ChE 344
Fall 2014
Mid Term Exam II + Solution
Wednesday, November 19, 2014

Open Book – Closed Notes (but one 3x5 note card),
Closed Computer, Web, Home Problems and In-class Problems

Name_____

Honor Code:

I have neither given nor received unauthorized aid on this examination, nor have I concealed any violations of the Honor Code.

_____
(Sign at the end of exam period)

	Point Totals
1)	____/ 5 pts
2)	____/10 pts
3)	____/10 pts
4)	____/15 pts
5)	____/15 pts
6)	____/20 pts
7)	____/25 pts
Total	____/100 pts

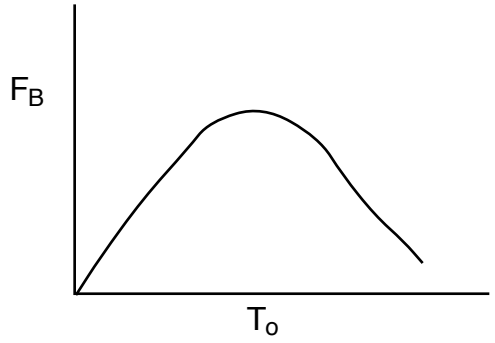
(5 pts) 1) The reactions

$$(1) \qquad A \rightleftharpoons B + C$$

$$(2) \qquad A \longrightarrow D + E$$

$$(3) \qquad A + C \longrightarrow F + G$$

are carried out in a packed bed reactor where B is the desired product. The flow rate of species B exiting the reaction is shown below as a function of the entering temperature, T_o



Circle the correct answer, true (T), False (F) or (CT) Can't tell from the information given.

T F CT a) The above figure could represent an adiabatic system where the reaction 1 is adiabatic exothermic and reversible.

T F CT b) The above figure could represent an adiabatic system where the reaction 1 is endothermic and reversible.

T F CT c) The above figure could represent an adiabatic system where all reactions are endothermic.

T F CT d) The above figure could represent a system where the reactions 1 and 3 are endothermic and reaction 2 is exothermic.

T F CT e) The above figure could represent a system where the reactions 1 and 2 are endothermic and reaction 3 is exothermic.

Solution

a) True. Possible because if reaction (1) is exothermic, at low T_0, rate of forward reaction (1) is low and at high T_0, equilibrium conversion is low.

b) True. Possible because if reaction (1) is endothermic, at low T_0, rate of forward reaction (1) is low and at high T_0, reaction (1) and (2) can take over.

c) True. Same as (b).

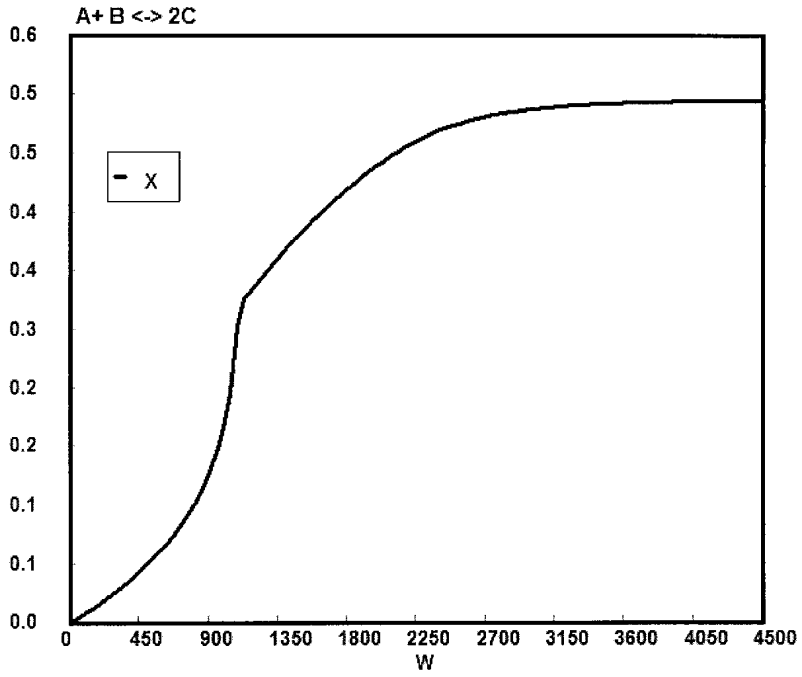
d) True. Possible.

e) True. Possible.

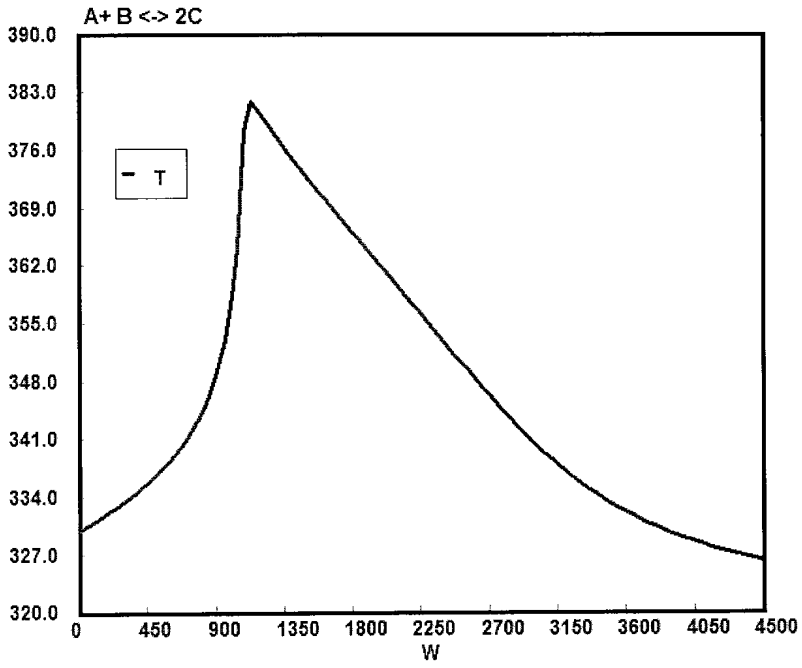
(10 pts) 2) The curves below show the conversion or temperature profiles for the Problem 12-3_B base case. Sketch the requested profiles for the parameters identified. Be sure to label which curve is the maximum and which is the minimum.

