

Dr Iolo Wyn Williams and Roger G Hacker

Design for an experiment: An introduction to kinetics

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Although kinetics has been introduced into many elementary syllabuses, it can be argued that no fully satisfactory standard experiment has been published. As examples, consider the introductory experiments in the Nuffield 0-level course. The first of these demonstrates the influence of particle size on the reaction between marble and hydrochloric acid. 20 g of powdered marble react more rapidly than 20 g of marble chips with 40 cm³ 2 M hydrochloric acid. This is an admirable experiment and the difference is quite obvious by observation alone. The method suggested is to weigh the flask on a top-pan balance and plot the weight against time. This results in a typical rate curve, the rate falling off to zero as the acid is used up. This, again, is an admirable introduction to the many rate experiments which plot and interpret such a continuously changing rate, but it is not the simplest of situations. We would prefer a first experiment where the effect of a stepwise variation of concentration on rate is studied.

This is what happens in the second experiment, the reaction between sodium thiosulphate solution and hydrochloric acid, which we have always found reliable. Apart from the fact that it is a rather unusual reaction – which is not a serious criticism – our only doubt about this experiment concerns exactly what is being measured. Is it an induction period before the reaction starts, or the time taken for a certain amount of sulphur to be precipitated (which would not amount to the same fraction of the total reaction in each case since in some of the specified mixtures thiosulphate is in excess and acid in others), or even the rate of coagulation of a sulphur sol?

We have investigated an introductory quantitative experiment for class use which takes account of the following criteria.

- 1** The reaction to be studied should be familiar and the technique used should be as simple as possible and not distract attention from the basic chemistry. If possible, it would be desirable to study the effects of particle size, concentration, temperature and catalysis on the same reaction.
- 2** A technique which requires several quick, independent determinations rather than a series of consecutive recordings or a lengthy experiment with a single determination at the end of it has several advantages. Two or three practice determinations are possible, a good number of determinations for averaging may be obtained, a slip or a faulty determination do not invalidate the whole experiment and additional values may be obtained or points checked quickly.
- 3** The results should have some quantitative significance and should be capable of interpretation at different levels of sophistication.
- 4** Some of the approximations and assumptions made in the experiment should be apparent at a level which the pupil can comprehend so that a sensible discussion of errors is possible. The technique should be capable of refinement by the pupils to minimize these errors.

We decided to study the rates of reaction of metals, particularly magnesium, with acids. This seemed such an obvious choice that we were rather surprised to find no mention of it in the many text-books and practical physical chemistry books that we examined. Was it that any results which might be obtained had been found

to be complicated and difficult to interpret, or was it simply that the absence of kinetics from elementary syllabuses had resulted in a lack of interest? In the past, pure chemists have certainly devoted most of their attention to homogeneous reactions, and the heterogeneous reactions have been more the province of corrosion chemists who, in turn, have been more interested in slow reactions than in rapid ones.¹⁻⁴

After our preliminary experiments had shown that interesting results could be obtained, we did find an experiment described in the Australian *Approach to chemistry* series⁵. This suggested finding the rate of reaction of magnesium ribbon with hydrochloric acid ranging from 0.1 M to 1.0 M, and the variation of the rate of reaction of iron nails with 5 M hydrochloric acid over a temperature range of 25–55 °C. The technique suggested was to collect the hydrogen liberated in a test-tube over water and measure the time taken for 10 or 20 cm³ of hydrogen to be produced. But with a rapid flow of hydrogen the meniscus in the tube would be badly agitated and it would be difficult to time the reaction accurately.

We set out to determine whether we could get meaningful results by dropping a short length of magnesium ribbon into a large excess of acid in an open flask, and measuring the time taken for it to react completely. Some preliminary experiments were carried out to determine the most appropriate conditions.

