

Chemistry 277

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University of Maryland, College Park

General Chemistry and Energetics

Hour Exam (100 points)

Your Name: \_\_\_\_\_

Key

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:

$$\sigma_Y^2 = \lim_{N \rightarrow \infty} \frac{1}{N} [\sum_i (Y_i - \bar{Y})^2]$$

$$\text{pH} = -\log([\text{H}^+])$$

$$\sigma_Y^2 = \left(\frac{\partial Y}{\partial u}\right)^2 \sigma_u^2 + \left(\frac{\partial Y}{\partial v}\right)^2 \sigma_v^2 + \dots$$

$$R = 0.08206 \text{ L}\cdot\text{atm/mole K}$$

$$T^2 = 4\pi^2 a^3 / GM$$

$$\ln K_{eq} = -\Delta H^\circ / (RT) + \Delta S^\circ / R$$

$$R = 8.314 \text{ J/mole K} = 1.987 \text{ cal/mole K} = N_A k_B$$

$$SEM = \frac{\sigma}{\sqrt{n}}$$

$$^\circ\text{C} = ^\circ\text{K} - 273.15$$

$$P(v)dv = Cv^2 \exp(-mv^2/2kT) \quad \ln k = (-E_a/RT) + \ln A$$

$$\text{pH} = \text{p}K_a + \log([\text{A}^-]/[\text{HA}])$$

$$K_p = K_c(RT)^{\Delta n}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$\text{Absorbance} = \epsilon c \ell$$

$$PV = nRT$$

$$\left[ \frac{-\hbar^2}{2\mu} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

$$\text{p}K_a = -\log(K_a)$$

$$\text{pH(e.p.)} = \frac{1}{2} (\text{p}K_{a1} + \text{p}K_{a2})$$

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)**

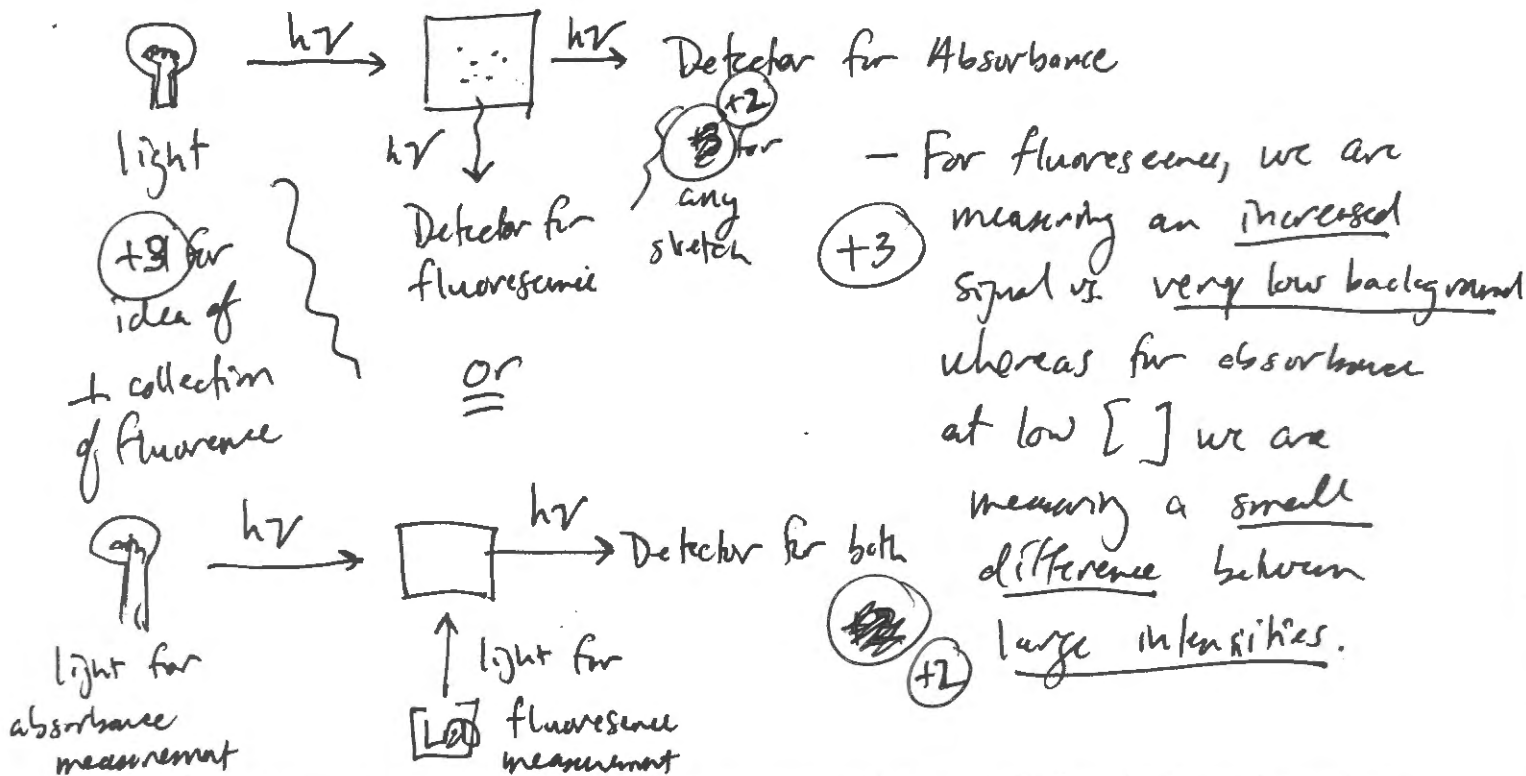
(a; 6 pts) The equilibrium constant for the reaction  $aA + bB \rightleftharpoons cC + dD$  is given by

