

# Experiment 15

## *Iodine Clock*



## The Task

The goal of this experiment is to identify the rate-determining step in a complex reaction mechanism.

## Skills

At the end of the laboratory session you should be able to:

- determine the concentration dependence of the rate of a reaction via the method of initial rates;
- use a micropipette;
- determine the order of a reaction with respect to each reactant;
- Use Excel® to graph experimental data.

## Other outcomes

You will become familiar with the use of chemical kinetics as a research tool.

## The Assessment

You will be assessed on your use of the micropipette. See Skill 4.9.

## Introduction

Chemical kinetics concerns the rates of chemical reactions. Some reactions can occur within times as fast as nanoseconds, *e.g.* some proton transfers (*i.e.* acid-base reactions), whereas other reactions can occur on the timescale of months to years, *e.g.* a battery gradually running flat or a car turning into a heap of rust. The time scale over which a reaction occurs is completely independent of its energetics. Thus, a reaction producing a product of lower free energy will always occur spontaneously, but the energy change associated with the reaction tells you nothing about how long the reaction will take. To find this out, you simply have to start the reaction and measure its rate experimentally.

The study of chemical kinetics is of major importance in chemical research. It is a powerful research tool for determining the reaction mechanism, *i.e.* how a reaction proceeds. For example, the reaction mechanism of complex biological enzymes, such as the  $\text{Na}^+, \text{K}^+$ -ATPase, and mechanisms of metabolic pathways, such as glycolysis, have been solved by kinetic experiments. The information gained from such experiments is of great value in devising therapeutic strategies for treating disease conditions, *e.g.* diabetes and cardiovascular disease, to name just two.

The use of chemical kinetics to solve reaction mechanisms is predominantly based on the concentration dependence of the rate of reactions. The rate of any chemical reaction will depend on concentration simply because, if the concentration of a reactant is zero, there is nothing there to react and hence the rate would be zero. The whole theory of chemical kinetics is based on probability. Consider the simplest possible reaction,  $\text{A} \rightarrow \text{B}$ , in which reactant A spontaneously changes into product B. (Radioactive decay is a typical example.) The rate of this reaction,  $v$ , is defined as the rate of change of the concentration of the reactant A or of the product B. For this simple reaction  $v$  is related mathematically to the concentration of A,  $[\text{A}]$ , by  $v = k[\text{A}]$ .  $[\text{A}]$  is simply a measure of the probability that a molecule of A is present in the volume of solution that you're measuring. As the concentration increases so does the probability that some A is present and hence the rate of reaction increases. The constant  $k$ , termed the rate constant, is a constant of proportionality and is equal to the rate that the reaction would have if the concentration of A were 1 M. The value of  $k$  depends on the chemical nature of A and on the experimental conditions, *e.g.* temperature and pressure.

Now let us consider a slightly more complicated reaction,  $\text{A} + \text{B} \rightarrow \text{C}$ . For this reaction, a molecule of A and a molecule of B must meet or collide with one another to react and form C. Therefore, again based on probability, the rate of the reaction must be proportional to the probability of finding a molecule of A and a molecule of B in the same unit volume at the same time, which is given by the probability of finding a molecule of A multiplied by the probability of finding a molecule of B (just like the probability of two heads when tossing coins is  $\frac{1}{2} \times \frac{1}{2}$ ). Using concentration again as a measure of the probability of finding a molecule, the rate of this reaction is given by  $v = k[\text{A}][\text{B}]$ . As in the previous example  $k$  is the rate the reaction would have if A and B were both present at a concentration of 1 M. Following the same logic, it is simple to show that for a reaction  $2\text{A} \rightarrow \text{B}$  (*i.e.*  $\text{A} + \text{A} \rightarrow \text{B}$ ), the rate would be given by  $v = k[\text{A}]^2$ .

