Chemistry 277 **Your Name:** _____

Prof. Jason Kahn

University of Maryland, College Park **Your SID #:** _____

General Chemistry and Energetics

Hour Exam (100 points) **Your Section # or time:** _____

March 11, 2019

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:

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

Thus,

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

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

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

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

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

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

$Absorbance = \varepsilon c \ell = \log(I_0/I)$ $\quad$ $PV = nRT$

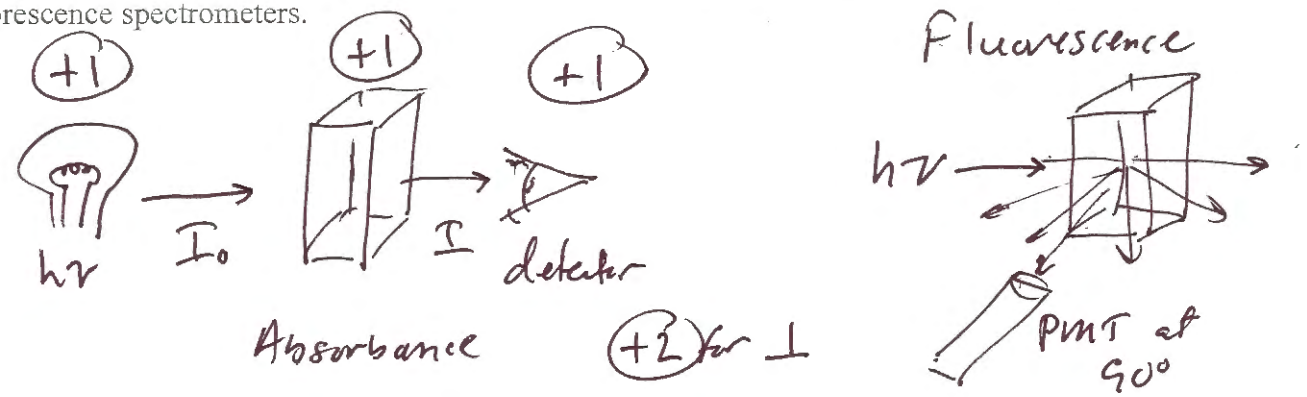
$\mathrm{p}K_a = -\log(K_a)$ $\quad$ $\mathrm{pH(e.p.)} = \frac{1}{2}(\mathrm{p}K_{a1} + \mathrm{p}K_{a2})$ $\quad$ $\left[\frac{-\hbar^2}{2\mu}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$

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 (40 pts):

(a; 5 pts) Sketch the two different geometries for excitation and observed light for absorbance vs. fluorescence spectrometers.



(b; 3 pts) From the definition of how we measure absorbance, how do we know it must be unitless?

$Abs = \log(I_0/I)$ is a logarithm (+2) – you cannot take a logarithm of a unit (+1)

+1 if opposite of c

(c; 6 pts) From Beer's law, show that the units of the molar extinction coefficient must be $M^{-1}cm^{-1}$.

$A = \varepsilon c l$ (+2) (+2)

$(\text{units less}) = \varepsilon\,(cm)(M)$ so units of ε must be $M^{-1}cm^{-1}$ (+1)

(+2) (+3)

by dimensional analysis or "to cancel" or any statement

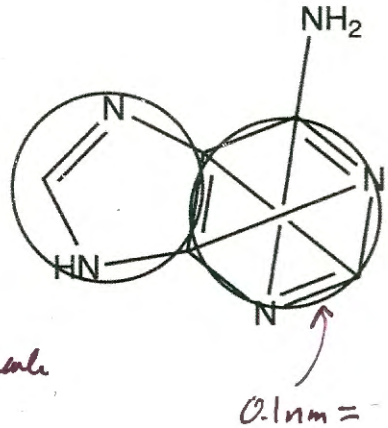
(d; 9 pts) The molar extinction coefficient of ATP is 15400 $M^{-1}cm^{-1}$. Convert this value into an area per molecule, and compare this value to the physical area of the ATP chromophore shown. Approximate the length of all bonds as 0.1 nm, the area of a hexagon as the area of the corresponding circle (πr^2), and the area of each ring as identical. What do you conclude?

$15400\ M^{-1}cm^{-1} = 15400\ \frac{\text{liter}}{\text{mole}} \cdot \frac{1}{cm}$

(+2)

(+3) $= 15400 \times \frac{1000\ cm^3}{\text{liter}} \times \frac{1\ \text{mole}}{6.02\times10^{23}\ \text{molecules}}$

$= \frac{1.54\times10^{7}}{6.02\times10^{23}}\ \frac{cm^2}{\text{molecule}} = 2.56\times10^{-17}\ cm^2/\text{molecule}$ (+3)



0.1 nm = 10^{-10} m = 10^{-8} cm

$\text{Area} = 2\times\pi r^2 = 2\times3.1415\times(10^{-8}cm)^2$

$= 6.28\times10^{-16}\ cm^2$ (+2)

(+2) Score for the page_____

Considering a photon as a particle, only about 1/30 of photons that "hit" an ATP are absorbed

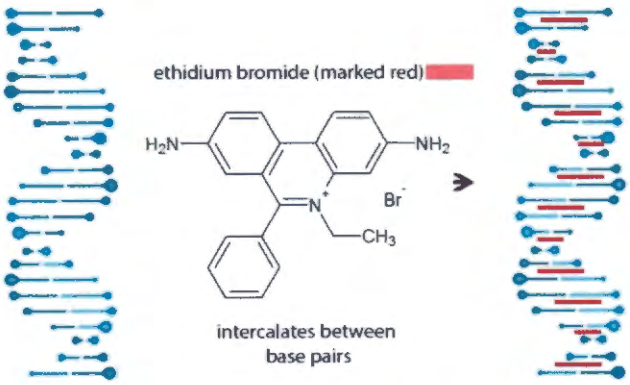
(e, 5 pts) For our protein lab we used an extinction coefficient in terms of micrograms per ml (× cm^{-1}) instead of a molar extinction coefficient. Why was the different unit appropriate?

(+2) – We don't know which protein(s) we are looking at, so we don't know molecular weights.

(+2) – To a first approximation, all proteins have similar absorbance (+CBBG) on a mass basis.

(+1) – So mass/volume (× cm^{-1}, cuvs) is appropriate for the desired measure – mass of dietary protein, whether or not it resembles BSA.

(f; 12 pts) Recall that fluorescence is a competition between loss of energy through emission of a photon vs. through any other means. In general, are most colored molecules fluorescent in the visible/IR or not? Give two possible reasons for the enhanced fluorescence of ethidium bromide when it is bound to DNA vs. free in solution, where it has more conformational freedom and is completely accessible to solvent. (I will be very surprised if anyone gives the answer accepted in the literature: this is about thinking.)



(From https://www.hoelzel-biotech.com/en/infothek/nucleic-acid-detection/

(+2) Most colored molecules are not fluorescent.

Possible answers: (+5 each)

1. Restricted vibrational modes of EthBr ~~regulon~~ intercalated slow down loss of energy to the environment.
2. Positively charged EthBr is sequestered away from Br^- so halide quenching is decreased.
3. Energy transfer from neighboring DNA bases ↑ apparent ε (but this wouldn't explain EB fluorescence upon exposure to 312nm light that DNA does not absorb.)
4. Drug is sequestered away from solvent and can't dump energy.
5. Rate of de-excitation via proton transfer to solvent is decreased upon binding (accepted answer).

Score for the page 17

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

(a; 20 pts) If you mix 2.57 ± 0.03 mL of a 1.523 M NaCl stock solution with 7.43 ± 0.04 mL of water, what is the final salt concentration? Give your reasoning for the error you impute to the stock solution [NaCl], and provide a final answer to the appropriate number of sig figs ± propagated uncertainty to one sig fig.

(+3) Final $[NaCl] = \frac{\text{moles}}{\text{volume}} = \frac{(2.57 \pm 0.03)\text{mL} \times (1.523 \text{ moles} \pm 0.005 \text{ moles/L})}{((2.57 \pm 0.03) + (7.43 \pm 0.04))\text{mL}}$

(+5) Estimate ± 0.005 as the uncertainty in [NaCl] because the last digit is uncertain but is worth reporting. One could also justify ± 0.002 or ± 0.008 or +0.002/-0.008 on this basis, but the choice of 0.005 does not depend on the value of the last digit, which is a priori unknown.

Eg Based on prop. eqn's, $\sigma_{denominator} = \sqrt{0.03^2 + 0.04^2} = 0.05$ (Pythagorean) (+3)

$$\frac{\sigma_{numerator}}{numerator} = \sqrt{\left(\frac{0.03}{2.57}\right)^2 + \left(\frac{0.005}{1.523}\right)^2} = \sqrt{1.36 \times 10^{-4} + 1.078 \times 10^{-5}} = 0.0121 \quad (+3)$$

note choice of error doesn't matter much b/c the rel. error in volume is much larger

so $\sigma_{numerator} = 0.0121 \times 2.57 \times 1.523 = 0.0474$

$[NaCl] = \frac{3.9141 \pm 0.0474}{10.00 \pm 0.05} = 0.391 \text{ M} \pm \sigma_{NaCl}$ (+3)

$\sigma_{NaCl} = 0.391 \sqrt{(0.0121)^2 + (0.05/10)^2} = 0.391 \times 0.013 = 0.005 \text{ M}$ (+3) (12%)

(rel. error of num.)

(b; 5 pts) Let's say that someone measures the chloride ion concentration of the diluted solution with an extremely precise method like atomic absorption to be 0.457321 M. Is the error in your concentration likely to be a systematic error or a random error? Speculate on what could cause it.

(+2 for reasoning) 0.391 ± 0.005 means that there is a 90+ % chance that the true value is within 0.01 (depending on whether the uncertainty is std. dev. or SEM)

(+1) 0.457321 is different by ~0.06, much larger → systematic error.

(+2) Could be... "NaCl" was not, for example what if it were a mixture of NaCl and NaBr or NaO_2 or something by mistake. Or the stock concentration was simply wrong due to sloppy weighing at the factory. Or you used a NaCl solution instead of H2O to dilute, or someone has boiled + concentrated the stock solution.

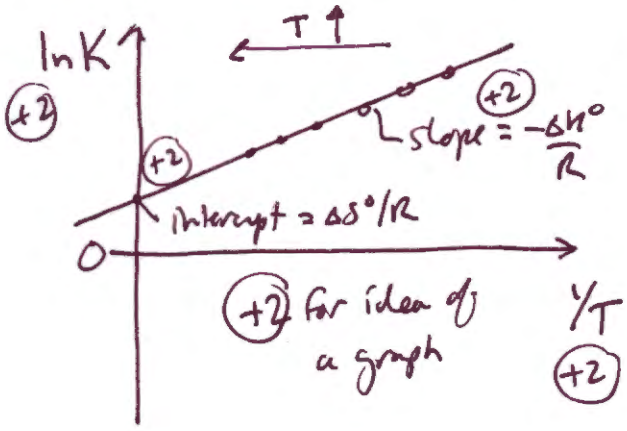
Score for the page 25

3. Plotting data (10 pts):

(a; 10 pts) Sketch a van't Hoff plot (based on $\ln K = (\Delta H° - T\Delta S°)/RT$) for an equilibrium with $\Delta H° < 0$ and $\Delta S° > 0$.

↳ D'oh! $\Delta G° = -RT \ln K = \Delta H° - T\Delta S°$

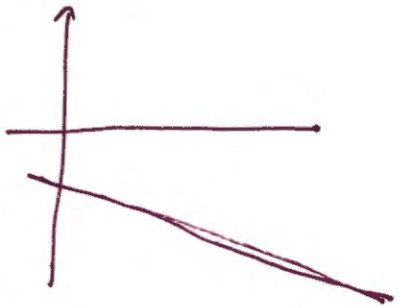
$\ln K = \left(-\frac{\Delta H°}{R}\right)\left(\frac{1}{T}\right) + \left(\frac{\Delta S°}{R}\right)$ is correct $\ln K = \left(-\frac{\Delta H°}{R}\right)\cdot\frac{1}{T} + \frac{\Delta S°}{R}$



$\Delta H° < 0 \Rightarrow \oplus$ slope

$\Delta S° > 0 \Rightarrow \oplus$ intercept

But



is full credit if labeled, due to my sign error

4. Random lab questions (25 pts)

(a; 5 pts) What was the purpose of the phenanthroline in the Fe/egg lab?

Phenanthroline changes (+2) color when it binds Fe^{+2}, allowing us to use absorbance to measure $[Fe^{+2}]$. (+3)

(b; 8 pts) If you run an enzymatic reaction until all the concentrations stops changing and then add additional enzyme, explain why there should be no further change if everything is going well. If something does happen, give a possible explanation.

(+3) If the reaction has reached equilibrium adding enzyme will not change anything - all an enzyme does is speeding arrival at equilibrium.

If something changed...

(+3) for any
- Enzyme could be unstable + died before rxn reached equilibrium,
- Enzyme could be inhibited by product so reaction slows down,
- Enzyme prep could contain additional cofactor that was unknown.

(+2) In any of these cases, adding fresh enzyme will give a pulse of rxn.

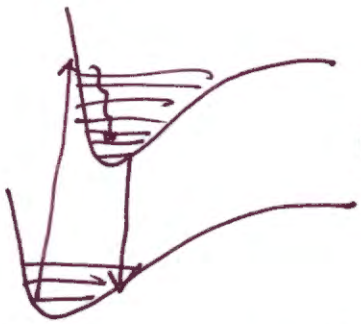
for idea (may be implicit)

Score for the page 23

(c; 4 pts) What was the basis of our measurement of acetaldehyde concentration in the alcohol dehydrogenase lab? (EtOH + NAD^+ ⇌ acetaldehyde + NADH)

We assumed no acetaldehyde to start and measured $[CH_3CHO]$ by stoichiometry, through measuring added [NADH] by absorbance. (+1) (+3) (+1) points add up to 5 – max 4 allowed.

(d; 8 pts) Explain briefly why fluorescence is to the red of absorbance for any given molecule.



(+3) the Jablonski diagram shows that vertical excitation gives an excited vibrational state of the excited electronic state.

(+3) Then internal conversion gives the lowest vibrational state of the 1st excited state, and fluorescence gives an excited vib. state of the ground state.

(+2) Therefore the emitted photon is of lower energy and longer wavelength than the absorbed photon, and fluorescence is to the red of absorption.

Page	Score
2	/23
3	/17
4	/25
5	/23
6	/12
Total	/100

Score for the page 12