TEAM

TEAM EXAM

WUCT 2019

Instructions & Rules

Clearly write your WUCT-assigned Team Name in "FIRST NAME" and TEAM ID number above. If team name exceeds the "FIRST NAME" box, continue in "LAST NAME". Your exam will not be graded if these cannot be read. Write darkly on your exam, and box your answers. 60 minutes are allotted for the team round. Team members are permitted and encouraged to work together on these questions. The team round will require answers that involve written explanations of students' thought processes in addition to numerical answers. Only responses written in the provided spaces on the front of exam pages will be graded. Students are not permitted to communicate with their coach in any way during this time, but they are encouraged to collaborate among themselves to work through the problems. Only the QR-coded packet will submitted for grading, so make sure that all work intended to be submitted is written there. Please be certain that you are submitting every page on the team exam, otherwise the team will lose all points for the page(s) that were not submitted. Cheating will NOT be tolerated.

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Question 1 (22 points)

The human body has developed several interesting ways to cope with changes in the amount of oxygen it receives. Here, we will investigate how the body adapts at high elevations as barometric pressure decreases, and how it adapts during intense exercise to combat acute acidosis.

a. **(5 points)** Use Henry's law ($C_{gas} = k_H \cdot P_{gas}$) to calculate the change in volume of dissolved Oxygen at 10,000 ft altitude relative to sea level (0 ft). Use the k_H constant of 0.03 $\frac{mL\ O_2}{mmHg \cdot L}$, assume a total blood volume of 5.00 L, and that P_{oxygen} is always 20.0% of $P_{Barometric}$. Report answers to 3 significant digits.
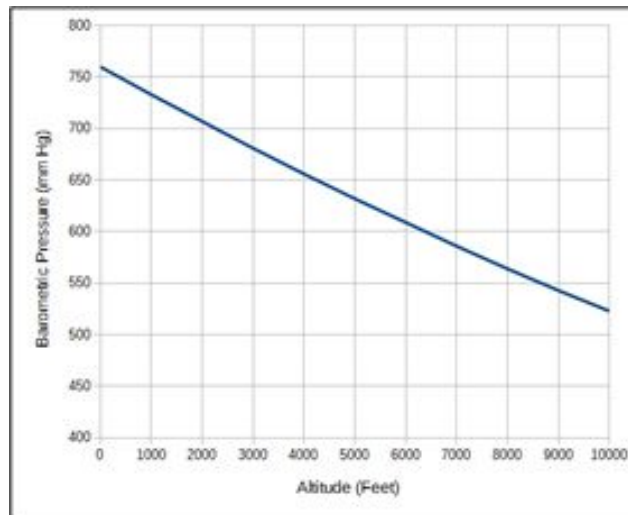
+1 pt, Identify the barometric pressure as changing from 760 mmHg to 525 mmHg

+1 pt, Calculating partial pressure of oxygen assuming that 20.0% of the air is oxygen, partial pressure at each altitude is 152 mmHg and 105 mmHg.

+1 pt, Amount of Oxygen at sea level:

$C_{gas} = P_{gas} * (k_H) = (152\ mmHg) * 0.03\ \frac{mL\ O_2}{mmHg \cdot L} = 4.56\ mL\ O_2$ per L of blood

22.8 mL in 5.00 L of blood

+1 pt, Amount of Oxygen at 10000 feet:

$C_{gas} = P_{gas} * (k_H) = (105\ mmHg) * 0.03\ \frac{mL\ O_2}{mmHg \cdot L} = 3.15\ mL\ O_2$ per L of blood

15.75 mL in 5.00 L of blood

+1 pt, The change in volume of oxygen is **7.05 mL**

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b. **(2 points)** Although the partial pressure of O_2 is lower at higher altitudes, people living at high altitudes do not have lower blood oxygen levels. This is due to the binding capabilities of hemoglobin in their red blood cells. Derive an expression for the concentration of oxyhemoglobin in the blood based on the total fraction of oxyhemoglobin (S_{O_2}) and the total concentration of hemoglobin in the blood ([Hb]). Support your expression with dimensional analysis

+1 pt, $S_{O_2} \cdot [Hb]$

+1 pt, $\frac{moles\ oxyhemoglobin}{total\ moles\ hemoglobin} \cdot \frac{total\ moles\ hemoglobin}{blood\ volume} = \frac{moles\ oxyhemoglobin}{blood\ volume}$

c. **(3 points)** Expand on your expression to come up with an equation that will give you the volume of oxygen in a given volume of blood. Support your equation with dimensional analysis.

+2 pt, Multiply by the volume of oxygen per total moles oxyhemoglobin

$C_{O_2} = S_{O_2} \cdot [Hb] \cdot \frac{volume\ oxygen}{total\ moles\ oxyhemoglobin}$

+1 pt, $\frac{moles\ oxyhemoglobin}{total\ moles\ hemoglobin} \cdot \frac{total\ moles\ hemoglobin}{blood\ volume} \cdot \frac{volume\ oxygen}{total\ moles\ oxyhemoglobin} = \frac{volume\ oxygen}{volume\ blood}$

d. **(5 points)** In addition to a decrease in atmospheric pressure, there is a decrease in temperature associated with higher altitudes. Amonton's law, $P_1/T_1 = P_2/T_2$, reveals a directly proportional relationship between pressure and temperature. Why does increasing temperature increase gas pressure? Explain why this law is not strictly upheld in the case of lungs?

+1 pt, Increasing temperature will increase the average kinetic energy of they system
+1 pt, this will cause more frequent and forceful collisions with the walls of the system
+1 pt, this increases the pressure

+2, lung volume changes as we breathe, and this means that P/T is not constant. Rearranging the ideal gas law, P/T = nR/V, we see that P/T depends on V.

e. **(5 points)** The bicarbonate buffer system is a crucial acid-base system for maintaining blood pH. Once dissolved in blood, CO_2 exists in the form of either carbonic acid, H_2CO_3, or bicarbonate, HCO_3^-. Where $[CO_2] = [HCO_3^-] + [H_2CO_3]$. Calculate the pH of

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blood when the total concentration of dissolved CO_2 is 37.6 mM and that of bicarbonate is 35.3 mM.
(Hint: The pKa of carbonic acid is 6.1)

+2 pt, calculation of $[H_2CO_3]$
37.6 mM = 35.3 mM + $[H_2CO_3]$
2.3 mM = $[H_2CO_3]$

+2, correct use of Henderson-Hasselbalch equation
pH = pKa$_{carbonic\ acid}$ + log ([HCO3-])/$[H_2CO_3]$)
pH = 6.1 + log(35.3 mM /2.3 mM)
pH = 6.1 + 1.2

+1, final answer
pH = 7.3

f. **(2 points)** The pH of blood normally ranges from 7.35 to 7.45. If you measure the blood pH of a patient to be 7.30, explain what gas must have accumulated to cause this.

