EXERCISE 2

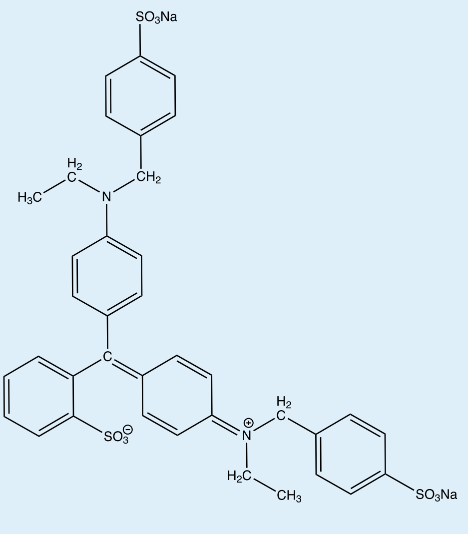
# Reaction of Blue Food Dye with Bleach

2

## INTRODUCTION

In the experiment, you will study the rate of the reaction of FD&C Blue #1 (Blue #1 is denoted by E number **E133** in food stuff) with sodium hypochlorite (NaClO). Since this reaction is very visible, you will use a spectrophotometer to quantitatively follow the rate of disappearance of the coloured reagent. Your data will allow you to determine the rate law and to propose a possible mechanism for the reaction.

Figure 1: FD&C Blue



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Because of the extended conjugation of alternating double bonds within the molecule, the $\Pi - \Pi^*$ absorption occurs in the visible region of the spectrum at 628 nm. When the dye reacts with hypochlorite, the colour disappears. Even though the product of this reaction is not completely known, we can still carry out rate studies with the reagents to determine the mechanism that occurs. One possible explanation for this reaction is that the bleach oxidises the central methylene carbon atom so that the molecule no longer has the extend conjugation system and the $\Pi - \Pi^*$ absorption of the less conjugated product occurs at a lower wavelength outside of the visible region of the spectrum.

The product might be an alcohol compound depicted in the reaction below. A study of how the concentration of the reactants affect the rate of the reaction gives insight into the mechanism and whether this simple explanation might be correct.

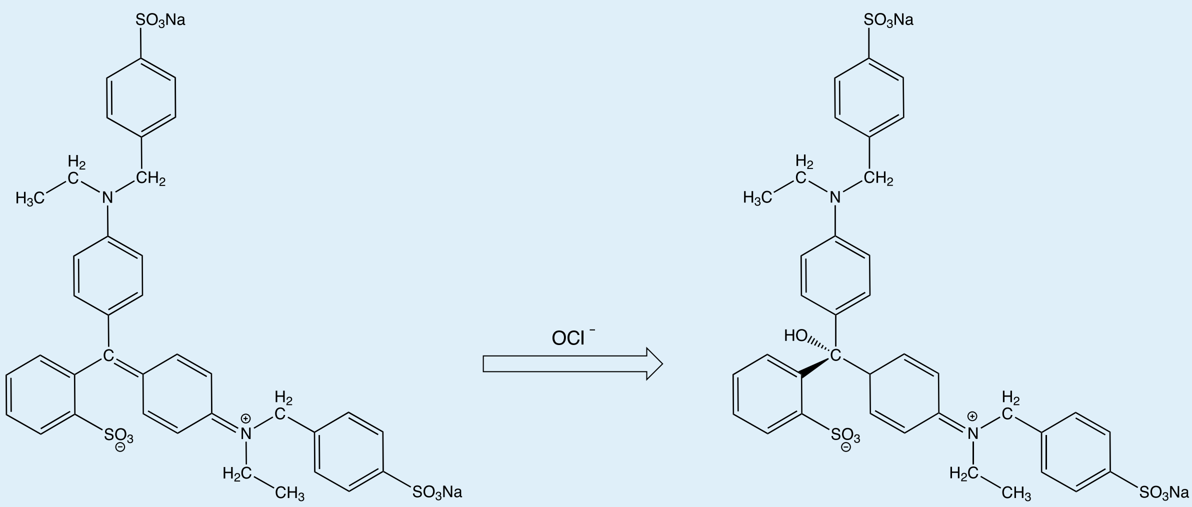



Figure 2: Possible mechanism of FD&C Blue #1 reacting with the hypochlorite ion

## The Rate Law:

The rate of a reaction can be represented either by the disappearance of reactants or the appearance of products. Since Blue #1 is the only coloured species in the reaction, we can monitor the rate of the reaction shown above by recording the decrease in the colour of solution with time. That is:

Where the exponents ***a*** and ***b*** indicate the order of the

$$\text{Rate} = -\frac{d[\text{Blue\#1}]}{dt} = k[\text{Blue\#1}]^a\,[\text{OCl}^-]^b$$

reaction with respect to each reagent, and ***k*** is the overall rate constant for the reaction at room temperature.
The overall rate of reaction is the sum of ***a*** and ***b***.
The square brackets, [ ], represent the concentration of the given reagent. The objective of this experiment is to determine the values of the exponents **a** and **b** and the value of ***k*** at room temperature.

