CBE 142: Chemical Kinetics & Reaction Engineering

Midterm #2

November 9th 2017

This exam is worth 90 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: KEY

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	10	
2	20	
3	25	
4	35	

TOTAL : ______ / 90

Key

POTENTIALLY USEFUL FORMULAS

Quadratic Formula:

Given $ax^2 + bx + c = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Integrals:

$$\int_0^x \frac{dx}{a + bx} = \frac{1}{b} \ln\left(\frac{a + bx}{a}\right)$$

$$\int_0^x \frac{dx}{(ax + b)^2} = \frac{1}{ab} - \frac{1}{a(ax + b)}$$

$$\int_0^x \frac{x}{x^2 + a^2} dx = \frac{1}{2} ln\left[\frac{|x^2 + a^2|}{|a^2|}\right]$$

$$\int_0^x \frac{ax + b}{cx + d} dx = \frac{ax}{c} + \frac{ad - bc}{c^2} \ln\left[\frac{|d|}{|cx + d|}\right]$$

$$\int_0^x \frac{x}{ax + b} dx = \frac{x}{a} + \frac{b}{a^2} \ln\left[\frac{|b|}{|ax + b|}\right]$$

$$\int_0^x \frac{1}{(ax + b)(cx + d)} dx = \frac{1}{ad - bc} ln\left[\frac{|d(ax + b)|}{|b(cx + d)|}\right]$$

$$\int_0^x \frac{x}{(ax + b)(cx + d)} dx = \frac{1}{ad - bc}\left(\frac{b}{a} ln\left[\frac{|b|}{|ax + b|}\right] + \frac{d}{c} ln\left[\frac{|cx + d|}{|d|}\right]\right)$$

Key

Problem #1: **[10 points]**

The desired liquid phase reaction

3 points to get want $C_A \uparrow$, $C_B \downarrow$

$A + B \rightarrow D$ (desirable) $\quad r_1 = k_1 C_A^{1.9} C_B^{0.2}$

is accompanied by the unwanted side reaction

$A + B \rightarrow U$ (undesirable) $\quad r_2 = k_2 C_A^{0.9} C_B^{1.7}$ $\boxed{+2}$

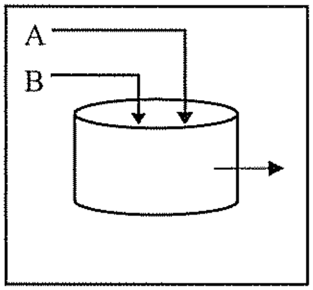
$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1 C_A^{1.9} C_B^{0.2}}{k_2 C_A^{0.9} C_B^{1.7}} \quad \boxed{+1}$$

$$S_{DU} = \frac{k_1}{k_2} \frac{C_A}{C_B^{1.5}} \quad \boxed{+1}$$

$\boxed{+1}$ Need to maximize A & minimize B Because of the 1.5 power in B, it is more important to minimize B.

Assume equal molar concentrations of A and B in the feed stream and equal numbers of total moles of A and B fed for each Scheme below. Order the schemes from lowest to highest selectivity which is defined as the ratio of the rate of desirable product formation to the rate of undesirable product formation. Explain your answer in a few short sentences. Answers without correct justification will receive no credit.

Scheme 1

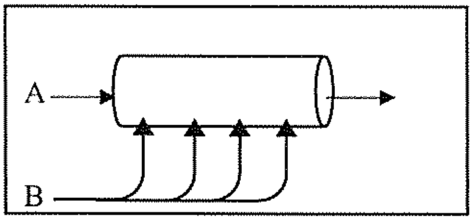


keeps C_A & C_B low, by dilution

better than PFR b/c keeps C_B low (important b/c 1.5 power)

