

ESCUELA TÉCNICA SUPERIOR DE INGENIEROS
INDUSTRIALES Y DE TELECOMUNICACIÓN

UNIVERSIDAD DE CANTABRIA



Trabajo Fin de Grado

CHEM-E-CAR: IODINE CLOCK REACTION

(Chem-E-Car: Reacción del reloj de yodo)

Para acceder al Título de

Graduado en Ingeniería Química

Autor: Guillermo Díaz Sainz

July-2015

TÍTULO	Chem-E-Car: Iodine Clock Reaction		
AUTOR	Guillermo Díaz Sainz		
DIRECTOR/CODIRECTOR	Antonio Domínguez Ramos / Andrés del Castillo Martín		
TITULACIÓN	Grado en Ingeniería Química	FECHA	23/07/2015

PALABRAS CLAVE/KEYWORDS

Chem-E-Car; iodine clock; detention mechanism.

PLANTEAMIENTO DEL PROBLEMA/SCOPE

Chem-E-Car is the AIChE's annual competition engaging college students in designing and constructing a car powered by a chemical reaction. The car must safely carry a specified load and stop after a priory unknown given distance. (*AIChE Chem-E-Car Competition™ 2015*). It is not allowed mechanical force to the wheel, gears, driveshaft or ground slow or stop the car, so a chemical reaction is selected as the detention mechanism of the car.

The aim of this work is the study of the chemical reaction between potassium iodate and sodium hydrogen sulfite selected as the detention mechanism which is the iodine clock reaction. When the reaction between potassium iodate and sodium hydrogen sulfite is completed, the color of the solution changes from colorless to blue/black color (*John A.Church et al. 1968*), so a photosensor that is in the iodine clock tank can send a signal to an electrovalve and turn-off the engine or the propulsion reaction, thus Chem-E-Car stops. The propulsion reaction is the reaction between potassium permanganate and sodium oxalate and its product is carbon dioxide that can move a pneumatic engine. For this purpose, a mathematical expression that relates concentrations of potassium iodate and temperature with the period of time needed to change the color of the solution was obtained.

RESULTADOS /RESULTS

The study considers the period of time needed to changing the color of the solution with different potassium iodate concentrations and temperatures. It studied the performance of the iodine clock at 6 temperature values (15 °C, 20 °C, 22.5 °C, 25 °C, 28 °C and 30 °C) and at 6 potassium iodate concentrations values (0.02 M, 0.018 M,

0.014 M, 0.01 M, 0.006 M and 0.002 M). For working at temperatures higher than ambient temperature, a thermostatic bath is used and for working at temperature less than ambient temperature, a cooling bath is used.

Using Matlab Curve Fitting Tool, mathematical expression is obtained. Firstly it is selected polynomial group. It has been chosen the polynomial expression with the lowest degree of polynomial, but at the same time balancing a proper goodness of fit. Poly 21 has been chosen, in which the concentration polynomial degree is 2 and the temperature polynomial degree is just 1. Poly 21 has 5 coefficients, so it is important reduce the number of coefficients in order to simplify and help at later operations. A lower number of coefficients leads to a worse fit. For this reason, a more simple mathematical expression is created with the Custom Equation option (only 3 coefficients) displaying an exponential form, and pursuing a better goodness of fit. General expression obtained is therefore (f as time (s), y as temperature (°C) and x as potassium iodate concentration (M)):

$$f(x,y) = 0.1014 * \exp\left(-\frac{-8.204}{y}\right) * x^{-1.105}$$

CONCLUSIONES / CONCLUSIONS

A exponential expression that relates the potassium iodate concentration and temperature with the period of time needed to change the color of the starch based solution is obtained showing a goodness of fit over $R^2 > 0.99$.

BIBLIOGRAFÍA/REFERENCES

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS. 2015. *AIChE Chem-E-Car Competition™ 2015*. [Consulted: 21th April 2015].

ALBERTO ROMERO LÓPEZ. Design of a Chem-E-Car prototype based on a chemical reaction. Final degree, July 2015.

JOHN A. CHURCH AND SANFORD A. DRESKIN, 1968.

ACKNOWLEDGMENT

I would like to acknowledge the support received throughout this stage to all those who have helped make this possible.

Specially, I would like to express my sincere gratitude to my supervisors: Antonio Domínguez Ramos, Andrés del Castillo Martín, Enrique Alvarez Guerra and Manuel Álvarez Guerra for giving me the opportunity to do this project, the advice received and dedication.

My thanks also to my family and friends for support, patience and understanding in the implementation of the same.

CONTENTS

1. INTRODUCTION	1
1.1 About the Chem-E-Car	1
1.2 Background of Chem-E-Car previous competitions.....	4
1.3 Objectives	10
2. DEVELOPMENT	11
2.1 Methodology	11
2.1.1 Selection of the detention mechanism: an iodine clock	11
2.1.2 Experimental procedure for carrying out the study of the concentration of KIO_3 and temperature	16
2.1.2.1 Material and reagents	17
2.2 Results and discussion	19
2.2.1 Performance of the iodine clock	19
2.2.2 Influence of concentration of KIO_3 and temperature	21
3. CONCLUSIONS	27
4. ANNEX.....	28
4.1 ANNEX 1.....	28
5. REFERENCES.....	39

LIST OF FIGURES

Figure 1. Sketch of typical performance course layout	2
Figure 2. Example of a NFPA diamond.	4
Figure 3. NFPA code of 1) acetylene	5
Figure 4. NFPA code of 1) methylamine, 2) ethylamine, 3) propylamine, 4) n-butylamine and 5) sec-butylamine.	6
Figure 5. NFPA code of 1) acetic acid and 2) hydrogen chloride.	8
Figure 6. NFPA code of 1) sulfuric acid, 2) potassium permanganate and 3) sodium oxalate.	9
Figure 7. Reaction sequence of iodine clock.	11
Figure 8. The "Old Nassau" modification of the iodine clock reaction.	12
Figure 9. Colorimetric method for carbon monoxide (I).....	14
Figure 10. Colorimetric method for carbon monoxide (I).....	15
Figure 11. Thermostatic bath (20 °C, 22.5 °C, 25 °C, 28 °C and 30 °C) (on the left) and cooling bath with thermostat (15 °C) (on the right).....	17
Figure 12. Material needed in experimental procedure.....	17
Figure 13. Molecular formula of amylose.	18
Figure 14. Molecular formula of amylopectin.	18
Figure 15. Reagents needed in experimental procedure.....	18
Figure 16. Surface plotted by Matlab for different potassium iodate concentration values, temperature values and time needed values to change the solution color (Poly 21).	22
Figure 17. Surface plotted by Matlab for different potassium iodate concentration values, temperature values and time needed values to change the solution color (Poly).	23

Figure 18. Parity diagram between calculated time (general mode) and experimental time..... 24

Figure 19. Surface plotted by Matlab (general mode) for different values of potassium iodate concentration, temperature and time needed to change the solution color (General Mode). 25

LIST OF TABLES

Table 1. Meaning of different number in health hazard, fire hazard and reactivity and meaning of different words in specific hazard.....	5
Table 2. Solution of different concentration of iodate prepared by diluting the original.	16
Table 3. Time needed to change the color of the solution with different potassium iodate concentration values at 15 °C.	19
Table 4. Time needed to change the color of the solution with different potassium iodate concentration values at 20 °C.	19
Table 5. Time needed to change the color of the solution with different potassium iodate concentration values at 22.5 °C.	19
Table 6. Time needed to change the color of the solution with different potassium iodate concentration values at 25 °C.	20
Table 7. Time needed to change the color of the solution with different potassium iodate concentration values at 28 °C.	20
Table 8. Time needed to change the color of the solution with different potassium iodate concentration values at 30 °C.	20
Table 9. Different degree polynomial and its goodness of fit.....	21
Table 10. Different coefficients values with 95% confidence bounds (Poly 21).....	22
Table 11. Different coefficients values with 95% confidence bounds (Poly).....	23
Table 12. The goodness of fit of this linear model (Poly).	23
Table 13. Different coefficients values with 95% confidence bounds (General Mode). 24	
Table 14. The goodness of fit of this linear model (General Mode).	24
Table A.1. Types of hazards and prevention of acetylene.....	28
Table A.2. Types of hazards and prevention of methylamine.	29

Table A.3. Types of hazards and prevention of ethylamine.	30
Table A.4. Types of hazards and prevention of propylamine.	31
Table A.5. Types of hazards and prevention of n-butylamine.	32
Table A.6. Types of hazards and prevention of sec-butylamine.	33
Table A.7. Types of hazards and prevention of hydrogen-chloride.	34
Table A.8. Types of hazards and prevention of acetic-acid.	35
Table A.9. Types of hazards and prevention of citric-acid.	36
Table A.10. Types of hazards and prevention of potassium-permanganate.	37
Table A.11. Types of hazards and prevention of sulfuric acid.	38

1. INTRODUCTION

1.1 About the Chem-E-Car

Chem-E-Car is an AIChE's annual competition engaging college students in designing and constructing a car powered by a chemical reaction. The car must safely carry a specified load and stop after a given distance (*AIChE Chem-E-Car Competition™ 2015*).

The competition, which involves multiple regional competitions and a final competition at the Annual Student Conference, increases awareness of the chemical engineering discipline among the public, industry leaders, educators and other students. The objectives of the AIChE Chem-E-Car Competition are: providing chemical engineering students with the opportunity to participate in a team on design and construction of a small chemical powered model car; demonstrating the ability to control safely a chemical reaction to carry a specified load and stop after a given distance; encouraging students to become actively involved in their professional society and increasing awareness of the chemical engineering discipline among the general public, industry leaders, educators and other students.

There are two general competitions. The first is held at spring regional conferences and the second is held at the AIChE Annual Meeting. Each year, the annual competition is held together with the Annual Student Conference at the site of the AIChE Annual Meeting. A host AIChE chapter, along with the AIChE staff and the competition sub-committee from the Student Chapters Committee, and SACHE provides support for the annual competition. There is a poster session, a video competition and a distance/performance session at each competition.

Each year the rules may be modified to address concerns that have developed at the past regional and annual competitions.

According to the Chem-E-Car Competition Rules in 2015, each car will be given two opportunities to go over a specified distance carrying a certain additional load. The required load (0 - 500 mL of water) and distance (15 - 30 m \pm 0.005 m) will be given to

each team one hour prior to the start of the performance competition. A judge from the student host chapter will measure out the prescribed water for each team. Teams may not add or remove any “load” to adjust their vehicle weight once the poster session has concluded. Teams are allowed to adjust “fuel” or chemical reactants used in the car’s chemical reaction.

