

Please answer all questions in a blue exam booklet and clearly identify the question (number/letter) that you are responding to! Good Luck!!

1) Please indicate the letter that best answers each of the following multiple choice questions (3 points each):

A) A fluoride ion-selective electrode based on a lanthanum fluoride crystal is an example of:

- a) An electrode of the first kind
- b) An electrode of the second kind
- c) A solid-state membrane electrode
- d) None of the above

B) The most widely used potassium selective membrane electrode employs the antibiotic valinomycin as an ionophore within a thin polymeric membrane at the distal end of the electrode. The presence of valinomycin enables the organic membrane to exhibit a voltage (EMF) that is highly dependent on the potassium activity in the sample, with relatively little interference from other common cations. The function of the valinomycin in this system is to:

- a) Sequester/bind all other cations present in the sample thus allowing only potassium to enter the organic membrane
- b) Selectively binds potassium to form a valinomycin/potassium complex within the membrane phase
- c) Serves as an anionic site within the membrane to neutralize the charge of potassium when it enters the membrane phase
- d) None of the above

C) Alkaline error associated with the use of glass membrane pH electrodes for pH measurements will yield:

- a) False high pH readings at low sample pH values due to the negative interference of Na^+ and other alkali cations on the potential (EMF) of the glass membrane
- b) False low pH readings at low sample pH values due to the positive interference of Na^+ and other alkali cations on the potential (EMF) of the glass membrane
- c) False high pH readings at very high sample pH values due to positive interference of Na^+ and other alkali cations on the potential (EMF) of the glass membrane
- d) False low pH readings at very high sample pH values due to positive interference of Na^+ and other alkali cations on the potential (EMF) of the glass membrane

D) For the following galvanic cell: $\text{Ag}/\text{AgCl}(s), \text{KCl}(0.1 \text{ M})/\text{KCl}(0.01 \text{ M}), \text{AgCl}(s)/\text{Ag}$,

addition of silver nitrate solution (0.1 M) to the right half-cell will cause the overall EMF of the cell (measured as $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$) to:

- a) Remain the same
- b) Become more positive (+)
- c) Become more negative (-)
- d) Increase during the addition of the AgNO_3 and then gradually become more negative as equilibrium is reached

E) The low detection limits obtained in stripping analyses are a result of

- a) Faster measurements, which increase flux of the analyte to the electrode surface.
- b) Preconcentration of the analyte at the hanging Hg drop electrode.
- c) Lower double layer charging currents than in pulse methods or cyclic voltammetry.
- d) The chemical interactions between the reduced analyte ion on the Hg drop.

F) Voltammetry is typically done in the presence of a large excess of an inert electrolyte, which ensures that a redox-active analyte arrives at the electrode surface primarily by

- a) Diffusion in a concentration gradient at the electrode surface.
- b) Migration in the electrical field at the electrode surface.
- c) Convective transport in a thermal gradient at the electrode surface. --
- d) Electrostatic attraction to an image charge in the electrode.

G) Which of the following statements is true about a modern potentiostat.

- a) A potential difference is applied between the working and counter electrodes, and the current flow between the working and reference electrodes is measured.
- b) A potential difference is applied between the working and reference electrodes, and the current flow between the working and counter electrodes is measured.
- c) A reference electrode with Luggin capillary and a parallel-plate counter electrode must be used to eliminate solution TR drops.
- d) The reference and counter electrodes are both nearly ideal non-polarizable electrodes.

H) Which statement is true about polarography?

- a) The diffusion current is caused by solution stirring.
- b) The addition of supporting electrolytes is necessary for a migration current.
- c) The diffusion current is proportional to the square root of the concentration of the electroactive species.
- d) The magnitude of the diffusion current is proportional to concentration of electroactive species.

I) Choose the best statement which describes the half-wave potential in polarography.

- a) It is often independent of concentration and it is characteristic of the electroactive species in a given electrolyte solution.
- b) It is dependent on concentration and is independent of the electroactive species
- c) It is only dependent on the type of electrode and independent of the electroactive species.
- d) It is only dependent on the type of electroactive species if the reduction involves the formation of an amalgam.

2) A) Neglecting liquid junction potentials and assuming ion activities equal concentrations, calculate the cell potential for the following galvanic cell that consists of a fluoride anion selective membrane (LaF₃ crystal), an internal Ag/AgCl reference electrode, an external calomel reference electrode and a sample solution composed of 0.001 M NaF. (10)

Hg/Hg₂Cl₂(s), KCl(0.3M)/sample /F⁻ sel. Mem./ NaCl (0.1 M), NaF (0.1M), AgCl(s) / Ag

B) If the sample solution also contained bromide ions at 0.1 M, and chloride at 0.1 M, in addition to the 0.001 M fluoride, what would be the % error in the measurement of fluoride ion concentration in the sample given $k_{PotFBr} = 10^{-4}$ and $k_{Pot FCl} = 10^{-3}$. (5)

3) Sketch the DC and differential pulse polarograms (voltammograms---relative current on y axis vs. E_{app} on x axis) you would expect to observe (two separate plots) for a solution containing a mixture of Pb²⁺ and Cd²⁺ at concentrations of 0.1 and 0.2 mM, respectively. Assume that there is no over potential for reduction of these two ions on an dropping Hg electrode, that the sample solution is adequately degassed and that the reference electrode used was a Ag/AgCl electrode with 1 M KCl as the inner electrolyte. Also assume that the E_0 for Pb²⁺ + 2 e⁻ -> Pb is -0.120 V (vs. NHE) and for Cd²⁺ + 2e⁻ -> Cd is -0.352 V (vs. NHE). (note: Make sure you label your x 2 axis in units of applied voltage relative to the Ag/AgCl reference electrode used in the experiment; the current need only be relative current---no need to calculate an actual current value for each species.). (10)

4) Please answer the following question True or False! (4)

B) It is necessary to use a three electrode potentiostat configuration to do voltammetry when the working electrode is much, much smaller in area than the reference electrode since this will enhance concentration polarization of the reference electrode.

C) In voltammetry, non-faradaic currents usually result from the oxidation or reduction of electroactive species at the working electrode.