

NOTE TO STUDENTS:

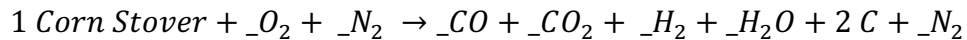
This exam will be a time crunch and there are a total of **200 points** available. The relative weights of each problem are defined below as well as the page number they can be found. The problems are selected to increase in difficulty. Many of these problems are very long and require long calculations. if you find your team short on time but know how to solve the problem, then write in words a written explanation as to how you would solve the problem being sure to include all steps, ideas equations that would be used to receive a large amount of partial credit. While we want you to be able to get a final answer, the showing us that you understand the overall process of a problem is more important.

Tiebreaker information: Due to the team exam being the longest and most challenging with points spread throughout, normal tiebreaking rules apply in the event two teams receive an equal number of points. However, the order of tiebreaker questions for this exam will be given to the students beforehand. The order is as follows:

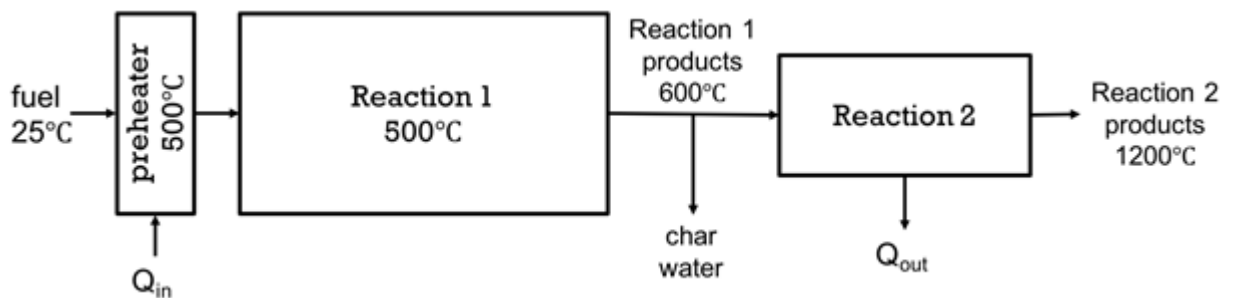
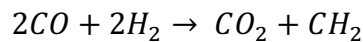
Question #1 → Question #2 → Question #3 → Question #5 → Question #6 → Question #4 →
Question #7

Problem #1: (28 Points)

Many scientists are investigating alternative sustainable energy sources from agricultural waste. More specifically, this problem we will be looking at corn stover (a byproduct of corn production) as a feedstock. This feedstock is mixed with air (assumed 80% N₂ and 20% O₂ by mole) and heated to 500°C before entering reactor #1. Assume the system is ideal and the reactor is isothermal and has a 100% conversion of corn stover and modeled by the unbalanced reaction below:



A key undesirable product produced is char (C) and for 1 mole of corn stover is experimentally known to produce 2 moles of char. After exiting reactor #1, the ratio of CO to CO₂ is 9 to 1 and the ratio of H₂O to H₂ is 1 to 7. This stream is then “de-charred” where 100% of all the water, char and excess corn stover are removed from the system. The remaining stream is then heated again to 600°C before it enters reactor #2 where the carbon monoxide and hydrogen gas react over an iron catalyst to produce methylene and CO₂ modeled below:



- a. Corn stover is in reality a combination of multiple hydrocarbons which many scientists approximate as being C₁₀H₂₂O₇N₂. The largest contributor to energy production of these types of “starchy” molecules is carbon content. After doing research, your team comes across a new substance which a 141g sample the contains the following:

36g C 12g H 79g O 14g N

Determine the molecular formula of this new carbon source (round subscripts when appropriate). **Circle final answer. (3 Points)**

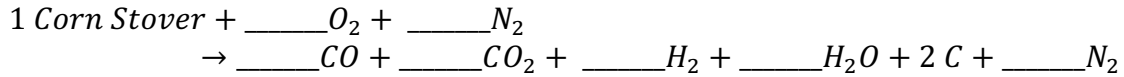
$$n = \frac{m}{MW}$$

$$C = \frac{36}{12.01} \approx 3 \text{ mol} \quad H = \frac{12}{1.01} \approx 12 \text{ mol} \quad O = \frac{79}{16.00} \approx 5 \text{ mol} \quad N = \frac{14}{14.01} \approx 1 \text{ mol}$$

$$\text{Molecular formula} = C_3H_{12}O_5N$$

+1 point if students had the correct approach to solving this problem
+2 points if students get the correct answer

b. Balance the first reaction above. Write your final answer in the reaction below in **decimal** form. **Show ALL work. (13 points)**



For simplicity, the following coefficient variables are assigned:

$$O_2 = \alpha, N_2 = \beta, CO = \gamma, CO_2 = \delta, H_2 = \varepsilon, H_2O = \zeta, N_2 = \eta$$

There are 7 unknowns which means we need 7 EQ's:

EQ#1: $4\alpha = \beta$	O ₂ /N ₂ Balance
EQ#2: $\gamma = 9\delta$	CO/CO ₂ Ratio
EQ#3: $7\varepsilon = \zeta$	Water/Hydrogen Ratio
EQ#4: $\varepsilon + \zeta = 11$	H-Balance
EQ#5: $\gamma + \delta + 2 = 10$	C-Balance
EQ#6: $2\alpha + 7 = \varepsilon + 2\delta + \gamma$	O-Balance
EQ#7: $2 + 2\beta = 2\eta$	N-Balance

+4 point if students have the correct 7 equations above

Immediately what pops out is that *EQ#3* and *EQ#4* only include unknowns! As a result we can easily solve for ε and ζ !

$$7\varepsilon = \zeta \\ 8\varepsilon = 11 \\ \varepsilon = \mathbf{1.375} \\ \zeta = \mathbf{9.625}$$

Similarly, *EQ#2* and *EQ#5* only include unknowns! As a result we can easily solve for γ and δ !

$$\gamma = 9\delta \\ \gamma + \delta + 2 = 10 \\ 10\delta + 2 = 10 \\ 10\delta = 8 \\ \delta = \mathbf{0.8} \\ \gamma = \mathbf{7.2}$$

Now that we have 4 unknowns determined, we can easily solve for the other 3 through plug-and-chug.

$$2\alpha + 7 = \varepsilon + 2\delta + \gamma \therefore \alpha = \frac{\varepsilon + 2\delta + \gamma - 7}{2} = \frac{1.375 + 2(0.8) + 7.2 - 7}{2}$$

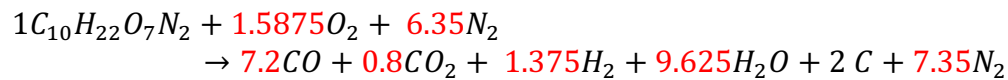
$$\alpha = 1.5875$$

$$4\alpha = \beta \therefore$$

$$\beta = 6.35$$

$$2 + 2\beta = 2\eta \therefore \eta = 1 + \beta = 7.35$$

$$\eta = 7.35$$



+1 point for each correct coefficient above (**7 points total**)

+2 points if students get ALL coefficients correct.