The car will start with its front end just touching the designated starting line. There will be a designated finish line. The distance will be measured with respect to the front point of the car. The goal of the competition is to have the car stopped as close as possible to the specified finish line while carrying the mentioned load. The path should be wedge-shaped with a starting line and the prescribed distance clearly marked in an arc of constant distance from the starting point. The physical site will dictate the exact course layout. An example of the course layout is in the next figure:

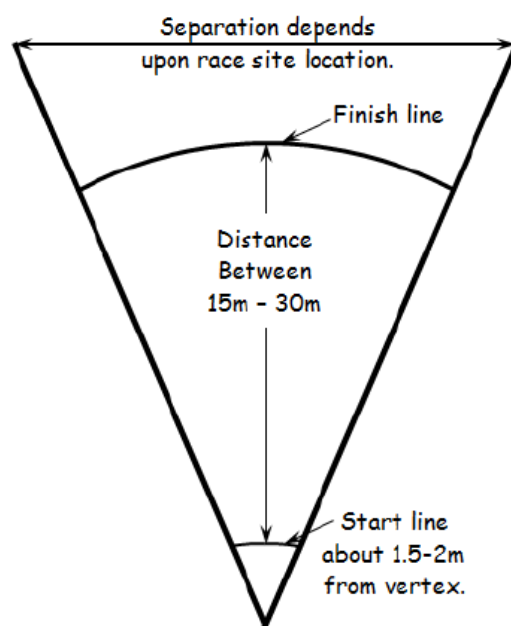


Figure 1. Sketch of typical performance course layout

A vehicle that goes outside the course (having the entire vehicle outside the side tape boundaries of the course) will have its distance measured to where it went out of bounds, and a penalty of 3.0 m will be added to the measured distance. Each car will have two attempts to complete the course, each attempts lasting no more than two minutes. About the vehicle drive system, the only energy source for the propulsion of

the car is a chemical reaction. The distance travelled by the car must be based on a quantifiable change and direct control of the concentration of chemical species. The chemical reactant species must be in a solid, liquid, or vapor state. No commercial batteries are allowed as the power source. The car must be an autonomous vehicle and cannot be controlled remotely. No mechanical force can be applied to the wheel, gears, driveshaft or ground to slow or stop the car (brakes). There can be no mechanical or electronic timing device(s) to stop the chemical reaction or the car. In addition, a timing device cannot utilize what is normally considered as an instantaneous reaction. Internal combustion engines using an alternative fuel are allowed and this fuel must be completely synthesized by the students.

About the size of the car, all components must fit into a box of dimensions no larger than 40 cm x 30 cm x 20 cm. The car may be disassembled to meet this requirement.

The cost of the contents of the “shoe box” and the chemicals must not exceed \$2,000. The vehicle cost includes the donated cost of any equipment. The time donated by university machine shops and other personnel will not be included in the total price of the car. It is expected that every university has equal access to these resources.

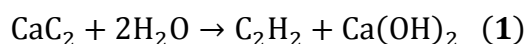
About the Chem-E-Car safety rules, the safe preparation and operation of vehicles during all phases of the competition, including construction, testing and competition, is mandatory. It is not permitted the use of open containers or used chemical pouring at the starting line with a National Fire Protection Association (NFPA) rating of 2 or more. For mixing chemicals to start a reaction, it is suggested that a small holding tank with a valve or a syringe be provided on your vehicle to add the chemical at the starting line (*Regional Chem-E-Car Safety Rules Spring 2015*). The appropriate pressure gauge range ranges from 0 to 400 psig. In any case no vehicle is permitted to have a pressure greater than 500 psig. About the chemical containment hazards, the primary containment must be adequate to prevent leakage of any chemicals during normal transport of the vehicle to the starting line and during the vehicle operation during the contest.

1.2 Background of Chem-E-Car previous competitions

Based on previous competitions, different alternatives have been evaluated regarding the choice of the chemical reaction responsible for causing the movement of the car. One of the products of those chemical reactions is a gas product that is used for moving a pneumatic engine. The most useful reactions for causing the movement of the car are:

Reaction of the carbide and water:

One of these alternatives is the reaction of the carbide and water to give acetylene, which is an exothermic reaction whose heat of reaction is $-31 \frac{\text{kcal}}{\text{mol}}$ or $-130 \frac{\text{kJ}}{\text{mol}}$. Mainly the group of carbide that reacts with water is calcium carbide. The stoichiometric reaction is shown next: (Weissermel, K. et al., 1981).



In this reaction, water can be added under a large excess (wet generator) or almost stoichiometrically (dry generator). The second type is usually preferred. However, the main issue is the dissipation of the heat of reaction.

The hazardous characteristics are frequently denoted using a NFPA diamond. A sample diamond is shown below (Regional Chem-E-Car Safety Rules Spring 2015):

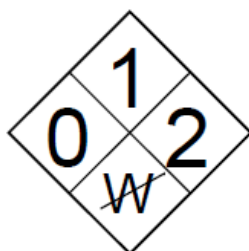



Figure 2. Example of a NFPA diamond.

The area with a “0” in the diamond denotes health hazard, the area with “1” denotes fire hazard and the area with a “2” denotes reactivity. The box at the bottom is used to denote specific hazards. The hazards in the NFPA diamond are indicated by numbers 0 through 4. Zero means minimal hazard while 4 means extreme hazard.

In the next table, it can be found the number in health hazard, fire hazard and reactivity and words in specific hazard.

Table 1. Number in health hazard, fire hazard and reactivity and words in specific hazard.

Health Hazard		Fire Hazard		Reactivity		Specific Hazard	
4	Deadly	4	Below 73 °F	4	May detonate	Oxidizer	OXY
3	Extreme danger	3	Below 100 °F	3	Shock and heat may detonate	Acid	ACID
2	Hazardous	2	Below 200 °F	2	Violent Chemical change	Alkali	ALK
1	Slightly hazardous	1	Above 200 °F	1	Unstable if heated	Corrosive	COR
0	Normal material	0	Will not burn	0	Stable	Use no water	W
						Radiation Hazard	

It is observed that in the reaction of carbide and water to give acetylene, acetylene has the next NFPA code: H 1; F 4; R 3 (*International Chemical Safety Cards (ICSC)*).

1)

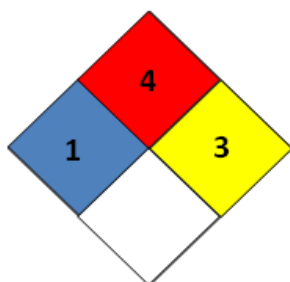
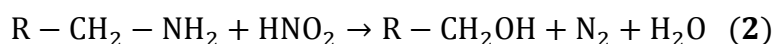


Figure 3. NFPA code of 1) acetylene

In the annex (Table A.1. Types of hazards and prevention of acetylene) it is observed the types of hazards of the acetylene and the prevention of those hazards.

Reaction of an amine and nitrous acid:

Another reaction studied is the formation of molecular nitrogen from the reaction of a primary amine and nitrous acid. The stoichiometric reaction can be expressed as (*John McMurry, 1994*):



Amines have basic character that is evidenced by the formation of salts. These salts are colorless solids, nonvolatile, water-soluble and insoluble in organic solvents. Some examples of primary amine that can be used are: methylamine, ethylamine,

propylamine, n-butylamine or sec-butylamine. Secondary or tertiary amines are not used, because they do not form any molecular nitrogen. It is observed that methylamine has the next NFPA code: H 3; F 4; R 0; ethylamine: H 3; F 4; R 0; propylamine: H 3; F 3; R 0; n-butylamine: H 3; F 3; R 0 and sec-butylamine: H 3; F 3; R 0 (*International Chemical Safety Cards (ICSC)*).

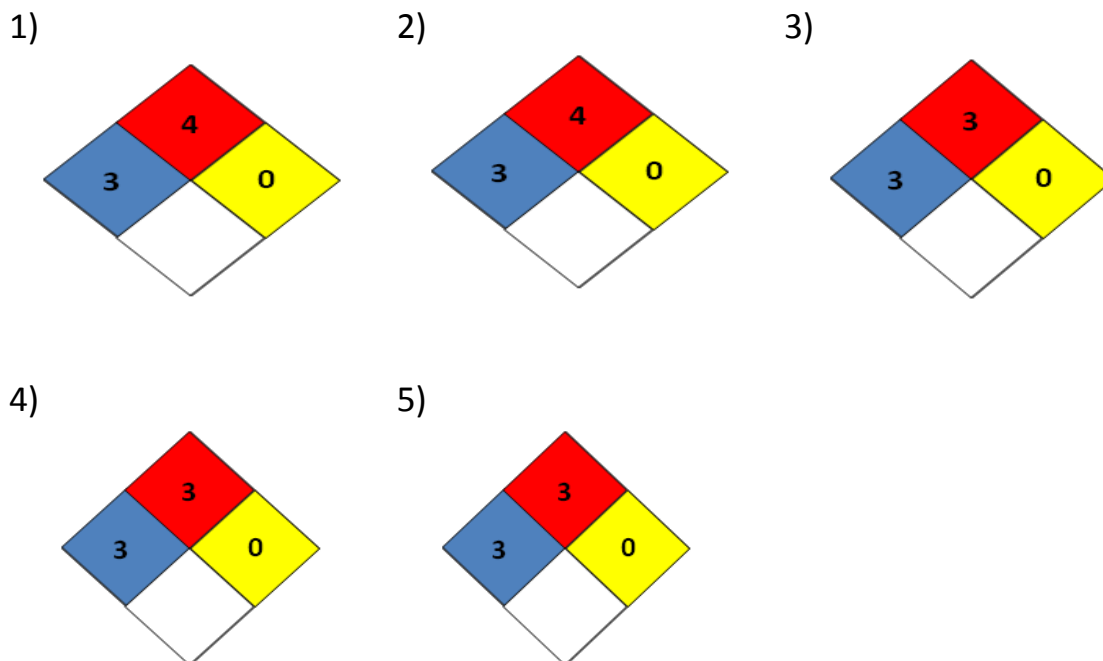


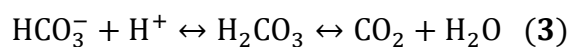
Figure 4. NFPA code of 1) methylamine, 2) ethylamine, 3) propylamine, 4) n-butylamine and 5) sec-butylamine.

In the annex (Tables A.2., A.3., A.4., A.5. and A.6. Types of hazards and prevention of methylamine, ethylamine, propylamine, n-butylamine and sec-butylamine) it is observed the types of hazards of the methylamine, ethylamine, propylamine, n-butylamine, sec-butylamine and the prevention of those hazards. For this case the main problem is to find a suitable primary amine to perform reaction. Moreover, the majority of primary amines are flammable and are dangerous for human health, so it is not the best reaction to cause the movement of the car.

Reaction of an acid and a carbonate:

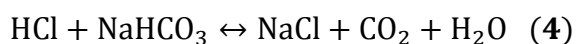
Other option is the reaction between an acid and a carbonate to produce carbon dioxide. This reaction has some drawbacks: - it does not meet the safety requirements

and the low amount of gas production. The stoichiometric reaction can be expressed as (Yueh-Huey Chen *et al.*, 2002).

