Kinetics of Dye Fading

Technology and Graphical Analysis

Introduction

Phenolphthalein is a dye that is used as an acid–base indicator. It is colorless in acidic or neutral solutions and turns bright red-violet as the solution becomes basic. In strongly basic solutions, the red color slowly fades and the solution again becomes colorless. The kinetics of this "fading" reaction can be analyzed by measuring the intensity of the red color and graphing the results.

Concepts

- Kinetics
- Reaction rate
- Order of reaction
- Colorimetry

Background

Phenolphthalein is a large organic molecule. In solutions where the pH < 8, it has the structure shown in Figure 1, which is colorless. As the solution becomes basic and the pH increases, the phenolphthalein molecule (abbreviated H_2P) loses two hydrogen ions to form the red-violet dianion (abbreviated P^{2-}) shown in Figure 2.

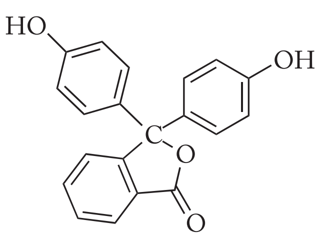


Figure 1. H_2P is colorless.

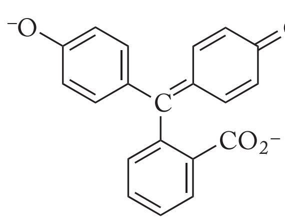


Figure 2. P^{2-} is red.

The colorless-to-red transition of H_2P to P^{2-} (Equation 1) is very rapid, and the red color develops instantly when the pH reaches the indicated range. Gradually, however, if the concentration of hydroxide ions remains high, the red P^{2-} dianion will combine with hydroxide ions to form a third species, POH^{3-} (Equation 2), which is also colorless. The rate of this second reaction is much slower than the first and depends on the concentration of phenolphthalein and hydroxide ions.

$$\underset{\text{Colorless}}{H_2P} \xrightarrow{\text{fast}} \underset{\text{Red}}{P^{2-}} + 2H^+ \qquad \textit{Equation 1}$$

$$\underset{\text{Red}}{P^{2-}} + OH^- \xrightarrow{\text{slow}} \underset{\text{Colorless}}{POH^{3-}} \qquad \textit{Equation 2}$$

The kinetics of the "fading" reaction can be followed by measuring the concentration of P^{2-} versus time and graphing the results. Figure 3 illustrates how the concentration of a reactant decreases with time over the course of a reaction. Notice that the graph of concentration versus time is a curved line, not straight. The curve levels off as it approaches the *x*-axis. This means that the reaction slows down as the reactant concentration decreases.

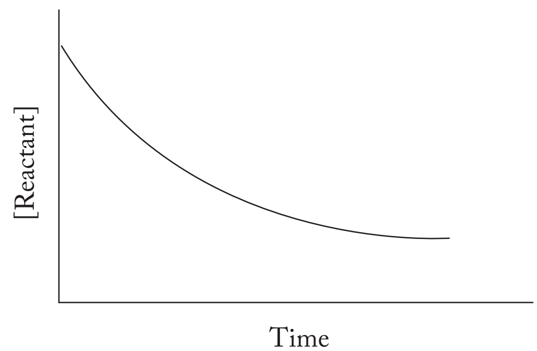


Figure 3.

Exactly how much the rate decreases as the reactant concentration decreases depends on the rate law for the reaction. In the case of the reaction of P^{2-} with OH^- ions, the rate law has the general form:

$$\text{Rate} = k[P^{2-}]^n[OH^-]^m \qquad \textit{Equation 3}$$

The exponents *n* and *m* are defined as the order of reaction for each reactant, and *k* is the rate constant for the reaction at a particular temperature. The values of the exponents *n* and *m* must be determined by experiment. If the reaction is carried out under conditions in which the concentration of OH^- does not change—by using a large excess of hydroxide ions—the rate law will reduce to the form:

$$\text{Rate} = k'[P^{2-}]^n \qquad \textit{Equation 4}$$

where k' is a new "pseudo" rate constant incorporating both the "true" rate constant *k* and the experimentally constant $[OH^-]^m$ term.

