CHEG 345
Spring 2021
Kinetics Laboratory

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UNIVERSITY OF DELAWARE

CHEG 345 Junior Laboratory – Spring 2021

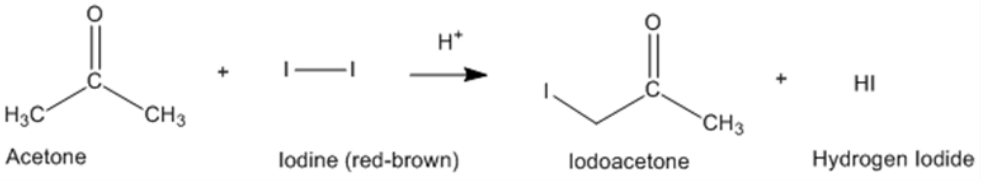
Two Experiments

- Kinetics (KIN) – Iodination of Acetone Experiment
- Thermodynamics (VLE) – Vapor Liquid Equilibrium Experiment

KIN Lab Objectives

1. Work effectively in a team, managing and documenting workload and time.
2. Design and analyze kinetics experiments to parametrize a proposed rate expression.
3. Consider operational precautions necessary to perform the designed experiments in a safe manner.
4. Use MATLAB and/or Aspen to simulate a network of multiple reactions and the steady-state operation of a CSTR.
5. Communicate in efficient, technical terms both orally and in writing, using a variety of formats (presentation, memorandum, short report).

Iodination of Acetone - Reaction



KIN Lab Structure

Phase 1

- **Familiarization and Planning**
- Deliverable: Pre-lab meeting with instructor to demonstrate knowledge of objectives, key information (safety, equipment, use of P-Code), and outline of experimental design.

Phase 2

- **Acetone Iodination Simulation and Data Analysis**
- Deliverable: short memo report with analysis of simulated data and provide in-person update

Phase 3

- **Reaction Network and CSTR Design**
- Deliverable: final report and presentation

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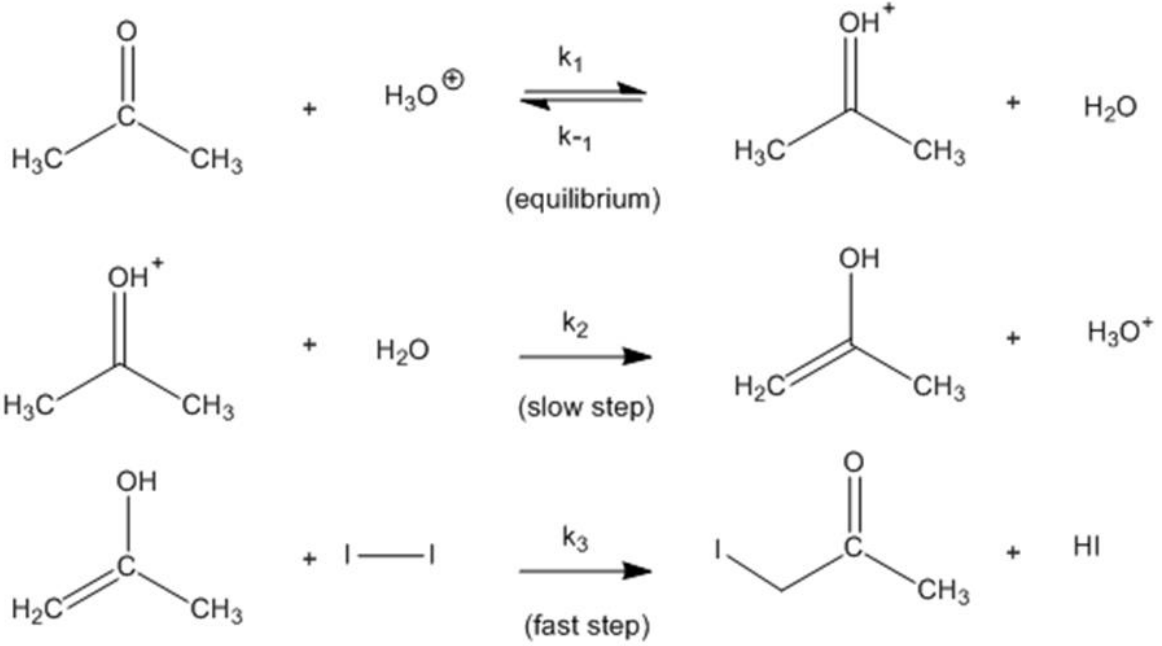
Iodination of Acetone - Mechanism