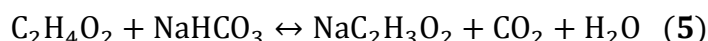


The first specie is a base from a (bi)carbonate or solid solution, more protons will be sequestered from an acid and the result is additional carbonic acid. Because carbonic acid is unstable, it breaks down into carbon dioxide and water. Next reactants can be used:

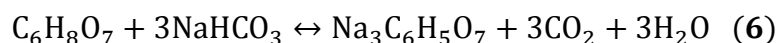
- 1- Hydrochloric acid and sodium bicarbonate



- 2- Acetic acid and sodium bicarbonate



- 3- Citric acid and sodium bicarbonate



The best option is the reaction between hydrochloric acid and sodium bicarbonate because it is the easiest reaction to be performed. The final product is water with sodium chloride dissolved so it is not aggressive to the environment. In the annex (Table A.7. Types of hazards and prevention of hydrogen chloride) it is observed the types of hazards of the hydrogen chloride and the prevention of those hazards.

For carrying out the reaction between acetic acid and sodium bicarbonate, the main drawback is that a huge amount of acetic acid for neutralize sodium bicarbonate is needed. In the annex (Table A.8. Types of hazards and prevention of acetic acid) it is observed the types of hazards of the acetic acid and the prevention of those hazards.

The main advantage to perform the reaction between citric acid and sodium bicarbonate is that the high production of carbon dioxide and a solution of sodium citrate in water, which is considered harmless to the environment. In the annex (Table A.9. Types of hazards and prevention of citric acid) it is observed the types of hazards of the citric acid and the prevention of those hazards.

It is observed that acetic acid has the next NFPA code: H 2; F 2; R 0 and hydrogen chloride: H 3; F 0; R 1 (*International Chemical Safety Cards (ICSC)*).

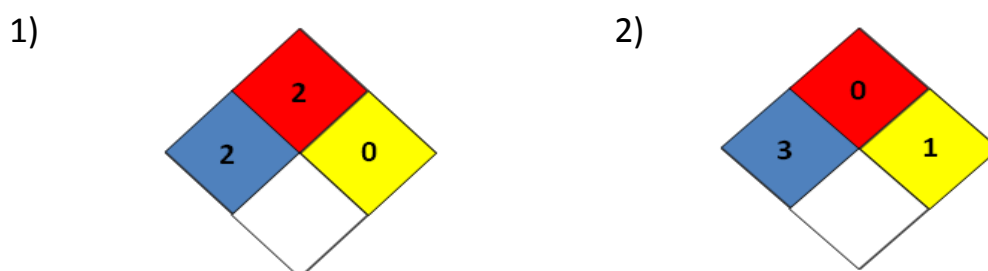
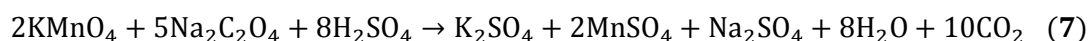


Figure 5. NFPA code of 1) acetic acid and 2) hydrogen chloride.

In conclusion, all the reactions previously reported are not suitable to impulse the car, because they have important disadvantages such as fire, health and reactivity hazards.

Reaction of potassium permanganate and sodium oxalate:

The reaction chosen to cause the movement of the car is the formation of carbon dioxide from potassium permanganate and sodium oxalate. The stoichiometric reaction can be expressed as (*Margaret J. Steffel et al., 1990*):



The reaction is accelerated by the increasing temperature and by the auto catalytic effect of the product, Mn^{+2} (*Krisztián A. Kovács et al., 2004*). The main advantage of this reaction is the fact that meets the requirements of safety and health. Other advantages are that this reaction produces a large amount of gas (carbon dioxide), when compared with the reaction of an acid and a carbonate. In this reaction the

limiting reactant is potassium permanganate. Per mol of potassium permanganate it is produced 5 mol of carbon dioxide. About the thermodynamics of this reaction, the heat of reaction is $-1,514 \text{ J / mol}$ and about chemical equilibrium, this reaction is virtually irreversible and reaction kinetics presents a complex reaction mechanism and energy activation allows to carry it out in 5 minutes at a temperature about $20 \text{ }^{\circ}\text{C}$ (*Gene E. Kalbus et al., 2004*). In the annex (Table A.10. and A.11. Types of hazards and prevention of potassium permanganate and sulfuric acid) it is observed the types of hazards of the potassium permanganate and sulfuric acid and the prevention of those hazards.

It is observed that sulfuric acid has the next NFPA code: H 3; F 0; R 2; No Water, potassium permanganate: H 1; F 0; R 0, sodium oxalate: H 2; F 1; R 0 (*International Chemical Safety Cards (ICSC)*).

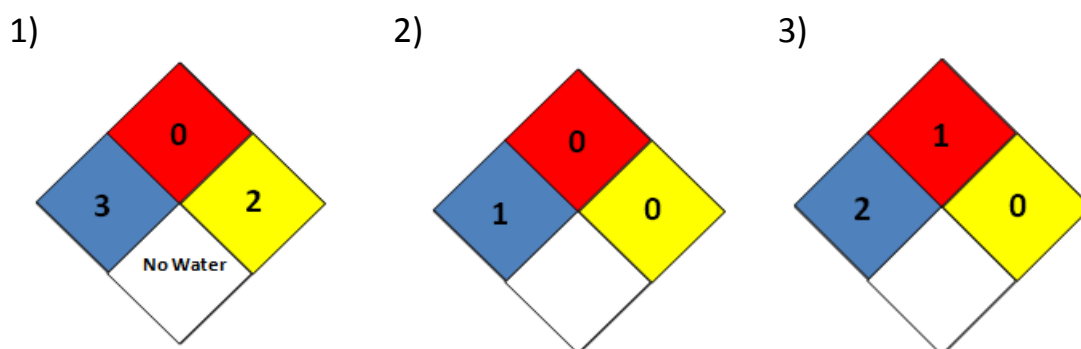


Figure 6. NFPA code of 1) sulfuric acid, 2) potassium permanganate and 3) sodium oxalate.

Those reactions have been chosen to impulse the car, but it is needed other chemical reaction that it is selected as the detention mechanism of the car. This final degree project focus on the chemical reaction that it is selected as the detention mechanism.

1.3 Objectives

The overall objective of this work is the study of the reaction that it is selected as the detention mechanism of Chem-E-Car. According to the AIChE Chem-E-Car CompetitionTM Performance Competition, the vehicle must stop by a quantifiable change, and direct control, of the concentration of chemical species in any solid, liquid or vapor state. It is not allowed applying mechanical force to the wheel, gears, driveshaft or ground to slow the car. It is not allowed stop the car with mechanical or electronic timing device neither.

The reaction selected as the detention mechanism of Chem-E-Car is the iodine clock, which is based on a reaction between potassium iodate and sodium hydrogen sulfite. When the reaction between potassium iodate and sodium hydrogen sulfite is completed, the color of the solution changes from colorless to blue/black color, so a photosensor that is in the iodine clock tank can send a signal to a electrovalve and the release of the produced carbon dioxide to a pneumatic engine is cut down, so the Chem-E-Car stops.

In this work it will be studied the performance of the iodine clock and the influence of the concentration of potassium iodate and temperature on the period of time needed to change the color of the solution. The goal is to obtain a mathematical expression that relates concentration of potassium iodate and temperature with the period of time needed to change the color of the solution. One hour prior to the start of the performance competition, it is given the specified load and distance so it is known the time needed to go over a specified distance carrying a certain additional load (*Alberto Romero López, 2015*). The period of time needed to change the color of the solution (reaction between potassium iodate and sodium hydrogen sulfite is completed) is the same as the time needed to go over a specified distance carrying a certain additional load, because it is mandatory to cut down the release of the produced carbon dioxide to a pneumatic engine when the car have gone over the specified distance carrying a certain additional load. Taking into account that the temperature is a known value, for a given time potassium iodate concentration could be obtained (or the amount of the potassium iodate) from the mathematical expression objective.

2. DEVELOPMENT

2.1 Methodology

2.1.1 Selection of the detention mechanism: an iodine clock

Iodine clock reaction:

The detention mechanism selected is the iodine clock reaction. The iodine clock reaction is characterized by vivid color changes. The iodine clock reaction involves a reaction sequence is shown nest (*Jack L. Lambert et al. 1984*):

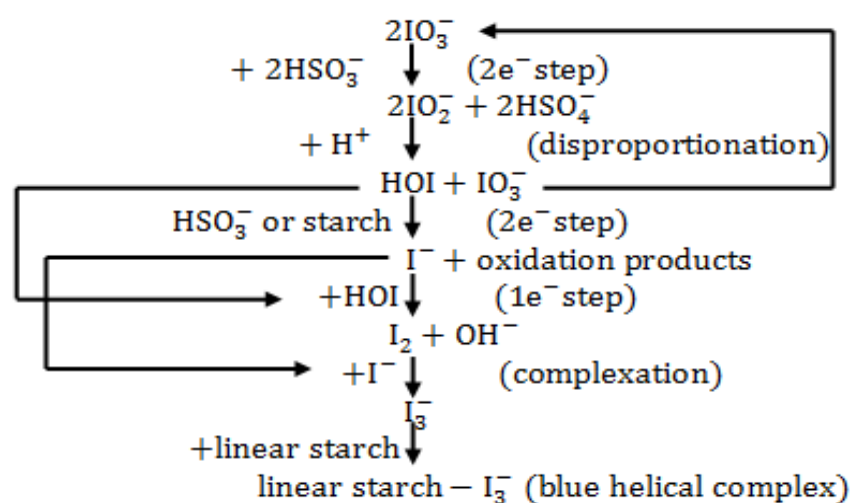
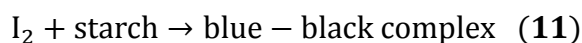
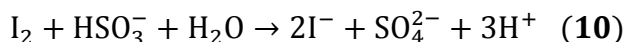
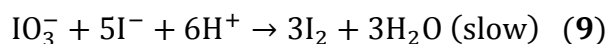


Figure 7. Reaction sequence of iodine clock.

The first two-electron reduction step to iodite is speculative, as other iodine species may be involved in a more complicated reaction sequence. The second two-electron reduction, the reduction of hypoiodous acid to iodide ion could be accomplished by either bisulfite or the secondary alcohol groups of the starch. Hypoiodous acid would be largely undissociated, under the moderately acidic conditions of the reaction. Successively lower concentrations of bisulfate merely extended the time to the appearance of the blue color, which was generated more sluggishly the lower the bisulfate concentration. As soon as the triiodide ion appears, the color of the solution changes from colorless to blue/black color.

In summary, the overall process that takes place can be described by the following very well-known reaction (*John A. Church et al., 1968*):



As indicated above, steps 1 and 2 are dominant as long as sodium hydrogen sulfite is in excess. Once it is consumed, step 3 can no longer occur and an appreciable concentration of molecular iodine becomes present. The starch indicator then rapidly combines with the iodine (triiodide ion, is actually present as well, in equilibrium with molecular iodine and iodine ion) to form the blue – black complex. One can easily see that color development will not occur if the molar ratio of sodium hydrogen sulfite to potassium iodate is greater than 3:1 (*Andre P. Oliveira et al., 2005*).

