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Development of a Novel Chemical Timer

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CHAPTER 1

INTRODUCTION

1.1 Background

The goal of this thesis is to develop a chemical timer for Chem-E Car (Chemical Engineering Car), that is as inherently safe as possible. Chem-E Car is an undergraduate competition held at the regional and national conferences of the American Institute of Chemical Engineers that, “increases awareness of the chemical engineering discipline among the public, industry leaders, educators, and other students” (“Chem-E-Car Competition,” 2020). Students are tasked to build a shoebox sized car powered and stopped by chemical reactions and this car must travel a distance between fifteen and thirty meters in under two minutes. Teams are scored on traveling the correct distance and creativity. The exact distance is not known until the day of the competition, so cars include a chemical mechanism to adjust how far the car travels before it stops. For this study a chemical timer was developed for the Chem-E Car competition.

1.2 Motivation

In 2006, Mississippi State students were working on a pressure-based propulsion system for Chem-E Car when a surge in pressure caused the reactor on the car to explode injuring two students (Elkins, 2006). The same year, AIChE’s Board of Directors temporarily suspended the competition, “due to reports of careless safety practices and inconsistent supervision” (Ellis, 2007). Since 2006, AIChE has implemented mandatory safety training and other measures to increase safety in Chem-E Car competitions. While these safety measures have been largely successful in preventing incidents like the one in 2006, most cars still use hazardous chemicals and operate at hazardous temperatures and pressures. No amount of safety measures can completely eliminate the potential for injury so long as these hazardous are present. That is why this thesis seeks to eliminate these hazards by developing a timer for Chem-E Car that is as inherently safe as possible.

1.3 Criteria for Success

The timer will be evaluated against three main criteria: safety, accessibility, and performance. Safety will be evaluated against the principles of inherently safer design. Accessibility is further divided into cost and ease of construction. The final timer should cost less than $50 to fabricate and $0.20 to run not including shipping and tax.[1] A run consists of charging the timing mechanism with reactants and operating the timer for a short period of time. Each run should cost less than $0.20 to run a single time to ensure that it is accessible to teams with a low budget, and it should be able to be built with common shop tools (e.g., a table saw, drill press, bandsaw). For performance, the timer will be considered successful if it is accurate to ±8.6 s, which is the median performance of cars at the 2018 national competition, exclusive of the cars that did not move from the starting line (see section 4.3 for an explanation of how this value was calculated).

[1] These costs were determined to be reasonable by the experimenter for a Chem-E Car design team with a limited budget

CHAPTER 2

SAFTEY IN CHEM-E CAR

2.1 Safety Design

At its most basic level, safety revolves around the minimization and mitigation of hazards which are defined as “an inherent chemical or physical characteristic that has the potential for causing damage to people, property, or the environment” (“Guidelines for engineering design for process safety”, 2012). Hazards can be classified as intrinsic hazards and extrinsic hazards. Intrinsic hazards, more commonly called “chemical hazards”, are hazards associated with a particular chemical that are independent of how that chemical is used (“Guidelines for engineering design for process safety”, 2012). In this context, chemical refers to, “any substance, or mixture of substances” (OSHA, 2016). Chemical hazards can be further divided into physical hazards and health hazards. Physical hazards are associated with the physical or chemical properties of a chemical (e.g., flammability, reactivity), and health hazards are the ability of a chemical to cause undesirable health effects (e.g., skin irritation, cancer) (OSHA, 2016). There are several different systems for identifying and classifying chemical hazards. The most widely used and the one Chem-E Car uses is the Globally Harmonized System (GHS) which is an internationally agreed upon standard managed by the United Nations. Extrinsic hazards are hazards that arise from how a chemical is used (e.g., operating conditions, quantity, geographic location) (“Guidelines for engineering design for process safety”, 2012). For Chem-E Car, the main extrinsic hazards are temperature and pressure. Both in intrinsic and extrinsic hazards can be mitigated with appropriate safety design.

Safety design follows a hierarchy given in order of decreasing robustness and reliability:

- Inherent – eliminates hazards by using less hazardous materials or operating conditions.
- Passive – minimize the frequency or consequence of a hazard using design features which do not rely on the active functioning of a device (e.g., secondary containment to contain spills)
- Active – minimize the frequency or consequence of a hazard using design features which rely on the active functioning of a device (e.g., pressure relief valves)
- Procedural – minimize the frequency or consequence of a hazard using procedures and policies (e.g., routine inspection)

The most important of these four safety strategies is inherent safety, more commonly referred to as inherently safer design. Inherently safer design follows four tenants:

- Minimize – minimize the inventory of hazardous chemicals and size of equipment operating at hazardous conditions.
- Moderate – operate at less hazardous conditions.
- Substitute – replace hazardous chemicals with less hazardous chemicals.
- Simplify – eliminate unnecessary complexity.

Because it seeks to eliminate hazards instead of controlling them, inherently safer design is the most robust and reliable safety design ("Guidelines for engineering design for process safety", 2012).

For this study, using the principles explained above, inherently safer design will drive design decisions. The process chemistry will be selected to eliminate chemical hazards and the equipment will be designed to mitigate physical hazards. Ideally, the timer should use non-hazardous chemicals and operate at ambient temperature and pressure. Only when inherent safety cannot be used to eliminate a hazard will other safety design measures be used. With this focus, several potential timer designs were considered.

2.2 Popular Timers

Before designing a new timer, it is helpful to examine what timing mechanisms Chem-E Car teams have used in the past to stop their cars. The most popular timers can be divided into two categories based on their chemistries: clock reactions, and gas generating reactions. A survey of the "Chem-E-Car in the Spotlight" videos posted by AIChE for the 2019 national conference showed that 69% of teams used a clock reaction to stop their car, 5% used gas generating reactions, 5% used another stopping mechanism, and 21% did not say how they stopped their car. This information is summarized in Figure 2.1 below and a detailed list of the timing mechanisms used by teams in the 2019 national competition is given in Appendix A.

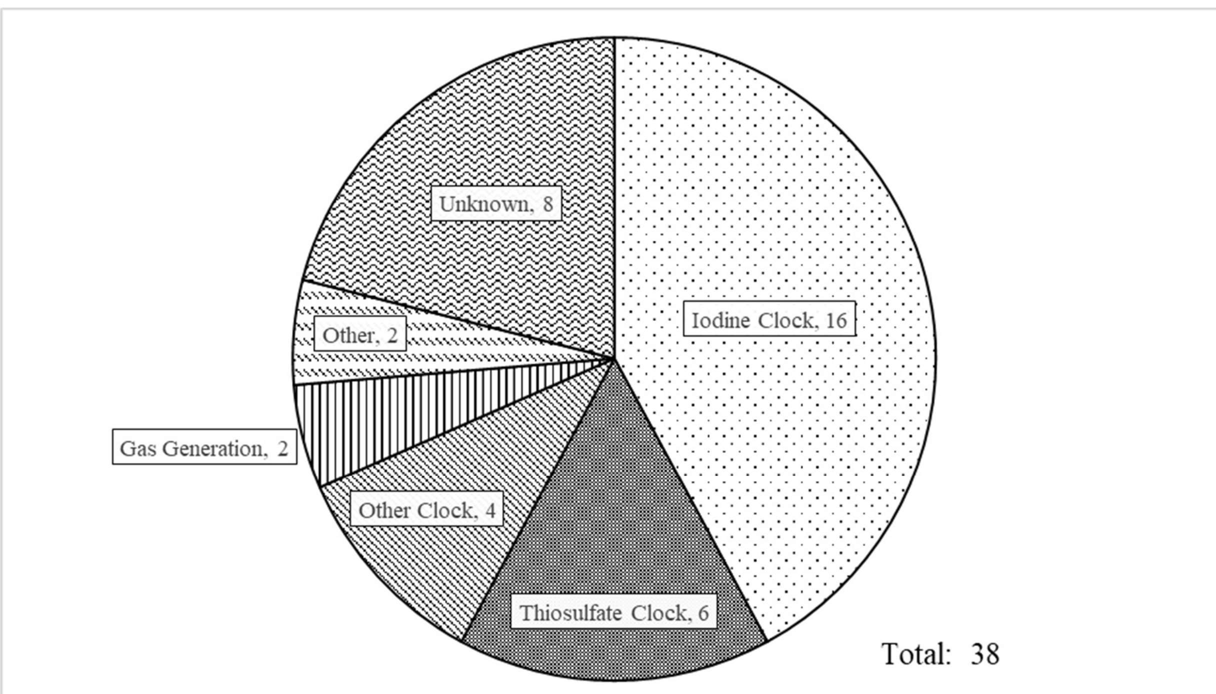

Figure 2.1 A summary of the types of timers used in the 2019 national Chem-E car Competition (Ewing, 2019)

2.2.1 Clock Reactions

There is no specific definition of a clock reaction, but generally a clock reaction is a liquid phase reaction that causes a change in the optical properties of the reaction mixture that can be measured by a photosensor. This change can be sudden with an induction period, or gradual. The two most popular clock reactions are the iodine clock, and the thiosulfate clock:

- **Iodine clock** – An aqueous solution of potassium iodide and ascorbic acid is mixed with another solution of hydrogen peroxide and a starch indicator. The hydrogen peroxide oxidizes the iodide to iodine which is immediately reduced by the ascorbic acid back to the colorless iodide. When the ascorbic acid is depleted, the iodine reacts nearly instantaneously with iodide and starch to form a dark blue complex. (Wright, 2002).
- **Thiosulfate clock** – a solution of sodium thiosulfate is mixed with an acid, usually HCl, causing the thiosulfate to slowly decompose into sulfur, sulfur dioxide, and water. The sulfur is insoluble in water causing the solution to slowly become opaque (Meacham, 2019).

