CBE 142: Chemical Kinetics & Reaction Engineering

Midterm #2
November 14th, 2019

This exam is printed on **double-sided** pages. It is worth 100 points and 24% of your course grade. You have 80 minutes to complete this exam, so please manage time wisely. Please read through the questions carefully before giving your response. **Make sure to SHOW ALL YOUR WORK and BOX your final answers! Answers without a clear and legible thought process will receive no credit**.

Name (Print clearly in box):

Student ID (Print clearly in box):

Section (Day/GSI) that you **attend**: ________________________________

You are allowed one 8.5''x11'' sheet of paper (front and back) and a calculator for this exam. **You should have more space than is needed to solve all problems.**

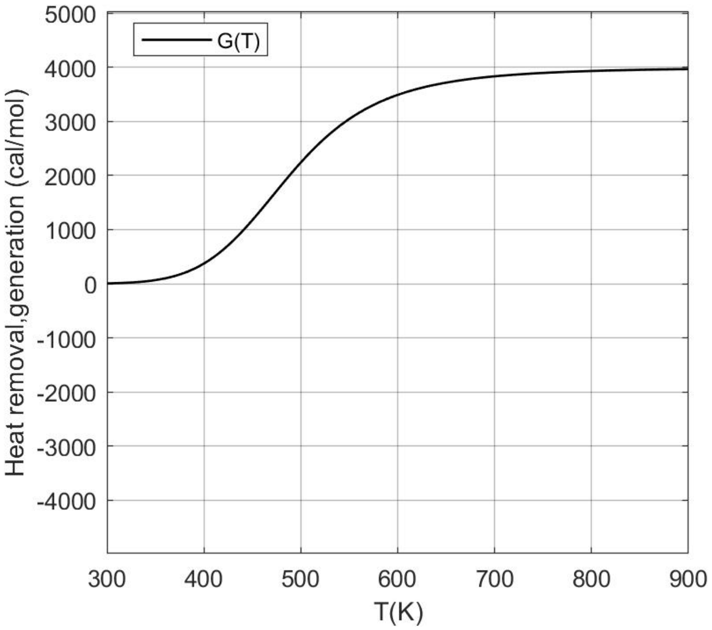
Problem	**Max Points**	**Points Earned**
1	25	
2	20	
3	30	
4	25	

TOTAL : ______ / 100

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 <u>must</u> be true:**
   i. The reaction is irreversible
   ii. Reactor is at steady state
   iii. ΔH_{rxn} can change with temperature
   iv. The reactor is well-mixed

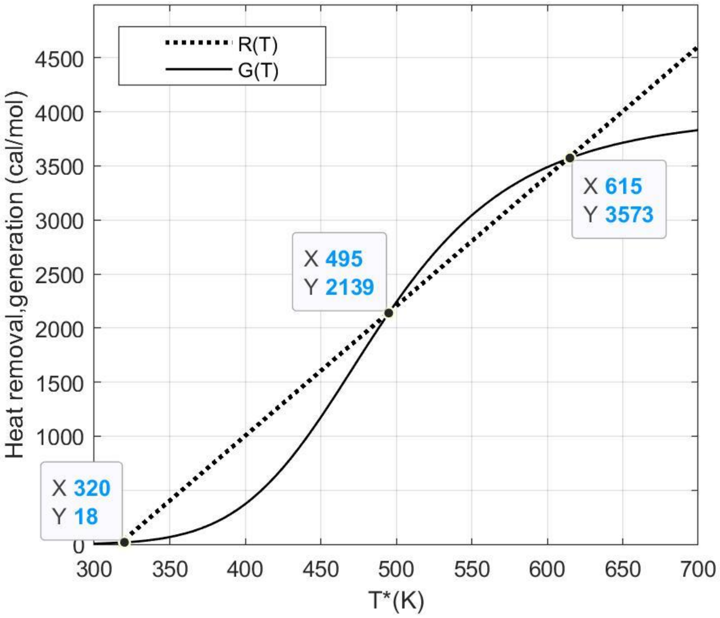
b) (6 points) Below is a reactor heat generation curve G(T) for a 1st-order, irreversible, liquid phase reaction with $\Delta H^o_{rxn} = -4000$ cal/mol.
   i. Sketch G(T) if the above reaction were instead reversible. **Label this curve A.**
   ii. Sketch G(T) for a reaction that is also 1st-order, irreversible, liquid phase and has a similar activation energy to the given G(T), but has $\Delta H^o_{rxn} = +2000$ cal/mol. **Label this curve B.**



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:

ΔH^{o}_{rxn} = -4000 cal/mol
Inlet temperature T_0 = 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.

