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 problems; they are equally weighted.
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

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.

$$\text{Acetic acid (AcAc)} + \text{ Propanol (PrOH)} \overset{H^+}{\rightleftharpoons} \text{ Propyl acetate (PrAc)} + \text{ Water } (H_2O)$$

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.

$$\text{AcAc} + \text{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{AcAc}_{\text{ads}}$$

$$\text{PrOH} + \text{S} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{PrOH}_{\text{ads}}$$

$$\text{PrAc} + \text{S} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{PrAc}_{\text{ads}}$$

$$\text{H}_2\text{O} + \text{S} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{H}_2\text{O}_{\text{ads}}$$

$$\text{AcAc}_{\text{ads}} + \text{PrOH}_{\text{ads}} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \text{PrAc}_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}}$$

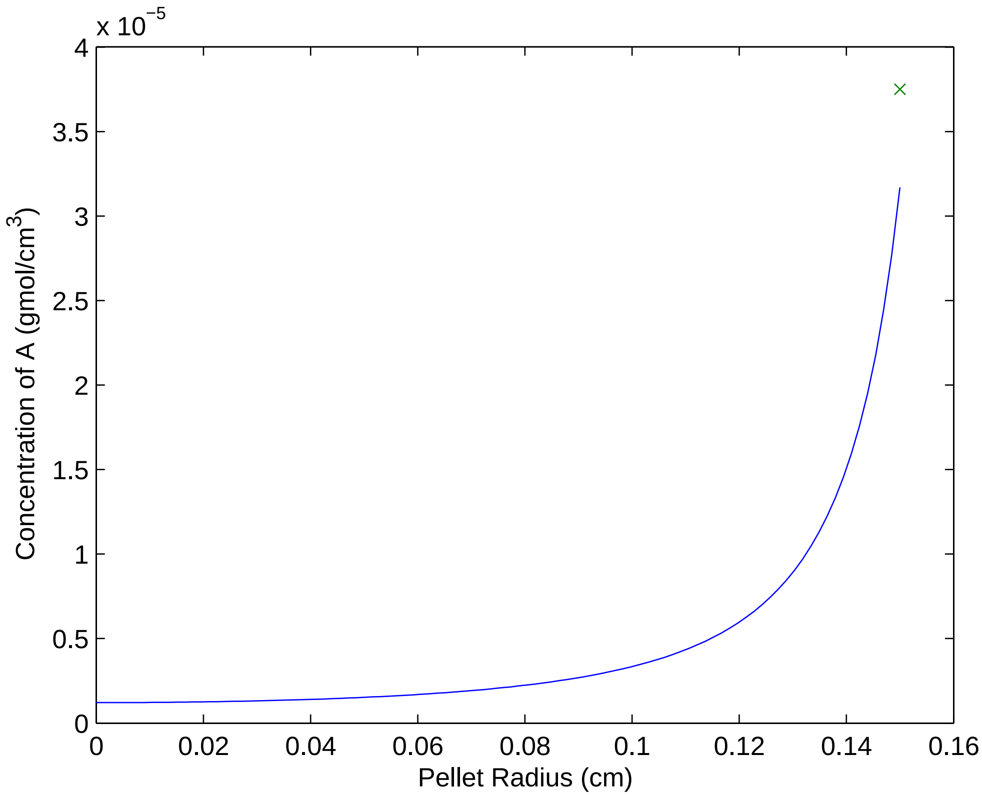

Figure 1: Concentration of A within the pellet versus pellet radius. The symbol × corresponds to the bulk fluid concentration.

Problem 2

Use Figure 1 and the information below to estimate the rate of the second order catalytic reaction

$$\mathrm{A} \rightarrow \mathrm{B} \qquad r = kc_A^2 \qquad k = 3.54 \times 10^6 \ \mathrm{cm^3/gmol\text{-}s}$$

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 × 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^2/s and the external mass transfer coefficient was $k_m = 4.0$ cm/s under the conditions of the experiment.

Problem 3

The following first-order catalytic reaction is conducted in a fixed-bed reactor. The reactant and product are gases.

$$\text{A} \rightarrow 2\text{B} \qquad r = kc_A$$

The intrinsic rate constant is $k = 2.35 \times 10^{13} \exp(-19,124/T)$ s^{-1}, where T is in Kelvin. The feed consists of pure A at 2 atm and a total molar flow rate of $N_{Af} = 12$ mol/s and a temperature of 578 K. At this feed rate there are no external limitations. The catalyst pellets are spherical with a radius of 0.3 cm. The effective diffusivity is $D_{\text{eff}} = 0.004$ cm^2/s. The bed has a void fraction of $\epsilon_B = 0.412$. The fixed bed reactor was designed to yield a conversion of A corresponding to $x_A = 0.9$.

There was a problem with the purity of the feed for several days, the catalyst was poisoned by the impurity and now the catalyst is ten times less active. For all practical purposes the intrinsic rate constant is now $k_{\text{poisoned}} = 2.35 \times 10^{12} \exp(-19,124/T)$. Assuming the diffusivity will not change with temperature, what new reactor temperature will you need to ensure the existing reactor continues to provide $x_A = 0.9$? You should assume you will heat the feed to this new temperature so the system is still isothermal.

Batch Reactor

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

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

Plug Flow Reactor

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

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

Stirred Tank Reactor

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

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

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

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

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

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

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

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

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

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

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

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 $\rightarrow$ 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

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