

CHEMICAL ENGINEERING LABORATORY
CHEG 4137W/4139W

Reaction Kinetics
Saponification of Isopropyl Acetate with Sodium Hydroxide

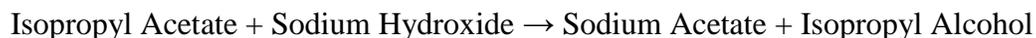
Objective:

The purpose of this experiment is to examine and determine the reaction kinetics of a simple homogenous liquid-phase system and to model this reaction in a continuously stirred-tank reactor (CSTR). Data from simple batch (flask) reactions will be provided to determine initial rate data from concentration versus time profiles before using the continuous reactor.

Major Topics Covered: Chemical reaction kinetics, reaction order, Arrhenius-style rate law.

Theory:

The reaction:



is an example of a saponification reaction (the reverse reaction would be esterification). This reaction may be either reversible or irreversible. For the irreversible case, the rate equation for a batch reactor may be written:

$$r_A = -d[A]/dt = k[A][B]$$

where k is the rate constant and $[A]$ and $[B]$ are the concentrations of the reactants in the appropriate units. If strictly equimolar concentrations of reactants are used, the rate equation can be simplified to a general n th-order reaction. $r_A = k_n [A]^n$ where $n \cong 2$. With good experimental data, this model allows the determination of the reaction order for an irreversible reaction.

The effect of temperature on the rate constant can be compared with that predicted by the Arrhenius expression: $k = Ae^{(-E/RT)}$, where A is the frequency factor, E is the activation energy of the reaction, R is the gas constant, and T is the absolute temperature. Rate data at various temperatures can be used to determine the frequency factor and activation energy of the reaction.

Once basic rate data is obtained, it can be used to size or design reactors, or determine the maximum conversion for a reactor of a given size. Design equations for different types of reactors are provided in the references.

Safety Precautions:

1. This lab uses both acids and bases. Use caution when handling these reagents, as well as when sampling from flasks or the reactor. Appropriate personal protective equipment should be used at all times.
2. Always make sure that the pump reservoirs are filled prior to turning on the pumps.
3. The ester solution should be mixed in a well-ventilated area.

Available Variables: Temperature, reactor residence time.

Procedure: See appendix for reagent preparation guide and procedure.

Analysis:

Your analysis **must include:**

1. A graphical determination of the reaction order as determined by the batch reaction experiment data.
2. Determination of the activation energy and frequency factor for the reaction, and a comparison with appropriate literature values.
3. A predictive model for CSTR results based on the batch results and intended CSTR operating conditions.
4. A comparison of CSTR experimental results with the predictive model, and a discussion surrounding the agreement/disagreement between theory and experiment.

Report:

Describe the design of your experiments and the results obtained, including an error analysis. Provide thoughtful and quantitative discussion of results, explain trends using physical principles and relate your experimental observations to predicted results (e.g. discrepancies between predicted CSTR results and experimental data). Express any discrepancies between observed and predicted results in terms of quantified experimental uncertainties or limitations of the correlations or computational software used.

Pro Tips:

1. Because of variations in density of the solutions, generate your calibration curves using the actual reagents, not pure water. The setup allows you to continuously recycle the reagents during the calibration phase.
2. For ease of taking data, it is recommended to start at lower temperatures and work incrementally upward.
3. Flush both pumps with pure water at the end of the experiment; this will prolong the life of the pump internals.
4. Carefully monitor the level in the reactor, and adjust the inlet or outlet flow rates to keep the level steady. Only take data when the system is at steady state.

References:

1. Fogler, H. S., *Elements of Chemical Reaction Engineering*, Prentice-Hall, Inc., Englewood Cliffs, NJ, 2nd Ed., 1992.
2. C. H. Bamford and C. F. H. Tipper, eds., *Comprehensive Chemical Kinetics*, vol. 10, "Ester Formation and Hydrolysis," Elsevier, New York, NY, 1972.
3. International Critical Tables, 7,129, "Influence of Constitution of Ester on Velocity of Hydrolysis; Titrimetric Method" (1930).

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Procedure and Checklist:

The batch experiment procedure can be found at the end of this document, to be used for reference.

CSTR Analysis:

Using your understanding of the saponification reaction, design a set of experiments to examine the continuous stirred tank reactor. Make up only the amounts of solutions you will need for the day.

The rate constant and the equilibrium constant (if the latter affects the reaction) should be experimentally determined beforehand as a function of temperature and compared to any available values from the literature and/or calculations based on the chemical structure of the ester. Use this kinetic information to design the runs for the continuous reactor, e.g., one set of conditions must result in conversion of the limiting component to at least 80%. Within the temperature chosen for this conversion, you also must be able to vary the flow rates over a sufficient range to check thoroughly your model for the reactor. Conditions (especially temperature) should be standardized, monitored and controlled so that accurate and precise process data are determined.

