Experiment 2: Kinetics of the Fading of Phenolphthalein

What lab skills will you practice?
- Using a spectrophotometer
- Collecting data in a timed experiment
- Pipetting and preparing solutions

What chemical concepts will you apply?
- Determining rate laws from concentration and time data — Silberberg: Chapter 14.4
- Examine experimental kinetic data — Chapter 14.3
- Dilutions — Silberberg: Chapter 3.5

What report writing skills will you use?
- Writing an Introduction
- Preparing data collection tables
- Presenting data in graphs and tables
- Interpreting data from a graph

Reminders:
- Complete the pre-lab quiz and flowchart at least **one hour before lab**
- Print & bring all Experiment 2 **and** Appendix H pages to lab
- Bring a "blue book" with data tables prepared

Objective
In this experiment, you will determine the rate law for the reaction of phenolphthalein in strongly basic solutions.

Introduction
Reactions of Phenolphthalein
Phenolphthalein (H_2Ph) is perhaps the most commonly used acid-base indicator (especially in undergraduate laboratories). In a mildly basic solution (pH 8-10), the weak acid phenolphthalein reacts with hydroxide ions to give a base form (Ph^{2-}) that has an intense pink color. This reaction can be written as:

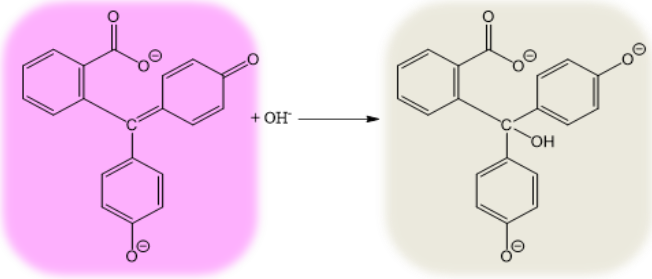
$$H_2Ph_{(aq)} + 2\,OH^- \rightarrow Ph^{2-} + 2\,H_2O_{(l)} \quad [1]$$

(colorless) (pink)

Reaction 1 is fast, and Ph^{2-} is intensely colored - so a small amount will produce a visible color change. These characteristics make the $H_2Ph \rightarrow Ph^{2-}$ reaction ideal for use as a color indicator in titrations. Reaction 1 is the dominant reaction in moderately basic conditions. If more OH^- is added, to a pH greater than 11 , the phenolphthalein can react further:

$$Ph^{2-}_{(aq)} + OH^-_{(aq)} \rightarrow PhOH^{3-}_{(aq)} \quad [2]$$

(pink) (colorless)



In Reaction 2 (shown symbolically and schematically above), the colored basic phenolphthalein is hydroxylated to form a colorless species. Reaction 2 is much slower than Reaction 1, and may take several minutes to reach completion. Since it is a slower reaction, it is possible to measure the reaction progress using typical laboratory equipment and techniques. By observing the disappearance of the pink colored Ph^{2-} species as a function of time, we can monitor the kinetics of Reaction 2. In order to follow the quantity of colored compound in solution, you will use a technique called **absorbance spectroscopy** (also known as colourimetry, since it is often used with colored compounds).

Absorbance and Color

Absorbance spectroscopy is a technique that relates the color intensity of a colored compound in solution (as measured by **absorbance**) to the concentration of that colored compound. Absorbance is the amount of light *of a specific wavelength* that is absorbed (i.e. does not pass through) by a sample. Most coloured species have a very strong absorbance at a characteristic wavelength.

Glass absorbs most UV (but not visible) wavelengths. So you can see out a window, but you don't get a sunburn indoors!

The absorbance of a solution depends directly on the concentration of the colored compound in that solution. You've probably seen this outside the lab – very concentrated solutions tend to have an intense color, while dilute solutions are more lightly colored. The relationship between absorbance and concentration is described by **Beer's Law** (given here for a phenolphthalein solution):

$$A = \epsilon \ell [Ph^{2-}] \quad [3]$$

Where: A is the measured absorbance – a unitless quantity.
ϵ is the *molar attenuation coefficient* (or "extinction coefficient" or "absorptivity") for the coloured compound (i.e. the base form of phenolphthalein)
ℓ is the length of the light path through the sample
$[Ph^{2-}]$ is the concentration (in M) of the colored compound (i.e. the base form of phenolphthalein)

