Problem 1 (25 points)

a) (4 points) In class, we derived expressions for heat generation G(T) and heat removal R(T) for non-isothermal reactors. Which of the following assumptions apply to these expressions? Circle all that must be true:



The reaction is irreversible -> not newssarily true, The reaction is irreversible -> not newssarily true. Reactor is at steady state -> underlying assumption for mole, energy balances ΔH_{rxn} can change with temperature > we we said $\Delta H(T) \sim \Delta H_{rxn}$ to simplify The reactor is well-mixed > MCS iv. The reactor is well-mixed > MSS analysis for (STRS, which are well-mixed Partial Credit: to if both correct answers circled and 1 incorrect. circled +2 if only 1 correct answer circled, no incorrect answers, b) (6 points) Below is a reactor heat generation curve G(T) for a 1st-order, irreversible, circled liquid phase reaction with $\Delta H^{o}_{rxn} = -4000$ cal/mol. i. Sketch G(T) if the above reaction were instead reversible. Label this curve A. ii. Sketch G(T) for a reaction that is also 1st-order, irreversible, liquid phase and has a similar activation energy to the given G(T), but has $\Delta H^{\circ}_{rxn} = +2000$ cal/mol. Label this curve B. Curve A: 5000 -must be same as G(T) 4000 irreversible curve at low Heat removal,generation (cal/mol) 3000 T, CONVERSIONS 2000 - cannot intersect 1000 given curve 0 - must have a local -1000 B maxima and decrease -2000 (does not plateau) -3000 -4000 700 800 900 400 500 600 300 T(K) Curve B: - plateau at -2000 cal/mol - gets more negative at higher. T, conversions Page 2 of 23

c) (15 points) The following questions pertain to the figure below, which shows heat generation G(T) and heat removal R(T) curves for a first-order, irreversible, liquid-phase reaction. The feed is a mixture of the reactant and inert solvent, both of which have the same heat capacity.

Additional information:

 $\Delta H^{o}_{rxn} = -4000 \text{ cal/mol}$ Inlet temperature T₀ = 322 K, T* = 318 K UA = 20 cal min⁻¹ K⁻¹ and α = 0.2



i. (3 points) During steady-state operation, the reactor operates at a conversion of about X = 0.89. Estimate the operating temperature of the reactor.

T = GIS 12, read off plot
X=0.89 tells you that it is the upper
branch steady state
$$G = -X_A \cdot SH^2rxn$$

 $\frac{3573}{4000} \approx 0.89$

ii. (3 points) The reactor is operating at steady state when a pulse-disturbance causes the reactor temperature to suddenly change to T = 500 K. After the disturbance, all reactor operating parameters immediately return to normal such that the G(T) and R(T) curves above still apply. Sketch the reactor temperature T as a function of time after this sudden temperature change, labeling the T value at very long times as T_{VL} .



500 K is close to the unstable steady state. At 500 K, G is only slightly larger than R So the initial dT is small. Full credit only awarded for 'S' shaped curve between correct initial and final T. iii. (6 points) Reactor extinction would cause a drastic decrease in plant productivity. Assuming an ambient temperature T_a the same as in part (c), estimate the feed temperature that would lead to extinction. Sketch the corresponding R(T) for that feed temperature in the same plot used for part c. What is the steady-state conversion after extinction? Hint: first calculate T_a.

See plot. T* for extinction is -30012.

$$T^{*} = \frac{T_0 + dT_a}{1 + 2} = 300 12 \qquad 0$$
We wont to find To, so we need to calculate
Ta first from the conditions provided:

$$318 = 322 + (0.2) \cdot T_a \qquad 0$$

$$T_a = 298 \text{ k}$$

$$1.2$$
Plug @ into (0) to get:

$$300 = T_0 + (0.2) \cdot (298) = 12 \quad T_0 - 300 \text{ k}$$
field temp
that leads to

extinction.

χ =

20.01

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At To = 300 k, COnversion Very low

1

- iv. (3 points) In this example, what else could cause reactor extinction if the feed temperature were fixed at 322 K? Circle all that apply:
 - i.) Decrease in reactor coolant temperature Ta

ii. Increase in feed flowrate

iii. Increase in reactor heat-exchange area

"What else could cause extinction" is another way of saying "what could cause an increase/shift in heat removal curr ?"

$$R(T) = \overline{C}_{po} (1+2)(T-T^*)$$

- d = UA if A1, then dT FAO Cpo and R(T) slope increases to cause
 - if Ta \downarrow , then $T^* \downarrow$, and R(T) shifts left, can (ause extinction

extinction

if Faot, & J and R(T) slope decreases, maintaining upper branch this may seem counterintaitive, steady state. but as Faot, the reactor becomes more adiabatic because the energy removed by cooling jacket is very Page 6 of 23 Small in comparison to heating of feed.