Mathematical treatment of the equations for the reaction rate and the rate law predicts the following outcomes:

- If the fading reaction is first order in $[P^{2-}]$ (i.e., $n = 1$), a graph of the natural log (ln) of $[P^{2-}]$ versus time will give a straight line. The slope of the line is equal to $-k'$.
- If the fading reaction is second order in $[P^{2-}]$ (i.e., $n = 2$), a graph of $1/[P^{2-}]$ versus time will give a straight line. The slope of the line is equal to $-k'$.

Experiment Overview

The purpose of this technology-based experiment is to use colorimetry and graphical analysis to determine how the rate of the phenolphthalein fading reaction depends on the concentration of the dye. A colorimeter is a special instrument that measures the absorbance of light. A known amount of phenolphthalein will be added to a large excess of sodium hydroxide, and the absorbance (Abs) of the red solution will be measured at specific time intervals. Absorbance is directly proportional to concentration, so a graph of absorbance versus time has the same characteristics as a graph of concentration versus time (Figure 3). Graphing the absorbance data—ln(Abs) versus time and 1/Abs versus time—should reveal whether the fading reaction is first or second order in phenolphthalein.

Pre-Lab Questions

Crystal violet (CV) is another indicator dye that combines with hydroxide ions to form a colorless product (Equation 5). Crystal violet was added to 0.10 M NaOH, and the solution immediately turned violet. After 10 minutes, the color faded and the solution was almost colorless. The absorbance measurements were recorded in Table 1.

$$CV^{+} + OH^{-} \rightarrow CVOH \qquad \textit{Equation 5}$$

Violet   Colorless

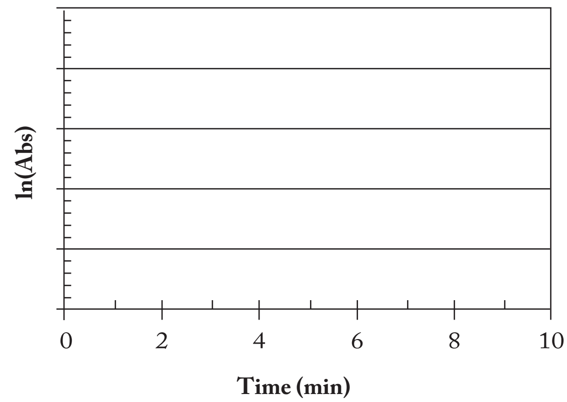
Table 1.

Reaction Time	Absorbance	ln(Abs)	1/Abs
1 min	0.366		
2 min	0.251		
3 min	0.176		
4 min	0.124		
5 min	0.089		
6 min	0.065		
7 min	0.048		
8 min	0.037		
9 min	0.029		
10 min	0.023		

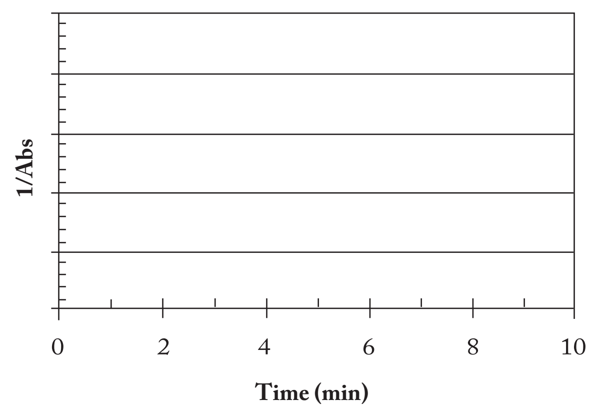
1. Calculate the values of ln(Abs) and 1/Abs for each absorbance measurement to complete Table 1.

2. Use the following graphs to plot ln(Abs) versus time (Graph 1) and 1/Abs versus time (Graph 2).

Graph 1



Graph 2



3. Which graph more closely approximates a straight line? Is the reaction of crystal violet with hydroxide ions (Equation 5) first or second order in crystal violet?

Materials

Phenolphthalein solution, 1 drop*

Sodium hydroxide, NaOH, 0.2 M, 5 mL

Water, distilled

Colorimeter sensor or spectrophotometer

Computer or calculator for data collection

Computer interface system (LabPro)

Cuvette with lid, 1

Data collection software (LoggerPro)

Thermometer

Tissues or lens paper, lint-free

Wash bottle

*The concentration of phenolphthalein is approximately 6×10^{-3} M.

