

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?

Answer: $k_1 \ll k_2$

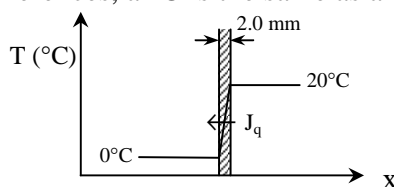
2. Thermal conductivity can be expressed as a linear flux-force relationship:

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

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.

Answer: Note that for temperature differences, a $^\circ\text{C}$ is the same as a degree K:

$$\frac{dT}{dx} = \frac{(T' - T)}{\delta}$$

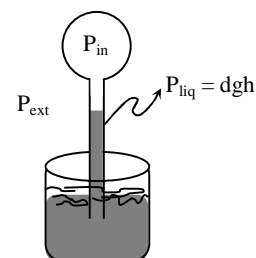


$$J_q = -\kappa \frac{dT}{dx} = -0.0252 \text{ J m}^{-1} \text{ K}^{-1} \text{ s}^{-1} (20.0 - 0.0^\circ\text{C}) / 2.00 \text{ mm} (1000 \text{ mm} / 1 \text{ m})$$

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

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°C , 0.9982 g mL^{-1} and the atmospheric pressure is 1.000 bar.

Answer: $P_{\text{ext}} = P_{\text{in}} + P_{\text{liq}}$ and $P_{\text{liq}} = dgh$.



The density of water at 20.0°C is needed in kg m^{-3} to match the units of g :

$$d = 0.9982 \text{ g mL}^{-1} (1 \text{ kg} / 1000 \text{ g}) (1 \times 10^3 \text{ mL} / 1 \text{ L}) (1000 \text{ L} / 1 \text{ m}^3) = 998.2 \text{ kg m}^{-3}$$

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 $P_{\text{ext}} = P_{\text{in}} + P_{\text{liq}}$ for P_{in} gives:

$$P_{\text{in}} = P_{\text{ext}} - P_{\text{liq}} = 1.00 \times 10^5 \text{ Pa} - 1958 \text{ Pa} = 98042 \text{ Pa} = 0.980 \text{ bar}$$

If you would like to see the pressure in torr:

$$P_{\text{in}} = 0.980 \text{ bar} (1 \text{ atm}/1.01325 \text{ bar})(760 \text{ torr}/1 \text{ atm}) = 735. \text{ torr}$$

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 $12,144. \text{ M}^{-1} \text{ cm}^{-1}$ 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.

Answer: $J = J_0 e^{-2.303 \epsilon l c}$

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

you can also use $J = J_0 10^{-\epsilon l c}$ or $A = \epsilon l c = \log(J_0/J) = 2.83$

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 $4.16 \text{ kWh m}^{-2} \text{ day}^{-1}$. 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: $1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$]

Answer: First convert the insolation into the equivalent averaged flux:

$$J = 4.16 \text{ kWh m}^{-2} \text{ day}^{-1} (3.6 \times 10^6 \text{ J}/1 \text{ kWh})(1 \text{ day}/24 \text{ hr})(1 \text{ hr}/3600 \text{ s}) = 173.3 \text{ J m}^{-2} \text{ s}^{-1}$$

Remember that $1 \text{ J s}^{-1} = 1 \text{ W}$ so $J = 173. \text{ W m}^{-2}$. 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 $2.80 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ 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.

Answer: The temperatures are 303.15 K and 323.15 K:

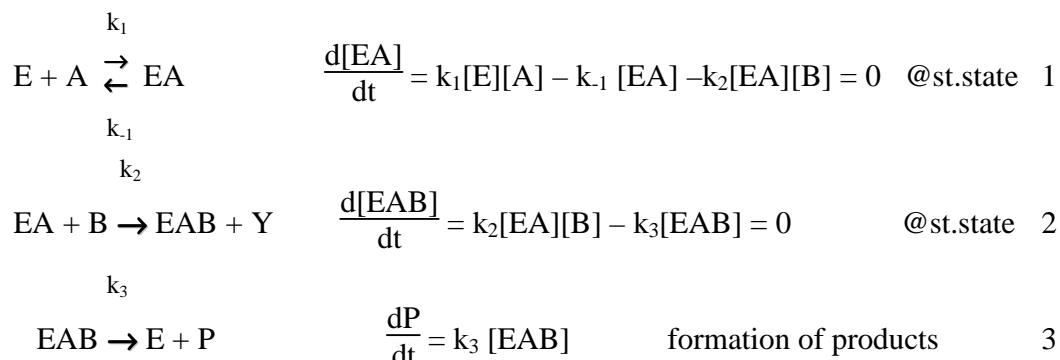
$$\ln\left(\frac{1.38 \times 10^{-2}}{2.80 \times 10^{-3}}\right) = -\frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{323.15 \text{ K}} - \frac{1}{303.15 \text{ K}}\right)$$