+2 pt, Increased CO_2 in the blood (caused by respiration) would decrease the blood pH due bicarbonate buffer system.

Question 2 (20 points)

A class of chemicals called endorphins are responsible for the so-called "runner's high" that many people experience after finishing a hard workout. These compounds are polymers of amino acids that are able to interact with receptors in our brains to relieve pain. These receptors are also targeted by drugs like morphine, which is commonly used as a pain medication in hospital settings.

a. **(4 points)** Shown below is the structure of a beta-Endorphin, an endorphin that is expressed in high levels in athletes. The structure of a generic amino acid is provided for your reference. Identify the number of amino acids that make up this beta-Endorphin, and circle the bonds that connect each amino acid to the adjacent amino acids.

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Beta-Endorphin   General Amino Acid
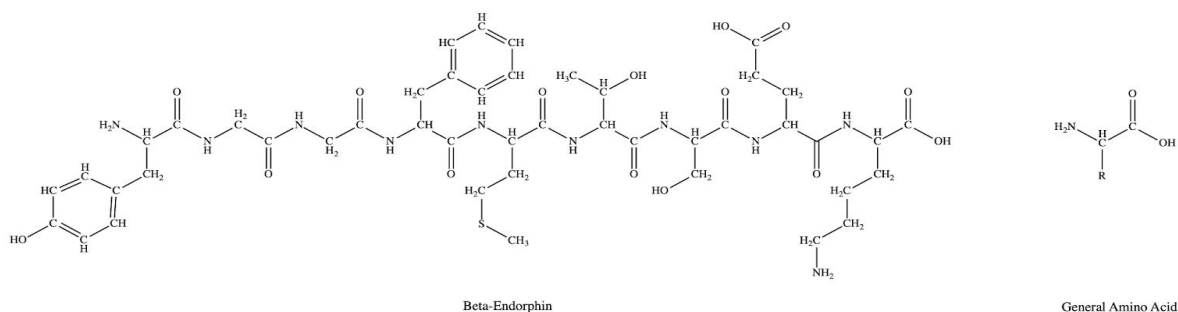
+2 pt, There are 9 amino acids present.
+2 pt, Bonds between each carbonyl carbon and amide nitrogen should be circled.

b. **(2 points)** Shown below is the chemical structure of morphine. Interestingly, morphine and endorphins are known to bind the same receptors because they share a similar structural element, or "motif". Clearly identify this motif by circling it in each structure, and briefly explain why it make sense that both molecules bind the same target.
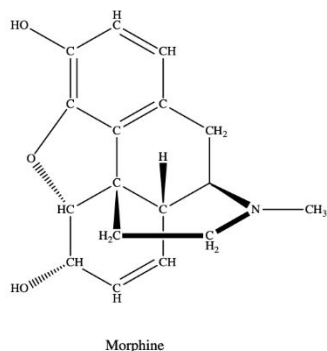

Morphine

+1 pt, Both structures have a phenolic moiety (six carbon conjugated ring + hydoxyl)
+1 pt, Similarly shaped molecules will often bind the same receptors

c. Now, we will turn our focus to the polymeric structure of beta-Endorphin itself. The bonds connecting individual amino acids are called peptide bonds. Above, we drew them as all single bonds, however, experimental evidence tells us that they are stronger than typical single bonds.

   i. **(3 points)** Draw a resonance structure for the generalized dipeptide shown below that justifies stabilization.
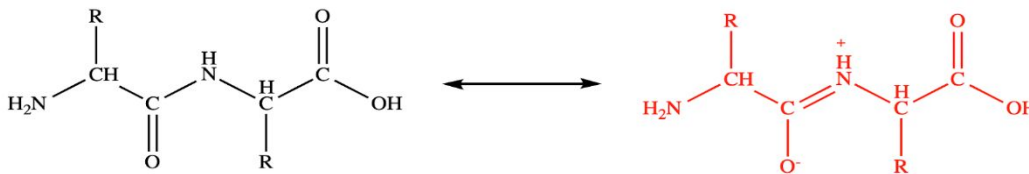
+3 pt, correct structure, shows charges and bonds

    ii. **(3 points)** Based on the resonance structure you drew, provide an explanation for why peptide bonds are stronger than C-N single bonds.

      +1 pt, The peptide bond can resonate to a double bond.
      +1 pt, Double bonds are stronger than single bonds.
      +1 pt, The actual bond character is a mixture of both these forms, so it will be stronger than a single bond.

d. Binding of ligands like morphine and beta-Endorphin to receptors can be modeled using some fairly simple equilibrium expression manipulations.

    i. **(3 points)** Using an equilibrium expression for the binding of a ligand "L" to a receptor "R" to form a ligand-receptor complex "LR", derive an expression for the dissociation constant, K_D.

      +1pt, $L + R \leftrightarrow LR$
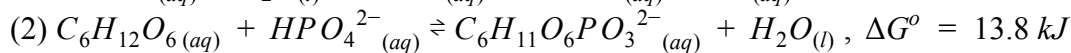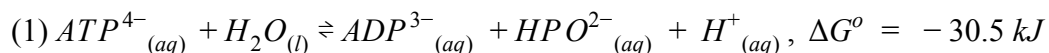   +2 pt, $K_D = \dfrac{[L][R]}{[LR]}$

    ii. **(5 points)** Often interesting to know the fraction "F" of receptors that have a ligand bound to them. Derive this expression. Your final expression for F should only be in terms of [L] and K_D (fully simplify your answer).

      +5 pt, accepting last or second to last expression
$$F = \frac{[LR]}{[R][LR]} = \frac{1}{(\frac{[R]}{[LR]})+1} = \frac{1}{(\frac{K_D}{[L]})+1} = \frac{[L]}{K_D+[L]}$$

Question 3 (23 points)

Glycolysis is one of the key energy-generating processes in cells, and it is comprised of several successive reactions. The first two of these reactions are given below:

$$(1)\; ATP^{4-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons ADP^{3-}{}_{(aq)} + HPO^{2-}{}_{(aq)} + H^+{}_{(aq)},\; \Delta G^o = -30.5\; kJ$$
$$(2)\; C_6H_{12}O_{6\,(aq)} + HPO_4{}^{2-}{}_{(aq)} \rightleftharpoons C_6H_{11}O_6PO_3{}^{2-}{}_{(aq)} + H_2O_{(l)},\; \Delta G^o = 13.8\; kJ$$

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This question will investigate the thermodynamics of these two reactions, and the structural thermodynamics of the enzyme that catalyzes it.

a. **(5 points)** Explain why the second reaction is able to proceed even though it is not spontaneous. Include a net reaction equation and interpretation of the Gibbs free energy in your explanation.

+2 pt, The second reaction can proceed because it is coupled to the first reaction which is highly favorable.

+1 pt, The total reaction is: $C_6H_{12}O_6 + ATP \rightarrow ADP + C_6H_{11}O_6PO_3 + H^+$.