Most of these clock reactions are reasonably safe. They occur at room temperature and do not produce large of amounts of gas that could generate pressure. However, all the popular clock reactions use one or more hazardous chemicals. The iodine clock uses hydrogen peroxide, and the thiosulfate clock uses hydrochloric acid. During operation, the concentration of these chemicals and therefore hazards they pose are usually small, but while preparing the clock the chemicals can be highly concentrated. Because most accidents occur during startup and shutdown, the risk posed by these clock reactions cannot be ignored (Chemical Safety Board, 2018).

2.2.2 Gas Generating Reactions

Gas generation timers measure the volume of gas produced by a chemical reaction and stop the car after a certain volume of gas is produced. If the right chemistry is selected, these timers can be as harmless as baking soda and vinegar. However, these timers have the potential to generate dangerous amounts of pressure. Because these gas generation timers are less popular than clock reactions, there are fewer examples to reference, but design teams have developed a few ways to measure the volume of gas produced by different reactions.

In 2019, Iowa State University used oxygen gas generated by catalytically decomposing hydrogen peroxide to displace an electrolyte solution. Submerged in the electrolyte were two copper electrodes connected to an Arduino™ microcontroller. As the electrolyte was displaced, the resistance between the electrodes increased, and at a specified resistance the microcontroller cuts power to the car (Burnett-Larkins, 2019). In 2017, Universiti Malaysia also used hydrogen peroxide to produce oxygen gas which they measured with a syringe. The oxygen pushed the plunger against a switch stopping the car (Tabri et al., 2017). In 2015 University of Wisconsin-Madison's timer added soap to decomposing hydrogen peroxide to make a foam. This foam filled a tube where it interrupted a laser beam stopping the car (Soesanto, 2016).

2.3 Timer Selection

After reviewing existing timers, it was decided that instead of developing a completely new type of timer it was more effective to focus on optimizing the safety of a clock reaction or gas generation timer. Using all the principles of safety design mentioned in section 2.1, two concepts were developed. The first proposed timer is a clock reaction where milk of magnesia, an opaque suspension of magnesium hydroxide in water, reacts with ascorbic acid to form water soluble magnesium ascorbate causing the mixture to turn transparent. This reaction is given below.

$$Mg(OH)_2\ (s) + 2\ C_6H_8O_6\ (aq) \rightarrow Mg(C_6H_7O_6)_2\ (aq) + 2\ H_2O\ (l) \qquad (2.1)$$

The change in transmittance of the system can be measured with a photosensor and an Arduino microcontroller. The advantages of this clock reaction are that it uses no hazardous chemicals and is entirely in the liquid phase; no gases are produced. The two potential problems with the timer are the difficulty building and calibrating a device to continuously measure the transmittance of the milk of magnesia and the cost of milk of magnesia. Over the counter milk of magnesia costs approximately $3.57 for a 746 mL bottle ("Equate Milk of Magnesia Saline Laxative", n.d.). Assuming the timer uses 50 mL of milk of magnesia per run, the timer would cost at least $0.24 for each run which is above the $0.20 per run goal.

The second proposed timer is a gas generating reaction between calcium carbonate antacid tablets and ascorbic acid. The calcium carbonate and ascorbic acid react to produce carbon dioxide gas. The volume of the carbon dioxide produced is measured by displacing water in a tube.

$$CaCO_3\ (s) + 2\ C_6H_8O_6\ (aq) \rightarrow Ca(C_6H_7O_6)_2\ (aq) + CO_2\ (g) + 2\ H_2O\ (l) \qquad (2.2)$$

The water level in the tube will be measured with an off the shelf conductivity-based level switch. This switch has two wires, and whenever there is water between these wires the switch is closed, and when one of the wires is removed from the water the switch opens stopping the car. The advantage of this gas generating reaction is that it is simple and easy to build:

- The volume of carbon dioxide produced by the reaction can be measured with a burette or with an inverted graduated cylinder in a beaker of water for determining the rate of reaction
- Antacid tablets are inexpensive compared to milk of magnesia
- Using an off the shelf level switch to measure the water level eliminates the need to program a microcontroller or calibrate sensors

The disadvantage of this timer is that there is the potential to generate unsafe pressures. This hazard is minimized by using solid antacid tablets that have a limited surface area, effectively limiting the rate at which gas can be produced. Using antacid tablets also makes it harder to accidentally measure out too much calcium carbonate which could overpressure the timer. With powdered calcium carbonate it is hard to tell the difference between one and two grams at a glance, but with antacid tablets it is clear if there is one tablet or two tablets being used in the timer.

Both proposed timers use only non-hazardous household chemicals. Milk of magnesia and antacid tablets are sold at pharmacies as digestive aids, and ascorbic acid is sold as Vitamin C powder at health food stores. Ascorbic acid is recommended because it is the only readily available acid that is non-hazardous under GHS. To determine which timer to pursue for the final design, a qualitative decision matrix was used (Table 2.1). Although the milk of magnesia clock is inherently safer, it was decided to pursue the antacid CO_2 timer because it is more accessible.

Table 2.1 The decision matrix that was used to decide which timer to pursue.†

Criteria	Milk of Magnesia Clock	Antacid CO_2 Timer	Explanation
Inherent Safety	X		The antacid CO_2 timer has the potential to generate pressure, the milk of magnesia clock does not.
Uses easy to obtain chemicals	-	-	Both timers use only household chemicals.
Technical Simplicity		X	The antacid CO_2 timer uses an off the shelf circuit while the milk of magnesia clock uses a microcontroller and a photosensor which must be calibrated.
Ease of Construction	-	-	Both timers are anticipated to be similarly difficult to build
Ease of Use		X	It is easier to count out antacid tablets than it is to measure liquid milk of magnesia
Cost		X	Milk of magnesia appears to be more expensive than antacid tablets. A microcontroller and sensors cost more than the level switch

† "X" indicates the better timer for that criteria, and "-" indicates a tie between the timers.

CHAPTER 3

DEVELOPING THE TIMER

3.1 Experimental Setup

The apparatus used to collect rate data for the proposed gas generating reaction consists of a 50 mL burette with the stopcock tip removed and submerged into a beaker of dyed water, so the 50.0 mL marking was at the water line. Tubing was connected to the top of the burette. This tubing teed and connected to a rubber stopper and a line with a valve connecting the pipette bulb. This apparatus is shown in Figure 3.1.

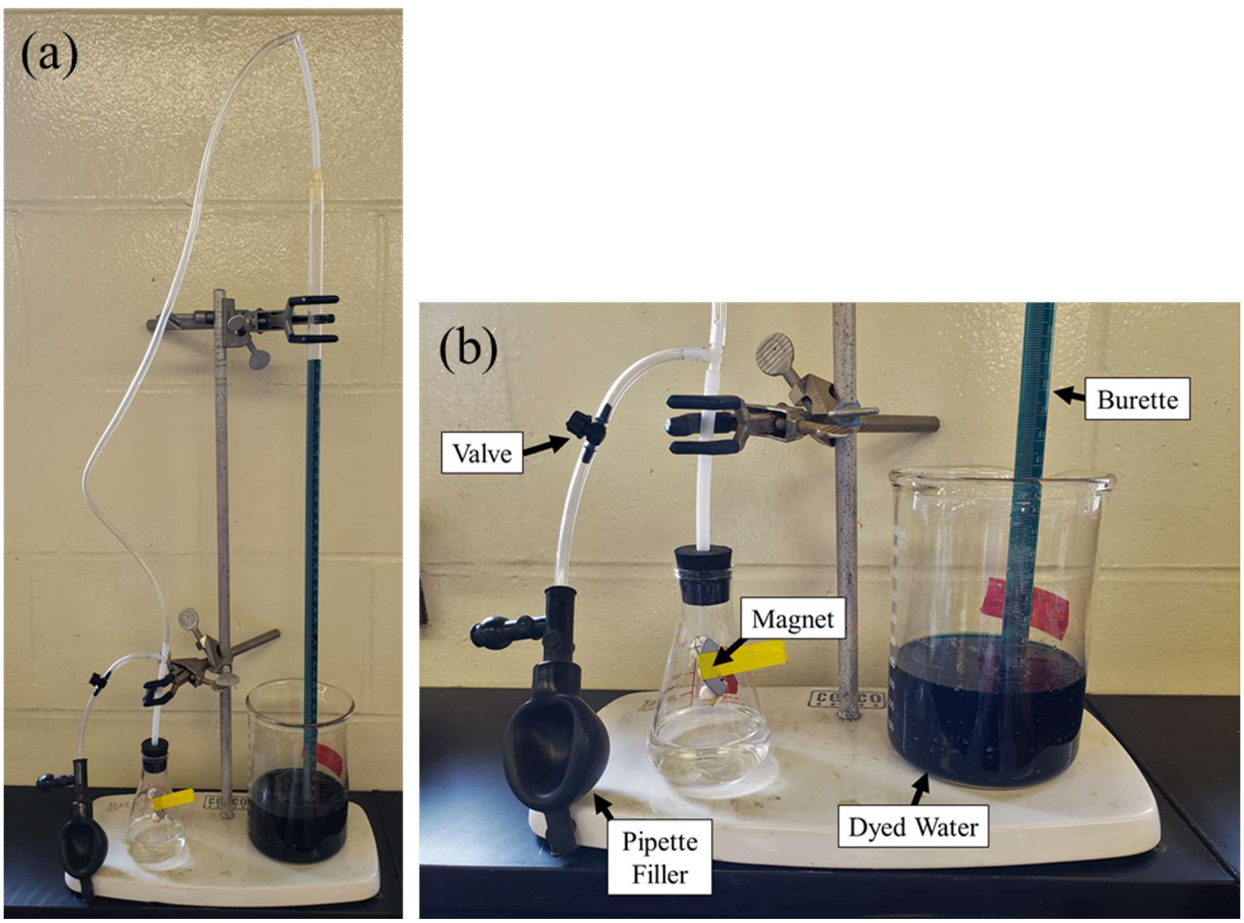

Figure 3.1 The apparatus used to collect rate data.

