Objective: Use spectrophotometry to determine the order of the kinetics of decolorization of phenolphthalein in alkaline solution.

Introduction: Phenolphthalein undergoes a transformation from clear in color to pink as a solution’s pH increases beyond a value of about 8. At higher pHs, the pink color will fade over time. In this experiment the kinetic order of the fading process will be determined.

The overall reaction may be considered to be (In stands for indicator – not indium):

\[
\begin{align*}
\text{HIn} & \rightarrow \text{In}^2- \rightarrow \text{InOH}^3-
\end{align*}
\]

pH<8  pH >8  pH >>8

Clear  Pink  Clear

The kinetics of the second step above will be studied in this experiment.

It is probably reasonable to assume that the kinetics of the second step will depend both on the concentration of phenolphthalein as well as the concentration of the hydroxide ion in the solution. A starting rate law might be:

\[
\text{Rate} = k [\text{OH}^-]^m [\text{In}^2-]^n
\]

where the presumed integers m and n represent the order of the reaction with respect to OH\(^-\) and In\(^2-\), respectively. Rather than using an initial rate method similar to the iodine clock reaction previously studied, the change in color as a function of time will be studied in this experiment.

The color in a solution arises because components of the solution absorb various wavelengths of the visible spectrum. A pink solution is pink because the wavelengths corresponding to that color are the primary ones passing through the solution – the other wavelengths are being absorbed. A spectrometer may be used to determine the light absorbed at different wavelengths. In the spectrometer a light of a particular wavelength is sent through the sample and the intensity of light emerging from the sample is determined. The absorbance, A, of the sample is defined as:

\[
A = \log \frac{I_{\text{initial}}}{I_{\text{after sample}}}
\]

where \(I_{\text{initial}}\) is the initial power of the light entering the sample and \(I_{\text{after sample}}\) is the power emerging from the sample. As the light emerging from the sample decreases the absorbance increases.

The absorbance is directly related to the concentration and the length of solution through which the light must pass. This relationship is summarized in Beer’s Law:
\[ A = \varepsilon bc \]

where \( \varepsilon \) is the molar absorptivity or molar absorption coefficient, \( b \) is the path length of the cell in units consistent with \( \varepsilon \), and \( c \) is the molar concentration. If one knows both \( \varepsilon \) and \( b \), it is possible to use an absorbance measurement to arrive at the concentration of a particular solution. In this experiment the molar absorptivity of phenolphthalein may be taken as \( 3.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1} \). (Reference 1) and the path length is 1.0 cm.

Determination of the orders \( m \) and \( n \) will be made by measuring the fading of the absorbance of the phenolphthalein (at 550 nm) at a variety of sodium hydroxide concentrations. The sodium hydroxide concentration chosen will be in large excess of the amount of phenolphthalein present so the hydroxide concentration effectively does not change during the course of the reaction and the fading of color can be related directly to the concentration of the phenolphthalein.

Absorbance-time data will be acquired over a period of time for each reaction and, through appropriate plots, the order of the reaction with respect to phenolphthalein may be determined. Recall a plot of \( \ln[A] \) vs. \( t \) will be linear with slope \(-k\) if a reaction is first order and one of \( 1/[A] \) vs. \( t \) will be linear with slope of \( k \) if a reaction is second order. The order with respect to phenolphthalein may actually be determined by one reaction. The rate constant determined from the slope is actually a “pseudo” rate constant. Since we have assumed the hydroxide ion concentration does not change much, the rate law may be considered as:

\[
\text{Rate} = \{k[OH^-]^m\} [In^{2-}]^n \approx k_1 [In^{2-}]^n
\]

where the quantity in curly brackets is effectively constant during the course of one run, but different between runs based on the sodium hydroxide concentration. The curly bracketed quantity has been replaced by \( k_1 \), a “pseudo” rate constant.

However, it is also of interest to determine the order with respect to hydroxide ion which will require further experiments. In looking at the rate law immediately above, it is evident that the value of \( k_1 \) changes for each different concentration of hydroxide ion. Since \( k_1 = k[OH^-]^m \), the following relationship holds:

\[
\ln k_1 = \ln k + m \ln[OH^-]
\]

A plot of \( \ln k_1 \) vs. \( \ln[OH^-] \) should be linear with slope \( m \) and intercept \( \ln k \). Thus, the entire rate law may be determined by a few straightforward experiments.

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1. Barnes, M.O. and LaMer, V. K., *Journal of the American Chemical Society*, 64, 2312 (1942).
**Experimental**

*Milton Roy Spectronic 21-D*

The spectrometer you will be using is pictured below:

In making absorbance measurements, you must make sure the Mode is set to absorbance. There will be one cuvette per spectrometer that will be filled with water and serve as a blank. Frequently during the day place the blank in the spectrometer and make sure the absorbance reads zero. If not, adjust using the knob on the lower left of the instrument.

**Solutions**

You will make absorbance-time readings on four solutions with sodium hydroxide concentrations ranging between 0.05 M and 0.30 M. You are provided with 10-mL volumetric flasks and an assortment of pipettes with which to make these solutions.

**Procedure**

1. Use a pipette to deliver the desired volume of NaOH into a 10-mL volumetric flask. Dilute to the mark with the 0.30 M NaCl solution provided, cap the flask, and invert it several times for good mixing.
2. Put two drops of phenolphthalein in the volumetric flask, cap the flask and invert several times. Immediately transfer some of the solution to the cuvette and place it in the spectrometer.
3. Take absorbance-time readings as the color of your solution fades. You do not need to have a particular reading as an initial reading – you will record your first reading as time zero.
4. Continue taking readings every few minutes until you have about 7-10 readings or until the absorbance levels off – whichever comes first. These readings do not have to be at specific time intervals. It is best to remove your solution between readings so it does not heat up. Since more than one group may be using a particular spectrometer, just stagger your readings as necessary.
5. Once you have terminated taking the readings, put the solution in the cuvette and the volumetric flask in the waste container.
6. Repeat the steps above to acquire absorbance-time data for four different concentrations of NaOH.
Data Table

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Data Analysis:

1. Make one plot that contains the ln (concentration phenolphthalein) vs. time for all four of your runs above. The concentration of phenolphthalein may be found from Beer’s Law with \( \varepsilon = 3 \times 10^4 \text{ M}^{-1}\text{s}^{-1} \) and a path length of 1 cm. From this plot determine the order with respect to phenolphthalein and the value of \( k_1 \), the pseudo rate constant.

2. Make a plot of the ln of \( k_1 \) vs. the ln [OH\(^-\)]. From this plot determine the order with respect to hydroxide concentration and the value of k.

Postlab

1. Write the rate law for this reaction including the values of the orders you have determined and the rate constant.

2. This is the first shot at conducting this experiment. (These aren’t graded for what you say – be honest.)
   a. Risky to ask before ever doing it, but what could improve the experiment?

3. Did the experiment help you understand anything better?