

CHEM 221
Instrumental Analysis
EXAM #2

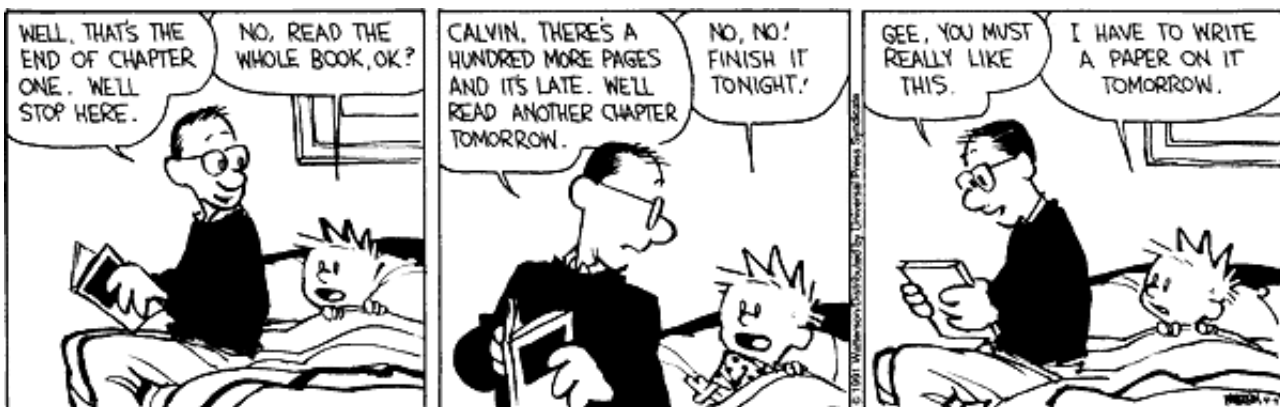
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INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself!

The entire exam is worth a total of 200 points. Provided are a periodic table and a formula sheet jam-packed with useful stuff!

Good Luck!



1. **a. (20 pts)** The Pd 4,4'-bis(dimethylamino)thiobenzophenone complex, in aqueous solution, absorbs very strongly in the UV/Vis spectral region, with a molar absorptivity of 2.12×10^5 . Assuming that the minimum measurable absorbance is 0.010 and that a cell with a 2.50-cm pathlength is available, what is the lowest possible concentration (**ppb**) of Pd that can be determined spectrophotometrically?

$$A = \epsilon bc, \text{ so: } c = A/\epsilon b = 0.010/[(2.12 \times 10^5)(2.50 \text{ cm})]$$

$$c = 1.886792 \times 10^{-8} \text{ mol/L}$$

Now, to convert mol/L to ppb:

$$\frac{1.886792 \times 10^{-8} \text{ mol Pd}}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.00 \text{ mL}}{\text{g}} \times \frac{106.4 \text{ g Pd}}{\text{mol}} \times 10^9 =$$

$$= 2.00755 \text{ ppb Pd}$$

$$= \boxed{2.0 \text{ ppb Pd}}$$

- b. (15 pts)** Assuming that the readout uncertainty of the spectrophotometer is $\pm 0.10\%$ -T, what is the %-relative uncertainty in making an absorbance measurement of 0.010?

$$s_T = 0.0010$$

$$A = 0.010$$

$$T = 10^{-A} = 0.9772372$$

$$\frac{s_A}{A} = \frac{(0.434)s_T}{T |\text{Log}T|} = \frac{(0.434)(0.0010)}{(0.9772372)(0.010)} = 4.441 \times 10^{-2}$$

$$\% \text{-rel uncert} = (s_A/A) \times 100 = \boxed{4.4 \%}$$

c. (15 pts) Assuming that the Pd 4,4'-bis(dimethylamino)thiobenzophenone system follows Beer's Law in this concentration range, calculate the detection limit for Pd with this system (i.e., the concentration of Pd, in ppb, that would give a S/N = 3).

$$S/N = 3 = A/s_A = 1/4.441 \times 10^{-2} = 22.51745$$

(for 2.00755 ppb Pd)

