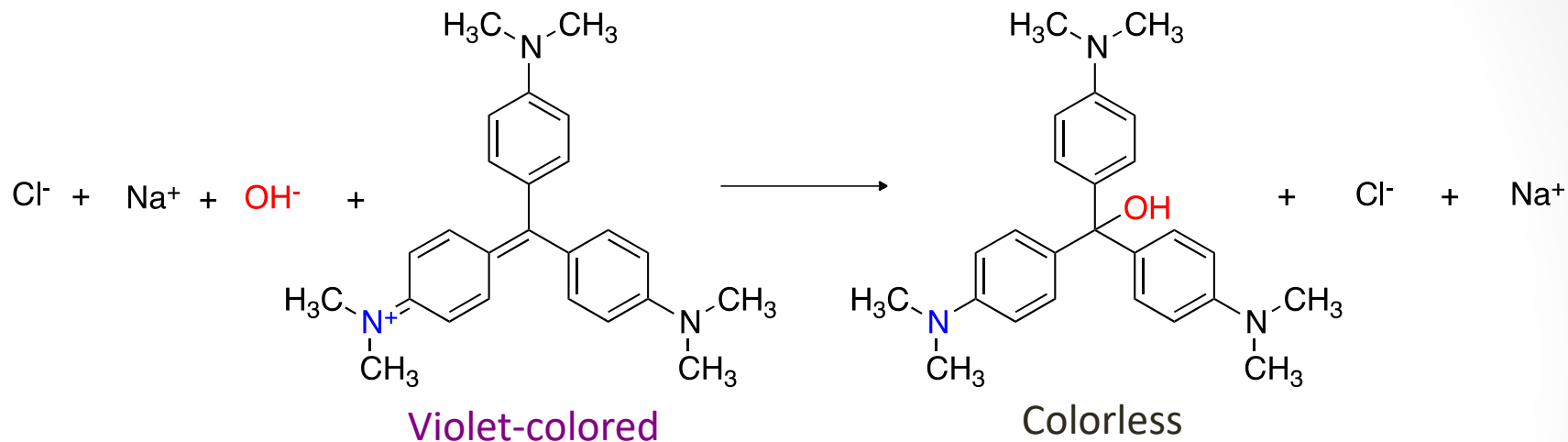


Integrated Rate Law Kinetics

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Reaction of Crystal Violet with NaOH



Crystal Violet – contains three six-membered rings with alternating double and single bonds. C. V. has extended resonance.

Molecules that are highly conjugated or in resonance tend to form **colored** solutions because they absorb visible light.

Disruption of the conjugation of C.V. by NaOH produces a **colorless** species.

We can monitor this reaction by UV-Vis spectroscopy.

UV-Vis Spectroscopy

- Instrument that measures the Absorbance (A) of light by a solution
- By measuring the absorbance of a species, we can find its concentration using **Beer's Law**:

$$A = \epsilon bc$$

A diagram illustrating the components of Beer's Law equation $A = \epsilon bc$. The equation is centered at the top. Three arrows point from labels below to the variables in the equation: 'Absorbance' points to 'A', 'Molar absorptivity (L mol⁻¹ cm⁻¹)' points to 'ε', and 'Concentration (mol L⁻¹)' points to 'c'. A fourth label, 'Path length (cm)', is positioned below the equation with an arrow pointing towards it, indicating its role in the calculation.

- Molar absorptivity and path length are constants for each experiment; therefore, **A(Abs)** and **c** are directly **proportional** to one another.

Rate Law Equations

- The Rate of reaction for $A + B \leftrightarrow C$ can be expressed by the following equations:

