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 equally weighted problems.
4. Useful integrals and equations are listed beginning on page 4.
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

Consider the gas phase reaction

$$\mathrm{A} \xrightarrow{k} \mathrm{B} + \mathrm{C} \qquad r = kc_A \qquad k = (7.94 \times 10^9 \text{ sec}^{-1}) \exp\left(\frac{-27,400 \text{ cal/mol}}{RT}\right)$$

This reaction will be conducted in an adiabatic plug flow reactor. The reactor operates at a constant pressure of 2 atm. The feed to the reactor is pure A at $T_f = 650$ K and a feed rate of $Q_f = 5 \times 10^4$ cm^3/sec. The heat capacities and heats of formation at 650 K are listed in the table.

Component	Variable	Value	Units
A			
	C_{pA}	75.2	cal/mol-K
	H_{fA}	-9,460	cal/mol
B			
	C_{pB}	37.7	cal/mol-K
	H_{fB}	16,710	cal/mol
C			
	C_{pC}	35.3	cal/mol-K
	H_{fC}	-11,000	cal/mol

Assuming the heat capacities and heats of formation are invariant with temperature, compute the reactor volume needed to realize a conversion of A corresponding to $x_A = 95$ %.

Problem 2

Determine the steady-state temperature and composition exiting a nonisothermal CSTR with a first-order, liquid-phase, series reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}, \qquad r_1 = k_1 c_A \qquad r_2 = k_2 c_B \tag{1}$$

The following variables and constants describe this system. The solution will involve solving more than one algebraic equation simultaneously and, if done by hand, a trial and error approach is needed. You will be given full credit if you use $T = 450$ K for your first guess AND you compute the composition, and then you make a stab at a solution by telling us what your next guess would be.

Parameter	Value	Units
T_f	298	°K
T_a	450	°K
c_{Af}	3.5	kmol/m^3
Q_f	60×10^{-6}	m^3/s
ΔH_{R1}	-2.09×10^7	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	1800	J/s °K
k_1	$4.48 \times 10^6 \quad \exp(-7550/T)$	s^{-1}; T in °K
k_2	$6.92 \times 10^5 \quad \exp(-8400/T)$	s^{-1}; T in °K

Problem 3

[adapted from Missen, Mims and Saville, *Chemical Reaction Engineering and Kinetics*, Wiley 1999.]
The pyrolysis of ethyl nitrate, $C_2H_5ONO_2$, to formaldehyde, CH_2O, and methyl nitrate, CH_3NO_2 is proposed to proceed as follows

$$C_2H_5ONO_2 \xrightarrow{k_1} C_2H_5O + NO_2$$

$$C_2H_5O \xrightarrow{k_2} CH_3 + CH_2O$$

$$CH_3 + C_2H_5ONO_2 \xrightarrow{k_3} CH_3NO_2 + C_2H_5O$$

$$2C_2H_5O \xrightarrow{k_4} CH_3CHO + C_2H_5OH$$

Methyl, CH_3, and ethoxy, C_2H_5O, are free radicals and can be assumed to be reaction intermediates.

(a) Develop a rate expression for the production of formaldehyde in terms of stable molecules.

(b) This reaction was studied in an isothermal CSTR and after solving the material balance for the change in ethyl nitrate one generates the following rate versus concentration data.

R_{CH_2O} mol m^{-3} s^{-1}	$c_{C_2H_5ONO_2}$ mol m^{-3}
0.0121	0.0713
0.0122	0.0759
0.0134	0.0975
0.0209	0.235
0.0230	0.271

Is the proposed mechanism consistent with the experimental data? Why or why not?

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)

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

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

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

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

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

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

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

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

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:

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