

Instructions

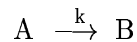
1. Write your name at the top of each answer sheet and on the front page of the exam questions.
2. Start each problem at the top of a new page.
3. The exam consists of three equally weighted problems.
4. Useful integrals and equations are listed beginning on page 5.
5. Return the exam questions or you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

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

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

**Problem 1**

Determine value of the rate constant for the second-order, heterogeneously-catalyzed reaction



if the following rate data ( $R_{Ap}$ ) were determined for isothermal, spherical pellets of different sizes ( $R_p$ ). In all cases the partial pressure of A was 2 atm and the temperature was 650 K. The effective diffusivity of A is  $D_A = 0.0095 \text{ cm}^2/\text{s}$ . You may assume the bulk fluid and the concentration of A at the external surface are equal.

$R_p$ (cm)	$R_{Ap}$ gmol/cm <sup>3</sup> -s
0.0488	$-2.093 \times 10^{-3}$
0.0397	$-2.491 \times 10^{-3}$
0.0334	$-2.857 \times 10^{-3}$

**Problem 2**

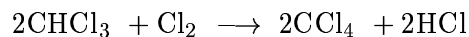
Determine the isothermal plug flow reactor volume needed to convert 90 % of A for the following gas-phase, second-order reaction at 475 K.



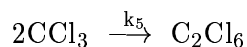
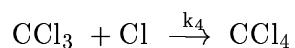
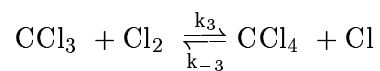
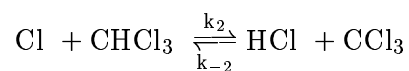
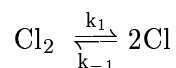
The feed consists of a 1:2 molar mixture of A in B, at a feed rate of  $Q_f = 8,000 \text{ cm}^3/\text{s}$  and a pressure of 3 atm.

**Problem 3**

One possible mechanism for the gas-phase chlorination of chloroform



involves the following set of elementary reactions.



**Part A)** Determine the rate of production of  $\text{CCl}_4$  in terms of stable molecules. The  $\text{Cl}$  and  $\text{CCl}_3$  radicals are reaction intermediates. Under the conditions of the experiments Reaction 1 is so fast it can be assumed to be at equilibrium.

**Part B)** This reaction has been studied in a batch reactor charged with 94.4 Torr of  $\text{Cl}_2$  and 22.3 Torr of  $\text{CHCl}_3$  (the total reactor pressure was 116.7 Torr initially). List the necessary design equations needed to determine the partial pressure of  $\text{Cl}_2$  versus time. You may assume the reactor is isothermal.

**Problem 4**

**Part A)** Consider two ideal reactors a PFR and a CSTR. These reactors will be arranged two different ways.

**Arrangement 1** The CSTR and PFR are in series, with the CSTR first in the series arrangement.

**Arrangement 2** The CSTR and PFR are in parallel.

Write down the residence time distribution function  $p(\theta)$  that describes the two arrangements and plot the distribution function versus time. On your plot clearly label the magnitude of values on the y-axis and indicate where on the x-axis zero begins and multiples of the reactor residence time appear. The CSTR and PFR have the same residence time,  $\tau$ .

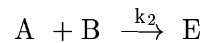
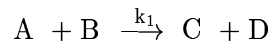
The distribution function for a PFR is

$$p(\theta) = \delta(\theta - \bar{\theta})$$

The distribution function for a CSTR is

$$p(\theta) = \frac{1}{\bar{\theta}} \exp\left(\frac{-\theta}{\bar{\theta}}\right)$$

**Part B)** Using the following two independent reactions,



the definitions of heats of reaction, and the conventions for reaction stoichiometry, reaction rates and rates of production, prove that

$$\sum_{j=1}^{n_{\text{species}}} H_j R_j = \sum_{i=1}^{n_{\text{rxns}}} \Delta H_{Ri} r_i$$

**Problem 5**

The liquid-phase series reactions



are to be carried out in a CSTR. The feed enters at 45 °C and consists of pure A at a concentration of  $c_{Af} = 5$  mol/L. Determine the temperature of the cooling fluid, which will be constant, that is required for the reactor to operate at 75 °C.

Parameter	Value	Units
$M_t$	93,000	g/min
$\Delta H_{R1}$	-6,200	cal/mol
$\Delta H_{R2}$	8,000	cal/mol
$V_R$	1000	liter
$Q_f$	100	liter/min
$C_{pf}$	0.22	cal/g-K
$U$	0.65	cal/min-cm <sup>2</sup> -K
$A$	15,400	cm <sup>2</sup>
$k_1$	$3.16 \times 10^{14} \exp(-12,500/T)$	min <sup>-1</sup> ; $T$ in K
$k_2$	$2.52 \times 10^9 \exp(-8,500/T)$	min <sup>-1</sup> ; $T$ in K

## Design Equations

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### 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

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

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

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

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

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

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

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

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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

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