

GEORGE MASON UNIVERSITY  
CHEMISTRY DEPARTMENT  
CHEM 321, FINAL EXAM  
FALL 2003

**TIME 10:30 -1:00**

NAME \_\_\_\_\_

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Honor code pledge:

I have neither given nor received aids in this examination.

Signed \_\_\_\_\_

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**Show complete work to receive full credits. You are allowed to use a piece of paper with anything written on it and a calculator. Turn off your cell phone.**

**1. (40 points)**

(a) Calculate the pH of a  $10^{-8.5}$  M LiOH aqueous solution without any approximations ( $pK_w = 15.00$ ).

(b) Calculate the pH of a solution prepared by mixing equal volumes of 0.01 M each of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ . (For  $\text{H}_2\text{CO}_3$ :  $pK_{a1} = 6.352$ ,  $pK_{a2} = 10.329$ )

(c) Calculate the pH of a solution prepared by mixing equal volumes of strong acid or base of  $\text{pH} = 5$  and  $\text{pH} = 8$ .

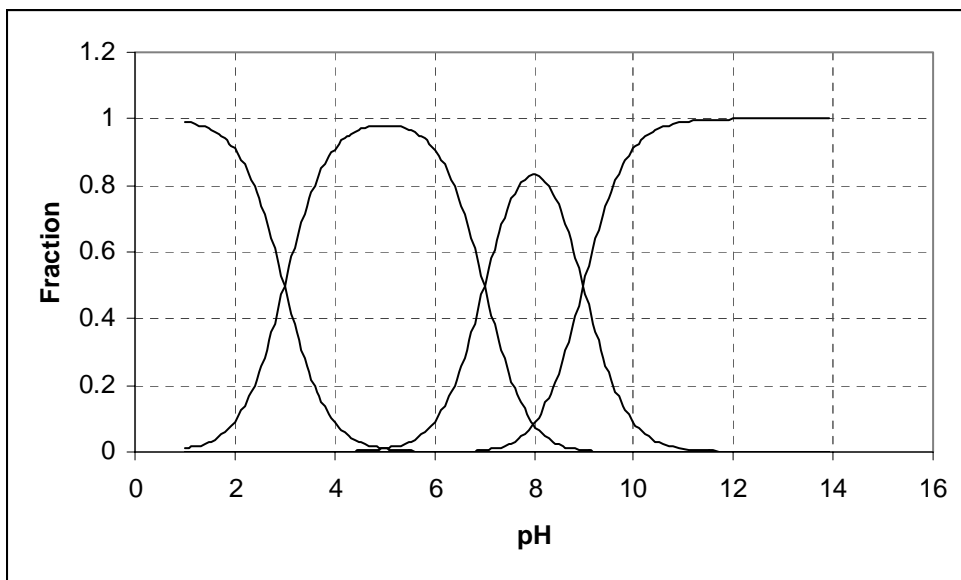
(d) What is the pH of a solution prepared by dissolving 0.10 mols of  $\text{H}_3\text{PO}_4$  in a liter of water? ( $pK_{a1} = 2.148$ ,  $pK_{a2} = 7.199$ ,  $pK_{a3} = 12.15$ ). What are the predominant species at  $\text{pH} 7.2$ ?

- (e) Excess  $\text{PbBr}_2(\text{s})$  was added to 0.025 M NaBr solution. Analysis of the equilibrium solution showed  $[\text{Pb}^{2+}] = 1.40 \times 10^{-2}$  M. What is the  $K_{\text{sp}}$  for  $\text{PbBr}_2(\text{s})$ ?
- (f) The metal ions,  $\text{Zn}^{2+}$ , is titrated with EDTA. If the concentration of the complex at the equivalence point is 0.025 M, calculate the concentration of free EDTA present in the solution. ( $\alpha_{\text{Y}^{4-}} = 0.36$ ,  $K_{\text{f}} = 10^9$ )
- (g) Show that the response of a  $\text{Cu}^{2+}$  ions selective electrode changes by 29.6 mV for a 10-fold change in concentration.
- (h) Solid  $\text{BaF}_2$  is in equilibrium with its species in aqueous solution. Identify all the species in solution and write the same number of equations to solve for the species concentrations. (mass balance, charge balance etc.)

**2. (15 points)**

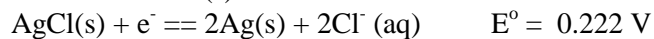
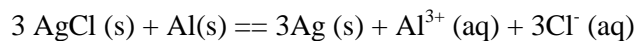
The graph below is the fractional composition diagram for a polyprotic acid ( $H_nA$ ). Given the initial concentration of the acid is 0.002 M, answer the following questions:

- Find  $n$ . Identify and estimate the acid dissociation constants.
- Calculate the equilibrium concentrations of all acidic or basic species at pH 2, pH 5, pH 7, and at pH 12.
- Identify two pH values where the buffer capacities of the acid are maximum



**3. (15 points)**

The following reaction can be studied by means of an electrochemical cell.



- Draw an electrochemical cell showing all the components of the cell and the direction of electron flow.
- Express the cell using line notation
- Calculate the equilibrium constant for the cell at 25 °C
- Calculate the concentration of  $\text{Al}^{3+}$  in the cell if the cell has 0.010 M KCl and the cell voltage is 2.000 V.



- f) Explain how electroosmotic flow drives the solution (solute+solvent) in a CZE separation of ionic species.
- g) Explain how the following detector works?
- h) The solvent hexane was used to prepare a standard solution of benzene by dissolving 30.0 mg of benzene (FW 78.114) in 250.0 mL of hexane. The sample has an absorbance of 0.312 at 256 nm in a 1.000 cm cell. Find the molar absorptivity of benzene.

**Extra Points****1. (10 points)**

A 1.000 g sample of an alloy steel sample is dissolved in perchloric acid, the manganese is oxidized to permanganate (purple in color), and the solution is diluted to 250.0 mL in a volumetric flask. The absorbance at 525 nm in a 1.00 cm cell is found to be 0.35. Calculate the percentage of Mn in steel. (Molar absorptivity of permanganate,  $\text{MnO}_4^-$ , is 2390. Atomic weight of Mn = 55)

**2. (10 points)**

Consider a 100.0 mL 0.10 M aqueous solution of  $\text{NaHCO}_3$ . (Data:  $\text{H}_2\text{CO}_3$ :  $\text{pK}_{\text{a}1} = 6.35$ ,  $\text{pK}_{\text{a}2} = 10.33$ )

- Identify all the species present in solution
- Calculate the pH of the solution.
- What is the pH of the solution if 10.0 millimols of HCl is added to it?