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The Effect of Sulfuric Acid, Persulfate and Acetic Anhydride on the Preparation of Chlorine Dioxide from Chlorite Solution

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A Thesis
Submitted to the Department of Materials Science and Engineering,
University of Rajshahi, Bangladesh, in partial fulfillment of the
requirements for the degree of Doctor of Philosophy

BY

MD. ABDUR ROUF

DEPARTMENT OF MATERIALS SCIENCE AND
ENGINEERING UNIVERSITY OF RAJSHAHI
BANGLADESH

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Examination Roll No. : 0193
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JUNE 2013

Dedicated

To

My Beloved Parents and Teachers

Certificate

This is to certify that the contents in the thesis entitled ***"The effect of sulfuric acid, persulfate and acetic anhydride on the preparation of chlorine dioxide from chlorite solution"*** *is original research work done by Md. Abdur Rouf under our guidance and supervision for the degree of Doctor of Philosophy. It contains no material previously published or submitted for any other degree.*

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June 2013
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DECLARATION

I do hereby declare that the research work produced in the thesis entitled, “The effect of sulfuric acid, persulfate and acetic anhydride on the preparation of chlorine dioxide from chlorite solution” and submitted in the Department of Materials Science and Engineering, University of Rajshahi for the Degree of Doctor of Philosophy is the result of my own investigation carried out under the supervision of **Dr. C. M. Mustufa**, Professor, Department of Applied Chemistry and Chemical Engineering, **Dr. Md. Azhar Ali**, Professor, Department of Chemistry, **Dr. Md. Golam Mostafa**, Professor, Institute of Environmental Science and **Dr. Md. Asadul Hoque**, Associate Professor, Department of Materials Science and Engineering, University of Rajshahi. The thesis has not been concurrently submitted for any other Degree.

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ABSTRACT

The study was attempted to generate ClO_2 from chlorite ion in a well stirred process aiming at a small scale production for the use of disinfection, sterilization and water purification etc. There were four reactants, H_2SO_4, $Na_2S_2O_8$, $(CH_3CO)_2O$ and a mixture of H_2SO_4 and $(CH_3CO)_2O$ reacted individually with $NaClO_2$ to produce ClO_2. The main objective of the study was to achieve the maximum percentage production of ClO_2 from chlorite solution. The analytical procedures were devised to determine chlorine dioxide, chlorite, chlorate and chloride ions in the composite reaction mixtures in order to determine the reaction order and propose possible chemical reactions for the formation and decomposition of ClO_2.

The reactions were carried out with various concentrations of $NaClO_2$ (0.01, 0.05, 0.1 and 0.2N) and H_2SO_4 (0.02, 0.1, 0.2, 0.4 and 1.0N) at different time intervals. The production of ClO_2 greatly depended on both the reactant concentrations and reaction time. The maximum percentage production of ClO_2 was found to be 75% from the reaction between 0.01N $NaClO_2$ and 1.0N H_2SO_4 in 240 minutes.

Similarly, other reactions for the production of ClO_2 from different reactants were illustrated as: a) about 60% ClO_2 was produced in the reaction of 0.01N $NaClO_2$ and 0.2N $Na_2S_2O_8$ in 240 minutes, b) about 78% ClO_2 was produced in the reaction of 0.01N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ within two minutes and c) about 91% ClO_2 was produced in the reaction of 0.01N $NaClO_2$ with a mixture of 0.1N $(CH_3CO)_2O$ and 0.02N H_2SO_4 concentrations within two minutes. Above results showed that 0.01N $NaClO_2$ was the most suitable concentration for the production of ClO_2 from chlorite solution.

About 78% and 2% ClO_2 were produced, respectively from $(CH_3CO)_2O$ and H_2SO_4 reacted individually with $NaClO_2$ within two minutes of reaction time and their sum was 80%, which was lower than that of the percentage production (91%) obtained in the reaction between $NaClO_2$ and the reactant mixture [$(CH_3CO)_2O$ and H_2SO_4]. The reaction between $NaClO_2$ and the mixture [$(CH_3CO)_2O$ and H_2SO_4] showed the better production efficiency of ClO_2 than sum of their individual effects. In this reaction, either $(CH_3CO)_2O$ or H_2SO_4 was not acted as a catalyst because they reacted individually with

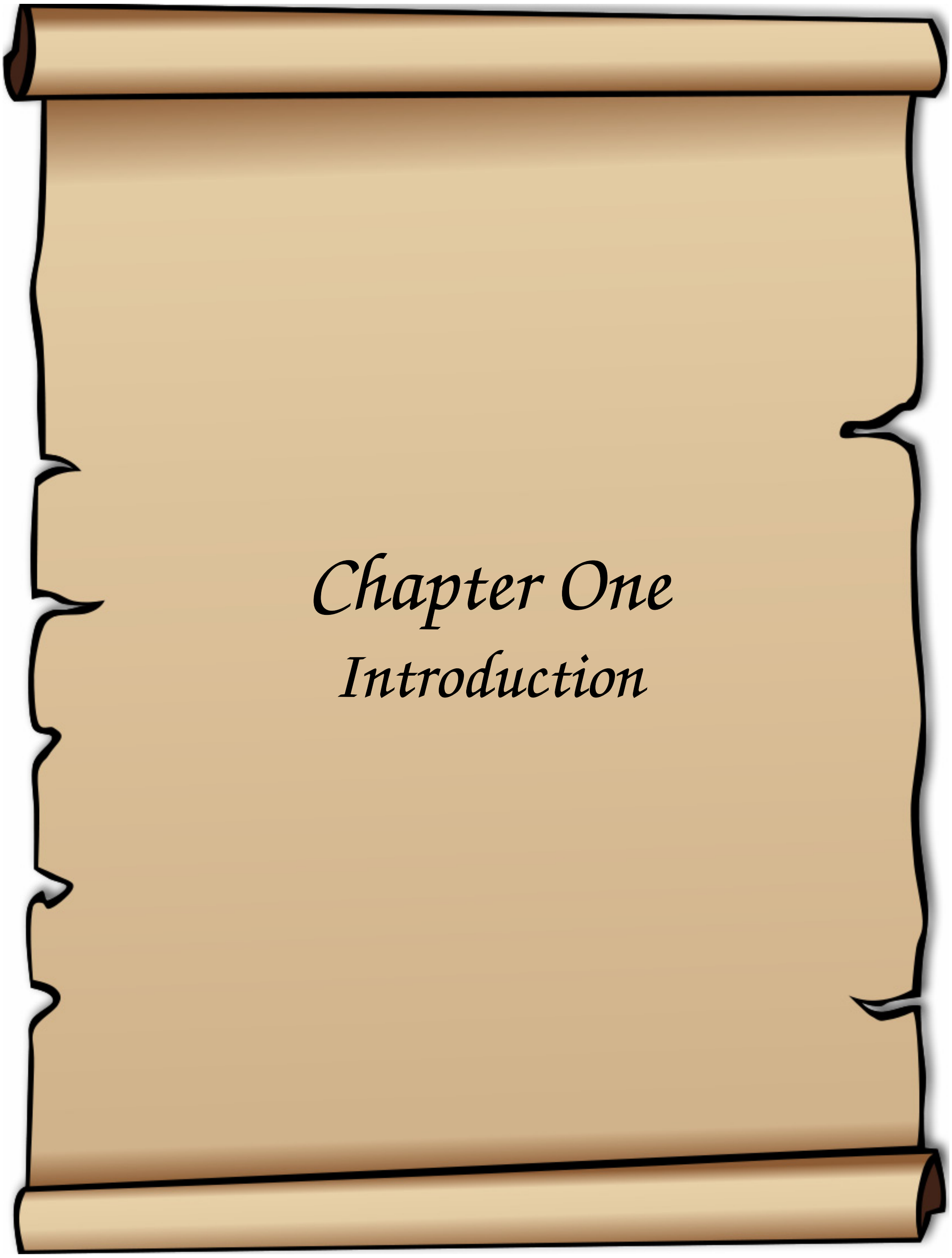
$NaClO_2$ to produce ClO_2. Thus the synergistic effect of $(CH_3CO)_2O$ and H_2SO_4 might be the cause of maximum production of ClO_2.

The study proposed reactions for ClO_2 generation and decomposition based on the experimental results of the reaction between $NaClO_2$ and H_2SO_4. It was observed that ClO_2 is a very unstable compound, decomposes readily and forms various chlorine species in a series of reactions, and at the end of the reaction, the decomposition amount of ClO_2 was almost equal to the formation amount of Cl^-. Thus the proposed reactions for ClO_2 generation and decomposition can be written as follows:

$$ClO_2^- \xrightarrow{H^+} xClO_2 +$$

$$ClO_2 \xrightarrow{H^+} Cl^- + 2H_2$$

The reaction order was determined using the reaction of $NaClO_2$ and H_2SO_4 at 30 ± 1^0C. On the basis of the rate law, and finally a plot of *dx/dt* against *(a-x)* gave a straight line indicating the first-order reaction. The results showed that the experimental data did not fit to the equations of other order reactions. Hence, it was concluded that the decomposition reaction of ClO_2^- ion for the generation of ClO_2 followed the first-order kinetics.



Chapter One

Introduction

INTRODUCTION

Chlorine dioxide is a chemical compound with the formula ClO_2. It was first prepared in the early nineteenth century by Sir Humphrey Davey (1811). By combining potassium chlorate ($KClO_3$) and hydrochloric acid (HCl) produced a greenish-yellow gas named "euchlorine". Later, this gas was found to be a mixture of chlorine dioxide and chlorine[1]**.** This yellowish-green gas crystallizes as orange crystals at −59°C. As one of several oxides of chlorine, it is a potent and useful oxidizing agent used in water treatment and in bleaching[2]. The molecule ClO_2 has an odd number of valence electrons and it is therefore a paramagnetic radical. Its electronic structure has baffled chemists for a long time because none of the possible Lewis structures are very satisfactory. In 1933 Brockway proposed a structure that involved a three-electron bond[3]. Acclaimed chemist Linus Pauling further developed this idea and arrived at two resonance structures involving a double bond on one side and a single bond plus three-electron bond on the other[4]. In Pauling's view the latter combination should represent a bond that is slightly weaker than the double bond. In molecular orbital theory this idea is commonplace if the third electron is placed in an anti-bonding orbital[5].

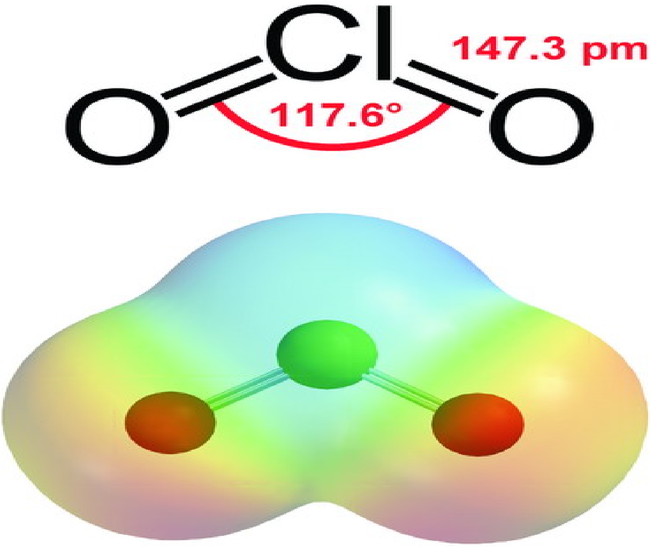


Fig. 1.1 Structure of ClO_2

This is doubtless that ClO_2 is widely used as a bleaching, oxidizing, disinfecting and strongly sterilizing agent. But aqueous ClO_2 is not stable, the gaseous ClO_2 remains unchanged in darkness, but it gradually decomposes in sunlight. It may explode when rapidly heated to 100°C. The aqueous solution is fairly stable in darkness. In sunlight it decomposes rapidly in few hours and diffuses slowly in day light in to chloric acid, chlorine and oxygen and the reaction is given below[6,7]:

$$6ClO_2 + 2H_2O \rightarrow HClO_3 + Cl_2 + O_2$$

Chlorine dioxide is toxic. If ClO_2 is inhaled, it can irritate the throat and lungs. The short term exposure limit for ClO_2 is 0.3 ppm (V/V)[8]. Because ClO_2 is volatile, the concentration of ClO_2 above concentrated solutions can exceed this limit. Therefore, solutions of ClO_2 should be prepared and handled under fume hoods to avoid inhalation[9]. Sometimes ClO_2 may be exploded due to the high concentration of aqueous ClO_2. It cannot be compressed or stored commercially as a gas because it is explosive under pressure. The danger of explosion is also associated with ClO_2 in the gas phase. At concentration greater than 10 percent of volume in air [10.1 k_{pa} (76 mm Hg)] it has been reported to be spontaneously explode[10,11]. One of the most important physical properties of ClO_2 is its high solubility in water, particularly in chilled water. In contrast to the hydrolysis of chlorine gas in water, ClO_2 in water does not hydrolyze to any appreciable extent but remains in solution as a dissolved gas[12]. It is approximately 10 times more soluble than chlorine (above 11^0C), while it is extremely volatile and can be easily removed from dilute aqueous solution with minimal aeration or recombination with carbon dioxide. Above 11 to 12^0C, the free radical is found in gaseous form. In the gaseous form, the free radicals also react slowly with water. The reaction rate is 7 to 10 million times slower than that of the hydrolysis rate for chlorine gas[13]. This characteristic may affect ClO_2 effectiveness when batching solutions and plumbing appropriate injection points. Additionally, as the following reaction indicates, in waters with high pH content, the chemical will disproportionate to ClO_2^- and ClO_3^- [14,15]:

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

At concentrations greater than 15% volume in air at STP, ClO_2 explosively decomposes into chlorine and oxygen. The decomposition is initiated by light. Thus, it is never handled in concentrated form, but is almost always used as a dissolved gas in water in a concentration range of 0.5 to 10 gm per liter. Its solubility increases at lower temperatures: it is thus common to use chilled water (5 °C or 41 °F) when storing at concentrations above 3 gm per liter. In many countries, such as the USA, chlorine dioxide gas may not be transported at any concentration and is almost always produced at the application site using a ClO_2 generator. In some countries, ClO_2 solution below 3 grams per liter in concentration may be transported by land, but are relatively unstable and deteriorate quickly**[16,17]**.

At a glance the physical properties of ClO_2 are as follows**[18-21]** :

Molecular weight	67.452 g/mol
Melting point	-59^{0}C
Boiling point	11^{0}C
Vapor pressure, 0^{0}C	490 mm Hg
Solubility limit, aqueous, 25^{0}C, 34.5 mm Hg	~3 g/L
Solubility limit, aqueous, $0\text{-}5^{0}$C, 70-100 mm Hg	~20 g/L
Solubility limit, aqueous, 20^{0}C, 760 mm Hg	~70 g/L
Solubility limit, hexane, 22^{0}C	~60 g/L
Miscibility limit, liquid .aqueous	~60 g/L
Heat of formation at STP	25 Kcal/mol
Heat of vaporization STP	6.52 Kcal/mol
Heat of solution STP	6.6 Kcal/mol
Explosion velocity, pure (non aqueous) ClO_2	1,250 m/s
Explosion velocity, ClO_2 in air	50 m/s
Molar absorptivity, $E_{(360\ nm)}$	1,250 cm^{-1} M^{-1}

Large quantities of ClO_2 are produced each day in the United States[22]. Although its primary application has been the bleaching of wood pulp, it is also used extensively for bleaching and dye stripping in the textile industry and for bleaching flour, fats, oils and waxes [23]. In the United States, ClO_2 was first used in 1944 at the water treatment plant in Niagara Falls, New York, to control phenolic tastes & odors arising from the presence of industrial wastes, algae and decaying vegetation[24,25]. ClO_2 was introduced as a drinking water disinfectant on a large scale in 1956, when Brussels, Belgium, changed from chlorine to ClO_2[26]. The use of ClO_2 in water treatment leads to the formation of the by-product chlorite which is currently limited to a maximum of 1 ppm in drinking water in the USA[27]. This EPA (Environmental protection Agency) standard limits the use of ClO_2 in the USA to relatively high quality water or water which is to be treated with iron based coagulants (Iron can reduce chlorite to chloride) [28].

ClO_2 is a strong oxidant which has been given increasing attention as an alternative to chlorine for the disinfection of water and waste water. ClO_2 is an alternative for chlorine in drinking water disinfection, because it effectively inactivates bacteria and viruses over a broad p^H range[29]. ClO_2 is an oxidizing compound which is a powerful disinfecting, sterilizing and bleaching agent[23]. The known disinfecting and sterilizing agents such as chlorine, glutaraldehyde and chloramines are not as effective as ClO_2. The well established chlorine works at low pH and end reaction product is chloride[30]**.** This factor is conducive to corrosion for metallic bodies. Chlorine also produces carcinogenic trihalomethane in the presence of ammonia and organic materials present in water[31,32]. Glutaraldehyde is used as a cold sterilant to disinfect and clean heat sensitive equipments, such as dialysis instruments, surgical instruments, suction bottles, but it is not safe for those instruments and exhibits objectionable corrosive attack. The same is true for chloramines. Highly effective ClO_2 works at near neutral aqueous media and it does not react with organic materials to produce trihalomethane[32,33]. It is safe for plastic piping and exhibits no objectionable corrosive attack on copper piping[34,35].

ClO_2 is more powerful sterilizing agent and requires lower dose levels than chlorine at both low and high pH. Stream-sterilizer is also a sterilizing agent but it is not as effective as chlorine dioxide because it works at high temperature and takes longer time[36]. It cannot sterilize plastic items such as plastic test tube caps. It is not safe for many metallic and plastic materials. The required contact time for ClO_2 is lower. It works at low concentration. Therefore ClO_2 is of necessity for more superior alternative than chlorine, chloramines, glutaraldehyde and steam sterilizer[37].

ClO_2 is an emerging biocide for heat surfaces, cooling tower components and reservoir intakes[38]. It is an effective biocide at concentrations as low as 0.1 ppm and over a wide pH range. Because or its biocidal characteristics chlorine dioxide is ideal for water hygiene. It controls Legionella, and other bacteria such as Salmonella, Shigella, E.Coli, other coliforms, sessile organisms and biofilm and provides a lasting residual through out the system[38,39].The high concentration range is pertinent to the ClO_2 generator product in which species, concentration on the order of 0.001 to 1 g/L are uncounted. Dosage and residual levels of ClO_2 in drinking water supply are likely to be on the order of 1mg/L or less as is common in European water treatment. The EPA of USA recommends a ClO_2 dosage of 1mg/L because of unresolved questions regarding health effect. The National Research Councils of Safe Drinking Water Committee has recommended seven-day suggested no adverse response levels of 0.125 mg/L for each of the following species chlorate, chlorite, ClO_2, and chlorine[40].

It can also be used for air disinfection,[41] and was the principal agent used in the decontamination of buildings in the United States after the 2001 anthrax attacks[42]. After the disaster of Hurricane Katrina in New Orleans, Louisiana and the surrounding Gulf Coast, ClO_2 was used to eradicate dangerous mold from houses inundated by water from massive flooding[43]. Stabilized ClO_2 can also be used in an oral rinse to treat oral disease and malodor[44]. There are multipurpose used of ClO_2 such include water storage systems cooling towers, air conditioning units in hotels, school, apartment and commercial buildings and health care facilities including hospitals.

ClO_2 provides excellent microbiological control for food industries such as brewing, fruits, vegetables, poultry, fish, meats and dairy. ClO_2 disinfects surfaces, fume scrubbers, flume-water and packaging operations. It is widely tested and used, and approved by the appropriate regulatory agencies in the United States and elsewhere[38].

In 1940's it was used primarily to control tastes and odors, a Manganese and Iron contents of water but today it is used almost exclusive as a substitute for chlorine at the head of the plant[45]. ClO_2 as a bactericidal agent can persist in clean water at least 48 hours. Superior disinfection power has been noted in swimming pools[46]. ClO_2 is also very often used to remove Iron and Manganese from ground water[47], which are as follows:

$$ClO_2 + 5Fe^{2+} + 13H_2O \rightarrow 5Fe(OH)_3 + Cl^- + 11H^+$$

$$2ClO_2 + 5Mn^{2+} + 6H_2O \rightarrow 5MnO_2(s) + 12H^+ + 2Cl^-$$

Normal dosages of ClO_2 in the treatment of wheat flour may be as high as 20 ppm, cereals require higher such as 40 to 160 gm per 100 kg[48,49]. The principal effect sought by the use of ClO_2 in the treatment of wood pulp is its high bleaching stability. The effect is secondarily accompanied by sterilization. Lignin is considered to be the wood pulp constituent who is the most sensitive to ClO_2[46].

ClO_2 is also used extensively as a bleaching agent in the pulp and paper industry. In fact in order to minimize the environmental effects of the bleaching process, ClO_2 is rapidly becoming the chemical of choice[50]. Chlorine is also used as a bleaching agent, but it is not as effective as ClO_2 because delicate articles like silk, wool etc. are not bleached by chlorine as they are damaged by it[23].

The major advantages of using ClO_2 as a disinfection method for drinking water treatment include[51-54]:

(1) It is more effective than chlorine and chloramines against certain viruses.

(2) It oxidizes iron, manganese and sulfides, enhancing the clarification process.

(3) It can control taste and odor phenomena resulting from algae.

(4) Under proper conditions, no harmful by-products are generated.

(5) Its disinfection ability is not influenced by pH.

Disadvantages include:

(1) It must be produced in situ, using suitable generators.

(2) It decomposes in sun-light.

(3) The cost of the equipment and sodium chlorite (as raw material) are high.

Water pollution is a major problem for the third world countries including Bangladesh. Most of the people specially the rural people suffer many diseases like, dysentery, diarrhea, etc. due to drinking of contaminated water. To minimize this problem, it is necessary to take a step for the purification of water. Due to limitations of chlorine, ClO_2 is the superior alternative. However literature shows that chlorites do not convert to ClO_2 completely, and there are also side reactions producing chlorine of chlorates etc. Normally inorganic acids, organic acids and aldehydride etc. are used for this production of ClO_2 from chlorites. Pure ClO_2 has become and important question now a day. And it has become very essential to find out the obstruction, which are responsible for the 100% production of pure ClO_2. If we want to take the maximum efficiency by the use of ClO_2, the production of pure ClO_2 without any objectionable side reaction is must. And for this, we should have got the knowledge, what is happening through out the reaction and also the happenings through out the elementary steps and why we can't get the maximum conversion of chlorite into ClO_2.

There are two main sources for the production of ClO_2 from chlorate and chlorite. ClO_2 can be generated in direct-acidification generators by acidification of sodium chlorite solution. Several stoichiometric reactions have been reported for such processes[53]. Production of ClO_2 from chlorite is also mostly carried out from these sources. However commercial production of ClO_2 from chlorate needs large industrial set-up. On the other hand ClO_2 is gaseous, unstable and at high concentration may cause explosion. So storage of ClO_2 and transportation to the site of application is a big problem for the production from large industrial plant[54-56].

Production of ClO_2 from chlorite needs simple oxidation.

$$[ClO_2^- \rightarrow ClO_2 + e^-].$$

So it is much easier to produce ClO_2 from chlorite. Chlorite based ClO_2 has a wide variety of small applications in drinking water, food processing, cooling towers, pulp bleaching etc.[23]. In these areas chlorite is the preferable source for the production of ClO_2. But chlorate based ClO_2 is used only in pulp and textile fabric bleaching[57].

Sulfuric acid, lactic acid, citric acid, nitric acid are an economically attractive source of acid instead of for the production of ClO_2 from chlorite[53]. More over using hydrochloric acid the conversion rate is not up to the mark. ClO_2 shows promise of good disinfection of performance without the disadvantage of forming large quantities of undesirable halogenated by products.

In this research, the considerable reactions are given below:

$$4NaClO_2 + 2H_2SO_4 \rightarrow 2ClO_2 + 2Na_2SO_4 + HCl + HClO_3 + H_2O$$

$$2NaClO_2 + Na_2S_2O_8 \rightarrow 2ClO_2 + 2Na_2SO_4$$

$$4NaClO_2 + (CH_3CO)_2O \rightarrow ClO_2 + NaClO_3 + NaCl + 2CH_3COONa$$

$$NaClO_2 + (CH_3CO)_2O + H_2SO_4 \rightarrow ClO_2 + NaClO_3 + NaCl + Na_2SO_4 + 2CH_3COONa + H_2O$$

Beyond folks reaction have selected for high conversion rate of ClO_2 from sodium chlorite and also helpful due to others byproducts of it, does not create a hinder of ClO_2 production & estimation.

