Experiment 10 - Kinetics of Decomposition of Dye

Overview

In this experiment, you will measure the rate at which bleach will decompose a dye, removing the color from solution. The reaction is easily followed using a spectrophotometer and a time-based data collection device. We will use the SpectraVis+ and LabQuest 2 from Vernier to collect and analyze the data. If you have the LoggerPro package installed on your laptop, you can control the experiment and analyze the data through that piece of software.

Chemical Kinetics

The rate of a chemical reaction can be defined in terms of the time rate of change of concentrations of the reactants and products of the reaction. For the reaction

$$A + 3\,B \rightarrow 2C$$

the **rate of reaction** can be defined by any of the ratios

$$rate = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{3}\frac{\Delta[B]}{\Delta t} = \frac{1}{2}\frac{\Delta[C]}{\Delta t}$$

where Δ[X] is the change in the concentration of compound X, and Δt is the time in which that change takes place. In differential form (the limit where Δt approaches 0), the expression becomes

$$rate = -\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

Example: The rate of a reaction

$$A + 3\,B \rightarrow 2\,C$$

Is determined to be 3.0 x 10^{-2} M/s. What is the rate at which C is being formed?

Solution: The rate of the reaction in terms of the time-rate of change of the concentration of C is given by

$$rate = \frac{1}{2}\frac{\Delta[C]}{\Delta t}$$

So

$$3.0 \cdot 10^{-2}\frac{M}{s} = \frac{1}{2}\frac{\Delta[C]}{\Delta t}$$

Or

$$6.0 \cdot 10^{-2}\frac{M}{s} = \frac{\Delta[C]}{\Delta t}$$

The measurement of chemical reaction rates can give a great deal of insight into the actual mechanism by which a chemical reaction progresses. In this experiment, the reaction we are looking at will by

$$Dye + OCl^{-} \rightarrow products$$

and the rate will depend on both the concentration of the dye and the concentration of hypochlorite (OCl^-) in the solution. We can write a **rate law** (A mathematical relationship between the concentrations of the reactants and time) in differential form

$$rate = -\frac{d[Dye]}{dt} = k[Dye][OCl^{-}]$$

where k is the **rate constant**. In the reaction, hypochorite (OCl^-) acts as a **catalyst**. As such, its concentration is essentially constant as the reaction progresses. Because of this, we can incorporate its concentration into the **effective rate constant** (k'),

$$k' = k[OCl^{-}]$$

and the rate law becomes

$$-\frac{d[Dye]}{dt} = k'[Dye]$$

This expression is easily integrated by separating the variables (placing concentration terms on one side, and time terms on the other)

$$\frac{d[Dye]}{[Dye]} = -k'\,dt$$

Integration yields

$$\int_{[Dye]_0}^{[Dye]} \frac{d[Dye]}{[Dye]} = -k' \int_0^t dt$$

$$\ln\left(\frac{[Dye]}{[Dye]_0}\right) = -k't$$

Exponentiation of both sides followed by solving for [Dye] produces the result

$$[Dye] = [Dye]_0 e^{-k't}$$

This suggests an exponential decay of the concentration of the dye. And since the concentration of the dye is proportional to the absorbance of the solution, we can simply fit the time-dependence of the absorbance to an exponential decay model to find a value for the effective rate constant *k'* from our measured data. And since

$$k' = k[OCl^-]$$

the value of k' should be independent of the initial concentration of the dye, but should be directly proportional to the concentration of hypochlorite. Thus, **halving the concentration of OCl^- should cut the value of the effective rate constant in half**. This will be the hypothesis of this experiment.

Experimental description

Procedure

1. Connect the SpectraVis+ to the LabQuest2 via the USB cable.
2. Calibrate the Spectravis+ to set the dark current and 100% transmission.
   a. You will need a cuvette with deionized water to use as a blank.
   b. Tap on the red box that displays the Absorbance, and follow the directions to calibrate the spectrophotometer.
3. Obtain a value of λ_{max}.
   a. In "Full spectrum" mode, obtain an absorption spectrum of the dye.
   b. Make a note the wavelength at which the absorbance the highest.
4. Collect kinetics data for the bleaching of the dye.
   a. Change the data collection mode to "Time based" by tapping on the "mode" box on the upper right side of the LabQuest2 display. The default values for this mode should be fine for this experiment.
   b. Make sure the device is set to collect
   c. Deliver 1.00 mL of dye solution to a clean cuvette. Note the concentration.
   d. Note the concentration of the bleach solution. Deliver 1.00 mL of bleach solution, wipe the sides of the cuvette (to remove any drops of solution on the outside.)

