Chemistry 277
Prof. Jason Kahn
University of Maryland, College Park
General Chemistry and Energetics
Hour Exam (100 points)

Your Name: ______________________________

Your SID #: ______________________________

Your Section # or time: ______________________________

March 9, 2020

You have 53 minutes for this exam.

Explanations should be concise and clear. There is lot of extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Generous partial credit will be given, *i.e.*, if you don't know, guess.

Useful Equations:

$\sigma_Y{}^2 = \lim_{N\to\infty} \frac{1}{N}\left[\sum_i (Y_i - \overline{Y})^2\right]$ pH = – log([H^+]) $\sigma_Y{}^2 = \left(\frac{\partial Y}{\partial u}\right)^2 \sigma_u{}^2 + \left(\frac{\partial Y}{\partial v}\right)^2 \sigma_v{}^2 + \cdots$

The sample standard deviation for *N* samples is $\sigma_X = \sqrt{\frac{1}{N-1}\sum_i \left(X_i - \overline{X}\right)^2}$

For $Y = au + bv$, $\sigma_Y = \sqrt{a^2\sigma_u{}^2 + b^2\sigma_v{}^2}$. For Y = $\frac{au}{bv}$, $\frac{\sigma_Y}{Y} = \sqrt{\frac{\sigma_u{}^2}{u^2} + \frac{\sigma_v{}^2}{v^2}}$

R = 0.08206 L·atm/mole K $T^2 = 4\pi^2 a^3/GM$ $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

R = 8.314 J/mole K = 1.987 cal/mole K = $N_A k_B$ $SEM = \frac{\sigma}{\sqrt{n}}$

$N_A = 6.02 \times 10^{23}$ particles/mole zepto-atto-femto-pico-nano-micro-milli-centi-deci-base

°C = °K – 273.15 $P(v)dv = Cv^2 exp(-mv^2/2kT)$ $\ln k = (-E_a/RT) + \ln A$

pH = pK_a + log([A^-]/[HA]) $K_p = K_c(RT)^{\Delta n}$ $K_w = [H^+][OH^-] = 10^{-14}$

$Absorbance = \varepsilon c \ell = \log(I_0/I)$ $PV = nRT$ $\left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$

pK_a = – log(K_a) pH(e.p.) = ½ (pK_{a1} + pK_{a2})

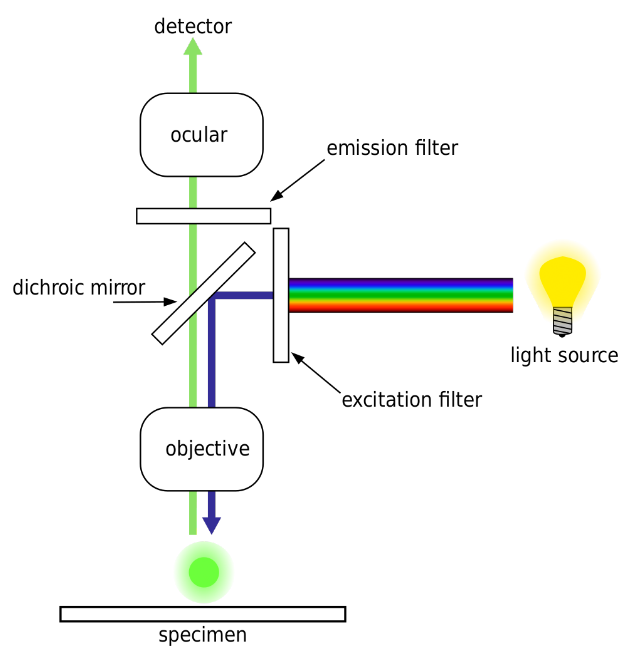
Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

1. Absorbance and Fluorescence (38 pts):

(a; 8 pts) Sketch the different spectrometer geometries for the excitation beam and the observed light for absorbance vs. fluorescence spectrometry. Explain why we collect fluorescence emission at 90° to the excitation beam.

(b; 6 pts) For simple imaging of fluorescence from a specimen, scattered light and fluorescence emerge from the sample together; only the florescence is shown in the picture at the right. What do you think the “emission filter” in the light path does, and why is it necessary?