## Beer-Lambert Law

In order to measure the concentration of the dye solution over the course of the reaction you will be using a spectrophotometer. The spectrophotometer will be set to a wavelength, which corresponds to an absorption peak of the dye (628 nm), and the absorbance will be measured over the course of reaction.

Looking at the Beer-Lambert law:

$$A = \varepsilon c l$$

It can be seen that the Absorbance (A) is directly proportional to the concentration (c); therefore, for this experiment the absorbance will be used instead of the concentration.

## Zero-order Reactions

These are reactions whose rate does not change when the concentration of a reactant changes. If this applies to reactant A whose rate equation is:

**Rate=k[A]$^x$**

Then the expression for [A]$^x$ must always equal 1. This is achieved by using the power zero; hence the reaction is a zero-order reaction.

**Rate=k[A]$^0$ which gives rate=k**

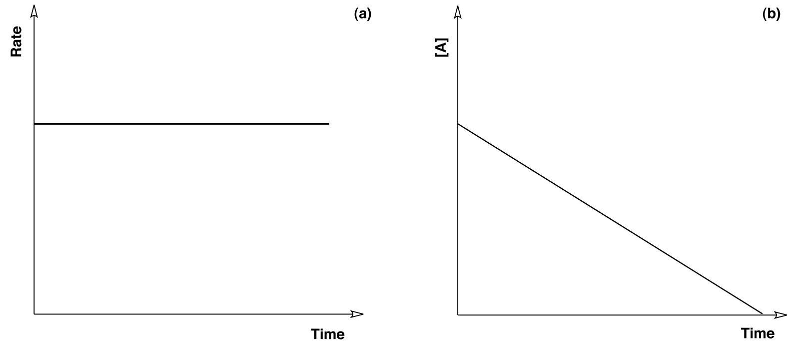



Figure: Graphs for a zero-order reaction (a) rate plotted against time, and (b) concentration plotted against time.

## First-order Reactions

This is where the rate of a reaction is directly proportional to the concentration of one species; taking this species to be A, the rate equation for reactant A is given as:

**rate =$k$[A]$^1$ or rate=$k$[A]**

Any such reaction is called a first-order reaction with respect to A, where [A] in the rate equation is the value for the concentration of A.

If the concentration doubles, the rate of the reaction will also double. Another way of determining if a reaction is first order with respect to A is plot a graph of ln[A] *versus* time. If the plot results in a straight line then the reaction is first order and the rate constant $k$ is equal to the slope of the line (i.e. $k$=-gradient).

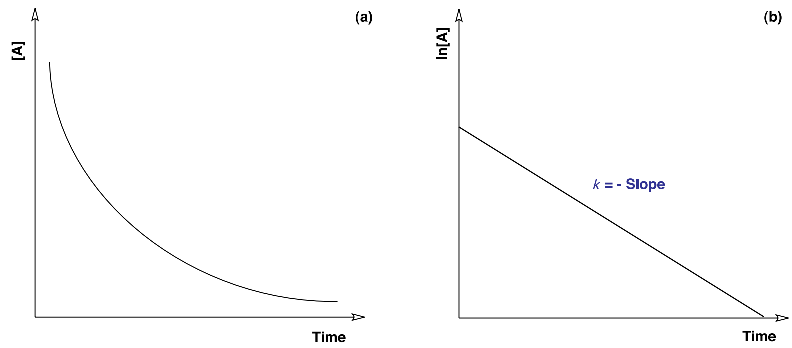



Figure: Graphs for a first-order reaction (a) concentration plotted against time, and (b) ln[A] plotted against time.

## Second-order Reactions

This is where the rate of a reaction is proportional to the concentration of one species by a factor of 2;
taking this species to be A, the rate equation for reactant A is given as:

**rate=$k$[A]$^2$**

If the concentration doubles, the rate of the reaction will quadruple. Another way of determining if a reaction is second order with respect to A is plot a graph of 1/[A] *versus* time. If the plot results in a straight line then the reaction is second order and the rate constant $k$ is equal to the slope of the line (i.e. $k$=gradient).