$\boxed{+1}$

Scheme 2



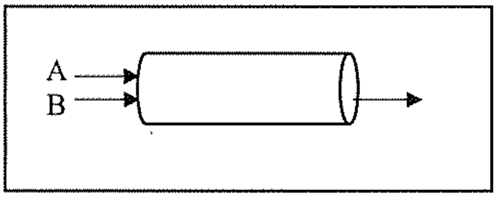
$\boxed{+1}$

best

C_B low, C_A high

feeding in B keeps C_B low

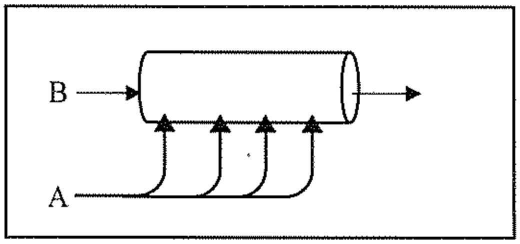
Scheme 3



keeps C_A & C_B high

$\boxed{+1}$

Scheme 4



$\boxed{+1}$

worst

C_A low; C_B high

feeding in C_A keeps it low

$\boxed{+1}$ for order written correctly if justification also correct

Lowest Selectivity			Highest Selectivity
4	3	1	2

partial credit

+2 for perfect backwards ordering ~~without justification~~ w ~~consistent~~

Key

Key

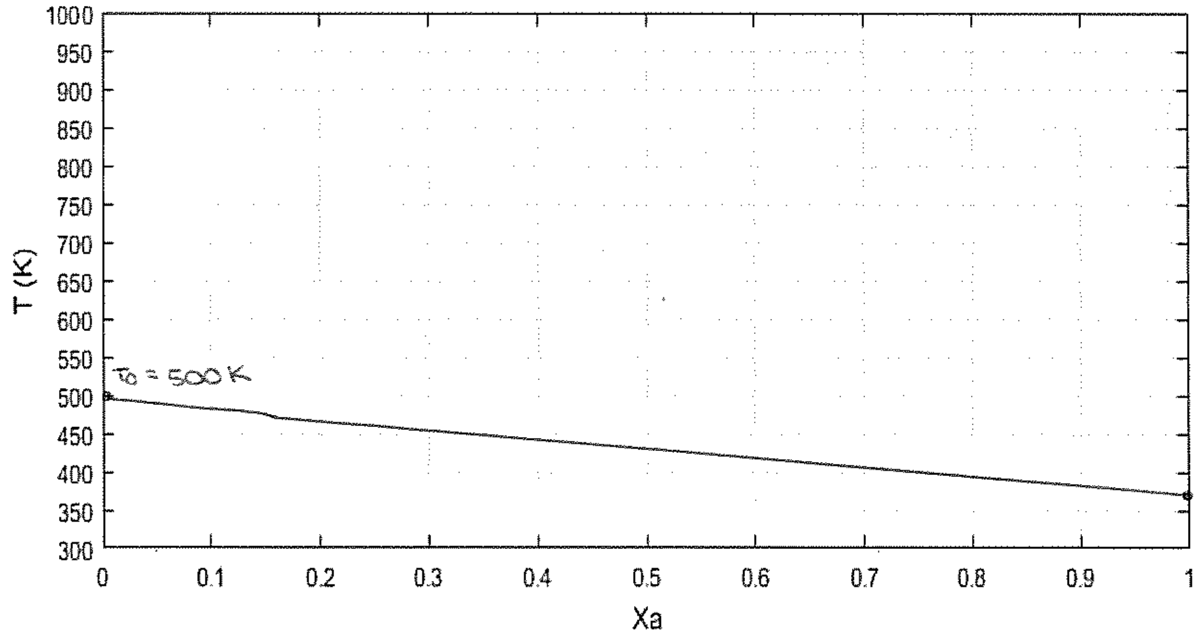
Problem #2: [20 points]

The ideal gas-phase, elementary reaction $A \xrightarrow{k} B$ takes place in an *unsteady*, constant-pressure BSTR. The reactor is charged with pure A. Variations in the PV term of the unsteady energy balance may be neglected.