Safety Precautions

Sodium hydroxide is a corrosive liquid. Avoid contact with eyes and skin, and clean up all spills immediately. Phenolphthalein is moderately toxic by ingestion. Wear chemical splash goggles and chemical-resistant gloves and apron. Wash hands thoroughly with soap and water before leaving the laboratory.

Procedure

Read the entire procedure before beginning the experiment.

1. Handle the cuvette by its ribbed sides or its top to avoid getting fingerprints on the surface.

2. Connect the interface system to the computer or calculator, and plug the colorimeter sensor into the interface.

3. Select Setup and Sensors from the main screen and choose "Colorimeter."

   Note: Many newer sensors have an automatic calibration feature that automatically readies the colorimeter before use. If the sensor has the autocalibration feature, set the wavelength on the colorimeter to 565 nm (green), press the autocalibration key, and proceed to step 9. If the sensor does not have the autocalibration feature, follow steps 4–8 to calibrate the colorimeter for 100% transmission (0 absorbance) with a "blank" cuvette containing only the sodium hydroxide solution.

4. Select Calibrate and Perform Now from the Experiment menu on the main screen.

5. Obtain a clean and dry cuvette, and fill it about ⅔ full with 0.20 M sodium hydroxide. Wipe the cuvette with a lint-free tissue, then place the cuvette in the colorimeter compartment.

6. Set the wavelength knob on the colorimeter to 0%T—the onscreen box should read zero. Press Keep when the voltage is steady.

7. Turn the wavelength knob on the colorimeter to 565 nm (green)—the onscreen box should read 100. Press Keep when the voltage is steady.

8. Return to the main screen and set up a live readout and data table that will record absorbance as a function of time.

9. Select Setup followed by Data Collection. Click on Selected Events to set the computer for manual sampling.

10. Remove the "blank" cuvette from the colorimeter compartment. Measure and record the initial temperature of the sodium hydroxide solution.

11. Add one drop of phenolphthalein to the cuvette, and immediately press Collect on the main screen to begin measuring time. This ensures that the absorbance versus time measurements will accurately reflect the time of reaction from the time of mixing.

12. Place the lid on the cuvette, and carefully invert the cuvette several times to mix the solution.

13. Place the cuvette in the colorimeter compartment. When one or two minutes have elapsed from the time of mixing, press Keep on the main screen to automatically record the absorbance.

14. Continue making absorbance measurements at regular time intervals (at least every two minutes). Press Keep on the main screen to automatically record the absorbance at each desired time.

15. When 16 minutes have elapsed from the time of mixing, press Stop on the main screen to end the data collection process.

16. If possible, save the data on the computer or calculator and obtain a printout of the absorbance versus time data table and graph. Otherwise, record the absorbance and time measurements in the data table.

17. Remove the cuvette from the colorimeter compartment. Measure and record the final temperature of the dye solution.

18. Rinse the cuvette several times with distilled water, and allow it to air dry.

19. (Optional) Calculations and graphical analysis may be done on the computer or calculator using either the data collection software that accompanies the technology interface system or a conventional spreadsheet program, such as Excel. See the *Post-Lab Questions* section.

Name ______________________________

Class/Lab Period ______________________________

Kinetics of Dye Fading

Data Table

Initial Temperature		Final Temperature	
Time	**Absorbance***	**ln(Abs)***	**1/Abs***

*Computer-generated tables and graphs may be substituted for the data table and *Post-Lab Questions* 1–3.

Post-Lab Questions

Use a separate sheet of paper to answer the following questions.

1. Plot or obtain a graph of absorbance versus time. Does the "rate of fading" of phenolphthalein depend on the concentration of the dye? Explain.
2. Calculate the values of ln(Abs) and 1/Abs for each absorbance measurement, and enter the results in the table. *Note:* This may be done directly with the data saved in the technology program or separately using a calculator or spreadsheet program.
3. Plot or obtain graphs of both ln(Abs) versus time and of 1/Abs versus time (see the *Background* section and the *Pre-Lab Questions*).
4. Which graph more closely approximates a straight line?
5. Is the reaction of phenolphthalein with hydroxide ions (Equation 2) first or second order in phenolphthalein?
6. Did the temperature of the solution change over the course of the reaction? What effect, if any, would the temperature change have on the results of the experiment?
7. The concentration of sodium hydroxide is assumed to be constant throughout the reaction and is thus included in the "reduced" rate law expression (see Equation 4 in the *Background* section). Is this assumption valid? Prove it.

