CHEM 133 Exam 2
Apr. 9, 2015
KEY

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

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

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 = 6.626×10^{-34} J·s, speed of light in a vacuum = c = 2.998×10^8 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 = 1.38×10^{-23} J/K

SHORT ANSWER SECTION: (Each question worth 4 points – **answers in bold**)

1. Which of the following is a common source of interference (limited selectivity) in ion selective electrodes.
a) the junction potential between the reference solution and the salt bridge
b) ions in the analyte solution of the same charge and similar size as the analyte ion
c) unstable reference electrodes d) current draw through the electrodes

2. Electron microscopes often have an attachment allowing elemental analysis to be performed on the sample being struck by electrons through spectroscopy perfomed on emitted X-rays. In this case, excitation of the atoms emitting X-rays occurs mostly by:
a) thermal excitation b) X-ray absorption
c) chemical reaction **d) by electrons knocking out inner shell electrons**

3. Which of the following changes to a UV-visible absorption spectrometer will increase its sensitivity? (ability to detect low concentrations of analyte)
a) use a more sensitive light detector **b) use a longer path length cell**
c) use a more intense light source d) analyze at a wavelength were absorptivity is smaller

4. List a source of monochromatic light OTHER THAN use of white light and a monochromator.
source = __*laser, LED, hollow cathode lamp, white light and interference filter*________

5. Give one component of a monochromator and describe its purpose
component _*1) entrance slit, 2) collimating optics, 3) dispersing element, 4) focusing optics, 5) exit slit* purpose _*1) let light in, 2) make light beams parallel, 3) disperse light, 4) focus light on exit slit, 5) allow monochromatic light to leave*_

6. Compared to elements in other forms (e.g. as ions in solution), atoms in the gas phase have:
a) very well defined energy states b) multiple vibrational and rotational states
c) no excited electronic states d) very slow velocities

7. The main advantage in using inductively couple plasma for emission measurements is:
a) increased ionization efficiency b) emission is better for charged species
c) high temperature increases the excited state populations
d) high temperatures result in narrower emission bands

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

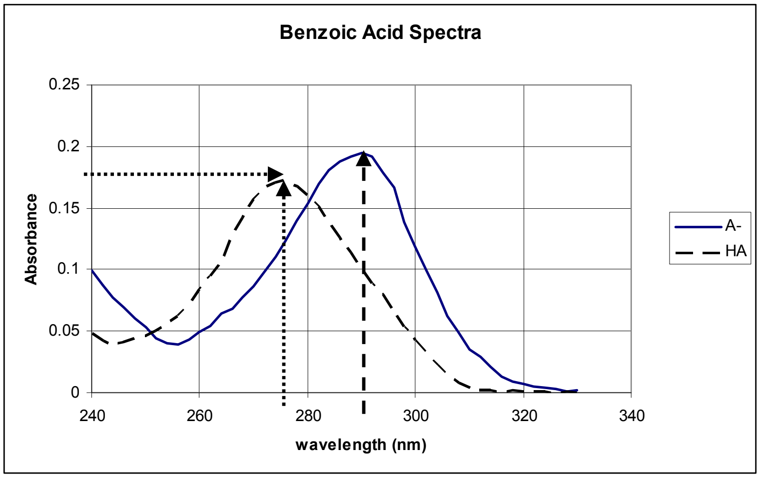
1. Calculate the expected potential for a cell (E_{Cell}) consisting of a reference electrode with E = 0.211 V attached to the plus end of a voltmeter and the minus end of the voltmeter attached to Pb/PbF_2 electrode (electrode notation: $Pb(s)|PbF_2(s)|F^-(aq)$) with the solution containing 0.0038 M NaF. The standard potential (E°) for the reduction of $PbF_2(s)$ to Pb(s) in the Pb/PbF_2 electrode is -0.350 V (10 pts)

$E_{Cell} = E_+ – E_-$ where + and – refer to the voltmeter electrodes, so
$E_{Cell} = E_{ref} – E_{Pb/PbF2}$
The reaction occurring in the Pb/PbF_2 electrode is: $PbF(s) + 2e^- \leftrightarrow Pb(s) + 2F^-$
$E_{Pb/PbF2} = E° – (0.05916/2)\log[F^-]^2 = -0.350\ V - (0.05916/2)\log(0.0038)^2$
$E_{Cell} = 0.211\ V – [-0.350\ V - (0.05916)(-2.42)] = 0.561\ V – 0.143\ V =$ ***0.418 V***

2. Some infrared detectors measure temperature increases (e.g. due to infrared light hitting a thermistor). If the minimum temperature increase detectable by a thermistor corresponds to a heat flux of 1.0×10^{-6} J (over a 1 s period), calculate the minimum number of photons needed for detection for infrared radiation with a wavenumber of 800 cm^{-1}. (8 pts)

$E_{Mindetect} = nE_{photon}$ where n = # photons and $E_{photon} = hc/\lambda$ and $\lambda = 1/\tilde{\nu} = 1/800$ cm
$E_{photon} = hc/\lambda = 6.626 \times 10^{-34}$ Js)$(2.998 \times 10^8$ m/s)/[(0.00125 cm)(1 m/100 cm)]
$= 1.59 \times 10^{-20}$ J/photon
$n = E_{Mindetect}/E_{photon} = 1.0 \times 10^{-6}\ J/ 1.59 \times 10^{-20}$ J/photon = **6.3×10^{13} photons**

3. Benzoic acid (e.g. HA) is a weak acid with a pK_a of 4.2. The spectra (shown below) are given for both forms with the acid form (assume 100% in acid form) for benzoic acid in an aqueous buffer with a pH of 1.0 and the basic form in an aqueous buffer with pH of 8.0 (assume 100% base form). These spectra were collected for a total benzoic acid concentration of 0.0010 M with a cell path length of 0.5 cm.