Reaction conditions

In experiments to determine a suitable range of concentration, 3 cm of magnesium ribbon were found to react with 2 M hydrochloric acid in about 12 s, with 1 M acid in about 1 min and with 0.5 M acid in about 4 min. Reactions much slower than this were not considered suitable for a class experiment. Using acid of about 1.2 M, the reaction time was found to vary from 66 s at 12 °C to 16 s at 45 °C, showing that an experiment to study temperature-dependence would be possible, preferably at a slightly lower concentration.

Table 1. Effect of acid volume on rate of magnesium–HCl (0.7 M) reaction

Volume (cm ³)	10	20	30	40	50	70	100
Reaction time (s)	270	190	181	170	165	164	163
Temperature rise (°C)	8.0	5.6	4.2	3.6	3.1	2.2	1.9

Using different volumes of 0.7 M acid the results shown in Table 1 were obtained. 3 cm of magnesium ribbon weigh about 0.03 g, nearly 0.001 mol, and will react with 0.002 mol of acid, equivalent to 2 cm³ of 1 M or 2.9 cm³ of 0.7 M acid. Both the temperature effect and the change in concentration during reaction could be minimized by using large volumes but in the interests of economy and on the basis of Table 1 we chose to use 50 cm³ of acid. With the weakest hydrochloric acid used, 0.5 M, there would be an overall change in concentration during a reaction of 8 per cent, or an average change of 4 per cent – within acceptable limits for an experiment of this sort.

It is worth asking a class to predict the effect on reaction time of doubling the amount of metal used before trying it out. We found that, using 50 cm³ 1 M acid and changing the amount of ribbon from 3 cm to 6 cm resulted in a difference of only 2 s in 50 s. (It may be fortuitous that the increased rise in temperature is balanced by greater dilution of the acid.) We conclude that there is no need to have an exact length but suggest 3 cm of ribbon is an appropriate length.

We examined the influence of stirring by determining the reaction time under various shaking and stirring conditions for two concentrations of acid. Results are given in Table 2 on page 3.

Table 2. Effect of agitation on rate of magnesium–HCl reaction

	0.6 M HCl	1.4 M HCl
No stirring	166 s	35 s
Gentle swilling of the acid	154	32
Swilling with some shaking	144	30
Stirring with a glass rod	145	30
Very vigorous shaking	140	29

A standard technique of swilling the acid in 100 cm³ wide-necked conical flasks with occasional shaking was adopted and gave very reproducible results within limits shown in Table 3. Nevertheless, this effect could be a limiting factor in a class experiment and results at slow reaction rates could be quite divergent.

Table 3. Reproducibility of results

Reaction time (s)	10–20	20–40	40–80	80–160	160–300
Reproducibility (s)	0.5	1	2	5	10

We compared the rate of reaction of fairly clean ribbon from a fresh supply, old and badly corroded ribbon, ribbon previously cleaned by immersion in dilute nitric acid and ribbon cleaned with steel wool. There was surprisingly little difference between them and so we used new ribbon, untreated.

A few experiments testing the effect of added sodium and magnesium chlorides indicated that high concentrations of added salt slow down the reaction considerably. There is other evidence⁶ that small concentrations of added sodium chloride increase the rate of reaction, and it is well known that sodium chloride solution alone is highly corrosive to magnesium, far more so than solutions of nitrates or sulphates. A more detailed study of the effect of added salts would be a worthwhile extension to this work.

Results

In figure 1 on page 4 the rate of reaction, taken as the reciprocal of the reaction time, is plotted against both the concentration and the square of the concentration. Instinctively one expects the rate to be proportional to the concentration, so that the curvature is a bit of a disappointment and it comes as a pleasant surprise to find a linear dependence on the square.

The experiment was repeated with nitric and sulphuric acids. The rate with nitric acid is considerably slower than with hydrochloric, but otherwise the results give a similar concentration dependence. The results are given in Table 4 on page 7 so that they may be checked at will, or used as an exercise.

