Chem 454 Exam I February 11,2000

Name: ____

Formulae

$E = h\nu$ $c = \nu\lambda$ $h = 6.626 \times 10^{-34}$ Js $c = 2.998 \times 10^{8}$ m/s $E = E^0 + \frac{0.0592}{n}\log\frac{[ox]}{[red]}$

$E_{cell} = E_{cathode} - E_{anode}$ Beer's Law: $A = \varepsilon bc$

Standard Deviation

$$\sigma = \sqrt{\frac{\sum\left(x_i - \bar{x}\right)}{n-1}}$$

variance = $(\sigma)^2$

Confidence Interval

$$\mu = \bar{x} \pm \frac{t_s}{\sqrt{n}}$$

1) Fill in the blanks (10 points)

a) The term, ________________________ describes the reproducibility of experiment.

b) The term, ________________________ describes how close the experimental result comes to the true value.

c) An active filter _______________________ the gain of the transducer output.

d) Selection rules only allow electronic transitions from the _________________ vibrational level of the electronic state.

e) Phosphorescence is the relaxation from a __________________ excited state to a singlet ground state.

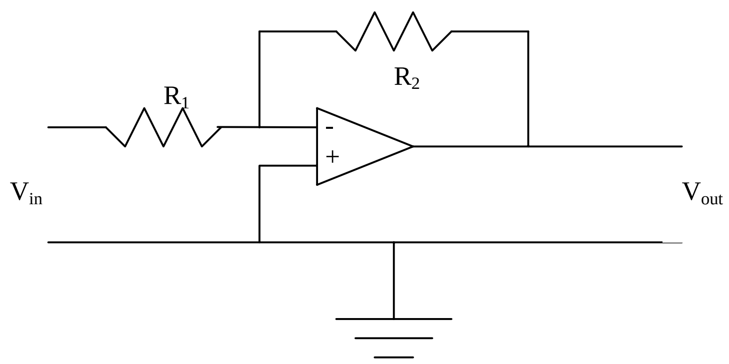
2) Why is the daylight sky blue? Conversely, why are sunsets red? (10 points)

3) Describe the real (not ideal) response of a pH electrode. A plot of ($pH_{ideal} - pH_{real}$) versus pH may help your description. (10 points)

4) Sketch the configuration of a modern commercial pH/reference electrode configuration. (10 points)

5) What is the frequency character of thermal noise? Give an example of a transducer that is susceptible to thermal noise. (10 points)

6) What is the voltage output relative to the voltage input for the following device? What is frequency characteristic of this circuit? What type of noise filtering characteristic does this circuit have? (10 points)



$R_2 = 1500\ \Omega$ $R_1 = 250\ \Omega$ Open Specifications: $A = 10^5$ $f_0 = 10^8$ Hz

7) Describe the basic principles of the interference filter used in spectroscopic applications. (10 points)

8) A 25.00 mL solution of an aqueous dye was diluted to 50.00 mL and found to have an absorbance of 0.416 at 348 nm in a 1.00 cm cuvette. A second 25.00 mL aliqout of this dye was mixed with 10.00 mL of 23.4 ppm standardized solution of the dye and diluted to 50.00 mL, this solution had an absorbance of 0.610 in the same cuvette. Calculate the concentration in ppm of this dye. (15 points)

9) A Hg anode coated with a thin layer of Hg_2SO_4(s) is in contact with a solution of unknown sulfate concentration. Completing the circuit is an SCE reference electrode. Calculate pSO_4 and $[SO_4^{2-}]$ if the potential between the two electrodes is –0.576 V. (15 points)

$E_{SCE} = 0.244$ V $Hg_2SO_4(s) + 2e = 2Hg(l) + SO_4^{2-}(aq)$ $E^0 = 0.615$ V

Chem 454 Exam II March 10, 2000

Formulae

Statistics

Standard Deviation

$$\sigma = \sqrt{\frac{\sum\left(x_i - \bar{x}\right)}{n-1}}$$

variance = $(\sigma)^2$

Confidence Interval

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Spectroscopy

E = hν c = νλ h = 6.626 x 10^{-34} Js c = 2.998 x 10^{8} m/s Beer's Law: A = εbc

$$\frac{N_j}{N_0} = \frac{P_j}{P_0} e^{-\frac{E_j}{kT}}$$

k = 1.28 x 10^{-23}J/K

Electrochemistry

$$E = E^0 + \frac{0.0592}{n} \log \frac{[ox]}{[red]}$$

$$E_{cell} = E_{cathode} - E_{anode}$$

Chromatography

$$H = \frac{L}{N} \qquad H = A + \frac{B}{u} + Cu \qquad u = \frac{L}{t_m} \qquad k' = \frac{t_r - t_m}{t_m} \qquad K = \frac{c_s}{c_m} = \frac{k' V_m}{V_s} \qquad V_m = t_m F$$