Note: Due to this being taken remotely, students must show sufficient work that they did not use a solver/excel to solve for these coefficients. If this is not present, then students can only get a maximum of **4 points total**.

- c. After the products leave reactor #2 they have to legally be passed through a heat exchanger to reduce their temperature before releasing them into the environment. Determine if running cooling water co-current or counter-current will have more effective heat transfer over a long distance. Circle an option below and explain (1-2 sentence). (**3 points**)

Co-current

Counter-current

Counter current is more effective form of heat transfer because there is a greater overall temperature gradient throughout the length of the heat exchanger than in co-current flow.

+3 points if students answer counter-current and give a reasonable explanation. Explanation must include something about there being “higher overall higher temperature gradient” for counter-current flow.

- d. If the net energy per kg of corn is 340.5 kJ, calculate the how many **square yards** of land that must be harvested to produce 100,000 kWh of energy. (4 points)

Useful Info:

One bushel of corn weighs roughly 25kg. Roughly 101 bushels of corn are harvested from an acre of land. 1 acre is $6.273 \cdot 10^6 \text{ in}^2$ and 1 yard is 36 inches.

$$10^6 \text{ kWh} = 10^6 \text{ kW} \cdot 1 \text{ hr} = \frac{1 \text{ kJ}}{\text{s}} \cdot 3600 \text{ s} = 3.6 \cdot 10^9 \text{ kJ} \cdot \frac{1 \text{ kg corn}}{340.5 \text{ kJ}} = 1.057 \cdot 10^7 \text{ kg}$$

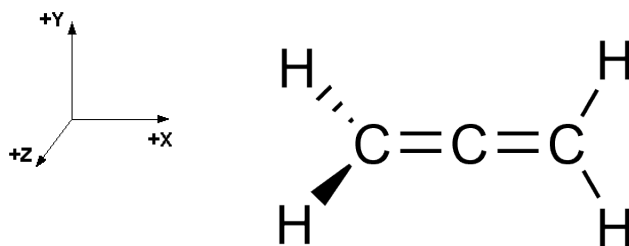
$$1.057 \cdot 10^7 \text{ kg corn} \cdot \frac{1 \text{ bushel}}{25 \text{ kg corn}} \cdot \frac{1 \text{ acre}}{101 \text{ bushels}} \cdot \frac{6.273 \cdot 10^6 \text{ in}^2}{1 \text{ acre}} \cdot \left(\frac{1 \text{ yd}}{36 \text{ in}}\right)^2$$

$$10^6 \text{ kWh} = 2.0267 \cdot 10^7 \text{ yd}^2 \text{ or } 20,267,225 \text{ yd}^2$$

+2 point for determining the needed mass of corn to produce this amount of energy

+2 points if students gets the correct final answer in the correct units of square yards

- e. A chemical produced in the second reaction is methylene which is a carbene molecule. Carbene chemistry is extremely important and through dimerization and further reaction forms allene show below with the addition CH_3Li . For allene, explain why two hydrogen atoms are not in the plane of the page (3-5 sentences). (5 points)



The reason the carbon atoms on the left side of allene are not in the plane of the page is because the pi bonds between the center and right carbon are between the $\pm z$ -p orbitals. This means the only empty p-orbitals for the left most carbon and center carbon are available in the $\pm y$ axis. This means that the hydrogen atoms are “forced” to be in not in the plane of the page.

+1 point mentioning pi bonds in any way!

+4 points for correct orbital explanation.

Problem #2: (22 points)

- a) Consider an idealized photoelectric effect experiment using a silver electrode with a work function of 4.26 eV and a light source that generates a **constant photon rate** with varying wavelength. If light with a wavelength of 275 nm generates a photocurrent of 1.38×10^{15} electrons per second, calculate the photocurrent (in electrons per second) that would be measured if the wavelength of the light was increased to 325 nm. Please show all work and **circle your final answer.** (6 points)

$$\Phi = 4.26 \text{ eV} \cdot \frac{1.602 \cdot 10^{-19} \text{ J}}{1 \text{ eV}} = 6.82 \cdot 10^{-19} \text{ J}$$

$$E_{ph} = \frac{hc}{\lambda} = \frac{(6.626 \cdot 10^{-34} \text{ Js})(2.998 \cdot 10^8 \text{ m/s})}{325 \cdot 10^{-9} \text{ m}}$$

$$E_{ph} = 6.11 \cdot 10^{-19} \text{ J}$$

$E_{ph} < \Phi$, therefore no electrons will be ejected

Alternate: Another correct way to answer this question includes calculating the threshold wavelength and demonstrating that $\lambda = 325 \text{ nm} > \lambda_0$, therefore, no electrons will be ejected.

+1 point for correct energy conversion

+1 point for correct E photon

+4 points for correct comparison and conclusion

- b) A gaseous N^{6+} ion is initially in the 9th excited state and undergoes a transition. The difference (in magnitude, $|\Delta r|$) in the radii of the two Bohr orbits due to this transition is 634.8 pm. Use the Bohr model of the atom to answer the following questions.
- i. Was the photon absorbed or emitted? **Circle your final answer.** (Note: no points will be given for a correctly circled answer with justification and calculations):

Circle One: The photon was.....

Absorbed

or

Emitted

Justify your answer with appropriate calculations **and** a written explanation in the space provided below. (8 points)

If the photon was absorbed, the radius would increase by 634.8 pm. An increase of 634.8 pm results in a non-integer quantum number $n=13.56$, which is not possible. **If the photon was emitted, the radius would decrease by 634.8 pm. A decrease of 634.8 pm results in an integer quantum number $n=4$. Hence, the photon was emitted.**

$$r_{initial} = 52.9 \text{ pm} \left(\frac{n^2}{Z} \right) = 52.9 \text{ pm} \left(\frac{10^2}{7} \right) = 755.7 \text{ pm}$$

$$\Delta r = r_{final} - r_{initial} \therefore r_{final} = 120.9 \text{ pm or } 1390.5 \text{ pm}$$

Now we can do the same calculation earlier, but instead solve for the quantum number.

$$r_{final} = 1390.5 \text{ pm} = 52.9 \left(\frac{n^2}{7} \right) \therefore n = 13.56$$

$$r_{final} = 120.9 \text{ pm} = 52.9 \left(\frac{n^2}{7} \right) \therefore n = 4$$

+2 points for correct $r_{initial}$ calculation

+2 points for correct quantum number calculations for **BOTH** scenarios

+4 points for correct and clear explanation that accurately describes why the photon was emitted.

