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 \( A \rightarrow B \rightarrow C \) can you always use the steady-state approximation, or if not, what must be true?
   
   Answer: \( k_1 \ll k_2 \)

2. Thermal conductivity can be expressed as a linear flux-force relationship:
   
   \[ J_\text{q} = -\kappa \frac{dT}{dx} \]

   where \( \kappa \) 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\(^\circ\)C and the inside is 20.0\(^\circ\)C. The thermal conductivity is 0.0252 J m\(^{-1}\) K\(^{-1}\) s\(^{-1}\) at 15\(^\circ\)C and 1 atm. Assume a linear temperature gradient.

   Answer: Note that for temperature differences, a \(^\circ\)C is the same as a degree K:
   
   \[ \frac{dT}{dx} = \frac{T' - T}{\delta} \]

   \[ J_\text{q} = -\kappa \frac{dT}{dx} = -0.0252 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1} \frac{(20.0 - 0.0\,^\circ\text{C})}{2.00 \text{ mm}} (1000 \text{ mm/1 m}) \]

   \[ = -252 \text{ J m}^{-2} \text{ s}^{-1} \] the flux direction is negative, that is \( \leftarrow \) (hotter to colder)

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\(^\circ\)C, 0.9982 g mL\(^{-1}\) and the atmospheric pressure is 1.000 bar.

   Answer: \( P_{\text{ext}} = P_{\text{m}} + P_{\text{liq}} \) and \( P_{\text{liq}} = dgh \).

   The density of water at 20.0\(^\circ\)C is needed in kg m\(^{-3}\) to match the units of g:
   
   \[ d = 0.9982 \text{ g mL}^{-1} \] \((1 \text{ kg/1000 g})(1 \times 10^3 \text{ mL/L})(1000 \text{ L/1 m}^3) = 998.2 \text{ kg m}^3 \)

   Then \( P_{\text{liq}} = dgh = 998.2 \text{ kg m}^{-3} (9.807 \text{ m} s^{-2})(0.200 \text{ m}) = 1958 \text{ Pa} \)

   Solving \( P_{\text{ext}} = P_{\text{m}} + P_{\text{liq}} \) for \( P_{\text{m}} \) gives:
\[ P_{in} = P_{ext} - P_{liq} = 1.00 \times 10^5 \text{ Pa} - 1958 \text{ Pa} = 98042 \text{ Pa} = 0.980 \text{ bar} \]

If you would like to see the pressure in torr:
\[ P_{in} = 0.980 \text{ bar} \left( \frac{1 \text{ atm}}{1.01325 \text{ bar}} \right) \left( \frac{760 \text{ torr}}{1 \text{ atm}} \right) = 735. \text{ torr} \]

So, by decreasing the pressure in your mouth, the atmosphere pushes the water up the straw.

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.

\[ J = J_0 e^{-2.303 \varepsilon c} \]
\[ J/J_0 = e^{-2.303(12,144. \text{ M}^{-1} \text{ cm}^{-1})(100.0 \text{ cm})(2.33 \times 10^{-6} \text{ M})} = 1.48 \times 10^{-3} \text{ or } 0.148\% \]

you can also use J = J_0 10^{-\varepsilon c} \text{ or } \Lambda = \varepsilon c = \log(J_0/J) = 2.83

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]

\[ J = 4.16 \text{ kWh m}^{-2} \text{ day}^{-1}(3.6x10^6 \text{ J/kWh})(1 \text{ day}/24 \text{ hr})(1 \text{ hr}/3600 \text{ s}) = 173.3 \text{ J m}^{-2} \text{ s}^{-1} \]

Remember that 1 J s\(^{-1}\) = 1 W so J = 173. W m\(^2\). The AC power from a 12% efficient solar photovoltaic cell is:

\[ \text{AC power} = (173.3 \text{ W m}^{-2})(0.12)(0.77) = 16.0 \text{ J m}^{-2} \text{ s}^{-1} = 16.0 \text{ W m}^{-2}. \]

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.

\[ \ln \left( \frac{1.38 \times 10^{-2}}{2.80 \times 10^{-3}} \right) = -\frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{323.15 \text{ K}} - \frac{1}{303.15 \text{ K}} \right) \\
1.5950 = -\frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (-2.0416 \times 10^{-4} \text{ K}^{-1}) \text{ or } E_a = 64.96 \text{ kJ mol}^{-1} \]

\[ k = A e^{-Ea/RT} = A e^{-64.96 \times 10^{-3} J \text{ mol}^{-1} / 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} / 303.15 \text{ K}} = 2.80 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1} \]
\[ A = 4.37 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \text{ or use } \ln k = \ln A - \frac{E_a}{RT} \]
7. The following mechanism has been proposed for an enzyme reaction with two substrates, A and B:

\[ E + A \overset{k_1}{\rightleftharpoons} EA \]
\[ \frac{d[EA]}{dt} = k_1[E][A] - k_{-1} [EA] - k_2[EA][B] = 0 \quad \text{@st.state 1} \]

\[ EA + B \rightarrow EAB + Y \]
\[ \frac{d[EAB]}{dt} = k_2[EA][B] - k_3[EAB] = 0 \quad \text{@st.state 2} \]

\[ EAB \rightarrow E + P \]
\[ \frac{dP}{dt} = k_3[EAB] \quad \text{formation of products} \]