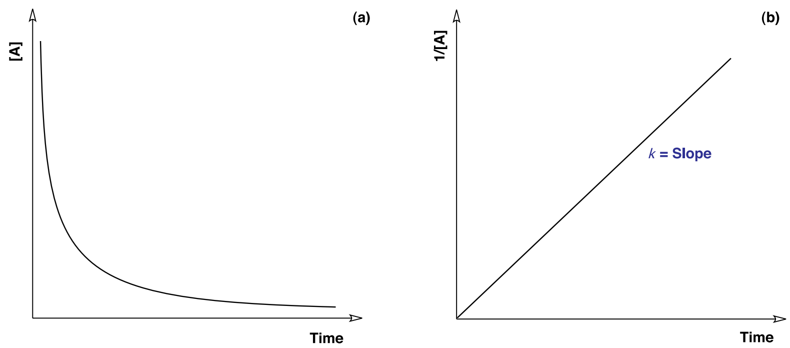



Figure: Graphs for a second-order reaction (a) concentration plotted against time, and (b) 1/[A] plotted against time.

# METHOD

## Group Allocation:

| GROUP | VOL. OF DYE SOLUTION (ml) | VOL. OF DISTILLED WATER (ml) | VOL. OF BLEACH (ml) |
|---|---|---|---|
| 1 | 3.0 | 1.0 | 0.5 |
| 2 | 4.0 | 0.0 | 0.5 |
| 3 | 3.0 | 0.5 | 1.0 |
| 4 | 2.0 | 1.5 | 1.0 |
| 5 | 2.0 | 0.5 | 2.0 |

## Solution Preparation:

1. Pour 10 ml of the dye solution in to a small labelled beaker. Pour 10 ml of the distilled water into a small labelled beaker. Pour 10 ml of the bleach into a small labelled beaker. These will be your stock solutions.
2. In cuvette **A** place 4.5 ml of distilled water into it. This will be your reference sample.
3. In cuvette **B**, place the volume of dye solution that is indicated in the table above.
4. In cuvette **B** place the volume of distilled water that is indicated in the table above.

   **DO NOT ADD YOUR BLEACH SOLUTION YET**

5. Take cuvette **A** and **B**, with your stock solution of bleach over to the spectrophotometer. A technician will help you with the running of the instrument.
6. Record a reference spectrum using your reference sample.
7. Prepare your kinetics sample by first measuring out the required volume of bleach. Quickly add the bleach to your kinetics solution. Place the lid on the cuvette and turn the cuvette over twice. Place the kinetics sample in the spectrometer and record the absorbance over a period time (i.e. two minutes) on your worksheet.

   **Practice run**
   Before carrying out the experiment using the spectrophotometer do a test run. Prepare a dye solution in a curvette and quickly add the bleach. Place the lid on curvette and turn the curvette over twice. Leave curvette on your workbench and observe the colour change.

8. Once the kinetic program has finished get a print-out of all the data.

# ANALYSIS OF RESULTS

1. On your worksheet find the natural logarithm of each absorbance value. (Note: On your calculator this is designated as "ln").
2. Again, in the same table find the inverse (reciprocal) of each absorbance value.
3. Plot (using the graph paper provided) a graph of **ln[Abs]** *versus* **Time**.
4. Plot (using the graph paper provided) a graph of **1/[Abs]** *versus* **Time**.
5. By inspection of the graphs, what is the order of the reaction with respect to the dye?
6. From the graph that appeared linear determine the gradient (the rate constant *k*) of the graph.
7. Once you have determined your rate constant place it on the group result table provided and take note of the other groups values.
8. Use the group results to determine **b** and the order of the reaction with respect to the hypochlorite concentration (**a**).

$$\textbf{Rate} = k\ [\textbf{Blue \#1}]^{a}\ [\textbf{OCl}^{-}]^{b}$$

# MATERIALS

### Chemicals

- FD&C Blue #1 Erioglaucine (Cas# 3844-45-9) Mw = 792.86 g/mol ($C_{37}H_{34}N_2O_9S_3$•2Na)
- Stock solution: 0.0104 g in 50 cm$^3$; c=2.263x10$^{-4}$ mol dm$^{-3}$
- 2 cm$^3$ of stock solution in 50 cm$^3$; c=9.05x10$^{-6}$ mol dm$^{-3}$ to give an absorbance of ~0.7 at $\lambda$max. (15 ml per student/pair)
- De-ionised water (15 ml per student/pair)
- Bleach solution – Hypochlorite 6% w/v (15 ml per student/pair)

### Apparatus (Per student or pair)

- 3 x 25 ml beaker
- 3 x 2 ml plastic disposable syringe ***without needle*** (Pipettes can be used instead but syringe quicker for taking kinetics measurements and to aid mixing)
- 2 x disposable plastic cuvettes and stoppers
- Tissues

### Instrument

- UV-visible Spectrometer (integral printer and paper) Initial scan 400 – 700 nm then set to single wavelength approximately 628 nm
- Laptop (*optional*)
- Printer (*optional*)
- Connection cables x 2 (*optional)*

### Set up for laptop and printer use:

- Connect UV-vis to laptop via left hand front USB port (Com 5)
- Connect printer to any USB port
- From spectrometer menu Select printer / auto print on / Computer USB / OK
- Open PVC program, set auto print to on or off depending on requirements.