From Mechanism to Rates

Question

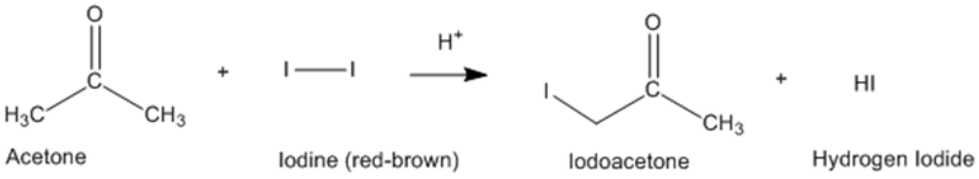
1a. Knowing that step 2 is the rate limiting step, write the rate expression for the overall reaction with the rate constant expressed in terms of k_1, k_{-1}, k_2, and k_3.

1b. What is the order dependence on the concentration of acetone?

1c. What is the order dependence on the concentration of iodine?

1d. What is the order dependence on the concentration of H_3O^+ (or H^+)?

Reaction



$$Ac + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AcH^+ + H_2O$$

(equilibrium)

$$Rate_1 = k_1[Ac][H_3O^+]$$

$$Rate_{-1} = k_{-1}[AcH^+][H_2O]$$

$$AcH^+ + H_2O \xrightarrow{k_2} Ac^* + H_3O^+$$

(slow step)

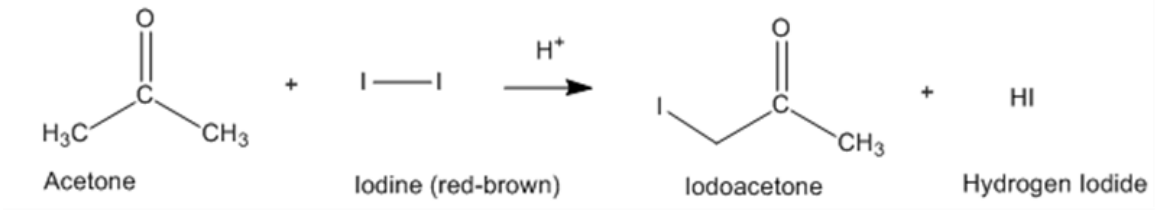
$$Rate_2 = k_2[AcH^+][H_2O]$$

$$Ac^* + I_2 \xrightarrow{k_3} AcI + HI$$

(fast step)

