1. Please answer the following questions True or False and provide a detailed 1-2 sentence explanation to justify your answer (4 points each).

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

b) When using a three electrode potentiostat to do electrochemistry, the counter or auxiliary electrode is always placed as close as possible to the working electrode to minimize $iR_{\text{solv}}$ drop due to the current that flows between these two electrodes.

c) If one neglects the effect of alkaline error due to selectivity constraints (i.e., assume complete selectivity for hydrogen ion over other cations), in highly basic solutions (pH > 12), the pH measured with a glass membrane electrode is likely to falsely low due to the difference in liquid junction potential between the calibrating buffer and the test sample.

d) An ideally polarized electrode is one in which the faradaic current increases proportionally to the applied voltage.

e) A carbon electrode is contact with an electrolyte solution of 0.1 M tetrabutylammonium chloride is likely to have a positive PZC value compared to placement of the same electrode into an aqueous solution that contains 0.1 M sodium chloride.

2. Calculate the transference number for sodium ions, $t_{\text{Na}^+}$, in an electrolyte solution composed of 0.01 M KCl and 0.05 M NaCl. (10)

3. Coupled chemical reactions represent one form of overpotential for faradaic electrochemical reactions. Explain what overpotential is, and give an example of how coupled chemical reactions could alter the applied potential required to reduce or oxidize and electroactive species. (15)

4. Calculate the absolute potential of the following electrochemical cell (as silver electrode minus calomel electrode):

$$\text{Hg / Hg}_2\text{Cl}_2(s), \text{NaCl (1 M)} / \text{NaCl (0.001 M)}, \text{AgCl}_{(s)} / \text{Ag}$$

Assume concentrations equal activities, and do not neglect liquid junction potentials! (15)
5. A carbon working electrode with an area of 0.2 cm$^2$ and a double layer capacitance of 10 µF/cm$^2$ was employed in a chronoamperometric experiment using a three electrode potentiostat. The sample solution contained an electroactive species present at 100 µM concentration in a background electrolyte of 0.1 M KCl. The electroactive species undergoes a 2 electron reduction at the carbon electrode with an $E_{1/2}$ value of –0.300 V vs. a saturated calomel reference electrode (when carrying out a steady-state voltammetric experiment). If the reference electrode was placed 2 cm away from the working electrode, **what would be the faradaic and charging currents 1 msec after application of a potential pulse of –0.500 V vs. SCE?** You may assume that this potential would fall within the limiting current regime under steady-state conditions. Recognize that the chronoamperometric experiment is performed under non-steady-state conditions (no solution convection). (20)

6. a) Explain the difference between the three main types of ionophores/carriers that can be used to prepare organic liquid/polymer membrane ion-selective electrodes. Discuss what controls the ultimate selectivity sequence of the resulting ion sensors for each type of ionophore and indicate what type of additional lipophilic sites would be required in the membrane to achieve optimal selectivity and response slopes when using the three classes of ionophores to develop anion selective electrodes, (15)

   b) In Professor Bachas’s lecture last Thursday, he described the potentiometric chloride response of anion electrodes based on mercurocarborand structures. Of the three types of ionophores you described above, which class does this type of ionophores belong to? Briefly justify your answer based on what was shown in his lecture! (5)