Additional information:

- $\sum_i N_i C_{P_i} = 200 \frac{\text{cal}}{\text{K}}$ (constant)
- $\Delta H_{rx} = 2{,}500 \frac{\text{cal}}{\text{mol}}$ (not a function of T)
- $N_{A0} = 10$ mol
- $T_0 = 500$ K

a) **[8 pts]** Sketch a plot of T vs. X_A for adiabatic operation of the reactor. For full credit, your sketch must:
   - Clearly indicate the value of T at the y-intercept
   - Clearly indicate the presence of maxima and/or minima in the graph (if any are present). If any maxima and/or minima are present, it is not necessary to calculate the value of X_A at which they occur
   - Show the correct general trend regarding the slope at every point (i.e., everywhere on the plot it should be clear if T vs. X_A is linear, quadratic, exponential, etc.)



+1 For $T_0 = 500$ K at $X_A = 0$

+2 For T at $X_A = 1 < 500$ K (aka monotonic T decrease in general)

+5 For linear everywhere

Partial credit: if missed linear trend

+2 For $T = T_0 + \frac{(-\Delta H_{rx})(N_{A0})}{\sum_i N_i C_{P_i}} X_A$ (okay if slightly off, but should show linear trend)

Partial credit contived: breakdown of +2 for $T = T_0 + \left(\frac{-\Delta H_{rx} N_{A0}}{\Sigma N_i C_{pi}}\right) X_A$

Key

Unsteady EB on $\overset{\text{adiabatic}}{\vee}$ BSTR: $\frac{dT}{dt} = \frac{(-\Delta H_{rx})(-r_A V)}{\Sigma N_i C_{pi}}$ +0.5

Mole balance: $\frac{dX_A}{dt} = \frac{-r_A V}{N_{A0}}$ +0.5

combine:

$\frac{dT}{dt} = \frac{-\Delta H_{rx} N_{A0}}{\Sigma N_i C_{pi}} \frac{dX_A}{dt} \Rightarrow dT = \left(\frac{-\Delta H_{rx} N_{A0}}{\Sigma N_i C_{pi}}\right) dX_A$ +0.5

integrate:

$T = T_0 + \left(\frac{-\Delta H_{rx} N_{A0}}{\Sigma N_i C_{pi}}\right) X_A$ +0.5

b) **[2 pts]** Calculate the reactor temperature when the reaction has gone to completion.

At $X_A = 1$,

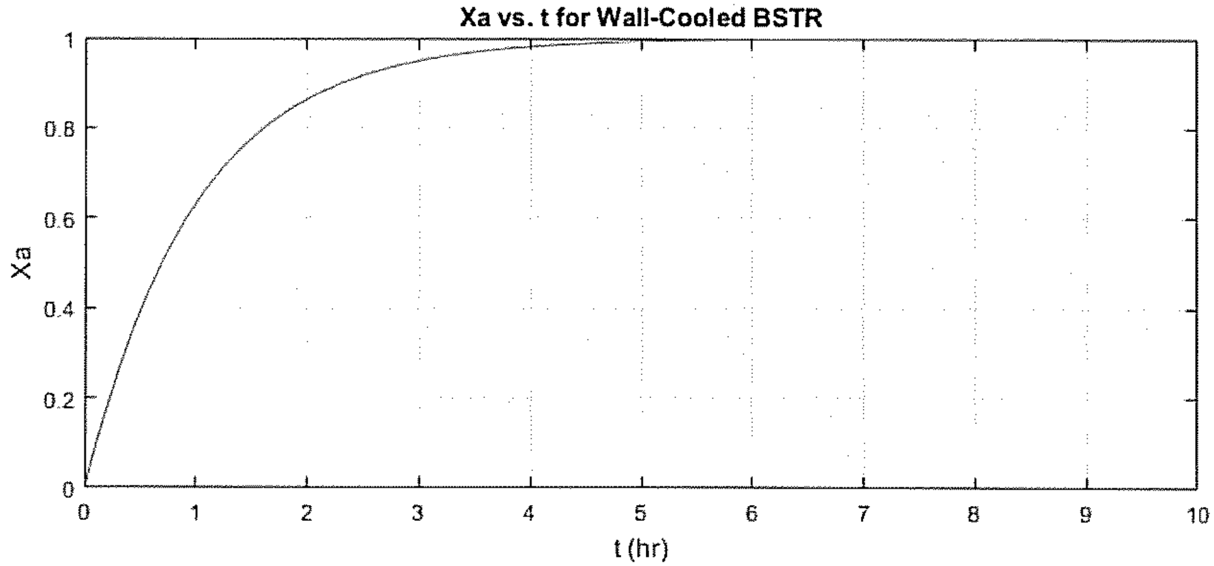
$\boxed{\text{+1 for eq}}$ $T = T_0 + \left(\frac{-\Delta H_{rx} N_{A0}}{\Sigma N_i C_{pi}}\right) X_A = 500 - 125 X_A$