As you can see, **absorbance is directly dependent on concentration** of the coloured compound. The combined quantity $\epsilon\ell$ depends on the compound and experimental setup you will use. For this laboratory (and Experiment 3, where you also use absorbance) you will determine this quantity experimentally by constructing a **calibration plot** in Part 1. By making a plot of *A* vs. $[Ph^{2-}]$, the slope will be $\epsilon\ell$ (fitting y=mx+b, and assuming A=0 when $[Ph^{2-}]$=0). You will use this value in Part 2 to determine phenolphthalein concentration from your absorbance measurements.

In order to have a known concentration of the coloured form of phenolphthalein, for the solutions used in making the calibration plot you will use a lower pH (less OH^-) so that Reaction 1 predominates, and all of the phenolphthalein in solution should be in the basic form.

Kinetics and Pseudo-Order Conditions

As you have seen in class and in your textbook (Silberberg sections 14-2 & 14.3), the rate of reaction can be related to the reactant concentrations through an expression called the **rate law** for a particular reaction. For the reaction of phenolphthalein in Reaction 2, the general form for the rate law would be:

$$Rate = k[Ph^{2-}]^p[OH^-]^n \quad [4]$$

Where: k is the **rate constant** for the reaction (temperature dependent)
p is the **order** with respect to phenolphthalein
n is the **order** with respect to hydroxide
We assume that p and n are whole numbers (most commonly 0, 1, or 2).

In this experiment, you will determine the values for *p, n,* and *k*. Solving a system with three unknown variables is possible, but is much easier if the experiments are designed so that only one variable changes at a time. Since *k* is already a constant value, we will control the reactant concentrations in order to manipulate the variables in the equation. There are many experimental designs that will accomplish this, but in the procedure of Part 2, you will approximate a constant hydroxide concentration by using a large excess of this reagent. Since the hydroxide and phenolphthalein react in a 1:1 ratio, if the hydroxide is 100 times more concentrated than the phenolphthalein, $[OH^-]$ changes only by 1% while the $[Ph^{2-}]$ is (nearly) completely consumed. In other words, $[OH^-]$ remains effectively constant, while the relative change in $[Ph^{2-}]$ is very large.

Using a small $[Ph^{2-}]$ works because phenolphthalein is very intensely colored, and can be detected at these low concentrations using absorbance.

If we make the (reasonable) assumption that [OH^-] is constant under the conditions described above, we can rewrite Equation [4] as:

$$Rate = k'[Ph^{2-}]^p \quad [5]$$

Where

$$k' = k[OH^-]^n \quad [6]$$

The constant *k'* is a **pseudo-order constant** – it behaves and can be treated as if it were a rate constant for a reaction of order *p*, but it is not a **true** rate constant because its value depends on the concentration of a reactant (in this case, hydroxide).

The value of *p* would typically be obtained by the *method of initial rates* (as described in Silberberg Section 14.3) – but then you would need to measure the reaction rate at a number of different initial reactant concentrations. In this experiment, you will take advantage of the **integrated rate laws** to allow you to use a simpler experimental procedure.

Integrated Rate Laws for Different Reaction Orders

The reaction of the fading of phenolphthalein is believed to be a first-order reaction with respect to phenolphthalein concentration [1]. To confirm (or refute!) this claim, you will compare the common whole-number orders for the reaction (i.e. *p* = 0, 1, or 2) and determine the one that most appropriately describes the observed behaviour.

If we take the rate law expression for the fading of phenolphthalein at each of these reaction orders (0th, 1st, and 2nd order) and integrate each form, we will obtain the following distinct integrated rate laws for each order:

p = 0:
$$[Ph^{2-}]_t = -k_0' \cdot t + [Ph^{2-}]_0 \quad [7]$$

p = 1:
$$\ln[Ph^{2-}]_t = -k_1' \cdot t + \ln[Ph^{2-}]_0 \quad [8]$$

p = 2:
$$\frac{1}{[Ph^{2-}]_t} = k_2' \cdot t + \frac{1}{[Ph^{2-}]_0} \quad [9]$$

In Equations 7-9, the subscript on *k'* indicates the order of the reaction described. Note that all of these integrated rate laws are presented as linearized equations of the form *y = mx+b*, with time (*t*) as the controlled variable, and the pseudo-order constant (*k'*) related to the slope.