(2 pt) (a) Sketch the conversion for the maximum flow rate, i.e., 8 mol/min, and for the minimum flow rate, i.e., 1 mol/min

Flow Rate: Base case shown below for $F_{A0} = 5$

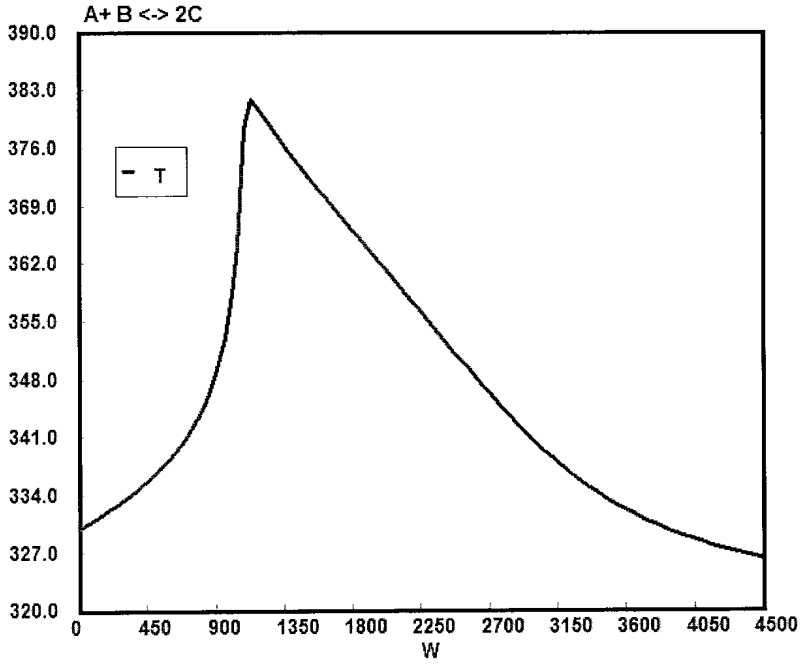


(2 pt) (b) Inert, Θ_I: Sketch the temperature profiles for $\Theta_I = 0.5$ and $\Theta_I = 4$. The base case shown below is for $\Theta_I = 1$

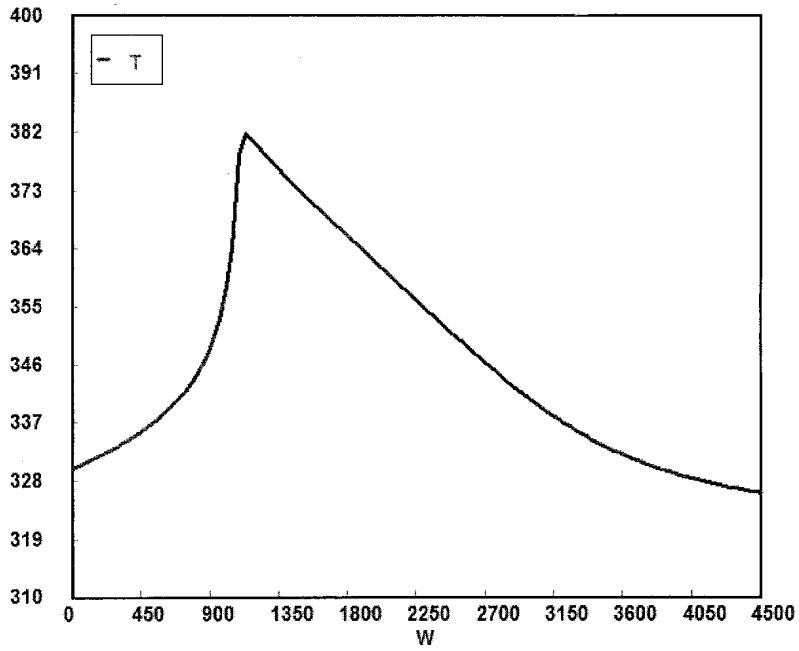


2) (continued)

(2 pt) (c) Sketch the temperature profiles for $\frac{Ua}{\rho_b} = 0.1\ \text{cal/kg} \bullet \text{s} \bullet \text{K}$ and for $\frac{Ua}{\rho_b} = 0.8 \text{cal/kg} \bullet \text{s} \bullet \text{K}$. The base case profile $\left(\frac{Ua}{\rho_b} = 0.5 \text{cal/kg} \bullet \text{s} \bullet \text{K}\right)$ is shown below

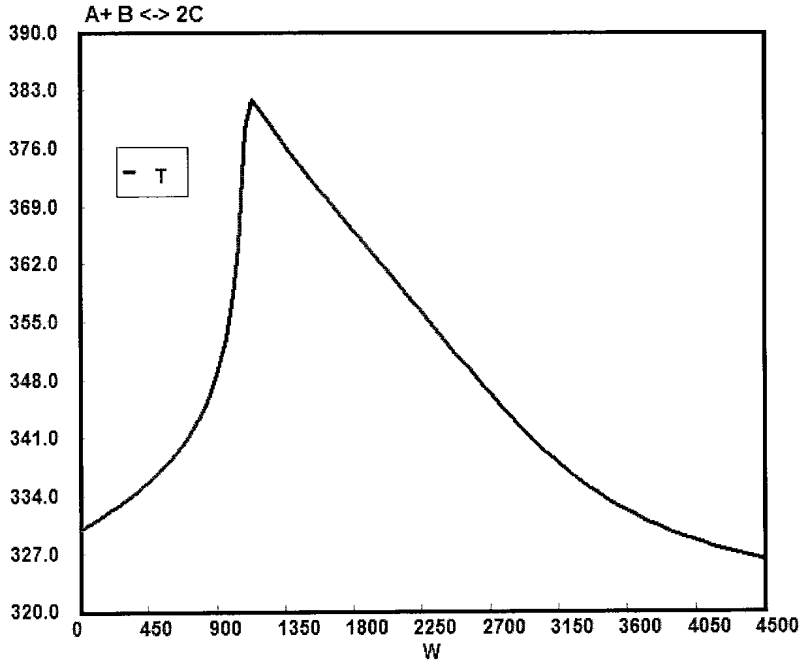


(2 pt) (d) Sketch the temperature profiles for an inlet temperature $T_0 = 310$ and for $T_0 = 350$ on the base case profile shown below for $T_0 = 330$K



