CHEM 133 Exam 2
SOLUTIONS

Equations and constants that you may find useful:
Nernst Equation:

$$E = E^o - \frac{RT}{nF}\ln Q = E^o - \frac{2.303RT}{nF}\log Q = E^o - \frac{0.05916}{n}\log Q \ (\mathrm{T} = 298\ \mathrm{K})$$

R = Universal Gas Constant = 8.314 J mol^{-1} K^{-1}; F = the faraday = 96,500 C/mol e^-; n = moles e^-

h = Planck's constant = 6.626 x 10^{-34} J·s, speed of light in a vacuum = c = 2.998 x 10^8 m/s
Dispersion of a grating monochromator:
constructive interference occurs for: $n\lambda = d(\sin\theta - \cos\phi)$
angular dispersion: $\frac{\Delta\phi}{\Delta\lambda} = \frac{n}{d\cos\phi}$ linear dispersion: $\frac{\Delta y}{\Delta\lambda} = \frac{F\Delta\phi}{\Delta\lambda}$
where n = order, θ = entrance angle from normal ϕ = exit angle from normal, F = focal length, and d = groove spacing

Boltzmann Distribution: $N^*/N_o = (g^*/g_o)e^{-E/kT}$ with Boltzman Constant = k = 1.38 x 10^{-23} J/K

SHORT ANSWER SECTION: (Each question worth 4 points)

1. An ion selective electrode is set up to measure the Ca^{2+} concentration in water. Its response is dependent on $\log[Ca^{2+}]$ over a wide range of concentrations. Give a possible example where its response could deviate from the log dependence.
Condition leading to deviation = _*1) Very high concentrations where sites in the membrane reach saturation, 2) low concentrations relative to interfering ions*___

2. Transitions in vibrational states occur with the absorption of ________ radiation.
a) X-ray b) visible c) infrared d) microwave

3. Which of the following can lead to apparent or real deviations from Beer's law:
a) compounds have ground and excited energy states with a wide range of energies
b) very low concentrations c) use of very monochromatic light
d) compounds that can exist in an acid or base form

4. Besides emission of light, give the name or describe a process by which a molecule at an excited energy state can transition to a lower energy state.
Name or process: *1) collisional deactivation, 2) inter system crossing, 3) photolysis, 4) photoionization (last two are a stretch as they result in a different molecule.*

5. Which of the following instruments typically has two monochromators?
a) a dual beam UV-Vis absorption spectrometer b) an FTIR
c) an NMR d) a fluorescence spectrometer

6. The wavelength of light emitted by a grating monochromator is adjusted by:
a) changing the entrance slit width b) rotating the grating
c) moving the focusing optics (e.g. mirror) d) changing the exit slit width

7. The two inherent advantages of performing atomic spectroscopy on atoms in the gas phase (vs. in aqueous or solid forms) are:

a) greater sensitivity and simpler instrument design
b) greater sensitivity and greater selectivity
c) greater selectivity and ease in determining metal charge state
d) it works and there are no spectroscopic methods for analyzing metals as solids

SECTION II. PROBLEM SECTION. Show work – use the back side if needed

1. Cyanide concentration is measured using a zinc/zinc cyanide electrode in which the reduction reaction is as follows: (14 points)

$Zn(CN)_2(s) + 2e^- \leftrightarrow Zn(s) + 2CN^-$

The standard reduction potential, E°, for the above reaction is -1.221 V. The above electrode is coupled to a reference electrode with fixed voltage of +0.197 V through a salt bridge and with the reference electrode attached to the plus side of the voltmeter (and $Zn/Zn(CN)_2$ electrode attached to the negative side of the voltmeter). If the voltmeter reads 1.139 V, what is the concentration of CN^-?

