15. Determination of the order of the reaction between hydrogen peroxide and iodide ions in the presence of sulphuric acid

Student Sheet

Intended lesson outcomes

By the end of this exercise you should be able to:

- measure liquid volumes using a burette
- use a stopclock
- adapt an experiment to measure the effect of a different variable
- analyse data graphically
- deduce rate orders, write a rate equation and calculate a value for the rate constant

Background information

The rate of formation of iodine in the reaction:

$$H_2O_2(aq) \ + \ 2I^-(aq) \ + \ 2H^+(aq) \ \rightarrow \ 2H_2O(l) \ + \ I_2(aq)$$

is given by:

$$\text{rate} = k[H_2O_2]^{\mathbf{a}}[I^-]^{\mathbf{b}}[H^+]^{\mathbf{c}}$$

where k is a constant at a given temperature and **a**, **b**, **c** represent the order of reaction with respect to the three reactants.

In the presence of sodium thiosulphate, the iodine liberated in the above reaction reacts with the sodium thiosulphate until no more sodium thiosulphate remains. As excess iodine forms, the solution becomes coloured. By adding a few drops of starch, the iodine is shown up more clearly as it forms a blue complex.

The initial rate for the above reaction is determined by allowing the reaction to proceed in the presence of a known, small amount of sodium thiosulphate. The time interval that elapses before this is used up, i.e. before excess iodine appears is measured. The reciprocal of this time (1/t) is used as a measure of the initial rate of reaction.

Note: This method of determining the initial rate assumes that the actual rate does not vary over this period of time. This is not strictly true, but the error in the initial rate measurement is unlikely to be significant.

The rate order with respect to individual components may be deduced from a graph of the initial reaction rate vs. the concentration of the component under investigation. If the rate order with respect to that component is zero, then the rate of reaction will be independent of the concentration of that component and a graph of rate vs. concentration will be a horizontal straight line. If the rate order is one, the rate vs. concentration graph will be straight, sloping and will pass through the origin. For rate orders higher than one, the rate vs. concentration graph, while still passing through the origin, would be curved, and a more complex graph would have to be drawn to determine the actual rate order.

Safety

MSDS sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident.

	You must wear eye protection throughout this experiment
	Hydrogen peroxide and sulphuric acid are **corrosive.**

Procedure

Experiment 1

1. Using burettes, measure out 10.0 cm^3 aqueous potassium iodide and 10.0 cm^3 of dilute sulphuric acid into a small conical flask; then add to this mixture 3-4 drops of starch.
2. Using burettes, measure out 3.0 cm^3 of aqueous sodium thiosulphate and 1.0 cm^3 of hydrogen peroxide into a test tube.
3. Add the contents of the test tube to the conical flask, start the stopclock immediately while swirling the contents of the flask.
4. Measure the time that elapses before a blue colour appears.
5. Record your result in the table.
6. Repeat the experiment, but using 8.0 cm^3, 6.0 cm^3, 4.0 cm^3 and 2.0 cm^3 of potassium iodide, and adding deionised water to keep the total volume constant throughout.
7. Complete the table by calculating the values for 1/t.

tube	volume of H_2O_2 / cm^3	volume of H_2SO_4 / cm^3	volume of KI / cm^3	volume of $Na_2S_2O_3$ / cm^3	volume of water / cm^3	time t / s	'rate' 1/t / s^{-1}
1	1.0	10.0	10.0	3.0	4.0		
2	1.0	10.0	8.0	3.0	6.0		
3	1.0	10.0	6.0	3.0	8.0		
4	1.0	10.0	4.0	3.0	10.0		
5	1.0	10.0	2.0	3.0	12.0		

Experiment 2

Repeat Experiment 1, but this time vary the volume of sulphuric acid by using 8.0 cm^3, 6.0 cm^3, 4.0 cm^3 and 2.0 cm^3 of acid, but keep the total volume constant by adding deionised/distilled water. Construct a suitable table for this experiment and use it to record your results. Complete your table by calculating the values for 1/t.

Note: Your **first** result from experiment **1** also forms part of this experiment.

Experiment 3

Repeat Experiment 1, but this time vary the volume of hydrogen peroxide by using 2.0 cm^3, 3.0 cm^3, 4.0 cm^3 and 5.0 cm^3 of the peroxide solution. As in experiment 1, keep the total volume constant by adding deionised/distilled water. Construct a suitable table for this experiment and use it to record your results. Complete your table by calculating the values for 1/t.

