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 first-order, heterogeneously catalyzed reaction

$$\mathrm{A} \rightarrow \mathrm{B} \qquad r = kc_A$$

will be carried out in a spherical pellet.

Using the data tabulated below, predict the isothermal fixed-bed reactor volume needed to convert 95% of A if the feed is pure A at 2.5 atm, 585 K, $N_{Af} = 12$ mol/s, and the spherical pellets have a radius of $R = 0.25$ cm. The experimental rate data ($r_{\mathrm{experimental}}$) were collected at 585 K and $P_A = 2.5$ atm over spherical pellets of different diameters. At the experimental conditions and at the conditions for the fixed-bed reactor the diffusivity of A in the pellet is $D_A = 0.004$ $cm^2$/s and you can assume the bulk fluid and the pellet exterior concentrations are equal. The pellet density is $\rho_p = 0.68$ g/$cm^3$ and the bed density is $\rho_B = 0.40$ g/$cm^3$ (*i.e.*, $\epsilon_B = 0.412$).

| Pellet radius (cm) | Experimental rate $r_{\mathrm{experimental}}$ (gmol/$cm^3$-s) |
|---|---|
| 0.01 | $1.98 \times 10^{-3}$ |
| 0.02 | $1.70 \times 10^{-3}$ |
| 0.03 | $1.41 \times 10^{-3}$ |
| 0.04 | $1.18 \times 10^{-3}$ |
| 0.05 | $1.01 \times 10^{-3}$ |
| 0.1 | $5.67 \times 10^{-4}$ |
| 0.2 | $2.99 \times 10^{-4}$ |
| 0.3 | $2.03 \times 10^{-4}$ |
| 0.4 | $1.53 \times 10^{-4}$ |
| 0.5 | $1.23 \times 10^{-4}$ |

**Problem 2**

An equimolar, gaseous mixture of A and B is in adsorption-desorption equilibrium on a catalyst surface. The adsorption-desorption reactions can be represented as

$$\mathrm{A} + \mathrm{S} \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} \mathrm{A}_{\mathrm{ads}} \qquad \Delta H_{ads} = -18,000 \text{ cal/gmol}$$

$$\mathrm{B} + \mathrm{S} \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} \mathrm{B}_{\mathrm{ads}} \qquad \Delta H_{ads} = -26,000 \text{ cal/gmol}$$

where S represents an adsorption site. At a total pressure $P = 1$ atm and 425 K the fractional coverages of A and B are $\theta_A = 0.214$ and $\theta_B = 0.643$.

What is the fractional coverage of A ($\theta_A$) and the fractional coverage of B ($\theta_B$) for the same gas mixture and pressure but a temperature of 500 K?

**Problem 3**

A cylindrical catalyst pellet is used for the following reaction in a fixed-bed reactor

$$\mathrm{A} \rightarrow \mathrm{B} \qquad r = kc_A \qquad k = 2.3 \text{ s}^{-1}$$

The catalyst pellets are too fragile and there is too much breakage when repacking the bed with fresh catalyst so you have asked the catalyst vendor to make the pellets more mechanically robust. In making the catalyst more robust mecahnically the vendor decided to change the aspect ratio of the pellets and the cylinder is now shorter and the diameter is larger. The changes have also changed the effective diffusivity of A in the pellet and the bed density. The relevant parameters are listed below.

| Parameter | Current catalyst | New catalyst |
|---|---|---|
| $\rho_p$ (g/cm$^3$) | 0.68 | 0.68 |
| $\rho_B$ (g/cm$^3$) | 0.53 | 0.58 |
| $\mathrm{D}_A$ (cm$^2$/s) | 0.008 | 0.0065 |
| pellet radius (cm) | 0.25 | 0.50 |
| pellet length (cm) | 1.0 | 0.60 |

By how much will the catalyst charge need to change (as a percentage fo the current mass of catalyst in the reactor) if the feed gas, operating temperature and pressure, and the conversion of A are held constant? The feed is pure, gaseous A. You should also determine if the existing reactor is large enough to hold the new catalyst charge.

**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**

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

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

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

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

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

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

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

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

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

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

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

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

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