

ChE 344
Fall 2014
Final Exam + Solution

Wednesday, December 17, 2014
4 p.m. – 6 p.m.

Open Book, Closed Web and Closed Notes

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) ____ / 5 pts

3) ____ / 15 pts

4) ____ / 20 pts

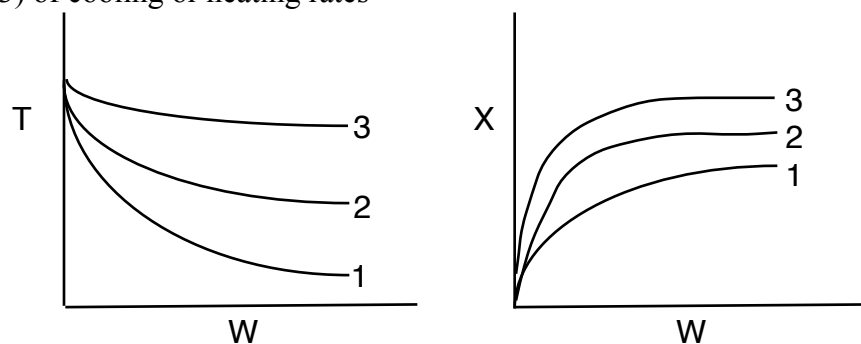
5) ____ / 25 pts

6) ____ / 25 pts

7) ____ / 35 pts

Total ____ / 130 pts

- (5 pts) 1) The conversion and temperature are shown below as a function of catalyst weight for three sets (1, 2, 3) of cooling or heating rates



Circle the correct answer.

- A) One of the curves could correspond to an exothermic irreversible reaction with too high of a cooling rate.
 True False Insufficient information to tell
- B) One of the curves could correspond to an endothermic reversible reaction with too high of a heating rate.
 True False Insufficient information to tell
- C) The reaction could be second order exothermic and carried out adiabatically.
 True False Insufficient information to tell

Solution

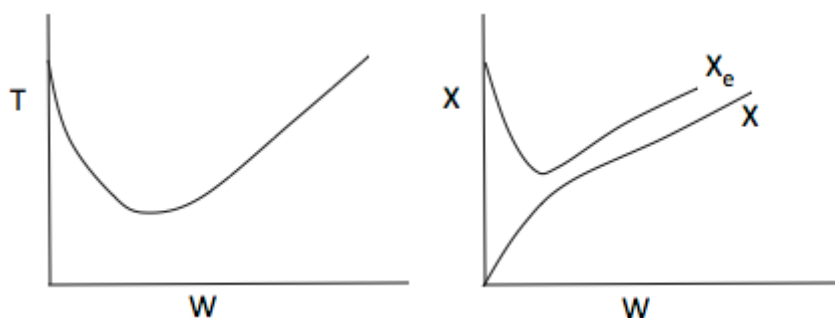
- A) True. $k(T)$ smaller $\therefore X$ smaller

$$\frac{dX}{dV} = \frac{k}{v_0}(1-X)$$

$$v_0 = \text{constant}$$

- B) False. For endothermic reactions conversion always increases with heating rate up to isothermal conditions.
- C) False. For exothermic adiabatic reaction T always increases with increasing W .

(5 pts) 2) Consider the following profiles for the reaction $A \rightleftharpoons B$



Which of the following statements are true? Circle all that apply.

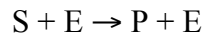
- A) The above reaction could be adiabatic.
- B) The above reaction could be exothermic with constant cooling temperature.
- C) The above reaction could be endothermic with constant heating temperature.
- D) The above reaction could be second order.
- E) The above reaction could be first order.

Solution

Answer: C and D

- A) The above reaction could be adiabatic. False.
 X_e could not increase if adiabatic.
- B) The above reaction could be exothermic with constant cooling temperature. False.
 T would increase then decrease follow slope temperature curve.
- C) The above reaction could be endothermic with constant heating temperature. True.
- D) The above reaction could be second order. True.
- E) The above reaction could be first order. True.