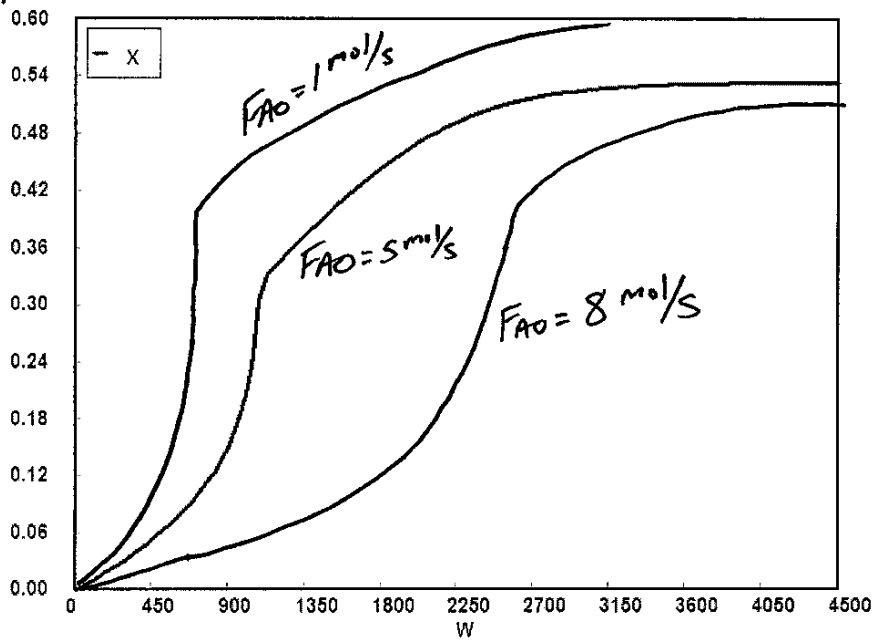
2) (continued)

(2 pt) (e) Sketch the temperature profiles for constant coolant temperatures of T_a = 300K and for T_a = 340K on the base case profile shown below for T_a = 320K

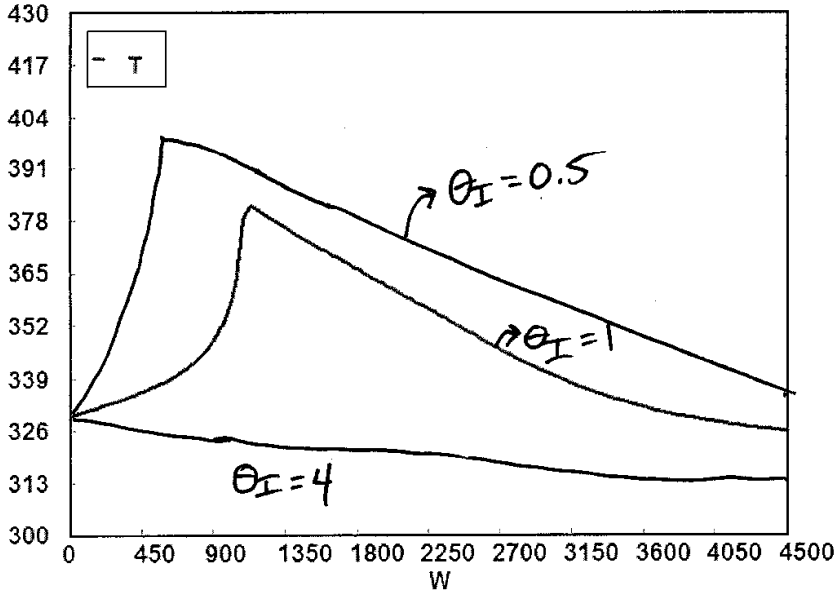


Solution

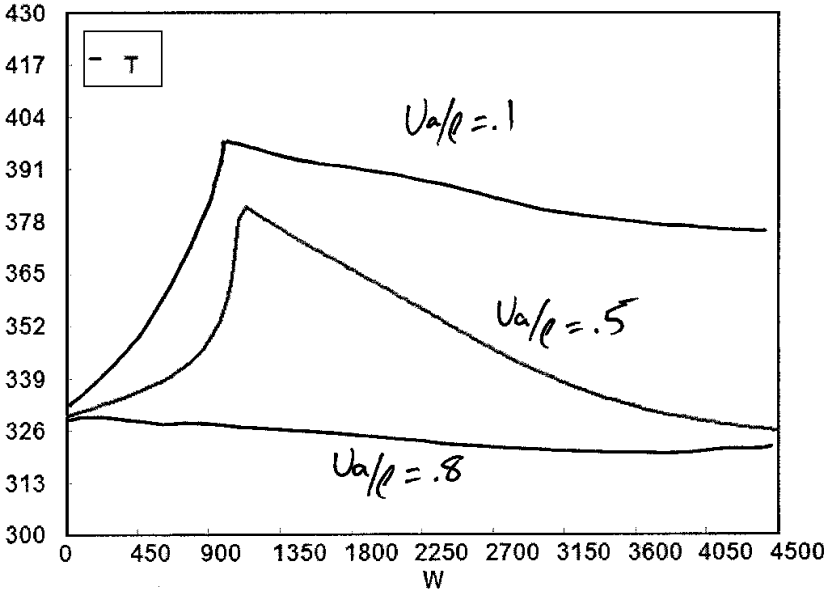
a) MIN : F_{A0} = 1 mol/s
BASE : F_{A0} = 5 mol/s
MAX : F_{A0} = 8 mol/s