As suggested above, the group results should be compared with a mathematical model of the continuous reactor to demonstrate that you have successfully modeled the reactor and the reaction system. Possible approaches are to: (1) predict the performance of the continuous reactor from the batch data alone, and then compare the observed performance against this prediction; or (2) derive kinetic information from the continuous- reactor data alone, and compare these results (e.g., order, rate constants, frequency factor and activation energy) against those found for the batch reactions. You may also wish to use literature rate constants, providing appropriate citations.

Using the continuous reactor, ambitious groups can try to model and experimentally verify startup conditions, reagent imbalance, temperature changes, etc. as an alternative to or in addition to the standard steady-state conditions.

Helpful questions to consider:

1. How would CSTR data be treated to determine kinetic parameters?
2. Derive a design equation for this reaction in a CSTR using two streams (reactants A and B) of equal molar feed rate. Express your answer in terms of (a) volume, (b) flow rate, (c) initial concentration, and (d) the reaction rate constant.
3. What assumptions are necessary to solve the model equations analytically?

4. How often should data points be taken during an experiment? Should you take more data points at the beginning or the end of the experiment?
5. How is the equilibrium constant of a reaction related to temperature?
6. Compare the kinetic parameters determined from the flask reactions with those determined from the continuous reactor. Can you explain any differences?

CSTR Standard Operating Procedure

I. Preparation of Reagents

1. Make 1L of 0.1M NaOH solution; this will be used for titration
2. Make 4L of 0.1M NaOH solution in the provided Caustic tank
3. Make 4L of 0.1M Isopropyl Acetate solution in the provided Ester tank
4. Make 1L 0.1M HCl solution

II. System Breakdown



Figure 1: CSTR System

A: Valve 1
B: Valve 2
C: Valve 3
D: Valve 4
E: Caustic flowmeter
F: Ester flowmeter
G: Ester collection tube
H: Caustic collection tube

I: Impeller
J: Glass reactor
K: Caustic pump
L: Ester pump
M: Outlet pump
N: Valve 5
O: Outlet collection tube
P: Waste bucket

III. Prepare system

1. Connect the chiller quick-connect fittings to the fittings on the back of the system, as shown in Figure 2 below.

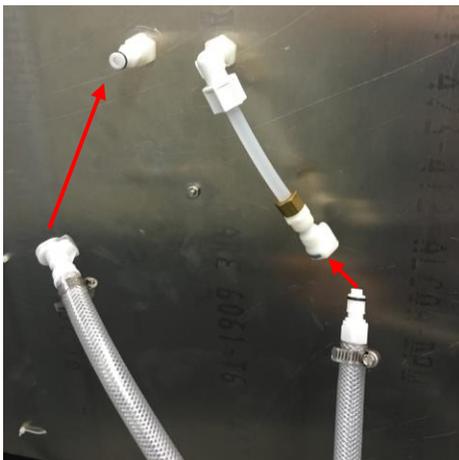


Figure 2: Chiller fittings

2. Turn on the chiller using the green switch and set to the desired temperature using the temperature control dial. Insert a thermometer into the chiller reservoir through the port to the right of the control panel
3. Connect the four quick-connect fittings between the containers and the system tubing
 - i. Red tubes connect with Ester; blue tubes connect with Caustic; green tubes connect with the outlet and waste bucket
4. Adjust the waste bucket lid so it is not completely airtight; this is to avoid pressure buildup.

IV. Calibrate the Flowmeters

1. Ensure that the valves are turned so the flow is through the closed loop (through the ester and caustic pumps, flowmeters, and containers), as shown in Figure 3
 - i. V1 should direct the flow to the ester container
 - ii. V2 should direct the flow to the caustic container
 - iii. V3 should direct the flow to V1
 - iv. V4 should direct the flow to V2

