

CHEMISTRY 321/323 EXAM 4 December 19, 2008

1. There are 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 scanning an applied voltage:
- electrogravimetry
 - coulometry
 - potentiometry
 - voltammetry
 - all of the above
2. The lifetime of the lead-storage batteries we use in automobiles would be shorter if there was not a high overvoltage for formation of hydrogen. The phenomenon that gives rise to the overvoltage is referred to as:
- migration
 - concentration polarization
 - convection
 - kinetic polarization
 - gaseous diffusion
3. Which of the following processes in an electrolysis experiment is generally minimized for the analyte via the use of a background electrolyte:
- convection
 - diffusion
 - migration
 - polarization
 - pre-concentration
4. A voltage of -0.820 V was applied to a cell with a cell potential of -0.775 V and a resistance of $30.2\ \Omega$. Assuming polarization to be negligible, what current would be expected to run through the cell?
- 52.8 mA
 - 1.49 mA
 - 27.2 mA
 - 25.6 mA
 - 1.36 A

$$E_{\text{applied}} = E_{\text{cell}} - IR - \eta$$

$$-0.820\text{ V} = -0.775\text{ V} - I(30.2\ \Omega)$$

$$I = 1.49\text{ mA}$$

5. In a linear sweep voltammetry experiment, the identity of the analyte that is undergoing reaction is reflected by:

- a) one-half the voltage at which the limiting current is reached
- b) the voltage at which current begins to flow
- c) the current at one-half the limiting current
- d) the limiting current
- e) the voltage at which the current is one-half the limiting current**

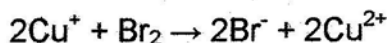
6. Which of the following methods is based on minimal current flow?

- a) coulometry
- b) voltammetry
- c) potentiometry**
- d) electrogravimetry
- e) amperometry

7. Traces of aniline can be determined by reaction with and excess of Br_2 generated electrochemically from bromide ion:



The polarity of the working electrode is then reversed and the excess Br_2 is determined via a Coulometric titration involving the generation of Cu^{2+} from Cu^+ in solution:



Excess quantities of KBr and Cu(II)SO_4 were added to a 25.0 mL aqueous solution containing aniline. Calculate the mass of aniline in solution based on the following information:

Working electrode function:	Generation time (s) with current = 1.00 mA:
Anode	226
Cathode	16.2

- $Q = It$
 $n_{\text{Br}_2} = \frac{Q}{nF} = \frac{It}{nF} = \frac{(0.001 \text{ A})(226 \text{ s})}{(2)(96,485 \text{ C/mole})} = 1.17 \times 10^{-6} \text{ mol Br}_2 \text{ produced}$
 a) 101 μg
 b) 67.4 μg
 c) 16.9 μg
 d) 50.6 μg
e) 33.7 μg
 Anode: $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$
 Cathode: $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+ = \frac{(0.001)(16.2)}{(1)(96,485)} = 1.68 \times 10^{-7} \text{ moles Cu}^+$

$$1.68 \times 10^{-7} \text{ moles Cu}^+ \times \frac{1 \text{ mol Br}_2}{2 \text{ mol Cu}^+} = 8.4 \times 10^{-8} \text{ moles left over Br}_2$$

$$1.17 \times 10^{-6} - 8.4 \times 10^{-8} = 1.086 \times 10^{-6} \text{ moles Br}_2 \text{ consumed}$$

$$1.086 \times 10^{-6} \text{ moles Br}_2 \times \frac{\text{mole aniline}}{3 \text{ moles Br}_2} \times \frac{93 \text{ g}}{\text{mole aniline}} = 33.7 \mu\text{g}$$

8. Which of the following properties is not generally useful as a basis for a physical separation?

- a) physical state
- b) solubility
- c) polarity
- d) vapor pressure
- e) molar absorptivity

