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 7.
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; R = 8.3144 J/gmole-K

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

Problem 1

(a) Determine the PFR reactor volume required to realize 95% conversion of A ($x_A = 0.95$) for the gas-phase reaction

$$2\text{A} \longrightarrow \text{B} \qquad r = kc_A^2 \qquad k = 2.9 \times 10^4 \text{ cm}^3\text{/gmol-sec}$$

The feed is a 1:1 molar mixture of A and an inert with a total molar flowrate of $N_{\text{feed}} = 10$ gmol/sec. The reactor operates at 2 atm total pressure and at a constant temperature of 600 K.

(b) List five assumptions used in modeling a PFR

(c) List four assumptions used in modeling a CSTR

Problem 2

A batch reactor is used for the liquid phase reaction.

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{1}$$

where

$$r = k_1 c_A - k_{-1} c_B \qquad k_1 = A_1 \exp(-E_1/RT) \qquad k_{-1} = A_{-1} \exp(-E_{-1}/RT)$$

The kinetic constants, thermodynamic data and reactor conditions are listed below. You may assume the heat capacity and heat of reaction are independent of temperature and that the density is constant.

Item	Units	Value
A_1	hr^{-1}	85.96×10^{15}
E_1	cal/gmol	30,400
A_{-1}	hr^{-1}	148.45×10^{18}
E_{-1}	cal/gmol	39,900
ΔH_R	cal/gmol	-9,500
$\hat{C}_p$	cal/g-K	0.95
T_o	K	368
ρ	$\mathrm{g/cm}^3$	0.9
c_{Ao}	$\mathrm{gmol/cm}^3$	5×10^{-2}
V_R	cm^3	18,000
U	$\mathrm{cal/hr\text{-}cm}^2\text{-K}$	54
A	cm^2	200
T_a	K	368

The concentrations of A and B (c_A and c_B) are plotted in Figure 1 and the temperature is plotted in Figure 2 versus reactor time.

(a) Develop the balances that are needed to generate the changes in the dependent variables with the independent variable. Specify/define all variables.

(b) Discuss why the curves for T, c_A and c_B change as they do with time.

(c) Is the equilibrium limit reached when the temperature is at the maximum value?

(d) If this reactor were to be operated adiabatically, would more A react? Why? Justify your anwser.