(15 pts) 3) The enzymatic reaction



follows Michaelis-Menten kinetics. The reaction is carried out in a batch reactor where the initial substrate concentration is 0.1 mol/dm^3 . When the substrate concentration is 0.02 mol/dm^3 the reaction rate is one half the maximum rate. If 20 minutes are necessary to reach one half the maximum rate, what is $V_{\max}$?

Solution

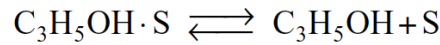
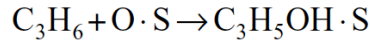
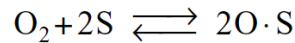
$$K_m = S = 0.02 \text{ mol/dm}^3$$

$$t = \frac{K_m \ln \frac{C_{S0}}{C_S} + C_{S0} - C_S}{V_{\max}} \quad \text{see equation (9-32) on page 9-22}$$

$$V_{\max} = \frac{0.02 \ln \frac{0.1}{0.02} + 0.1 - 0.02}{20 \text{ min}} = \frac{(0.02)(1.6) + (0.098)}{20 \text{ min}^{-1}} = 0.0065 \text{ min}^{-1}$$

(20 pts) 4) Study Problem

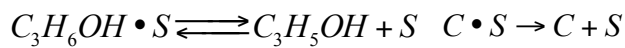
P10-6B The formation of propanol on a catalytic surface is believed to proceed by the following mechanism



At low concentrations of oxygen, the initial rate is half order in O_2 and first order in propylene. Suggest a rate-limiting step and derive a rate law.

Solution

P10-6B



$$-r_B = r_S = k_3 P_B C_{A \cdot S}$$

$$r_{AD} = k_A \left[P_{A_2} C_V^2 - \frac{C_{A \cdot S}^2}{K_A} \right]$$

Assume surface reaction is the rate-limiting step

$$\frac{r_{AD}}{k_A} = 0$$

Replace all P_A with P_{A_2}

$$C_{AgS} = C_V \sqrt{K_A P_A}$$

$$-r_B = r_S = k_3 P_B C_V \sqrt{K_A P_A}$$

$$r_{C \cdot S} = k_D \left[C_{C \cdot S} - \frac{P_C C_V}{K_D} \right] = k_D [C_{C \cdot S} - K_C P_C C_V]$$

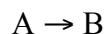
$$\frac{r_{C \cdot S}}{k_D} = 0$$

$$C_{C \cdot S} = K_C P_C C_V$$

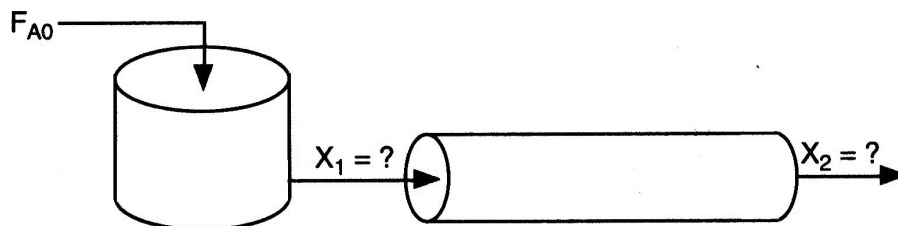
$$C_T = C_V + C_{A \cdot S} + C_{C \cdot S} = C_V \left[1 + \sqrt{K_A P_A} + K_C P_C \right]$$

$$-r_B = r_S = \frac{k_3 C_T P_B \sqrt{K_A P_A}}{1 + \sqrt{K_A P_A} + K_C P_C}$$

- (25 pts) 5) Study Problem P5-20_B, Modified California Registration Exam Problem
The elementary gas phase reaction



takes place isobarically and isothermally in a PFR where 63.2% conversion is achieved. The feed is Pure A. It is proposed to put a CSTR of equal volume upstream of the PFR, i.e.,



Based on the entering molar flow rate to A to the first reactor, what will be the intermediate from the CSTR, X_1 and exit conversions from the PFR based on feed to first reactor? The entering flow rates and all other variables remain the same as that for the single PFR.

