Problem 1. (25 points)

a. Circle the case(s) below in which multiple steady states are possible.

5 points

+1	+1	+1		
Exothermic, wall-cooled PFR	Endothermic, adiabatic CSTR	Exothermic, adiabatic semi-batch reactor	[✓ Exothermic, wall-cooled CSTR]	[✓ Exothermic, adiabatic PFR with large recycle ratio]
			+1	+1

b. Given the elementary reaction steps: $A \xrightarrow{k1} B \xrightarrow{k2} C$, can you achieve a higher concentration of B in a PFR or a CSTR if $k_1 \approx k_2$? Explain your answer in two sentences or less.

5 points

(+2)

Higher concentration of B is expected in a PFR. A PFR operates at conditions that change down the length of the reactor; ~~A~~ A CSTR operates at the exit conditions and would allow the reaction to progress to the formation of C at the max rate of consumption of B (at the max. B concentration).

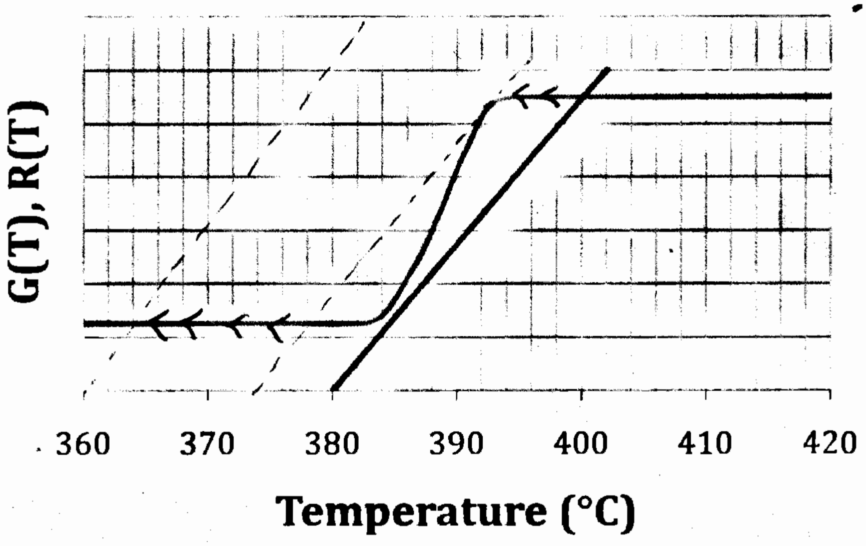
c. On the curve below, draw arrows indicating how the adiabatic CSTR temperature responds to a 20°C decrease in inlet temperature, given an initial inlet feed temperature of 380°C. Make sure that you draw the path of operating reactor temperatures that the system follows as the inlet temperature decreases from 380°C to 360°C. Assume that the heat of reaction and heat capacities are independent of temperature.