$$\text{Rate} = k[A]^m[B]^n \quad \& \quad \text{Rate} = -\Delta[A]/\Delta t$$

- where m & n is called the “order of reaction” with respect to A or B

Zero Order

$$\text{Rate} = -\frac{\Delta A}{\Delta t} = k[A]^0[B]^y$$

$$\int_{[A]_o}^{[A]} \Delta A = \int_0^t -k[B]^y \Delta t$$

$$[A] - [A]_o = -k[B]^y (t - 0)$$

$$[A] = -k[B]^y t + [A]_o$$

First Order

$$\text{Rate} = -\frac{\Delta A}{\Delta t} = k[A]^1[B]^y$$

$$\frac{\Delta[A]}{[A]} = -k[B]^y \Delta t$$

$$\int_{[A]_o}^{[A]} \frac{\Delta[A]}{[A]^1} = \int_0^t -k[B]^y \Delta t$$

$$\int_{[A]_o}^{[A]} \ln[A] = \int_0^t -k[B]^y t$$

$$\ln[A] - \ln[A]_o = -k[B]^y t$$

$$\ln[A] = -k[B]^y t + \ln[A]_o$$

Second Order

$$\text{Rate} = -\frac{\Delta A}{\Delta t} = k[A]^2[B]^y$$

$$\int_{[A]_o}^{[A]} -\frac{\Delta[A]}{[A]^2} = \int_0^t k[B]^y \Delta t$$

$$\int_{[A]_o}^{[A]} \frac{1}{[A]} = \int_0^t k[B]^y t$$

$$\frac{1}{[A]} - \frac{1}{[A]_o} = k[B]^y t$$

$$\frac{1}{[A]} = k[B]^y t + \frac{1}{[A]_o}$$

Integrated Rate Laws

<i>Order</i>	<i>Integrated Rate Law Equations</i>	<i>y vs. x</i>
<i>Zero, $m = 0$</i>	$[A] = -k[B]^n t + [A]_o$	$[A]$ vs. t
<i>First, $m = 1$</i>	$\ln [A] = -k[B]^n t + \ln [A]_o$	$\ln [A]$ vs. t
<i>Second, $m = 2$</i>	$\frac{1}{[A]} = k[B]^n t + \frac{1}{[A]_o}$	$1/[A]$ vs. t

- All equations are written in the form $y = mx + b$
- The order of the reaction with respect to “A” (here A = Crystal Violet) can be found by plotting $[A]$, $\ln [A]$, or $1/[A]$ versus t (time);
- The equation that provides a linear slope is evidence of the order of the reaction

Goals for Experiment: [C.V.]&t

1. Make a calibration curve for Crystal Violet:

- Prepare 3 C.V. solutions of different concentration([C.V.])
- Measure the absorbance (A) of 4 C.V. solutions
- Draw calibration curve: Abs v. [C.V.]

