UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATIONS, APRIL 2001

Third Year - Program 5 - Environmental/Biomed

CHE392S - KINETICS AND REACTOR DESIGN

Examiner - C. A. Mims

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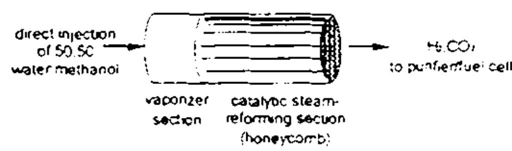
*Instructions: Work all questions in the exam booklet(s) provided. Indicate prominently the number of each question by its solution. 100 total marks in 4 questions. Have fun and **DON'T PANIC!** There is less work than meets the eye - read and think first (redundant advice by 3rd year, I'm sure). Integrals on last page.*

Question 1. (43 total marks) Storage of hydrogen is difficult and dangerous. In order to enable more widespread use of fuel cells in the home and on board motor vehicles, there is significant interest in being able to supply hydrogen on demand from "reforming" of safer liquid fuels. Methanol (CH_3OH) is a favourite candidate for these applications. One embodiment (an important word in patent literature) is shown here.

At moderate temperatures (~200°C), the process can be treated as a single reaction (however, see later)-



$$\text{(I)} \qquad H_2O + CH_3OH \rightarrow CO_2 + 3\,H_2 \qquad\qquad r_I = k_I P_{CH3OH} P_{H2O} P_{H2}^{-1}$$

A copper-based catalyst is coated on the walls of the honeycomb monothlith in the reformer section .

<u>*Assume the following:*</u>

Ideal gas behaviour (all 4 components)

Total pressure in the reactor = 1.5 atm.

Cu content on the monolith = 20 g/L of monolith.

Feed is 1:1 molar mixture of methanol:water.

Isothermal reactor at 200°C

$k_I = 1.44 \times 10^2$ mol atm^{-1}s^{-1} kg$_{Cu}^{-1}$. at 200°C

Ideal plug flow in the monolith

<u>*Apply the following engineering constraints:*</u>

The maximum H_2 supply rate required is 0.5 mol/s (to power a 100kW fuel cell).

The conversion of the methanol at this maximum supply rate is required to be 98%.

(1a, 20marks) What volume of monolith is required to meet these requirements?

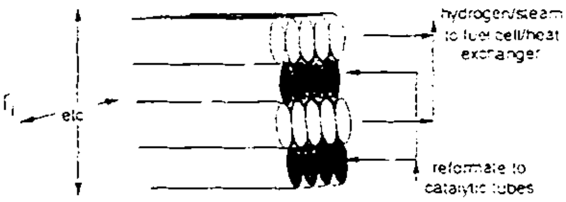
(1b, 4 marks) Tests show that the rate constant can be expected to decrease by a factor of 2 after 100,000 hours of use. What volume of monolith is required to assure the requirements are met in this eventuality?

(1c, 8 marks) The rate law in part (a) can result from a Type II Langmuir-Hinshelwood mechanism where H, H_2O and methanol all adsorb on the catalyst surface and the rate- limiting surface step is between adsorbed

H_2O and methanol. Write the steps of this mechanism, their individual rate laws, and the full rate law that results. Describe the conditions under which this rate law simplifies to the simpler one in part (a), and what mechanistic constants make up the overall rate constant, k_I in part (a) in this limit.

(1d, 8 marks) This question deals with a more realistic case (you will probably see these in operation in the next decade). Please write just the differential equations for each species and for the gas temperature

The feed is the same as in part (a) .
(1) Three catalytic reactions occur simutaneously.
(I) $CH_3OH + H_2O \rightarrow CO_2 + 3\,H_2$ Heat of reaction ΔH_I , rate r_I
(don't worry about the rate laws here - but just imagine!)
(II) $CO_2 + H_2 \rightarrow CO + H_2O$ Heat of reaction ΔH_{II} , rate r_{II}
(III) $3H_2 + CO \rightarrow CH_4 + H_2O$ Heat of reaction ΔH_{III} , rate r_{III}



The honeycomb is a manifold where half the channels form a hydrogen delivery system (see diagram) and the methanol + reformate flows through the other (shaded) half which have the catalystt. The contact area between the flow systems = A' (m^2 per L of the monolith).