$$Rate_3 = k_3[Ac^*][I_2]$$

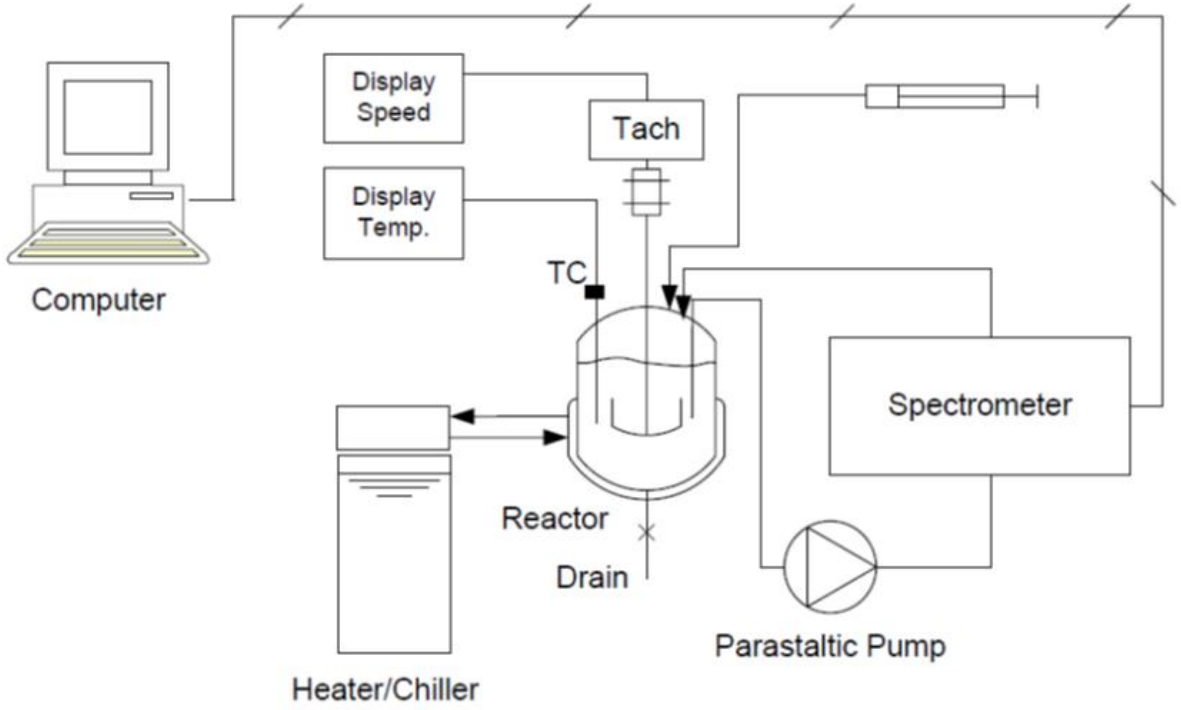
Rate Expression



$$r = k[acetone]^a[I_2]^b[H^+]^c$$

$$k = A\,exp\left(\frac{-E_a}{RT}\right)$$

Reactor Schematic



Equipment

Spectrophotometer (1), Sipper Pump (2), Reactor (3), Impeller (4), Circulating Water for Temperature Regulation (5), Sampling and Return Needles (6), Thermocouple (7), Impeller Motor (8), Syringe Port (9), Waste Beaker (10), Impeller Speed Control (11), Impeller Speed Readout (12), Thermocouple Readout (13), Water Bath (14), Computer Monitor (15), Keyboard (16), Computer Mouse (17), Spectrophotometer Dust Cover (18), Secondary Container (19)

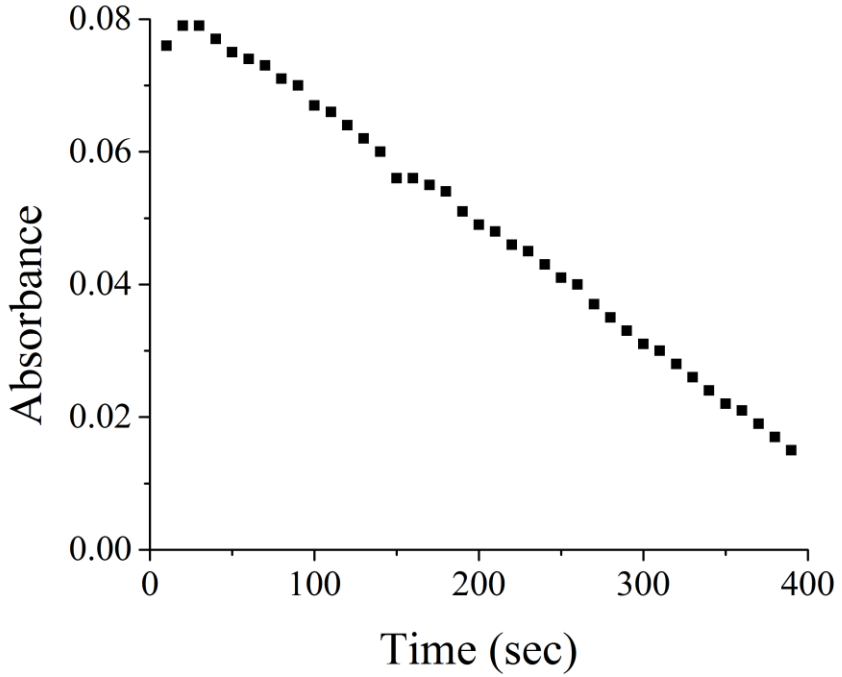
Iodination of Acetone

Safety

Standard Run

Standard Run		
	Concentration (mol/L)	Concentration SD (mol/L)
Acetone	1.98	0.002
Iodine	0.00162	4.9E-07
HCl	0.0199	5.6E-06
Water	45.42	0.01

