<u>Investigating the effect on the rate of reaction when changing the acid</u> <u>that is reacting with magnesium</u>

Aim

The aim of this investigation is to determine the order of reaction of monobasic, dibasic and tribasic acids with magnesium. The second part of my research in this area concerns the effect of acid strength on the order of reaction.

Proposed Procedure

When reacting an acid with a metal the following reaction takes place:-

From this we can see that a gas is given off. I decided that to measure how the rate of the reaction varies I will have to make a record of the amount of hydrogen gas given off during time intervals.

These results will show me the varying rate but I need to establish the order and therefore I have to make sure the experiment will provide data which will enable me to work out the order of the reaction.

How will I work out the order of the reaction?

Higher concentrations of acids lead to a greater chance of reactants colliding. The more often these reactants collide the faster the rate will be. The order of a reaction is the power to which the concentration of a reactant must be raised in order to satisfy the rate kinetics found by the experiment. There are many ways to work out this order, I have chosen to monitor the hydrogen gas given out over a set period of time. Then to find out the order of the reaction I will be able to plot a graph of concentration against time and study the curve produced. Concentration will be assumed to be proportional to the gas volume given off.

I am looking at how this order changes as I change the type of acid that I am reacting with magnesium. This means that every other variable will remain the same. I will keep a fixed amount of solution at the same concentration, to this will be added the same mass of magnesium. When added I will take a reading of the gas given out, that is collected in a gas syringe, at regular intervals.

Monobasic acids [H⁺]

Hydrochloric acid [strong, (HCL)] Ethanoic acid [weak, (CH₃CO₂H)]

Dibasic acids [2H⁺]

Sulphuric acid [strong, (H_2SO_4)] Ethanedioic acid [weak, $(C_2O_4H_2)$]

Tribasic acid [3H⁺]

Phosphoric acid [strong, (H₃PO₄)]

[1]In the nineteenth century it was the Swedish chemist Arrhenius who put forward the definition of an acid,

'Acids are substances which dissociate in water to produce hydrogen ions, H^* The strength of these acids depend on how much they disassociate their hydrogen ions. Some dissociate far greater percentages than others when in water.

This dissociation in water is an equilibrium reaction, the measure of this equilibrium is the K_{α} value.

$$K_{\alpha} = [H^{+}][A^{-}]$$
 [H-] hydrogen ion concentration [H-] resultant ion concentration [HA] un-dissociated acid

The greater the dissociation the stronger the acid, this will produce a higher K_{α} value.

[2]Example

$$HCL_{(g)} + H_2O_{(I)} \xrightarrow{100\%} CL_{(aq)} + H_3O_{(aq)}^{+}$$

As the H+ ion is fully dissociating into the water then the Ka value is very high(greater than 1).

$$1 \times 10^{-5}$$

$$CH_2CO_2H_{(I)} + H_2O_{(I)} \xrightarrow{less than 1\%} CH_2CO_2^{-}_{(aq)} + H_3O^{+}_{(aq)}$$

As the H+ ion doesn't dissociate into the water that much then the Ka value is low.

$$1.7 \times 10^{-5}$$

Varying the concentration of an acid will change the pH value but wont affect the K_a value. This is why it is a better gauge of the strength of the acid.

For both monobasic and dibasic acids I have chosen a strong and weak acid. I have determined that they are strong and weak by studying their K_{α} values^[3]. I tried to keep consistency between strong acids and also between weak acids

with this value. We had a limited choice of acids but the ones I have chosen have the best consistency. I will only looking at one tribasic acid as this is all that I have available for my use at my school laboratory.

Preliminary experiments

The aim of my preliminary experiments is to find the right amount and molar concentration of acid to use. It has to be a compromise so I will be able to get results for the whole range of my acids.

In my preliminary experiments I will also be trying to determine the right mass and type of magnesium to use. Available to use are strips, turnings and powder. Each of these have different surface areas and one would imagine that these may be the key to balancing the rate of reaction to make it possible to take readings for such a variety of acids.

Method

[Diagram]

As I am investigating the order of the reaction with respect to the acid the magnesium has to be in excess. I had to make sure that it was in excess for my tribasic reaction, phosphoric acid, as this will require the most amount of magnesium to react with the same volume of acid.

$$2H_3PO_4 + Mg \longrightarrow Mg(PO_4)_2 + 3H_2$$

As you can see from the equation, the tribasic reaction, with phosphoric acid, is going to give off the greatest volume of hydrogen gas. The monobasic will give off the least. Therefore in my preliminary experiments I tried to balance my reactants to be able to take readings from these to

Results:

25 cm³ 0.1 molar phosphoric acid 0.7g magnesium powder

Time/seconds	Volume/ cm³
10	16
20	22
30	24
40	24
50	24

This reaction had a fast initial rate but levelled off extremely quickly. The maximum volume of gas given out was quite low, this is due to the fact that all of the acid has been used up. It was also clear that this reaction was exothermic

from this reaction. The conical flash became hotter when being held.

