

Instructions

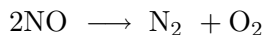
1. Write your name at the top of each answer sheet and on the front page of the exam questions.
2. Start each problem at the top of a new page.
3. The exam consists of three equally weighted problems.
4. Useful integrals and equations are listed beginning on page 4.
5. Return the exam questions or you will receive a grade of zero.

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

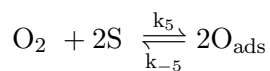
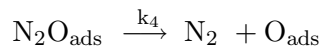
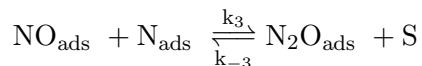
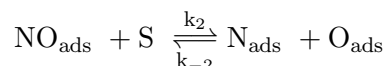
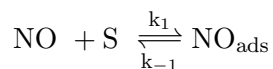
The van't Hoff relation is  $\frac{\partial \ln K}{\partial T} = \frac{\Delta H^\circ}{RT^2}$

**Problem 1**

Develop a rate expression for the nitrogenation of NO over metals in terms of gas phase concentrations of reactants and/or products. The mass action statement for this reaction is



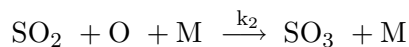
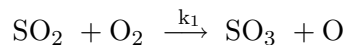
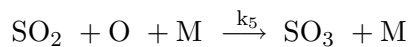
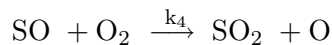
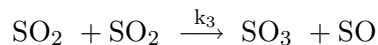
The following mechanism has been proposed to describe the reaction.



Reaction 4 is considered to be the rate limiting step and the other reactions are fast enough that they may be assumed at equilibrium.

**Problem 2**

[Adapted from Kee, Coltrin, and Glarborg, "Chemically Reacting Flow: Theory and Practice, Wiley, 2003.] In most combustion processes sulfur released by the fuel is quantitatively oxidized to  $\text{SO}_2$ , which may be subsequently oxidized to  $\text{SO}_3$  in the flue gas. Gaseous oxidation of  $\text{SO}_2$  by  $\text{O}_2$  has been experimentally determined in an oxygen-rich gas mixture to have a rate of  $\text{SO}_3$  formation that increases roughly linearly with the concentration of sulfur dioxide and only slightly with the concentration of oxygen at temperatures ranging from 1200 to 1300 K and 1 atm total pressure. There are two possible reaction mechanisms

**Mechanism I****Mechanism II**

In these mechanisms the component M is any gas phase molecule, *i.e.*, its concentration is  $P/RT$ , and it only serves to carry the excess energy of the collision away so the reaction can proceed; as such it is both a reactant and a product of an elementary reaction. Assuming that SO and O are reaction intermediates, determine if either Mechanism is consistent with the experimental data. After you derive your rate equation for each mechanism determine if, or how, it can match the experimental data and describe how or how not.

**Problem 3**

- (a) What is the rate of reaction in a cylindrical pellet (pellet radius = 0.2 cm and pellet length = 0.75 cm) for the reaction



at 3 atm of total pressure (pure A) and 750 K if the diffusivity of A is  $D_A = 0.0063 \text{ cm}^2/\text{s}$  and the value of the rate constant at 750 K is  $k = 0.25 \text{ gmol}^{0.25} \text{ cm}^{-0.25} \text{ s}^{-1}$ . You may assume the bulk and pellet surface concentrations are equal.

- (b) One of the possible boundary conditions for reaction with diffusion in a porous pellet is

$$D_j \frac{dc_j}{dr} = k_m(c_{jf} - c_j), \quad r = R$$

For a 0.3 cm radius pellet, a value of  $D_j = 0.008 \text{ cm}^2/\text{s}$ , and a value of  $k_m = 1.5 \text{ cm/s}$ , do you expect the bulk fluid and the pellet surface concentrations to be approximately equal so you could neglect the external differences. Why or why not? Be sure to justify your answer.

- (c) List the differential equation and boundary conditions that will allow you to compute  $R_{Ap}$  for the reaction in a spherical pellet.



Be sure to define all terms.

**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)**

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

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

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

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

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

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

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

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

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:

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

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 ( $A \rightarrow B$ ) 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

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