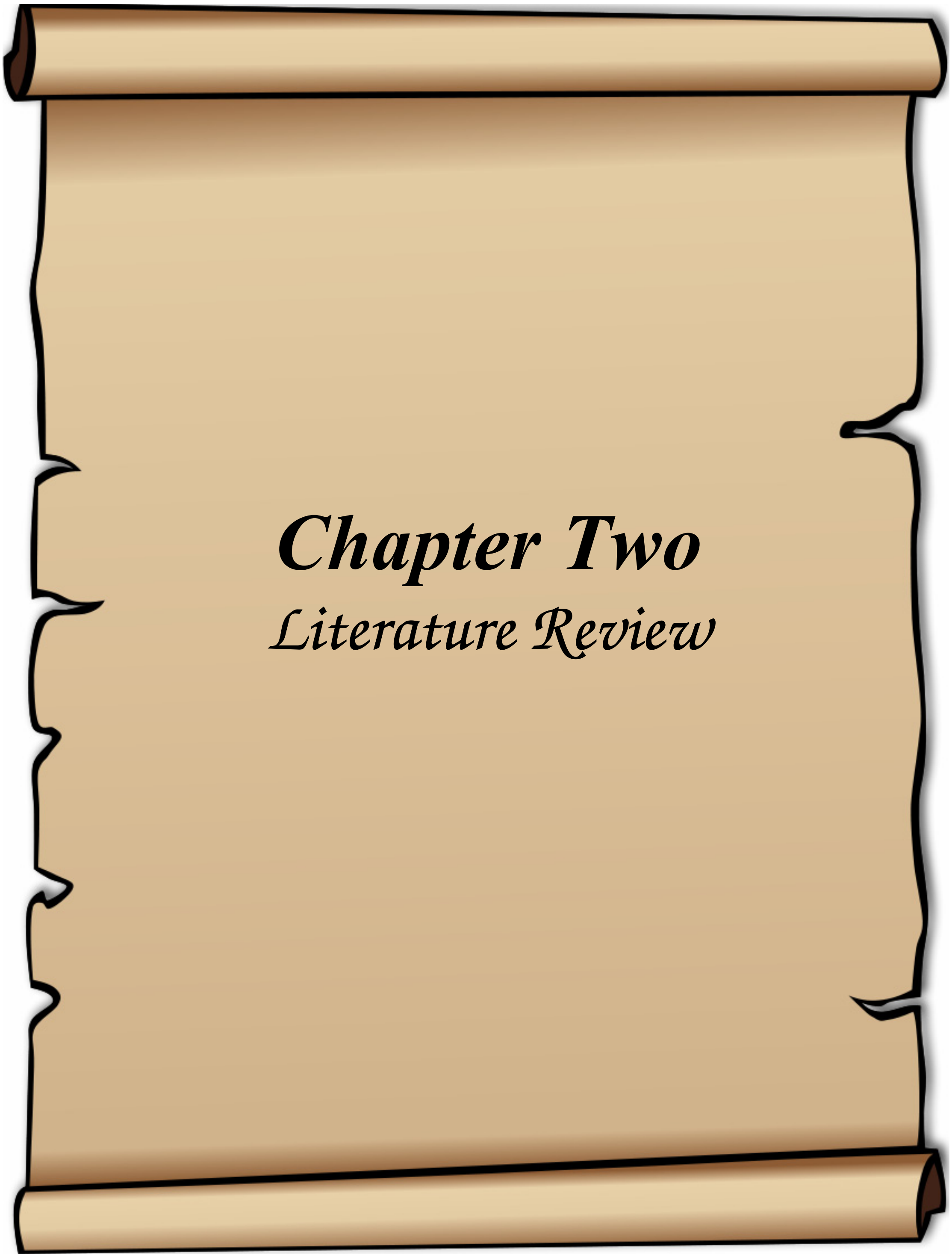
Although the manufacturing cost of ClO_2 from sodium chlorite is higher than sodium chlorate. But the main advantage derives from its each of application or from the purity of ClO_2 produced. However, research shows that chlorites do not convert to ClO_2 completely, and there are also side reactions producing chlorine, chloride, chlorate etc. Normally inorganic acids, organic acids, acetic anhydride and aldehydes etc. are used for this production of ClO_2 from chlorite. Masschelein[58] reported that the generation of ClO_2 in the laboratory is simple and fast for the reaction of $NaClO_2$ with acetic anhydride. Hydrochloric acid is not suitable because apart from producing ClO_2 it also produces substantial amount of chlorine. This fact grows an interest to carry out experiments in this research to investigate the possibility of complete conversion of chlorite to ClO_2 by using sulfuric acid, sodium per sulfate ($Na_2S_2O_8$), acetic anhydride, and a mixture of sulfuric acid and acetic anhydride also to minimize side reactions.

From the literature survey, it was apparently shown that most of the researcher used sodium chlorate as a source chlorine for the production of chlorine dioxide. Chlorine dioxide is produced by the reaction of sodium chlorate and different types of inorganic and organic acids. But commercial production of chlorine dioxide from chlorate needs large industrial set up. Sodium chlorite is an alternative and attractive source for the preparation of chlorine dioxide. The preparation of chlorine dioxide from chlorite is perfectly adapted for small and average quantities of the former. Unfortunately there is no or little research on ClO_2 production from chlorite solution so far has been reported in Bangladesh.

SCOPE AND OBJECTIVES

The study was attempted to reduce the literature gap and investigate the possibility in finding new reactants composition for the maximum production of ClO_2 from chlorite solution. The main object of the present investigation was to improve chlorine dioxide production from chlorite solution. This study also attempted to understand the reaction kinetics, reactor order and proposed chemical reactions for the generation and decomposition of ClO_2 from chlorite solution.

The effect of time and concentrations of reactants on the production of chlorine dioxide from chlorite solution was measured.



Chapter Two

Literature Review

LITERATURE REVIEW

Chlorine dioxide (ClO_2) is an oxidizing compound with powerful disinfecting, sterilizing and bleaching action[59]. The literature reports are vast as regards the most important and brilliant development of the extensive studies of the chlorine dioxide chemistry. A substantial amount of investigations are related to the chemistry of ClO_2, production of ClO_2, mechanism, uses and catalyst effect on the preparation of ClO_2 which were published as expressed bellow:

Chlorine dioxide is a very reactive species. Above –40°C it is unstable in pure form [60,61]. It undergoes explosive decomposition if its concentration exceeds 10% by volume in air[60,62]. Chlorine dioxide readily dissolves in water, but unlike chlorine, ClO_2 does not undergo a chemical reaction[60,62,63]. While at 20^0C and atmospheric pressure the solubility of chlorine is about 7 g/L that of ClO_2 is about 70 g/L[64]. Chlorine dioxide is toxic. If ClO_2 is inhaled, it can irritate the throat and lungs. The short term exposure limit for ClO_2 is 0.3 ppm (v/v). Chlorine dioxide has been retained in the reactor for up to 15 minutes without significant loss of chlorine dioxide[65]. Chlorine dioxide reacts with phenolic compounds and as a result, ClO_2 is very effective in removing phenolic tastes and odors from treated water[61]. Chlorine dioxide reacts rapidly with organic sulfides and tertiary amines. The reactions between ClO_2 and primary and secondary amines alcohols, and carbonyl compounds are slow [66,67]. It can also be used for air disinfection[68], and was the principal agent used in the decontamination of buildings in the United States after the 2001 anthrax attacks[69]. Chlorine dioxide can effectively remove Cryptosporidium cysts that are resistant to chlorine[70]. During disinfection of chlorine dioxide, chlorite and chlorate ions form as inorganic disinfection byproducts [71,72]. Due to health concerns, the maximum concentration of ClO_2 and its inorganic disinfection byproducts (DBP), chlorite and chlorate ions, are regulated by the disinfectants and disinfection byproducts Rule (DBPR)[73,74]. The current regulations set the maximum residual disinfectant concentration (MRDL) for ClO_2 at 0.8 mg/L. Oral rinses containing ClO_2 are now utilized in dental practices as a topical antiseptic for the oral cavity or for dentures[75-77].

Chlorate (ClO_3^-), Chlorite (ClO_2^-) and Chlorous acid ($HClO_2$) may be used to generate chlorine dioxide[78-81]. The reduction of chlorate is the more efficient process, and is generally used when large volumes and high concentrations of chlorine dioxide are needed. Commercial processes that are used for the pulp and paper industry in North America for large-scale production of chlorine dioxide are based on the three reactions given below[82]:

(1) $2NaClO_3 + H_2SO_4 + SO_2 \rightarrow 2ClO_2 + 2NaHSO_4$

(2) $2NaClO_3 + CH_3OH + H_2SO_4 \rightarrow 2ClO_2 + Na_2SO_4 + HCHO + 2H_2O$

(3) $NaClO_3 + H_2SO_4 + NaCl \rightarrow ClO_2 + 1/2Cl_2 + Na_2SO_4 + H_2O$

Chlorine dioxide can be produce by chemical, electrochemical and photochemical methods from chlorite solution. Several method of generating chlorine dioxide by the photochemical oxidation of chlorite has been reported[83-85]. Low concentrations of ClO_2 gas are produced by this procedure. The chlorite solution is irradiated using a light source and the chlorine dioxide generated is swept from the solution using an inert gas stream. In another method, ultraviolet light is used in conjunction with salts or hydrogen ions to produce a chlorine dioxide[86]. Nabar et al.[87] reported that the photo decomposition of sodium chlorite solutions. They found that the extent of photodecomposition decreased with the increase of pH and initial sodium chlorite concentration. Chloride ion has no effect on the photodecomposition reaction. Sodium chlorite is the preferred raw material for chlorine dioxide production in quantities less than about 2000 kg/d. This is typical for water treatment and disinfection applications and other applications not requiring high purity chlorine dioxide. Launer et al.[88] reported that at pH 2.4, (maintained with an orthophosphoric acid dihydrogen phosphate buffer) at temperature 50°C and 8×10^{-4}N sodium chlorite, even low levels of light illumination increases the rate of decomposition of cholorous acid to chlorine dioxide. The thermal decomposition products of $NaClO_2$ in the 175^0C to 200^0C temperature range are sodium chlorate and sodium chloride which are given below[78,89]:

$$3NaClO_2 \rightarrow 2NaClO_3 + NaCl$$

The electrochemical oxidation[90-95] of sodium chlorite is an old, but not well-used method for generating chlorine dioxide. Concentrated aqueous sodium chlorite, with or with-out added conductive salts, is oxidized at the anode of an electrolytic cell having a porous diaphragm-type separator between the anode and cathode compartments[96-101]. The anodic reaction is given below:

$$ClO_2^- \rightarrow ClO_2 + e^-$$

The generated chlorine dioxide must be air stripped from the anode compartment in order to achieve high chlorite conversion efficiency. Sodium ion from the anode compartment are transported into the cathode compartment with co-products sodium hydroxide and hydrogen gas which as follows[96-98]:

$$2NaClO_2 + 2H_2O \rightarrow 2ClO_2 + H_2 + 2NaOH$$

The anode often used is graphite and the cathode is copper or nickel[102]. However the iron cathode and Fe_2O_3 anode are also used[102,103]. At the working voltage of 4V with anodic current is 0.6A in an aqueous solution containing 100g/L chlorite. The chlorine dioxide produced is free of chlorine gas. Flis[104] and Hausmann et al.[105] reported that a typical patented scheme for the electrolytic production of ClO_2, Cl_2, NaOH and H_2. The most recent development is use of platinum or ruthenium oxide activated titanium anodes for the chlorite electrolysis to produce chlorine dioxide. An alternative electrochemical process producing aqueous chlorine dioxide and co-product sodium hydroxide from the in-situ acid activation of sodium chlorite has been developed[106]. New electrochemical generation technology employing high surface area anodes have also been developed for the production of chlorine free aqueous chlorine dioxide solution from dilute chlorite solution. Chlorite to chlorine dioxide conversion efficiencies have been demonstrated in a single flow-through pass with no by-product chlorate-chlorite waste streams[107-110]. Chlorite ion is oxidized by using electrochemical methods. The overall reaction that takes place in the generator is the following[72]:

$$2ClO_2^- + 2\,H_2O \rightarrow 2ClO_2 + 2OH^- + H_2$$

The advantage of the electrochemical generators is that they require only one chemical for the generation of ClO_2. These generators are well suited for the generation of low amounts of ClO_2, for example for the generation of ClO_2 in the laboratory. Mild alkaline solutions of sodium chlorite are stable for periods up to a year, and even with prolonged boiling no decomposition occurs if light is excluded[111,112]. In hot, strongly alkaline solution, chlorine dioxide is not formed but chlorate ion is the principal product of the decomposition[113,114]. As the pH is lowered, the chlorite solution becomes less stable. Neutral solutions of sodium chlorite are reasonably stable if they are kept away from light and heat, but the solution will decompose slowly if heated[87,112,113,115]. As in the case of the alkaline solution, the decomposition of a neutral solution of the chlorite produces no chlorine dioxide, only chlorate ion and chloride ion are formed[112,114,116]. In contrast to alkaline or neutral solutions, solutions of acidic chlorite decompose at measurable rates, and the rate generally increases with decreasing pH[86,87,112,117-120] and increasing temperature[87,112,116,118,121]. The products of the decomposition reaction of chlorite are chlorate ion, chlorine dioxide and chloride ion. Kieffer et al.[118] observed that the relative amount of chlorine dioxide formed decreases as the hydrogen ion concentration is decreased form 2.0 to 0.49N. As the hydrogen ion concentration is further decreased to 10^{-3}N, relatively more chlorine dioxide is produced.

Chlorine dioxide[122,123] was the main product in the decomposition of sodium chlorite in acetic acid-sodium acetate buffer over the entire pH region studied (pH 2-7), but less chlorine dioxide was formed as the pH was decreased. No chlorate ion was found above pH 5, but below this pH its formation becomes increasingly important. The rate of disproportion of acidified chlorite solutions varies with the pH. The reaction is very slow at a pH greater than 4. Less than 10^{-5}N chlorine dioxide is formed in 2 hour if the initial sodium chlorite concentration is 3 x 10^{-3}N. Only if the pH is less than 3 more than 1% of the sodium chlorite decomposes within 10 minutes[116]. Nakamori et al.[124] reported that the stoichiometry is independent of the acid used to acidify the chlorite solution. Neither the addition of chlorate ion nor chlorine dioxide affects the stoichiometry. The acidification of sodium chlorite, at moderate acid pH 5 up to 6 to generate chlorine dioxide gas, has a mechanism as follows[125]:

$$5NaClO_2 + 4H^+ \rightarrow 4ClO_2 + 4Na^+ + Na^+Cl^- + 2H_2O$$

Kim et al.[126] reported that the production and stability of chlorine dioxide from sodium chlorite in organic acid solutions and its effectiveness in killing bacillus cereus spores.

They suggested that the amount of ClO_2 produced is higher as the concentration of sodium chlorite is increased and as the pH of the organic acid solutions is decreased. However, the stability in production of ClO_2 is enhanced by increasing the pH of the organic acid solutions.

Chlorite ion can be proton to form chlorous acid, which undergoes a self-decomposition reaction[127]. Chlorous acid is a weak acid but its pure substance is unstable, with degradation to chloride, chlorate and chlorine dioxide[121,128-133]. This reaction is catalyzed by chloride ion. In low pH solutions, chlorous acid decomposes into chlorine dioxide and chlorate ion. Chloride ion has both inhibiting and accelerating effects on the formation of chlorine dioxide from chlorous acid[121]. The rate of formation of chlorine dioxide from chlorous acid goes through a maximum at around pH 2 according to the following reactions[116]:

$$H^+ + ClO_2^- \rightarrow HClO_2 \qquad (pKa = 1.72) \text{ ---------(A)}$$

$$4HClO_2 \rightarrow 2ClO_2 + ClO_3^- + Cl^- + 2H^+ + H_2O \text{ ------------- (B)}$$

$$5HClO_2 \rightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O \text{ -----------------------(C)}$$

There was reported[127,128] equation (B) describes the uncatalyzed reaction and equation (C) describes the chloride ion catalyzed decomposition reaction. Because the uncatalyzed reaction produces chloride ion, the catalyzed pathway becomes significant as the reaction proceeds. A problem with acid-based generators is that chlorate ion is produced. Another shortcoming of this method is that part of the chlorite ion is converted to chloride or chlorate ions. Barnett[134] and Taube[85] were proposed a mechanism involving HOCl, Cl_2O_2, and Cl_2 as intermediates for the disproportionation of chlorous acid. In the absence of chloride, the reaction is controlled by two simultaneous processes given below:

$$2HClO_2 \rightarrow H^+ + HOCl + C1O_3^-$$

and

$$HClO_2 + CIO_2^- \rightarrow HOCl + ClO_3^-$$

Chloride has a catalytic effect and an inhibiting effect as well on the formation of chlorine dioxide.

Bandi[135] and Beuermann[136] investigated the reaction of hydrochloric acid with sodium chlorite. They reported that, in the range 0.3 to 1.5N $NaClO_2$, the rate constant of the reaction depends only on the concentration of hydrochloric acid and the stoichiometry is as follows:

$$NaClO_2 + HCl \rightarrow HClO_2 + NaCl$$

$$5HClO_2 \rightarrow 4ClO_2 + HCl + 2H_2O$$

At pH <0.5 the reaction was complete within 5 minutes but at pH> 1 the reaction was not complete even after 60 min. Yields of 100% chlorine dioxide could be obtained by optimizing the hydrochloric acid and sodium chlorite concentrations, reaction time, and temperature. It has been reported[112] that sodium chlorite reacts with concentrated hydrochloric acid to produce chlorine and chlorine dioxide. Glabisz et al.[137] proposed that the decomposition of chlorite in concentrated hydrochloric acid proceeds according to the reaction:

$$ClO_2^- + H^+ \Leftrightarrow HClO_2$$

$$HClO_2 + 3H^+ + 3Cl^- \Leftrightarrow 2Cl_2 + 2H_2O$$

Kepinski et al.[138] indicated that with 0.1N $NaClO_2$ and 5.0N HCl the decomposition of chlorite is complete within 1 min but no chlorine is detected. Beuermann[136] found that only small amounts (ca. 2%) of chlorine were produced when hydrochloric acid reacted with sodium chlorite. If any chlorine were formed it would react immediately with chlorite, since the chlorite-chlorine reaction is known to be rapid in an acidic solution. The addition of a strong inorganic acid into an aqueous sodium chlorite solution produces chlorous acid, which rapidly disproportionate into chlorine dioxide. One proposed set of reaction using hydrochloric acid is given below[139]:

$$NaClO_2 + HCl \rightarrow HClO_2 + NaCl$$

$$HClO_2 + 3HCl \rightarrow 2Cl_2 + 2H_2O$$

$$4NaClO_2 + 2Cl_2 \rightarrow 4ClO_2 + 4NaCl$$

Yielding the overall reaction as follows:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$$

Masschelein et al.[140] proposed a net secondary reaction path produces by-product chlorate is as follows:

$$4NaClO_2 + 2HCl \rightarrow 2ClO_2 + NaClO_3 + 3NaCl + H_2O$$

Chlorine dioxide is produced from the oxidation of sodium chlorite by hypochlorous acid (HOCl). Hypochlorous acid is prepared by combining solutions of sodium hypochlorite and hydrochloric acid which as follows[141]:

$$2NaClO_2 + NaOCl + 2HCl \rightarrow 2ClO_2 + 3NaCl + H_2O$$

Chlorine dioxide is produced by the acidification of sodium chlorite solution with sulfuric acid according to the following reaction[141]:

$$4NaClO_2 + 2H_2SO_4 \rightarrow 2ClO_2 + HCl + HClO_3 + 2Na_2SO_4 + H_2O$$

Mussari et al.[142] reported above the reaction only 50% chlorite was converted to chlorine dioxide. Chlorine dioxide is removed from the reaction flask solution as gas by air stripping, purified by scrubbing with sodium chlorite solution and recovered by absorbing in chilled deionized water. It was reported[141,143] that chlorine dioxide can be prepared by mixing sodium hypochlorite bleaching solution with sodium chlorite and an acid which as follows:

$$2NaClO_2 + NaOCl + H_2SO_4 \rightarrow 2ClO_2 + NaCl + Na_2SO_4 + H_2O$$

The reaction with sulfuric acid as shown in the above reaction produces the highest purity of chlorine dioxide. White et al.[114] proposed the above reaction could take place in the following way firstly chlorite was converted to chlorous acid, and then the chlorous acid converted to chlorine dioxide in a manner analogous to that which occurred in the hydrochloric acid conversion, where 5 molecules of chlorous acids yield 4 molecules of chlorine dioxide, with one chlorous acid reverting to chloride, this reactions are as follows:

$$2NaClO_2 + H_2SO_4 \rightarrow 2HClO_2 + Na_2SO_4$$

$$5HClO_2 \rightarrow 4ClO_2 + HCl + 2H_2O$$

Lenzi et al.[144] made an extensive study of the byproducts reaction between chlorate ion and chloride ion in strong sulfuric acid solutions. They found that the rate of formation of chlorine dioxide is second order with respect to chloride ion. The order of reaction with respect to chlorate ion changes with acidity being approximately first order at high acidity and second order at low acidity.

The chemistry of sulfuric acid conversion is reported to give only 50% conversion of chlorite to chlorine dioxide. While chloride is a by-product of this reaction and would be expected to catalyze conversion and change the chemistry to that yielding 80% conversion, the concentration of by-product chloride is apparently insufficient to effect significant catalysis in the brief time the reactants would remain in the reaction chamber before injection into dilution water. Concentrated sulfuric acid cannot be combined directly with chlorite, as it reacts too violently and generates a significant amount of heat, which lends to volatilization of produced chlorine dioxide and possible damage to plastic generation equipment[71].

Chlorine dioxide yields from chlorite by acidification using sulfuric acid generally does not exceed about 60-70% of the theoretical 80% molar yield[114]. The methods using hydrochloric acid give increased conversion yields because of the presence of chloride ion. The acid-chlorite generating systems are commonly used in very small-scale operation for convenience.

The oxidation of chlorite with per-sulfate is well adapted to the laboratory generation of chlorine dioxide[145]. No acid is produced in the reaction and, for this reason, the formation of chlorine need not to be feared. Masschelein[146] pointed out that per-sulfate oxidized sodium chlorite according to the following reaction:

$$2ClO_2^{-} + S_2O_8^{2-} \rightarrow 2ClO_2 + 2SO_4^{2-}$$

Hefti[122] studied the decomposition of a sodium chlorite solution in an acetic acid sodium acetate buffer. As 95°C with 0.2N buffer, the decomposition reaction was slow at pH 5 to 7, but below pH 5 the reaction was fast. Hemker et al.[147] reported a method for point-of-use generation of chlorine dioxide wherein sodium chlorite is oxidized with sodium persulfate in an aqueous reaction mixture. According to them, the molar ratio of sodium chlorite and sodium persulfate is 1:2 or smaller should be avoided because they decrease the reaction rate. The generation reaction of chlorine dioxide from sodium chlorite with sodium persulfate is provided below[148]:

$$2NaClO_2 + Na_2S_2O_8 \rightarrow 2ClO_2 + 2Na_2SO_4$$

It was reported[146,149] the production of chlorine dioxide by the reaction of an aldehyde with aqueous chlorite solutions at neutral or slightly acidic pH according to the reaction:

$$H^+ + RCHO + 3ClO_2^- \rightarrow 2ClO_2 + RCO_2^- + Cl^- + H_2O$$

Subsequent examination of this reaction has indicated that the proper stoichiometric reaction most likely is as follows:

$$4NaClO_2 + (CH_3CO)_2O \rightarrow 2ClO_2 + NaClO_3 + NaCl + 2CH_3CO_2Na$$

The rate of acidified chlorite decomposition was increased four times by decreasing the buffer concentration from 0.1N to 0.5N.

