

To study

The relationship between the concentration of a reactant and the rate of reaction with respect to that reactant can be shown using **rate-time** graphs.



To discuss

Rate cannot be directly measured, so instead chemists often measure the concentration of a reactant or volume of gaseous product as the reaction progresses.

Look at the graphs below. They are the **concentration-time** graphs for two different chemical reactions. Study each graph carefully and decide whether the rate is zero order, first order or second order.

Explain your decision.





Method 1 Using a conical flask and a balance

You are going to collect and analyse data to find the order of this reaction with respect to hydrochloric acid.

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(I)$

The calcium carbonate you will use is in the form of marble. Fairly large pieces are used so that the surface area does not change significantly during the reaction. However, the quantity and concentration of hydrochloric acid is such that it is almost all used up during the reaction.

Wear eye protection

- **1** Put the following items on a top-pan balance:
- small conical flask containing about 10 g of marble in six or seven lumps.
- measuring cylinder containing 20 cm³ of 1 M hydrochloric acid.
- plug of cotton wool for the top of the conical flask.

2 Pour the acid into the conical flask, plug the top with the cotton wool, and put the measuring cylinder back on the balance pan.

3 Allow a few seconds to pass so that the solution is saturated with carbon dioxide. Then start timing and taking mass readings. Record the total mass of the whole reaction mixture and apparatus (m) at intervals of 10 seconds at the start, increasing to 30 seconds, until the reaction is over and the mass no longer changes. Record the final mass (m_{final}) .

Record your results in a table like the one below.

Time <i>t</i> /s	Total mass m _t /g	$m_{\rm t}-m_{\rm final}/{\rm g}$	

4 When the reaction is over, the total mass of carbon dioxide evolved and lost to the atmosphere can be found by subtracting m_{final} from m_{t} at time = 0 s. This is proportional to the concentration of the hydrochloric acid at the moment when timing started. So $(m_{\text{t}} - m_{\text{final}})$ is proportional to the concentration of hydrochloric acid at each time *t*. Complete the third column.

5 Plot a graph of $(m_t - m_{final})$ against *t*, putting *t* on the horizontal axis.

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The effect of concentration on rate – Student sheet

Method 2 Using a side-arm test tube and a gas syringe

You are going to collect and analyse data to find the order of this reaction with respect to hydrochloric acid.

 $CaCO_3(s) + 2HCI(aq) \rightarrow CaCI_2(aq) + CO_2(g) + H_2O(I)$

The calcium carbonate you will use is in the form of marble. Fairly large pieces are used so that the surface area does not change significantly during the reaction. However, the quantity and concentration of hydrochloric acid is such that it is almost all used up during the reaction.

Wear eye protection

Take care with the gas syringe

1 Set up the apparatus as shown in the diagram.

2 Place about 10 g of marble in six or seven lumps in the test tube.

3 Use a measuring cylinder to measure 10 cm³ of 1 M hydrochloric acid.

4 Put the acid into the test tube. Allow a few seconds for the solution to become saturated with carbon dioxide. Put the stopper in place and start timing.

5 Take readings of volume (V_t) every 30 seconds, until the reaction is over and the volume no longer changes. Record the final volume as well.

Record your results in a table like the one below.

Time t/s	Volume of $CO_2 V_t/cm^3$	$V_{\rm final} - V_{\rm t}/{\rm cm}^3$

6 When the reaction is over, the total volume of carbon dioxide collected (V_{final}) is proportional to the concentration of the hydrochloric acid at the moment when timing started. So ($V_{\text{final}} - V_t$) is proportional to the concentration of hydrochloric acid at each time *t*. Complete the third column.

7 Plot a graph of $(V_{\text{final}} - V_t)$ against *t*, putting *t* on the horizontal axis.







Methods 1 and 2

To discuss

- Are there any anomalous results in your data (outliers)?
- Are you satisfied with the validity of the data you have collected?
- If you think it necessary, repeat the procedure to give you a second set of readings.

To answer

1 Describe in words how the rate changes as the concentration of the hydrochloric acid changes.

2 Compare the shape of your graph with the shapes of the three graphs below.



Is the reaction of calcium carbonate with hydrochloric acid zero order, first order, or second order with respect to hydrochloric acid?³ Is the evidence sufficient for you to draw a firm conclusion? (You can use evidence from others in your class too if necessary.)