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Many reactions, however, proceed in a number of small steps. Let us consider the hypothetical composite reaction  $2A + B \rightarrow D$ . Of the many possible ways this reaction might occur, two are given below:

mechanism (1)  $A + A \rightarrow C$ , followed rapidly by  $C + B \rightarrow D$ , or

mechanism (2)  $A + B \rightarrow C$ , followed rapidly by  $C + A \rightarrow D$

To determine which of these two possible mechanisms is operating, one could carry out kinetic experiments on the dependence of the rate of formation of D on the concentrations of the reactants A and B. Because in each mechanism the first step is much slower than the second step, it will be a “bottleneck” and totally determine the rate of formation of D. Under these conditions the rate of formation of D,  $v$ , for the two mechanisms would be given by:

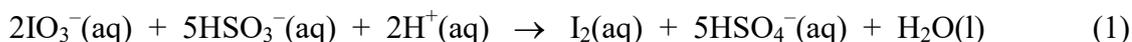
rate of formation of D *via* mechanism (1):  $v = k[A]^2$ , or

rate of formation of D *via* mechanism (2):  $v = k[A][B]$ .

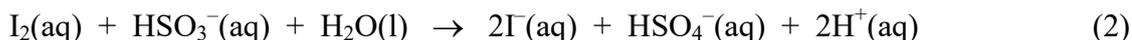
Therefore, measurements of the rate of the reaction at different concentrations of A and B would allow one to distinguish easily between the two mechanisms. If the rate depended on the square of the concentration of A and not at all on the concentration of B, this would support mechanism (1). If the rate of the reaction were directly proportional to the concentrations of both A and B, this would support mechanism (2). If the reaction rate does not conform to either of these relationships, then some other mechanism must apply. This is a simple example of how kinetics research can be used to determine how a reaction occurs.

### *Iodine Clock Reaction*

The iodine clock reaction was discovered by the Swiss chemist Hans Heinrich Landolt in 1886. There are a number of variations of it, but all of them involve the mixing of two colourless solutions. Initially there is no visible reaction, but after a certain period of time the mixed solution suddenly turns dark blue. In this experiment you will study the iodate variation of the iodine clock reaction, which involves the reaction between iodate ions,  $\text{IO}_3^-$ , hydrogensulfite ions,  $\text{HSO}_3^-$ , and hydronium ions,  $\text{H}^+$ . The stoichiometry of the **overall** reaction is as follows:



If the solution contains starch, it will react with  $\text{I}_2$ , the elemental iodine produced by the reaction, and form a blue starch-iodine complex. But why doesn't the blue colour appear immediately? The trick is that as soon as any  $\text{I}_2$  is formed, it immediately reacts with any  $\text{HSO}_3^-$  still present and is converted into colourless  $\text{I}^-$ :



Thus, reaction (2) efficiently removes any  $\text{I}_2$  produced by reaction (1). Only after **all** of the  $\text{HSO}_3^-$  has been consumed by reactions (1) and (2) will the  $\text{I}_2$  concentration increase and its reaction with the starch begin. This not only explains the sudden appearance of the blue colour, but it also allows us to determine the rate of the reaction. A measure of the rate of  $\text{HSO}_3^-$  consumption can be made by dividing the initial concentration of  $\text{HSO}_3^-$  by  $t$ , the time it takes for the blue colour to appear,  $[\text{HSO}_3^-]_0/t$ .

Now, here is the problem for you to consider in this experiment. Does reaction (1) occur in a single step? To answer this question you need to consider the following:

If reaction (1) were a single-step reaction, how would you expect the overall rate to depend on the concentrations of the reactants  $\text{IO}_3^-$ ,  $\text{HSO}_3^-$  and  $\text{H}^+$ ?

This question demonstrates a fundamental principle of kinetic research. Solving reaction mechanisms always involves making a theoretical prediction and then doing experiments to test your prediction. If the prediction turns out to be wrong, then you must modify your mechanism and make a new prediction, until you have a mechanism that is consistent with the experimental result. A word of warning, however; consistency doesn't necessarily mean a mechanism is right, simply that it agrees with the data currently available. Further experiments could still prove it to be wrong.

## Safety

### *Chemical Hazard Identification*

**0.20 M sodium hydrogensulfite solution** – non-hazardous.

**0.20 M sodium iodate solution** – non-hazardous.

**starch** – non-hazardous.

**hydrochloric acid (0.004 M - 0.006 M)** – non-hazardous.

### *Risk Assessment and Control*

Minimal risk.