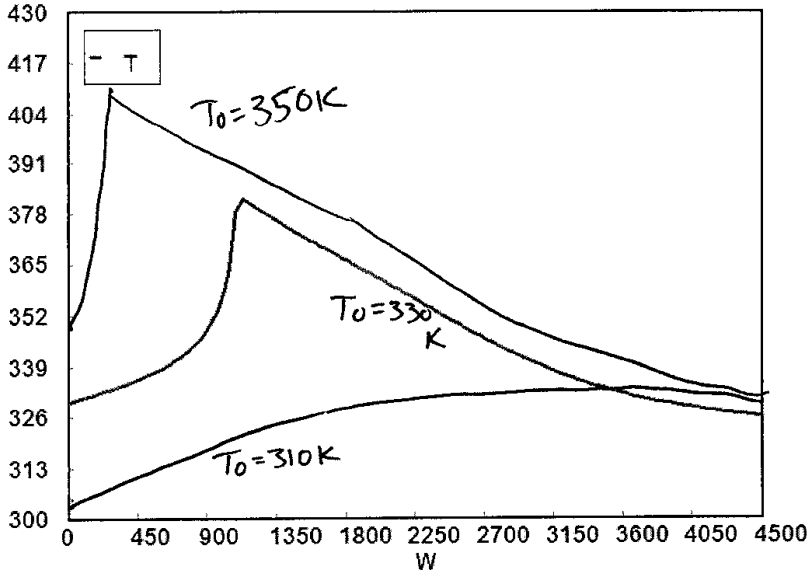
b) MIN: $\theta_I = 0.5$
BASE: $\theta_I = 1$
MAX: $\theta_I = 4$



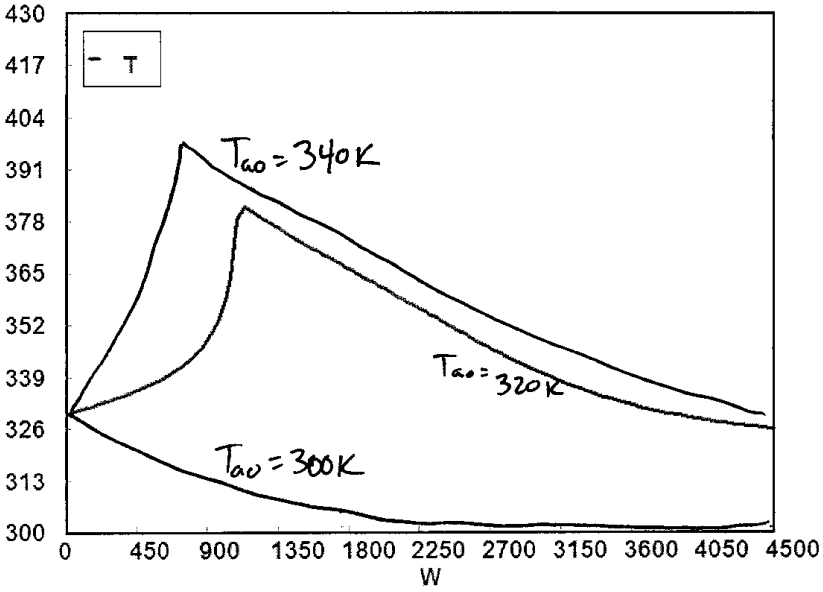
c) MIN: $U_a/\ell = .1$
BASE $U_a/\ell = .5$
MAX $U_a/\ell = .8$



d) MIN: $T_o = 310$ K
BASE: $T_o = 330$ K
MAX: $T_o = 350$ K



e) MIN: $T_{ao} = 300$K
BASE: $T_{ao} = 320$ K
MAX: $T_{ao} = 340$ K



(10 pts) 3) **What's wrong with this solution?** The liquid phase dimer-quadmer series addition reaction

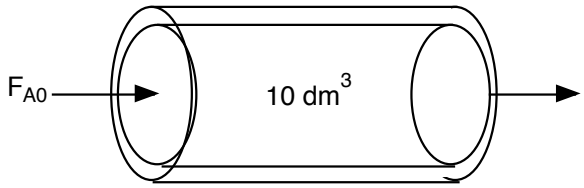
$$4A \rightarrow 2A_2 \rightarrow A_4$$

can be written as

$$2A \rightarrow A_2 \qquad -r_{1A} = k_{1A}C_A^2 \qquad \Delta H_{Rx1A} = -32.5\frac{\text{kcal}}{\text{mol A}}$$

$$2A_2 \rightarrow A_4 \quad -r_{2A_2} = k_{2A_2}C_{A_2}^2 \quad \Delta H_{Rx2A_2} = -27.5\frac{\text{kcal}}{\text{mol A}_2}$$

and is carried out in a 10 dm^3 PFR.



The mass flow rate through the heat exchanger surrounding the reactor is sufficiently large that the temperature of the coolant in the exchanger is constant at T_a = 315K and the entering temperature T_0 is 300K. Pure A is fed to the rector at a volumetric flow rate of 50 dm^3/s and a concentration of 2 mol/dm^3.
[Hint: to avoid any confusion in the subscripts let B = A_2, C = A_4.]

$$4A \rightarrow 2B \rightarrow C$$

Plot F_A, F_B, F_C, T, Q_g and Q_r as a function of reactor volume V.

Additional Information

$$k_{1A} = 0.6\frac{dm^3}{mol\,s} \text{ at 300 K with } E_1 = 4{,}000\frac{cal}{mol}$$

$$k_{2A_2} = 0.35\frac{dm^3}{mol \bullet s} \text{ at 320 K with } E_2 = 5{,}000\frac{cal}{mol}$$

$$C_{P_A} = 25\frac{cal}{mol A\,K}, C_{P_{A_2}} = 50\frac{cal}{mol A_2\,K}, C_{P_{A_4}} = 100\frac{cal}{mol A_4\,K}$$

$$Ua = 1{,}000\frac{cal}{dm^3 s\,K}$$

What 5 things (lines of code) are wrong with the solution? See next page.

	Line Number	**Is**	**Should be**
1			
2			
3			
4			
5			

3) (continued)