25 cm³ 0.5 molar phosphoric acid 0.7g magnesium powder

Time/seconds	Volume/cm ³
10	-off scale-
20	-off scale-
30	-off scale-

By using 0.5 molar acid it made the reaction go far to quick and I wasn't able to get any results.

When I added my magnesium powder a second time a lot of it stuck to the edges before it reached the acid, this is because it was wet. Therefore I tried my experiment with a conical flask.

25 cm³ 0.5 molar phosphoric acid 0.7g magnesium turnings

Time/seconds	Volume/ cm³
10	13
20	34
30	52
40	81
50	-off scale-

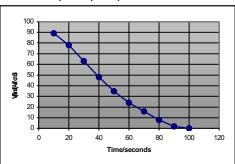
The reaction was still taking place to quickly. I had changed to trying to use magnesium turnings as this would give less surface area to react with and slow the reaction down. The flask worked a lot better as no magnesium was now able to

stick to the edge, I made sure I dried the entrance to the flask.

25 cm³ 0.25 molar phosphoric acid 0.7g magnesium turnings

Time/seconds	Volume/ cm³	$V_{(final)}-V_{t}/cm^{3}$
10	4	89
20	15	78
30	30	63
40	45	48
50	58	35
60	69	24
70	77	16
80	85	8
90	91	2
100	93	0

Graph A-phosphoric acid order



With this combination of 0.25 molar phosphoric acid and 0.7g magnesium turnings there is a balance that means the experiment didn't go too fast and a reasonable amount of readings were able to be taken.

By looking at graph A it is hard to determine whether the order is first or zero order. During the experiment many different variables come into the rate of the reaction that make it hard to draw conclusions. To try and minimise the effect of the exothermic nature of the reaction on the

Water bath- To put the test tube in a water bath I filled a beaker full of tap water. This reason for this was to see whether it would stabilise the heating effect of the exothermic reaction.

order I did the same experiment but the conical flask was in a water bath. The general curve on the graph however wasn't changed. This water bath was added to see whether it would stabilise the exothermic affect but it didn't work as expected.

After I had found out that this combination worked well I then tested this same combination with ethanoic acid, as this is my weakest monobasic acid. I couldn't get the reaction to produce enough results unless I shook the mixture. I couldn't stir the mixture as it was in a sealed container to collect gas but this action seemed to have the same affect. I didn't have a magnetic stirrer available otherwise this would have produced the fairest test.

The ethanoic acid reaction was considerably slower than my other reaction. This loss of speed also affected the gas syringe. With such little hydrogen being given off they had a tendency to stick then jump. To alleviate this problem I found that twisting the plunger on the gas syringe stopped all sticking.

Modifications due to Preliminary experiments:-

- I have decided that in my actual experiment I will not use the planned test tube but instead a small conical flask. This has a major advantage as when the magnesium has past the entrance of the flask there is no test tube edge to stick to. I also will make sure that the entrance of the flask is dry at the beginning of the experiment to prevent unnecessary sticking.
- I have decided that I will shake the flask whenever I am taking readings.
 This is so it is possible for me to obtain readings with my ethanoic acid. I
 must therefore do the same shaking with all my experiments or it will no
 longer be a fair test.
- I found that twisting the gas syringe would stop all sticking and therefore this would be part of my procedure for all types of acids.

Chosen amounts/concentration

Magnesium:-0.7g turnings

Acid:-

25 cm³ 0.25 molar concentration

Control of variables

To keep my investigation a fair test I must make sure that the only variable that is changing is the one that I am deliberately varying. I therefore think it is important that I go to special lengths to make sure that no other variables are altered in any of my experiments.

Temperature:-

When the temperature of the solution goes up this will have a direct relationship on the rate of the reaction. As this is what we are measuring it is of great importance that we take this into account. From the preliminary experiments it is known that the reaction is exothermic. This means that as the reaction goes on the temperature will increase and the rate of reaction will therefore be greater than if no temperature rise had taken place. As shown earlier I tried to restrict this from happening by placing the conical flask in a water bath during the experiment. I thought this would have the affect of stabilising the temperature increase. I found that the benefit that was gained from this didn't out weigh the fact that I couldn't shake my reaction. This meant that I didn't keep this water bath in my actual experiment. To make sure that this temperature is taken into account though I will take a control reading of how the temperature goes up for all of the acids done. This will let me compare it to my graph of hydrogen produced and will be possible to see any correlation.

Concentration:-

As the reaction progresses the concentration of the acid will decrease, it is because of this fact that we can analyse the order of the reaction of concentration against time. However, as the different types of acids are being compared in this investigation it is important that the starting concentration of these acids are the same.

