CLB321: Chemical Kinetics 2019

***Warning:** Please read **all** of this document. If a question directed to me reveals that you have not read this document, marks will be subtracted from the group effort.*

Administration

Schedule

You are supplied with a general schedule (see schedule on Click-Up) specifying the dates of the Kinetics experiment and feedback session. **There will be no contact sessions prior to the experiment**, all the detail is supplied in this document. **You mark will mainly be awarded on the group performance during the feedback session** (see detail on feedback session below).

PLEASE NOTE THAT A PEER REVIEW SYSTEM HAS BEEN IMPLEMENTED IN WHICH YOUR PERFORMANCE DURING THE EXPERIMENT WILL BE ASSESSED BY YOUR PEERS IN THE GROUP. THIS WILL BE USED TO CALCULATE A SCALING FACTOR FOR YOUR INDIVIDUAL MARKS.

Experimental Session

For details on the specific experiment number (1-6) of your group, see the back of this document. The table below gives the experiment number of your group.

Group	1	2	3	4	5	6	7	8	9	10	11	12
Exp no	1	2	1	2	3	4	5	6	5	3	4	6

Group	13	14	15	16	17	18	19	20	21	22	23	24
Exp no	1	2	3	4	5	6	5	6	3	4	1	2

Feedback Session

Make a 100% sure that you have addressed the following!

Group feedback will be assessed in a combined session on the days allocated for feedback, e.g. Group 1 and 2 will be assessed in a combined session on 07 August 2019.

The feedback session will be in the form of a presentation by the respective groups. Each group member will be allocated a specific experimental role in the group (decided by the group) and will have to give individual feedback on that role. The groups will be questions by the lecturer and the students from the other group to assess the group members' understanding. Each group member will be expected to ask and answer at least one question. The groups will be given 15 minutes for presentation and 15 minutes for answering questions each.

In preparation for the feedback, the following should form part of the presentation

1) Experimental procedures required to acquire the data
2) **Graphs showing**:

- Conversion vs. time data for the batch runs – with corresponding fits/predictions.
- Conversion vs. residence time (V/Q) data for the continuous runs – with corresponding fits/predictions. Give the experimental data as points and the theoretical solution – based on a given rate equation - as a line on the x vs. τ plot. Carefully choose the scale/range on both axes so that the results are well presented. **Plot ALL the continuous results on ONE very neat graph**. You also need a theoretical solution for the two CSTR's in series.

3) The **value** of the rate constant at ambient temperature (with units, use seconds for time)
4) You also need **good reasons** for:
   - Differences between experimental and theoretical results.
   - Differences between a similar volume CSTR and PFR (as well as 2 CSTR's in series)

Experimental

Background

In this experiment you will study the homogeneous (non catalysed) saponification reaction of ethyl acetate with sodium hydroxide to form sodium acetate and ethanol:

$$CH_3COOCH_2CH_3 + NaOH \rightarrow CH_3COONa + CH_3CH_2OH$$
$$(A + B \rightarrow C + D)$$

The reaction is irreversible and accordingly the reaction rate is only a function of the two reactant concentrations and the temperature. The reaction will start whenever the ethyl acetate mixture gets in contact with the sodium hydroxide mixture. You will be studying this reaction in three types of reactors namely a batch reactor (BR), a continuous stirred tank reactor (CSTR) and a plug flow reactor (PFR).

The aim of the experiment is to assess the claim: "Reaction rate expression (kinetics) describing this reaction is independent of the reactor type used". This implies that one reactor type will be enough to determine the reaction kinetics and after this the reaction kinetics can be used to model the outcome (in this case conversion or outlet concentration) of any of the other reactor types. You will thus be developing rate model using one type of reactor, while you will test the model using another type of reactor. The more accurate you work to develop the model, the better your prediction will be for the other type of reactors, the more marks you will get!

