UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATIONS, DECEMBER 2001

Third Year - Program 6 - Chemical

CHE332F - APPLIED REACTION KINETICS

Examiner - C. A. Mims

Instructions: There are 5 questions, 4 with multiple parts. Total marks = 100. Indicate ***prominently*** the number and part (a,b,c, etc.)) of each question by its solution in the exam booklet(s).

DON'T PANIC!

17 total marks	**1. Theories of reactions:** The reaction of oxygen atoms with methane [1] $O + CH_4 \rightarrow OH + CH_3$ has a rate constant of 1.3×10^6 L mol s^{-1} at 500K.
10marks	➤**(a)**Estimate the rate constant for the reaction of O atoms with neo-pentane (tetramethylmethane. $C(CH_3)_4$ at 500K, i.e. $O + C(CH_3)_4 \rightarrow C(CH_3)_3(CH_2) + OH$ Molecular diameters: neo-pentane = 600pm; methane = 400pm; O atom = 150pm Molar masses: neopentane = 0.072kg; methane = 0.016 kg; O atom = 0.016 kg. Energy needed (energy barrier) with neopentane is 6 kJ/mol lower than for methane (because of slightly weaker C-H bond in neopentane). State any assumptions you made in the calculation above and justify them..
2 marks	➤**(b)**➤Draw a qualitative structure for the transition state in reaction [1] above.
3 marks	➤**(c)**➤True or false? A smaller pre-exponential factor in the rate constant corresponds to a more positive entropy of activation in transition state theory. Explain in 25 words or less.
2 marks	➤**(d)**➤How are theories of elementary reactions useful to the applied chemist/engineer? *(be brief).*

50 total marks

2. Ideal reactors: The following data were obtained in a laboratory CSTR for the reforming of methanol.

	mass of catalyst	FA_o CH_3OH (liquid, 25C)	Feed ratios (mole basis)			Dry gas (no H_2O, CH_3OH) Outlet mole fraction				
T (°C)	g	mol min^{-1}	H_2O/ CH_3OH	N_2/ CH_3OH	CO_2/ CH_3OH	H_2	CO_2	$(CH_3)_2O$	CO	N_2
256	35	0.46	1.1	0.4	0.1	0.565	0.188	0.00534	0.0006	0.241

7 marks ➤**(a)**➤Calculate the reaction rate (mol $kg_{cat}^{-1}min^{-1}$) for production of CO_2, H_2, CO, and dimethyl ether $(CH_3)_2O$ in this reactor. Use the N_2 tracer.

8 marks ➤**(b)**➤Calculate the methanol conversion and the carbon-based selectivities to CO, CO_2, and dimethyl ether. (Assume there are no unmeasured carbon-containing products).

3 marks ➤**(c)**➤Why are CSTRs useful for laboratory investigations of reaction kinetics to determine rate laws? Make a comparison to PFRs in your answer.

The following reaction network is fit to data on this system.

$$[1]\quad CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad r_1 = k_1 P_{CH3OH}^{1/2} P_{H2O}^{1/2}$$
$$[2]\quad 2\,CH_3OH \rightarrow (CH_3)_2O + H_2O \qquad r_2 = k_2 P_{CH3OH} P_{H2O}^{-1/2}$$
$$[3]\quad CO_2 + H_2 \rightarrow CO + H_2O \qquad r_3 = k_3 P_{CO2} P_{H2}^{1/2} P_{H2O}^{-1/2}$$

k_1 (300°C) = 71 mol atm^{-1} kg_{cat}^{-1} min^{-1}
k_2 (300°C) = 0.45 mol atm$^{-1/2}$ kg_{cat}^{-1} min^{-1}
k_3 (300°C) = 0.013 mol atm^{-1} kg_{cat}^{-1} min^{-1}

A 1:1 mixture of CH_3OH:H_2O (only) is fed at 300°C and at 1 atm pressure in the reactor. Answer the following, using these conditions and the rate laws above.

6 marks ➤**(d)**➤What are the initial (at very low conversion) carbon-based selectivities to the three products: CO, CO_2, and dimethyl ether.

6 marks ➤**(e)**➤Sketch (qualitatively) the dependence of the selectivities to CO, CO_2, and dimethyl ether as a function of the methanol conversion in a PFR.

17marks ➤**(f)**➤Assume only reaction 1 is occuring. Calculate how much catalyst will be needed to react 0.100L/min of liquid methanol feed (density = 0.8 g cm^{-3}) to 98% conversion

3 marks ➤**(g)**➤Discuss the importance of selectivity in chemical process engineering. *(be brief)*

15 total marks

3. **Rate Laws:** The following data were obtained for the oxidation of soot (solid carbon) by NO_2 at 350°C on an active diesel exhaust catalytic filter.

$$C(solid) + 2\,NO_2 \rightarrow CO_2 + NO$$

P_{NO2} / *atm*	rate / *mol C (mol $C_{present}$)$^{-1}$ hour^{-1}*
0.000300	0.073
0.000800	0.317
0.002700	1.96

6 marks

➤(a)➤ Show that this reaction obeys a power law in P_{NO2} over the measured range. Calculate the best reaction order and value for the rate constant (with units).

At 390°C, the rate is 0.745 mol C (mol $C_{present}$)$^{-1}$ hour^{-1} in the presence of .000500 atm of NO_2. Assume the rate law is separable (temperature - composition) and Arrhenius temperature dependence is followed.

6 marks

➤(b)➤ Calculate the values (with units) of the activation energy and pre-exponential factor for this reaction.

3 marks

➤(c)➤ What other parameters besides temperature and P_{NO2} could the rate of this reaction depend on?

15 total marks

4. The mechanism of a simple reaction $A \rightarrow 2C$ involves the following steps

$A \rightarrow 2B^*$; rate constant k_1
$2B^* \rightarrow A$; rate constant k_2
$B^* \rightarrow C$; rate constant k_3

5 marks

➤(a)➤ Treat B* as a reactive intermediate and derive the rate law for the reaction applying the stationary state approximation

5 marks

➤(b)➤ What is the simplified rate law if $k_1, k_2 >> k_3$? and what activation energy would be measured in this case if E_{A1} = 95kJ/mol, E_{A2} = 35kJ/mol and E_{A3} = 112 kJ/mol?

5 marks

➤(c)➤ Reaction 2 in question 2 is equilibrium limited (i.e. reversible). The equilibrium constant is 0.04 at 300°C. Write a general equation for the net rate of this reaction taking the equilibrium limit into account. Discuss the relevance to reactor design.

3 marks

➤*4.*➤ Compose a short quantitative question (about reaction kinetics) for next year's class. Base it on something I didn't ask about on this exam.

Enjoy your vacation/holiday !

POSSIBLY USEFUL INTEGRALS:

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

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

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