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:

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

**Answer:** Solving Eq. 1 for \([EA]\) gives: \([EA] = \frac{k_1[E][A]}{k_1 + k_3[B]}\)

Solving Eq. 2 for \([EAB]\) gives: \([EAB] = \frac{k_2}{k_3} [EA][B]\)

Substituting Eq. 4 into Eq. 5 gives: \([EAB] = \frac{k_1 k_2 [E][A][B]}{k_3 (k_1 + k_2[B])}\)

Substituting the concentration of the reactive intermediate from Eq. 6 into the rate law for the formation of product, Eq. 3, gives the final rate law:

\[ \frac{dP}{dt} = \frac{k_3}{k_1 + k_2 [B]} \]

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

**Answer:** Separating variables gives: \(- \int \frac{1}{[A]^3} d[A] = \int k_3 \ dt. \) Note that \(- \int \frac{1}{x^3} dx = \frac{1}{2x^2} \)

Combining the integration constants: \( \frac{1}{2[A]^2} = k_3 t + c \)

The boundary condition is at \( t = 0, [A] = [A]_o \), the initial concentration: \( c = \frac{1}{2[A]_o^2} \)

Substituting the integration constant back in to the integrated rate law gives the linear form:

\[ \frac{1}{2[A]^2} = k_3 t + \frac{1}{2[A]_o^2} \quad \text{or} \quad \frac{1}{2[A]^2} - \frac{1}{2[A]_o^2} = k_3 t \]
9. The *cis-trans* isomerization of 1-ethyl-2-methylcyclopropane is first order in the forward and reverse directions:

$$k_1 \text{ cis} \rightarrow \text{ trans} \quad k^{-1}$$

<table>
<thead>
<tr>
<th>t (s)</th>
<th>0.01679</th>
<th>0.01102</th>
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<tbody>
<tr>
<td>[cis] (M)</td>
<td>0.01679</td>
<td>0.01102</td>
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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 \((k_1 + k^{-1})\).

**Answer:**

\[
\ln \left( \frac{[A] - [A]_\infty}{[A]_0 - [A]_\infty} \right) = (k_1 + k^{-1}) t
\]

\[
\ln \left( \frac{0.01102 - 0.00443}{0.01679 - 0.00443} \right) = (k_1 + k^{-1}) \times 1000 \text{ s} \quad (k_1 + k^{-1}) = 6.29 \times 10^{-4} \text{ s}^{-1}
\]

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:

\(A = \varepsilon_A [A] + \varepsilon_B [B]\), where \(\varepsilon_A\) and \(\varepsilon_B\) are the molar extinction coefficients of A and B, respectively. Show that:

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

**Answer:**

\[
[\varepsilon_A [A]_0 + \varepsilon_B [B]_0 - \xi] - [\varepsilon_B [B]_0 - \varepsilon_B [B]_0 - [A]_0 - [A]_0 - \xi]
\]

\[
[\varepsilon_A [A]_0 + \varepsilon_B [B]_0] - [\varepsilon_B [B]_0 - [A]_0 - [A]_0 - \xi]
\]

\[
\frac{\varepsilon_A [A]_0 - \xi + \varepsilon_B [B]_0 - \xi - \varepsilon_B [B]_0 - [A]_0}{\varepsilon_A [A]_0 + \varepsilon_B [B]_0 - [A]_0 - [A]_0 - \xi}
\]

\[
\frac{\varepsilon_A [A]_0 - \xi + \varepsilon_B [B]_0 - \xi - \varepsilon_B [B]_0 - [A]_0}{[A]_0 - [A]_0 - \xi}
\]

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:**

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

**Answer:**

\[
|M| = 4(0.5) - 1(1) = 1
\]

\[
M^{-1} \begin{pmatrix} 2 \\ 1 \end{pmatrix} = \begin{pmatrix} 0.5 & -1 \\ 1 & 4 \end{pmatrix} \begin{pmatrix} 2 \\ 1 \end{pmatrix} = \begin{pmatrix} (0.5)(2) + (-1)(1) \\ (1)(2) + (4)(1) \end{pmatrix} = \begin{pmatrix} 0 \\ 6 \end{pmatrix}
\]

\[
M^{-1} \begin{pmatrix} 2 \\ 1 \end{pmatrix} = \begin{pmatrix} 0.5 & -1 \\ 1 & 4 \end{pmatrix} \begin{pmatrix} 2 \\ 1 \end{pmatrix} = \begin{pmatrix} (0.5)(2) + (-1)(1) \\ (1)(2) + (4)(1) \end{pmatrix} = \begin{pmatrix} 0 \\ 6 \end{pmatrix}
\]