Absorbance



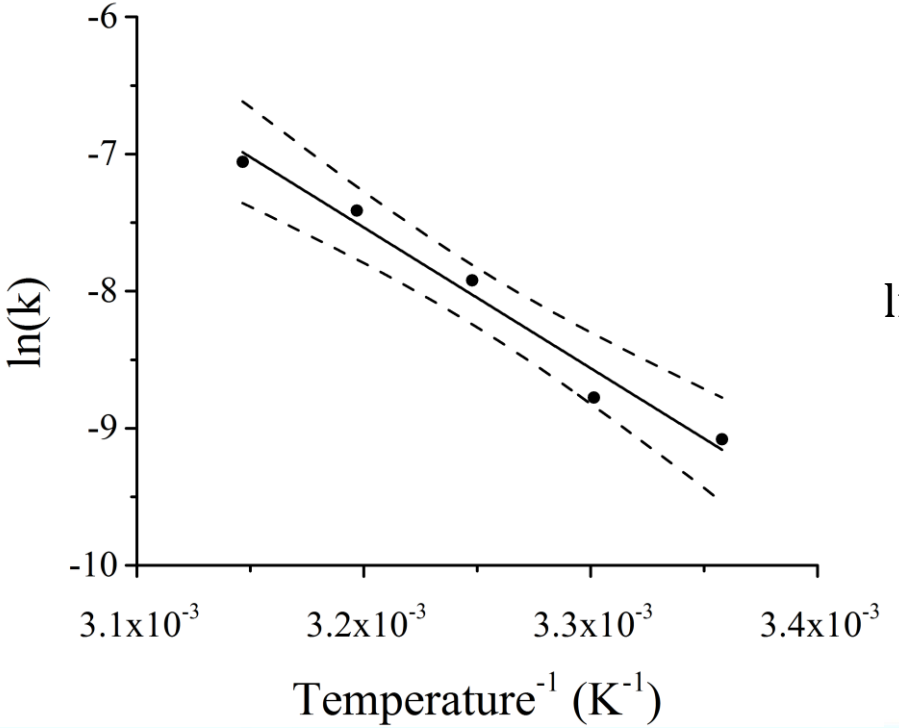
Initial Rates Method

$$r = k[Ac]^a[HCl]^b[Iodine]^c$$

$$r_0 = k[Ac]_0{}^a[HCl]_0{}^b[Iodine]_0{}^c$$

$$\ln r_0 = \ln k + a\ln[Ac]_0 + b\ln[HCl]_0 + c\ln[Iodine]_0$$

Temperature Dependence (Determine E_a and A)



$$\ln(k) = \frac{-E_a}{RT} + \ln(A)$$

A One-Parameter Function that Can Fit **Any** Data!

$$f_\alpha(x) = \sin^2\left(2^{x\tau}\, arcsin\left(\sqrt{\alpha}\right)\right)$$

arXiv:1904.12320

"Real numbers, data science and chaos: How to fit any dataset with a single parameter" by Laurent Boué

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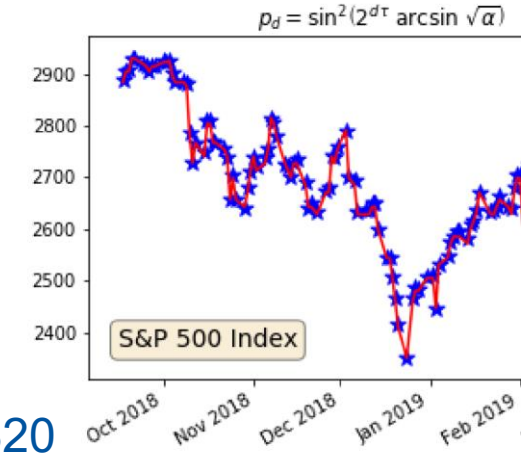

α=0.9186525008673170697061215177743819472103574383504939864690954692792184358812098296063847317394708021665491910117472119056871470143410398692872752461892785029829514157709738923288994766865216570536672099485574178884250989741343121…

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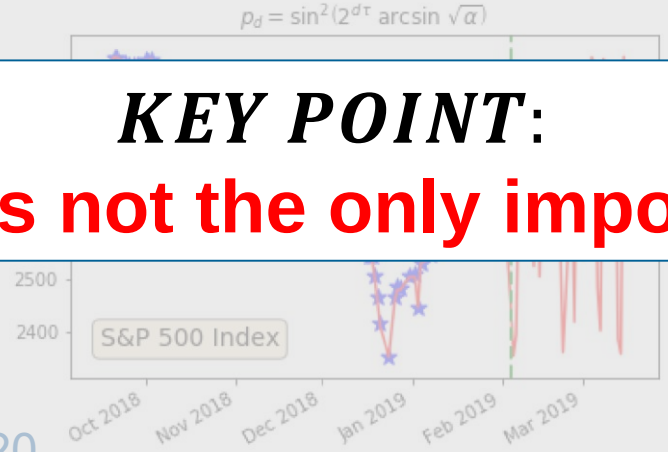

***KEY POINT*:**

Goodness of fit is not the only important metric!!!