Take care so as not to break the micropipettes. Do not wind them above a setting of 1000  $\mu\text{L}$  nor below 100  $\mu\text{L}$ .

### *Waste Disposal*

All solutions in this experiment can be washed down the sink.

The plastic micropipette tips should be thrown in the rubbish bin at the end of the experiment.

## Experimental

*This experiment is to be completed in pairs.*

### Part A Hypothesis Formation

Research in chemical kinetics requires a lot of care and thought. The meaning of experimental results may often not be immediately obvious. Therefore, the first step is to form a hypothesis of what behaviour you would expect for a particular mechanism. Reaction (1) in the Introduction describes the reaction you will be investigating. Based on the general information given to you in the Introduction about the way in which the rate of a chemical reaction depends on the concentration of species involved in the rate-determining step, try to answer the following questions in your logbook. If necessary, your demonstrator can give you some guidance.

***For your logbook:***

*If reaction (1) were a single- step reaction, how would you expect the overall rate to depend on the concentrations of the reactants  $\text{IO}_3^-$ ,  $\text{HSO}_3^-$  and  $\text{H}^+$ ?*

Since the iodine clock reaction involves the reaction of  $\text{IO}_3^-$  with  $\text{HSO}_3^-$  and  $\text{H}^+$ , the overall rate of the reaction can be written in the following form:

$$-d[\text{HSO}_3^-]/dt = v = k [\text{IO}_3^-]^x [\text{HSO}_3^-]^y [\text{H}^+]^z \quad (3)$$

Your goal is to determine the values of the exponents, x, y and z, and by comparing with your theoretical predictions from Part A, to determine if reaction (1) is a single step reaction. The exponents x, y and z are termed the *reaction order* with respect to each reactant. For example, for a reaction  $\text{A} + 2\text{B} \rightarrow \text{C}$ , for which the rate equation might be  $v = [\text{A}][\text{B}]^2$ , the reaction would be 1<sup>st</sup> order with respect to A, 2<sup>nd</sup> order with respect to B, and 3<sup>rd</sup> order overall.

If you vary two or more things simultaneously it is impossible to know what change is causing any of the differences that you observe. So, to determine how the reaction rate depends on  $[\text{HSO}_3^-]$ , it is important to vary  $[\text{HSO}_3^-]$  only and keep the concentrations of all of the other reactants constant.

## Part B Dependence of rate on $[\text{HSO}_3^-]$

Read Skill 4.1 on storage and transfer of stock solutions of known concentrations. The high level of precision needed for volumetric analysis is not required in this experiment, so a single rinse (rather than 3 rinses) with the stock solution is sufficient.

Read Skill 4.9 on the correct usage of the micropipette.

(B1) Collect two 250 mL beakers. Make sure they are clean by rinsing with tap water and drying them with paper towel. Label one  $\text{NaIO}_3$  and the other  $\text{NaHSO}_3$ .

(B2) Collect about 20 mL of the 0.20 M  $\text{NaIO}_3$  stock solution in a small labelled conical flask. Similarly collect about 20 mL of the 0.20 M  $\text{NaHSO}_3$  stock solution. These two reagents will be measured out using micropipettes. To avoid contamination, use a different pipette tip for each solution, alternating them as appropriate.

(B3) Now collect about 500 mL of the 0.006 M HCl stock solution in a labelled conical flask.

(B4) Construct a table in your logbook to record your results. It needs 4 columns, headed [HCl],  $\text{NaIO}_3/\text{mL}$ ,  $\text{NaHSO}_3/\text{mL}$  and time/s. (Including Parts C and D, you will be running 8 separate experiments, so leave enough room to record all your results.)

(B5) Use a measuring cylinder to transfer 50. mL of the HCl to each of the 2 dry beakers.

(B6) Add 1.0 mL of the 0.20 M  $\text{NaHSO}_3$  solution to the appropriately labelled beaker. Similarly, add 1.0 mL of the 0.20 M  $\text{NaIO}_3$  solution to the other beaker.

(B7) Dissolve a small amount of starch ( $\sim \frac{1}{4}$  Ni spatula) in the beaker containing  $\text{NaIO}_3$ .

