Instructions

1. Write your name at the top of the exam questions. You must turn in these questions or you will receive a grade of **ZERO** on the final.
2. Write your name at the top of each answer sheet.
3. Start each problem at the top of a new page.
4. The exam consists of five equally weighted problems.
5. Useful equations and integrals are provided after the questions.

R = 82.06 cm^3-atm/gmole-K; R = 1.987 cal/gmole-K

Problem 1

A pulse input experiment was performed on a flow reactor. The effluent pulse data ($c_{\text{pulse}}(\theta)$) and the corresponding residence time distribution are tabulated below. Determine the effluent concentration of A for this reactor if $c_{\text{A}f} = 0.07$ gmole/liter and $k = 16.56$ lit/gmole-min for the following liquid-phase reaction

$$\text{A} \xrightarrow{k} \text{B} \qquad r = kc_{\text{A}}^2$$

θ (min)	$c_{\text{pulse}}(\theta)$ (μmole/liter)	$p(\theta)$ (min^{-1})	θ (min)	$c_{\text{pulse}}(\theta)$ (μmole/liter)	$p(\theta)$ (min^{-1})
0	0.00	0.000	14	2.50	0.029
2	1.40	0.016	16	1.70	0.020
4	5.60	0.065	18	1.00	0.012
6	9.10	0.106	20	0.60	0.007
8	9.50	0.111	22	0.20	0.002
10	6.90	0.081	24	0.00	0.000
12	4.60	0.054			

In general:

$$\overline{\theta} = \int_0^\infty \theta p(\theta) d\theta \qquad \sigma^2 = \int_0^\infty (\theta - \overline{\theta})^2 p(\theta) d\theta$$

For segregated flow:

$$c_s(\theta) = \int_0^\infty p(\theta) c(\theta) d\theta$$

For CSTRs-in-series:

$$p(\theta) = \left(\frac{n}{\overline{\theta}}\right)^n \frac{\theta^{n-1}}{(n-1)!} \exp^{n\theta/\overline{\theta}} \qquad n = \frac{\overline{\theta}^2}{\sigma^2}$$

Problem 2

Determine the isothermal (450 K) plug flow reactor volume required for 90 % of A to react for the following second-order gas phase reaction.

$$A \longrightarrow B + C$$

Where

$$r = k \times c_A^2$$

and the rate constant is ($k = 1000$ cm^3/(gmole-sec)). The feed contains a 50:50 mixture of A in an inert at a total pressure of 4 atm and a molar feed rate of 6.0 gmole/sec.

Problem 3

The first-order, heterogeneously catalyzed reaction

$$A \longrightarrow B \qquad r = kc_A$$

will be carried out in a spherical pellet.

Using the data below predict the isothermal, fixed-bed reactor volume needed to convert 95% of A if the feed is pure A at 2.5 atm, 585 K, $N_{Af} = 12$ mol/s, and a pellet radius $R = 0.25$ cm. The data ($r_{\text{experimental}}$) were collected at 585 K and $P_A = 2.5$ atm over pellets of different diameters. At the reactor and experimental conditions, the diffusivity of A in the pellet is $D_A = 0.004$ cm^2/s and you can assume the bulk fluid and the pellet exterior concentrations are equal. The pellet density is $\rho_p = 0.68$ g/cm^3 and the bed density is $\rho_B = 0.40$ g/cm^3 (*i.e.*, $\epsilon_B = 0.412$).

Pellet radius (cm)	Experimental Rate $r_{\text{experimental}}$ (gmole/cm^3-s)
0.01	2.20×10^{-4}
0.02	1.88×10^{-4}
0.03	1.57×10^{-4}
0.04	1.31×10^{-4}
0.05	1.12×10^{-4}
0.1	6.28×10^{-5}
0.2	3.31×10^{-5}
0.3	2.25×10^{-5}
0.4	1.70×10^{-5}
0.5	1.37×10^{-5}

Problem 4

Allyl chloride is to be produced in a 25-ft long 2-in ID tube operating as a PFR. The feed is a 4:1 molar ratio of propylene to chlorine and it enters at a feed rate of 0.85 lbmol/hr, 2 atm of pressure, and 392 °F . The reactor pressure may be assumed constant.

