

CH 341, Physical Chemistry
Fall 2009

Test 1

Name _____

Constants: $R = 8.314$ or 0.08206 you know the units.
 $g = 9.80665 \text{ m s}^{-2}$

$1 \text{ atm} = 1.0135 \times 10^5 \text{ Pa}$
 $1 \text{ bar} = 1 \times 10^5 \text{ Pa}$

Part 1: Answer 4 of the following 5 questions. If you answer more than 4 cross out the one you wish not to be graded. Otherwise only the first 4 will be graded. 9 points each.

1. For the reaction mechanism $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ can you always use the steady-state approximation, or if not, what must be true?

2. Thermal conductivity can be expressed as a linear flux-force relationship:

$$J_q = -\kappa \frac{dT}{dx}$$

where κ is the thermal conductivity. A thermopane window is constructed from two sheets of glass with a narrow spacing. Calculate the thermal flux in a thermopane window with a spacing of 2.00 mm between the panes of glass. Assume the outside air temperature is 0.0°C and the inside is 20.0°C . The thermal conductivity is $0.0252 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$ at 15°C and 1 atm. Assume a linear temperature gradient.

3. Calculate the pressure inside your mouth that would be necessary to drink a soft drink through a straw of length 20.0 cm. Assume the drink has the density of water at 20.0°C , 0.9982 g mL^{-1} and the atmospheric pressure is 1.000 bar.

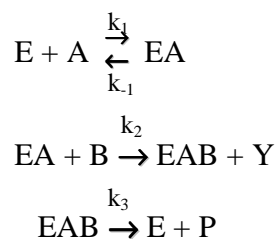
4. A substance with a molar absorption coefficient of $12,144. \text{ M}^{-1} \text{ cm}^{-1}$ and a concentration of $2.33 \times 10^{-6} \text{ M}$ is found in a lake. Calculate the fraction of the light incident at the surface of the lake that remains at a depth of 1.00 m.

5. A photovoltaic panel can convert at best 12% of the light flux into DC electrical power. The conversion of the DC power from a solar panel to AC power that can be used to power appliances or to feed into the power grid is about 77% efficient. The yearly average insolation for Boston is $4.16 \text{ kWh m}^{-2} \text{ day}^{-1}$. Calculate the AC power available per square meter from photovoltaic cells operating at 12% efficiency in Boston. Express your results in joules per second and also watts. [Hint: $1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$]

Part 2: Answer 4 of the following 6 questions. If you answer more than 4 cross out the ones you wish not to be graded. Otherwise only the first 4 will be graded. 16 points each.

6. The rate constant for the decomposition of a certain substance is $2.80 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ at 30.0°C and $1.38 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ at 50.0°C . Calculate the activation energy and pre-exponential factor.

7. The following mechanism has been proposed for an enzyme reaction with two substrates, A and B:

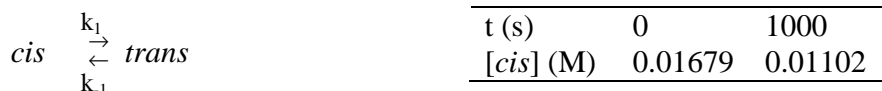


where EA and EAB are enzyme substrate complexes. Assuming that k_2 and k_3 are large compared to k_1 , show that the mechanism gives the rate law:

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [E][A][B]}{k_{-1} + k_2 [B]}$$

8. Find the integrated rate law for a third-order reaction with stoichiometry $A \rightarrow B$ and rate law $-d[A]/dt = k_3 [A]^3$. (Give the linearized form, for example for a second order reaction the linear form of the integrated rate law is $1/[A] - 1/[A]_0 = k_2 t$)

9. The *cis-trans* isomeration of 1-ethyl-2-methylcyclopropane is first order in the forward and reverse directions:



The reaction, starting with only *cis* isomer has the time course given in the table, above. The long-time value for the *cis*-isomer concentration is 0.00443 M. Determine ($k_1 + k_{-1}$).

10. Consider a reaction with the stoichiometry: $A + B \rightarrow C + D$. Assume that both A and B absorb at a specific wavelength, while C and D do not. Assume also that A is the limiting reagent, $[A]_0 < [B]_0$. Remember that the concentration of A is determined by the extent of the reaction: $[A] = [A]_0 - \xi$. Assume that the absorbance of the mixture is the sum of the absorbances: $A = \epsilon_A l [A] + \epsilon_B l [B]$, where ϵ_A and ϵ_B are the molar extinction coefficients of A and B, respectively. Show that:

$$\frac{[A]}{[A]_0} = \frac{[A]_0 - \xi}{[A]_0} = \frac{A - A_\infty}{A_0 - A_\infty}$$

11. Solve the matrix equation $\begin{pmatrix} 4 & 1 \\ 1 & 0.5 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 2 \\ 1 \end{pmatrix}$ for x and y.

$$\left[\text{Hint: } \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}^{-1} = \frac{1}{|M|} \begin{pmatrix} M_{22} & -M_{12} \\ -M_{21} & M_{11} \end{pmatrix} \right]$$