# RESULTS

| GROUP | RATE CONSTANT (s$^{-1}$) | VOL. OF BLEACH (ml) |
|---|---|---|
| 1 | 0.00889 | 0.5 |
| 2 | 0.00882 | 0.5 |
| 3 | 0.01498 | 1.0 |
| 4 | 0.01577 | 1.0 |
| 5 | 0.02692 | 1.5 |

## Order of the reaction

Order with respect to dye is 'first order' as a plot of ln(Abs) vs. Time gives a straight line.

Looking at the rate constants and the volume of bleach one can work out the order the reaction with respect to the bleach. If the reaction is first order with respect to the bleach, then doubling the volume of the bleach will double the rate constant. From the group data table above you can see this does in fact happen, e.g. Group 1 and Group 3.

Therefore, the reaction is first order with respect to the bleach. Furthermore, taking Group 1 and Group 5, triple the volume of bleach, triples the rate constant.

The overall order of the reaction is second order.

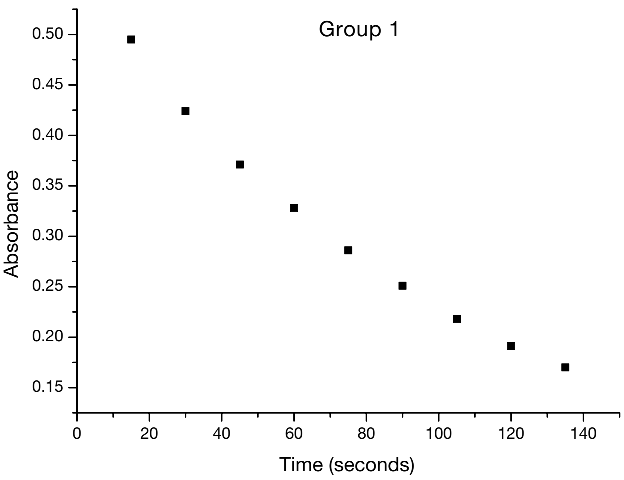
# RESULTS - RAW DATA

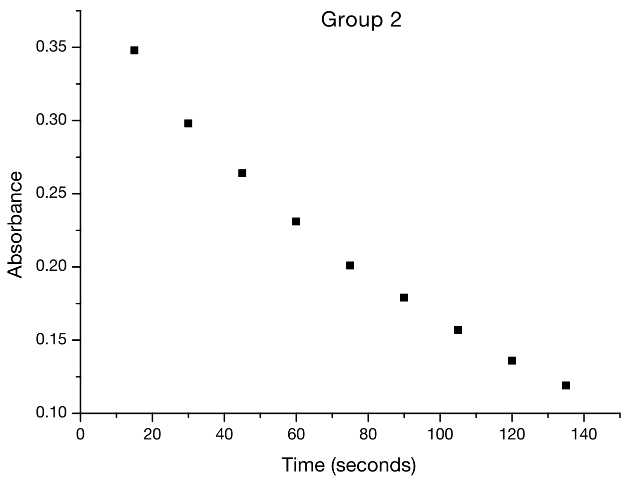
## Group 1

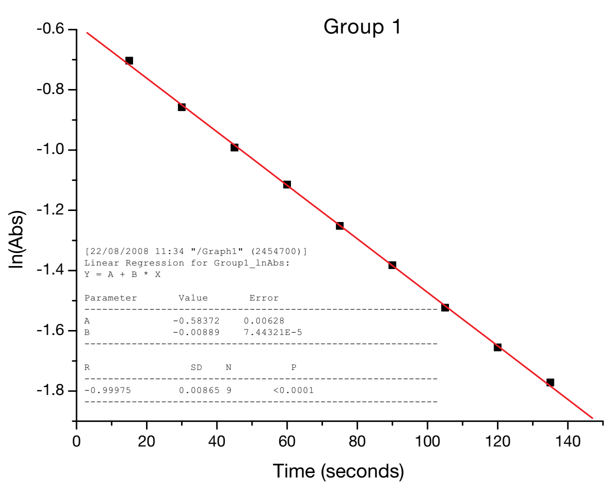
| TIME(s) | ABS | LN(ABS) | 1/(ABS) |
|---|---|---|---|
| 15 | 0.495 | -0.7032 | 2.0202 |
| 30 | 0.424 | -0.85802 | 2.35849 |
| 45 | 0.371 | -0.99155 | 2.69542 |
| 60 | 0.328 | -1.11474 | 3.04878 |
| 75 | 0.286 | -1.25176 | 3.4965 |
| 90 | 0.251 | -1.3823 | 3.98406 |
| 105 | 0.218 | -1.52326 | 4.58716 |
| 120 | 0.191 | -1.65548 | 5.2356 |
| 135 | 0.17 | -1.77196 | 5.88235 |