$$Cl_2 + C_3H_6 \xrightarrow{k_1} C_3H_5Cl + HCl \quad (1)$$

$$Cl_2 + C_3H_6 \xrightarrow{k_2} C_3H_6Cl_2 \quad (2)$$

The rate constants have units of lbmol/(hr ft^3 atm^2) and are

$$k_1 = 2.06 \times 10^5 \exp\left(-27200/(RT)\right)$$

$$k_2 = 11.7 \times \exp\frac{-6860}{RT}$$

in which T is in °R and R is in Btu/(lbmol °R). The rate expressions are

$$r_1 = k_1 P_{C_3H_6} P_{Cl_2}$$

$$r_2 = k_2 P_{C_3H_6} P_{Cl_2}$$

The thermodynamic data for this reaction are listed below

Component	$H_f^{298°K}$ kcal/mol	A	B ($\times 10^2$)	C ($\times 10^5$)	D ($\times 10^9$)
Cl_2	0.00	6.432	0.8082	−0.9241	3.695
C_3H_6	4.88	0.866	5.602	−2.771	5.266
C_3H_5Cl	−0.15	0.604	7.277	−5.442	17.42
HCl	−22.06	7.235	−0.172	0.2976	−0.931
1,2-$C_3H_6Cl_2$	−39.60	2.496	8.729	−6.219	18.49

The partial molar heat capacities are expressed in units of cal/mol °K and can be calculated using

$$C_{pj} = A_j + B_j T + C_j T^2 + D_j T^3$$

List all the differential equations needed to calculate the molar flow rates of the dichloropropane and allyl chloride, and the temperature as a function of position in a nonadiabatic reactor. Be sure to provide enough information so we can tell how you will compute the various variables your equations. For nonadiabatic operation a constant wall temperature of 392°F can be realized by boiling ethylene glycol on the outer surface of the reactor wall. The inside heat-transfer coefficient is 5 Btu/hr ft^2 °F for a feed rate of 0.85 lbmol/hr and 2 atm total pressure.

Problem 5

Use equations to explain your answers to Parts 1 and 2. Be precise and show how the equations support or provide the answers.

1. Why does the equilibrium constant decrease with increasing temperature for an exothermic reaction.

2. For a set of parallel reactions such as

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{C} \qquad r_1 = k_1 c_A c_B$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} \mathrm{D} \qquad r_2 = k_2 c_A c_B$$

   What reactor would you choose, what would influence the temperature of operation, and what would influence the mode of operation (such as isothermal, nonisothermal, nonisothermal and adiabatic) if you were interested in maximizing the production of component C and minimizing the production of component D?

3. A homogeneous reaction is taking place in a tubular flow reactor. What assumptions are necessary for you to model this as a plug flow reactor?

4. A homogeneous reaction is taking place in a stirred vessel to which fluid is added and removed at a constant mass flow rate. What assumptions are necessary for you to model this as a CSTR?

5. Sketch the residence time distribution function, $p(\theta)$, you would expect for a reactor that can be modeled as 8 CSTRs-in-series. Clearly define where on your plot where the mean residence time is located. Discuss why you have proposed the shape you have drawn.

6. Why do we write the rate of the elementary reaction

$$\mathrm{H} + \mathrm{NO} \xrightarrow{\mathrm{k}_1} \mathrm{HNO}$$

   as

$$r = k_1 c_{\mathrm{H}} c_{\mathrm{NO}}$$

Useful Integrals

$$\int \frac{1}{a+bx}dx = \frac{1}{b}\ln(a+bx)$$

$$\int (a+bx)^n\,dx = \frac{(a+bx)^{n+1}}{(n+1)b} \qquad ;n \neq -1$$

$$\int \frac{dx}{(a+bx)(a'+b'x)} = \frac{1}{ab'-a'b}\ln\left(\frac{a'+b'x}{a+bx}\right)$$

$$\int \frac{a+bx}{a'+b'x}dx = \frac{bx}{b'} + \frac{ab'-a'b}{b'^2}\ln\left(a'+b'x\right)$$

$$\int \frac{(a+bx)^m}{(a'+b'x)^n}dx = \frac{-1}{(n-1)b'}\left[\frac{(a+bx)^m}{(a'+b'x)^{n-1}} - mb\int \frac{(a+bx)^{m-1}}{(a'+b'x)^{n-1}}dx\right]$$

$$\int x^m\,(a+bx)^n\,dx = \frac{x^{m+1}\,(a+bx)^n}{m+n+1} + \frac{an}{m+n+1}\int x^m\,(a+bx)^{n-1}\,dx$$

