

C Nolan Lab report 4

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Investigation of effects of reaction conditions on magnesium redox kinetics

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List of abbreviations:

Abbreviation	Definition
m	Gradient
Δ	Change in
y	Cartesian Y coordinate
x	Cartesian X coordinate
t	Time
V	Volume
°C	Degrees Celsius
E_a	Activation energy
k	Rate
mol	Moles
dm	Decimetres
s	Seconds
HCl	Hydrochloric acid
Mg	Magnesium
MgCl ₂	Magnesium chloride
H ₂	Hydrogen
OME	Ordnance Munitions and Explosives
PBX	Polymer-Bonded Explosive

Introduction

The rate of a reaction can depend on a multitude of factors. It is understood that rate carries a direct proportionality to the concentration of reactants, however the exact nature of the order of proportionality is not necessarily known. For this experiment it can be hypothesized that by adjusting the concentration of one of the reactants as an independent variable, the time of reaction and volume of gas produced can be measured as dependent variables to deduce the order of the relationship between reactant concentration and rate. The mass of the other reactant will be used as a control variable. Additionally, it can be hypothesized that the

independent variables of temperature and surface area can also be used to observe the effect they have on the rate of reaction.

A typical rate equation of unknown order with arbitrary reactants A and B is present in [eq. 1], where k is the rate constant, the square brackets represent concentration, and the unknown orders of reaction are given as n and m.

$$(1) \text{ rate} = k[A]^n[B]^m$$

In order to find the order of the reaction with respect to [A], the rates of reactions with varying concentrations of reactant A must be plotted against their respective concentrations to observe the proportionality relationship in [eq.2]. The order can be gleaned from the linearity of the trendline.

$$(2) \text{ rate} \propto [A]^n$$

The rates necessary for the plot can be found by plotting volume of gas evolution against time and calculating the instantaneous rate either by differentiation or direct interrogation of a line of best fit [eq.3], where m is the gradient, c is the y-intercept, Δy is the change in the cartesian y coordinate and Δx is the change in the cartesian x coordinate. The gradient of such a plot would be considered a proxy for the rate of reaction in the form of [eq.4] where V is volume of gas evolved, and t is time.

$$(3) m = \frac{\Delta y}{\Delta x} \text{ when } y = mx + c$$

$$(4) \text{ rate} \propto \frac{\Delta V}{\Delta t}$$

The reaction being investigated is the redox reaction between magnesium (Mg) and hydrochloric acid (HCl) [eq.5], wherein magnesium metal in an oxidation state of 0 is oxidised to +2 by two stoichiometry equivalents of HCl, while hydrogen goes from +1 to 0.



Results

The data from each experiment was collected and plotted. Each reaction was given an individual plot during its fastest period of reaction, and an instantaneous reaction rate was calculated, with each being listed in [table 1]. The rates of the differing particle size experiments were not calculated, as explained in the discussion.

Concentration mol dm ⁻³	Rate	Temperature °C	Rate
0.5	0.0683	36.6	0.9941
1.0	0.705	38.2	1.0982
1.5	1.4263	48.1	1.1164
2.0	2.1891		

Concentration dependence

The rate for each concentration was plotted individually [fig.1,2,3,4] and combined [fig.5]. Then the calculated rates were plotted against the concentrations to find a 1st order rate relationship, indicated by the direct linearity of rate with respect to concentration [fig.6].

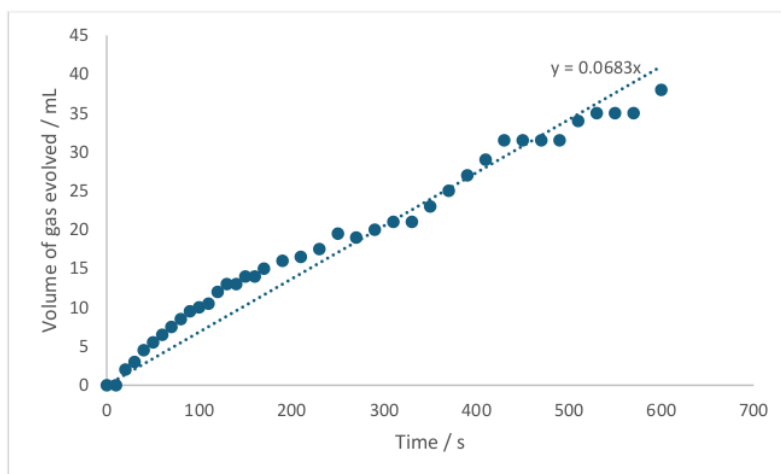


Figure 1: Plot of volume of hydrogen gas evolved against time for 0.5 mol dm⁻³

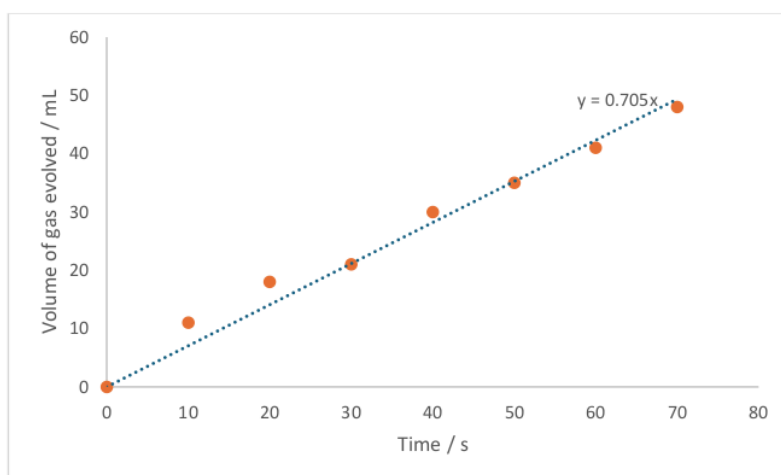


Figure 2: Plot of volume of hydrogen gas evolved against time for 1 mol dm⁻³

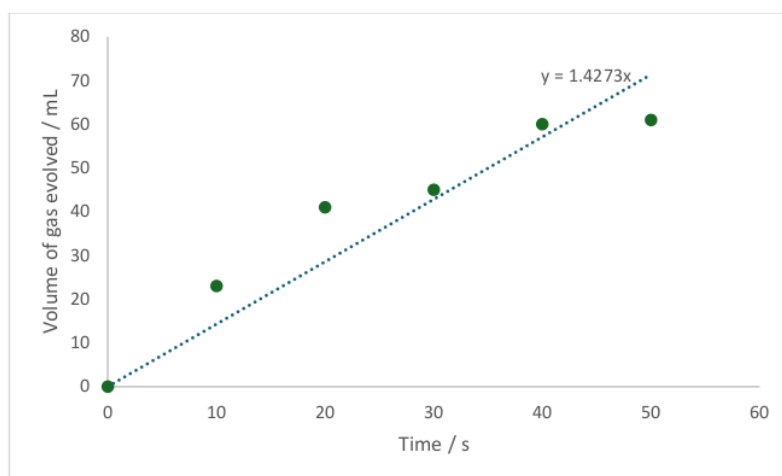


Figure 3: Plot of volume of hydrogen gas evolved against time for 1.5 moldm⁻³

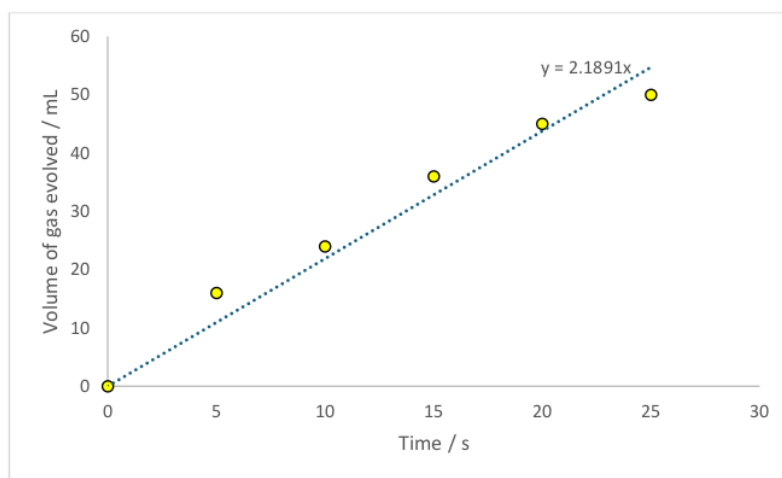


Figure 4: Plot of volume of hydrogen gas evolved against time for 2 moldm⁻³

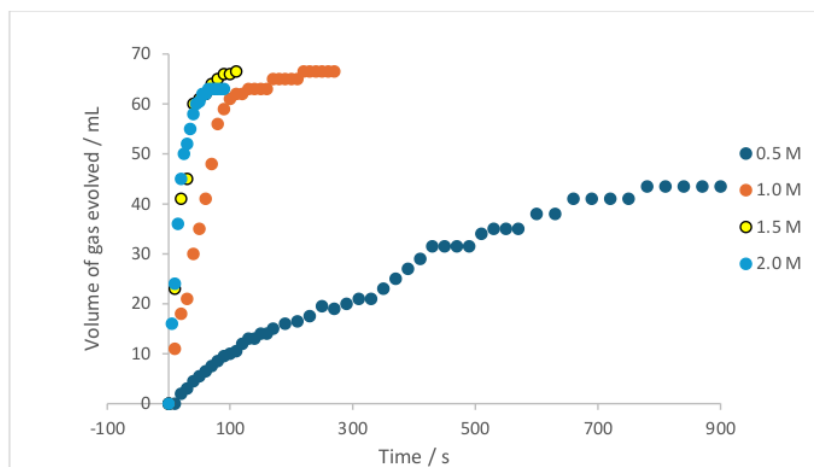


Figure 5: Plot of all concentrations for general comparison

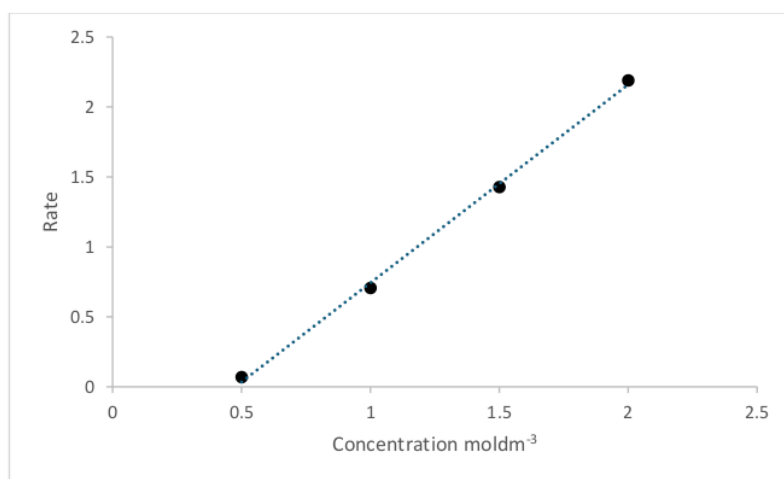


Figure 6: Plot of rate proxies against concentration

Temperature

The rate for each temperature was plotted individually [fig.7,8,9] and combined [fig.10]. A positive correlation between temperature and rate can be observed in [fig.11].

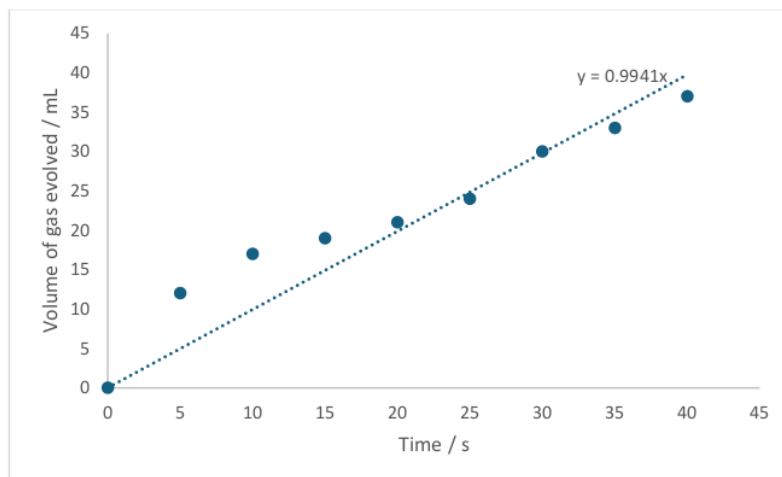


Figure 7: Plot of volume of hydrogen gas evolved against time for 36.6 °C

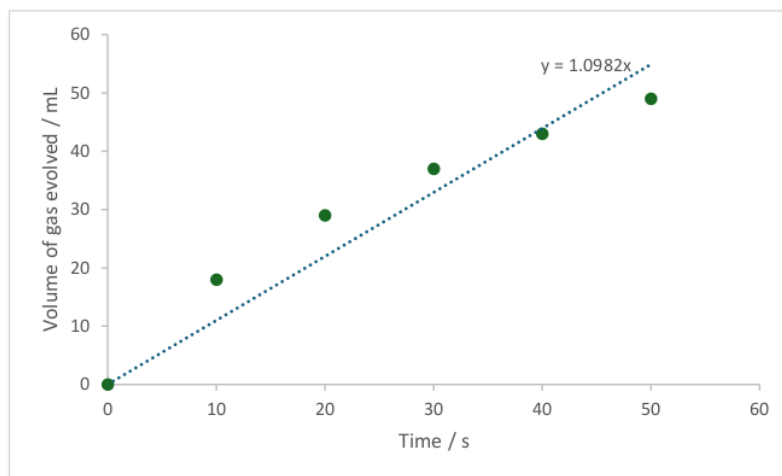


Figure 8: Plot of volume of hydrogen gas evolved against time for 38.2 °C

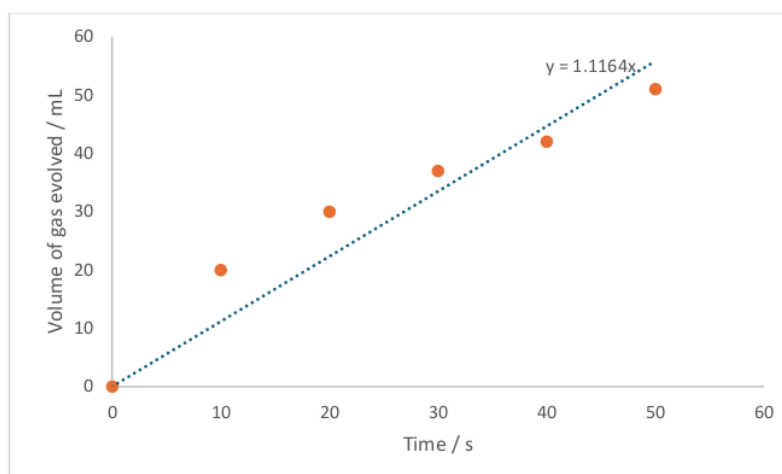


Figure 9: Plot of volume of hydrogen gas evolved against time for 48.1 °C

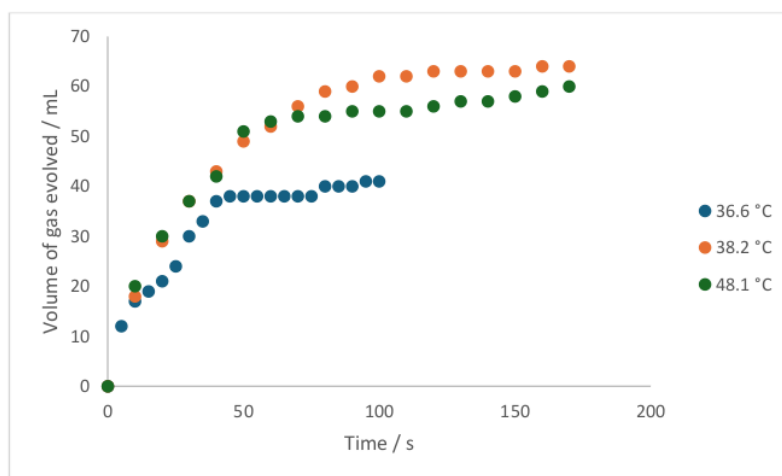


Figure 10: Plot of all temperatures for general comparison

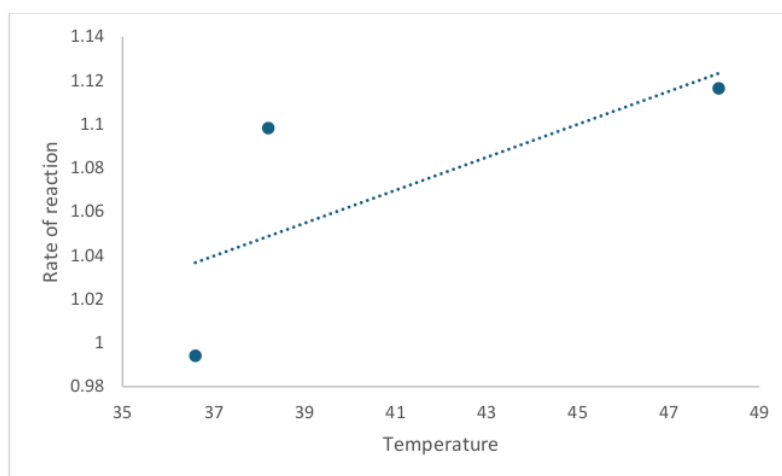


Figure 11: Plot of rate proxies against temperature

Surface area

The rate for the increased surface area reaction was plotted can be compared with the smaller surface area equivalent in [fig.12]. This appears to incorrectly indicate that there is a negative correlation between surface area and reaction rate, which will be addressed in the discussion.

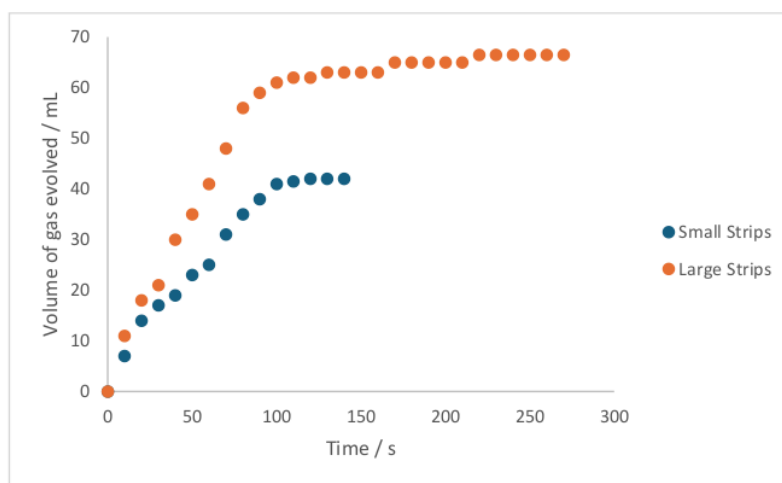


Figure 12: Plot of volumes of hydrogen evolved against time for small and large strips of magnesium

Discussion

Accuracy and Error

The effects of concentration, temperature and surface area on reaction kinetics are well understood [1]. The findings of varying concentration are consistent with the notion that the redox of magnesium and HCl is first order with respect to HCl concentration, and this is generally known to be true.

Temperature is known to have a positive correlation with reaction rate due to its proportionality relationship with the rate constant (k) [eq.6], however the data presented in this experiment does not demonstrate this relationship accurately. This is likely the result of the methodological errors discussed later.

$$(6) k = Ae^{\frac{-E_a}{RT}}, \therefore k \propto e^{-\frac{1}{T}}$$

The surface area of a reactant is known to positively correlate with reaction rate as well, although the data obtained from this experiment would conclude the opposite. This is also likely due to methodological errors.

While many avenues for inaccuracy exist due to the nature of the experimental setup, two major sources of error stand out.

The first is the efficacy of the gas syringes used. These syringes would sporadically become jammed and suddenly increase greatly in measurement over the reaction time, significantly affecting the recorded rates. Such an issue could be avoided in the future by ensuring gas syringes are adequately lubricated before use, or simply by choosing a different method of determining the rate, such as direct concentration monitoring via a digital probe.

The second methodological flaw occurred during the addition of smaller pieces of magnesium for the increased surface area experiment. The diameter of the reaction vessel used was far too small for complete addition of magnesium without spillage. Additionally, the system was not able to be closed in time to ensure complete gas capture, an issue which was likely present in every faster rate experiment, resulting significant losses of gas. While the use of a funnel would likely prevent the first part of this issue, simply using an addition funnel to add a liquid reagent to HCl would avoid all issues associated with this methodology.

Ordnance, Munitions and Explosives (OME) applications

The utility of the field of reaction kinetics cannot be understated in the OME industry. As acknowledged by Liu et al. [2] in their investigation of a polymer-bonded explosive (PBX), “the reaction rate model is crucial since it controls the process of the explosive”. Knowing the kinetics of an explosive reaction in this manor can allow for a greater understanding of the resultant physical effects it will have after detonation. Liu et al. constructed a mathematical model to describe how the reactions of the different explosive substances

present in their PBX propagated through the material in and proceeded in accordance with known rate laws such as the Arrhenius law.

Explosive compounds react too quickly and energetically to practically or safely measure their rates directly, as such, Loboiko & Lubyatinsky [3] used the novel technique of measuring reaction rate via the recording of shock-wave luminosity to gain insight into the nature of high explosive (HE) detonations. It was found that by recording the intensity of the of radiation emission of a HE detonation shockwave, the velocity of the gases can be calculated. This in turn can be used under the ZND detonation model to calculate the rate at which the detonation reaction travels via the Chapman–Jouguet condition, which states that the propagation velocity just reaches the velocity of sound in the medium of the leading shockwave.

The implications of the physical dimensions of reactants also extend to the OME industry. Jones [4] found that rate of detonation of explosives in cylindrical tubes depended on the radius of those tubes. The finding that constricting the diameter of a tube containing an explosive would increase the rate of reaction has obvious implications on the manufacture of explosives.

Conclusion

While the initial hypothesis was found true via the confirmation of a 1st order reaction rate with respect to HCl concentration, the secondary hypothesis of temperature and surface area dependence lack adequate evidence to be truly supported by this experiment, although common scientific consensus suggests it would be true. Significant improvements to the reaction methodology were suggested and applications of kinetics analysis were found to be abundant, and of significant interest.

References

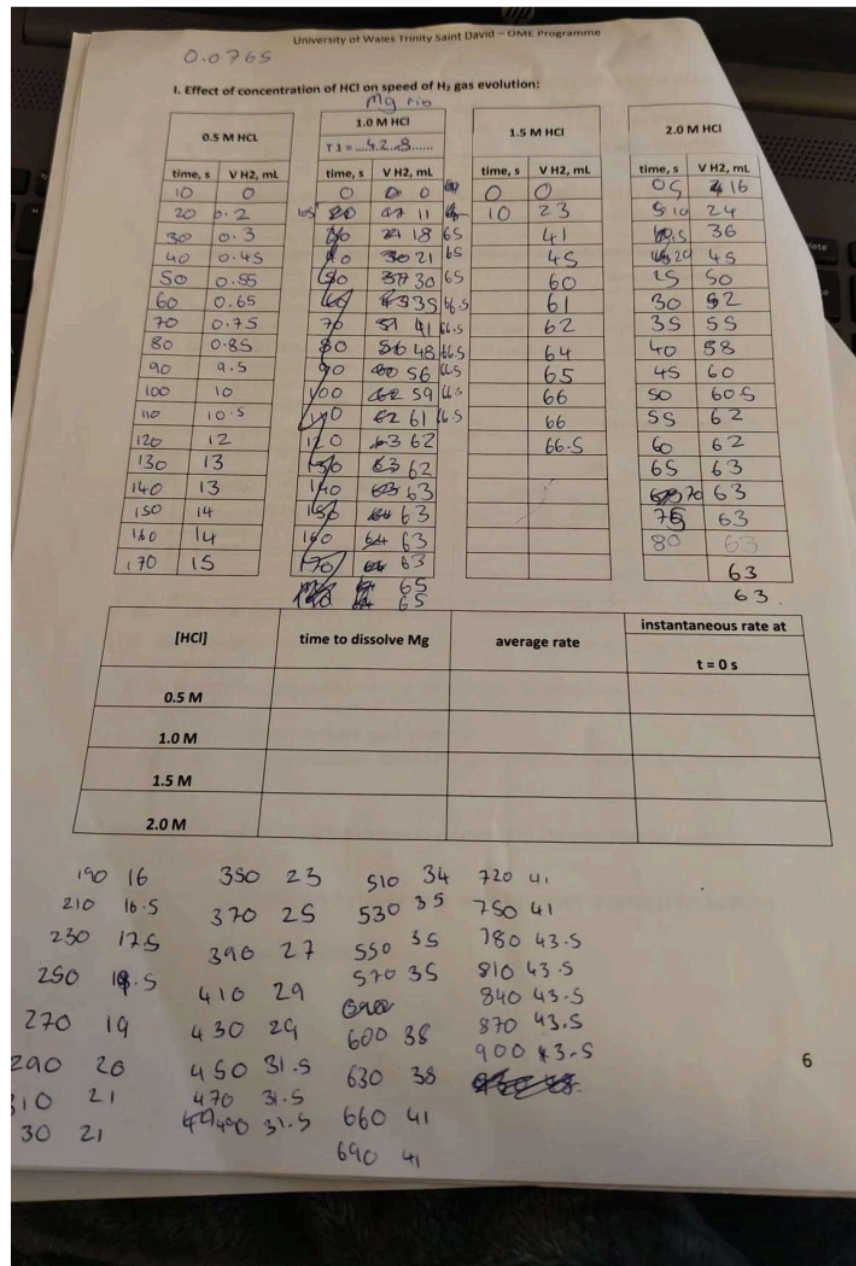
- [1] P. Flowers, Klaus Theopold, R. Langley, W. R. Robinson, and O. College, *Chemistry*. Houston, Texas: Openstax, Rice University, 2018, p. 606.
- [2] Y. R. Liu, Z. P. Duan, Z. Y. Zhang, Z. C. Ou, and F. L. Huang, "A mesoscopic reaction rate model for shock initiation of multi-component PBX explosives," *Journal of hazardous materials*, vol. 317, pp. 44–51, Nov. 2016, doi: <https://doi.org/10.1016/j.jhazmat.2016.05.052>.
- [3] B. G. Loboiko and S. N. Lubyatinsky, "Reaction Zones of Detonating Solid Explosives," *Combustion, Explosion, and Shock Waves*, vol. 36, no. 6, pp. 716–733, 2000, doi: <https://doi.org/10.1023/a:1002898505288>.
- [4] H. Jones, "A theory of the dependence of the rate of detonation of solid explosives on the diameter of the charge," *Proceedings of the Royal Society of London A Mathematical and Physical Sciences*, vol. 189, no. 1018, pp. 415–426, May 1947, doi: <https://doi.org/10.1098/rspa.1947.0049>.

Appendix

Method:

Equipment:

Copies of worksheet:



ii. Effect of temperature on speed of H_2 gas evolution

other group.

T2 = 36.6

time, s	V H_2 , mL
5	12
10	17
15	19
20	21
25	24
30	30
35	33
40	37
45	38
50	38
55	38
60	38
65	38
70	38
75	38
80	40
85	40

90 40
95 41
100 41

T3 = 38.2

time, s	V H_2 , mL
0	0
10	18
20	29
	37
	43
	49
	52
	56
	59
	60
	62
	62
	63
	63
	63
	64

64

T4 = 48.1

time, s	V H_2 , mL
0	0
10	20
20	30
	32
	42
	51
	53
	54
	54
	55
	55
	55
	56
	57
	52
	58
	59

60

61
62
62
62
63
63
64
64

temperature	time to dissolve Mg	average rate	instantaneous rate at
			t = 0 s
T1			
T2			
T3			
T4			

$$T_1 = 46.6$$

time, s	VH2, mL
10	7
20	14
30	17
40	19
50	23
	25
	31
	35
	38
	41
	41.5
	42
	42
	42

[illegible]