

Instructions

1. Write your name at the top of each answer sheet and on the front page of the exam questions.
2. Start each problem at the top of a new page.
3. The exam consists of three problems; they are equally weighted.
4. Useful integrals and equations are listed beginning on page 5.
5. Return the exam questions or you will receive a grade of zero.

$$R = 82.06 \text{ cm}^3\text{-atm/gmole-K}; R = 1.987 \text{ cal/gmole-K}$$

$$\text{The van't Hoff relation is } \frac{\partial \ln K}{\partial T} = \frac{\Delta H^\circ}{RT^2}$$

Problem 1

Determine the operating temperature of a steady-state CSTR for the following set of liquid-phase reactions. The solution requires simultaneous solution of a set of equations and if you do not have a programmable calculator capable of solving the set of equations, you should show you have properly defined the problem by performing TWO iterations of a trial and error solution. In this trial and error solution, using a guess of $T = 370$ K determine, if this was the right guess and make one more iteration. If you have a programmable calculator, give us the answer.

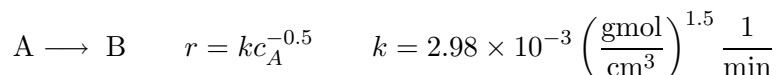
		k_o (min^{-1})	E_a (cal/gmol)	ΔH_R (cal/gmol)
A $\xrightarrow{k_1}$ B	$r_1 = k_1 c_A$	8.25×10^{12}	19,500	-23,000
B $\xrightarrow{k_2}$ C	$r_2 = k_2 c_B$	2.27×10^{10}	17,500	-27,000
B $\xrightarrow{k_3}$ D + E	$r_3 = k_3 c_B$	1.28×10^9	15,800	-19,000

The process parameters are listed below. The feed is pure A.

Parameter	Value	Units
\bar{C}_{pA}	45	cal/gmol-K
V_R	1,000	liter
Q_f	100	liter/min
T_f	338	Kelvin
T_a	323	Kelvin
UA	377,300	cal/min-K
c_{Af}	5.0	gmol/liter

Problem 2

Determine the volume of a single isothermal PFR and a single steady-state CSTR to realize 95% conversion of A for the reaction



The volumetric feed rate is $Q_f = 6 \times 10^4 \text{ cm}^3/\text{min}$. The reactant and products are liquids and the concentration of A in the feed is $c_{Af} = 0.08 \text{ gmol/cm}^3$. The volumes will not be the same. Does your answer make sense? Explain why.

Problem 3

Your team has been asked to prepare a preliminary design of a reactor to produce cyclohexane by the hydrogenation of benzene. Cyclohexane is a raw material for producing adipic acid and caprolactam needed in the manufacture of several types of nylon. You are to consider a fixed-bed reactor using 0.32-cm diameter pellets supporting a Ni catalyst. The pellet density is $\rho_p = 1.892 \text{ g/cm}^3$.

The apparent rate equation for the hydrogenation of benzene to cyclohexane from the gas phase has been reported on the supported nickel catalyst to be of the form:

$$r = \frac{k_p(K_H^3 K_B P_H^3 P_B - (K_C P_C / K))}{(1 + K_H P_H + K_B P_B + K_C P_C)^4},$$

$$\ln k_p = \frac{-13,300}{RT} + \frac{33.5}{R},$$

$$\ln K_H = \frac{15,500}{RT} - \frac{31.9}{R},$$

$$\ln K_B = \frac{11,200}{RT} - \frac{23.1}{R},$$

$$\ln K_C = \frac{8,900}{RT} - \frac{19.4}{R},$$

$$K = \exp(25,980/T - 46.87)$$

where K_H , K_B and K_C are apparent adsorption equilibrium constants for benzene, hydrogen and cyclohexane, respectively, and have units of atm^{-1} . The reaction equilibrium constant K has units of atm and the rate constant k_p has units of $\text{gmol/gcat}\cdot\text{sec}$. Temperature T is in degrees Kelvin and $R = 1.987 \text{ cal/gmol}\cdot\text{K}$.

