Chem. 210 Third Hour Exam Answers

Apr. 19, 2001

Write your answers on the blank pages. Number each page in sequence and write your name at the top of each page. Answer all of the questions. Points assigned to each question are stipulated.

Some possibly useful equations: $2.3RT/F = 0.05916$ V F = 96485 coul/mol

$\Delta E = K + S\cdot\log(a_A)$ % rel. error $= \pm 100\%\cdot(10^X - 1)$ where $X = \Delta E_{err}/S$

$S = +(2.3RT/zF)$ Q/nF = # moles of analyte $i = i_o\cdot e^{-t/\tau}$

$R = (t_R(B) - t_R(A))/(W_A/2 + W_B/2)$ $k' = t_R'/t_M$ $\alpha = t_R'(B)/t_R'(A)$

$R = k\sqrt{N} = k\sqrt{L}$ $N = L/H = 16(t_R/W)^2$ $H = A + B/u + Cu$

Calculations: SHOW ALL OF YOUR WORK! Points will be deducted if I cannot see how you got your final answer. Underline or circle your final answers.

1. (5) A combination pH electrode was calibrated in pH 7.00 and 4.00 buffers. The pH meter displayed voltages of −10.7 mV in the pH 7.00 buffer and +153.7 mV in the pH 4.00 buffer. A sample of water from Bear Creek (stocked trout stream near Friendsville, MD) yielded a voltage of +74.2 mV. Calculate the pH of the water.

$E = K - S(pH)$ (note: all units are mV)

$-10.7 = K - S(7.00)$

$+153.7 = K - S(4.00)$

subtract: $-164.4 = -S(3.00)$ $S = 54.8$ mV (ideal is 59.2 mV)

$-10.7 = K - (54.8)(7.00)$ $K = +372.9$ mV

$+74.2 = (372.9) - (54.8)pH$ pH = **5.45**

2. (6) Two similar compounds, **A** and **B**, were separated by HPLC using a 15.0 cm long column. Detector output for **A** showed a peak at 10.4 min and a base width of 1.5 min. Detector output for **B** showed a peak at 11.6 min and a base width of 1.7 min. The dead time was 1.3 min. Calculate (i) the resolution of the two peaks and (ii) the length of column needed to increase the resolution to 1.5.

(i) $R = (11.6 - 10.4)/((½)(1.5 + 1.7) =$ **0.75**

(ii) $R/\sqrt{L}$ = constant; $0.75/\sqrt{15.0} = 1.5/\sqrt{L}$ $L = (1.5/0.75)^2(15.0) =$ **60. cm**

3. (5) A sample of tapwater was tested for lead by anodic stripping voltammetry. 20.0 mL of the tapwater spiked with concentrated HNO_3 and $Hg(NO_3)_2$ (negligible volume change) was place in a

cell containing a MFE WKG electrode. The solution was stirred and deposition was carried out for 1.0 minutes. During the stripping step, a current peak of 1.4 μA was obtained. 5.0 mL of 1.0 ppm Pb standard was added to the cell and mixed thoroughly. Upon repeating the ASV experiment, a current peak of 2.5 μA was obtained. Calculate the Pb concentration in the tapwater.

This is a standard addition problem. Assume that the blank signal is zero.

1st measurement	$1.4 = mC$
2nd measurement	$2.5 = m((20.0/25.0)C + (5.0/25.0)(1.0))$
	$2.5 = (1.4/C)((4/5)C + (1.5))$
	$1.4/(5C) = 2.5 - 5.6/5 = 1.38$
	$C =$ **0.20 ppm**

4. (8) In a controlled potential coulometry experiment, Cu^{2+} was reduced to Cu at a mercury pool WKG electrode. The electrolyte volume was 40.0 mL, the initial current was 90.0 mA and the electrolysis time constant τ was 170 s.

(a) At what time did the current decay to 0.09 mA?

$i = i_o \cdot e^{-t/\tau}$

$0.09 = (90.0)e^{-t/170}$

$\ln(0.09/90.0) = -6.91 = -t/170$ $t =$ **1175 s** (slightly less than 20 minutes)

(b) The charge passed during electrolysis was 15.3 coul. What was the original Cu^{2+} concentration in mg/mL? AW for Cu = 63.546.

The half-reaction is: $Cu^{2+} + 2e^- \rightleftharpoons Cu$ so, $n = 2\ e^-/Cu^{2+}$

$Q/nF = (15.3\text{ coul})/((2)(96485\text{ coul/mol})) = 7.93 \times 10^{-5}$ mol Cu^{2+}

$C = (7.93 \times 10^{-5}\text{ mol})/(0.0400\text{ L}) = 1.98 \times 10^{-3}$ M

$(1.98 \times 10^{-3}\text{ mol/L})(64.546\text{ g/mol})(1000\text{ mg/g})(1\text{ L}/1000\text{ mL}) =$ **0.126 mg/mL**

Short answer: Provide a word, phrase, formula, sketch, or a few sentences. Each question is worth 5 points.

5. Suggest 3 ways that the electrolysis time constant in Q. #4 could be made smaller.

Larger area WKG electrode, smaller electrolyte volume, faster stirring rate.

