ | $^{\circ}C = K - 273.15$ | $R = 0.0821 L atm mol^{-1} K^{-1}$ |
|--|---------------------------------------|--|
| $F = 96485 \text{ C mol}^{-1}$ | $1 \text{ A} = 1 \text{ C sec}^{-1}$ | $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ |
| $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -RTlnK$ | $\Delta G = \Delta G^{\circ} - RTlnQ$ | $\Delta G = -nFE$ |
| $pH = pK_a + log\left(\frac{[conjugatebase]}{[weakacid]}\right)$ | pH + pOH = 14 | $K_a K_b = K_w = 1.00 \text{ x } 10^{-14}$ |
| $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$ or $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$ | $E=E^{o}-\frac{2.303RT}{nF}\log Q$ | $E = E^{o} - \frac{0.05916V}{n} \log Q$ |

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



TABLE 20.1 Some Selected Standard Electrode (Reduction) Potentials at 25 $^\circ\text{C}$

Reduction Half-Reaction

Acidic solution

E°, **V**

| $F_2(g) + 2 e^- \longrightarrow 2 F^-(aq)$ | +2.866 |
|--|--------|
| $O_3(g) + 2 H^+(aq) + 2 e^- \longrightarrow O_2(g) + H_2O(l)$ | +2.075 |
| $S_2O_8^{2-}(aq) + 2 e^- \longrightarrow 2 SO_4^{2-}(aq)$ | +2.01 |
| $H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l)$ | +1.763 |
| $MnO_4^{-}(aq) + 8 H^+(aq) + 5 e^- \longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$ | +1.51 |
| $PbO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow Pb^{2+}(aq) + 2 H_2O(l)$ | +1.455 |
| $\operatorname{Cl}_2(g) + 2 e^- \longrightarrow 2 \operatorname{Cl}^-(aq)$ | +1.358 |
| $Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$ | +1.33 |
| $MnO_2(s) + 4 H^+(aq) + 2 e^- \longrightarrow Mn^{2+}(aq) + 2 H_2O(l)$ | +1.23 |
| $O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow 2 H_2O(l)$ | +1.229 |
| $2 \operatorname{IO_3^{-}(aq)} + 12 \operatorname{H^+(aq)} + 10 \operatorname{e^-} \longrightarrow \operatorname{I_2(s)} + 6 \operatorname{H_2O(l)}$ | +1.20 |
| $Br_2(l) + 2 e^- \longrightarrow 2 Br^-(aq)$ | +1.065 |
| $NO_3^{-}(aq) + 4 H^+(aq) + 3 e^- \longrightarrow NO(g) + 2 H_2O(l)$ | +0.956 |
| $Ag^+(aq) + e^- \longrightarrow Ag(s)$ | +0.800 |
| $Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$ | +0.771 |
| $O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow H_2O_2(aq)$ | +0.695 |
| $I_2(s) + 2 e^- \longrightarrow 2 I^-(aq)$ | +0.535 |
| $Cu^{2+}(aq) + 2 e^{-} \longrightarrow Cu(s)$ | +0.340 |
| $SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^- \longrightarrow 2 H_2O(l) + SO_2(g)$ | +0.17 |
| $\operatorname{Sn}^{4+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \longrightarrow \operatorname{Sn}^{2+}(\operatorname{aq})$ | +0.154 |
| $S(s) + 2 H^+(aq) + 2 e^- \longrightarrow H_2S(g)$ | +0.14 |
| $2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$ | 0 |
| $Pb^{2+}(aq) + 2e^{-} \longrightarrow Pb(s)$ | -0.125 |
| $\operatorname{Sn}^{2+}(\operatorname{aq}) + 2 \operatorname{e}^{-} \longrightarrow \operatorname{Sn}(\operatorname{s})$ | -0.137 |
| $Fe^{2+}(aq) + 2e^{-} \longrightarrow Fe(s)$ | -0.440 |
| $Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$ | -0.763 |
| $Al^{3+}(aq) + 3 e^{-} \longrightarrow Al(s)$ | -1.676 |
| $Mg^{2+}(aq) + 2 e^{-} \longrightarrow Mg(s)$ | -2.356 |
| $Na^+(aq) + e^- \longrightarrow Na(s)$ | -2.713 |
| $Ca^{2+}(aq) + 2e^{-} \longrightarrow Ca(s)$ | -2.84 |
| $K^+(aq) + e^- \longrightarrow K(s)$ | -2.924 |
| $Li^+(aq) + e^- \longrightarrow Li(s)$ | -3.040 |