Hydrogen is transported through the wall (by dissolving in it - some materials do this!) with the following rate:

$$\Phi_{H2} = k_{H2}\,(P^{1/2}_{H2,\,catalytic} - P^{1/2}_{H2,\,delivery}) \text{ moles } atmH_2^{-1/2}\ m^{-2}$$

and thermal energy is also transported at the rate

$$\Phi_J = k_J\,(T_{catalytic} - T_{delivery}) \text{ joules Kelvin}^{-1}\ m^{-2}$$

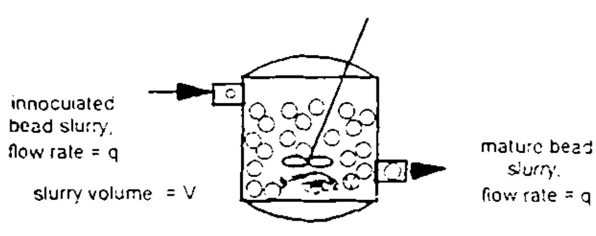
The temperature and P_{H2} in the hydrogen delivery system are maintained at a constant level by feedback from the fuel cell and recirculation. Assume k_{H2} and k_J are independent of T (k_{H2} is really not!). Include other necessary information needed in the differential equations.

(1e, 3 marks) For this system, write an expression for the carbon-based selectivity (overall fractional yield) to CO_2 as a function of the molar flow rates of the various species.

Question 2. (32 total marks)

It is desired to use a continuous process to innoculate open-lattice polymer beads with bone-cell colonies for use in implants (the same process could possibly be used to produce colonies for indroduction into water streams for environmental remediation).

The beads are innoculated with 0.1mg of cell mass per g polymer (x = 0.1) and fed as a slurry (in a nutrient broth) to a reactor/incubator/nursery with the mixing conditions of a CSTR. Under these conditions cell mass growth follows the rate law



$$dx/dt = k_g\, x\,(b-x)/\,b$$

which causes x to grow exponentially until it saturates at b. Given the following, answer the questions below:

$k_g = 0.7\ h^{-1}$ $b = 50$ mg / g polymer cells only on beads

(2a, 7 marks) How long would it take a given bead to reach 90% of the saturated value of cell mass concentration ($x = 0.9\ b$)?

(2b, 9 marks) What value of the average reactor residence time (V/q) would be required in order to assure that 90% of the beads have reached or exceeded the 90% level discussed in part (a)?

(2c, 6 marks) What measurements would you make and what results would you expect in order to assure that the reactor in (a) is well mixed? How would incomplete mixing show up in your measurement?

(2d, 5 marks) Describe how incomplete mixing in the slurry would effect the results and how you might treat this in a process model. Be as quantitative as possible under exam pressure/constraints and use diagrams where useful.

(2e, 5 marks) How might this continuous (no BR's allowed) process be improved (i.e. smaller reactor / holdup time) ? Elaborate on how this would improve things.

Answer me these questions 3. (30 total marks)

(3a, 3 marks) What is the general form of the exit age distribution, E(t) for N tanks in series?

(3b, 3 marks) The concept of less than one "tanks in series" was discussed. What is the significance of this concept and how is it used?

(3c, 3 marks) What is the value of the integral of E(t)dt from $t = 0$ to $t = \infty$ for $N = 2$?

(3d, 3 marks) The effects of concentration and temperature are separable in a rate law if the same activation energy is measured at various fluid compositions - T or F? Explain if unsure.

(3e, 3 marks) Transition State Theory assumes that the molecular groupings in the transition state configuration are in equilibrium with the products - T or F?

Question 4. (10 total marks). Take only 10-15 minutes on this one.

(4a, 8 marks) Please describe a concept or information that "clicked" or was re-inforced by working on your project.

(4b, 2 marks) Would you like to take a final exam (or part) in a course like this in which work is done on a computer (no communications features, of course)? Please explain (very briefly).

Best of luck this summer, CM (:^)

Possibly useful integrals:

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

2. $$\int \frac{dx}{(a+bx)^2} = -\frac{1}{b(a+bx)}$$

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

4. $$\int \frac{x\,dx}{(a+bx)^2} = \frac{1}{b^2}\left[\ln(a+bx) + \frac{a}{a+bx}\right]$$

5. $$\int \frac{x\,dx}{(a+bx)^n} = \frac{1}{b^2}\left[\frac{-1}{(n-2)(a+bx)^{n-2}} + \frac{a}{(n-1)(a+bx)^{n-1}}\right];\ n = 3 + \text{higher}$$

6. $$\int \frac{x^2\,dx}{a+bx} = \frac{1}{b^3}\left[(a+bx)^2 - 2a(a+bx) + a^2\ln(a+bx)\right]$$

7 $$\int \frac{x^2\,dx}{(a+bx)^2} = \frac{1}{b^3}\left[a+bx - 2a\ln(a+bx) - \frac{a^2}{(a+bx)}\right]$$