Chem 447---Electrochemistry---Problem Set # 2

1) Please answer the following questions True or False---**and** provide a sentence or two to support your answer. (4 each)

a) In highly acidic samples, the pH measured by glass electrode with a Ag/AgCl reference (with 0.1M KCl as internal reference electrolyte) is likely to be falsely low due to the error caused by the liquid junction potential.

b) When using a lanthanum fluoride crystal based fluoride ion selective electrode to measure the fluoride concentration of drinking water, if the pH of the water sample were to be adjusted <4 the measured fluoride level would be falsely low.

c) When using a three electrode potentiostat configuration to do electrochemistry, the purpose of the auxilliary electrode is to control the potential of the working electrode, since the potentiostat effectively measures the potential between the working electrode and the auxiliary electrode.

d) Enzyme electrodes can be prepared to measure biologically important species that are nonionic (not charged) by immobilizing highly selective enzymes at the surface of appropriate working electrodes.

e) For the reduction of an electroactive species at a small area micro-stationary electrode at constant applied potential, the current will always decrease rapidly with time (e.g. $t^{-1/2}$), even if the solution is well stirred.

2) Neglecting liquid junction potentials, assuming unity activity coefficients, and given that the potassium selective membrane exhibits a potentiometric selectivity coefficient of $K_{K,Na} = 10^{-4}$, calculate the absolute cell potential of the following potassium electrode-based galvanic cell when the sample is a solution containing 10^{-2} M KCl and 10^{-2} M NaCl: (10)

$Hg/Hg_2Cl_{2(s)}$, KCl (1M)/ sample / K^+selective membrane / KCl (0.1M), $AgCl_{(s)}/Ag$

If this cell were allowed to discharge spontaneously, which electrode (Ag or Hg) would be the true cathode of the cell?

3) Plot the i vs E_{appl} you would expect to observe for the simultaneous measurement of Zn^{+2} and Pb^{+2} by conventional D.C. polarography at a dropping mercury electrode. Make sure to indicate on the axis the approximate $E_{1/2}$ potential values and the relative magnitude of the currents for the two reduction reactions. Assume that the sample is adequately degassed (to remove O_2) and that the $[Zn^{+2}] = 1 \times 10^{-5}$ M and $[Pb^{+2}] = 3 \times 10^{-5}$ M. Also the reference electrode used was a Ag/AgCl with 1M KCl as the internal electrolyte, and that there are no overpotentials for the $2e^-$ reductions of Pb^{+2} and Zn^{+2} on a mercury electrode. (10)

4) The selective determination of sulfite represents a challenging analytical problem (e.g., in wines, etc.). One approach which can be used involves acidifying the sample to liberate $SO_2(g)$ in accordance with the following reaction:

$$SO_3^{-2} + 2H^+ \leftrightarrow H_2O + SO_2 \text{ (g)}$$
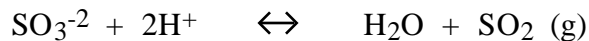
The concentration of SO_2 can be directed with a potentiometric SO_2 gas sensor. The key reaction within the sensor is:

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$$
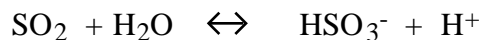
The equilibrium constant for this reaction is 1×10^{-2}.

Please sketch a schematic diagram of the SO_2 sensor which would be used to measure sulfite in complex samples. Specifically label the various components and membranes and indicate the likely chemical compositions of the internal solutions present within the sensor.   Briefly explain how the sensor is able to respond to sulfur dioxide (10).