

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.

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

**Problem 1**

The rate of a heterogeneously catalyzed, first-order reaction

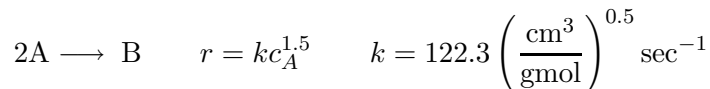


in a 0.75-cm diameter spherical pellet is  $R_{Ap} = -3.25 \times 10^{-5}$  gmol/cm<sup>3</sup>-sec when the catalyst is exposed to pure, gaseous A at a pressure of 1 atm and a temperature of 525 K. This reaction is known to have an activation energy of  $E_a = 18,600$  cal/gmol. Further, we know the effective diffusivity of A in the pellet is  $D_A = 0.009$  cm<sup>2</sup>-sec at 525 K and that diffusion is in the regime of Knudsen flow. We also know the bulk fluid and the external surface concentrations can be assumed the same.

Find the rate of reaction if the catalyst is changed to a cylindrical pellet that is 0.5 cm in diameter and 1.0 cm in length, and the temperature is increased to 600 K.

**Problem 2**

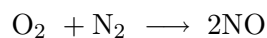
Determine the mass of catalyst required to realize 90% conversion of A for the heterogeneously-catalyzed reaction



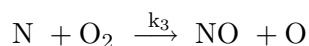
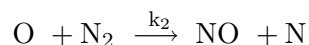
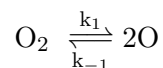
The fixed-bed reactor operates at constant pressure (1 atm) and temperature (575 K). The catalyst is spherical with a radius of  $R = 0.65$  cm, and the reactor when filled with these pellets, has a void fraction  $\epsilon_B = 0.31$  and a density of  $\rho_B = 0.76$  g/cm<sup>3</sup>. The effective diffusion coefficient for A in the pellet is  $D_A = 0.0075$  cm<sup>2</sup>/sec. You may neglect external transport limitations between the bulk fluid and the catalyst exterior surface. The inlet feed rate of pure A is  $N_{Af} = 12$  gmol/sec

**Problem 3**

**Part A** Develop an expression for the rate of NO production in terms of stable molecules. The homogeneous, high temperature reaction to produce nitric oxide is described by the following mass action statement

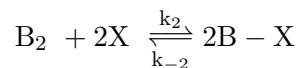
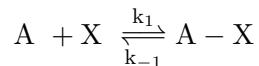


The following elementary reactions have been proposed to describe the chemical transformations required to generate NO. In this reaction scheme, the atoms O and N are reaction intermediates. We also know that the first reaction is so fast it can be approximated as being at equilibrium.



**Part B** Determine the fractional coverages of A, B and vacant sites for the following set of adsorption reactions that are equilibrated. The gas mixture of A and B<sub>2</sub> in contact with the catalyst surface is at 1 atm total pressure, 525 K and consists of a molar ratio of A:B<sub>2</sub>:Inert that is 1:3:1. The equilibrium adsorption constants are  $K_1 = 250,000 \text{ cm}^3/\text{gmol}$  and  $K_2 = 700,000 \text{ cm}^3/\text{gmol}$ .

Also if the heat of adsorption of B<sub>2</sub> is 3× that of A, what do you expect will happen to the relative coverages of A and B as the temperature is increased by 50 K. Explain your reasoning.



## Design Equations

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### 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)

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

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

## Useful Integrals

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

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

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

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

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

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

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:

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

## General Information on Mass Transfer with Reaction

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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  $\longrightarrow$  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

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