Old Nassau modification of the iodine clock reaction:

There are some modification of the iodine clock reaction that is identical down to the production of iodine ion, which is complexed as precipitated by mercury (II) until the mercury (II) is exhausted before resuming the pathway leading to the blue starch-polyiodite complex (*Jack L. Lambert et al. 1984*), well known as the Old Nassau modification of the iodine clock reaction.

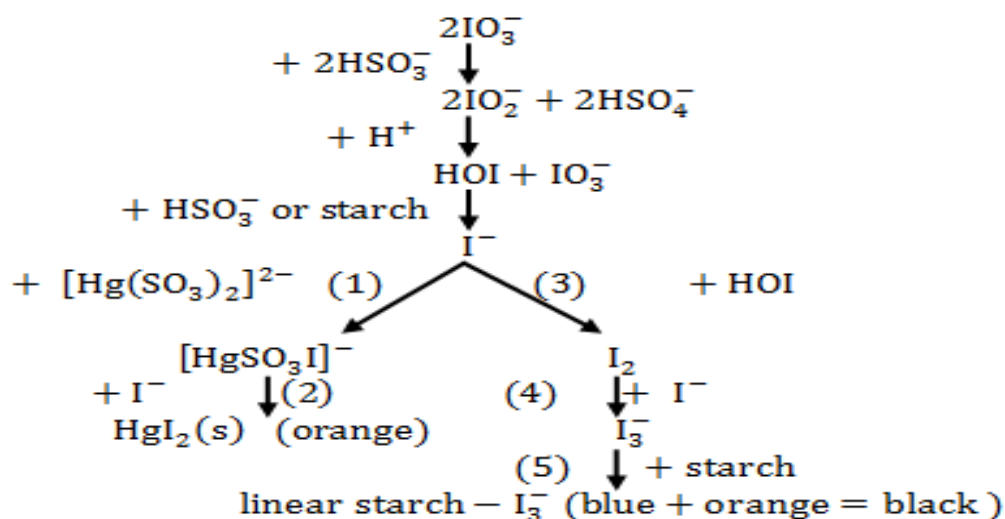


Figure 8. The "Old Nassau" modification of the iodine clock reaction.

Reactions 1, 2, 3, 4 and 5 take place sequentially. Mercury (II) chloride is largely undissociated in aqueous solution, but it forms a more stable-complex with sulfite into $[\text{Hg}(\text{SO}_3)_2]^{2-}$ and even more with iodite into $[\text{HgI}]^+$ and by the precipitation of HgI_2 . The

generated iodide first forms the colorless mixed iodosulfite complex, followed by precipitation of the orange mercury (II) iodite. It is attributed the rapid appearance of HgI_2 to supersaturation, but the bimolecular reaction of iodite with the mercury (II) iodosulfite complex probably, would be rapid enough to account for its nearly instantaneous appearance. When the mercury (II) has all been precipitated as HgI_2 , the extremely rapid production of triiodide produces the blue starch-triiodide complex, and the complementary orange and blue colors appear black (*Jun Ye et al., 2001*).

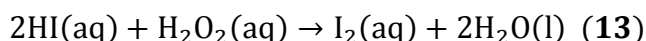
The rate – determining slow step in the clock reactions may involve the migration and reaction between iodite species that have been generated by reduction of iodate by bisulfite. One of the two – electron reactions or the disproportionation step in the reaction sequence that produces iodide ion must be relatively slow, and the iodite-iodite interaction would seem to be a likely candidate (*Jack L. Lambert et al. 1984*). This slow step must account for the interval before the appearance of the blue color and a portion of the interval before the appearance of the orange precipitate. The interval between the appearance of the orange precipitate and the black color in the latter is the time needed for all the mercury (II) to react with steadily generated iodide ion. The reaction of hypoiodite with iodide ion to produce iodine, the reaction of iodine with iodide ion to produce polyiodide anion, the reaction of polyiodide anion with linear starch to produce the blue helical complex, and the interactions of mercury (II) with iodide ion all are known or presumed to be rapid (*Jun Ye et al., 2001*).

Vitamin C clock reaction:

Other alternative is the “Vitamin C Clock Reaction”. In this case, it is needed ascorbic acid (vitamin C), hydrogen peroxide, iodide ion and starch. Ascorbic acid reacts with iodine according to the following equation (*Stephen W. Wright et al. 2006*):



The byproduct of the ascorbic acid oxidation is hydriodic acid (HI), which is oxidized to elemental iodine and water by many oxidizing agents, including hydrogen peroxide:



When the ascorbic acid is exhausted, the iodine produced in the second equation reacts with starch to produce a blue-black color.

Colorimetric method for carbon monoxide (I):

Other option is the colorimetric method for carbon monoxide in the parts – per – million range, iodate ion is reduced in a similar sequence by the generated, atomically dispersed, palladium metal in the presence of leuco crystal violet at pH 3.1 and using bisulfite ion as a two – electron reductant and thus a transient iodite, species must be assumed (*Jack L. Lambert et al. 1984*).

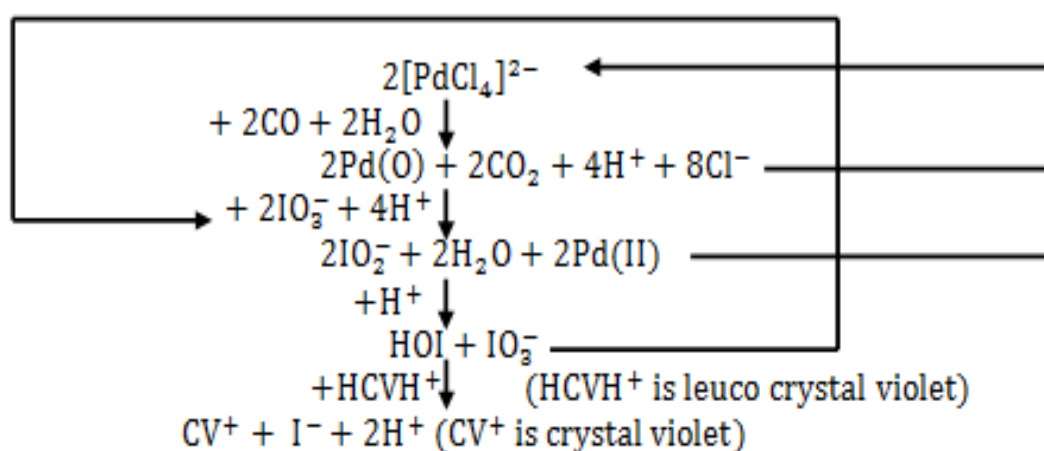
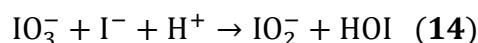


Figure 9. Colorimetric method for carbon monoxide (I)

In the colorimetric method for carbon monoxide, iodate ion is considered to be reduced by finely dispersed palladium metal and by iodide ion. The production of hypoiodous acid is demonstrated by its specific reaction to oxidize leuco crystal violet to crystal violet. Reduction of iodate ion by iodide ion is inferred to explain the autocatalytic production of crystal violet. However, it is a common observation that the reaction of iodate and iodide ions in acid solution results in the production of elemental iodide whose end product occurs only when an excess of iodide ion is present. When iodate ion is present in large excess, iodate apparently is reduced to iodite, and iodide oxidized to hypoiodite, in a simultaneous two – electron redox reaction:



2.1.2 Experimental procedure for carrying out the study of the concentration of KIO_3 and temperature

In this work it will be studied the performance of the iodine clock and the influence of the concentration of potassium iodate and temperature on the period of time needed to change the color of the solution. To study the influence of potassium iodate concentration and temperature, the following steps within the experimental procedure have to be performed:

- 1) Firstly it is prepared a 0.02 M potassium iodate solution.
- 2) Then 5 mL of 0.02 M potassium iodate solution are prepared and later poured into a test tube. It is needed to prepare other 5 potassium iodate solutions by diluting 0.02 M potassium iodate solution being poured into a test tube.

Table 2. Solutions of different concentration of potassium iodate (diluting the original solution).

[NaHSO ₃]	[KIO ₃]	mL of KIO ₃	mL of deionized water
0.01 M	0.02 M	5 mL	0 mL
0.01 M	0.018 M	4.5 mL	0.5 mL
0.01 M	0.014 M	3.5 mL	1.5 mL
0.01 M	0.01 M	2.5 mL	2.5 mL
0.01 M	0.006 M	1.5 mL	3.5 mL
0.01 M	0.002 M	0.5 mL	4.5 mL

- 3) Next it is prepared 0.01 M sodium hydrogen sulfite solution; 2 g/L starch solution and a 0.05 M sulfuric acid solution.
- 4) Secondly, 5 mL of 0.01 M sodium hydrogen sulfite solution, 2.5 mL of 2 g/L starch solution and 2 mL of 0.05 M sulfuric acid solution and are poured into a test tube.
- 5) It is mandatory to measure accurately the time when it is poured the solution of potassium iodate into the solution of sodium hydrogen sulfite, starch and sulfuric acid until the solution's color changes to the expected blue-black color.
- 6) Same experiments were repeated at different temperatures for studying the influence of temperature. The temperatures selected for this work are: 15 °C, 20 °C, 22.5 °C, 25 °C, 28 °C and 30 °C.

2.1.2.1 Material and reagents

For carrying out the experimental procedure about the iodine clock, it is needed the next material described below:

- 1) Thermostatic bath for working at temperatures higher than ambient temperature (20 °C, 22.5 °C, 25 °C, 28 °C and 30 °C) and a cooling bath for working at temperature less than ambient temperature (15 °C).
- 2) For each value of temperature, it is needed 6 test tubes where it is mandatory to pour the potassium iodate solution and others 6 test tubes where it is mandatory to do the same operation with sodium hydrogen sulfite solution, the starch solution and the sulfuric acid solution.



Figure 11. Thermostatic bath (20 °C, 22.5 °C, 25 °C, 28 °C and 30 °C) (on the left) and cooling bath with thermostat (15 °C) (on the right).

- 3) A chronometer for measuring time when it is poured the solution of potassium iodate into the solution of sodium hydrogen sulfite, starch and sulfuric acid until the solution's color changes to the characteristic -blue-black color.
- 4) Micropipettes, beaker, balance and volumetric flask were also used.