+2 pt, The free energy of the process is -16.7 kJ. Since this value is negative, we know that the overall reaction is spontaneous.

    i. **(4 points)** Calculate ΔG at 273.15 K for a mixture of 2.0 M glucose, 1.0 M ATP (aq), 1.5 M glucose-6-phosphate (aq), 1.0 M ADP and 1.2 M H^+ (aq). Will the reaction proceed spontaneously?

        +1 pt, correct equation
        +1 pt, correct plug in
        +1 pt, correct answer
        +1, statement of spontaneity
        $\Delta G = \Delta G^o + RT \ln(Q)$
        $\Delta G = -16.7\ kJ + (8.314 \frac{J}{mol*K})\ (273.15\ K)\ \ln(1.0*2.0)/(1.5*1.0*1.2))$
        $\Delta G = -16.5\ kJ$
        The reaction will proceed spontaneously.

    ii. **(3 points)** Assuming $\Delta S > 0$ in reaction (2), is this reaction endothermic or exothermic? Explain in 1-2 sentences.

        +1 pt, indicating reaction is endothermic
        +2 pt, reasoning
        ΔG is positive and ΔS is positive, the sign of enthalpy can be determined by $\Delta H = \Delta G + T\Delta S$. ΔH must be positive indicating an endothermic reaction.

b. For the remainder of this question, we will investigate the kinetics and thermodynamics involved in protein folding.

    i. **(4 points)** Small proteins often exist in two states, folded and unfolded. Calculate the equilibrium constant, K, for this equilibrium. The average stability of a small protein, is $7\ \frac{kcal}{mol}$ ($R = 2\ \frac{cal}{K \cdot mol}$, $T = 298\ K$). Interpret this result.

        +3 pt, calculation
        +1 pt, interpretation

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$\Delta G = -RT\ln(K) = -7000\ cal = -(2\ \frac{cal}{K \cdot mol})(298\ K)\ln(K)$

$K = 1.26 \times 10^5$

A large value of K indicates that the products (folded protein) are favored over reactant (unfolded protein). It is essential to notice that the $7\ \frac{kcal}{mol}$ is a *stability* and therefore is a negative quantity.

ii. **(5 points)** We can further dissect this by examining the forward (folding) and reverse (unfolding) reaction rates. If the rate of protein folding is in the neighborhood of 1.0 s^{-1}, what is the rate of protein unfolding? Additionally, determine the half-life of both the folding and unfolding of this protein.

+3 pt, calculation of k(unfolding)

$K = \frac{k(folding)}{k(unfolding)}$

$1.26 \times 10^5 = \frac{1.0\ s^{-1}}{k(unfolding)}$

$k(unfolding) = 7.93 \times 10^{-6}\ s^{-1}$

+2 pt, half-life calculations

$t_{1/2} = \frac{ln(2)}{k}$

Folding: $\frac{ln(2)}{1\ s^{-1}} = 0.693\ s$

Unfolding: $\frac{ln(2)}{7.93 \times 10^{-6}\ s^{-1}} = 8.74 \times 10^4\ s$

iii. **(2 points)** From part ii, you should see that there is a non-zero rate of protein folding and protein unfolding. Knowing that most proteins in your body are folded, explain how we can reconcile these calculations in a biologic context.

+2 pt, general understanding
While we see non-zero rates of protein unfolding, the rate of folding is much larger than the rate of unfolding. Additionally, based on the half-life calculations, we see that proteins fold much faster than they unfold. Overall, this indicates that most proteins in our body are folded.

Question 4 (43 points)

When dealing with a binary chemical system in liquid-vapor equilibrium, Raoult's law is often used. A key assumption of this law is that both the vapor and the liquid are acting as ideal mixtures. In reality however the liquid solutions often do not act ideal while the gas system does. To account for the deviation from ideality, chemists and chemical engineering use activity models and a modified Raoult's law. An activity coefficient (ɣ) is a unitless correction term for each chemical of the mixture that varies with mixture composition and can be determined by activity models such as a 2 parameter Margules model. The 2 parameter Margules model, as its

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name suggests, has two parameters (A_{12} and A_{21}) which are constants valid and unchanging for **all** compositions of the liquid solution. Use this information to solve the problem below:

<u>Modified Raoult's Law Equations:</u>

<u>2 Parameter Margules Equations:</u>

$$y_i \cdot P_{TOT} = x_i \cdot \gamma_i \cdot P_{SAT, i}$$

$$\ln(\gamma_1) = (x_2)^2 \cdot [A_{12} + 2x_1(A_{21} - A_{12})]$$

$$P_{TOT} = \sum x_i \cdot \gamma_i \cdot P_{SAT, i} \text{ for all i species in a mixture}$$

$$\ln(\gamma_2) = (x_1)^2 \cdot [A_{21} + 2x_2(A_{12} - A_{21})]$$

   a. **(11 points)** You are working at a chemical plant and are trying to separate bromoform (1) and 1,4 dioxane (2). An isothermal flash tank is used to achieve this separation which operates at 50°C and 24.95 kPa. The vapor pressures at these temperatures are $P_{SAT, 1}$ = 69.40 kPa and $P_{SAT, 2}$ = 15.80 kPa. The vapor exit stream has a composition of y_1 = 0.6200, and the liquid exit stream has a composition of x_2 = 0.6400. You can assume that the system is at steady state and that it is well mixed such that the pressure and composition of the liquid and vapor in the tank are equal to the exit stream compositions. If your boss says to make the liquid benzene composition (x_1) to be 0.4000, what do you change the pressure of the tank to? Give your final answer in units of **kPa** and **circle your final answer**.

+2 pt:
P_{TOT} new $= \sum x_i \cdot \gamma_i \cdot P_{SAT} = x_1 \cdot \gamma_1 \cdot P_{SAT,1} + x_2 \cdot \gamma_2 \cdot P_{SAT,2}$
P_{TOT} new $= (0.4)(\gamma_1)(69.40\text{kPa}) + (0.6)(\gamma_2)(15.8\text{kPa}) \therefore$ need to find new gamma 1 and gamma 2 value.

+2 pt:
To do this we need to use the 2 Parameter Margules Equations, but to use them we need A_{12} and A_{21}.