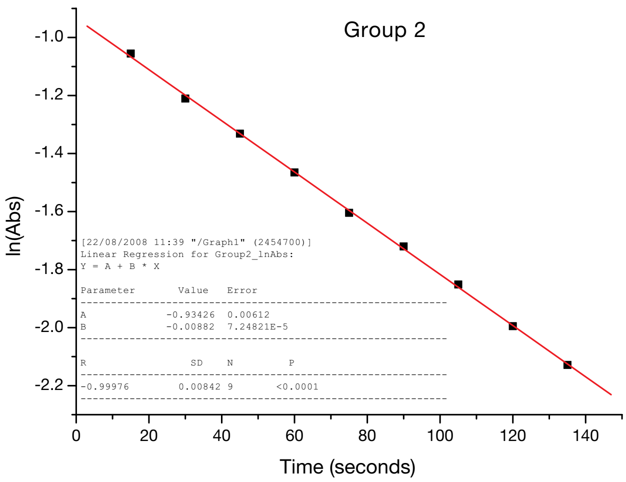
## Group 2

| TIME(s) | ABS | LN(ABS) | 1/(ABS) |
|---|---|---|---|
| 15 | 0.348 | -1.05555 | 2.87356 |
| 30 | 0.298 | -1.21066 | 3.3557 |
| 45 | 0.264 | -1.33181 | 3.78788 |
| 60 | 0.231 | -1.46534 | 4.329 |
| 75 | 0.201 | -1.60445 | 4.97512 |
| 90 | 0.179 | -1.72037 | 5.58659 |
| 105 | 0.157 | -1.85151 | 6.36943 |
| 120 | 0.136 | -1.9951 | 7.35294 |
| 135 | 0.119 | -2.12863 | 8.40336 |



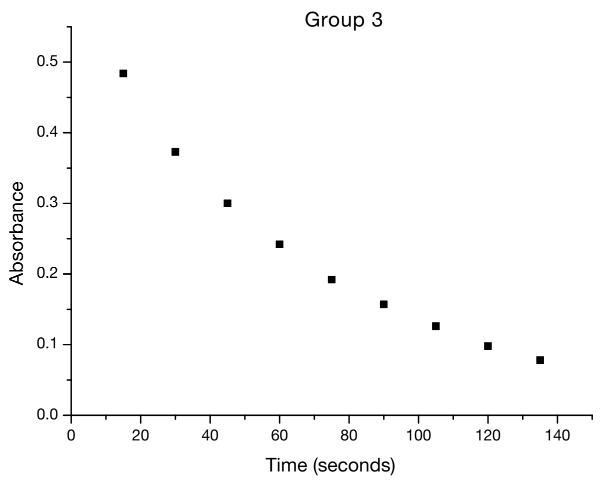



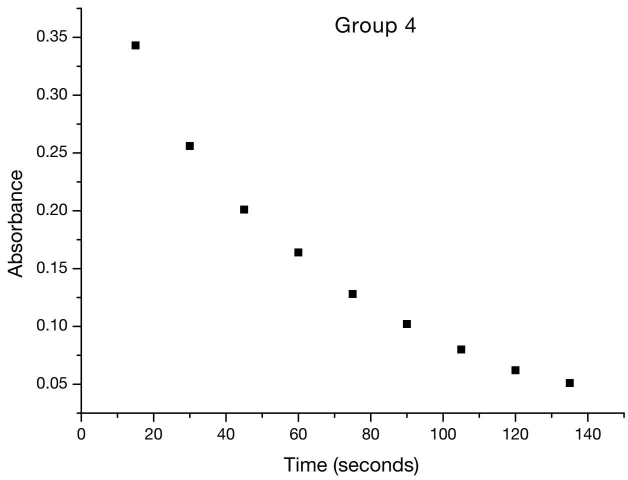
## Group 3

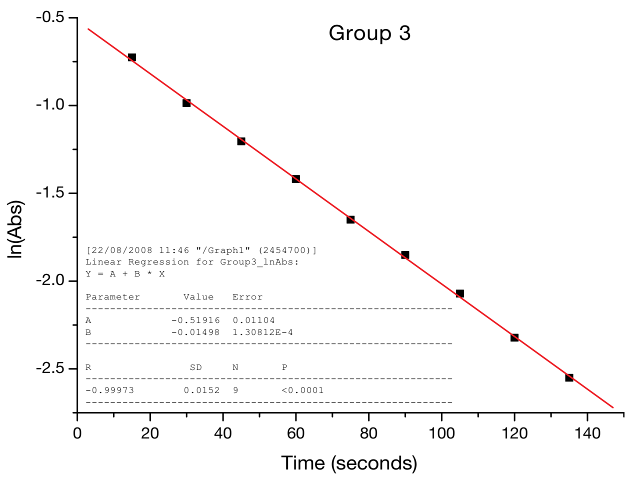
| TIME(s) | ABS | LN(ABS) | 1/(ABS) |
|---|---|---|---|
| 15 | 0.484 | -0.72567 | 2.06612 |
| 30 | 0.373 | -0.98618 | 2.68097 |
| 45 | 0.3 | -1.20397 | 3.33333 |
| 60 | 0.242 | -1.41882 | 4.13223 |
| 75 | 0.192 | -1.65026 | 5.20833 |
| 90 | 0.157 | -1.85151 | 6.36943 |
| 105 | 0.126 | -2.07147 | 7.93651 |
| 120 | 0.098 | -2.32279 | 10.20408 |
| 135 | 0.078 | -2.55105 | 12.82051 |

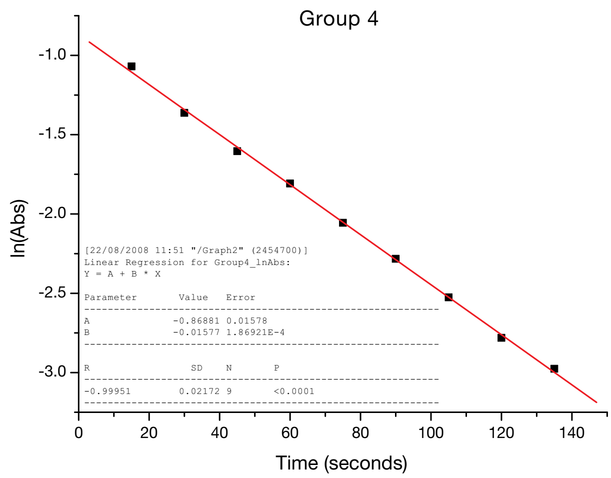
## Group 4

| TIME(s) | ABS | LN(ABS) | 1/(ABS) |
|---|---|---|---|
| 15 | 0.343 | -1.07002 | 2.91545 |
| 30 | 0.256 | -1.36258 | 3.90625 |
| 45 | 0.201 | -1.60445 | 4.97512 |
| 60 | 0.164 | -1.80789 | 6.09756 |
| 75 | 0.128 | -2.05573 | 7.8125 |
| 90 | 0.102 | -2.28278 | 9.80392 |
| 105 | 0.08 | -2.52573 | 12.5 |
| 120 | 0.062 | -2.78062 | 16.12903 |
| 135 | 0.051 | -2.97593 | 19.60784 |



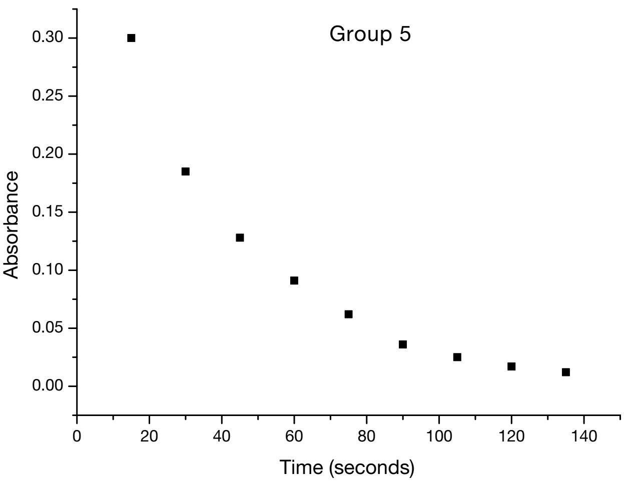



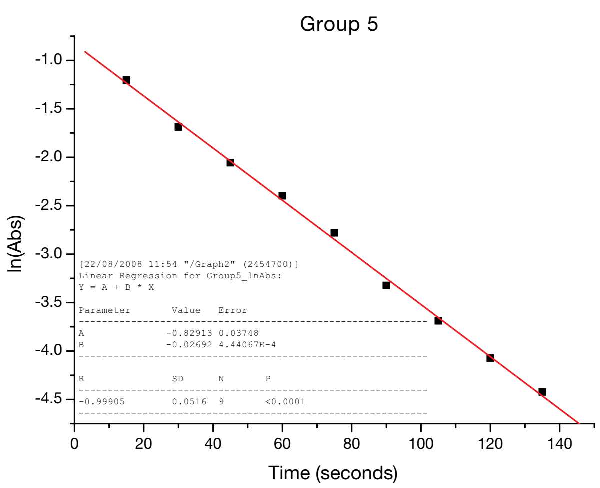



# Group 5

| TIME(s) | ABS | LN(ABS) | 1/(ABS) |
|---|---|---|---|
| 15 | 0.3 | -1.20397 | 3.33333 |
| 30 | 0.185 | -1.6874 | 5.40541 |
| 45 | 0.128 | -2.05573 | 7.8125 |
| 60 | 0.091 | -2.3969 | 10.98901 |
| 75 | 0.062 | -2.78062 | 16.12903 |
| 90 | 0.036 | -3.32424 | 27.77778 |
| 105 | 0.025 | -3.68888 | 40 |
| 120 | 0.017 | -4.07454 | 58.82353 |
| 135 | 0.012 | -4.42285 | 83.33333 |



# STUDENT WORK SHEET

| TIME (s) | ABSORBANCE | LN(ABSORBANCE) | 1/(ABSORBANCE) |
|---|---|---|---|
| 0 | | | |
| 15 | | | |
| 30 | | | |
| 45 | | | |
| 60 | | | |
| 75 | | | |
| 90 | | | |
| 105 | | | |
| 120 | | | |

## Calculations

### Determining k

Gradient of Line (k) = ______________________ units: ______________________

### Rate of the reaction with respect to the hypochlorite

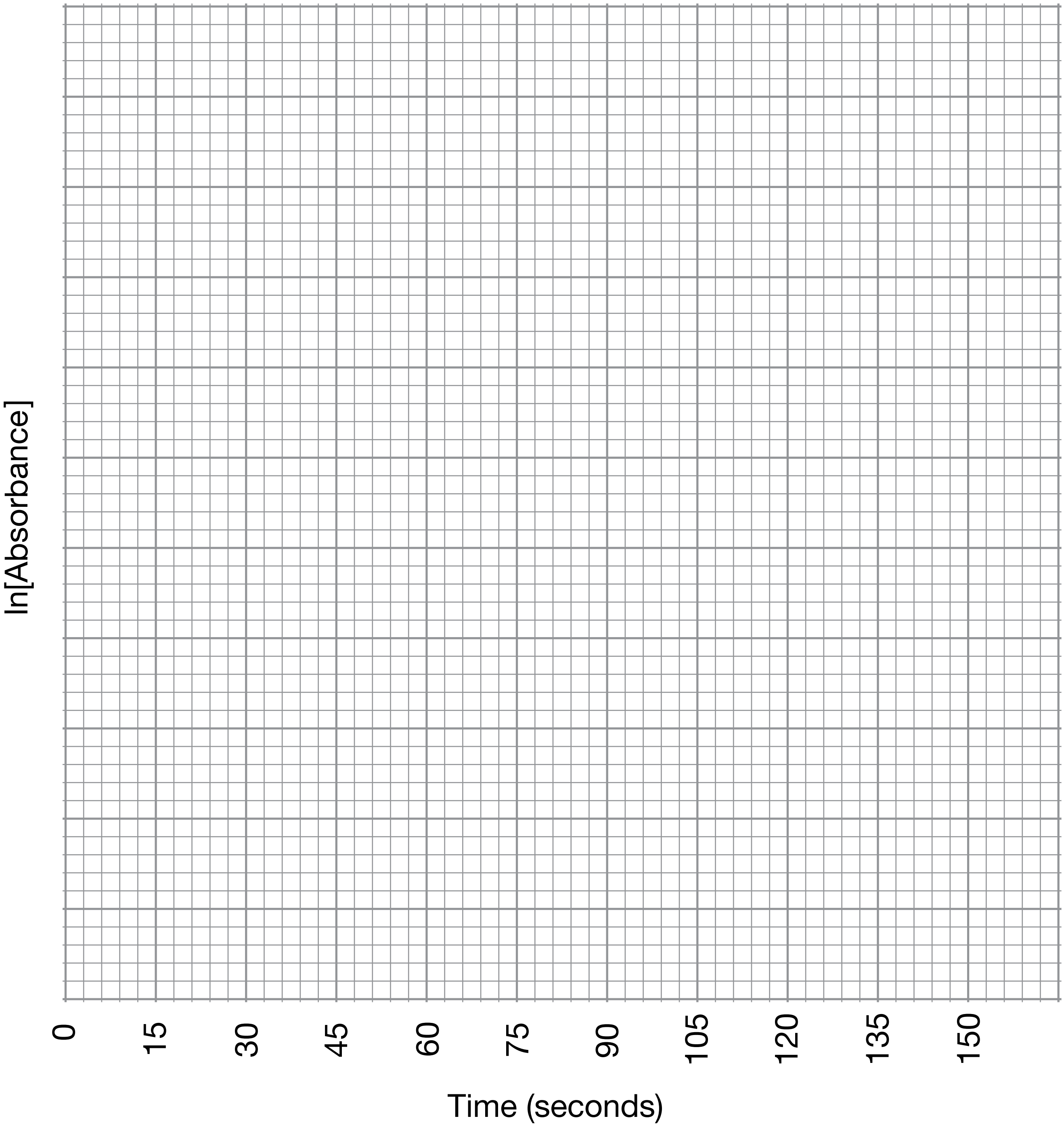
**1.** Using the rate constants determined from the other groups determine b, the order of the reaction with respect to the hypochlorite concentration.

