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; 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

Determine the volume required to realize 80% conversion of A in an isothermal PFR for the following gas phase reaction

$$\text{A} \longrightarrow \text{2B} \qquad r = kc_A^2 \qquad 1.8 \times 10^3 \text{ cm}^3\text{/gmol-s}$$

The reactor pressure is constant at $P = 3$ atm and the temperature is constant at $T = 500$ K. The inlet is pure A at a molar flowrate of $N_{Af} = 5$ gmol/s.

Problem 2

Consider the liquid-phase reaction

$$\text{2A} \longrightarrow \text{B} \qquad r = kc_A^2 \qquad k = 4.15 \times 10^{15} \exp(-26,000/RT)$$

The units on k are liter/gmol-min, T is in degrees Kelvin and $R = 1.987$ cal/gmol-K.

The reactor is operated isothermally at 358 K, at steady state, and you may assume constant density. The inlet stream has a volumetric flow rate of $Q_f = 100$ liter/min and the concentration of A in the feed is $c_{Af} = 5$ gmol/liter.

You are to maximize the conversion of A and you have a total of three reactors with which to work. Using one or all, and in any arrangement you choose (*i.e.*, you are free to arrange them in series or parallel) what is the maximum conversion possible?

There is a PFR with a total volume of 300 liters. There is a CSTR with a total volume of 200 liters. There is a CSTR with a total volume of 50 liters.

NOTE: you can employ a brute force solution or you can think for a few minutes and limit your calculations. Before you plow into this, you should provide a qualitative reason for how various arrangements or individual reactors will maximize the conversion and then you might be able to save some yourself some work and time.

Component	$H_f^{298\ ^\circ K}$ kcal/mol	A	B ($\times 10^2$)	C ($\times 10^5$)	D ($\times 10^9$)
Cl_2	0.00	6.432	0.8082	−0.9241	3.695
C_3H_6	4.88	0.866	5.602	−2.771	5.266
C_3H_5Cl	−0.15	0.604	7.277	−5.442	17.42
HCl	−22.06	7.235	−0.172	0.2976	−0.931
$1,2{-}C_3H_6Cl_2$	−39.60	2.496	8.729	−6.219	18.49

Table 1: Thermodynamic data for allyl chloride example.

Problem 3

Allyl chloride is to be produced in a 0.83 ft^3 steady-state, constant volume CSTR

$$\mathrm{Cl_2} + \mathrm{C_3H_6} \xrightarrow{k_1} \mathrm{C_3H_5Cl} + \mathrm{HCl}$$
$$\mathrm{Cl_2} + \mathrm{C_3H_6} \xrightarrow{k_2} \mathrm{C_3H_6Cl_2}$$

The feed is a 4:1 molar ratio of propylene to chlorine and it enters at a feed rate of 0.85 lbmol/hr, 2.0 atm of pressure, and 392°F. The reactor pressure may be assumed constant.

The rate constants have units of lbmol/(hr ft^3 atm^2) and are

$$k_1 = 206000 \times \exp\frac{-27200}{RT}$$
$$k_2 = 11.7 \times \exp\frac{-6860}{RT}$$

where T is in degrees Rankine and R is in Btu/(lbmol°R). The rate expressions are

$$r_1 = k_1 P_{\mathrm{C_3H_6}} P_{\mathrm{Cl_2}}$$
$$r_2 = k_2 P_{\mathrm{C_3H_6}} P_{\mathrm{Cl_2}}$$

The thermodynamic data for this reaction are listed in Table 1. The partial molar heat capacities can be calculated using $C_{Pj} = A_j + B_j T + C_j T^2 + D_j T^3$ cal/mol K

Develop all the equations you would need to compute the molar flowrates of Cl_2, C_3H_5Cl and $C_3H_6Cl_2$, and the reactor temperature for adiabatic operation. Be sure to specify the values for the coefficients or define them in terms of quantities given in the problem statement. Tell how you would solve the equations, *i.e.*, what approach would you use.

Problem 4

The catalyst used in a fixed-bed reactor for the following reaction

$$\text{A} \longrightarrow \text{B} \qquad r = kc_A \qquad k = 2.3 \text{ s}^{-1}$$

is a cylindrical pellet and it keeps breaking everytime the bed needs to be repacked so you have asked the catalyst vendor to make it more mechanically robust. By how much will the catalyst charge need to change (as a percentage of the current mass of catalyst in the reactor) if the feed gas, operating temperature and pressure, and conversion of A are held constant? The feed is pure A. Also determine if the existing reactor is large enough for the new catalyst charge.

In making the catalyst more robust the vendor has decided to make the pellet cylinder shorter and with a larger diameter. This has the effect of changing the effective diffusivity and the bed density. The relevant catalyst parameters are listed in the table.

Parameter	Current Catalyst	New Catalyst
ρ_p (g/cm^3)	0.68	0.68
ρ_B (g/cm^3)	0.53	0.58
D_A (cm^2/s)	0.008	0.0065
pellet radius (cm)	0.25	0.50
pellet length (cm)	1.0	0.60

Problem 5

(a) **66% of the Problem points.** The rate of phosgene ($COCl_2$) production from CO and Cl_2

$$CO + Cl_2 \longrightarrow COCl_2$$

is found to follow the empirical rate expression

$$R_{COCl_2} = k c_{CO} c_{Cl_2}^{1.5}$$

The production of phosgene is thought to proceed by the following set of elementary reactions.

$$Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl$$

$$CO + Cl \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} COCl$$

$$COCl + Cl_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} COCl_2 + Cl$$

In these reactions Cl and COCl are radicals and can be treated as reaction intermediates. Further the reactions are reversible but this does not necessarily mean they are at equilibrium.

Show that this mechanism is consistent with the empirical rate expression. In doing this you will need to argue for the relative importance of certain reactions (or relative magnitude of certain rate constants). How is the empirical rate constant defined in terms of the elementary rate constants?

(b) **33% of the Problem points.** Why does the equilibrium coverage for adsorbed A (A_{ads})

$$A_{(g)} + S \rightleftharpoons A_{ads}$$

decrease with increasing temperature?

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)

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

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

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

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

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

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

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

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

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.

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

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

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