Use the given conditions to find the Margules Parameters.
Initial $\gamma_1 = y_1 \cdot P_{TOT} / x_1 \cdot P_{SAT, 1} = (0.6200)(24.9\text{kPa})/(0.3600)(69.4\text{kPa}) = 0.6179$
Initial $\gamma_2 = y_2 \cdot P_{TOT} / x_2 \cdot P_{SAT, 2} = (0.3800)(24.9\text{kPa})/(0.6400)(15.8\text{kPa}) = 0.9357$

+3 pt:
Margules EQ's:
EQ#1: -0.482 = $(0.64)^2[A_{12} + 2(0.36)(A_{21} - A_{12})] \therefore$ -1.175 = $[0.72A_{21} + 0.28A_{12}]$
EQ#2: -0.0665 = $(0.36)^2[A_{21} + 2(0.64)(A_{12} - A_{21})] \therefore$ -0.513 = $[-0.28A_{21} + 1.28A_{12}]$

Solve system of EQ:
A_{12} = -0.699, A_{21} = -1.363

+2 pt:

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Use Margules Equation to find new $\ln(\gamma)$ values:

$\ln(\gamma_1) = (0.6)^2 \cdot [(-0.699) + 2(0.4)(-1.363 - (-0.699)] \therefore \ln(\gamma_1) = -0.4428 \therefore \gamma_1 = 0.6422$

$\ln(\gamma_2) = (0.4)^2 \cdot [-1.363 + 2(0.6)(-0.699 - (-1.363)] \therefore \ln(\gamma_2) = -0.0904 \therefore \gamma_1 = 0.9133$

+2 pt:

P_{TOT} new $= (0.4)(0.6422)(69.4\text{kPa}) + (0.6)(0.9133)(15.8\text{kPa}) = 26.49\text{kPa}$

b. **(6 points)** While the primary use of activity coefficients is to calculate deviations from ideality for non-ideal solutions, their values can also be used to quickly detect properties of the solution. In a binary mixture system both activity coefficients can either be greater than 1 or less than one. However, activity coefficients can never be negative. A different solution composed of 50% cis-2-butene and 50% trans-2-butene have activity coefficients less than 1. Determine if the boiling point of this non-ideal mixture is greater than, less than or equal to the boiling point of this solution if it was ideal. **Circle one of the options below and fully explain your answer.**

Greater than   **Equal to**   **Less than**

At a boiling point $P^{SAT} = P^{TOT}$. This can be extended to a binary ideal and non-ideal mixture with the equations $P_{TOT} = \sum x_i \cdot P_{SAT}$ and $P_{TOT} = \sum x_i \cdot \gamma_i \cdot P_{SAT}$. This means that if the activity coefficients (γ_i) are both less than 1, $P_{TOT, BP, IDEAL} > P_{TOT, BP, NON-IDEAL}$. Since the non-ideal solution has a lower total vapor pressure, this means its bp temperature is higher than that of the ideal solution.

Alternate solution: Student identifies from equations that when both γ values are less than one shows the cis-2-butene and trans-2-butene are more attracted (stronger IMF) to each other than themselves (pure solution). This means they are harder to separate/move to vapor phase. This would make the non-ideal solution boiling point to be greater than the ideal mixture.

1 point for selecting **Greater than**
5 points for a detailed explanation that clearly demonstrates to the greater students understand the process.
This point distribution prevents awarding guessing.
NOTE: If students answer with **Equal to** or **Less than,** the students will receive 0 points without exception.

c. **(12 points)** The isomerization of chemical compounds is a widely used process in industry to produce compounds on a large scale. An interesting process that this problem will focus on is the isomerization of a 50/50 mixture of cis-2-butene (A) and trans-2-butene (B) into isobutane (C) and 1-butene (D). This process occurs at 623K and 1 atm where all compounds are gaseous and are assumed to act ideally. What makes this process complex is that there are four equilibrium reactions occurring simultaneously as

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both compound (A) and (B) can be converted into (C) and (D). The reaction quotients (K) are given below at the desired temperature and pressure. Determine the final mole fractions of (A),(B),(C), and (D) based on their equilibrium expressions. Comment on how increasing the pressure will affect the final mole fractions of the products?

$$K_{(A)⇄(C)} = 4.27 \quad K_{(A)⇄(D)} = 0.666 \qquad K_{(B)⇄(D)} = 3.90 \quad K_{(B)⇄(D)} = 0.608$$

RXNS:

$(A)⇄(C): K_{(1)} = (P_C / P_A) = (yC/yA)*(Ptot/Ptot)$

$(A)⇄(D): K_{(2)} = (P_D / P_A) = (yD/yA)*(Ptot/Ptot)$

$(B)⇄(C): K_{(3)} = (P_C / P_B) = (yC/yB)*(Ptot/Ptot)$

$(B)⇄(D): K_{(4)} = (P_D / P_B) = (yD/yB)*(Ptot/Ptot)$

Pressures cancel in all of the expressions

Final System has : $yA + yB + yC + yD = 1$

This means that $yA + yB + K_{(3)}yB + K_{(4)}yB = 1$

$yC/K_{(1)} + yB(1 + K_{(3)} + K_{(4)}) = 1$

$yB (K_{(3)}/K_{(1)}) + yB(1 + K_{(3)} + K_{(4)}) = 1$

$yB = 1/(1 + K_{(4)} + K_{(3)} + (K_{(3)}/K_{(1)}))$

yB = 0.156

**yC = K_{(3)} ⬚ yB = 0.607**

yD = K_{(4)} ⬚ yB = 0.0947

yA = yD/K_{(2)} = 0.142

Observed in the equilibrium expressions, an increase in pressure will have **no effect** on the final mole fractions of the products.

+4 points for correctly writing all 4 equilibrium equations in terms of mole fractions
+2 points correctly identifying that pressure changes will not affect the system
+2 points for sum of all mole fractions = 1 equation
+4 points for correctly solving for the mole fractions.

d. **(3 points)** Assume the process above calculated its equilibrium constants at T = 623K through 3 steps. The first step was calculating the $\Delta G_{FORMATION}$ at standard temperature and pressure of all molecules using G_f of values from a textbook. The second step was using the equation $\Delta G = RTln(K)$ to calculate the equilibrium coefficient at the standard temperature and pressure. The third step involved using the Van't Hoff equation (shown below) to determine the equilibrium coefficients at the desired 623K. Unfortunately you notice that one of your equilibrium constants (A)⇄(C) is incorrect despite no arithmetic errors. Given the plot below of this reaction, determine which why <u>step 3</u> resulted in the incorrect calculation of its equilibrium constant? **Explain your answer.**

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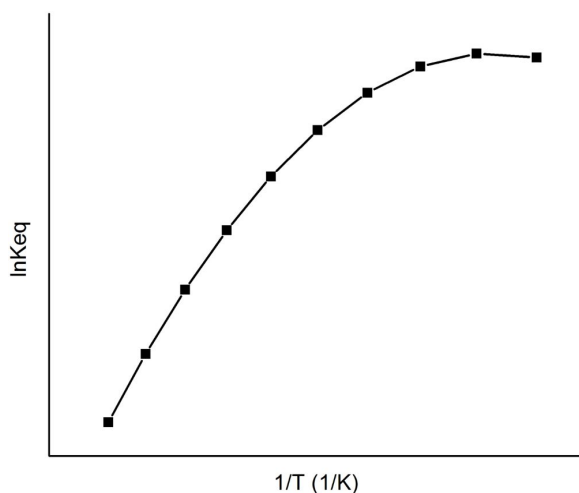
$$\ln\left(\frac{K_1}{K_2}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The graph's slope is negative enthalpy divided by ideal gas constant. Since the slope is not constant, this means that the enthalpy is a temperature dependent making the Van't Hoff equation not valid