$T = 500 + \frac{(-2500)(10)}{(200)}(1)$

$\boxed{\text{+1 for final answer}}$ $\boxed{T = 375 \text{ K}}$

Key

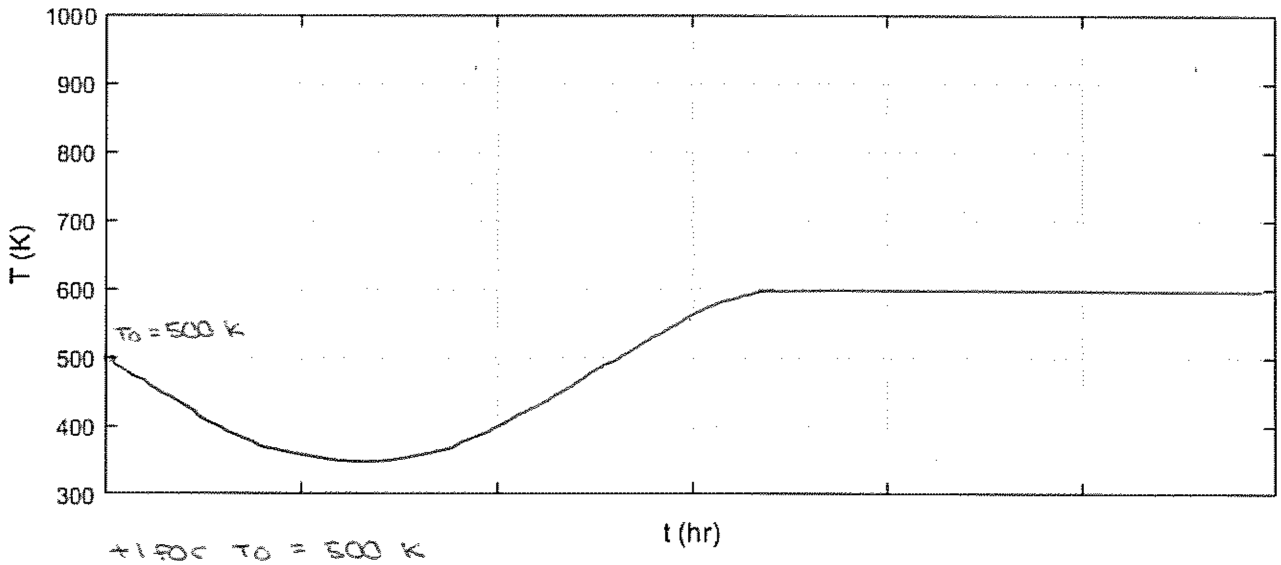
c) **[10 pts]** Now, this reaction will be carried out in a wall-cooled BSTR with $UA = 10\ \text{cal}/(\text{hr}\cdot\text{K})$ and $T_a = 600\ K$ (constant). All other parameters ($N_{A0},\ \Delta H_{rx}$, etc.) remain unchanged. Below is a plot of X_A vs. t for the wall-cooled BSTR.



Qualitatively sketch T vs. t for the wall-cooled BSTR. For full credit, you must:

- Clearly indicate the value of T at $t = 0$
- Clearly indicate the final value of T
- Clearly indicate the presence of maxima and/or minima in the graph (if any are present). If any maxima and/or minima are present, it is not necessary to calculate the value of t at which they occur.

