

Spectroscopy Problem Set # 2

1. Define the following terms:
 - a) bathochromic shift
 - b) hypsochromic shift
 - c) auxochrome
 - d) chromophore
 - e) isobestic point
 - f) quantum yield
2. A solution containing 4.48 ppm KMnO_4 has a transmittance of 0.309 in a 1 cm cell at 520 nm. Calculate the molar absorptivity of KMnO_4 .
3. Two species A and B are present in a solution. The molar absorptivities for A and B at 450 nm are 6,000 and 2500 $\text{L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$, respectively. At 550 nm, the molar absorptivities are 3,500 for A and 7,000 for B. If a sample containing both species had absorbance values at 550 nm = 0.45 and at 450 nm = 0.65, what concentrations of A and B are present in the unknown solution? Assume that measurements were made using a cell with 1 cm pathlength.
4. With respect to fluorescence measurements, explain the difference between an excitation spectrum and an emission spectrum.
5. Explain, in semi-quantitative terms, why quantum efficiency for a fluorescent species will depend strongly on the sample environment (e.g., solvent, temperature, etc.).
6. The absolute error in transmittance for a particular photometer is 0.005 and is independent of the magnitude of T. Calculate the % relative error in concentration that is caused by this source of error when $A = 0.585$ and in a second experiment when $T = 99.25\%$
7. In UV-Vis spectrophotometry, explain why a calibration curve for a given species at a fixed wavelength will become more non-linear at higher absorbance values if the slit width of the monochromator is made very wide.
8. In fluorescence instruments, why is sensitivity dependent on the intensity or power of the source?
9. Explain why a double beam spectrophotometer is usually required to obtain high quality absorption spectra in the UV-Vis range. Why can't one simply scan the monochromator of a simple Spectronic 20 spectrophotometer to obtain an accurate Visible spectrum in the visible region?