3 points for identifying the slope of the line is $-\Delta H/R$ and that its non constant making Van't Hoff invalid.

e. **(4 points)** Using the graph above determine if the reaction of $(A)\rightleftarrows(C)$ is exothermic or endothermic at high temperatures. **Circle one of the options below and fully explain your answer.**

      Endothermic   **Exothermic**

4 points all or nothing for correct circled answer **with** a correct explanation
Looking at the graph high temperatures are when (1/T) is small. At these points the graph has a positive slope ($-\Delta H/R$) meaning that $\Delta H < 0$.

f. **(7 points)** The Van't Hoff equation given above assumes that the reaction is reversible or that $\Delta S = 0$. This however is rarely the case. Using the equation $\Delta G = RT\ln(K)$ derive the Van't Hoff equation that does not assume $\Delta S = 0$. **Circle your final answer.**

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$$\Delta G = RT\ln(K) \ and \ \Delta G = \Delta H - T\Delta S \ \therefore \ \Delta H - T\Delta S = RT\ln(K)$$

$$\frac{\Delta H}{RT} - \frac{\Delta S}{R} = \ln(K) \ \therefore \ change \ in \ \ln(K) \ as \ a \ funciton \ of \ \left(\frac{1}{T}\right)$$

$$\frac{\Delta H}{R}\left(\frac{1}{T2} - \frac{1}{T1}\right) - \frac{\Delta S}{R} = \ln(K2) - \ln(K1)$$

$$-\frac{\Delta H}{R}\left(\frac{1}{T2} - \frac{1}{T1}\right) + \frac{\Delta S}{R} = \frac{\ln(K1)}{\ln(K2)}$$

2 points for equating RTln(K) = ΔH - TΔS, **3 points** for correctly applying Δ to equations, **2 points** for correct final answer.

Question 5 (16 points)

The second law of thermodynamics states that the entropy of an isolated system never decreases. As you saw in question 4, while we often try to use "ideal" systems, "real" systems are often much more complex. This question will investigate some properties of entropy, and how they apply to chemical systems.

a. **(4 points)** The entropy of a system is closely related to the number of microscopic states, Ω, that are consistent with the macroscopic quantities such as volume, pressure and temperature. This relation is encapsulated by the Boltzmann equation, $S = k_B\ln(\Omega)$. Derive an equation for the ΔS of a process.

+4 pt, correct derivation

For a generalized process $\Delta S = k_B\ln(\Omega_{final}) - k_B\ln(\Omega_{initial}) = k_B\ln(\frac{\Omega_{final}}{\Omega_{initial}})$

   i. **(3 points)** For each of the three cases: $\Omega_{final} > \Omega_{initial}$, $\Omega_{final} = \Omega_{initial}$, $\Omega_{final} < \Omega_{initial}$ describe how ΔS differs.

   +3 pt:
   $\Omega_{final} > \Omega_{initial}$: $\Delta S > 0$
   $\Omega_{final} = \Omega_{initial}$: $\Delta S = 0$
   $\Omega_{final} < \Omega_{initial}$: $\Delta S < 0$

   ii. **(2 points)** For a system consisting of 1 mole of CO_2 in a box, suggest two ways that you could decrease the entropy of the system.

   +1 pt, each case
   Option 1: decrease the volume of the box
   Option 2: decrease the temperature of the box

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b. **(5 points)** Table salt, NaCl, readily dissolves in water. Use a drawing to show how water arranges around each of the resultant ions. Is the entropy of the water molecules surrounding the ions greater or less than that of the bulk solvent? Why?

+1 pt for each drawing (2 pt total)
+3 pt for explanation
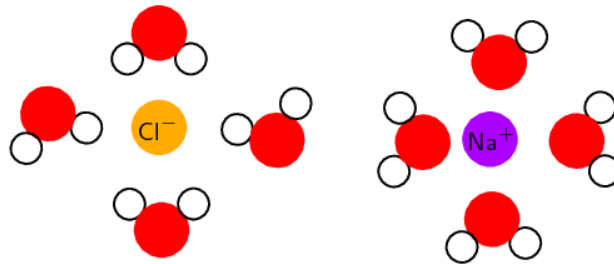
The oxygen atoms will face towards the sodium ions, and the hydrogen atoms will face towards the chloride ions. The entropy of the water surrounding these ions is less than that of the bulk solvent. This is because around the ions, the structure of the solvation shell is much more ordered than the bulk solvent.

c. **(2 points)** Below is a graph showing a function for the free energy of mixing two ideal gases. We know that ideal gasses will mix in all proportions. On this graph, plot a line describing the entropy of mixing.

+2 pt, plot showing general negative parabola form with entropy maximized at the minimum of the free energy function.
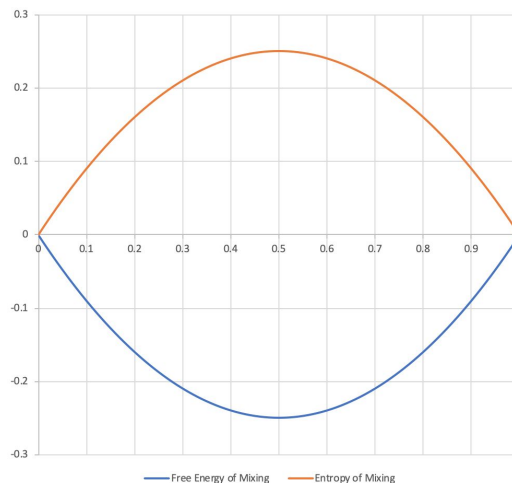
Question 6 (## points)

Silicone rubber is an incredibly versatile cross-linked polymer. It has applications ranging from automotive components to food storage. No matter the context, it is essential to have a pure product so that there are no heavy metals or otherwise dangerous impurities. In the 1990s,

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scientists discovered that an interesting compound, xenon tetrafluoride will decompose the silicone rubber matrix to gaseous products, leaving behind any impurities.

a. **(6 points)** At very high temperatures xenon tetrafluoride is able to react with xenon gas to form xenon difluoride. Draw the lewis dot structure of xenon tetrafluoride and xenon difluoride and state the geometry predicted by VSEPR theory.