In 2-3 sentences, explain physically why your graph looks the way it does. *Plots without correct justification will receive no credit.*



+1 for To = 500 K

+2 for Tfinal = 600 K and plateau

+7 for a minimum in T vs. t with correct physical explanation and math to justify

Partial credit:

+1 for unsteady BSTR wall-cooled EB

calculate $\frac{dT}{dt}$ at $X_A = 0$: need to know if pos. or neg. Key

$$\frac{dT}{dt} = \frac{UA(T_a - T) + (-r_AV)(-\Delta H_{rx})}{\Sigma N_iC_{p_i}} = \frac{Q_g - Q_r}{\Sigma N_iC_{p_i}}$$

what is $-r_AV$? $N_{A0}\frac{dX_A}{dt} = -r_AV$

$Q_r = -UA(T_a - T) = -10(600-500) = -1000$ cal/hr

→ adding 1000 cal/hr heat

$Q_g = (-\Delta H_{rx})N_{A0}\frac{dX_A}{dt}$

Estimate $\frac{dX_A}{dt} \approx \frac{0.4}{0.5} = 0.8$

$\Rightarrow Q_g = (-2500)(10)(0.8) = -20,000$

clearly heat added is much less than heat gen by rxn:

at $t = 0$, $\frac{dT}{dt}$ is negative.

The final temp has to be that of the cooling fluid. This occurs after a sufficiently long time.

So at first, $\frac{dT}{dt} < 0$, so rxr temp. drops. But the final T is 600 K, so T vs. t goes through a minimum before reaching 600 K, where it plateaus.

key

Problem #3: [25 points]

You are to design a steady-state, wall-cooled isobaric CSTR in which the exothermic, ***0^{th} order***, liquid-phase A → B reaction will occur. The feed will be pure A at concentration C_{A0}, and some unspecified temperature T_o.

The cooling fluid is not yet determined. Hence the values for the heat transfer quantity UA and the temperature of the cooling fluid T_{Am} are not yet known numerically, but we will assume they are constant and independent of the temperature. The following data are given:

ΔH_{rxn} (@T_R = 300 K) = -10 kcal/mol
$C_{P,A} = C_{P,B}$ = 10 cal/(mol K)
$A_o = 4.7*10^5$ mol min^{-1} L^{-1} (Arrhenius prefactor)
E = 10,000 cal/mol
R = 1.987 cal/(mol K)
C_{A0} = 2 mol/L
τ = 0.1 min
V = 1 L

(a) [**3 pts**] Express the conversion of A, X_A, in this reactor in terms of the CSTR operating temperature, T, and the constants above that have a given numeric quantity. Use this expression to determine the value of X_A when T = 300 K.

$$F_{A0} - F_A + r_A V = \frac{dN_A}{\cancel{dt}}^{\nearrow 0} \quad \boxed{+1 \text{ MB}}$$

$$F_{A0} X - kV = 0$$

$$X = \frac{kV}{F_{A0}}$$

$$\boxed{+1 \text{ PT } x(T)}$$

$$X = \frac{k\tau}{C_{A0}} = \frac{A_o \exp\left(\frac{-E}{RT}\right)\tau}{C_{A0}} = \underbrace{23500 \exp\left(\frac{-5632.7}{T}\right)}$$

$$x(T=300) = 0.0012 \quad \boxed{+1 \text{ PT for } x(T=300)}$$

(b) [**2 pts**] Using your expression from part (a), at what operating temperature will the conversion of the reactor reach X_A=1?