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}.

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.

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 T_a
  ii. Increase in feed flowrate
  iii. Increase in reactor heat-exchange area

Problem 2 (20 points)

The zeroth-order reaction A → 2B (reaction 1) occurs in a liquid phase, adiabatic flow reactor at steady state. 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, $\Delta H^o_{rxn,1}(T_{Ref})$ (with units of kcal/mol of A), θ_I, $C_{p,I}$, k_2, $\Delta H^o_{rxn,2}(T_{Ref})$ (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 explicitly; do not leave an implicit equation.

b. (7 points) Write an **implicit** expression that can be used to solve for the operating temperature of the flow reactor, but do not solve it. Use any answers deemed relevant from part (a) for this part of the problem.

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 a zeroth-order rate constant k_2 and heat of reaction ΔHrxn,2 (units of kcal/mol of A): 2A → 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. Because this question involves multiple reactions, the typical conversion X will not work. Instead, evaluate the rate in terms of the rate law, and use this rate for each relevant reaction.

Additional space for Problem 2 if needed. If you use this space, make sure to indicate which part of the problem you're using it for.

Problem 3 (30 points)

Consider the following reversible, ideal gas-phase reaction:

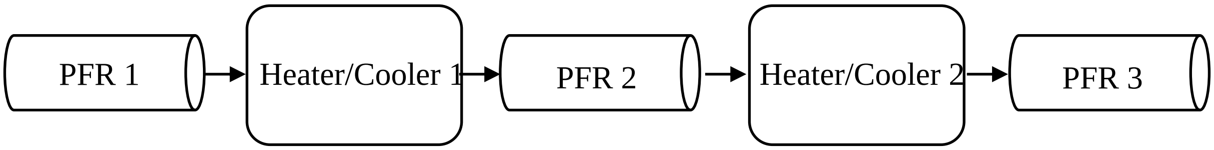
$$A_{(g)} + B_{(g)} \leftrightarrow C_{(g)} + 3D_{(g)}$$

The reaction is carried out adiabatically and isobarically at steady state in a flow reactor system, 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, for the forward reaction at 648 K is 1.842×10^{-9} (kmol)/(kg_{cat}*hr*bar^2), the heat of reaction at 648 K is 200 kJ/mol, the activation energy for the forward reaction is 240.1 kJ/mol, and the rate law (in terms of partial pressures) is:

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

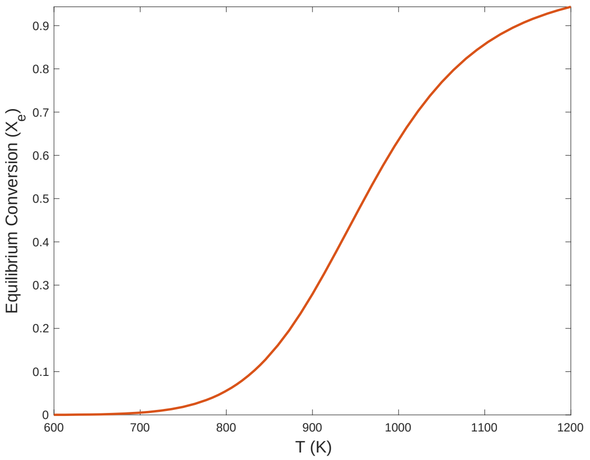
The molar heat capacities for A, B, C, and D are 60, 60, 60, and 20 J/(mol*K), respectively, and are independent of temperature. Note that ΔC_p of reaction is 0. The ideal gas constant is 8.314×10^{-2} (L*bar)/(K*mol). Note that there are no phase transitions involving any of the chemical species in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

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

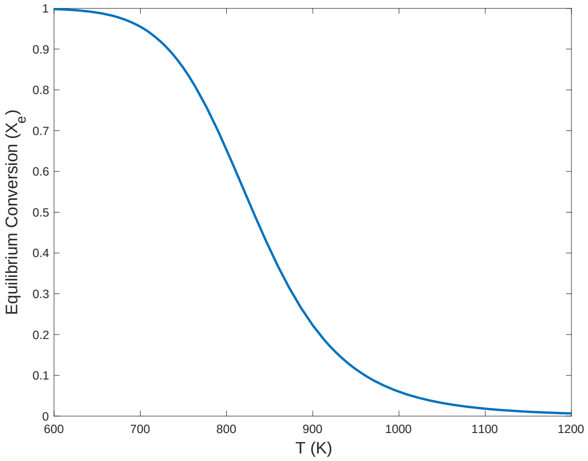


a) (5 points) For this reaction:
    i) (3 points) Should you use coolers or heaters between the PFRs to maximize conversion? You must justify your answer to receive credit.

ii) (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.



