

Name: \_\_\_\_\_

Please see additional tables and equation sheet at the end of this exam to assist in answering all questions and problems!

1. True/False----Indicate whether the following statements are **True** or **False** in the space next to the statement. Make sure you carefully read each statement ! (2 points each)

False a) EDTA titrations are a good methodology to determine the concentration of alkali metal ions (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ) that bind EDTA very tightly (large equilibrium constant for complexation).

True b) A solution containing 0.01 M of the free base amine form of Tris (tris-hydroxymethyl)aminomethane) will have a pH that is somewhat lower than that of a solution containing 0.05 M of this same species.

False c) The charge balance equation says that the sum of the concentrations of all cations in solution equals the sum of the total concentrations of each anion in the same solution.

False d) The anode of a galvanic cell (if allowed to discharge spontaneously) is always the half-cell electrode that has the more positive voltage.

True e) The true pH of a solution containing 0.01 M HCl will be increased if 0.1 M of potassium bromide is added to the solution.

False f) The titration of a monoprotic weak acid with a  $\text{pK}_a = 8.0$  with a strong base (e.g., NaOH) is likely to have an endpoint pH of approx. 6.0

True g) At very high ionic strengths (e.g.,  $> 0.5 \text{ M}$ ), activity coefficients can be greater than the values they are at a total ionic strength of 0.1 M.

False h) In the titration of a diprotic acid with strong base, the first equivalence point after removing the first proton will occur at the  $\text{pK}_1$  value for that diprotic acid.

False i) For buffers prepared from diprotic acids, the maximum buffering capacity will always occur when the pH is adjusted to a value that is half-way between the two  $\text{pK}_a$  values of the acid.

True j) For the same ionic strength, the activity coefficient of ion A will be greater than ion B if the hydrated radius of ion A is greater than the hydrated radius on ion B.

2. For the following galvanic cell, please indicate whether the overall cell potential (measured as  $E_{\text{cath}} - E_{\text{anode}}$  (or  $E_{\text{right}} - E_{\text{left}}$ ) will **increase**, **decrease** or **remain the same** for the following actions. Assume activities equal concentrations, neglect any junction potentials in the cell, and assume that the volume of solution in each half-cell is 100 mL) (10). Note the relevant half-cell equilibria, written as reductions follow (note you do not need  $E^\circ$  values to answer this problem!!) ( $\text{H}^+ + 1 \text{e}^- \leftrightarrow 1/2 \text{H}_{(2)}$ ;  $\text{AgCl}_{(s)} + 1 \text{e}^- \leftrightarrow \text{Ag}^0 + \text{Cl}^-$ )

**Pt / H<sub>2</sub> (1 atm), HCl (0.01 M) // NaCl (0.01 M), AgCl<sub>(s)</sub> / Ag**

↓ Decrease a) addition of 9 grams of NaCl (FM=58.5) into the right half-cell solution.

- r/o change b) addition of 10 grams of AgCl<sub>(s)</sub> into the right half-cell solution

↓ Decrease c) increasing the concentration of HCl in the left half-cell to 0.05 M.

↑ Increase d) adding 5 grams of AgNO<sub>3</sub> (soluble salt) to the right half-cell.

↓ Decrease e) decreasing the pressure of hydrogen gas in the left half cell to 0.5 atm.

### 3. Multiple Choice Questions:--Please circle the best answer for each question or the best choice to finish the phrase (4 points each).

-The Debye Huckel equation provides a means to estimate the activity coefficients of single ions in solution, but requires knowledge of:

a) the ionic strength of the solution and the hydrated radius the ion of interest.

b) the sizes of the hydrated ionic species that most determine the total ionic strength of the solution.

c) which ions most influence the total ionic strength and the charge on these ions.

d) the ionic strength of the solution, the size of the hydrated ion for which the activity coefficient is being calculated, and its charge.