Simpson's three-eighth's rule for numerical integration:

$$\int_{X_0}^{X_3} f(X)dX = \frac{3h}{8}\left[f(X_0) + 3f(X_1) + 3f(X_2) + f(X_3)\right]$$

where:

$$h = \frac{X_3 - X_0}{3} \qquad X_1 = X_0 + h \qquad X_2 = X_0 + 2h$$

Integration of $N+1$ points, where N is even:

$$\int_{X_0}^{X_N} f(X)dX = \frac{h}{3}\left[f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \ldots + 4f_{(N-1)} + f_N\right]$$

where:

$$h = \frac{X_N - X_0}{N}$$

Design Equations

Batch Reactor

$$\frac{d(V_R c_j)}{dt} = \sum_i^{n_{rxns}} \nu_{ij} r_i V_R$$

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \sum_i^{n_{rxns}} r_i \Delta H_{Ri} V_R}{V_R \sum_j^{n_{components}} c_j C_{pj}}$$

Plug Flow Reactor

$$\frac{d(Qc_j)}{dV} = \sum_i^{n_{rxns}} \nu_{ij} r_i$$

$$\frac{dT}{dV} = \frac{\frac{2}{R} U(T_a - T) - \sum_i^{n_{rxns}} r_i \Delta H_{Ri}}{Q \sum_j^{n_{components}} c_j C_{pj}}$$

Stirred Tank Reactor

$$\frac{d(V_R c_j)}{dt} = Q_f c_{jf} - Qc_j + \sum_i^{n_{rxns}} \nu_{ij} r_i V_R$$

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \sum_i^{n_{rxns}} r_i \Delta H_{Ri} V_R + Q_f \sum_j^{n_{components}} c_{jf}(H_{jf} - H_j)}{V_R \sum_j^{n_{components}} c_j C_{pj}}$$

Continuous Stirred Tank Reactor (constant phase)

$$0 = Q_f c_{jf} - Qc_j + \sum_i^{n_{rxns}} \nu_{ij} r_i V_R$$

$$0 = UA(T_a - T) - \sum_i^{n_{rxns}} r_i \Delta H_{Ri} V_R + \sum_j^{n_{components}} Q_f c_{jf} \int_T^{T_f} C_{pj} dT$$

General Information on Mass Transfer with Reaction

For heterogeneous reactions one must determine the rate per unit volume of pellet.

$$R_{jp} = \frac{1}{V_p} \int_{V_p} R_j dV$$

The dimensionless steady-state concentration within a symmetrical pellet is found with

$$\overline{\nabla}^2 \overline{c} + \left[\frac{a^2 \mathrm{R_{js}}}{c_{js} D_j} \right] \overline{R} = 0 \qquad \overline{R} = \frac{R_j}{R_{js}}$$

For a first-order reaction (A $\longrightarrow$ B) with a spherical pellet surface concentration of $c_{\mathrm{A}s}$

$$c_{\mathrm{A}} = c_{\mathrm{A}s} \frac{R}{r} \times \frac{\sinh\left(\Phi(\frac{3r}{R})\right)}{\sinh(3\Phi)}$$

$$R_{\mathrm{A}p} = \frac{1}{\Phi} \left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right] \times (-k_1 c_{\mathrm{A}s})$$

$$\Phi = \frac{R}{3} \times \sqrt{\frac{k_1}{D_e}}$$

For some heterogeneous cases it is appropriate to use

$$\eta = \frac{R_j}{R_{js}}$$

$$\eta \approx \frac{1}{\Phi} \left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right]$$

$$\Phi = \frac{V_p}{S_p} \left[\frac{n+1}{2} \times \frac{k_n c_s^{n-1}}{D_e} \right]^{0.5}$$

where

$$\tanh x = \frac{\mathrm{e}^x - \mathrm{e}^{-x}}{\mathrm{e}^x + \mathrm{e}^{-x}}$$