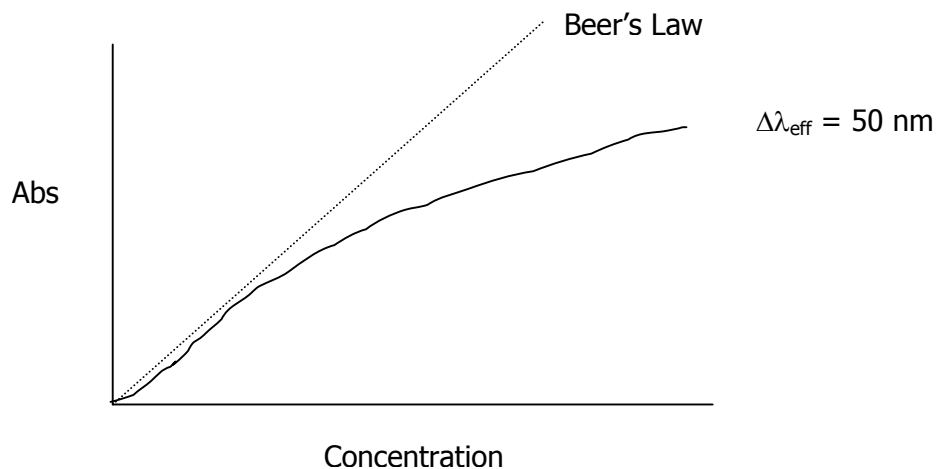
Since Beer's Law gives a linear relationship:

$$\frac{2.00755 \text{ ppb Pd}}{22.51745} = \frac{x}{3} \Rightarrow x = 0.267466 \text{ ppb Pd}$$

$$= \boxed{0.27 \text{ ppb Pd}}$$

d. (10 pts) Assuming that the Pd 4,4'-bis(dimethylamino)thiobenzophenone absorption bandwidth is 50 nm and the monochromator $\Delta\lambda_{\text{eff}}$ is 5 nm, what effect would a 10x increase in the slitwidth of the monochromator have on the applicability of Beer's Law with this system? Illustrate with a Beer's Law plot.

Beer's Law assumes that ϵ is invariant across the instrumental bandwidth ($\Delta\lambda_{\text{eff}}$), so that the sample is illuminated with, effectively, "monochromatic" light. The rule of thumb is that $\Delta\lambda_{\text{eff}}$ should be less than or equal to 10% of the absorption bandwidth in order for Beer's Law to hold - this is the case here, initially. As the slitwidth is increased, however, this condition is NOT met and *negative deviations* from Beer's Law will be observed at higher concentrations (as shown in the Beer's Law plot below):



2. One of the dispersive devices in my laboratory is a 1.0-meter focal length monochromator equipped with a 3600-gr/mm grating. The grating measures 75 mm x 75 mm.

- a. **(15 pts)** Calculate the first-order reciprocal linear dispersion, D^{-1} , ($\text{\AA}/\text{mm}$) for this monochromator.

Assuming that the angle r is small: $D_a = dr/d\lambda = n/d$

So: $D = F \times D_a = (F \times n)/d$

And: $D^{-1} = d/(F \times n)$

$$d = 1/3600 \text{ mm}^{-1} = 2.778 \times 10^{-4} \text{ mm} \times (10^7 \text{ \AA}/\text{mm}) \\ = 2.778 \times 10^3 \text{ \AA}$$

Substituting:

$$D^{-1} = 2.778 \times 10^3 \text{ \AA}/[(1.0 \times 10^3 \text{ mm}) \times 1]$$

$$D^{-1} = 2.778 \text{ \AA}/\text{mm} = \boxed{2.8 \text{ \AA}/\text{mm}}$$

- b. **(10 pts)** Copper has two emission lines at 2199.58 \AA and 2199.75 \AA ; is it theoretically possible for me to *just resolve* these two spectral features using the grating described in the first part of this problem? Assume operation in the first-order.

$$\text{Grating Resolving Power } (R_{\text{grating}}) = nN = (1)(3600 \text{ gr}/\text{mm})(75 \text{ mm}) \\ R_{\text{grating}} = 270,000$$

$$\text{Resolving Power Needed } (R) = \lambda_{\text{avg}}/\Delta\lambda = 2199.665 \text{ \AA}/0.17 \text{ \AA} \\ R = 13,000$$

Since $R_{\text{grating}} > R$, grating is capable of resolving the two copper lines.

