CH 341, Physical Chemistry **Test 1**
Fall 2009 Name _____

Constants: R = 8.314 or 0.08206 you know the units. 1 atm = 1.0135×10^5 Pa
g = 9.80665 m s^{-2} 1 bar = 1×10^5 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 J m^{-1} K^{-1} 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. M^{-1} cm^{1} and a concentration of $2.33x10^{-6}$ 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 kWh m^{-2} 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 kWh = $3.6x10^{6}$ 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 $2.80x10^{-3}$ L mol^{-1} s^{-1} at 30.0°C and $1.38x10^{-2}$ L mol^{-1} 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:

$$E + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} EA$$

$$EA + B \xrightarrow{k_2} EAB + Y$$

$$EAB \xrightarrow{k_3} E + P$$

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 $1/[A] - 1/[A]_o = k_2 t$)

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

$$cis \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} trans$$

t (s)	0	1000
[*cis*] (M)	0.01679	0.01102

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, $[A]_o < [B]_o$. Remember that the concentration of A is determined by the extent of the reaction: $[A] = [A]_o - \xi$. Assume that the absorbance of the mixture is the sum of the absorbances: $A = \varepsilon_A \ell [A] + \varepsilon_B \ell [B]$, where ε_A and ε_B are the molar extinction coefficients of A and B, respectively. Show that:

$$\frac{[A]}{[A]_o} = \frac{[A]_o - \xi}{[A]_o} = \frac{A - A_\infty}{A_o - A_\infty}$$

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.

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