Since your reaction can only have one true order, **only one of these equations will correctly describe your experimental data**. Which rate law best represents the experimental data is conveniently determined by plotting each of Equations [7], [8], and [9] ([Ph^{2-}] vs. *t*, ln[Ph^{2-}] vs. *t*, and 1/[Ph^{2-}] vs. t, respectively). The integrated rate laws are expected to show a linear relation *if* the equation correctly describes the data – if you are attempting to describe 0th order data with a 0th order plot ([Ph^{2-}] vs. *t*), for example. If the true reaction order *does not* match the integrated rate law being plotted – if you have plotted data from a 0th order reaction on a 1st order plot (ln[Ph^{2-}] vs. *t*), for example – the plot will not be linear.

For both of the data sets you will generate during lab, you will determine whether or not the reaction is pseudo-first-order (as believed by Barnes and LaMer [1]) by plotting the data according to 0th, 1st, and 2nd order integrated rate laws and determining which plot is most linear. You will also determine *k'* from the slope of the linear plot.

Equilibrium Correction

The fading of phenolphthalein is an equilibrium reaction with a K_{eq} that is large, but not infinite. At each stage of the reaction, there is a small but measurable "back reaction" occurring, and even after letting the reaction sit for a very long time, some phenolphthalein will remain in the coloured form. To account for this 'unreacted' phenolphthalein, you will make a measurement at "infinite time" ($[Ph^{2-}]_\infty$, really taken after about 20 minutes) and use it to correct all of the $[Ph^{2-}]$ values you obtain by absorbance measurements:

$$[Ph^{2-}]_{t,(corrected)} = [Ph^{2-}]_{t,(measured)} - [Ph^{2-}]_\infty \quad [10]$$

$$[Ph^{2-}]_{0,(corrected)} = [Ph^{2-}]_{0,(true)} - [Ph^{2-}]_\infty \quad [11]$$

Important! You will use collaborative class data to determine *n* and *k* for the reaction. After lab, you will need to determine your two values for *p* and *k'*, and send them to your TA by **email before 5 PM the day after your lab.** Your TA will then average the data and distribute it to the class so that you may finish the rest of your report.

References

1. Barnes, M.D.; LaMer, V.K.; Kinetics and Equilibria of the Carbinol Formation of Phenolphthalein. *J. Am. Chem. Soc.* [online] **1942**, *64*, 2312 – 2316.

Preparing for Lab

Before coming to lab, make sure you have:

- Read Experiment 2 and Appendix H (print and bring both to lab)
- Completed the online pre-lab quiz – *at least one hour before lab*
- Completed the procedure flow chart on Page 11 of this experiment
- Obtained a "blue book" lab report notebook and prepared tables for entering your raw data as described below
- Prepared yourself by wearing appropriate clothing and bringing a lab coat.

See information on D2L and in the Introduction chapter for details on 'blue books' and appropriate lab attire.

Tables for Raw Data

On the **last two pages** of your "blue book", prepare **neat, labelled tables** to use for entering your raw data during lab. Remember to include units and titles for all tables.

Part 1: Calibration

Provide space to record the precise concentrations of all reagents used.

Prepare one table with the following headings:

Sample #	$[Ph^{2-}]$ (M)	A

You will need space for 5 measurements.

Part 2: Kinetic Runs

You will be assigned **two** of the Kinetic runs from Table 2 by your TA. For **each run**, prepare a table with the following headings:

Reaction Time (s)	Time mm:ss	A	$[Ph^{2-}]_{measured}$ (M)	$[Ph^{2-}]_{corrected}$ (M)	$\ln[Ph^{2-}]$	$\frac{1}{[Ph^{2-}]}$ (M^{-1})	$[OH^-]$ (M)

You will need space for 12 measurements in each run.

The stopwatches in lab display time as mm:ss so be prepared to convert between seconds and minutes.

Experimental Procedure

For this experiment you will work in pairs.
Each partner must submit an individually written lab report.