Immediately place the cuvette (taking care to ensure the proper orientation of the smooth cuvette surfaces!) in the SpectraVis+. Tap the start button to begin data collection.

   e. Collect data for at least 90 seconds. You should see an exponential decay of the absorbance signal.

5. Fit the data to an exponential decay curve.
   a. Under the *Analyze* menu, select “curve fit”.
   b. Select “Natural Exponential” as the model. This will fit the data to a function of the form

$$y = Ae^{-Bt} + C$$

   c. Make a note of the Initial Absorbance (parameter A in your fit) and the rate constant (parameter B in the fit.)
6. Repeat from step 4 for each set of concentrations you wish to investigate.

Vocabulary and Concepts

References

[1] J. Randall, Advanced Chemistry with Vernier, 3rd ed., Beaverton, OR: Vernier Software and Technology, 2013.

[2] M. Perona, "Chemical Kinetics to Dye For," *CSU Stanislaus Chemistry Department.*

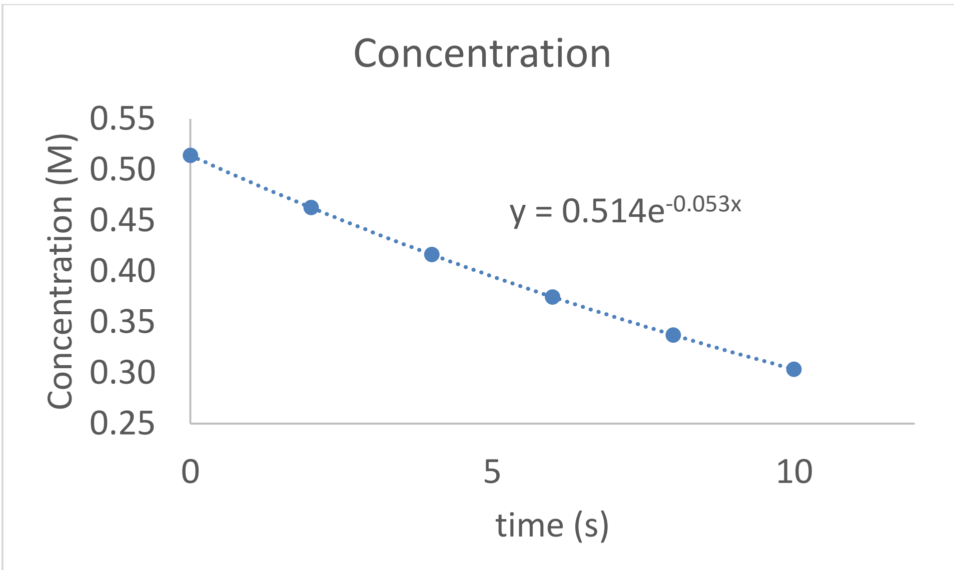
Pre-Laboratory Assignment – Kinetics

Name ______________________________ Section ___________________________

Randall collects data for a first-order decomposition reaction

$$A \rightarrow products$$

He plots the concentration of A vs time and fits the data to an exponential decay as shown below:



1. What is the rate constant (k) for the decomposition?

2. What is the initial concentration (the concentration at time t = 0) in Randall's experiment?

3. What will the concentration be after 25 seconds?

Report Sheet – Kinetics

Name ________________________________ Date ______________________________

Lab Partner(s) ____

Color of dye solution __________________________

λ_{max} (nm) __________________________

For each run, write down the equation for the exponential decay.

1.

2.

3.

4.

Run	[Dye]	[bleach]	Initial Absorbance (parameter A)	k' (s^{-1}) (parameter B)
1	50%	50%		
2				
3				
4				

Did k' depend on a) the concentration of the dye? b) the concentration of the hypochlorite? Or c) both?

Was the hypothesis of the experiment supported by your data, or was your data inconsistent with the hypothesis?