(a) Overall View
(b) Closeup View of the Base

The procedure used to determine rate data is as follows:

1. Fill a 125 mL Erlenmeyer flask with 50 mL of the aqueous ascorbic acid solution.
2. Wrap the antacid tablet in a steel wire holder.
3. Secure the holder (containing the tablet) to the inside of the flask above the aqueous solution using a magnet on the outside of the flask.
4. Stopper the flask.
5. Open the valve and use the pipette filler to fill the burette with dyed water to the 10.0 mL mark.
6. Close the valve.
7. Watch the water level for fifteen seconds to see if it falls indicating a leak.
8. If there are no leaks pull the magnet away from the flask dropping the tablet(s) in the ascorbic acid solution.
9. Record the water level in the burette every fifteen seconds after removing the magnet for a total of two minutes.

3.2 Testing the Repeatability of Antacid Tablets

Before committing to extensive testing to collect rate data, the ascorbic acid and antacid tablet chemistry was tested for repeatability. Three bottles of TUMS® Ultra Strength Antacid Tablets Assorted Fruit (labelled bottle A, bottle B, and bottle C) were tested for repeatability both between the bottles and between the different colors of tablets. Assorted fruit TUMS® come in four colors: red, orange, yellow, and green. Five tablets of each color from each bottle were tested using procedure outlined in the previous section. All the antacid tablets were tested in a 90 g/L ascorbic acid solution that was prepared in one large batch to minimize the variability.

Bottle A and bottle B were from the same batch, and bottle C was from a different batch as determined by their labels. The average flowrate of carbon dioxide produced by the reaction, Q_{CO_2} was calculated by performing a linear regression on the volume measurements taken with the burette versus time and taking the slope. An example of the data collected from a single tablet is shown in Figure 3.2 below, and a summary of all the measurements is given in Figure 3.3.

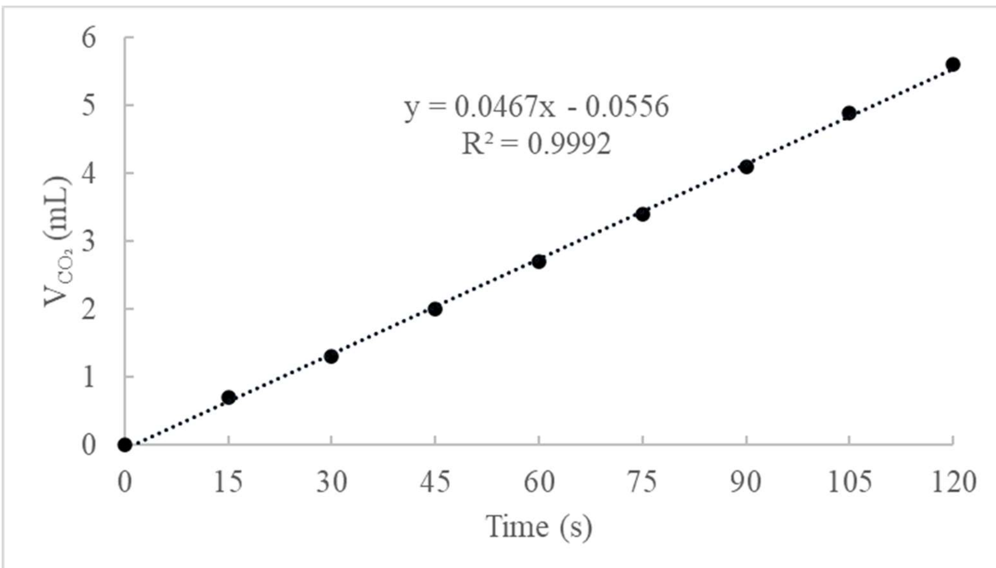

Figure 3.2 The volume of carbon dioxide produced by a single red TUMS® Ultra Strength Assorted Fruit antacid tablet from bottle A in a 90 g/L ascorbic acid solution at 21 °C as a function of time.

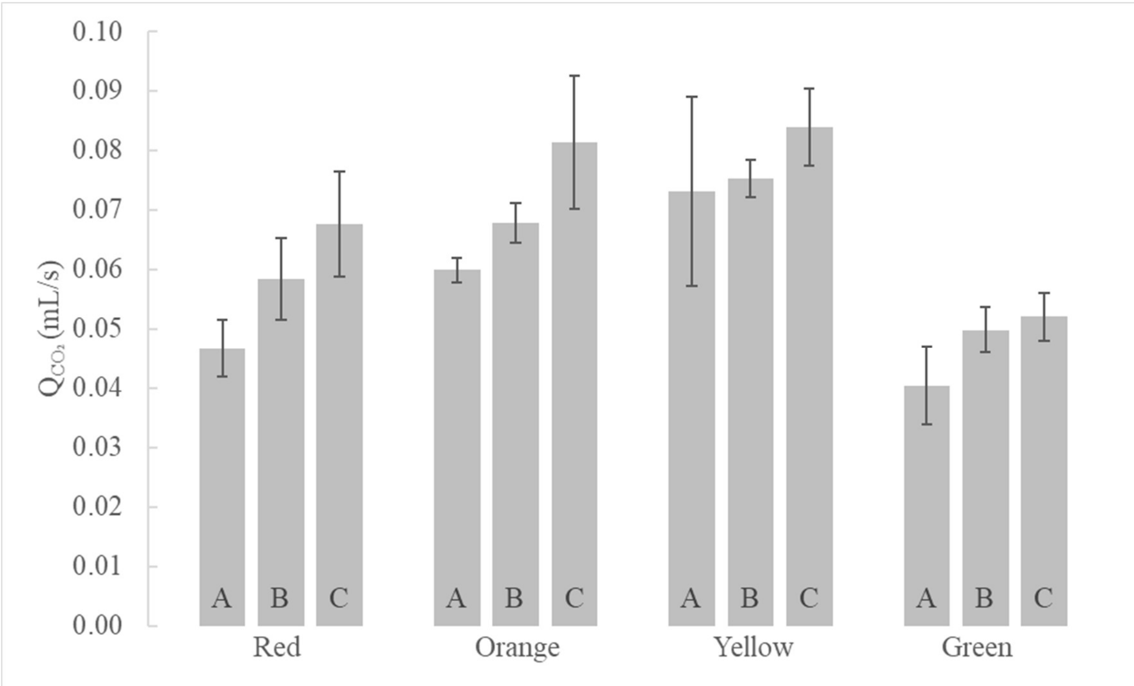

Figure 3.3 Testing TUMS® Ultra Strength Assorted Fruit antacid tablets for consistency with a 90 g/L ascorbic acid solution at 21 °C.

Note. The bars are the average of the five tests for each color/bottle combination. Error bars indicate one standard deviation. The letters at the base of each bar indicate which bottle the antacid tablets were from.

There was significant variation in gas production between both the different colors of tablets and the different bottles. This could be because there are small variations in the composition of the tablets, so some tablets have more calcium carbonate than others. Or the different color dyes could be participating in the reaction. The manufacturer of TUMS®, GlaxoSmithKline, was contacted about these results, but they declined to comment (see Appendix B). Generic Kroger brand antacid tablets were also tested, but they barely reacted with the ascorbic acid. For these reasons, the original plan to use antacid tablets and an ascorbic acid solution was abandoned.

3.3 Ascorbic Acid Tablets and Aqueous Sodium Bicarbonate

Not wanting to abandon the gas generation timer, another gas generating reaction was tried that is essentially the inverse of the reaction between antacid tablets and an ascorbic acid solution. 500 mg vitamin C pills were tested in a solution of 50.0 g/L sodium bicarbonate. Three of 500 mg tablets were used per run to have approximately the same number of moles of ascorbic acid as there was calcium carbonate in the antacid tablets. Two different bottles of brand 500 mg bottles were tested, and both bottles were as consistent as the four most consistent TUMS® color/bottle combinations as shown in Figure 3.4.

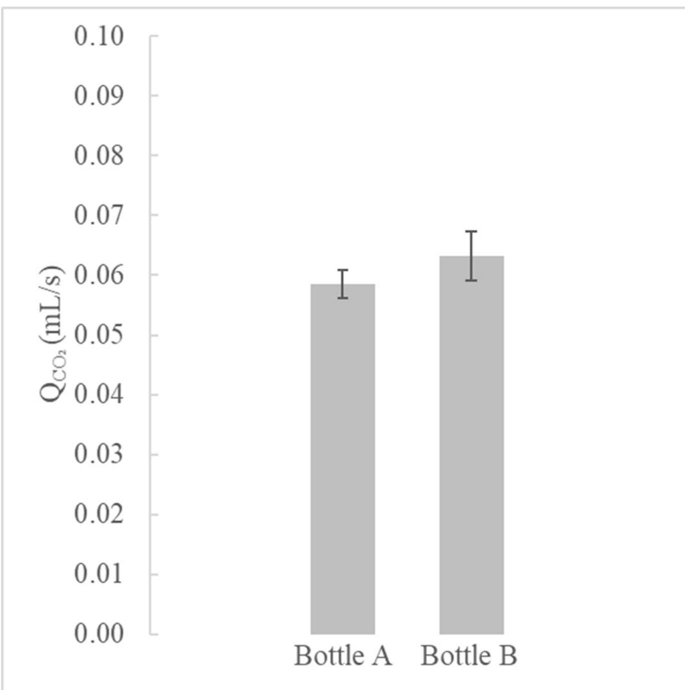

Figure 3.4 The results of the consistency tests for the 500 mg Vitamin C pills shown on the same scale as Figure 3.3

Note. The bars are the average of the five tests for each bottle. Error bars indicate one standard deviation.