Before you go into the lab

For each reactor type you will need to have a numerical solver for the mole balance. For the batch reactor this will imply that for a given set of initial reactant concentrations and a given or fitted rate constant and rate order, you will be able to generate a concentration theoretical profile (for any component) as a function of time. For simplicity we assume that the reaction kinetics follow a simple power law model:

$$r_A = -kC_A^m C_B^n$$

From your batch reactor experiment you will also obtain an experimental concentration profile. The idea is to have an experimental and theoretical profile that are very similar. The batch reactor mole balance will reduce to the following:

$$\frac{dN_A}{dt} = r_A V$$

For the PFR the mole balance will reduce to:

$$\frac{dF_A}{dV} = r_A$$

Remember:

$$\frac{F_A}{Q} = C_A$$

Note that this is a steady state mole balance and that the experimental reactor takes time to achieve steady state. Since the above equation is a differential equation you will be able to obtain a theoretical concentration as a function of reactor volume (given the rate constant and reaction

Finally, the CSTR mole balance:

$$F_{Ao} - F_A = -r_A V$$

Remember: This is also a steady state mole balance.

Background

In this experiment you will study the homogeneous (uncatalysed) saponification reaction of ethyl acetate with sodium hydroxide to form sodium acetate and ethanol:

$$CH_3COOCH_2CH_3 + NaOH \rightarrow CH_3COONa + CH_3CH_2OH$$
$$(A + B \rightarrow C + D)$$

The reaction is irreversible and accordingly the reaction rate is only a function of the two reactant concentrations and the temperature. The reaction will start whenever the ethyl acetate mixture gets in contact with the sodium hydroxide mixture. You will be studying this reaction in three types of reactors namely a batch reactor (BR), a continuous stirred tank reactor (CSTR) and a plug flow reactor (PFR). You should prove to yourself that the reaction rate describing this reaction is independent of the reactor type used. This implies that one reactor type will be sufficient to determine the reaction rate (sometimes called the reaction kinetics) and after this the reaction kinetics can be used to model the outcome (in this case conversion or outlet concentration) of any of the other reactor types. You will thus be developing rate model using one type of reactor, while you will test the model using another type of reactor. The more accurate you work to develop the model, the better your prediction will be for the other type of reactors, the more marks you will get!

Experimental setup and operation

Batch reactor

You are supplied with 5 liter each of 0.08 mol/l ethyl acetate and 0.04 mol/l sodium hydroxide in separate glass flasks. The batch reactor is a plain 200 ml glass beaker placed on the stirrer hotplate. Apart from the stirring magnet a conductivity sensor will be placed in the beaker. The reaction starts as soon as the two separate reagents (**2x100 ml** of each) get mixed. ***Note that both reagent concentrations will halve upon mixing***. Use the supplied 100 ml measuring flasks.

The insertion of the conductivity probe is very important, since no bubbles should be present in the sensor hole (at the bottom of the sensor). Insertion at an angle helps to achieve this but does not always work. One should re-insert until no bubbles are present. Make sure that the

probe readings are recorded before the reaction starts (see data recording below). You can follow the conductivity readings on the LABVIEW interface as the reaction proceeds. You can run the batch experiment for 10-15 minutes.

PFR and CSTR

You are supplied with 5 liter each of 0.08 mol/l ethyl acetate and 0.04 mol/l sodium hydroxide in the feed tanks. The peristaltic pump can be adjusted by using the arrow buttons (even during operation), please check if the respective volumetric flowrates are equal. The flow rate for a single pump should always be **between 5 and 60** (the reading on the pump is the volumetric flow rate in ml/min – remember to check this). Make sure that the pump is connected to the correct reagent. The pump can be started with the green button and stopped by the red button. The moving curved arrow on the interface indicates that the pump is on. Make sure the feed tank valve is open before starting the pump.

For the flow reactors experiments will only be performed at ambient temperature. Make sure that you constantly monitor the ambient temperature. The exit from the two pumps can either be connected to the PFR or CSTR. The PFR lines goes through the transparent tube to the PFR, while the CSTR lines runs over the bench to the CSTR situated on one of the stirrer hotplates (make sure only the stirrer and not the heater is on).