POLYMATH Report
Ordinary Differential Equations

Calculated values of DEQ variables

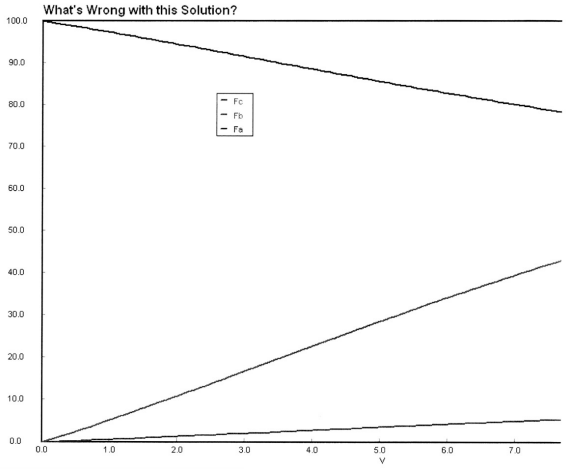
	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	2.	1.459847	2.	1.459847
2	Cb	0	0	1.080307	1.080307
3	Cpa	25.	25.	25.	25.
4	Cpb	50.	50.	50.	50.
5	Cpc	100.	100.	100.	100.
6	DH1a	-3.25E+04	-3.25E+04	-3.25E+04	-3.25E+04
7	DH2b	-2.75E+04	-2.75E+04	-2.75E+04	-2.75E+04
8	E1	4000.	4000.	4000.	4000.
9	E2	5000.	5000.	5000.	5000.
10	Fa	100.	72.99233	100.	72.99233
11	Fb	0	0	54.01534	54.01534
12	Fc	0	0	6.751918	6.751918
13	k1	0.6	0.6	0.6	0.6
14	k1a	0.6	0.6	1.026949	1.026864
15	k2	0.35	0.35	0.35	0.35
16	k2b	0.35	0.35	0.6851962	0.6851254
17	Qg	1.2E+04	1.094E+04	1.497E+04	1.094E+04
18	Qr	-1.5E+04	-1.5E+04	1.112E+04	1.111E+04
19	r1a	-2.4	-2.994262	-2.188403	-2.188403
20	r1b	2.4	2.188403	2.994262	2.188403
21	r2b	0	-0.7995845	0	-0.7995845
22	ra	-2.4	-2.994262	-2.188403	-2.188403
23	rb	2.4	2.188403	2.994262	2.188403
24	rc	0.6	0.5471007	0.7485654	0.5471007
25	sumCp	2500.	2500.	5200.767	5200.767
26	T	300.	300.	326.1184	326.114
27	T1	300.	300.	300.	300.
28	T2	320.	320.	320.	320.
29	Ta	315.	315.	315.	315.
30	Ua	1000.	1000.	1000.	1000.
31	V	0	0	10.	10.
32	vo	50.	50.	50.	50.

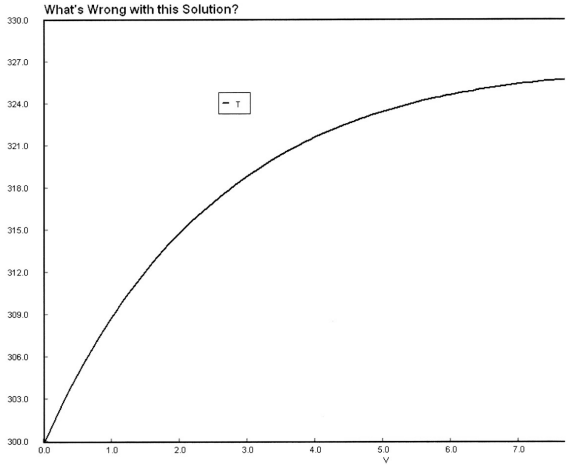
Differential equations

1 d(T)/d(V) = (Qg-Qr)/sumCp
2 d(Fc)/d(V) = rc
3 d(Fb)/d(V) = rb-ra
4 d(Fa)/d(V) = ra

Explicit equations

1 Cpc = 100
2 Cpb = 50
3 Cpa = 25
4 k2 = .35
5 Ta = 315
6 Ua = 1000
7 DH2b = -27500
8 DH1a = -32500
9 T1 = 300
10 E1 = 4000
11 k1 = .60
12 T2 = 320
13 E2 = 5000
14 k2b = k2*exp((E2/1.987)*(1/300-1/T))
15 vo = 50
16 Cb = Fb/vo
17 Ca = Fa/vo
18 sumCp = (Fa*Cpa+Fb*Cpb+Fc*Cpc)
19 k1a = k1*exp((E1/1.987)*(1/300-1/T))
20 r1a = -k1a*Ca^2
21 r2b = -k2b*Cb^2
22 r1b = -r1a
23 rc = -r1a/4
24 rb = r1b
25 ra = r1a
26 Qg = ra*DH1a+rb*DH2b
27 Qr = Ua*(T-Ta)





Solution

Line Number	Is	Should be
3	$r_b - r_a$	r_b
14	$k_{2b} = k_2 * \exp\left[\frac{E2}{1.987}\left(\frac{1}{300} - \frac{1}{T}\right)\right]$	$k_{2b} = k_2 \exp\left[\frac{E2}{1.987}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right], T_2 = 320$
21	$r_c = -\frac{r_{2b}}{4}$	$r_c = -\frac{r_{2b}}{2}$
22	$r_{1b} = -r_{1a}$	$r_{1b} = -\frac{r_{1a}}{2}$
24	$r_b = r_{1b}$	$r_b = r_{1b} + r_{2b}$
26	$Q_g = r_A DH_{1a} + r_b DH_{2b}$	$Q_g = r_{1a} DH_{1a} + r_{2b} DH_{2b}$

(15 pts) 4) (***Reactor selection and operating conditions***) For the following set of liquid reactions, describe <u>all</u> possible reactor systems and conditions to maximize the selectivity to D. Make sketches where necessary to support your choices. The rates are in (mol/dm^3 • s), and concentrations are in (mol/dm^3).

(1) $A + B \rightarrow D \qquad -r_{1A} = 10\exp(-8{,}000\ \text{K}/T)C_A C_B$

(2) $A + B \rightarrow U \qquad -r_{2A} = 100\exp(-1{,}000\ \text{K}/T)C_A^{1/2} C_B^{3/2}$

Solution

P8-9

Reactor selection

$A + B \rightarrow D \qquad r_D = -r_{1A} \qquad r_{1A} = 10\exp(-8000K/T)C_A C_B$

$A + B \rightarrow U \qquad r_U = -r_{2A} \qquad r_{2A} = 100\exp(-1000K/T)C_A^{1/2} C_B^{3/2}$

$$S_{DU} = \frac{r_D}{r_U} = \frac{10\exp(-8000\text{K}/\text{T})C_A C_B}{100\exp(-1000\text{K}/\text{T})C_A^{1/2}C_B^{3/2}} = \frac{\exp(-8000\text{K}/\text{T})C_A^{1/2}}{10\exp(-1000\text{K}/\text{T})C_B^{1/2}}$$

At T = 300K

$k_1 = 2.62 \times 10^{-11}$ & $k_2 = 3.57$ $\qquad S_{D/U} = \dfrac{7.35\times10^{-12}C_A^{1/2}}{C_B^{1/2}}$