With confidence that the 500 mg tablets were consistent, the next step was to collect rate data for the reaction.

3.4 Determining the Rate of Reaction

The overall reaction between the Vitamin C pills and aqueous sodium bicarbonate is:

$$C_6H_8O_6\ (s) + NaHCO_3\ (aq) \rightarrow NaC_6H_7O_6\ (aq) + CO_2\ (g) + H_2O\ (l) \quad (3.1)$$

Assuming this reaction irreversible and elementary, i.e., first order with respect to sodium bicarbonate, the rate of formation of carbon dioxide can be written:

$$r_{CO_2} = kC_{NaHCO_3} \quad (3.2)$$

Where:

k = rate constant [L/(m^2·s)]
C_{NaHCO_3} = molar concentration of sodium bicarbonate (mol/L)

The mole balance for carbon dioxide in the Erlenmeyer flask in Figure 3.1 can be written:

$$F_{CO_2,in} - F_{CO_2,out} + r_{CO_2}S = \frac{dN_{CO_2}}{dt} \quad (3.3)$$

Where:

$F_{CO_2,in}$ = molar flowrates of carbon dioxide into the flask (mol/s)
$F_{CO_2,out}$ = molar flowrate of carbon dioxide leaving the flask (mol/s)
S = surface area of the Vitamin C pills (m^2)
dN_{CO_2}/dt = rate of accumulation of carbon dioxide in the flask (mol/s)

No carbon dioxide enters the flask and there is no accumulation of carbon dioxide in the Erlenmeyer flask since any carbon dioxide formed is immediately removed from the flask by the falling water in the burette, so $F_{CO_2,in}$, and dN_{CO_2}/dt are zero and (3.3) simplifies to:

$$F_{CO_2,out} = SkC_{NaHCO_3} \quad (3.4)$$

The molar mass of sodium bicarbonate can be used to relate the molar concentration of sodium bicarbonate, C_{NaHCO_3}, to the mass concentration of sodium bicarbonate, C'_{NaHCO_3}.

$$C_{NaHCO_3} = \frac{C'_{NaHCO_3}}{M_{NaHCO_3}} \tag{3.5}$$

The ideal gas law can be used to relate $F_{CO_2,out}$ to the volumetric flowrate of carbon dioxide leaving the flask, Q, in mL/s as measured by the burette.

$$Q_{CO_2} = \frac{RT}{P} F_{CO_2,out} \tag{3.6}$$

Substituting (3.5) and (3.6) into (3.4)gives:

$$Q_{CO_2} = \frac{RTSk}{PM_{NaHCO_3}} C'_{NaHCO_3} \tag{3.7}$$

If the surface area of the tablets and the temperature and pressure inside the burette are assumed to be constant, the fraction in (3.7) can be combined into a new rate constant, k', with units of mL·L/(g·s):

$$Q_{CO_2} = k' C'_{NaHCO_3} \tag{3.8}$$

k' could be written with units of $L^2/(g\cdot s)$, but it was decided to use units of mL·L/(g·s) for k' since the sodium bicarbonate concentration was measured in g/L and the rate of carbon dioxide production was measured in mL/s.

Equation (3.8) assumes that the temperature and pressure and therefore molar volume of the gas in the burette are constant. In reality, as the water level falls in the burette, the pressure in the tube increases and so the molar volume of the gas decreases. With the water level in the burette at 10.0 mL, the water level in the burette is 45.7 cm above the water level in the beaker which corresponds to an absolute pressure of 96.8 kPa. If the water level in the burette was at the same level as the water in the beaker, the pressure in the burette would be at atmospheric pressure which was assumed to be 101.3 kPa. At 101.3 kPa, the molar volume of an ideal gas is 4.4% lower than at 96.8 kPa. Considering the water level in the burette rarely dropped below the

30.0 mL mark, the assumption that the molar volume of the gas inside the burette is constant is reasonable. Equation (3.8) also assumes that the surface area of the vitamin C pills is constant. In reality, the surface area changes as the tablet reacts with the acid and dissolves, but in testing the vitamin C pills did not appear to dissolve appreciably after two minutes so the change in surface area was ignored.

If equation (3.8) and its assumptions are correct, there will be a linear relationship between the sodium bicarbonate concentration and the volumetric flowrate of carbon dioxide produced by the reaction. To examine this, vitamin C pills from bottle A were tested in six solutions of sodium bicarbonate with varying concentrations; the results are shown in Figure 3.5.

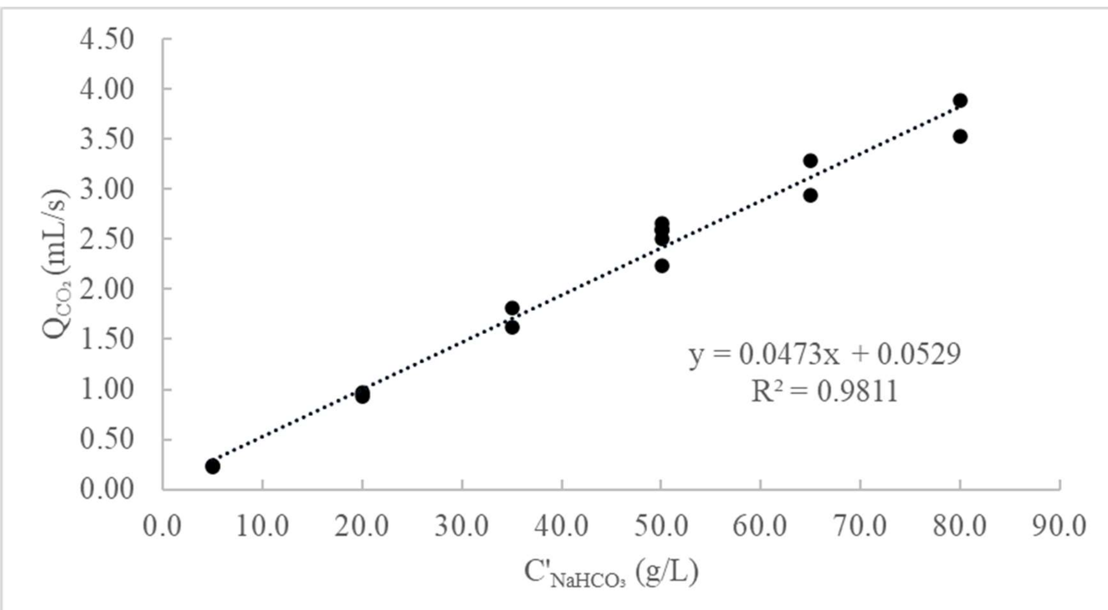

Figure 3.5 Determining the order of the reaction between aqueous sodium bicarbonate and three 500 mg Vitamin C pills from bottle A with respect to sodium bicarbonate at 17 °C

A linear regression gives a good fit (R^2 = 0.9811) to Q_{CO_2} v. C'_{NaHCO_3} in Figure 3.5 suggesting that equation (3.8) is the correct approach and the assumptions are valid. This regression assumes that the concentration of sodium bicarbonate in the liquid phase does not change over the two minutes. With 50 mL of 50.01 g/L (0.5953 M) sodium bicarbonate, the vitamin C pills from Bottle A produced an average of 7.9 mL of carbon dioxide in 2 minutes at 17 °C. Assuming an ideal gas at 1 atm, this volume of carbon dioxide corresponds to 1.1% conversion of sodium bicarbonate which is low enough that the concentration of sodium bicarbonate can be treated as constant.

3.5 Temperature Dependence

When preparing the solutions of sodium bicarbonate there was a noticeable drop in the temperature of the solutions. An 80 g/L solution decreased from 17 °C to 14 °C in the time it took to dissolve the sodium bicarbonate. If this temperature drop significantly affects the rate of reaction, it could pose a problem for using the timer in the Chem-E Car competition. In this study, solutions were prepared and then left for several hours to warm back up to room temperature and therefore the temperature drop was not an issue. At the Chem-E Car competition teams only have one hour to prepare their car after the distance the car must travel is announced. One hour may not be enough time to prepare the sodium bicarbonate solutions and warm them back up to room temperature. So, it was necessary to measure the effect of temperature on the rate of reaction to see if these drops in temperature would be an issue. Rate data was collected at three different temperatures and Figure 3.6 was used to calculate the rate constants at these temperatures.