+2 pt each structure (4 pt total)
+1 pt each geometry (2 pt total)
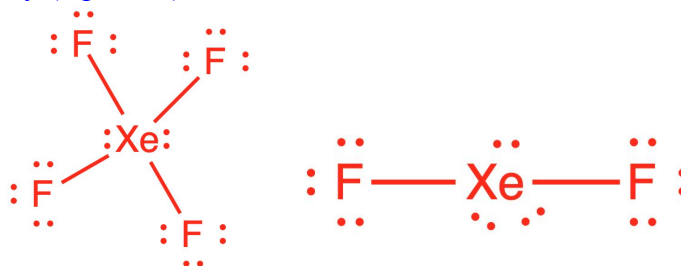
The xenon tetrafluoride takes on a square planar structure and the xenon difluoride takes on a linear structure.

b. **(8 points)** On the diagrams below, fill in the standard (left) and hybridized (right) electron configurations of xenon in xenon tetrafluoride. You may add energy levels as needed; however, you must clearly **label** them. Briefly, explain how your hybridized diagram confirms the Lewis structure you drew in part a.

+3 pt each, correctly filling and labeling diagrams
+2 pt explanation
Left diagram shows the standard configuration, and right shows the hybridized configuration. The student must fill in sp^3d^2 orbitals. Based on the Lewis structure in A, there are two lone pairs around the Xe atom, these correspond to the two pairs of electrons in the sp^3d^2 orbitals. The four lone electrons in the sp^3d^2 orbitals correspond to electrons that are forming the bonds between Xe and the pendant fluorine atoms.
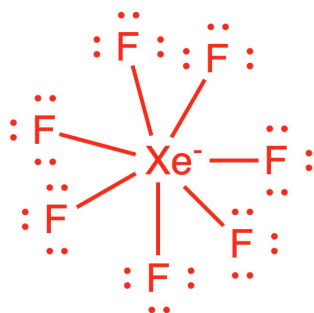
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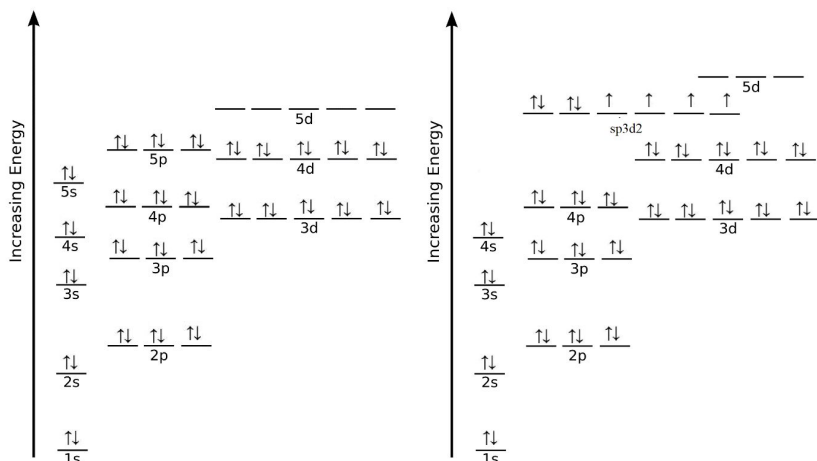
c. **(8 points)** Another interesting xenon compound is xenon hexafluoride which reacts with fluoride ions to form xenon heptafluoride. For xenon heptafluoride:
   i.   Draw the corresponding Lewis structure
   ii. Calculate the formal charge of the xenon and each fluorine
   iii. Determine where the most negative charge is located
   iv. Based on your knowledge of electronegativity, where do you think the negative charge of the molecule really is? Explain why this is the case.

+2 pt, structure
+1 pt, each formal charge calculation
+1 pt, determination of most negative atom
+3 pt, explanation and justification

The formal charge of Xe is -1 (8 valence electrons - (7 bonded +2 unbonded))

The formal charge of each F is 0 (7 valence electrons - (1 bonded - 6 unbonded))

Formal charges indicate that the Xe atom carries the negative charge.

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d. **(4 points)** What does it mean to have an expanded octet, and how it is possible? Include a discussion of orbital energy levels in your explanation.

+4 pt, explanation
An expanded octet is a state that can only be achieved by elements in period 3 or above. In the case of Si, P, S and Cl all of these elements can bond more than four atoms because they can accommodate additional electrons in the 3d orbital, even though the 3d orbital has a higher energy level than the 4p

e. **(2 points)** In the reaction of xenon hexafluoride in part c, does xenon hexafluoride act as an acid? If so, which definition of acid does it fall under and why?

+1 pt, identification
+1 pt, reasoning
It can be called a lewis acid because it can accept electrons.

f. During quality control testing of a silicone rubber sample, a 1.0 L solution of impurities is generated. Fortunately, the identities of some of the impurities are known: 4.6 g Aluminum, 2.3 g Copper, and 5.6 g Nickel.

   i. **(12 points)** In the lab, you have unlimited access to OH^- ions and following handy K_{sp} table. What is the minimum concentration of OH^- ions needed to precipitate all impurities? List all sources from which this concentration is determined. Which ion will precipitate first and last?

Metal	Ksp of Metal-Hydroxide Compound
Aluminum	4.60E-33
Copper (II)	2.60E-19
Iron (II)	8.00E-16
Magnesium	1.80E-11
Nickel (II)	2.00E-15
Zinc	2.10E-16

+1 Point for stating that the common ion effect is present
+1 Point for stating the concentrations of metal ions present
+3 Points for determining the max [OH⁻] prior to ppt for each metal hydroxide compound (1 point each)

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+4 Points for listing each of the contributors for the min [OH⁻] concentration needed
+1 Point for the correct minimum [OH-] concentration
+2 Points for ion species that ppt first and last (1 point each)
Here we leverage the Common Ion effect:
Let's first calculate the concentrations of the metal ions in solution:
0.17 M Al^{3+}, 0.036 M Cu^{2+}, and 0.095 M Ni^{2+}

These ions form the following compounds with OH⁻: $Al(OH)_3$, $Cu(OH)_2$, and $Ni(OH)_2$.

Thus, [OH⁻] to precipitate the ions are as follows:
Al: $Ksp=[Al^{3+}][OH^-]^3$, thus [OH⁻] = 3.00e-11 M
Cu: $Ksp=[Cu^{2+}][OH^-]^2$, thus [OH-] = 3.00e-9 M
Ni: $Ksp=[Ni^{2+}][OH^-]^2$, thus [OH-] = 1.45e-7 M
Thus, Al will precipitate first and Ni will precipitate last.

Since the goal is to add enough [OH-] to precipitate all compounds we will need 0.51 mol of OH⁻ to ppt all Al^{3+} and 0.072 mol of OH⁻ to ppt all Cu (since their OH⁻ levels for ppt are below that of Ni^{2+} and thus OH⁻ will be pulled out of soln by these two ions until all metal is used up). In addition to this amount of OH⁻, we need to add 0.19 mol of OH⁻ to ppt all Ni^{2+}. However, to drive all eq. to ppt and make sure no ppt is converted back into ionic species, we need to add an additional 1.45e-7 mol of OH- to ensure the ion conc is greater than/equal to the necessary conc. of OH- to facilitate precipitation. Thus, the answer is 0.775 M OH-

      ii.   **(5 points)** Given the above Ksp table, what ion(s), if any, would remain in solution after the three aforementioned impurities are precipitated? Assume each of the three ion species not listed in i. are present at 0.050 mol each.