Note: If student concluded that the photon was absorbed, then the maximum points possible is **4 points**. These points will only be awarded if the student had the correct process, and only circled it due to a math error.

- ii. What was the wavelength (in nm) of the photon that was either emitted or absorbed in part a) of this question? If you were unable to solve for part i), assume that the gaseous ion (N^{6+}) ends in the 12th excited state. Show work and circle your final answer. (8 points)

Note: Bonus points will be awarded if you use your correct answer from part i) to get a correct answer in part ii).

$$|\Delta E_{ion}| = \Delta E_{ph} \therefore \left| -2.18 \cdot 10^{-18} \text{ J} (Z^2) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right| = \frac{hc}{\lambda}$$

+2 points for using the equation above with your answer from i) **OR** with the given info in part ii)

If correct part a)

$$\left| -2.18 \cdot 10^{-18} \text{ J} (Z^2) \left(\frac{1}{4^2} - \frac{1}{10^2} \right) \right| = \frac{(6.626 \cdot 10^{-34} \text{ Js})(2.998 \cdot 10^8 \text{ m/s})}{\lambda}$$

$$\lambda = 35.4 \text{ nm}$$

+2 points for substituting in the correct quantum numbers.

+2 points for correct final wavelength

-1 point if units are incorrect

+2 points if student used their correct solution in part a) to get a correct solution in part i)

OR

$$\left| -2.18 \cdot 10^{-18} \text{ J } (Z^2) \left(\frac{1}{13^2} - \frac{1}{10^2} \right) \right| = \frac{(6.626 \cdot 10^{-34} \text{ Js})(2.998 \cdot 10^8 \text{ m/s})}{\lambda}$$

$$\lambda = 455 \text{ nm}$$

+2 points for substituting in the correct quantum numbers.

+2 points for correct final wavelength

-1 point if units are incorrect

Problem #3: (30 points)

a) A buffer solution can be prepared by starting with a weak acid, HA, and converting some of the weak acid to its salt (for example, NaA) by titration with a strong base. The fraction of the original acid that is converted to the salt is designated as “ f ”.

i) Devise an equation similar to the Henderson-Hasselbalch Equation but expressed in terms of f rather than concentration. (4 points)

$$pH = pKa - \log_{10} \frac{[HA]_0}{[A^-]_0} = pKa - \log_{10} \frac{(1-f)[HA]_0}{f[HA]_0}$$

$$pH = pKa - \log_{10} \left(\frac{1-f}{f} \right)$$

+2 points for correctly stating the Henderson-Hasselbalch equation.

+2 points for correct expression in terms of f

ii) What is the pH at the point in the titration of cyanic acid (HOCN) with NaOH when $f = 0.27$? (3 points)

$$K_a(\text{HCON}) = 3.5 \times 10^{-4}$$

$$pKa = \log_{10}(K_a) = 3.46$$

$$pH = pKa - \log_{10} \left(\frac{1-f}{f} \right) = 3.46 - \log_{10} \left(\frac{1-0.27}{0.27} \right)$$

$$pH = 3.03$$

+1 point for correctly calculating the pKa

+2 points for correctly calculating the pH

iii) Can you use your equation to calculate pH at the limits (that is, $f = 0$ and $f = 1$)? Provide a **chemical** explanation in 1-2 sentences using the space below. (3 points)

No, because at the limits stated in this problem, the solution is no longer a buffer as only the weak acid or its conjugate base will be present. At these conditions the Henderson-Hasselbalch equation is no longer valid.

+1 point for mentioning the fact that the solution is no longer a buffer

+2 points for stating that the H-H equation is not valid unless the solution is a buffer

- iv) Calculate the pH at $f = 1$. You may assume that the solution being titrated initially contains 0.075 mol of HOCN in 500 mL of water. The NaOH titrant solution is prepared at a standard concentration of 0.20 M. This process is performed at standard temperature and pressure. Show all work and **circle your final answer.** (8 points)

$f = 1$ means that all HOCN has been converted to OCN^- .

$$\text{Volume of titrant required for neutralization} = \frac{0.075 \text{ mol}}{0.20 \text{ mol/L}} = 0.375 \text{ L}$$

$$\text{At equivalence point, } \frac{0.075 \text{ mol } \text{OCN}^-}{(0.500 \text{ L} + 0.375 \text{ L})} = 0.0857 \text{ M } \text{OCN}^-$$

	$\text{OCN}^-_{(\text{aq})}$	+	$\text{H}_2\text{O}_{(\text{l})}$	\rightleftharpoons	HOCN	+	$\text{OH}^-_{(\text{aq})}$
I	0.0857				0		0
C	-x				+x		+x
E	0.0857 - x				x		x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.86 \times 10^{-11}$$

$$K_b = 2.86 \times 10^{-11} = \frac{[\text{HOCN}][\text{OH}^-]}{[\text{OCN}^-]} = \frac{x^2}{0.0857 - x} \quad x = [\text{OH}^-] = 1.56 \times 10^{-6}$$

$$\text{pOH} = -\log(1.56 \times 10^{-6}) = 5.81 \quad \text{pH} = 14.0 - 5.81 = 8.19$$

+1 point for correct volume of titrant needed to neutralize the acid

+3 points for correct ICE table setup or written in an equivalent way

+1 point for correct K_b calculation

+1 point for correct hydroxide concentration

+2 points for correct final pH

- b) You come across two labeled beakers which contain two different basic solutions. These species were dissolved in water at 25°C. The initial concentrations of each species as well as the pH of the solutions **after** equilibrium is established are provided below. Using this information in the table below, classify each species as a strong or weak base. If the base is weak, calculate its K_b value. Show all work and **circle** the one of the options below. If the base is weak write the K_b for the base on the line provided below:

	Species	Initial Concentration (M)	pH of the solution at equilibrium	Conjugate Acid	Conjugate Base (if applicable)
1	XO_2^-	0.34 M	12.55	HXO_2	
2	HYO_3^-	0.40 M	8.34	H_2YO_3	YO_3^{2-}

i) Species 1 (XO_2^-) (6 points)