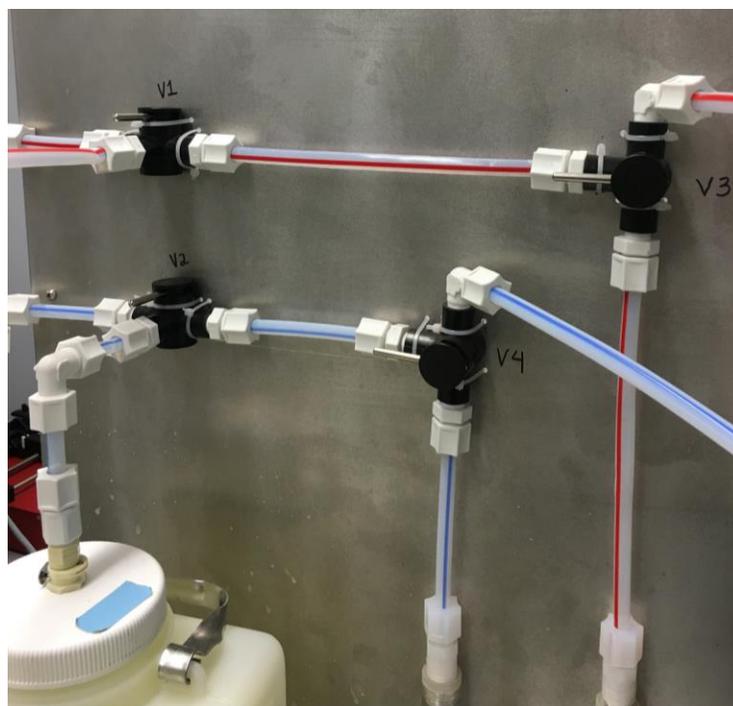


Figure 3: Closed-loop configuration

2. Start the system by switching on the caustic pump and ester pump
3. Set the desired flowrate using the pump knobs
 - i. Make sure to read the flowmeter float at its widest point
4. Ensure the temperature is at the setpoint
5. Allow the system to equilibrate by running the system for the equivalent of one residence time
6. Label and weigh 2-4 50-mL Erlenmeyer flasks; these will be the liquid collection vessels
7. Turn V1 all the way to the right and collect a sample of liquid through the ester collection tube, timing the entire collection process. Turn V1 back to the center when done collecting.
 - i. Weigh the collected liquid and record the weight
 - ii. Return the collected liquid back to its container
8. Repeat step 7 for V2, using the caustic collection tube
9. Perform steps 7-8 two more times for a total of three data points
10. Repeat steps 3-9 for 3-5 different flowrates

V. Run the system

1. Precool the HCl by placing it in an ice bath
2. Turn V3 and V4 so the flow is through the glass reactor, as seen in Figure 4. Make sure V5 is flowing into the waste bucket, as seen in Figure 5

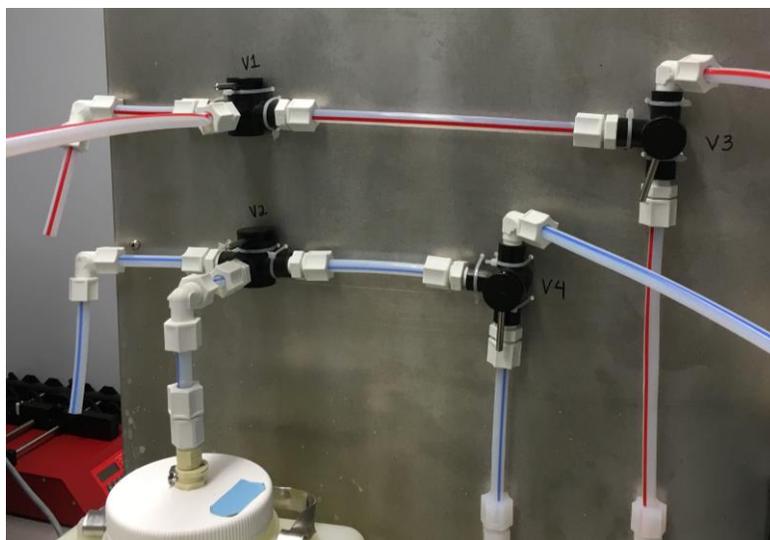


Figure 4: V1, V2, V3, & V4 open-loop configuration

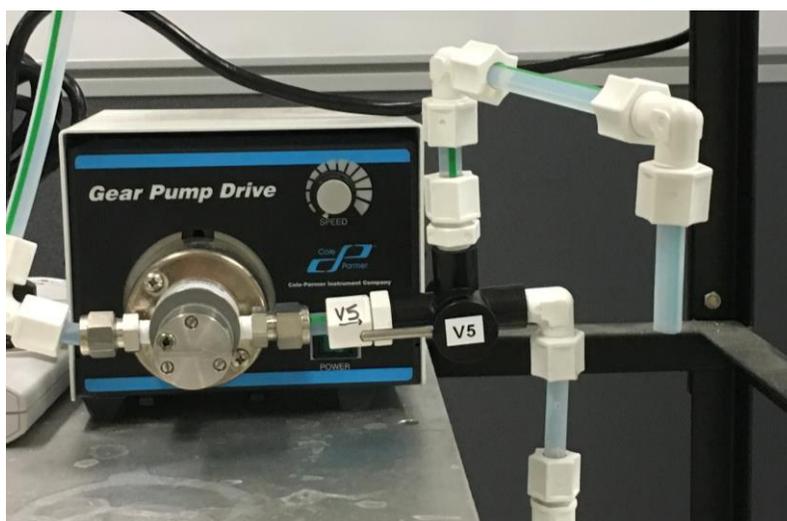


Figure 5: V5 configuration into waste bucket

3. Set the desired flowrate and temperature
4. Place a thermometer in the glass reactor via a port through the plastic cover
5. Make sure the valve at the bottom of the glass reactor is open
6. Once liquid begins to accumulate in the bottom of the glass reactor, switch on the outlet pump but keep the dial turned down to 0
7. Allow the glass reactor to fill to exactly 1L solution
8. Turn on the impeller and set to the desired speed
9. Use the dial to start the outlet pump. Manipulate the dial to keep the level in the glass reactor at 1L
10. Once the temperature is stable, begin collecting 10-mL samples from the outlet sample tube at timed intervals using a 50-mL Erlenmeyer flask