Chlorine reacts rapidly with acidified or neutral solutions of chlorite ion to form chlorine dioxide. In alkaline solution, the reaction is very slow[86,150,151]. There were initiated that relatively more chlorate ion and less chlorine dioxide formed as the solution was made more basic. There was reported[112] that in the pH 8 to 10 region, chlorination is the predominant product but at pH 4 chlorine dioxide is the main product. It has been observed generally that, as the hydrogen ion concentration increases, the relative amount of chlorine dioxide produced also increases. High concentrations hydrogen and chloride ions favor the formation of relatively more chlorine. Emmenegger et al.[150] noted that with chlorite in excess there was a marked improvement in the production of chlorine dioxide. In another series of experiments where the ratio of chlorite and hypochlorite ion was 1:2 and 1:4, the chlorine dioxide that was immediately formed disappeared with time; and the chlorate concentration increased, such that with hypochlorous acid in excess, the entire chlorine dioxide was eventually converted into chlorate ion. Gordon et al.[152] reported the preparation of chlorine dioxide by reacting aqueous sodium chlorite with chlorine. There is report for the production of chlorine dioxide by the reaction of chlorite with chlorine according to the following reaction:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl.$$

Hypochlorous acid-chlorite system, chlorine gas is extract into water forming a hypochlorous acid solution which then reacts with aqueous sodium chlorite to produce chlorine dioxide**[153-155]**. Hypochlorous acid, formed from the disproportionation of chlorine gas in water reacts with sodium chlorite to produce chlorine dioxide as follows:

$$Cl_2 + H_2O \Leftrightarrow HOCl + HCl$$

$$2NaClO_2 + HOCl + HCl \rightarrow 2ClO_2 + NaCl + H_2O$$

Chlorine dioxide yield from chlorite is 95% or higher in properly operated systems. Excess hypochlorous acid is commonly used to achieve a high conversion. High purity chlorine dioxide gas (7.7% in air or nitrogen) can be produced by the gas-solid method, which reacts dilute chlorine gas with solid sodium chlorite according to reaction**[98]**:

$$2NaClO_{2(S)} + Cl_{2(g)} \rightarrow 2ClO_2 + 2NaCl$$

It was reported that in the laboratory, ClO_2 is prepared by oxidation of sodium chlorite. Hicks**[156]** reported that chlorine gas reacts directly with a concentrated sodium chlorite solution under a vacuum and chlorine dioxide gas is removed from the reaction chamber using a water-based extract. The reaction has a 100% theoretical molar conversion of chlorite to chlorine dioxide.

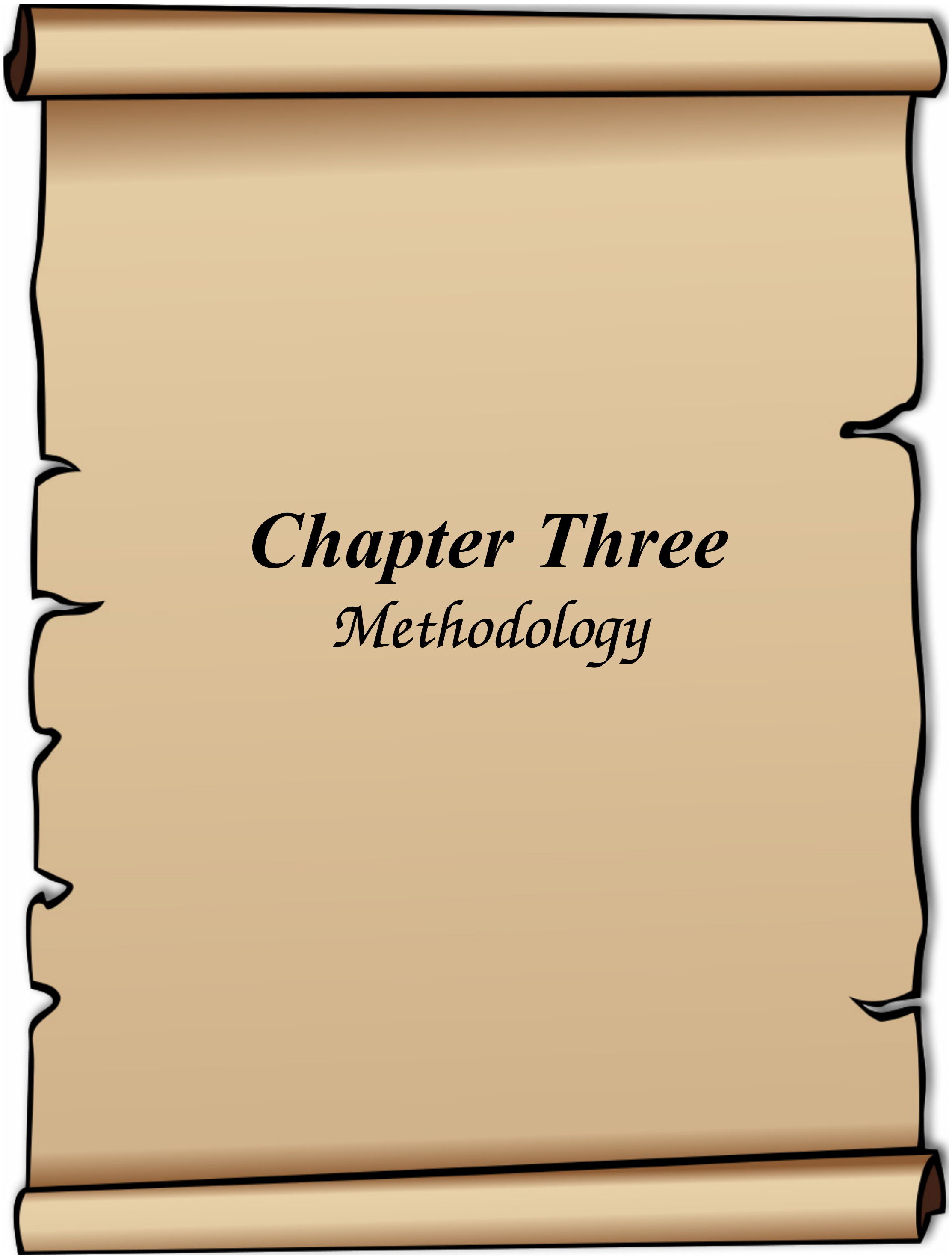
Sodium chlorite can be oxidized by ozone to form chlorine dioxide under acidic conditions, but the generated chlorine dioxide has a competing reaction with excess ozone to form chlorate according to the following reactions**[139,157]**:

$$2NaClO_2 + O_3 + H_2O \rightarrow 2ClO_2 + 2NaOH + O_2$$

$$2ClO_2 + O_3 + H_2O \rightarrow 2ClO_3^- + O_2 + 2H^+$$

Chlorine dioxide is generated from an aqueous solution of sodium chlorite in the presence of a catalyst having a reduced rate of deactivation. According to the experiment

[158], the catalyst is preferably a Pd/Al_2O_3 or palladium and another platinum group metal (e.g., PdPt/ Al_2O_3) or palladium and a Group IB metal (e.g., PdAu/ Al_2O_3) catalyst containing La_2O_3 and Nd_2O_3 which has increased the formation of chlorine dioxide from chlorite solution and a slower rate of deactivation. Daniel[159] suggested that the catalyst is preferably palladium, or palladium together with another platinum group metal (e.g., Pd+Pt), or palladium together with a Group IB metal (e.g., Pd+Au) or a Group IIA carbonate salt (e.g., $CaCO_3$) or a magnesium salt that can be converted to MgO for the generation of chlorine dioxide from chlorite solution. Ionnalagadda et al.[160] reported that Ru(III) or $RuCl_3$ used as a catalyst for the generation of chlorine dioxide from chlorite ions. According to them, the rate of disproportion of acidic chlorite was dependent on the catalyst concentration and indicating that for the catalyzed reaction, the orders with respect to chlorite and H^+ are also first-order.



Chapter Three

Methodology

METHODOLOGY

3.1. Introduction

The analytical chemistry of chlorine dioxide, especially in solution, is complicated by chlorine dioxide's sensitivity to light and instability over time, complex chlorine chemistry and interference from related redox species[161]. Attempts have been made to determine chlorine dioxide by different methods, such as spectrophotometric, colorimetric, iodometric titration, amperometric titration, potentiometric titration and gas chromatographic method etc.[162-167]. All of these methods have advantages and disadvantages, and many are not selective in the presence of other oxychlorine species. Methodology section of this chapter reviews the literature reports on the estimation of chlorine dioxide with emphasis on spectrophotometric and iodometric methods.

3.2. Spectrophotometric Method

Chlorine dioxide has a relatively wide absorbance spectrum in the UV-visible region. The spectrum is observed in the range between 240 to 440 nm, having the maximum absorbance at 360 nm[168-171]. It has been reported[172] that the molar absorptivity of ClO_2 solutions is 1250 $mole^{-1}cm^{-1}$ at 360 nm, and it is independent of temperature in the range 25°C to 50°C, chloride ion concentration up to 0.3N, and hydrogen ion concentration in the range of 0.2N to 4N. Hong et al.[173] reported that chlorine dioxide in aqueous solution has an absorption maximum at 360 nm with a high molar absorptivity. Another investigation[174] reveals that the molar absorptivity of chlorine dioxide has only a slight variation with the acidity of the medium, and remains unchanged in the presence of chloride ion, chlorate ion and chlorine. Kortvelyesi[175] reported that the concentration range of ClO_2 that can be determined in a 1 cm cell at 360 nm is from 2.7 mg/L to 108 mg/L. By using different path length cells 10 cm to 0.1 cm, the range can be extended from 0.27 mg/L to 1080 mg/L. High ClO_2 concentrations are generally measured at higher wavelengths than 360 nm. This wavelength can be as high as 450 nm or even 500 nm, because in this region the molar absorptivity of ClO_2 is low. According to these report wavelengths of the maximum molar absorptivities of the various chlorine species are hypochlorous acid at 235 nm, chlorite ion at 260 nm, hypochlorite ion at 292 nm, chlorate ion at 225 nm and ClO_2 at 358 nm. This reveals that there may be negligible effect of other oxychlorine species for the estimation of chlorine dioxide at 360 nm. Crawford[176] observed that the spectrophotometric measurement of ClO_2 at higher wavelengths was grossly inaccurate in the presence of high concentrations of chlorite ion due to $Cl_2O_4^-$ complex formation between chlorine dioxide and chlorite ion. The absorption spectrum of this complex slightly overlaps with the spectrum of ClO_2 and is shifted to longer wavelengths. This indicates that above about 400 nm, the $Cl_2O_4^-$ complex has higher molar absorptivity than that of ClO_2. However, in the presence of high concentration of chlorite ion the absorption of chlorine dioxide will be lower at 360 nm due to formation of $Cl_2O_4^-$ complex at the expense of ClO_2. Farr and Mustafa[177] have also reported that chlorite ion produces interference in the spectrophotometric estimation of ClO_2 at 360 nm especially when the concentration of ClO_2^- is three times or higher than the concentration of chlorine dioxide. At this wavelength there is no or negligible interference from chlorite, chlorate and chloride ions. According to them the typically encountered interferences from chlorine (free and combined) generally found in potable water are not the problem in the spectrophotometric estimation of ClO_2. Watanabe et al.[178] have been reported that in spectrophotometric estimation of ClO_2 at 360nm the concentrations of chlorine up to 10 mg L^{-1} has no or negligible effect. It has been reported[73,179] that estimation of ClO_2 at 360 nm from a mixture of free available chlorine (FAC) (e.g. elemental chlorine, hypochlorous acid and hypochlorite ion) and ClO_2 solution FAC has no interference up to 6 mg/L, and even concentration higher than this has negligible interference. Literature report[180] reveals that the spectrophotometric measurement presents a simple, fast, and reliable method for measuring ClO_2 concentrations in a wide range. This method can be used for measuring a variety of samples, for example measuring ClO_2 concentration in the field or for measuring it in the generator effluent. A general problem with ClO_2 analytical methods is that it is volatile and highly reactive in nature. Nonetheless spectrophotometric method is relatively free of interferences, easy to perform, and accurate (if the correct molar absorptivity is used). Rapid determination of ClO_2 is necessary in the kinetic measurements due to the fast decomposition of chlorine dioxide to other chlorine species[181]. Spectrophotometric measurements are normally used to follow the concentration changes during the kinetic studies as this method can be used to determine changes in the concentration rapidly.

3.3. Iodometric Titration Method

Aieta et al.[182] have reported a detailed method for the iodometric estimation of ClO_2 and other oxychlorine species in the solution. Chlorine dioxide can be measured by indirect iodometric titration method at pH 7 .This method is not able to distinguish the two FAC species (HOCl and OCl^-) from each other .There are reports[183,184] on simplified methods for the iodometric estimation of ClO_2, chlorite ion, and chlorine present in the aqueous solution. The indirect iodometric titration method deals with the titration of iodine liberated in chemical reaction of ClO_2 with iodide solution. ClO_2 and other oxychlorine species oxidize iodide salts to liberate iodine. The gaseous iodine reacts with excess iodide in the solution to from highly soluble tri-iodide according to the reaction:

$$I_2\,(aq) + I^- \rightarrow I_3^-$$

Iodine in turn is titrated with standard sodium thiosulfate ($Na_2S_2O_3$) solution using starch as indicator and ClO_2 is estimated following the procedure given elsewhere[24]. This method is very useful for measuring different chlorine species in aqueous medium because iodine liberation is pH dependent oxidation of iodide by individual chlorine species. Clesceri et al.[185] have reported pH dependent oxidation of potassium iodide to selectively distinguish various oxychlorine species from each other. Another report[182] shows the reaction of the oxy-chlorine species with aqueous iodide ion at various pH buffered conditions as:

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^- \qquad \text{pH } 7.2, <0.1$$

$$2ClO_2 + 2I^- \rightarrow I_2 + 2ClO_2^- \qquad \text{pH } 7.$$

$$2ClO_2 + 10I^- + 8H^+ \rightarrow 5I_2 + 2Cl^- + 4H_2O \qquad \text{pH } 2, <0.1$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow 2I_2 + Cl^- + 2H_2O \qquad \text{pH } 2, <0.1$$

$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O \qquad \text{pH } <0.1$$

Chlorine and chlorine dioxide react with iodide at pH 7 to liberate iodine and therefore are estimated together. After this the pH of the solution is lowered to 2 so that chlorite ion and ClO_2 oxidize iodide ion to iodine and these are estimated together. For the next step, a new sample is used with the pH adjusted to 7. Chlorine dioxide and the volatile portion of chlorine are purged by nitrogen gas from this sample. The sample is titrated to the end point to remove any remaining chlorine. The sample pH is lowered to 2 and in this case only chlorite ion is estimated. If chlorate ion is also present a new sample is used, and its pH is lowered to about 0.1 by using concentrated HCl. At this pH all chlorine species (free available chlorine, ClO_2, chlorite ion, chlorate ion) react with iodide ion.

Farr and Mustafa[177] reported that at pH 7 only chlorine or hypochlorous acid interfere with the chlorine dioxide estimation. This can be overcome by two separate titrations. The first titration carried out on a pH 7 buffered samples determines combined chlorine and chlorine dioxide. For the second titration the sample pH is raised to 12.5 and held for 10 minutes, at which point ClO_2 disproportionate according to the reaction:

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O.$$

It was reported[184,186] that chlorite reacts with potassium iodide only slowly at pH 7; hence, it interferes only slightly in the determination of chlorine dioxide. However, no interference was observed in the titrometric determination in the presence of as high as 10 times higher levels of chloride, chlorate and perchlorate ions individually or combined[177]. Wheeler et al.[187] explore this chemistry in an attempt to find a specific analytical reagent for ClO_2, and developed chlorophenol red (CPR), a pH indicator, as a selective titrant for chlorine dioxide. This reagent was proposed for the rapid and direct determination of as low as 0.05 mg/L of ClO_2 in the presence of other active chlorine compounds and commonly occurring oxidizing agents. Reports[175] show that iodometric measurements made it possible to determine the concentration changes of all three species (FAC, ClO_2, and chlorite ion) in the aqueous solution. Further kinetic studies were performed by following the changes in the concentrations of the various species by iodometric titration. Eaton et al.[167] and Gordon et al.[188] suggested that iodometric titrations could be performed based on utilization of the pH dependent reactivity of the various chlorine species. Harp et al.[189] reported estimation of all chlorine species on the bass of oxidation of iodide to tri-iodide ion. Potential sources of errors related to the iodide / tri-iodide reaction include: (i) air oxidation of the iodide reagent,

(ii) volatilization of produced iodine, (iii) iodine or iodated contamination in the iodide reagent and (iv) consumption of tri-iodide by sample components

In sprite of this the iodometric method is the most suitable titration method for the estimation of chlorine dioxide in the presence of other oxychlorine species.

3.4. Colorimetric Method

This method is generally based on the reaction between ClO_2 and a dye that results in a decrease in the absorbance of the dye. Due to this reaction, colorimetric methods can be selective for the measurement of ClO_2[190,191]. It has been reported[192] that colorimetric method has higher sensitivity in addition to selectivity. It was reported[167,190] that chlorophenol red (CPR) was specific for the estimation of chlorine dioxide without interference from chlorine. The colorimetric estimation of chlorine dioxide by CPR was also suggested by Farr and Mustafa[177]. The United States Environmental Protection Agency[193] (US EPA) has developed a new colorimetric method for the measurement of ClO_2 and chlorite ion. This method is based on the decolorization of the dye Lissamine Green B (LGB) by ClO_2. It was reported[194] that the variety of existing suitable reagents for colorimetric analyses led to the considerable number of analytical procedures. Most of the published works are based on color-fading oxidation reactions of dyes with chlorine dioxide.

In one report[195] for the estimation of ClO_2 was based on the decolorization of the dye amaranth measured at 522 nm. The response was linear in the 0.1 to 1.0 mg/L concentration range. Amaranth method is selective for measuring ClO_2 in the presence of free available chlorine (FAC). This method has a good selectivity and the detection limit is considerally low. Acid chrome violet potassium salt (ACVK) method[196-198] was used for the estimation of ClO_2. In this method no interference was observed from free or combined chlorine, chlorite and chlorate ions. The problem with this method is the complicated reagent preparation.

The colorimetric method requires strict control of pH, temperature and reaction time and will be affected by turbidity[189]. In addition, the selectivity of the indicator for chlorine dioxide is questionable. But this method can not fully satisfy the estimation of chlorine dioxide.

A significant problem of the colorimetric methods is the purity of the dyes[175,199]. The purity of these dyes can be as low as 40-50% or as high as 90-95%. Furthermore, the stability of the dye either in the solid form or in the reagent can be influenced by the impurities.

3.5. Amperometric Titration Method

Amperometric titration[200] is an electrochemical technique that measures the current (amperes) at a constant voltage. As titrant is added to the titration cell, the current will change based on a series of chemical reactions. When complete reaction is attained, a constant current is recorded and the end point is reached. Aieta et al.[201] reported the use of amperometric titration for the determination of chlorine dioxide, chlorine, chlorite, and chlorate water disinfection by chlorine dioxide. The amperometric analysis of ClO_2 estimation is analogous to the iodometric method with the exception in the amperometric analysis, phenyl arsine oxide (PAO) is the titrant instead of sodium thiosulfate as used in the iodometric method[202]. The difference between the results obtained by two methods is not significant. Desai[203] revealed that the amperometric titration method was more cumbersome and time-consuming for the estimation of chlorine dioxide.

The titration can be usually carried out rapidly, since the end point is found graphically and a few current measurements at constant applied voltage before and after the end point suffice[204,205]. In this method, other oxychlorine species have interferences in the determination of chlorine dioxide, so it is not suitable for the determination of ClO_2 in the mixture of oxychlorine species.

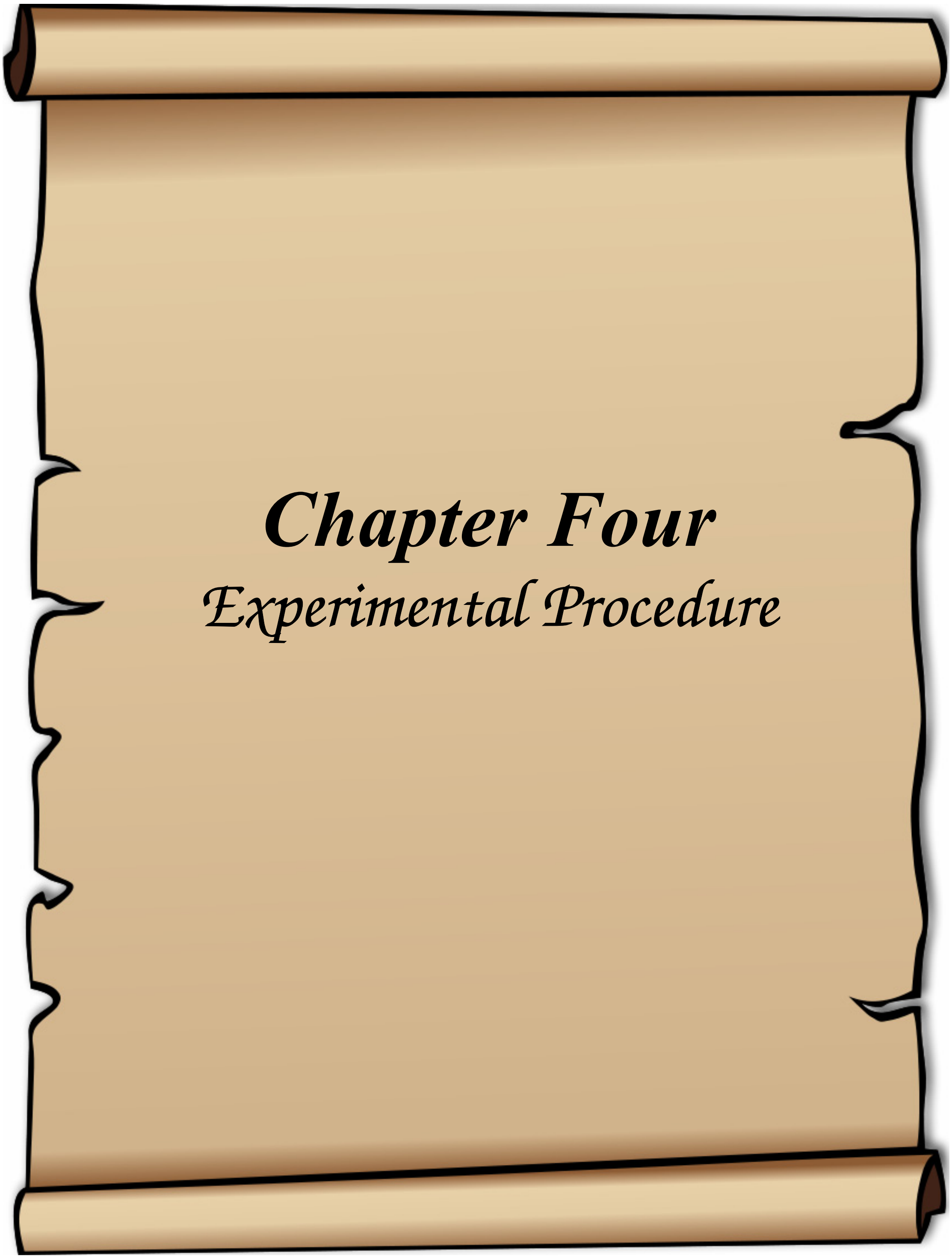
3.6. Potentiometric Titration Method

Prince[206] and Barbolani et al.[207] reported that the estimation of chlorine dioxide, chlorite, chlorate and chlorine in water by the potentiometric titration. A potentiometric titration[208] is one in which the end-point is detected by measuring the change in potential of a suitable electrode during the titration. It is a technique similar to the direct titration of a redox reaction. However no indicator is used, instead the voltage across the analyte, typically an electrolyte solution, is measured. To do this, two electrodes are used, a neutral electrode and standard reference electrode. The voltage is recorded at intervals as the titrant is added. A titration is the use of carefully measured amounts of a known solution to determine the concentration of other. There were reports[209-212] of the determination of chlorine dioxide and oxychlorine species by potentiometric method. The advantages of potentiometric titration are that it gives a sharp end-point in every case and it is easy to handle[213]. The main disadvantage of this method is its high temperature dependent.

3.7. Gas Chromatographic Method

This method has been used for measuring chlorine and chlorine dioxide in gases[214]. It was reported[215] as an adjunct to the determination of chlorine dioxide in the paper chromatographic separation of chloride and oxyanions of chlorine from one another. Shin et al.[216] reported the development of a sensitive gas chromatographic method for the determination of chlorine dioxide in water. Richardson et al.[217] reported identification and estimation of chlorine dioxide disinfection byproducts in drinking Water by using gas chromatography method.

In this study, all common methods of chlorine species analyses display some lack of specificity and are not adequately selective to be completely free of interferences. For above of the problem we considered to be iodometric titration and spectrophotometric method for the analysis of various chlorine species. In addition to the selectivity, the sensitivity and suitability of spectrophotometric method is also higher than that of others method for the determination of very high or very low concentrations of ClO_2.



Chapter Four

Experimental Procedure

EXPERIMENTAL PROCEDURE

4.1. Introduction

Chlorine dioxide was prepared by reacting aqueous sodium chlorite (80% purity) solution with sulfuric acid or sodium persulfate or acetic anhydride. Effect of reactant concentrations, their relative ratios, pH and time were investigated on the percentage productions of chlorine dioxide. Reaction rate was followed and mechanism of chlorine dioxide production was determined. The quantitative estimation of chlorine dioxide and other oxychlorine species was made by iodometric titration and UV pectrophotometric method. This chapter has been divided into the following sections:

i) Used Chemical, their sources and specifications.
ii) Preparation of solutions.
iii) Standardization of sodium thiosulfate solution by potassium dichromate.
iv) pH measurement.
v) Generation of chlorine dioxide from chlorite solution.
vi) Determination of chlorine dioxide by iodometric titration method.
vii) Prepared standard curve by UV spectrophotometer.
viii) Analysis of chlorine species in the sample.

4.2. Chemicals Used, Sources and Specification

The purity of chemicals used in this investigation and their sources are as follows -

Chemicals	Sources	Purity
Sodium chlorite	BDH limited Poole (England)	About 80%
Nitric acid	BDH limited Poole (England)	67.71%
Hydrochloric acid	BDH limited Poole (England)	35-38%
Potassium iodide	BDH limited Poole (England)	99%

Sodium thiosulfate	BDH limited Poole (England)	99%
Potassium Dichromate	Peking Chemical (China)	99.8%
Sulfuric acid	E. Merck (Germany)	98%
Starch soluble	E. Merck (Germany)	
Disodium hydrogen Phosphate	E. Merck (Germany)	99%
Potassium dihydrogen Phosphate	E. Merck (Germany)	99.5%
Sodium persulfate	E. Merck (India)	98%
Acetic anhydride	E. Merck (India)	98%
Sodium bicarbonate	E. Merck (India)	99.5%
Silver nitrate	E. Merck (Germany)	98%
Sodium chloride	E. Merck (India)	99.5%
Sodium bicarbonate	E. Merck (India)	99%

4.3. Preparation of Solutions

4.3.1. Preparation of sodium chlorite solution

Sodium chlorite was 80% pure. Impurities were taken into calculation in the preparation of sodium chlorite solution.

Exactly 11.304 g sodium chlorite was weighed out in 500 mL volumetric flask and made up to the mark with distilled water to prepare 0.2N solution. This was considered as the stock solution for the preparation of different concentration of solution.

12.5, 62.5 and 125 mL portions of the stock solution of sodium chlorite were taken in three different 250 mL volumetric flasks. The flasks were then made up to mark with distilled water and the solution was mixed thoroughly after shaking well to prepare 0.01, 0.05 and 0.1N sodium chlorite solution.

4.3.2. Preparation of H_2SO_4 solution

Accurately 6.94 mL concentrate H_2SO_4 (98% purity, sp.gr. 1L=1.84 kg) was taken in 250 mL volumetric flask and distilled water was added up to the mark to prepare 1N stock solution of H_2SO_4.

5, 25, 50 and 100 mL portions of the above solution of sulfuric acid were taken in four (4) different 250 mL volumetric flasks. The flasks were then made up to mark with distilled water with well shaking to prepare 0.02, 0.1, 0.2 and 0.4N sulfuric acid (H_2SO_4) solution.

4.3.3 Preparation of HCl solution

Accurately 51.8 mL of concentrate HCl (1L=1.84 kg and 37%) was taken in 250 mL volumetric flask and up to the mark with distilled water to prepare 2.5N HCl.

4.3.4. Preparation of $Na_2S_2O_8$ solution

Sodium persulfate was 80% pure and molecular weight was 238.09. Impurities were taken into calculation in the preparation of persulfate solution.

Exactly 31.328 gm of sodium persulfate was weighed out in 250 mL volumetric flask and made up to the mark with distilled water to prepare 1.0N solution. After 1, 5, 10, 20 and 40 mL portions of the above solution of sodium persulfate were taken in five different 100 mL volumetric flasks. The flasks were then made up to mark with distilled water and the solution was mixed thoroughly after shaking well. The flasks were then contained 0.01, 0.05, 0.1, 0.2 and 0.4N of sodium persulfate solution.

4.3.5. Preparation of 0.01N sodium thiosulfate solution

Sodium thiosulfate ($Na_2S_2O_3 . 5H_2O$) is obtainable in a state of high purity, but there is always some uncertainty as the exact water content, because of the efflorescence nature of the salt and for other reasons. The substance is therefore unsuitable as a primary standard. It is a reducing agent by virtue of the half-cell reaction:

$$2S_2O_3^{2-} = S_4O_6^{2-} + 2e^-$$

The equivalent weight of sodium thiosulfate pentahydrate is its molecular weight, or 248.18. An approximately 0.1N solution was prepared by dissolving 6.2045 gm. A. R crystallized sodium thiosulfate in 250 mL volumetric flask and up to the mark with distilled water. Then the solution was standardized by potassium dichromate solution.

4.3.6. Preparation of 0.1N potassium dichromate solution

Exactly 2.45 gm of A. R potassium dichromate was weighed out and dissolved in 100 mL volumetric flask and made up to the mark with distilled water to prepare 0.1N solution .

4.3.7. Preparation of starch solution

1-2 gm of soluble starch was made paste with little water. This was poured with constant stirring into 100 mL of boiling water, and boiled for one minute. The solution was allowed to cool down, and 2-3 gm of potassium iodide was added to it. This was stored in a stopper bottle.

4.3.8. Preparation of 0.1N potassium iodide solution

About 8.3 gm of A. R potassium iodide was dissolved in 500 mL distilled water to prepare 0.1N potassium iodide solution.

4.3.9. Preparation of pH 7 buffer solution

2.1425 gm of potassium dihydrogen phosphate and 8.735 gm of disodium hydrogen phosphate were dissolved in 1 liter volumetric flask and made up to the mark with distilled water to make pH 7 buffer solution.

4.4. Standardization of sodium thiosulfate solution by potassium dichromate

Potassium dichromate is reduced by an acid solution of potassium iodide, and equivalent amount of iodine is set free:

$$Cr_2O_7^{2-} + 6I^- + 14H^+ = 2Cr^{3+} + 3I_2 + 7H_2O$$

3 gm of iodate free potassium iodide and 2 gm of sodium carbonate were dissolved in 100 mL cold distilled water in a 500 mL conical flask. 6 mL of concentrated hydrochloric acid was slowly added to it, whilst gently rotating the flask in order to mix the liquids. 25 mL of 0.1N potassium dichromate solution was mixed with it. The flask was covered with a small watch glass, and allowed to stand it dark for 5 minutes in order to complete the reaction. The watch glass was rinsed and the solution was diluted to 300 mL. The liberated iodine was titrated with 0.1N sodium thiosulfate solution contained in burette, whilst constantly rotating the liquid so as to thoroughly mix the solution. When most of the iodine had reacted as indicated by the solution acquiring a yellowish-green color, 2 mL of starch solution was added to change the color to blue.

Drop wise addition of thiosulfate solution was continued with constant swirling of the liquid, until 1 drop changed the color from greenish blue to light green. This was the end point of titration.

4.5. pH measurement

For the pH measurement a Mettler-Toledo 320 pH meter (England) was used. The pH meter was furnished with a combined glass electrode having an ATC mode (automatic temperature compensator). Before each pH measurement, the pH meter was standardized using standard buffers. After standardization of the pH meter, the electrode was rinsed with sufficient distilled water, and the residual water present on the surface of the electrode was removed by a piece of filter paper. It was then placed within the test solution and pH was read from the digital display of the pH meter. In this investigation, the electrode was dissolved in a stock solution and then adding drop by drop phosphate buffer solution to adjust the pH 7.

4.6. Generation of chlorine dioxide from chlorite solution

Chlorine dioxide was prepared from sodium chlorite by reacting separately with sulfuric acid (H_2SO_4), sodium persulfate ($Na_2S_2O_8$), acetic anhydride and a mixture of acetic anhydride and H_2SO_4.

A definite concentration of sulfuric acid reacts separately with different concentrations of sodium chlorite solution and similarly for a definite concentration of sodium chlorite reacts separately with different concentrations of sulfuric acid. Sulfuric acid concentrations of 0.02, 0.1, 0.2, 0.4, 1.0N and sodium chlorite concentrations of 0.01, 0.05, 0.1, 0.2N were used in this study.

In these experiments, sodium persulfate of 0.01, 0.05, 0.1, 0.2N and sodium chlorite concentrations of 0.01, 0.05, 0.1, 0.2N were used. The definite concentration of sodium persulfate react separately with different concentrations of sodium chlorite solutions and similarly for a definite concentration of sodium chlorite react separately with different concentrations of sodium persulfate.

In this investigation, sodium chlorite concentrations of 0.01, 0.05, 0.1, 0.2N and acetic anhydride of 0.025, 0.05, 0.1, 0.2 and 0.4N were used. The definite concentration of acetic anhydride react separately with different concentrations of sodium chlorite solutions and similarly for a definite concentration of acetic anhydride react separately with different concentration of acetic anhydride.

4.7. Determination of chlorine dioxide by iodometric titration method

20 mL of test solution containing chlorine dioxide was taken in a 250 mL conical flask. The solution pH was raised to the range pH at 6.7 to 6.8 by adding (drop by drop) appropriate volume of phosphate buffer solution (Na_2HPO_4-KH_2PO_4). Approximately 10 mL 0.1N potassium iodide was added to the solution and kept in dark for 5 minutes. The side of the conical flask was rinsed down with distilled water and the solution was titrated by standard sodium thiosulfate solution. When most of iodine was reacted as indicated by the solution acquiring a light color, 2-3 drops of starch solution was added which changed the color to blue. Drop wise addition of thiosulfate was continued, until 1 or 2 drops changed the color from blue to colorless.

Concentration of chlorine dioxide in percent from chlorite solution was calculated according to the following relations:

$$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^-$$

$$S_2O_3^{2-} \equiv I^-$$

And,

$$2ClO_2 + 2\,I^- = I_2 + 2ClO_2^-$$

$$2ClO_2 = 2I^-$$

$$ClO_2 \equiv I^-$$

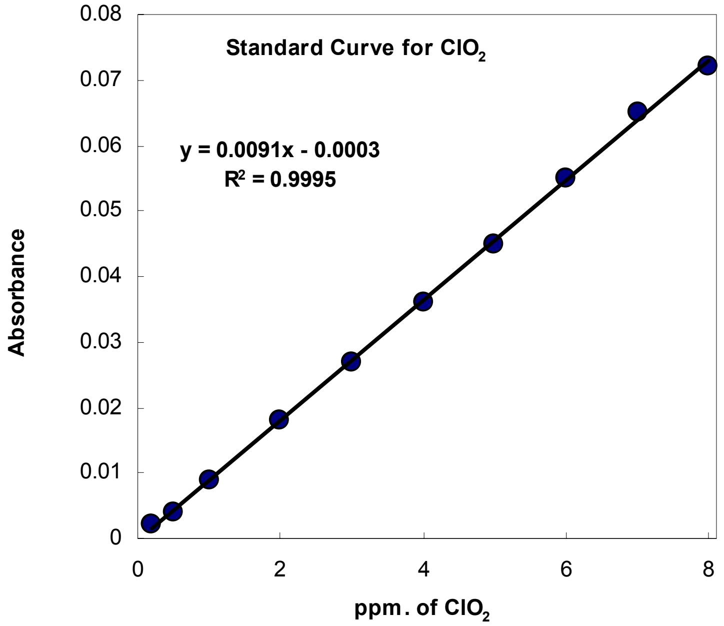
$$\text{Finally, } S_2O_3^{2-} \equiv I^- \equiv ClO_2 \quad \text{............................(A)}$$

Where the number of equivalent amount of sodium thiosulfate required to reduced the iodine which was equivalent of chlorine dioxide.

4.8. Prepared standard curve by UV spectrophotometer

Chlorine dioxide was prepared from chlorite solution by reacting with sulfuric acid. In this investigation, 25 mL 0.1N sodium chlorite solution and 25 mL 0.4N sulfuric acid were used, because these pair of conc. showed the maximum production of chlorine dioxide. Initially the chlorine dioxide solution was divided in two parts; one part (25 mL) was used for iodometric titration to measure the amount of chlorine dioxide. The result of the estimation shows that 41.6563 mg of chlorine dioxide was present.

The other part of chlorine dioxide solution was taken in 250 mL volumetric flasks and then made up to mark with distilled water. Then the strength of the solution was 166.625 ppm of chlorine dioxide (according to part one solution). Thus 0.12, 0.3, 0.6, 1.2, 1.8, 2.4, 3.0, 3.6, 4.2, and 4.8 mL of the above solutions of chlorine dioxide were taken in ten (10) different 100 mL volumetric flasks. The flasks were then made up to mark with distilled water and the solution was mixed thoroughly after shaking well. The flasks were thus contained 0.2, 0.5, 1, 2, 3, 4, 5, 6, 7 and 8 ppm of chlorine dioxide solution. Then different ppm of chlorine dioxide solution were used to measure the absorbance (360 nm) by UV spectrophotometer and plot a absorbance against ppm of chlorine dioxide solution to get a standard graph which is showed below:



ppm.	Abs.
0.2	0.002
0.5	0.004
1	0.009
2	0.018
3	0.027
4	0.036
5	0.045
6	0.055
7	0.065
8	0.072

4.9. Analysis of chlorine species by iodometric titration method

Chlorine dioxide (ClO_2) was generated by reacting between aqueous sodium chlorite solution and sulfuric acid (H_2SO_4) or, sodium persulfate ($Na_2S_2O_8$) or, acetic anhydride $(CH_3CO)_2O$. In the aqueous Solution of ClO_2 was present along with other chlorine species such as, ClO_2, Cl_2, ClO_2^- and ClO_3^- in the reaction vessel. These solutions were indicated as a sample and used for the determination of various chlorine species in this study.

Sample was taken for directly estimation of chlorine dioxide using UV spectrophotometer at 360 nm of wave length.

All chlorine species (e.g. ClO_2, Cl_2, ClO_2^- and ClO_3^-) in the reaction vessel were analyzed by iodometric titration in step by step which were given below -

Step-1

10 mL of sample was taken in a 250 mL volumetric flask and adjusted pH at 7 by phosphate buffer. Then 1 g KI granules were added keeping in the dark for 5 minutes and titrated with 0.1N $Na_2S_2O_3$.

The reduction reaction of chlorine and chlorine dioxide to chloride (Cl^-) and chlorite (ClO_2^-) respectively were given below:

$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$ (pH 7, 2 and <0.1)

$2ClO_2 + 2I^- \rightarrow I_2 + 2CO_2^-$ (pH 7)

[Record reading, A = mL of titrant / mL of Solution.]

Step-2

Continuing with the sample from step 1 and adjusted pH 2 by adding 2 mL of 2.5N HCl and allowed the mixture to react in the dark for 5 minutes. Then the mixture was titrated with 0.1N $Na_2S_2O_3$ to end point. The reactions were considered to be occurred in step 2 which were giving below:

$2ClO_2 + 10I^- + 8H^+ \rightarrow 5I_2 + 2\,Cl^- + 4\,H_2O$ (pH 2)

$ClO_2^- + 4I^- + 4H^+ \rightarrow 2I_2 + Cl^- + 2\,H_2O$ (pH 2)

[Record reading, B = mL of titrant / mL of sample.]

Step-3

Again, 10 mL sample was taken in a 250 mL volumetric flask and adjusted pH at 7 according to step 1. Then ClO_2 was purged from the sample using N_2 gas and added 1 g KI granules and kept in the dark for 5minutes. Then the sample was titrated with 0.1N $Na_2S_2O_3$ to end point.

[Record reading, C = mL of titrant / mL of sample.]

Step-4

Continuing with the sample from step 3 and added 2 mL of 2.5N HCl to adjust pH 2 and allowed the mixture to react in the dark for 5 minutes. Then the mixture was titrated using 0.1N $Na_2S_2O_3$ to end point. Chlorite was reduced to chloride (Cl^-) as follows:

$$ClO_2^- + 4I^- + 4H^+ \rightarrow 2I_2 + Cl^- + 2\,H_2O \qquad (pH\ 2)$$

[Record reading, D = mL of titrant / mL of sample.]

Step-5

Once again, 1 mL KBr and 10 mL of 12N HCl were taken in a 50 mL reaction flask and added 15 mL sample carefully to above mixture and stopper the reaction flask immediately. Allowed the mixture to react in the dark for 20 minutes and 1 g KI granules was added to the reaction vessel, which indicated as a solution (A).

25 mL of saturated Na_2HPO_4 Solution was taken in a 250 mL titration flask and added the reaction mixture (A). This reaction flask was rinsed thoroughly and added the rinsed water to titration flask. Thus the sample was titrated with 0.1N $Na_2S_2O_3$ to end point.

Step-5 was repeated for blank titration, 15 mL distilled demonized water was added to reaction flask instead of a sample. The following reducing reaction was considered to be occurred in this step:

$$ClO_3^- + 6I^- + 6H^+ \rightarrow 3I_2 + Cl^- + 3H_2O; \qquad (pH < 0.1)$$

[Record reading, E = (mL of titrant sample – mL of titrant blank) / mL of sample.]

Concentrations of ClO_2, Cl_2, ClO_2^- and ClO_3^- were estimated using the following equation:

ClO_2^- concentration (mg/L) = $D \times N \times 16.863$

ClO_3^- concentration (mg/L) = $[E-(A+B)] \times N \times 13.908$

ClO_2 concentration (mg/L) = $(B-D) \times N \times 13.49$

Cl_2 concentration (mg/L) = $[A-(B-D)] \times N \times 35.45$

Where, N is the normality of the titrant ($Na_2S_2O_3$) which was illustrated as equivalents per liter.

4.10. Estimation of chloride ion by the Mohr's titration method

The Mohr method uses chromate ions as an indicator in the titration of chloride ions with a silver nitrate standard solution. This silver nitrate solution was standardized against NaCl. The end point of the titration occurs when all the chloride ions are precipitated. Then additional silver ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate. In this experiment, the amount of chloride ion in an unknown sample was determined by Mohr titration.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

$$2Ag^{+}_{(aq)} + CrO_4{}^{2-}{}_{(aq)} \rightarrow Ag_2Cr_2O_4\ (s)$$

The pH of the sample solutions should be between 6.5 and 10.

By knowing the stoichiometry and moles consumed at the end point, the amount of chloride in an unknown sample can be determined.

Methods:

Preparation of 5% K_2CrO_4 (indicator): 1.0 g of K_2CrO_4 was dissolved in 20 mL of distilled water.

Preparation of standard $AgNO_3$ solution: 9.0 g of $AgNO_3$ was weighed out, transferred to a 500 mL volumetric flask and made up to volume with distilled water. The resulting solution was approximately 0.1N. This solution was standardized against NaCl. Reagent-grade NaCl was dried overnight and cooled to room temperature. 0.25 g portions of NaCl were weighed into Erlenmeyer flasks and dissolved in about 100 mL of distilled water. In order to adjust the pH of the solutions, small quantities of $NaHCO_3$ were added until effervescence ceased. About 2 mL of K_2CrO_4 was added and the solution was titrated to the first permanent appearance of red Ag_2CrO_4.

Determination of Cl^- in sample: The unknown was dried at 110^{o} C for 1 hour and cooled in a desiccator's. Individual samples were weighed into 250 mL Erlenmeyer flasks and dissolved in about 100 mL of distilled water. Small quantities of $NaHCO_3$ were added until effervescence ceased. About 2 mL of K_2CrO_4 was introduced and the solution was titrated to the first permanent appearance of red Ag_2CrO_4. An indicator blank was determined by suspending a small amount of chloride free $CaCO_3$ in 100 mL of distilled water containing 2 mL of K_2CrO_4.

Calculations for standardization

Molecular mass of NaCl = 58.44 g/mol.

$$\text{m.mol. of } AgNO_3 = \frac{\text{W g NaCl}}{58.44 \text{ g mol.}^{-1}} \times 1000 \frac{\text{m.mol. NaCl}}{\text{1 mol. NaCl}} = \text{ m.mol.}$$

$$\text{Normality of } AgNO_3 = \frac{\text{m.mol. } AgNO_3}{\text{mL } AgNO_3} = \text{N } AgNO_3 \text{ (Reagent volume corrected for blank)}$$

Determination of Chloride ion

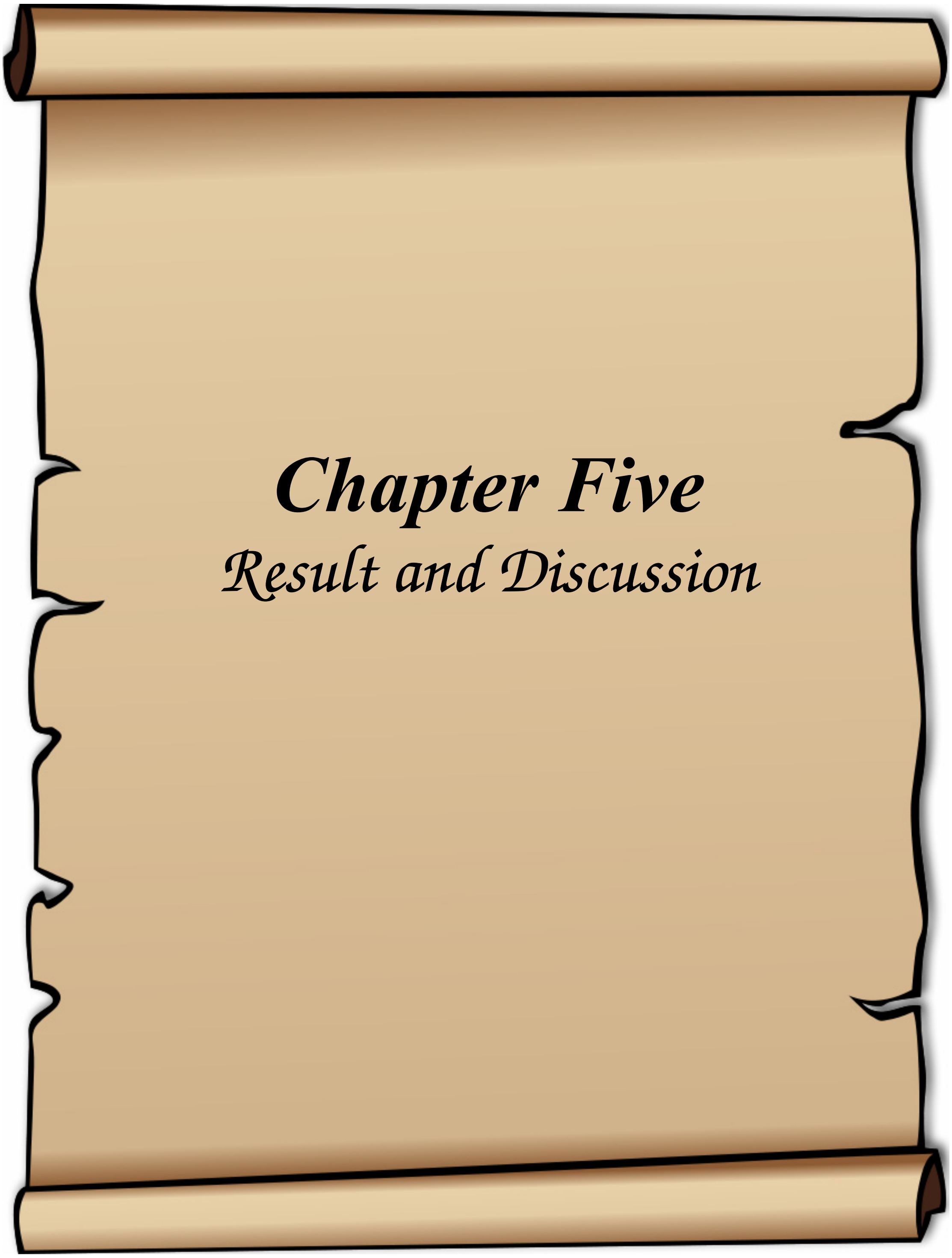
Atomic mass of Cl^- = 35.45 g/mol.

m.mol. of Cl^- = N $AgNO_3$ × **V** $AgNO_3$ = m.mol.

$$\text{mass of Cl} = \text{ m.mol.} \times \frac{35.45 \text{mg } AgNO_3}{1 \text{m.mol.}} = \text{ mg}$$

$$\% \text{of } Cl^- = \frac{\text{mg } Cl^-}{\text{mg sample}} \times 100 = \% Cl^-$$

[Where, N = Normality, W = Weight and V = Volume]



Chapter Five

Result and Discussion

RESULT AND DISCUSSION

5.1. Preparation of chlorine dioxide from sodium chlorite and sulfuric acid

This study was attempted to generate chlorine dioxide by a reaction of sodium chlorite ($NaClO_2$) and sulfuric acid (H_2SO_4). The effects of reactants concentration and reaction time on the production of chlorine dioxide are discussed here. This study also describes the formation of various chlorine species in different time intervals during the reaction period. The reaction was carried out at a temperature 30 ± 1^0C and the volume ratio of H_2SO_4 and $NaClO_2$ was 1:1(v/v).

5.1.1. The effect of $NaClO_2$ concentration on the percentage production of ClO_2

The study results show that the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentration (Fig. 5.1.). The results also illustrate that the percentage production of ClO_2 increased with increasing reaction time and the highest percentage production was shown in 240 minutes for all cases. In lower H_2SO_4 (0.02N) concentration and reaction time intervals of 60 and 240 minutes, the percentage production of ClO_2 decreased rapidly with increasing $NaClO_2$ concentration, but the other graph lines of the figure show that the percentage production of ClO2 decreased slowly with time (Fig. 5.1.A). The other figures (Figs. 5.1.B-1.E) show a similar trend, where the percentage production of ClO_2 decreased slowly with increasing concentration of $NaClO_2$. The highest conversion was achieved to be 75% in a reaction of 0.01N $NaClO_2$ and 1.0N H_2SO_4 for 240 minutes (Fig. 5.1.E). The figures illustrate that the percentage production of ClO_2 depended on both the $NaClO_2$ concentration and reaction time. As the percentage production of ClO_2 is the ratio of the product (ClO_2) to initial $NaClO_2$ concentration, and $NaClO_2$ was the only source of chlorite species, thus it is obvious that the production of ClO_2 was not proportional to $NaClO_2$ concentration for a definite H_2SO_4 concentration. Hence the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentration as expected.

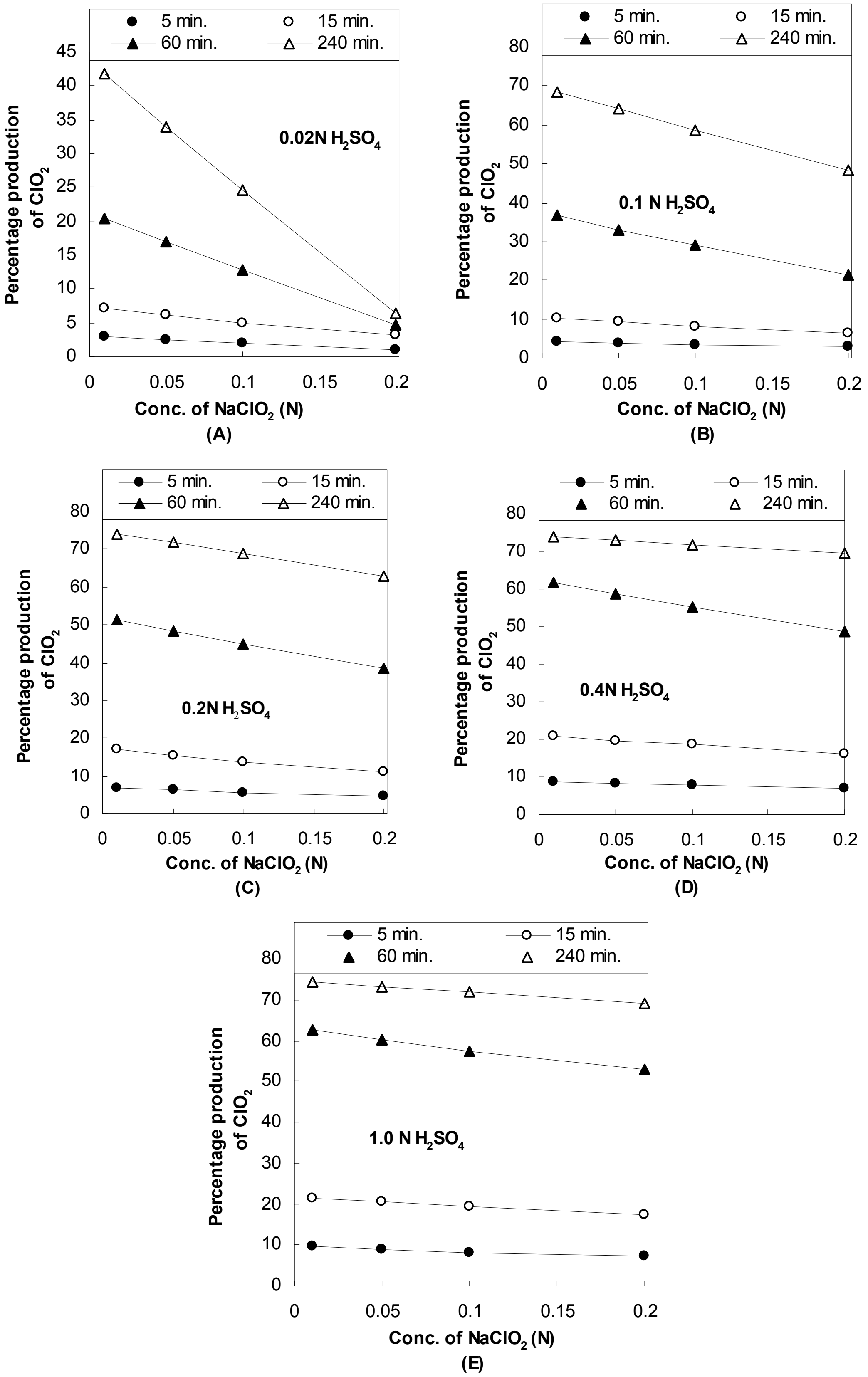
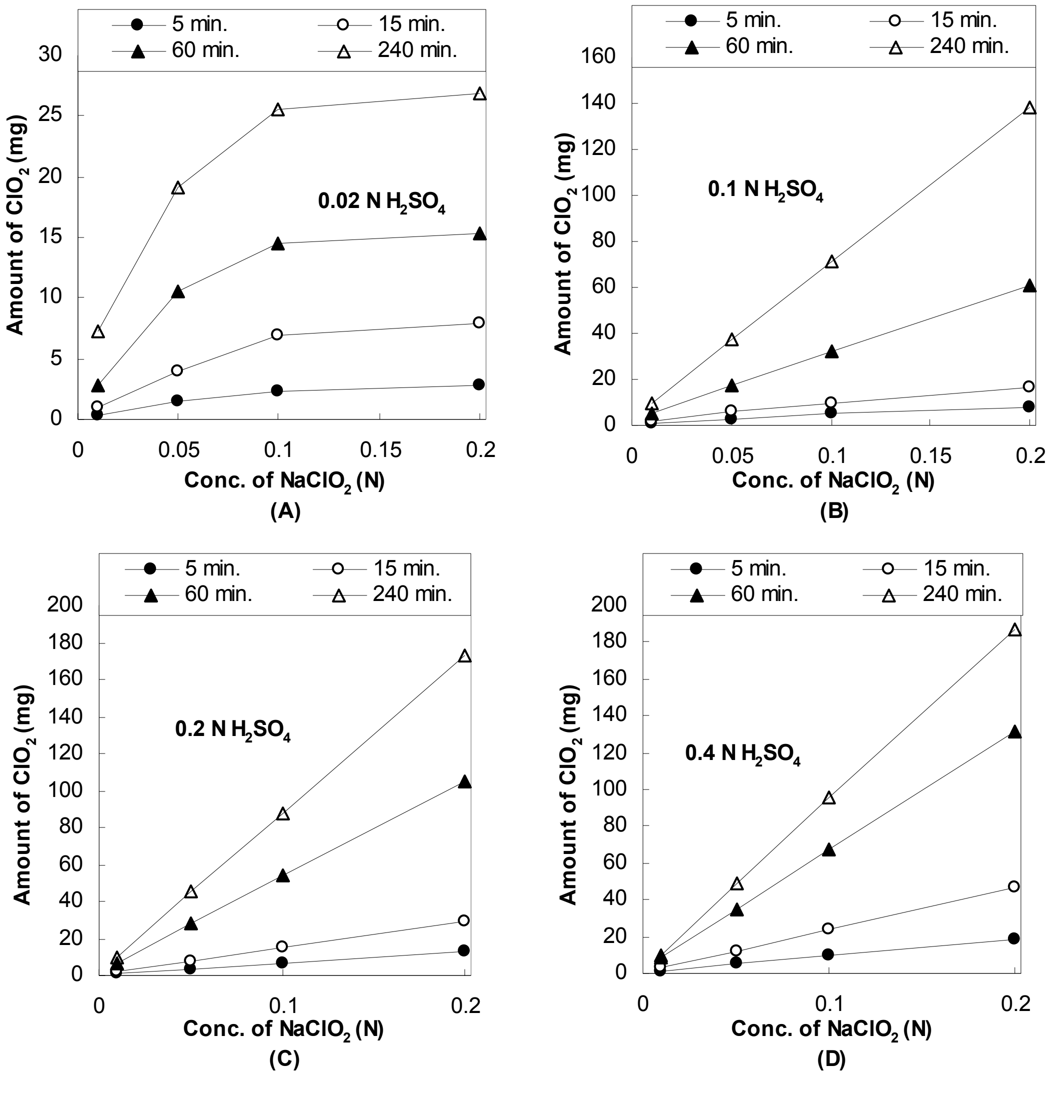


Fig. 5.1. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2
Reaction conditions: H_2SO_4: $NaClO_2$ (v/v) 1: 1; temperature, 30 ± 1^0C
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4; D = 0.4N H_2SO_4; E = 1.0N H_2SO_4
[APPENDIX, Table-5.1 for experimental data]

5.1.2. The effect of $NaClO_2$ concentration on the amount of ClO_2

The study results show that the amount of ClO_2 increased with increasing of $NaClO_2$ concentration (Fig. 5.2.). The results also illustrate that the amount of ClO_2 increased with reaction time and the highest amount of ClO_2 was obtained in 240 minutes for all cases. In Fig. 5.2.A, the line of graphs show that the amount of ClO_2 increased almost sharply until reaching 0.1N of $NaClO_2$ concentration and then increased very slowly with increasing $NaClO_2$ concentration. But the other figures show an almost similar trend, where the amount of ClO_2 increased with increasing $NaClO_2$ concentration (Fig. 5.2.B-2.E). The highest amount of ClO_2 was found to be 195 mg in the reaction of 0.2N $NaClO_2$ and 1.0N H_2SO_4 for 240 minutes (Fig. 5.2.E). $NaClO_2$ was the only source of chlorite ion hence; it is obvious that the concentration $NaClO_2$ had a great effect on the production of ClO_2.



(A) (B)

(C) (D)

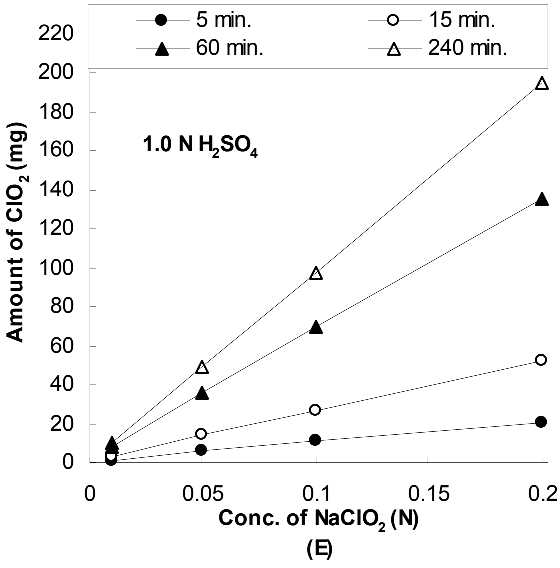
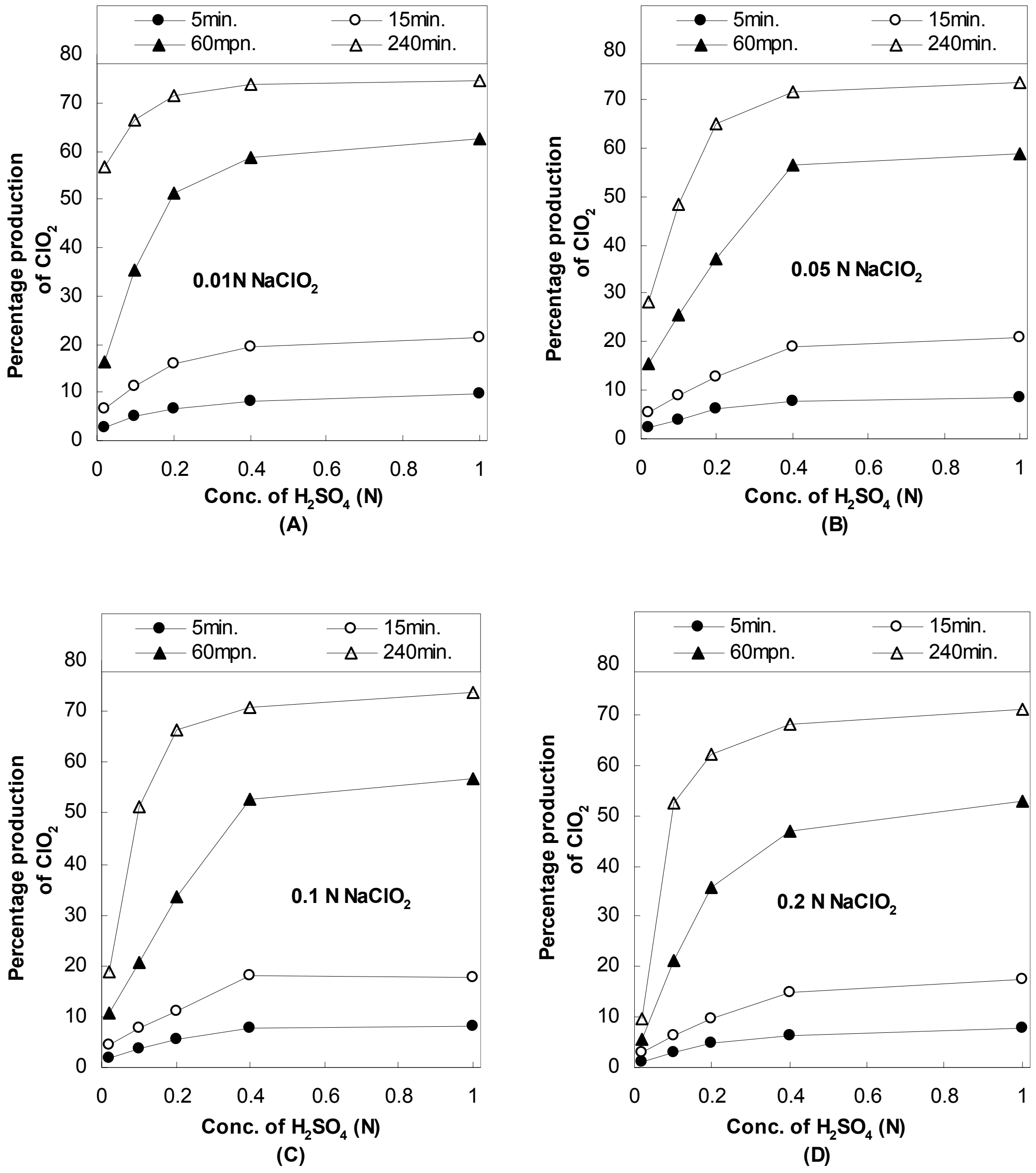


Fig. 5.2. The effect of $NaClO_2$ concentrations on the amount of ClO_2
Reaction conditions: H_2SO_4 : $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4; D = 0.4N H_2SO_4; E = 1.0N H_2SO_4
[APPENDIX, Table-5.2 for experimental data]

5.1.3. The effect of H_2SO_4 concentration on the percentage production of ClO_2

The study results show that the percentage production of ClO_2 increased with increasing H_2SO_4 concentration up to 0.4N and become almost constant with increasing H_2SO_4 concentration (Fig. 5.3.). The results also illustrate that the percentage production of ClO_2 increased with increasing reaction time and the highest percentage production of ClO_2 was found in 240 minutes for all cases. The highest conversion was found to be 75% in a reaction of 0.01N $NaClO_2$ and 1.0N H_2SO_4 in 240 minutes (Fig. 5.3.A). The line of graphs for 5 and 15 minutes of reaction times show that the percentage production of ClO_2 increased slowly with increasing H_2SO_4 concentration up to 0.4N and become almost constant with H_2SO_4 concentrations, but the other line of graphs for 60 and 240 minutes of reaction times show that the percentage production of ClO_2 increased sharply with H_2SO_4 concentration up to 0.4N and then increased very slowly or almost constant with H_2SO_4 concentrations (Figs. 5.3.A-3.D). The experiment results illustrate that 0.4N H_2SO_4 was the optimum concentration for the production of ClO_2 from $NaClO_2$ solution.



(A)
(B)
(C)
(D)

Fig. 5.3. The effect of H_2SO_4 concentrations on the percentage productions of ClO_2
Reaction conditions: H_2SO_4 and $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$
[APPENDIX, Table-5.3 for experimental data]

5.1.4. The effect of H_2SO_4 concentration on the amount of ClO_2

The study results show that the amount of ClO_2 increased with increasing H_2SO_4 concentration up to 0.4N and become almost constant with H_2SO_4 concentration (Fig. 5.4.). The results also illustrate that the amount of ClO_2 increased with increasing reaction time and the highest amount of ClO_2 was shown in 240 minutes for all cases. The line of graphs for 5 and 15 minutes of reaction times show that the amount of ClO_2 increased slowly with H_2SO_4 concentration up to 0.4N and become almost constant with H_2SO_4 concentrations, but the other line of graphs for 60 and 240 minutes of reaction times show that the amount of ClO_2 increased sharply with H_2SO_4 concentration up to 0.4N and then increased very slowly or almost constant with H_2SO_4 concentrations (Figs. 5.4.A-4.D). The highest amount of ClO_2 was found to be 195 mg from the reaction of 0.2N $NaClO_2$ and 1.0N H_2SO_4 for 240 minutes (Fig. 5.4.D). The experiment results illustrate that 0.4N H_2SO_4 was the optimum concentration for the production of ClO_2 from $NaClO_2$ solution.

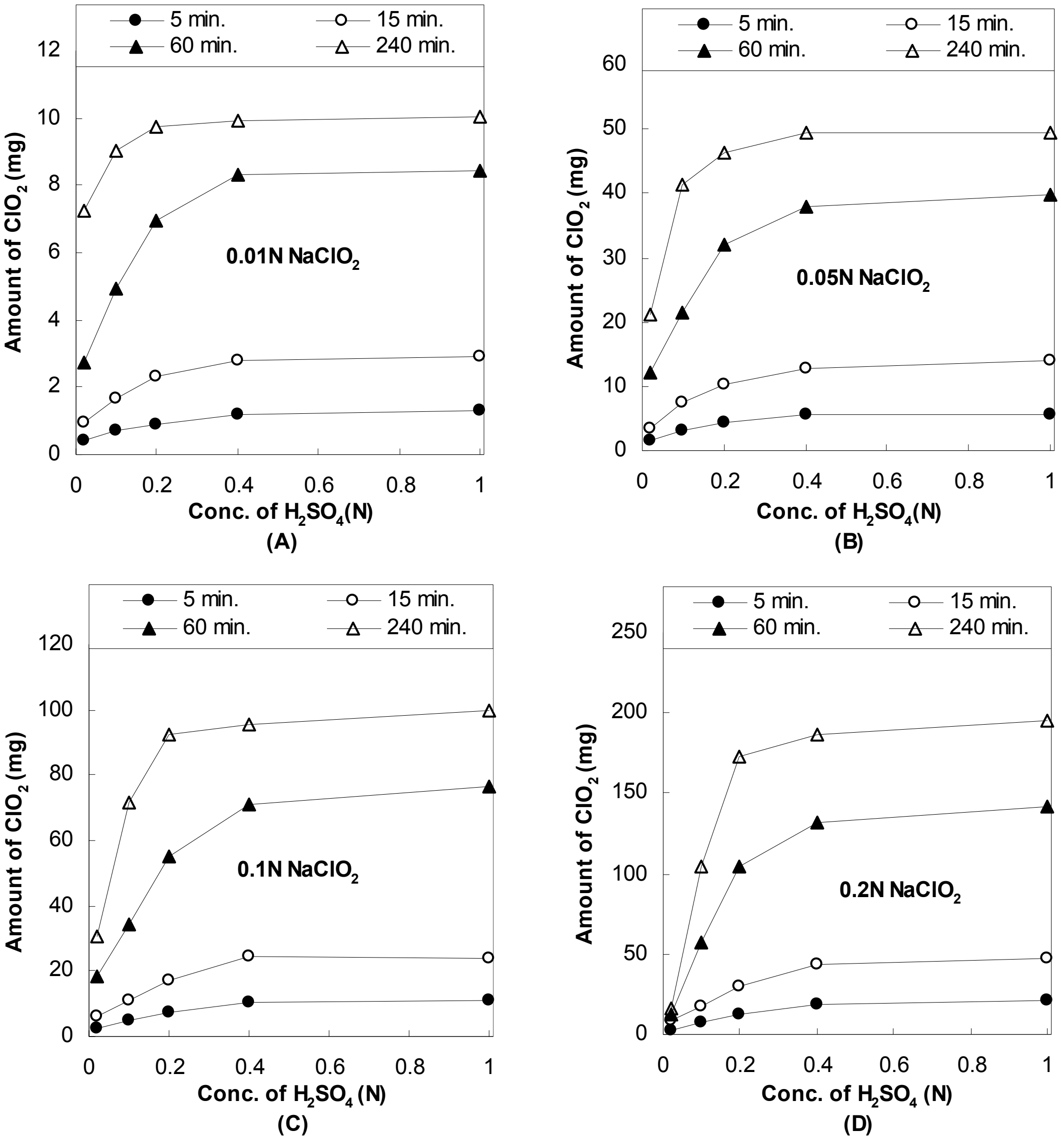


Fig. 5.4. The effect of H_2SO_4 concentrations on the amount of ClO_2
Reaction conditions: H_2SO_4 : $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
A = 0.01N $NaClO_2$; B = 0.05 N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$
[APPENDIX, Table-5.4 for experimental data]

5.1.5. The effect of time on the percentage production of ClO_2 at various H_2SO_4 concentrations

The effects of time on the percentage production of ClO_2 for a fixed $NaClO_2$ and various H_2SO_4 concentrations were shown in Figs. 5.5.-5.8. The study observes that in the beginning, the percentage production of ClO_2 increased sharply with time until reached the maximum and then decreased with time (Figs. 5.5.-5.8.). The results also illustrate that for a definite $NaClO_2$ concentration, percentage production of ClO_2 increased with increasing H_2SO_4 concentration. The figures show that for a definite $NaClO_2$ concentration, the time to reach the peak (maximum percentage production) was reduced with increasing H_2SO_4 concentration and the peak height was increased with increasing H_2SO_4 concentration. The figures (Figs. 5.5.-5.8.) also illustrate that the maximum percentage production of ClO_2 for various H_2SO_4 concentrations was achieved to be between 240 and 1440 minutes and then percentage production decreased with time, this could be happened due to unstable nature of ClO_2[121,128-133] and moreover report showed that it was readily decomposed to chloride ions since it was formed[116,117,181]. The overall observation of these figures illustrate that the percentage production of ClO_2 was largely dependent on time and reactants concentration. The highest conversion was achieved to be 75% in a reaction of 0.01N $NaClO_2$ and 1.0N H_2SO_4 for 240 minutes (Fig. 5.5.).

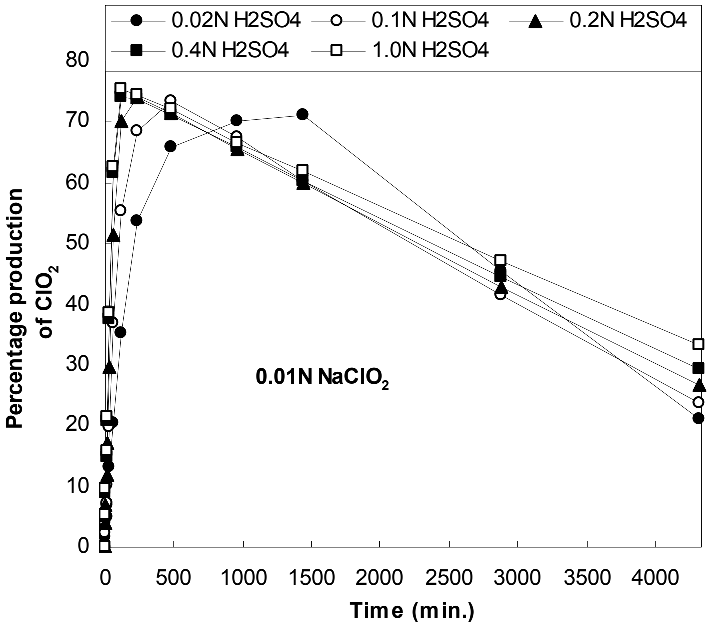


Fig. 5.5. The effect of time on the percentage production of ClO_2
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.5.A for experimental data]

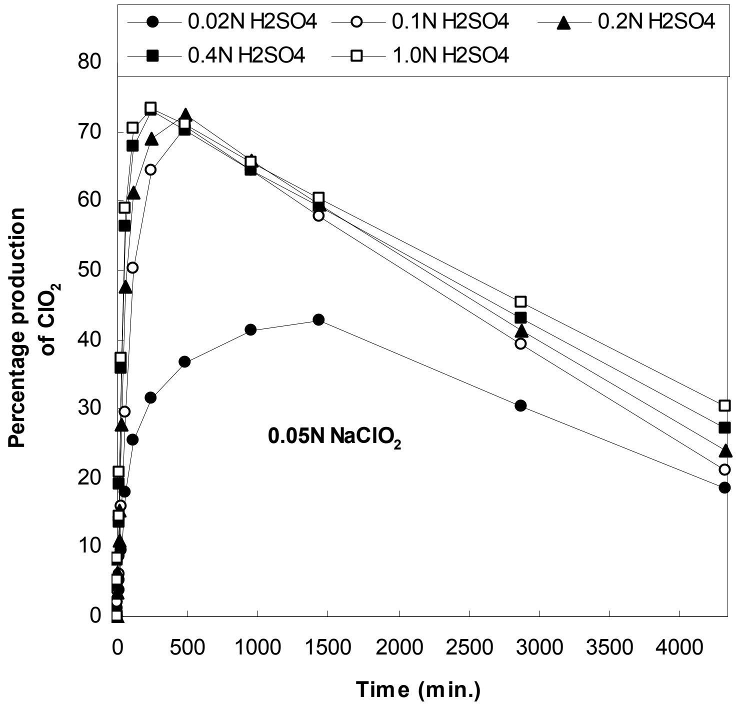


Fig. 5.6. The effect of time on the percentage production of ClO_2
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C.
[APPENDIX, Table-5.5.B for experimental data]

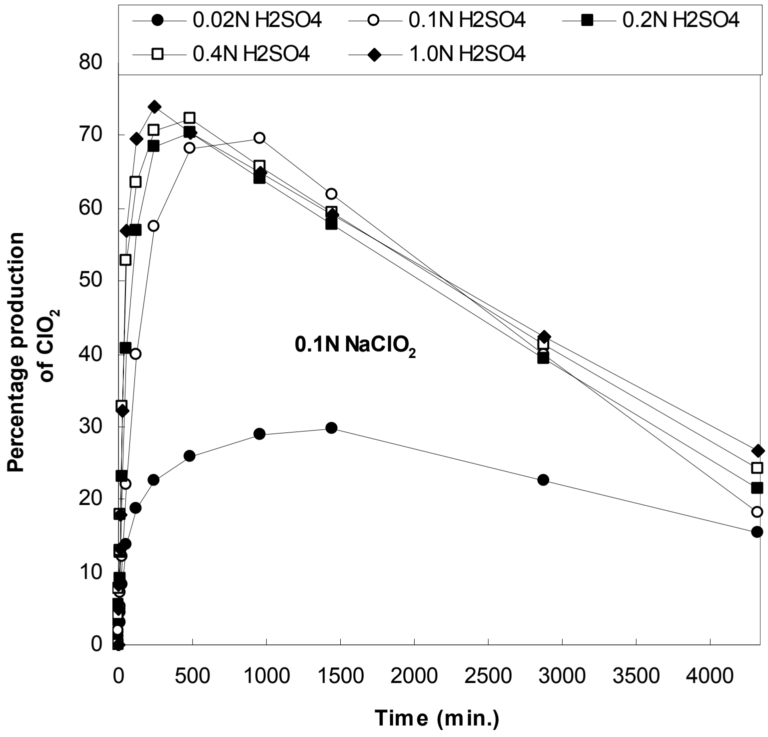


Fig. 5.7. The effect of time on the percentage production of ClO_2
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1, at temperature 30 ± 1^0C.
[APPENDIX, Table-5.5.C for experimental data]

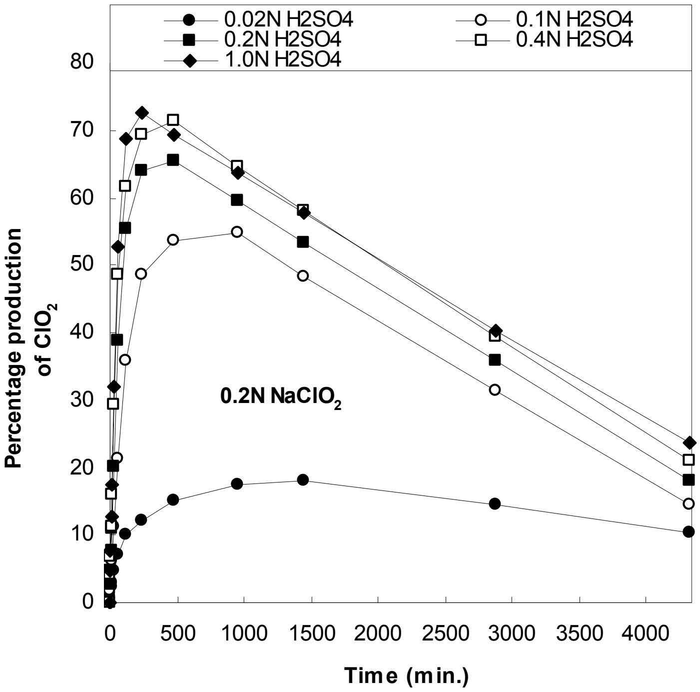


Fig. 5.8. The effect of time on the percentage production of ClO_2
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.5.D for experimental data]

5.1.6. The effect of time on the amount of ClO_2 at various H_2SO_4 concentrations

The effects of time on the amount of ClO_2 for a fixed $NaClO_2$ and various H_2SO_4 concentrations were shown in Figs. 5.9.-5.12. The study observes that in the beginning, the amount of ClO_2 increased sharply with increasing time until reached the maximum and then decreased with time (Figs. 5.9.-5.12.). The results also illustrate that for a definite $NaClO_2$ concentration, the amount of ClO_2 increased with increasing H_2SO_4 concentration. The results show that for a definite $NaClO_2$ concentration, the time to reach the peak (maximum percentage production) was reduced with increasing H_2SO_4 concentration and the peak height was increased with increasing H_2SO_4 concentration. The overall observation of these figures illustrate that the amount of ClO_2 was largely dependent on time and reactants concentration. The figures (Figs. 5.9.-5.12.) also illustrate that the maximum percentage production of ClO_2 for various H_2SO_4 concentrations were achieved to be between 240 and 1440 minutes and then the amount of ClO_2 decreased with time, this could be happened due to unstable nature of ClO_2. The highest conversion was achieved to be 195 mg in the reaction of 0.2N $NaClO_2$ and 1.0N H_2SO_4 for 240 minutes (Fig. 5.12.).

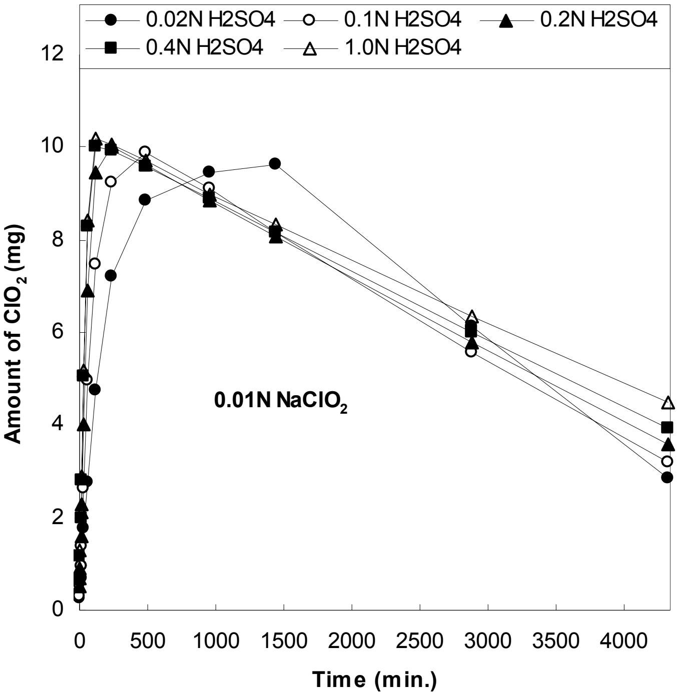


Fig. 5.9. The relation between the amount of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.6.A for experimental data]

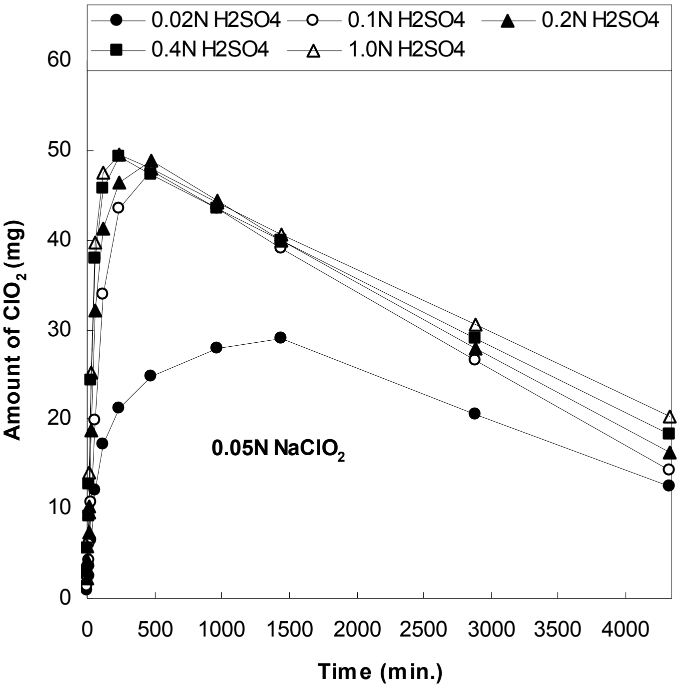


Fig. 5.10. The relation between the amounts of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.6.B for experimental data]

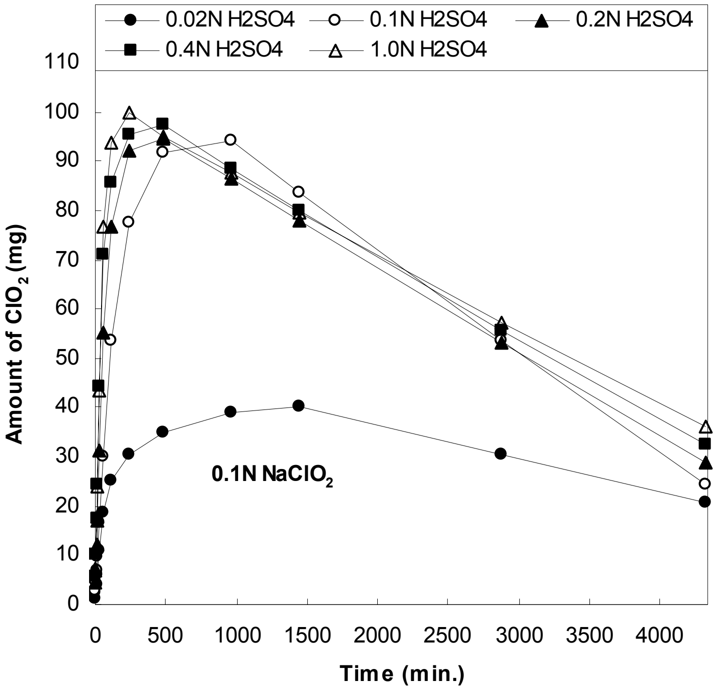


Fig. 5.11. The relation between the amounts of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.6.C for experimental data]

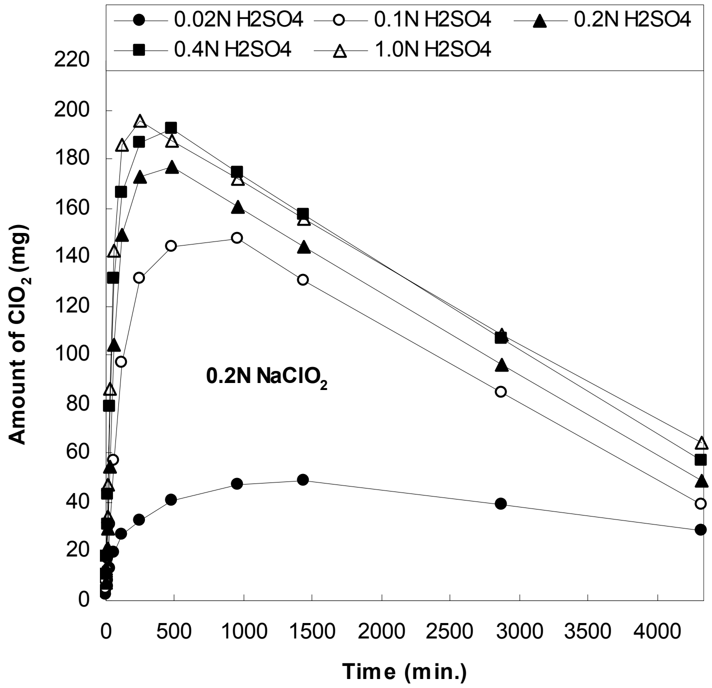


Fig. 5.12. The relation between the amounts of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.6.D for experimental data]

5.1.7. The effect of time on the percentage production of ClO_2 at various $NaClO_2$ concentrations

The effects of time on the percentage production of ClO_2 for a fixed H_2SO_4 and various $NaClO_2$ concentrations were shown in Figs. 5.13.-5.17. The study observes that in the beginning, the percentage production of ClO_2 increased sharply with time until reached the maximum and then decreased with time (Figs. 5.13.-5.17.). In Fig. 5.13., the percentage production of ClO_2 increased sharply in the beginning and then slowly until reached the maximum and finally decreased with time. The figure also shows that the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentrations. Similar trend was found in Figs. 5.14.-5.17., where the percentage production of ClO_2 increased sharply in the beginning until reaching the maximum and then decreased with time. The figures (Figs. 5.13.-5.17.) also illustrate that the percentage production of ClO_2 for various $NaClO_2$ concentrations was achieved to be between 240 and 1440 minutes and then the percentage production decreased with time, this could be happened due to unstable nature of ClO_2 and moreover report showed that it was readily decomposed to chloride ions since it was found. The overall observation of these figures illustrate that the percentage production of ClO_2 was largely dependent on time and reactants concentration. The highest conversion was achieved to be 75% in a reaction of 0.01N $NaClO_2$ and 1.0N H_2SO_4 for 240 minutes (Fig. 5.17.).

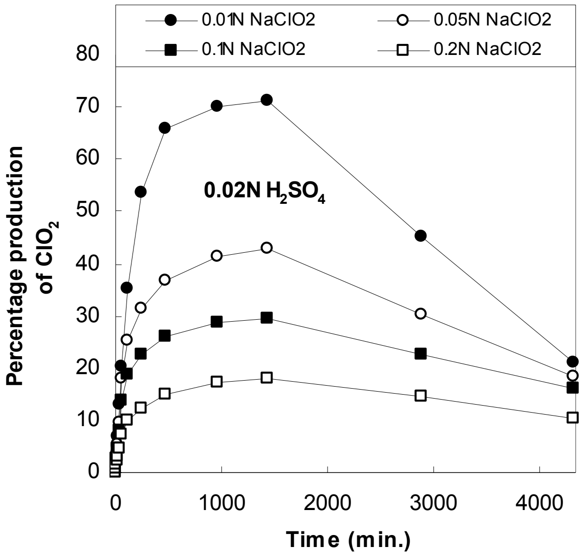


Fig. 5.13. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.7.A for experimental data]

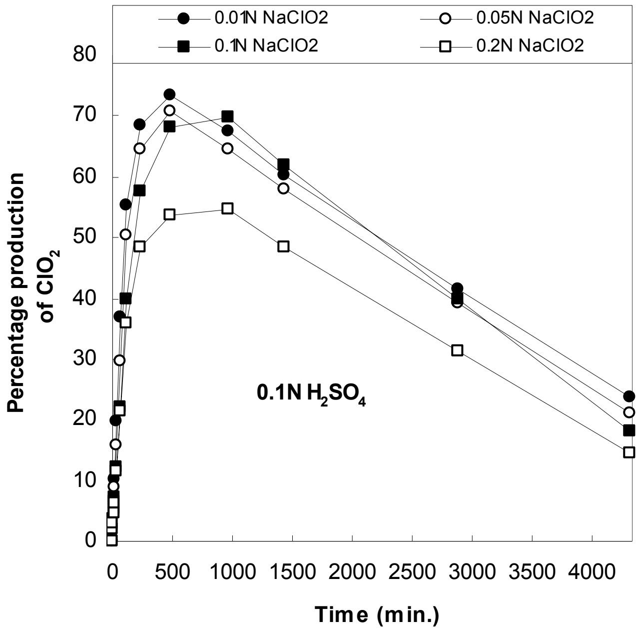


Fig. 5.14. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.7.B for experimental data]

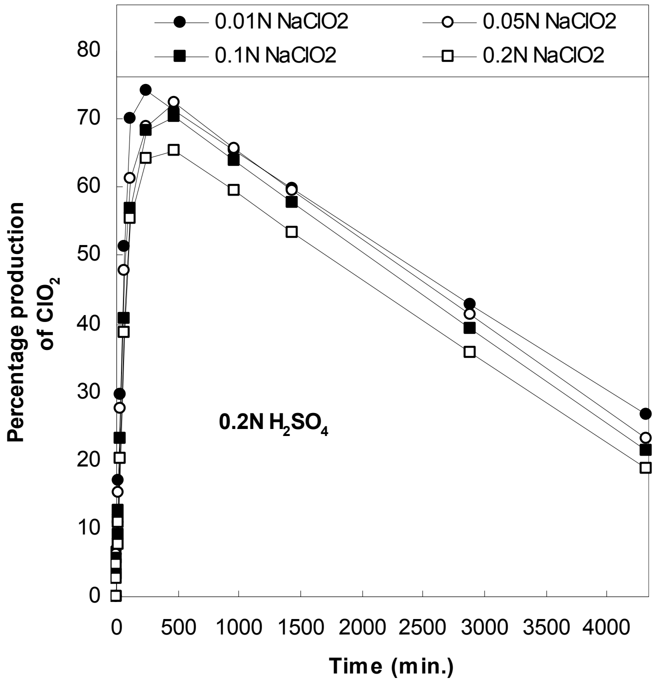


Fig. 5.15. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.7.C for experimental data]

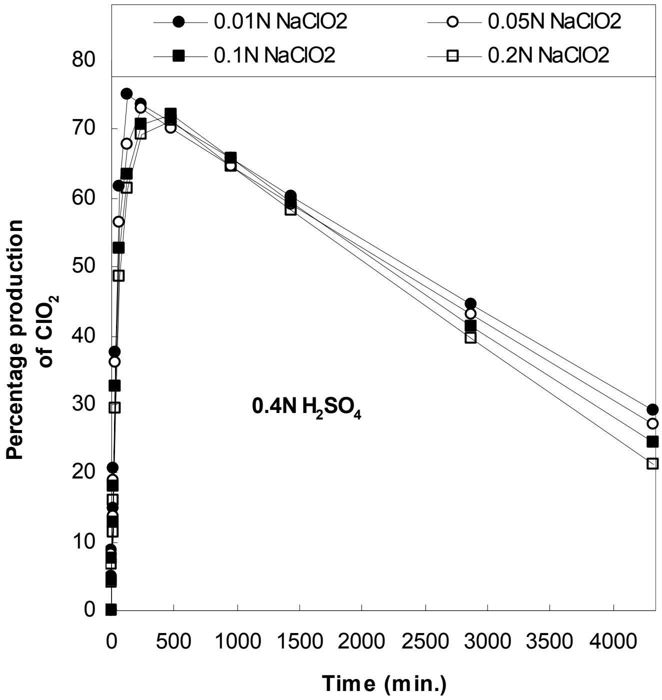


Fig. 5.16. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^{0}C
[APPENDIX, Table-5.7.D for experimental data]

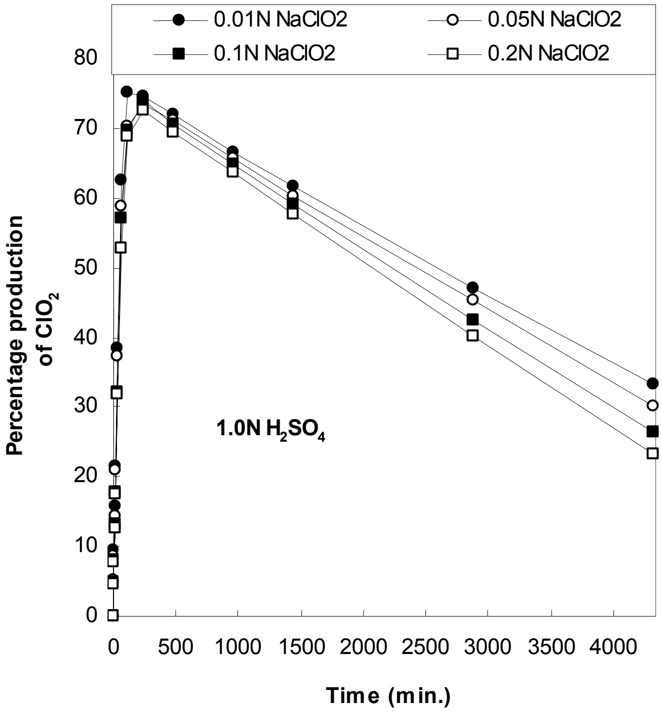


Fig. 5.17. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^{0}C
[APPENDIX, Table-5.7.E for experimental data]

5.1.8. The effect of time on the amount of ClO_2 at various $NaClO_2$ concentrations

The effects of time on the amount of ClO_2 for a fixed H_2SO_4 and various $NaClO_2$ concentrations were shown in Figs. 5.18.-5.22. The study observes that in the beginning, the amount of ClO_2 increased sharply with increasing time until reached the maximum and then decreased with time (Figs. 5.18.-5.22.). The results also illustrate that for a definite H_2SO_4 concentration, the amount of ClO_2 increased with increasing $NaClO_2$ concentration. The results show that the time to reach the peak (maximum percentage production) was reduced with increasing H_2SO_4 concentration and the peak height was increased with H_2SO_4 concentration (Figs. 5.18.-5.22.). The overall observation of these figures illustrate that the amount of ClO_2 was largely dependent on time and reactants concentration. The figures (Figs. 5.18.-5.22.) also illustrate that the maximum amount of ClO_2 for various $NaClO_2$ concentrations was achieved to be between 240 and 1440 minutes and then the amount of ClO_2 decreased with time, this could be happened due to unstable nature of ClO_2 and moreover report showed that it was readily decomposed to chloride ions since it was formed. The highest conversion was achieved to be 195 mg in a reaction of 0.2N $NaClO_2$ and 1.0N H_2SO_4 for 240 minutes (Fig. 5.22.).

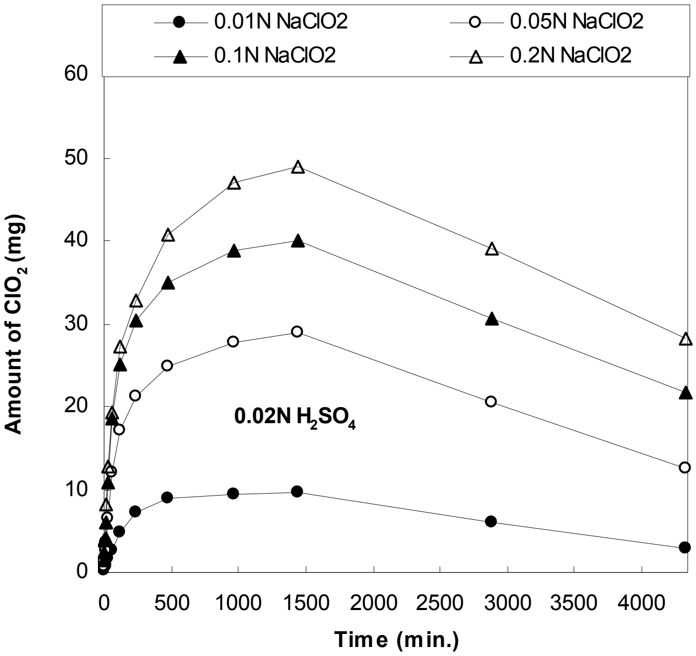


Fig. 5.18. The relation between the percentage productions of ClO_2 with time (min.) The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C [APPENDIX, Table-5.8.A for experimental data]

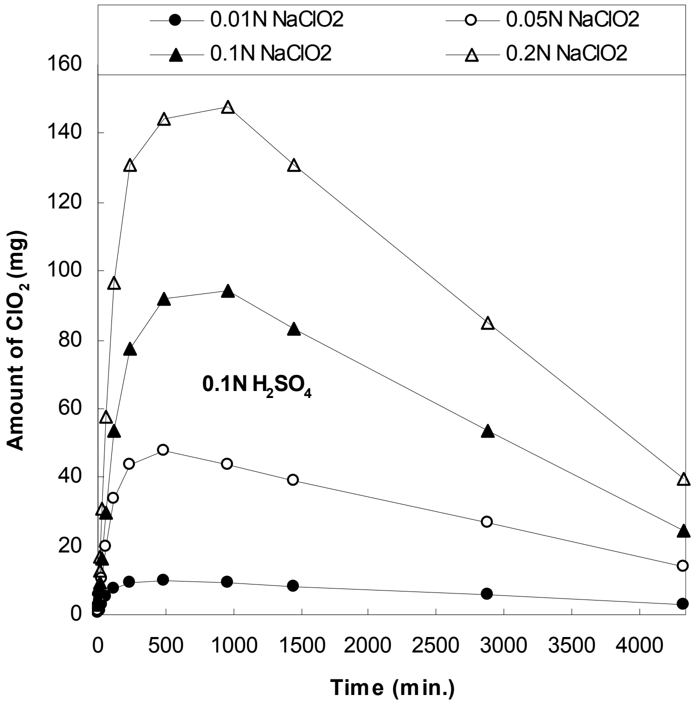


Fig. 5.19. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.8.B for experimental data]

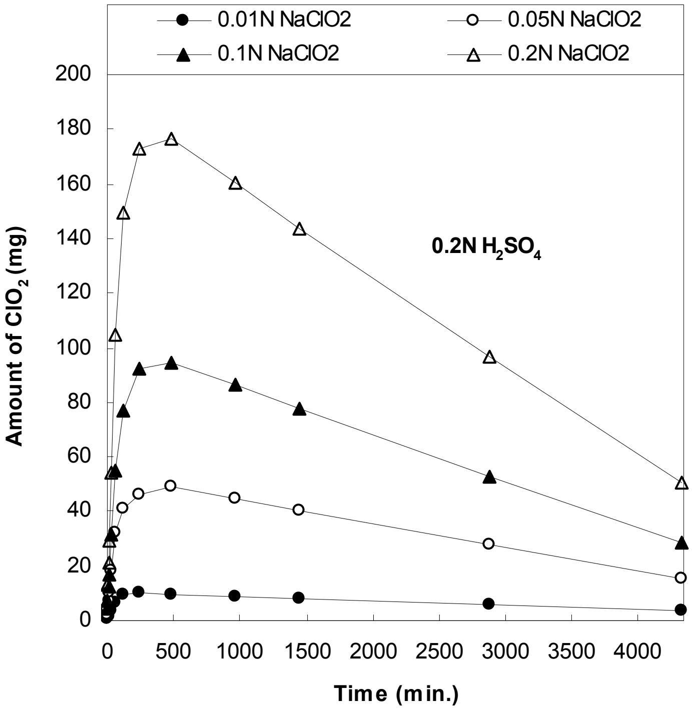


Fig. 5.20. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.8.C for experimental data]

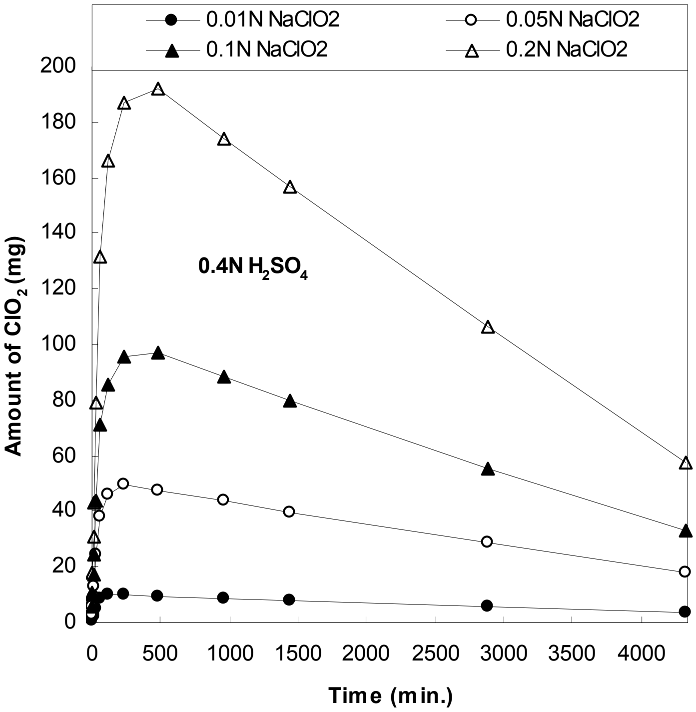


Fig. 5.21. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.8.D for experimental data]

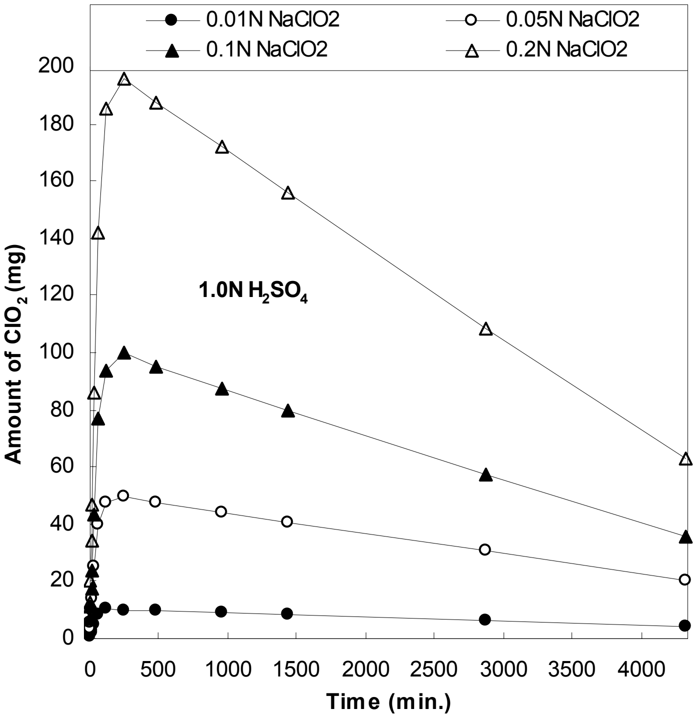


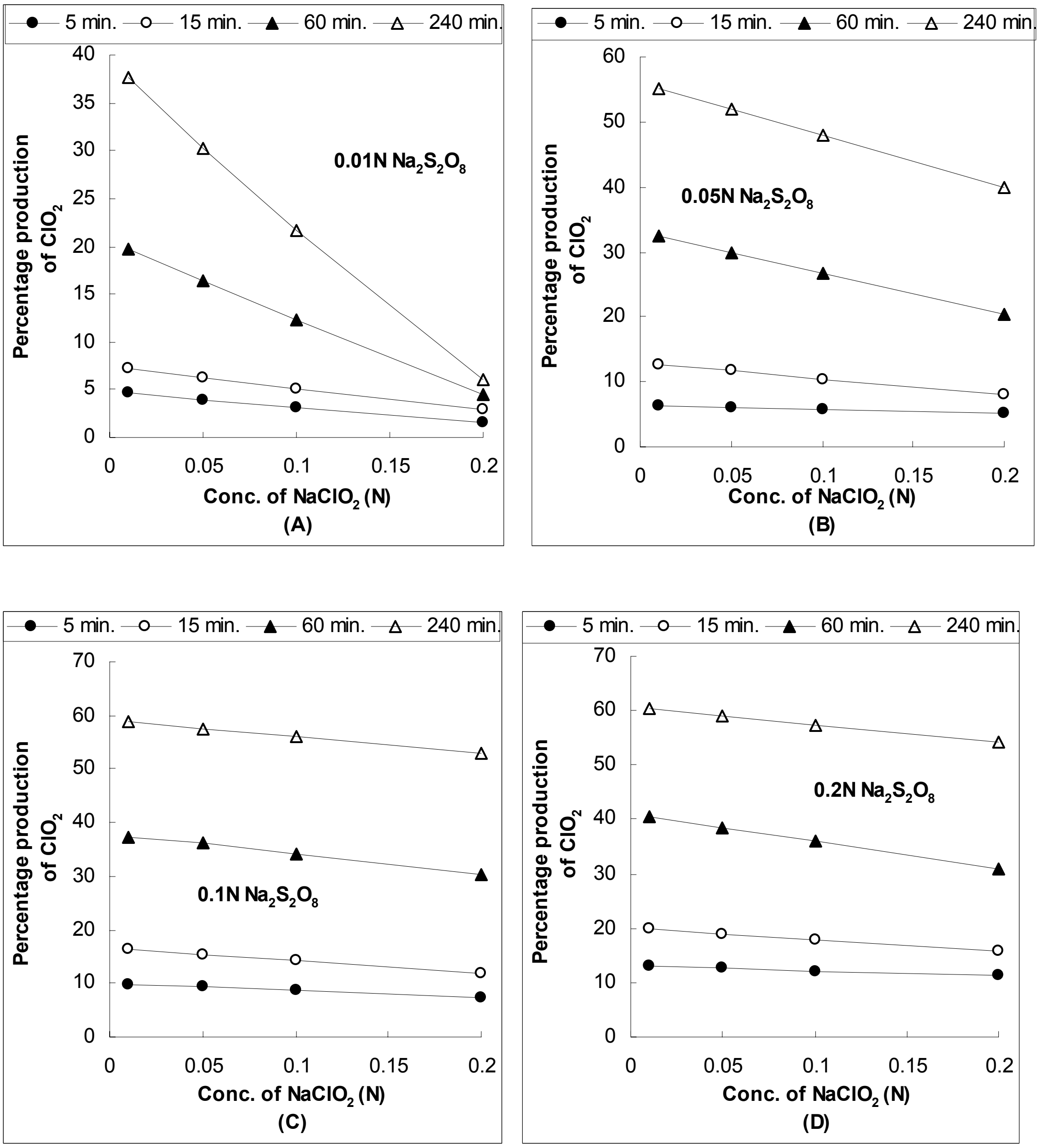
Fig. 5.22. The relation between the percentage productions of ClO_2 with time (min.)
The reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1:1; at temperature 30 ± 1^0C
[APPENDIX, Table-5.8.E for experimental data]

5.2. Preparation of chlorine dioxide from sodium chlorite and sodium per sulfate

This study was attempted to generate chlorine dioxide by a reaction of sodium chlorite and sodium per sulfate ($Na_2S_2O_8$). The effects of reactants concentration and reaction time on the production of chlorine dioxide are discussed here. The reaction was carried out at a temperature 30 ± 1^0C and the volume ratio of $NaClO_2$ and $Na_2S_2O_8$ was 1:1(v/v).

5.2.1. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2

The study results show that the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentration (Fig. 5.23.). The results also illustrate that the percentage production of ClO_2 increased with reaction time and the highest percentage production was shown in 240 minutes for all cases. In lower $Na_2S_2O_8$ (0.01N) concentration, the line of graph for 60 and 240 minutes of reaction times show that the percentage production of ClO_2 decreased rapidly with increasing $NaClO_2$ concentration, but the other line of graph for 5 and 15 minutes of reaction times show that the percentage production of ClO_2 decreased slowly with increasing $NaClO_2$ (Fig. 5.23.A). The almost similar trends were observed in other figures (Figs. 5.23.B-23.D), where the percentage production of ClO_2 slowly decreased with increasing concentration of $NaClO_2$. The overall observation of these figures illustrate that the percentage production of ClO_2 dependent on both the $NaClO_2$ concentration and reaction time. The highest percentage production of ClO_2 was found to be 60% in a reaction of 0.01N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes (Fig. 5.23.D). As the percentage production of ClO_2 is a ratio of a product (ClO_2) to initial $NaClO_2$ concentration, and $NaClO_2$ was the only source of chlorite species, thus it is obvious that the amount of ClO_2 was not proportional to $NaClO_2$ concentration for a definite $Na_2S_2O_8$ concentration. Hence the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentration as expected.



(A) (B) (C) (D)

Fig. 5.23. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2
Reaction conditions: $Na_2S_2O_8$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C.
A = 0.01N $Na_2S_2O_8$; B = 0.05N $Na_2S_2O_8$; C = 0.1N $Na_2S_2O_8$; D = 0.2N $Na_2S_2O_8$
[APPENDIX, Table-5.9 for experimental data]

5.2.2. The effect of sodium chlorite concentration on the amount of ClO_2

The study results show that the amount of ClO_2 increased with increasing $NaClO_2$ concentration (Fig. 5.24.). The results also illustrate that the amount of ClO_2 increased with reaction time and the highest amount of ClO_2 was obtained in 240 minutes for all cases. In Fig. 5.24.A, the lines of graph for 60 and 240 minutes of reaction times show that the amount of ClO_2 increased rapidly until reaching 0.1N of $NaClO_2$ concentration and then increased slowly with increasing concentration of $NaClO_2$, but the other lines of graph for 5 and 15 minutes of reaction times show that the amount of ClO_2 increased slowly with increasing $NaClO_2$ concentration. The other figures show an almost similar trend (Fig. 5.24.B-24.D), where the amount of ClO_2 increased sharply with increasing $NaClO_2$ concentration. The highest amount of ClO_2 was found to be 146 mg in the reaction of 0.2N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes (Fig. 5.24.D). $NaClO_2$ was the only source of chlorite ion hence; it is obviously the concentration of $NaClO_2$ had a great effect on the production of ClO_2.

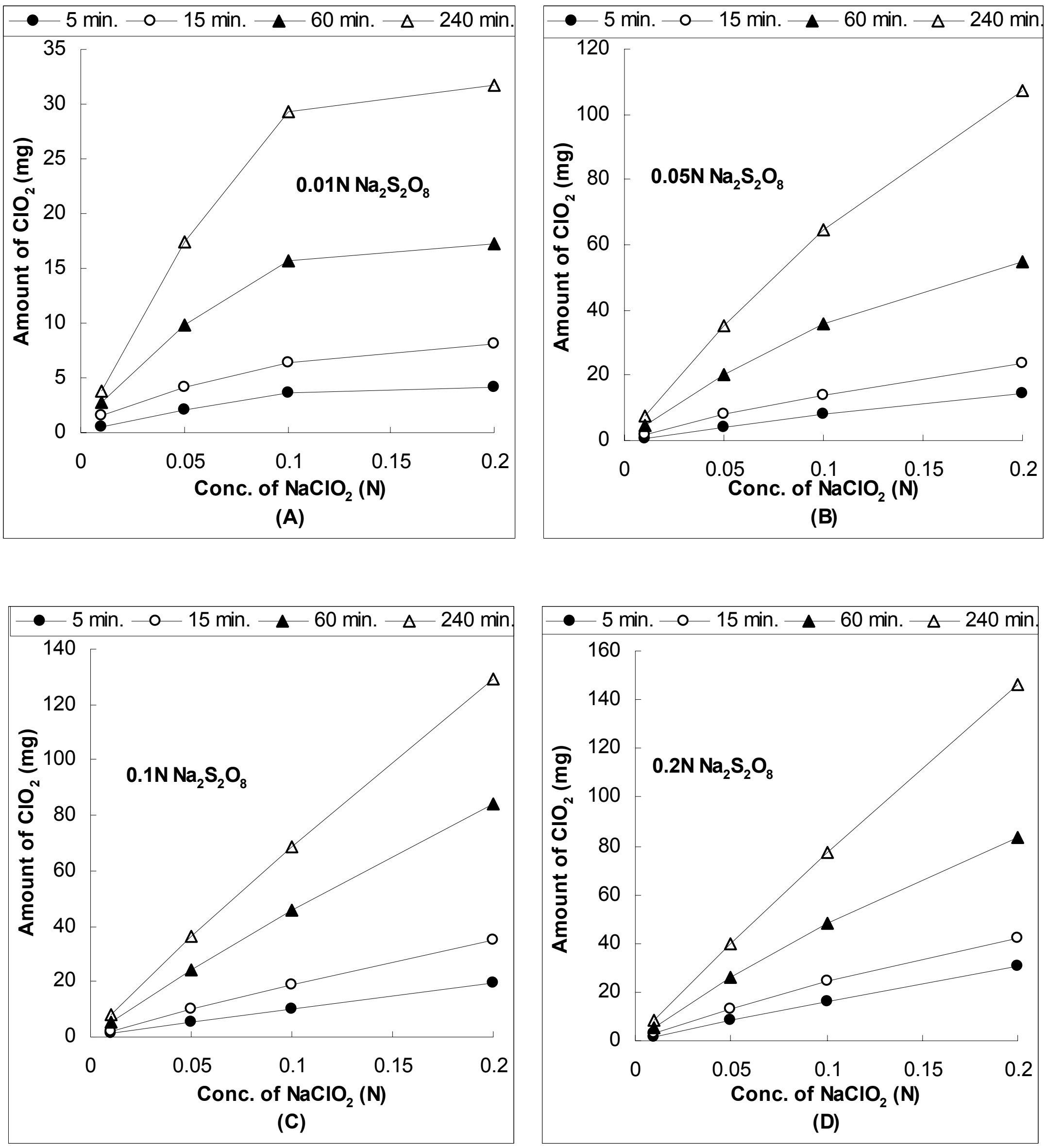
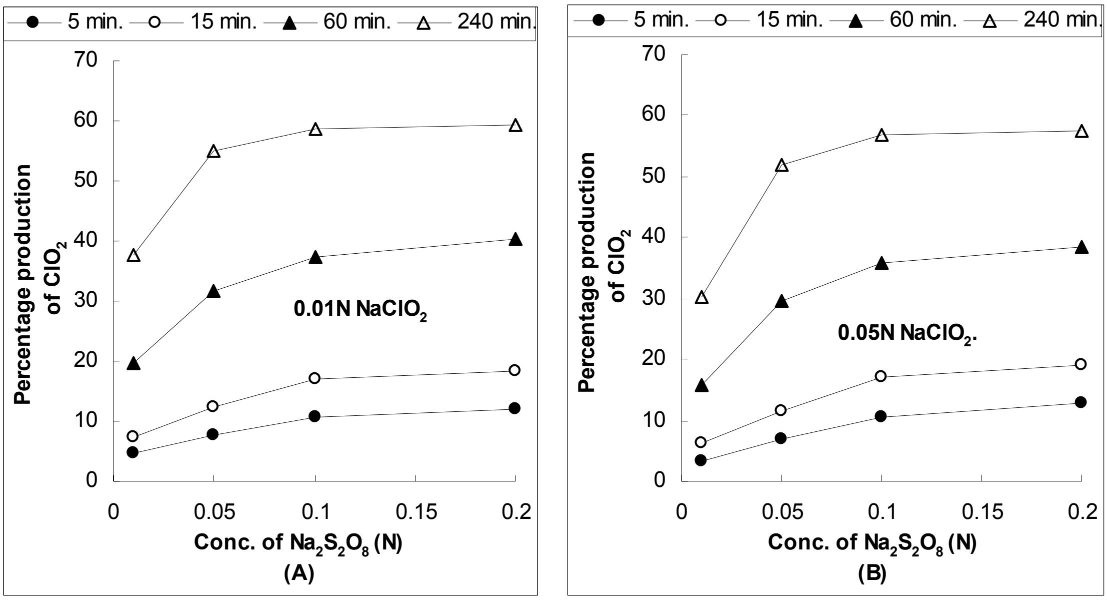


Fig. 5.24. The effect of $NaClO_2$ concentrations on the amount of ClO_2
Reaction conditions: $Na_2S_2O_8$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C.
A = 0.01N $Na_2S_2O_8$; B = 0.05N $Na_2S_2O_8$; C = 0.1N $Na_2S_2O_8$; D = 0.2N $Na_2S_2O_8$
[APPENDIX, Table-5.10 for experimental data]

5.2.3. The effect of $Na_2S_2O_8$ concentration on the percentage production of ClO_2

The study results show that the percentage production of ClO_2 was increased with increasing $Na_2S_2O_8$ concentration up to 0.1N and become almost constant with $Na_2S_2O_8$ concentration (Fig. 5.25.). The results also illustrate that the percentage production of ClO_2 increased with reaction time and the highest percentage production of ClO_2 was found in 240 minutes for all cases. The lines of graph for 5 and 15 minutes of reaction times show that the percentage production of ClO_2 increased slowly with increasing $Na_2S_2O_8$ concentration up to 0.1N and become almost constant with increasing $Na_2S_2O_8$ concentrations, but the other lines of graph for 60 and 240 minutes of reaction times show that the percentage production of ClO_2 increased rapidly with $Na_2S_2O_8$ concentration up to 0.1N and then increased very slowly or almost constant with $Na_2S_2O_8$ concentrations (Figs. 5.25.A-25.D). The highest conversion was achieved to be 60% in a reaction of 0.01N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes (Fig. 5.25.A). The experiment results illustrate that 0.1N $Na_2S_2O_8$ was the optimum concentration for the production of ClO_2 from $NaClO_2$ solution.



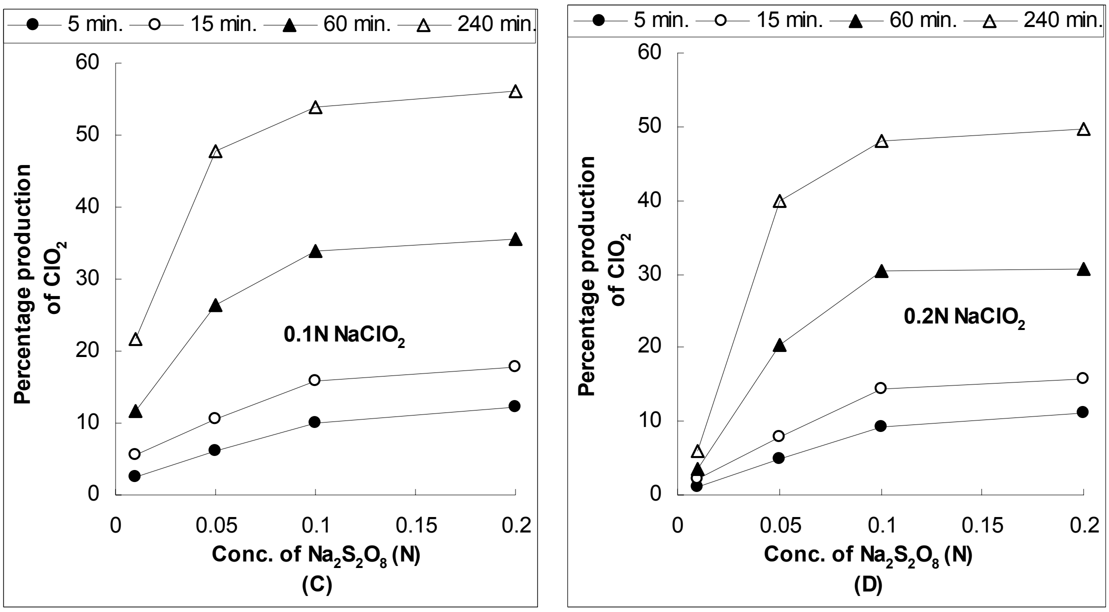


Fig. 5.25. The effect of $Na_2S_2O_8$ concentrations on the percentage production of ClO_2
Reaction conditions: $Na_2S_2O_8$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^{0}C.
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$
[APPENDIX, Table-5.11 for experimental data]

5.2.4. The effect of sodium per sulfate concentration on the amount of ClO_2

The study results show that the amount of ClO_2 increased with increasing $Na_2S_2O_8$ concentration up to 0.1N and become almost constant with $Na_2S_2O_8$ concentration (Fig. 5.26.). The results also illustrate that the amount of ClO_2 increased with reaction time and the highest amount of ClO_2 was found in 240 minutes for all cases. The lines of graph for 5 and 15 minutes of reaction times show that the amount of ClO_2 increased slowly with increasing $Na_2S_2O_8$ concentration up to 0.1N and become almost constant with increasing $Na_2S_2O_8$ concentrations, but the other lines of graph for 60 and 240 minutes of reaction times show that the amount of ClO_2 increased rapidly with $Na_2S_2O_8$ concentration up to 0.1N and then increased very slowly or almost constant with $Na_2S_2O_8$ concentrations (Figs. 5.26.A-26.D). The experiment results illustrate that 0.1N $Na_2S_2O_8$ was the optimum concentration for the production of ClO_2 from $NaClO_2$ solution. The highest amount of ClO_2 was found to be 146 mg in a reaction of 0.2N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes (Fig. 5.26.D).