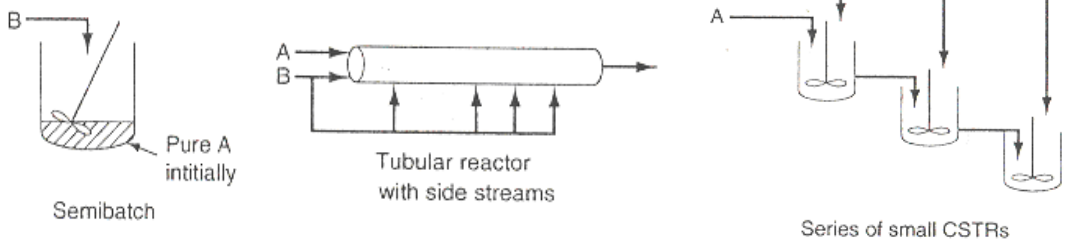
At T = 1000K

$k_1 = 3.35 \times 10^{-3}$ & $k_2 = 36.78$ $\qquad S_{D/U} = \dfrac{9.2\times10^{-5}C_A^{1/2}}{C_B^{1/2}}$

(6 pts) Hence In order to maximize S_{DU}, use higher concentrations of A and lower concentrations of B. This can be achieved using:

1) A semibatch reactor in which B is fed slowly into a large amount of A
2) A tubular reactor with side streams of B continually fed into the reactor

(6 pts) 3) A series of small CSTR's with A fed only to the first reactor and small amounts of B fed to each reactor.

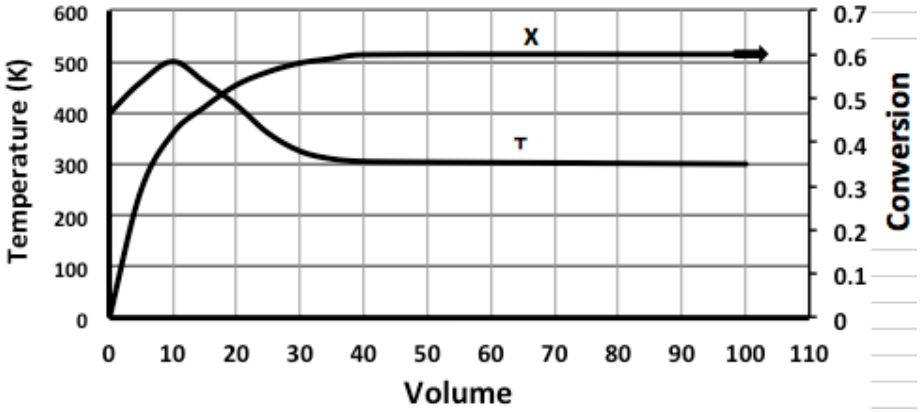


(3 pt) Also, since $E_D > E_U$, so the specific reaction rate for D increases much more rapidly with temperature. Consequently, the reaction system should be operated at highest possible temperature to maximize $S_{D/U}$. Note that the selectivity is extremely low, and the only way to increase it is to keep $\left(\dfrac{C_B}{C_A}\right)^{1/2} < 10^{-6}$ and add B drop by drop.

(15 pts) 5) The temperature and conversion in a very long (i.e., virtually infinite) PFR are shown below as a function of the reactor volume. The reactor is surrounded by a jacket for heat transfer. The value of Ua is 100 cal/(sec • m^3 • K) with T_a being constant. The elementary gas-phase, reversible reaction is

$$2\,A \rightleftharpoons B + 2C$$

and pure A is fed to the reactor at 0.05 mol/dm^3. The absolute value of the heat of reaction is 20,000 cal/mol of A at 500K, and the heat capacities of A, B, and C are 10, 10, and 5 cal/mol/K, respectively.



(7 pt) (a) What is the rate of disappearance of A at V = 10 m^3?

$-r_A$ = _____ mol/m^3•s

(7 pt) (b) What is the total amount of heat removed (in cal/mol) from the entire reactor per mol of A fed in cal/mol?

Q = _____ cal/mol A

(1 pt) (c) What is the equilibrium conversion at 300 K

X_e = _____

Solution

(a) $-r_A$ = _____

At maximum

$Q_g = Q_r$

$\dot{Q}_r = Ua\,(T - T_a) = 100\,(500 - 300) = 20{,}000$ cal/s•m^3

$Q_g = (-r_A)(-\Delta H_{Rx})$

$(-r_A)(-\Delta H_{Rx}) = Q_r = 20{,}000$ cal/s•m^3

$$-r_A = \frac{20{,}000\,\frac{\text{cal}}{\text{s}\bullet\text{m}^3}}{20{,}000\,\frac{\text{cal}}{\text{mol}}} = 1\,\frac{\text{mol}}{\text{m}^3\bullet\text{s}}$$

(b) $\dot{Q} - F_{A0}\sum\Theta_i C_{P_i}\left(T - T_0\right) - \left[\Delta H^\circ_{Rx} + \Delta C_P\left(T - T_a\right)\right]F_{A0}X = 0$ Eqn. (8-28)

Per Mole A

$$\frac{\dot{Q}}{F_{A0}} = C_{P_A}\left[T - T_0\right] + \left[\Delta H_{Rx} + \Delta C_P\left(T - T_R\right)X\right]$$

$$A \underset{\leftarrow}{\overset{\rightarrow}{}} \frac{B}{2} + C$$

$$\Delta C_P = C_{P_C} + \frac{C_{P_B}}{2} - C_{P_A} = 5 + \frac{10}{2} - 10 = 0$$

$$= 0$$

$$\frac{\dot{Q}}{F_{A0}} = 10\left(300 - 400\right) + \left[-20{,}000\right]\left[0.6\right] = -1000 - 12{,}000 = -13{,}000\,\frac{\text{cal}}{\text{mol}}$$

(c) At ∞ reactor length $X_e = 0.6$

(20 pts) 6) The reversible liquid phase reaction

$$A \rightleftharpoons B$$

is carried out in a 12 dm^3 CSTR with heat exchange. Both the entering temperature, T_0, and the heat exchange fluid, T_a, are at 330 K. An equal molar mixture of inerts and A enter the reactor.

(a) Choose a temperature, T, and carry out a calculation to find G(T) to show that your calculation agrees with the corresponding G(T) value on curve shown below at the temperature you choose.

