

May 2013
04-Chem-A4, Chemical Reactor Engineering
3 hours duration

NOTES:

1. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper, a clear statement of any assumptions made.
2. This is an OPEN BOOK EXAM. Any non-communicating calculator is permitted.

You may bring to this examination

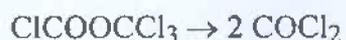
- a) the official textbook by Fogler, Elements of Chemical Reaction Engineering (4th Edition – however an earlier edition can be used) (annotated in margins, flagged, etc. as desired).
- b) your own unit conversion tables and/or mathematical tables (such as a CRC Handbook).
- c) a non-communicating, 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. Graph paper will be provided.

3. Four (4) questions constitute a complete exam paper. Complete 4 of 5 questions. Clearly indicate which questions are to be marked.
4. Each question is of overall equal value.
5. Most questions require an answer in problem solution format. Clarity and organization of the answer are important. Technical content is the key factor in the answers. Thus it is expected that you clearly outline and document your problem solution strategy. All equations used must be clearly documented prior to the use of specific values for the variables, and the parameters must be identified with appropriate units and significant figures. Citation of the origin of significant formulas used (e.g., Fogler, eq. (3-44)) would be of value to the examiner. Please treat all the data provided as exact and give your answers to three significant figures.
6. Each question is worth 20 marks. Marking schemes are indicated by the numbers in brackets such as "{5 marks}" following each part of a problem. Total for the exam is 80 marks. Complete 4 of 5 questions.

Marking Scheme (ONLY complete 4 of 5 questions for a total of 80 marks)

1. (a) 5 marks, (b) 5 marks, (c) 5 marks, (d) 5 marks
2. (a) 8 marks, (b) 8 marks, (c) 4 marks
3. (a) 15 marks, (b) 5 marks
4. (a) 10 marks, (b) 10 marks
5. (a) 8 marks, (b) 8 marks, (c) 4 marks

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

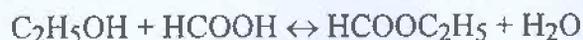


In the table below, total pressure data are provided for this reaction under batch conditions.

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 the activation energy be for this process in kJ/mol?

2. At a temperature of 25°C, a mixed ethanol-water solvent has a concentration of 0.0677 molar in formic acid (HCOOH). Some HCl is then added as a catalyst. The resulting esterification reaction is carried out in a batch reactor and monitored by titration. The resulting change in the formic acid concentration with time are reported in the table below. Initially no ester is present.



During this process, ethanol concentration is much in large excess relative to that of formic acid, and the water concentration is in great excess of that of the ester. Ethanol and water concentrations are in some constant (though unknown) ratio. Effectively, the reaction is HCOOH becomes HCOOC₂H₅ 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 $A \rightarrow B$, one of the integrated forms of the rate expression for such a reaction is given as

$$\ln[(A-A_e)/(A^\circ-A_e)] = -(k_f + k_r)t$$

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 $K = k_f/k_r$ 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

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

- [15] 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 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.

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

- [5] b) How would an increase in pressure of 20% affect the result in part (a)? Please explain.

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



The reactor used in this study has a 3.3 cm inside diameter and 80 cm 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 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 by chemical reaction when the concentration of A is close to its value in the feed stream. (The dimensions of both sides of the equation are therefore those of volume.)

5. 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 liquid 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, Design "a" or Design "b"? Please explain your reasoning.