Circle One: Strong Base **Weak Base**

K_b of XO_2^- (if weak) $4.13 \cdot 10^{-3}$

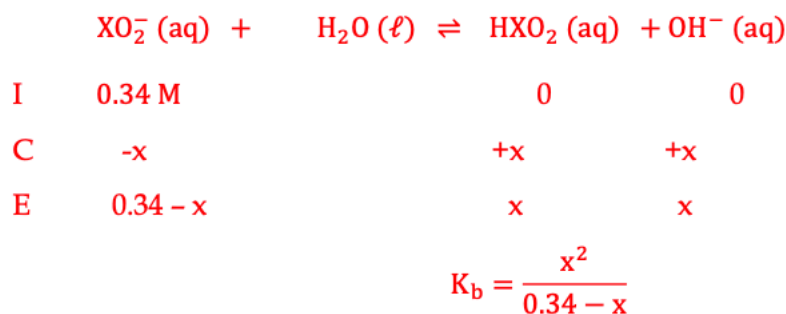
Supporting Work: If the base was strong, $[XO_2^-] = [OH^-]$ in solution and resulting pOH would be:

$$-\log_{10}(0.34 M) = 0.469 = pOH$$

$$pH = 14 - pOH = 13.53$$

Since the pH is not 13.53, we can conclude that species 1 must be a weak base.

+3 points for circling weak base **AND** having work that supports this claim
(No points awarded simply for circling weak base)



$$pOH = 14 - pH = 14 - 12.55 = 1.45 \quad [OH^-] = 10^{-1.45} = 0.03548 M$$

$$K_b = \frac{[OH^-]_{eq}[HXO_2]}{[XO_2^-]} = \frac{(0.03548)(0.03548)}{(0.34 - 0.03548)} = 4.13 \times 10^{-3}$$

Note: For clarity, this solution presented a full ICE Table, ICE table is not necessary for full credit.

+2 points for correct equilibrium hydroxide concentration
+1 point for K_b answer

ii) Species 2 (HYO_3^-) (6 points)

Hint: For species 2, $\text{pK}_{a_2} = 10.32$

Circle One: Strong Base **Weak Base**

K_b of XO_2^- (if weak) _____

Supporting Work: This is an amphiprotic salt meaning that its pH can be determined as:

$$\text{pH} = \frac{1}{2}(\text{pK}_{a_1} + \text{pK}_{a_2}) \therefore 8.34 = \frac{1}{2}(\text{pK}_{a_1} + 10.32)$$

$$\text{pK}_{a_1} = 6.36 \therefore \text{K}_{a_1} = 10^{-6.36} = 4.365 \cdot 10^{-7}$$

$$\text{K}_b(\text{HYO}_3^-) = \frac{\text{K}_w}{\text{K}_{a_1}} = \frac{10^{-14}}{4.365 \cdot 10^{-7}} = 2.29 \cdot 10^{-8}$$

Alternate:

$$\text{pH} = \frac{1}{2}(\text{pK}_{a_1} + \text{pK}_{a_2}) \therefore 8.34 = \frac{1}{2}(\text{pK}_{a_1} + 10.32)$$

$$\text{pK}_{a_1} = 6.36 \therefore \text{pK}_b = 14 - 6.36 = 7.64$$

$$\text{K}_b(\text{HYO}_3^-) = 10^{-7.64} = 2.29 \cdot 10^{-8}$$

+3 points for circling weak base **AND** having work that supports this claim

(No points awarded simply for circling weak base)

+1 point for correctly calculating the pK_{a1}

+2 point2 for correctly calculating the K_{b1} of the weak base

Problem #4: (10 points)

A solution of naphthalene (1) and Biphenyl (2) have the following properties shown below:

	Melting Temperature (°C)	Enthalpy of Fusion (kJ/mol)
1	80.2	18.8
2	69.2	18.58

These two chemicals are known to form a 2 phase diagram with a key eutectic point. When dealing with such complicated non-ideal mixtures of chemicals, the activity coefficients of both chemicals must be utilized. Below is the equilibrium criteria for the solubility of each chemical in the other.

$$\ln(x_i^{Liquid} \gamma_i) = -\frac{\Delta H_i^{fus}}{R} \left(\frac{1}{T} - \frac{1}{T_{m_i}} \right)$$

- a) Explain what a Eutectic point is **(3 points)**

A Eutectic point is a key location in a phase diagram which is the lowest temperature a liquid can exist for the solution of two chemicals. It also at this point that the composition of (1) and (2) has the lowest melting temperature.

+3 points for a reasonable answer that mentions something with respect to lowest melting temperature composition.

- b) Assuming that the naphthalene and biphenyl are ideal, determine the eutectic composition (in mole fraction form) and eutectic temperature. **(8 points)**

Since the solution is ideal we can ignore the activity coefficients!

+2 point for identifying that the activity coefficients of both become 1.

Now we know that both equations should give the same eutectic temperature since it is one point. This means that we can rearrange the equation above for both species to be:

$$T_e = \left[\frac{1}{T_{m_1}} - \frac{R}{\Delta H_1^{fus}} \ln(x_1^{Liquid}) \right]^{-1}$$
$$T_e = \left[\frac{1}{T_{m_2}} - \frac{R}{\Delta H_2^{fus}} \ln(1 - x_1^{Liquid}) \right]^{-1}$$

+2 points for correctly rearranging both equations to be equal to the eutectic temperature.
+1 point for equating the two equations to solve for the composition

$$\left[\frac{1}{T_{m_1}} - \frac{R}{\Delta H_1^{fus}} \ln(x_1^{Liquid}) \right]^{-1} = \left[\frac{1}{T_{m_2}} - \frac{R}{\Delta H_2^{fus}} \ln(1 - x_1^{Liquid}) \right]^{-1}$$

$$x_1^e = 0.447 \text{ \& } x_2^e = 0.553$$

+2 points for correctly solving for both eutectic mole fractions

Now the student can use either of the above two equations and solve for the eutectic temperature

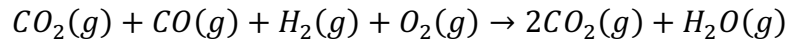
$$T_e = 313.7 \text{ K}$$

+1 point for correctly solving for the eutectic temperature

Problem #5: (30 points)

21.3 kg of syngas comprising 50%CO, 35%H₂ and 15%CO₂ by mole (mixture average molecular weight = 21.3kg/kmol) undergoes complete, adiabatic, stoichiometric combustion with oxygen ($\phi = 1.0$). What is the final temperature? The gas properties are given in the table below. The reactants have a temperature of 380K before combustion. The reference temperature is 298K. Select either a molar or mass based approach and use the corresponding values.