+1 Point for correct answer
+3 Points (1 each) for Ksp calculations showing that Q>Ksp for Fe and Zn and Q<Ksp for Mag
+1 point for recognizing that the conc. of OH⁻ will be 1.45e-7 M and that is what the calculations should be based off of
Since the concentration of OH- left from the previous question is 1.45e-7 M, any product of this OH- concentration and the 0.05 M ion concentration that is greater than the ions respective Ksp will precipitate.
Thus, magnesium is the only ion that will remain in solution.

      iii.   **(3 points)** Time to prove it! You need to prove that each of three known metal ions have precipitated. To do so, you are given a photon beam of which has an energy of your choosing. Further, you are given an instrument that informs you of all speeds of ejected electrons only. The work functions of these metals are given below in a table. What is the minimum energy of light required to ensure you

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have properly removed the impurities? How would you go about designing this test?

Compound	Work Function (eV)
Aluminum Hydroxide	4.51
Copper Hydroxide	3.22
Nickel Hydroxide	7.82

+1 Point for correct minimum energy
+2 Points for correct experimental design
Here, you will detect if the impurities have been precipitated out of solution by seeing what speeds of electrons are ejected at some arbitrary energy of photon beam. At a minimum, you will need a photon beam with energy >7.82 eV as we need to be able to detect electrons ejected by all three impurities. At whatever energy chosen, you must calculate the KE of the electrons using the KE=E-work function formula to determine what the expected KE (and thus electron speed) will be. Based on which of the predicted speeds for the three impurities you detect, you can determine which ppt has formed.

iv. **(3 points)** Would you be able to determine how much of each precipitate in present in the solution with this technique? Why or why not?

+1 Point for correct answer
+2 Points for correct explanation (either solutions 1 or 2 works)
No, as:
1) You can only capture electron speed - not #, you are unable to determine how much ppt exists in solution.
2) Varying photon beam energy will only change the KE of the electrons ejected

Thus there is no way in the designed system to vary a controllable variable to gather information regarding ppt amount.

Question 7 (37 points)
Fluorescent molecules are often an easy way for chemists and biochemists to monitor reactions and cellular processes. This question will introduce you to the concepts behind several fluorescence-based techniques.

a. mCardinal is a synthetic, far-red fluorescent protein that has the potential to aid in the process of non-invasive biopsies. A group of researchers analyzing the protein have discovered that it is fairly unstable, and have generated the following questions.

i. **(4 points)** At 310.15 K mCardinal has an enthalpy of 1803.5 J and an entropy of 5.26 J/K. Please explain why mCardinal might be unstable based on this data.

+2 pt, calculation

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G = H - TS
G = 1803.5 J - (310.15 K)(5.26 J/K) = 172.11 J

+2 pt, explanation
The free energy is positive. This indicates that the structure is not favorable and that it will likely explore other conformations in order to lower its energy.

ii. **(4 points)** Further research shows that the mCardinal often self-aggregates during *in vitro* (inside aqueous cell culture) experiments. Analysis of the 3-D crystal structure of mCardinal shows that several interfaces on the protein's surface contain large amounts of alanine, valine, leucine, and isoleucine as amino acids, all of which are hydrophobic in nature. Explain why this protein may self-aggregate.

+4 pt, explanation demonstrating understanding
This phenomenon is a classic example of the hydrophobic effect which states that nonpolar/hydrophobic materials tend to associate in aqueous environments to exclude water molecules. By self-aggregating, mCardinal minimizes the amount of hydrophobic area in contact with polar water molecules, and thus maximizes favorable hydrogen-bonding interactions between water molecules and water molecules and polar amino acid residues.

b. Many fluorescent proteins, like mCardinal, are characterized by their excitation/emission spectra--the wavelengths of light that are able to excite the protein to fluorescence and the wavelength of light the protein emits, respectively. The excitation/emission plot of mCardinal is given below.
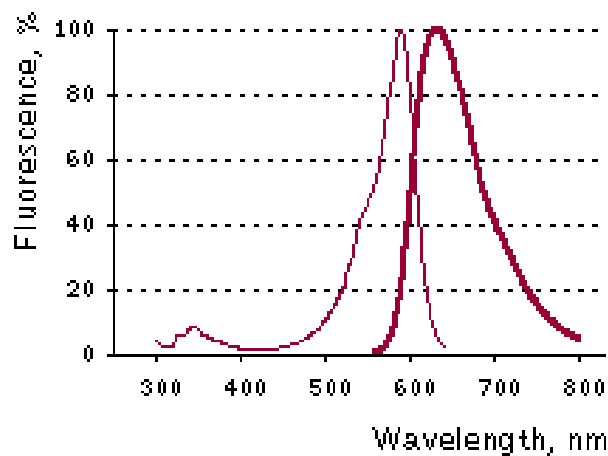

i. **(3 points)** Explain why the excitation spectra is left-shifted in comparison to the emission spectra on the mCardinal plot.

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ii. **(6 points)** Often times, two fluorescent proteins are used in conjunction with one another in a technique called Fluorescence Resonance Energy Transfer (FRET) microscopy. In this process, one protein (donor protein), when excited by a photon, can excite the other protein (acceptor protein). In the space below, plot the excitation/emission spectra (intensity vs. wavelength) of both proteins. Clearly indicate that lines correspond to each protein and whether it is excitation or emission. Below your graph, state all final destinations of energy and energy loss within the system.
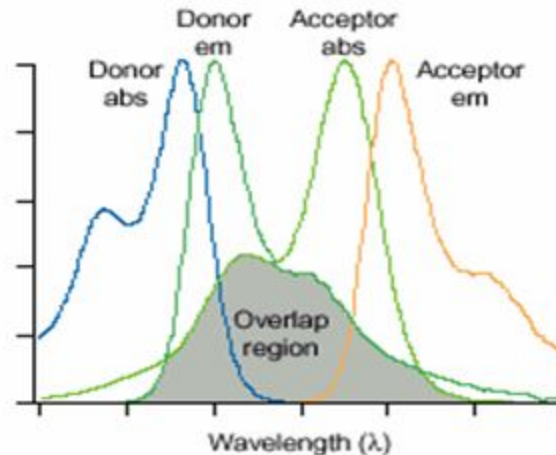
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c. Unlike the fluorescent proteins from parts a and b, thioflavin T (ThT) is a small molecule fluorescent dye that binds stoichiometrically to amyloid protein fibrils. As such, it is often used to detect and monitor amyloid fibril formation. Amyloid fibrils are formed when proteins misfold into a form that allows many copies of the same protein to stack together into fibers.

i. **(5 points)** Based on the structure of ThT below, hypothesize why ThT only emits a strong fluorescent signal when it is attached to amyloid fibrils and does not when it is freely floating in solution.

