

University of Wales Trinity Saint David

# An Investigation Into Rates of Reaction

To Equilibrium and Beyond

## Abstract

In this experiment the effect of concentration, temperature, and surface area on the rate of chemical reaction was evaluated. Using solid magnesium metal and hydrochloric acid as reactants the volume of hydrogen gas produced against time was measured thereby allowing the calculation of rate of reaction with the  $H_2$  gas as the quantitative variable measured with respect to time and its time derivative being the instantaneous rate at any given point.

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## Introduction

The aim of this experiment is to examine factors that influence the rate of chemical reaction between magnesium metal and hydrochloric acid. These factors are the concentration of hydrochloric acid in solution, the temperature at which the reactants are introduced and the surface area of the magnesium metal when it is introduced to the solution of HCl.

The hypotheses with regards to these factors are as follows:

- 1- By increasing the concentration HCl, the rate of reaction will also increase.
- 2- Increasing the temperature of the HCl will increase rate of reaction.
- 3- A larger surface area of Mg will increase rate of reaction.

By measuring the volume of hydrogen gas evolved during the reaction in equation 1.1 below and plotting it as a function of time we can use said volume to work out the instantaneous rate of reaction at any given point for the 3 differing hypothesis parameters by taking the derivative of our function for volume produced with respect to time.



For a truly accurate study of the rate of a chemical reaction one must require the solution of a multi body problem involving the motion, electrostatic and quantum interactions of all subsequent molecules, electrons and atomic nuclei that are involved within the reaction. Of which one could dedicate a lifetime of scholarly endeavour. To account for this in practicality we apply collision theory to a given chemical reaction which is a simplified model with the primary assumption that for a reaction to occur the individual molecules or atoms must collide in a macroscopic sense. That is like in the case of two snooker balls hitting or a multi car pile up on a motorway.<sup>[1,2]</sup> Continuing with the car analogy, from our 3 hypothesis, a higher concentration means there are more cars in a given stretch of road and so the likelihood of a collision increases meaning the rate at which collisions occur will also increase. For temperature this is the speed of our cars (or molecules) and for the same stretch of road, increasing the speed of the vehicles will mean there is likely to be more collisions as there is more traffic per unit of time and the cars have more kinetic energy when they do collide. In turn meaning the rate at which collisions occur is higher. Finally, the third assumption is possibly counter intuitive as increasing the surface area means reducing the physical size of the road (or reactant) without reducing the amount of traffic, again having a higher likelihood of collisions occurring as there is now more traffic per unit area than before.

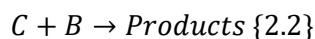
Just as with collisions with cars, not every small bump will cause a catastrophic failure of the structural integrity, that's why reactants that collide must also have sufficient energy to overcome their own structural bonds, and this is known as the activation energy. The activation energy ( $E_a$ ) is the minimum energy required for a chemical reaction to occur. It is the energy that takes a set of reactant species to another product species via the movement, breaking, formation and or stretching of chemical bonds<sup>[3,4]</sup>.

## Concentration and Temperature

The activation energy and rate constant  $k(T)$  are mathematically linked and are present in the formulae known as the Arrhenius equation.

$$k(T) = Ae^{\frac{-E_a}{RT}} \{2.1\}$$

Where rate constant is given by  $k$ ,  $A$  is the Arrhenius constant,  $E_a$  is the activation energy,  $R$  is the gas constant  $8.142\text{Jmol}^{-1}\text{K}^{-1}$  and  $T$  is temperature K. The rate constant is linked to the rate of reaction as the larger the value of  $k$ , the faster the rate of reaction. The rate of reaction is given by the general reaction solution below:

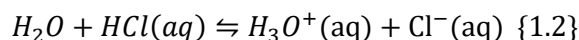
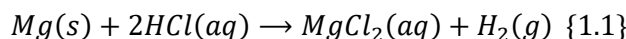


$$\text{Rate} = k[C]^n[B]^m, \quad m, n \in \mathbb{R} \{2.3\}$$

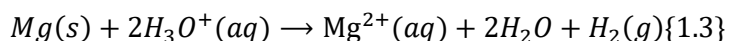
$$\text{Rate} = Ae^{\frac{-E_a}{RT}}[C]^n[B]^m \{2.4\}$$

From 2.1 and 2.3 we can see that temperature should play a significant factor in the rate of reaction, as temperature increases the activation energy diminishes as a barrier as if  $RT \gg E_a$  then 2.4 becomes,  $\text{Rate} = A[C]^n[B]^m \{2.5\}$ , but this is very much a fringe case. With temperature being an inverse negative exponent as seen in eqn 2.4 it can be hypothesised that all other factors being constant increasing temperature should exponentially increase rate of reaction for the general case {2.2} and the specific reaction 1.1.

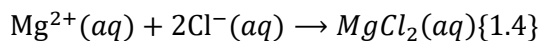
Now equation 1.1 only tells us half the story, HCl in solution is a strong acid and is assumed to completely dissociate into a water solution and so we get the following chloride ion formation<sup>[5]</sup>.