Using sulphuric acid a rather surprising result was obtained. In the first instance we used acid of 0.5 M–1.5 M (or 1.0 M–3.0 M in hydrogen ion, neglecting partial ionization for the moment). The relevant part of figure 2 shows that there is a linear dependence on concentration rather than on the square of the concentration, suggesting that some different mechanism is operating even though the rate of dissolution of magnesium is entirely within the range encountered in the HCl experiment. The range of concentrations was therefore extended and, since in one or two cases the acid was more dilute, the whole series was repeated using 100 cm³ acid in each case. As before, the timing at each concentration represents the mean of at least three determinations.

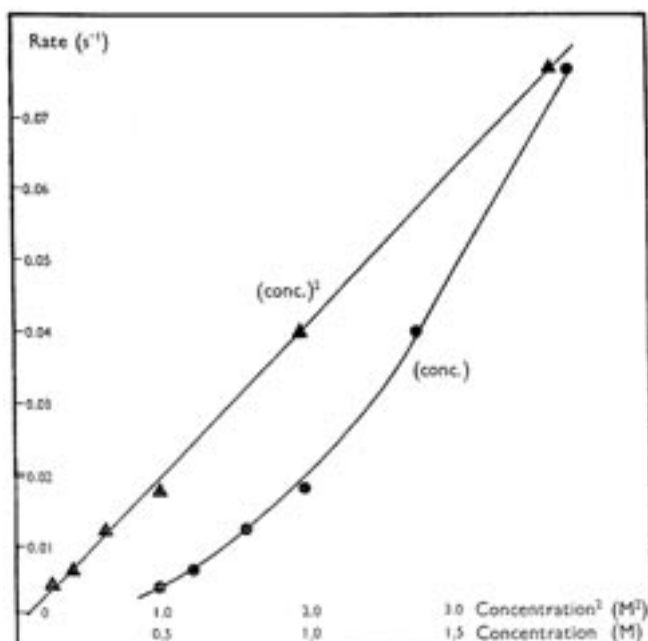


Figure 1 Rate of reaction plotted against concentration for magnesium in hydrochloric acid at 21.4 °C.

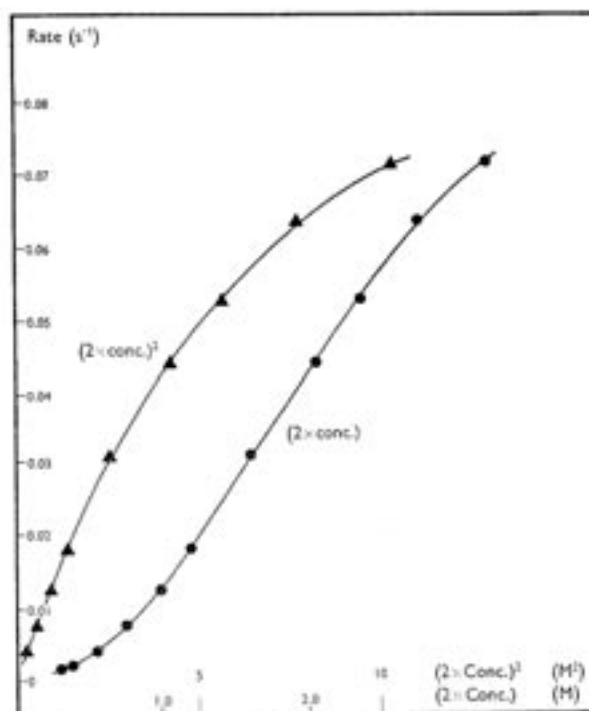


Figure 2. Rate of reaction plotted against concentration and the square of concentration for magnesium in sulphuric acid at 19.6 °C.

In figure 2 it will be seen that the rate is proportional to the square of the concentration in dilute solutions but proportional to the concentration in the more concentrated solutions (excluding the uppermost point which falls off a straight line). In this situation a slightly more sophisticated treatment yields more information. From the basic rate equation;

$$\text{rate} = k \times (\text{concentration})^n$$

where k is the rate constant and n the order of the reaction, by taking the logarithm of both sides:

$$\log(\text{rate}) = \log k + n \log(\text{concentration})$$

A graph of log rate against log concentration will give a straight line so long as the order of the reaction remains constant and the slope of the graph will be equal to the order. Figure 3 on the next page is the log–log plot for both hydrochloric and sulphuric acids. The slope of both straight lines is about 2, but in sulphuric acid the points deviate from the line at high rates and it is not possible to draw any one line through them with any confidence. Thus a graph such as figure 2 can be misleading.