11. Add 5mL 0.1M HCl and one drop of phenolphthalein to your 10mL collected sample
12. Titrate the sample with 0.1M NaOH
13. Record the volume needed to titrate to completion
14. Discard solution into the designated waste bucket
15. Repeat as needed

VI. Flush the system

1. Turn off the pumps, chiller, and impeller
2. Disconnect the quick-connect fittings and empty the containers (ester, caustic, and waste) into the designated hazardous waste bucket
3. Rinse the ester and caustic containers with tap water
4. Fill the ester and caustic containers with approximately 5L distilled water each
5. Reconnect the ester, caustic, and waste containers to their quick-connect fittings
6. Turn V1, V2, V3, and V4 so the flow is through the closed loops
7. Run the caustic and ester pumps for approximately 5 minutes to flush the closed loop lines with distilled water
 - i. Make sure to also rinse the sample-collection tubing!
8. Turn V3 and V4 to direct the flow into the glass reactor
9. Allow the glass reactor to fill to just above the 1L mark, then turn on the impeller and the outlet pump
 - i. Maintain a volume of approximately 1L in the glass reactor
10. Run all the pumps until the level in the ester and caustic containers reaches the outlet ports. At that point, turn off the caustic and ester pumps before any air enters the pumps! **Do not let any air enter the pumps!**
11. Turn off the impeller
12. Drain the glass reactor by allowing the solution to drain into the waste bucket via the outlet pump
 - i. **Don't let any air enter the pump! Turn off the outlet pump before any air enters the pump!**
13. Empty the three containers (caustic, ester, and waste) into the sink
14. Clean all used glassware with soap/alconox and water

Batch Experiment Procedure – FOR REFERENCE ONLY!

For preliminary determination of the kinetic parameters, run batch reactions in flasks immersed in a temperature controlled water bath. Check the temperatures with an accurate laboratory thermometer. It is good practice to cover as wide a temperature range as practical, given the equipment.

Initial Reaction Procedure:

Recommended temperature range of 25-50°C

To determine the extent of reaction (conversion) with time:

1. Make the following solutions:
 - a. 1-L of 0.1M NaOH
 - b. 1-L of 0.1M HCl
 - c. 1-L of 0.1M Isopropyl Acetate
2. Preheat for 10 min 100 mL of ester and 100mL alkali at the test temperature in separate stoppered 250-mL Erlenmeyer flasks with lead donuts for support during immersion.
 - a. Use the water bath of the chiller for immersion. Insert a thermometer into the chiller reservoir through the port to the right of the control panel to record water bath temperatures
3. At zero-time, mix together and stopper.
4. At timed intervals, swirl the flask and transfer a 10.0-mL sample with a volumetric pipette, to an Erlenmeyer flask containing 5.0 mL of 0.1N HCl and one drop of phenolphthalein. The HCl should be precooled in an ice bath.
5. Rapidly titrate with 0.1 N NaOH to a pink end point with phenolphthalein indicator.
6. Plot the reaction curve as you do the experiment. If the reaction rate is too fast or slow, rerun with improved time intervals for sampling. Continue sampling until the reaction is substantially complete.

One way of estimating the zero-time data point is by inverse addition of the reagents. Mix 5.0 mL HCl with 5.0 mL NaOH. Add 5.0 mL of ester solution, mix, cool, and titrate with NaOH.

Calculations:

In principle at $t = 0$, only isopropyl acetate and sodium hydroxide are present. Adding a slight excess of HCl over the alkali gives: ester + NaCl + water + HCl excess. Back titration with NaOH gives the HCl excess, V_1 .

Determine the experimental order of reaction. Assuming second-order kinetics, use a numerical or graphical method to estimate the reaction rate constant. Repeat at various temperatures, and compare the observed effect of temperature on the rate constant with the predictions of the Arrhenius theory. Report the derived frequency factor and activation energy. Compare with data available in the literature.

Questions:

Somewhere in your report you should address the following:

1. Why is it necessary to titrate cold samples?
2. Why should titration end points be reached rapidly?
3. What would you expect to be the effect of alcohol chain length on reaction rate?
4. Is there any significant indication that the reaction is not second order?
5. Does your data contradict the hypothesis that the reaction is irreversible?