The balanced chemical equation that describes this process is:



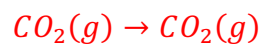
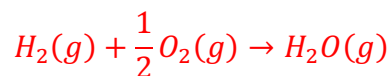
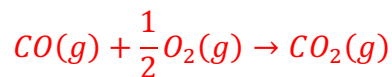
Hint: You can assume the reaction above can be split into two independent reactions occurring in parallel plus an inert chemical balance.

	CO	H ₂	CO ₂	O ₂	H ₂ O
M _k (kg/kmol)	28	2	44	32	18
C _p (kJ/kmol-K)	29.18	28.64	37.18	29.41	33.61
H _f ^o (kJ/kmol)	-110537	0	-393538	0	-241838

In addition to the information given above, you have access to the following:

	CO	H ₂	CO ₂	O ₂	H ₂ O
<i>m</i> _{IN} (kmol)	0.5	0.35	0.15	0.425	0
<i>m</i> _{OUT} (kmol)	0	0	0.65	0	0.35

Since we are given the moles of everything entering and exiting the reaction, we need to determine what the three parallel reactions actually are:



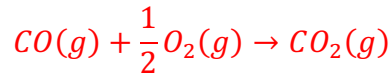
+1 point for RXN#1

+1 point for RXN#2

Reaction #3 is just an inert balance and not vital to this problem. As a result no points are awarded or removed for not including it.

Now that the reactions are determined, we can now look to see how much energy is produced from each of these reactions at STP.

RXN#1:



$$\Delta H_{RXN,1}^{\circ} = -393,538 \frac{kJ}{kmol} - \left(-110,537 \frac{kJ}{kmol} \right) = -283,001 \frac{kJ}{kmol \text{ rxn}\#1}$$

+3 point for the standard enthalpy of reaction per unit kmol

Find the extent of reaction #1:

$$\xi_1 = \frac{|(n_{CO})_{out} - (n_{CO})_{in}|}{|v_{CO}|} = \frac{|0.5 \text{ kmol} - 0 \text{ kmol}|}{|1|} = 0.5 \text{ kmol rxn}\#1$$

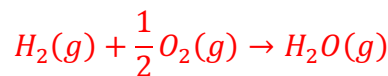
$$\Delta \hat{H}_{RXN,1}^{\circ} = \Delta H_{RXN,1}^{\circ} \xi_1 = \left(-283,001 \frac{kJ}{kmol \text{ rxn}\#1} \right) 0.5 \text{ kmol rxn}\#1$$

$$\Delta \hat{H}_{RXN,1}^{\circ} = -141,500.5 \text{ kJ}$$

This means that the first reaction is responsible for releasing 141,500.5 kJ of energy into the system.

+3 points for determining the correct total energy produced from RXN#1

RXN#2:



$$\Delta H_{RXN,2}^{\circ} = -241,838 \frac{kJ}{kmol} - \left(0 \frac{kJ}{kmol} \right) = -241,838 \frac{kJ}{kmol \text{ rxn}\#2}$$

+3 point for the correct standard enthalpy of reaction per unit kmol

Find the extent of reaction #2:

$$\xi_2 = \frac{|(n_{H_2})_{out} - (n_{H_2})_{in}|}{|v_{H_2}|} = \frac{|0.35 \text{ kmol} - 0 \text{ kmol}|}{|1|} = 0.35 \text{ kmol rxn}\#2$$

$$\Delta \hat{H}_{RXN,2}^{\circ} = \Delta H_{RXN,2}^{\circ} \xi_2 = \left(-241,838 \frac{kJ}{kmol \text{ rxn}\#2} \right) 0.35 \text{ kmol rxn}\#2$$

$$\Delta \hat{H}_{RXN,2}^{\circ} = -84,643.3 \text{ kJ}$$

+3 points for determining the correct total energy produced from RXN#2

This means that the combination of these two reactions occurring in parallel assuming that both reach 100% completion results in:

$$\Delta \hat{H}_{RXN}^{\circ} = \Delta \hat{H}_{RXN,2}^{\circ} + \Delta \hat{H}_{RXN,1}^{\circ} = -84,643.3 \text{ kJ} - 141,500.5 \text{ kJ} = -226,143.8 \text{ kJ}$$

+2 points for correct overall heat of reaction

Next, find the enthalpy of the reactants at 380K entering reactor.

$$\hat{H}_{1,IN} = n_1 C_{p,1} \Delta T = (0.35 \text{ kmol}) \left(28.64 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (380\text{K} - 298\text{K}) = 821.968 \text{ kJ}$$

$$\hat{H}_{2,IN} = n_2 C_{p,2} \Delta T = (0.425 \text{ kmol}) \left(29.41 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (380\text{K} - 298\text{K}) = 1024.9385 \text{ kJ}$$

$$\hat{H}_{3,IN} = n_3 C_{p,3} \Delta T = (0.50 \text{ kmol}) \left(29.18 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (380\text{K} - 298\text{K}) = 1,196.38 \text{ kJ}$$

$$\hat{H}_{4,IN} = n_4 C_{p,4} \Delta T = (0.15 \text{ kmol}) \left(37.18 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (380\text{K} - 298\text{K}) = 457.314 \text{ kJ}$$

$$\hat{H}_{5,IN} = n_5 C_{p,5} \Delta T = (0.00 \text{ kmol}) \left(33.61 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (380\text{K} - 298\text{K}) = 0 \text{ kJ}$$

$$\begin{aligned} \hat{H}_{IN} &= \hat{H}_{1,IN} + \hat{H}_{2,IN} + \hat{H}_{3,IN} + \hat{H}_{4,IN} + \hat{H}_{5,IN} \\ &= 821.968 \text{ kJ} + 1024.9385 \text{ kJ} + 1,196.38 \text{ kJ} + 457.314 \text{ kJ} + 0 \text{ kJ} \end{aligned}$$

$$\hat{H}_{IN} = 3500.60 \text{ kJ}$$

+3 points for having the overall process above (even if calculations are wrong)

+3 points for correct total enthalpy in

Find the enthalpy of the reactants at leaving the reactor at an unknown temperature.

