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 3.
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**

The second-order, heterogeneously-catalyzed reaction

$$2A \longrightarrow B \qquad r = kc_A^2$$

was studied at 675 K and with pure A at 1 atm. Both A and B are gases at this temperature. The rate of production of A was determined to be $-2.87 \times 10^{-6}$ gmol/$cm^3$-sec in a spherical catalyst pellet of radius $R = 0.4$ cm. From the experimental conditions we can neglect any external mass transfer limitations. Given that the diffusivity of A in the pellet is $D_A = 0.002$ $cm^2$/sec, what is the value of the rate constant at 675 K?

**Problem 2**

Determine the mass of catalyst required to reach a conversion of A of $x_A = 0.85$ if the heterogeneously-catalyzed reaction

$$A \longrightarrow 2B \qquad r = kc_A \qquad k = 548.4 \text{ min}^{-1}$$

is conducted in an isothermal fixed-bed reactor having an inlet flow of pure A of $N_{Af} =$ 258 gmol/min, at a temperature of $T = 650$ K and pressure of $P = 1.5$ atm. Both A and B are gases at the reaction conditions. The catalyst is a spherical pellet with a radius of $R = 0.8$ cm and the diffusivity of A is $D_A = 0.0065$ $cm^2$/sec. The bed porosity is $\epsilon_B = 0.35$ and the bed density is $\rho_B = 0.4$ g/$cm^3$. You may neglect external mass transfer limitations and my assume the pressure drop is negligible.

**Problem 3**

**Part (a)** Explain how you would use information on the catalyst pore structure (*e.g.*, pore radius and pore size distribution) along with the chemical and physical properties of the diffusing molecules to estimate an effective diffusion coefficient for an equimolar counter diffusion situation in a catalyst pellet. What do you need to know and why does it matter?

**Part (b)** List the possible boundary conditions at the pellet surface that can be used to solve

$$\overline{\nabla}^2\overline{c} + \left[\frac{a^2\mathrm{R_{js}}}{c_{js}D_j}\right]\overline{R} = 0 \qquad \overline{R} = \frac{R_j}{R_{js}}$$

in a spherical pellet. What process condition or additional information do you need to determine which boundary condition would be most appropriate? Be specific and provide enough detail that you convince the reader you would be making an informed choice and not a random guess.

**Part (c)** List at least three different cases where it is appropriate to use

$$\eta = \frac{R_j}{R_{js}}$$

$$\eta \approx \frac{1}{\Phi}\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right]$$

to describe the reaction rate in a catalyst pellet.

**Part (d)** List at least three different cases where it is inappropriate to use

$$\eta = \frac{R_j}{R_{js}}$$

$$\eta \approx \frac{1}{\Phi}\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right]$$

to describe the reaction rate in a catalyst pellet, *i.e.*, when does this approach fail to be a sensible thing to do.

**Part (e) - Extra no points bonus** Who got voted off the island while you were taking this exam?

**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)

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

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

## Useful Integrals

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

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

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

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

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

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

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 $c_{As}$

$$c_A = c_{As}\frac{R}{r} \times \frac{\sinh\left(\Phi(\frac{3r}{R})\right)}{\sinh(3\Phi)}$$

$$R_{Ap} = \frac{1}{\Phi}\left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi}\right] \times (-k_1 c_{As})$$

$$\Phi = \frac{R}{3} \times \sqrt{\frac{k_1}{D_e}}$$

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

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