$$\alpha = \frac{k_B^{'}}{k_A^{'}} = \frac{K_B}{K_A} \qquad R_s = \frac{(t_{r,B} - t_{r,A}\}}{W_{av}} = \frac{\sqrt{N}}{4}\left(\frac{\alpha}{\alpha - 1}\right)^2 \left(\frac{k_B^{'}}{k_B^{'} + 1}\right) \qquad t_{r,B} = \frac{16 R_s^2 H}{u}\left(\frac{\alpha}{\alpha-1}\right)^2 \frac{\left(1 + k_B^{'}\right)^3}{\left(k_B^{'}\right)^2}$$

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

Name: ____

1) Fill in the blanks (20 points)

a) CCD array spectrometers use an ____________________ grating for wavelength dispersal.

b) Fluorescence is based on a singlet to _________________ electronic transition.

c) Molecular rigidity ___________________ fluorescence efficiency.

d) The purpose of the flame in flame AA, AF, and AE is to ______________________ the sample.

e) The hollow cathode lamp is the source for _____________________ spectroscopy

f) Raman active transitions are based __________________________ changes of the atom/molecule/ion.

g) IR active transitions are based on _________________________ changes of the molecule.

h) The partition coefficient is based concentration of a solute in the __________________ and _______________ phases.

i) Chromatographic band broadening ______________________with plate height.

j) A chromatographic resolution value of ________________ indicates complete separation of solute species.

2) Sketch and describe the major optical components of a Michelson inferometer. What is the purpose of the moveable mirror? (10 points)

3) Describe the principal source or sources of Doppler broadening in AA spectroscopy. (10 points)

4) Describe the transitions that give rise to Stokes and anti-Stokes lines in Raman spectroscopy. Why is it generally necessary that a laser must serve as a source for Raman spectroscopy? (10 points)

5) Describe how the “A” term of the van Deemter equation contributes to band broadening. (5 points)

6) Describe how the “B/u” term of the van Deemter equation contributes to band broadening. Why is it inversely proportional to mobile phase flow rate? (5 points)

7) Describe how the “Cu” term of the van Deemter equation contributes to band broadening. Why is it directly proportional to mobile phase flow rate? (5 points)

8) What advantages does ICP hold over flame AE? What disadvantage does it have when compare to flame AA or AE? (10) points

9) Why is the flame necessary in flame AA? (5 points)

10) Why is the detection limit lower for AA spectroscopy based on an electrothermal oven versus a flame? (5 points)

11) A 10.00 mL sample of blood was analyze for lead by flame AA. After this sample was filtered for proteins, a 5.00 mL sample was aspirated into the AA spectrometer which gave an absorbance of 0.445 at 283.3 nm. The remaining 5.00 mL sample was treated with 2.00 mL of 0.250 ppm standardized lead solution. This solution gave an absorbance of 0.683 at 283.3 nm. Assuming that Beer's law is obeyed, what is the concentration of lead in this sample? (15 points).

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

$$R_s = \frac{(t_{r,B} - t_{r,A}\}}{W_{av}} = \frac{\sqrt{N}}{4}\left(\frac{\alpha}{\alpha-1}\right)^2\left(\frac{k_B^{'}}{k_B^{'}+1}\right)$$

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

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Name: ____

1) Fill in the blanks (20 points)

a) Ionization of solids and non-volatile liquids require ________________________ techniques.

b) Reversed phase separations in HPLC involve the use of ___________________ stationary phase and ___________________ mobile phase.

c) The acronym, FID, stands for ____.

d) Gel filtration chromatography is used for the separation of ______________ molecular weight ______________- soluble compounds.

e) The relative population of the excited and ground state levels of the nuclear spin states in applied magnetic field are very nearly ____

f) Saturation in NMR refers to a situation in which the population of__________________________________

g) The relaxation mechanism in NMR is a _______________________________________

h) The acronym, TOF, refers to ____

i) An example of a universal detector for GC is the ____

j) Capillary columns hold an advantage over packed columns in GC due to considerations of __________________________________.