The main purpose of using KCl as an electrolyte in a Ag/AgCl or calomel reference electrode, is to:

a) make sure you have a pure source of and given concentration of chloride ion to determine the half cell potential.

b) provide a given concentration of chloride ion to establish the half-cell potential and also minimize the junction potential due to the similar mobilities of chloride and potassium ions

c) provide a means to make a saturated solution even at high temperatures, that has a constant chloride concentration, no matter what the temperature is.

d) none of the above

- The conditional formation constant of Cu(II) binding to EDTA at pH 7.0 is:

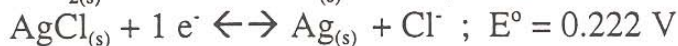
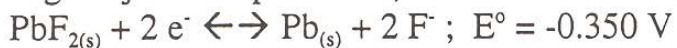
a)  $6.31 \times 10^{18}$

b)  $3.15 \times 10^{14}$

c)  $6.31 \times 10^{11}$

d)  $3.15 \times 10^{15}$

-The voltage of the following galvanic cell (assume concentrations = activities and neglect junction potentials) is best estimated by the following  $E_{\text{cell}}$  value:



$\text{Pb}_{(s)} / \text{PbF}_{2(s)}, \text{F}^- (0.01 \text{ M}) // \text{Cl}^- (0.1 \text{ M}), \text{AgCl}_{(s)} / \text{Ag}_{(s)}$

a) +572 mV

b) +749 mV

c) -128 mV

d) +128 mV



-L-Histidine is a naturally occurring amino acid with three ionizable groups (1 carboxyl, and two amines). The  $pK_a$  value for the carboxylic acid group is 1.70. The  $pK_a$  values for the protonated forms of the amine groups are 6.02 and 9.08, respectively. At which of the following pH values will histidine be closest to its isoelectric point (pI value)?

a) pH 3.86

b) pH 6.02

c) pH 5.38

d) pH 7.55

4. With concerns about use of cyanide in a possible terrorist attack, there is great interest in methods that can be used to determine cyanide concentration. One classical method is based on forming a complex with excess nickel ( $Ni^{+2}$ ) in accordance with the following reaction:



and then titrating the excess  $Ni^{+2}$  with EDTA in the presence of an appropriate colorimetric indicator. In practice for potential contamination of water supplies with  $CN^-$  in the state of Michigan, a new lab-tech in the state forensics laboratory decided to test the accuracy of this method. He/she prepared a "test" sample with a given amount of KCN in pH 8 buffer. In the test run of the method, he/she took 15 mL of this solution and added 25 mL of a standard solution containing  $Ni^{+2}$  to form the complex. The excess  $Ni^{+2}$  in this solution required 18 mL of 0.015 M EDTA to get the color endpoint. In a separate experiment, 40 mL of the standard  $Ni^{+2}$  solution required 45 mL of the same EDTA solution to reach the endpoint. Calculate the molarity of  $CN^-$  in the 15 mL of the test sample. (10)

First determ.  $[Ni^{+2}]$  in standard soln:

$$45 \text{ mL} \times 0.015 \text{ M} = 0.675 \text{ mmoles}$$

$$\frac{0.675 \text{ mmoles}}{40 \text{ mL}} = \boxed{0.0169 \text{ M}} = [Ni^{+2}] \text{ - std. soln}$$

$$\therefore \text{total } Ni^{+2} \text{ added} = 25 \text{ mL} \times 0.0169 \text{ M} = 0.4225 \text{ mmoles}$$

$$\text{excess } Ni^{+2} = 18 \text{ mL} \times 0.015 \text{ M} = 0.2700 \text{ mmoles}$$

$$Ni^{+2} \text{ used to complete } CN^- = 0.1525 \text{ mmoles}$$

Since 4  $CN^-$  react with 1  $Ni^{+2}$

$$\text{mmoles } CN^- = 4 \times 0.1525 \text{ mmoles} = 0.610 \text{ mmoles}$$

$$[CN^-] = \frac{0.610}{15 \text{ mL}} = 0.0407 \text{ M}$$

5. Calculate the  $[Ag^+]$  and  $[I^-]$  (concentrations) in water solutions that are saturated with  $AgI_{(s)}$  ( $K_{sp} = 8.3 \times 10^{-17}$ ) and are prepared in the absence and presence of 0.05 M  $KNO_3$ . (10)

Absence: assume  $\gamma_{Ag^+}$  and  $\gamma_{I^-} = 1.0$

$$\therefore K_{sp} = [Ag^+][I^-] = x^2 = 8.30 \times 10^{-17}$$

$$[Ag^+] = [I^-] = x = 9.11 \times 10^{-9} M$$

In presence:

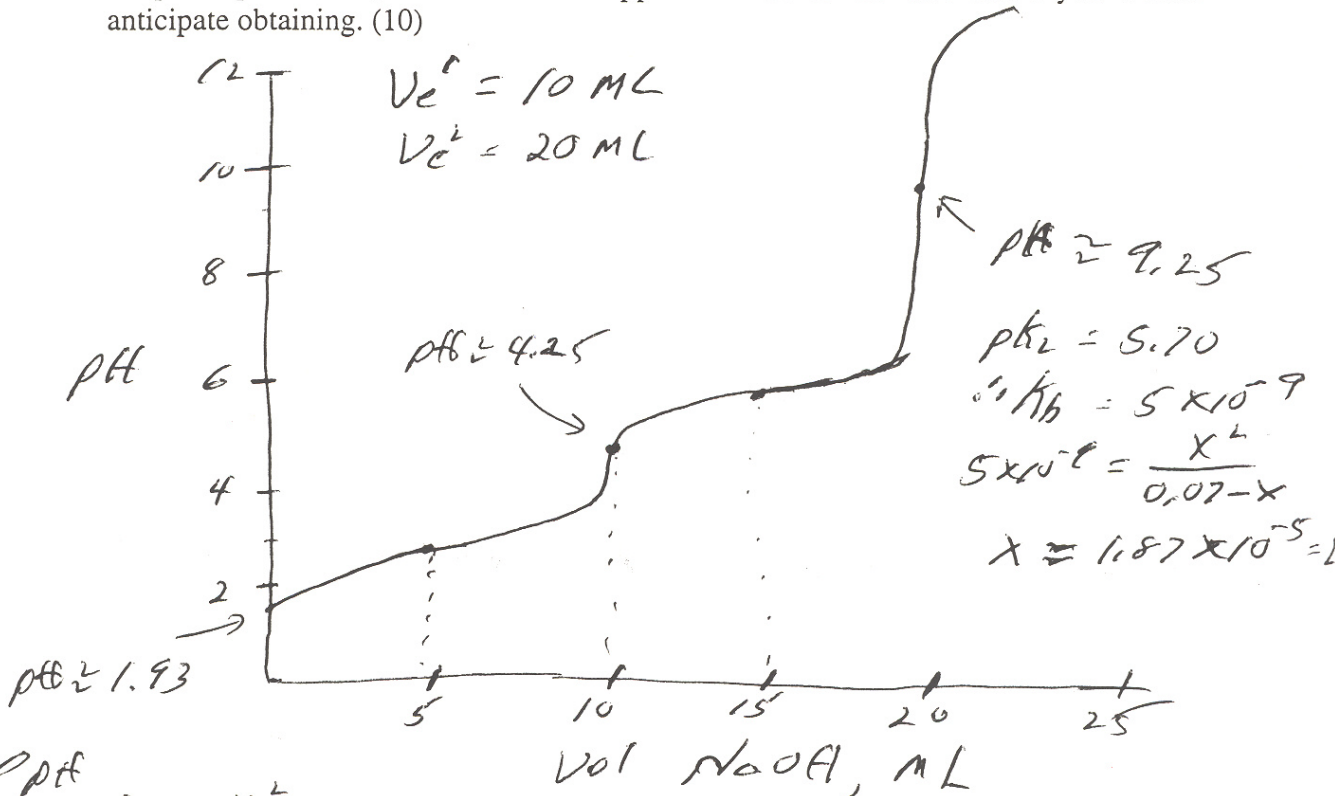
$$\mu = 0.05 M; \quad \gamma_{Ag^+} = 0.80, \quad \gamma_{I^-} = 0.805$$

$$\therefore K_{sp} = 8.30 \times 10^{-17} = [Ag^+] \gamma_{Ag^+} \cdot [I^-] \gamma_{I^-}$$

$$= x^2 (0.80)(0.805)$$

$$x = \boxed{1.14 \times 10^{-8} M} = [Ag^+] = [I^-]$$

6. Malonic acid (propanedioic acid— $HO_2CCH_2CO_2H$ ) has a  $pK_1 = 2.85$  and a  $pK_2 = 5.70$ . Sketch the titration curve you would expect to see if a 50 mL solution of 0.10 M of this diprotic acid is titrated with a 0.50 M NaOH. Make sure you label your axes (pH on y axis, mL NaOH on x axis) and try to draw the titration curve starting pH, endpoint pH values, etc. to a close approximation to the true curve you would anticipate obtaining. (10)



