

Chem 344 Final Exam

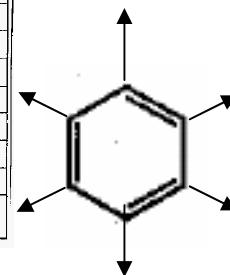
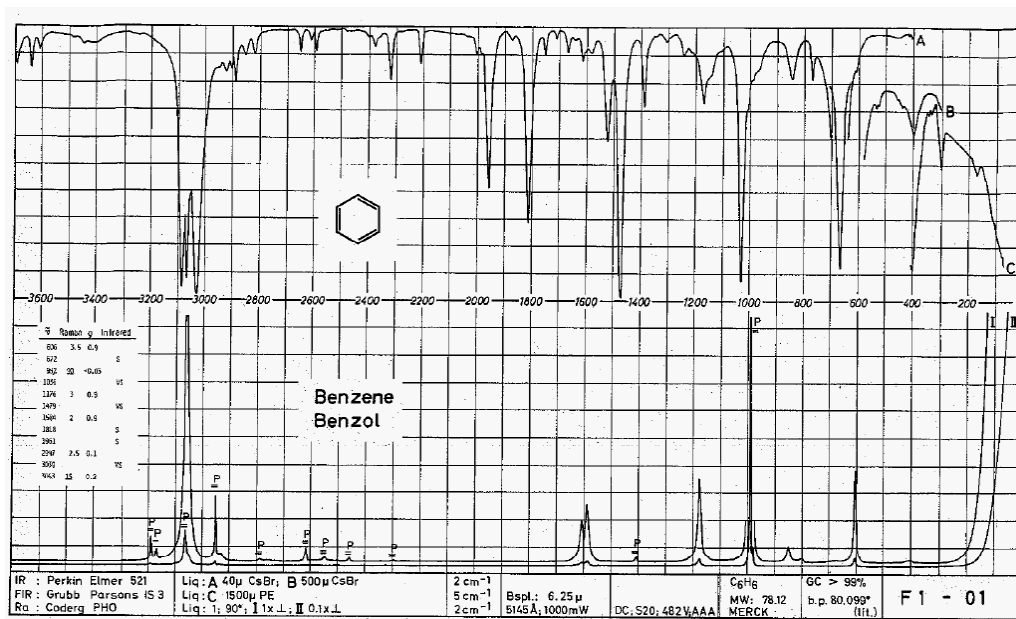
Wednesday, Dec. 13, 2006, 6-8 PM

Closed book exam, only pencils and calculators permitted. No Computers. Put all of your work in the answer book. If you need graph paper there are sheets available. If you work out graphical values like slope and intercept on your calculator, you should fully explain your method, put in intermediate values and describe the result. "Floating" answers without substantiation receive little credit. Possibly useful information is at the end of the exam.

Good Luck!!

1. When we do protein crystal structures with conventional x-ray source, we often use Cu $K\alpha$ x-rays with a wavelength of 1.54 Å (154 pm) because the wavelength has to be of the order of the spacing of molecules and atoms in the crystal. Longer wavelength radiation would result in less resolution. We can also get similar structural data with electron diffraction. What electron energy would be needed to get equivalent resolution data as with Cu $K\alpha$ x-rays (please express answer in eV)?
2. Bohr made a model for the H-atom by making some obvious and some radical assumptions.
Answer only 2 of the following:
 - a. State his assumptions for balancing forces on the orbiting electron and briefly explain why they are reasonable.
 - b. Charged particles traveling in a circle radiate (that is the basis of synchrotron radiation). Why is this a problem for Bohr's classical atom? Briefly explain.
 - c. Bohr made a radical assumption about angular momentum. What was it and why special? What important characteristic did it bring to the energy determination?
 - d. How did Bohr relate his solution for the energy to the Balmer series of spectral lines? What assumption was required? Answer beyond that it worked!
3. We used a postulate approach to learning quantum mechanics
Answer only 3 of the following:
 - a. Briefly explain the restrictions on the wavefunction and how they relate to the Born interpretation in terms of probability.
 - b. Briefly discuss the role of the operator, and formulate it for angular momentum: $\mathbf{L}_z = (\mathbf{r} \times \mathbf{p})_z$ (**bold** implies vector, \times is cross product, but only take the component along the z direction, around the z-axis).
 - c. What is the total angular momentum of the electron in the H-atom $2p_z$ state? Explain your answer (*one line answer*).
 - d. Explain how you would determine the dipole moment of the H-atom $2p_z$ electron? (*set up , do not solve*)
 - e. Explain how you would determine the fraction of the electron density that would lie within the Bohr radius for an H-atom $2p_z$ electron. (*set up , do not solve*)
 - f. Briefly explain the difference between the radial function for the H-atom and the radial distribution function and their relative purpose.