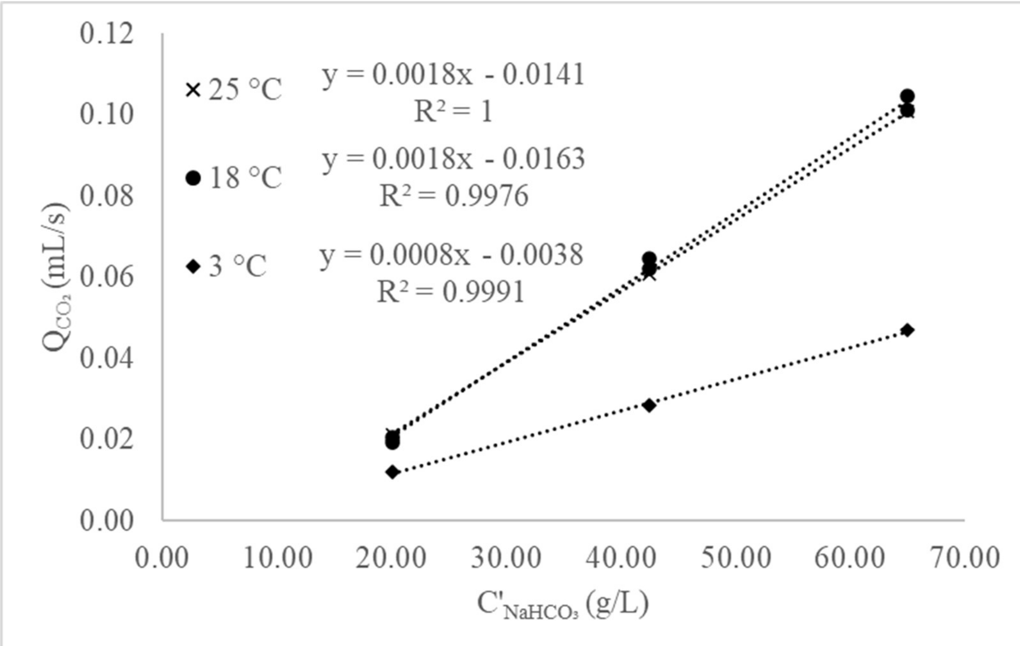

Figure 3.6 The rate of reaction versus sodium bicarbonate concentration at different temperatures for vitamin C pills from bottle C

Then, the linear form of the Arrhenius equation (3.9) was used to calculate the activation energy of the reaction in Figure 3.7.

$$\ln k' = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \tag{3.9}$$

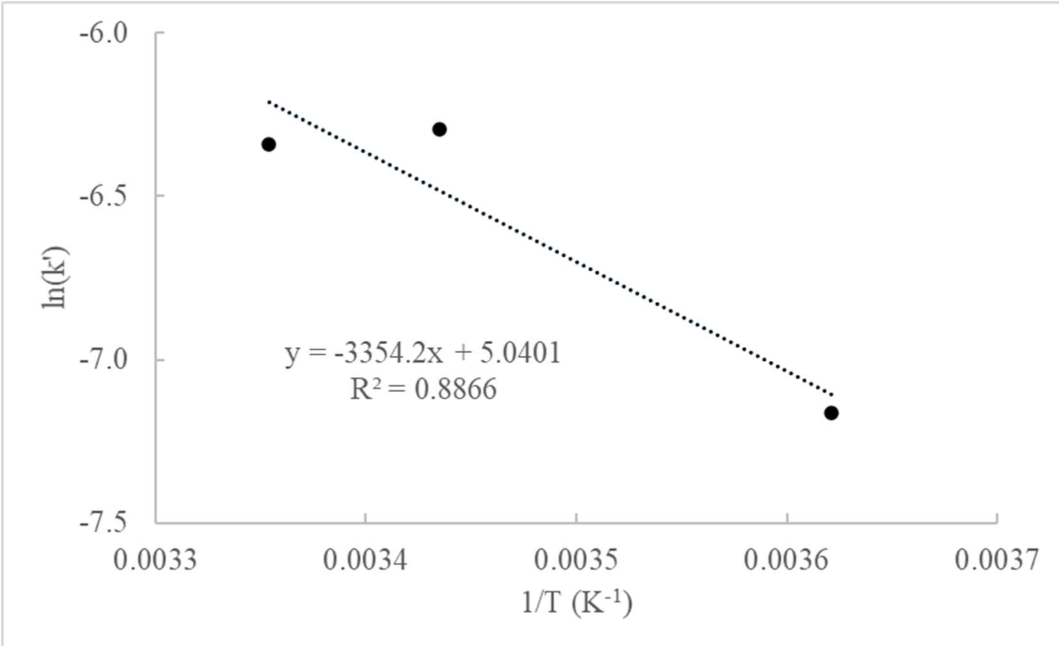

Figure 3.7 Arrhenius plot of the rate constants at different temperatures

The activation energy for the reaction was calculated to be 27 kJ/mol. With this activation energy, the rate of reaction increases 12% every for every 1 °C increase in temperature and doubles every 17 °C. This shows that the effect of temperature on the rate of reaction is not negligible, and the temperature of the solutions used in the timer must be carefully controlled.

3.6 Designing the Timer

Based on all the previously collected data, a timer was fabricated like the one described in section 2.3. Photos of this timer are given in Figure 3.8.

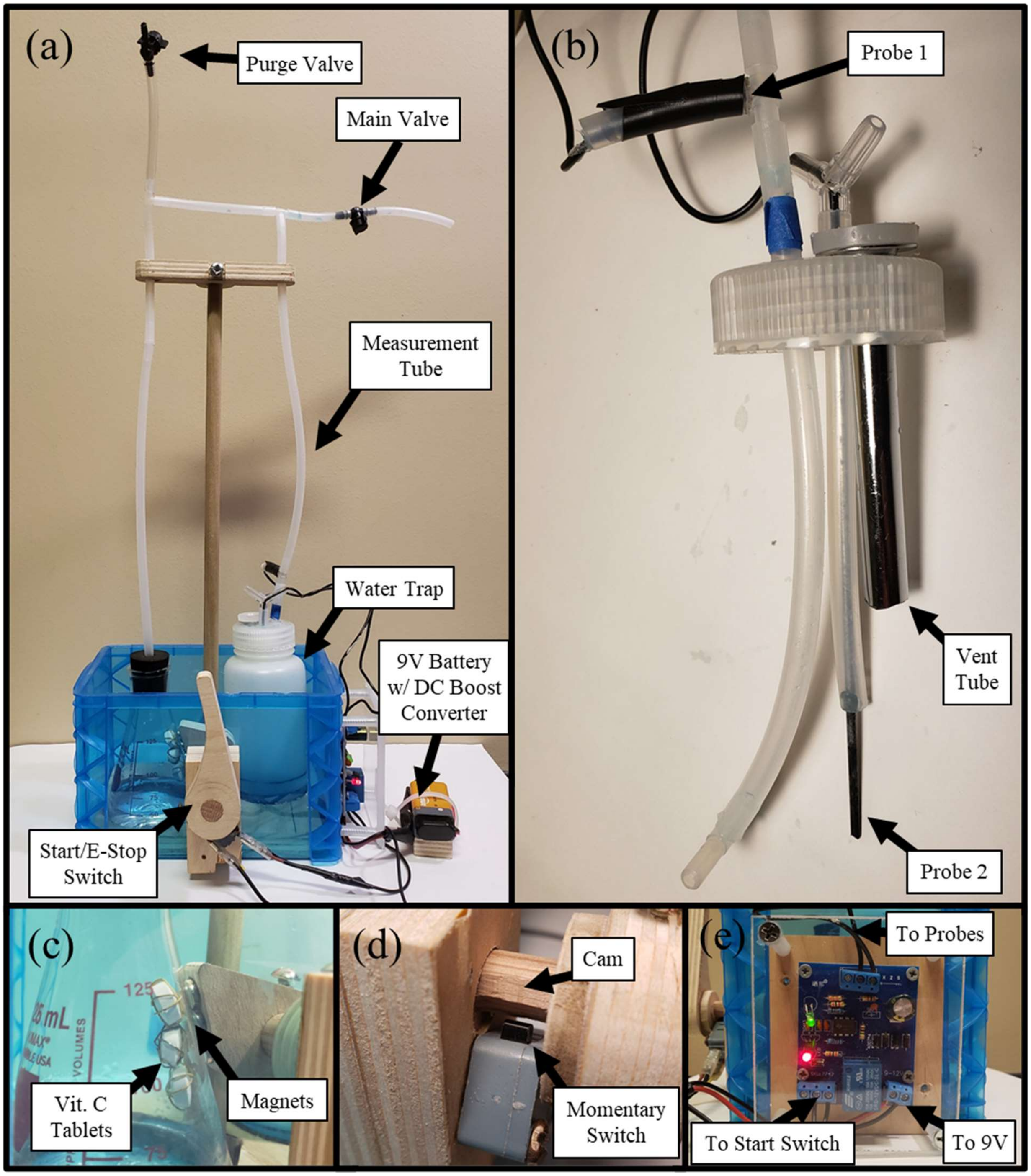

Figure 3.8 Different views of the timer with labels

(a) Overall View of the timer
(b) Wires and tubes inside the water trap
(c) The Erlenmeyer flask with the magnets holding the tablets
(d) The cam on the start/emergency stop switch
(e) The level control circuit

The procedure for using the timer is as follows:

1. Use a calibration curve to determine the required concentration of sodium bicarbonate solution.
2. Prepare required concentration of sodium bicarbonate solution.
3. Measure out 50 mL of the sodium bicarbonate solution and pour it into the flask making sure not to get any solution on the upper walls of the flask where it could react prematurely with the vitamin C pills.
4. Put the flask in the timer.
5. Rotate the start switch clockwise until the magnets are resting against the wall of the flask.
6. Wrap three Vitamin C pills in tripwire.
7. Slide the three Vitamin C pills inside the flask, making sure they are held securely by the magnets.
8. Stopper the flask.
9. Open the main valve and using the pipette filler, suck up the water to the tee by the main valve.
10. Close the main valve and remove the pipette filler.
11. Rotate the start switch clockwise to release the tablets and start the timer

3.6.1 Level Switch

The part of the timer that stops and starts the car is a level switch that is sold for controlling small pumps connected to sumps, rainwater collection tanks, etc. The circuit has two probes that are put in the body of water to be controlled. If there is water between these probes, the relay in the circuit closes, and if there is no water between the probes the relay opens. In the timer, when there is water in the measurement tube, there is water between probe 1 and probe 2 in Figure 3.8b and the relay on the level switch is closed. When water falls below probe 1 in the measurement tube, there is no longer water between probe 1 and probe 2, and the relay opens. The level switch runs on 12 V which is supplied by a 9V battery with a DC boost converter.