Before beginning, sign out a *Supplementary Equipment Tray* from your TA, containing:

- 1 digital stopwatch
- 1 digital thermometer
- 3 13×100 mm spectrophotometer cuvettes
- 5 18×150 mm test tubes with rubber stopper

By 'signing out' this equipment, you are responsible for it (similar to the equipment in your drawer) until you and your TA sign it back in at the end of lab.

Part 1: Calibration

You will build a calibration curve by measuring the absorbance of a series of solutions of known $[Ph^{2-}]$ concentration, and plotting the absorbance vs. concentration. You will make this plot *in lab*, since you cannot complete the lab report if there is a significant error in Part 1.

1. **Turn on the spectrophotometer** to let it warm up.
2. **Prepare your solutions**. You will prepare 5 solutions according to the volumes in Table 1 below. For each solution:
   - ↪ Dispense 1.00 mL of phenolphthalein from the bottle on the rear bench into a 100 mL graduated cylinder and add two drops of 0.75 M NaOH.
   - ↪ Add 0.75 M NaCl to the cylinder until the desired total volume is reached (*do not* remove solution from the cylinder if you overshoot).
   - ↪ Mix thoroughly by pouring the solution back and forth several times between the graduated cylinder and a clean, dry beaker.

Do not change the dispenser settings – it automatically delivers 1.00 mL.

NaCl is used to dilute the solution, since absorbance is affected by *ionic strength* – the total concentration of ions in solution.

TABLE 1: COMPOSITION OF CALIBRATION MIXTURES

Sample #	3×10^{-4} M Ph^{2-} (mL)	0.75 M NaCl (mL)	Total Volume (mL)
1	1.00	99.0	100.0
2	1.00	49.0	50.0
3	1.00	34.0	35.0
4	1.00	24.0	25.0
5	1.00	19.0	20.0

3. **Measure the absorbance**. Refer to **Appendix H** and your TA's demo for instructions on using the spectrophotometer.
   - ↪ In one of the cuvettes in your supplementary equipment kit, prepare your blank. Rinse the cuvette with 0.75 M NaCl, then fill it halfway with the same solution. Use this cuvette as your blank.
   - ↪ Use the other cuvette to measure the absorbance of Solution 1. Rinse the cuvette with a small amount of Solution 1, then fill it about ½ full with Solution 1. Measure the absorbance and record it in your blue book.
   - ↪ Discard the solution from the cuvette, and repeat the measurement for Solutions 2-5.

Make all absorbance measurements (Parts 1 & 2) at **545 nm.**

4. **Plot your data.** Using the *full sheet* of graph paper in your blue book, plot the data from Part 1 immediately after finishing. You may use pencil or erasable pen *for plotting this graph only*. Draw a line of best fit through your data, determine the slope (see Calculations section) and have your TA review and initial your graph **before moving on to Part 2.**

Your plot should have a y-intercept of 0. (*why?)*

Part 2: Kinetic Runs

Each pair of students will do **two** of the kinetic runs described in Table 2, as assigned by your TA during lab. Repeat the steps below for **each run** that you are assigned.

Timing is **very important** for these measurements. Make sure you record the exact time you make each measurement in your data table.

Once you're assigned your runs, fill in the "time" column of your data table so you know when to measure.

TABLE 2: COMPOSITION OF REACTION MIXTURES

Run	3×10^{-4} M **Ph^{2-}** (mL)	0.75 M **NaCl** (mL)	0.75 M **NaOH** (mL)	Total Reaction Time (s)	Measurement Interval (s)
1	1.00	6.0	3.0	500	50
2	1.00	5.0	4.0	400	40
3	1.00	4.0	5.0	300	30
4	1.00	3.0	6.0	250	25
5	1.00	2.0	7.0	200	20
6	1.00	1.0	8.0	180	18