Two points must be raised here. The first concerns the use of concentrations rather than activities in what are, by thermodynamic standards, quite concentrated solutions. Activities are normally invoked when the use of concentrations fails to give satisfactory results, *e.g.* in equilibrium constants, but in the present circumstances the use of concentrations appears to give perfectly straightforward results, *e.g.* the straight line plots obtained for the HCl reactions in figures 1 and 3. If the log–log plot for HCl (figure 3) is drawn in terms of activities rather than concentrations the straight line is lost and the plot shows a distinct curve. We feel instinctively that the straight line is too good to tamper with, and that it would be foolish to introduce a correction factor (activity) where none is called for. If this were an equilibrium constant exercise where activities are known to be necessary and useful we could not justify such a stand but we wonder whether other factors may not be significant in heterogeneous reaction kinetics.

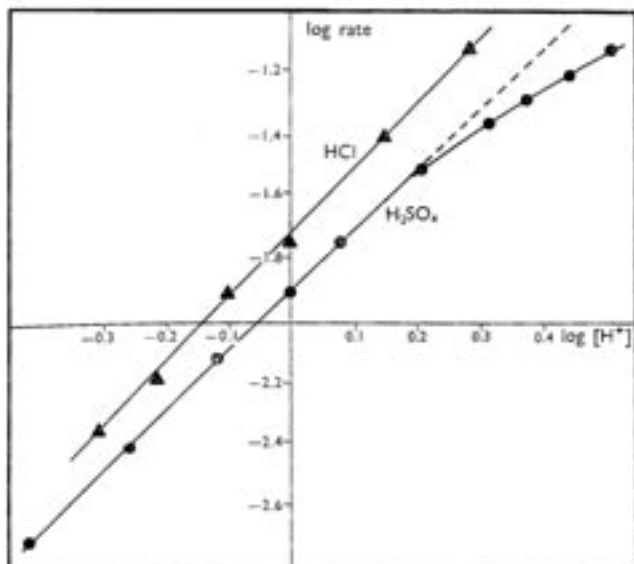


Figure 3 (above). Log rate against log concentration plots for magnesium in hydrochloric and sulphuric acid.