Teacher's Notes

Kinetics of Dye Fading

Master Materials List

(for 30 students working in pairs)

Phenolphthalein, dilute solution, 2 mL

Sodium hydroxide, NaOH, 0.2 M, 75 mL

Water, distilled

Colorimeter sensors, 15

Computers or calculators for data collection, 15

Computer interface system (LabPro), 15

Cuvettes with lids, 15

Data collection software (LoggerPro)

Thermometers, 15

Tissues or lens paper, lint-free

Wash bottles, 15

Preparation of Solutions

- Sodium Hydroxide, 0.20 M: Carefully add 0.80 g of sodium hydroxide to 50 mL of distilled or deionized water and stir to dissolve. Dilute to 100 mL with water.

- Phenolphthalein Dilute Solution: Prepare or obtain a standard 1% solution of phenolphthalein in ethyl alcohol (Flinn Catalog No. P0020). Dilute this standard phenolphthalein solution by a factor of five with ethyl alcohol—5 mL of standard 1% solution and 20 mL of ethyl alcohol, for example. *Note:* The final concentration of phenolphthalein is about 6×10^{-3} M.

Safety Precautions

Sodium hydroxide is a corrosive liquid. Avoid contact with eyes and skin, and clean up all spills immediately. Phenolphthalein is moderately toxic by ingestion. Wear chemical splash goggles and chemical-resistant gloves and apron. Wash hands thoroughly with soap and water before leaving the laboratory. Please consult current Safety Data Sheets for additional safety, handling and disposal information.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. The dye solutions may be flushed down the drain with excess water according to Flinn Suggested Disposal Method #26b.

Lab Hints

- The actual amount of lab time needed for this experiment is about 30–40 minutes. An additional 20–30 minutes of computer time will be required if the calculations and graphing are done using the data collection software that accompanies the technology interface system. Alternatively, the calculations and graphing may be assigned as homework. The difference between the ln(Abs) and 1/Abs graphs is very distinct even in less precise hand-drawn graphs. The ln(Abs) versus time graph gives an excellent straight-line fit whereas the 1/Abs versus time graph is curved.

- It is important to wash and rinse the plastic cuvettes immediately after the timed run is over. Sodium hydroxide will react with or be absorbed by the plastic if left in the cuvette too long.

- Although this experiment serves a useful role in helping meet technology goals for the curriculum, it is very challenging conceptually. Graphical analysis of kinetic data to determine whether a reaction is first or second order is usually reserved for honors-level or even Advanced Placement chemistry courses. The *Background* section contains a summary of the use of graphical analysis in kinetic studies. A more detailed explanation is provided in the *Supplementary Information* section.

- A review of the principles of light absorption and transmission will be necessary if this is the first colorimetry experiment in your lab program. The phenolphthalein solution absorbs light in the 350–600 region. The wavelength of light used in this experiment is 565 nm, corresponding to green light. The beam of light is passed through the sample, and the intensity of the light that is transmitted is measured electronically. The greater the concentration of phenolphthalein in solution, the more green light the solution will absorb. See the "Color and Light Spectrum" Demonstration Kit (Flinn Catalog No. AP6172) for a large-scale demonstration of the relationship between the color of absorbed and transmitted light.

- Absorbance data may also be collected continuously via a timed run as opposed to manually at selected time intervals. The drawback is that the temperature of the solution may increase more if the light source is on continuously.

- The experiment may also be performed using a conventional spectrophotometer rather than colorimetry to measure absorbance as a function of time.

Teaching Tips

- This experiment can be extended to determine the reaction order with respect to hydroxide ions. Have different student groups collect absorbance data at different hydroxide ion concentrations. For each hydroxide ion concentration, a graph of ln(Abs) versus time should be linear with a slope equal to $-k'$ (see the *Background* section), where k' incorporates the hydroxide concentration ($k' = k[OH^-]^m$). The classroom data collected by different student groups can be compared to determine the reaction order in hydroxide ion. A graph of k' versus $[OH^-]$ is linear and demonstrates that the reaction is first order with respect to hydroxide ions ($m = 1$). See the *Supplementary Information* section for results and graphical analysis of the effect of hydroxide ion concentration on the rate of fading of phenolphthalein.
- Many teachers prefer to have students draw their own graphs. Graphing the data themselves will help students practice an important skill and may, in fact, make it easier for students to interpret the data and results.
- The LabPro interface system for collecting laboratory data may be used with a computer, a calculator or alone. The steps in the *Procedure* represent the computer-interface instructions. This will need to be modified slightly if the LabPro is used as a calculator interface or if a different type of interface system is used.