Then there is magnesium ion formation because of the  $\text{H}_3\text{O}^+$  ion which appears to be the rate determining step as no Mg can react to form  $\text{MgCl}_2$  (and hydrogen gas) until it is oxidised and in solution.



Leaving our Mg and Cl ions to finally react, again as HCl is a strong acid we assume a large excess of chloride ions so the Mg ion formation given in eqn 1.3 must be the rate determining step leaving the following.



Therefore from {1.3} and {2.4} the rate equation depends on the concentration of HCl or more accurately the  $\text{H}_3\text{O}^+$  ions.

$$\therefore \text{Rate} = k[\text{HCl}]^2 = Ae^{\frac{-E_a}{RT}}[\text{HCl}]^2 \equiv k[\text{H}_3\text{O}^+]^2 = Ae^{\frac{-E_a}{RT}}[\text{H}_3\text{O}^+]^2 \{1.5\}$$

■

## Surface Area

For hypothesis 3 the assumption is that all the surface area for a given magnesium sample is available for reaction to take place, and that our pieces are perfect cubes of magnesium (the

same result for spheres also). If the mass of our Mg remains the same but the volume of the individual cubes of magnesium decreases, then the volume to surface area ratio increases.

Volume (V) and Surface area (A) of cube of side length  $l$  is given by:

$$V = l^3, \text{ and } A = 6l^2 \quad \{3.1\}$$

Dividing the cube into  $n$  smaller cubes each will have a side length of  $l(n)^{\frac{-1}{3}}$ .

$$V_{\text{smaller}} = \left( \frac{l}{\sqrt[3]{n}} \right)^3 = \frac{l^3}{n} \quad \{3.2\}$$

The sum total volume of the small cubes and one big cube will be the same

$$\Sigma V_{\text{smaller}} = \frac{l^3}{n} \times n = l^3 = V \quad \{3.3\}$$

However the Surface area of one small cube is:

$$A_{\text{smaller}} = 6 \times \left( \frac{l}{\sqrt[3]{n}} \right)^2 = 6l^2 n^{\frac{-2}{3}} \quad \{3.4\}$$

$$\Sigma A_{\text{smaller}} = 6l^2 n^{\frac{-2}{3}} \times n = 6l^2 n^{\frac{1}{3}} \quad \{3.5\}$$

Resulting in the ratio of surface areas being:

$$n^{\frac{1}{3}} : 1, \text{ where } n^{\frac{1}{3}} > 1 \quad \{3.6\}$$

Say We split the cube of unit length 1m into 4 or 1000 then we get,

$$l = 1\text{m}, \quad n = 1, \quad A = 6\text{m}^2, \quad V = 1\text{m}^3 \quad \{3.7.1\}$$

$$n = 4, \quad \Sigma A_{\text{smaller}} = 6(1)^2(4)^{\frac{1}{3}} \approx 9.52\text{m}^2, \quad \Sigma V_{\text{smaller}} = 1\text{m}^3 \quad \{3.7.2\}$$

$$n = 1000, \quad \Sigma A_{\text{smaller}} = 6(1)^2(1000)^{\frac{1}{3}} = 60\text{m}^2, \quad \Sigma V_{\text{smaller}} = 1\text{m}^3 \quad \{3.7.3\}$$

So as the number of divisions or the finer of a powder we create the rate of reaction should scale with  $n^{\frac{1}{3}}$  divisions and if the number of divisions is unknown then one can find the difference in rates of reaction and approximate  $n$ .

■

Accounting for all 3 hypotheses, assumptions and factors the following theoretical specific solution for the given acid-metal rate of reaction is:

$$\text{Rate} = S_A k [H_3O^+]^2 = S_A A e^{\frac{-E_a}{RT}} [H_3O^+]^2 \quad \{4.0\}$$

$S_A$  is the surface area factor where  $S_A = n^{\frac{1}{3}}$ , with  $n$  being the divisions from the original bulk solid where  $n = 1$ ,  $A$  is the Arrhenius constant,  $E_a$  is the activation energy,  $R$  is the gas constant  $8.142\text{Jmol}^{-1}\text{K}^{-1}$ ,  $T$  is temperature K and  $[H_3O^+]$  is the concentration of acid.

## Results and Discussion

Group 1: concentration \*

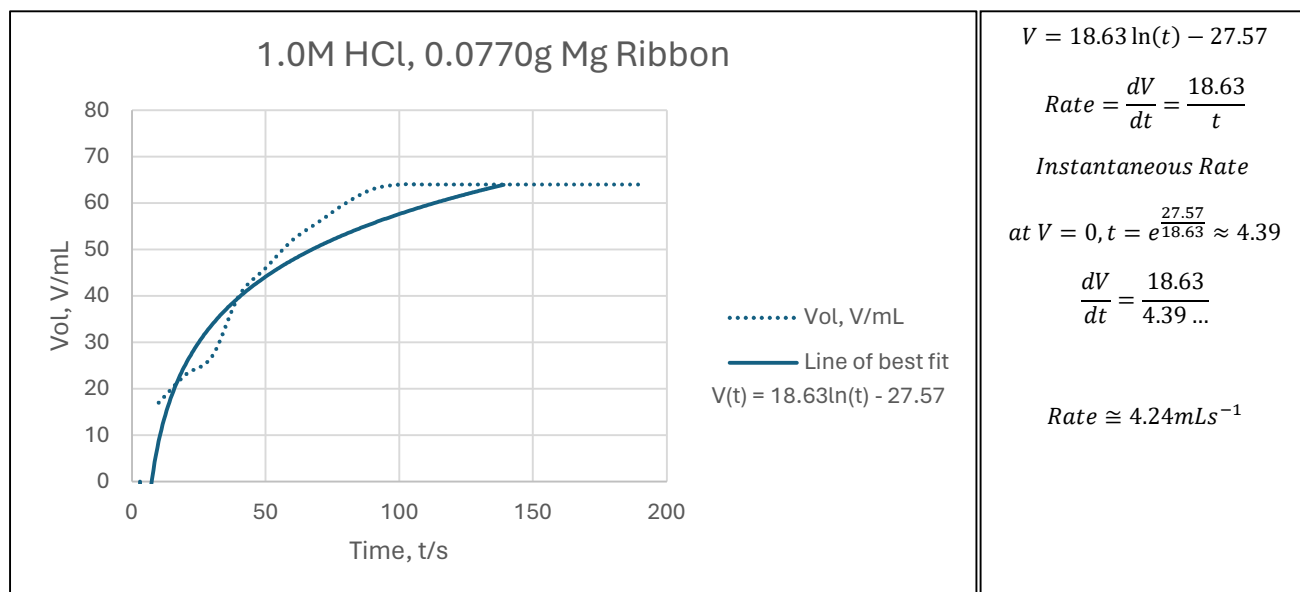


Figure 1 Volume of evolved  $\text{H}_2$  gas as a function of time from the reaction with HCl. The dashed line is volume raw data with the solid line the function calculated for that data set given algebraically above.

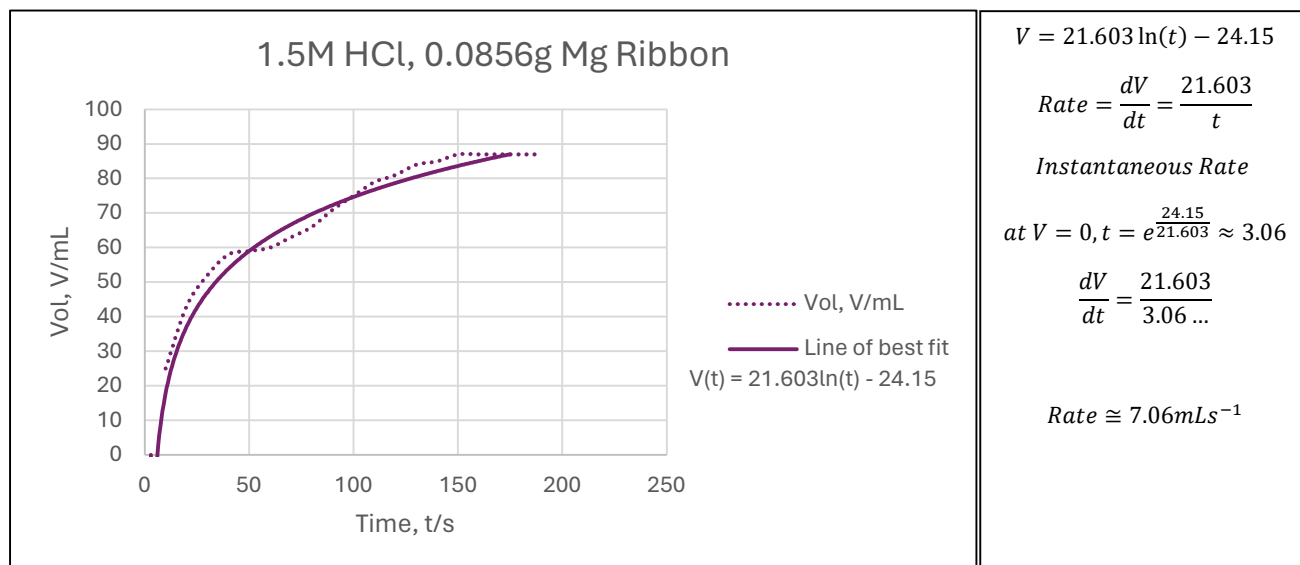


Figure 2 volume of evolved gas as a function of time for 1.5M HCl. There is a definite sharper curve as opposed to figure 1.

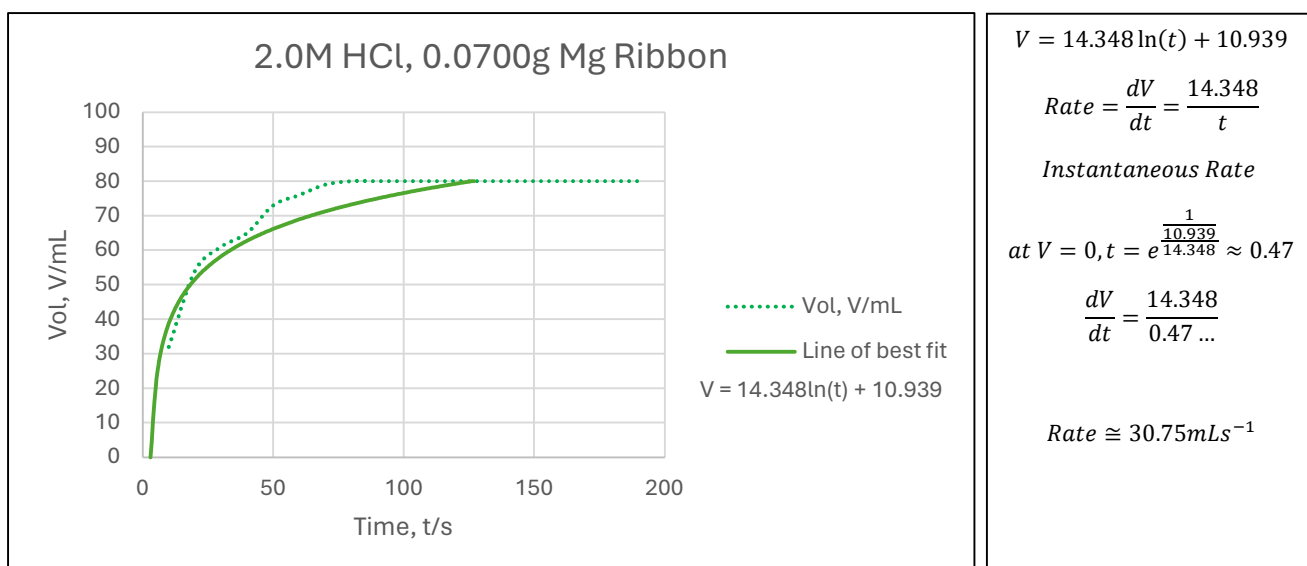


Figure 3 Third and final graph for group 1 again visually showing a sharper evolution of  $H_2$  gas indicating a faster rate of reaction than the previous 2.

The functions show a clear logarithmic growth as shown with the calculated instantaneous rate of reaction on the right as the volume derivative with respect to time. Mathematically this posed an issue as when  $t=0$ ,  $V$  cannot be negative as the case would be with figures 1&2 therefore the true instantaneous rate of reaction must take place at  $V=0$ . Yielding the rates:

- 1- Rate of reaction 1.0M HCl =  $4.24 \text{ mL s}^{-1}$
- 2- Rate of reaction 1.5M HCl =  $7.06 \text{ mL s}^{-1}$
- 3- Rate of reaction 2.0M HCl =  $30.75 \text{ mL s}^{-1}$

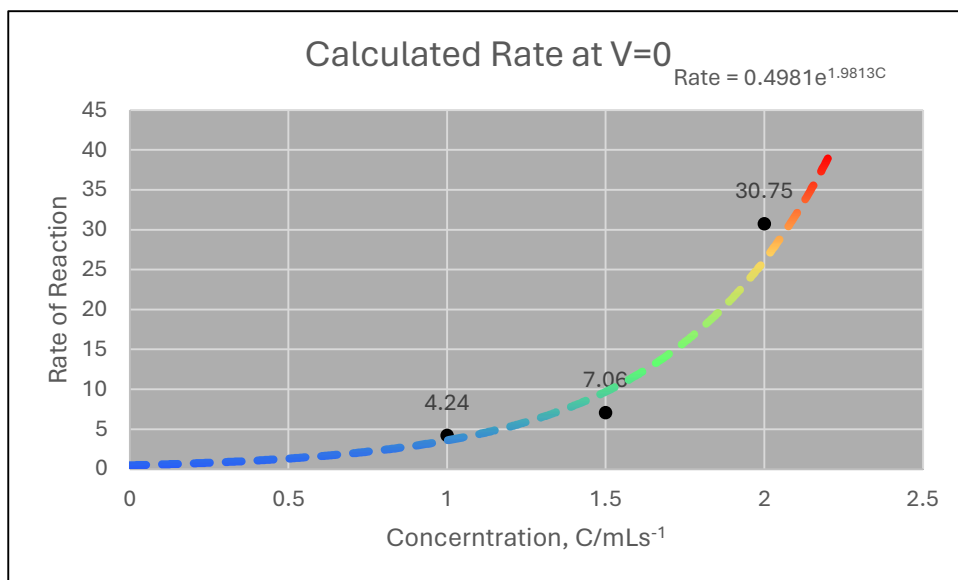


Figure 4, Rate of reaction as a function of concentration.

From the calculated rates of reaction at  $V=0 \text{ mL}$  we there is an exponential or possibly quadratic increase in the instantaneous rate of reaction. From the previously derived rate equation 4.0 this experimentally derived result supports the hypotheses that we have a 2<sup>nd</sup> order rate of reaction

regarding the HCl being the driving factor with the  $1.98C \approx 2C$  in the exponent being our 2<sup>nd</sup> order contribution. Therefore, the concentration portion of the experiment we arrive at the following expression, where C is the concentration (molarity) of HCl.

$$\text{Instantaneous Rate}_{V=0} = 0.4981[e^C]^{1.9813} \{5.1\}$$

Which is very close to the predicted 2<sup>nd</sup> order dependence on concentration of:

$$\text{Rate} = k[\text{HCl}]^2$$

For the average rate of reaction each of the calculated rates of reaction in figures 1,2 &3 will use the mean function  $\bar{f} = \frac{1}{b-a} \int_a^b f(x)dx$ , in the bounds  $0.001s \leq t \leq 50s$  in 10s increments. 50s was chosen as on all graphs this appears to be where all 3 of the concentrations begin to slow down. T cannot be 0 as the derived rate equations of the form  $\text{rate} = N/t$ , where N is an arbitrary constant, goes to infinity when  $t=0$ , and so I have chosen 1ms to be the starting point as the reactions were observed using a stopwatch and human reaction times are in the order of milliseconds.

$$\text{RateMean}_{1.0M} = \frac{1}{50 - 0.001} \int_{0.001}^{50} \frac{18.63}{t} dt \cong 4.0$$

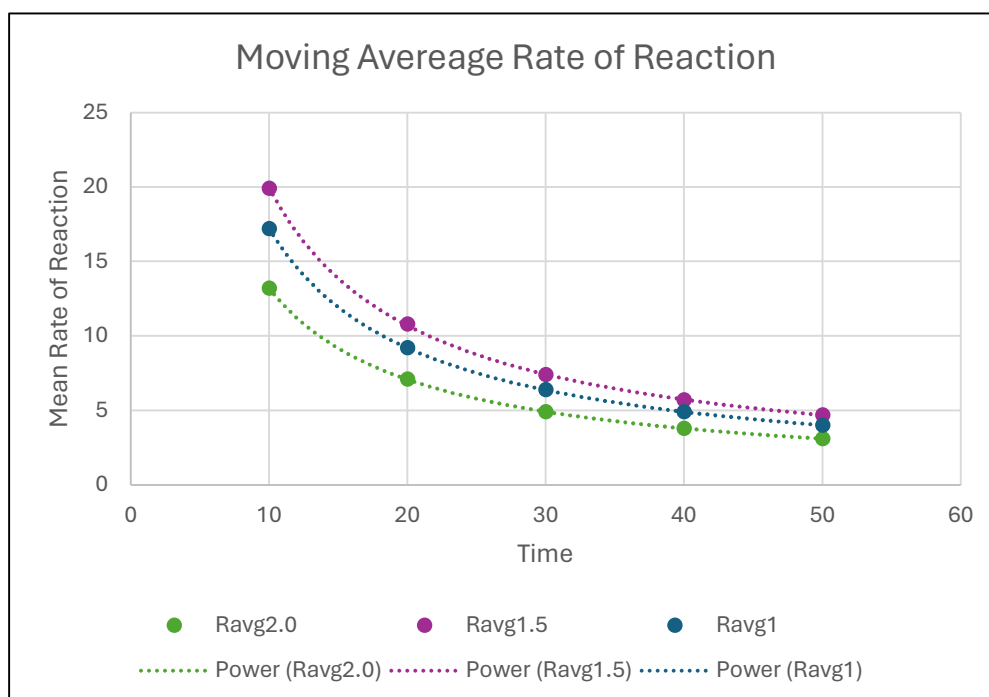


Figure 5: Average rate of reaction as a function of time.

While at first glance it may be counterintuitive and could possibly be an error as to why the average rate of reaction for the 1.5M solution has a consistently higher rate of reaction over the 2.0M and to a lesser extent the 1.0M. That is because there was a larger mass of Mg available to react and this holds true irrespective of the concentration for our samples. The more magnesium to react which in turn produced more H<sub>2</sub> gas over time thereby increasing the average rate of reaction, which makes logical sense.

## Group 2: Temperature

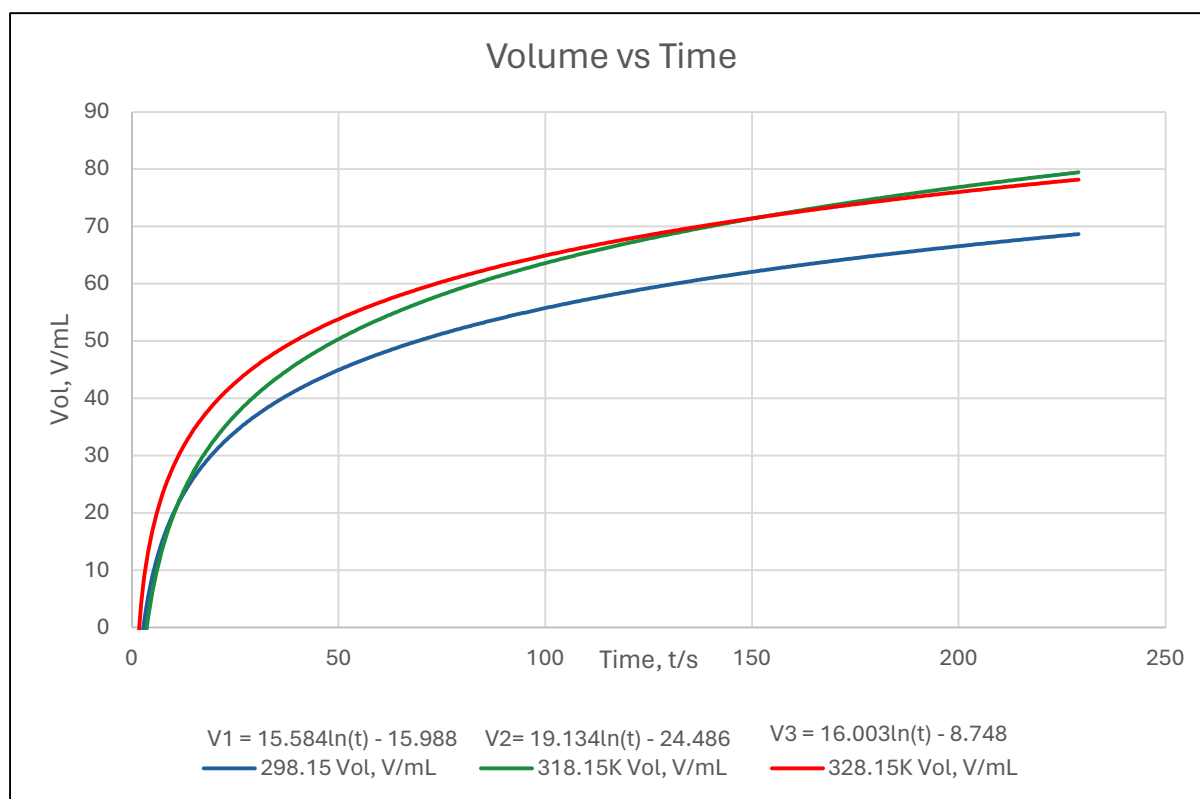


Figure 6: Plots of volume as a function of time varying the temperature in each case, blue = 25°C, green = 45°C and red = 55°C.

Here the concentration remains the same at one molar solution of hydrochloric acid with the temperature varying from 25°C to 55°C. Initially as expected the higher temperature evolved the most gas the fastest by quite a margin although this gradually gets beaten out by the calculated 45°C curve. By weight  $V_1 = 0.0770\text{g}$ ,  $V_2 = 0.0796\text{g}$  and  $V_3 = 0.0812\text{g}$ . The higher mass of  $V_2$  evolving more hydrogen gas than  $V_1$  is to be expected as  $(\text{mass}) v_1 < v_2 < v_3$  however  $V_2$  evolving more gas over all as  $V_3$  could be down to experimental error. A prominent source of said error was due to the Mg strip getting stuck to the side of the test tube during reaction.

Instantaneous rate at  $V=0$  calculated as before in figures 1, 2 & 3 yields:

$$\text{Rate Temp1} = 5.57 \text{ mL s}^{-1}, \text{ temp} = 298.15 \text{ K}$$

$$\text{Rate Temp2} = 5.32 \text{ mL s}^{-1}, \text{ temp} = 318.15 \text{ K}$$

$$\text{Rate Temp3} = 9.26 \text{ mL s}^{-1}, \text{ temp} = 328.15 \text{ K}$$

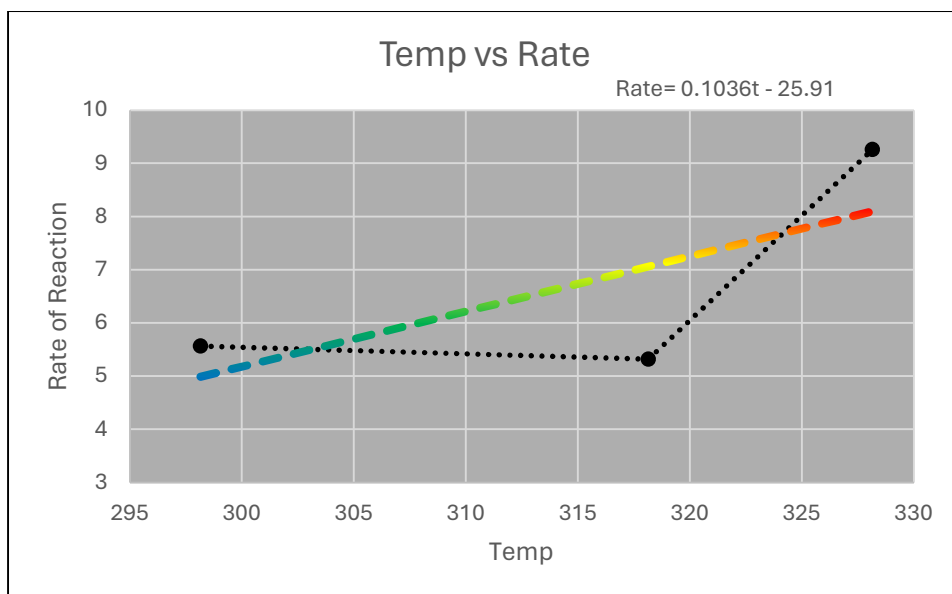


Figure 7 Rate as a function of temperature.

From the graph and data above we see that there is a slight decrease followed by a significant increase in right reaction as a function of temperature. This rate of reaction does not increase uniformly with temperature suggesting potential anomaly as in accordance with collision theory collision frequency and energy should increase as temperature increases as individual molecules have a higher kinetic energy leading to a greater frequency of collisions and collisions of a higher energy meaning the reaction should increase as temperature increases. Although the anomalous result doesn't take away from the overall trend seen in the gradient line where the dramatic increase in rate of reaction at 328.15K suggests that this kinetic energy is more than enough to overcome the activation energy barrier for our magnesium hydrochloric acid reaction overall aligning with the concepts laid out in collision theory primarily that a higher temperature of reaction will increase the rate of reaction as only collisions with a high enough energy to overcome the activation energy barrier will result in a successful reaction. Potential sources of error as previously mentioned magnesium sticking to the test tube, inconsistent temperature measurements. The part of the test tube where temperature was measured could have been warmer than the majority of it simply measurements in accuracies or inconsistencies with taking measurements on the part of humans or indeed the reaction dynamics as impurities such as magnesium oxide will interfere with the reaction laid out in equation set 1.

### Group 3: Surface area

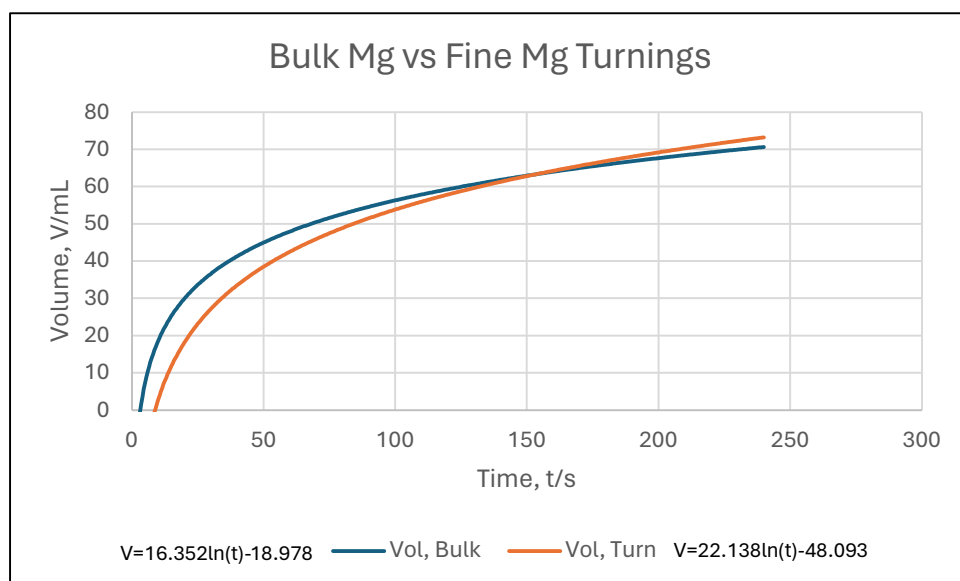


Figure 8: Bulk magnesium ribbon compared with fine Mg turnings, clearly showing a slower evolution of gas from the turnings which is contrary to what is expected behaviour as derived in equation set 3.

Rate Bulk = 5.12

Rate Fine=2.52

The results of reaction here are unexpected as the larger pieces of magnesium the bulk have a smaller surface area to volume ratio this should mean that fewer magnesium atoms are exposed to acid at any given time resulting in a lower rate of reaction which is not what we have found. The likely cause of this is that the fine magnesium particles had been sat idle in a oxygen rich atmosphere and so had built up a layer of magnesium oxide which in turn has inhibited the reaction between hydrochloric acid and magnesium metal. The reason this is more pronounced thereby reducing the rate of reaction more in the finer magnesium is exactly because of the reasons set out previously the finer magnesium reacts more readily with the oxygen in the air thereby having a greater inhibiting effect on the acid metal reaction down the line. To account for this in the future the magnesium turnings or powder will either ideally be kept in an inert atmosphere off say nitrogen kept under oil or indeed only prepared when immediately to be used. The data suggesting that the bulk magnesium ribbon having a faster rate of reaction at  $V=0$  is contrary to the usual expectation of the larger surface area of the fine magnesium.

## Conclusions

The data indicates that increasing the concentration of hodgepodge acid has a marked and clear increase in the rate of reaction with magnesium and this agrees with collision theory where having physically more reactant available increases the frequency and thereby effective collisions thus increasing the overall reaction rate. The exponential or quadratic rate of reaction increase alludes to the more complicated chemistry going on with the acid dissociation in solution and thereby the more complex kinetics that would be involved to truly gain insight into the overall rate of reaction more of these steps must be evaluated to speak with confidence on the system as a whole. We've got the temperature the doctor suggests that increasing temperature overall increases the rate of reaction despite the unexpected decrease in reaction from 298.15K to 318.15K. However with a significant increase in temperature at 328.15K the typical Arrhenius behaviour as expected from the Arrhenius equation and collision theory takes over once more. Again, Surface area had an unexpected result also with the bulk magnesium reacting faster and having a higher instantaneous rate of reaction than the fine magnesium likely being due to magnesium oxide formation.

Overall the experiment was unable to successfully account for all factors in a neat equation as outlined in equation 4 however this was likely due to experimental errors as outlined above and more research must be done before a definitive statement on the effects of surface area and temperature on rate of reaction however concentration showed clear and expected results, namely being a second order dependence on concentration in regard to rate of reaction.

## Rates of Reaction in Ordnance, Munitions and Explosives

The impact of safety is often the critical factor when evaluating the cost/benefit of using specific energetic compounds. In academia and industry there is a large focus on LOVA (low vulnerability) energetic materials as seen in S. Delbarre et al<sup>[6]</sup>. Materials with high rates of reaction could pose a safety risk as they could be more susceptible to stimuli, like friction impact and shock or just degrade more readily. In addition tuning of energy release is paramount when designing with energetic materials in mind. For example a detonating explosive will have a higher rate of reaction than a deflagrating one however for applications such as propellants a detonating material is a poor choice as a controlled burn is required to accurately get an item to move in a repeatable way without destroying what you intend to move in the first place, gradual release of gas and energy and so lower rates of reaction are essential in rocket, motor and gun propellants for this very reason. For special kinds of ammunition a desired chemical reaction can occur leaving the armour more vulnerable to subsequent shots or having completely failed due to a chemical reaction brought upon by a munition and so the rate of reaction will need to have a known and consistent effect. Finally for non-military applications controlling the rate of an explosive reaction is absolutely essential in modern demolition or mining, carefully selected energetic materials with precise and accurately calculated rates of reaction are needed to prevent collateral damage.

## Bibliography

- [1] "6.1.6: The Collision Theory," Chemistry LibreTexts, Oct. 02, 2013.  
[https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Supplemental\\_Modules\\_\(Physical\\_and\\_Theoretical\\_Chemistry\)/Kinetics/06%3A\\_Modeling\\_Reaction\\_Kinetics/6.01%3A\\_Collision\\_Theory/6.1.06%3A\\_The\\_Collision\\_Theory#:~:text=Collision%20theory%20explains%20why%20different,on%20the%20frequency%20of%20collisions.](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/06%3A_Modeling_Reaction_Kinetics/6.01%3A_Collision_Theory/6.1.06%3A_The_Collision_Theory#:~:text=Collision%20theory%20explains%20why%20different,on%20the%20frequency%20of%20collisions.)  
(accessed May 19, 2024).
- [2] Autor: St G Khristov, *Collision theory and statistical theory of chemical reactions*. Editora: Berlin ; New York: Springer-Verlag, 1980, p. 1.
- [3] D. G. Truhlar, "Interpretation of the activation energy," *Journal of Chemical Education*, vol. 55, no. 5, p. 309, May 1978, doi: <https://doi.org/10.1021/ed055p309>.
- [4] Admin, "Activation Energy - Definition, Formula, SI Units, Examples, Calculation," BYJUS, Oct. 16, 2019. <https://byjus.com/jee/activation-energy/> (accessed May 20, 2024).
- [5] Y. Mei, W. Liu, J. Brugger, D. M. Sherman, and J. D. Gale, "The dissociation mechanism and thermodynamic properties of HCl(aq) in hydrothermal fluids (to 700 °C, 60 kbar) by ab initio molecular dynamics simulations," *Geochimica et cosmochimica acta*, vol. 226, pp. 84–106, Apr. 2018, doi: <https://doi.org/10.1016/j.gca.2018.01.017>.
- [6] S. Delbarre, Léo Courty, and Mame William-Louis, "Thermal analysis of the decomposition of a LOVA gun propellant based on RDX and Nitrocellulose," *Hal.science*, 2023, doi: <https://hal.science/hal-04501346>.

## Appendix

### Materials and Method

- Long test tube with arm
- Gas syringe
- Rubber bung and delivery tube to fit the test tube
- Two large beakers for the water bath and reaction mixture
- Pipette and pipette filler
- Two clamp stands
- Test tube holder
- Thermometer
- Ring stand, Bunsen burner, clay triangle
- Stopwatch
- Graph paper
- Magnesium ribbon cut into 4 cm length and weighed

- Magnesium turnings (same mass as ribbon)
  - Hydrochloric acid (2.0 M and 1.0 M)
  - DI water
- 
- Three solutions of HCl were prepared, 1.0M 1.5M and 2.0M.
  - 20ml of 1.0M HCl was placed in the test tube with gas arm connected.
  - Mg ribbon was weighed and then added to HCl in test tube, the timer was simultaneously started.
  - The volume of gas evolved in 10s increments was taken.
  - This was repeated for 1.5M and 2.0M solutions of HCl.
  - This procedure was also repeated another three times using 1.0M HCl but this time varying the temperature being, 298.15K, 318.15K and 328.15K respectively.
  - Finally, the procedure was repeated using the finer Mg turnings with 1.0M HCl.

Care is to be taken on each part to avoid loss of hydrogen gas by ensuring a swift and timely application of a cap or bung to the live experimental test tube.