

HOMEWORK #6

HANDOUT #9

CHMY 361

Nov. 13, 2018. Updated Mon. Nov. 19

Problem 5 has 2 essential numbers added in bold.

Problem 4.(a) 310--> 300;

Due Tue. Nov 20, 9 am

1. For the reaction $2A + B \rightarrow 3C$, the following data is collected:

Initial Concentrations (M)		Initial Rate
A	B	
0.3	0.1	18.0 Ms ⁻¹
0.1	0.1	2.0 Ms ⁻¹
0.3	0.2	36.0 Ms ⁻¹

- (a) What are the orders of this reaction with respect to [A] and [B] and the overall order?
- (b) What is the numerical value and units of the rate constant from the above data if the rate is defined as: rate = rate of disappearance of A?
- (c) If we define the rate as = appearance of the product C, what will be the numerical value of the rate constant?
2. If 1.02 mg of the radioisotope, ³²P (half life 14.29 days), is absorbed into a leaf during a study of plant metabolism:
- (a) How many radioactive disintegrations (emission of a high energy electron) per second will there be from the leaf?
- (b) How long will it take until the fraction of the original ³²P remaining is 0.356?

3. For the reaction $A_2 + B_2 \rightarrow 2AB$ (stoichiometric), the following mechanism is proposed:

Step 1: $B_2 \rightleftharpoons B + B$ (forward rate constant = k_1 , back rate constant = k_{-1} , where (importantly) *if* B is formed, it cannot be observed experimentally (and therefore cannot appear in a proposed rate law).

Step 2: $B + A_2 \rightarrow AB + A$ (forward rate constant = k_2 , back rate constant is negligible).

Step 3: $B + A \rightarrow AB$

- (a) What is the rate law predicted if Step 1 is the rate determining step?
- (b) What is the rate law predicted if Step 2 is the rate determining step?

4. Enzymes selectively catalyze reactions by as much as 10^{17} fold faster than the same reaction in water at body temperature without enzyme, where they are unmeasurably slow. A common explanation is that the enzyme electrostatic environment lowers the Arrhenius activation energy (E_a) enough to provide this rate enhancement. Experiments have concluded that the rate of a certain reaction at 300 K has a rate constant of **100 years⁻¹** in the absence of an enzyme, but that the rate constant is **100 s⁻¹** with the enzyme.

(a) What **difference** in E_a is required to create a ratio of enzyme-catalyzed to un-catalyzed rate constants at **300 K**, assuming that the A factor in the Arrhenius equation is the same for both cases?

(b) If the difference in E_a were expressed as the electrostatic energy of two ions of charge +1 and -1, how far apart in Angstroms would they be to give the lowering of the E_a found in (a)?

5. On a summer day the UV flux at 300 nm can be $200 \times 10^{-5} \text{ Js}^{-1}$ on an area the size of a human face. At this wavelength, DNA absorbs most of this light. If you forget to put on sunscreen, and if the quantum yield for causing thymine dimers is 2×10^{-4} and a Y chromosome has about 59 million DNA base pairs, and if the face has surface area of **500 cm²**, and if there are **6 million Y chromosomes per cm²**, what fraction of the base pairs in a chromosome would suffer thymine dimer formation in 3 hours?

(Full disclosure: I don't know if this is reasonable or not because the numbers come from the internet without fact checking)

6. If one journal article states that for a certain enzyme, $K_M = 1 \times 10^{-2} \text{ M}$ and k_2 (i.e., k_{cat}) = $1 \times 10^6 \text{ s}^{-1}$, and another states for the same enzyme that $K_M = 1 \times 10^{-5} \text{ M}$ and $k_2 = 2 \times 10^6 \text{ s}^{-1}$, is there any way to tell whether one, both or neither are credible values? Show your calculations and state your reasoning that form the basis for your conclusion.

7. (a) Show that Boltzmann's constant at 300 K = 0.697 cm^{-1} by dividing k_B in $\text{JK}^{-1}\text{molecule}^{-1}$ by hc , where c is the speed of light in cm s^{-1} and h is Planck's constant in J s.

(b) Show that $k_B T$ at 300 K = 209 cm^{-1} .

(c) From the Boltzmann distribution using the value and units of k_B from (b), what is the ratio of molecules in the first vibrational excited state to those in the ground state, if the energy difference between these states = $k_B T$ at 300K, assuming the degeneracy = 1, which is typical. For your information, the energy spacing between vibrational energy states is $\Delta E = h\nu_{\text{vib}}$, where ν_{vib} is the classical vibrational frequency of the bonds (not relevant to this question).

(d) Answer the same question as in (c) for the probability of finding a chlorophyll molecule in its excited state if the lowest excited electronic state can be excited with 700 nm light. Do this by first changing 700 nm to cm^{-1} and using the value and units of k_B from (b)

(e) Answer the same question as in (c) for the ratio of spin up and spin down protons in a high magnetic field such that the frequency of radiation that gives resonance between the two energy states ($\Delta E = h\nu$) is 600 Mhz (= $6 \times 10^6 \text{ s}^{-1}$).