$$X_1 = \underline{\hspace{2cm}}$$

$$X_2 = \underline{\hspace{2cm}}$$

Solution

Base Case PFR above. Find τk

$$\text{Mole Balance } \frac{dX}{dV} = -r_A$$

$$\text{Rate Law } -r_A = kC_A$$

Stoichiometry

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

Combine

$$\frac{dX}{dV} = \frac{kC_{A0}}{F_{A0}}(1 - X) = \frac{k}{v_0}(1 - X)$$

$$\ln \frac{1}{1 - X} = k\tau$$

$$X = 0.632$$

$$\ln 2.73 = \tau k$$

$$k\tau = 1$$

CSTR added upstream of PFR

$$V = \frac{F_{A0}X}{kC_{A0}(1-X)}$$

$$\tau k = \frac{X}{1-X}$$

$$\frac{kV}{v_0} = \frac{X}{1-X} = 1$$

$$X = 0.5$$

$$X_1 = 0.5$$

Now find X_2

$$V = F_{A0} \int_{X_1}^{X_2} \frac{dX}{-r_A} = v_0 C_{A0} \int_{X_1}^{X_2} \frac{dX}{kC_{A0}(1-X)}$$

$$\tau k = \int_{X_1}^{X_2} \frac{dX}{1-X}$$

$$= \ln \frac{1}{1-X_2} - \ln \frac{1}{1-X_1}$$

$$1 = \ln \frac{1}{1-X_2} - \ln \frac{1}{1-0.5}$$

$$1 + \ln 2 = 1.69 = \ln \frac{1}{1-X_2}$$

$$5.44 = \frac{1}{1-X_2}$$

$$0.18 = 1 - X_2$$

$$X_2 = 0.82$$

(25 pts) 6) Study Problem from California Professional Engineers Exam

P7-8_A In order to study the photochemical decay of aqueous bromine in bright sunlight, a small quantity of liquid bromine was dissolved in water contained in a glass battery jar and placed in direct sunlight. The following data were obtained at 25°C:

Time (min)	10	20	30	40	50	60
ppm Br ₂	2.45	1.74	1.23	0.88	0.62	0.44

- (10 pts) **(a)** Determine whether the reaction rate is zero or first order in bromine using any technique you choose (e.g., trial and error, plotting) and calculate the reaction rate constant in units of your choice.
- (15pts) **(b)** Assuming identical exposure conditions, calculate the required hourly rate of injection of bromine (in pounds per hour) into a sunlit body of water, 25,000 gal in volume, in order to maintain a sterilizing level of bromine of 1.0 ppm. [If you are unable to determine the rate constant in part (a) assume it is equal to 1.0 in appropriate units.]
(Note: ppm = parts of bromine per million parts of brominated water by weight. In dilute aqueous solutions, 1 ppm = 1 milligram per liter).

Solution

P7-8 (a)

Photochemical decay of bromine in bright sunlight:

t (min)	0	10	20	30	40	50	60
C _A (ppm)		2.45	1.74	1.23	0.88	0.62	0.44

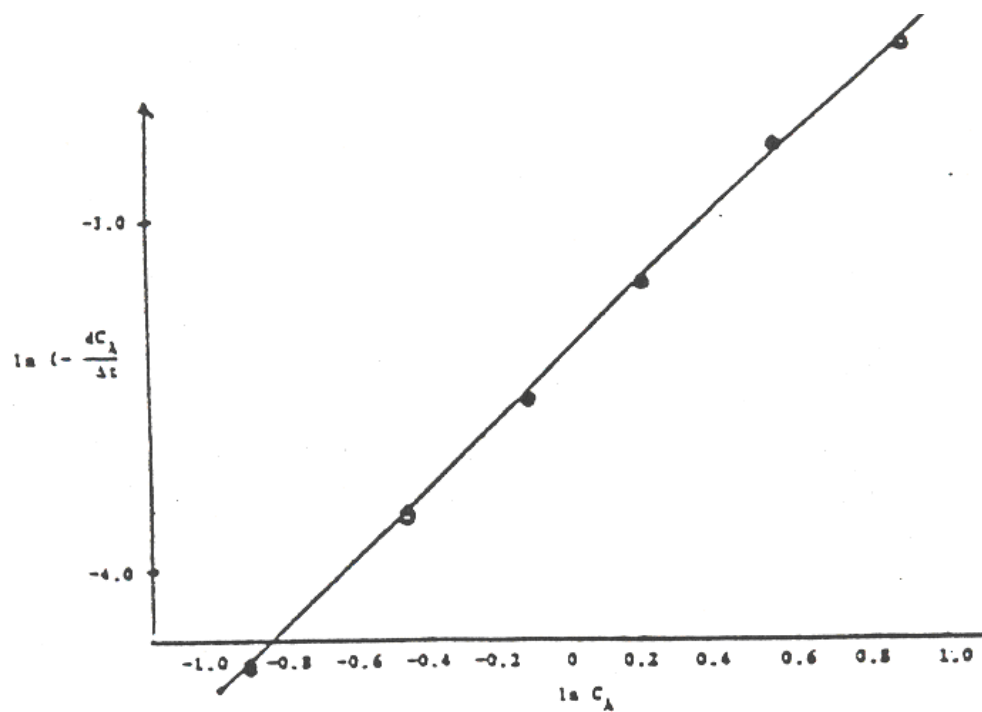
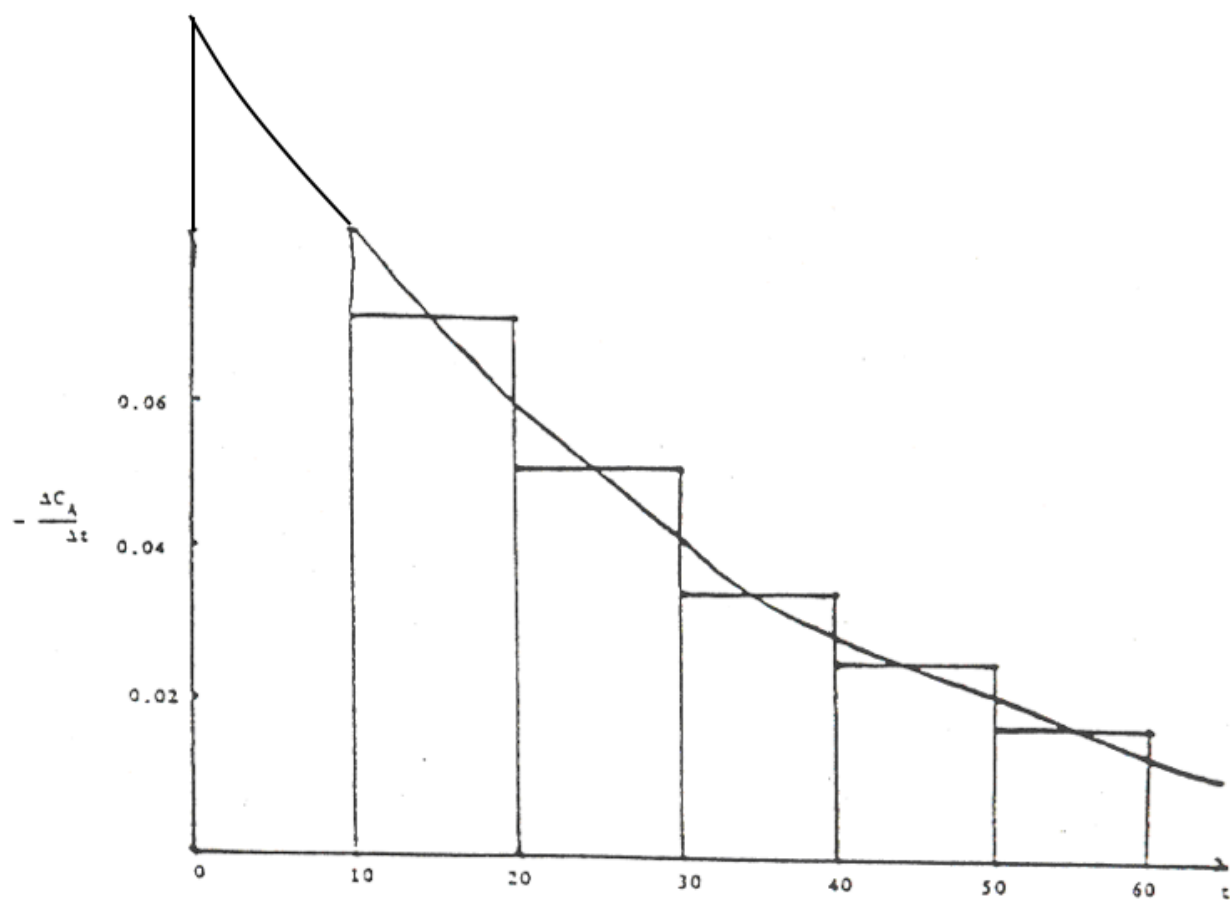
Mole balance: constant V

