Ultrasonic measurements of gas syringe positions for the kinetic study of reactions between acids and aluminium

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ABSTRACT

Gas syringe measurements are commonly used to study the rate of reactions of gas-producing reactions but it often involves manual reading and leads to possible human error. In this study, we report the use of Arduino and an ultrasonic sensor HC-SR04 to allow for continuous and real-time monitoring of gas-producing reactions. The reaction studied here is the reaction of aluminium with solutions of acids (hydrochloric and sulfuric acid) to elucidate the effect of anion and concentration on the rate of reaction as it is not well reported in the literature. Herein, we find that there is an induction time before the hydrogen gas is produced and this could be due to the oxide layer that needs to be reacted before the aluminium surface can be reacted with acid. The reaction of aluminium and hydrochloric acid is much faster than that of sulfuric acid and this suggests that there is a selective anion effect that chloride activates the surface more than the sulfate.

INTRODUCTION

The measurement of gas volumes is an important and accessible way in laboratories [1] to gain insights into the kinetics of reactions involving the production of gas. Typically, gas volumes can be measured using a graduated gas syringe, which allows the volumes at different timings to be recorded. However, this is often limited by the precision of the gas syringe (0.5mL for a 35mL gas syringe) and parallax errors from manually reading the plunger positions. Furthermore, there is also a lack of automated gas volume measurement that is available readily and cheaply and the construction of the glass syringe might be prone to warping if not properly maintained. Alternately, gas flow sensors can be used to continuously measure the flow rate of gas such that gas production can be determined [2]. However, apart from its excessive costs [3], they have defined working ranges and accuracy.

Aluminium, is a common metal used in the external facades of buildings, aircraft and spacecraft components as it is lightweight and strong, allowing an aircraft to carry more weight and become more fuel efficient. Furthermore, it has properties of corrosion resistance, as well as its resistance to water and immunity to the harmful effects of UV rays, thus ensuring a longer lifespan of the buildings [4]. Therefore, it is the second most used metal in the world after steel [5]. However, in the presence of a corrosive environment like acid rain that contains chloride ions, aluminium is still susceptible to corrosion, prompting the need for protective coatings to prevent this corrosion [6].

The effects of concentration on the rate of reaction between acids and aluminium are often studied and tested [7], however, studies on the effect of anion on reaction of acid and aluminium are much less common. Some similar studies involving acid reactions of aluminium include the effect of anions on the reaction with the study of corrosion inhibitors, in which the corrosion inhibition of aluminium in the presence of ethyl trimethyl ammonium bromide was studied. [8] The corrosion behaviour of A*l* in 2 M HC*l* solution in the presence of various corrosion inhibitors were similar investigated using different chemical and electrochemical techniques [9].

In this project, we report the use of a glass syringe as the gas syringe and an ultrasonic distance sensor HC-SR04, triggered and monitored using Arduino to determine the volume of gas produced and its application towards studying the rate of gas production for a reaction between aluminium and two acids, namely hydrochloric acid and sulfuric acid.

MATERIALS AND METHODS

A) Ultrasonic distance measurement of the gas syringe plunger and calibration of gas syringe

