CHEMISTRY 321/323 EXAM 4 December 14, 2007

1. There twenty (20) multiple-choice questions. Code answers for the multiple-choice questions on the scan sheet.
2. Write your name and student ID number on the answer sheet.
3. Write your Graduate Instructor's name on the line for "Instructor" on the answer sheet.
4. Use a #2 HB pencil to code all information onto the answer sheet.
5. Code your name and student ID number on the answer sheet.
6. Code 0321 or 0323 as the "Section Number" on the answer sheet.
7. Code the **best** answer to each question on the answer sheet.
8. Relevant equations are listed at the end of the exam.
9. Each multiple-choice question is worth ten (10) points. The total score for this exam is two hundred (200) points.

CONFIRM THAT YOUR EXAM INCLUDES ALL TWENTY (20) QUESTIONS

1.   Which of the following measurements involves electrolysis:

   a)   The measurement of pH with a pH electrode
   b)   A redox titration using a redox indicator
   c)   A stripping analysis of uranium in water
   d)   A titration in which the analyte solution potential is measured as a function of added titrant relative to the standard hydrogen electode.
   e)   All of the above.

2.   Which of the following electrochemical methods requires the formation of an insoluble form of the analyte?

   a)   electrogravimetry
   b)   coulometry
   c)   potentiometry
   d)   voltammetry
   e)   polarography

3.   Which of the following phenomena is not a factor that affects polarization at an electrode?

   a)   diffusion of the analyte to the electrode surface
   b)   diffusion of the product from the electrode surface
   c)   convection
   d)   the standard cell potential for the redox couple
   e)   a significant activation barrier for the reaction

4.   The limiting current in a linear sweep voltammogram is related to:

   a)   The standard reduction potential for the redox couple under investigation
   b)   The reduction potential of the reference electrode
   c)   The point at which concentration polarization begins
   d)   The concentration of the analyte of interest
   e)   The reduction potential of water

5. A potential of -0.788 V was applied to a cell with a cell potential of -0.734 V. The internal resistance of the cell was 18.0 Ω and an initial current of 1.78 mA was measured. What value can be assigned to an overpotential for this cell?

   a) There is no overpotential associated with this cell.
   b) An overpotential cannot be determined from the information provided.
   c) 0.032 V
   d) 0.022 V
   e) 0.054 V

$$E_{applied} = E_{cell} - IR - \pi$$

$$\pi = E_{cell} - IR - E_{applied}$$

$$0.022 = -.734 - (0.00178)(18) - (-.788)$$

6. Which of the following forms of electrochemistry seeks to obtain the condition of full polarization?

   a) potentiometry
   b) voltammetry
   c) coulometry
   d) electrogravimetry
   e) ohmetry

7. In the coulometric titration of U^{4+} in the presence of excess Ce^{3+}, it was found to require 652 seconds to reach the equivalence point using a constant current of 100.0 mA. How many moles of U^{4+} were present in the solution?

$$U^{4+} + 2Ce^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2Ce^{3+} + 4H^+$$
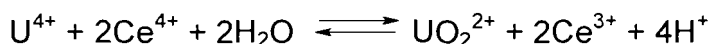
   a) 6.76×10^{-4} moles
   b) 3.38×10^{-4} moles
   c) 1.35×10^{-3} moles
   d) 1.69×10^{-4} moles
   e) none of the above

$$n_A = \frac{Q}{nF} = \frac{It}{nF} = \frac{(0.100)(652)}{(2)(96,485)}$$

8. Which of the following properties is not used as a basis for physical separation of analyte species in analytical chemistry?

   a) mass
   b) polarity
   c) molar absorptivity
   d) physical state
   e) size

9. What is the main difference between HPLC and UPLC?

   a) HPLC is reverse-phase whereas UPLC is normal-phase
   b) UPLC employs smaller stationary-phase particle size
   c) HPLC and UPLC employ different mobile phases
   d) HPLC and UPLC employ different detection methods
   e) HPLC operates at higher mobile phase pressures

10. Which of the following statements is accurate?

    a) Capillary column GC generally has higher efficiencies than HPLC because of a lower plate height in GC
    b) HPLC has higher efficiencies than capillary column GC because the column length is longer
    c) Gradient elution is an important approach in capillary GC to deal with the general elution problem
    d) Capillary column GC generally has higher efficiencies than HPLC because of a much greater column length in GC
    e) Mobile phase composition is an important experimental variable in both GC and LC

11. A good reason to increase flow rate in chromatography is

    a) to minimize band broadening due to mobile phase mass transport.
    b) to minimize band broadening due to mass transport in the stationary phase.
    c) to minimize eddy diffusion.
    d) to minimize column bleed.
    e) to minimize band broadening due to longitudinal diffusion.

Use the following information as needed for questions 12 and 13:

A weak organic acid has a K_a value of 6.2×10^{-5} M^{-1}. The distribution constant, K_D, for this acid between an organic solvent and water is 5.2.