9. Acetic acid ($K_a=1.75 \times 10^{-5}$ M) and formic acid ($K_a=1.80 \times 10^{-5}$ M) are both present at equimolar concentrations in 50.0 mL of water (i.e., [acetic acid]/[formic acid] = 1.00). If the pH of the solution is 4.5, what will the concentration ratio, [acetic acid]/[formic acid], be after two extractions with 25.0 mL each of chloroform? K_D value for acetic acid = 5.5; K_D value for formic acid = 4.2

- ~~a) 1.00~~
- b) 0.22
- ~~c) 0.17~~
- ~~d) 0.67~~
- ~~e) 0.47~~

$$D_{\text{acetic}} = \frac{3.2 \times 10^{-5}}{3.2 \times 10^{-5} + 1.75 \times 10^{-5}} \cdot (5.5) = 3.54$$

$$D_{\text{formic}} = \frac{3.2 \times 10^{-5}}{3.2 \times 10^{-5} + 1.8 \times 10^{-4}} \cdot (4.2) = 0.63$$

$$\frac{\{ \text{acetic} \}_2}{\{ \text{acetic} \}_0} = \left(\frac{50}{50 + 25(3.54)} \right)^2 = 0.13$$

$$\frac{\{ \text{formic} \}_2}{\{ \text{formic} \}_0} = \left(\frac{50}{50 + 25(0.63)} \right)^2 = 0.58$$

$$\frac{0.13}{0.58} = 0.22$$

all answers accepted for #9

incorrect K_a for formic was given. Using given K_a 's 0.71 would result

10. Which of the following values of aqueous solution pH would allow for the removal of both acids with the fewest number of extractions?

- a) pH = 3
- b) pH = 5
- c) pH = 7
- d) pH = 9
- e) pH = 11

of question 9

low pH forces most of the acid to be neutral

11. In chromatography, an adequate separation of two components can be achieved when the rate of peak broadening is less than the rate of peak separation. Which of the following plays the most important role in rate of peak separation in reverse phase liquid chromatography?

- a) the diameter and uniformity of the packing material
- b) the magnitude of the difference in the distribution constants
- c) flow rate
- d) the magnitude of the difference in the longitudinal diffusion coefficients
- e) the magnitude of the difference in the eddy diffusion factor

12. The relative peak areas for a mixture of four steroids separated by HPLC, along with relative response factors for each of the components, is given in the following table. Based on this information, what percentage of the total steroid content is comprised of estradiol?

Compound	Relative peak area	Relative detector response
Estradiol	32.4	0.72
Estrone	47.1	0.68
Testosterone	40.6	1.00
Estriol	27.3	0.95

- a) 32.4 %
 b) 15.6 %
 c) 24.5 %
 d) 19.1 %
 e) 22.0 %

$$\frac{32.4}{0.72} = 45$$

$$\frac{45}{183.64} = .245$$

$$\frac{47.1}{0.68} = 69.3$$

$$.245 \times 100 = 24.5\%$$

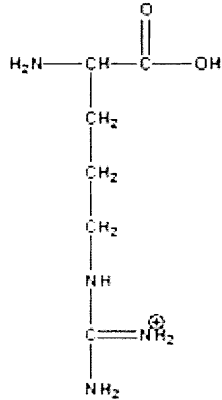
$$\frac{40.6}{1} = 40.6$$

$$\frac{27.3}{0.95} = \frac{28.7}{183.64}$$

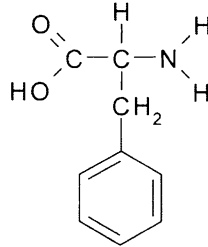
13. In comparing HPLC with capillary gas chromatography (GC) as discussed in class, which of the following statements is generally true:

- a) GC has smaller H values and lower efficiencies than HPLC
 b) GC has larger H values and lower efficiencies than HPLC
 c) GC has larger H values and higher efficiencies than HPLC
 d) GC has smaller H values and higher efficiencies than HPLC
 e) GC and HPLC have different H values and lengths but similar efficiencies