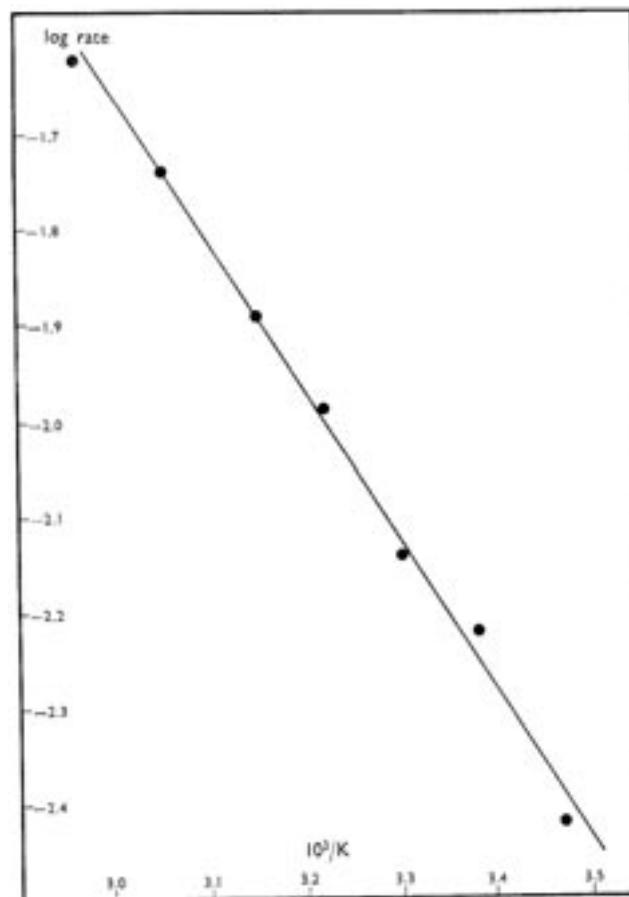


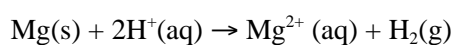
Figure 4 (right). Log rate plotted against reciprocal of temperature for magnesium in 0.66 M hydrochloric acid.

The second point concerns our use of the full stoichiometric concentration of hydrogen ion in sulphuric acid, ignoring the known incomplete dissociation of the hydrogensulphate ion. The linear part of the log–log plot (figure 3) is rather convincing, and there is other evidence³ that the hydrogen ion is not the only active species so that the hydrogensulphate ion may also be playing some part in the reaction. This is more apparent in the case of weaker acids, *e.g.* ethanoic. At 21 °C, 2 M ethanoic acid takes 360 s to react, and 1 M ethanoic acid takes 840 s. These rates are slower than in HCl, but far in excess of what would be expected on the basis of hydrogen ion concentration: in 1.0 M ethanoic acid, $[H^+] = 4.2 \times 10^{-3}$ molar. We have assumed that the use of the full stoichiometric acid concentration is justified in a simple treatment.

The dependence of the rate upon temperature was studied by holding the flask of acid in a 1-litre beaker containing water at the appropriate temperature, from room temperature to 65 °C. During the short reaction time the cooling of the beaker did no more than offset the energy from the exothermic of the reaction. For the results shown in Table 4 on page 7, 0.66 M hydrochloric acid was used. Figure 4 (above) is a graph of log rate plotted against the reciprocal of the temperature in degrees absolute.

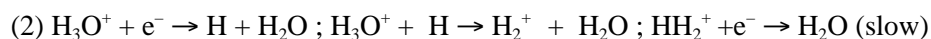
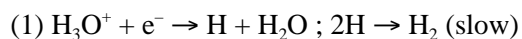
Reaction mechanisms

The interpretation of these results in mechanistic terms is by no means straightforward. It would be dangerously easy to relate the observed second-order rate to the stoichiometric equation:



but the various steps involved in the reaction must be considered in order to determine the rate-controlling factor. First, the hydroxonium ion H_3O^+ migrates to the metal. Factors which might affect this include the concentration of acid, the film of discharged hydrogen atoms and/or molecules on the metal surface, the physical presence of gaseous hydrogen and the ease with which the magnesium ions can migrate away.

The next step is transfer of the proton from the hydroxonium ion to the metal surface, its discharge and the formation of molecular hydrogen. Two mechanisms have been suggested for this step:



The first is called the catalytic mechanism and is said to apply to hydrogen evolution at transition-metal electrodes in electrolysis and the second, the electrochemical mechanism, at electrodes made of silver, mercury and lead.⁵ No one seems to have hazarded a guess for magnesium. For our purposes it does not matter, since both are second-order processes – even though the slow step in the second mechanism involves a single ion its concentration is directly dependent upon the previous step which is bimolecular. Finally, the hydrogen gas is desorbed from the metal and detached as bubbles.

If the rate of a reaction is dominated by the first step, the rate is said to be diffusion controlled or concentration polarized. If the second step predominates, the rate is activation controlled or activation polarized. The two effects may overlap. The first might be said to be a physical and the second a chemical effect.

It is not immediately apparent what order of reaction the diffusion control will give but Coates¹ showed that an order of 1.5, which he observed for magnesium and hydrochloric acid between 0.05 M and 0.3 M, is compatible with the diffusion mechanism. Boey⁶ has also observed that the order in this concentration differs from that found at higher concentrations. The reaction is very slow in this range and Coates used no stirring. Other evidence that the reaction is diffusion controlled is that the rate is inversely proportional to the viscosity of the solution,² and that the temperature coefficient – 1.3 per 10 °C in our experiment – is much lower than the factor of two usually associated with chemical reactions.

