

Exam 4 is on Friday, Dec. 2, 7:55-8:55 AM in the usual meeting room. You may bring a 4 x 6" sheet of notes for use during the exam.

This is important: All numerical answers to problems should make physical sense. If you are computing energies, velocities, rates, molecular weights, times, etc., be aware of what is a reasonable answer and what is physically impossible (in a normal chemical environment on the Earth's surface). If you are unable to find a mistake you know must be there, explain why you know the answer is suspect, and estimate the answer along with justification.

Know or be able to:

Problems of the type given for homework #6 and #7.

Chapter 9

1. Given a balanced chemical reaction, write expressions for the rate of change in concentrations of the reactants and products. This is just stoichiometry (nothing to do with mechanism)
2. Concept of rate law and definition of order of reaction with respect to reactants and overall. Given data on rate as a function of concentrations of reactants, determine the rate law and the rate constant.
3. Definition of an *elementary step* and how to deduce the rate law for an *elementary step*. Know what is meant by unimolecular, bimolecular and termolecular. Know that you *cannot* derive the rate law from the overall *stoichiometric* chemical equation.
4. Significance of the rate determining step. For a simple mechanism, deduce the rate law if you are given which is the rate determining step for two cases: 1) the first step is rate determining; 2) the second step is rate determining and the first step is at equilibrium, or 3) the 3rd step is rate determining and the first two steps are at equilibrium. Understand that steps happening after the rate determining step have no bearing on the rate law.
5. Use the Arrhenius equation to determine the ratio of rate constants at two different temperatures if given the activation energy, E_a ; or if given E_a and two different temperatures, calculate the ratio of rates; or if given the rate constant, T , and the E_a , find the temperature at which a certain rate constant will be attained. (Realize that the procedure is isomorphic with using the Vant Hoff equation to find the ratio of equilibrium constants from the ΔH^0 for a reaction.)
6. Know that the reactant in a first order reaction decays exponentially. Find the fraction remaining after a given time if you are given the rate constant, half life, or *relaxation time (i.e., lifetime)*. Compute the half life from the rate constant. With the same equations with a change of sign, be able to *compute exponential growth*, where doubling time takes the place of half life.

Know that light intensity decays exponentially with distance traveled through an absorbing solution, and that the fraction remaining after travelling a distance x is 10^{-A} , where A is the absorbance for path length x .

7. Concept of diffusion controlled reaction and that the 2nd order rate constant for such is maximally about 10^9 to 10^{10} $M^{-1}s^{-1}$ for medium to small molecules in water at room temperature (when H^+ or OH^- are not involved).
8. Planck's equation, $\Delta E = h\nu = hc/\lambda$ and how to use it to convert between energy differences, frequency, wavenumber, and wavelength. How this equation relates to energy per photon. Calculate the Boltzmann factor when the energy difference is given as a photon wavelength, wavenumber, or frequency.
9. Definition of quantum yield of a photochemical reaction. Be able to calculate a quantum yield if given the moles or molecules of product obtained from a given amount of energy absorbed at a given wavelength.

Chapter 10

1. How does an enzyme greatly increase the rate of a reaction?
2. Michaelis-Menten enzyme kinetics. The meaning of V_{\max} and K_m . Know how to find V_{\max} and K_m from doing a Lineweaver-Burke plot.
3. Understand the significance of the specificity constant (k_{cat}/K_m) with respect to limits imposed with regard to maximum possible diffusion controlled encounters of substrate and enzyme (which is pertinent at very low substrate concentrations; see # 7. under Chapter 9 above).

Chapter 12

Calculate the total Coulombic potential *energy* of a collection of a few charges, if given their charges (in Coulombs or as fractional proton charges) and the distance between each pair of charges in Angstroms or meters. (***This will be much quicker if you use the 1389 kJ/mol per elementary charge squared per Angstrom constant, because those will be the units given on the exam.***)

Chapter 13

1. Know the approximate wavelength of light (and therefore the energy per photon) which causes: nuclear and electron spin flips in a high magnetic field, rotations and vibrations of molecules, excitations of electrons in large conjugated molecules and in small molecules, ionization of core electrons (X-rays and gamma rays).
2. Definitions of transmittance and absorbance. Beer's law: $A = \epsilon Cl$. Given any three of the four variables, calculate the fourth. Calculate transmittance from absorbance and vice versa. Do a problem like Problem 13, Chapter 13.
3. Concept of fluorescence (spontaneous emission). Kasha's Rule: Fluorescence is almost all from the lowest vibrational level of the lowest excited electronic singlet state, ***regardless*** of excitation wavelength, and that the fluorescence spectrum will be approximately the mirror image of the ***longest*** wavelength absorption band (in liquids or solids), with a small overlap of the absorption and fluorescence spectra.
4. Vibrational Spectroscopy: With simple diagrams, describe the difference between infrared absorption and Raman spectroscopy. Understand how bond energy and mass of the atoms making the bond contribute to the vibrational frequency. Know the basic range of vibrational frequencies and an example for the extremes.

Chapter 14

NMR: What causes the spectra? Difference between NMR spectrum and MRI. Predict the MRI of a simple geometric object filled with water for a given direction of magnetic field gradient relative to the object.

From Lectures:

List **3** of the 5 quantum concepts presented in class and the corresponding equation for each. Define terms and symbols used.