

Instructions

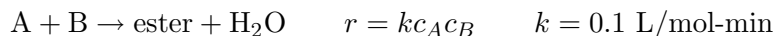
1. Write your name at the top of each answer sheet and on the front page of the exam questions.
2. Start each problem at the top of a new page.
3. The exam consists of five problems; they are equally weighted.
4. Useful integrals and equations are listed beginning on Page 6.
5. Return the exam questions or you will receive a grade of zero.

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

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

**Problem 1**

Consider the liquid-phase organic esterification reaction taking place in the CSTR depicted in Figure 1. Two streams, an acid containing no base, and a base stream containing no acid, are fed into the CSTR. The esterification reaction and its rate are given by



in which A is the organic acid and B is the organic base. The acid and base are dissolved in an organic solvent and the acid and base streams have feed concentrations of  $c_{Af}$  and  $c_{Bf}$ , respectively. You may assume constant density of the fluid and a constant reactor volume. Find the steady state effluent concentration of ester when

$$Q_A = Q_B \quad c_{Af} = 8 \text{ mol/L} \quad c_{Bf} = 4 \text{ mol/L} \quad \tau = 10 \text{ min}$$

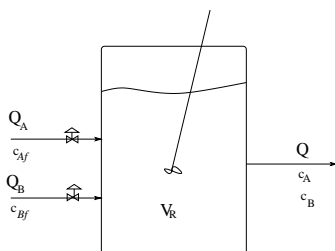
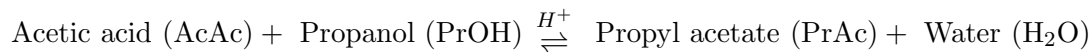


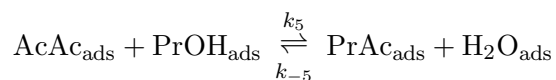
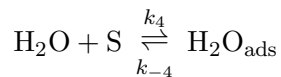
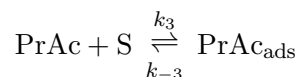
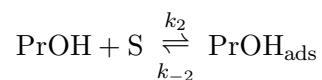
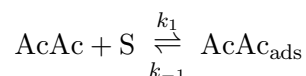
Figure 1: Organic acid and base streams fed into a CSTR.

**Problem 2**

Y-S. Huang and K. Sundmacher [International J. Chem. Kinet. DOI 10.1002/kin.20236 (2007)] have studied the kinetics of propyl acetate synthesis over Amberlyst 15, a commercial cation-exchange resin.



This acid-catalyzed reaction of liquid-phase reagents and products takes place on the surface of the resin, which has acid sites on it. One of three proposed mechanisms involves the adsorption of the reagents and the products on the resin and the bimolecular coupling of the adsorbed reagents. In this proposed mechanism, the adsorption and desorption steps are assumed to be at equilibrium, and the bimolecular coupling reaction, which is reversible, is assumed to be the slow (rate-limiting) step. The symbol "S" represents the active acid sites. Develop an expression for the rate of production of propyl acetate in terms of the liquid phase components.



**Problem 3**

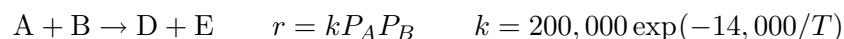
There were 20 technical areas covered in the course this semester. Here are 20 quickies and each is worth one point of credit. Provide a short answer to each.