Answers to Pre-Lab Questions

Student answers will vary.

Crystal violet (CV) is another indicator dye that combines with hydroxide ions to form a colorless product (Equation 5). Crystal violet was added to 0.10 M NaOH, and the solution immediately turned violet. After 10 minutes, the color faded and the solution was almost colorless. The absorbance measurements were recorded in Table 1.

$$CV^+ + OH^- \rightarrow CVOH$$ *Equation 5*

Violet — Colorless

Table 1.

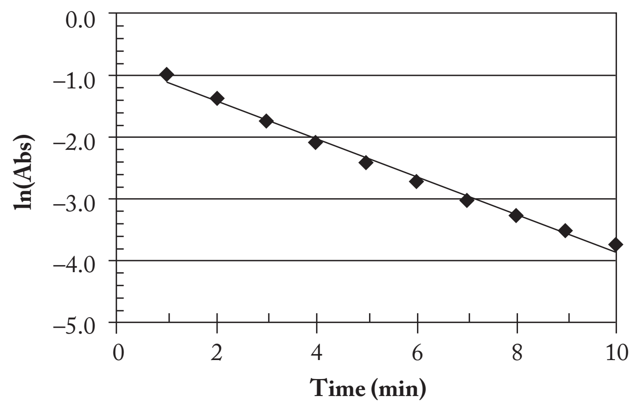
Reaction Time	Absorbance	ln(Abs)	1/Abs
1 min	0.366	–1.01	2.73
2 min	0.251	–1.38	3.98
3 min	0.176	–1.74	5.68
4 min	0.124	–2.09	8.06
5 min	0.089	–2.42	11.2
6 min	0.065	–2.73	15.4
7 min	0.048	–3.04	20.8
8 min	0.037	–3.30	27.0
9 min	0.029	–3.54	34.5
10 min	0.023	–3.77	43.5

1. Calculate the values of ln(Abs) and 1/Abs for each absorbance measurement to complete Table 1.

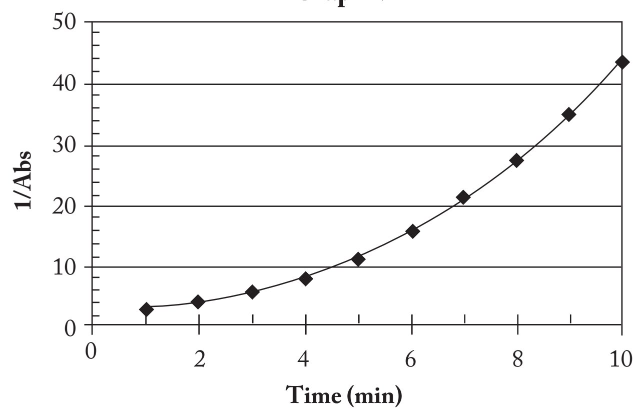
   See Table 1.

2. Use the following graphs to plot ln(Abs) versus time (Graph 1) and 1/Abs versus time (Graph 2).

Graph 1



Graph 2



3. Which graph more closely approximates a straight line? Is the reaction of crystal violet with hydroxide ions (Equation 5) first or second order in crystal violet?

   The graph of ln(Abs) versus time gives a straight line. The graph of 1/Abs versus time is curved. The reaction is first order in crystal violet.

Sample Data

Student data will vary.