(B8) With a stopwatch at the ready, take the beaker containing  $\text{NaIO}_3$  and pour it rapidly into the beaker containing  $\text{NaHSO}_3$ , mix well with a clean stirring rod and start the stopwatch. Measure the time,  $t$ , it takes for the appearance of the blue/black colour.

**Record your results in your logbook.**

(B9) Discard your reaction down the sink, rinse both beakers with tap water and dry them with paper towel, ready for the next experiment.

(B10) Repeat steps (B5) - (B9) using the following different volumes of 0.20 M  $\text{NaHSO}_3$  in (B6): 0.75 mL, 0.50 mL and 0.25 mL.

### ***For your logbook:***

*For each of your reactions calculate the final concentrations of  $\text{NaIO}_3$  and  $\text{NaHSO}_3$  after mixing.*

*You can assume that dilution of the HCl by the relatively small volumes of  $\text{NaIO}_3$  and  $\text{NaHSO}_3$  doesn't significantly change the  $[\text{H}^+]$  of the solution.*

*From your measured times for the appearance of the blue/black colour,  $t$ , and the initial  $[\text{HSO}_3^-]$ , calculate the rate of the reaction,  $v$ . Check with your Demonstrator that you're doing it correctly.*

*Construct a table in your logbook of  $[\text{HSO}_3^-]$ ,  $[\text{IO}_3^-]$ ,  $[\text{H}^+]$ ,  $t$  and  $v$ .*

### Part C Dependence of rate on $[\text{IO}_3^-]$

To determine how the reaction rate depends on  $[\text{IO}_3^-]$ , we now vary  $[\text{IO}_3^-]$  keeping the concentrations of all of the other reactants constant.

(C1) Rinse the beakers you used for Part B thoroughly with tap water and make sure that they're completely dry on the inside by wiping with a small amount of paper towel.

(C2) Repeat the experiment as in Part B, but with the following volumes of reagents:

HCl; 0.006 M, 50. mL in each beaker (You will need to replenish your stock.)

NaHSO<sub>3</sub>; 1.0 mL

NaIO<sub>3</sub>; varying volumes of 0.75 mL and 0.50 mL.

#### ***For your logbook:***

*For each of your reactions calculate the final concentrations of NaIO<sub>3</sub> and NaHSO<sub>3</sub> after mixing.*

*From your measured times for the appearance of the blue/black colour,  $t$ , and the initial  $[\text{HSO}_3^-]$ , calculate the rate of the reaction,  $v$ , as you did in Part B.*

*Construct a table in your logbook of  $[\text{IO}_3^-]$ ,  $[\text{HSO}_3^-]$ ,  $[\text{H}^+]$ ,  $t$  and  $v$ . In your table you can include one of your measurements from Part B, for which the initial  $\text{HSO}_3^-$  and  $\text{H}^+$  concentrations were the same as in this section.*

### Part D Dependence of rate on $[\text{H}^+]$

To determine how the reaction rate depends on  $[\text{H}^+]$ , we now vary  $[\text{H}^+]$  keeping the concentrations of all of the other reactants constant. For this all we need to do is to take an HCl solution of a different concentration.

(D1) Collect about 120 mL of the other HCl stock solutions in appropriately labelled conical flasks.

(D2) Repeat the experiment as in Part B, but with the following volumes of reagents:

NaIO<sub>3</sub>; 1.0 mL

NaHSO<sub>3</sub>; 1.0 mL

HCl; 50. mL in each beaker. Use 0.005 M for one experiment and 0.004 M in the other.

#### ***For your logbook:***

*Calculate the final concentrations of NaIO<sub>3</sub> and NaHSO<sub>3</sub> after mixing.*

*From your measured times for the appearance of the blue/black colour,  $t$ , and the initial  $[\text{HSO}_3^-]$ , calculate the rate of the reaction,  $v$ , as you did in Parts B and C.*

*Construct a table in your logbook of  $[\text{IO}_3^-]$ ,  $[\text{HSO}_3^-]$ ,  $[\text{H}^+]$ ,  $t$  and  $v$ . In your table you can include one of your measurements from Part B, for which the initial  $\text{HSO}_3^-$  and  $\text{IO}_3^-$  concentrations were the same as in this Part.*