$$-\frac{R}{E} \ln\left(\frac{x C_{A0}}{A_o \tau}\right) = \frac{1}{T}$$

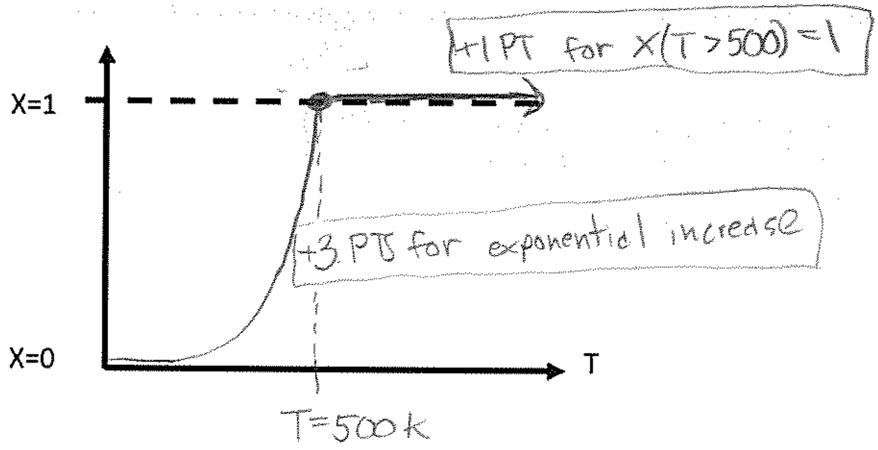
$$T = \frac{1}{\ln\left(\frac{x C_{A0}}{A_o \tau}\right)\left(-\frac{R}{E}\right)} \overset{\text{or}}{=} \frac{1}{\ln\left(\frac{x}{23500}\right)\frac{1}{(-5032.7)}} \quad \boxed{+1 \text{ PT for } T(x)}$$

$$T = 500.03 \text{ K}$$

$$\boxed{T = 500 \text{ K}} \quad \boxed{+1 \text{ PT for } T(x=1)}$$

Key

(c) [**4 pts**] On the graph below, qualitatively sketch $X_A(T)$ according to your equation from part (a). Make sure to mark the temperature you solved in part (b) on the x-axis.



(d) [**5 pts**] What is the maximum value of the ***derivative*** of the heat generation term, dG/dT? At which operating temperature and conversion does this maximum most correspond to?

+1 Def. of G(T)

+1 Derivative of X(T)

$$\frac{dG}{dT} = \frac{d(-\Delta H_{rxn} X_A(T))}{dT} = -\Delta H_{rxn} \frac{dX_A}{dT}$$

$$\left.\begin{aligned}\frac{dG}{dT} &= -\Delta H_{rxn} \frac{A_0 \tau}{C_{A0}} \left(\frac{E}{RT^2}\right) \exp\left(\frac{-E}{RT}\right) \\ &= 10000(23500)\left(\frac{5032.7}{T^2}\right) \exp\left(\frac{-5032.7}{T}\right)\end{aligned}\right\} \boxed{+1 \ \frac{dG}{dT} \text{ final expression}}$$

- Max of $\frac{dG}{dT}$ occurrs when $\overset{\boxed{+0.5}}{X=1}$ or $\overset{\boxed{+0.5}}{T=500K}$;

$$\max\left(\frac{dG}{dT}\right) = \left.\frac{dG}{dT}\right|_{T=500} = 10000(23500)\left(\frac{5032.7}{500.03^2}\right) \exp\left(-\frac{5032.7}{500.03}\right)$$

$$= 201.28 \ \frac{cal}{mol K}$$

$$= 201 \ \frac{cal}{mol K} \quad \boxed{+1 \ \max \text{ of } \frac{dG}{dT}}$$

Key

(e) [**6 pts**] Now determine the range of heat transfer quantities UA with units [=] cal/(min K) that is guaranteed to eliminate the possibility of multiple steady states, regardless of the composite temperature T* which is also the x-intercept of R(T).

let Y = max of $\frac{dG}{dT}$, answer from part (d)

To guarantee elimination of MSS:

$$Y < \frac{dR}{dT}$$

+ 2 PTS (alternatively can get partial +1 for word explanation)

$$R(T) = \overline{C}_{p0}(1+\kappa)(T-T^*) \text{, where } \overline{C}_{p0} = \Sigma\Theta_i C_{pi} = C_{pA} = 10 \frac{\text{cal}}{\text{mol K}}$$

+0.5 for $\overline{C}_{p}$

$$\frac{dR}{dT} = \overline{C}_{p0}(1+\kappa)$$

$$\kappa = \frac{UA}{F_{A0}\overline{C}_{p0}}$$

+0.5 for κ

$$\kappa = \frac{UA}{C_{A0}\left(\frac{V}{\tau}\right)\overline{C}_{p0}}$$

+1 PT for F_{A0}

$$\frac{dR}{dT} = \overline{C}_{p0} + \frac{UA}{\underset{F_{A0}}{\underset{|||}{C_{A0}\left(\frac{V}{\tau}\right)}}}$$

