

CHEM 133 Exam 2
Apr. 9, 2015

Name _____

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

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

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

h = Planck's constant = $6.626 \times 10^{-34} \text{ J}\cdot\text{s}$, speed of light in a vacuum = $c = 2.998 \times 10^8 \text{ m/s}$
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 = $k = 1.38 \times 10^{-23} \text{ J/K}$

SHORT ANSWER SECTION: (Each question worth 4 points)

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 performed 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 where absorptivity is smaller

4. List a source of monochromatic light OTHER THAN use of white light and a monochromator.

source = _____

5. Give one component of a monochromator and describe its purpose

component _____ purpose _____

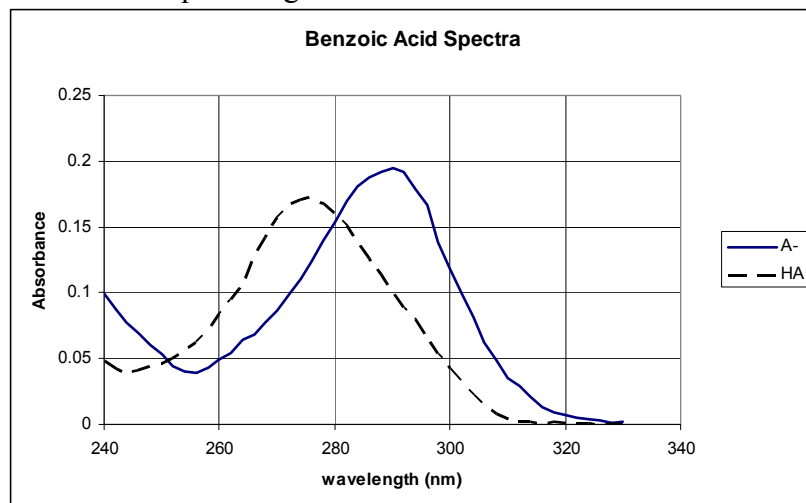
6. Compared to elements in other forms (e.g. as ions in solution), atoms in the gas phase have:
- a) very well defined energy states
 - b) multiple vibrational and rotational states
 - c) no excited electronic states
 - d) very slow velocities
7. The main advantage in using inductively couple plasma 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 $E = 0.211 \text{ V}$ attached to the plus end of a voltmeter and the minus end of the voltmeter attached to Pb/PbF₂ electrode (electrode notation: Pb(s)|PbF₂(s)|F⁻(aq)) with the solution containing 0.0038 M NaF. The standard potential (E°) for the reduction of PbF₂(s) to Pb(s) in the Pb/PbF₂ electrode is -0.350 V (10 pts)

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 $1.0 \times 10^{-6} \text{ J}$ (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)

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.



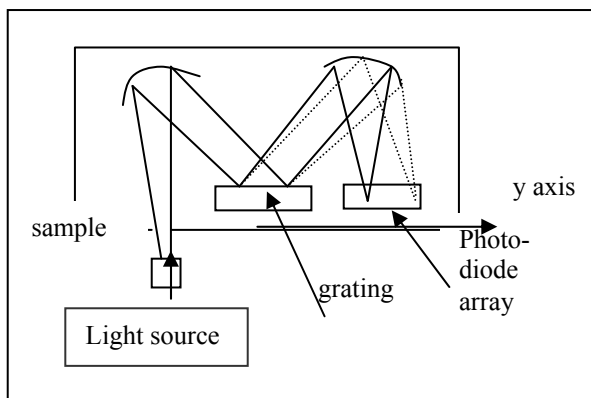
a) At a wavelength of 275 nm, estimate the molar absorptivity (in $M^{-1} \text{ cm}^{-1}$) of the HA species. (6 pts)

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 ($\Delta\lambda = 1 \text{ nm}$). Is a linear Beer's law plot expected? If not, explain why not and what sort of plot would be expected. (8 pts)

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

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)

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)



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.

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)