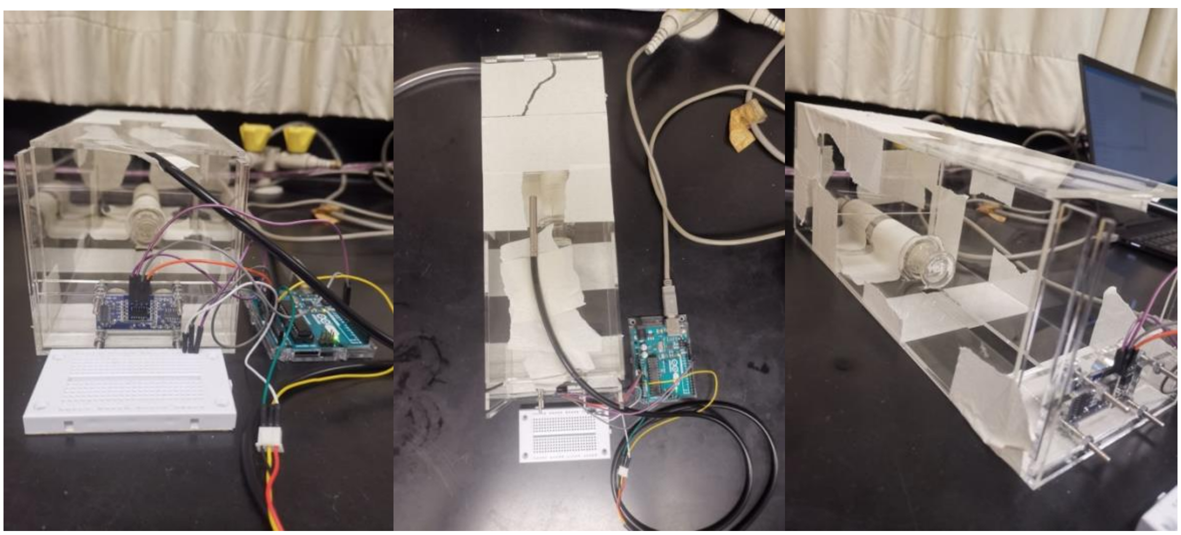

Figure 1: Setup of ultrasonic sensor aligned to measure distance of plunger away from sensor, connected to Arduino which then sends a serial output of the readings to the computer.

As shown in Figure 1, the ultrasonic sensor HC-SR04 with a glass syringe to Arduino as shown in Figure 1. A glass syringe was used instead of a plastic syringe as there was more friction in the in the plastic syringe due to its rubber seal of the plunger, causing it to become stuck with insufficient gas pressure and be less responsive.

The glass syringe was enclosed in an acrylic box to minimize by ultrasonic noise from the surrounding that can result in erroneous readings. By using the HC-SR04 ultrasonic sensor which has an integrated circuit to easily program with Arduino, the distance between the sensor and the plunger can be measured automatically and continuously without the need for human interference [10]. Furthermore, the usage of the ultrasonic sensor removes the need to manually measure the volume of gas in the syringe's barrel, eliminating inaccuracies stemming from parallax errors. An acrylic cut-out was used to fixed the position of the sensor and sleeves to ensure that any changes in the distance is largely due to the movement of the plunger.

By connecting the ultrasonic sensor HC-SR04 and Arduino, the sensor is able to measure the total time taken for a single ultrasound pulse of 40 kHz to travel from the sensor to the plunger and back to the sensor. We coded the Arduino from New.ping library [11] to obtain ten repeats before returning the median to avoid extremes values due to noise. The program loops and returns in a new data point approximately every 1310 seconds. Thereafter, the time taken for the pulse to travel to the plunger and back into the sensor is converted to the distance between them using the formula:

$$d = \frac{vt}{2}$$

where d is the distance between the plunger and sensor

v is the speed of sound

t is the time taken for the pulse to travel

The calibration of the 35mL gas syringe was attempted by producing hydrogen gas from the reaction of limiting amounts of magnesium and hydrochloric acid into the gas syringe. However, due to the oxide layer on the magnesium strips, there was errors in the measurement of the mass of magnesium used despite our efforts to sand it down. Instead, we calibrated the glass gas syringe by injecting air from a 5 mL plastic syringe through a tubing. The plastic syringe was calibrated by measuring volumes of water (1mL increments) measured using the plastic syringe and weighing it accordingly. The glass syringe was calibrated by measuring volumes of water (5mL increments) measured using the glass syringe and weighed accordingly.

B) Monitoring hydrogen gas production from reactions of aluminium and acids

Figure 2: Setup of round-bottom flask with dropping funnel. The top of the dropping funnel is connected to a tubing adaptor of which a Tygon tubing is connected to a gas syringe.

Aluminium foil of thickness 0.41mm was obtained from UNI-CHEM. Concentrated hydrochloric acid and sulfuric acid were obtained from Asia Scientific Apparatus Co, and diluted to the desired concentrations. Potassium hydrogen phthalate was obtained from Sigma-Aldrich and was titrated using bromothymol blue indicator and used to standardize the acid concentration with NaOH using published procedures [12].

For a sample experiment, the respective acids are reacted with aluminium in a 100-mL round-bottom flask with a dropping funnel attached as shown in Figure 2. A mass of 0.0225 g of aluminium foil is kept constant in each experiment. The mass of metal and concentrations of acids are chosen such that the concentration of the acid does not deviate too much from its original value when the metal is fully reacted. The aluminium is submerged in 50 mL of hydrochloric acid (acid will be introduced via the dropping funnel and the measurements will start once the dropping funnel is emptied). The reaction mixture will be stirred via a stir bar and magnetic stirrer throughout the experiment and the temperature is kept at about 300K by keeping it in a water bath with a temperature of 299.7 ± 0.6 K as determined by a LM35DT temperature sensor. No noticeable increase in water bath temperature due to the reaction of acid and metal even at the higher concentrations of 1.2 M HC*l*.