$$\hat{H}_{1,OUT} = n_1 C_{p,1} \Delta T = (0 \text{ kmol}) \left(28.64 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (T_f - 298\text{K}) = 0 \text{ kJ}$$

$$\hat{H}_{2,OUT} = n_2 C_{p,2} \Delta T = (0 \text{ kmol}) \left(29.41 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (T_f - 298\text{K}) = 0 \text{ kJ}$$

$$\hat{H}_{3,OUT} = n_3 C_{p,3} \Delta T = (0.00 \text{ kmol}) \left(29.18 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (T_f - 298\text{K}) = 0$$

$$\hat{H}_{4,OUT} = n_4 C_{p,4} \Delta T = (0.65 \text{ kmol}) \left(37.18 \frac{\text{kJ}}{\text{kmol} - \text{K}} \right) (T_f - 298\text{K})$$

$$= \left(24.167 \frac{\text{kJ}}{\text{K}} \right) T_f - 7201.77 \text{ kJ}$$

$$\begin{aligned}
\hat{H}_{5,OUT} &= n_5 C_{p,5} \Delta T = (0.35 \text{ kmol}) \left(33.61 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \right) (T_f - 298\text{K}) \\
&= \left(11.76 \frac{\text{kJ}}{\text{K}} \right) T_f - 3505.523 \text{ kJ} \\
\hat{H}_{OUT} &= \hat{H}_{1,OUT} + \hat{H}_{2,OUT} + \hat{H}_{3,OUT} + \hat{H}_{4,OUT} + \hat{H}_{5,OUT} \\
&= 0 \text{ kJ} + 0 \text{ kJ} + 0 \text{ kJ} + \left(24.167 \frac{\text{kJ}}{\text{K}} \right) T_f - 7201.77 \text{ kJ} + \left(11.76 \frac{\text{kJ}}{\text{K}} \right) T_f \\
&\quad - 3505.523 \text{ kJ} \\
\hat{H}_{OUT} &= \left(35.927 \frac{\text{kJ}}{\text{K}} \right) T_f - 10,707.3 \text{ kJ}
\end{aligned}$$

+3 points for correct total enthalpy out as a function of an unknown temperature.

$$\Delta \hat{H}_{RXN}^{380\text{K}} = \Delta \hat{H}_{RXN}^{298\text{K}} + \hat{H}_{OUT} - \hat{H}_{IN} = 0$$

+1 point for including the equation above.

+1 point for equating the equation above to 0 due to adiabatic system.

This relationship above is due to the fact that the system is operating adiabatically.

$$0 = -226,143.8 \text{ kJ} + \left(35.927 \frac{\text{kJ}}{\text{K}} \right) T_f - 10,707.3 \text{ kJ} - 3500.60 \text{ kJ}$$

$$226,143.8 \text{ kJ} + 10,707.3 \text{ kJ} + 3500.60 \text{ kJ} = \left(35.927 \frac{\text{kJ}}{\text{K}} \right) T_f$$

$$240,351.7 \text{ kJ} = \left(35.927 \frac{\text{kJ}}{\text{K}} \right) T_f$$

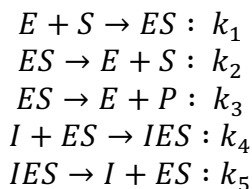
$$\underline{T_f = 6690.0 \text{ K}}$$

+3 points for correct final answer!

NOTE: Since this is a very long and computationally heavy problem, if the students' overall process is correct, well laid out, and easy to follow, then regardless if they make computational mistakes, these should not propagate through the problem and should be accounted for by the grader.

Problem #6: (36 Points)

During WW2, it was common for spies to keep potassium cyanide pills on their person in case they were ever caught. Cyanide as a poison is extremely lethal as it acts as a non-competitive inhibitor of cytochrome c oxidase, which halts cellular respiration and causes hypoxic anoxia. In this system the enzyme cytochrome c oxidase (E) combines with substrate (S) to form an enzyme-substrate complex (ES) which produces product (P). However, when cyanide enters the system, it acts as an inhibitor (I) forming an inhibited enzyme-substrate complex (IES). This system can be denoted by the five equations and their rate constants below:



- a. Assuming that it only takes an acute amount of cyanide to kill an adult in 1-3 minutes, how does the relative magnitude of k_3 compare to k_4 ? How does the relative magnitude of k_5 compare to k_4 ? **Explain (3-6 sentences) (6 Points)**

Since a small $[I]$ is needed to kill someone, it is clear that $k_3 < k_4$ as the rapid deactivation of the ES is what causes death. In addition, it can be seen that $k_5 < k_4$ since a total lack of cellular respiration causes death meaning the IES has a much harder time going back to ES.

+3 points if students state that $k_3 < k_4$ with a reasonable explanation that shows they did not guess.

+3 points if students state that $k_5 < k_4$ with a reasonable explanation that shows they did not guess.

If students simply state:

$$k_3 < k_4 \text{ \& } k_5 < k_4$$

Then only 1 point will be awarded!

- b. After close analysis we find that this system can be modelled using a pseudo steady-state analysis (PSSA) with a **constant amount of enzyme**. This results in the following reaction mechanism:

$$r_p = \frac{V_{max}[S]}{K_M + [S] \left(1 + \frac{[I]}{K_I}\right)}$$

Using the rate expressions given below, determine V_{max} , K_M , and K_I in terms of rate constants and the total amount of enzyme present denoted as $[E]_{TOT}$. **Circle final answer for full credit. (25 Points)**

Given Rate Expressions:

$$\begin{aligned} -r_s &= r_p = k_3[ES] \\ r_{ES} = 0 &= k_1[E][S] - k_2[ES] - k_3[ES] - k_4[ES][I] + k_5[IES] \\ r_{IES} = 0 &= k_4[ES][I] - k_5[IES] \end{aligned}$$

First find $[IES]$:

$$\begin{aligned} k_4[ES][I] &= k_5[IES] : \text{This will be used later for } [ES] \\ [IES] &= \frac{k_4[ES][I]}{k_5} \end{aligned}$$

+4 points if students get correct expression for $[IES]$

Next find $[ES]$:

$$\begin{aligned} &\text{From previous} \\ 0 &= k_1[E][S] - k_2[ES] - k_3[ES] - k_4[ES][I] + k_4[ES][I] \\ 0 &= k_1[E][S] - k_2[ES] - k_3[ES] \\ [ES] &= \frac{k_1[E][S]}{(k_2 + k_3)} \end{aligned}$$

