HOMEWORK #6

CHMY 361 **HANDOUT #9**
Nov. 13, 2017

Due Tue. Nov 21, 9 am

1. For the reaction 3A + B --> C, the following data is collected:

Initial Concentrations (M)

A	B	Initial Rate
0.2	0.1	6.0 Ms^{-1}
0.1	0.1	3.0 Ms^{-1}
0.1	0.2	12.0 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 = <u>appearance</u> of the product C, what will be the numerical value of the rate constant?

2. The famous **Carbon 14** is a radioactive isotope of carbon. It has too many neutrons, which allows an electron to quantum mechanically tunnel out of the nucleus to freedom, gaining tremendous kinetic energy in the process (called a beta particle). The first order rate constant for this is obtainable from the useful (not too long, not too short) half-life of 5,730 years. ^{14}C has a fairly constant level of abundance equal to about 1 part per trillion in the upper the reaches of the atmosphere by bombardment of N_2 by high energy particles from deep space. Therefore the carbon in all living things (e.g., us) is 1 part per trillion ^{14}C. We are radioactive!

Now the actual question:
From the half-life, compute the number of disintegrations per second from the 13 kg of carbon in a small human body. Note, that a "disintegration" is the same as the loss of one <u>atom</u> of ^{14}C, and recall that in a first order process changing units does not affect the rate constant because the units of k are s^{-1}.

3. For the reaction 2A + B ---> C (stoichiometric), the following mechanism is proposed:

Step 1: 2A <---> D (forward rate constant = k_1, back rate constant = k_{-1}, where (importantly) *if* D is formed, it cannot be observed experimentally (and therefore cannot appear in a proposed rate law).

Step 2: B + D ---> C (forward rate constant = k_2, back rate constant is negligible).

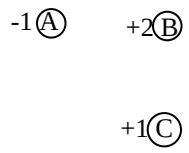
(a)What is the rate law predicted if Step 1 is the rate determining step?
(b) What is the rate law predicted if Step 2 is the rate determining step?

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. Such numbers come from applying the Arrhenius equation to extract the activation energy at temperatures up to 200-300 ^{o}C (473-573 K).
What **difference** in E_a is required to create a ratio of enzyme-catalyzed to uncatalyzed rate constants = 1×10^{16} at 300 K, assuming that the A factor in the Arrhenius equation is the same for both cases.

5. On a summer day the UV flux at 300 nm can be 200×10^{-5} 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 0.0015 for your skin, how many moles of thymine dimers will be formed in 3 hours?

6. If one journal article states that for a certain enzyme, $K_M = 1 \times 10^{-2}$ M and that k_2 (i.e., k_{cat}) $=1 \times 10^6$ s^{-1}, and another states for the same enzyme that $K_M = 1 \times 10^{-3}$ M and that $k_2 = 2 \times 10^4$ s^{-1}, is there any way to tell whether one, both or neither are credible values? State the basis for your conclusion.

7. Given 3 charges, A, B, C forming a right triangle.



The charges shown are in units of elementary charge. The distance between A and B = distance between B and C = 1.0. Angstrom. Calculate the electrostatic potential energy of interaction in kJ/mole of this charge distribution.

8. (a) Show that Boltzmann's constant at 300 K = 0.697 cm^{-1} by dividing k_B in $JK^{-1}molecule^{-1}$ 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_BT at 300 K = 209 cm^{-1}.

(c) The vibrational frequency of the I_2 molecule is about 212 cm^{-1}. 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. (Degeneracy= 1 for all vibrational states of I_2)

(d) Answer the same question as in (c) for the probability of finding a visual pigment in the retina of an eye in its excited state, if the lowest excited electronic state can be excited with 500 nm light by first changing 500 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 probability of finding a water molecule in its lowest rotational excited state, if the lowest excited rotational excited state can be excited with 5 cm^{-1} light.