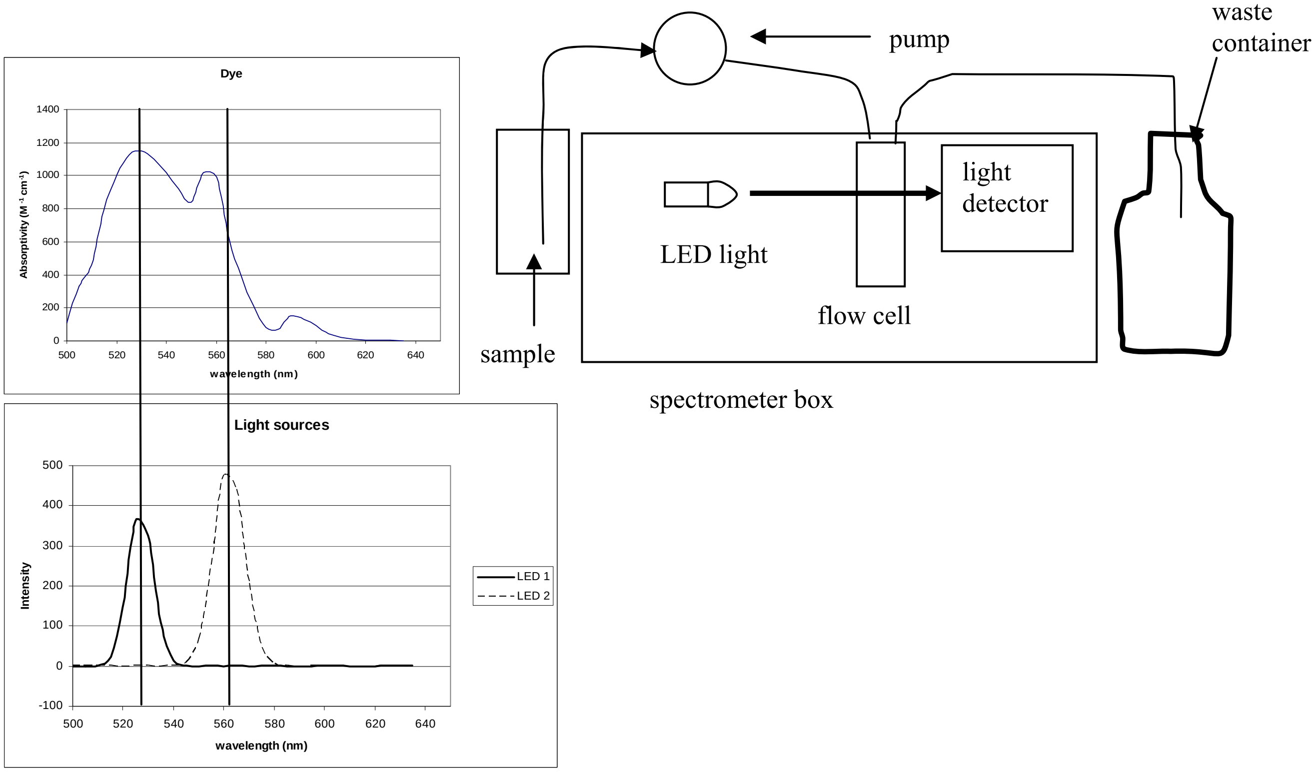
$E_{meas} = E_+ - E_-$ where $E_+ = E_{ref} = 0.197V$ and $E_- = E(Zn/Zn(CN)$ electrode)
$E(Zn/Zn(CN)$ electrode$) = E^o - 0.05916/2\log[CN^-]^2$
$E_- = E_+ - E_{meas} = 0.197 - 1.139\ V = -0.942\ V = -1.221 - 0.05916/2\log[CN^-]^2$
$0.279\ V = -0.05916/2\log[CN^-]^2$ or $\log[CN^-]^2 = -(0.279)(2/0.05916) = -9.43$
$[CN^-] = (10^{-9.43})^{0.5} =$ ***1.9×10^{-5} M***

2. A compound of interest, in a mixture containing other organic molecules, is known to absorb light and fluoresce. Describe two advantages in using fluorescence spectroscopy over absorption spectroscopy for analyzing this compound in a sample. (8 pts)

1) Because most organic compounds don't fluoresce, fluorescence spectroscopy should be MORE SELECTIVE (or reduce interferences) relative to absorption spectroscopy.

2) The problem doesn't mention concentrations, but fluorescence spectroscopy also is MORE SENSITIVE which could be an issue if the compound of interest is present at low concentrations.

