Chemistry 5640 - Instrumental Analysis

2nd Take-home Examination

April 11, 2005

Due Monday, April 18, at 11:30 AM

Instructions: Answer the following 4 equal-valued questions on your own. Answers may be turned in either neatly hand written or typed (printed). Be sure to put your name on your response. Most everything required for successful performance is in the book. You may not share your results with other students prior to the examination being graded and returned. You can ask me questions, either in person, or by e-mail (Stephen.Bialkowski@usu.edu). If the information is important, it will be shared with the class, by me only, either verbally or by posting on the Chemistry 5640 internet home page at www.chem.usu.edu/~sbialkow/Classes/5640/Chem5640.html

1) Optical Spectroscopy Instrumentation

A. Refer to Problem 7-3 and 7-4 in your book. Calculate the wavelength of maximum emission of a tungsten filament light bulb operating at the usual temperature of 2870 K and at a temperature of 3000 K. What are the total irradiances of the bulb at these two temperatures?

B. Why is glass better than a fused silica as a prism material for a monochromator to be used in the 400 to 800 nm region?

C. A monochromator with a focal length of 0.5 m is equipped with a 1200 blaze/mm echellette grating;
   - Calculate the reciprocal linear dispersion of the instrument for first-order spectra.
   - What is the first-order resolving power of the monochromator if 4 cm of grating is illuminated?
   - In theory, what minimum wavelength difference could be resolved at 500 nm by the instrument?

D. Describe the basis for radiation detection with both the silicon and vacuum photodiode transducers. How does the photomultiplier tube improve upon the response of the vacuum photodiode?

2) Atomic Spectroscopy

A. A chemist attempts to determine strontium with an atomic absorption instrument equipped with an oxygen-acetylene burner. The sensitivity associated with the 460.7 nm atomic line is not satisfactory. Suggest at least three things that might be tried to increase sensitivity.

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

C. Why are ion interferences sometimes less severe in ICP than flame emission spectroscopy?

D. What is an internal standard? Describing how one might use Li internal standards to obtain more accurate Na and K measurements in a flame emission spectrometer.

3) Visible/Ultraviolet Spectrophotometry

A. List and describe 3 sources of nonlinear (e.g., non-Beer's law) behavior in spectrophotometry.

B. How does optical bandwidth affect the measurement of absorbance? What gives a more accurate reading of absorbance; an interference filter with an optical bandwidth 10 nm, or one with a bandwidth of 0.1 nm?

C. The following questions refer to molecular luminescence spectrometry:
- Why is fluorescence spectrometry generally much more sensitive than absorption spectrophotometry? What type of noise (e.g., shot, thermal, or flicker) is reduced in luminescence spectrometry versus absorption spectrophotometry?
- What is the difference between fluorescence and phosphorescence?
- List two spectroscopic "features" of phosphorescence that distinguishing it from fluorescence.

4) Vibrational Spectroscopy

A. Fourier-Transform infrared spectrophotometers (FTIR)
- What is the main difference between the scanning-dispersive infrared spectrophotometer and the FTIR?
- What are some of the advantages to using the FTIR?
- When might the twin-beam scanning disperse instrument be advantageous?

B. Define the terms: fundamental; hot-band; overtone; combination band, Stokes v. anti-Stokes, and virtual states as used in vibrational spectroscopy.

C. Using Equation 16-9 calculate the spring constant for $H^{35}Cl$. (v=0 to v=1 occurs at 2886 cm^{-1}) Based on this spring constant and the atomic masses, predict the vibration frequencies for $H^{19}F$ (2907 cm^{-1}), $H^{79}Br$ (2559 cm^{-1}), and $H^{127}I$ (2230 cm^{-1}). Are these predictions accurate? Why or why not?

D. Use the Boltzmann Equation (8-1) to calculate the N (v=1)/N (v=0) excited-to-ground state population ratios for the 459 cm^{-1} band of CCl_4 at 20 °C and 40 °C. Predict the Stokes to anti-Stokes intensity ratios of the Raman spectra obtained at the two temperatures.