(b) Find the exit conversion and temperature from the CSTR. X = _____ T = _____.

(c) What entering temperature T_0 would give you the maximum conversion?
T_0 = _____ X = _____

(d) What would the exit conversion and temperature be if the heat exchange system failed (i.e., UA = 0)?

Additional information

The G(T) curve for this reaction is shown below

$C_{P_A} = C_{P_B} = 100$ cal/mol/K, $C_{P_I} = 150$ cal/mol/K

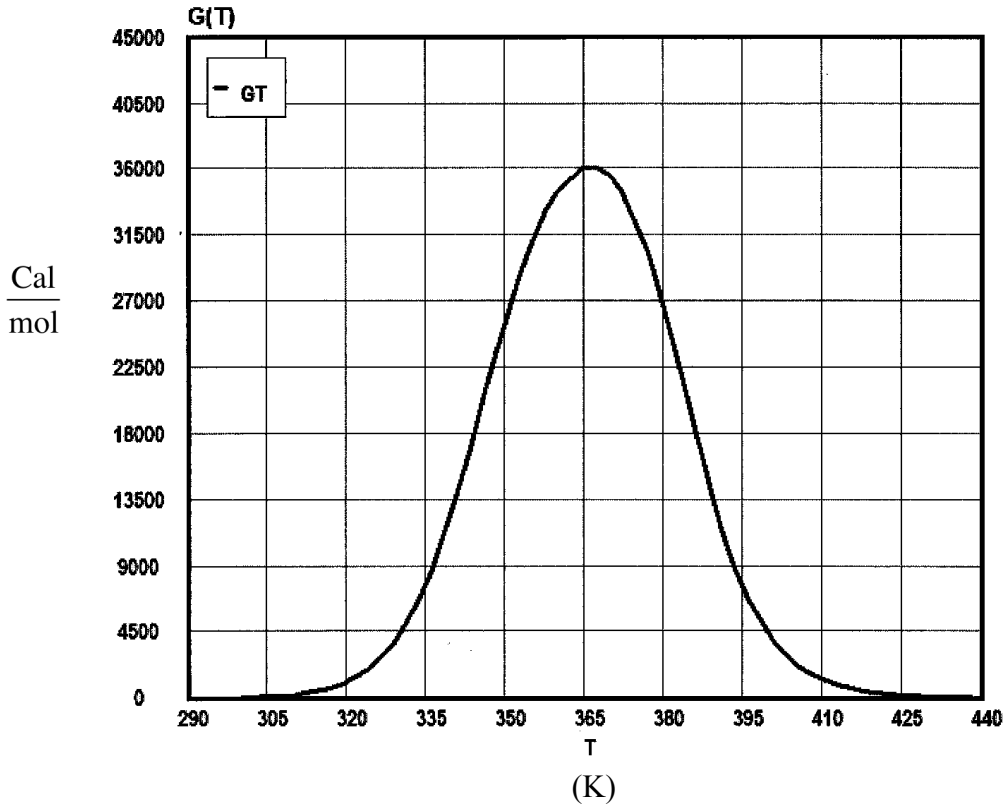
$F_{A0} = 10$ mol/h, $C_{A0} = 1$ mol/dm^3, $v_0 = 10$ dm^3/h

$\Delta H_{Rx} = -42,000$ cal/mol

$UA = 5{,}000$ cal/h/K

$k = 0.001\ h^{-1}$ at 300 K with $E = 30,000$ cal/mol

$K_C = 5,000,000$ at 300 K



Solution

(a) Mole balance for CSTR:

$$V = \frac{F_{A0}X}{-r_A}$$

Rate Law:

$$-r_A = k(C_A - \frac{C_B}{K_C})$$

Stoichiometry:

$$C_A = C_{A0}(1 - \mathrm{X})$$

$$\mathrm{C}_B = C_{A0}X$$

Combine:

$$V = \frac{F_{A0}X}{k(C_{A0}(1 - \mathrm{X}) - \frac{C_{A0}X}{K_C})}$$

$$\frac{VkC_{A0}}{F_{A0}} = \frac{X}{(1 - \mathrm{X}) - \frac{X}{K_C}}$$

$$k\tau[(1 - \mathrm{X}) - \frac{X}{K_C}] = \mathrm{X}$$

$$(\frac{1}{k\tau} + \frac{1}{K_C} + 1)\mathrm{X} = 1$$

$$X = \frac{1}{\frac{1}{k\tau} + \frac{1}{K_C} + 1}$$

Therefore,

$$\mathrm{G(T)} = -\Delta H^{\circ}_{Rx}X = \frac{-\Delta H^{\circ}_{Rx}}{\frac{1}{k\tau} + \frac{1}{K_C} + 1}$$

For example, let T = 380 K, then

$$k = k_{300K}\exp[\frac{E}{R}(\frac{1}{300} - \frac{1}{380})]$$

$$= (0.001)\exp[\frac{30000}{1.987}(\frac{1}{300} - \frac{1}{380})]$$

$$= 39.942\ \mathrm{h}^{-1}$$

$$K_C = K_{C300K}\exp[\frac{\Delta H^o_{Rx}}{R}(\frac{1}{300}-\frac{1}{380})]$$

$$= (5000000)\exp[\frac{-42000}{1.987}(\frac{1}{300}-\frac{1}{380})]$$

$$= 1.807$$

$$\mathrm{G(T)} = \frac{-\Delta H^o_{Rx}}{\frac{1}{k\tau}+\frac{1}{K_C}+1} = \frac{42000}{\frac{1}{(39.942)(12/10)}+\frac{1}{1.807}+1} = 26680 \text{ cal/mol}$$

The calculation agrees with the corresponding G(T) value on curve.