+3 points if students get correct expression for $[ES]$

This problem requires us to give answers in terms of $[E]_{TOT}$ not, $[E]$ which means we need to perform an enzyme mass balance:

$$[E]_{TOT} = [E] + [ES] + [IES]$$

+3 points if students get correct expression for $[E]_{TOT}$ from a mass balance

$$[E]_{TOT} = [E] + \frac{k_1[E][S]}{(k_2 + k_3)} + \frac{k_4[ES][I]}{k_5} = [E] + \frac{k_1[E][S]}{(k_2 + k_3)} + \frac{k_4 k_1 [E][S][I]}{k_5 (k_2 + k_3)}$$

$$[E]_{TOT} = [E] \left[1 + \frac{k_1[S]}{(k_2 + k_3)} + \frac{k_4 k_1 [S][I]}{k_5 (k_2 + k_3)} \right] \therefore [E] = \frac{[E]_{TOT}}{\left[1 + \frac{k_1[S]}{(k_2 + k_3)} + \frac{k_4 k_1 [S][I]}{k_5 (k_2 + k_3)} \right]}$$

+5 points if students get correct expression for $[E]$ in terms of rate constants, $[E]_{TOT}$, $[S]$, and $[I]$.

Plug into r_p :

$$r_p = k_3[ES] = \frac{\frac{k_3 k_1}{(k_2 + k_3)} [E]_{TOT} [S]}{\left[1 + \frac{k_1[S]}{(k_2 + k_3)} + \frac{k_4 k_1 [S][I]}{k_5 (k_2 + k_3)} \right]}$$

+4 points if students get a correct expression r_p

Now manipulate the rate law to resemble the observed form by factoring:

$$r_p = \frac{\frac{k_3 k_1}{(k_2 + k_3)} [E]_{TOT} [S]}{\frac{k_1}{(k_2 + k_3)} \left[\frac{(k_2 + k_3)}{k_1} + [S] + \frac{k_4 [S][I]}{k_5} \right]}$$

$$r_p = \frac{k_3 [E]_{TOT} [S]}{\left[\frac{(k_2 + k_3)}{k_1} + [S] \left(1 + \frac{k_4 [I]}{k_5} \right) \right]} \therefore r_p = \frac{V_{max} [S]}{K_M + [S] \left(1 + \frac{[I]}{K_I} \right)}$$

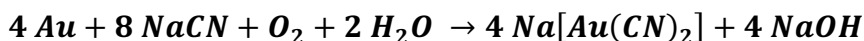
$$K_M = \frac{(k_2 + k_3)}{k_1}, \quad K_I = \frac{k_5}{k_4}, \quad V_{max} = k_3 [E]_{TOT}$$

+2 points if students get a correct expression K_M

+2 points if students get a correct expression V_{max}

+2 points if students get a correct expression K_I

- c. As a result of its uses during WW2 as well as its inherent lethality, cyanide is a notorious chemical. However, it still has its uses in industries such as gold mining. There, sodium cyanide is used to extract gold from raw ore due to cyanide having a high affinity for gold. This process can be modeled by the following reaction:



A common idea in reaction chemistry is to determine the rate of reactions for each product and reactant. However, certain chemicals are much easier to detect. In this case, the rate of formation of NaOH is easiest to track because of its immediate impact on pH readings. However, the most important rates of reactions are that of the gold depletion and that of the gold complex formation. A person suggests the

following relationship for the rates of reactions below which is incorrect. Correct this relationship. (5 points)

INCORRECT Relationship: $r_{Au} = r_{NaCN} = r_{O_2} = r_{H_2O} = r_{Na[Au(CN)_2]} = r_{NaOH}$

$$-\frac{r_{Au}}{4} = -\frac{r_{NaCN}}{8} = -r_{O_2} = -\frac{r_{H_2O}}{2} = \frac{r_{Na[Au(CN)_2]}}{4} = \frac{r_{NaOH}}{4}$$

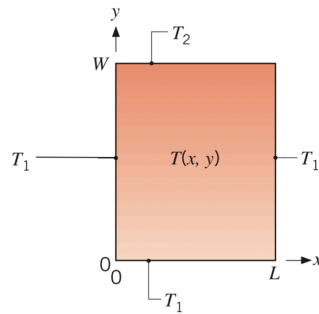
+2 points if students gets ALL the negative signs correct

+3 points if students gets ALL the coefficients correct

Problem #7: (44 Points)

Heat transfer is an extremely important topic to both chemists and chemical engineers, and an extremely common system is a square hot plate. Assume you turn on a hot plate and let it run for a long time such that the system reaches steady state with no internal heat generation. Your teacher tells you that 3 sides of the hot plate are maintained at a temperature T_1 , and the fourth side is maintained at T_2 with $T_2 > T_1$. An image is provided below. Since your teacher knows you cannot solve a partial differential equation, she gives you the following exact solution shown below which describes the temperature at any (x, y) coordinate of the hot plate:

$$\theta(x, y) = \frac{T(x, y) - T_1}{T_2 - T_1} = [C_1 \cos(\lambda x) + C_2 \sin(\lambda x)][C_3 e^{-\lambda y} + C_4 e^{\lambda y}]$$



- a) State the boundary conditions (BCs) in terms of $\theta(x, y)$. Write answers on lines below. (4 points)

$$\theta(0, y) = \underline{\quad 0 \quad}$$

$$\theta(L, y) = \underline{\quad 0 \quad}$$

$$\theta(x, 0) = \underline{\quad 0 \quad}$$

$$\theta(x, W) = \underline{\quad 1 \quad}$$

Because of the nature of this problem, this problem is **ALL OR NOTHING**

(+4 points if all boundary conditions above are correct)

- b) Apply these boundary conditions from part a) to the exact solution and determine if $C_1, C_2, C_3,$ and C_4 are zero or non-zero. For convenience the solution to the PDE has been copied from the previous page. **Circle all final answers for full credit. (10 points)**

$$\theta(x, y) = [C_1 \cos(\lambda x) + C_2 \sin(\lambda x)][C_3 e^{-\lambda y} + C_4 e^{\lambda y}]$$

Apply condition #1: $\theta(0, y) = 0$

$$\begin{aligned} \theta(0, y) &= [C_1 \cos(0) + C_2 \sin(0)][C_3 e^{-\lambda y} + C_4 e^{\lambda y}] = 0 \\ \sin(0) = 0, \cos(0) = 1 &\therefore \theta(0, y) = [C_1][C_3 e^{-\lambda y} + C_4 e^{\lambda y}] \therefore C_1 = 0 \end{aligned}$$

(+2 points for determining that $C_1 = 0$)

Apply condition #2: $\theta(L, y) = 0$

$$\theta(L, y) = [C_2 \sin(\lambda L)][C_3 e^{-\lambda y} + C_4 e^{\lambda y}] = 0$$

From this we can see that $C_2 \neq 0$ since then it will mean that $\theta(x, y) = 0$ for all x and y .