1. **Prepare your solution**. Use the volumes assigned in Table 2 for the run your TA has assigned. Start with the first (longest) run listed.
   - ↪ Use graduated pipets to deliver the required amounts of 0.75 M NaOH and NaCl into a clean, dry test tube.
   - ↪ At the rear bench, add 1.00 mL Ph^{2-} to the test tube, and **activate the stopwatch at the same time**. All reaction times are measured starting from the instant of Ph^{2-} addition. Complete the next steps quickly so you do not miss your first time for measurement.
   - ↪ Mix the solution by gently swirling. Hold the cuvette by the rim.
   - ↪ Use a small amount (1-2 mL) of the solution to rinse a clean cuvette, then fill the cuvette half-full.
2. **Measure the absorbance**.
   - ↪ Place the cuvette in the spectrophotometer. **Use the same instrument** that you used in Part 1 or your $\epsilon\ell$ value may be invalid. You should not need to re-blank the spectrophotometer.
   - ↪ Wait until the end of the first time interval for your run (as specified in Table 2). While you wait, record your initial temperature reading (using your remaining solution in the test tube).
   - ↪ At the time interval, record the absorbance and the exact time of measurement (if different from the intended time) in your blue book.
   - ↪ Leave the cuvette in the instrument while you wait until the next measurement interval, then record absorbance again. Repeat for 11 measurements total – until the "total time" for your run has been reached.
   - ↪ After 11 measurements, move your cuvette to any empty spot in the spectrophotometer, let the reaction mixture rest for **at least 20 minutes**, and take a final measurement of absorbance and temperature. This is your "infinite time" measurement.
   - ↪ While you are waiting for the 20 minutes to elapse, repeat the steps of Part 2 for the second (faster) run assigned by your TA. Use your second cuvette for these measurements – do not dump the first one.

It helps if one partner handles solutions while the other runs the stopwatch.

If you miss a time-point, skip it or take a measurement as soon as possible and record the actual reaction time at measurement (rather than the intended time).

Do not put the thermometer into the cuvette. Use a beaker or test tube.

After both runs have been completed **and** both "infinite time" points have been recorded, dispose of all solutions properly, clean all your glassware and tidy your bench. Return all supplementary equipment to your TA and sign for its return.

Calculations

Graphs for Part 2 may be done on a computer using Excel or similar software, if you like. The calibration curve for Part 1 is completed during lab. Remember to show sample calculations for **each** type of calculation in Part 1 and 2 in your blue book, as part of your lab report. *You do not need to re-do this graph at home*.

Calibration (*done during lab*)

Make a plot of A vs. [Ph^{2-}] using the graph paper included in your blue book, and use a ruler to hand-draw a line of best fit through your data. Your graph should:

- Use as much of the plot area as possible – at least half of the page by length and by width. Choose your axis scaling appropriately.
- Have axis labels and a title.
- Include your blank (A=0, [Ph^{2-}]=0) as a data point.

It is possible that none of your data points lie exactly on your line of best fit. Calculate slope from points that are **actually on** the best-fit line. (they do not have to be measured data points)

From your line of best fit, determine the slope of your plot (and so $\varepsilon\ell$). Mark the points that you used for the slope calculation. Label the slope **on your plot.** You can show your sample calculation on the plot or with your other sample calculations, as long as it is clearly labelled.

Kinetic Runs 1 (*done at home, **before 5PM** the day after lab*)

*Start with analyzing your **faster (shorter)** run:*

Use the $\varepsilon\ell$ value you found during lab to determine the $[Ph^{2-}]$ from each absorbance measurement. Equation [3] will help you.

You can complete these calculations on the computer (attach a printout of the table) – but you still need to show a sample calculation for each, handwritten in your blue book.

Once you have found $[Ph^{2-}]$, determine $\ln[Ph^{2-}]$ and $1/[Ph^{2-}]$ for each measurement point.

Prepare **three plots**:

- $[Ph^{2-}]$ vs. t
- $\ln[Ph^{2-}]$ vs t
- $1/[Ph^{2-}]$ vs t

You can plot these by hand or by computer. All plots should follow these guidelines:

- Make your graph **large** – it should take up as much of one letter-size page as possible. You can staple as many pages as needed into your blue book.
- Have **dense gridlines** – if you are plotting by hand, use metric graph paper with 1-mm gridlines (like in your blue book). If you are plotting on a computer, aim for a similar line density when your plot is printed (it may look odd on-screen).
- **Hand-draw** your line or curve of best fit, whether or not you plot your data points on the computer.

Remember, readings from your graph can only be as precise as your gridlines!

Determine which of the three plots is **most linear**. By comparing with Equations 7-9, determine the experimental order of reaction with respect to $[Ph^{2-}]$.

If "most linear" is hard to determine, compare *y*-intercepts to see which is closest to the one predicted by Equation 7, 8 or 9.