If the reactor is operated at 525 K with a feed having a partial pressure of benzene of 5 atm and 8.5 atm of hydrogen, determine if you can assume the concentration within the pellet is the same as the surface concentration. Base your answer on the inlet reactor conditions. The effective diffusivity of either hydrogen or benzene can be approximated as $D = 0.009 \text{ cm}^2/\text{sec}$.

Problem 4

Your supervisor walks into your office and informs you the company is keen to make investment decisions on a new product line of antiviral drugs and the CEO needs a technical briefing at the end of the day. Your boss reminds you that the CEO is a stickler for details and technical and analytical rigor, so you need to be prepared to back up any recommendation by considering alternatives and all possible scenarios; he instructs you to be prepared to present one recommendation. Specifically, you are to select the reactor, probable operating conditions, specify inlet and outlet flowrates, if any (including temperatures and pressures), specifications for heat transfer equipment, and estimates of product purity exiting the reactor. The product in question is from a class of phosphonofosphate-amino acid conjugates. You are to focus on a key intermediate N-[(methoxycarbonyl)hydroxyphosphiny]-L-Valine, which is formed in a reaction of a dianionic phosphonofosphate (PO_5CH_3) and L-valine ethyl ester hydrochloride in a sodium hydroxide-buffered solution.

Your supervisor has arranged for the team of chemists that developed the chemical process to visit with you in a conference call in 1 hour. Your supervisor wants to review your proposal and calculations in 4 hours.

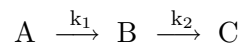
You decide to begin by making a list of questions to ask the chemists and separately your supervisor so you can settle on a reactor and develop estimates needed for the briefing. Answer this exam question by sharing your list of questions, and for each, provide a possible answer you expect and tell how you will use this to prepare for your briefing. If a question's answer leads to a new question, provide that question (and its possible answer and how it will be used).

Problem 5

A pulse experiment was performed on a stirred reaction vessel operating at steady state. The effluent concentration of the tracer is listed below from the time of injection.

Time(sec)	0	120	240	360	480	600	720	840	960	1080
Concentration (gm/m ³)	0.0	6.5	12.5	15.0	11.0	6.0	2.5	1.0	0.5	0.0

This reactor will be used, under the same steady state conditions to carry out the series first-order liquid-phase reaction.



$$r_1 = k_1 c_A \quad k_1 = 0.0033(\text{sec}^{-1})$$

$$r_2 = k_2 c_B \quad k_2 = 0.0051(\text{sec}^{-1})$$

The feed to the reactor is pure A at a concentration of 8 gmol/liter. Determine the effluent concentrations of A, B, and C from this reactor.

In general:

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

For segregated flow:

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

For CSTRs-in-series:

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

Design Equations

Batch Reactor

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

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

Plug Flow Reactor

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

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

Stirred Tank Reactor

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

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

Continuous Stirred Tank Reactor (steady-state and constant phase)

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

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

Useful Integrals

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

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

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

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

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

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

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

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

where:

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

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

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

where:

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

General Information on Mass Transfer with Reaction

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

$$R_{jp} = \frac{1}{V_p} \int_{V_p} R_j dV = -\frac{S_p}{V_p} D_j \left. \frac{dc_j}{dr} \right|_{r=R_p}$$

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

$$\nabla^2 \bar{c} + \left[\frac{a^2 |R_{js}|}{c_{js} D_j} \right] \bar{R} = 0 \quad \bar{R} = \frac{R_j}{R_{js}}$$

For a first-order reaction (A \rightarrow B) with a spherical pellet surface concentration of c_{As}

$$c_A = c_{As} \frac{R}{r} \times \frac{\sinh\left(\Phi\left(\frac{3r}{R}\right)\right)}{\sinh(3\Phi)}$$

$$R_{Ap} = \frac{1}{\Phi} \left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right] \times (-k_1 c_{As})$$

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

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

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