

98-CHEM-A4, Chemical Reactor Engineering

Duration: 3 hours

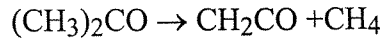
NOTES:

1. If you have any doubt as to the interpretation of a question, please submit with your answer a clear statement of any assumptions you make, if possible, underlined or enclosed in a box.
2. **OPEN BOOK EXAM**
You may bring to this examination
 - a) your own unit conversion tables and/or mathematical tables (such as a CRC Handbook).
 - b) a non-communicating, programmable electronic calculator including a small operating guide. Please indicate the name and model of your calculator on the first inside left-hand sheet of the exam work book.
3. Graph paper will be provided.
4. Any **FOUR** of SIX questions constitute a complete paper and, unless you indicate otherwise, only the first four answers will be marked.
5. Technical content is the key factor in your answers. It is essential, however, that you express yourself clearly: the examiner will not interpret remarks that are unclear.
6. Each question is worth 20 marks. The total exam is out of 80 marks. Marking schemes are indicated by the numbers in brackets such as [5] in the left margin of each part of a problem.
7. It would help the examiner if you would cite the origin of significant formulas used, e.g., Fogler, eq. (3-44).
8. Please treat all the data provided as exact and give your answers to three significant figures.

1. A first-order reaction of A in the liquid phase has a rate constant of 0.020 min^{-1} . The reaction of A to product is to be carried out isothermally at 200°C in two identical CSTRs-in-series, each vessel having a volume of exactly 100 L. The feed rate of reactant is 0.7884 L/min . You may assume there is neither an expansion nor a contraction of the reacting liquid during reaction.

- [8] a) Calculate the conversion leaving the second CSTR. (Call this Design "a".)
- [8] b) To achieve the same conversion in a single 200-L CSTR, what feed rate (in L/min) would be needed? (Call this Design "b".)
- [4] c) Which design would you expect to convert the larger quantity of A for a given feed rate, Design "a" or Design "b"? Please explain your reasoning.

2. Acetone is pyrolyzed isothermally and irreversibly to ketene in a plug flow reactor at 520°C and 1.00 atm total pressure:



The reactor used in this study was 3.3 cm inside diameter and 80 cm in length. Molar mass of acetone is 58 g/mol. The table below provides conversions (X_A) for a feed of pure acetone to the reactor.

Feed Flow, g/h	X_A
126	0.05
46	0.13
21	0.24
12	0.35

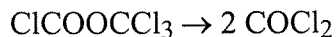
- [10] a) Show that a first-order kinetic model is reasonable for this reaction and calculate the rate constant in units of 1/h.
- [10] b) Check your result for k by means of a "differential reactor" analysis, in which you assume

$$\Delta V / \Delta X \approx F_{A^0} / (-r_A)$$

for changes in concentration that are differential (by convention less than about 10%). For such low conversions, it is permissible to neglect volume changes due to stoichiometry.

In this equation, ΔV is the volume of the reactor, ΔX is the fractional conversion of reactant A, F_{A^0} is the molar feed rate of reactant A, and $(-r_A)$ is the rate of disappearance of A (i.e., the change in its concentration per unit of time) by chemical reaction when A is close to its feed concentration. (The dimensions of both sides of the equation are therefore those of volume.)

3. The decomposition of pure diphosgene at 280°C occurs in the gas phase with the following stoichiometry

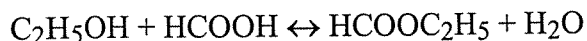


In the table below, total pressure data are provided on this decomposition.

Time, s	Total pressure, torr
0	15
500	18.9
800	20.7
1300	23
1800	24.8

- [5] a) Show by plotting the data to the integrated form of a second order reaction that this model does **not** adequately fit the data. (Graphical or tabular solutions are equally acceptable.)
- [5] b) Show by means of a differential method of data analysis that the data do fit a first order rate law.
- [5] c) Report the mean rate constant in appropriate units.
- [5] d) If the rate constant at 265°C were half as large as the value reported in c), what would be the activation energy for this process in kJ/mol?