3. A simple absorption photometer is shown in the diagram below to measure the concentration of a dye added to sodas. The dye spectrum and LED spectral responses are also given. The dye concentrations are expected to range from 0.30 to 1.00 mM and the cell path is 0.40 cm.



a) What is the energy of a typical photon originating from LED 2 (dashed line)? (6 pts)

E = hc/λ = $(6.63 \times 10^{-34}$ Js$)(3.00 \times 10^{8}$ m/s$)/(562 \times 10^{-9}$ m$) =$ $\mathbf{3.5 \times 10^{-19}}$ **J**

b) Which LED should be selected (LED 1 or LED 2)? Consider possible deviations to Beer's law and whether typical A values are in a good range in explaining your answer. (8 pts)

Can look at expected A values (A = εbC): for LED 1,

A(LED1 range) = $(1150\ M^{-1}\ cm^{-1})(0.4\ cm)(3 \times 10^{-4}\ M)$ *= 0.14 to 0.46*

vs. A(LED2 range) = $(600\ M^{-1}\ cm^{-1})(0.4\ cm)(3 \times 10^{-4}\ M)$ *= 0.072 to 0.24*

Best region is around 0.4 to 0.8, so ***LED1 is better***

Can look at deviations to Beer's law. Both LEDs are not very narrow emitters, but at λ (LED2), Δε/Δλ is larger compared to at λ (LED1). Thus larger deviations are expected for LED 2, and ***LED 1 should be used.***

c) Using the LED selected in b), estimate the concentration of a dye if the measured absorbance is 0.38. (6 pts)

LED 1: C = A/εb = 0.38/[$(1150\ M^{-1}\ cm^{-1})(0.40\ cm)$*] =* ***0.83 mM***

If using LED 2, ***C = 1.58 mM***

4. A monochromator is used with a grating that has 120 lines/mm, a focal length of 25 cm, and the grating set so that second order light exits the grating at an angle of 62° to normal.

a) What slit width (in mm) is needed to obtain a resolution of 250 for 731 nm light? (12 pts)

combining two dispersion equations, $\Delta y/\Delta\lambda = Fn/(d\cos\phi)$ *where* $n = 2$ *(second order),* $F = 250$ *mm,* $d = 1/120$ *mm = 0.00833 mm and* $\phi = 62$*. Resolution =* $\lambda/\Delta\lambda = 250$ *so*
$\Delta\lambda = 731$ *nm/250 = 2.92 nm*
The slit width = $\Delta y = Fn\Delta\lambda/(d\cos\phi)$
The slit width = (250 mm)(2)(2.92 x 10^{-6}*mm)/[(0.00833 mm)(cos62)] =* ***0.37 mm***

b) What will be the wavelength at which first order light exits the exit slit with the other conditions being the same? (6 pts)

The diffraction equation is: $n\lambda = d(\sin\theta - \cos\phi)$
Although θ *is not given, we know* θ *and* ϕ *are constant so* $n\lambda$ *= const. = 2(731 nm)*
const. = 1462 nm = 1λ *(for 1st order light) so* $\boldsymbol{\lambda}$ ***= 1462 nm***

5. Spectrometers commonly use monochromators to select a specific wavelength of light that is sent to the sample. **Give the name of a spectrometer** that doesn't use a monochromator (but still allows analysis of light over a range of wavelengths), and **describe how wavelength discrimination occurs** without the monochromator. (12 pts)

A number of spectrometers don't use monochromators including:
1) FTIR, 2) FTNMR, 3) spectrometers with polychromators (UV-Vis or atomic spectrometers), 4) X-ray instruments (XRF or Xray spectrometer attachments) with energy dispersive detectors, and 5) Atomic absorption spectrometers (which do use a monochromator, but also discriminate light through lamp selection). [5 is a stretch]

Wavelength discrimination occurs by: 1), 2) collecting time dependent signals of "white" light and Fourier transforming them to frequency dependent signals, 3) using a detector array in place of an exit slit in a monochromator (multiple wavelengths sent to each detector), 4) using a detector that produces a current that is proportional to the X-ray energy.