• same slope for each line

+1 just line

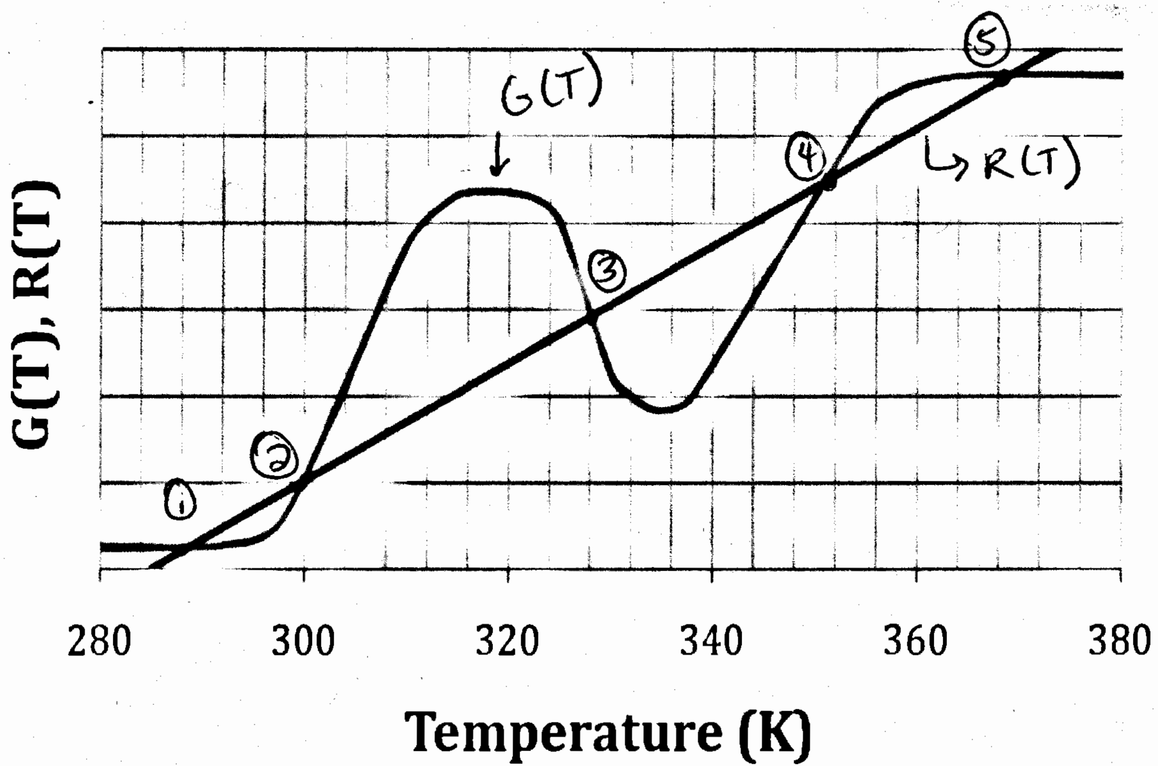
+2.5 show moves

+5 arrows + line



max 5 points

d. A non-ideal steady state, wall-cooled reactor is described by the G(T) and R(T) curves below. Indicate the steady states by clearly numbering each one. Determine the stability of each steady state and justify your choices in two or three sentences. Assume that the heat of reaction and heat capacities are independent of temperature.



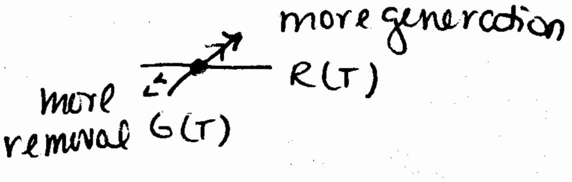
① ③ ⑤ } stable +3

② ④ } unstable +2

with explanation!

For each stable steady state, a small perturbation returns the system to the steady state.

For unstable steady states:



small perturbation - move to a stable steady state.

e. How does the mole balance curve (i.e. X_{MB} vs. temperature) shift for a first-order reaction in a CSTR when you increase the inlet concentration and keep all other parameters constant? Indicate and justify your answer with a sentence or a qualitative graph.

First order reaction: $X_A = \dfrac{k\tau}{1+k\tau}$ (+1)

No shift, mole balance does not depend on concentration for first order reaction.

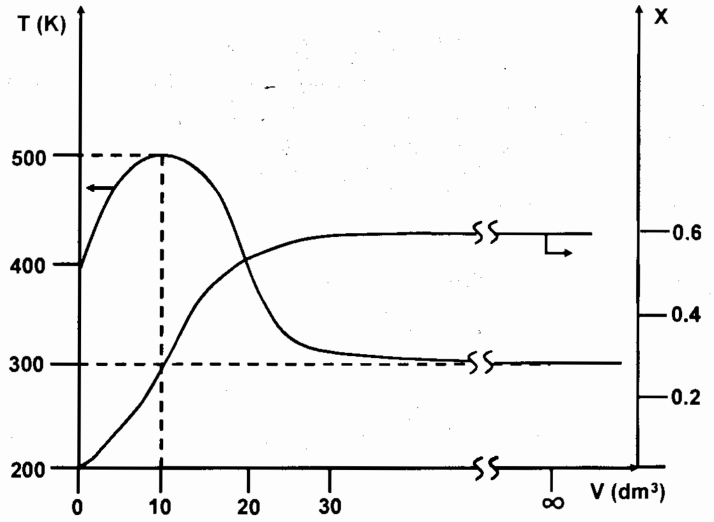
(Full credit possible if assumed τ changed, but full explanation required).