4. Sketch only 2 of the following H-atom wavefunctions:
- $R_{nl}(r)$ for $n = 2, l = 0$, and $n = 2, l = 1$
 - $4\pi r^2 R_{nl}(r)$ for the same values of n, l as in part a
 - $Y_{lm}(\theta, \phi)$ for $l = 2, m = 0$ and $l = 2, m = 2$
 - $2p_x$ and $3d_{xy}$ orbitals
5. Consider the LiH diatomic molecule in its ground state. This question is about vibrational spectra: **Answer only 3 of the following**
- If r is the distance from Li to H, the harmonic potential energy for LiH vibrations is: $V = \frac{1}{2}k(r-r_e)^2$. What is the equilibrium bond distance? i.e. explain how to determine.
 - If the fundamental frequency of LiH is 2400 cm^{-1} , what is k ? (watch your units!, MW: Li = 7, H = 1)
 - What is the fundamental vibrational frequency of LiD? (MW: D = 2)
 - In the gas phase, the LiH IR spectrum has rotational structure. Describe which bands are observed and to what transitions they correspond.
 - What is the spacing of the transitions in part d, if $r_e = 1.1 \text{ \AA}$ (110 pm)?
 - Briefly explain what would happen to the predicted vibrational spectrum if the potential were more realistic, i.e. anharmonic.
6. Consider Benzene vibrational spectra: **Answer only 2 of the following**
- Explain why for benzene the ring breathing mode (where all Cs move in and out in phase) is not observed in the IR spectrum but it is in the Raman. (see below)
 - Explain why the out-of-phase C-H stretch (where two C-H bonds opposite each other move so that one contracts while the other stretches) is seen in the IR. (see below)
 - For the benzene spectrum below, briefly explain the nature of the vibrational motion leading to transitions at $\sim 3000 \text{ cm}^{-1}$ and at $\sim 1500 \text{ cm}^{-1}$.
 - Determine the total number of fundamental vibrational modes for benzene.



a)

7. Harmonic oscillator question:

- a. Sketch the harmonic oscillator potential surface, include
 - i. the energy levels, with quantum numbers and energies
 - ii. the wavefunctions for the first four levels.

Do only one of b or c following (*it is not required to work an integral to get the answers if you see the relationship*): (skip **d** and **e**)

- b. Show that the wavefunctions for $v = 0$ and $v = 1$ are orthogonal.
- c. Using the general principle of orthogonality, show that the dipole moment operator $\mu = er$ will lead to an allowed transition from $v = 0$ to $v = 1$.
- ~~d. Explain why the wavefunctions penetrate the potential surface at each energy level, i.e. go past the classical turning point~~
- ~~e. Describe how the solutions to the quantum mechanical harmonic oscillator approach the expected behavior of a classical oscillator for high v values.~~

~~8. Real molecules are anharmonic oscillators. **Do not do the following**— skip~~

- ~~a. Briefly explain how this anharmonic potential for nuclear motion is related to the solution of the electronic Hamiltonian for the molecule~~
- ~~b. Briefly explain how this anharmonic, real potential can be related to the simple harmonic oscillator potential in #5a?~~

9. **For only one of the UV absorbance spectra** below (**a**, **b**, or **c**; each representing a transition from $S_0 \rightarrow S_1$) sketch the relative ground and excited state potential surfaces that would be consistent with the shapes observed according to the Franck Condon principle.