3.6.2 Start Switch

The start switch has a normally open momentary switch that is wired in series with the relay on the level switch. When the start switch is rotated all the way to the left with the magnets resting against the Erlenmeyer flask, a cam depresses the momentary switch. When the start switch is rotated clockwise to drop the tablets, the cam releases the momentary switch, closing the circuit and energizing the car.

3.6.3 Water Trap

The tube below probe 1 extends to the bottom of the water trap. The water trap is a bottle filled to 2 cm of water to ensure that the outlet of the measurement tube is always submerged.

3.6.4 Purge Valve

Sometimes when using the pipette filler to fill the measurement tube with water, the water overshoots and water enters the horizontal tube between the main valve and the purge valve in Figure 3.8a. The purge valve gives a way to clear this tube of water without having to unstopper the Erlenmeyer flask and risk dropping the vitamin C pills into the baking soda solution.

3.6.5 Sizing the Measurement Tube

The length of the measurement tube on the timer can be adjusted depending on how fast the reaction produces carbon dioxide. The procedure below was used to determine the length of the measurement tube. This procedure assumes that the car the timer is used with travels at a constant speed which can be fixed at any value.

1. Measure the rate constant for the reaction as shown in Figure 3.9

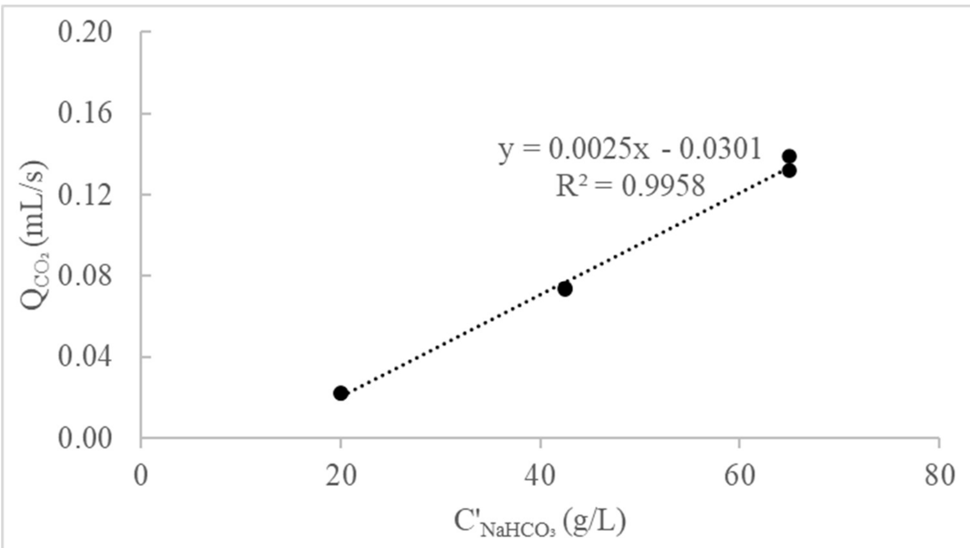

Figure 3.9 The calibration curve used to size the measurement tube; measured using vitamin C pills from bottle D at 20 °C

2. Calculate the speed the car needs to travel at by dividing the maximum distance the car needs to travel (30 m is the maximum distance for the Chem-E Car competition) by the maximum time it has to travel this distance (120 s is the maximum time cars can run in the Chem-E Car competition, but this includes the time it takes to start the car, so 110 s is the time used to calculate the speed of the car) to get a speed of 0.273 m/s.

3. Calculate the minimum time at which the timer needs to trigger based on the speed of the car and the minimum distance the car must travel (15 m is the minimum distance for the Chem-E Car competition).
4. Arbitrarily set the measurement tube volume to be 5 mL
5. Calculate the minimum and maximum gas rates needed to trigger the timer based on the 5 mL measurement tube volume, the minimum time calculated previously, and a maximum time of 120 s (the full 120 s is used in this calculation instead of the 110 s used in step 2 to ensure that the timer can be slowed down if needed).
6. Using the rate constant, calculate the sodium bicarbonate solution concentrations that correspond to the calculated minimum and maximum gas rates.
7. Adjust the tubing volume and repeat steps 3-6 until the calculated minimum sodium bicarbonate concentration is 25 g/L.
8. Using the inside diameter of the tube (0.170 in), calculate the length of tube with the volume determined in step 7.

3.6.6 Calibrating and Testing the Timer

The actual volume of the measurement tube will be close but not the same as the calculated volume from section 3.6.5 so the timer must be calibrated. How long it took the timer to trigger was measured at the same concentrations used to calculate the rate constant when sizing the measurement tube. The reciprocal of these times was plotted against the sodium bicarbonate solution concentration in Figure 3.10 to give a linear calibration curve.

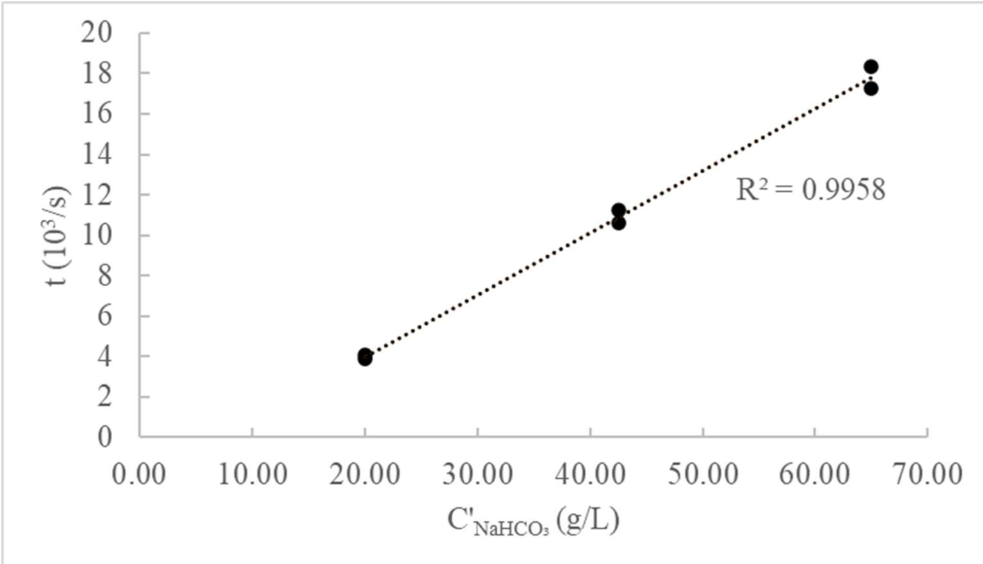

Figure 3.10 The calibration curve for the timer using vitamin C pills from Bottle D at 20 °C

Then, to test the timer, four random sodium bicarbonate concentrations between the calibration concentrations were tested to see how they compared to the calibration curve. The results of these tests are shown in Figure 3.11 and discussed in the next section.

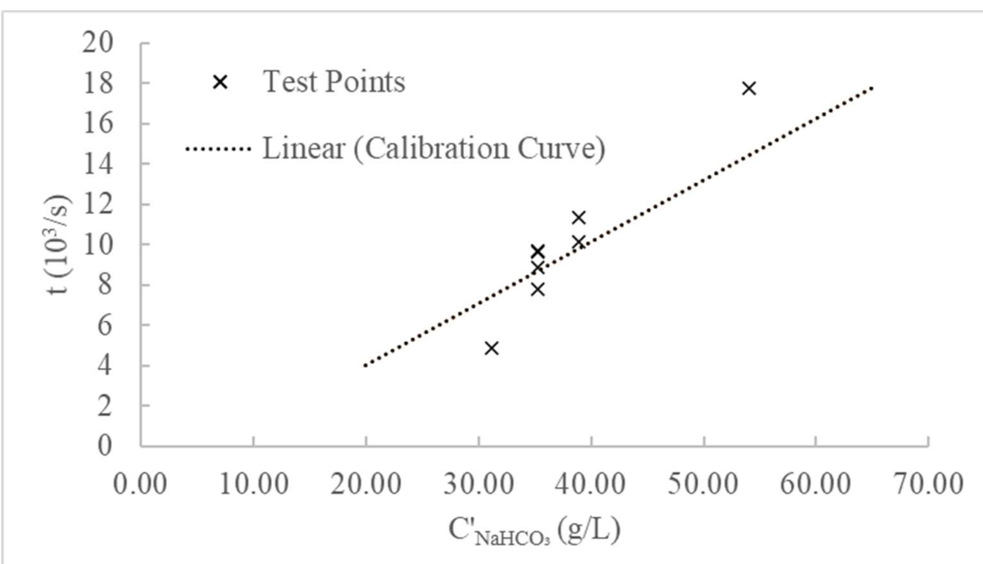

Figure 3.11 Testing the timer and comparing it to the calibration curve.

CHAPTER 4

EVALUATING THE SUCCESS OF THE TIMER

With the timer built and tested, it was evaluated against the criteria for success outlined in the section 1.3. These criteria are safety, accessibility which is divided into cost and ease of construction, and performance. An evaluation of the timer against these criteria is summarized in Table 4.1. The timer met three of the five criteria and almost met one criteria. The individual criteria are discussed in greater detail in the following sections.

Table 4.1 A summary of the final timer compared to the criteria for success.

Criteria	**Goal**	**Result**
Safety	Follows Principles of Inherently Safer Design	Follows Principles of Inherently Safer Design
Cost to Build	\$50	\$55
Cost to Use	\$0.20	\$0.10
Can be built with common tools	Yes	Yes
Performs better than the median car at the 2018 national competition	Accurate to ±8.6 s	Generally accurate to ±14.0 s

4.1 Safety

The safety of the timer was evaluated based on its adherence to the four principles of inherently safer design: minimize, moderate, substitute, and simplify.

<u>Minimize</u>

- The amount of ascorbic acid and sodium bicarbonate used in the timer is below the maximum daily intake recommended by Mayo Clinic the America association

(Zeratsky 2020; "How much sodium should I eat per day?," n.d.). A person could safely drink the reaction mixture.

<u>Moderate</u>

- The timer operates at atmospheric temperature and pressure.
- The pH of the reaction mixture is between 2 and 9, and if the concentration of the sodium bicarbonate solution is greater than 14 g/L, the pH of the reaction mixture should not fall below 7 (NOAA, n.d., "Ascorbic Acid," n.d.).
- The electronics on the timer operate at 12 V.

<u>Substitute</u>

- The timer uses only non-hazardous chemicals.

<u>Simplify</u>

- The magnets that hold the tablets to the wall of the Erlenmeyer flask can only hold three vitamin C pills. If a person tries to add more than three tablets to the flask, they will fall into the solution before the flask can be stoppered. This effectively limits the maximum rate at which gas is produced.
- Only one valve and one switch are used to arm the timer simplifying the startup procedure.
- The same switch used to start the timer can also be used to stop the timer in an emergency.

Additionally, the timer includes a few passive safety measures where inherent safety was not possible. The tubing used in the timer is semi-rigid polyethylene that resists kinking that could cause pressure to build inside the system. The water trap is large enough to hold the entire volume of liquid the system. Lastly, the bottom of the vent tube on the water trap sits in the middle of the bottle so that if the timer were to be knocked over, only a small amount of water would leak out of the water trap. The only major hazard present in the design is the potential to generate pressure if the tubing leaving the Erlenmeyer flask or the vent tube in the water trap were to become blocked. This is not believed to be a significant risk since the stopper on the Erlenmeyer flask will pop out before the flask or the tubing fails, but if the buildup of pressure was a concern, a pressure relief valve could be installed in-line with the tubing above the Erlenmeyer flask.

4.2 Accessibility

Accessibility is how easy it is for a person to build and use the timer. For the timer to be considered accessible it was said it should cost less than \$50 to build, cost less than \$0.20 to run, and be able to be built with common shop tools.

4.2.1 Cost

In total, the timer would cost \$92.48 to build, and \$0.10 to run. A cost breakdown is given in Table 4.*2*. \$92.48 is well above the \$50 goal, however, this is the maximum price to buy everything new. With some resourcefulness the actual cost can be much lower. Most undergraduate labs will have a 125 mL Erlenmeyer flask, rubber stoppers, and a pipette bulb filler that can be borrowed. The micro limit switch, 9V battery snap connector, magnets, and speaker wire can be salvaged from broken electronics. The 3/8” copper riser can be substituted with any similar rigid tubing, even a large drinking straw would work. Lastly, the small amount of plywood used in the timer can probably be found as a cutoff from another project. This brings the actual cost of the timer is closer to \$55. The timer costs \$0.10 to run assuming each run uses three 500 mg vitamin C pills and 50 mL of sodium bicarbonate solution with an average concentration of 40 g/L.

Table 4.2 A cost breakdown of all the components used to build and run the timer not including tax and shipping.

Item	Price	Quantity	Extended	Source
250 count 500 mg Vitamin C pills	$7.71	1	$7.71	Amazon
Arm and Hammer Baking Soda, 1 lb.	$0.82	1	$0.82	Amazon
SEOH 125 mL Erlenmeyer Flask	$3.95	1	$3.95	Amazon
#5 Rubber Stoppers	$8.23	1	$8.23	Amazon
25 ft 0.170 in ID polyethylene tubing	$4.58	1	$4.58	Lowes
Fluval Air Valve	$1.49	2	$2.98	Amazon
Airline Tubing Connectors 40 pcs	$4.99	1	$4.99	Amazon
KOOBOOK Liquid Level Controller	$11.99	1	$11.99	Amazon
9V Battery, 2 pack	$5.98	1	$5.98	Lowes
9V Battery Snap Connector	$0.99	1	$0.99	eBay
Adjustable DC Boost Converter, 2pc	$2.95	1	$2.95	eBay
Micro Limit Switch, 12 pc	$6.10	1	$6.10	Amazon
Steel Tripwire	$2.99	1	$2.99	Army Surplus Store
Rare Earth Magnets, 10 Pc.	$2.79	1	$2.79	Harbor Freight
7/16" Dowel Rod	$1.68	1	$1.68	Lowes
Plastic Tub	$5.00	1	$5.00	Unknown
Three Way Pipette Suction Bulb	$7.19	1	$7.19	Amazon
250 mL Nalgene Bottle	$7.50	1	$7.50	Amazon
3/8 in Nickel Plated Copper Riser	$3.88	1	$3.88	Lowes
18 AWG Speaker Wire, 1 ft	$0.41	3	$1.23	Lowes
15/32" Pine Plywood 2'x2'	$7.48	1	$7.48	Lowes

4.2.2 Ease of Construction

The timer was built using only a drill, drill press, jigsaw, bandsaw, and table saw, all common shop tools, although it could be built with just a drill and jigsaw. The only additional equipment needed to test the timer not listed in Table 4.2 is a burette, volumetric flask, scale, and beaker which should be available in any undergraduate teaching lab.

4.3 Performance

For performance, the timer was said to be successful if it is accurate to ±8.6 s, which is the median performance of cars at the 2018 national competition, exclusive of the cars that did not move from the starting line. This time is calculated from the distance the cars stopped from the starting line (see Appendix C) divided by the assumed speed of the car (0.273 m/s) used to size the measurement tube in Section 3.5.5. Based on the measurements in 3.5.6, the timer is not accurate to ±8.6 s. Only two of the eight times measured by the timer at different concentrations of sodium bicarbonate could have been predicted by the calibration curve to within ±8.6 seconds as shown in Figure 4.1. The timer is generally accurate ±14.0 s with seven of the eight measurements being within ±14.0 s of the time predicted by the calibration curve.

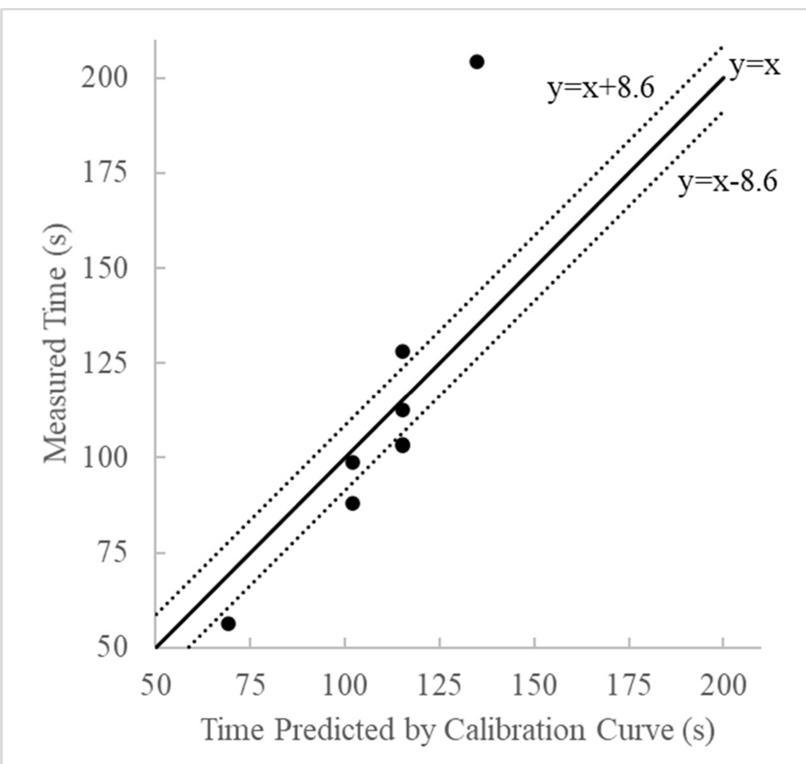

Figure 4.1 A comparison of the times predicted by the calibration curve based on sodium bicarbonate solution concentration to the times measured by the timer.

CHAPTER 5

CONCLUSION

This study was successful in developing a timer for the Chem-E Car competition that is inherently safe and easy to build. The timer would be easy to integrate into any existing Chem-E Car that is powered by electricity. While the timer did not meet the performance criteria, it is a prototype and future studies may be needed to optimize the timer. The performance of the timer may be improved with different diameter measurement tubes or a different number of vitamin C pills. Additionally, the size of the timer may be reduced by using a smaller Erlenmeyer flask and a smaller bottle for the water trap. It is recommended that Chem-E Car design teams use the timer presented in this study in their cars to make their cars safer.

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APPENDIX A

SUMMARY OF CARS AT THE 2019 NATIONAL COMPETITION

Table A.1 Summary of the cars at the 2019 national competition (Ewing, 2019)

School	**Power Source**	**Timer**	**Timer Type**
Auburn	Magnesium Air Battery	Iodine Clock	Iodine Clock
HKUST	Alkaline Battery	Thiosulfate Clock	Thiosulfate Clock
China University of Petroleum-Beijing	Alkaline Battery	Iodine Clock	Iodine Clock
Lamar University	Alkaline Battery	Iodine Clock	Iodine Clock
CSULB	Aluminum Air Battery	Iodine Clock	Iodine Clock
Ohio State University	Unspecified Battery	Iodine Clock	Iodine Clock
University of Florida	Lead Acid Battery	Iodine Clock	Iodine Clock
Virginia Tech	Lead Acid Battery	Iodine Clock	Iodine Clock
University of Toledo	Lead Acid Battery	Chemical Chameleon Clock	Other Clock
Cal Poly Pomona	Aluminum Air Battery	Thiosulfate Clock	Thiosulfate Clock
City College of New York	Unspecified Battery	Thiosulfate Clock	Thiosulfate Clock
SENAI CIMATEC	Cu-Al Battery	Elephant Toothpaste	Gas Generation
Michigan State University	Cu-Al Battery	Thiosulfate Clock	Thiosulfate Clock
Iowa State University	Hydrogen Fuel Cell	H_2O_2 Decomposition	Gas Generation
Nanjing Tech University	Unknown	Unknown	Unknown
KAIST	Hydrogen Fuel Cell	Iodine Clock	Iodine Clock
Missouri S&T	Lead Acid Battery	Luminol Clock	Other Clock
Rutgers University	Unspecified Battery	Unknown	Unknown
Northwest University	Zinc Air Battery	Iodine Clock	Iodine Clock

School	**Power Source**	**Timer**	**Timer Type**
Northeastern University	Methanol Fuel Cell	Galvanic Cell	Other
Texas A&M University at Qatar	Hydrogen Fuel Cell	Iodine Clock	Iodine Clock
Stony Brook University	Zinc Air Battery	Iodine Clock	Iodine Clock
Trine University	Daniel Cell	Iodine Clock	Iodine Clock
University of North Alabama	Aluminum Air Battery	Iodine Clock	Iodine Clock
University of Puerto Rico at Mayagüez	H_2O_2 Decomposition Pressure Engine	Thiosulfate Clock	Thiosulfate Clock
University of New Mexico	Aluminum Air Battery	Iodine Clock	Iodine Clock
University of Michigan	Dry Cell Battery	Chemical Chameleon Clock	Other Clock
National Taiwan University	Air Battery	Iodine Clock	Iodine Clock
University of Illinois at Chicago	Lead Acid Battery	Iodine Clock	Iodine Clock
University of Colorado Boulder	Pneumatic DC Generator	Acid/Base Neutralization Thermistor	Other
Universidad Nacional de Colombia	Unknown	Unknown	Unknown
University of California, Los Angeles	Alkaline Battery	Thiosulfate Clock	Thiosulfate Clock
Cornell	Unknown	Unknown	Unknown
Lodz University of Technology	Unknown	Unknown	Unknown
Kansas State University	CO_2 Driven Pneumatic Motor	Unknown	Unknown
McGill University	Unknown	Unknown	Unknown
Oregon State University	Unknown	Unknown	Unknown
Texas Tech University	Lead Acid Battery	Luminol Clock	Other Clock

APPENDIX B

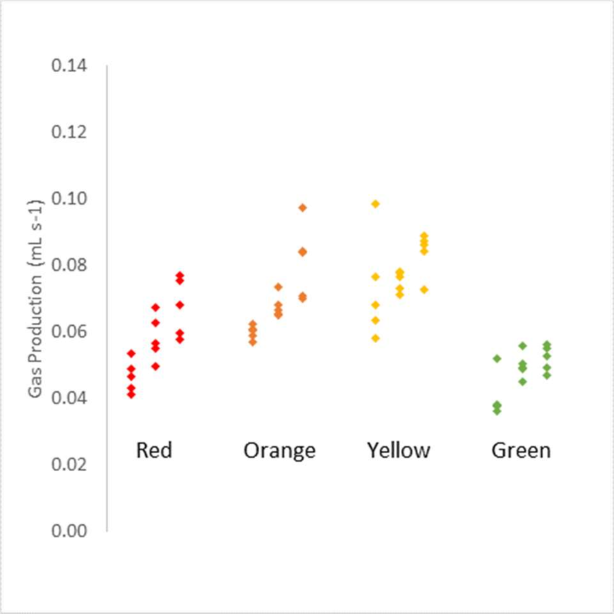
EMAIL CORRESPONDENCE WITH GLAXOSMITHKLINE

From: Harvey, Mitchell
Sent: Friday, January 15, 2021 3:11 PM
To: Consumer.Communications@gsk.com
Subject: Tums Assorted Fruit Antacid Question

I am a senior chemical engineering student at Mississippi State University. Each year the American Institute of Chemical Engineers hosts a competition where students design a shoebox sized car that is powered and stopped by chemical reactions. The car must carry a payload and stop after traveling a specified distance. Over the past few months I have been developing a timer for this car based on the reaction between Tums antacid tablets and Vitamin C (ascorbic acid) that produces carbon dioxide gas. I have been getting some interesting results and I was wondering if there was an engineer or chemist who could give me more insight into my results which are summarized below.

In my experimentation, I found that the different colors of Tums ultra-strength assorted fruit antacid tablets do not react at the same rate. When I drop a red tablet in acid it produces gas at one rate, and when I drop a yellow tablet from the same bottle in the same strength acid it produces gas at a different rate. I also noticed variation in the rate of reaction for the same color tablets from different bottles. I tested each color in a bottle five times with the same strength acid and repeated this for three different bottes and I got the results graphed below. Each column of data points represents a specific color from a specific bottle. The order of the columns with respect to the bottle is the same for each color. I expected there to be some variation between tablets, but not this much between colors and bottles. The first two bottles I tested came from the same store and had the same expiration date so I would have expected them to react the same but they did not. Do you have any insight?

Thank you,
Mitchell Harvey



From: USA GSK Consumer Relations <consumer.communications@consumerrelations-mail.gsk.com>
Sent: Friday, January 22, 2021 8:55 AM
To: Harvey, Mitchell <mah1269@msstate.edu>
Subject: Case number: 01586892

Dear Ms. Harvey,

Thank you for your enquiry on TUMS Assorted Fruit Chewable Tablets. We appreciate your work and the information you have provided from the findings of your project. We will share this information with the relevant team to look further in to this and will reach out to you if further information is needed.

Furthermore, the results and outcomes of studies is proprietary to GSKCH hence we cannot throw further light on this.

For more information on TUMS products please visit our website www.tums.com

Please be assured that GSKCH only uses ingredients of the highest quality, and all products and raw materials undergo rigorous testing to ensure they are fully compliant with local regulations.

If we may be of future assistance, please call us at 1-800-245-1040, weekdays between 8:00 A.M. to 6:00 P.M. EST.

Yours sincerely,

Merrill
GSK Consumer Relations Healthcare
184 Liberty Corner Road, Warren, NJ, 07059, United States

APPENDIX C

CAR PERFORMANCES AT THE 2019 NATIONAL COMPETITION

Table A.2 Final Run Results for the 2018 national competition. The distances are the distances are the distance from the stop distance (25.3 m) in meters (Ewing, 2018)

Final Runs 2018	**Run #1**	**Run #2**
The Cooper Union	0.27	0.16
University of Massachusetts, Amherst	6.935	10.05
Cal Baptist University	5.125	1.3
Centro Universitario Senai Cimatec	25.3	25.3
Hong Kong University of Science and Technology	25.3	25.3
Iowa State University	4.05	0.88
Texas Tech University	25.3	25.3
University of Colorado Boulder	22.57	1.15
Tianjin University	0.64	1.86
Louisiana State University	0.96	6.19
McGill University	13.6	0.63
City College of New York	0.87	0.12
Virginia Tech	8.035	1.62
University of Toledo	25.3	8.4
University of British Columbia	13.755	4.77
The Ohio State University	1.865	2.73
Texas A&M University at Qatar	18.765	14.97
Rose-Hulman Institute of Technology	3.265	5.25
UC Berkeley	3.54	22.26
University of Patras	25.3	25.25
Cal Poly Pomona	10.05	9.25
Georgia Institute of Technology	0.305	0.01
Institut Teknologi Sepuluh Nopember	6.14	0.97
Michigan State University	25.3	25.3
Oklahoma State University	10.385	1.98
University of Tennessee at Chattanooga	14.86	0.27
Tsinghua University	0.99	0.22
University of Utah	3.215	1.53
University of Tulsa	25.3	1.75
University of Tennessee, Knoxville	0.67	0.25
Rutgers University	25.3	0.05
Michigan Technological University	25.3	25.3
Clarkson University	0.16	2.41
Colorado State University	7.5	7.12
KAIST	0.58	0.5
University of Pittsburgh	25.3	2.35
University of South Florida	25.3	25.3
VIT University	25.3	25.3
Oregon State University	5.485	1.84