4 Write a rate equation for the reaction.

5 Draw and complete a table, like the one below, to compare collision theory and rate equations as models for the rate of a reaction.

Collision theory	Rate equation



Card sort

To do

Cut out the cards below and arrange into three groups; zero order, first order and second order reactions.



Nuffield Practical Work for Learning: Model-based Inquiry • The effect of concentration on rate • Student sheet © Nuffield Foundation 2013 • downloaded from www.nuffieldfoundation.org



The effect of concentration on rate: Assessing learning

1 Label the following equation as fully as you can.

$$r_{A} = k[A]^{a}[B]^{b}$$

2 Information about the effect of changes of concentration on the rates of some reactions is given below. For each example, use the information to write the rate equation for the reaction.

a
$$CH_2 \longrightarrow CH_2(g) \longrightarrow CH_2CH=CH_2(g)$$

cyclopropene

The rate is proportional to the concentration of cyclopropene.

b $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$

The rate is proportional to the concentration of nitrogen(I) oxide.

c $H_2(g) + I_2(g) \rightarrow 2HI(g)$

The rate is proportional to the concentration of hydrogen and to the concentration of iodine.

d $2HI(g) \rightarrow H_2(g) + I_2(g)$

The rate is proportional to the square of the concentration of hydrogen iodide.

e $C_{12}H_{22}O_{11}(aq) + H_2O(I) \xrightarrow{H^+} 2C_6H_{12}O_6(aq)$

The rate is proportional to the concentration of sucrose and to the concentration of hydrogen ions.



3 Use the rate equation for the following reactions to write down the order of the reaction with respect to each of the reactants.

a The elimination of hydrogen bromide from bromoethane.

$$CH_2CH_2Br + OH^- \rightarrow CH_2 = CH_2 + Br^- + H_2O$$

Rate $_{(CH_3CH_2Br)} = k[CH_3CH_2Br]$

What would be the effect on the rate of doubling the concentration of hydroxide ions?

b One of the propagation steps in the radical substitution of an alkane by chlorine.

 $CH_3 \bullet + Cl_2 \rightarrow CH_3Cl + Cl^{\bullet}$

Rate $(CH_3^{\bullet}) = k[CH_3^{\bullet}][Cl_2]$

What would be the effect on the rate of doubling the concentration of the methyl radicals *and* the chlorine gas?

4 When hydrogen peroxide solution reacts with iodide ions in aqueous acid, iodine is liberated.

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

The following table gives some experimental results for the reaction.

Run	Initial reactant concentration / mol dm ⁻³		Initial rate of formation of I ₂	
	[H ₂ O ₂]	[17]	[H⁺]	/ mol dm ⁻³ s ⁻¹
1	0.010	0.010	0.10	1.75 x 10 ⁻⁶
2	0.020	0.010	0.10	3.50 x 10 ⁻⁶
3	0.030	0.010	0.10	5.25 x 10 ⁻⁶
4	0.030	0.020	0.10	1.05 x 10 ⁻⁵
5	0.030	0.020	0.20	1.05 x 10 ⁻⁵

a Use the results of runs 1, 2 and 3 to deduce the order of reaction with respect to $H_2O_2(aq)$. Explain how you arrived at your answer.

b Use the results of runs 3 and 4 to deduce the order of reaction with respect to I⁻(aq), giving an explanation as in part **a**.

c Use the results of runs 4 and 5 to deduce the order of reaction with respect to $H^+(aq)$, giving and explanation as before.

d What is the rate equation for the reaction?