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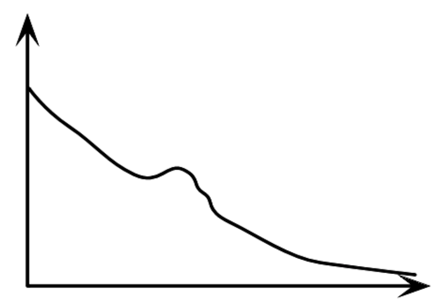
(c; 8 pts) Draw a sketch and explain why the number of photons absorbed by a sample is NOT proportional to the number of absorbing molecules in the sample, except for very dilute samples.

(d; 8 pts) Why is an absorbance reading >3 likely to be meaningless (for our specs)? How can you obtain an accurate absorbance reading for such a sample?

(e, 8 pts) Sketch the absorbance spectrum that your group obtained in the egg lab, in which we used phenanthroline to chelate iron and give a red color. For the sample spectrum shown, explain why the absorbance value at the top of the middle "peak" doesn't mean much and what might have gone wrong in the workup.



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2.0 ± 0.3 Accuracy, precision, error analysis (25.0000 ± 0.0001 pts):

(a; 17 pts) You perform three measurements of absorbance for three 1:5 dilutions of the same stock solution of a dye, and record 0.7822, 0.7964, and 0.7633. What is the estimated mean ± SEM of the values (for σ, use the formula with the N–1)? Given that the original stock solution is at 1.451 ± 0.003 M, calculate the extinction coefficient of the dye and report it to the appropriate number of significant figures ± propagated uncertainty to one sig fig. Path length = 1 cm, considered exact.

(b; 8 pts) From looking at the experimental values, do you think their uncertainty was due to uncertainty in the spectrometer reading or to random pipetting errors in the dilution step, and why? Describe one additional experiment you could you do to test your conclusion.

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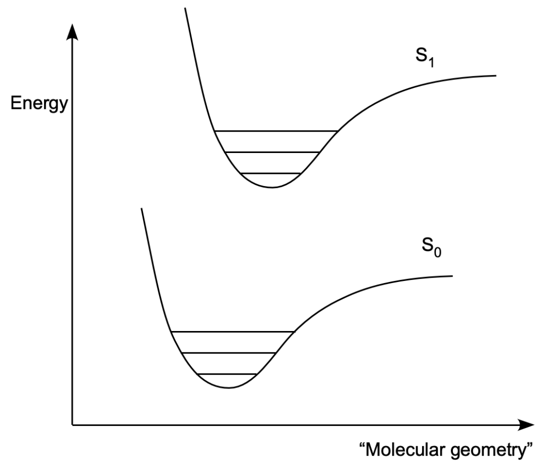
3. Spectroscopy (18 pts)

(a; 6 pts) On the Franck-Condon diagram below, add in two lines, representing the process of absorption of a UV/vis photon followed by fluorescence. S_0 and S_1 are the ground electronic state and the first excited electronic state respectively.



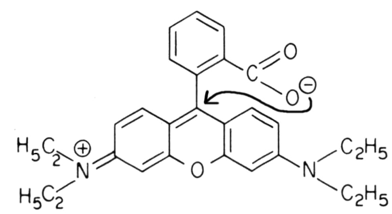
(b; 12 pts) Refer to your diagram to explain why fluorescence emission is to the red of absorbance (or fluorescence excitation). The "Stokes shift" is the energy difference between the absorbance λ_{max} and the fluorescence λ_{max}. The Stokes shift is different for different molecules. Sketch a Franck-Condon diagram for a different molecule corresponding to a larger Stokes shift than the molecule in (a). Speculate on possible physical origins of the large shift (many possible answers).

4. Random lab questions (19 pts)

(a; 6 pts) If you run an enzymatic reaction until all the concentrations stop changing and then add additional substrate, explain what should happen if everything is going well. If, instead, nothing actually happens, give a possible explanation.

(b; 5 pts) What was the basis of our measurement of the remaining NAD^+ concentration in the alcohol dehydrogenase lab? (EtOH + $NAD^+ \rightleftharpoons$ acetaldehyde + NADH)

(c; 8 pts) In the rhodamine lab, the measurement of concentration of the Z form shown at the right is based on absorbance, and the [L] is calculated by difference. Imagine that you used a lot more of the stock than you thought you did for one measurement. How could this give you a physically impossible number for [L]? How could we modify the experiment to fix this problem? (Hint: one possible solution involves the use of expensive and fragile quartz cuvettes that allow measurement in the UV.)



Page	Score
2	/14
3	/24
4	/25
5	/18
6	/19
Total	**/100**

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