Data Table

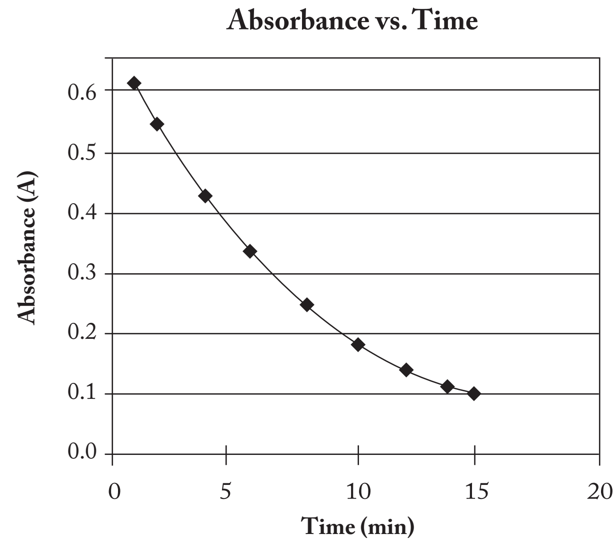
Initial Temperature	21.5 °C	**Final Temperature**	22.8 °C
Time	**Absorbance***	**ln(Abs)***	**1/Abs***
1 min	0.610	–0.49	1.64
2 min	0.545	–0.61	1.84
4 min	0.428	–0.84	2.34
6 min	0.327	–1.12	3.06
8 min	0.247	–1.40	4.05
10 min	0.188	–1.67	5.31
12 min	0.146	–1.93	6.86
14 min	0.116	–2.16	8.66
15 min	0.104	–2.27	9.66

*Computer-generated tables and graphs may be substituted for the data table.

Answers to Post-Lab Questions

Student answers will vary.

1. Plot or obtain a graph of absorbance versus time. Does the "rate of fading" of phenolphthalein depend on the concentration of the dye? Explain.

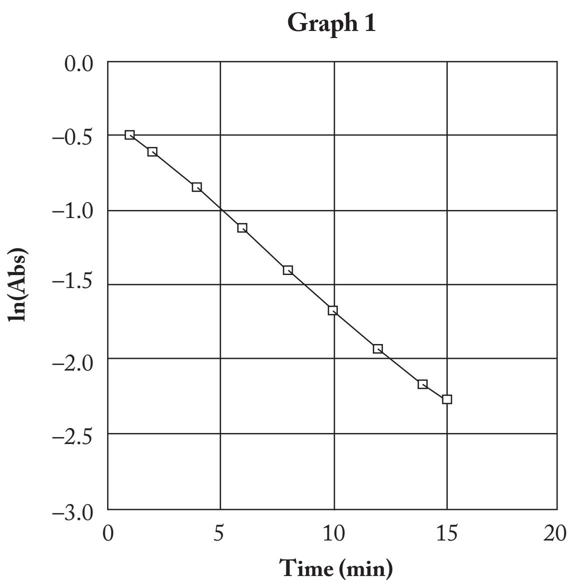


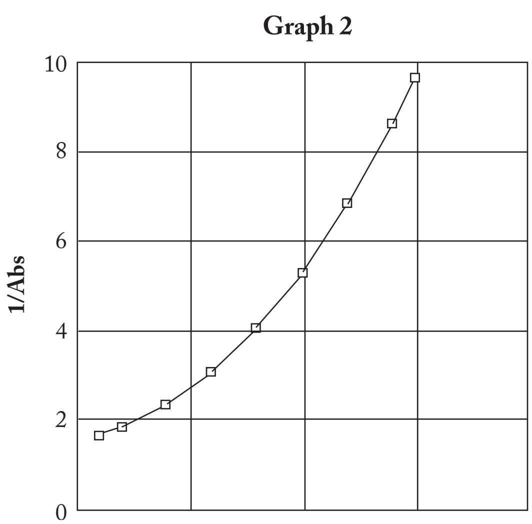
Yes, the "rate of fading" depends on the concentration of the dye. The graph of absorbance vs. time is curved, suggesting that the rate decreases as the concentration of phenolphthalein decreases over the course of the reaction.

2. Calculate the values of ln(Abs) and 1/Abs for each absorbance measurement, and enter the results in the table. *Note:* This may be done directly with the data saved in the technology program or separately using a calculator or spreadsheet program.

See the data table.

3. Plot or obtain graphs of both ln(Abs) versus time and of 1/Abs versus time (see the *Background* section and the *Pre-Lab Questions*).





The graph of ln(Abs) vs. time is linear with a slope = –0.129 (k' = 0.129) and correlation coefficient = 0.999.

4. Which graph more closely approximates a straight line?

   The points on the ln(Abs) versus time graph all fall on a straight line. The 1/Abs versus time graph is curved.

5. Is the reaction of phenolphthalein with hydroxide ions (Equation 2) first or second order in phenolphthalein?

   The reaction is first order in phenolphthalein.

6. Did the temperature of the solution change over the course of the reaction? What effect, if any, would the temperature change have on the results of the experiment?