10. We used a Jablonski diagram to describe electronic energy transfer between states in a molecule.

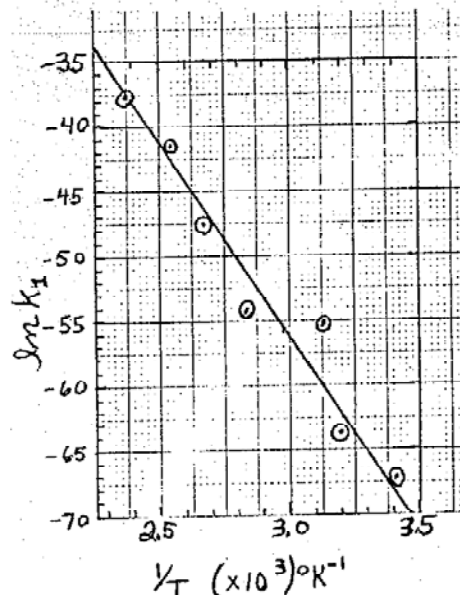
Do only two of the following

- a. Explain why molecular fluorescence is normally at a longer wavelength than the corresponding absorbance spectrum
- b. Briefly explain why fluorescence and absorbance spectra often do not overlap at all, i.e. sometimes have a spectral gap.
- c. Briefly explain why phosphorescence is much weaker and has a much longer lifetime than fluorescence.
- d. Explain how the molecule gets rid of the vibrational energy to relax down to the lowest energy level ($v = 0$).
- e. Explain why heavier atoms facilitate phosphorescence.

11. The plot at right was made for the 1st order decomposition of chloroethane:



Determine the activation energy for this reaction [note: temperatures are around room temp, 300 K, and $\ln k_1$ is natural log, base e]



Choose only 1 of the following 2 kinetics questions (# 12 or 13)

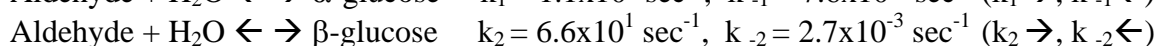
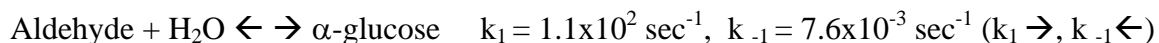
12. Consider the following mechanism where C is the product whose formation you wish to follow.



- Determine a rate law consistent with this mechanism involving two parallel channels. You may assume that k_{-2} is negligible (very slow).
 - Describe the overall order of the limiting rates for high A or High B concentration.
13. Consider the following reaction
- $$\text{A} + \text{B} \xrightarrow{k_f} \text{Products}$$
- If this reaction is 1st order in A and 2nd order in B write the overall rate law in terms of disappearance of A. What is the overall order?
 - Describe how could you determine the rate of the reverse reaction?

Choose only 1 of the following 2 kinetics questions (# 14 or 15)

14. The aldehyde form of glucose can be reversibly converted to both α - and β -glucose:



If 1.0 mole of pure aldehyde is placed in 1.0 liter of water, what will be the equilibrium concentration of aldehyde, α -glucose and β -glucose ?

15. A competitive inhibitor reversibly binds to the enzyme active site.
- Explain what mechanistic step this adds to the Michaelis-Menten enzyme mechanism model.
 - How will it affect the rate of the enzyme reaction? Does this appear in V_{max} or in K_m ? How? (use of a Lineweaver-Burk plot may assist your answer)