4. At a temperature of 25°C, a mixed ethanol-water solvent is 0.0677 molar in formic acid (HCOOH), some HCl added having been added as a catalyst. The resulting esterification reaction is monitored by titration, and the formic acid concentrations as a function of time are reported in the table below. Initially no ester is present.



During this process, ethanol concentration is much in excess of that of formic acid. The water concentration is greatly in excess of that of the ester. Ethanol and ester concentrations are in some constant (though unknown) ratio. Effectively, the reaction is $\text{HCOOH} \leftrightarrow \text{HCOOC}_2\text{H}_5$ at the given $[\text{C}_2\text{H}_5\text{OH}]/[\text{H}_2\text{O}]$ ratio.

- [8] a) Show that the reaction is reversible pseudo-first order. For $\text{A} \leftrightarrow \text{B}$, one of the integrated forms for such a reaction is given as

$$\ln[(\text{A}-\text{A}_e)/(\text{A}^\circ-\text{A}_e)] = -(\text{k}_f + \text{k}_r)t$$

where A° is the starting concentration of A, and A_e is its equilibrium concentration. k_f and k_r are the forward and reverse rate constants respectively.

- [8] b) Calculate individual rate constants k_f and k_r for the given $[\text{C}_2\text{H}_5\text{OH}]/[\text{H}_2\text{O}]$ ratio.
- [4] c) Calculate the pseudo-equilibrium constant $\text{K} = \text{k}_f/\text{k}_r$ for this particular solvent ratio.

t, min	Formic acid, mol/L
0	0.0677
50	0.0615
100	0.0562
160	0.0509
290	0.0428
∞	0.0292

5. A problem on adiabatic conversion in a plug flow reactor

- [10] a) Gaseous reactant A is flowing into an adiabatic plug flow reactor at 0.0020 kmol/s carried by STEAM entering at 0.020 kmol/s. The (absolute) pressure of the combined stream is 105 kPa. The heat of reaction of A is -150 kJ/mol (i.e., is exothermic). The heat capacity of STEAM is 2.3 kJ/kg•K, a value that may be assumed to describe the heat capacity of the entire stream. Also, the molar mass of the stream may be assumed to be that of the STEAM. The temperature of the feed is exactly 600 K. At that temperature, the rate constant for the reaction is 0.3 s^{-1} . The energy of activation for the reaction is 80,000 kJ/mol. (Note that STEAM is in upper-case letters to distinguish it from "stream".)

Calculate the temperature of the stream leaving the reactor if 80% of the A has been reacted to product.

- [4] b) How would an increase in pressure of 20% affect the result in part (a)? Please explain.
- [3] c) How does the answer to part (a) depend on the rate constant of the reaction? Please explain.
- [3] d) How does the answer to part (a) depend on the kind of reactor (plug flow, CSTR) in which the conversion occurs? Please explain.

6. The dimerization of the monomer 2,5-dimethyl-3,4-diphenylcyclopentadienone in the liquid phase may be monitored by a colour change during its reaction. The spectrometer readings of its concentration provide us with the following concentration data of the monomer from a batch dimerization at 20 °C.

t, min	C _{monomer} , mmol/L
0	5.35
5	4.90
10	4.45
15	3.96
20	3.61
25	3.43
30	3.21
35	2.98
45	2.63
55	2.40
65	2.14
75	2.00
120	1.47

These data are to be the basis for the design of a continuous flow stirred-tank reactor.

- [8] a) What is the order (hint: try an integral value) and rate constant for this reaction?
- [8] b) What “holding time” would be needed for a PFR reactor in order to achieve a dimerization of 90% of the incoming feed of monomer if its entering concentration is exactly 4.50 mmol/L?
- [8] c) If the result in part (b) seems unrealistic, can you suggest a course of action that could increase the rate of reaction?