## Part E Data Analysis

Now comes the point where you compare your measured data to the predictions of your hypotheses from Part A. To determine the order of the reaction with respect to each of the reactants  $\text{IO}_3^-$ ,  $\text{HSO}_3^-$  and  $\text{H}^+$ , the simplest method is to take the logarithm of equation (3). This yields:

$$\log v = \log k + x \log[\text{IO}_3^-] + y \log[\text{HSO}_3^-] + z \log[\text{H}^+] \quad (4)$$

If two of the reactant concentrations have been held constant and only one varied, then equation (6) reduces to the equation for a straight line. For example, if only  $[\text{IO}_3^-]$  had been varied, then the equation would reduce to:

$$\log v = \text{constant} + x \log[\text{IO}_3^-] \quad (5)$$

Therefore, for a set of data in which only  $[\text{IO}_3^-]$  had been varied, a plot of  $\log v$  versus  $\log[\text{IO}_3^-]$  should yield a straight line, and the slope of the line,  $x$ , will equal the order of the reaction with respect to  $\text{IO}_3^-$ .

Take your logbook containing all your experimental results to the computer room at the back of either Lab A or Lab B. Use Excel\* to graph  $\log v$  (y-axis) against  $\log[\text{IO}_3^-]$  (x-axis). Include a linear line of best fit and its equation. Hence determine the slope of the line and the order of the reaction with respect to  $\text{IO}_3^-$ . Print the worksheet and paste into your log book. Repeat to determine the order of the reaction with respect to  $\text{HSO}_3^-$  and  $\text{H}^+$ .

\*Instructions for using Excel can be found in Appendix 5.1 on page E5-10.

### ***For your logbook:***

*Compare your orders of reaction to those predicted if reaction (1) is a single step reaction.*

## Group Discussion

Did you all come to the same conclusion concerning the order of the reaction with respect to  $\text{IO}_3^-$ ,  $\text{HSO}_3^-$  and  $\text{H}^+$ ?

Based on your results, do you think that reaction (1) occurs as a single step?

If not, which species do you think are involved in the rate-determining step?

## Appendix 15.1

The following instructions are for Excel2007.

Start a new worksheet and give it a title.

Construct a table with the following headings in cells A5 to E5:

[HSO<sub>3</sub><sup>-</sup>], t, v, log[HSO<sub>3</sub><sup>-</sup>], log v.

Give the table an appropriate heading (in cell A4).

*e.g.* Part B, [HCl] = 0.006 M, [IO<sub>3</sub><sup>-</sup>] = 0.002 M

Complete the entries for [HSO<sub>3</sub><sup>-</sup>], t and v. You should have 4 sets of data which will occupy cells A6 through C9.

In cell D6, enter **=log10(A6)**

In cell E6, enter **=log10(C6)**

Fill down to complete the table. (Use the cursor to highlight both cells D6 and E6. Move the cursor so that it is over the small solid square at the bottom right of cell E6. The cursor will change shape to a small + sign. Now either double-click or click and hold and pull the cursor down to the bottom of the table.)

We now need to graph the data in the last 2 columns. Click the Insert tab.

Select cells D5 to E9. (Either use the cursor or click in D5 then press shift and click in E9.)

Select “Scatter with smooth lines with markers” from the range of charts shown.

Place the cursor on the line linking 2 of the data points and right click.

Select “Add trendline”. Select “Linear” from the Trendline Options and check the box near the bottom which says “Display equation on chart”. Click “Close”.

An equation of the form  $y = mx + b$  will be displayed somewhere on the chart. Use the cursor to pull it to the far right where it is not overlapping any of the other data.

The value of m in the above equation is the slope of the line, *i.e.* the order of the reaction with respect to HSO<sub>3</sub><sup>-</sup>.

We now need to print the worksheet.

Make sure you do a Print Preview, so that you know that what you’re about to print is the right size, is what you want, *etc.* Depending how you’ve set out the worksheet, you may need to use the cursor to highlight just a portion of the worksheet and then use the “Print Selection” option.

Repeat the whole process to determine the order of the reaction with respect to IO<sub>3</sub><sup>-</sup> and H<sup>+</sup>.