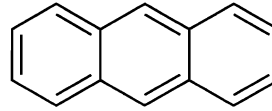
14. Arginine, phenylalanine, and anthracene are to be separated via reverse phase liquid chromatography. Predict the elution order:



arginine



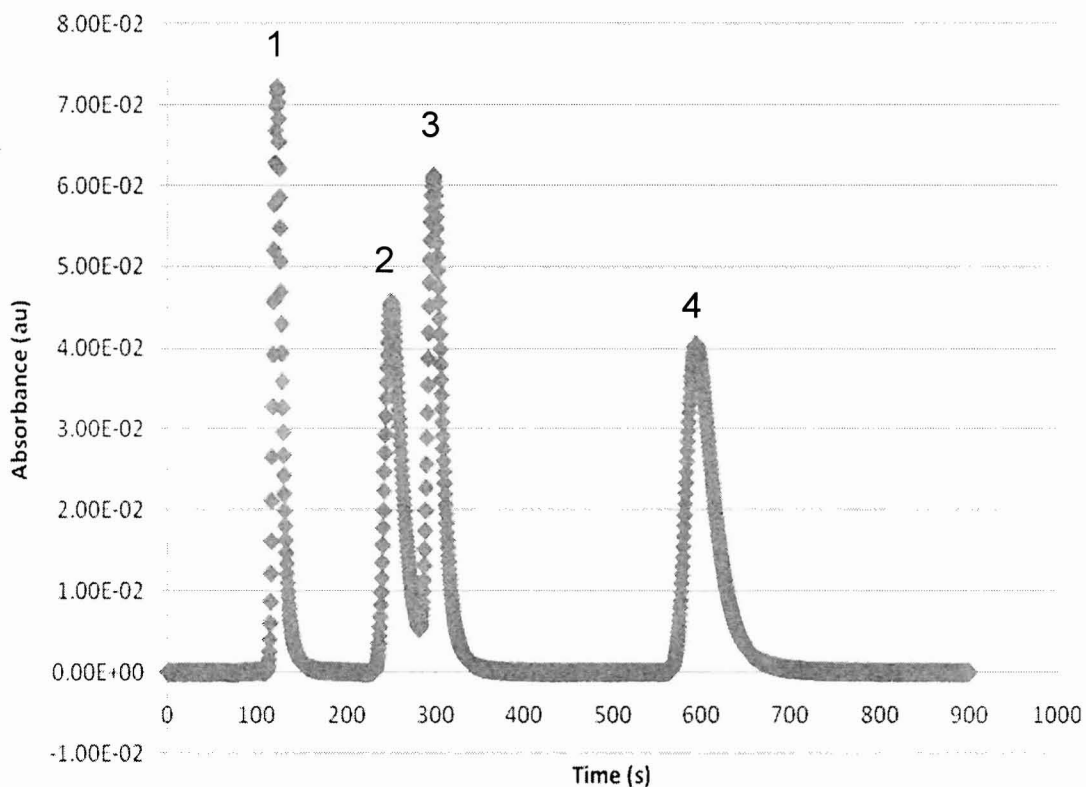
phenylalanine



anthracene

- a) anthracene first, arginine second, phenylalanine third
b) phenylalanine first, arginine second, anthracene third
c) anthracene first, phenylalanine second, arginine third
d) arginine first, phenylalanine second, anthracene third
e) the elution order cannot be predicted with any confidence
15. Which of the following is not a factor in determining column efficiency in liquid chromatography:
- a) flow rate
b) column length
c) detector response
d) packing particle size
e) diffusion coefficient of the analyte

Use the following information to answer questions 16-20. The figure is a liquid chromatogram of the four deoxy mononucleotides.



The following information relates details of the separation:

Column length: 25.0 cm

Column diameter: 0.46 cm

Stationary phase: C-18

Mobile phase: aqueous buffered at pH = 7.2

Flow rate: 1.2 mL/min

Dead time: 16.7 s

Quantity	Component 1	Component 2	Component 3	Component 4
Peak height (au)	0.072	0.046	0.061	0.041
Elution time (s)	120	255	310	608
Peak width at base (s)	28	70	55	98

16. What is the elution order (first to last) for the four mononucleotides (dAMP = deoxyadenosine monophosphate; dCMP = deoxycytidine monophosphate; dGMP = deoxyguanosine monophosphate; dTMP = deoxythymidine monophosphate):

- a) dAMP:dCMP:dGMP:dTMP
- b) dCMP:dTMP:dGMP:dAMP
- c) dCMP:dTMP:dAMP:dGMP
- d) dAMP:dGMP:dCMP:dTMP
- e) none of the above

17. What is the retention factor for component 4?

- a) 35.4
 - b) 36.4
 - c) 6.20
 - d) 591
 - e) 0.97
- $$\frac{t_r - t_m}{t_r} = \frac{608 - 16.7}{608} = 35.4$$

18. What is the efficiency of the column for component 4?

- a) 508
 - b) 99.3
 - c) 581
 - d) 616
 - e) insufficient information is provided
- $$N = 16 \left(\frac{t_R}{w} \right)^2 = 16 \left(\frac{608}{98} \right)^2 = 616$$

19. Assuming an average value of H = 0.08 cm, at what approximate distance after injection of the sample were components 1 and 4 separated with a resolution of 1.5?

- a) 162 cm
 - b) 4.4 cm
 - c) 11 cm
 - d) 1.5 cm
 - e) insufficient information is provided
- $$u = 25 \text{ cm} / 16.7 \text{ s} = 1.5 \text{ cm/s}$$
- $$V_4 = 25 \text{ cm} / 608 \text{ s} = 0.041 \text{ cm/s}$$
- $$\alpha = \frac{608 - 16.7}{120 - 16.7} = 5.72$$

$$t_{R,4} = \frac{16 R_s^2 H}{u} \left(\frac{\alpha}{\alpha - 1} \right)^2 \frac{(1 + k_0)^3}{k_0^2} \quad k_0 = \frac{608 - 16.7}{16.7} = 35.4$$

$$= \frac{16 (1.5)^2 (0.08)}{1.5} \left(\frac{5.72}{5.72 - 1} \right)^2 \frac{(1 + 35.4)^3}{(35.4)^2} = 108 \text{ s}$$

$$108 \text{ s} \times 0.041 \text{ cm/s} = 4.4 \text{ cm}$$

20. Assuming a value of $H = 0.08$ cm for each component, what column length would be needed to separate components 2 and 3 with a resolution of 2.0, assuming all other performance characteristics are the same?

- a) 163 cm
 b) 3041 cm
 c) 2028 cm
 d) 173 cm
 e) 86 cm

$$k_3 = \frac{310 - 16.7}{16.7} = 17.6$$

$$\alpha = \frac{310 - 16.7}{255 - 16.7} = 1.23$$

Note: Varying the length of a column is generally not a practical approach to improving a separation in HPLC. Simpler alternatives include changing mobile or stationary phase composition, particle packing size, etc., as discussed in class.

May you have a safe, enjoyable, and restful break.

$$t_3 = \frac{16(2.0)^2(0.08)}{1.5} \left(\frac{1.23}{.23} \right)^2 \frac{(1 + 17.6)^3}{(17.6)^2} = 2028 \text{ s}$$

$$V_3 = \frac{25 \text{ cm}}{310 \text{ s}} = .0806 \text{ cm/s} \quad \text{dist.} = 2028 \times .0806 = 163.5$$

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

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

for $aA + bB + \dots \rightleftharpoons cC + dD + \dots$

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

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

$$E = IR$$

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

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:

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

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

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

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

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

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

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

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

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

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

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

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

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

$$area = \pi r^2$$

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

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

$$t_R = t_S + t_M$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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