Chem 310
3rd Homework Set Answers

1. A double line labeled $\mathbf{S_0}$ represents the _*ground electronic*_ state and the _*ground vibrational*_ 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 _S_1 *or higher excited*_ state. Light absorption in the IR spectral domain results in transition from the $\mathbf{S_0}$ state to _*an excited vibrational*_ 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.

   The three assumptions are: (a) analyte absorbance over the bandpass of the transmitted beam, (b) the analyte molecules do not interact with each other, and (c) the concentration is uniform across the sample. The first assumption is invalid if (i) the bandwidth of the transmitted beam is wide compared to the half-width of an absorption peak (example: IR absorption spectroscopy, where half-widths can be as small as 1 cm^{-1}*), or (ii) the center wavelength corresponds to a region where the molar absorptivity is changing rapidly with wavelength. The second assumption is invalid when the concentration of the analyte is too high. Example: flat aromatic or conjugated molecules in water tend to form dimers and oligomers at concentrations above* 10^{-5} *M. The third assumption can invalid in solids, poorly stirred solutions, or samples where the color analyte is being generated at one point.*

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.

   The general factor is chemical equilibrium. The analyte exists in a chemical equilibrium of two or more forms which shifts with changing concentration. Deviations from Beer s Law can be positive or negative for the general factors. Examples include dimerization, acid-base, and complexation equilibria. The instrumental factors include non-constant absorbance over the instrumental bandpass (second assumption), and stray light. Both factors lead to excess light reaching the detector, causing negative deviations of Beer s Law plots at higher concentrations.

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.

   When the bandwidth is too large, absorption peaks are broader (greater half-width) and not as *high as in the accurate absorption spectra. Overlapping peaks can appear as one peak. Decreasing the bandwidth decreases the amount of distortion. When the bandwidth reaches less than one-tenth of the half-width of the narrowest peak, the true shape (height and peak half-width) is observed in the absorption spectrum. The sketch should show an overlay of an accurate absorption spectrum (A vs λ) and the distorted spectrum.*

5. (a) Convert 0.379 absorbance to %T.

   $T = 10^\wedge(-0.379) = 0.418$ or 41.8%

   (b) Convert 37.9% transmittance to absorbance.

   $A = -\log(0.379) = 0.421$

   (c) Calculate the %T of a solution having twice the concentration of the solution in part (a).

   From Beer s Law ($A = \epsilon bC$), the absorbance of the solution will double. $A = 2(0.379) = 0.758$; $T = 10^\wedge(-0.758) = 0.175$ or 17.5%

   (d) Calculate the absorbance of a solution having 1/3 the transmittance of the solution in part (b).

   $\%T = (37.9\%)/3 = 12.63\%$; $A = -\log(0.1263) = 0.898$

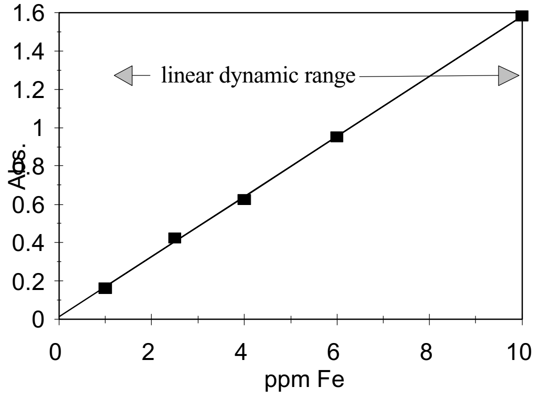
6. A 1.35×10^{-4} M solution of $[Ru(NH_3)(pyridine)]^{2+}$ has a transmittance of 13.2% at 406 nm in a 1.00 cm. cell. What is the molar absorptivity of the complex?

   $A = -\log(0.132) = 0.879 = \epsilon(1.00\ cm)(1.35\times10^{-4}\ M)$; $\epsilon = 6.51\times10^{3}\ M^{-1}cm^{-1}$

7. At 580 nm, the complex $[Fe(SCN)]^{2+}$ has a molar absorptivity of $7.00\times10^3\ M^{-1}cm^{-1}$. What is the absorbance of 2.50×10^{-5} M solution of the complex in a 5.00 cm cell? What is the transmittance?

   $A = (7.00\times10^3\ M^{-1}cm^{-1})(5.00\ cm)(2.50\times10^{-5}\ M)$
   $= 0.875$; $T = 10^\wedge(-0.875) = 0.133$ or 13.3%

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 (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. *All data points are in the linear dynamic range.*

(b) Give the slope and intercept of the linear regression line and the standard deviation of the slope and intercept. *Slope* $= 0.157 \pm 0.002/\text{ppm}$*; intercept* $= 0.014 \pm 0.014$.