In the PFR the reagents join up at the T-piece at the top of the PFR plate. At this point the reaction starts as the mixture flows through the blue 6mm tube that is more than 20m long. The volume of the PFR can be taken as 300 ml – please confirm this. At the exit of the PFR the reaction mixture flows over the conductivity probe (inserted in the silicon tube at the top of the PFR plate). As in the batch reactor you should ensure that there are no air bubbles trapped in the hole of the conductivity sensor. After the conductivity measurement, the mixture exits into the drain (make sure the outlet tube is in the basin).

In the first CSTR (the glass beaker with the outlet tube at approximately 300 ml) both reagents enter the reactor from the top. Make sure that the thermocouple seals in its hole and that the tip is inserted in the liquid. At steady state the stirrer speed should exceed 250 rpm. The conductivity probe should be submerged directly into the vessel for concentration measurement.

There is the option of connecting two CSTR's in series (use the glass beakers with the outlet tube at approximately 150ml). The outlet from the first CSTR can be directly fed to the second CSTR. The outlet should be connected to the drain. Note that there is only one conductivity probe, so when performing an experiment with 2 CSTR's in series, you should move the conductivity probe to get the steady state readings of both reactors.

Relating conductivity readings to concentration.

The demis will show you how to work with the LABVIEW interface and how to take conductivity readings from LABVIEW to text.

The only molecules in the system that gives a conductivity reading is Sodium Hydroxide (NaOH) and Sodium Acetate (NaAc). NaOH gives a higher conductivity reading than NaAc at the same concentration, this results in a decreased conductivity as the reaction proceeds. The LABVIEW interface will record the mixture conductivity and you should copy the relevant readings into Python to perform the fits.

In order to calculate the NaOH concentration in the reaction mixture (using Python), the following procedure should be followed.

- The conversion of the reaction can be obtained by using the following:

$$x = \frac{K_{START} - K}{K_{START} - K_{FINAL}}$$

- The NaOH concentration will be given by:

$$C_{NaOH} = 0.02 \cdot (1 - x)$$

- K represents your conductivity data, while K_{START} and K_{FINAL} are constants at a specific temperature (will differ for setup A and B)
- Note that for a batch reactor run you will not be able to determine K_{START} accurately upon mixing. It takes a few seconds before the correct reading is displayed, **although time zero should be taken on the instant of mixing**.
- To obtain K_{START} use the carefully measured 0.02 mol/l NaOH solution.
- The K_{FINAL} value can be obtained by leaving the ambient batch reaction for 1 hour. (The demi might supply you with a completely reacted mixture – make sure the conductivity remains constant – no reaction)

Before you leave the bench

Make sure

- all the spills are cleaned
- all glassware are clean
- the pumps are not running
- that that the conductivity sensors have been **thoroughly washed** with distilled water and placed on the bench (dry)

Nomenclature

Ci	reactant concentration in the reactor (not in the inlet streams prior to mixing)
t	time
ri	rate of formation (mol/time/volume)
k	rate constant (units dependant on overall rate order
A	Ethyl Acetate
B	Sodium hydroxide
C	Sodium Acetate
D	Ethanol
n,m	rate orders
Q	total volumetric flow rate to the PFR/CSTR
V	volume of reactor
K	conductivity reading in mS/cm

Experimental details

Experiment 1

Part 1: Determine the ambient temperature kinetics using:

- A batch reactor.

Part 2: Test the ambient kinetics using:

- The PFR and CSTR (at 300ml) using a **total** inlet flow rate (two streams combined) of 30 and 50 ml/min.
- Two CSTR's (150ml each) in series using a **total** inlet flow rate (two streams combined) of 30 and 50 ml/min. Measure the concentration in both reactors once steady state is achieved.

Note the following: It will take at least the residence time (V/Q) before you reach steady state. Since you will have free time you can predict your measurements beforehand by using the measured kinetics from part1 in the mole balances.

Experiment 2

Part 1: Determine the ambient temperature kinetics using:

- A batch reactor.