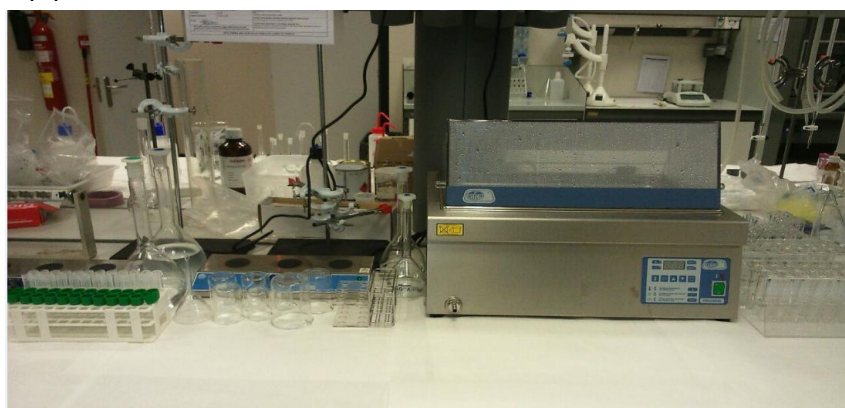


Figure 12. Material needed in experimental procedure.

For carrying out the experimental procedure about the iodine clock, the next reagents were used:

- 1) Potassium iodate supplied by Panreac; molecular formula: KIO_3 ; purity: 100%.
- 2) Sodium hydrogen sulfite supplied by Panreac; molecular formula: NaHSO_3 ; purity: 40% p/v.
- 3) Sulfuric acid supplied by Panreac; molecular formula: H_2SO_4 ; purity: 93 – 98%.
- 4) Starch supplied by Panreac. Molecular formula: starches contain 10-20% amylose and 80-90% amylopectin.

Amylose, which has the next molecular formula:

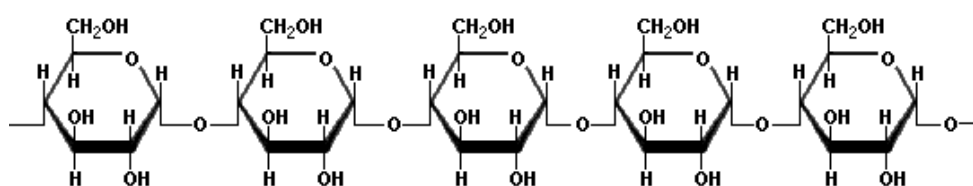


Figure 13. Molecular formula of amylose.

Amylopectin, which has the next molecular formula:

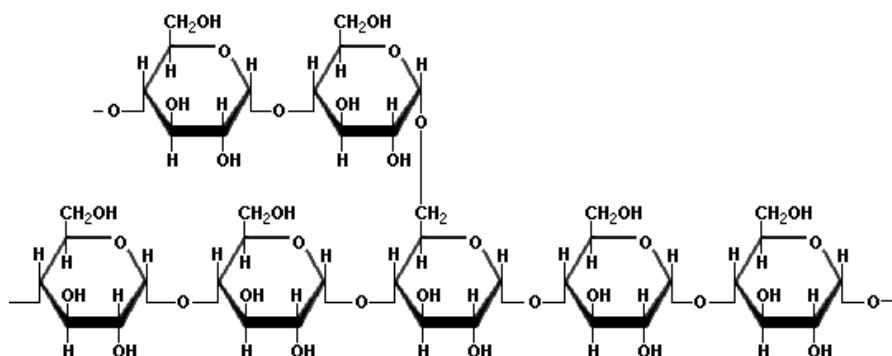


Figure 14. Molecular formula of amylopectin.



Figure 15. Reagents needed in experimental procedure.

2.2 Results and discussion

2.2.1 Performance of the iodine clock

The study considers the period of time needed to changing the color of the solution with different potassium iodate concentrations and temperatures. It will be studied: i) the influence of the concentration of potassium iodate and ii) the influence of temperature. It will be studied the performance of the iodine clock at 6 temperature values (15 °C, 20 °C, 22.5 °C, 25 °C, 28 °C and 30 °C) and at 6 potassium iodate concentration values (0.02 M, 0.018 M, 0.014 M, 0.01 M, 0.006 M and 0.002 M). The period of time needed to changing the color of the solution with different potassium iodate concentration values and temperature values are presented in the tables 3-8.

Table 3. Time needed to change the color of the solution with different potassium iodate concentration values at 15 °C.

Temperature 15 °C = 288 K				
[NaHSO ₃] M	[KIO ₃] M	Time Experiment 1 (s)	Time Experiment 2 (s)	Time average (s)
0.01	0.02	15.3	14.9	15.1
0.01	0.018	15.8	15.5	15.6
0.01	0.014	21.4	21.1	21.2
0.01	0.01	29.6	28.5	29.1
0.01	0.006	43.9	51.0	47.4
0.01	0.002	163.5	176.2	169.9

Table 4. Time needed to change the color of the solution with different potassium iodate concentration values at 20 °C.

Temperature 20 °C = 293 K				
[NaHSO ₃] M	[KIO ₃] M	Time Experiment 1 (s)	Time Experiment 2 (s)	Time average (s)
0.01	0.02	13.1	13.3	13.2
0.01	0.018	14.3	14.0	14.2
0.01	0.014	17.6	17.7	17.7
0.01	0.01	24.0	23.9	24.0
0.01	0.006	41.5	40.5	41.0
0.01	0.002	143.8	145.0	144.4

Table 5. Time needed to change the color of the solution with different potassium iodate concentration values at 22.5 °C.

Temperature 22.5 °C = 295.5 K				
[NaHSO ₃] M	[KIO ₃] M	Time Experiment 1 (s)	Time Experiment 2 (s)	Time average (s)
0.01	0.02	12.0	11.6	11.8
0.01	0.018	13.5	13.0	13.3
0.01	0.014	16.7	16.4	16.5
0.01	0.01	23.9	23.7	23.8
0.01	0.006	39.1	38.9	39.0
0.01	0.002	139.2	135.5	137.4

Table 6. Time needed to change the color of the solution with different potassium iodate concentration values at 25 °C.

Temperature 25 °C = 298 K				
[NaHSO ₃] M	[KIO ₃] M	Time Experiment 1 (s)	Time Experiment 2 (s)	Time average (s)
0.01	0.02	12.1	12.1	12.1
0.01	0.018	13.6	13.0	13.3
0.01	0.014	16.0	16.2	16.1
0.01	0.01	23.6	23.5	23.5
0.01	0.006	39.9	40.0	39.9
0.01	0.002	137.8	137.2	137.5

Table 7. Time needed to change the color of the solution with different potassium iodate concentration values at 28 °C.

Temperature 28 °C = 301 K				
[NaHSO ₃] M	[KIO ₃] M	Time Experiment 1 (s)	Time Experiment 2 (s)	Time average (s)
0.01	0.02	12.0	11.8	11.9
0.01	0.018	13.2	13.2	13.2
0.01	0.014	15.9	16.5	16.2
0.01	0.01	22.8	23.2	23.0
0.01	0.006	39.4	37.1	38.3
0.01	0.002	139.3	134.9	137.1

Table 8. Time needed to change the color of the solution with different potassium iodate concentration values at 30 °C.

Temperature 30 °C = 303 K				
[NaHSO ₃] M	[KIO ₃] M	Time Experiment 1 (s)	Time Experiment 2 (s)	Time average (s)
0.01	0.02	10.4	10.7	10.6
0.01	0.018	11.4	11.3	11.3
0.01	0.014	14.9	14.1	14.5
0.01	0.01	20.8	20.6	20.7
0.01	0.006	35.3	35.6	35.4
0.01	0.002	124.1	124.3	124.2

The maximum period of time needed to change the color of the starch based solution must be two minutes, which is the maximum allowed time for each run so it is expected to obtain period of time needed to change the color of the solution lower than 2 minutes. It is important to consider the human error for each experimental time measurement. The human error was estimated to be lower than a second. The human error must be considered as the interval between (pressing the chronometer to start and pressing the button again to stop it) due to the reaction time to see the color change of the solution.

2.2.2 Influence of concentration of KIO_3 and temperature

The aim of this study is to obtain a mathematical expression that relates the concentration of potassium iodate and temperature with the period of time needed to change the color of the starch based solution. This mathematical expression is obtained by means of Curve Fitting Tool from Matlab (*MathWorks, Matlab R2013B*).

Firstly the period of time needed to change the color of the solution values and potassium iodate concentration as well as the temperature values are introduced. Potassium iodate concentration is selected as X data; temperature is selected as Y data and time is selected as Z data. Curve Fitting Tool has different types of settings available. Firstly it is selected a polynomial group. In the following table 9, it can be found different degree polynomial and the goodness of the fit.

Table 9. Different degree polynomial and its goodness of fit

Degree polynomial	Goodness of fit			
	SSE	R-square	Adjusted R-square	RMSE
Poly 11	$5.49 \cdot 10^4$	0.643	0.633	28.21
Poly 21	$1.27 \cdot 10^4$	0.917	0.912	13.78
Poly 12	$5.40 \cdot 10^4$	0.649	0.628	28.4
Poly 22	$1.27 \cdot 10^4$	0.918	0.911	13.85
Poly 31	2307	0.985	0.984	5.958
Poly 32	2177	0.986	0.984	5.878
Poly 13	$5.39 \cdot 10^4$	0.650	0.617	28.8
Poly 23	$1.22 \cdot 10^4$	0.921	0.911	13.91
Poly 33	2101	0.986	0.984	5.824
Poly 41	680.9	0.996	0.995	3.287
Poly 42	524.2	0.997	0.996	2.956
Poly 43	379.2	0.998	0.997	2.557
Poly 14	$5.38 \cdot 10^4$	0.650	0.606	29.23
Poly 24	$1.21 \cdot 10^4$	0.922	0.907	14.2
Poly 34	1898	0.988	0.985	5.72
Poly 44	359.1	0.998	0.997	2.51
Poly 51	523.1	0.997	0.996	2.93
Poly 52	357.3	0.998	0.997	2.5
Poly 53	189.7	0.999	0.998	1.87
Poly 54	159	0.999	0.999	1.75
Poly 15	$5.38 \cdot 10^4$	0.650	0.593	29.7
Poly 25	$1.20 \cdot 10^4$	0.922	0.902	14.5
Poly 35	1852	0.988	0.984	5.86
Poly 45	295.5	0.998	0.997	2.38
Poly 55	158.9	0.999	0.999	1.77

Poly A⁽¹⁾ B⁽²⁾

(1): Concentration polynomial degree

(2): Temperature polynomial degree

From the results obtained in Table 9, it has been chosen the polynomial expression with the lowest degree of polynomial, but at the same time balancing a proper goodness of fit. It has been chosen Poly 21, in which the concentration polynomial degree is 2 and the temperature polynomial degree is just 1.

The linear model of Poly 21 is therefore:

$$f(x, y) = p00 + p10 \cdot x + p01 \cdot y + p20 \cdot x^2 + p11 \cdot x \cdot y \quad (15)$$

where different coefficients values with 95% confidence bounds are in the following table 10:

Table 10. Different coefficients values with 95% confidence bounds (Poly 21).

Coefficients	Confidence bounds
p00	217.6 (184.2, 251.1)
p10	$-2.49 \cdot 10^4$ ($-2.822 \cdot 10^4$, $-2.158 \cdot 10^4$)
p01	-1.951 (-3.302, -0.5994)
p20	$7.501 \cdot 10^5$ ($6.487 \cdot 10^5$, $8.516 \cdot 10^5$)
p11	100.4 (-1.105, 202)

Figure 16 shows surface plotted by Matlab (Poly 21) for different potassium iodate concentration values, temperature values and time needed values to change the solution color.

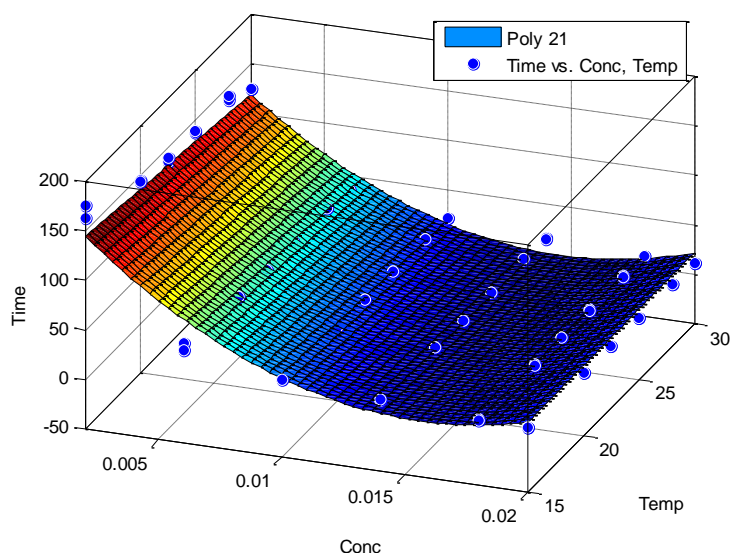


Figure 16. Surface plotted by Matlab for different potassium iodate concentration values, temperature values and time needed values to change the solution color (Poly 21).

The goodness of fit of Poly 21 can be found in Table 9. Poly 21 has 5 coefficients, so it is recommended reduce the number of coefficients in order to simplify and help at

later operations. Coefficient p11 should be removed, because it may have a value of zero. In this case the linear model of poly is therefore:

$$f(x,y) = p00 + p10 * x + p01 * y + p20 * x^2 \quad (16)$$

where different coefficients values with 95% confidence bounds are in the following table 11:

Table 11. Different coefficients values with 95% confidence bounds (Poly).

Coefficients	Confidence bounds
p00	190.2 (171.1, 209.3)
p10	$-2.255 \cdot 10^4$ ($-2.493 \cdot 10^4$, $-2.018 \cdot 10^4$)
p01	-0.7777 (-1.439, -0.1163)
p20	$7.506 \cdot 10^5$ ($6.471 \cdot 10^5$, $8.542 \cdot 10^5$)

The goodness of fit of Poly is very similar as the goodness of fit of Poly 21. The goodness of fit of this linear model is in the next table:

Table 12. The goodness of fit of this linear model (Poly).

Goodness of fit	
SSE	$1.347 \cdot 10^4$
R-square	0.9124
Adjusted R-square	0.9086
RMSE	14.07

Figure 17 shows surface plotted by Matlab (Poly) for different potassium iodate concentration values, temperature values and time needed values to change the solution color.

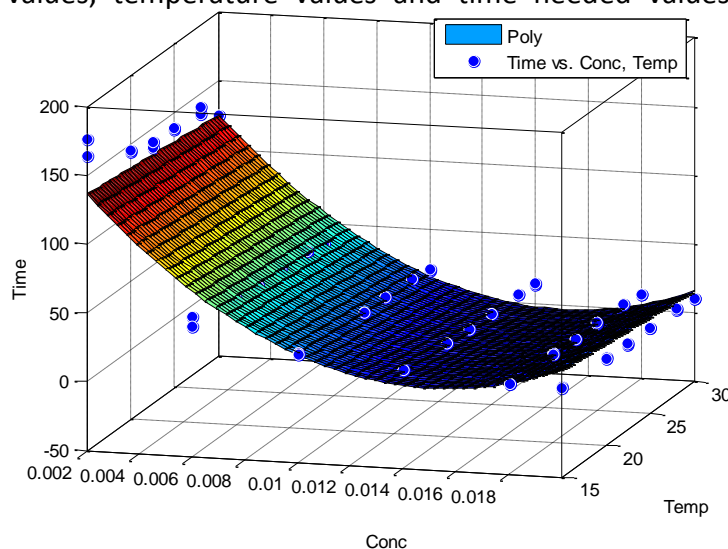


Figure 17. Surface plotted by Matlab for different potassium iodate concentration values, temperature values and time needed values to change the solution color (Poly).

It is important reduce the number of coefficients for simplifying and helping at later operations, but a lower number of coefficients leads to a worse fit, so a tailored

mathematical expression is created with the Custom Equation option with 3 coefficients displaying an exponential form, pursuing a better goodness of fit. General expression suggestion is therefore:

$$f(x,y) = p1 * \exp\left(-\frac{p2}{y}\right) * x^{p3} \quad (17)$$

where different coefficients values with 95% confidence bounds are in the following table 13:

Table 13. Different coefficients values with 95% confidence bounds (General Mode).

Coefficients	Confidence bounds
p1	0.1014 (0.08927, 0.1135)
p2	-8.204 (-8.961, -7.446)
p3	-1.105 (-1.124, -1.086)

The goodness of fit of this general expression is in the next table:

Table 14. The goodness of fit of this linear model (General Mode).

Goodness of fit	
SSE	395.5
R-square	0.9974
Adjusted R-square	0.9974
RMSE	2.394

In the next parity diagram (Figure 18), it is demonstrated that the time obtained with last equation (general mode) is very similar as the time obtained experimentally in laboratory.

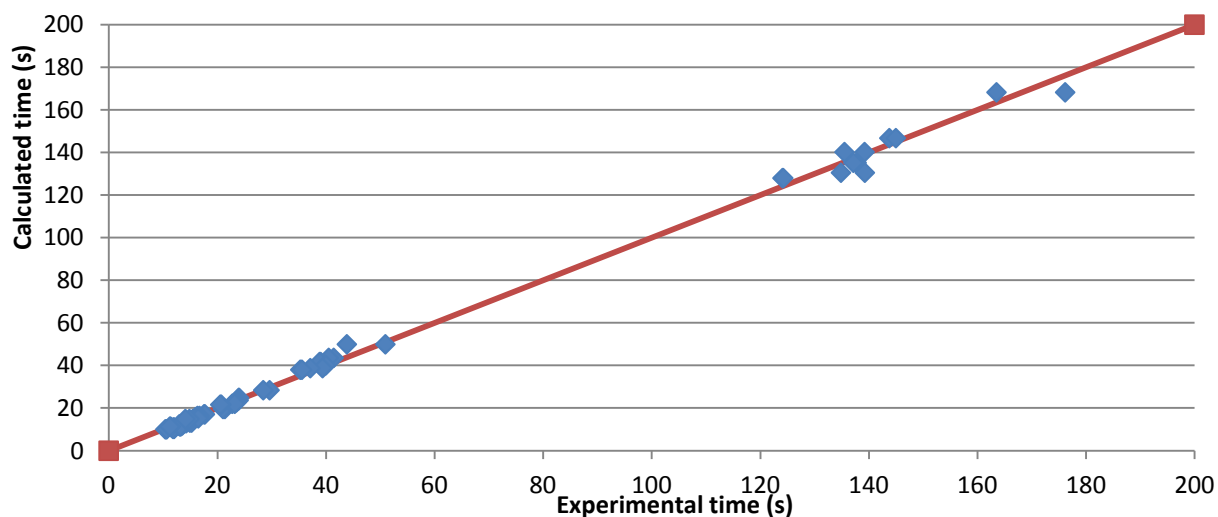


Figure 18. Parity diagram between calculated time (general mode) and experimental time.

Figure 19 shows surface plotted by Matlab (general mode) for different potassium iodate concentration values, temperature values and time needed values to change the solution color for the equation 17 with the parameters on table 13.

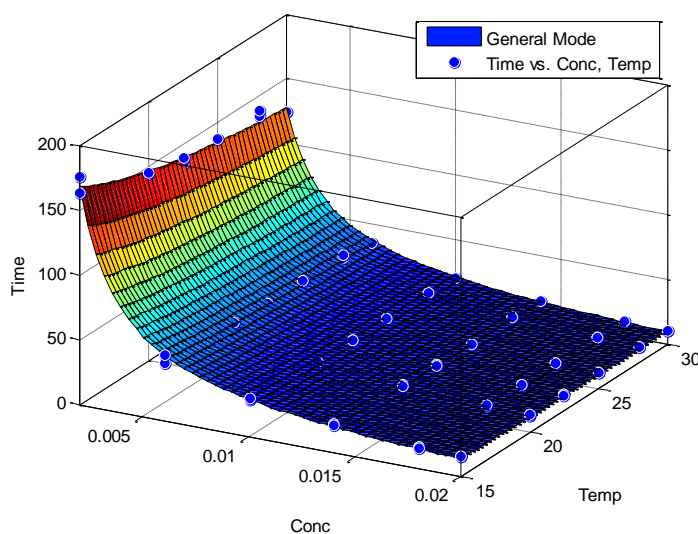


Figure 19. Surface plotted by Matlab (general mode) for different values of potassium iodate concentration, temperature and time needed to change the solution color (General Mode).

The aim of this final degree project is used a chemical reaction as a detention mechanism of the car. The period of time needed to change the color of the solution (reaction between potassium iodate and sodium hydrogen sulfite is completed) is the same as the time needed to go over a specified distance carrying a certain additional load (*Alberto Romero López, 2015*) because it is mandatory to cut down the release of the produced carbon dioxide to a pneumatic engine when the car have gone over the specified distance carrying a certain additional load. Taking into account that the temperature is a known value, for a given time potassium iodate concentration (x) could be obtained (or the amount of the potassium iodate) from the mathematical expression objective, whose units is mol/L.

It is mandatory to prepare the potassium iodate solution whose concentration is x. It is also prepared 0.01 M sodium hydrogen sulfite solution, 0.05 M sulfuric acid solution and 2 g/L starch solution and poured it into the volume tank (5 mL of sodium hydrogen sulfite solution, 2 mL of sulfuric acid solution and 2.5 mL of starch solution). At the same time the Chem-E-Car start going over a specified distance carrying a certain additional load by the injection of carbon dioxide to the pneumatic engine, 5

mL of potassium iodate solution is poured into the iodine clock tank. When the reaction between potassium iodate and sodium hydrogen sulfite is completed, the color of the solution changes from colorless to blue/black color, so a photosensor that is in the iodine clock tank can send a signal to a electrovalve and the release of the produced carbon dioxide to a pneumatic engine is cut down, so the Chem-E-Car stops (Chem-E-Car is expected to stop in a specified distance carrying a certain additional load).

The time obtained by the Chem-E-Car modeling (*Alberto Romero López, 2015*) in the most restrictive situation is approximately 36.1 seconds (specified distance of 30 and an additional load of 500 mL of water)), then it is needed a potassium iodate concentration between 0.0080 M and 0.0063 M (temperature between 15 ° C and 30 ° C). For the least restrictive situation, time obtained is approximately 18 seconds (specified distance of 15 m and an additional load of 0 mL of water)), then it is needed a potassium iodate concentration between 0.015 M and 0.011 M (temperature between 15 ° C and 30 ° C).

3. CONCLUSIONS

The experimental procedure has demonstrated that the proposed iodine clock reaction can be used as the detention mechanism in the Chem-E-Car project discussed in this work because the period of time needed to change the color of the starch based solution is below two minutes, which is the maximum allowed time for each run, according to the existing rules. Therefore iodine clock is used to stop the injection of carbon dioxide to the pneumatic engine, thus the Chem-E-Car is expected to stop in a specified distance carrying a certain additional load.

It is obtained a mathematical expression that relates the potassium iodate concentration and temperature with the period of time needed to change the color of the mentioned above starch based solution. This mathematical expression request only three coefficients while showing a goodness of fit over $R^2 > 0.99$.

4. ANNEX

4.1 ANNEX 1

Table A.1. Types of hazards and prevention of acetylene.

ACETYLENE			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Extremely flammable.	No open flames, no sparks, and no smoking.	Shut off supply; if not possible and no risk to surroundings, let the fire burn itself out; in other cases extinguish with powder, carbon dioxide
EXPLOSION	Gas / air mixtures are explosive.	Closed system, ventilation, explosion – proof electrical equipment and lighting. Prevent build-up of electrostatic charges. Use non-sparking handtools. Use flame arrester to prevent flash-back from burner to cylinder.	In case of fire: keep cylinder cool by spraying with water.
EXPOSURE			
-INHALATION	Dizziness. Dullness. Headache. Suffocation.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Artificial respiration may be needed. Refer for medical attention.
- SKIN			
- EYES			First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION		Do not eat, drink, or smoke during work.	
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Evacuate danger area. Consult an expert. Ventilation. Remove all ignition sources. (Extra personal protection: self-contained breathing apparatus).		Fireproof. Separated from - see Chemical Dangers. Cool.	Special insulated cylinder. F symbol; R: 5-6-12, S: 2-9-16-33, Un Hazard Class: 2.1.

Table A.2. Types of hazards and prevention of methylamine.

METHYLAMINE			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Extremely flammable. Gives off irritating or toxic fumes (or gases) in a fire.	No open flames, no sparks, and no smoking.	Shut off supply; if not possible and no risk to surroundings, let the fire burn itself out; in other cases extinguish with powder, carbon dioxide.
EXPLOSION	Gas / air mixtures are explosive.	Closed system, ventilation, explosion – proof electrical equipment and lighting. Use non-sparking handtools.	In case of fire: keep cylinder cool by spraying with water. Combat fire from a sheltered position.
EXPOSURE			
-INHALATION	Burning sensation. Cough. Headache. Laboured breathing. Shortness of breath. Sore throat.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer for medical attention.
- SKIN	On contact with liquid: frostbite.	Cold-insulating gloves. Protective clothing.	On frostbite: rinse with plenty of water, do not remove clothes. Refer for medical attention.
- EYES	Redness. Pain. Blurred vision. Severe deep burns.	Safety goggles, or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION		Do not eat, drink, or smoke during work.	
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Evacuate danger area. Consult an expert. Ventilation. Remove all ignition sources. Personal Protection: complete protective clothing including self-contained breathing apparatus. Never direct water jet on liquid. Remove vapour with fine water spray.		Fireproof. Cool.	F+ symbol. Xn symbol. R: 12-20-37/38-41. S: 2-16-26-39. UN Hazard Class: 2.1.

Table A.3. Types of hazards and prevention of ethylamine.

ETHYLAMINE			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Extremely flammable. Gives off irritating or toxic fumes (or gases) in a fire.	No open flames, no sparks, and no smoking.	Shut off supply; if not possible and no risk to surroundings, let the fire burn itself out; in other cases extinguish with dry powder, carbon dioxide.
EXPLOSION	Gas / air mixtures are explosive.	Closed system, ventilation, explosion – proof electrical equipment and lighting.	In case of fire: keep cylinder cool by spraying with water. Combat fire from a sheltered position.
EXPOSURE			
-INHALATION	Cough. Laboured breathing. Sore throat.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer for medical attention.
- SKIN	On contact with liquid: frostbite.	Cold-insulating gloves. Protective clothing.	On frostbite: rinse with plenty of water, do not remove clothes. Refer for medical attention.
- EYES	Redness. Pain. Blurred vision.	Safety goggles, or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION		Do not eat, drink, or smoke during work.	
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Evacuate danger area. Consult an expert. Ventilation. Remove all ignition sources. Never direct water jet on liquid. (Extra personal protection: complete protective clothing including self-contained breathing apparatus).		Fireproof. Cool.	F+ symbol. Xn symbol. R:12-36/37. S: 2-16-26-29, UN Hazard Class: 2.1.

Table A.4. Types of hazards and prevention of propylamine.

PROPYLAMINE			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Extremely flammable. Gives off irritating or toxic fumes (or gases) in a fire.	No open flames, no sparks, and no smoking.	Powder, alcohol-resistant foam, water in large amounts, carbon dioxide.
EXPLOSION	Vapour / air mixtures are explosive.	Closed system, ventilation, explosion – proof electrical equipment and lighting. Do not use compressed air for filling, discharging, or handling.	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE		Prevent generation of mists. Avoid all contact.	
-INHALATION	Cough. Laboured breathing. Sore throat. Burning sensation. Shortness of breath.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest.
- SKIN	Redness. Skin burns. Pain. Blisters.	Cold-insulating gloves. Protective clothing.	Remove contaminated clothes. Rinse skin with plenty of water or shower. Refer for medical attention.
- EYES	Redness. Pain. Loss of vision. Severe deep burns.	Face shield, or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION	Abdominal pain. Burning sensation. Headache. Shock or collapse.	Do not eat, drink, or smoke during work.	Rinse mouth. Do not induce vomiting. Give plenty of water to drink. Refer for medical attention.
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Evacuate danger area. Consult an expert. Ventilation. Remove all ignition sources. Collect leaking liquid in sealable containers. Wash away spilled liquid with plenty of water. (Extra personal protection: chemical protection suit, including self-contained breathing apparatus).		Fireproof. Separated from strong oxidants, acid, food and feedstuffs. Well closed.	Do not transport with food and feedstuffs. UN Hazard Class: 3. Un Subsidiary Risks: 8. UN Packing Group: II

Table A.5. Types of hazards and prevention of *n*-butylamine.

N-BUTYLAMINE			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Highly flammable. Gives off irritating or toxic fumes (or gases) in a fire.	No open flames, no sparks, and no smoking.	Powder, alcohol-resistant foam, water in large amounts, carbon dioxide.
EXPLOSION	Vapour / air mixtures are explosive.	Closed system, ventilation, explosion – proof electrical equipment and lighting.	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE		Avoid all contact.	In all cases consult a doctor.
- INHALATION	Cough. Laboured breathing. Sore throat. Burning sensation. Shortness of breath. Headache. Flushing of the face. Vomiting. Dizziness. Symptoms may be delayed.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer for medical attention.
- SKIN	May be absorbed. Redness. Skin burns. Pain. Blisters.	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse skin with plenty of water or shower. Refer for medical attention.
- EYES	Redness. Pain. Loss of vision. Severe deep Burns.	Face shield, or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove Contact lenses if easily possible), then take to a doctor.
- INGESTION	Abdominal pain. Burning sensation. Diarrhoea. Nausea. Headache. Shock or collapse..	Do not eat, drink, or smoke during work.	Rinse mouth. Do not induce vomiting. Give plenty of water to drink. Refer for medical attention.
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Evacuate danger area. Consult an expert. Ventilation. Collect leaking and spilled liquid in sealable containers as far as possible. Absorb remaining liquid in sand or inert absorbent and remove to safe place. Do not let this chemical enter the environment. Personal protection: chemical protection suit including self-contained breathing apparatus.		Fireproof. Separated from food and feedstuffs.	Unbreakable packaging; put breakable packaging into closed unbreakable container. Do not transport with food and feedstuff. F symbol. C symbol. R: 11-20/21/22-35. S: 1/2-3-16-26-29-36/37/39-45. Un Hazard Class: 3. Un Subsidiary Risks: 8. Un Packing Group: II.

Table A.6. Types of hazards and prevention of sec-butylamine.

SEC-BUTYLAMINE			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Highly flammable.	No open flames, no sparks, and no smoking.	Powder, alcohol-resistant foam, water in large amounts, carbon dioxide.
EXPLOSION	Vapour / air mixtures are explosive.	Closed system, ventilation, explosion – proof electrical equipment and lighting.	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE		Strict hygiene.	In all cases consult a doctor.
-INHALATION	Cough. Laboured breathing. Sore throat. Shortness of breath.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer for medical attention.
- SKIN	Redness. Skin burns. Pain. Blisters.	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse skin with plenty of water or shower. Refer for medical attention.
- EYES	Redness. Pain. Loss of vision. Severe deep burns.	Safety spectacles, face shield, or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION	Diarrhoea. Sore throat. Vomiting. Abdominal pain. Burning sensation. Shock or collapse.	Do not eat, drink, or smoke during work.	Rinse mouth. Do not induce vomiting. Refer for medical attention.
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Evacuate danger area. Consult an expert. Remove all ignition sources. Collect leaking and spilled liquid in sealable containers as far as possible. Absorb remaining liquid in sand or inert absorbent and remove to safe place. Chemical protection suit including self-contained breathing apparatus.		Fireproof. Separated from strong oxidants, strong acids. Cool. Dry. Keep in a well-ventilated room.	Note: C. F symbol. C symbol. N symbol. R: 11-20/22-35-50. S: 1/2 -9-16-26-28-36/37/39-45-61. Un Hazard Class: 3. Un Subsidiary Risks: 6.1. Un Packing Group: II.

Table A.7. Types of hazards and prevention of hydrogen-chloride.

HYDROGEN CHLORIDE			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Not combustible		In case of fire in the surroundings: use appropriate extinguishing media.
EXPLOSION			In case of fire: keep cylinder cool by spraying with water.
EXPOSURE		Avoid all contact.	In all cases consult a doctor.
-INHALATION	Corrosive. Burning sensation. Cough. Laboured breathing. Shortness of breath. Sore throat.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer for medical attention.
- SKIN	On contact with liquid: frostbite. Corrosive. Serious skin burns. Pain.	Cold-insulating gloves. Protective clothing.	First rinse skin with plenty of water, then remove contaminated clothes and rinse again. Refer for medical attention.
- EYES	Corrosive. Pain. Blurred vision. Severe deep burns.	Safety goggles or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION			
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Evacuate danger area. Consult an expert. Remove gas with fine water spray. Personal protection: complete protective clothing including self-contained breathing apparatus.		Separated from combustible and reducing substances, strong oxidants, strong bases, metals. Keep in a well-ventilated room. Cool. Dry.	T symbol. C symbol. R: 23-35. S: 1/2-9-26-36/37/39-45. Un Hazard Class: 2.3. Un Subsidiary Risks: 8

Table A.8. Types of hazards and prevention of acetic-acid.

ACETIC ACID			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Flammable.	No open flames, no sparks and no smoking.	Powder, alcohol-resistant foam, water spray, carbon dioxide.
EXPLOSION	Above 39 °C explosive vapor/air mixtures may be formed.	Above 39 °C use a closed system, ventilation, and explosion-proof electrical equipment.	In case of fire: keep drums, etc., cool by spraying with water
EXPOSURE		Avoid all contact.	
- INHALATION	Sore throat. Cough. Burning sensation. Headache. Dizziness. Shortness of breath. Laboured breathing.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Half-upright position. Refer for medical attention.
- SKIN	Pain. Redness. Blisters. Skin burns.	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse and then wash skin with water and soap. Rinse skin with plenty of water or shower.
- EYES	Redness. Pain. Severe deep burns. Loss of vision.	Face shield or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION	Abdominal pain. Burning sensation. Diarrhoea.	Do not eat, drink, or smoke during work.	Rinse mouth. Do not induce vomiting. Give plenty water to drink. Refer for medical attention.
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Collect leaking liquid in sealable containers. Cautiously neutralize spilled liquid with sodium carbonate only under the responsibility of an expert. Wash away remainder with plenty of water. Personal protection: chemical protection suit-including self-contained breathing apparatus.		Fireproof. Separated from froom and feedstuffs. See Chemical Dangers. Keep in a well ventilated room.	Do not transport with food and feedstuffs. Note: B. C symbol. R: 10-35. S: 1/2-23-26-45. Un Hazard Class: 8. Un Subsidiary risks: 3. Un Packing Group: II.

Table A.9. Types of hazards and prevention of citric-acid.

CITRIC ACID			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Combustible.	No open flames.	Powder, water spray, foam, carbon dioxide
EXPLOSION	Finely dispersed particles form explosive mixtures in air.	Prevent deposition of dust; closed system, dust explosion-proof electrical equipment and lighting.	
EXPOSURE		Prevent dispersion of dust.	
-INHALATION	Cough. Shortness of breath. Sore throat.	Ventilation (not if powder).	Fresh air, rest. Refer for medical attention.
- SKIN	Redness. Pain. Severe deep burns. Loss of	Protective gloves.	Rinse skin with plenty of water or shower. Refer for medical attention.
- EYES	Redness. Pain.	Safety goggles.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION	Abdominal pain. Sore throat.	Do not eat, drink, or smoke during work.	Rinse mouth. Refer for medical attention.
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Sweep spilled substance into containers; if appropriate; moisten first to prevent. Wash away remainder with plenty of water. (Extra personal protection: P2 filter respirator for harmful particles).		Separated from strong oxidants, strong bases, metal nitrates and metals. Dry.	

Table A.10. Types of hazards and prevention of potassium-permanganate.

POTASSIUM PERMANGANATE			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Not combustible, but enhances combustion of other substances. Gives off irritating or toxic fumes (or gases) in a fire.	No contact with flammable substances.	In case of fire in the surroundings: use appropriate extinguishing media.
EXPLOSION	Risk of fire and explosion on contact with combustible substances and reducing agents.		In case of fire: keep cylinder cool by spraying with water.
EXPOSURE		Prevent dispersion of dust. Strict hygiene.	
-INHALATION	Burning sensation. Cough. Sore throat. Shortness of breath. Laboured breathing.	Avoid inhalation of dust. Local exhaust or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer for medical attention.
- SKIN	Redness. Skin burns. Pain	Protective gloves. Protective clothing.	First rinse skin with plenty of water, then remove contaminated clothes and rinse again. Refer for medical attention.
- EYES	Redness. Pain. Severe deep burns.	Face shield or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
- INGESTION	Burning sensation. Abdominal pain. Diarrhoea. Nausea. Vomiting. Shock or collapse.	Do not eat, drink, or smoke during work.	Rinse mouth. Give plenty of water to drink. Do not induce vomiting. Refer for medical attention.
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Sweep spilled substance into covered containers. Carefully collect remainder, and then remove to safe place. Do not absorb in saw-dust or other combustible absorbents. Personal protection: chemical protection suit including self-contained breathing apparatus. Do not let this chemical enter the environment.		Separated from combustible and reducing Substances, powdered metal. Well closed.	O symbol. Xn symbol. N symbol. R: 8-22-50/53. S: 2-60-61. Un Hazard Class: 5.1. Un Packing Group: II

Table A.11. Types of hazards and prevention of sulfuric acid.

SULFURIC ACID			
TYPES OF HAZARD / EXPOSURE	ACUTE HAZARDS / SYMPTOMS	PREVENTION	FIRST AID / FIRE FIGHTING
FIRE	Not combustible. Many reactions may cause fire or explosion. Gives off irritating or toxic fumes (or gases) in a fire.	No contact with flammable substances. No contact with combustibles.	No water. In case of fire in the surroundings: powder, foam, carbon dioxide.
EXPLOSION	Risk of fire and explosion on contact with bases(s), Combustible substances, oxidants, reducing agents or water.		In case of fire: keep drums, etc., cool by spraying with water but no direct contact with water.
EXPOSURE		Prevent generation of mists. Avoid all contact.	In all cases consult a doctor.
- INHALATION	Corrosive. Burning sensation. Sore throat. Cough. Laboured breathing. Shortness of breath.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Half-upright position. Artificial respiration may be needed. Refer for medical attention.
- SKIN	Corrosive. Redness. Pain. Blisters. Serious skin burns.	Protective gloves. Protective clothing.	Remove contaminated clothes. Rinse skin with plenty of water or shower. Refer for medical attention.
- EYES	Corrosive. Redness. Pain. Severe deep burns.	Face shield or eye protection in combination with breathing protection.	First rinse with plenty of water for several minutes (remove Contact lenses if easily possible), then take to a doctor.
- INGESTION	Corrosive. Abdominal pain. Burning sensation. Shock or collapse.	Do not eat, drink, or smoke during work.	Rinse mouth. Do not induce vomiting. Refer for medical attention.
SPILLAGE DISPOSAL		STORAGE	PACKAGING & LABELLING
Consult an expert. Evacuate danger area. Do not absorb in saw-dust or other combustible Absorbents. Personal protection: complete protective clothing including self-contained breathing apparatus. Do not let this chemical enter the environment.		Separated from combustible and reducing Substances, strong bases, food and feedstuffs, incompatible materials. May be stored in stainless steel containers. Store in an area having corrosion resistant concrete floor.	Unbreakable packaging; put breakable packaging into closed unbreakable container. Do not transport with food and feedstuffs. Note: B. C symbol. R: 35 S: 1/2-26-30-45 Un Hazard Class: 8; Un Packing Group: II

5. REFERENCES

- [1] AMERICAN INSTITUTE OF CHEMICAL ENGINEERS. 2015. *AICHE Chem-E-Car Competition™ 2015*. [Consulted: 21th April 2015]. Available in: http://www.aiche.org/sites/default/files/docs/pages/a_-_chem-e-car_official_rules_regionals_2015.pdf.
- [2] AMERICAN INSTITUTE OF CHEMICAL ENGINEERS. 2015. *Regional Chem-E-Car Safety Rules Spring 2015*. [Consulted: 21th April 2015]. Available in: http://www.aiche.org/sites/default/files/docs/pages/b_-_chem-e-car_safety_rules_regionals_2015.pdf.
- [3] WEISSERMEL, K.; ARPE, H. J. 1981. *Química orgánica industrial. Productos de partida e intermedios más importantes*. Capítulo 4, Acetileno.
- [4] CENTERS FOR DISEASE CONTROL AND PREVENTION. 2015. *International Chemical Safety Cards (ICSC)*. [Consulted: 20th April 2015] Available in: <http://www.cdc.gov/niosh/ipcs/icstart.html>
- [5] JOHN MCMURRY, 1994. *Química orgánica*. 5ª Ed.
- [6] YUEH-HUEY CHEN, JING-FUN YAUNG. 2002. Alka-Seltzer Fizzing-Determination of Percent by Mass of NaHCO_3 in Alka-Seltzer Tablets. An Undergraduate General Chemistry Experiment. *J. Chem. Educ.*, 2002, 79 (7), p 848
- [7] MARGARET J. STEFFEL, GEORGE VOLPE, J.T. MALOY. 1990. Reduction of Permanganate: A Kinetics Demonstration for General Chemistry. *Journal of Chemical Education*, Volume 67, Number 7, July 1990.
- [8] KRISZTIÁN A. KOVÁCS, PAL GRÓF, LÁSZLÓ BURAI, MIKLÓS RIEDEL. 2004. Revising the Mechanism of the Permanganate/Oxalate Reaction. *J.Phys. Chem. A* 2004, 108, 11026 – 11031.

- [9] GENE E. KALBUS, VAN T. LIEU, LEE H. KALBUS. 2004. A Spectrophotometric Study of the Permanganate-Oxalate Reaction. An Analytical Laboratory Experiment. *Journal of Chemical Education*, Vol. 81, No. 1, January 2004.
- [10] ALBERTO ROMERO LÓPEZ. Design of a Chem-E-Car prototype based on a chemical reaction. Final degree, July 2015.
- [11] JACK L. LAMBERT AND GARY T.FINA. Iodine Clock Reaction Mechanisms. Kansas State University, Manhattan, KS 66506. Volume 61, Number 12, December 1984.
- [12] JOHN A. CHURCH AND SANFORD A. DRESKIN, 1968.
- [13] ANDRE P. OLIVEIRA AND ROBERTO B. FARIA. 2005. The Chlorate-Iodine Clock Reaction. Instituto de Química, Universidade Federal do Rio de Janeiro, Caixa Postal 68563, Rio de Janeiro, RJ, 21945-970 Brazil (Received October 17, 2005).
- [14] STEPHEN W. WRIGHT, MARSHA R.FOLGER AND MATTHEW A.RICE. A Clock Reaction Sympathetic Ink from consumer Chemicals. Vol. 83, No. 10, October 2006, *Journal of Chemical Education*.
- [15] JUN YE, LONG SHENG MA, AND JOHN L. HALL. 2001. Molecular Iodine Clock. JILA, National Institute of Standards and Technology and University of Colorado, Department of Physics, University of Colorado, Boulder, Colorado 80309-044 (Received 15 June 2001; published 13 December 2001)