6. Describe the MFE mentioned in Q. #3. What are its advantages over a HMDE?

A glassy carbon WKG electrode is used. Since Hg^{2+} is added to the sample, mercury metal is deposited onto the glassy carbon to form a Mercury Film Electrode. The Pb forms an amalgam in the mercury film. There are two advantages over a HMDE: (i) higher preconcentration factor because the volume of mercury is smaller, and (ii) sharper stripping peaks leading to better resolution of closely spaced stripping peaks.

7. What the 3 functions of a potentiostat?

(i) control the applied potential E_{WKG} vs E_{REF}.
(ii) pass current through the WKG and CTR electrodes (no current through the REF electrode).
(iii) convert the current signal to a voltage for the recorder.

8. Sketch a gas chromatograph and label the parts.

The sketch should show a gas tank, filters/traps, pressure/flow regulation, heated injector, column inside programmable oven, and heated detector.

9. Sketch a FID. What gases are used? What is the nature of the signal?

The sketch should show a cone burner with a tube just above it. Hydrogen is introduced into the mobile phase, which flows into the cone burner. Air is introduced around the burner. A flame above the burner flows into the tube. The burner is the cathode and the tube is the anode, with several hundred volts being applied. Hydrogen/air flames have low ion content, so little current passes. Any reduced carbon compounds entering the flame increases the ion content of the flame. The signal is an increase in current.

10. How and why is dissolved air removed from the mobile phase in HPLC?

Dissolved air is removed either by (i) sparging the solvent with helium (lowest solubility) or by (ii) applying reduced pressure to the solvent for a few minutes. These procedures prevent bubble formation in the mobile phase during pressure changes.

11. Sketch a chromatogram that shows peak tailing. What causes peak tailing?

The sketch should show the signal rising sharply to the peak and decaying slowly to baseline after the peak. Peak tailing is caused by active sites (exposed silanols Si/-OH) on the support not covered by the stationary phase. These sites strongly bind polar analytes (acids, amines, alcohols), causing them to desorb slowly.

12. What is a typical stationary phase for reverse phase HPLC?

Bonded alkane silanes with chain lengths of 4, 8 or 18 methylenes.

Discussion: Give as much detail as possible. Each question is worth 12 points.

13. List the assumptions of hydrodynamic voltammetry and state which assumptions lead to steady-state behavior. Sketch a steady-state voltammogram (American convention) for the following half reaction when the analyte is $Co(bpy)_3^{2+}$:

$Co(bpy)_3^{3+} + e^- \rightleftharpoons Co(bpy)_3^{2+} \quad E^{0\prime} = -0.15$ V vs SCE

State how the steady-state voltammogram provides information about the identity, concentration, and oxidation state of the analyte.

The four assumptions:

(i) The analyte is part of a half-reaction.
(ii) The solution is stirred (combined diffusion and convection).
(iii) The area of the WKG electrode is small and the volume of electrolyte is large.
(iv) The Nernst equation is obeyed at the electrode surface (reversibility).

Assumptions (ii) and (iii) lead to steady-state behavior.

The voltammogram should have correctly labeled axes (i_{cat} up, $-E$ to the right). The current is zero at potentials negative of −0.15 V and is equal to the anodic limiting current at potentials positive of −0.15 V. The half-wave potential should be indicated and close to −0.15 V.

The identity of the analyte is obtained by the half-wave potential (identifies the half-reaction). The concentration is obtained from the limiting current, which is proportional to concentration. The oxidation state is obtained from the sign of the current; anodic current indicates the analyte is the Reduced form.

14. What is the van Deemter equation? What are the 3 factors which cause band broadening in chromatography and how do they relate to the van Deemter equation? What parameter can be optimized when viewing a van Deemter plot?

$H = A + B/u + Cu$ where H is the theoretical plate height and u is the linear flow velocity of the mobile phase.

A is the multipath factor for packed columns; different molecules follow different paths. B is the diffusion factor; molecules move from high to low concentration spontaneously. C is the mass transfer factor; different molecules enter and leave the stationary phase at different times.

The van Deemter plot shows H decreasing sharply and then rising slowly as u increases. For best resolution, H should be as small as possible ($N = L/H$), so the best linear flow rate is found at the minimum of the plot.

15. Sketch a fluorescence HPLC detector (dual monochromator design) and discuss its operation, its advantages and its disadvantages. How can the detector be made selective for one compound? Is the detector destructive?

The sketch should show a continuum source (D_2 lamp or Xe arc), an excitation monochromator, optics to focus light onto a transparent capillary carrying the mobile phase, optics to collect the emission at right angles to the excitation, an emission monochromator, and a detector (probably a PMT).

The excitation monochromator is tuned to a wavelength corresponding to an absorption peak for the analyte. The emission monochromator is tuned to a wavelength corresponding to the emission peak of the analyte. Signal is related to emission intensity as the analyte flows through the capillary.

Advantages: very selective (only fluorescent compounds are detected), very sensitive (more sensitive than absorbance by several orders of magnitude in concentration), low LOD, wide dynamic range (wider than absorbance), non-destructive, can handle gradient elution.

Disadvantages: subject to inner filter effects at high concentrations of analyte; the signal is no longer linear with concentration. Need UV-transparent and fluorescent-free mobile phase.

The detector can be selective to one fluorescent compound in a mixture of fluorescent compounds by setting the excitation and emission wavelengths to peak absorbances and peak emissions of the desired analyte.