(+2 points for determining that C_2 does not equal 0)

Apply condition #3: $\theta(x, 0) = 0$

$$\theta(x, 0) = [C_2 \sin(\lambda x)][C_3 e^0 + C_4 e^0] = [C_2 \sin(\lambda x)][C_3 + C_4] = 0$$

From this we know that since $C_2 \neq 0$, and since x does not have to be an integer means the only way to have this boundary condition work is if $C_3 = -C_4$, and that **neither are zero**.

(+4 points for determining that C_3 and C_4 are not zero)

(+2 points for determining that $C_3 = -C_4$ are not zero)

- c) Determine all possible values for λ . Explain your answer (1-2 sentences). (3 points)

We know from the previous problem that $[C_2 \sin(\lambda L)] = 0$ and that $C_2 \neq 0$. As a result we know that $\sin(\lambda L) = 0$. Since the sine function is periodic we know that $\sin(n\pi) = 0$ where n is all real integers. This means that:

$$\lambda = \frac{n\pi}{L} \text{ where } n = 0, \pm 1, \pm 2, \pm 3, \dots$$

+3 point for determining the correct values of lambda, (the \pm symbol is not necessary for full credit) **AND** a proper explanation that shows the student did not simply go to part e) and copy the answer.

Note, if the student only writes the answer, no points will be awarded!

- d) Through the application of orthogonality, and the definition of the hyperbolic sine function, the finalized form of the PDE can be solved and is given below:

$$\sinh(\phi) = \frac{e^{\phi} - e^{-\phi}}{2} \quad C_n = \frac{2}{n\pi} \cdot \frac{(-1)^{n+1} + 1}{\sinh(\lambda W)}$$

$$\theta\left(\frac{L}{2}, \frac{L}{2}\right) = \sum_{n=1}^{\infty} C_n \left[\sin\left(\frac{n\pi}{2}\right) \right] \left[\sinh\left(\frac{n\pi}{2}\right) \right]$$

The solution form above is accurate for a system where $L = W$, $T_1 = 100^\circ\text{C}$, and $T_2 = 150^\circ\text{C}$. determine what the fewest number of terms in the infinite summation that are needed to give a “good approximation” (relative error less than **0.005%**) for the temperature of the plate at the center location. Use this approximation to calculate the temperature at the center of the plate to **three** decimal places. Justify your answer (1-2 sentences). (24 points)

When looking for this series to somewhat converge student should note that it is the constant C_n that will have the biggest impact on the term of the series.

When n = even integer, $C_n = 0$

+2 points for determining that all even terms in the infinite sum cancel out

This means only the odd modes contribute to the final temperature distribution

$$C_1 = \frac{2}{\pi} \cdot \frac{(-1)^2 + 1}{\sinh\left(\frac{\pi}{L}W\right)} = \frac{2}{\pi} \cdot \frac{2}{\sinh(\pi)} = 0.11025$$

$$C_3 = \frac{2}{3\pi} \cdot \frac{(-1)^2 + 1}{\sinh\left(\frac{3\pi}{L}W\right)} = \frac{2}{3\pi} \cdot \frac{2}{\sinh(3\pi)} = 6.85 \cdot 10^{-5}$$

$$C_5 = \frac{2}{5\pi} \cdot \frac{(-1)^2 + 1}{\sinh\left(\frac{5\pi}{L}W\right)} = \frac{2}{5\pi} \cdot \frac{2}{\sinh(5\pi)} = 7.675 \cdot 10^{-8}$$

+2 points correctly calculating each of the constants above (6 points total)

From this we can easily see that C_n decreases extremely quickly. This means we probably do not need many terms for a good approximation, but we can also note that the sinh term in the exact solution increases quickly as well.

$$\theta_1\left(\frac{L}{2}, \frac{L}{2}\right) = (0.1102 \cdot 2.313) = 0.253716$$

$$\theta_3\left(\frac{L}{2}, \frac{L}{2}\right) = (0.11025 \cdot 2.313) + (6.85 \cdot 10^{-5} \cdot -55.6544) = 0.24228$$

$$\theta_5\left(\frac{L}{2}, \frac{L}{2}\right) = (0.1102 \cdot 2.313) + (6.85 \cdot 10^{-5} \cdot -55.6544) + (7.675 \cdot 10^{-8} \cdot -1288) = 0.24277$$

+2 points correctly calculating each of the theta values above (6 points total)

$$T_{1Term} \left(\frac{L}{2}, \frac{L}{2} \right) = 100^{\circ}\text{C} + 50^{\circ}\text{C} \cdot \theta_1 = 112.69^{\circ}\text{C}$$

$$T_{3Term} \left(\frac{L}{2}, \frac{L}{2} \right) = 100^{\circ}\text{C} + 50^{\circ}\text{C} \cdot \theta_3 = 112.495^{\circ}\text{C}$$

$$T_{5Term} \left(\frac{L}{2}, \frac{L}{2} \right) = 100^{\circ}\text{C} + 50^{\circ}\text{C} \cdot \theta_5 = 112.500^{\circ}\text{C}$$

+2 points correctly calculating each of the center temperature values above (6 points total)

Check relative error of the terms:

$$\text{RelError } T_{3Term} = \frac{|112.69^{\circ}\text{C} - 112.495^{\circ}\text{C}|}{112.495^{\circ}\text{C}} = \mathbf{0.17\%}$$

$$\text{RelError } T_{5Term} = \frac{|112.5^{\circ}\text{C} - 112.495^{\circ}\text{C}|}{112.5^{\circ}\text{C}} = \mathbf{0.004\%}$$

+4 points correctly calculating and determining that three terms gives us the desirable relative error!

- e) What is the heat flux at the corners (0, W) and (L, W) of the hot plate? Give a one sentence explanation for each. **(3 points)**

Heat flux is infinite at point (0, W) and (L, W) because the finite temperature difference occurs across an infinitesimal distance.

+3 points for correctly identifying that the heat flux at these two points on the hot plate are infinite AND give a proper explanation as to why.

- f) What is the heat flux at the corners (0, W) and (L, W) of the hot plate? Give a one sentence explanation for each. **(3 points)**

Heat flux is infinite at point (0, W) and (L, W) because the finite temperature difference occurs across an infinitesimal distance.

+3 points for correctly identifying that the heat flux at these two points on the hot plate are infinite AND give a proper explanation as to why.