+1 PT for $\frac{dR}{dT}$

$$Y < \overline{C}_{p0} + \frac{UA}{C_{A0}\left(\frac{V}{\tau}\right)}$$

$$\left(\frac{C_{A0}V}{\tau}\right)(Y - \overline{C}_{p0}) < UA$$

$$UA > \left(\frac{2\frac{\text{mol}}{\text{L}}\cdot 1\text{L}}{0.1\text{ min}}\right)\left(201\frac{\text{cal}}{\text{mol K}} - 10\frac{\text{cal}}{\text{mol K}}\right)$$

$$\boxed{UA > 3820 \frac{\text{cal}}{\text{min K}}}$$

+ 1 PT final answer

key

(f) **[5 pts]** Unlike part (e), the cooling fluid has now been specified and will have a heat transfer quantity UA = 2000 cal/(min K). Now an inert species is available with heat capacity $C_{P,I} = 30$ cal/(mol K) and will be fed to the reactor with some concentration C_{IO} in conjunction with the $C_{A0} = 2$ mol/L specified in the original problem statement. Determine the ***minimum*** inert inlet concentration, C_{IO}, that is guaranteed to eliminate the possibility of multiple steady states regardless of the composite temperature T*. As always in this class, assume a zero volume of mixing of all species.

$$Y < \frac{dR}{dT} \qquad \boxed{\text{+1 PT}}$$

$$Y < \overline{C_{p0}} + \frac{UA}{F_{A0}}$$

$$\overline{C_{p0}} > Y - \frac{UA}{F_{A0}} \qquad \boxed{\text{+1 PT for inequality w/ } C_p\text{'s}}$$

$$\overline{C_{p0}} > 201 \frac{cal}{mol K} - \frac{2000 \frac{cal}{min K}}{20 \frac{mol}{min}}$$

$\boxed{\text{+0.5 for } \overline{C_{p0}}}$

$$\overline{C_{p0}} = \sum \Theta_i \tilde{C}_{pi} = C_{p,A} + \frac{C_{I0}}{C_{A0}} C_{p,I}$$

$\boxed{\text{+0.5 for } \Theta_I}$

$$\overline{C_{p0}} > 101 \frac{cal}{mol K}$$

$$C_{p,A} + \frac{C_{I0}}{C_{A0}} C_{p,I} > 101$$

$\boxed{\text{+1 PT for inequality w/} C_{I0}}$

$$\begin{cases} C_{I0} > (101 - C_{p,A}) \dfrac{C_{A0}}{C_{p,I}} \\ C_{I0} > \left(Y - \dfrac{UA}{F_{A0}} - C_{p,A}\right) \dfrac{C_{A0}}{C_{p,I}} \end{cases}$$

$$C_{I0} > \left(201 \frac{cal}{mol K} - \frac{2000 \frac{cal}{min K}}{20 \frac{mol}{min}} - 10 \frac{cal}{mol K}\right) \frac{2 \frac{mol}{L}}{30 \frac{cal}{mol K}}$$

$$\boxed{C_{I0} > 6.1 \frac{mol}{L}} \qquad \boxed{\text{+1 PT for final answer}}$$

Key

Problem #4: [35 points]

The following irreversible elementary exothermic liquid-phase reaction is taking place in a well-stirred batch reactor.

$2A \rightarrow B$, k = 0.5 L/(mol-hr) at 310 K

The batch reactor is surrounded by a refrigeration unit. The job of this refrigeration unit is to maintain isothermal operation of the reactor at the initial temperature. Assume this refrigeration unit provides the only communication between the reactor and its surroundings; there is no other mode of heat transfer with the surroundings. At time t = 0, there was only A in the reactor, with a concentration 1 mol/L and at temperature 310 K. The volume of the reactor is constant at 500 L. Assume that all liquids are incompressible and at the same density.