+3 points for "no change"
+2 explain.

5 points total

Problem 2. (35 points)

The temperature and conversion in an infinitely long isobaric 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 dm^{-3} s^{-1} K^{-1}. The gas-phase elementary, reversible reaction is $2A \leftrightarrow B + 2C$ and pure A is fed to the reactor at a concentration of 0.05 mol dm^{-3} and a volumetric flow rate of 1 dm^{3} s^{-1}. The **absolute value** of the heat of the reaction is 20,000 cal (mol of A)$^{-1}$ at 500 K, and the heat capacities of A, B, and C are 1.0, 1.0, and 0.5 cal mol^{-1} K^{-1}, respectively.



a. The coolant temperature is constant. What is the coolant temperature? If you cannot find T_a and need it in a later section, take $T_a = 325$ K (Note: This is an incorrect answer).

At the exit of the reactor:

3 points total

$${}_{0}\cancel{\frac{dT}{dV}} = \frac{Ua(T_a - T) + \overset{0}{\cancel{r_A}}\,\Delta H_{rxn}(T)}{F_{A0}\overline{C}_{p0}}$$

$$\boxed{T = T_a = 300K}$$

b. Is the reaction exothermic or endothermic? Briefly justify your answer.

Exothermic b/c the temperature initially increases. This increase must come from the reaction since $T_a < T_0$.

3 points total

c. What is the instantaneous rate of consumption of A at V = 10 dm^3?

5 points total

$$\underset{0}{\cancel{\frac{dT}{dV}}} = \frac{Ua(T_a - T) + r_A \Delta H_{rxn}(T)}{\tilde{C}_{p0} F_{A0}} \quad @ \; V = 10\,dm^3$$

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

$$r_A\big|_{V=10} = \frac{-Ua(T_a - T)}{\Delta H_{rxn}^{\circ}} = \frac{-100 \frac{cal}{dm^3 s K}(300 - 500K)}{-20{,}000 \; cal/mol}$$

$$\boxed{r_A = 1 \frac{mol}{dm^3 s}}$$

d. What is the numerical value of the equilibrium constant, including the units? You may give the value at any temperature you choose, but the temperature must be specified.

Rate: $-r_A = 2k_f C_A^2 - 2k_r C_B C_C^2 = 0$ @ equi

Stoich:

$$C_A = \frac{F_{A0}(1-X)}{\upsilon}$$

$$C_B = \frac{F_{A0}(\tfrac{1}{2}X)}{\upsilon}$$

$$C_C = \frac{F_{A0}X}{\upsilon}$$

Gas-phase:

$$\upsilon = \upsilon_0 (1 + \varepsilon X)\left(\frac{T}{T_0}\right)\underset{1}{\cancel{\left(\frac{P_0}{P}\right)}}$$

$$\varepsilon = \delta y_{A0} = \left(\tfrac{1}{2}\right)(1)$$

$$C_A = \frac{C_{A0}(1-X)}{1 + \frac{1}{2}X}\left(\frac{T_0}{T}\right)$$

12 points total

$$C_B = \frac{C_{A0}(\frac{1}{2}X)}{1 + \frac{1}{2}X}\left(\frac{T_0}{T}\right)$$

$$C_C = \frac{C_{A0}X}{1 + \frac{1}{2}X}\left(\frac{T_0}{T}\right)$$

@ equi:

$$\frac{k_f}{k_r} = K_{eq} = \frac{C_C^2 C_B}{C_A^2}$$

$$= \frac{C_{A0}^{\cancel{3}}(X)^2\left(\frac{1}{2}X\right)}{\left(1+\frac{1}{2}X\right)^{\cancel{3}}}\left(\frac{T_0}{T}\right)^{\cancel{3}}\frac{\cancel{\left(1+\frac{1}{2}X\right)^{2}}}{\cancel{C_{A0}^{2}}(1-X)^2}\cancel{\left(\frac{T}{T_0}\right)^{2}}$$

$$= \frac{C_{A0}\,\frac{1}{2}\,X^3\,(T_0/T)}{\left(1+\frac{1}{2}X\right)(1-X)^2} = \frac{0.05\left(\frac{1}{2}\right)(0.6)^3\left(400/300\right)}{(1+0.3)\,(1-0.6)^2}$$

$$\boxed{K_{eq} = 0.034\ \frac{mol}{dm^3}\ @\ 500K}$$

e. What is the total amount of heat removed from the reactor? (This part is worth 12 points.)

$$\frac{dT}{dV} = \frac{Ua(T_a-T) + r_A \Delta H^\circ_{rxn}}{F_{A0}\bar{C}_{p0}}$$

$$F_{A0}\bar{C}_{p0}\,dT = Ua(T_a-T)\,dV + r_A \Delta H^\circ_{rxn}\,dV$$

$$F_{A0}\bar{C}_{p0}\int_{T_0}^{T} dT = \underbrace{\int_0^{\infty} Ua(T_a-T)\,dV}_{Q_{NET}} + \Delta H^\circ_{rxn}\int_0^{\infty} r_A\,dV$$

$$r_A = -F_{A0}\frac{dX}{dV}$$ from mole balance.

$$F_{A0}\bar{C}_{p0}(T-T_0) = Q_{NET} + \Delta H^\circ_{rxn}\int_V^{\infty}\left(-F_{A0}\frac{dX}{\cancel{dV}}\right)\cancel{dV}$$

$$Q_{NET} = F_{A0}\bar{C}_{p0}(T-T_0) + F_{A0}\Delta H^\circ_{rxn}\int_0^{0.6} dX$$

$$= 0.05(1)(1)(300-400) + 0.05(1)(-20000)(0.6-0)$$

$$\boxed{Q_{NET} = -605\ \frac{cal}{min}}$$ ← neg b/c heat removed.

Problem 3. (30 points)

An elementary, liquid-phase reaction A + B → 2C is to be carried out in an isothermal CSTR. A and B enter the reactor at 27°C, with a total flow of 2 $dm^3\ s^{-1}$, and equal concentrations of 1 mol dm^{-3}. The rate constant at 27°C is 0.01 $dm^3\ mol^{-1}\ s^{-1}$ and the standard heat of the reaction at 25°C is -60 kJ (mol of A)$^{-1}$. The reactor coolant temperature is constant at 10°C and U = 2.0 kJ $m^{-2}\ s^{-1}\ K^{-1}$. The heat capacities of A, B, and C are 2, 1, and 1.5 kJ $mol^{-1}\ K^{-1}$, respectively.

a. Determine the reactor volume required to achieve a 45% conversion of A.

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

4 points total

Rate: $-r_A = k C_A C_B$

Stoich: $C_A = C_{A0}(1-X)$

$C_B = C_{A0}(1-X)$

$$V = \frac{\cancel{C_{A0}} v_0 X}{k C_{A0}^{\cancel{2}} (1-X)^2} = \frac{0.2(0.45)}{(0.01)(1)(0.55)^2} = \boxed{298\ dm^3}$$

b. Determine the heat transfer area needed to run the reactor isothermally at 45% conversion of A.

$$X_{EB} = \frac{\frac{UA}{F_{A0}}(T - T_a) + \tilde{C}_{p0}\overset{0\ (\text{isothermal})}{\cancel{(T - T_0)}}}{-\Delta H^\circ_{rxn} \leftarrow \Delta \hat{C}_p = 0}$$

4points total

$$A = \frac{X_{EB}(-\Delta H^\circ_{rxn})(F_{A0})}{U(T - T_a)} = \frac{0.45(60)(2)(1)}{2(300-283)} = \boxed{1.58\ m^2}$$

2 points total

c. Would the answer to part b) be higher or lower (choose one) if we had included shaft work? Justify your answer in one sentence.