12. If the aqueous phase is buffered to a pH of 4.61, what will the distribution ratio, D, be for this acid between water and the organic phase?

a) 1.47
b) 2.41
c) 3.72
d) 5.21
e) No response is correct.

$[H^+] = 10^{-4.61} = 2.46 \times 10^{-5}$

$D = \dfrac{[H^+]}{[H^+] + K_a} \cdot K_D$

$= \dfrac{2.46 \times 10^{-5}}{2.46 \times 10^{-5} + 6.2 \times 10^{-5}} \cdot (5.2)$

$= 1.47$

13. An increase in the pH of the aqueous phase would be expected to:

a) decrease the fraction of the acid in the aqueous phase.
b) have no effect on either K_D or D.
c) decrease the analytical concentration in the aqueous phase but have no effect on the actual concentration.
d) increase the fraction of the acid in the aqueous phase.
e) have no effect on the acid concentration in either phase.

Use the following information as needed for questions 14 and 15:

The distribution constant, K_D, for I_2 between chloroform and water is 87.

$750\ M^{-1} = K_f$ for $I_2 + I^- \rightleftharpoons I_3^-$

14. What fraction of I_2 initially present in 50 mL of water is expected to partition into the organic phase after a single extraction with 50 mL of chloroform?

a) 0.01
b) 0.03
c) 0.50
d) 0.99
e) 0.97

$1 - \dfrac{n_{1,aq}}{n_{0,aq}} = \dfrac{K_D V_{org}}{V_{aq} + K_D V_{org}}$

$= \dfrac{(87)(50)}{50 + 87(50)}$

$= 0.99$

15. What aqueous concentration of I^- should be used to remove roughly 99% of the I_2 initially present in 50 mL of chloroform using 5 extractions with 50 mL volumes of water?

Step 1 - Determine D
Step 2 - Determine $[I^-]$

$$5 \cdot \log_5\left(\frac{V_{aq}}{V_{aq}+V_{org}D}\right)$$

$$\frac{\log(0.01)}{5} = \log\frac{50}{50+50D}$$

$$\frac{[I_2]_{aq,5}}{[I_2]_{aq,0}} = \left(\frac{V_{aq}}{V_{aq}+V_{org}D}\right)^5$$

$$10^{-0.4}(50+50D) = 50$$

$$D = 1.51$$

$$D = \frac{K_D}{1+K_f[I^-]} = 1.51 = \frac{87}{1+750[I^-]}$$

$$[I^-] = 0.174 M$$

- (a) 0.174 M
- b) 0.075 M
- c) 0.288 M
- d) 11.48 M
- e) None of the above.

USE THE FOLLOWING INFORMATION TO ANSWER QUESTIONS 16 THRU 20

Table 1. Peak positions, heights, and widths for four components separated isocratically using a 10 cm reverse phase column and a flow rate of 0.2 cm/s. Detection was via UV-vis absorption.

Quantity	Non-retained species	Analyte A	Analyte B	Analyte C	Analyte D
Peak height (au)	0.1	2.30	0.22	0.52	1.16
Elution time (s)	53	67	102	147	217
Peak width at base (s)	7	10	15	22	33

16. Assuming equal molar absorptivities, which of the analytes is of highest concentration in the sample?

peak area $\approx \frac{1}{2}(base)(height)$

$D > A > C > B$

- a) A
- b) B
- c) C
- (d) D
- e) insufficient information provided.

17. What is the selectivity associated with species B and C?

$$\alpha = \frac{t_{R,C} - t_M}{t_{R,B} - t_M} = \frac{147-53}{102-53} = 1.92$$

- a) 1.88
- b) 0.69
- c) 1.44
- d) 0.52
- (e) 1.92

18. For which component is the efficiency greatest?

$N = 16 \left(\frac{t_R}{w}\right)^2$

a) A $\qquad$ $N_A = 718$

(b) B $\qquad$ $N_B = 734$

c) C $\qquad$ $N_C = 714$

d) D $\qquad$ $N_D = 691$

e) For a given column and mobile phase, the efficiency is the same for all analytes.

19. Assuming a plate height of 0.014 cm, at what distance along the column was component B separated from component A with a resolution of 1.5?

a) 10.0 cm

b) 6.1 cm

c) 8.2 cm

(d) 4.3 cm

e) insufficient information provided.

20. How much time did component C spend in the mobile phase?

a) 94 s

b) 147 s

(c) 53 s

d) 7 s

e) insufficient information is provided.

$R = 1.5$

$H = 0.014$

$u = 10cm/53s = 0.19 \, cm/s$

$K_B = \dfrac{102-53}{53} = 0.92$

$\alpha = \dfrac{102-53}{67-53} = 3.5$

$t_{R,B} = \dfrac{16(1.5)^2(0.014)}{0.19} \left(\dfrac{3.5}{3.5-1}\right)^2 \dfrac{(1+0.92)^3}{0.92^2}$

$\bar{V}_B = \dfrac{10cm}{102s} = 0.098 \, cm/s$

distance $= \bar{V}_B \cdot t_{R,B} = 0.098 \, cm/s \times 43.5s = 4.3 \, cm$

$$\Delta G = -nFE_{cell}$$

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} = -RT \ln K_{eq}$$

for aA + bB +... ⇆ cC + dD + ...

