

3. For the reaction $A + 2B \rightarrow C$ (stoichiometric), the following mechanism is proposed:

Step 1: $A + B \rightleftharpoons D$ (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: $B + D \rightarrow C$ (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. The uncatalyzed rate of hydrolysis of certain gluconopyranosides at room temperature can be estimated by observing the rate at very high temperatures and using the Arrhenius equation to extrapolate to room temperature (300 K). At 250 °C the rate constant = 10^{-5} s^{-1} and at 200 °C the rate constant = 10^{-6} s^{-1} . What is the expected rate at room temperature? (The same reaction in the presence of an enzyme proceeds at a rate that is 10^{16} times faster at room temperature!

5. On a summer day the UV flux at 300 nm can be $200 \times 10^{-5} \text{ J s}^{-1}$ on an area the size of a human face. At this wavelength, DNA absorbs most of this light. If the quantum yield for causing thymine dimers is 0.001, how many moles of thymine dimers will be formed in 5 hours?

6. If one journal article states that for a certain enzyme, $K_M = 1 \times 10^{-5} \text{ M}$ and that k_2 (i.e., k_{cat}) = $2 \times 10^6 \text{ s}^{-1}$, and another states for the same enzyme that $K_M = 1 \times 10^{-4} \text{ M}$ and that $k_2 = 2 \times 10^4 \text{ s}^{-1}$, 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 in a straight line, in which the charges shown are in units



of elementary charge, the distance between A and B = 2.0 Angstrom, and the distance between B and C = 1.0 Angstroms. Calculate the electrostatic potential energy of interaction in kJ/mole of this charge distribution. Use the form of Coulomb's Law given in lecture and in the text with units kJ/mol in which the charges are in units of elementary charge, and distances are in units of Angstroms.

8. (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) What is the name of the electromagnetic radiation for which the minimum energy to put a molecule into the first excited state = $2k_B T$ at 300 K? (*thermal* energy is constantly exciting everything, with no need of a beam of light, but will be less successful the larger the energy jump).

(d) What type of energy of the molecule is being excited, (e.g., translational, rotational, vibrational, electronic, nuclear spin)?

(For the next exam you will be asked to do this for *any* wavelength of light.)