Part 2: Test the ambient kinetics using:

- The PFR and CSTR (at 300ml) using a **total** inlet flow rate (two streams combined) of 24 and 40 ml/min.
- Two CSTR's (150ml each) in series using a **total** inlet flow rate (two streams combined) of 24 and 40 ml/min. Measure the concentration in both reactors once steady state is achieved.

Note the following: It will take at least the residence time (V/Q) before you reach steady state. Since you will have free time you can predict your measurements beforehand by using the measured kinetics from part1 in the mole balances.

Experiment 3

Part 1: Determine the ambient temperature kinetics using:

- The PFR with a **total** inlet flow rate (two streams combined) of 24, 40, 50, 60 ml/min. Note than you need to integrate each run separately with a chosen value of m,n and k. Start with an elementary guess.

Part 2 :Test the ambient kinetics using:

- a Batch reactor. This will result in a concentration profile (that you can predict beforehand).
- a CSTR (at 300ml) using a **total** inlet flow rate (two streams combined) of 24 and 40 ml/min.
- two CSTR's (150ml each) in series using a **total** inlet flow rate (two streams combined) of 24 and 40 ml/min. Measure the concentration in both reactors once steady state is achieved.

Note the following: It will take at least the residence time (V/Q) before you reach steady state. Since you will have free time you can predict your measurements beforehand by using the measured kinetics from part1 in the mole balances.

Experiment 4

Part 1: Determine the ambient temperature kinetics using:

- The PFR with a **total** inlet flow rate (two streams combined) of 30, 40, 50, 75 ml/min. Note than you need to integrate each run separately with a chosen value of m,n and k. Start with an elementary guess.

Part 2 :Test the ambient kinetics using:

- a Batch reactor. This will result in a concentration profile (that you can predict beforehand).
- a CSTR (at 300ml) using a **total** inlet flow rate (two streams combined) of 30 and 50 ml/min.
- two CSTR's (150ml each) in series using a **total** inlet flow rate (two streams combined) of 30 and 50 ml/min. Measure the concentration in both reactors once steady state is achieved.

Note the following: It will take at least the residence time (V/Q) before you reach steady state. Since you will have free time you can predict your measurements beforehand by using the measured kinetics from part1 in the mole balances.

Experiment 5

Part 1: Determine the ambient temperature kinetics using:

- A CSTR (at 300ml) with a **total** inlet flow rate (two streams combined) of 24, 30, 50, 60 ml/min. Note than you need to solve each run separately with a chosen value of m,n and k. Start with an elementary guess.

Part 2 :Test the ambient kinetics using:

- a Batch reactor. This will result in a concentration profile (that you can predict beforehand).
- The PFR using a **total** inlet flow rate (two streams combined) of 30 and 50 ml/min.
- two CSTR's (150ml each) in series using a **total** inlet flow rate (two streams combined) of 30 and 50 ml/min. Measure the concentration in both reactors once steady state is achieved.

Note the following: It will take at least the residence time (V/Q) before you reach steady state. Since you will have free time you can predict your measurements beforehand by using the measured kinetics from part1 in the mole balances.

Experiment 6

Part 1: Determine the ambient temperature kinetics using:

- A CSTR (at 300ml) with a **total** inlet flow rate (two streams combined) of 24, 40, 60, 75 ml/min. Note than you need to solve each run separately with a chosen value of m,n and k. Start with an elementary guess.

Part 2 :Test the ambient kinetics using:

- A Batch reactor. This will result in a concentration profile (that you can predict beforehand).
- The PFR using a **total** inlet flow rate (two streams combined) of 24 and 40 ml/min.
- Two CSTR's (150ml each) in series using a **total** inlet flow rate (two streams combined) of 24 and 40 ml/min. Measure the concentration in both reactors once steady state is achieved.

Note the following: It will take at least the residence time (V/Q) before you reach steady state. Since you will have free time you can predict your measurements beforehand by using the measured kinetics from part1 in the mole balances.