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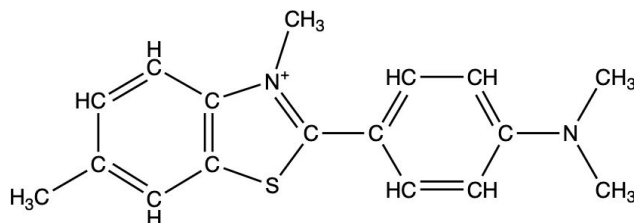
In solution, ThT is able to rotate freely around the C-C bond that links the bicycle on the left, and the 6-membered ring on the right. When ThT is bound to an amyloid fibril, this rotation is "locked" so that the molecule it not allowed to rotate. This allows the p-orbitals of the two sides share electron density, which allows fluorescent emission when excited by a particular wavelength of light.
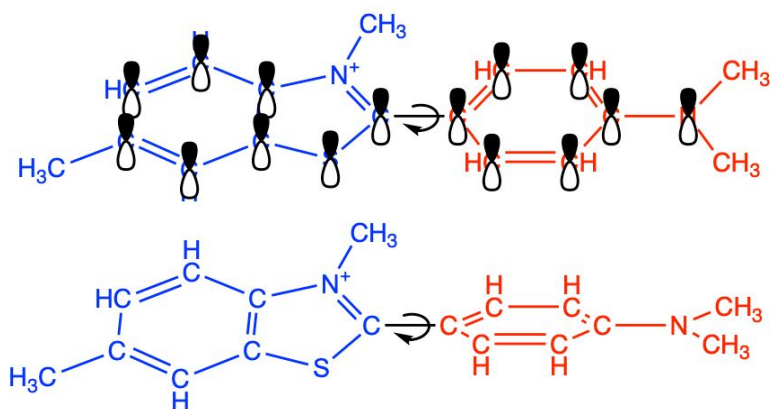
ii. **(6 points)** The kinetics of amyloid fibril formation can be described by the graph below. ThT fluorescence is used as a proxy for the percentage of protein monomers that have been incorporated into fibrils.

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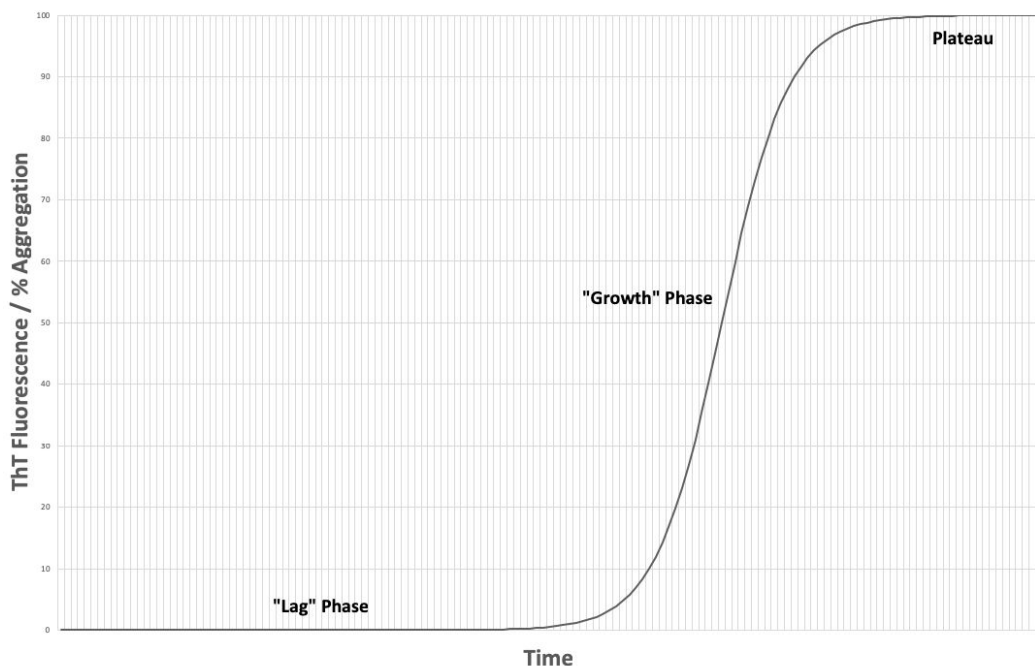
Amyloid fibrils are interesting in that they can be "seeded" by the addition of preformed oligomeric species. Here, we will investigate how these "seeds" affect the kinetics of fibril formation.

Using the data below, determine two different rate laws. The first rate law, R_1, should be in terms of [monomer] and [dimer]. The second rate law, R_2, should be in terms of [monomer] and [pentamer]. Final answers should take the form $R_x = C \, [y]^m[z]^n$ where C is a constant.

[monomer]	[dimer]	[pentamer]	Rate (AU)
100.5	--	--	1.0
99.7	101.1	--	20381.1
101.2	199.8	--	80798.2
202.3	100.2	--	40622.0
98.9	--	100.1	49548.9
100.1	--	199.3	198801.1
199.0	--	100.0	99500.0

+3 pt, each correct rate law
Analyzing the data, we see that the reaction is first order with respect to [monomer], and that the reaction is second order with respect to [dimer] and [pentamer].
$R_1 = C_1 \, [\text{monomer}][\text{dimer}]^2$
$R_2 = C_2 \, [\text{monomer}][\text{pentamer}]^2$
Solving for C_1 and C_2:

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$R_1 = 0.02$ [monomer][dimer]^2
$R_2 = 0.05$ [monomer][pentamer]^2

iii. **(3 points)** The two rate laws determined in B.i. should look fairly similar, differing only in the "C" ahead of the $[y]^m[z]^n$ terms. Using this, generate a generalized rate law that can be applied to both the dimer and pentamer situations. This will require incorporating an "N" term where N describes the composition of the seed.

+3 pt, correct derivation
As stated, the rate laws R_1 and R_2 are the same except for the constant. Thus, we can generalize them to **R = C [monomer][seed]^2**. Additionally, we see that the C term is proportional to the number of units in the seed, so we can further refine our rate law to **R = 0.01 N [monomer][seed]^2**.

iv. **(6 points)** Using the graph above and your newfound knowledge from b.ii. and b.iii., describe how this graph will change when a "seed" like the dimeric and pentameric species above is added to the original solution of monomers. Can the dimers and pentamers be considered catalysts?

+3 pt, description and explanation
Adding a dimer or pentamer seed to a solution of monomers increases the rate of fibrillization. This means that the time it takes for all monomers in solution to be incorporated into a fiber is decreased. This will manifest in a leftward shift in the above curve, while maintaining a similar shape.

+3 pt, explanation
No, the dimer and pentamer do not fit the definition of a catalyst--they are consumer in the reaction and not able to be recycled. Even though the do increase the rate of reaction, they are just combinations of monomers, which are the reactants.