- 1) The stoichiometric matrix  $\nu$  is a  $(n_{\text{reaction}} \times n_{\text{species}})$  matrix. If one particular  $(6 \times 8)$  matrix has a rank of 4, what does that mean?
- 2) How does the equilibrium constant change with system pressure for a gas?
- 3) Under what condition is the volume of the reaction mixture in a batch reactor constant?
- 4) What is the Arrhenius rate expression?
- 5) List two different assumptions that are used in describing a CSTR.
- 6) What assumptions for the PFR lead to the design equation being a first order ordinary differential equation?
- 7) For a system of reactions consisting of two or more linearly independent reactions, why is it not possible to reduce the isothermal problem to one material balance expression to find the effluent composition?
- 8) For a second order reaction, why is the conversion of the limiting reagent greater in a PFR than in a steady state CSTR of equal volume?
- 9) Consider a system of two independent, irreversible, exothermic reactions, with activation energies of 24,000 and 26,000 cal/gmole for Reactions 1 and 2, respectively. The desired product is formed in Reaction 1. If you were to carry out the reaction in a nonisothermal batch reactor and assuming the initial conditions are identical, would you operate it adiabatically or not?
- 10) One method to determine if a CSTR is operating at a stable or unstable steady-state condition was developed by van Heerden. At an operating condition, what must be true about the slope of the rate of heat generation vs. the slope of the rate of heat removal for the reactor to be stable?
- 11) A plot of temperature versus reactor volume increases from an initial value and appears to asymptotically approach a constant value in a PFR. List two possible scenarios that would lead to such a plot.
- 12) What does the reaction coordinate represent within the context of transition state theory?

- 13) Can a catalyst change the rate of a reaction, the equilibrium condition for a reaction, or both?
- 14) Almost without exception, adsorption is exothermic. Why is this so?
- 15) What variable establishes the type of diffusion, Knudsen or molecular, a gas molecule will experience in a cylindrical pore?
- 16) Why did we define the characteristic length to be the ratio of the pellet volume to the pellet surface area when applying the Thiele analysis to reaction with diffusion in heterogeneous catalysts?
- 17) How are the reactor bed density,  $\rho_B$ , the reactor pellet density,  $\rho_p$ , and the bed porosity,  $\epsilon_B$  related?
- 18) The first moment of the residence time distribution function is also equal to what physical process parameter?
- 19) If a reactor has a large dispersion parameter, would you expect it to be represented by a CSTR-in-series model with a large or small number of CSTRs?
- 20) In fitting data to a model one generally defines an objective function to be minimized, such as the sum of the squares of the residuals, where the residuals are the differences between the model prediction and the experimental data. Why is it a good idea to examine the residuals and what should you look for when you do this?

**Problem 4**

An adiabatic PFR will be used for the gas phase reaction



The units for the rate are  $\text{lbmol/hr-ft}^3$ ,  $P_j$  is in atm and  $T$  is in  $^\circ\text{R}$ . The feed enters at  $500^\circ\text{F}$  and 2 atm total pressure. The inlet molar feed rate of B is  $N_{Bf} = 0.17 \text{ lbmol/hr}$ . The feed only contains A and B. The heat of reaction is  $\Delta H_r = -58,000 \text{ Btu/lbmol}$  and the molar average heat capacity of the fluid is  $\tilde{C}_p = 95 \text{ Btu/lbmol-R}$ . You may assume  $\Delta H_r$  and  $\tilde{C}_p$  remain constant.

- (a) Determine the maximum temperature if the feed consists of a 4:1 molar mixture of A:B (*i.e.*, the molar flow rate of A is 4 times the molar flow rate of B).
- (b) For a fixed molar feed rate of  $N_{Bf} = 0.17 \text{ lbmol/hr}$ , what ratio of A:B will give the maximum possible reactor temperature? What is that temperature?