2. Determine the Order of Reaction with respect to C. V.:

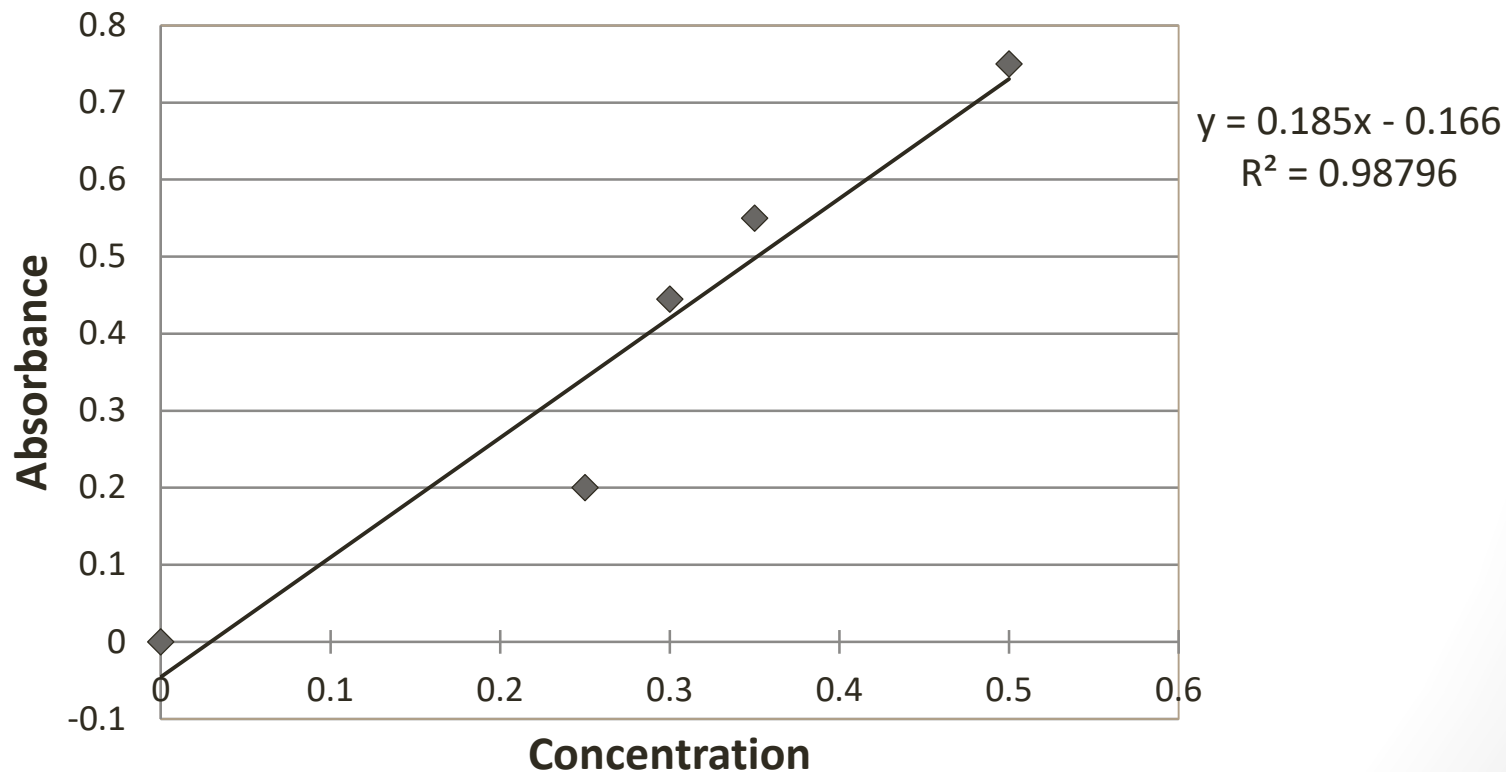
- Follow the reaction using the spectrophotometer by recording the absorbance (Abs) of C.V. every 10 seconds for 2 min (t).
- Repeat twice (perform a total of 3 times)

3. Determine the Order of Reaction with respect to NaOH:

- The same way as in goal #2, except with a different concentration of NaOH.

Calibration Curve

Beer's Law Plot: Absorbance vs Concentration



Experimental Details

- Preparing C.V. stock solutions – using one 10.0 mL volumetric flask
 - Use LESS THAN 20 mL of 8×10^{-6} M C.V. in total
 - Solvent: 5% EtOH/H₂O
 - Put the prepared solution in a cuvette; rinse the flask thoroughly; then move on to next preparation
- Transferring solutions – using graduated pipets
 - Rinse with solutions for 3 times
 - Don't draw solutions into the bulb
- Syringes:
 - get rid of bubbles at the tip first



Spectrophotometers



- “cuvette” : 13 x 100 mm test tube
- **Blank** the spectrophotometer between each trial
 - 5% EtOH H₂O for part 1 (calibration curve)
 - 0.050 M NaOH for part 2 (order for CV)
 - 0.025 M NaOH for part 3 (order for NaOH)

Contamination Prevention

- Rinse glassware several times with DI water and EtOH/H₂O
- HCl & NaOH will react with Crystal Violet!
- Use new cuvettes (don't need to rinse)
- label graduated pipets, beakers and cuvettes
- Use your own beakers to get solutions.
Never put your graduated pipets into public solutions!

Safety & Waste

Waste

- Keep a labeled **Waste beaker** in your hood.
- Dispose of waste solutions in the liquid waste container.
- Dispose of syringes in the solid waste.

Safety

- Wear safety glasses and gloves at all times!
- NaOH and Crystal Violet are eye irritants.
Crystal Violet can **stain** your skin or clothes.

Clean up

- Return cleaned 10.0 mL volumetric flasks to front hood at the end of the period
- Czar duty: Hood# 4&5
 - Wipe down hoods and sashes

Reminders

- Notebook pages are due **Dec 2nd** (Mon) at 1:25 PM to the drop box.
- Last day to turn in Assignments: **Dec 2nd** (Mon)
- Last day to report mistakes on Sakai: **Dec 9th** (Mon)