a) At a wavelength of 275 nm, estimate the molar absorptivity (in M^{-1} cm^{-1}) of the HA species. (6 pts)

$A = 0.175$ (see dotted line in chart) $= \varepsilon bC$ or $\varepsilon = A/bC = 0.175/[(0.5\ \text{cm})(0.0010\ \text{M})]$

$\varepsilon = 350\ M^{-1}\ cm^{-1}$

b) A chemist prepares benzoic acid standards by diluting benzoic acid in water over the range 10^{-4} to 10^{-2} M and analyzes the samples at a wavelength of 290 nm with fairly monochromatic light ($\Delta\lambda = 1$ nm). Is a linear Beer's law plot expected? If not, explain why not and what sort of plot would be expected. (8 pts)

See dashed line in plot. $A(HA) = 0.10$ and $A(A^-) = 0.195$. So for range, max A (100% A^-) = 1.95 and min = 0.01 (100% A^-). This is a reasonable range. At the highest A values (>1), there could be non-linearity for non-monochromatic light, but this should be minimal because $d\varepsilon/d\lambda l$ is only large fore HA, which has lower A values and $\Delta\lambda$ is small. The highest concentration is low for real deviations to Beer's law. The biggest source of deviation to Beer's law comes from dissolving a weak acid. This is because if it is unbuffered, the fraction present in the two forms (HA and A^-) will change with concentration (goes from 8% A^- at max conc. to 54% A^- at min). This will result in a greater A value at lower concentrations or a curvature toward decreasing A with increasing C.

c) Which species (HA or A^-) shows a larger gap in energy between the ground and excited electronic states? Explain your answer. (4 pts)

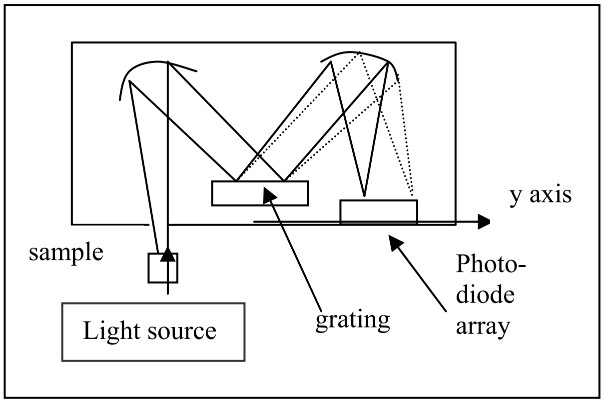
HA has a larger gap because its maximum occurs at lower wavelengths (E is proportional to$1/\lambda$)

6. Sodium can emit 589 nm light with an electronic transition going from a 3p to a 3s (ground) state. Given that there are 3 3p orbitals and 1 3s orbital, calculate the ratio of Na atoms in the excited state to ground state in a plasma at 6000 K. (8 pts)

$N^*/N = (g^*/g_o)e^{-E/kT}$ with $g^*/g_o = 3/1$ with $E = hc/\lambda = 3.37 \times 10^{-19}$ J

*$N^*/N = 3\exp[-3.37 \times 10^{-19}\ \text{J}/(1.38 \times 10^{-23}\ \text{J/K})(6000\ \text{K})] = 3e^{-4.07} =$ **0.051***

4. A photodiode array instrument has a polychromator as shown in the figure below. The polychromator's first order linear dispersion ($\Delta y/\Delta\lambda$) is 0.083 mm/nm, and the photodiode array consists of 512 elements each of 0.10 mm width (along the y axis). Assume a constant linear dispersion value (not perfect because of the change in ϕ). A sodium lamp emitting at 589 nm is detected at element number 300 (with element 1 being closest to the grating). **Give the bandwidth associated with each element** of the array (in nm) and **give the wavelength reaching element 1**. Also **give one advantage** this type of instrument has over a spectrometer using a monochromator. (20 points)



In the polychromator, Δy corresponds to the width of a detector element
Thus, the bandwidth, $\Delta\lambda = \Delta y/(\Delta y/\Delta\lambda)$
or $\Delta\lambda = 0.1 \text{ mm}/(0.083 \text{ mm/nm})$
$\Delta\lambda = 1.2$ nm

Since $\Delta y/\Delta\lambda$ is positive, it means that lower λ values occur toward the grating (element 1)
*Thus, element 1 should be (300 – 1)(**1.2 nm**) below element 300 or 360 nm less than the 589 nm or at 589 – 360 = **229 nm***

The biggest advantage is that all of the light is detected simultaneously.

Bonus (3 pts) Would you actually expect the linear dispersion to increase or decrease with element number (considering the change in ϕ as drawn in the diagram). Explain your answer.
The angle normal to light exiting the grating, ϕ, will be greater for greater elements.
From the linear dispersion equations, $\Delta y/\Delta\lambda$ depends on $1/\cos\phi$. So as ϕ increase, $\cos\phi$ decreases and $1/\cos\phi$ increases. Thus $\Delta y/\Delta\lambda$ increases with element number. [The assumption is pretty good for small ϕ, though]

5. The atomization process in electrothermal (graphite furnace) atomic absorption (AA) is significantly different from flame AA. Describe the atomization process through sample placement and heating steps. (8 pts)
A liquid sample is placed into a graphite tube (typically on a L'vov platform), and then the tube is heated through a series of steps to ensure uniform atomization. The heating has 4 steps: drying, charring, atomization, and clean-up, in which the temperature is ramped up.