A



B

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**: $C_{P,A}$, $C_{P,B}$, $C_{P,C}$, $C_{P,D}$, $\Delta H_{rxn}(T_{ref})$, X, V, F_{A0}, T, T_0, k’, E_a, R, ν, ν_0, P_A, P_B, P_C, P_D, Θ_A, Θ_B, Θ_C, Θ_D, r’, r_A.

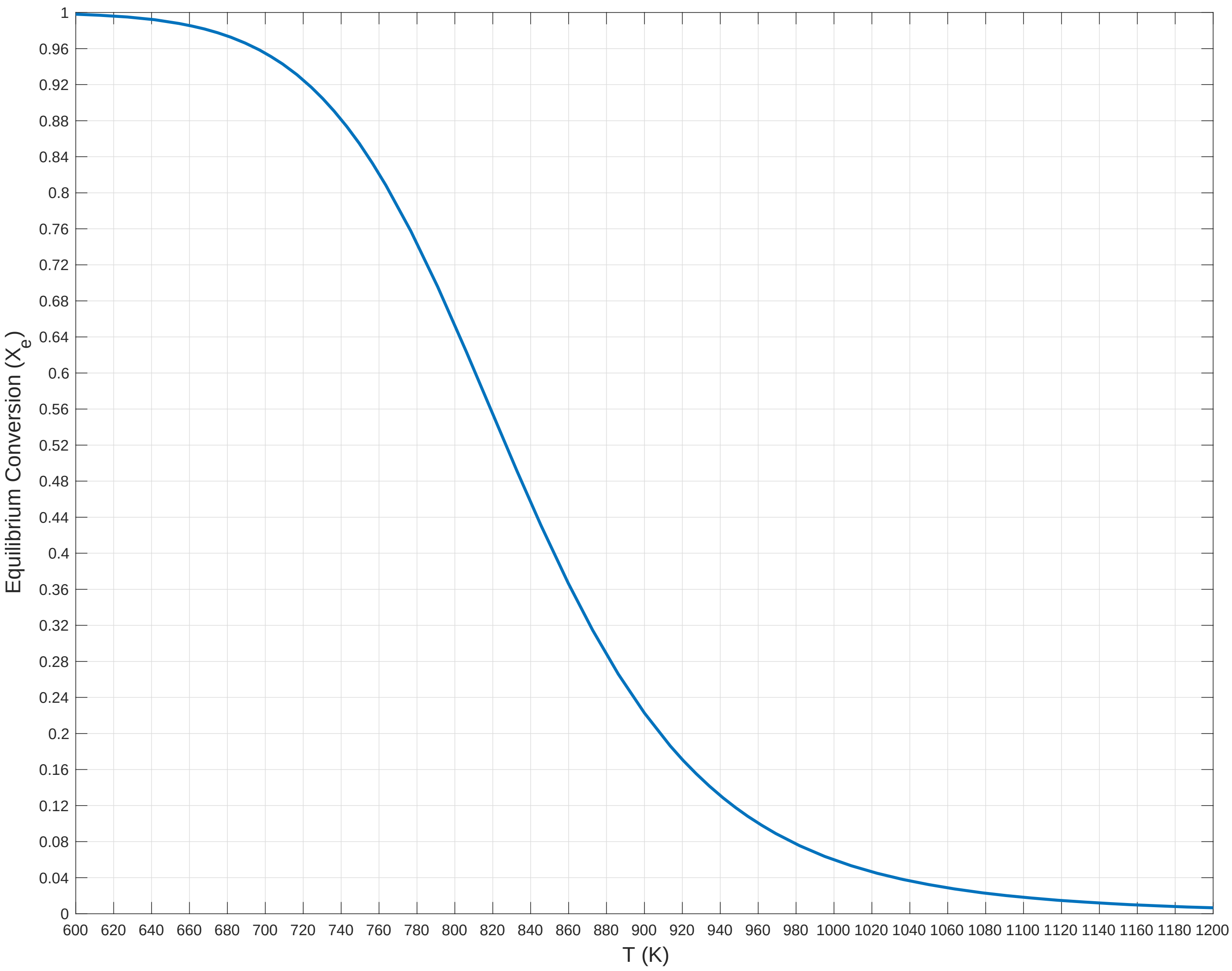
Additional space for (b) if needed