A good test between diffusion control and activation control is that the former should be strongly influenced by stirring and agitation whereas the latter should be unaffected. In our preliminary experiments we observed a small stirring effect, but Roald and Beck⁴ observed a considerable stirring effect although it diminished sharply above 0.3 M acid concentration. The vigorous rate of evolution of hydrogen from the metal surface in our experiment probably provided its own agitation in the crucial diffusion layer, and so destroyed the diffusion control. The excellent second-order plots that we have found certainly support the view that the rate is activation controlled in this concentration range.

An explanation for the falling off in rate in the more concentrated sulphuric acid solutions is more difficult to find, particularly whilst the corresponding HCl rates seem to be regular. Roald and Beck suggest that the hydrogen ion concentration at the magnesium surface is reduced to such a point that a transitory formation of magnesium hydroxide takes place on the metal surface. Presumably this is most likely at high rates of reaction and it must happen in both acids. However, the strong corrosive action of chlorides on magnesium compared with sulphates has already been mentioned: it is thought that the chloride ion breaks down the surface layer, and if this is so, it explains why the rate is maintained in hydrochloric and not in sulphuric acid. It would be interesting to compare the effect of added sodium chloride on the rates in the two acids.

Reactions of zinc

Reactions of zinc with hydrochloric acid can show particle size or catalysis effects. We used zinc foil cut into 1 cm squares, each square being slightly bent so that it would not lie flat on the bottom of the flask.

In the first experiment, to study the effect of a catalyst on the rate, we used 50 cm³ of 5 M HCl, with different amounts of copper sulphate dissolved in each. The catalyst is the copper displaced by the zinc as soon as it enters the solution. Since the foils weigh about 0.25 g (approximately 0.005 mol) copper displacement alone could account for the whole of the zinc in the solution where the copper sulphate concentration is 0.1 M. The catalytic effect is most pronounced at the lower concentration. For subsequent experiments all the acid solutions were made 0.001 M in copper sulphate.

Rates for the Zn foil–HCl reaction are given in Table 5. When plotted they show a reasonably linear dependence upon the square of the concentration up to 6.25 M, but they are notable for the extremely fast rates in the two most concentrated solutions. Having previously come out in favour of concentrations as against activities, we have to admit that this phenomenon is strikingly similar to the rapid increase in the activity of HCl solutions above 6 M, *e.g.* 6.25 M hydrochloric acid has an activity of 28 whereas in 11.4 M solutions the activity is 550.

The rates from temperature variation experiments (Table 5) using 5 M HCl give a good Arrhenius plot: the rate is doubled between 13 °C and 23 °C.

To examine the particle size effects, the rate of reaction of zinc powder with hydrochloric acid was determined. This required a slightly different technique. 0.25 g of powder was introduced into the acid and the end point was taken when the solution clarified sufficiently for a black cross on paper beneath the flask to become visible. This was quite reproducible.

Table 4. Reaction rates for magnesium in various acids

Hydrochloric acid (Temperature 21.4 °C)							
Concentration (M)	1.94	1.40	1.00	0.794	0.614	0.495	
Reaction time (s)	13.0	25	55	81	152	224	
Nitric acid (Temperature 24.5 °C)							
Concentration (M)	2.28	1.68	1.30	1.01	0.828		
Reaction time (s)	25	55	88	151	248		
Sulphuric acid (Temperature 19.6 °C)							
Concentration (M)	1.62	1.39	1.19	1.04	0.81	0.60	
[H ⁺] (M)	3.24	2.78	2.38	2.08	1.62	1.20	
Reaction time (s)	14.0	15.8	19.0	23	32	55	
Concentration (M)	0.498	0.381	0.278	0.193	0.159		
[H ⁺] (M)	0.996	0.762	0.556	0.386	0.318		
Reaction time (s)	80	132	254	510	675		
Hydrochloric acid (0.66 M)							
Temperature (°C)	15.6	23.4	30.0	37.4	45.0	55.0	65.0
Reaction time (s)	265	165	137	97	77	55.5	41.5

