Chem 310
3rd Homework Set
Due Date: Feb. 10, 2004

1. A double line labeled $\mathbf{S_0}$ represents the _____ state and the _____ state of a molecule in an excitation state diagram. Light absorption in the UV, sometimes the VIS and occasionally the near IR spectral domain results in transition from the $\mathbf{S_0}$ state to _____ state. Light absorption in the IR spectral domain results in transition from the $\mathbf{S_0}$ state to _____ state.

2. What are the three assumptions that must be true for Beer s law to be valid? Under what circumstances would each of the assumptions be invalid? Be specific in your examples. This is a discussion question.

3. What are the factors (both general and instrumental) that cause deviations from linearity in a Beer's law plot? This is a discussion question, and your answer should refer to the assumptions in Question 2 where possible.

4. How is a spectrum distorted if the bandwidth of the monochromator is too large? Include sketches of the spectra with and without the distortion. This is a discussion question.

5. (a) Convert 0.379 absorbance to %T.
   (b) Convert 37.9% transmittance to absorbance.
   (c) Calculate the %T of a solution having twice the concentration of the solution in part (a).
   (d) Calculate the absorbance of a solution having 1/3 the transmittance of the solution in part (b).

6. A 1.35×10^{-4} M solution of $[Ru(NH_3)(pyridine)]^{2+}$ has a transmittance of 13.2% at 406 nm in a 1.00 cm. cell. What is the molar absorptivity of the complex?

7. At 580 nm, the complex $[Fe(SCN)]^{2+}$ has a molar absorptivity of 7.00×10^{3} $M^{-1}cm^{-1}$. What is the absorbance of 2.50×10^{-5} M solution of the complex in a 5.00 cm cell? What is the transmittance?

8. Calibration curve problem. Iron in aqueous solution can be measured at ppm levels by converting all of the iron to iron(II), adjusting the pH to 5, and then adding excess 1,10-phenanthroline, a chelating ligand. The bright orange-red solution exhibits an absorption maximum at 510 nm.

Conc. (ppm)	Absorbance in a 1.00 cm cell
1.00	0.164
2.50	0.425
4.00	0.628
6.00	0.951
10.00	1.582

(a) Use a spreadsheet to generate a graph of the data as symbols. Keep the concentration axis in ppm Fe. Calculate and plot the linear regression line over that part of the data which you judge to be linear. Attach the plot and a printout of your spreadsheet to your homework. On your plot, indicate the linear dynamic range on the concentration axis.

(b) Give the slope and intercept of the linear regression line and the standard deviation of the slope and intercept.

(c) What is the sensitivity of this calibration (including units)?

(d) Calculate the concentration of Fe in ppm in a sample if the measured absorbance is 0.500.

(e) Calculate the molar absorptivity of the Fe phenanthroline complex.

9. A 25.0 mL aliquot of an aqueous quinine solution was diluted to 50.0 mL and the absorbance was measured at 348 nm in a 2.00 cm cell. A second 25.0 mL aliquot of quinine solution was mixed with 10.0 mL of 23.4 ppm quinine and then diluted to a final volume of 50.0 mL and its absorbance measured in a 2.00 cm. cell. If the absorbance of the first solution is 0.832 and the absorbance of the second solution is 1.220, calculate the concentration of quinine in the original aqueous solution. Do not convert concentrations to molar; the answer should be in ppm.

10. A simultaneous determination of cobalt and nickel is based on light absorption of their respective 8-hydroxyquinolinol complexes. The molar absorptivities are given in the following table:

	Molar absorptivities ϵ	
Element	365 nm	700 nm
Co	3529	428.9
Ni	3228	10.2

Given the following data obtained in 1.00 cm cells, calculate the concentrations of Co and Ni:

Wavelength	Absorbance
365 nm	0.598
700 nm	0.039

11. Fig.13-20 on p. 323 of SH&N is a diagram of a double-beam scanning UV-VIS-near IR spectrometer. Answer the following questions with respect to that figure:
    (a) Why is there a tungsten source and a deuterium source?
    (b) At approximately what wavelengths would the instrument switch the source?
    (c) What is the role of the filter assembly?
    (d) What is the role of the optical chopper?
    (e) What should the reference cuvette contain?
    (f) What two light detectors would be used as the transducer? Explain why there are two detectors, and indicate at what wavelengths the detector would be switched.

12. Harris, Problem 19-3.

13. Sketch a UV-VIS diode array spectrophotometer and label the parts. What is the source? What is the detector? What determines the wavelength resolution of this instrument? What determines the wavelength range of this instrument? What are the advantages and disadvantages of the multi-channel design relative to the double beam design?