The volume of gas produced into the gas syringe by each reaction is measured over time with the ultrasonic sensor setup and the rate of gas production is recorded. The experiment is then repeated at the different concentrations of acids (0.8 M, 0.9 M, 1.0 M, 1.1 M HC*l* and 0.6 M H_2SO_4) as well as combinations with NaC*l* or Na_2SO_4 with hydrochloric acids to investigate the effect of anions. To compare the reactions, graphs of 10-point averages of the volumes calculated are plotted against time. The averaging will smooth out fluctuations due to electrical noise.

On top of comparing the graphs of the volume of gas produced, two more parameters are evaluated: the induction time before production of hydrogen gas is observed, average speed of gas production. Studying the induction time allows us to understand how the acid concentration affects the activation of the surface before the acid reacts with bare surface metal. The average speed of gas production can provide an indicator of the relative rates of reaction and allow us to account for the difference in volume of gases produced between the different experiments.

RESULTS AND DISCUSSION

<u>A) Calibration of glass gas syringe</u>

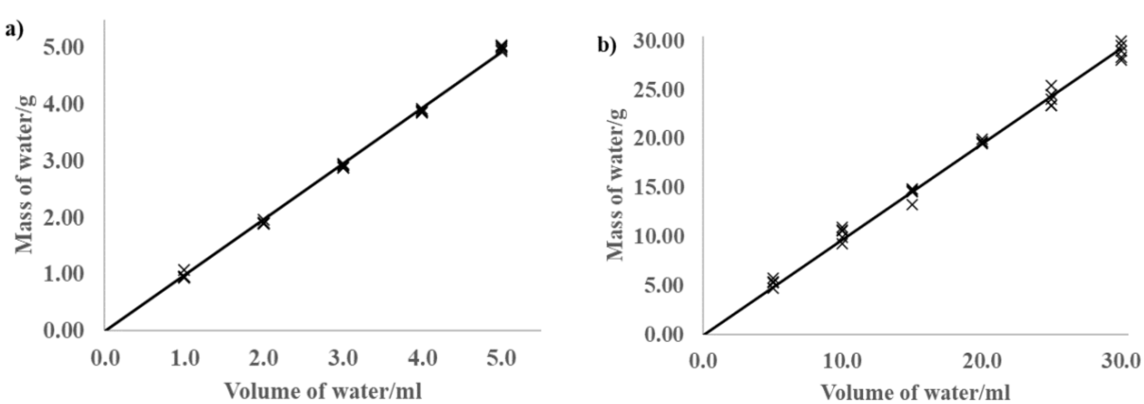

Figure 3: Mass-volume of water graphs for the calibration of a) the plastic syringe and b) the glass gas syringe (bottom). The error bars are not shown but the uncertainty due to the measurement of volume is about 1% and 0.01 g for the mass of water.

The mass of water increased linearly with volume for both syringes (Figure 2) and the density of water was calculated to be 0.984 g/mL and 0.974 g/mL for the plastic and glass syringes respectively. These values deviate from the reported density of water (0.996 g/mL) at 28.0°C [25]. This deviation is likely due to the uncertainty of the volume measurement at ±0.1 mL for the plastic syringe and ±0.5 mL for the glass syringe leading to about 1% uncertainty for each measurement. However, the larger deviation of the glass syringe implies that the glass syringe cannot be taken as calibrated and this also highlight the problem of inaccurate calibration of the glass syringe if left unchecked. In addition, there was a larger spread of values for the glass syringe owing to the difficulty of keeping the smoother plunger in place when transferring the liquid.

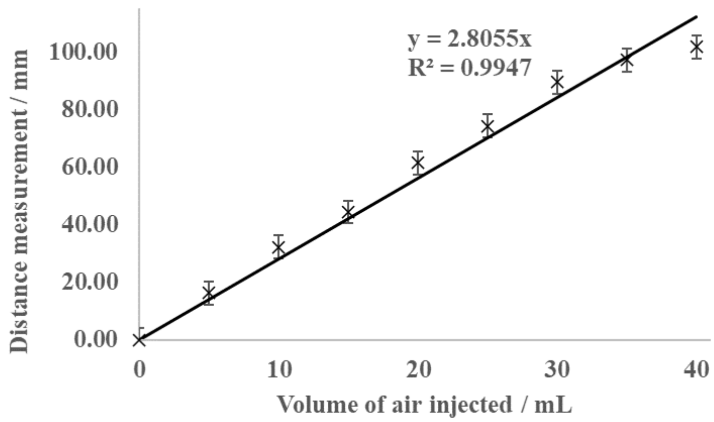

Figure 4: Distance measured by the ultrasonic sensor setup when volume of air is injected into the syringe. The vertical error bars (not shown) are about 1%.