Higher b/c more energy is being put into the reactor, that needs to be removed.

d. The feed temperature is no longer 27°C. If the reactor were to operate adiabatically and is at 27°C and 45% conversion of A, what new feed temperature would be required?

$$X_{EB} = \frac{\cancelto{0}{\dot{Q}} + \overline{C_{p0}}(T - T_0)}{-\Delta H^\circ_{rxn}}$$

$$T_0 = T - \frac{X_{EB}(-\Delta H^\circ_{rxn})}{\overline{C_{p0}}} = 300 - \frac{(0.45)(60)}{3}$$

$$\boxed{T_0 = 291\,K}$$

4 points total

e. The reactor is still run adiabatically and the inlet temperature is changed to 27°C. When this is performed, the conversion increases to 93%. Based on this observation, what is the activation barrier for this reaction?

8 points total

$$X_{EB} = \frac{\overline{C_{p0}}(T-T_0)}{-\Delta H^{\circ}_{rxn}}$$

$$T = T_0 + \frac{X_{EB}(-\Delta H^{\circ}_{rxn})}{\overline{C_{p0}}} = 300 + \frac{(0.93)(60)}{3} = 319\,K$$

$$V = \frac{v_0 X}{k C_{A0}(1-X)^2}$$

$$k = \frac{v_0 X}{V C_{A0}(1-X)^2} = \frac{(2)(0.93)}{298(1)(0.07)^2} = 1.28 \frac{dm^3}{mol\ s}$$

Arrhenius:

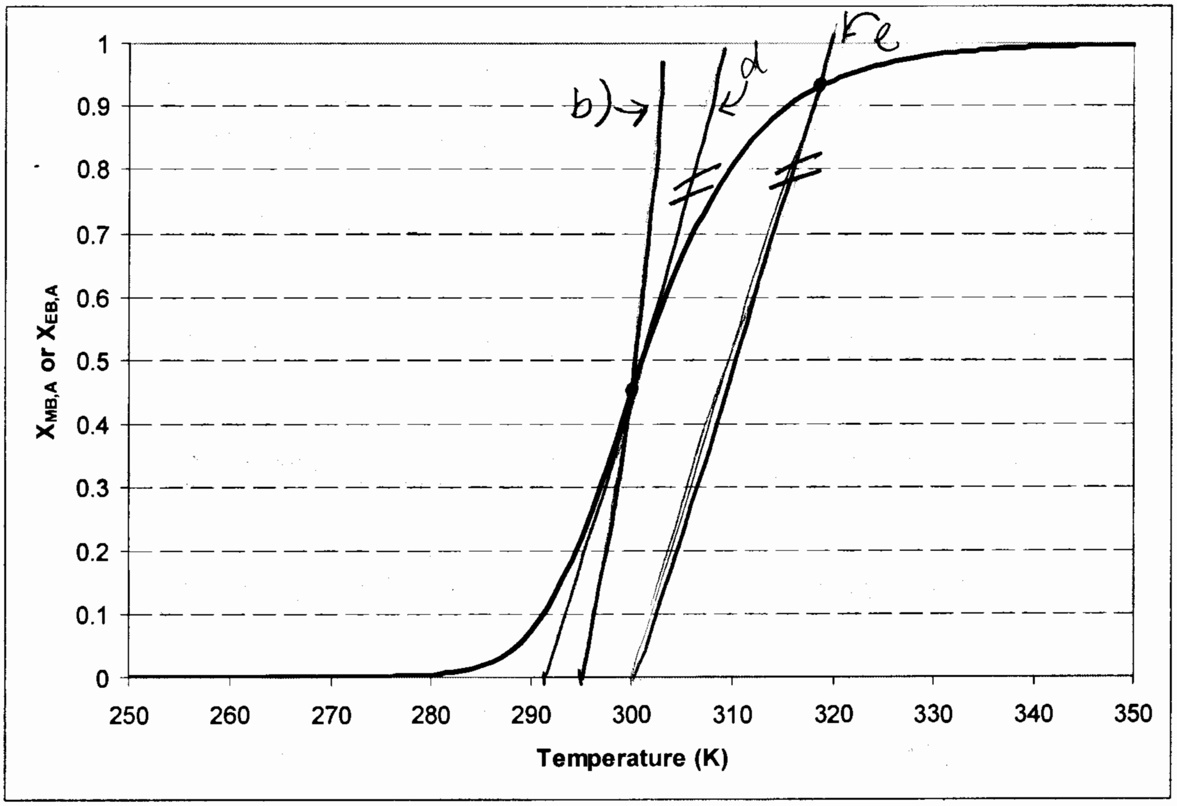
$$\frac{k_1}{k_2} = \exp\left(\frac{-E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