2) The refractive index detector is very nearly a universal one for HPLC. Explain its basis of operation. What is its major drawback? (10 points)

3) What is electro-osmotic flow and what advantage does it hold over the flow produce by mechanical pumping? (10 points)

4) A solute was found to have a retention time of 25 minutes on a C-18 column with ethanol as a mobile phase. Which solvent, methanol or isopropanol will decrease the retention time of this solute? For full credit you must have an explanation. (5 points)

5) When designing a binary (CH_3CN:H_2O) mobile phase for gradient elution on using a C-18 stationary phase would it be best to increase or decrease the proportion of water during elution? Why? (5 points)

6) Describe at least three advantages supercritical CO_2 has over typical HPLC mobile phases. (10 points)

7) Describe the interface for LC-MS. What is the major difficulty encountered in the combination of these two techniques? How is this problem addressed? (10 points)

8) What type of molecular information is derived from tandem M.S.? What advantage does MS-MS hold over GC-MS? (10 points)

9) Describe in detail how the free induction decay is produced and measured for FT-NMR. (10 points)

10) What further information is obtained from 2D-NMR techniques when compare to standard NMR? How does the information obtained from COSY differ from NOESY? (10 points)

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

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

Name: ____

200 total points

1) Fill in the blanks (40 points)

a) An example of a universal detector for HPLC is a(n)_____________________________________

b) An example of an analytical technique based on light scattering is _______________________________

c) The FID is a detection system sensitive for _____________________ containing compounds

d) The pH limits of the glass pH electrode are ______________ and _______________

e) 60 Hz noise is an example of _______________________ noise.

f) A device aimed at filtering 60 Hz noise is known as a ______________________ filter

g) The IR active stretch is based on __________________________ changes of a molecule.

h) Flicker noise is _________________ frequency in nature.

i) A suppression column is required to neutralize ions generated by the__________________ column in IC.

j) The excited-state lifetime of fluorescence is ____________________ than the lifetime for phosphorescence.

k) Soft ionization in mass spectrometry produces _____________________________________ ions.

l) The retention time for ______________ions is the longest in capillary electrophoresis.

m) In general the detection limit for an analytical technique is when the signal to background ratio is __________

n) The acronym ESCA stands for ____

o) Increasing the column temperature in HPLC tends to improve separation efficiency by increasing

____

p) A common interference for the Cl^- ISE is _________________________________

q) A GC detector selective for organics with electron-withdrawing groups, especially halogenated organics is the

____

r) An example of a desorption method for MS is _________________________________

s) A light scattering technique that results is a change of wavelength is known as

____

t) The CCD is usually coupled with a _________________________ grating in order to obtain wavelength dispersion.

2. Explain why it is beneficial to decrease the stationary phase depth for both HPLC and GC. (10 points)

3. Auger and XRF are both relaxation techniques. Explain how they differ and what types of information can be obtained from each technique. (10 points)

4. What is micellar electrokinetic chromatography? How does it differ from standard CE? What is its basis for the sepration of solutes? What major advantage does it hold over CE? (10 points)

5. What is the major difference in the information obtained by the 2-D NMR techniques of NOESY and COSY? (10 points)

6. What would be the effect of the following on band broadening in GC? Explain your answer. (10 points)

a. Increasing the mobile phase flow rate.

b. Decreasing the injection port temperature below the BP of your solute.

c. Decreasing the rate of sample injection.

7. Explain why high pressures are necessary for HPLC. (10 points)

8. Sketch the configuration of the modern pH/reference elctrode configuration. (10 points)

9. Describe in enough detail to explain why only certain wavelengths of light are allowed to pass in an interference filter. (10 points)

10. Using a graph explain the difference between detection limit and sensitivity. (10 points)

11. Sketch and describe the 5 major optical components of the Michelson inferometer. (10 points)

12. Why is the detection limits for electrothermal AA lower than flame AA? (10 points)

13. Draw a schematic for the flame ionization detector used in GC. How does it work? What type of species does it detect? What are the relative advantages and disadvantages of the FID when compare to a TCD? (10 points)

14. Molecular fluorescence is generally more sensitive than absorption spectrophotometry, why is this so? (10 points)

15. What are the advantages of capillary columns over packed columns in GC? (10 points)

16. Aliquots of 5.00 mL of an optically absorbing species were pipetted into five 100.00 mL volumetric flasks. Exactly 0.00 2.00, 4.00, 6.00, 8.00 mL of a 1.00 mM standard solution of the same absorbing species were added to each aliquot of sample and diluted to 100.00 each. The absorbances were measured at 410 nm and found to be 0.20, 0.30, 0.40, 0.50, and 0.60 respectively. Calculate the concentration of the unknown sample assuming Beer's law is obeyed. You may find the following equation helpful. (20 points)

$$A = \frac{\varepsilon b V_x C_x}{V_t} + \frac{\varepsilon b V_s C_s}{V_t}$$