   The temperature of the solution increased from 21.5 to 22.8 °C over the course of the reaction. In general, the rate of a reaction increases as the temperature increases. However, the temperature increase in this case is fairly small and does not seem to affect the results. *Note:* The temperature effect is probably due to the "heating" of the sample by the light source. To reduce the temperature effect, remove the cuvette from the colorimeter compartment between measurements. The temperature change does not seem to be large enough to warrant the increased probability that the solution might spill as it is repeatedly inserted and removed.

7. The concentration of sodium hydroxide is assumed to be constant throughout the reaction and is thus included in the "reduced" rate law expression (see Equation 4 in the *Background* section). Is this assumption valid? Prove it.

   The initial concentration of phenolphthalein in the cuvette is roughly 1×10^{-4} M—one drop of 0.006 M phenolphthalein is diluted with about 3 mL (60 drops) of sodium hydroxide. The initial concentration of sodium hydroxide is 0.2 M, more than 1000X greater than the phenolphthalein concentration. The amount of sodium hydroxide consumed during the reaction is insignificant—the assumption is valid.

Supplementary Information

Graphing Exercises

Graphical analysis of first and second order reactions is based on combining the equations for the disappearance of reactant (Equation 6) and the rate law for a pseudo-first order reaction (Equation 7).

$$\text{Rate} = \frac{-\Delta[\text{A}]}{\Delta t} \qquad \textit{Equation 6}$$

$$\text{Rate} = k'[\text{A}]^m \qquad \textit{Equation 7}$$

The resulting equation is

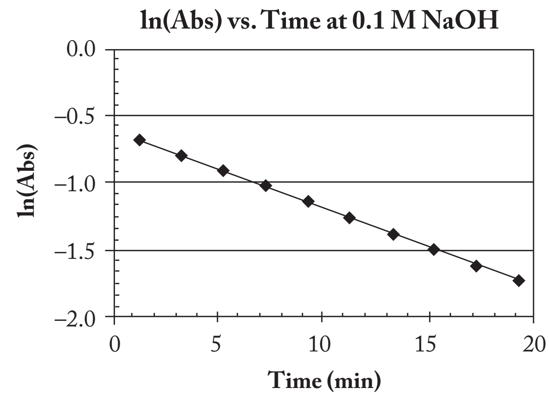
$$\frac{-\Delta[\text{A}]}{\Delta t} = k'[\text{A}]^m \quad \text{or} \quad \frac{-\Delta[\text{A}]}{[\text{A}]^m} = k'\Delta t$$

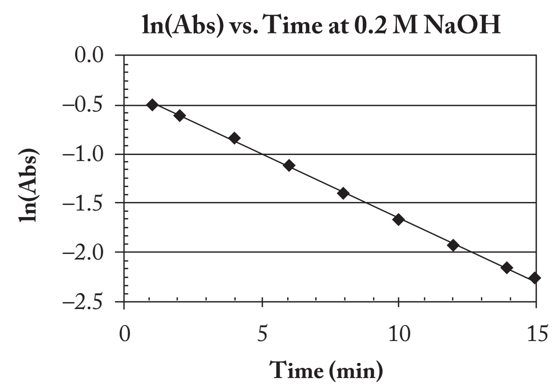
Using calculus, it can be shown that if $m = 1$, the so-called integrated rate equation is $\ln[\text{A}] = -k't + \ln[\text{A}]_o$. A graph of ln[A] versus time will be linear with slope $-k'$.

If $m = 2$, the integrated rate equation has the form $1/[\text{A}] = k't + 1/[\text{A}]_o$. A graph of 1/[A] versus time will be linear with slope k'.

Order of Reaction in Hydroxide Ion

The following ln(Abs) vs. time graphs were obtained for different hydroxide ion concentrations.





The value of k' was equal to 0.13 for 0.2 M NaOH and 0.061 for 0.1 M NaOH. Substituting these values into the equation for the pseudo-rate constant ($k' = k[\text{OH}^-]^m$) gives the following results:

At 0.2 M NaOH: $0.13 = k' = k[0.2]^m$

At 0.1 M NaOH: $0.061 = k' = k[0.1]^m$

$$\frac{0.13}{0.061} = 2 = \left(\frac{0.2}{0.1}\right)^m$$

$$m = 1$$

The fading reaction of phenolphthalein is first order in sodium hydroxide.