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d ...}{[A]^a [B]^b ...}$$

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{[C]^c [D]^d ...}{[A]^a [B]^b ...} \text{ at } 25\ ^0C$$

$$E = IR$$

$$E_{applied} = (E_{cathode} - E_{anode}) - IR - \Pi$$

96,485 C = 1 faraday (F)
(charge of 1 mole of elementary charges)

$$n_A = \frac{Q}{nF}$$

$I = Q/t$ where I is constant current, Q is charge, t is time
$Q = It$

Separations equations:

$$K_D = \frac{(a_A)_{org}}{(a_A)_{aq}} = \frac{[A]_{org}}{[A]_{aq}}$$

$$n_1 = \left(\frac{V_{aq}}{V_{aq} + V_{org}K_D}\right) n_0$$

$$n_i = \left(\frac{V_{aq}}{V_{aq} + V_{org}K_D}\right)^i n_0$$

$$[A]_{aq} = [A]_{org}\left(\frac{V_{aq}}{V_{aq} + V_{org}K_D}\right)$$

$$\frac{n_{org}}{n_0} = \left(1 - \frac{n_1}{n_0}\right) = \left(1 - \frac{V_{aq}}{V_{aq} + V_{org}K_D}\right) = \frac{K_D V_{org}}{V_{aq} + K_D V_{org}}$$

$$\frac{[A]_{aq,i}}{[A]_{aq,0}} = \left(\frac{V_{aq}}{V_{aq} + V_{org}K_D}\right)^i$$

$$\frac{[A]_{org,i}}{[A]_{org,0}} = \left(\frac{K_D V_{org}}{V_{aq} + V_{org}K_D}\right)^i$$

$$D = \frac{C_{org}}{C_{aq}}$$

$$\frac{C_{A,aq,i}}{C_{A,aq,0}} = \left(\frac{V_{aq}}{V_{aq} + V_{org}D}\right)^i$$

$$\frac{C_{A,org,i}}{C_{A,org,0}} = \left(\frac{DV_{org}}{V_{aq} + V_{org}D}\right)^i$$

$$D = \frac{K_D}{1 + K_a/[H^+]_{aq}} = \frac{[H^-]}{[H^+] + K_a} \cdot K_D \qquad \text{for organic acids}$$

$$D = \frac{K_D}{1 + K_f[I^-]} \qquad \text{and} \quad K_f = \frac{[I_3^-]}{([I_2][I^-])} \text{ for } I_2 + I^- \leftrightarrows I_3^-$$

$$K_C = \frac{(a_A)_S}{(a_A)_M} = \frac{[A]_S}{[A]_M}$$

$$u = \frac{L}{t_M}$$

$$\overline{v} = \frac{L}{t_R}$$

$$t_R = t_S + t_M$$

$$\overline{v} = \frac{L}{t_R} = \frac{L}{t_M} \cdot \frac{t_M}{t_R} = u \cdot \frac{t_M}{t_R}$$

$$\overline{v} = u\left(\frac{V_M}{V_M + V_S K_C}\right)$$

$$k_A = \left(\frac{t_R - t_M}{t_M}\right) = \frac{t_S}{t_M}$$

$$\alpha = \frac{k_B}{k_A} = \frac{(t_{R.B} - t_M)/t_M}{(t_{R.A} - t_M)/t_M} = \frac{(t_{R.B} - t_M)}{(t_{R.A} - t_M)} = \frac{K_B}{K_A}$$

$$N = \frac{L}{H}$$

$$H = \frac{\sigma^2}{L}$$

$$N = \frac{L^2}{\sigma^2}$$

$$\tau = \frac{\sigma}{L/t_R}$$

$$\sigma = \frac{LW}{4t_R}$$

$$N = 16\left(\frac{t_R}{W}\right)^2$$

$$H = \frac{\sigma^2}{L} = \frac{LW^2}{16t_R^2}$$

$$H = A + \frac{B}{u} + (C_S + C_M)u$$

$$R_S = \frac{2[t_{R,B} - t_{R,A}]}{W_A + W_B}$$

$$R_S = \frac{\sqrt{N}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_B}{1 + k_B}\right)$$

$$\frac{V_S K_B}{V_M} = \left(\frac{t_R - t_M}{t_M}\right) = \frac{t_S}{t_M} = k_B$$

$$\alpha = \frac{k_B}{k_A} = \frac{K_B}{K_A}$$

$$N = 16R_S^2\left(\frac{\alpha}{\alpha - 1}\right)^2\left(\frac{1 + k_B}{k_B}\right)^2$$

$$t_{R,B} = \frac{16R_S^2 H}{u}\left(\frac{\alpha}{\alpha - 1}\right)^2 \frac{(1 + k_B)^3}{k_B^2}$$