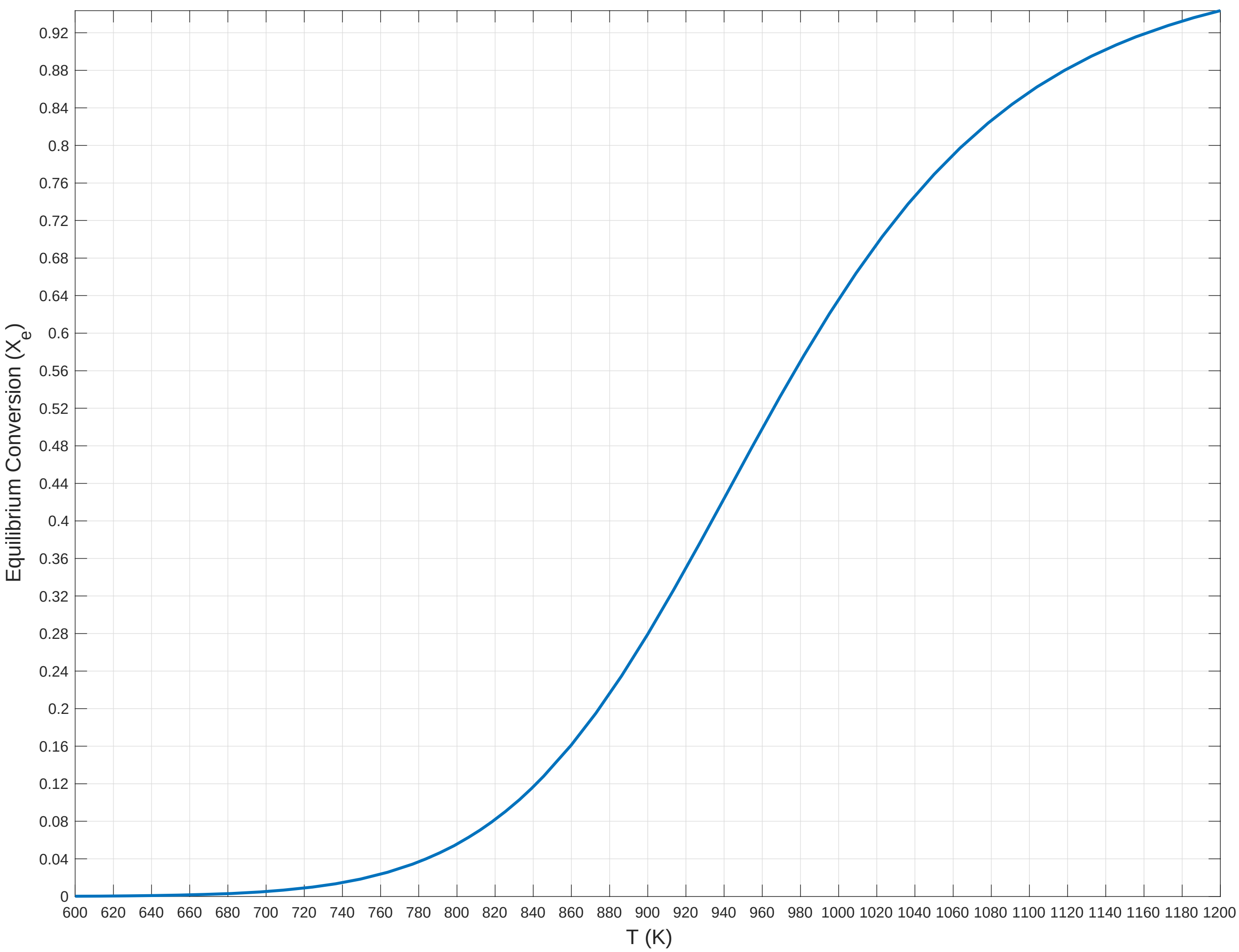
c) (8 points) Determine the maximum final outlet conversion resulting from the process shown in the diagram above if the following is known:

   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 Cal1 card to produce straight lines.