Learning structure of the lesson

The big picture This lesson sequence is designed to exemplify a model-base practical work in which students evaluate collision theory a models for explaining rates of reactions. Understanding the rates of chemical reactions is important industry. In this lesson sequence students will evaluate collis predicting rates of reactions. They then collect data to deter reaction of calcium carbonate and hydrochloric acid, and deter They use the rate equation to make and istings.	Age range: 16–18 Timing: 1 h 40 min (If the lesson needs to be divided into two parts, a good place to break is just before students start the practical activity).	
Learning episode 1 (teacher-led) 10 mins Class discussion about why chemists study rates of reaction. Introduce learning outcomes for lessons. Learning episode 2 (student-led) 15 mins	Learning outcomes Students will be able to:	Equipment and materials Teacher guidance Practical guidance Slide presentation Interactive Student sheet
hydrochloric acid. This is followed by an activity in which students organise what they already know about rates of reaction.	evaluate different	Per class Eye protection
Introduce a mathematical model for describing rates of reaction and use the interactive to ensure students know how to find half life.	models for explaining the rates of reactions • use experimental data	Marble, acid washed chips, 0.5– 1 g each Hydrochloric acid (1 M), 50 cm ³ Beaker (250 cm ³) Stopclocks
Learning episode 4 (teacher-led) 25 mins Present the problem to students who then follow one of	to identify how the concentration of each	Per group/pair
two practical methods to find the order of the reaction between calcium carbonate and hydrochloric acid. Learning episode 5 (teacher-led) 15 mins Students analyse the collected data to find the order of reaction and write the rate equation for the reaction.	reactant affects the rate of a reaction	Hydrochloric acid (1 M), 20 cm ³ Cotton wool Measuring cylinder (25 cm ³) Conical flask (100 cm ³) Balance to weigh to +/- 0.001 g or Hydrochloric acid (1 M), 10 cm ³ Measuring cylinder (10 cm ³)
Learning episode 6 (student-led) 15 mins The model is generalised and students see how they can write a rate equation for any reaction, given the relevent data. A card sort activity can be used to reinforce learning. Key words Rate equation, [A], order of reaction, k		Test tube with side arm, 150 x 25 mm, or equivalent Glass gas syringe (100 cm ³) Rubber stopper to fit test tube Rubber connecting tubing Refer to the health and safety advice and practical guidance



Prior knowledge

It is assumed that students know the following.

- The rate of a reaction can vary with changes in temperature, concentration, surface area, and with the presence of catalysts.
- Collisions are required for chemical reactions to take place and the rate depends on the number of successful collisions per second.

Background information

In a reaction of the type

 $xA + yB \rightarrow products$

the rate of change of concentration of substance A will be found by experiment to follow a mathematical expression of the form:

 $r_{A} = k[A]^{m}[B]^{n}$

An expression of this kind is called a rate equation. The terms in the equation are defined below.

Sometimes the rate equation includes the concentration of substances which do not appear as reactants in the chemical equation. These substances may be, for example, catalysts. Catalysts are not reactants but they do affect the rate.

Terminology

The terms which students need to understand and use in this lesson are:

rate equation – this is used to show how rate varies with concentration of reactants. It takes the form: rate = $k[A]^m[B]^n$.

[A] – the square brackets [] around substance A denote concentration of A in mol dm $^{-3}$.

order of reaction – the order of reaction is the power to which the concentration of a reactant is raised in the rate equation. If rate = $k[A]^m[B]^n$ the order of reaction with respect to A is m, and the order of reaction with respect to B is n. Any term raised to the power zero equals 1, so for a zero order reaction, rate = $k[A]^0 = k$.

k – a constant of proportionality called the rate constant.

Differentiation

For students requiring additional support in recalling what they already know about the collision theory, the following table can be copied onto cards and cut out. These form the basis of an activity which could be used prior to the lesson or as a further starter.

There are six cards each featuring a different reaction. Place students in groups of three or four and give each group one or two cards. Ask them to explain what is going on as fully as possible using collision theory.



Sugar dissolves quicker in hot water than cold water	A lump of flour is difficult to catch alight but an explosion in a custard factory ripped the place apart
Magnesium reacts very slowly with cold water but extremely vigorously with steam	A jelly baby can be added to molten potassium chlorate and a violent reaction occurs. It is not safe to use sugar for this reaction.
Chlorine can be made by reacting concentrated hydrochloric acid with potassium manganate(VII), but the reaction is very slow with 1 mol dm ⁻³ acid	In the Haber process to make ammonia, the reaction is carried out at high pressures: $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

Students' explanations should include points such as:

- An increase in the concentration/pressure leads to an increase in the number of collisions. This leads to an increased chance of successful collisions taking place which will increase the rate of the reaction.
- An increase in temperature leads to an increase in both the number of collisions and the energy with which they collide. This leads to an increased chance of successful collisions taking place. Maxwell Boltzmann graphs could be used.
- An increase in particle size increases the number of collisions. This leads to an increased chance of successful collisions taking place which will increase the rate of the reaction.
- For the custard power factory see: www.guardian.co.uk/uk/2006/oct/22/schools.education
- For the jelly baby reaction see <u>www.cleapss.org.uk</u>. The sugar has a higher surface area and the reaction is so fast as to be unsafe. When the sugar is trapped in the jelly the reaction speed is slower and the reaction can be carried out safely in the laboratory.
- For the reaction between potassium manganate(VII) and glycerol see: <u>www.rsc.org/learn-chemistry/resource/res00000742/spontaneous-</u> <u>exothermic-reaction</u>

Optional extension activities

This lesson sequence is probably best followed up by giving students the opportunity to carry out another reaction to find the order, probably involving two reactants this time.

One possibility would be the kinetics of the reaction between iodine and propanone in acid solution. See Nuffield Advanced Chemistry Teachers' guide page 157 and student book page 249. Download this from the STEM centre elibrary: <u>http://stem.org.uk/cx36t</u>

The concept of the rate-determining step could be introduced, as could various methods for obtaining data for the study of reaction rates.



Lesson details – lesson 1







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Slide 4	Task: Ask students to organise their ideas into the three categories listed on slide 4 .
What you already know Organise what you know about the reaction of marble chips with hydrochloric acid into three categories. Practical techniques equipment and methods	They do not need to have something in every category. Where one idea falls into two categories, the content can be rewritten onto two pieces of paper.
Observations / data / summaries of data including from previous experimental work, e.g. graphs, or statements summarising a trend/pattern Explanations inferences, models, type of reaction, equations	Task: Get students to share some of their ideas with the class. Ensure that they all understand the difference between data and explanations.
Extensioner 202	
Slide 5	Optional: slide 5 'What is rate of reaction?' could be used at this point.
<text><text><text><text><text><text></text></text></text></text></text></text>	 Task: Students' explanations are likely to include models. Collision theory is a model for explaining rates of reaction. Draw together what students know about collision theory. Questions for discussion: Does the collision theory model have any limitations? What kind of predictions does it allow you to make? What kind of predictions can you not make? Differentiation: If students are having trouble identifying limitations, ask them to draw a graph predicting the volume of CO₂ gas produced by the reaction of marble with acid, against time. How accurately can they draw the graph? They will not be able to put numbers on the graph (even if they know the mass of marble and concentration of acid) and they do not know the exact gradient of the line at any point.
	Explain: Collision theory goes part of the way to explaining the effect of concentration on the rate of a reaction, but does not allow you to make quantitative predictions. That is, if you double the concentration, what happens to the rate: does it double? does it treble?

The effect of concentration on rate – Teacher guidance





The effect of concentration on rate – Teacher guidance









The effect of concentration on rate – Teacher guidance







Student sheet: Answers

1 The rate increases as the concentration of hydrochloric acid increases.

2 The graph is most similar to the first order graph. By calculating the half life it can be shown that it is indeed first order with respect to hydrochloric acid.

3 Answers will depend on the quality of the evidence collected.

4 No, it is not possible to predict the order of the reaction from the chemical equation. The order of reaction is an experimental quantity which must be measured.

5 The rate equation is: $r_{HCI} = k[HCI]$

Assessing learning: Answers

1 Diagram labelled with:

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r<sub>A</sub> = rate of reaction with respect to A
k = rate constant
[A] = concentration of A
[B] = concentration of B
n = order of reaction with respect to B
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2a Rate = k[cyclopropane(g)]

- **b** Rate = $k[N_2O(g)]$
- **c** Rate = $k[H_2(g)][I_2(g)]$
- **d** Rate = $k[HI(g)]^2$
- **e** Rate = $k[C_{12}H_{22}O_{11}][H^+]$

3a First order with respect to CH_3CH_2Br . Zero order with respect to OH^- .

Doubling the concentration of hydroxide ions would have no effect on the rate.

b First order with respect to CH_3 , first order with respect to Cl_2 .

Doubling the concentration of methyl radicals and the chlorine gas would increase the rate by four times.

