CHEM 322 **Name**_____
Spring 2013 **Due In Class Friday, May 3**

Complete the following on separate paper. Show your work and **clearly identify your answers**.

1. Calculate the frequency in hertz, the wavelength, the energy in joules and the energy in kJ/mol associated with the 1685 cm^{-1} C=O vibrational absorption band of an amide.

$$\lambda = \frac{1}{1685\ cm^{-1}} \times \frac{10^4\ \mu m}{1\ cm} = 5.93\ \mu m$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8\ m/s}{5.93 \times 10^{-6}\ m} = 5.06 \times 10^{13}\ s^{-1}$$

$$E = h\nu = 6.63 \times 10^{-34} Js \times 5.06 \times 10^{13}\ s^{-1} \times \frac{6.02 \times 10^{23}\ photons}{1\ mol} = \frac{20.2\ kJ}{mol}$$

2. A compound has a molar absorptivity of 1.24×10^4 L $cm^{-1}mol^{-1}$. What concentration of the compound would be required to produce a solution that has a transmittance of 10.2% in a 2.50 cm cell? What absorbance does this correspond to?

   $A = -\log T = abc = -\log(0.102) = 0.991$

   $c = (-\log T)/ab = (-\log 0.102)/(1.24 \times 10^4\ L\ cm^{-1}mol^{-1} \times 2.50\ cm) = 3.20 \times 10^{-5} M$

3. A monochromator with a focal length of 0.58 m was equipped with an echellette grating of 2500 blazes per millimeter. (a) Calculate the reciprocal linear dispersion of the instrument for first order spectra. (b) If 2.0 cm of the grating were illuminated, what is the first order resolving power of the monochromator? (c) At approximately 430 nm, what minimum wavelength difference could in theory be completely resolved by the instrument?

   (a) $D^{-1} = \dfrac{(1\ mm/2500\ lines) \times 10^6\ nm/mm}{1 \times 0.78\ m \times 10^3\ mm/m} = 0.69\ nm/mm$

   (b) $R = \mathbf{n}N = 1 \times 2500\ lines/mm \times 2.0\ cm \times 10\ mm/cm = 5.0 \times 10^4$

   (c) $\lambda/\Delta\lambda = R = 5.0 \times 10^4 = 430/\Delta\lambda$

   $\Delta\lambda = 430/5.0 \times 10^4 = 8.6 \times 10^{-3}\ nm$

4. Why to quantitative and qualitative analyses often require different monochromator slit widths?

   For qualitative analysis, it is important to resolve as many absorption bands as possible for identification purposes. This consideration often means that slit widths should be as narrow as possible. On the other hand, for quantitative methods, better signal-to-noise ratios, and hence higher precision, can be obtained with wider slit widths.

5. For Na^+ and Mg^+ compare the ratios of the number of ions in the 3p excited state to the number in the ground state in (a) a natural gas-air flame (1800 K), (b) a hydrogen-oxygen flame (2950 K), (c) an inductively coupled plasma source (7250 K).

The energies of the $3p$ states can be obtained from the emission wavelengths shown in

Figure 8-1. For Na, we will use an average wavelength of 5893 Å and for Mg^+, 2800 Å.

For Na, the energy of the excited state is

$$E_{3p,Na} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{5893\ \text{Å} \times 10^{-10}\ \text{m/Å}} = 3.37 \times 10^{-19}\ \text{J}$$

For Mg^+

$$E_{3p,Mg^+} = \frac{6.626 \times 10^{-34}\ \text{J s} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{2800\ \text{Å} \times 10^{-10}\ \text{m/Å}} = 7.10 \times 10^{-19}\ \text{J}$$

(a) Substituting into Equation 8-1, gives at 1800 K

$$\left(\frac{N_j}{N_0}\right)_{Na} = 3 \exp\left(-\frac{3.37 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 1800\ \text{K}}\right) = 3.85 \times 10^{-6}$$

$$\left(\frac{N_j}{N_0}\right)_{Mg^+} = 3 \exp\left(-\frac{7.10 \times 10^{-19}\ \text{J}}{1.38 \times 10^{-23}\ \text{J K}^{-1} \times 1800\ \text{K}}\right) = 1.16 \times 10^{-12}$$

Proceeding in the same wave we obtain for Na and Mg^+

(b) $N_j/N_0 = 7.6 \times 10^{-4}$ and 8.0×10^{-8}

(c) $N_j/N_0 = 0.10$ and 2.5×10^{-3}

6. In the concentration range of 500 to 2000 ppm of U, there is a linear relationship between absorbance at 351.5 nm and concentration. At lower concentrations the relationship is nonlinear unless about 2000 ppm of an alkali metal salt is introduced to the sample. Explain.