Additional information:
$H_A(T_R)$ = -10 kJ/mol, $H_B(T_R)$ = -40 kJ/mol, T_R = 298 K
C_{pA} = 10 J/mol-K, C_{pB} = 20 J/mol-K

a) [**6 pts**] Starting with the mole balance equation, express C_A as a function of time for this reactor.

Assume: isothermal $\Rightarrow \Delta T = 0$
$V = 500\text{L}$ (constant)

$$acc = \cancel{in} - \cancel{out} + gen$$

$$\frac{dN_A}{dt} = r_A V \quad \boxed{+1}$$

$$\cancel{V}\frac{dC_A}{dt} = r_A \cancel{V} \qquad r_A = -2kC_A^2 \quad \boxed{+1}$$

$$\frac{dC_A}{dt} = -2kC_A^2 \quad \boxed{+2}$$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = -2kt$$

$$-\frac{1}{C_A} + \frac{1}{C_{A0}} = -2kt$$

$$C_A = \frac{C_{A0}}{1+2kC_{A0}t} \quad \boxed{+2}$$

Key

b) **[11 pts]** Calculate the time-dependent heat load on the refrigeration unit $\dot{Q}_{\text{cooling}}$ with units kJ/hr needed for isothermal operation of the reactor at 310 K, as a function of time t and known constants.

$\boxed{+2}$ Heat gen = Heat removed

$\Delta C_p = 0$ $\boxed{+1}$

$\boxed{+4}$ $\dot{Q}_{cooling} = -2 k C_A^2 \, \Delta H_{Rx} \cdot V$

$$\Delta H_{Rx} = \frac{1}{2} H_B - H_A$$
$$= \frac{1}{2}(-40) - (-10)$$
$$= -10 \text{ kJ/mol A} \quad \boxed{+1}$$

$\boxed{+1}$ $\dot{Q}_{cooling} = -2k\left(\frac{C_{A0}}{1+2kC_{A0}t}\right)^2 \cdot V \cdot \Delta H_{Rxn}$

$$= (-2)\left(\frac{1}{2}\right)\left(\frac{1}{1+t}\right)^2 (500)(-10)$$

$$\dot{Q}_{cool} = 5000\left(\frac{1}{1+t}\right)^2 \text{ kJ/hr} \quad \boxed{+2}$$

c) **[4 pts]** Calculate the ***average*** heat load on the refrigeration unit between t=0 to 1 hr. Express your answer in kJ/hr.

$\boxed{+3}$

$$\dot{Q}_{Avg} = 5000\int_0^1 \frac{1}{(1+t)^2}\,dt = 5000\left[\frac{1}{2}\right] \quad +$$

$$\dot{Q}_{Avg} = 2500 \text{ kJ/hr} \quad \boxed{+1}$$

Key

d) **[2 pts]** Now, after 1 hour of operation, suddenly the refrigeration unit stops working altogether. The batch reactor starts operating adiabatically rather than isothermally, starting at this time. Calculate the conversion of A (X_A) in the batch reactor at time t = 1 hour which is the time of power failure.

$$C_A(t) = \frac{1}{1+t} = \frac{1}{1+1} = 0.5\,\text{mol/L}$$

$$X = 1 - \frac{C_A}{C_{A0}} = 1 - \frac{.5}{1} = .5$$

$$\boxed{X_A = .5}$$

Key

e) [**12 pts**] Assuming the refrigeration malfunction that is described in part (d), what is the temperature (T) in the batch reactor at a conversion $X_A = 0.6$? This conversion is in the regime of after the refrigeration unit has broken down.

Heat gen = Heat remove

$$(-\Delta H_{rxn})(x - x^*) = C_{pA}(T - T_0) \quad \boxed{+6}$$

$$T = \frac{-\Delta H_{Rx}(x - x^*)}{C_{pA}} + T_0 \quad \boxed{+4}$$

$$T = \frac{-(-10{,}000)(.6 - .5)}{10} + 310$$

$$\boxed{T_f = 410\ K} \quad \boxed{+2}$$

Key