$$\ln\left(\frac{.01}{1.28}\right) = \frac{-E_A}{0.0083}\left(\frac{1}{300} - \frac{1}{319}\right)$$

$$\boxed{E_A = 203\ kJ/mol}$$

8 points total →

f. Below is the curve of $X_{MB,A}$ (mole balance conversion of A) vs. T. Draw the lines for $X_{EB,A}$ (energy balance conversion of A) vs. T for parts b), d), and e) and label them. You must accurately indicate the T* values (Fogler calls this T_C) for all cases. Clearly show lines with parallel slopes by drawing equal signs through them.



X-intercepts are T*:

part b. $T^* = \frac{T_a \alpha + T_0}{\alpha + 1}$

$\alpha = \frac{UA}{C_{p0} F_{A0}} = \frac{(2)(1.58)}{3(1)(2)} = 0.527$

$T^* = \frac{(283)(0.527) + 300}{1.527} = 294$

part d&e (adiabatic)

$T^* = T_0$ $(\alpha = 0)$

T = 291 K for part d

= 300 K for part e

Lines drawn by connecting T* to solution along X_{MB} given in problem.

Problem 4. (10 Points)

An adiabatic, liquid-phase semibatch reactor initially at $T_o = 325$ K is charged with $N_{Ao} = 100$ mol of pure liquid A. At time t = 0, an equimolar liquid feed of B and inert I at temperature $T_{feed} = 300$ K is fed to the semibatch reactor at a total molar flow rate $F_T = 10$ mol hr^{-1}. The reaction $A + B \rightarrow 2C$ occurs in the reactor. Assume a temperature independent heat of reaction of -100 kJ mol^{-1} of A, a $C_p = 1$ kJ mol^{-1} K^{-1} for all species, and A to be the limiting reactant for all times. Also assume an Arrhenius temperature dependence for k where E_a is 30 kJ mol^{-1}. Given that a 50% conversion of A is achieved after 10 hrs, write out a thermochemical cycle and use it to calculate the reactor temperature at this time.

Energy Balance:

$$(N_{Ao} + F_B t + F_I t) C_p \cdot (T - T_o) = -\Delta H_{rxn} N_{Ao} X_A$$
$$+ (F_B t + F_I t) \cdot C_p \cdot (T_o - T_{feed})$$

$$(100 + 10(10))\text{ mol} \cdot 1 \frac{\text{kJ}}{\text{mol}\cdot\text{K}} \cdot (T - 325\text{K})$$
$$+ (10)(10)\text{ mol} \cdot 1 \frac{\text{kJ}}{\text{mol}\cdot\text{K}} \cdot (325\text{ K} - 300\text{ K})$$
$$= 100 \frac{\text{kJ}}{\text{mol A}} (100\text{ mol A})(0.5)$$

$$\boxed{T = 337.5\text{ K}}$$