As shown in Figure 4, the volume of gas in the glass syringe increased linearly, with the exception towards the end, at about 40 mL as measured by the ultrasonic sensor. In addition, the ultrasonic sensor shows that the measuring range of the gas syringe can be increased from 35 mL to 40 mL without the plunger falling off. However, the ultrasonic measurements still produce an error of about 0.5 mL for volume measurements due to electrical noise in the signal generated in the setup.

B) Monitoring hydrogen gas production from reactions of aluminium and acids

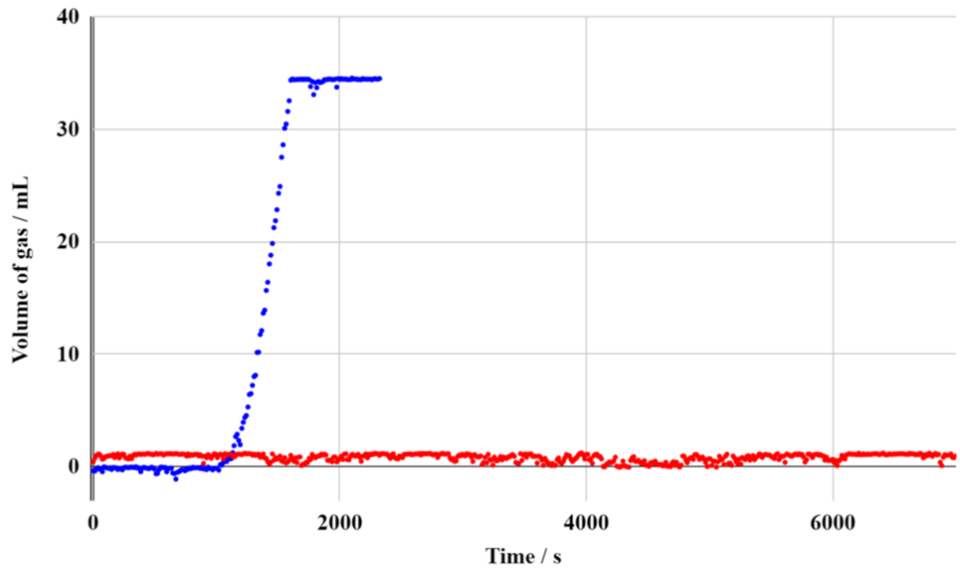

Figure 5: Volumes of gas measured over time for the reaction of aluminium with 1.2 M HC*l* (•) and 0.6 M H_2SO_4 (•).

As shown in Figure 5, the reaction of 1.2 M HC*l* with aluminium took place with two stages: an initial induction period of about 1030 s before the gas production started and the eventual gas production which ended after 1700 s. The total volume of gas produced is also much lower than the expected volume of 90 mL if the aluminium is pure. This points to the presence of an oxide layer that both affect the purity of the aluminium and necessitates an induction time before the acid has access to the aluminium metal underneath the oxide. This is supported by the fact that the rate of hydrogen gas production gradually increases at the onset of hydrogen gas production, instead of having the same gradient throughout the experiment.

On the other hand, 0.6 M H_2SO_4 did not react with aluminium at all within the measurement time frame of 7000s. This implies there is an anion effect that Cl^- has an effect on the reaction of acids with aluminium likely due to a faster reaction with the oxide surface before the acid reacts with aluminium to produce hydrogen gas, while the reaction between H_2SO_4 and aluminium oxide is much slower. This is in line with the reports of enhancement of corrosion of aluminium oxide using Cl^- and other ions [13] due to adsorption of Cl^- on the oxide surface and penetration of Cl^- through the oxide film. The SO_4^{2-} might not be able to penetrate as well as Cl^- but the reason is uncleared and suggests an inhibiting effect by the sulfate on the aluminium surface.

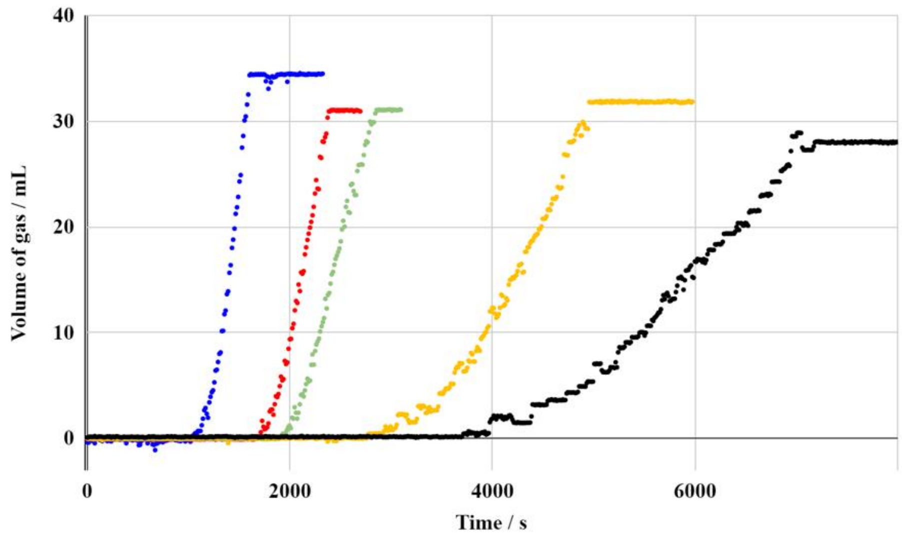

Figure 6: Volumes of gas measured over time for the reaction of aluminium with different concentrations of HC*l*. (0.8 M (•), 0.9 M (•), 1.0 M (•), 1.1 M (•) and 1.2M (•))

As shown in Figure 6, the varying concentrations of the HC*l*, has resulted in different average volumes of hydrogen gas produced as well as a difference in the induction time of each experiment. As the concentration of HC*l* increases, the average volume of gas produced increases, and the induction period decreases. As seen in the graph, 1.2 M HC*l* has produced the highest volume of hydrogen gas, and had the shortest induction period to break down the oxide layer on the aluminium foil before it could react with the aluminium itself. On the other hand, 0.8 M HC*l* has produced the lowest volume of hydrogen gas, and had the longest induction period. Thus, this shows the direct relationship between the concentration of HC*l* and the volume of hydrogen gas produced, as well as the inverse relationship between the concentration of HC*l* and the length of the induction period.

Table 1: Induction time before hydrogen gas production and average rate of gas production from the reaction between HC*l* and aluminium for the concentration of HC*l* between 0.8 M and 1.2 M

Concentration of HC*l* / M	**Induction Time / s**	**Average rate of gas production mL / s**
0.8	3720	0.0087
0.9	2700	0.0137
1.0	2000	0.0365
1.1	1760	0.0470
1.2	1030	0.0596

When the concentration of HC*l* was varied between 0.8 M and 1.2 M, the graphs (Figure 6) shows that the induction time decreases from 3720 s to 1030 s (Table 1) as the concentration decreases from 0.8 M to 1.2 M. This is expected as the increase in acid concentration results in the faster depletion of the oxide surface. The average rate of gas production increases with concentration as well and indicates a concentration dependence on the rate of reaction. The volumes of H_2 differ between the different concentrations likely due to differences in the oxide surface area on the aluminium foil.

On close examination, there are still observed dips in the volume measurements over time despite the 10-point averaging. This is likely due to an instrumentation error of the glass syringe barrel that might have localized ballooning that gave space for the gas to leak into and giving rise to fluctuating values. The ultrasonic sensor is also prone to ambient noise in the ultrasonic frequencies (for example, when rain was approaching, we noticed that there were fluctuations in a stationary value measurement**)**

As the concentration of HC*l* increases from 0.8 M to 1.2 M, the induction time decreases from 3720 s (about 1 hour) to 1030 s. This could be due to the increased rate of reaction between the oxide layer and the acid with increasing concentration of HC*l*, decreasing the time taken for the oxide layer to be activated sufficiently before the HCl can act on the metal surface. In addition, as the concentration of HC*l* increases, there was a corresponding increase in the average rate of hydrogen gas production and this is likely due to the increase in rate of reaction between the higher concentration of hydrogen ions around the exposed aluminium surface.

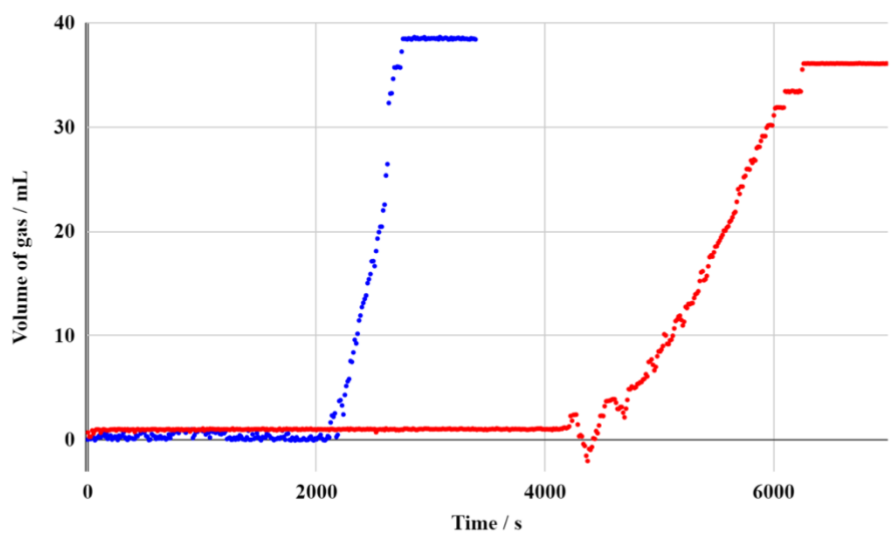

Figure 7: Volumes of gas measured over time for the reaction of aluminium with 1.2 M HC*l* in the presence of added 1.2 M NaC*l* (•) and (b) 0.6 M Na_2SO_4 (•)

As shown in Figure 7, the graph of 1.2 M HC*l* in the presence of added 1.2 M NaC*l* has a shorter induction period than the graph of 0.6 M Na_2SO_4. This is in line with the experiment comparing the kinetics of respective reactions of hydrochloric acid and sulfuric acid with the aluminium foil and suggests that the sulfate does inhibit the acid and aluminium oxide reaction, rather than just a pure activation by the C*l*$^-$ ions.

What is more interesting is that there was a longer induction time upon adding 1.2 M NaC*l*, suggests that the Na^+ cation might have an inhibiting effect on the reaction of the aluminium oxide layer with the acid. This effect is unexpected and may warrant more studies to understand the effect of both the Cl^- and its accompanying cation. This can allow us to isolate the effect of SO_4^{2-} or Cl^- anion from the Na^+ cation. There were large fluctuations for the reaction between 4210s and 4780s for the reaction with the added Na_2SO_4 but this is likely an isolated event as it was not observable during other experiments.

Looking at the rate of hydrogen gas production, it is noteworthy that the rate increased slightly with added Na*Cl* and decreased by 3 times for added Na_2SO_4. This implies that once the oxide layer is reacted away, the sodium ion has little effect on the rate of reaction between the acid and aluminium. The decrease in rate of reaction for the added Na_2SO_4 might be due to either a direct effect of the sulfate or due to a carryover effect from having less surface area to allow for the acid to react with the metal.

CONCLUSION

In conclusion, the use of ultrasonic sensor HC-SR04 along with the gas syringe set up connected to Arduino aided our experiments. It extended the measuring range of the gas syringe and allowed for the automated collection of data (volume of gas produced). However, the precision may be off by 0.3 mL to 0.5 mL, and there may be some inaccuracies due to the construction and calibration of the gas syringe.

By using the setup for studying reactions of acids and aluminium, we can conclude that there is an anion effect, with Cl^- anion possibly catalyzing the reaction of acids and the aluminium oxide layer over SO_4^{2-}. We have also observed that the induction time of an experiment is dependent on the concentration of hydrochloric acid, as the concentration of hydrochloric acid increases, the induction time decreases. The average rate of production of hydrogen gas also increases with the concentration of hydrochloric acid.

Through our experiments, we were also able to investigate the effect of added salt Na*Cl* and Na_2SO_4 on the reaction of H*Cl* and aluminium metal. In the investigation, we have found that the addition of either salts increased the induction period to break down the aluminium oxide layer, and that Na_2SO_4 had a larger effect than Na*Cl* on the induction time. Furthermore, we have found that the production of gas is slower when Na_2SO_4 is added rather than when Na*Cl* is added, thus this implies that the sulfate ion does affect even the kinetics of reaction between acid and aluminium beyond the reaction with the oxide layer.

For future experiments, determining the solubility constant of both salts and if solubility is a main reason for the anion effect is an area that can be covered. We have also found that it is important to strip the aluminium oxide layer through sanding in an inert environment to reduce the chances of an oxide layer from forming again.

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APPENDIX

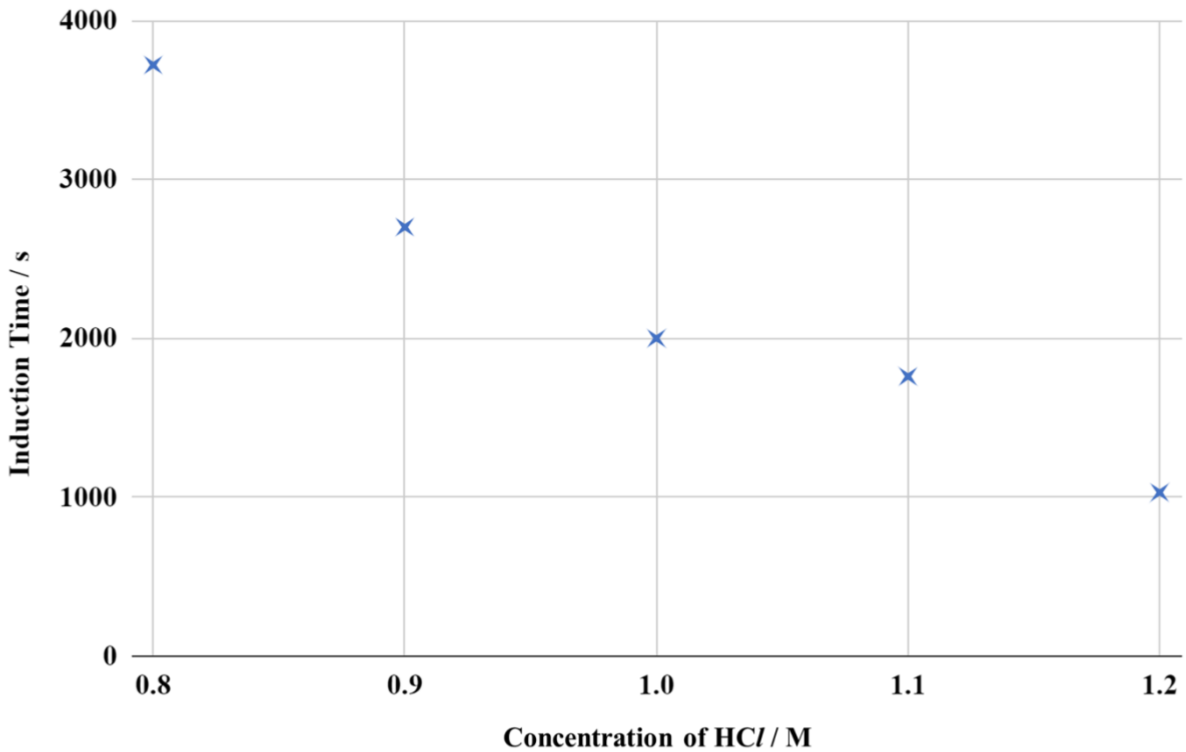
Arduino Code for Distance Measurement using HC-SR04 Ultrasonic Sensor (ref) and NewPing library (ref) coupled with temperature measurement using LM35DT (ref)

```
#include <NewPing.h>
#define TRIGGER_PIN  9
#define ECHO_PIN     10
#define MAX_DISTANCE 140

NewPing sonar(TRIGGER_PIN, ECHO_PIN, MAX_DISTANCE);
int analogVal;
int tempPin = A0;
float voltage, temp;
const int trigPin = 9;
const int echoPin = 10;
float duration;
void setup() {
  Serial.begin(9600); // Starts the serial communication
}

void loop() {
analogVal = analogRead(tempPin);
voltage = (analogVal*5.000)/1024;  // Converts analog reading from LM35 to voltage reading
float tempC = voltage*100; // Converts voltage reading from LM35 to temperature in °C
float temp = (tempC + 273);  // Converts temperature in °C to K
Serial.print(temp);
delay(50);
Serial.print(" ");
Serial.print(millis()); // Prints the time in millisec and distance in mm on the Serial Monitor
Serial.print(" ");
```

```
Serial.println(sonar.ping_median(10)); //Do 10 pings and return median in microseconds
delay (1000);
}
```


4000
3000
2000
1000
0
Induction Time / s
0.8
0.9
1.0
1.1
1.2
Concentration of HC*l* / M

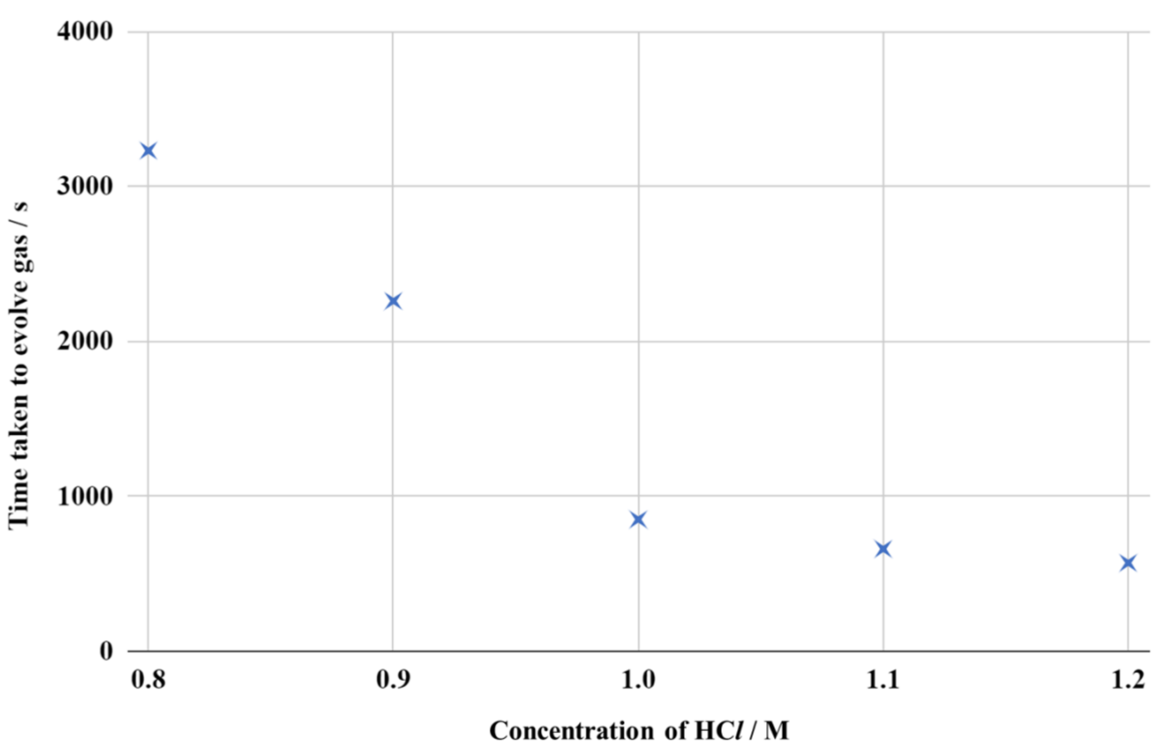

4000
3000
2000
1000
0
Time taken to evolve gas / s
0.8
0.9
1.0
1.1
1.2
Concentration of HC*l* / M

Figure A1: Decrease in a) induction time when the concentration of HC*l* increases and b) time taken for complete evolution of H_2 gas when the concentration of HC*l* increases.

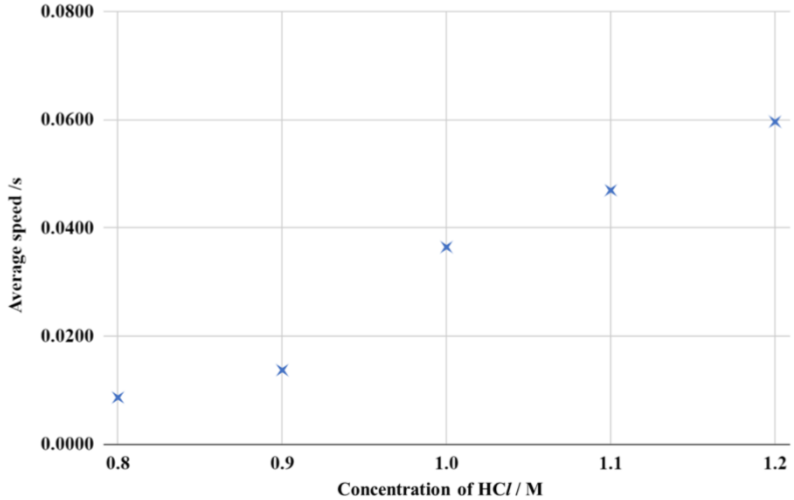


Figure A2: The increase in average speed of gas production when the concentration of HC*l* increases.