$$1.5950 = -\frac{E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (-2.0416 \times 10^{-4} \text{ K}^{-1}) \quad \text{or } E_a = 64.96 \text{ kJ mol}^{-1}$$

$$k = A e^{-E_a/RT} = A e^{-64.96 \times 10^3 \text{ J mol}^{-1}/8.3145 \text{ J K}^{-1} \text{ mol}^{-1}/303.15 \text{ K}} = 2.80 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$A = 4.37 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \quad \text{or use } \ln k = \ln A - E_a/RT$$

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:

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

Answer: Solving Eq. 1 for [EA] gives: $[EA] = \frac{k_1[E][A]}{k_{-1} + k_2[B]}$ 4

Solving Eq. 2. for [EAB] gives: $[EAB] = \frac{k_2}{k_3} [EA][B]$ 5

Substituting Eq. 4 into EQ. 5 gives: $[EAB] = \frac{k_1 k_2 [E][A][B]}{k_3 (k_{-1} + k_2[B])}$ 6

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:

$$\frac{dP}{dt} = \frac{k_1 k_2 [E][A][B]}{(k_{-1} + k_2[B])}$$

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 $1/[A] - 1/[A]_0 = k_2 t$)

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

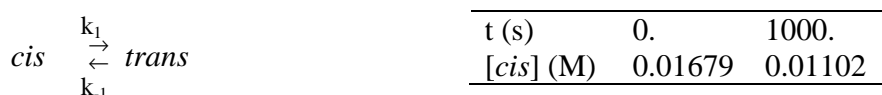
Combining the integration constants: $\frac{1}{2[A]^2} = k_3 t + c$

The boundary condition is at $t = 0$, $[A] = [A]_0$, the initial concentration: $c = \frac{1}{2[A]_0^2}$

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

$$\frac{1}{2[A]^2} = k_3 t + \frac{1}{2[A]_0^2} \quad \text{or} \quad \frac{1}{2[A]^2} - \frac{1}{2[A]_0^2} = k_3 t$$

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 $(k_1 + k_{-1})$.

$$\text{Answer: } \ln\left(\frac{[A] - [A]_{eq}}{[A]_o - [A]_{eq}}\right) = (k_1 + k_{-1}) t \quad [A]_o = 0.01679 \text{ M}$$

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

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, $[A]_o < [B]_o$. 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: $A = \epsilon_A l [A] + \epsilon_B l [B]$, where ϵ_A and ϵ_B are the molar extinction coefficients of A and B, respectively. Show that:

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

$$\begin{aligned}
 \text{Answer: } A &= \epsilon_A l [A] + \epsilon_B l [B] = \epsilon_A l ([A]_o - \xi) + \epsilon_B l ([B]_o - \xi) \\
 A_o &= \epsilon_A l [A]_o + \epsilon_B l [B]_o \quad t \rightarrow \infty \quad \xi \rightarrow [A]_o \quad [A] \rightarrow 0 \\
 A_\infty &= \epsilon_A l (0) + \epsilon_B l ([B]_o - [A]_o)
 \end{aligned}$$

$$\begin{aligned}
 \frac{A - A_\infty}{A_o - A_\infty} &= \frac{\epsilon_A l ([A]_o - \xi) + \epsilon_B l ([B]_o - \xi) - \epsilon_B l ([B]_o - [A]_o)}{\epsilon_A l [A]_o + \epsilon_B l [B]_o - \epsilon_B l ([B]_o - [A]_o)} \\
 &= \frac{\epsilon_A l [A]_o - \epsilon_A l \xi + \epsilon_B l [A]_o - \epsilon_B l \xi}{\epsilon_A l [A]_o + \epsilon_B l [A]_o} = \frac{(\epsilon_A l + \epsilon_B l) ([A]_o - \xi)}{(\epsilon_A l + \epsilon_B l) [A]_o} = \frac{[A]_o - \xi}{[A]_o}
 \end{aligned}$$

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.

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

$$\text{Answer: } |M| = 4(0.5) - 1(1) = 1 \quad M^{-1} \begin{pmatrix} 2 \\ 1 \end{pmatrix} = \begin{pmatrix} 0.5 & -1 \\ -1 & 4 \end{pmatrix} \begin{pmatrix} 2 \\ 1 \end{pmatrix} = \begin{pmatrix} (0.5)(2) + (-1)(1) \\ (-1)(2) + (4)(1) \end{pmatrix} = \begin{pmatrix} 0 \\ 2 \end{pmatrix}$$