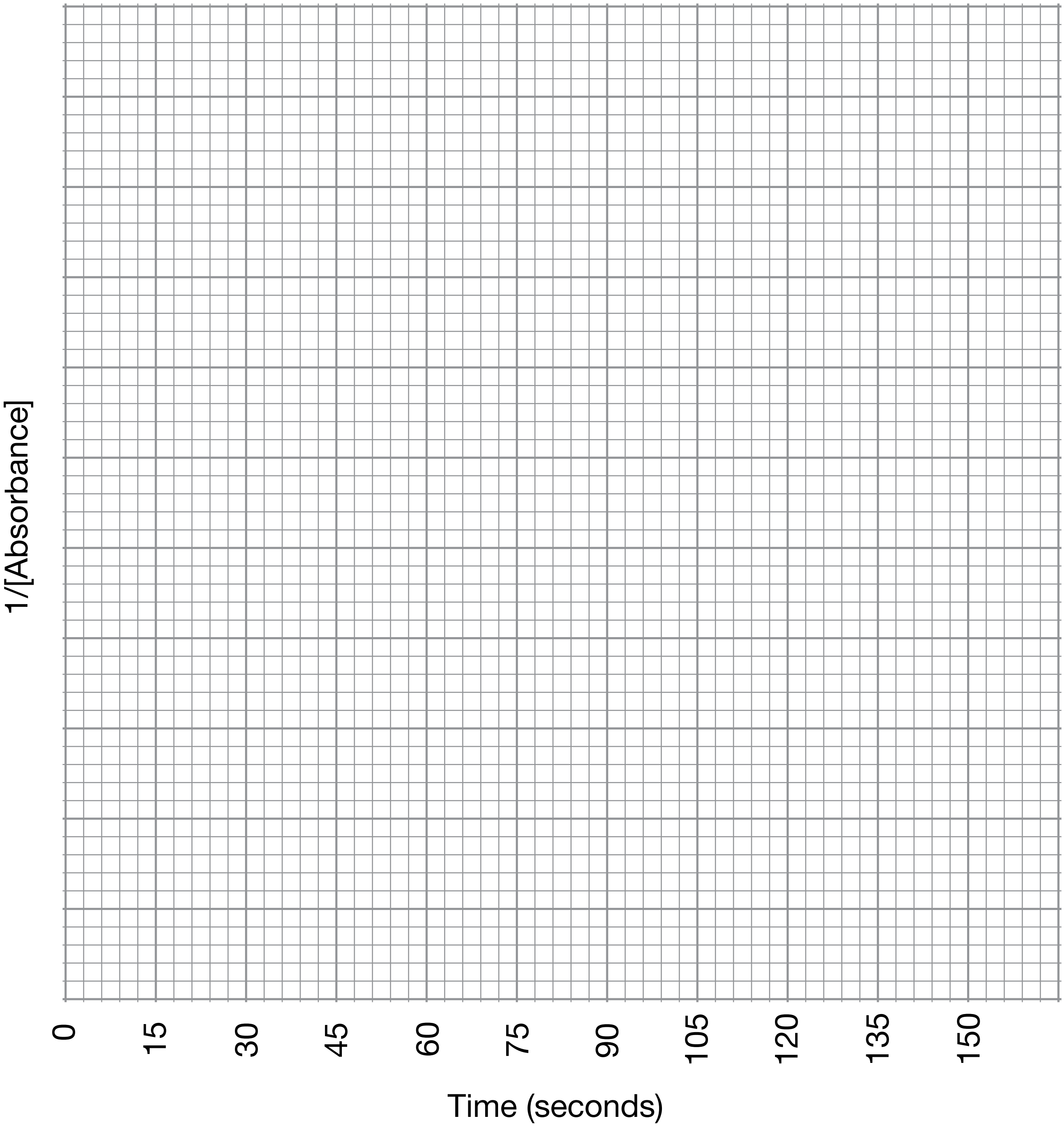
### Overall Rate Law

**Rate= k [Blue #1]$^a$ [OCl$^-$]$^b$**

a= ______________________ b= ______________________

Overall order = ______________________


ln[Absorbance]
0
15
30
45
60
75
90
105
120
135
150
Time (seconds)


1/[Absorbance]
0
15
30
45
60
75
90
105
120
135
150
Time (seconds)