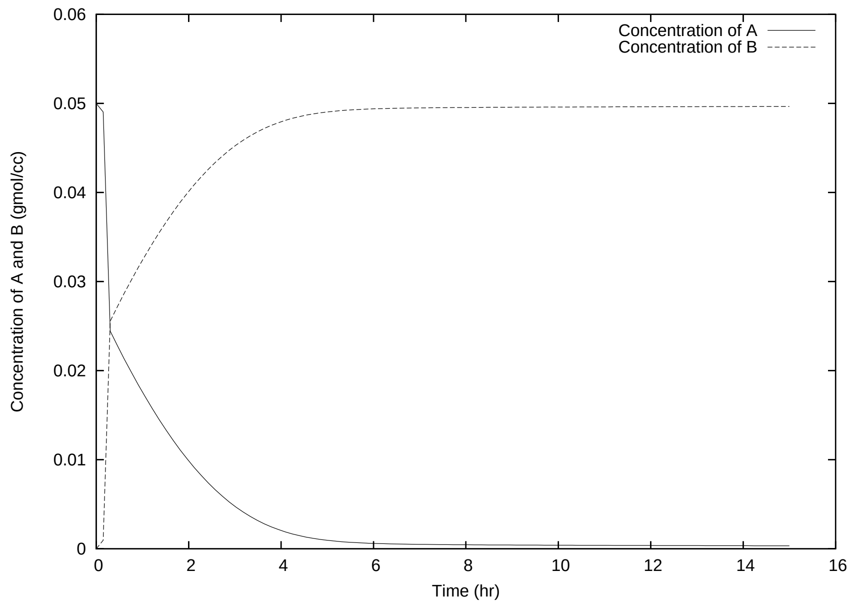

Figure 1: Concentration of A and B versus time

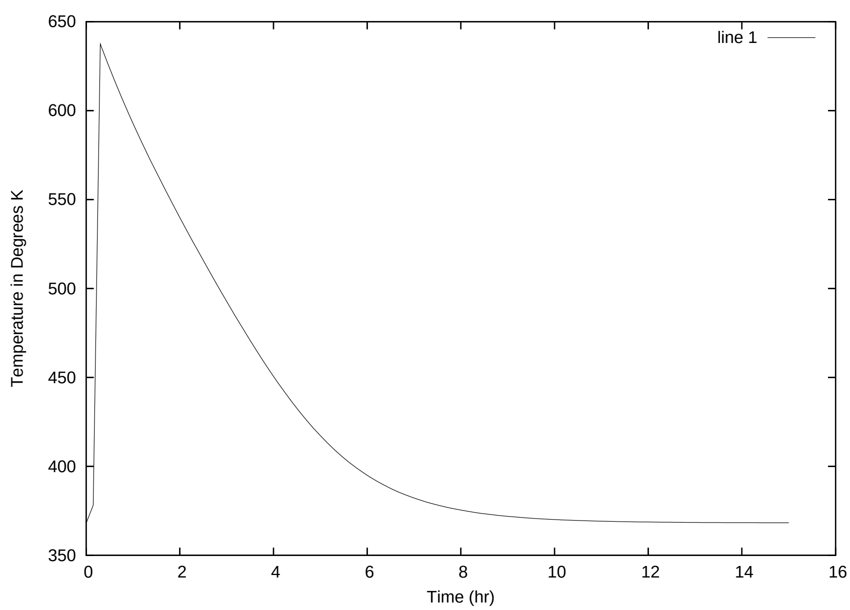

Figure 2: Temperature versus time

Problem 3

Using the data below for a pulse experiment, determine the effluent concentration of A for the second order liquid phase reaction.

$$\mathrm{A} \longrightarrow \mathrm{B} \qquad r = kc_A^2 \qquad k = 0.245 \text{ liter/gmol-min}$$

The same volumetric feed rate to the reactor, $Q_f = 5$ liter/min, applies to both the pulse experiment and the chemical reaction. The inlet concentration of A for the reaction is $c_{Af} = 1.5$ gmol/liter.

Time (min)	Effluent concentration (gmol/liter)	Time (min)	Effluent concentration (gmol/liter)
0	0.000	20	0.075
2	0.003	22	0.079
4	0.010	24	0.070
6	0.017	26	0.058
8	0.021	28	0.040
10	0.028	30	0.019
12	0.033	32	0.012
14	0.047	34	0.010
16	0.058	36	0.002
18	0.067	38	0.000

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 4

A heterogeneously-catalyzed reaction will be conducted in a spherical pellet loaded into a fixed-bed reactor. The reactants and products are gases

$$\mathrm{A} \longrightarrow \mathrm{B} + \mathrm{C} \qquad r = kc_A^2 \qquad k = 2.7 \times 10^5 \mathrm{cm}^3/\mathrm{gmol\text{-}s}$$

Find the mass of catalyst required to reach a conversion of A of $x_A = 0.90$ if the reactor is isothermal. You may assume the bulk fluid and surface concentrations are equal and may neglect pressure drop within the reactor. The feed consists of pure A at 650 K, a molar feed rate of $N_{Af} = 1.2$ gmol/s, and the reactor pressure is 2.0 atm. The pellet has a radius of $R_P = 0.40$ cm and a density of $\rho_p = 0.7$ g/cm^3. The bed has a density of $\rho_B = 0.4$ g/cm^3. The effective diffusivity of A in the pellet is $D_e = 0.006$ cm^2/s.

Problem 5

(Adapated from: R. Tripathi and S. K. Upadhyay, Int. J. Chem. Kinetics, online edition (2004).)

The kinetics for the oxdiation of reducing sugars, such as glucose, galactose, fructose, maltose, and lactose by osmium VIII was determined in the presence of sodium metaperiodate ($Na^+IO_4^-$) in an alkaline medium. The authors made the following experimental observations

Observation 1 The reaction rate is zero order in periodate concentration.

Observation 2 The reaction order with respect to the sugar concentration (the substrate) and the reaction order with respect to the hydroxyl (OH^-) concentration decreases from unity to zero as the substrate and as the hydroxyl concentration is increased.

Observation 3 The rate is proportional to the osmium VIII concentration.

The following mechanism of elementary steps was proposed. The terms in the [ ] brackets contain symbolic short-hand terms for different species, such as [S] for sugar and [E⁻] for enediol anion.

$$\text{Sugar[S]} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Enediol anion } [E^-] + H_2O \qquad \text{fast and at equilibrium}$$

$$[E^-] + Os_4(OH)_2^{2-}[Os^{VIII}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex[X]} \qquad \text{fast and at equilibrium}$$

$$[X] \xrightarrow{k_3} HCHO + RCOO^- + OsO_3(OH)_2^{2-}[Os^{VI}] \qquad \text{slow}$$

$$[Os^{VI}] + IO_4^- \xrightarrow{k_4} IO_3^- + [Os^{VIII}] \qquad \text{fast}$$

Develop a reaction rate expression for this general oxidation reaction. Discuss how it is consistent with the three experimental observations. Note that the overal reaction stoichiometry is

$$\text{Sugar} + OH^- + IO_4^- \longrightarrow HCHO + RCOO^- + IO_3^-$$

Also note in the heterogeneous problems this semester we performed a site balance $\bar{c}_m = \bar{c}_v + \sum \bar{c}_j$. Here we must satisfy a different balance, one over the total catalyst, $c_T = c_{Os^{VIII}} + c_X$.

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)

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

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

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

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

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

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

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

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

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:

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

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

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

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

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