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 5.
5. Return the exam questions or you will receive a grade of zero.

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

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

Problem 1

Determine the concentration of C in the effluent from the series arrangement of two, identical CSTRs in series. The reactors are isothermal, each reactor has a volume of V_R = 750 liters and the total volumetric flow rate to the first reactor is Q_f = 50 liter/min. The feed consists of A in a solvent at a concentration of c_{Af} = 4.2 mol/l. The compound of interest is formed in the liquid-phase series reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \xrightarrow{k_3} \mathrm{D}$$

The reaction kinetics are

Reaction	Rate Expression	Rate Constant Value
1	$r_1 = k_1 c_A$	$k_1 = 0.047$ min^{-1}
2	$r_2 = k_2 c_B^2$	$k_2 = 0.53$ l/mol-min
3	$r_3 = k_3 c_C$	$k_3 = 0.047$ min^{-1}

Problem 2

Determine the reactor volume required to realize 90% conversion of A for the heterogeneously catalyzed reaction

$$2\text{A} \xrightarrow{k} \text{B} \qquad r = kc_A^2 \qquad k = 25,000 \text{ cm}^3/\text{mol-sec}$$

The reactant and product are gases. The reactor is charged with pure A. The inlet pressure is 1 atm and the temperature is 675 K. The reactor is isothermal. The molar feed rate of A is $N_{Af} = 3.7$mol/sec. The bed density is $\epsilon_B = 0.425$, the spherical catalysts have a radius of $R = 0.4$ cm, and the effective diffusivity of A in the pellet is $D_A = 0.002$ cm^2/sec.

Problem 3

A pulse input experiment was performed on a flow reactor. The effluent pulse data ($c_{\text{pulse}}(\theta)$) are presented below. Determine the mean residence time and the variance for this reactor.

θ (min)	$c_{\text{pulse}}(\theta)$ (μmole/liter)	θ (min)	$c_{\text{pulse}}(\theta)$ (μmole/liter)	θ (min)	$c_{\text{pulse}}(\theta)$ (μmole/liter)
0	0.000	7	2.340	14	0.072
1	6.480	8	1.584	15	0.020
2	7.920	9	1.080	16	0.000
3	7.740	10	0.900		
4	6.696	11	0.648		
5	4.752	12	0.468		
6	2.880	13	0.180		

In general:

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

Problem 4

The catalytic conversion of NO to N_2 requires CO to remove the oxygen as CO_2. The overall stoichiometery of the reaction is

$$\mathrm{NO} + \mathrm{CO} \rightleftharpoons \frac{1}{2}\mathrm{N_2} + \mathrm{CO_2}$$

This reaction proceeds by the following set of surface reactions.

$$\mathrm{NO} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO-S}$$

$$\mathrm{NO-S} + \mathrm{S} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{N-S} + \mathrm{O-S}$$

$$\mathrm{2N-S} \overset{k_3}{\longrightarrow} \mathrm{N_2} + \mathrm{2S}$$

$$\mathrm{CO} + \mathrm{S} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{CO-S}$$

$$\mathrm{CO-S} + \mathrm{O-S} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{CO_2-S} + \mathrm{S}$$

$$\mathrm{CO_2} + \mathrm{S} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{CO_2-S}$$

where S designates a surface site and adsorbed species are designated with a "-S", such as NO-S.
Using the Hougen-Watson formalism, develop a rate expression for the reaction of NO to N_2. The reactants and products are gases. Reaction 3 is the rate limiting step.

Problem 5

Part (a) In the energy balance for a plug flow reactor the book lists the following equation for an ideal gas and for which the pressure can be assumed constant

$$Q\rho\hat{\mathrm{C}}_p \frac{dT}{dV} = -\sum_i \Delta H_{Ri} r_i + \dot{\mathrm{q}}$$

What is $\hat{\mathrm{C}}_p$? Can you assume it is constant for this reaction in a nonisothermal reactor, if the feed consists of a 2:1 mixture of propylene:chlorine?

$$\mathrm{C_2H_6} + \mathrm{Cl_2} \longrightarrow \mathrm{C_2H_5Cl} + \mathrm{HCl}$$

What are some of the ways you can also express this variable?

Part(b) Consider a reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$$

in a nonisothermal plug flow reactor. The reaction is exothermic. Figure 1 shows the temperature profile in a the reactor for three different cases. There are three cases represented: a reference case, one in which the heat transfer surface temperature is higher than the reference case and a third in which there is added diluent to the reference case. Using equations and concepts developed in this class argue for which curve (Curve 1 or Curve 2) is associated with the increased heat transfer surface temperature, and which curve (Curve 1 or Curve 2) is associated with the added diluent.

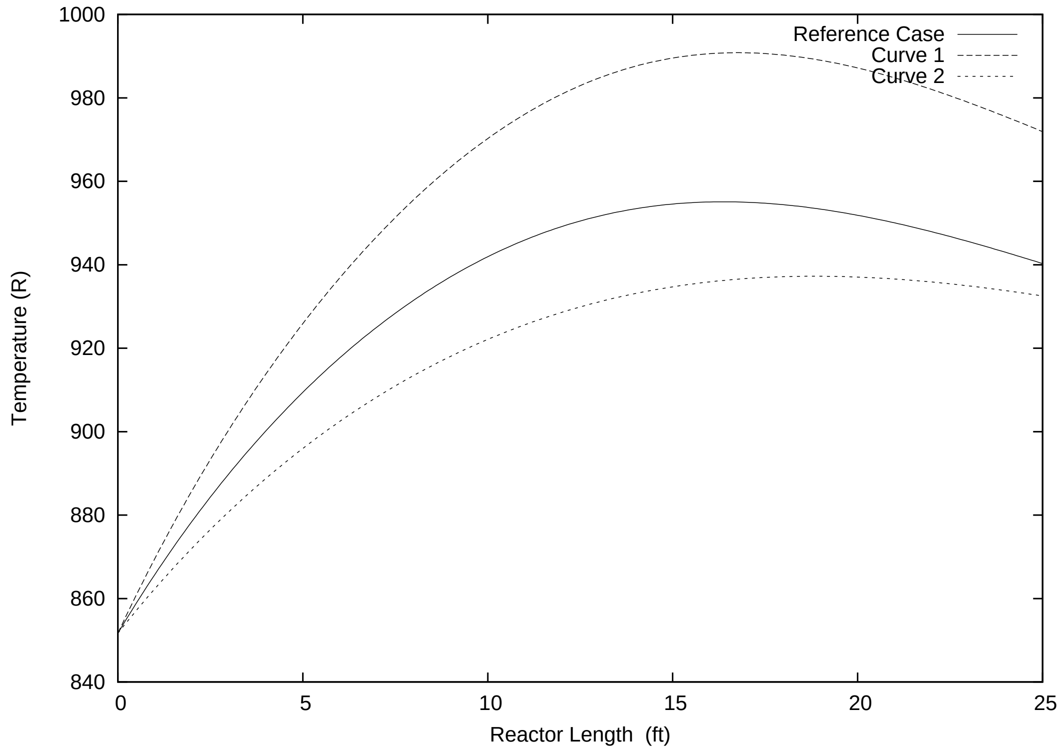

Figure 1: Temperature versus reactor length for three cases, a reference case, one in which the heat transfer surface temperature is higher than the reference case and a third in which there is added diluent. Note that Curve 1 is the topmost curve and the reference case is the middle curve.

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)

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

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

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

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

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

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

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

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

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:

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

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

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

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

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

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

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