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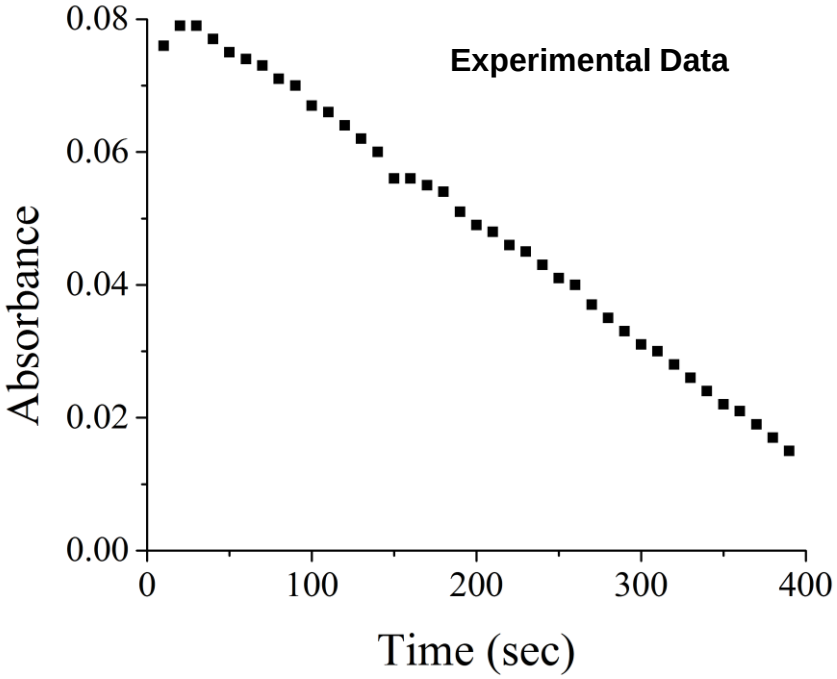
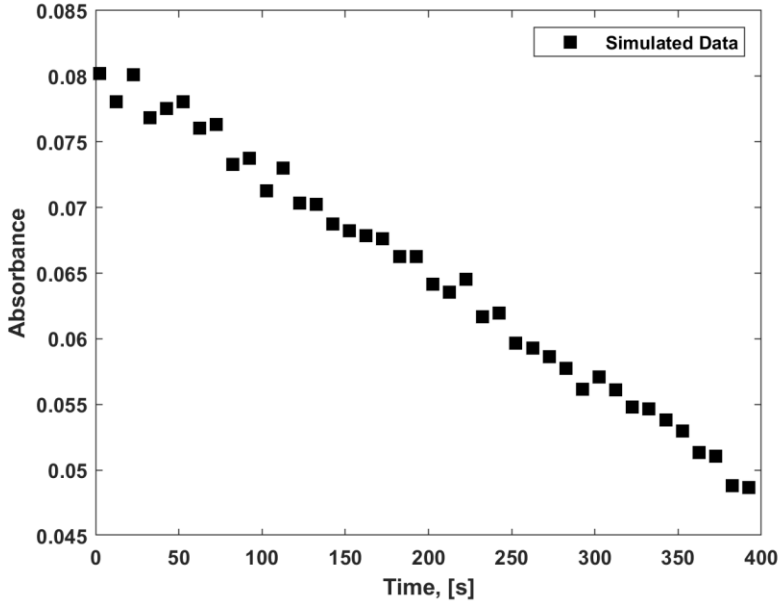
Experimental vs. Simulated Data

