

Instructions

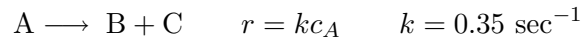
1. Write your name at the top of each answer sheet and on the front page of the exam questions.
2. Start each problem at the top of a new page.
3. The exam consists of five equally-weighted problems.
4. Useful integrals and equations are listed beginning on page 6.
5. Return the exam questions or you will receive a grade of zero.

$R = 82.06 \text{ cm}^3\text{-atm/gmole-K}$; $R = 1.987 \text{ cal/gmole-K}$; $R = 8.3144 \text{ J/gmole-K}$

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

Problem 1

Consider the following gas-phase reaction in an isothermal 750 K PFR



You will be asked to consider how the volume changes with process conditions and these comparisons will be made against the Reference Case. For the Reference Case the feed consists of a 1:1 molar mixture of A:Inert, the feed rate of A is $N_{Af} = 6 \text{ gmol/sec}$, and the total pressure is 1 atm. By how much will the reactor volume change from the Reference Case if:

- The concentration of A in the feed is increased by a factor of two by doubling the total pressure to 2 atm and retaining the 1:1 A:Inert feed strategy;
- The concentration of A in the feed is increased by a factor of two by feeding pure A and operating at a total pressure of 1 atm?

In both new strategies the molar feed of A is unchanged at $N_{Af} = 6 \text{ gmol/sec}$. In all three cases the conversion of A is $x_A = 0.95$.

Problem 2

A steady-state temperature of 367.53 K is found for a nonisothermal CSTR with a first-order, liquid-phase, series reaction

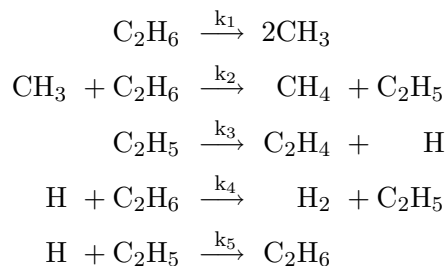


Determine if this is a stable or unstable operating temperature. The following variables and constants describe this system.

Parameter	Value	Units
T_f	298	°K
T_a	300	°K
c_{Af}	3.5	kmol/m ³
Q_f	60×10^{-6}	m ³ /s
ΔH_{R1}	-2.09×10^8	J/kmol
ΔH_{R2}	-5.90×10^7	J/kmol
C_{pA}	2.02×10^5	J/kmol °K
V_R	18×10^{-3}	m ³
UA	360	J/s °K
k_1	$4.48 \times 10^6 \exp(-7550/T)$	s ⁻¹ ; T in °K
k_2	$6.92 \times 10^5 \exp(-8400/T)$	s ⁻¹ ; T in °K

Problem 3

Ethane pyrolysis to produce ethylene and hydrogen also generates methane as an unwanted reaction product. The overall stoichiometry for the process is not a simple balance of ethane and the products. The following mechanism and their kinetics have been proposed for ethane pyrolysis



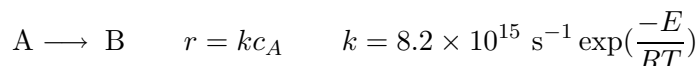
The rate constants are listed below in the table for the elementary reactions, in which $k = A_0 \exp(-E/RT)$. The preexponential factor A_0 has units of s^{-1} or $\text{cm}^3/\text{mol s}$ for first- and second-order reactions, respectively.

Reaction	A_0	$E(\text{kJ/mol})$
1	1.0×10^{17}	356
2	2.0×10^{11}	44
3	3.0×10^{14}	165
4	3.4×10^{12}	28
5	1.6×10^{13}	0

What is the rate of ethylene production at the inlet conditions to an isothermal PFR operating at a constant pressure of 1.0 atm and at 925 °K. The feed consists of ethane in a steam diluent. The inlet partial pressure of ethane is 50 torr and the partial pressure of steam is 710 torr. The feed enters at a flowrate of 35 cm^3/s . The reaction intermediates in this reaction mechanism are the radicals CH_3 , C_2H_5 and H .

