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 12, 2018

You have 53 minutes for this exam.

Explanations should be concise and clear. There is 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:

$\sigma_Y{}^2 = \lim_{N\to\infty} \frac{1}{N}\left[\sum_i \left(Y_i - \overline{Y}\right)^2\right]$	$pH = -\log([H^+])$	$\sigma_Y{}^2 = \left(\frac{\partial Y}{\partial u}\right)^2 \sigma_u{}^2 + \left(\frac{\partial Y}{\partial v}\right)^2 \sigma_v{}^2 + \cdots$
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 = $N_A k_B$		$SEM = \frac{\sigma}{\sqrt{n}}$
°C = °K – 273.15	$P(v)dv = Cv^2 exp(-mv^2/2kT)$	$\ln k = (-E_a/RT) + \ln A$
$pH = pK_a + \log([A^-]/[HA])$	$K_p = K_c(RT)^{\Delta n}$	$K_w = [H^+][OH^-] = 10^{-14}$
$Absorbance = \varepsilon c \ell$	$PV = nRT$	$\left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$
$pK_a = -\log(K_a)$	$pH(e.p.) = ½ (pK_{a1} + pK_{a2})$	

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. Straightforward questions (20 pts)

(a; 6 pts) The equilibrium constant for the reaction aA + bB ⇌ cC + dD is given by

K_{eq} =

(b; 10 pts) Sketch the instrument geometry used for detecting fluorescence vs. absorbance, and based on your diagram, explain why fluorescence is able to measure much smaller concentrations than absorbance.

(c; 4 pts) Besides its advantage in sensitivity, fluorescence is much more useful than absorbance for tracking biomolecules in cells because…

Score for the page____________

2. Accuracy, precision, error analysis (20 pts)

(a; 5 pts) Give a physical rationale for the addition of standard deviations in quadrature, i.e. explain why when we add a set of numbers a, b, c with associated uncertainties σ_a, σ_b, σ_c the uncertainty of the sum (a + b + c) is $\sqrt{\sigma_a{}^2 + \sigma_b{}^2 + \sigma_c{}^2}$, not $\sigma_a + \sigma_b + \sigma_c$ as one might naively expect.

(b; 15 pts) Sketch a histogram of measurements that obey the usual normal distribution = Gaussian = bell curve. Explain the distinction between the standard deviation of the set of measurements and the standard error of the mean for the set of measurements. Which one decreases as you make more measurements, and why?

Score for the page____________

3. A bit of mathematical reasoning that explains a physical concept (24 pts)

Relationships among absorbance, transmittance, concentration, and intensity are not trivial. Recall that

$$Abs = \varepsilon c \ell = log_{10}\left(\frac{I_o}{I}\right) = \frac{1}{\ln(10)} ln\left(\frac{I_o}{I}\right) = \frac{1}{2.303} ln\left(\frac{I_{trans} + I_{abs}}{I_{trans}}\right) = \frac{1}{2.303} ln\left(1 + \frac{I_{abs}}{I_{trans}}\right)$$

where I_{trans} is the intensity of the transmitted light and I_{abs} is the intensity of the light absorbed by the sample.

Taylor series: $\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots$

(a; 12 pts) For very dilute solutions that absorb very little of the incident light, use the Taylor series expansion at the right to show that the measured absorbance *Abs* is directly proportional to I_{abs}, and derive the relationship between concentration *c* and I_{abs}.

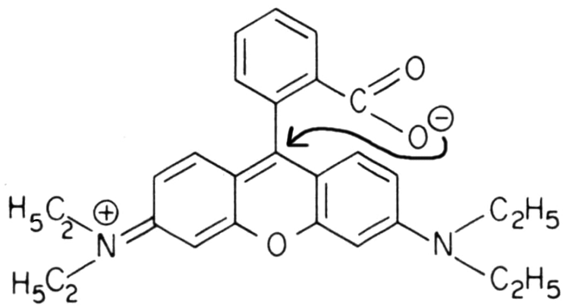
(b; 6 pts) Physically, in terms of what each molecule in the cuvette "sees," why does the proportionality between *c* and I_{abs} hold true in dilute solution?

(c; 6 pts) Physically, why is does this relationship not hold true at higher concentrations?

Score for the page____________

4. Chromophores and fluorophores (22 pts)
As you recall, Rhodamine B can exist either as a lactone or zwitterion form, with the latter shown below.

(a; 6 pts) On the right, draw the lactone form. The arrow pushes an electron pair as part of the mechanism of interconversion. Another hint: "Spiro" but not Nixon's vice president.



(b; 4 pts) Explain why the lactone form is not colored (at least to human eyes).

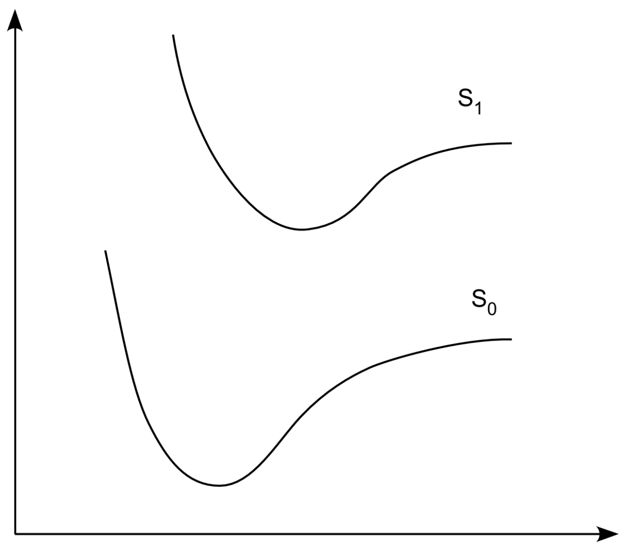
(c; 8 pts) List two features of the rhodamine B molecule that help make the zwitterion highly absorbent and also fluorescent.

(d; 4 pts) When you calculated the purity of Rhodamine B by measuring its absorbance in chloroform, you needed to assume that it is exclusively in the Z form in chloroform. Why?

Score for the page____________

5. Spectroscopy (14 pts)

(a; 8 pts) On the Franck-Condon diagram below for absorption and emission of light by a fluorophore, add in labels for the axes and a sketch of the process of absorption of a visible light photon followed by fluorescence. S_0 and S_1 are the ground electronic state and the first excited electronic state respectively.



(b; 6 pts) Refer to the diagram to explain why fluorescence emission is to the red of absorbance (or fluorescence excitation).

Page	Score
2	/20
3	/20
4	/24
5	/22
6	/14
Total	**/100**

Score for the page____________