I have to make sure that that when I am diluting down the acid to the right concentration great care is taken and I must be very precise. In my plan it has been said that I will be washing out the measuring cylinder with the acid that is being diluted. This is so no contamination is left from any substance that was in it before. Even though all of these precautions will be taken if the acid that I am diluting down is not at the stated concentration then all of mine will be out as

well. We are provided with these acids and I will make sure that I take this possible inaccuracy into account in my analysis.

Amount/volume used:-

The initial amount of magnesium and volume of acid that react together plays a major part in how the results of my reaction go. I have spent a fair time with preliminary experiments making several alterations to my proposed value for these to make sure that I was working on the right scale. For example, I didn't want to be only looking at the first 100cm^3 given off if the reaction was going to carry on and give out another 700cm^3 . On the other hand I had to make sure that I had a great enough quantity given off to take sensible readings. I was using a 25cm^3 measuring pipette which has an accuracy of ± 0.05 cm³, which is 0.002%, to measure out my 25cm^3 portions of acid. I was also using a balance that has an accuracy of ± 0.01 g therefore have an error of 0.0004%. This means that my percentage error for this volume of acid and amount of magnesium is 0.0024%. This will have to also be taken into account during my analysis.

Plan

1. Experiment 1

[Diagram]

For my investigation I will be monitoring the hydrogen gas given off when different acids are added to magnesium (I have chosen 0.7g magnesium turnings, determined from earlier experiments).

The magnesium turnings will be added to a conical flask with my prepared acid and then all hydrogen that is given off will be collected in a gas syringe. For the duration of the reaction the conical flask will be shaken.

The amount of hydrogen gas that has been given off will be recorded at regular intervals. All readings will be repeated three times to make sure I have no anomalous results.

My experiment includes testing 5 different acids; hydrochloric acid, ethanoic acid, sulphuric acid, ethanedioic acid and phosphoric acid. All these acids were used in 25cm³ portions and at a concentration of 0.25 molar.

At our school laboratory only higher concentration acids are available and therefore these will have to be diluted down. My 0.25 molar acids will have to be made from either 1 or 2 molar initial solutions, they can be made by using these ratios:

1 molar ratio 1:3, acid to water 2 molar ratio 1:7, acid to water

To dilute the acid the right proportions will be added in a 50 cm³ measuring cylinder, before any solutions of the acid is made first the measuring cylinder should be washed out with the acid that is being made up. This is to eliminate the chance of a possible contamination of the acid.

The 25cm³ portion of the diluted acid will be extracted using a 25cm³ measuring pipette.

Equipment list:

- Stop Watch
- Conical flask with delivery tube
- Gas syringe
- 25cm³ Measuring pipette
- 50 cm³ Measuring cylinder
- Beaker
- Retort stand
- 2. Experiment 2

[Diagram]

As spoken about in my control of variable it is known that the reaction is going to be exothermic and therefore a record of the temperature increase is necessary. The method is trying to keep as many variables as possible the same as Experiment 1 as its aim is to find out the temperature increase of the reactions from this experiment.

The same concentration and amount of acid as well as the same quantity of magnesium will be used as in Experiment 1. The magnesium will be added to a

conical flask with the acid in it. This conical flask however will not be connected to a gas syringe via delivery tubing, it will have a thermometer (-10 - $50^{\circ}C$) in it. The flask will be shaken in the same way as in *Exp*eriment 1 to make the results as meaningful as possible.

The temperature readings will also be taken at regular intervals.

Equipment list:

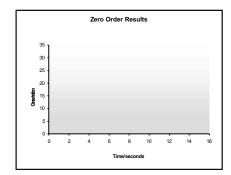
- Stop Watch
- Conical flask
- 25cm³ Measuring pipette
- 50 cm³ Measuring cylinder
- Beaker
- Thermometer $(-10 50^{\circ}C)$

Data Analysis

To make sense of the results that I collect they need to be interpreted the right way. To do this I will be manipulating them in two ways to help me find out the order of reaction.

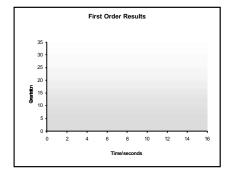
Concentration against Time graph^[1]

By looking at these graphs produced I will be able to compare the results that I receive to the known, published, curves for the respective orders.



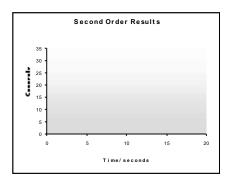
Zero order-

Will be a straight line as the gradient of the reaction is the rate. The concentration has no effect on the rate when zero order and therefore the rate will remain constant throughout this reaction.



First order-

The curve will be such that the time taken for the concentration to half (half-life) remains constant.