Problem 4

The following heterogeneously catalyzed reaction



is to be conducted in an isothermal fixed-bed reactor operating at a constant pressure of 1.5 atm. The reactant and product are gases. When the feed to the reactor is pure A and $N_{Af} = 4.3$ gmol/sec and the temperature is 650K, the reactor volume is 108,200 cm³ for 80% conversion of A. What will the reactor volume be for 80% conversion of A if the feed composition and molar flowrate stay the same and the temperature is decreased to 600K?

For this catalyst the bed porosity is $\epsilon_B = 0.35$, the pellet radius is $R = 0.8$ cm, and the diffusivity of A is $D_A = 0.0065$ cm²/sec. You may neglect external gradients.

Problem 5

- (a) The effluent concentrations listed in below were recorded following a pulse injection into a flow reactor. On the basis of these data, do you expect the flow reactor to be more like a CSTR or a PFR? Explain your reasoning.

time (min)	C (mg/dm ³)	time (min)	C (mg/cm ³)
0	112	40	34.5
5	95.8	50	26.3
10	82.2	70	15.7
15	70.6	100	7.67
20	60.9	150	2.55
30	45.6	200	0.90

- (b) The residence time distribution curves for two different reactors, each having the same residence time, are shown in Figure 1. A second order reaction was studied in each of these reactors and conversion for the limiting reactant of 0.695 and 0.702 were realized. Determine which reactor, A or B, had the lower conversion. Explain your reasoning.

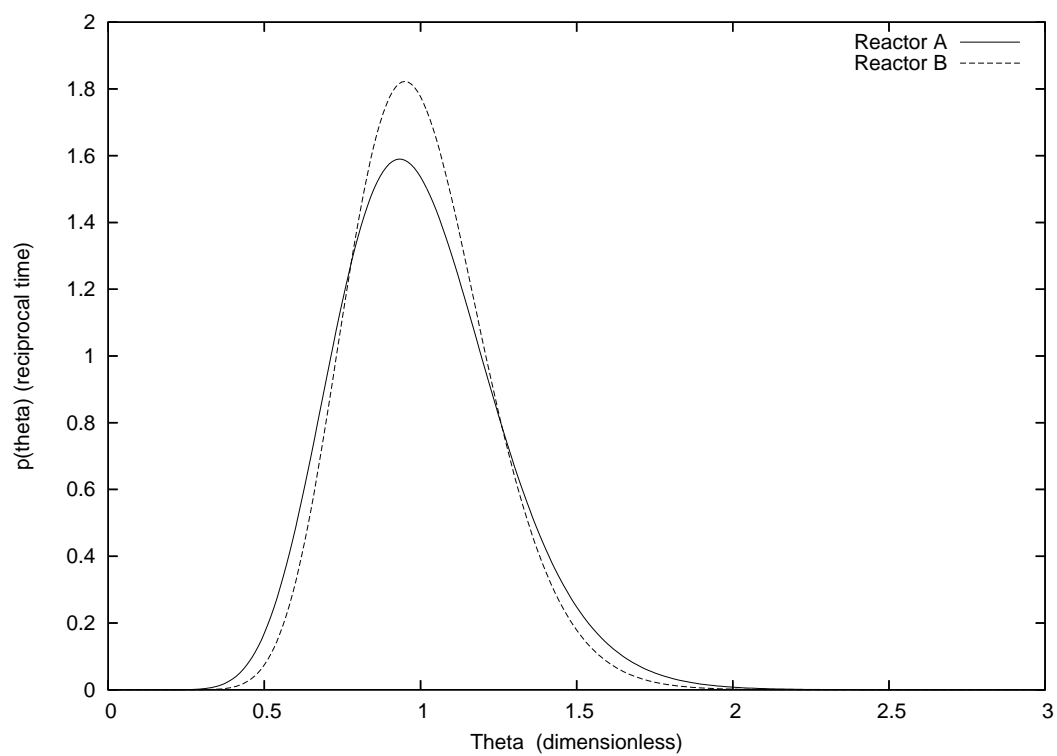


Figure 1: The residence time distribution function versus dimensionless time, $\Theta = \theta/\bar{\theta}$, for two different reactors with equal mean residence times, $\bar{\theta}$.

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

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

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

Continuous Stirred Tank Reactor (constant phase)

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

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

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

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