Equilibrium Conversion (X_e)
T (K)
1
0.96
0.92
0.88
0.84
0.8
0.76
0.72
0.68
0.64
0.6
0.56
0.52
0.48
0.44
0.4
0.36
0.32
0.28
0.24
0.2
0.16
0.12
0.08
0.04
0
600 620 640 660 680 700 720 740 760 780 800 820 840 860 880 900 920 940 960 980 1000 1020 1040 1060 1080 1100 1120 1140 1160 1180 1200


Equilibrium Conversion (X_e)
T (K)
0
0.04
0.08
0.12
0.16
0.2
0.24
0.28
0.32
0.36
0.4
0.44
0.48
0.52
0.56
0.6
0.64
0.68
0.72
0.76
0.8
0.84
0.88
0.92
600
620
640
660
680
700
720
740
760
780
800
820
840
860
880
900
920
940
960
980
1000
1020
1040
1060
1080
1100
1120
1140
1160
1180
1200

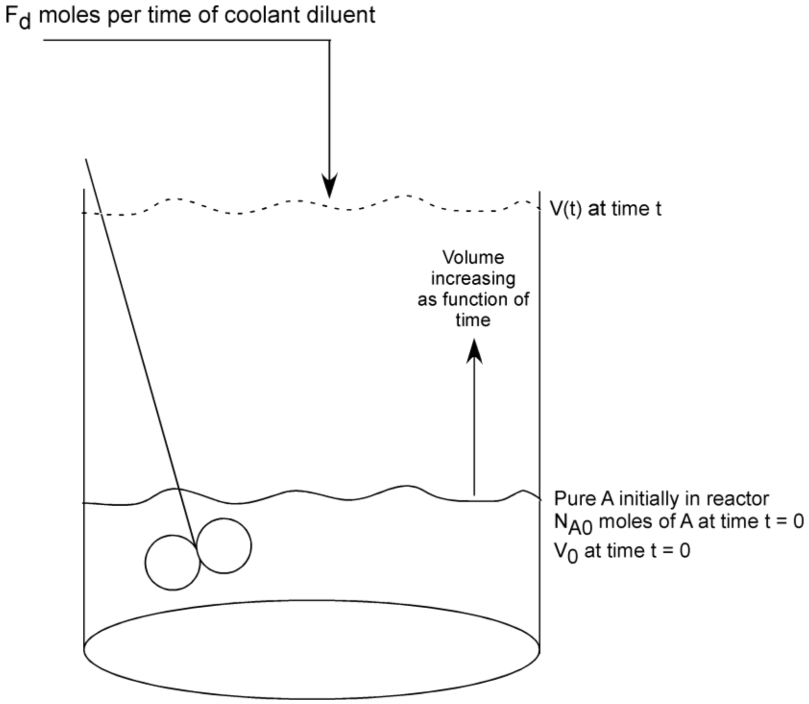
d) (2 points) Estimate the temperature of the contents exiting the second PFR in your optimized process from (c).

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

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.

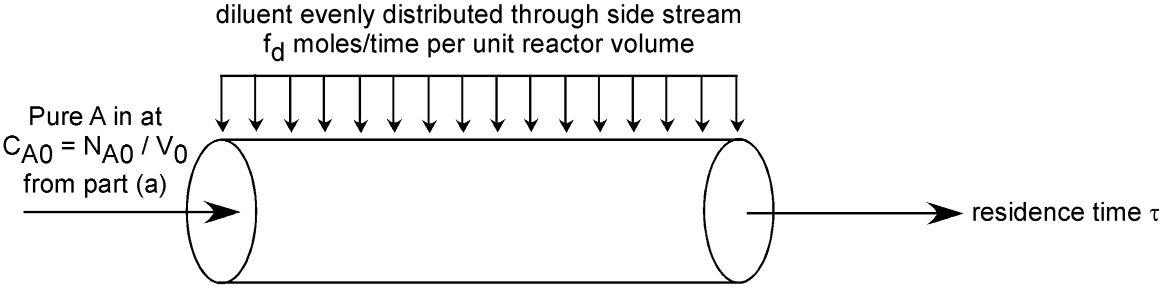
Note that there are no phase transitions involving any of the chemical species in the temperature ranges relevant to the problem.



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

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).



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.