7. How many mL of 1.40 M HCl should be added to 5.00 g of Tris(hydroxyamino)methane (FM=157.6;  $pK_1 = 8.08$ ) dissolved in 500 mL of water, to give a pH of 8.00? What would be the ionic strength of this buffer, after the total volume was diluted to 1 L? (10). (neglect activity coefficients)

$$\text{moles Tris} = \frac{5g}{157.6} = 0.0317 \text{ moles}$$

$$pH = pK_a + \log \frac{Tris}{Tris-H^+} = 8.00 = 8.08 + \log X$$

$$-0.08 = \log X$$

$$X = 0.832$$

$$0.832 = \frac{0.317 - X}{X}$$

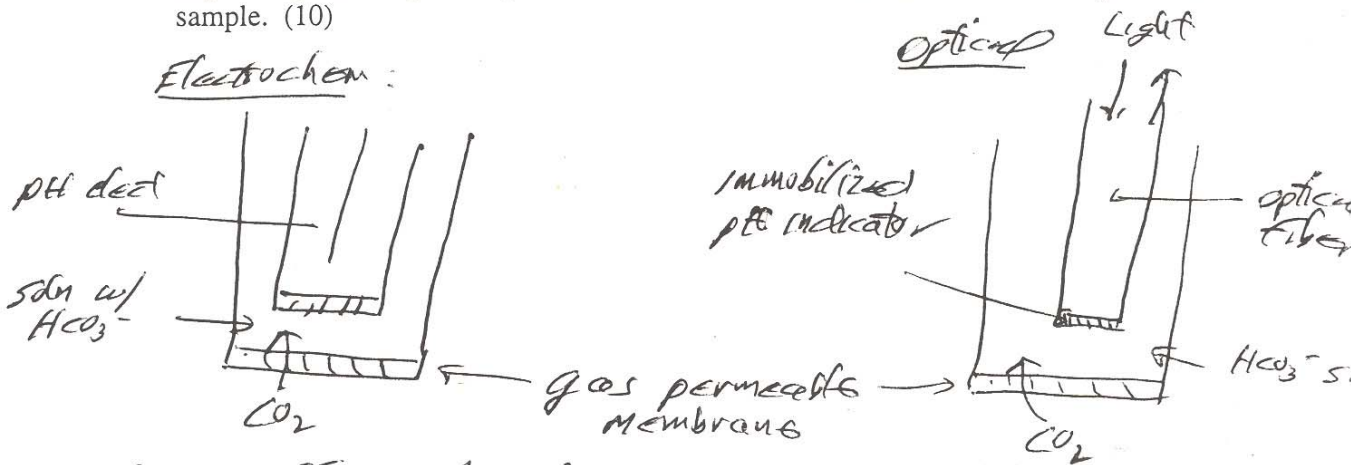
$$X = 0.0173 \text{ moles Tris-H}^+ = \text{moles HCl needed}$$

$$0.0173 = X L \cdot 1.4 M = X L \cdot 1.4 M$$

$$X = 0.0124 L = \boxed{12.4 \text{ mL}}$$

Ionic strength: since total  $[Tris-H^+]$  and  $[Cl^-] = 0.0173 M$  (after dilute to 1L) -  
 then  $I = \boxed{0.0173 M}$

8. Sketch the design of either an electrochemical or optical carbon dioxide sensor, and label the important components. Briefly explain how the output signal changes depending on the partial pressure/concentration of carbon dioxide in a given test sample. (10)



$CO_2$  diffuses through gas permeable membrane into layer of soln with  $HCO_3^-$ .  $CO_2$  reacts with  $H_2O \rightleftharpoons H_2CO_3$   
 $H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ ;  $\therefore$  increase in  $CO_2$  increases pH of internal  $HCO_3^-$  solution in accordance with  $H_2O$  eqn:  $pH = pK + \log \frac{HCO_3^-}{H_2CO_3} \leftarrow \text{const.}$