Table 5. Reaction rates for zinc in hydrochloric acid**Zn foil – 5 M hydrochloric acid (Temperature 21 °C)**

Concentration of copper sulphate (M)	0.1	0.05	0.01	0.005	0.001
Reaction time(s)	291	317	337	355	424

Zn foil – hydrochloric acid (Temperature 23.5 °C)

Acid concentration (M)	11.4	8.47	6.25	5.64	4.95	4.14	3.76
Reaction time(s)	13	42	186	228	442	880	1318

Zn foil – hydrochloric acid (5 M)

Temperature (°C)	1	13	23	29	39	45	55
Reaction time (s)	1415	840	430	340	205	160	110

Zn powder – hydrochloric Acid (Temperature 22.8 °C)

Acid concentration (M)	4.96	4.55	3.85	3.41	2.83	2.24
Reaction time (s)	59	71.5	106	143	222	391

Figure 5 shows that the rate is again proportional to the square of the concentration rather than to the concentration. The log-log plot gives an excellent straight line, but with the rather strange slope of 2.4. If activities are used the linearity is lost but the slope of the best line appears to be about 1.1.

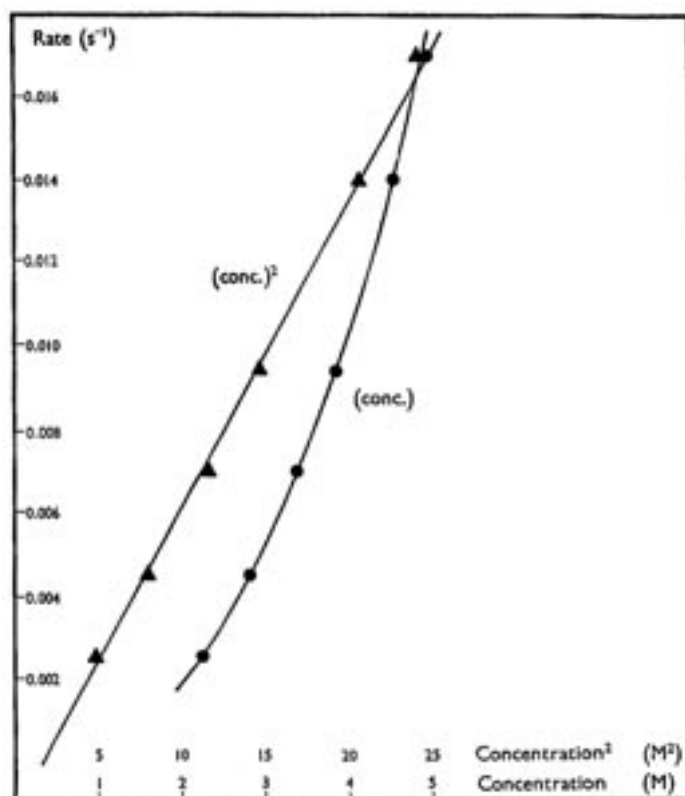


Figure 5. Graphs of rate of reaction against concentration for zinc powder in hydrochloric acid at 22.8 °C.

Conclusion

The magnesium reaction with hydrochloric acid is simple and reliable, and the reaction with sulphuric acid makes an interesting variant. The possibilities of extension to zinc have been demonstrated and, in view of its greater reactivity with acid, iron would also be worth trying. Studies on the effect of stirring and of added salts; salts with some oxidizing power, *e.g.* nitrates, might make interesting projects. Studies of the rate dependence in weak and moderately weak acids would also be interesting.

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The work described was carried out by Mr Hacker during, and after, taking the Postgraduate Certificate in Education at the University of Waterloo, Canada, where he is doing postgraduate research. Welsh-speaking Dr Williams is the author of two earlier *Education in Chemistry* articles (1968, **5**, 220; 1969, **6**, 120).