4a First order with respect to H_2O_2 ; rate is doubled if $[H_2O_2]$ doubled, rate trebled if $[H_2O_2]$ trebled.

b First order with respect to I⁻; rate is doubled if [I⁻] doubled.



- **c** Zero order with respect to H^+ ; rate unchanged if $[H^+]$ doubled.
- **d** Rate = $k[H_2O_2][I^-]$



The teacher demonstration is used at the start of the lesson to remind students of the familiar reaction:

 $CaCO_{3}(s) + 2HCI(aq) \rightarrow CaCI_{2}(aq) + CO_{2}(g) + H_{2}O(I)$

In the class practical, students collect data to find the order of the reaction with respect to hydrochloric acid.

Students follow one of the two methods provided. Which one you use will depend on the apparatus available.

Equipment and materials

Teacher demonstration

Eye protection Marble, small acid washed chips, 0.5–1 g each, 10 g Hydrochloric acid (1 M), 50 cm³ Beaker (250 cm³)

Class practical: Method 1 Using a conical flask and a balance

Eye protection

per group/pair

Marble, acid washed chips, 1–1.5 g each, 10 g Hydrochloric acid (1 M), 20 cm³ Cotton wool Measuring cylinder (25 cm³) Conical flask (100 cm³) Balance to weigh to +/- 0.001 g Stopclock

Class practical: Method 2 Using a side-arm test tube and a gas syringe

Eye protection

per group/pair

Marble, as in method 1 Hydrochloric acid (1 M), 10 cm³ Measuring cylinder (10 cm³) Test tube with side arm, 150 x 25 mm, or equivalent Glass gas syringe (100 cm³) Rubber stopper to fit test tube Rubber connecting tubing Stopclock

Health and Safety and technical notes

Before carrying out this practical, users are reminded that it is their responsibility to carry out a risk assessment in accordance with their employer's requirements, making use of up-to-date information.

Read our standard health & safety guidance.

1 The marble chips should be washed briefly in dilute hydrochloric acid to remove any surface powder. They should then be rinsed in pure water and allowed to dry at room temperature.

2 Take great care handling the gas syringes.

Procedure

Demonstration

Wear eye protection

1 Add 50 cm³ of 1 M hydrochloric acid to a 250 cm³ beaker, and drop in a few marble chips. Students should observe the bubbles forming on the surface of the marble chips.

Class practical: Method 1 Using a conical flask and a balance

Wear eye protection.

1 Put the following items on the pan of a direct-reading, top-pan balance: small conical flask containing about 10 g of marble in six or seven lumps.

measuring cylinder containing 20 cm³ of 1 M hydrochloric acid.

plug of cotton wool for the top of the conical flask.

2 Adjust the balance so that it is ready to weigh all these items.

3 Pour the acid into the conical flask, plug the top with the cotton wool, and replace the measuring cylinder on the balance pan.

4 Allow a few seconds to pass so that the solution is saturated with carbon dioxide; then start timing and taking mass readings. Record in a table the mass of the whole reaction mixture and apparatus at intervals of 30 seconds until the reaction is over and the mass no longer changes.

5 Complete the table by carrying out the calculations as described in the Student sheet and plot a graph of the results.

Class practical: Method 2 Using a side-arm test tube and a gas syringe

Wear eye protection

1 Set up the apparatus as shown in the diagram.

2 Remove the stopper and place about 10 g of marble in six or seven lumps in the test tube.

3 Use a measuring cylinder to measure 10 cm³ of 1 M hydrochloric acid.

4 Put the acid into the test tube and allow a few seconds for the solution to become saturated with carbon dioxide. Then, replace the stopper and start timing.

5 Take readings of volume every 30 seconds until the reaction is over and the volume no longer changes. Record the results in a table.

Teaching notes

Fairly large pieces of marble are used so that the surface area does not change appreciably during the reaction.

On the other hand the hydrochloric acid is arranged to be in such quantity and concentration that it is almost all used up during the reaction.

For both Methods 1 and 2 it is important that the acid is saturated with



carbon dioxide before readings are begun.

In Method 2 the maximum volume of carbon dioxide obtainable from 10 cm^3 of 1 M hydrochloric acid is about 120 cm^3 . Therefore the timing must not be started too early or the syringe will be overfilled.

Sample results are shown below.





Method 2 Using a side-arm test tube and a gas syringe