Problem 2 (20 points)

The zeroth-order reaction $A \rightarrow 2B$ (reaction 1) occurs in a liquid phase, adiabatic, and steady-state reactor. There are no phase transitions in any of the temperature ranges relevant to this problem. Express all your answers using one or more of the following known terms:

 F_{Ao} , T_o , $C_{p,A}$, $C_{p,B}$, T_{Ref} , k_1 , θ_A , θ_B , V, $\Delta H_{rxn,1^o}$ (T_{Ref}) (with units of kcal/mol of A), θ_I , $C_{p,I}$, k_2 , $\Delta H_{rxn,2^o}$ (T_{Ref}) (with units of kcal/mol of A)

a. (5 points) Write a mole balance on A and find an expression for the conversion. Solve for conversion, and do not leave an implicit equation.

$$\frac{dN_A}{dt} = 0 = F_{A0} - F_A + r_A V$$

$$\frac{dF_A}{dV} = r_A, \text{ divide by volume (small change in volume)}$$

$$X = \frac{F_{A0} - F_A}{F_{A0}}, \quad F_{A0} \frac{dX}{dV} = -r_A, \text{ this differential is for a general flow reactor}$$

$$\int \frac{dV}{F_{A0}} = \frac{V}{F_{A0}} = \int \frac{dX}{-r_A} = \frac{1}{k_1} \int dX = \frac{X}{k_1}, \text{ if 0th order, we end up getting something similar to}$$
a CSTR design equation

$$X = \frac{k_1 V}{F_{Ao}}$$

b. (7 points) What is the operating temperature? Your answer should be an explicit expression for the temperature, but not a numeric answer. Use any answers deemed relevant from part (a) in order to solve this part of the problem.
Start with a generic energy balance:

$$Q - W_{s} - F_{Ao} \sum \Theta_{i} C_{pi} (T - T_{io}) - [\Delta H^{o}_{rxn}(T_{R}) + \Delta C_{p} (T - T_{R})] F_{Ao} X_{A} = (\frac{dE}{dt})_{sys}$$

$$- F_{Ao} \sum \Theta_{i} C_{pi} (T - T_{io}) - [\Delta H^{o}_{rxn}(T_{R}) + \Delta C_{p} (T - T_{R})] F_{Ao} X_{A} = 0$$

$$0 = - F_{Ao} \sum \Theta_{i} C_{pi} (T - T_{io}) - [\Delta H^{o}_{rxn}(T_{R}) + \Delta C_{p} (T - T_{R})] (-r_{A}V)$$

$$T = \frac{-F_{Ao} \sum \Theta_{i} C_{pi} (-T_{io}) - [\Delta H^{o}_{rxn}(T_{R}) + \Delta C_{p} (-T_{R})] (-r_{A}V)}{F_{Ao} \sum \Theta_{i} C_{pi} + \Delta C_{p} (-r_{A}V)}$$

$$\frac{r_{A}}{1} = \frac{-r_{B}}{2} = -0.5k_{1}$$

$$T = \frac{-F_{Ao} (-T_{o}) [\Theta_{A} C_{pA} + \Theta_{B} C_{pB}] - [\Delta H^{o}_{rxn,1} (T_{Ref}) + (2C_{pB} - C_{pA})] (-T_{Ref})] (k_{1}V)}{F_{Ao} [\Theta_{A} C_{pA} + \Theta_{B} C_{pB}] - (2C_{pB} - C_{pA})k_{1}V}$$

c. (8 points) It was discovered that during operation, A reacts on its own to form a side product, U, in a second, separate reaction with rate constant k_2 and heat of reaction $\Delta H_{rxn,2}$

(units of kcal/mol of A): $2A \longrightarrow U$. There is no U initially in the feed. Find an expression to determine the operating temperature. You do not have to solve for an explicit expression for the temperature for this part, as long as every other term in the equation is in terms of constants that are known. Do not use conversion (X), but rather use the overall rate of reaction for a given reaction.

The term accounting for the heats of reactions (generation).

$$\begin{split} 0 &= -F_{Ao} \sum \theta_i C_{pi} (T - T_o) - V \sum [\Delta H_i^o (T_{Ref}) + \Delta C_p (T - T_{Ref})] (-r_i) \\ \frac{r_A}{2} &= \frac{-r_U}{1} = -k_2 \\ 0 &= -F_{Ao} (\theta_A C_{pA} + \theta_B C_{pB} + \theta_U C_{pU}) (T - T_o) - V [k_1 (\Delta H_1^o (T_R) + (2C_{pB} - C_{pA}) (T - T_{Ref})) + 2k_2 (\Delta H_2^o (T_{Ref}) + (C_{p,U} - 2C_{pA}) (T - T_R))] \end{split}$$

Don't need to include theta U since there is no initial U

Consider the following reversible, ideal gas-phase reaction:

$$A_{(g)} + B_{(g)} \leftrightarrow C_{(g)} + 3D_{(g)}$$

The reaction is carried out adiabatically at steady state in an isobaric PFR with an inlet pressure of 5 bar, inlet temperature of 1100 K, and inlet volumetric flow rate of 500 L/h, with a molar ratio of 3:1 B:A. The rate constant, k, at 648 K is $1.842 \times 10^{-9} (\text{kmol})/(\text{kg}_{cat}*\text{hr}*\text{bar}_2)$, the heat of reaction at 648 K is 200 kJ/mol, the activation energy is 240.1 kJ/mol, and the rate law (in terms of partial pressures) is:

$$r = k \left(P_A P_B - \frac{P_C P_D^3}{K_p} \right)$$

The molar heat capacities for A, B, C, and D are 60, 60, 60, and 20 J/(mol*K), respectively, and are independent of temperature (note that ΔC_p of reaction is 0). The ideal gas constant is 8.314*10-2 (L*bar)/(K*mol). Note that there are no phase transitions involving any of the chemical species in the temperature ranges relevant to the problem.

You would like to design a three-stage PFR system, with interstage **cooling** or **heating** (your choice) to maximize overall conversion. In other words, your process contains three reactors and two coolers/heaters as shown in the following diagram.



- a) (5 points) For this reaction:
 - i) (3 points) Should you use coolers or heaters between the PFRs to maximize conversion? You must justify your answer to receive credit.

use heaters ble the reaction is endothermic, which means A+ B + every = C+ 3D According to Le Chatelier's principle for reactions @ equilibrium, increasing the amount of reactants (energy here using heating), we can shift the reaction forward to increase conversion of the reactants.

 i) (2 points) Which of the following equilibrium conversion curves is a correct representation of the reaction defined above? Circle A or B and justify your answer to receive credit. You may refer to your explanation in (i) to justify your answer, but answers without justification receive no credit.



Note that receiving points for (ii) hinged on your explanation in (i).

b) (12 points) Write all of the equations that would need to be solved to determine the reactor volume needed to achieve a specified conversion in any one of the PFRs. Your equations should be symbolic and **in terms of all or some of the following**: CP,A, CP,B, CP,C, CP,D, $\Delta H_{rxn}(T_{ref})$, X, V, FA0, T, T0, k', Ea, R, ν , ν_0 , PA, PB, PC, PD, Θ_A , Θ_B , Θ_C , Θ_D , r', rA.

1) Mole balances a= molar rate $==-r_1 \quad \frac{dF_B}{dV} = -r_1 \quad \frac{dF_E}{dV} = r_1$ dFo $\frac{dX}{dV} = \frac{-F_A}{F_{AQ}}$ (1b) 2) rate law (2 a and b $r' = K' \left(P_A P_B - \frac{P_c P_b^3}{K_e} \right) / [K'(T) = 1.842 \times 10^{-9} exp$ 3) <u>stoichiometry</u> Since r' is in terms of P_i , we P_i to molar Flow rates OR We Know $P_s = F_s RT$ $V = v_0 \frac{F_T}{F_s}$

Additional space for (b) if needed

3) <u>Mole balance (contrd</u>) $F_{j} = F_{Ao} \left(\Theta_{j} + \frac{j}{1 + 1} X \right)$ j>0 for product $T_{A} = F_{AO} \left(\Theta_{j} + \frac{j}{1 + 1} X \right)$ j>0 for product $\Theta_{j} = \frac{F_{AO}}{F_{AO}}$ $F_{J} = F_{AO} \left(1 - X \right)$ $F_{c} = F_{AO} \cdot X$ $F_{B} = F_{AO} \left(3 - X \right)$ $F_{O} = 3F_{AO} X$ 4) Every balance $X = \frac{\frac{2}{5}\Theta_{5}(T-T_{5,0})(e_{1,5})}{-\left[\Delta H_{0,0}^{\circ}(T_{R}) + (T-T_{R})\Delta(e_{RX,0})\right]}$ (4 a and

- c) (8 points) Determine the maximum final outlet conversion resulting from the process shown in the diagram above if the following is known:
 - i) 99.9% of the equilibrium conversion of A is reached in each reactor.
 - ii) You are able to **heat** or **cool** the feed to the second and third reactors back to the inlet temperature of 1100 K rather than leaving the feed at the previous reactor's outlet temperature.

Hint: You will need to use one of the curves in (a) to answer this question, so they are conveniently reproduced for you below. Use the one you chose in (a). And be sure to use a ruler or your Call card to produce straight lines.





d) (2 points) Estimate the temperature of the contents exiting the second PFR in your optimized process from (c).

Tz ≈ 945 K From part (d) graph

e) (3 points) Estimate the molar flow rate of D at the outlet of the third PFR in your optimized process from (c).

X3= 0.58 $F_{0} = 3F_{A0}(0.58)$ PAO DO = FAO R TO PAO = 10 FAO = FAO PO =Potro = 1 Po =) $F_{Ao} = \frac{(\frac{1}{4}k_{o})(v_{o})}{k T_{o}} = \frac{(\frac{1}{4})(5 her)(500 \frac{k}{6})}{(8.314 \times 10^{-2} \frac{k.5mr}{m(m)})(1100 \text{ K})}$ = 6.834 mol/hr Thus $F_{0} = (3)(6.834)(0.58)$ $F_{0} = 11.89 \text{ mol/hr}$

Problem 4 (25 points)

A semi-batch stirred tank adiabatic reactor initially contains N_{A0} moles of pure A at a known volume V_0 and temperature T_0 . The liquid-phase reaction $A \rightarrow 2B$ occurs in the reactor. The standard heat of reaction ΔH_R^0 per mole of A reacted for this exothermic reaction at a reference temperature T_{ref} is known, as are the temperature-independent (average) constant-pressure molar heat capacities for all components, denoted as $C_{P,i}$ for any chemical species i; i.e. for diluent d defined below the heat capacity is $C_{P,d}$ whereas for components A and B above it is $C_{P,A}$ and $C_{P,B}$, respectively. In order to cool the reactor, a liquid stream of cool diluent d is added to the reactor, at a known molar flowrate of F_d , volumetric flowrate v_0 , and temperature T_d . There is no outlet stream in this reactor. A scheme is shown below.

Note that there are no phase transitions involving any of the chemical species in the temperature ranges relevant to the problem.



a) (19 points) A technician can measure the conversion X_A at a known time t in this reactor. Assuming adiabatic operation of the reactor, find an expression that explicitly gives the reactor temperature T as a function of X_A , t, and other parameters given in the problem. Additional space for (a) if needed

19.6. Sugar a P.S. 4. S. Sugar S. C. S. S. S.

Adiabatic reactor, so energy released by rxn
must go into heating the reactor feed
energy absorbed by feed and reactants:

$$\sum Ni Cpi (T-T_{io}) =$$

 $NAO (pA (T-T_o) + Nd Cpd (T-Td))$ where $Nd = Fa \cdot t$
 $theragy released by rxn = -NAO \cdot XA \cdot \Delta Hrxn(T)$
 $= -NAO \cdot XA [\Delta H^{O}xn + (2Cp, B - CpA)(T-Tret)]$
 $Fequate and solve for T (XA, t)$
 $T \cdot (NAO (pA + Fa t \cdot Cpid + NAO \cdot XA \cdot \Delta Cp) = -(To NAO \cdot CpA + Td Fat Cpid + NAO \cdot XA (\Delta H^{O}xn - \Delta Cp Tret))$
 $T (XA, t) = -(To NAO CpA + Td Fa t \cdot Cpid + NAO \cdot XA \cdot \Delta Cp)$

b) (4 points) You wish to build a steady-state adiabatic and isobaric PFR that comprises a side-stream inlet of diluent d at temperature T_d, which operates under otherwise similar operating conditions and achieves the same conversion after residence time τ as achieved in the semi-batch reactor in part (a). What should the molar flowrate per unit reactor volume of diluent d be, f_d in the figure below, in order for the moles of d added per initial moles of A to be the same in both reactors, after the same residence "cooking" time τ? Your final answer should be an explicit equation that relates f_d to parameters defined in the problem statement in part (a).

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c) (2 points) Instead of adiabatic operation as in part (a), the semi-batch reactor is now a walled-cooled semi-batch reactor, with now two modes to relieve the exothermicity of the reaction: heating up of the cool diluent, which is continuously being added at T_d, as in part (a), as well as transfer of heat to surroundings. The overall heat transfer coefficient is known to be U, and the heat transfer area is known to be A. The ambient temperature of the heat sink is known to be T_{am}. What is the temperature of the reactor at infinitely long time? Physically justify your answer in a single sentence. Answers without justification receive no credit.

As t>00, T> Tam

Rate of heat generation by rxn goes to zero as reactant is consumed and heat remained MA(T-Tam) will occur until italso approaches zero (T-Tam). へどかたらとないで、大いないたいというというという