(c) What is the sensitivity of this calibration (including units)? *Same as the slope.*

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

$0.500 = 0.157C + 0.014;\ C = (0.500 - 0.014)/0.157 = 3.10 \text{ ppm Fe}$

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

Need to convert the slope from ppm^{-1} *to* M^{-1}*, since the cell path length is 1.00 cm.*

$0.157/\text{ppm} = [0.157\ \text{L}/(0.001\ \text{g Fe})][55.85\ \text{g Fe/mol Fe}] = 8.77\times10^3\ M^{-1}\text{cm}^{-1}$

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.

This is a standard addition problem with the final volume being constant. Recall the equations for standard addition to a fixed volume:

Equations: $S_1 = mC_x(V_x/V_t)$ *and* $S_2 = m(C_x(V_x/V_t) + C_s(V_s/V_t))$ *Let* $S = \text{Abs}$.

Then $0.832 = mC_x(25.0/50.0)$ *and* $1.220 = m(C_x(25.0/50.0) + (23.4)(10.0/50.0))$

$1.220 = 0.832 + m(23.4)(10.0/50.0);\ m = 0.0829/\text{ppm}$

$0.832 = 0.0829C_x(25.0/50.0);\ C_x = 20.1\ \text{ppm}$

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

Two analytes requires two equations:

$A_1 = b(\epsilon_{x1}C_x + \epsilon_{y1}C_y)$ *(at* λ_1*)* *and* $A_2 = b(\epsilon_{x2}C_x + \epsilon_{y2}C_y)$ *(at* λ_2*)*

$0.598 = (1.00)(3529C_{Co} + 3228C_{Ni})$ *and* $0.039 = (1.00)(428.9C_{Co} + 10.2C_{Ni})$

I solved this by rearranging the second equation into an expression for [Ni], substituting it into the first equation, and solving for [Co]. Plugging [Co] into either equation gives [Ni]. I get: $[Co] = 8.88\times10^{-5}$ *M;* $[Ni] = 8.81\times10^{-5}$ *M*

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:

Sorry, this question wasn t meant to be on this homework set. Just for your information, here are the answers.

(a) Why is there a tungsten source and a deuterium source? *The tungsten source has very little continuum emission in the UV domain, so a deuterium arc source is used to provide the continuum in the UV.*

(b) At approximately what wavelengths would the instrument switch the source? *Typically it is around 330 - 350 nm.*

(c) What is the role of the filter assembly? *To remove higher order wavelengths passed by the grating monochromator. As the wavelength is scanned, the cutoff filters are changed to correctly block 2nd order wavelengths without attenuating 1st order wavelengths.*

(d) What is the role of the optical chopper? *To alternately direct the light through the sample and reference cuvets, so that the instrument can measure P and* P_o *automatically. The signal from the PMT is amplified at the chopper frequency to eliminate any signals due to stray light entering the spectrometer after the chopper; this process is known as synchronous detection.*

(e) What should the reference cuvette contain? *In order to compensate for reflection losses in the sample cuvette, the reference cuvette should contain the solvent (i.e., a blank).*

11. (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. *A PMT works well for the UV-VIS domains, but may have a poor response in the near IR (depending on the photocathode material). A good near-IR detector is the PbS photoconductivity transducer . The switch should be about 700-900 nm.*

12. Harris, Problem 19-3.
Isosbectic points are observed in absorption spectra (plots of molar absorptivity vs wavelength) when the analyte exists as two species in equilibrium. Varying the concentration or some other condition (e.g., pH) causes the equilibrium to shift, resulting in a change in the absorption spectrum. The overlaid absorption spectra often cross at a single wavelength regardless of the position of the equilibrium. At the isosbectic point, the two species in the equilibrium have the same molar absorption coefficient ϵ. *Observation of an isosbectic point in overlaid spectra is used as evidence for the existence of an equilibrium between two species. Harris discusses isosbectic points in terms of a chemical reaction converting one species to another; this discussion is equivalent to the equilibrium discussion above.*

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?
The sketch should show one or more sources, light passing through a cuvette and into a concave grating monochromator. Light from the entrance slit is focused on a linear diode array. Possible sources include a W filament, D_2 *arc, or Xe high pressure arc. Wavelength resolution is determined by the linear reciprocal dispersion* $d\lambda/dx$ *and the dx spacing of the linear diode array; typically the resolution is 1 or 2 nm. Advantages include (a) no moving parts, (b) excellent wavelength reproducibility at each diode detector, and (c) rapid acquisition of a spectrum (circa 1 second). The primary disadvantage is that the instrument is inherently single beam; a reference spectrum must be recorded with a blank, and then a sample spectrum recorded. Stray light at the wavelength extremes can be a problem with this design.*