- c. **(10 pts)** Calculate the slitwidth (μm) needed in order to *baseline resolve* the two copper lines. Again, assume operation in the first-order.

To *baseline resolve* the two lines, we need $\Delta\lambda_{\text{eff}} = \frac{1}{2}\Delta\lambda$

$$\text{So: } \Delta\lambda_{\text{eff}} = \frac{1}{2}(0.17 \text{ \AA}) = 0.085 \text{ \AA}$$

Since: $\Delta\lambda_{\text{eff}} = D^{-1} \times w$, $w = \Delta\lambda_{\text{eff}}/D^{-1} = (0.085 \text{ \AA})/(2.778 \text{ \AA}/\text{mm})$

$$w = 3.06 \times 10^{-2} \text{ mm} = \boxed{31. \mu\text{m}}$$

3. Lets assume that we have a light source that emits only at 2199.58 Å (wavelength in vacuum) and we are directing the beam into a Michelson interferometer.

a. (5 pts) Calculate the frequency of the light.

$$\nu = c/\lambda = (2.9979 \times 10^8 \text{ m/sec})/(2199.58 \times 10^{-10} \text{ m})$$

$$\nu = 1.362942 \times 10^{15} \text{ Hz} = \boxed{1.3629 \times 10^{15} \text{ Hz}}$$

b. (10 pts) The first surface that the light strikes is a beam splitter made out of fused silica (refractive index = 1.553). Calculate the percent of the light intensity that is reflected *at the flat surface* of the beamsplitter (assume that all of the light hitting the beamsplitter is orthogonal to its surface).

$$n_i \text{ (fused silica)} = 1.553$$

$$\text{Assume that } n_i \text{ (air)} = 1.00$$

$$\frac{I_r}{I_o} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} = \frac{(1.553 - 1.00)^2}{(1.553 + 1.00)^2} = \frac{0.30581}{6.5187} = 0.04692$$

$$\% \text{-reflected} = 0.04692 \times 100 = \boxed{4.7\%}$$

- c. (15 pts) Calculate the distance (cm) that the moving mirror needs to travel in order to "barely resolve" the two copper emission lines at 2199.58 Å and 2199.75 Å.

$$\bar{\nu}_1 = 1/(2199.58 \times 10^{-8} \text{ cm}) = 45,463.2 \text{ cm}^{-1}$$

$$\bar{\nu}_2 = 1/(2199.75 \times 10^{-8} \text{ cm}) = 45,459.7 \text{ cm}^{-1}$$

$$\Delta\bar{\nu} = 45,463.2 - 45,459.7 \text{ cm}^{-1} = 3.5 \text{ cm}^{-1}$$

$$\Delta\bar{\nu} = 1/2x \text{ so: } x = 1/2\Delta\bar{\nu} = 1/[(2)(3.5 \text{ cm}^{-1})]$$

$$\text{So: } x = 1/7.0 \text{ cm}^{-1} = 0.14286 \text{ cm} = \boxed{0.143 \text{ cm}}$$

- d. (5 pts) If the moving mirror in the interferometer travels at a velocity of 0.50 cm/sec, how long does it take to acquire a single interferogram capable of resolving the two copper lines (in part c, above)?

$$0.50 \text{ cm/sec} = 0.143 \text{ cm}/x \text{ sec}$$

$$x = 0.286 \text{ seconds} = \boxed{0.29 \text{ seconds}}$$

- e. (10 pts) Give two advantages (relative to dispersive spectrometry) to using FT-interferometry to acquire spectra.