Second order-

The curve will again be a curve yet this time it will be slightly deeper. The half-life of the reaction will not remain constant, it will increase drastically as the reaction goes on.

To work out the concentration the formula I used was: Concentration = $V_{(max)}$ - $V_{(t)}$

I could use this equation as the volume given off is directly proportional to the concentration of the acid.

This is a fine way to analyse my results but as you can see I may find some problems in saying whether my reaction is first or second order as these curves are not that different when errors come into experiments. I have therefore decided to look at a different type of graph as well.

Rate against time graphs^[4]

These will help me differentiate between first and second order. Zero order- straight horizontal line, as rate is remaining constant. First order- angled straight line, as rate is changing proportionally Second order- curved line, as the rate isn't changing proportionally This shows a greater difference between first and second order as one should produce a straight line and the other curved and therefore I feel it should be a better gauge.

To work out the rate at each time period the following calculation will be made:

Rate = <u>volume of hydrogen gas given off</u>
Time taken

Hypothesis

From the information that I have gathered I believe that when I change from monobasic to dibasic and tribasic acids this will have an affect on the order of the reaction.

I also believe that the strength of the acid could be a deciding factor. Both the monobasic acids should act as first order. I would expect sulphuric acid to be second order yet ethanedioic acid to be first order. Phosphoric acid

being my only tribasic acid is fairly strong. However, I would expect it to act as second order like sulphuric acid.

Explanation of Hypothesis

The most important data that was needed to make the hypothesis were the K_a values. These gave me all the information I needed on how each of the H^{+} ions from the acids were going to dissociate.

Monobasic

Acid	K _a values ^[3]
Hydrochloric acid (HCL)	1×10^6
Ethanoic acid (CH3CO2H)	1.7×10^{-5}

Both hydrochloric acid and ethanoic acid only have one $H^{\scriptscriptstyle T}$ ion to dissociate. For and acid to satisfy first order, the rate must go down proportionally to the concentration. Both these acids will have one $H^{\scriptscriptstyle T}$ ion and therefore it would follow that these direct relationship should appear.

Hydrochloric acid has a far greater K_a value, this means that is will be a stronger acid and I would expect the reaction to go faster. But also it may be easier for me to receive results that show it is first order. The ethanoic acid H^{\dagger} ion doesn't dissociate much and therefore the combination of slow reaction due to the weak acid may make it hard to record.

Dibasic

When deciding what the order of our dibasic acids should be we have more to look into. Not only do we have the dissociation of the first H ion but also how easily it will get rid of its second one.

Acid	1 st H ⁺ dissociation K _a values ^[3]	2 nd H⁺ dissociation K _a values ^[3]
Sulphuric acid (H ₂ SO ₄)	Very large	1.0×10^{-2}
Ethanedioic acid	5.89 x 10 ⁻²	Not published
(C ₂ O ₄ H ₂)		

For our acids to act as second order the rate must be proportional to $[concentration]^2$. For this to happen the acids must have both of their H^* ions dissociated into aqueous solution.

I would fully expect that sulphuric acid will act as second order, this is because the values of dissociation for both of its H^{+} ions are very high and therefore a

great proportion of them will be dissociated. I think that this will make it act as second order.

Ethanedioic acid on the other hand does not have such high K_a values and therefore I would not expect the same out come. In its formula it may appear to have two H^{\star} ions available just like sulphuric acid but by further study we see that it being such a weak acid and the extremely small dissociation value of its 2^{nd} H^{\star} ion makes it highly likely that this will have any affect on the reaction. This will make the acid behave as it has one H^{\star} ion and will act as a first order acid. As it is so weak I also believe that to find this relationship will not be easy. The reaction has to give off enough gas for it to be measurable under my laboratory conditions.

Tribasic

Acid	dissociation K _a	2 nd H ⁺ dissociation K _a	3 rd H⁺ dissociation K _a
	value ^[3]	value ^[3]	value ^[3]
Phosphoric acid	7.9×10^{-3}	6.2 x 10 ⁻⁸	4.4×10^{-13}
(H₃PO₄)			

Our one tribasic acid has 3 H † ions that it could dissociate. It is a fairly strong acid as you can see from its high 1st K_a value. For us to decided what order it will act as however we have to look at how well the next two H † ions dissociate. The second H † ion does dissociate reasonably well but not even as much as the 1st H † ion from ethanoic acid which is our example of a weak monobasic acid. Therefore I wouldn't expect it to have the greatest second order characteristics. Its 3rd and final H † ion hardly dissociates at all, its value is merely greater than K_a value of H_2O . This ion will not have any affect on out experiment at all.

Even though the second H^{\dagger} ion doesn't dissociate greatly I feel that it may still make my results show that it is a second order reaction.