From the "most linear" plot, determine the slope of the line of best fit, and from this slope, *k'* for this run.

*For your **slower run**:*

Determine the $[Ph^{2-}]$ from the absorbance measurements.

Based on the order you determined from your faster run, make **one** plot from your slow-run data that will produce a straight line. (i.e. if you determined the reaction to be zero-order earlier, you only need to plot $[Ph^{2-}]$ vs t here)

Draw a line of best fit through your slow-run data, and use the slope to determine *k'* for your second run.

You now have two values for *k'* and one *p* value. Email them to your TA **before 5 PM on the day after your lab** (don't forget to note which run each value corresponds to).

Failure to submit your data on time will result in a **1-point deduction** from your lab report, since late submission prevents everyone from completing their lab reports.

Kinetic Runs 2 (*after receiving aggregate data from your TA*)

Your TA will email you the complete list of experimental pseudo-rate constants (*k'*) for your lab section within 2 days after your lab. From this data, you can determine *n* (the order of reaction with respect to hydroxide) and *k*, the true rate constant.

Equation [6] can be converted into a linear form:

$$\ln k' = n \cdot \ln[OH^-] + \ln k \qquad [10]$$

From a plot of ln*k'* vs ln[OH^-], you can find the value of *n* (slope) and ln*k* (-intercept), and from there, the value of *k* itself.

This plot can be done by hand or on the computer, but should follow the same guidelines given above.

Lab Report

You will have **one week** to complete your formal lab report. Your report must be handwritten in a blue lab notebook (with the exception of graphs and tables, as noted above – these can be hand-drawn in pencil or plotted by computer and stapled into the book).

Submit your completed report to your lab section's dropbox outside SA 116. If your report Is late, hand it in to the *Late Report Box* outside SA 116, and notify your TA and the Lab Coordinator when you have submitted it. Marks will be deducted for late reports: 1 mark per half-day and 1 mark per weekend day.

Marks Breakdown

The general marking scheme for the lab report is as follows:

Criteria	Marks
Introduction Objective is clear, techniques and analyses are described	2
Procedure Statement of procedure, including additions or changes.	1
Data Data tables copied neatly into Results section and formatted appropriately	1
Data: Plots Graphs for Parts 1 and 2 have correct formatting, display relevant information, and any values used are clearly labelled	3
Data: Results & Calculations Sample calculations are shown for all steps, intermediate values (e.g. [Ph^{2-}], ln[Ph^{2-}]) tabulated , final results clearly shown	2
Discussion Discussion questions (given below) answered clearly and correctly	5
Conclusion & References Objectives, results, and their reliability are summarized. Reference list is consistently formatted, includes all required sources, and makes use of in-text citations.	2

Specific Guidelines

A sample introduction section (for Experiment 1) is posted on D2L to help you write your introduction for this lab. Use this sample and the types of questions asked in Experiment 1 to guide your writing for Experiment 2.

Refer to the lab manual Introduction chapter for details on formal reports.

Since this is your first time writing an introduction for Chem 209, you will be given the opportunity to rewrite the Introduction section (after it is graded and returned) in order to improve your writing skills and the mark received on this section.

To submit your Introduction for re-grading:

- Attach your new introduction to your original lab report *including* the gradesheet.
- Submit this package to your lab section's dropbox **within 24 hours** of the lab period where your reports were returned.
- A maximum of **half of the grades originally 'lost'** on your Introduction section may be returned, based on your TA's assessment, in increments of 0.5 points.

