Key

CBE 142: Chemical Kinetics & Reaction Engineering

Midterm #2

November 5th 2015

This exam is worth 160 points and 20% 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: ____

Student ID: ____

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. Any additional paper you wish to be graded must have your NAME and STUDENT ID written on each page.

Problem	**Max Points**	**Points Earned**
1	15	15
2	10	10
3	40	40
4	40	40
5	55	55

TOTAL : 160/160

1.) [15 PTS TOTAL] Adiabatic, steady-state reactor operation

An adiabatic vessel of unknown reactor type and unknown volume is operating at steady state and contains the following elementary gas phase decomposition reaction:

$$A \overset{k}{\rightarrow} 2B$$

You also know that there is no shaft work in the vessel. The reactor feed is pure A and the total inlet molar flow rate is 10 mol/s with a volumetric flowrate of 100 liter/s and an inlet temperature of $T_o = 300$ K. Additionally, the following data is known:

$\Delta H^o_R(300\text{ K}) = -10000$ cal / mol
$E = 10{,}000$ cal / mol
$k(300\text{ K}) = 0.6$ liter /mol-s
$C_{pA} = 30$ cal /mol K
$C_{pB} = 15$ cal/mol-K

a.) [5 PTS] If the outlet temperature is measured at T = 500 K, what conversion have you achieved in the vessel?

Integral Energy Balance

$$\cancelto{0}{\dot{Q}} - \cancelto{0}{\dot{W}_s} + \sum F_i H_i\big|_{in} - \sum F_i H_i\big|_{out} = \cancelto{0}{\frac{dE_{sys}}{dt}} \qquad \boxed{+\ 1\ \text{PT}}$$

$$\sum \Theta_i \hat{C}_{pi}(T - T_o) = -\Delta H_{rxn}(T)\, X \qquad \boxed{+\ 2\ \text{PTS}}$$

$$\downarrow \Delta \hat{C}_p = 0$$

$$X = \frac{C_{pA}(T - T_o)}{-\Delta H_{rxn}} = \frac{30\ \frac{\text{cal}}{\text{mol K}}(500\text{K} - 300\text{K})}{10000\ \text{cal/mol}}$$

$$\boxed{X = 0.6} \qquad \boxed{+\ 2\ \text{PTS}}$$

b.) [5 PTS] Now imagine placing a cooling unit around this vessel. What would be the total heat load, $\dot{Q}$, placed on the coolant in order to maintain isothermal reactor operation?

If isothermal w/ integral cooling:

$\dot{Q} - \overset{0}{\cancel{\dot{W}_s}} + \sum F_i H_i|_{in} - \sum F_i H_i|_{out} = 0$ $\boxed{+1\ \text{PT}}$

$\dot{Q} = \dot{W}_s - F_{A0}\sum \Theta_i \overset{0}{\cancel{C_{p_i}}}(T-T_0) - F_{A0}X[\Delta H^\circ_{rxn} + \cancel{\Delta C_p}(\overset{0}{T-T_R})] = 0$ $\boxed{+2\text{PTS}}$

$\dot{Q} = +F_{A0}\Delta H^\circ_{rxn} X$ b/c $T = T_0$ $\boxed{+1\ \text{PT}}$

$\dot{Q} = -10\ \text{mol/s} \cdot 10{,}000\ \frac{\text{cal}}{\text{mol}} \cdot 0.6 = 100{,}000\ \frac{\text{cal}}{\text{s}} \cdot 0.6$

$\boxed{\dot{Q} = -60\ \text{kcal/s}}$ $\boxed{+1\ \text{PTS}}$

c.) [5 PTS] Continuing from part (b), you now know that the coolant is available at $T_A = 270$K, and the overall heat transfer coefficient from the reactor to the fluid is given by 2,000 cal/(s m^2 K). How much surface area must your reactor have if the temperature rise is to be limited to 100 K above the inlet temperature? **NOTE:** If there is a piece of information missing that you need to solve the problem, please tell us in one succinct sentence what is preventing you from obtaining a numerical answer.

We need to know the reactor type, if T is uniform throughout (CSTR) or if T varies as a function of location in the reactor (PFR) will dictate how we handle $\dot{Q}$. without this info we can't solve for the surface area required.

$\boxed{+5\ \text{PTS}}$

or

If you assumed CSTR and said $\dot{Q} = UA(T_A - T)$ $\boxed{+1\ \text{PTS}}$ → $\boxed{+2\text{PTS}}$ Calculating a numerical answer

or

If you said we needed to know volume (or volume/area) and used $\frac{dQ}{dV} = U_{av}(T_A - T)$ $\boxed{+3\ \text{PTS}}$

2.) [10 PTS TOTAL] PFR and CSTR comparison for adiabatic reactors

Suppose we have two steady-state reactors, a PFR and a CSTR, that *both* achieve $x_A = 0.7$ for the following *elementary*, irreversible, liquid-phase reaction:

$$A + B \xrightarrow{k} C + D$$

Both reactors are adiabatic, and the $\Delta H_{rxn} << 0$, i.e. it is strongly exothermic.

Given that the reaction has positive order kinetics, is it possible to have a scenario where the volume of the aforementioned CSTR is less than the volume of the aforementioned PFR? Respond **no** or **yes** and provide a justification for your answer in just a few sentences or less.

This is a conceptual question only, **no math required**! Responses that guess the correct answer but provide an incorrect justification will not receive credit.

+10 PTS

Yes, the reactor T must increase from the inlet conditions due to exothermicity and adiabatic operation and the rate constant increases exponentially w/ this T. B/c of mixing in a CSTR, the feed is immediately raised to outlet T, causing an immediate increase in rate (whereas in a PFR the T increase is gradual down the reactor volume) meaning a CSTR could achieve the same conversion with less volume if the rate increase from T effects outplays the dilution effects.

can get +5 for each of underlined statements

---

or wrong answer but still thinking:

+2 PTS

No, dilution effects in a CSTR always make $V_{CSTR} > V_{PFR}$ (But this ignores rate dependence on T, which must be greater than inlet rxtr T for this problem!)