-Multiplex Advantage (Fellgett's Advantage)

-increased S/N

-Jacquinot's Advantage (Throughput Advantage)

-increased S/N

-Self-Calibrating

-Simple/Compact

4. QUICKIES - No more than 2 sentences! – 10 points each

- a.** Diffraction gratings are usually used with a small angle of diffraction (r). Give the most significant advantage and the most significant disadvantage of using a small angle r .

For a diffraction grating: $D_a = n/d\cos(r)$

Advantage: If r is small, then $\cos(r) \approx 1$, so the angular dispersion is *independent of wavelength*.

Disadvantage: If r were allowed to increase, $\cos(r)$ will *decrease* causing the angular dispersion to *increase*, so by keeping r small, we limit the dispersion attainable.

- b.** Why is the sky blue? (This is a *serious* question!)

Sunlight is scattered by particulates in the atmosphere – since scattering is more efficient at shorter wavelengths ($I_s \propto 1/\lambda^4$), more blue light is scattered than is longer wavelength light . . . so the sky is blue.

- c.** What is usually the most likely decay route to the ground state after a molecule or atom absorbs a photon of electromagnetic radiation (EMR)? Does this decay process result in the emission of a photon of EMR?

-Quenching (collisional decay) is the most likely route to the ground state.

-No photons are released by this process (energy is released as heat).

5. **TRUE or FALSE.**

Indicate whether the following statements are **TRUE** or **FALSE** and briefly explain **WHY**. **10 points each.**

- a. UV/Vis absorption bands due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions shift to longer wavelengths with increasing solvent polarity.

False! Increasing solvent polarity stabilizes (lowers the energy of) the *n-electrons* most significantly, so the $n \rightarrow \pi^*$ transitions *increase* in energy and the $\pi \rightarrow \pi^*$ transitions *decrease* in energy. So, $n \rightarrow \pi^*$ bands shift to shorter wavelengths; only the $\pi \rightarrow \pi^*$ bands shift to longer wavelengths with increasing solvent polarity.

- b. The absorbance maximum for hexatriene is observed at a *longer* wavelength than is the absorbance maximum for 1,3-butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$).

True! Hexatriene is more *conjugated*, stabilizing the π -orbitals, lowering the energy of the π^* states and *decreasing* the energy of $\pi \rightarrow \pi^*$ transitions, shifting their absorption bands to longer wavelengths.

- c. Charge transfer bands arise from $d \rightarrow d$ electronic transitions of the metal ion in metal-ligand complexes.

False! Charge transfer bands result from transitions involving the transfer of an electron within a complex (e.g., electron transfer between a metal ion and ligand in a metal-ligand complex). They are easily distinguishable from bands resulting from $d \rightarrow d$ transitions in that their molar absorptivities are considerably greater (10^4 versus 10^2).

BONUS! EXTRA CREDIT! – 10 points, maximum

Where (city and state) was the Pittsburgh Conference (PittCon) held this year?

Orlando, Florida

Where (city and state) and *in what year* was the **first** Pittsburgh Conference held?

Pittsburgh, PA in 1950

The first Pittsburgh Conference had 14 exhibitors and 56 technical papers, but this year's Pittcon had more than 1300 exhibitors and more than 1200 technical papers! If one were to stop at EACH of the 1300 exhibitors' booth(s), how much time (minutes) would you be able to spend with each exhibitor if you spent 30 hours (the number of hours that the exhibition hall is open during the entire conference) visiting exhibitor booths?

$$\frac{30 \text{ hours}}{1300 \text{ booths}} \times \frac{60 \text{ minutes}}{1 \text{ hour}} = 1.3846 \text{ minutes} = \boxed{1.4 \text{ minutes}}$$

This year, there were two conference plenary lectures, one by a recent Nobel Laureate (and analytical chemist!) and the other by a very distinguished and well known analytical chemist. Name each of these distinguished lecturers and identify the analytical research area common to both.

The two speakers were:

Professor John Fenn (Virginia Commonwealth Univ.) – Nobel Prize 2002

Professor Fred McLafferty (Cornell University)

Both have made significant contributions to mass spectrometric methods of analysis.