Discussion Questions

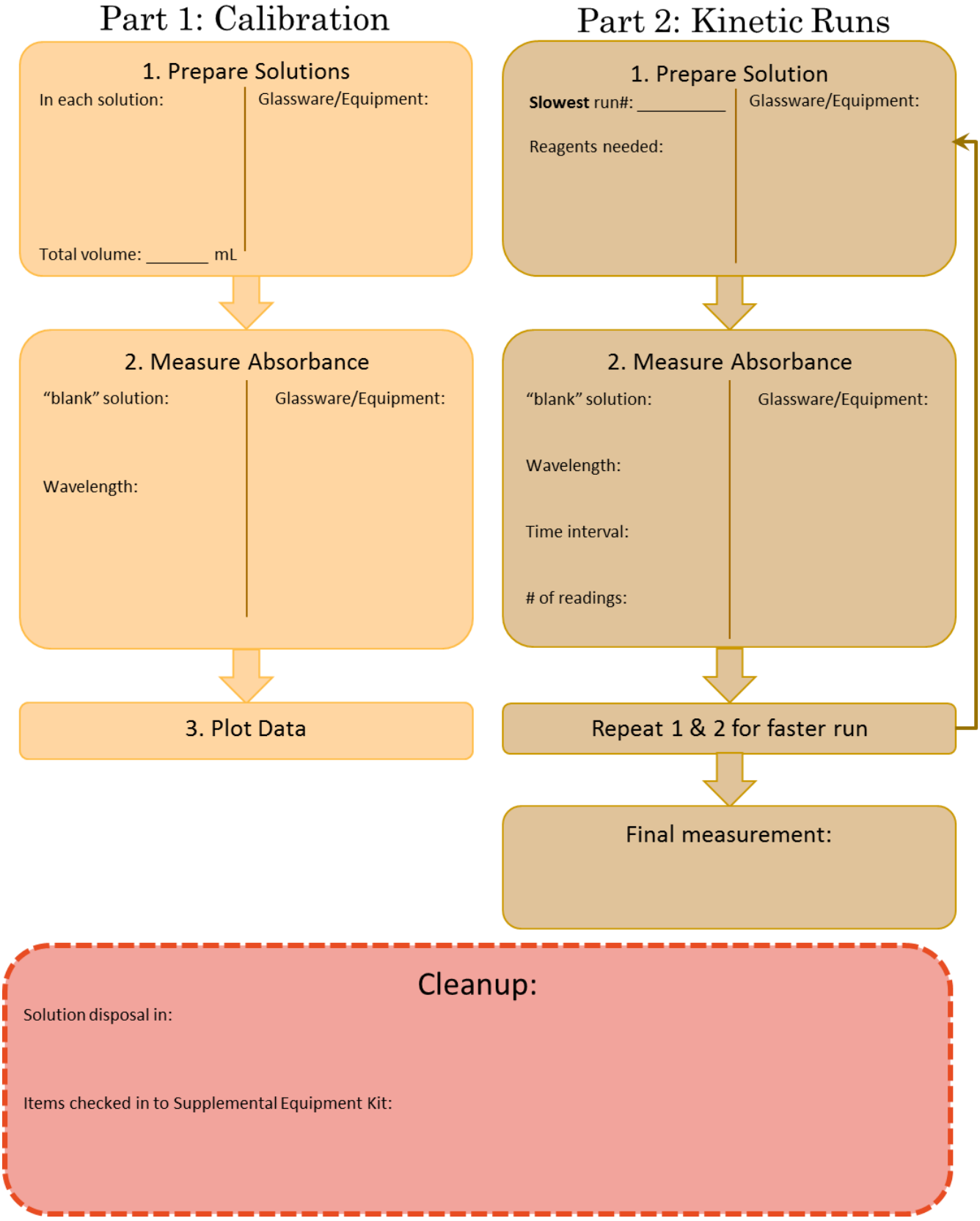
In lieu of a long-form Discussion section, for Experiment 2 only, you should answer the following discussion questions in your report:

1. *State your findings:* What is the overall rate law (including all constants) for the fading of phenolphthalein?
2. *Significance of your results:* If this reaction was carried out at 10°C instead of room temperature, how would the values of the order of reaction with respect to phenolphthalein (*p*) and the rate constant (*k*) be affected?
3. *Accuracy of your results:* Compare your experimentally determined order and rate constant to that found in literature. Justify your comments numerically.

   Suggested source: Nicholson, L; Kinetics of the Fading of Phenolphthalein in Alkaline Solution; *J. Chem. Ed.* **1989,** 66 (9), p. 725-726 – also linked on D2L.
4. *Precision of your results*: Comment on the precision and reproducibility of your results, justifying your comments numerically where possible.
5. *Sources of Error/Uncertainty*: Describe any errors or assumptions made in this experiment, and their potential effect on your final results.

Procedure Flow Chart – Pre-Lab Assignment

Fill in the flowchart below with all relevant experimental details (use the flowchart in Experiment 1 as a guide):



Attach this flowchart to the inside cover of your lab report.