---

or wrong answer but still thinking:

+3 PTS

No, dilution effects. But still mentions T rise in rxtr and interplay of T effects in rxtr

3)[40 POINTS TOTAL] Wall-cooled CSTR with Multiple Steady States

The elementary, reversible, liquid-phase reaction A<->B takes place in a steady-state, wall-cooled CSTR. Pure A enters the reactor. Use the following data to answer the parts of this problem:

- $V = 10\ dm^3$
- $v_0 = 1\ dm^3/min$
- $F_{A0} = 10$ mol/min
- UA= 3600 cal/(min-K)
- $C_{pA} = 40$ J/mol/K
- $C_{pB} = 40$ J/mol/K
- $\Delta H_{rxn}^{o} = -80{,}000$ cal/mol A
- $K_{400\ K} = 100$
- $k_{400K} = 1\ min^{-1}$
- Feed temperature $T_0 = 37^{o}C$
- Ambient temperature $Ta = 37^{o}C$
- The Temperature dependencies of the rate and equilibrium constants are given below by the Arrhenius and Vant Hoff Equations Respectively:

$$k(T) = A_0 \exp\left(-\frac{E_a}{RT}\right)\frac{1}{\min} with \frac{E_a}{R} = 20{,}000K$$

$$\ln\left(\frac{K_2(T)}{K_1(T)}\right) = -\frac{\Delta H_{rxn}^{o}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

a) [10 pts] Derive the heat generated per mole of A reacted, G(T), as a function of the reactor operating temperature (T), CSTR Residence time ($\tau = V/v_0$) and constants given in the data above.

Mol Bal / CSTR Design eqtn:

$$V = \frac{v_0 C_{A0} X}{k\left[C_A - \frac{C_B}{\underline{K}}\right]} = \frac{v_0 C_{A0} X}{k\left[C_{A0}(1-X) - \frac{C_{A0}X}{\underline{K}}\right]} \Rightarrow \frac{kV}{v_0} = \frac{C_{A0}X}{C_{A0}(1-X) - \frac{C_{A0}X}{\underline{K}}} \Rightarrow \frac{X}{1-X-\frac{X}{\underline{K}}} = k\tau$$

$$\Rightarrow X = \frac{k\tau}{1+k\tau\left(1+\frac{1}{\underline{K}}\right)}$$

$$\ln\left[\frac{\underline{K}(T)}{\underline{K}(T_1)}\right] = \frac{\Delta H^\circ_{RXN}(T_R)}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)$$

Van't Hoff: $\underline{K}(T) = \underline{K}(T_1)\exp\left[\frac{\Delta H^\circ_{rxn}(T_R)}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$

Arrhenius: $k = 1\ \text{min}^{-1}\exp\left[20{,}000\left(\frac{1}{400} - \frac{1}{T}\right)\right]$

from E.B. take nonlinear Generation term wrt T, $\div F_{A0}$

$$G(T) = -\Delta H^\circ_{rxn}\, X(\tau,T) \rightarrow \text{Mole Bal}$$

$$= -80{,}000\ \frac{\text{cal}}{\text{mol A}}\left[\frac{\tau k_0 \exp\left[\frac{E_a}{R}\left(\frac{1}{400} - \frac{1}{T}\right)\right]}{1 + \tau k_0 \exp\left[\frac{E}{R}\left(\frac{1}{400} - \frac{1}{T}\right)\right]\left(\frac{1}{\underline{K}(T)} + 1\right)}\right]$$

+ 2.5 POINTS	Mole Balance / CSTR Design equation (Mention)
+ 2.5 POINTS	For correct $X(T)$ expression
+ 2.5 POINTS	$G(T) = -\Delta H_{rxn} X$ (is the nonlinear term in E.B. wrt T)
+ 2.5 POINTS	Final expression for G(T) in terms of $\tau, k_0, E_a, \underline{K}(T)$ (or other variations)

Partial credit given if underlying logic shown.

b) [10 pts] The G(T) behavior you found from part (a) is shown on the graph on the adjacent page. Now on the same graph, plot the heat removed per mole A fed, R(T). Indicate on the plot the location of the three steady-state operating temperatures and explain why each steady state is locally stable or not. Clearly label and calculate T* as well as the relevant slope of R(T). 1 cal = 4.18 J (no points deducted for wrong conversion factors)

$$\alpha = \frac{UA}{C_{pA} F_{A0}} = \frac{3600}{9.6(10)} = 37.5$$

$$T^* \text{ or } T_c = 310 \quad (\because T_0 = T_a)$$

$$R(T) = 9.6\,(1+37.5)(T-310)$$

$$\Rightarrow \quad R(T) = 385\,(T-310)$$

To plot: <u>2 pts</u>

$T = 310$ $\quad R(T) = 0$

$T = 400$ $\quad R(T) = 34650$

No points deducted for minor variations in values read / calculated. (nor for conversion factors associated w/ J ↔ cal)

+ 3 POINTS α, T_c, correct calculation

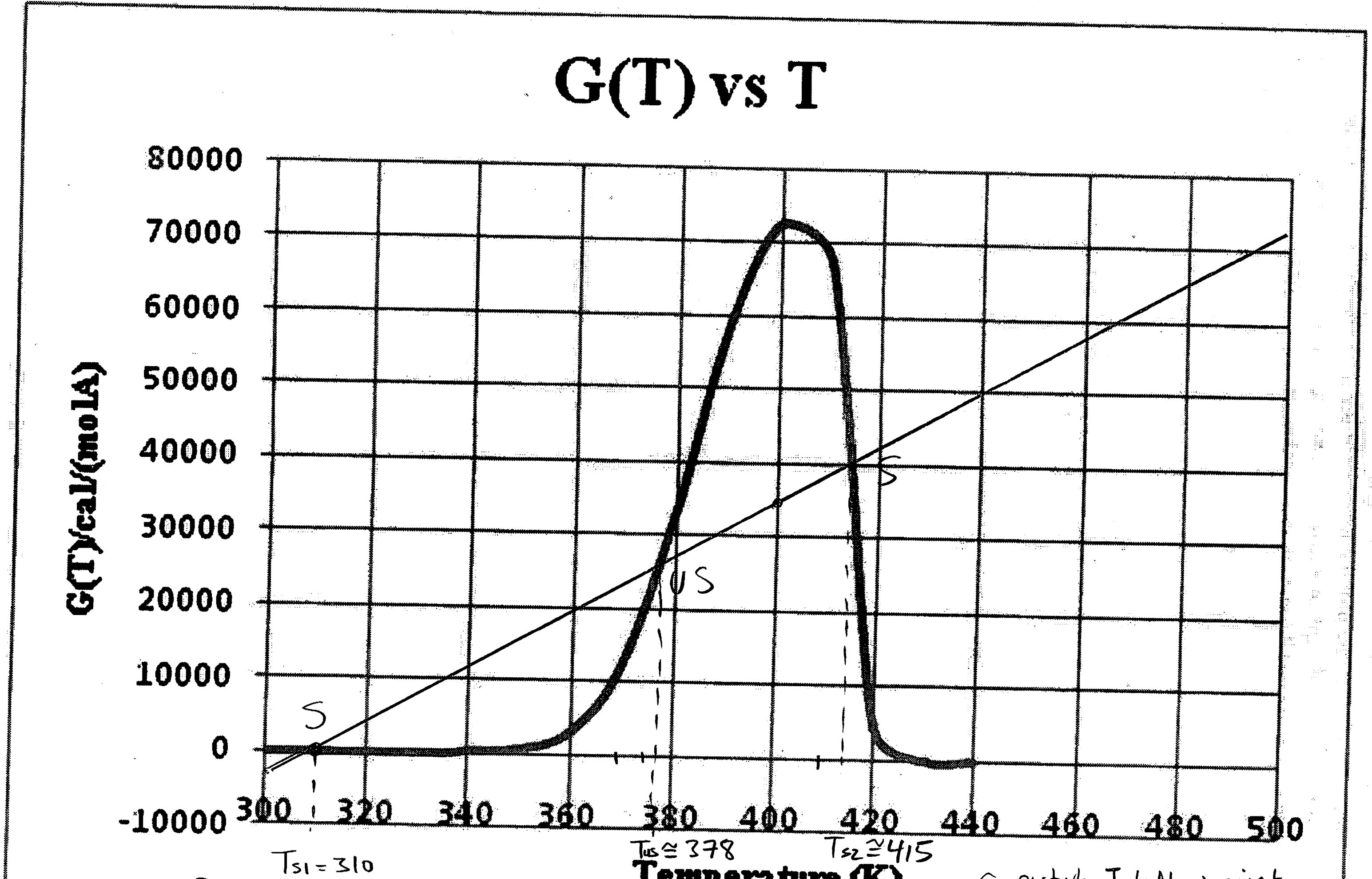
+ 3 POINTS $R(T) = G(T)$ correct application of concept

+ 3 POINTS 3 steady states + explanation for stability

(the two lines above: overlap)

+ 1 POINT $T_{\text{operating}}$ points identified on plot / values provided.

Partial credit given if underlying logic shown



For T_{S1} & T_{S2}

perturb T left => pt moves right ∵ G(T) > R(T)

perturb T right => pt moves left ∵ R(T) > G(T)

=> stays put
STABLE

For T_{US}

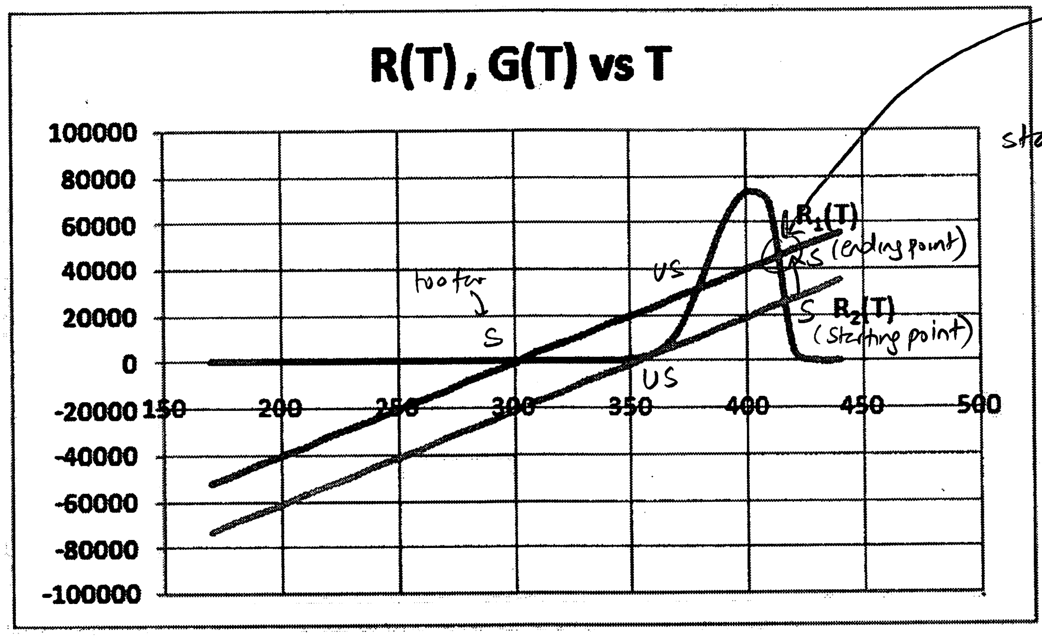
perturb T left => point moves left ∵ R(T) > G(T)

perturb T right => point moves right ∵ G(T) > R(T)

=> doesn't stay put
=> UNSTABLE

c) [5 pts] Assume that you are operating on the $R_2(T)$ line and the $G(T)$ curve below. Suddenly T^* decreases and you are now operating on the $R_1(T)$ line instead. Clearly label the temperature, T, of the new steady state.

Why?



✓ Stable

✓ closest to last stable operating point on $R_2(T)$

+ 2 POINTS SELECTING STABLE POINT(S)

+ 3 POINTS SELECTING CORRECT/NEXT CLOSEST STABLE POINT

Partial credit given on answers if underlying logic shown

d) [15 pts] Determine the heat exchanger product, UA, which gives the maximum conversion of the reactor for the T_o and T_A values given in part (a). Clearly show all reasoning and work – answers without explanation receive zero credit.

* $G(T)$ max @ $\frac{dG(T)}{dT} = 0 \rightarrow \boxed{X_{max}}$ $\because$ rxn exothermic.

$$\therefore \quad G(T) \cong 73000 \quad @ \quad T \cong 400\ K$$

$$= -\Delta H_{rxn} X$$

$$= 80{,}000\ \frac{cal}{mol\ A}\ X_{max}$$

$$\Rightarrow \quad X_{max} = 0.919$$

excel values

* $G(T) = R(T) = 73533.6 = 9.6\,(1+\alpha')(404.6-310)$

$$\Rightarrow \quad \alpha' \cong 80$$

* $\alpha' = \frac{UA'}{C_{pA} F_{A0}} \cong 80 \quad \Rightarrow \quad \boxed{UA' \cong 7680\ \frac{cal}{min\ K}}$

Full Credit provided for values in the range of 6000 – 9000 $\frac{cal}{min\ K}$ if correct logic

+5 POINTS X_{max} @ $G(T)_{max}$ calculation

+5 POINTS α', UA' correct calculation from energy

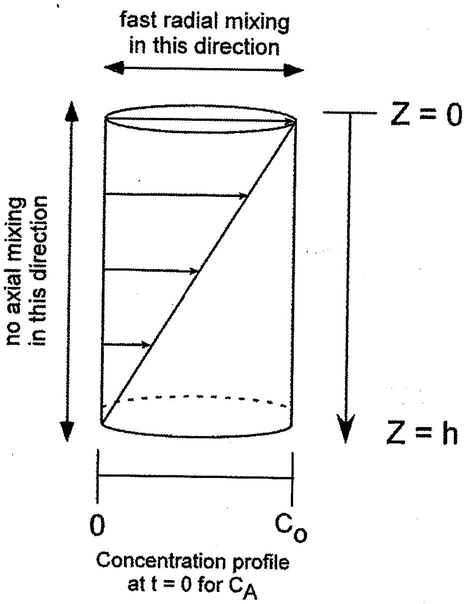
+2.5 POINTS $R(T)$ slope changes, T^* same – concept application

+2.5 POINTS $R(T) = G(T)$ / E.B. – concept application

Partial credit given for any work of remote relevance to solving problem

4.) [40 PTS] Adiabatic batch reactor

The elementary reaction A→B occurs in a tall and thin adiabatic batch reactor, which has no stirring, and as a result, no mixing in the axial direction and fast radial mixing. Reactant A is fed to the reactor in such a way that its profile at time t = 0 as a function of the axial Z direction is shown below and given by: $C_A = C_O (1 - Z/h)$. Assume liquid phase and mercury as solvent in which A is very dilute. Due to the high thermal conductivity of mercury, the temperature within the reactor is uniform everywhere.



Using the data given below, derive an expression for: (a) Reactor temperature at 90% conversion of A and (b) Time it takes to reach 90% conversion of A. Your answer for part (a) should be a number. Your answer for part (b) should be left as an expression that can be evaluated numerically involving either numerical integration and/or numerical evaluation of a nonlinear algebraic equation. However, all terms in the equation should be clearly written out so as to enable evaluation.

Data of possible usefulness for parts (a) and (b) is below. Assume all heat capacities to represent the temperature averaged heat capacity for the temperature window of interest to this problem.

$C_{P\ \text{Mercury Solvent}}$ = 28 J/(mol°C)
$C_{P\ \text{Reactant A}}$ = 30 J/(mol°C)
$C_{P\ \text{Product B}}$ = 30 J/(mol°C)
$C_{\text{Mercury Solvent}}$ = solvent concentration = 67 mol/L
C_O = scaling factor of initial concentration of A according to equation above = 3.35 mol/L
ΔH^{o}_{RXN}= -62,220 J/(mol A reacted °C) = -62.220 kJ/(mol A reacted °C)
$T_O = T_{\text{ambient}}$ = initial reactor temperature = 20 °C
k = 0.1 * exp(-7000/T) min^{-1} where T is the absolute temperature for elementary reaction A→B

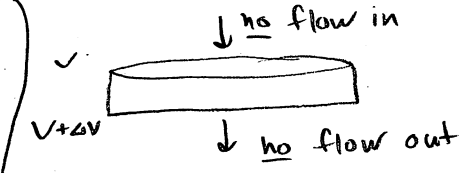
If you need something for solving this problem and do not have it, clearly define it in a box and proceed with solution.

b.) [20 PTS] Derive an expression for the time it takes to reach 90% conversion of A. Leave your answer as an expression that can be evaluated either by numerical integration and/or numerical evaluation of a nonlinear algebraic equation. Does the time to achieve this conversion vary spatially in the reactor? Explain why.

+3 PTS

Display knowledge of problem physics

- Key is extremely fast radial mixing with no axial mixing
- If we draw differential elements down the z-axis they don't communicate w/each other:



} b/c of no axial mixing

- Each differential element is just a batch reactor

. Mole balance on A:

Stoichiometry:

$C_A = C_{A0}(1-x)$ +2 PTS

+2 PTS

$$\frac{dN_A}{dt} = r_A \cdot \Delta V$$

$$-N_{A0}\frac{dx_A}{dt} = -k(T)\,C_A \cdot \Delta V$$

$$-\cancel{C_{A0}}\cancel{\Delta V}\frac{dx_A}{dt} = -k(T)\,\cancel{C_{A0}}(1-x)\cancel{\Delta V}$$

$$\frac{dx_A}{k(T)(1-x)} = dt$$

+3 PTS

$$\frac{dx_A}{(0.1e^{-7000/T})(1-x)} = dt$$

But we have T = fcn(x) from part (a)

$$T = 293 - \frac{(-62200 \cdot 3.35)}{2 \cdot 67.28}x$$

$$T = 293 + 55.5x$$ +3 PTS

Get T = fcn(x)

$$\boxed{t = \int_0^{0.9} \frac{dx_A}{(0.1e^{-7000/(293+55.5x)})(1-x)}}$$

+2 PTS

We can see the time to achieve x = 0.9 does not depend on position b/c there is no C_{A0} = fcn(z) in our final expression. This is a direct result of the rxn being 1st order. If it were 2nd order then your expression for t would depend on C_{A0}

+5 PTS

OR +2-5 if logic makes sense despite wrong answer a.) [20 PTS] Derive an expression for the reactor temperature at 90% conversion of A. Evaluate this expression and give a number for your final answer.

- Uniform T in rxtr allows us to use integral E balance for batch:

B/c $\Delta\hat{C}_p = 0$:

$$T = T_o - \frac{\Delta H_{rxn}^{\circ} X}{\Sigma \Theta_i \tilde{C}_{pi}} \quad \boxed{+10 \text{ PTS}}$$

if $T = T_o - \frac{\Delta H_{rxn} X}{C_{pa}}$ ✗ wrong

or similar can earn 5 – 7 pts for formula depending on mistakes

If no other Eqn or T work, up to +3 pts for realizing need to use E balance

NOTE: If you didn't see you could use the integral E balance from the beginning, would need to derive it:

(1) Batch E balance:

$$\frac{dT}{dt} = \frac{\overset{0}{\dot{Q}} - \overset{0}{\dot{W}_s} + (-\Delta H_{rxn})(-r_A V)}{\Sigma N_i C_{pi}}$$

w/ $\Delta\hat{C}_p = 0$:

$$\frac{dT}{dt} = \frac{\Delta H_{rxn}^{\circ}(r_A V)}{N_{Ao} \Sigma \Theta_i \tilde{C}_{pi}} \quad \boxed{+3 \text{ PTS}}$$

(2) Couple to mole balance:

$$N_{Ao} \frac{dx_A}{dt} = -r_A V \quad \boxed{+3 \text{ PTS}}$$

(3) Sub into E balance:

$$\frac{dT}{dt} = \frac{-\Delta H_{rxn}^{\circ} \frac{dx}{dt}}{N_{Ao} \Sigma \Theta_i \tilde{C}_{pi}}$$

→ cancel dt
→ separate
→ integrate $\boxed{+2 \text{ PTS}}$

(4) Integrate:

$$T - T_o = \frac{-\Delta H_{rxn}^{\circ} X}{\Sigma \Theta_i \tilde{C}_{pi}}$$

$$T = T_o - \frac{\Delta H_{rxn}^{\circ} X}{\Sigma \Theta_i \tilde{C}_{pi}} \quad \boxed{+2 \text{ PTS}}$$

1-3 pts for other relevant simplifications in derivation

$$T = T_o - \frac{\Delta H_{rxn}^{\circ} \cdot X_A}{1 \cdot C_{pA} + \underset{0}{\cancel{\frac{N_{BO}}{N_{Ao}}}} C_{p,B} + \frac{N_{Hg,S}}{N_{Ao}} C_{p,Hg}}$$

→ A is very dilute: $\frac{N_{Hg,o}}{N_{AO}} C_{p,Hg} >> C_{p,A}$ $\boxed{+2 \text{ PTS}}$

($C_{Hg} = 67$, $C_{Ao} < 3.35$ for all z)

$$T \approx T_o - \frac{\Delta H_{rxn}^{\circ} X_A N_{Ao}}{N_{Hg,s} C_{p,Hg}}$$

• Now we need N_{A0}:

$\boxed{+\ 2PTS}$

$$N_{A0} = \int_0^h C_A(z;t=0)\,dz \cdot A_c$$

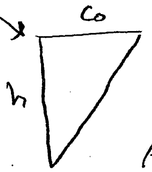
$$N_{A0} = \int_0^h \left(C_0\left(1-\frac{z}{h}\right)\right) dz \cdot A_c$$

$$N_{A0} = C_0\left(z - \frac{z^2}{2h}\right)\Big]_0^h \cdot A_c$$

$$N_{A0} = C_0\frac{h}{2}\cdot A_c = \frac{C_0 V}{2}$$

$\boxed{+3PTS}$

-or-



$A = \frac{1}{2} b\cdot h$

$A = \frac{C_0 h}{2}$

$N_{A0} = A\cdot A_c$

$N_{A0} = \frac{C_0 h\cdot A_c}{2}$

$\rightarrow N_{A0} = \frac{C_0 V}{2}$

• Plug back into T to see that we can cancel V and solve:

$$T = T_0 - \frac{\Delta H_{rxn}^\circ\, x_A\, \frac{C_0 \cancel{V}}{2}}{C_{Hg,s}\cdot \cancel{V}\cdot C_{p,Hg}}$$

$$T = T_0 - \frac{\Delta H_{rxn}^\circ\, x_A\, C_0}{2\cdot C_{Hg,s}\cdot C_{p,Hg}}$$

$\boxed{+\ 2PTS}$

• Evaluate:

$$T = 293K - \frac{\left(-62{,}220\,\frac{J}{mol\,A\cdot K}\cdot 0.9\cdot 3.35\,\frac{mol\,A}{L}\right)}{2\cdot 67\,\frac{mol\,Hg}{L}\cdot 28\,\frac{J}{mol\,Hg\cdot K}}$$

$\boxed{T = 343\ K}$ $\boxed{+1\ PT}$

70 °C

+1 for plugging in even if you forgot $N_{A0} / N_{Hg,0}$

5.) [55 PTS TOTAL] Constant Pressure BSTR

The elementary gas-phase reaction:

A (gas) + B (gas) → C (liquid)

proceeds with rate constant *k*. Non-volatile species C condenses immediately upon formation, such that C occupies no volume in the gas phase, and it can be safely assumed that the volume occupied by liquid C is also negligible.

You employ an isobaric non-isothermal BSTR with initial volume V_0, wherein the reactor volume changes freely at constant pressure. You may assume that shaft work contributes negligibly to the total energy of the system. The initial temperature of reactants is T_0 and temperature-averaged heat capacities of the species are such that $C_{P,A} = C_{P,B} = \frac{1}{2}C_{P,C}$. The reactor is initially charged with equal number of moles $N_{A0} = N_{B0}$.

(a) [10 pts] Derive an expression for the rate of change in conversion (dX_A/dt) as a function of conversion X_A, temperature T, and given constants. HINT: You need only consider a mole balance for part (a), and consider working with N_A rather than C_A as your variable.

mole balance:

$$\frac{dN_A}{dt} = -\overset{(+2)}{k C_A C_B V} = -k \overset{(+1)}{\frac{N_A}{V}\frac{N_B}{\cancel{V}}} \cancel{V} = -\frac{k N_A N_B}{V} \quad +3 \text{ mole balance}$$

$$\text{But } V = V_0 \overset{+1}{\overline{(1-X_A)}}\overset{+1}{\overline{\left(\frac{T}{T_0}\right)}} \text{ where } \varepsilon = 1 \text{ from stoichiometry since C condenses.}$$

[+2 V change, 1pt for T and 1pt for x dependence)

$$N_A = N_B = N_{A0}(1-x_A) \quad +1 \text{ for } N_i(x_A)$$

$$\therefore \frac{d[\cancel{N_{A0}}(1-x_A)]}{dt} = -\frac{k N_{A0}^{\cancel{2}}(1-x)^{\cancel{2}}}{V_0 \cancel{(1-x)} \left(\frac{T}{T_0}\right)} \quad + 1 \text{ solving}$$

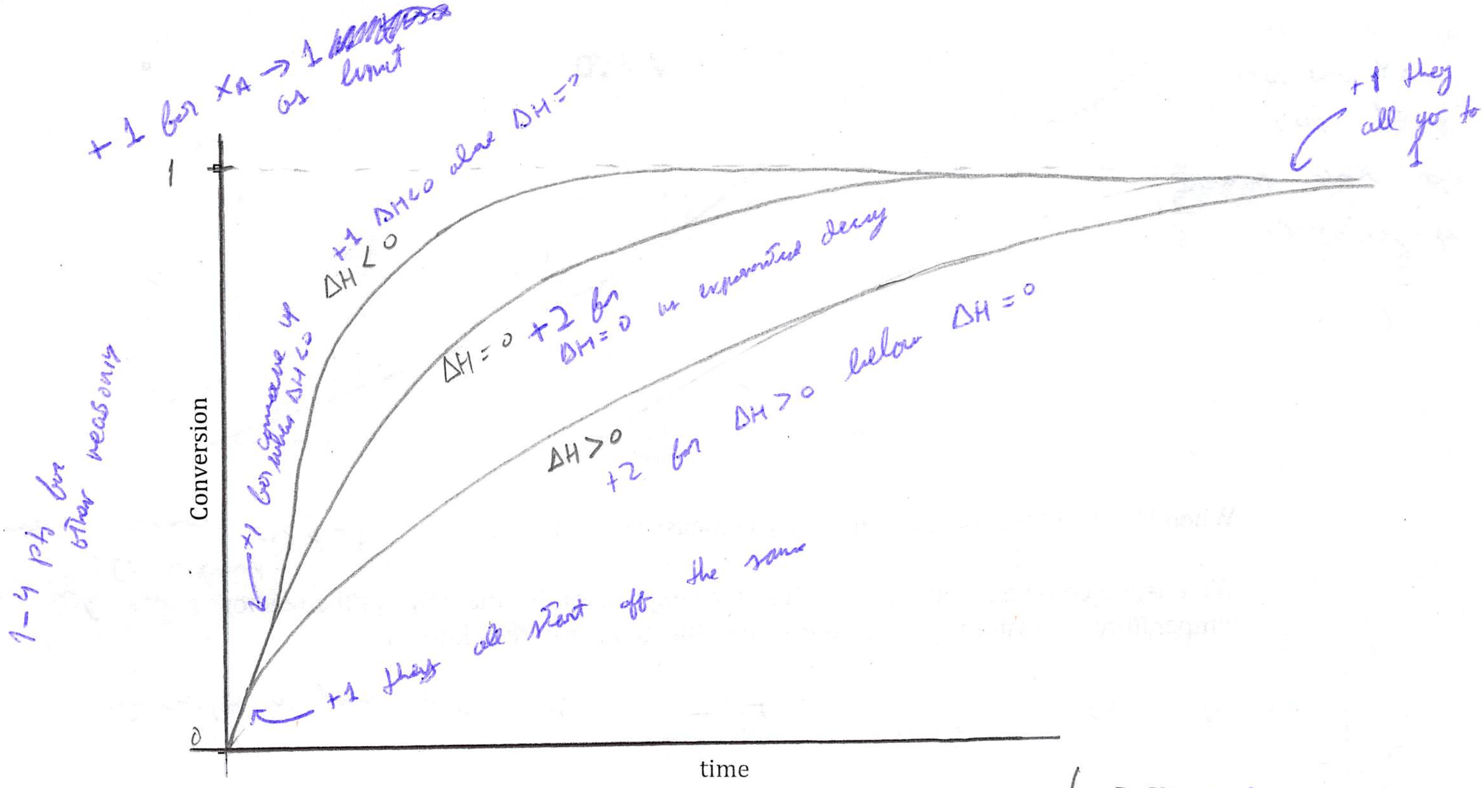
$$\boxed{\frac{dX_A}{dt} = \frac{k N_{A0}}{V_0}\left(\frac{T_0}{T}\right)(1-x)} \quad +1 \text{ find answer}$$

$$\boxed{k = A e^{-\frac{E_a}{RT}}} \quad +2 \text{ T dependence of k}$$

Could also have $PV = nRT \quad \therefore V = \frac{2N_{A0}(1-x)RT}{P_0} \Rightarrow \frac{dX_A}{dt} = \frac{k P_0}{2RT}(1-x)$

+1-2 pts for other reasoning

(b) [10 pts] Sketch the conversion as a function of time for $\Delta H_{rxn} = 0, \Delta H_{rxn} < 0, \Delta H_{rxn} > 0$ if the reactor is operated adiabatically. Label the numerical limits on your plot. Clearly explain and justify any limiting behaviors. Answers without a concise and logical explanation receive no credit.



$t \to \infty$ +1

$t \to \infty$

$\Delta H = 0$ isothermal $X = 1 - e^{-kt}$ exponential decay!

All curves go to 1 as $t \to \infty$

$\Delta H > 0$ implies cooling, so lower T, thus slower conversion.

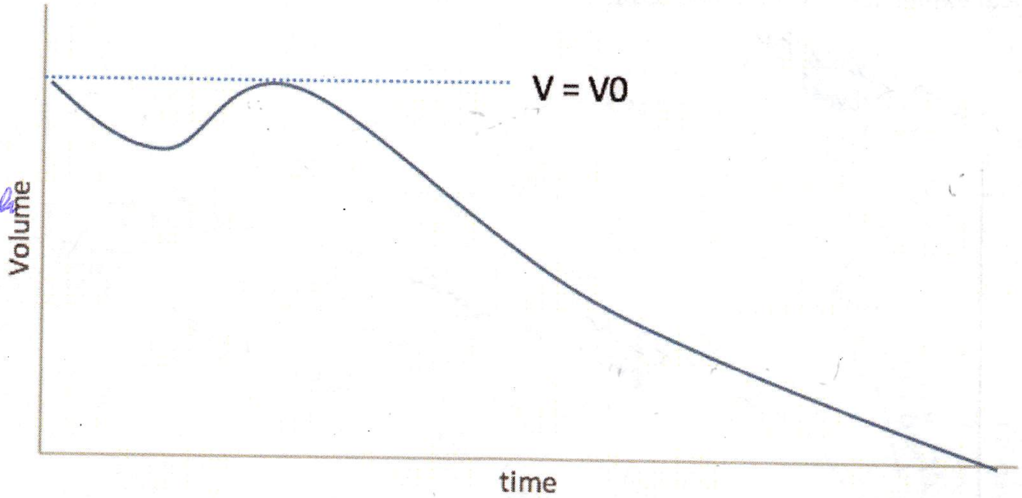
$\Delta H < 0$ has an exponential increase in conversion at early times because $k \propto e^{-\frac{E_A}{RT}}$ so it increases exponentially with temperature. It's thus above $\Delta H = 0$ curve.

At low t, they all start ~~off~~ on the same linear curve since T changes are small.

-1 for confusing endo and exo thermic.

(c) [10 pts] You perform an experiment in which the reactor from (a) is run adiabatically and you measure the volume of the reactor as a function of time:

Up to 3 pts in X^* and ΔH (total 6 pts) for other approaches if justified.



When V = V_0 at the local maximum, you measure T = T*.

1-5 pts awarded if some thought process in right direction

What is the conversion at T = T*? Derive an expression for the ΔH_{rxn} at the reactor temperature T* assuming the conversion at this temperature is known.

+5 for X^*

$$V = V_0 (1-X)\left(\frac{T}{T_0}\right)$$ + 2 realize you need V expression

Since $V = V_0$ @ T^*, then

$$\cancel{V_0} = \cancel{V_0}(1-X^*)\left(\frac{T^*}{T_0}\right) \Longrightarrow \boxed{X^* = 1 - \frac{T_0}{T^*}}$$ +1 final answer

+2 realize volumes are equal

+3 for ΔH_{rx}

For an adiabatic reactor,

$$T = T_0 + \frac{(-\Delta H_{Rx}(T_0))X}{\sum_i \Theta_i C_{p_i} + X \cancel{\Delta C_p}^{=0}}$$

+ 2 adiabatic energy balance (note at these conditions we are back at V_0 so no PV work)

+1 for $\Delta C_p = 0$

But $\Delta C_p = 2C_{P,A} - C_{P,A} - C_{PA} = 0$, so and ΔH_{rx} is T independent

$$T^* = T_0 - \frac{\overset{\text{known} = 1 - T_0/T^*}{X^*}\,\Delta H_{rx}}{\frac{1}{2}C_{P,A} + \frac{1}{2}C_{PA}}$$

+1 carry through.

→ initially $N_{A0} = N_{B0}$

acceptable

$$-\Delta H_{rxn} = \frac{(T^* - T_0)C_{P,A}}{X^*} = \frac{\cancel{T^* - T_0}}{\frac{\cancel{T^* - T_0}}{T^*}} C_{P,A} = \boxed{-\Delta H_{rx} = C_{P,A} T^*}$$

+1 final answer

(d) [5 pts] Now an extremely good controller is used such that T **is constant** throughout the course of the reaction. What is the total gas-phase concentration in the system if the conversion of A is equal to 0.5?

$PV = nRT$ +2 gas law

+2 realize = constant

$\frac{n}{V} = C = \frac{P}{RT} =$ constant since P is constant and $T = T_o$

$$\boxed{C = \frac{P_o}{RT_o}}$$

+1 final answer.

$C = \frac{2N_{A0}}{V_0}$ also acceptable $= 2C_{A0}$

+1 if some reasoning

(e) [20 pts] You now introduce a cooling coil with heat transfer coefficient *UA* and cooling fluid at T_a. Derive an expression for the rate of change in temperature (*dT/dt*) as a function of conversion X_A, temperature *T* and given constants.

Start with unsteady energy balance

$$\dot{Q} - \underbrace{\cancel{W_s}}_{\text{no shaft}} + \underbrace{\overset{=0}{\cancel{\sum_i F_i H_{i,in}}} - \overset{=0}{\cancel{\sum F_i H_{i,out}}}}_{\text{batch}} = \frac{d\hat{E}}{dt}$$

$$\downarrow$$

$$\dot{Q} = UA(T_a - T)$$

$$\therefore \frac{d\hat{E}}{dt} = UA(T_a - T)$$

(+2 if no further work)

+5 for starting from fundamental energy balance

⊛

Note $\hat{E} = \sum_i N_i U_i = \sum_i N_i H_i - PV$ ← P = constant

+ 3 pts for recognizing PV is important

$$\frac{d\hat{E}}{dt} = -P\frac{dV}{dt} + \sum_i \left[\frac{dN_i}{dt} H_i + N_i \frac{dH_i}{dt}\right]$$ (+3 for this derivative)

$$V = V_0\left(\frac{T}{T_0}\right)(1-x) \Longrightarrow \frac{dV}{dt} = -\frac{V_0}{T_0} T \frac{dx}{dt} + \frac{V_0}{T_0}\frac{dT}{dt}(1-x)$$

And $\frac{dN_i}{dt} = \nu_i r_A V$ (+3), $\frac{dH_i}{dt} = C_{p,i}\frac{dT}{dt}$ (+2)

$$= \frac{P_0 V_0}{T_0}\left[(1-x)\frac{dT}{dt} - T\frac{dx}{dt}\right] + \sum_i \left[V r_A \overset{\equiv \Delta H_{rxn}}{\left[\nu_i H_i\right]} + \overset{\text{plug in in terms of conversion}}{N_i C_{p,i}\frac{dT}{dt}}\right]$$

(+4 rest of plugs in)

But $r_A V = -\frac{k N_{A0}^2}{V_0}(1-x)\left(\frac{T_0}{T}\right)$ from (a) and we know $\frac{dx}{dt}$ from (a)

$$= \frac{P_0 V_0}{T_0}\left[(1-x)\frac{dT}{dt} - \cancel{T}\frac{k N_{A0}}{V_0}\left(\frac{T_0}{\cancel{T}}\right)(1-x)\right] + (-\Delta H_{rxn})\frac{k N_{A0}^2}{V_0}\left(\frac{T_0}{T}\right)(1-x)$$

$$+ \left(N_{A0}(1-x)C_{PA} + N_{A0}(1-x)C_{P,A} + N_{A0}X \cdot 2C_{P,A}\right)\frac{dT}{dt}$$

+10 pts for making it through $\frac{dE}{dt}$

$$= \frac{P_0 V_0}{T_0}(1-x)\left[\frac{dT}{dt} - \frac{k N_{A0} T_0}{V_0}\right] + (-\Delta H_{rx})\frac{k N_{A0}^2}{V_0}\left(\frac{T_0}{T}\right)(1-x) + N_{A0} C_{p,A}(2)\frac{dT}{dt}$$

$$= \frac{dT}{dt}\left[\frac{P_0 V_0}{T_0}(1-x) + 2 N_{A,0} C_{p,A}\right] + \frac{k N_{A0}^2 T_0 (1-x)}{V_0}\left(\frac{\Delta H_{rxn}}{T} - \frac{P_0 V_0}{T_0 N_{A0}}\right)$$

$$= UA(T_a - T)$$

$$\boxed{\frac{dT}{dt} = \frac{\left[UA(T_a - T) + \frac{k N_{A0}^2 T_0 (1-x)}{V_0}\left(\frac{\Delta H_{rxn}}{T} + \frac{P_0 V_0}{T_0 N_{A0}}\right)\right]}{\frac{P_0 V_0}{T_0}(1-x) + 2 N_{A,0} C_{p,A}}}$$

$$k = A e^{-\frac{E_a}{RT}}$$

+2 pts final answer

~~(total +15 pts if close to~~

up to +10 pts Partial credit

Partial credit:

+ 5pts if wrote $\frac{dT}{dT} = \frac{\dot{Q} - W_s - F_{A0}\sum \Theta_i C_{p_i}(T - T_0) + \Delta H_r r_A V}{\sum N_i C_p}$

and recognized $\underline{\dot{Q} = UA(T - T_0)}$, $W_s \overset{?}{=} 0$, and simplified

+2

↳ up to +5 pts for simplification

+2pts for $r_A V$ simplification, +1 for Θ_i, N_i simplification

Up to 15 pts partial credit for recognizing, apart from the above that PV is important (+3 for recognizing this, +2 for solving $P\frac{dV}{dt}$ in terms of T, x)