$$\frac{dC_A}{dt} = r_A = -kC_A^\alpha$$

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln(k) + \alpha \ln(C_A)$$

Differentiation

T (min)	10	20	30	40	50	60
Δt (min)	10	10	10	10	10	10
C _A (ppm)	2.45	1.74	1.23	0.88	0.62	0.44
ΔC _A (ppm)	-0.71	-0.51	-0.35	-0.26	-0.18	
$\frac{\Delta C_A}{\Delta t} \left(\frac{\text{ppm}}{\text{min}} \right)$	-0.071	-0.051	-0.035	-0.026	-0.018	



After plotting and differentiating by equal area

$-dC_A/dt$	0.082	0.061	0.042	0.030	0.0215	0.014
$\ln(-dC_A/dt)$	-2.501	-2.797	-3.170	-3.507	-3.840	-4.269
$\ln C_A$	0.896	0.554	0.207	-0.128	-0.478	-0.821

Using linear regression: $\alpha = 1.0$

$\ln k = -3.3864$

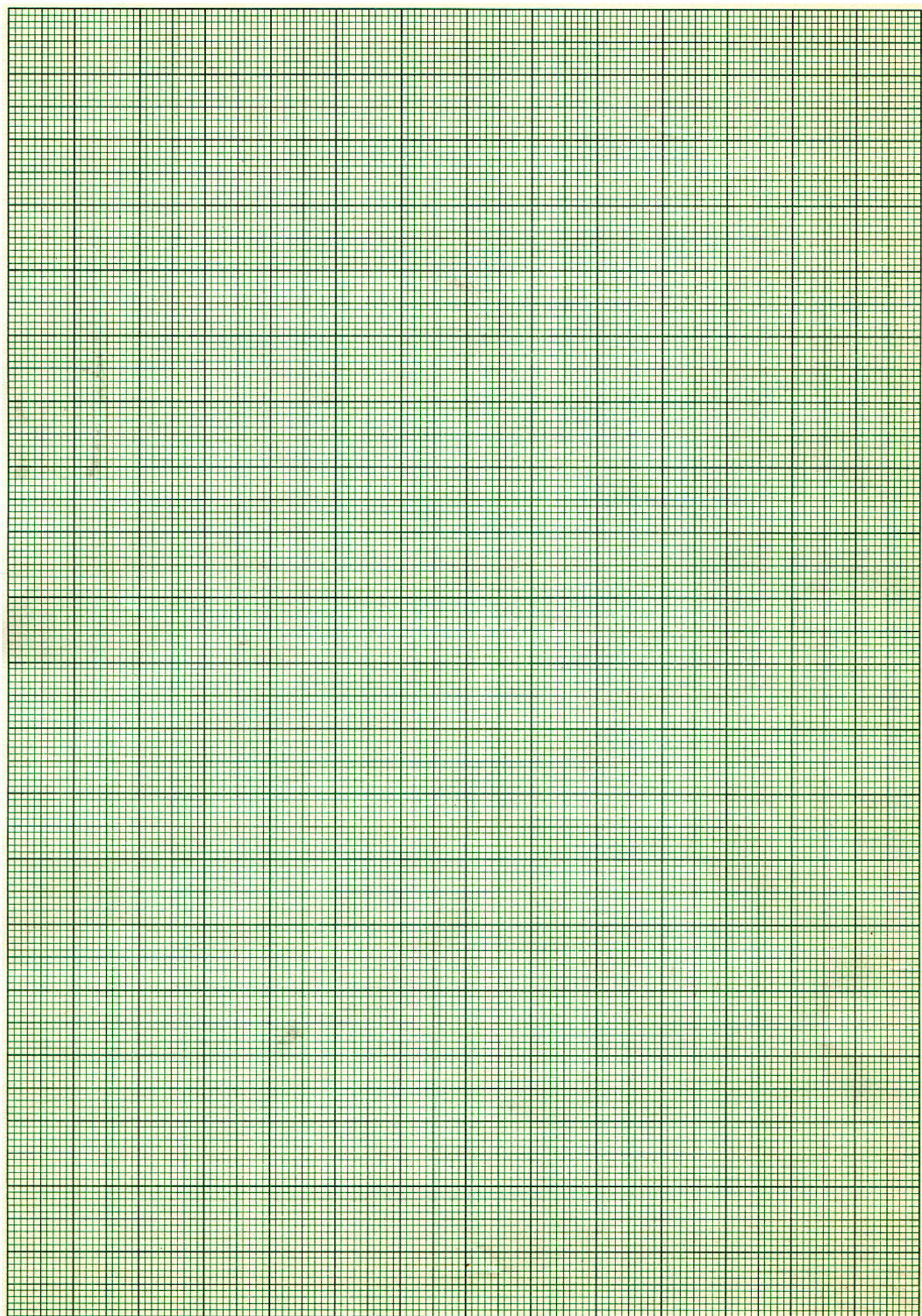
$k = 0.0344 \text{ min}^{-1}$

P7-8 (b)

$$\frac{dN_A}{dt} = -Vr_A - F_B = 0$$

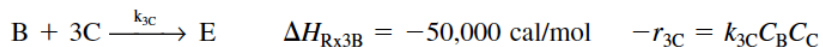
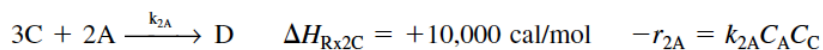
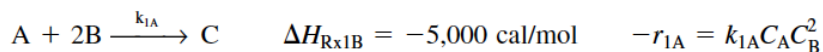
$$r_A = -0.0344 \frac{\text{ppm}}{\text{min}} = -0.0344 \frac{\text{mg}}{\text{l min}} \text{ at } C_A = 1 \text{ ppm}$$

$$F_B = (25000 \text{ gal}) \left(0.0344 \frac{\text{mg}}{\text{l min}} \right) \left(60 \frac{\text{min}}{\text{hr}} \right) \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) \left(\frac{3.7851 \text{ l}}{1 \text{ gal}} \right) \left(\frac{1 \text{ lbs}}{453.6 \text{ g}} \right) = 0.426 \frac{\text{lbs}}{\text{hr}}$$



(35 pts) 7)

P13-7_B The following reactions are taking place in a 2,000 dm³ liquid phase batch reactor under a pressure of 400 psig



The initial temperature is 450 K and the initial concentrations of A, B and C are 1.0, 0.5 and 0.2 mol/dm³ respectively. The coolant flow rate was at its maximum value so that $T_{a1} = T_{a2} = T_a = 400$ K so that the product the exchange area and overall heat transfer coefficient, UA , is $UA = 100 \text{ cal/s} \cdot \text{K}$.

- (a) If $Q_r > Q_g$ at time $t = 0$, and there is no failure of the heat exchange system, is there any possibility that reactor will run away? Explain

- (b) What is Q_r at $t = 0$? $Q_r = \underline{\hspace{2cm}}$

- (c) What is Q_g at $t = 0$? $Q_g = \underline{\hspace{2cm}}$

- (d) What is the initial rate of increase in temperature, (i.e., dT/dt) at $t = 0$?

$$\frac{dT}{dt} = \underline{\hspace{2cm}}$$

- (e) Suppose that the ambient temperature T_a is lowered from 400 K to 350 K, what is the initial rate of reactor temperature change?

$$\frac{dT}{dt} = \underline{\hspace{2cm}}$$

Additional Information:

As a first approximation, assume all heats of reaction are constant (i.e., $\Delta C_{p_{ij}} \cong 0$) Specific reaction rates at 450 K are

$$k_{1A} = 1 \times 10^{-3} \text{ (dm}^3\text{/mol)}^2\text{/s} \quad C_{p_A} = 10 \text{ cal/mol/K} \quad C_{p_D} = 80 \text{ cal/mol/K}$$

$$k_{2A} = \frac{1}{3} \times 10^{-3} \text{ (dm}^3\text{/mol)}^2\text{/s} \quad C_{p_B} = 10 \text{ cal/mol/K} \quad C_{p_E} = 50 \text{ cal/mol/K}$$

$$k_{3C} = 0.6 \times 10^{-3} \text{ (dm}^3\text{/mol)}^2\text{/s} \quad C_{p_C} = 50 \text{ cal/mol/K}$$

Solution

Part (a)

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{N_A C_{p_A} + N_B C_{p_B} + N_C C_{p_C}}$$

If $Q_r > Q_g$ then the temperature can only decrease causing the specific reaction rates k_i to decrease, hence runaway is unlikely.

Part (b)

$$Q_r = UA(T - T_a) = 100 \frac{\text{cal}}{\text{s} \cdot \text{K}} [450 - 400] \text{K} = 5,000 \frac{\text{cal}}{\text{s}}$$

Part (c)

$$Q_g = V[r_{1B}\Delta H_{R_{x1B}} + r_{2C}\Delta H_{R_{x2C}} + r_{3B}\Delta H_{R_{x3B}}]$$

Initially $T = 350 \text{ K}$

$$\text{Reaction 1: } \frac{r_{1A}}{-1} = \frac{r_{1B}}{-2} = \frac{r_{1C}}{1} \quad r_{1B} = 2r_{1A}$$

$$\text{Reaction 2: } \frac{r_{2A}}{-2} = \frac{r_{2C}}{-3} = \frac{r_{2D}}{1} \quad r_{2C} = \frac{3}{2}r_{2A}$$

$$\text{Reaction 3: } \frac{r_{3B}}{-1} = \frac{r_{3C}}{-3} = \frac{r_{3E}}{1} \quad -r_{3B} = \frac{1}{3}r_{3C}$$

$$Q_g = V[2k_{1A}C_A C_B^2][-\Delta H_{R_{x1B}}] + V\left[\frac{3}{2}k_{2A}C_A C_C\right][-\Delta H_{R_{x2C}}] + V\left[\frac{1}{3}k_{3C}C_B C_C\right][-\Delta H_{R_{x3C}}]$$

$$= (2,000) \left[\underbrace{(2)(10^{-3})(1)(0.5)^2 5,000}_{5,000} \right] + 2,000 \left[\underbrace{\frac{3}{2} \left(\frac{1}{3} \times 10^{-3} \right) (1)(0.2) [10,000]}_{-2,000} \right] +$$

$$+ 2,000 \left[\underbrace{\frac{1}{3} (0.6 \times 10^{-3}) (0.5)(0.2)}_{+2,000} \right] \cdot [50,000] = 5,000$$

$$Q_g = 5,000 \text{ cal/s}$$

$$\frac{dT}{dt} = \frac{Q_r - Q_g}{N_{A0}C_{PA} + N_{B0}C_{PB} + N_{C0}C_{PC}} = \frac{5,000 - 5,000}{N_{A0}C_{PA} + N_{B0}C_{PB} + N_{C0}C_{PC}} = 0$$

Part (d)

$$N_{A0}C_{PA} = C_{A0}VC_{PA} = (1)(2,000)(10) = 20,000$$

$$N_{B0}C_{PB} = C_{B0}VC_{PB} = (0.5)(2,000)(10) = 10,000$$

$$N_{C0}C_{PC} = C_{C0}VC_{PC} = (0.2)(2,000)(50) = 20,000$$

$$\frac{dT}{dt} = \frac{Q_g - Q_r}{50,000} = \frac{5,000 - 5,000}{50,000} = 0$$

Part (e)

Drop T_a by 50

$$Q_r = UA(T - T_a) = 100(450 - 350) = 10,000$$

$$\frac{dT}{dt} = \frac{5,000 - 10,000}{50,000} = -0.1$$

Blank Sheet