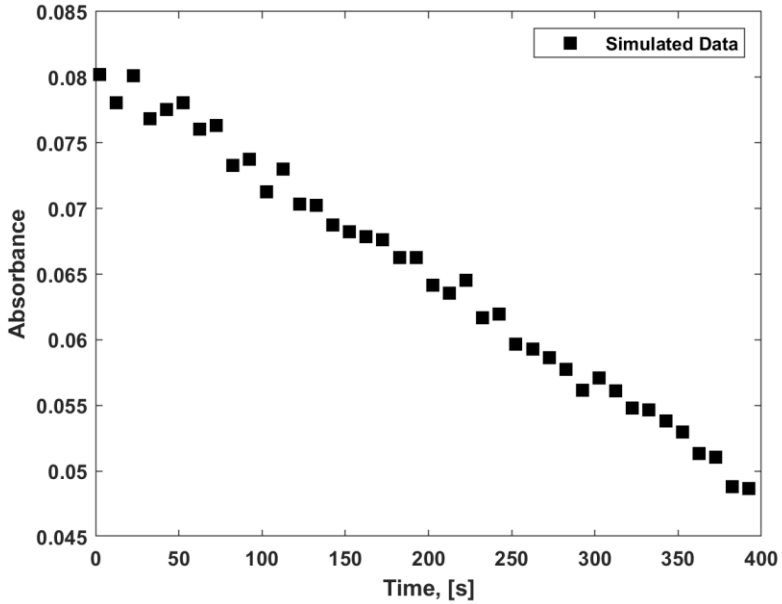




Similar but not identical conditions

Obtaining Simulated Data

- You will use a provided MATLAB P-Code function to simulate the experiment
- .p files are similar to .m files in use, but obscure source code (you won't be able to open up the files and see the key parameters – you will need to measure these yourself!)



Obtaining Simulated Data

- You will obtain simulated time-dependent 510 nm absorbance data by calling the AcetoneIodinationPCODE.p as function using the following syntax:

```
[t,Absorbance]=AcetoneIodinationPCODE(Temperature,[Acetone],[HCl],[I2],t_final);
```

Temperature – temperature of the reactor, in Kelvin.
[Acetone] – initial acetone concentration, in mol/L
[HCl] – initial hydrochloric acid concentration, in mol/L
[I2] – initial iodine concentration, in mol/L
t_final – duration of the experiment, in seconds (Please keep this reasonable – original labs were to be completed within 4 hours, using two parallel reactors)

t – time elapsed in seconds, from 0 to **t_final** in 5 second intervals
Absorbance – the absorbance at 510 nm. Use the provided calibration curve to determine the corresponding iodine concentration (**$Absorbance_{510nm}$** = 96.654***$[I_2]$** +0.0476) .

Phase 1 Key Objectives

- READ ALL HANDOUTS
- Watch the lab orientation video(s)
- Come up with plan for running **at most 15 simulated experiments** in total to determine the reaction orders for iodine, hydrochloric acid, and acetone, as well as the Arrhenius pre-exponential constant and activation energy. (This reduces the amount of available data, and puts a lower limit on your uncertainties)
- Schedule a short virtual meeting with the TA's for a Q&A about the physical lab and the simulated experiments – must be done prior to pre-lab meeting w/ prof. Orazov
- Google Doc will be sent to schedule pre-lab presentations (~ 15 min presentation + plus questions). Grading rubric will be available through CANVAS.

Questions / Points to consider for Pre-Lab meetings (not necessarily in this order)

- What is your objective for this lab cycle?
- How is your group organized? What are key tasks and who is responsible for each?
- What is your experimental plan? What are the most important data to gather? Why?
- What safety concerns are there, if any (were you to do the actual experiment)? What safety precautions would you use?
- What is your time-management plan for: (1) the day of the experiment; (2) preparing the initial report: (3) preparing the final report
- Are there any key tasks that can be performed prior to the actual experiment?
- What will actually be done with the data that are gathered?
- Others that anyone would like to discuss...?

Phase 2 Key Objectives

- Calculate **the reaction orders for iodine, hydrochloric acid, and acetone, as well as the Arrhenius pre-exponential constant and activation energy** using the simulated data and the initial rates method.

- An example / template Matlab script is provided (CANVAS) to allow you to solve for fitted parameters *and* statistical confidence intervals using non-linear regression. This can simply be modified (with a bit of thought) to deal with any of the equations you need to fit.

- **Be sure to include all sources of error in determining reported values of your experimental data and any parameters or key quantities that result from both the experimental data and subsequent analysis.**

Phase 3 Key Objectives

- **Specific instructions for Phase 3 will be made available during Phase 2**

- You will be asked to use the kinetic parameters determined in Phase 2 to infer the kinetic behavior of another reaction, occurring simultaneously with iodination of acetone. For this, you will need to construct a MATLAB or an Aspen model to simulate the reaction kinetics

- Using your kinetic expression, you will be asked to size a CSTR reactor to produce a desired amount of iodoacetone, given certain operational constraints.