(b)

$$\mathrm{R(T)} = C_{P0}(1+\kappa)(\mathrm{T}-\mathrm{T}_C)$$

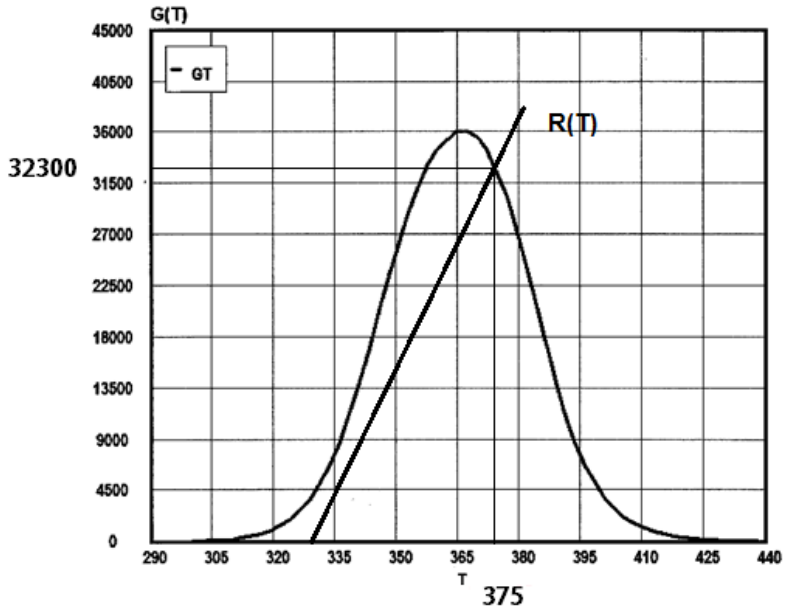
$$C_{P0} = C_{PA} + C_{PI} = 250 \text{ cal/mol/K}$$

$$\kappa = \frac{UA}{C_{P0}F_{A0}} = \frac{5000}{(250)(10)} = 2$$

$$\mathrm{T}_C = \frac{\kappa T_a + T_0}{1+\kappa} = 330 \text{ K}$$

So

$$\mathrm{R(T)} = (250)(1+2)(\mathrm{T}-330) = 750(\mathrm{T}-330)$$



The exit conversion and temperature are:

$$X = \frac{G(\mathrm{T})}{-\Delta H^o_{Rx}} = \frac{32300}{42000} = 0.77$$

$$T = 375\ K$$

(c)

$$R(T) = C_{P0}(1+\kappa)(T - T_C)$$

$$= 750(T - \frac{(2)(330) + T_0}{1+2})$$

$$= 750(T - \frac{T_0}{3} - 220)$$

At maximum conversion, R(T) curve should pass the maximum of G(T): (366, 36000), so

$$36000 = 750(366 - \frac{T_0}{3} - 220)$$

$$T_0 = 294\ K$$

(d) Heat exchange system failure

UA = 0

K = 0

Now: $R(T) = C_{p0}\,(T - TC)$

$R(T) = 250\,(T - TC)$

G(T) = R(T) G(T) = 14000 cal/mol, T = 386 K

$$X = \frac{14\,\text{cal/mol}}{42\,\text{cal/mol}} = 0.33$$

at

$$\boxed{\begin{array}{l} T \approx 386\ K \\ X \approx 0.33 \end{array}}$$

(25 pts) 7) The following elementary reactions are to be carried out in a PFR with a co-current heat exchange with constant T_a

$$2A + B \rightarrow C \qquad \Delta H_{Rx1B} = -10 \frac{kJ}{mol\ B}$$

$$A \rightarrow D \qquad \Delta H_{Rx2A} = +10 \frac{kJ}{mol\ A}$$

$$B + 2C \rightarrow E \qquad \Delta H_{Rx3C} = -20 \frac{kJ}{mol\ C}$$

The reactants all enter at 400 K. Only A and B enter the reactor. The entering concentration of A is 3 molar and that of B is 1 molar at a volumetric flow rate of 10 dm^3/s

Additional information

$Ua = 1{,}000\ J/dm^3/s/K$

$k_{1A}(400\ K) = 1\left(\frac{dm^3}{mol}\right)^2 \Big/ s$

$k_{2A}(400\ K) = 0.5\ s^{-1}$

$k_{3B}(400\ K) = 2\left(\frac{dm^3}{mol}\right)^2 \Big/ s$

$C_{P_A} = 10\ J/mol/K$

$C_{P_B} = 20\ J/mol/K$

$C_{P_C} = 30\ J/mol/K$

$C_{P_D} = 20\ J/mol/K$

$C_{P_E} = 80\ J/mol/K$

What coolant temperature T_a is necessary such that at the reactor entrance, i.e., V = 0, that

$$\frac{dT}{dV} = 0$$

T_a = _____

Solution

$$\frac{dT}{dV} = \frac{r_{1B}\Delta H_{Rx1B} + r_{2A}\Delta H_{Rx2B} + r_{3C}\Delta H_{Rx3C} - Ua(T - T_a)}{F_A C_{P_A} + F_B C_{P_B} + F_C C_{P_C} + F_D C_{P_D} + F_E C_{P_E}}$$

at V = 0, T = T_0 = 400 K for $\frac{dT}{dV} = 0$

$$T_a = T - \left[\frac{r_{1B}\Delta H_{Rx1B} + r_{2A}\Delta H_{Rx2A} + r_{3C}\Delta H_{Rx3C}}{Ua}\right]$$

$-r_{1A} = k_{1A} C_A^2 C_B$

$-r_{2A} = k_{2A} C_A$

$-r_{3B} = k_{3B} C_B C_C^2$

(1)

$$\frac{r_{1B}}{1} = \frac{r_{1A}}{2}$$

$$\Delta H_{Rx1B} r_{1B} = \Delta H_{Rx1B} \frac{r_{1A}}{2} = (-10{,}000)\left(-\frac{1}{2} k_{1A} C_{A0}^2 C_{B0}\right)$$

$$= (5{,}000)(1)(3)^2(1) = 45{,}000$$

(2)

$$\Delta H_{Rx2A} r_{2A} = (-\Delta H_{Rx2A})(-r_{2A})$$

$$= (-10{,}000) k_{2A} C_{A0} = (-10{,}000)(0.5)(3)$$

$$= -15{,}000$$

(3)

$$\Delta H_{Rx3C} r_{3C}$$

$$\frac{r_{3B}}{1} = \frac{r_{3C}}{2}$$

$$\Delta H_{Rx3C} r_{3C} = \Delta H_{Rx3C} 2 r_{3B} = (-20{,}000)\left(-2 k_{3B} C_{B0} C_{C0}^{\ 2}\right) = 0$$

$$T_a = 400 - \left[\frac{45{,}000 - 15{,}000}{Ua}\right] = 400 - \frac{30{,}000}{100}$$

$\boxed{T_a = 370 \text{ K}}$