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

+4  
6 pts ~~either way~~ for correct  
+2 for "products / reactants"

(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.

Cuvette (top view)



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

- Most molecules are not fluorescent so we can track the labeled molecules against an invisible soup of unlabeled stuff and see only the molecules we care about.  
 +2

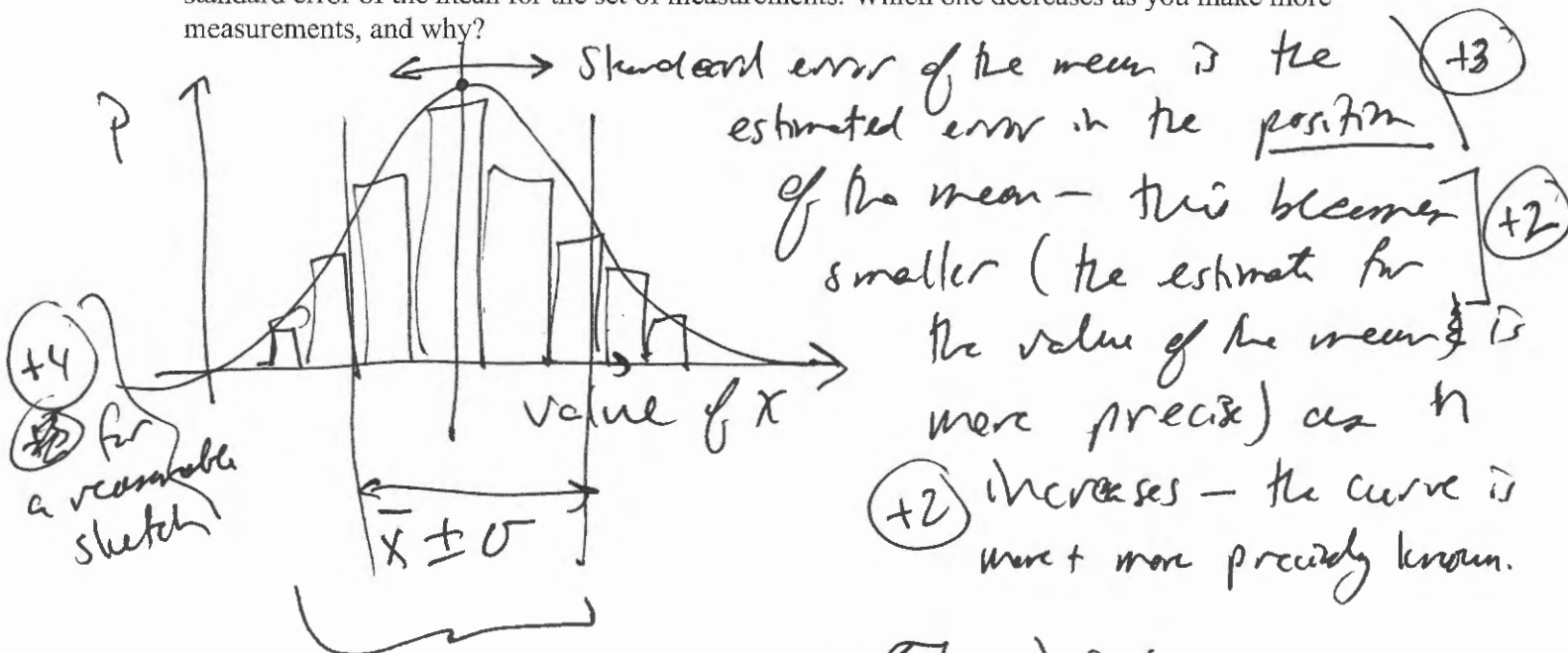
**2. Accuracy, precision, error analysis (20 pts)**