This behavior would result from ionization of U. At low concentrations, the fraction of U that is ionized is greater giving a nonlinear relationship between concentration and absorbance. The alkali metal salt suppresses the ionization of U.

7. Why is an electrothermal atomizer more sensitive than a flame atomizer?

The electrothermal atomizer is a more efficient atomizer. It requires much less sample and keeps the atomic vapor in the beam for a longer time than does a flame.

8. Use equation 7-13 in your text for the resolving power of a grating monochromator to estimate the theoretical minimum size of a diffraction grating that would provide a profile of an atomic absorption line at 500 nm having a line width of 0.002 nm. Assume that the grating is to be used in the first order and that it has been ruled at 2400 grooves/mm.

$$R = \frac{\lambda}{\Delta\lambda} = \mathbf{n}N = \frac{500\text{ nm}}{0.002\text{ nm}} = 2.5 \times 10^5 = 1 \times N$$

$$N = \text{no. of blazes} = 2.5 \times 10^5$$

$$\text{Size of grating} = \frac{2.5 \times 10^5 \text{ grooves}}{2400 \text{ grooves/mm}} = 104 \text{ mm}$$

9. A portable photometer with a linear response to radiation registered 63.8 μA with the solvent blank in the light path. The photometer was set to zero with no light striking the detector. Replacement of the solvent with an absorbing solution yielded a response of 41.6 μA. Calculate: (a) the percent transmittance of the sample solution, (b) the absorbance of the sample solution, (c) the transmittance expected for a solution in which the concentration of the absorber is one half that of the original solution, (d) the transmittance to be expected for a solution that has twice the concentration of the sample solution.

(a) $\%T = P/P_0 \times 100\% = I/I_0 \times 100\% = 256\text{ mV}/498\text{ mV} \times 100\% = 51.4\%$

$A = 2 - \log \%T = 2 - \log(51.4) = 0.289$

(b) $A = 0.289/2 = 0.144 \quad T = 10^{-A} = 10^{-0.144} = 0.717$

(c) $A = 2 \times 0.289 = 0.578 \quad T = 10^{-0.578} = 0.264$

10. Why are atomic emission methods with an ICP source better suited for multi-element analysis than flame atomic absorption methods?

Flame atomic absorption requires a separate lamp for each element, which is not convenient when multiple elements are to be determined.

11. Why does a deuterium lamp produce a continuum rather than a line spectrum in the ultraviolet?

In a deuterium lamp, the lamp energy from the power source produces an excited deuterium molecule that dissociates into two atoms in the ground state and a photon of radiation. As the excited deuterium relaxes, its quantized energy is distributed between the energy of the photon and the energies of the two atoms. The latter can vary from nearly zero to the energy of the excited molecule. Therefore, the energy of the radiation, which is the difference between the quantized energy of the excited molecule and the kinetic energies of the atoms, can also vary continuously over the same range. Consequently, the emission spectrum is a spectral continuum.

12. Explain the difference between a fluorescence emission spectrum and a fluorescence excitation spectrum. Which more closely resembles an absorption spectrum?

In a fluorescence emission spectrum, the excitation wavelength is held constant and the emission intensity is measured as a function of the emission wavelength. In an excitation spectrum, the emission is measured at one wavelength while the excitation wavelengths are scanned. The excitation spectrum closely resembles an absorption spectrum since the emission intensity is usually proportional to the absorbance of the molecule.

13. What are the advantages of an FTIR spectrometer compared to a dispersive instrument?

The advantages of FTIR instruments over dispersive spectrometers include (1) superior signal-to-noise ratios, (2) speed, (3) higher resolution, (4) highly accurate and reproducible frequency axis, and (5) freedom from stray radiation effects.

14. What length of mirror drive in a spectrometer with a Michelson interferometer would be required to provide a resolution of (a) 0.050 cm^{-1} (b) 0.40 cm^{-1} (c) 4.0 cm^{-1} (d) 1 nm

$$\Delta\bar{\nu} = \bar{\nu}_2 - \bar{\nu}_1 = \frac{1}{\delta}$$

(a) $$\delta = \frac{1}{\Delta\bar{\nu}} = \frac{1}{0.05\ \text{cm}^{-1}} = 20\ \text{cm}$$

and the length of mirror movement = 50 cm/s = 25 cm

(b) In the same way, length = 1.25 cm

(c) Length = 0.125 cm