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

Consider the first-order irreversible reaction (A $\longrightarrow$ B) taking place in a 0.3 cm radius spherical pellet. The rate constant is $k = 25.61\ \text{s}^{-1}$. The diffusivity of A in the pellet is $D_A = 0.007\ \text{cm}^2/\text{s}$. The external mass transfer coefficient is $k_m = 5.0$ cm/s. The concentration profile of A in the pellet as a function of radial position, r, is given by the following analytical relation

$$c_A = \frac{1.39 \times 10^{-13}\ \text{gmol/cm}^2}{r} \times \sinh(60.5\ \text{cm}^{-1} \times r)$$

Determine the concentration of A in the bulk fluid, *i.e.,* what is c_{Af}. Note you will have to determine if the bulk fluid concentration and the surface concentration are the same.

The $\sinh u = \frac{1}{2}(\text{e}^u - \text{e}^{-u})$, $\cosh u = \frac{1}{2}(\text{e}^u + \text{e}^{-u})$, and

$$\frac{d(\sinh u)}{dx} = \cosh u \frac{du}{dx}$$

Problem 2

Consider two different reaction mechanisms for the H_2 - I_2 reaction. The mass action statement for this reaction is

$$H_2 + I_2 \rightleftharpoons 2HI$$

Develop reaction rate expressions from the elementary reactions that are consistent with the information provided. In each case determine the rate of HI production, *i.e.*, R_{HI}, in terms of stable molecules. The stable molecules are H_2, I_2, and HI. You should consider H, I and H_2I to be reaction intermediates.

1. This mechanism assumes the first two elementary reactions are reversible and very fast relative to the third elementary reaction, and that the third elementary reaction is the rate limiting step.

$$I_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I$$

$$I + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2I$$

$$H_2I + I \xrightarrow{k_3} 2HI$$

2. This mechanism assumes the first elementary reaction is reversible. This mechanism does not make any assumptions about the relative rates of any of the elementary reactions.

$$I_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 2I$$

$$I + H_2 \xrightarrow{k_5} HI + H$$

$$H + I_2 \xrightarrow{k_6} HI + I$$

Problem 3

A heterogeneously-catalyzed reaction will be conducted in a spherical pellet loaded into a fixed-bed reactor. The reactants and products are gases

$$\text{A} \longrightarrow \text{B} + \text{C} \qquad r = kc_A^2 \qquad k = 1.2 \times 10^7 \text{ cm}^3/\text{gmol-s}$$

Find the mass of catalyst required to reach a conversion of A of $x_A = 0.85\%$ if the reactor is isothermal. You may assume the bulk fluid and surface concentrations are equal and may neglect pressure drop within the reactor. The feed consists of pure A at 650 K, a molar feed rate of $N_{Af} = 1.2$ gmol/s, and the reactor pressure is 2 atm. The pellet has a radius of $R_P = 0.30$ cm and a density of $\rho_p = 0.7$ g/cm^3. The bed has a density of $\rho_B = 0.4$ g/cm^3. The effective diffusivity of A in the pellet is $D_e = 0.007$ cm^2/s.

Design Equations

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

$$\frac{d(Q c_j)}{dV} = \sum_{i}^{n_{rxns}} \nu_{ij} r_i$$

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

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)

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

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

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

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

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

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

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

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

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

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