(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  $\sigma_a, \sigma_b, \sigma_c$  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.

+3 Random errors ~~stand~~ tend to cancel out in repeated measurements; it is unlikely that all of them will be in the same direction, ~~so the sum of~~.

+2 The math works out to the quadrature rule assuming that errors are not correlated w/ each other.

(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?



+4 The standard deviation (~~is~~  $\sigma$ ) is the measure of the width of the distribution - it is characteristic of the underlying distribution and does not change w/ sample size (the estimate of the true population  $\sigma$  gets more precise, though).

Score for the page

20

**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

$$Abs = \epsilon c l = \log_{10} \left( \frac{I_0}{I} \right) = \frac{1}{\ln(10)} \ln \left( \frac{I_0}{I} \right) = \frac{1}{2.303} \ln \left( \frac{I_{trans} + I_{abs}}{I_{trans}} \right) = \frac{1}{2.303} \ln \left( 1 + \frac{I_{abs}}{I_{trans}} \right)$$

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

(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  $I_{abs}$ .

$Abs = \frac{1}{\ln 10} \cdot \ln \left( 1 + \frac{I_{abs}}{I_{trans}} \right)$  where  $\frac{I_{abs}}{I_{trans}} \ll 1$  and  $I_{trans} \approx I_0$

$\approx \frac{1}{\ln 10} \left( \frac{I_{abs}}{I_{trans}} - \frac{1}{2} \left( \frac{I_{abs}}{I_{trans}} \right)^2 + \dots \right) \approx \frac{1}{2.303} \frac{I_{abs}}{I_{trans}} \approx \frac{I_{abs}}{2.303 I_0}$

(+3) for idea of plugging in  
 therefore  $c = \frac{Abs}{\epsilon l} \approx \frac{I_{abs}}{2.303 \epsilon l I_0}$  (+3) (or  $I_{trans}$ ) (+3) (I<sub>trans</sub> OK for I<sub>0</sub>)

(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?

(+2) The probability of a photon being absorbed is directly proportional to concentration because every molecule sees the same amount of incident light ( $\approx I_0$ ) and the probability of absorption at concentration is equally likely to absorb.

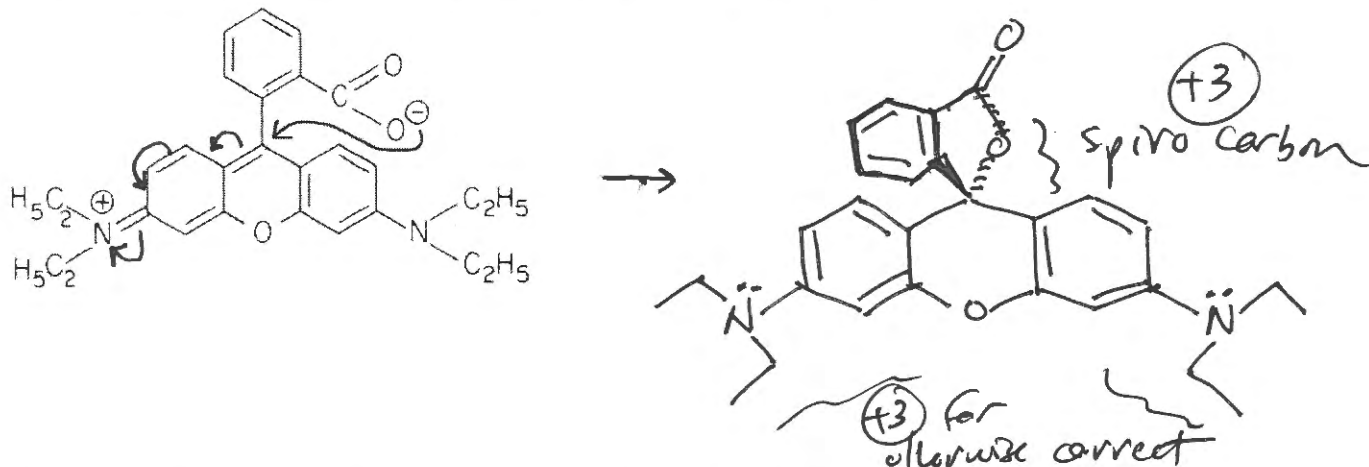
(c; 6 pts) Physically, why is does this relationship not hold true at higher concentrations?

(+3) At higher concentration the molecules at the front of the cuvette "shadow" the molecules at the back, so they "see" lower intensity, so each molecule is less likely to absorb a photon and  $Abs$  is not  $\propto [C]$ . (+3)

**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).

(+4) - There are no resonance forms that share electrons through orbitals larger than just one ring as in aniline or benzoic acid, which absorb in the UV.

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

(+4) - Extended ring system with extra lone pairs to add more polarizability.

(+4) - Rigid system that prevents loss of electronic energy to vibrational modes (because of bridging  $\pi$ )

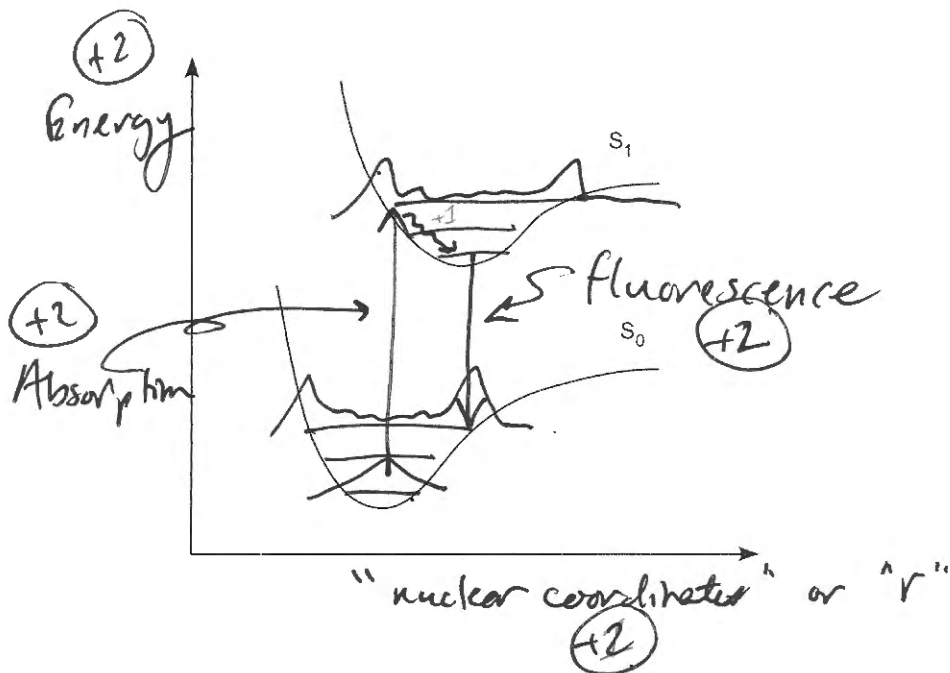
(d; 4 pts) When you calculated the purity of Rhodamine B by measuring its absorbance in chloroform, you needed to assume that it is exclusively in the Z form in chloroform. Why?

- We ~~measure~~ Absorbance < nominal absorbance -

(+4) we ~~cannot~~ cannot tell from one measurement whether this is due to decreased actual [RhB] or a lactone form that does not absorb.

**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.



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

- The emission is likely to give an excited vibrational state of the  $S_1$  electronic state.
- Internal conversion gives the ground vibrational state of  $S_1$ .
- Emission goes to an excited vib. state of  $S_0$ .
- Therefore the energy of the emitted photon is  $<$  the energy of the excitation photon, and emission is to the red of excitation.

Page	Score
2	/20
3	/20
4	/24
5	/22
6	/14
<b>Total</b>	<b>/100</b>

Score for the page 14