Note: Your **first** result from experiment **1** also forms part of this experiment.

Interpretation

You are now going to interpret your results graphically. You will use your values for the reciprocal of time, 1/t, as a measure of the rate of reaction, and the volume of the independent variable as a measure of its concentration.

1 Plot separate graphs of rate vs. concentration (1/t vs. volume used) for each of the above experiments.
2 By considering the shape of each graph, deduce the rate order with respect to each component and hence find values for **a**, **b** and **c** in the rate expression.
3 Explain why it is acceptable to use volume rather than concentration data in your graphs.
4 Use your data from tube 1, Experiment 1, and your rate expression from point 2, to deduce the value of the rate constant, *k*.
5 Identify any limitations of your experiment and suggest ways of overcoming them.

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Teachers' Notes

Students should be instructed to prepare each mixture only when it is required. Once a reaction is complete, the conical flasks must be washed thoroughly, otherwise contamination left behind in a flask may cause a subsequent experiment to start prematurely.

If preferred, the hydrogen peroxide could be measured out into a test tube and added quickly, with the clock being started simultaneously, rather than using a burette. Doing it this way will ensure easier access to the communal supply of hydrogen peroxide, as the time of collection will not be so critical.

The iodine produced by the reaction below, reacts immediately with the thiosulphate ions, $S_2O_3^{2-}$, present in each mixture.

$$H_2O_2(aq) \ + \ 2I^-(aq) \ + \ 2H^+(aq) \ \rightarrow \ 2H_2O(l) \ + \ I_2(aq)$$

$$I_2(aq) \ + \ 2S_2O_4^{2-}(aq) \ \rightarrow \ S_4O_6^{2-}(aq) \ + \ 2I^-(aq)$$

Only when all the thiosulphate ions are removed, will an excess of iodine accumulate, resulting in the deep blue colour of the starch/iodine complex being formed. The blue colour develops rapidly; this is the endpoint of the reaction.

It is vital that the same amount of sodium thiosulphate is present each time. Great emphasis should be placed on accurate burette use, especially with regard to measuring the sodium thiosulphate solution.

Interpretation answers

3 The initial concentration, *c*, of a given component in a reaction mixture is given by

$$c \ = \ \frac{\text{volume of solution of that component } (vol)}{\text{total solution volume}} \ = \ \frac{vol}{28}$$

i.e. $c \propto vol$

4 The value of the rate constant, *k*, could be used as a measure of experimental accuracy. Rather than comparing the results obtained by the students with a book value (which will be temperature dependent anyway), it would be better to use the value obtained from the teacher's trial. This would have the advantage of compensating for any inaccuracies there might be in solution concentrations.

5 Suggested potential sources of error, and their remedies, should be sensible, specific and supported by sound argument.

This exercise is appropriately called the '*iodine clock experiment*'. With care, it is possible to achieve remarkably consistent and accurate results. At the conclusion of the exercise, you may wish to randomly choose a time, in seconds, and challenge your students to deduce the recipe for a solution, which would turn blue at this specified time. This will help develop their planning skills under time pressure. The ensuing race, in which each student/group mixes their reagent on your command, can be quite entertaining. It is likely that the winner will be within a second or two of your selected time.

Materials (per student)

- Thermometer (range –10 °C to +110 °C)
- Communal burettes for chemicals (1) to (5)
- New test tubes for hydrogen peroxide
- Stopclock

- 150 cm^3 of 0.50 mol dm^{-3} sulphuric acid
- 120 cm^3 of 0.10 mol dm^{-3} potassium iodide
- 50 cm^3 of 0.010 mol dm^{-3} sodium thiosulphate
- 30 cm^3 of 2.0 volume hydrogen peroxide
- Deionised/distilled water
- Fresh starch solution (0.5 g in 25 cm^3 H_2O)

Test solutions

10.0 cm^3 potassium iodide
10.0 cm^3 sulphuric acid
3.0 cm^3 sodium thiosulphate
1.0 cm^3 hydrogen peroxide

30–40 seconds

Safety

The main points are included on the Student Sheet but it is the teacher's responsibility to ensure that a full risk assessment is carried out prior to the practical session. MSDS sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident.