The Decomposition of Hydrogen Peroxide in Acidic Copper Sulfate Solutions

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A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfillment of the requirements for the degree of Master of Science in Engineering

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DECLARATION

I hereby declare that the work set out in this dissertation is the result of my own unaided work, and that it has not been submitted for another degree at any other university or institution.

Signed: …………………..  

Bongani Mlasi

Date:………………….. 2015
ABSTRACT

The effects of copper sulfate on the kinetics of the decomposition of hydrogen peroxide in a sulfuric acid solution were investigated. This was done by measuring the change in temperature as a function of time in a well-stirred batch reactor (vacuum flask) immersed in a temperature controlled water bath. The cooling curve when no reaction was taking place was used to determine the heat loss from the reactor. The temperature that was measured during reaction was then corrected to account for heat losses and this corrected temperature profile corresponds to that which would be found in an effectively adiabatic reactor. The corrected temperature is related to the extent of reaction and thus by following the corrected (adiabatic) temperature profile one can monitor the extent as a function of time.

It was found that at lower temperatures (below 58°C) the rate of reaction was too slow to measure in the equipment. The reaction rate was sufficiently fast so as to allow accurate measurements of temperatures when the initial temperature was increased to 67°C. Unlike what had been expected there was not a single reaction but an exothermic reaction followed by an endothermic reaction. It was shown that both the adiabatic temperature rise and fall were proportional to the amount of hydrogen peroxide added.

The amount of copper sulfate present in the solution affected the exothermic part of the rate of the decomposition of peroxide. However, the amount of copper sulfate had no effect on the rate of the endothermic reaction. A simple model that had an asymptote was chosen to model the effect of the copper sulfate on the rate of the exothermic reaction and it was shown to fit the results very well. A possible
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explanation for the exothermic reaction followed by the endothermic reaction was proposed.
DEDICATION

To the Mlasi family, my wife Mrs Stella Marope Mlasi and our son Siyeza Olaniyi Mlasi, and beloved friends in COMPS
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I would like to express gratitude to my supervisors, Professor Diane Hildebrandt and Professor David Glasser, for their motivation and guidance over the past two years. Their encouragement, advice, insight and creativity have been valuable. I am indebted to both of them for all their contributions to my studies and beyond.
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CHAPTER 1

1. Introduction

Chemical kinetics is one of the prerequisites for designing any production process that includes chemical reactions. This study of reaction kinetics is governed by the factors on which the rates of reaction depend, including the nature of the reactants (acidic or basic), the amount of the reactants involved (which is known as the concentration), the temperature of the system and pressure. The last of these, pressure, can play an important role if the reaction system concerned uses compressive mediums like gases (rather than liquids) or heterogeneous reactions.

In the metal recovery industries, kinetics are of vital use in processes involving heterogeneous reactions between the metal deposited in solid ore and a liquid lixiviate, resulting in dissolved metal and a by-product, normally an ionic salt. Such processes are energy- and resource-intensive, and thus are responsible for a significant portion of the costs of minerals processing plants. If the nature of the reactions involved in the process is not thoroughly understood, then most of the energy and materials required will be squandered. The important contribution kinetics studies can make is to provide the knowledge necessary to optimizing the process in question. This includes an understanding of the reaction mechanism, the nature of the reactants, and their relation to the final product.

1.1. Statement of the problem

Most of the mineral leaching processes in common use involve a process with a relatively slow reaction of several hours’ duration. One of the ways in which such processes can be improved (and made more rapid) is to use oxidizing agents. Of the
several types of oxidizing agent that have been considered for metal recovery, the most common are air, chlorine and hydrogen peroxide (Haiyu, Jingyang and Jiakuan 2011; Olubambi, Borode and Ndlovu 2006).

Most mineral recovery plants find hydrogen peroxide the most suitable oxidant because of its reaction products. It decomposes to water and oxygen, which makes it eco-friendly (Li and Sheng 2008). Because it is in liquid form it is easier to handle than oxygen/air, which is a cheaper oxidant than peroxide (Haiyu, Jingyang and Jiakuan 2011). However, it has certain disadvantages that limit its use: it is expensive, and it is not regenerable (Li and Sheng 2008), which implies that it cannot be reused.

1.2. Research objectives

Our interest in the reaction kinetics for decomposition of hydrogen peroxide in sulfuric acid solution with copper sulfate is the effects that the presence of copper sulfate imposes on the peroxide in this system. These effects are studied using temperature–time profile technique in an adiabatic batch reactor. The determination of an empirical model relating the effects of mass of copper sulfate to the rate of decomposition of hydrogen peroxide is also studied. The determination of this relationship might be more easily understood when a better understanding of the effect of temperature on the decomposition rate of peroxide and the contribution of excess of peroxide in the solution is attained. If determined such knowledge might have important consequences in the optimization of the use of peroxide in copper leaching processes where sulfuric acid system is utilized.
1.3. Structure of the dissertation

Chapter 2
In this chapter the writer provides an account of the discovery and significance of hydrogen peroxide. The literature on the decomposition of peroxide is reviewed, and particular attention is paid to description of the kinetic mechanism involved when the peroxide is exposed to a catalytic reaction.

Chapter 3
The chapter starts by introducing the published work on temperature–time measurements, and then sets out the equations derived from the batch reactor energy and mass balances and discusses the correction required to take into account the heat loss. The data is then corrected so that it is effectively models an adiabatic batch reactor. The writer compares and discusses concentration–time and temperature–time profiles for the various experimental conditions. The linear dependency of the log of temperature versus time for the cooling curve is explained, as is the estimation of the heat transfer coefficient of the system.

Chapter 4
This section describes the experimental apparatus and methods used, the procedures followed and the variables measured.

Chapter 5
In this chapter the results obtained from the experiments are presented, discussed and compared with the predictions arising from the theoretical analysis.
Chapter 6

The conclusions derived from the analysis in the previous chapter are presented in this chapter. The overall conclusion is based on the experimental findings and evaluation of the data imparted by previous researchers.
CHAPTER 2

2. Literature review

This chapter covers the discovery and manufacturing processes of hydrogen peroxide. It presents the history of the manufacturing processes and the drawback encountered in an attempt to advance those processes. The uses of peroxides are further explained, with its contribution to environmental effects. The decomposition of the peroxide is a function of its environment. This is significant in metal recovery.

2.1. The discovery and formation processes of hydrogen peroxide

Hydrogen peroxide was discovered in 1818 by a French chemist Louis Jacques Thenard. He used the reaction of barium peroxide with nitric acid to produce a low concentration of aqueous hydrogen peroxide (Strukul 1992). His process produced a 3% m/m solution of aqueous hydrogen peroxide. The production cost for this process was high, therefore there was only a limited market. This was one of the major disadvantages of its production. Later, in the year 1853, Meidinger discovered that hydrogen peroxide can be produced from an electrochemical process using aqueous sulfuric acid. The sulfuric acid in electrolysis was later replaced by ammonium sulfate. By 1924 the annual production as a 100% m/m of aqueous hydrogen peroxide had reached approximately $3.5 \times 10^6$ kilograms. Further research on the production processes of peroxide was conducted using different reactants, and with tests such as the use of hydroquinones or hydrazobenzenes in alkaline conditions (Jones 1999). Peroxide was produced from the treatment of hydroquinone with oxygen, and also from the hydrogenation of an anthroquinone in the presence of a catalyst. Another production process was the direct synthesis of hydrogen peroxide.
from H₂ and O₂ using a range of Au-Pd which was supported by alumina (Lunsford 2003; Solsona, et al. 2006; Yildiz and Akin 2007).

2.2. The uses of hydrogen peroxide

Hydrogen peroxide has been useful in various ways, from biological functions and domestic uses to therapeutic uses (Abdollahi and Hosseini 2014). Although the familiar use of peroxide for more than a century has been as a popular bleaching agent (Beeman and Reichert 1953), this study investigates its use as an oxidizing agent. This is due to the present industry focus on recovering metals.

2.2.1. The activation of hydrogen peroxide

In many applications the decomposition of hydrogen peroxide is an aided process because it is a relatively weak oxidant. Especially when used alone in a mild condition, it requires activation (Salem, El-Maazawi and Zaki 2000). The objective of this activation is to increase its reactivity by converting peroxide into a different, more active species (Strukul 1992).

One of the ways in which peroxide is activated is through radical decomposition. A clear description is shown in Fenton’s reagent. In this case the iron catalyzes the peroxides to generate a highly reactive species called hydroxyl radicals (OH⁻) (Schmidt, et al. 2011):

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^- + \text{OH}^- + \text{Fe}^{3+}
\]

(2.1)

In situ chemical oxidation (ISCO) is an increasingly popular technology for the treatment of contaminated soils. It is also based on this equation in which the highly reactive hydroxyl radical rapidly reacts with most contaminants of concern (Buxton,
et al. 1988; Haag and Yao 1992). ISCO includes catalyzed H$_2$O$_2$ propagation (CHP), which differs slightly from Fenton’s reagent. The peroxide is used in a relatively high concentration, together with alternative catalysts (e.g. iron (III), chelated iron, and naturally occurring iron and manganese minerals). Other reactive oxygen species are then generated through promotion of propagation reactions, namely, superoxide anion (O$_2^-$) and hydroperoxide anion (HO$_2^-$).

\[
H_2O_2 + OH \cdot \rightarrow HO_2 \cdot + H_2O \quad 2.2
\]

\[
H_2O_2 + Fe^{3+} \rightarrow HO_2 \cdot + H^+ + Fe^{2+} \quad 2.3
\]

\[
HO_2 \cdot \leftrightarrow O_2 \cdot^- + H^+ \quad pK_a = 4.8 \quad 2.4
\]

\[
HO_2 \cdot + Fe^{2+} \rightarrow Fe^{3+} + HO_2 \cdot^- \quad 2.5
\]

These oxygen species contribute to the CHP potential for rapid treatment of almost all biorefractory compounds. However, its disadvantage lies in the rapid decomposition of peroxide, which greatly reduces its effectiveness (Watts and Teel 2006).

The generation of metal peroxy or hydroperoxy species from the reaction of peroxide and metal is also the mode of activation for H$_2$O$_2$ (Strukul 1992). This reaction is essential to increase either the electrophilic or the nucleophilic character of the peroxygens. An appropriate reaction for the formation of hydroperoxyl species is found in the research investigating the decomposition of azo dye by the UV/H$_2$O$_2$ process (Chang, et al. 2010). Hydroxyl radicals that were generated by the UV irradiation according to Equation 2.6 are being consumed to form hydroperoxyl radical that has a lower oxidation capability, as shown in Equation 2.7.
\[ \text{H}_2\text{O}_2 \xrightarrow{hv} 2\text{OH} \cdot \]  
\[ \text{H}_2\text{O}_2 + \text{OH} \cdot \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O} \]

Thus the excess of peroxide favours the consumption of hydroxyl radicals and decreases the dye reaction rate.

Croiset, Rice and Hanush (1997) studied the kinetics of the decomposition of hydrogen peroxide in supercritical water. In their research they used supercritical water oxidation (SCWO). This is a promising alternative technology for destroying hazardous waste using the hydrothermal oxidation process. The technology is made possible by the fact that above a critical point (at 374°C and 22.1MPa) water causes organic compounds (e.g. H₂O₂) to oxidize rapidly in a single phase. However, this supercritical water experiment consumes a lot of energy in order to attain the high temperatures required.

2.3. The metal recovering processes

In the process of recovering metals several methods have been found to be appropriate and have been thoroughly investigated. The methods include mechanical processes, pyrometallurgy and hydrometallurgy. Mechanical/physical processes are familiar separation methods in the recycling industry though they cause dust emission and noise pollution, and require tremendous energy usage (Li and Sheng 2008). Most importantly, the use of this method has never recovered high purity metals. Pyrometallurgy uses high temperature combustion to get the high temperatures required and, thus leads to serious air pollution. Also, due to the smelters, like for copper, being located in remote areas away from urban centres, the cost of the operation rises tremendously from energy consumption and transportation of feedstock (Oishi, et al. 2007). Hydrometallurgy is a process in which metal
contents are dissolved into leachants such as acids or alkalis (Olubambi and Potgieter 2009). This process has potentially lower costs and can be operated economically even on a small scale (Li and Sheng 2008). Due to the flexibility, simplicity of operations and energy saving, hydrometallurgical processing has become a substantial aspect of the metal recovery industries.

Notwithstanding these positive features in hydrometallurgy, there have been drawbacks in the operations of this process. These problems include low recovery of extracted metal and difficulties in separating solids from liquids; in addition, the ease of purification is affected by impurities (Olubambi and Potgieter 2009). The problem with for instance a sulfide ore in hydrometallurgical processing is its low solubility in many leaching solutions. In principle it was essential to simplify the dissolution of the constituent metal and an appropriate leachant needed to be selected for the recovery of the targeted metal.

In assessing the dissolution capacity of a leaching reagent, the primary criteria for making this selection are the cost and the effects that such a medium might have on the environment. Previously, in the processes of copper leaching, several reagents have been studied for their effectiveness in recovering this base metal. These reagents included the following. Halogen salts of chlorides and bromides were studied by Stanley and Subramanian (1977). Frankiewicz and Lueders (1979) researched using nitrogen dioxide and chlorine gas-saturated water was studied by Ekinci, et al. (1998). All of these solutions were used to recover copper from a chalcopyrite ore. However, these reagents are relatively slow in the rate of recovering copper metal. They are also used in the removal of other available metals such as zinc and iron. In 1998 the effectiveness of sulfuric acid compared with hydrochloric acid, nitric acid, ferric chloride and ferrous sulfate was reviewed by Prasad & Pandey (1998). In this study, nitric acid and hydrochloric acid were
the most effective. However, both nitric acid and hydrochloric acid cause corrosion. Therefore corrosion resistant equipment is required, but it is expensive.

Sulfuric acid is not as effective as other stronger oxidizing acids like nitric acid (Copur 2001; Copur 2002; Prasad and Pandey 1998). However, it is preferred to all other reagents in terms of cost, corrosion wear and the ease of regeneration during electro winning (Biswas and Davenport 1980). Besides, sulfuric acid is easily available and is a relatively cheap reagent for base metal recovery (Antonijevic and Bogdanovic 2004). Therefore optimization of sulfuric acid for a better recovery in leaching metals had to be considered.

2.3.1. Hydrogen peroxide in a sulfuric acid system for metal recovery

In assisting or optimizing the dissolution kinetics of sulfuric acid solution, hydrogen peroxide became very useful. This is because peroxide is a strong oxidizing agent that promotes the oxidation and leaching potential of the sulfuric acid system (Olubambi, Borode and Ndlovu 2006). The leaching of ores/metals using sulfuric acid in conjunction with hydrogen peroxide has been studied and successful results were obtained. The dissolution kinetics of manganese-silver associated ores in the solution of $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}_2$ were studied, and the recovery of silver was increased by the presence of hydrogen peroxide (Tao, et al. 2002). In addition silver leaching was noted as diffusion controlled with the kinetic model: 

$$1-2x/3-(1-x)^{2/3}=kt$$

($x$ is the mole fraction, $t$ is the time (min), and $k$ is a mass transfer coefficient). The kinetics of the dissolution of chalcopyrite by hydrogen peroxide in sulfuric acid was researched by Antonijevic, Dimitrijevic and Jankovic (1997). The presence of hydrogen peroxide with sulfuric acid again showed a significant increase in the amount of copper recovered.
Olubambi, Borode and Ndlovu (2006) also using the sulfuric and hydrogen peroxide system, investigated the effectiveness of hydrogen peroxide as an oxidant. Their research was on the leaching of zinc and copper from a Nigerian bulk sulfide ore. In this case they observed that the leaching rate of zinc and copper increased with an increase in hydrogen peroxide concentration. The dissolution kinetics of chalcopyrite in sulfuric acid and hydrogen peroxide were also investigated by Adebayo, Impinmoroti and Ajayi (2003). They found that the increase in stirring speed attributed to the faster decomposition of hydrogen peroxide. They speculated that the molecular oxygen evolved is adsorbed onto the surface of the chalcopyrite particles, and this hinders the contact between the particles and the hydrogen peroxide solution.

2.3.2 Copper ions in a leaching solution of hydrogen peroxide and sulfuric acid

The leaching solution for copper metal recovery, using a sulfuric acid and hydrogen peroxide system results in copper ions in solution with the remaining hydrogen peroxide in diluted sulfuric acid. It is important to find out the nature of the processes which take place in the remaining solution. There have been several research studies on some combinations of this solution.

In the late 1960s Grant, Harwood and Wells (1968) reported that copper (Cu^{2+}) in solution contributes to the decomposition of hydrogen peroxide. That proceeds by a combination of a molecular mechanism comprising the formation of free radicals like HO\textsubscript{2} and OH. Sigel, Flierl and Griesser (1969) confirmed the catalytic activity of Cu\textsuperscript{2+} on hydrogen peroxide decomposition. They add that the activity of the catalyst is a function of the concentration of the ligand of the copper ions. Their justification lies in the activity of Cu^{2+}-2', 2'-bipyridyl and Cu^{2+}-2', 6', 2''terpyridyl.
The kinetics and mechanism of the catalysis of the reaction between hydrogen peroxide and hydrazine or hydroxylamine, by Cu$^{2+}$ and Cu$^{2+}$-2, and 2'-bipyridyl complex, were also studied (Erlenmeyer, Flierl and Sigel 1969). This system was represented by Equation 2.2 below:

$$2\text{H}_2\text{O}_2 + \text{NH}_2\text{NH}_2 \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$$  \hspace{1cm} 2.2

In this case it was discovered that in the decomposition of peroxide in the presence of copper ion without a ligand, a precipitate was formed; the experiment was therefore rendered difficult. However, the kinetics of the system was derived from the proportionality of the initial velocity of the decreasing concentration of H$_2$O$_2$ to the concentration of H$^+$ in the reaction between H$_2$O$_2$ and NH$_3$OH. In Figure 2.1 the plots show the results in which the concentration of copper ion (Cu$^{2+}$) was varied at constant concentration of H$_2$O$_2$ and NH$_3$OH$^+$ (8X10$^{-4}$ M each):
Figure 2.1: (a) is the graph of Cu\textsuperscript{2+}-NH\textsubscript{3}OH-H\textsubscript{2}O\textsubscript{2} system at constant initial concentration of H\textsubscript{2}O\textsubscript{2} and NH\textsubscript{3}OH\textsuperscript{+} with the concentration of Cu\textsuperscript{2+} varied, as a function of pH (Erlenmeyer, Flierl and Sigel 1969); (b) is the evaluation of Figure 2.1.(a) at pH of 4.5.

Onuchukwu (1984) used copper and nickel ferrites to study the heterogeneous catalytic decomposition of hydrogen peroxide. The findings revealed that under the same experimental conditions the activity of copper superseded that of the nickel catalyst. This shows that copper is a better catalyst in decomposing peroxide than nickel. Furthermore the decomposition of peroxide in potassium hydroxide (KOH) obeyed the first order rate equation with respect to total hydrogen peroxide content; such a trend concurred with several reports of previous authors for peroxide decomposition in an alkaline media.

The catalytic action of copper (II) on the hydrogen peroxide decomposition which is in near neutrality aqueous solution is activated by halide ions (Perez-Benito 2001). Though the effect of fluorine (F\textsuperscript{-}) ion could only be studied at relatively low
concentrations (up to 0.360M), its increase in concentration contributes to an increase in pH. This is caused by the formation of HF, which is a weaker acid than the other hydrogen halides. Thus the activation effect of the halide ions was found to follow this sequence: Cl>F>Br. KCl was more efficient as activator of the catalyst while KBr had an inhibiting effect. However, I\(^-\) yielded a precipitate Cu\(_2\)I\(_2\) when reacting with Cu (II) which affects the homogeneity of the solution.

Figure 2.2 shows the effect of the increment of Cu (II) on the decomposition of peroxide in the presence of the solution constituents. The inset graph displayed the effect of Cu (II) on the rate constant. It is worth noting that at \([\text{Cu (II)}]=0\text{M}\), the graph has a zero coordinate, which implies that copper ion is the driving force behind the decomposition of hydrogen peroxide.
The Decomposition of Hydrogen Peroxide in acidic Copper Sulfate Solutions

Figure 2.2: The plot of the dependence of the initial rate on the concentration of copper sulfate (Perez-Benito 2001); main figure: $[\text{H}_2\text{O}_2]_0=0.196$ (empty circles) M and 0.392 (filled circles and triangles) M, $[\text{KHPO}_4]=1.20$ (triangles) and 6.00 (empty and filled circles) $\times 10^{-2}$ M, pH=6.31 (triangles) and 6.7 (empty and filled circles), $[\text{KNO}_3]=0$ (empty and filled circles) and 1.80 (triangles) M, at temperature of 25°C; inset: initial rate in $10^{-7}$ circles, $[\text{KNO}_3]=2.64$ M at $[\text{H}_2\text{O}_2]_0=0.392$ M, $[\text{KH}_2\text{PO}_4]=[\text{K}_2\text{HPO}_3]=1.20\times 10^{-2}$ M, pH=6.16 (circles) and 6.26 (triangles) also at 25°C.

2.3.3 The reaction kinetics for Hydrogen peroxide decomposition in a sulfuric acid system

The reaction kinetics for hydrogen peroxide decomposition has been studied for a long time especially with respect to catalytic decomposition using transition metals (Haber and Weiss 1934; Sigel, Flierl and Griesser 1969; Kanungo, Parida and Sant 1981; Borrull and Cerda 1987; Strukul 1992). Due to the increasing interest in the use of hydrogen peroxide as an oxidant for specific organic transformations, it
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seems suitable to review the research based on transition metal catalyzed oxidation especially with copper which is the metal of interest for this research. Nevertheless, what is significant is the researchers’ findings, the procedures which were followed in studying the kinetics and the relevance of their findings relevant to our research studies.

In the study of the kinetics of hydrogen peroxide decomposition the measuring of the initial velocity, $v_o$, of the decreasing concentration of $\text{H}_2\text{O}_2$ with temperature at 25°C was used (Erlenmeyer, Flierl and Sigel 1969; Sigel, Flierl and Griesser 1969). Kanungo, Parida and Sant (1981) similarly studied the kinetics of peroxide; however, they considered the oxygen liberated as the $\text{H}_2\text{O}_2$ decomposed at various temperatures (20°C - 40°C). Borrull and Cerda (1987) used temperature–time profiles while Jiang et al. (2002) and Choudhary and Gaikwad (2003) considered the relationship between the rate of reaction and the concentration of the reactants at various temperatures 8°C-40°C and 30°C -60°C respectively.

So far the kinetics of sulfuric acid and peroxide system had been studied relating their concentrations with the rate of the reacting metal (Antonijevic and Bogdanovic 2004). Also the effect of copper ions in solution had been shown by previous researchers to promote catalytic decomposition. Furthermore, peroxide had been recommended in the metal recovery industries rather than other oxidants.

However, in the previous research findings a gap remained unfilled as far as the leaching of metal using peroxide is concerned, which prompted the current research. First of all, though the sulfuric acid system had been examined, the effect of the copper concentration on the peroxide decomposition was still to be investigated. This was because the report on the effects of copper ions on the
peroxide was based on a different system and no thorough research had been done. The present research looks at the effect of copper in solution on the hydrogen peroxide decomposition.
CHAPTER 3

3. The description of the temperature–time technique

This chapter provides a contextual background on the use of temperature–time profiles for kinetic analysis of chemical reaction processes. It explains the theory behind the analysis of the measured temperature versus time profiles, and sets out the relevant equations derived from the mass and energy balances in a batch reactor system. It also explains the writer’s reasons for choosing to use this method. The measured temperature–time profiles were corrected for heat loss so as to predict the effective temperature vs time curves that would have been measured if the reactor was adiabatic. This allows us to relate the corrected adiabatic temperature to the reaction conversion which allows us to determine the reaction kinetics.

3.1. Adiabatic batch reactor measurement

Although continuous (flow) reactors are dominant in the chemical industry (Schmidt 1998), a batch reactor is preferable for experiments undertaken at the laboratory scale. It is worth noting that the equations describing batch and plug flow tubular reactors are very similar (Schmidt 1998). Previous researchers (Hartridge and Roughton 1924) utilized temperature profiles for an improved apparatus for measuring the velocity of very rapid chemical reactions. To enhance their understanding of this apparatus, they also used the neutralization of sodium hydroxide and monitored the time it takes to reach completion (calling it the theoretical temperature rise). However, a flow reactor has been generally used for fast reactions (La Mer and Read 1930).
Dyne, Glasser and King (1967) studied reaction rates using an automatically controlled adiabatic reactor using temperature-time measurements. In this experiment, the wall temperature was maintained at the same level as that of the mixture in the reactor by means of a direct heating current, thereby making the reactor effectively adiabatic.

In the study of homogeneous liquid phase kinetics, also carried out in a batch reactor, Glasser and Williams (1971) considered temperature as a variable against time. In this case, the kinetic parameters were obtained by means of regression analysis, using the corrected experimental temperature–time curve. It is worth noting that regression analysis is appropriate when the concentration of the contents and the temperature are varied simultaneously, and therefore can be expressed by the differential equation 3.1 (Scott, Glasser and Nicol 1975).

\[
\Delta H_{rxn} \frac{dx}{dt} = UA(T - T_s) + MC_P \frac{dT}{dt} - Q
\]

where:

\(\Delta H_{rxn}\) is the heat of reaction

\(x\) is the extent of reaction

\(M\) is the total mass of the reactor and its contents

\(C_P\) is the heat capacity of the reactor and the contents

\(Q\) is the rate of heat generated by the mechanical stirrer

\(U\) is the heat transfer coefficient between the contents of reactor and the surroundings

\(T\) is the temperature of the contents of the reactor
is the temperature of the surroundings; and

\(A\) is the external area of the reactor, corresponding to the surface through which heat transfer between the reactor and the surroundings occurs.

In order to ensure that the heat loss to the surroundings could be controlled and modelled, the reactor was placed in a constant temperature bath so that the temperature of the surroundings was constant.

The technique developed by Glasser and Williams (1971) for the estimation of the rate of reaction for a homogeneous reaction is known as the classical method. In this research the temperature of the walls of the reactor was automatically controlled in order to keep the temperature of the walls the same as that of the contents. Most importantly, the classical method enabled the temperature–time curve to be converted directly into concentration versus time data. The data can therefore be analyzed to determine reaction kinetics. Notwithstanding, there was discrepancy at higher temperature, which they presumed was attributable to their having halted the reaction from time to time to take samples for concentration measurement. This might have diminished the accuracy obtainable by the classical method.

3.2. Mathematical Analysis of Adiabatic batch system

Heat is released (or absorbed) when a reaction occurs, and this leads to an increase (decrease) in temperature in an adiabatic reactor. The differential equation appropriate to such curves is derived from the combination of the mass and energy balance for the reaction and the following assumptions:

The law of mass and energy conservation
The Arrhenius equation described the temperature dependence of reaction rates;
that the heat change is almost entirely attributable to a single reaction;
that the heat of reaction is not a function of temperature; and
the specific heat of the system is independent of temperature and composition of the reacting mixture.

The equation of the mass balance can be related to that of the energy balance. There is proportionality between the temperature of the single reaction and its extent of reaction. This results in a differential equation in terms of temperature–time variations for an adiabatic system. This is shown in section 3.3 below.

3.3. The energy balance equation for adiabatic batch reactor

In this section, the derivation of the equation produced from energy and mass balance, which relates the kinetics and thermodynamic parameters of a reaction, is set out. The relationship between reaction kinetics and the temperature of the reacting constituents is explicitly defined.

A batch reactor that is perfectly mixed, meaning that the concentration of the reacting constituents is spatially uniform (Fogler 1999), has the molar balance in terms of the concentration of the reactant:

\[-r_A = - \frac{1}{V} \frac{dN_A}{dt} = - \frac{dC_A}{dt} \]  

(3.2.)

where \(-r_A\) is the rate of formation of species A

V is the volume of the reacting solution
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\( N_A \) is the moles of A in the reacting solution

\( t \) is time

\( C_A \) is the concentration of reactant A in the solution.

The energy balance around a reactor can be clearly expressed through the consideration of these terms:

- the energy produced by the reactants;
- the energy generated by the mechanical stirrer in mixing the solution;
- the absorbed energy by the reactor contents;
- the energy due to heat transfer to the surrounding through the reactor walls.

Thus for a small time interval the mathematical equation relates the energy generated with that absorbed and released for a steady state process according to Equation 3.3:

\[
(-\Delta H_{rxn})(-r_A)V dt + Q_s dt = MC_p dT + UA(\Delta T)dt
\]  \hspace{1cm} (3.3)

Shatynski and Hanesian (1993) considered the heat due to stirring in Equation 3.3 \((Q_s dt)\) to be negligible, and this is the assumption considered in this investigation since according to them compared to the other terms of Equation 3.3, it is relatively small. The remaining equation becomes:

\[
(-\Delta H_{rxn})(-r_A)V dt = MC_p dT + UA(\Delta T)dt
\]  \hspace{1cm} (3.4)

since also in terms of extent of reaction the rate equation can be written thus:

\[
(-r_A)V = \frac{d\epsilon}{dt} = \text{rate of reaction}
\]  \hspace{1cm} (3.5)

In this case \( \epsilon \) is the extent of reaction.

Therefore Equation 3.5 is substituted into Equation 3.4 to yield Equation 3.6:
\[ (-\Delta H_{\text{rxn}}) \frac{d\varepsilon}{dt} dt = MC_p \ dT + UA(\Delta T) dt \] (3.6)

The boundary conditions for integrating Equation 3.6 are:

\[ t = 0, T = T_0 \text{ and } \varepsilon = \varepsilon_o, \text{ if } t \to t, T \to T_{\infty} \text{ and } \varepsilon \to \varepsilon. \]

Thus integrating Equation 3.6 with boundary condition leads to Equation 3.7

\[ (-\Delta H_{\text{rxn}}) \int_{\varepsilon_0}^{\varepsilon} d\varepsilon = MC_p \int_{T_0}^{T} dT + UA \int_{0}^{t} (T - T_S) dt \] (3.7)

Note that \( \Delta T = T - T_S \), is the difference in the temperature of the reactor contents (T) from the surrounding water bath temperature (T_S). This tends to zero as t tends to infinity after the overall heat transfer between the reactor contents and the surroundings is complete.

Equation 3.7 as t tends to infinity can be rearranged to give Equation (3.8) below.

Note also that \((\Delta \varepsilon = \varepsilon - \varepsilon_0)\)

\[ (T - T_o) + \frac{UA}{MC_p} \int_{0}^{\infty} (T - T_S) dt = \frac{(-\Delta H_{\text{rxn}})}{MC_p} \Delta \varepsilon \] (3.8)

Thus if we have a value of \( \frac{UA}{MC_p} \) we can correct the temperature-time curve to get information on the extent of reaction.
3.4. Determination of the heat transfer coefficient

Consider Equation 3.4 above in which there is no reaction occurring, that simply means that the heat generated by the reaction mechanism is equal to zero \((-\Delta H_{\text{rxn}})(-r_A)V\,dt = 0\). Therefore the resulting equation becomes:

\[ MC_p \, dT + UA(\Delta T)\,dt = 0 \]

\[ \text{(3.9)} \]

Consider the boundary conditions:

t=0, T=T_0 and when t→t, T=T

\[ \int_{T_0}^{T} \frac{dT}{T-T_S} = -\frac{UA}{MC_p} \int_{0}^{t} dt \]

\[ \text{(3.10)} \]

Integrating Equation 3.10 gives:

\[ \ln(T - T_S) - \ln(T_0 - T_S) = -\frac{UA}{MC_p} \cdot t \]

\[ \text{(3.11)} \]

Rearranging Equation 3.11 produces Equation 3.12

\[ \ln \left( \frac{T-T_S}{T_0-T_S} \right) = -\frac{UA}{MC_p} \cdot t \]

\[ \text{(3.12)} \]

This can be used to estimate the heat transfer coefficient \(\frac{UA}{MC_p}\)

3.5. Analysis of the nature of the order of the reaction

An adiabatic batch reactor with constant volume has an energy balance equation according to Equation 3.13

Boundary conditions: t=0, T=T_0 and t=t, T=T^{ad}
The Decomposition of Hydrogen Peroxide in acidic Copper Sulfate Solutions

\[ \text{MC}_p \frac{dT^{ad}}{dt} = (-\Delta H_{Rxn})(-r_A V) \quad (3.13) \]

For a perfectly insulated batch reactor no heat loss occurs and \((T^{ad})\) is the difference between the temperature in the adiabatic reactor at time \(t\) and the temperature in the reactor initially.

For a constant volume reaction, the rate equation in terms of concentration is written in this way (see Equation 3.2):

\[ r_A = \frac{dC_A}{dt} \quad (3.14) \]

Note that \(A\) represents a reactant, thus \(C_A\) is the concentration of \(A\) and \(r_A\) the rate of formation of \(A\). Now substituting equation 3.14 in 3.13 leads to Equation 3.15 below:

\[ \frac{MC_p d(T^{ad})}{dt} = \frac{\Delta H_{Rxn} V dC_A}{dt} \quad (3.15) \]

Now rearranging Equation 3.15 gives Equation 3.16:

\[ \frac{d(T^{ad})}{dC_A} = \frac{\Delta H_{Rxn} V}{MC_p} \quad (3.16) \]

To integrate Equation 3.16 the boundary condition should be specified.

Boundary conditions: at \(t=0\), \(T(0) = T_0\) and \(C_A(0) = C_{A0}\); at \(t=t\), \(T(t) = T^{ad}\) \(C_A(t) = C_A\)

\[ \int_{T_0}^{T^{ad}} \frac{d(T^{ad})}{dC_A} = \frac{\Delta H_{Rxn} V}{MC_p} \int_{C_{A0}}^{C_A} dC_A \quad (3.17) \]

Therefore Equation 3.17 gives Equation 3.18:
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\[ \Delta T^{ad} = T^{ad} - T_0 = \frac{\Delta H_{\text{Rxn}} V}{MCP} (C_A - C_{AO}) \]  \hspace{1cm} (3.18)

if we assume that the rate equation is first order and the change in temperature is fairly small so that we can assume isothermal conditions so that the rate constant remain constant since it is a function of temperature, we can write:

\[ C_A = C_{Ao} \exp(-kt) \]  \hspace{1cm} (3.19)

The combination of Equation 3.19 and 3.18 results in Equation 3.20

\[ T^{ad} - T_0 = \left( \frac{(C_{Ao} - C_{AO} \exp[-kt]) \Delta H_{\text{Rxn}} V}{MCP} \right) \]  \hspace{1cm} (3.20)

If we consider the steady state solution, i.e. as \( t \to \infty \) where \( T^{ad} \to T^{\infty} \):

\[ T^{\infty} = T_0 - \frac{\Delta H_{\text{Rxn}} V}{MCP} C_{Ao} \]  \hspace{1cm} (3.21)

Then the combination of Equations 3.20 and 3.21 gives:

\[ T^{\infty} - T^{ad} = \frac{\Delta H_{\text{Rxn}} V}{MCP} C_{Ao} \exp[-kt] \]  \hspace{1cm} (3.22)

Rearranging Equation 3.22 leads to Equation 3.23 thus a plot of \( \ln(T^{\infty} - T^{ad}) \) versus time \( t \) will give a straight line with slope \( k \). This slope is considered to be the estimated rate constant for the reaction in question.

\[ \ln(T^{\infty} - T^{ad}) = \ln \left( \frac{\Delta H_{\text{Rxn}} V C_{Ao}}{MCP} \right) - kt \]  \hspace{1cm} (3.23)
CHAPTER 4

4. Experimental section

This chapter outlines the mode in which experimental data was brought together and also explains the apparatus that was used to perform the experiments. The focus of these experiments was on the hydrogen peroxide decomposing in copper leaching solution. According to the display of Equation 4.1 (Khandpur 2005) the dissolution of copper in sulfuric acid solution, with peroxide as an oxidant, yields a metal salt called copper sulfate, and water:

\[
\text{Cu} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{CuSO}_4 + 2\text{H}_2\text{O}
\]

In order to maintain a high reaction rate most industrial processes normally run with an excess of the reagent. Because of this excess of reactant/s, the final solution can still contain unreacted reagents. Thus these experiments were performed with an excess of the reagents in the solution. The solution prepared comprised dissolved copper sulfate and hydrogen peroxide in dilute sulfuric acid. The schematic diagram of the tasks performed in sequence is shown in Figure 4.1.

---

**Figure 4.1:** The summarised flowchart of the experimental procedure.
4.1. Sample preparation

4.1.1. Copper sulfate sample
Copper sulfate is a chemical compound which is found in blue crystallized (CuSO$_4$.5H$_2$O) form. To use it in homogeneous reactions, different amounts of copper sulfate were weighed, i.e. 5g, 8g, 11g 15g and 20g, and dissolved them in distilled water, with a total volume of 100ml of the solution for each sample. This is later mixed with diluted sulfuric acid.

4.1.2. Sulfuric acid sample
Sulfuric acid comes in a 98% concentration, and the following amounts were measured out: 0ml, 5ml (0.353M), 15ml (1.05M), 20ml (1.41M) and 30ml (2.12M). Each sample was then diluted in distilled water to obtain a total volume of 250ml of solution. These prepared samples were then mixed with the copper sulfate solution. Each mixed sample was then placed on a hot plate. The temperature of the solution was increased to 50°C, 65°C, 70°C and 75°C before hydrogen peroxide was added.

4.1.3. Water bath used for surrounding temperature
The samples were put in a reactor vessel, which was immersed in a bath of water that was maintained at a constant temperature of 30°C. This was to keep the temperature surrounding the reactor the same throughout the experiments. The temperature of the water bath was monitored by a temperature controller to ensure that the temperature could not rise above or fall below the set point.
4.1.4. Addition of hydrogen peroxide

In all the experiments performed, the hydrogen peroxide used was 30% in concentration. Peroxide was injected at room temperature into the reactor by means of a syringe with a volume of 50ml. The amounts injected were 0ml, 5ml, 15ml, 20ml and 30ml, depending on the experiment.

The details of the solution components used are summarized in Table 4.1 below. In this case the molarity of each component is included.

Table 4.1: The concentration and the amounts of the components that were used for the experiments

<table>
<thead>
<tr>
<th>grams in 250ml</th>
<th>Copper sulfate</th>
<th>Hydrogen peroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MW</td>
<td>Conc%</td>
</tr>
<tr>
<td>250</td>
<td>100</td>
<td>moles</td>
</tr>
<tr>
<td>moles</td>
<td>moles/l</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>32</td>
<td>128</td>
</tr>
<tr>
<td>11</td>
<td>44</td>
<td>176</td>
</tr>
<tr>
<td>15</td>
<td>60</td>
<td>240</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>320</td>
</tr>
</tbody>
</table>
4.2. Reaction mechanism

4.2.1. The Reaction Vessel

The reaction vessel used was a 500ml thermos flask with a removable cap lid made of expanded polystyrene to minimize heat losses. The lid was pierced to make two holes small enough to allow a probe and syringe to be passed through. Stirring was carried out in the flask by means of a magnetic stirrer. Figure 4.2 is a photograph of the flask used.

A heated solution of sulfuric acid and copper sulfate was poured into the reaction vessel, and a temperature probe was inserted through the lid. The temperature recorded by the probe was displayed on the computer monitor. The temperature in the reaction vessel was allowed to stabilize prior to the addition of peroxide. Hydrogen peroxide was then slowly injected through the second hole to avoid the formation of bubbles inside the reactor.
The hydrogen peroxide was introduced at room temperature. The temperature of the solution in the reactor dropped relative to the amount of the oxidant used. The nature of the reaction that follows determines the resultant temperature of the solution: an exothermic reaction has a positive temperature gradient, while an endothermic reaction has a negative gradient. The pH of the solution was not considered an important parameter in these experiments.

4.3. Temperature profile

4.3.1. The thermocouple sensitivity
Sulfuric acid is a very strong acid which reacts with most metals. Since the thermocouple (type K) used is chromel/alumel (metallic) (Wang 1990), it is sheathed in a blown glass container to act as an insulator against the acidity of the solution. However, as the air surrounding the thermocouple inside the glass reduces the sensitivity of the thermocouple, a small amount of water was poured into the glass to increase the contact surface between the glass and the thermocouple. This insulation sheath caused a delay in the measurement by the thermocouple when it was inserted into the medium.

The thermocouple was immersed in two media, each of a different temperature, in order to measure the delay of the response. In the first instance, this device was immersed in tap water at 20°C. After three minutes it was removed and immediately afterwards plunged into a mixture of water and crushed ice at a temperature of 0°C. The temperature detected by the probe dropped from 20°C to -0.008°C in just under four minutes, as shown in Figure 4.3. The Figure shows that the probe took approximately 20 seconds to read the temperature of the new medium, it follows that
any reaction that occurs within less than 20 seconds will not be accurately read by the thermocouple sensor. As the reaction examined in this research project lasted for almost 50 minutes, this probe was appropriate for measuring the temperature change during the reaction.

![Graph showing temperature change over time](image)

Figure 4.3: The rate at which the probe responds when immersed in two solutions of different temperatures.

### 4.3.2. Thermocouple calibration

A calibrated, certified mercury thermometer was used to calibrate the thermocouple. A range of temperature from 0°C to 81°C was used for this purpose. Both thermometer and thermocouple were immersed in water at different temperatures, and the temperature readings of each were recorded. Figure 4.4 plots these results so that the readings from each can be compared. For example, when the thermometer recorded 0°C the thermocouple read ~2°C.
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Figure 4.4: The graphical presentation of the temperature obtained from thermocouple and thermometer.

The two probes plot shows a linear relationship thus equation 4.1 is derived from this plot in which the thermometer temperature is expressed in terms of the thermocouple:

$$T_C = (T_t) + 2 \quad 4.1$$

where $T_C$ is the corrected temperature equivalent to the thermometer reading and $T_t$ is the temperature recorded by the thermocouple.

4.4. Data analysis

In this section an appropriate simple model was chosen (one that could in principle give a curve of the shape of the experimental results) and the constants in the model found by non-linear regression. In order to evaluate the proposed model certain aspects had to be considered such as the coefficient of determination ($R^2$),
confidence interval and error bars to know how scientifically plausible values the best fit values are.

4.4.1. Coefficient of determination (R²)

By definition the coefficient of determination (R²) is considered as the amount of the variation in the dependent variable that is explained by the regression line in terms of the predictor variable (Katubilwa 2012). This in short is used to quantify the goodness of the proposed model to the experimental data fit. As the rule of thumb a value of R² ≥ 0.99 is recommended for a fit to be very good. Nonetheless a value of R² ≥ 0.95 is considered as a standard value that can be accepted by statisticians worldwide (Palm 2001). Though the coefficient of determination (R²) describes the goodness of fit of the curve to practical data, this does not determine the accuracy of the estimated parameters.

4.4.2. Confidence intervals of parameters

The point of regression is basically to find a best fit between the model and the experimental results using parameters in the model. However, one of the other key factors to draw a plausible scientific conclusion is the precision of the values of the parameters. For this to be achieved one introduces confidence interval.

Laboratory gathered data is subject to change every time a new experiment is performed; this is due to the environmental factors surrounding such an investigation. It is therefore essential to define best-fit parameters and an estimate of their confidence interval to allow one to take the variability inherent to the measurements into account in the regression (Motulsky and Christopoulos 2003).
The concept of variability in experimentally collected data is best handled by use of a confidence level. It is recommended that a 95% confidence level serves as a good balance between precision and reliability of the estimate relative to the experimental data. This means that every time a non-linear regression is performed the probability of getting the true value within the confidence level is 95% of the time; however, once in twenty times the true value may not be included within the confidence level.

A confidence band is normally also used in curve fitting. This is considered to be the enclosed region in which the true values lie with a certain probability. In a region in which the confidence band is considered to be 95% it simply implies that the chances of not finding the best fit values in that region is 5% (Motulsky and Christopoulos 2003). In other words, 95% of the time in that region, one will find the combination of the best fit values.

4.4.3. Error bars

The error bar normally highlights how accurate the experimental data is. It focuses on the reproducibility of the experimental data. This concept operates almost like the confidence band since it also uses regions in which the reproducibility of the data point lies would one want to repeat the experiment under the same conditions. The reproducible region is represented by bars on each coordinate. This is because the dependent variable is a function of external effects rather than the independent variable. The longer the bar around the point the larger is the region of uncertainty.
This plotting is done using the plotting capabilities of the Curve Fitting Toolbox of MATLAB. The confidence band considered is 95% and the variability of the best fit parameters is assessed.
CHAPTER 5

5. Results and discussion

5.1. Introduction

This chapter presents the results obtained from the temperature measurements of the homogeneous liquid phase reactions using temperature–time measurements in vacuum flasks. The pure water cooling curve experiments were done to provide reference curves that are used to compare with reaction processes to help to specify their reactivity. Thus for instance if the long time linearized curve (logarithm of the temperature difference from the bath temperature versus time, Eq 3.12) of the reacting process lies parallel to that of the cooling water curve, one can infer that the reaction was effectively complete by then; if it is not parallel then some reaction is still in progress.

The heat transfer coefficient per the effective specific heat of the system $\frac{UA}{MC_p}$ for the apparatus was estimated from the long time linear plot as described above, then later used to compensate for the heat lost in order to produce an approximate adiabatic curve. The reaction experiments were done at different initial temperatures and with different concentrations of constituents. Thus sufficient information was obtained to propose an explanation of what was occurring. A cooling curve was measured for each experiment under the assumption that the reaction was complete. As mentioned above, this could be compared with the pure water curve, to test whether the assumption that the reaction was effectively complete was valid.
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The choice of copper sulfate was motivated by the fact that it is the metal salt produced during the copper leaching processes in the presence of sulfuric acid and hydrogen peroxide. Because hydrogen peroxide is an expensive chemical, it is useful to know its rate of decomposition under different conditions so as to be able to minimize its use in copper leaching.

The batch reactor was a vacuum flask to minimize the heat lost to the surroundings so that the correction to effectively adiabatic conditions was as small as possible. The temperature–time profile for each experiment was recorded. A change in temperature under adiabatic conditions is a common feature of almost all chemical reactions because of their heat of reaction. Temperature is an easily measurable parameter and a variety of thermometric techniques can be used. The changes in temperature become a useful method to follow these reactions. This is particularly helpful in a study of chemical reactions from a kinetic point of view, which can be difficult if reactions happen quickly.

5.1.2. The heat transfer coefficient for water

Figure 5.1 illustrates a cooling curve for pure water that started at a temperature of 67°C. When cooling, the temperature of the reactor's contents tends to approach that of the surrounding medium, which in this case is 30°C as described in Eq 3.9.
Figure 5.1: Temperature–time profile for the 250ml water contained in a batch reactor cooling from an initial temperature of 67°C which is immersed in a water batch at a controlled temperature of 30°C.

The cooling process of water in this experiment is due to heat transfer only as there is no reaction taking place. The natural logarithm of the difference between the temperature of the reactor contents and the water in the bath (Eq 3.12) is plotted against time in Figure 5.2. In every other result that follows, this plot will be referred to as “the linear plot”. The linear trend line gives a coefficient of determination ($R^2$) of 0.9999, which is shown to be an excellent fit for this curve. The slope of the linear curve in Figure 5.2 is estimated from the trend line and found to be $-1.846 \times 10^{-3}$ min$^{-1}$. This is the value of $\left(\frac{UA}{MC_p}\right)$ for the non-reactive situation described in Equation 3.12.
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Figure 5.2: The logarithm curve of the cooling water with an initial temperature of 67 °C in a water bath of 30 °C.

A true adiabatic reactor has no transfer of energy from the reactor contents to its surrounding medium. In the presence of heat loss from a real reactor, the heat transfer coefficient is estimated, and is used to compensate for the heat that has been lost, producing an effective adiabatic process curve. The slope estimated from Figure 5.2 is the heat transfer coefficient with respect to the specific heat of the system. Therefore if it is used as in Eq 3.12 and added to the system to compensate for the heat loss in the energy balance equation for a non-reactive system, the extent of the reaction in the right hand side is zero. Thus Figure 5.3 shows that the corrected adiabatic temperature rise of the system temperature plotted against time is horizontal and null, as required.
Figure 5.3: Adiabatic temperature of the cooling water with initial temperature of 67 °C. The water bath temperature is 30 °C.

An adiabatic curve in reaction experiments (the equivalent of graphs as in Figure 5.3) can show endothermic or exothermic behaviour, or no temperature change (corresponding to no reaction). If the trend shows a rise in temperature, this indicates that heat generation is taking place inside the reactor. Therefore the reaction occurring is exothermic. In the case where a fall is recorded below the initial temperature, the reaction is endothermic. Since the corrected adiabatic temperature curve for the water experiment in Figure 5.3 shows a horizontal curve, no heat is released or absorbed.
5.2. The rate of decomposition of hydrogen peroxide

In this section the decomposition of hydrogen peroxide is evaluated as a function of different initial temperatures. The initial temperature of the reactor contents was varied from 47°C to 67°C, while the amounts of hydrogen peroxide injected were varied between 5ml and 30ml. The mass of copper sulfate used was also varied (i.e. 5g to 20g). All other constituents were kept constant, and the water bath temperature was controlled at 30°C throughout the experiments. The changes in temperature inside the reactor were recorded.

5.2.1. The effect of temperature

In this set of experiments, 5ml of hydrogen peroxide is injected into a solution of 1M of sulfuric acid solution and 0.3144M of copper sulfate at different initial temperatures (47°C, 53°C, 58°C and 67°C). Throughout the experimentation, the reactor’s content was stirred, using a removable magnetic stirrer, at constant speed to keep the temperature and composition of the solution uniform. A thermocouple was used as the temperature measuring device.

Figure 5.4 displays the measured temperatures as a function of time. Note that the concentration of the constituents of the solution was kept constant, and only the initial temperatures were varied. The effects of the initial temperature on the reacting solution showed an increment in the heat generated. It is evident that the change in initial temperature results in the change of the rate of decomposition of hydrogen peroxide. At the lowest temperature of 47°C there is very little temperature rise and this initial increase gets larger as the initial temperature increases. However, the rise
in temperature for the graph starting at 58°C seemed to be slowly rising. As would be expected the rise for the graph with initial temperature of 67°C is the fastest.

Figure 5.4: Temperature–time profile of the 1.0 M solution of sulfuric acid and 0.3144M of copper sulfate with 5ml of hydrogen peroxide injected at different initial temperatures (47°C, 53°C, 58°C and 67°C) with water bath at 30°C.

The results in Figure 5.4 suggest that the reaction might be complete after 300min. The linear plots for these experimental results were drawn on the basis of this finding. These plots were then compared to that for the water experiment linear plot (see Figure 5.4) and are presented in Figure 5.5. The graph with an initial temperature of 67°C has a slope experimentally similar to that of the cooling water since they differ by 1.08%. This means that only heat is lost during this part of the experiment; or, in other words, effectively no reaction occurs after about 300min.

It is evident that as the initial temperature of the reaction solution decreases, the slope increases. The slope of these graphs at 47°C, 53°C and 58°C depart from that
of the pure water (Figure 5.5). This suggests that what is taking place is not only the heat transfer for the cooling process but also a relatively slow rate of exothermic decomposition of peroxide.

Figure 5.5: This displays the tail after 5 hours for the logarithm vs time curves of the solution of 1.0M sulfuric acid and 0.3144M of copper sulfate with 5ml of peroxide at different initial temperatures. Water bath is at 30°C.

The experiments with an initial temperature of 47°C, 53°C and 58°C would need to be run for a longer time than 300 min in order to ensure that reaction is complete. Because the reaction rate would be lower at the lower temperature, the increase in temperature would be smaller over a longer time and the results would be more
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difficult to analyze. This reasoning suggests that the experiment should be performed at an initial temperature of 67°C. At a temperature higher than 67°C, decomposition takes place very fast; this would impair the ability of the temperature probe to respond rapidly and make accurate recordings of the results.

Table. 5. 1: The linear trend line slopes from Figure 5.5 with their initial temperatures.

<table>
<thead>
<tr>
<th>Pure-water slope(67°C)</th>
<th>-1.848X10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor solution</td>
<td>Linear slopes</td>
</tr>
<tr>
<td>1.0 M H₂SO₄,5mlH₂O₂, 5g-CuSO₄</td>
<td>x10^{-3}</td>
</tr>
<tr>
<td>Initial temperatures(°C)</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>-1.232</td>
</tr>
<tr>
<td>53</td>
<td>-1.528</td>
</tr>
<tr>
<td>58</td>
<td>-1.690</td>
</tr>
<tr>
<td>67</td>
<td>-1.826</td>
</tr>
</tbody>
</table>

The experimental results were then corrected using Equation 3.8. The corrected adiabatic temperature rises, based on the slopes in Table 5.1, are shown in Figure 5.6. It is worth noting that the decomposition of hydrogen peroxide is a function of temperature and also that an increase in initial temperature leads to an increase in the initial rate of change of temperature with time.
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Figure 5.6: The corrected (adiabatic) curves for the solution of 1.0M of sulfuric acid and 0.3144 M of copper sulfate and 5ml peroxide with initial temperature varying from 47°C to 67°C

The total temperature rise for the initial temperature of 67°C is 3°C while that of initial temperature of 47°C is below 0.5°C. This is not altogether surprising as the runs done at the lower initial temperature were corrected using curves that probably did not represent heat transfer alone but heat transfer with reaction as well. Clearly then these curves are not entirely credible. It might have been possible to try to correct the curves with the water experimental heat transfer rate but as one would not be able to interpret these curves, these results are not presented.
It is of interest to note that the curves at the higher initial temperatures seem to show an initial exothermic reaction followed by an endothermic one. This will be discussed again later.

5.2.2. The effect of various environments on the decomposition of hydrogen peroxide

In this section the effect of the medium on the decomposition of hydrogen peroxide are investigated. The effect of pure water; copper sulfate and diluted sulfuric acid all at same initial temperature of 67°C were studied.

In Figure 5.7, the experimental results for 5ml of hydrogen peroxide decomposition in the presence of copper sulfate, sulfuric acid and water have been plotted. The pure water curve was included for comparison purposes. Note that the total volume of the solution in the reactor is the same for all the experiments, which is 250ml. In this case the first experiment contained 5ml of pure water injected into the pure water in the reactor. The second experiment was of 5ml hydrogen peroxide added into the reactor vessel filled with pure water. The third run was of 5ml of peroxide in a diluted solution of 1.0M sulfuric acid. In the fourth experiment the same amount of peroxide was injected into an aqueous solution of copper sulfate. The last run was made of same amount of peroxide injected into a solution of 5g CuSO$_4$ and 15ml of H$_2$SO$_4$(=1.0M). Therefore each experiment was ran for at least 15 hours (= 900min)
Figure 5.7: The results of 5ml of peroxide decomposing in the presence of 250ml water (red); 1.0M sulfuric acid (light green) and 0.3144M copper sulfate (purple). Pure water curve (light blue) and the solution of CuSO₄ and H₂SO₄ with 5ml H₂O₂ (Black). All at initial temperature of 67°C and total volume of 250ml. Water bath at 30°C.

The cooling curves of Figure 5.7 are displayed in the linear plots in Figure 5.8 in which the tails after the experiments recorded in Figure 5.7 had been run for 5h are shown. It can been seen here that the reaction was probably complete after 5h, because the regressed slopes for each curve are close to that of the pure water run of \(-1.848 \times 10^{-3} \text{ min}^{-1}\).
Figure 5.8: The linear plots of the cooling curves after five hours from Figure 5.7.

The slopes of each curve in Figure 5.8 serve as the estimated heat transfer coefficient for each corresponding curve in Figure 5.7. The resulting corrected adiabatic curves with the heat loss compensated for are shown in Figure 5.9.
Figure 5.9: Corrected adiabatic curves from Figure 5.7 for the addition of 5ml solution of peroxide in various media containing 1M sulfuric acid, 250ml water and 0.3144M copper sulfate at initial temperature of 67°C.

It appears inconsistent that the curves in Figure 5.9 all have different temperature increases at long times. One would expect all of the decomposition reactions to be the same, and therefore to have the same heat of reaction as well as the same total temperature rise. As these experiments were conducted at different times, it is surmised that the hydrogen peroxide had decomposed while being stored between experiments. Because 5ml of what was thought to be 30% hydrogen peroxide solution was used in all experiments, it seems likely that by the time all the experiments had been completed the hydrogen peroxide had partially decomposed.
To confirm this, it was decided to obtain a fresh sample of hydrogen peroxide, and to carry out the replicate experiments for comparison in a reasonably rapid sequence.

As a consequence of this these results from these curves will not be used other than to note that the hydrogen peroxide at this temperature (initial temperature of 67°C) undergoes decomposition in all these cases.

5.2.3. The effects of varying volume of hydrogen peroxide

This section discusses the decomposition curves of hydrogen peroxide when the amount of hydrogen peroxide is varied. The concentration of sulfuric acid in these experiments was 1.0M and the amount of copper sulfate 5g (0.3144M). The amounts of peroxide considered were 5ml, 15ml, 20ml and 30ml and the duration of each experiment was 15 h. the initial temperature of the solution in the reactor was 67°C.

Figure 5.10 shows the resulting temperature–time profiles. One can see from these graphs that the increase in the amount of peroxide in the solution results in a commensurate rise in temperature.
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Figure 5.10: Temperature–time profile for 1.0 M of sulfuric acid, 0.3144 M of copper sulfate solutions at initial temperature of 67°C. Volume of peroxide added: 0ml (purple), 5ml (blue), 15ml (dark red), 20ml (light green) and 30ml (light blue). Water bath temperature is 30°C.

The linear plot is shown in Figure 5.12. As before, the tail is considered as having been achieved (reaction essentially complete) only after 5h. Thus, the estimate of the value of \( \frac{UA}{M Cp} \) is obtained from the slope of the trend line for each experiment according to equation 3.8. It is shown relative to the slope of the pure water experiment at the same initial temperature of 67°C. The five lines are parallel to each other and hence have almost equal slopes. Note that the volume of hydrogen peroxide added in the solutions has negligible effect on the heat transfer at this stage. After 5h of reaction most of the peroxide has decomposed, thus the remaining
amount is insignificant. And that is confirmed by the slope of each curve which is close to that of the pure water experiment.

Figure 5.11: The linear plot of the tails of the curves from Figure 5.10 starting after 5h.

Figure 5.13 shows the corrected plots for the adiabatic temperature rise (using Equation 3.8) obtained from the experimental curves in Figure 5.11. The increase in the amount of peroxide in the reaction solution contributed to an increase in the adiabatic temperature rise. Interestingly, there is a drop in temperature after the maximum temperature has been reached. As the amount of peroxide in the reactor solution increases, so does the drop in temperature. This suggests that the endothermic process could also depend on the amount of the peroxide added.
Table 5.2 below shows the amount of peroxide added, with the temperature rise to the maximum, and the subsequent drop for each graph. Each of the curves in Figure 5.12 shows a sharp change in slope at about 200min. This could be attributable to a slight inaccuracy in the correction to adiabatic temperature, as no allowance was made for the endothermic reaction. It is also believed that the correction does not make any significant difference up to this point, and that therefore the results are credible.

Figure 5.12: The corrected adiabatic curves of the decomposition reaction of hydrogen peroxide from the results in Figure 5.11.

The change in temperature between the initial and maximum temperature (rise) and between the maximum and the asymptotic temperature (drop) is shown in Table 5.2,
The Decomposition of Hydrogen Peroxide in acidic Copper Sulfate Solutions

and these are plotted versus the amount of hydrogen peroxide added (shown in Figure 5.13). The linearity of these results indicates that the increase in the amount of peroxide in the reaction has a direct proportionality to the rise in temperature for both the exothermic and endothermic parts.

Table 5.2: Change in the temperature between the initial and maximum temperature (rise) in Figure 5.12, between the maximum and asymptotic temperature (drop) in Figure 5.12 together with the corresponding amount of peroxide added.

<table>
<thead>
<tr>
<th>Volume of H$_2$O$_2$ ml</th>
<th>Rise (°C)</th>
<th>Drop (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2.946</td>
<td>0.4168</td>
</tr>
<tr>
<td>15</td>
<td>7.469</td>
<td>1.139</td>
</tr>
<tr>
<td>20</td>
<td>10.11</td>
<td>1.374</td>
</tr>
<tr>
<td>30</td>
<td>14.62</td>
<td>1.756</td>
</tr>
</tbody>
</table>

All the corrected curves show a rapid temperature increase followed by a slower temperature decrease. This implies a fast exothermic reaction followed by a slower endothermic one. This is contrary to what was expected to happen with a simple decomposition of the hydrogen peroxide. However, this will be discussed in detail later. This effect may affect the accuracy of the corrections made, but should not affect the general conclusions.
5.2.4. The effect of varying the amount of copper sulfate

Figure 5.14 illustrates the change in temperature caused by the reaction of hydrogen peroxide in sulfuric acid when the amount of copper sulfate in the solution was varied. An amount of 30ml of peroxide was added to a 1.0M solution of diluted sulfuric acid, and the mass of copper sulfate was varied from 5g to 20g in this series of experiments. The initial temperature was maintained at 67°C for each run.
Figure 5.14: The temperature–time profile for 1.0M sulfuric acid with 30ml hydrogen peroxide added in the presence of different amount of copper sulfate: 0g (green), 5g (dark red), 8g (light green), 11g (purple), 15g (light blue) and 20g (orange), all with initial temperature of 67°C and the water bath was kept at 30°C.

In Figure 5.15 the linear curves from the tails of the curves in Figure 5.14 have been plotted. As before these tails are plotted after 5h.
The Decomposition of Hydrogen Peroxide in acidic Copper Sulfate Solutions

Figure 5.15: The linear plot of the tail of the curves from Figure 5.14.

As all the lines for reacting systems in Figure 5.15 are essentially parallel and almost identical to that for the cooling water, it was safe to assume that the reaction is essentially complete after 5h. These slopes could then be used to correct the curves in Figure 5.14 to obtain the corrected adiabatic curves in Figure 5.16.A.

As before, Figure 5.16A shows an exothermic reaction followed by an endothermic one. The increase in the amount of copper sulfate caused a slightly greater rise in the maximum temperature rise, but the final temperature seemed to be unaffected.
Figure 5.16A: The corrected adiabatic curves of the results from Figure 5.14.

Figure 5.16B displays the corrected adiabatic temperature rise for the first 15min of the six experiments that form the subject of Figure 5.14. The results plotted below show that during this initial period the adiabatic temperature rises to its maximum, and that in this case the increase in the amount of copper sulfate results in an acceleration of the initial temperature rise.
Figure 5.16B: The adiabatic temperature rise plot from Figure 5.14 in which only the first 15 minutes duration is considered.

The curves in Figure 5.16B exhibit a slight S-shape but in the latter part they look as if the temperature might approach the maximum temperature exponentially. This is probably due to the rate constant increasing with temperature as the temperature range of about 13°C is quite large to consider the system as isothermal.

In order to study the exothermic reaction, the natural logarithm of the difference between the highest temperature that the graph reaches in Figure 5.16 B (\(T^\infty\)) and the corrected adiabatic temperature rise (\(T^{ad}\)) are plotted against time in Figure 5.17. The curves are all reasonably linear, indicating a first order reaction is occurring. A regression was done to obtain a first order rate constant for each
experiment. Equation 5.1 probably describes the exothermic reaction taking place in this system (Costa, et al. 2006). For the generation of heat which results in a rise in temperature of the system is probably from this catalytic decomposition of peroxide.

\[
\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2
\]  \hspace{1cm} 5.1

5.2.4.1. Effects of copper on reaction constant
It is evident from Figure 5.17 that the greater the amount of copper sulfate, the greater the first order rate constant for decay will be. The values of these rate constants with the amount of copper sulfate added are shown in Table 5.3.

It should be noted that doing these plots to get the so-called first order rate constants is contingent on the fact that the exothermic reaction is essentially complete before the endothermic reaction starts. These results appear to justify this assumption.
Figure 5.17: The $\ln(T^\infty - T^{ad})$ for the decomposition of hydrogen peroxide with different amounts of copper sulfate against time. In this case 0g (Orange), 5g (Blue), 8g (Dark red), 11g (Light green), 15g (Purple) and 20g (Green) of copper sulfate is in solution with 1.0M sulfuric acid and 30ml of peroxide is added. The experiments are done with an initial temperature of 67°C.

As previously mentioned the slopes of the regression curves in Figure 5.17 provide the estimated rate constants for first order reaction for each corresponding amount of copper sulfate. Table 5.3 contains the mass of copper sulfate with the corresponding estimated rate constants which is plotted in Figure 5.18.
The Decomposition of Hydrogen Peroxide in acidic Copper Sulfate Solutions

Table 5.3: The estimated rate constants with the corresponding amount of copper sulfate added.

<table>
<thead>
<tr>
<th>Mass (g) of CuSO₄</th>
<th>Estimated rate constant (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.03858</td>
</tr>
<tr>
<td>5</td>
<td>0.2659</td>
</tr>
<tr>
<td>8</td>
<td>0.3145</td>
</tr>
<tr>
<td>11</td>
<td>0.3999</td>
</tr>
<tr>
<td>15</td>
<td>0.4331</td>
</tr>
<tr>
<td>20</td>
<td>0.4637</td>
</tr>
</tbody>
</table>
The Decomposition of Hydrogen Peroxide in acidic Copper Sulfate Solutions

Figure 5.18: The graph of the change in mass of copper sulfate with the estimated first order rate constant of the solution in which the mass of copper sulfate used was 0g, 5g, 8g, 11g, 15g and 20g in 1.0M of sulfuric acid at an initial temperature of 67°C and with 30ml of peroxide added.

It can be seen that the curve in Figure 5.18 shows a saturation effect in that as more copper sulfate is added there a smaller effect of each addition and the rate constant seems to asymptote to a maximum value.

5.3. Model selection
From Figure 5.18, one can see that the rate constant initially depends linearly on the concentration of copper sulfate but then saturates, that is, the rate constant becomes
independent of the concentration of copper sulfate. A simple function that has this property is described below:

\[
k - k_0 = \frac{aM_{\text{CuSO}_4}}{1 + bM_{\text{CuSO}_4}}
\]

where:

\(k\) is the rate constant which is a function of the mass of copper sulfate present in solution.

\(k_0\) is the rate constant when no copper sulfate is added in the reacting solution.

\(M_{\text{CuSO}_4}\) is the mass of copper sulfate added in the reacting solution

\(a, b\) are the fitting parameters of the empirical model

The estimated rate constant is not only a function of the added copper sulfate since when no copper sulfate added the rate constant is:

\[
k(M_{\text{CuSO}_4} = 0g) = k_0
\]

Thus \((k_0)\) is read off as the y-intercept in Figure 5.18. At low concentration of copper sulfate \((bM_{\text{CuSO}_4} \ll 1)\), the reaction constant becomes linearly dependent on the mass of copper sulfate, that is:

\[
k - k_0 = aM_{\text{CuSO}_4}
\]

Thus the initial slope of rate constant curve in Figure 5.18 gives the value of the parameter \(a\), furthermore, if \(M_{\text{CuSO}_4}\) is increased \((M_{\text{CuSO}_4} \gg 1)\) then the equation for the rate constant becomes:
\[
k = \frac{a}{b} + k_0 \tag{5.5}
\]

Thus the reaction constant does not depend on the mass of copper sulfate at high concentration and asymptotes to \(\frac{a}{b} + k_0\). Now the graph for Equation 5.2 inserted in Figure 5.18 is displayed in Figure 5.19. This is performed at a confidence level of 95% and the coefficient of determination \(R^2\) is 0.99. The variability of each point is analysed using error bars while the solid line represents the proposed empirical model of Equation 5.2. The solid line crosses the error bars in the last five points of the experimental data. This signifies that the fitted model curve is within the margin of the error associated with each measurement. However, the initial point at 0g mass of copper sulfate no significant variability was detected so there is no error bar plotted on the graph.
Figure 5.19: The graph of the amount of copper sulfate against the reaction rate constants estimated in Figure 5.17 in comparison with the theoretical best fit model at a confidence level of 95%.

5.3.1. Confidence on the optimized parameters (a, b) for model

The constraints in Equation 5.2 have been optimized at a confidence level of 95% and are listed in Table 5.4. The value of (a) is estimated to be 0.08333 while (b) is 0.1278.

Table 5.4: Values of optimized parameters in Equation 5.2 computed at a confidence level of 95%

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_o$ (min$^{-1}$)</td>
<td>3.858X10$^{-2}$</td>
<td></td>
</tr>
<tr>
<td>$a$ (g$^{-1}$min$^{-1}$)</td>
<td>8.333X10$^{-2}$</td>
<td>±0.03158</td>
</tr>
<tr>
<td>$b$ (g$^{-1}$min$^{-1}$)</td>
<td>1.278X10$^{-2}$</td>
<td>±0.07643</td>
</tr>
</tbody>
</table>
In reality the experimental data does not coincide perfectly with the theoretical. The deviation is due to discrepancies encountered during the performing of the experimental exercise. The k in Table 5.5 cannot be accurate and precise since it is derived from experimental findings. Therefore a degree of uncertainty around k has been allocated based on the allowable error of 5% chosen. This makes the acceptable region that k can be considered to be enclosed by the maximum and minimum values. Therefore k+ is the highest acceptable value that k can reach, k- being the lowest value reachable by k. The ∆k is the amount in which k can increase or decrease and still be in the accepted region. The region between k+ and k- is produced by the 5% error which connotes that outside this region the error is higher than 5%, which is not acceptable. Such evidence in Figure 5.19 is illustrated by the vertical bars on each coordinate.

Table 5.5: Data for the plot of the mass of copper sulfate against estimated rate constant (k) showing 95% error bands

<table>
<thead>
<tr>
<th>Mass(g) of CuSO4</th>
<th>k</th>
<th>k+</th>
<th>k-</th>
<th>∆k</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.03858</td>
<td>0.04104</td>
<td>0.03612</td>
<td>0.00246</td>
</tr>
<tr>
<td>5</td>
<td>0.2659</td>
<td>0.291</td>
<td>0.2408</td>
<td>0.0251</td>
</tr>
<tr>
<td>8</td>
<td>0.3145</td>
<td>0.3398</td>
<td>0.2893</td>
<td>0.0253</td>
</tr>
<tr>
<td>11</td>
<td>0.3999</td>
<td>0.4287</td>
<td>0.3711</td>
<td>0.0288</td>
</tr>
<tr>
<td>15</td>
<td>0.4331</td>
<td>0.4687</td>
<td>0.3976</td>
<td>0.0356</td>
</tr>
<tr>
<td>20</td>
<td>0.4637</td>
<td>0.5004</td>
<td>0.427</td>
<td>0.0367</td>
</tr>
</tbody>
</table>

The Endothermic Reaction

Up until now the focus has only been on the exothermic part of the curves in Figure 5.16A. However, it is evident that a substantial endothermic part follows the
exothermic reaction. When this work was started, it was believed that there was only a single exothermic reaction taking place, which is seen in Equation 5.1. But, clearly something more complex is happening.

As this reaction happens when there is no copper sulfate present it is likely to be as a result of the presence of the sulfuric acid. Nevertheless the investigation on the endothermic reaction requires more thorough research. This could entail concentration of the hydroxyl radicals produced, the peroxides and superoxide. This part of the reaction was not covered in this research. Now it is known that hydrogen peroxide can react with sulfuric acid to produce Caro’s Acid (Olubambi, Borode and Ndlovu 2006). Caro’s acid (or peroxymonosulfuric acid) is an equilibrium product obtained by mixing hydrogen peroxide with sulfuric acid.

\[
H_2O_2 + H_2SO_4 \leftrightarrow H_2SO_5 + H_2O
\]

This is usually thought to occur only in concentrated solutions at low temperature, but as these reactions at 67°C are quite fast, maybe some is produced and nearly immediately decomposed. If this is the case its decomposition must be endothermic. This point has not been followed at this stage but could be the focus of more work in the future.
Chapter 6

6. Conclusions

In this research the effect of copper sulfate on the decomposition of hydrogen peroxide was investigated. This was done in the solution of diluted sulfuric acid. An insulated batch reactor (vacuum flask) was used. The reactor was immersed in a temperature controlled water bath in order to keep the surrounding temperature of the reactor constant at 30°C. Three variables were considered in doing these experiments, namely the initial temperature of the reactor contents, the volume of hydrogen peroxide used, and the amount of copper sulfate added to the process solution. In each experiment the temperature change of the reactor contents was monitored as a function of time after the addition of hydrogen peroxide. The exponential tail of the curves was used to measure the apparent heat loss rate from the reactor. By measuring the heat transfer rate when only water was present, or after a long time when it was assumed reaction was essentially complete, the experimental rate could be corrected to obtain an effective adiabatic curve. These effective adiabatic curves were then used to interpret the results. In cases when the apparent heat loss rate did not agree with the one from water it was assumed that the reaction was too slow and was not essentially complete and so the corrected results were not that meaningful.

6.1.1. Effect of initial temperature

Four different initial temperatures of the solution, 47°C, 53°C, 58°C and 67°C were used and the same concentration was maintained at 1.0M of sulfuric acid; 5g of copper sulfate was added and 5ml of injected peroxide. At all the temperatures except 67°C it was observed that the apparent cooling rate was lower than that for
the pure water, and so it was presumed that the reaction was not complete when the cooling rate was estimated (after 300 minutes) and hence the lower initial temperature experiments were not suitable for estimating the kinetics. As a consequence, all later experiments were done at 67° C.

6.1.2. Effects of reaction components on peroxide at 67° C
At an initial temperature of 67° C, 5ml of hydrogen peroxide was tested in four different solutions, namely, 250ml of hot water alone; 1.0M of sulfuric acid; 0.3144M of copper sulfate in a solution of 1.0M of sulfuric acid; and finally with copper sulfate alone. In this case all the cooling curves were essentially parallel so it was believed the corrected adiabatic curves could be used. The adiabatic temperature rise for each of the reaction in the different solutions was very different. This means either the reaction was not complete when the correction was made or, as was surmised, because the measurements were done at different times the peroxide had decomposed while being stored. It was therefore decided that in future fresh peroxide would be used. Experiments that were to be compared were done as soon after each other as possible.

6.1.3. Varying the volume of peroxide
The volumes of the hydrogen peroxide added to the reaction solution of 1.0M sulfuric acid and 5g of copper sulfate were 0ml, 5ml, 15ml, 20ml and 30ml respectively. The peroxide that was at room temperature was added to the reactor contents at 67° C. All the cooling curves were essentially the same as for the cooling water and therefore a correction was done to the experimental data. It was very clear from the experiments that the reaction was not a straightforward exothermic decomposition as there was both an exothermic followed by an endothermic reaction. It was shown
that the maximum adiabatic temperature rise was proportional to the amount of peroxide added, so was the subsequent adiabatic temperature drop. It was therefore concluded that there are at least two reactions occurring, both a function of the amount of peroxide present.

6.1.4. The role of copper sulfate in the reaction
Different amounts of copper sulfate were used, namely 0g, 5g, 8g, 11g, 15g and 20g, which were added to a 1.0M of diluted sulfuric acid with an initial temperature of 67°C. Then 30ml of hydrogen peroxide which was at room temperature was injected into the solution at 67°C initial temperature. It was observed that the change in the amount of copper sulfate affected the rate of decomposition of peroxide since the higher the amount of copper sulfate the faster the reaction occurred. It is worth noting that the change in the amount of copper sulfate had no effect on the rate of the side reaction.

6.1.5. Rate determination
This study has shown that an increase in the amount of copper sulfate in the reacting solution increases the rate of decomposition of peroxide. It was further found that for each experiment the decomposition of peroxide followed a first order rate. When the first order rate constants were plotted against the amount of copper sulfate present, the constant increased steeply initially as the copper catalyzes the peroxide but tailed off as the amount of copper sulfate increased. A simple rate expression that showed a saturation effect was chosen with two constants. The constants were estimated and the model was shown to give a good fit to the experimental results.
As the endothermic part was unaffected by the presence of copper it was not further analyzed. It was suggested that the decomposition of the hydrogen peroxide was not a simple process, as it was possible that Caro’s acid was formed, and what we saw was the decomposition of this as well as of the hydrogen peroxide directly.

6.2. Overall conclusion

The effect of copper sulfate on the kinetics of the decomposition of hydrogen peroxide was investigated and a model elucidating the effect of the amount of copper sulfate on the decomposition of peroxide was proposed. The primary decomposition of peroxide followed a first order rate law as reported in the literature (Croiset, Rice and Hanush 1997). As would be expected, it was also found that in an adiabatic reactor the maximum temperature rise of the reacting solution was found to be proportional to the amount of hydrogen peroxide added. Furthermore it was shown that copper sulfate served as a catalyst for the decomposition of hydrogen peroxide in a sulfuric acid solution (Perez-Benito 2004). The decomposition was also shown to contain an exothermic as well as an endothermic part and a possible explanation for this was proposed.

Because the copper in solution catalyses the decomposition of the hydrogen peroxide it would be desirable to keep the copper in industrial leaching solutions as low as possible. Therefore one would like to continuously remove the copper in solution during the leaching process. This could for instance be done by the addition of solvent extraction and electro-winning units in a recycle system with the leaching unit.
Solvent extraction provides high concentrations of copper ions (Cu$^{2+}$) in a solution using extractants such as aldoximes and ketoximes (Beltran 2009). The solution with the high concentration of copper is then taken for further purification of copper in an electro-winning unit while the stream with the lower copper concentration is returned to the leaching unit for further processing. Thus the amount of peroxide used in copper leaching solution could be minimized.
7. **References**


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