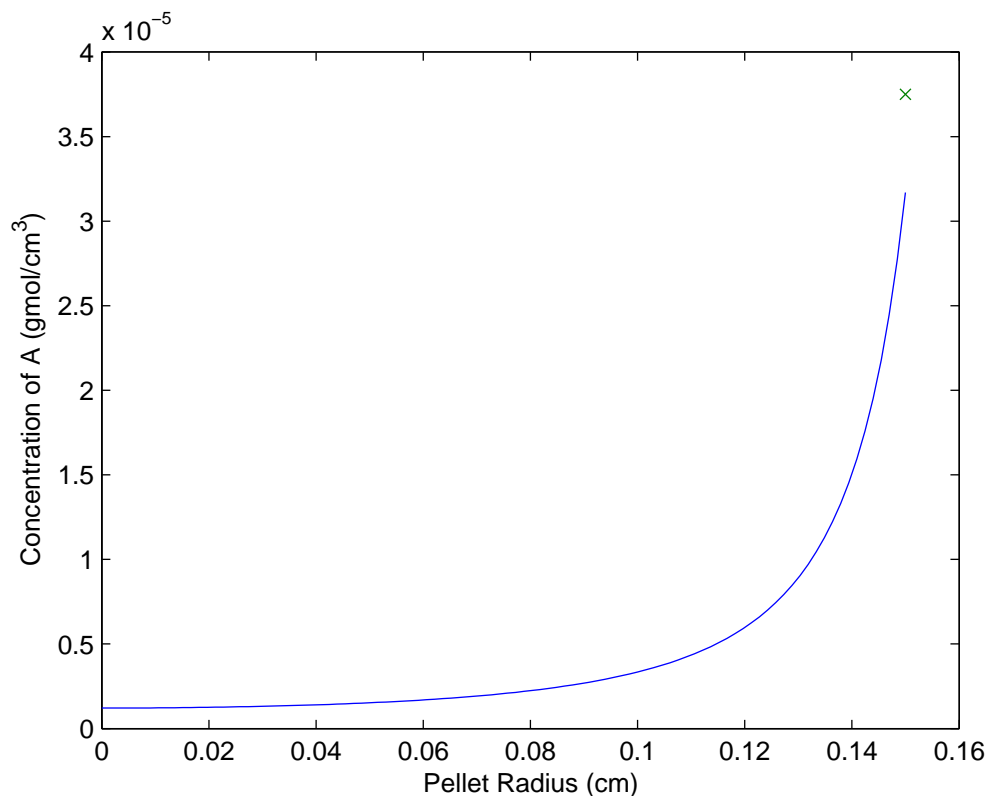
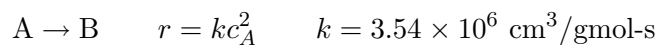


Figure 2: Concentration of A within the pellet versus pellet radius. The symbol  $\times$  corresponds to the bulk fluid concentration.

### Problem 5

Use Figure 2 and the information below to estimate the rate of the second order catalytic reaction



that was carried out in a spherical pellet of radius  $R = 0.15$  cm. This plot shows the concentration of A within the pellet and the symbol  $\times$  indicates the bulk fluid concentration. The reaction was carried out at a temperature of 650 K and at a partial pressure of A corresponding to 2 atm. The effective diffusion coefficient of A in the pellet is  $D_e = 0.008$  cm<sup>2</sup>/s and the external mass transfer coefficient was  $k_m = 4.0$  cm/s under the conditions of the experiment.

**Batch Reactor**

$$\frac{d(V_R c_j)}{dt} = \sum_i^{n_{rxns}} \nu_{ij} r_i V_R$$

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \sum_i^{n_{rxns}} r_i \Delta H_{Ri} V_R}{V_R \sum_j^{n_{components}} c_j \bar{C}_{pj}}$$

**Plug Flow Reactor**

$$\frac{d(Qc_j)}{dV} = \sum_i^{n_{rxns}} \nu_{ij} r_i$$

$$\frac{dT}{dV} = \frac{\frac{2}{R}U(T_a - T) - \sum_i^{n_{rxns}} r_i \Delta H_{Ri}}{Q \sum_j^{n_{components}} c_j \bar{C}_{pj}}$$

**Stirred Tank Reactor**

$$\frac{d(V_R c_j)}{dt} = Q_f c_{jf} - Q c_j + \sum_i^{n_{rxns}} \nu_{ij} r_i V_R$$

$$\frac{dT}{dt} = \frac{UA(T_a - T) - \sum_i^{n_{rxns}} r_i \Delta H_{Ri} V_R + Q_f \sum_j^{n_{components}} c_{jf} (\bar{H}_{jf} - \bar{H}_j)}{V_R \sum_j^{n_{components}} c_j \bar{C}_{pj}}$$

**Continuous Stirred Tank Reactor (steady-state and constant phase)**

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

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

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

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

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

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

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

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

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

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

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:

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