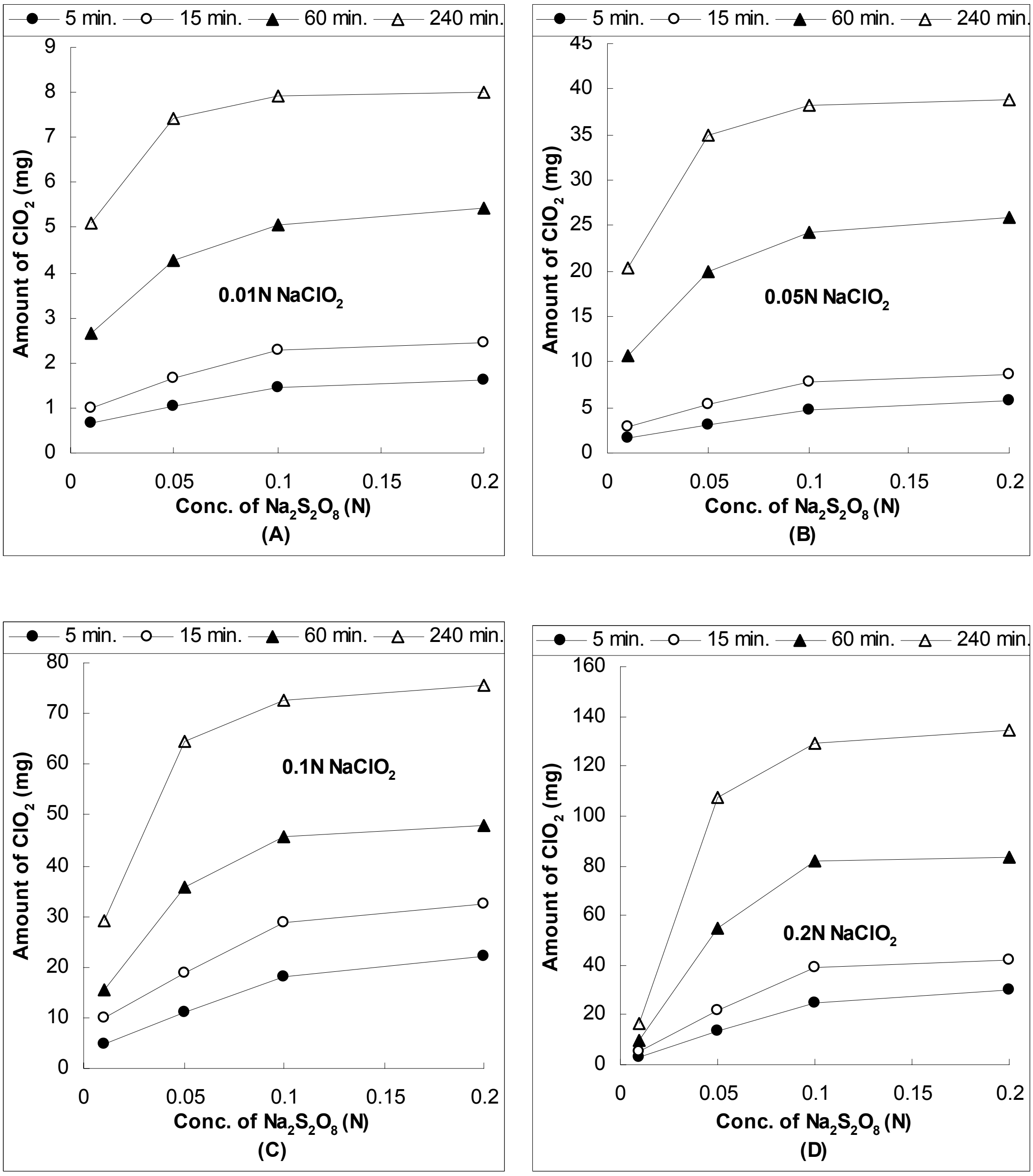
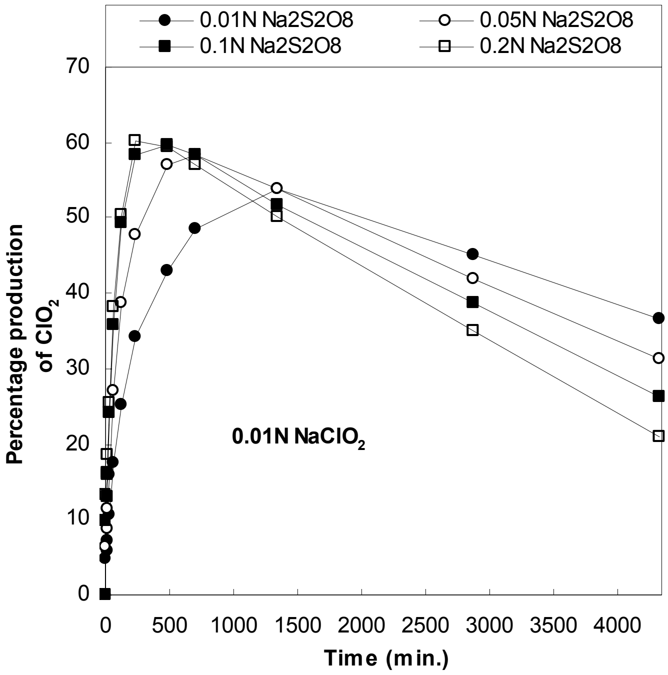


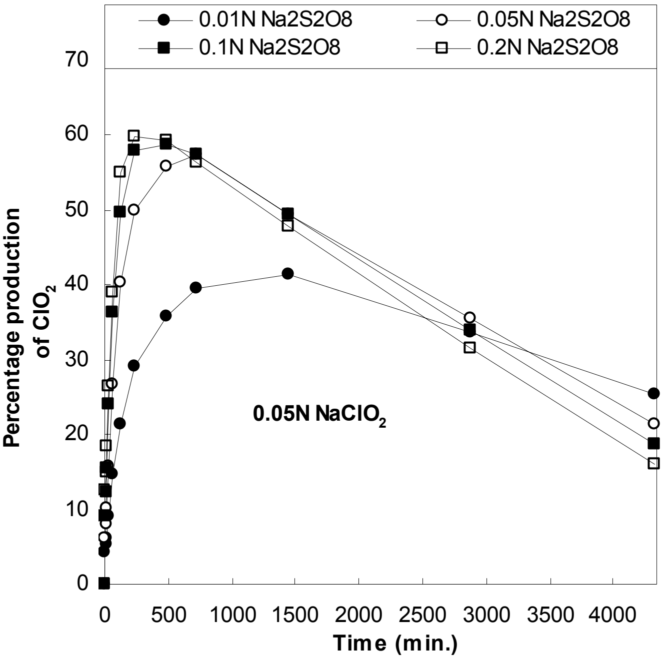
Fig. 5.26. The effect of $Na_2S_2O_8$ concentrations on the amount of ClO_2
Reaction conditions: $Na_2S_2O_8$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$
[APPENDIX, Table-5.12 for experimental data]

5.2.5. The effect of time on the percentage production of ClO_2 at various $Na_2S_2O_8$ concentrations

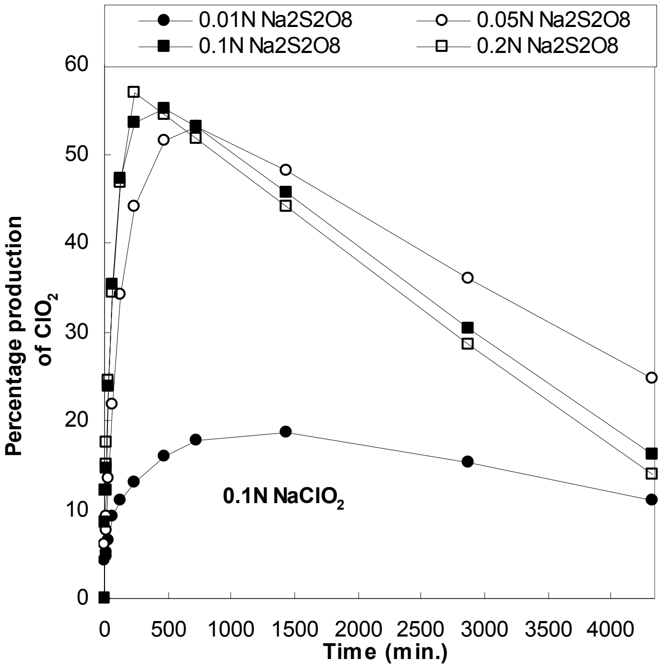
The effect of time on the percentage production of ClO_2 for a definite $NaClO_2$ and various $Na_2S_2O_8$ concentrations were shown in Fig. 5.27. The study observes that in the beginning, the percentage production of chlorine dioxide increased sharply with time until reached the maximum and then decreased with time (Figs. 5.27.A-27.D). The results also illustrate that for a definite $NaClO_2$ concentration, the percentage production of chlorine dioxide increased with increasing $Na_2S_2O_8$ concentrations. The figures show that for a definite $NaClO_2$ concentration, the time to reach the peak (maximum percentage production) was reduced with increasing $Na_2S_2O_8$ concentration and the peak height was increased with increasing $Na_2S_2O_8$concentration. The figures showed that for a definite $Na_2S_2O_8$ concentration the percentage production of ClO_2 was decreased with increasing $NaClO_2$ concentration. The figures (Figs. 5.27.A-27.D) also illustrate that the maximum percentage production of ClO_2 for various $Na_2S_2O_8$ concentrations was achieved to be between 240 and 1440 minutes and then the percentage production of ClO_2 decreased with time, this could be happened due to unstable nature of ClO_2 and moreover report showed that it was readily decomposed to chloride ions since it was found[116,117,181]. The overall observation of these figures illustrate that the percentage production of ClO_2 was largely dependent on time and the concentration of reactants. The highest conversion was achieved to be 60% in a reaction of 0.01N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes (Fig. 5.27.A).



(A)


0.01N Na2S2O8
0.05N Na2S2O8
0.1N Na2S2O8
0.2N Na2S2O8
0.05N NaClO$_2$
Percentage production of ClO$_2$
Time (min.)
0
10
20
30
40
50
60
70
0
500
1000
1500
2000
2500
3000
3500
4000

(B)


0.01N Na2S2O8
0.05N Na2S2O8
0.1N Na2S2O8
0.2N Na2S2O8
0.1N NaClO$_2$
Percentage production of ClO$_2$
Time (min.)
0
10
20
30
40
50
60
0
500
1000
1500
2000
2500
3000
3500
4000

(C)

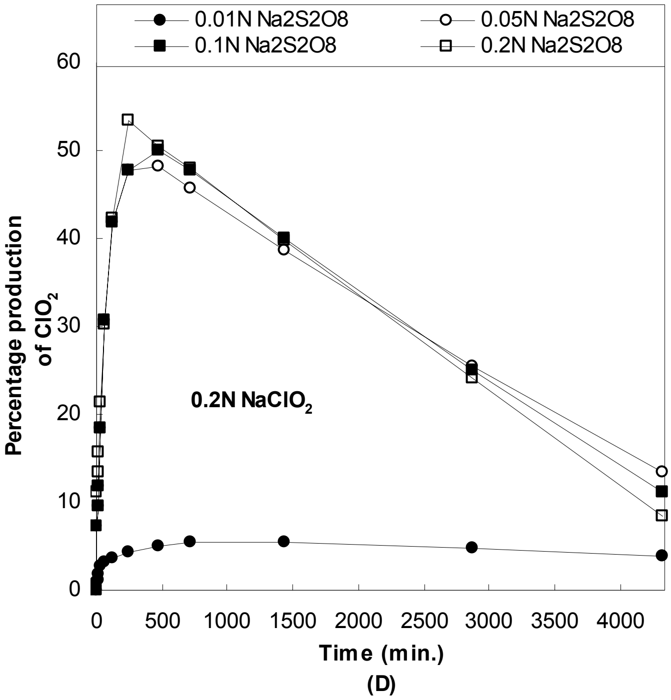
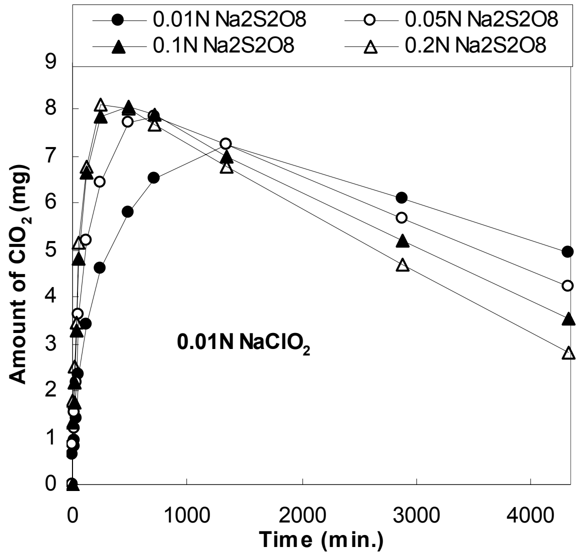


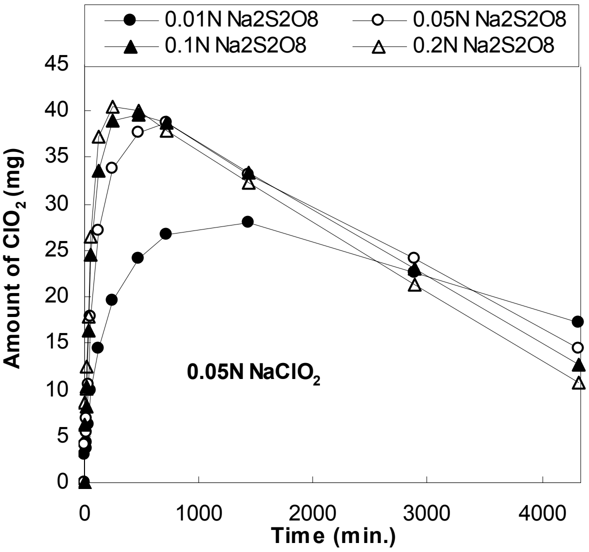
Fig. 5.27. The effect of time on the percentage productions of ClO_2
Reaction conditions: $Na_2S_2O_8$: $NaClO_2$ (v/v) 1: 1; temperature, 30 ± 1^0C.
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$
[APPENDIX, Table-5.13 for experimental data]

5.2.6. The effect of time on the amount of ClO_2 at various $Na_2S_2O_8$ concentrations

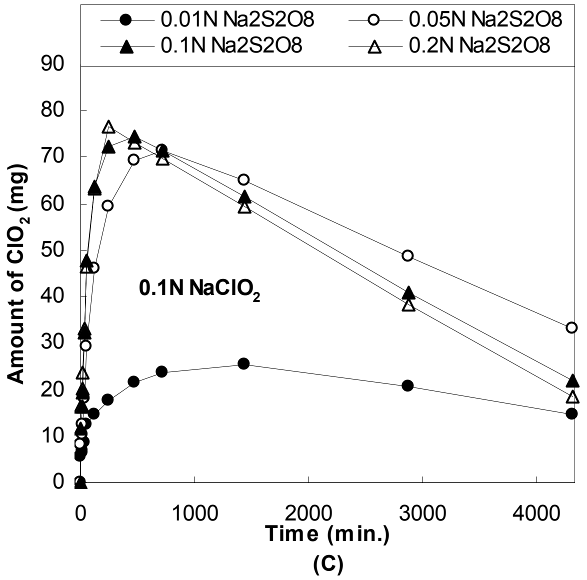
The effect of time on the amount of ClO_2 for a definite $NaClO_2$ and various $Na_2S_2O_8$ concentrations were shown in Fig. 5.28. The study observes that in the beginning, the amount of ClO_2 increased sharply with increasing time until reached the maximum and then decreased with time (Figs. 5.28.A-28.D). The results also illustrate that for a definite $NaClO_2$ concentration, the amount of ClO_2 increased with increasing $Na_2S_2O_8$ concentration. The results show that for a definite $NaClO_2$ concentration, the time to reach the peak (maximum percentage production) was reduced with increasing $Na_2S_2O_8$ concentration and the peak height was increased with $Na_2S_2O_8$ concentration. The overall observation of these figures illustrate that the amount of ClO_2 was largely depended on time and reactants concentration. The figures (Figs. 5.28.A-28.D) also illustrate that the maximum amount of ClO_2 for various $Na_2S_2O_8$ concentration was achieved to be between 240 and 1440 minutes and then the amount of ClO_2 decreased with time; this could be happened due to unstable nature of ClO_2. The highest amount of ClO_2 was found to be 146 mg in a reaction of 0.2N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes (Fig. 5.28.D).


0.01N Na2S2O8
0.05N Na2S2O8
0.1N Na2S2O8
0.2N Na2S2O8
Amount of ClO_2 (mg)
0.01N $NaClO_2$
Time (min.)
0
1
2
3
4
5
6
7
8
9
0
1000
2000
3000
4000

(A)


0.01N Na2S2O8
0.05N Na2S2O8
0.1N Na2S2O8
0.2N Na2S2O8
Amount of ClO_2 (mg)
0.05N $NaClO_2$
Time (min.)
0
5
10
15
20
25
30
35
40
45
0
1000
2000
3000
4000

(B)


0.01N Na2S2O8
0.05N Na2S2O8
0.1N Na2S2O8
0.2N Na2S2O8
Amount of ClO_2 (mg)
0.1N $NaClO_2$
Time (min.)
0
10
20
30
40
50
60
70
80
90
0
1000
2000
3000
4000

(C)

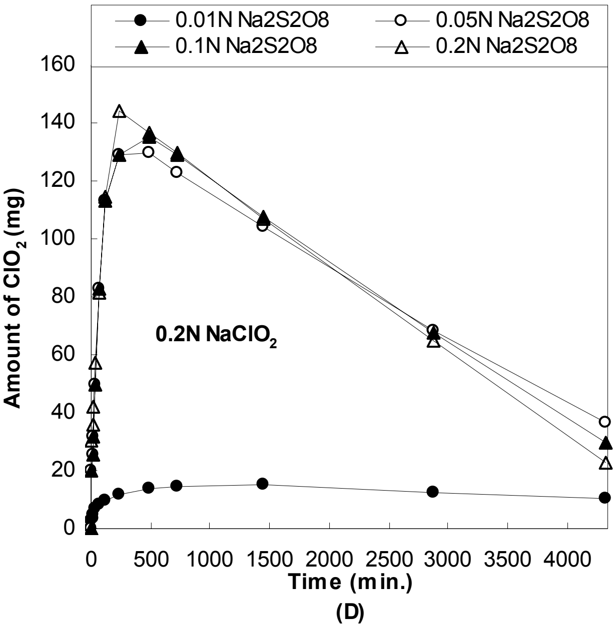
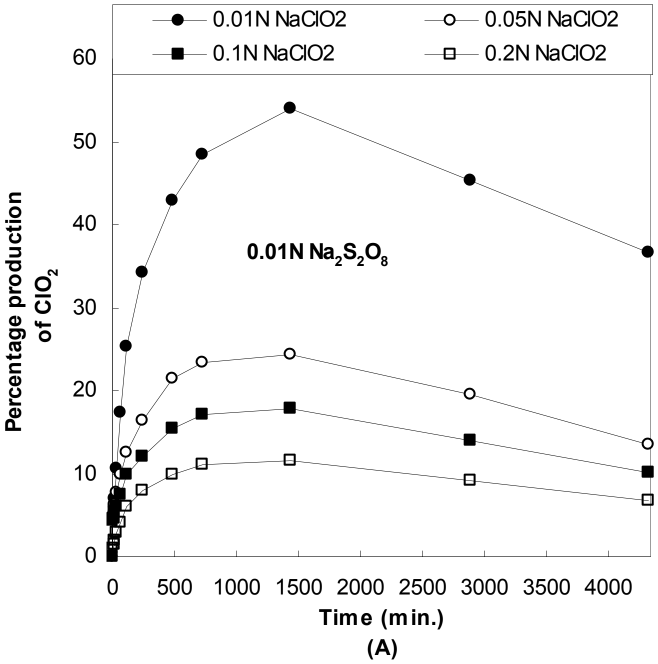
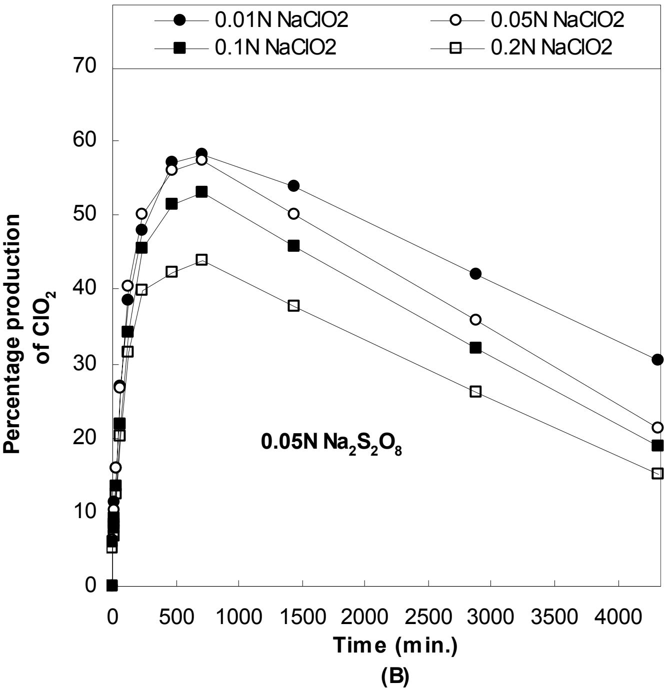


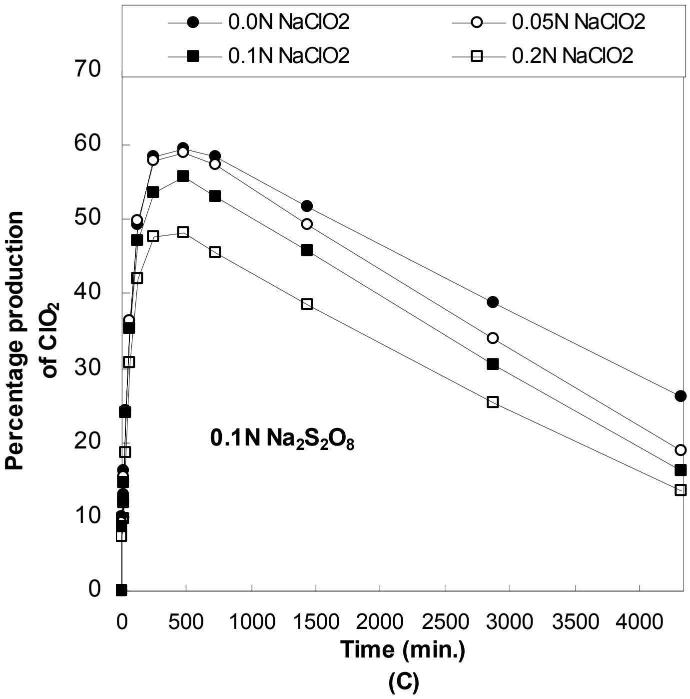
Fig. 5.28. The effect of time on the amount of ClO_2
Reaction conditions: $Na_2S_2O_8$: $NaClO_2$ (v/v) 1: 1, temperature, 30 ± 1^0C
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$
[APPENDIX, Table-5.14 for experimental data]

5.2.7. The effect of time on the percentage production of ClO_2 at various $NaClO_2$ concentrations

The effects of time on the percentage production of ClO_2 for a definite $Na_2S_2O_8$ and various $NaClO_2$ concentrations were shown in Fig. 5.29. The study observes that in the beginning, the percentage production of ClO_2 increased sharply with increasing time until reached the maximum and then decreased with time (Figs. 5.29.A-29.D). In Fig. 5.29.A, the percentage production of ClO_2 increased sharply in the beginning and then slowly until reaching the maximum and finally decreased with time. The figure also shows that the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentrations. Similar trend was found in Figs. 5.29.B-29.D, where the percentage production of ClO_2 increased sharply in the beginning until reaching the maximum and then decreased with time. The figures (Figs. 5.29.A-29.D) also illustrate that the maximum percentage production of ClO_2 for various $NaClO_2$ concentrations was achieved to be between 240 and 1440 minutes and then the percentage production decreased with time, this could be happened due to unstable nature of ClO_2 and moreover report showed that it was readily decomposed to chloride ions since it was found. The overall observation of these figures illustrate that the percentage production of ClO_2 was largely dependent on time and reactants concentration. The highest conversion was achieved to be 60% in a reaction of 0.01N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes (Fig. 5.29.D).







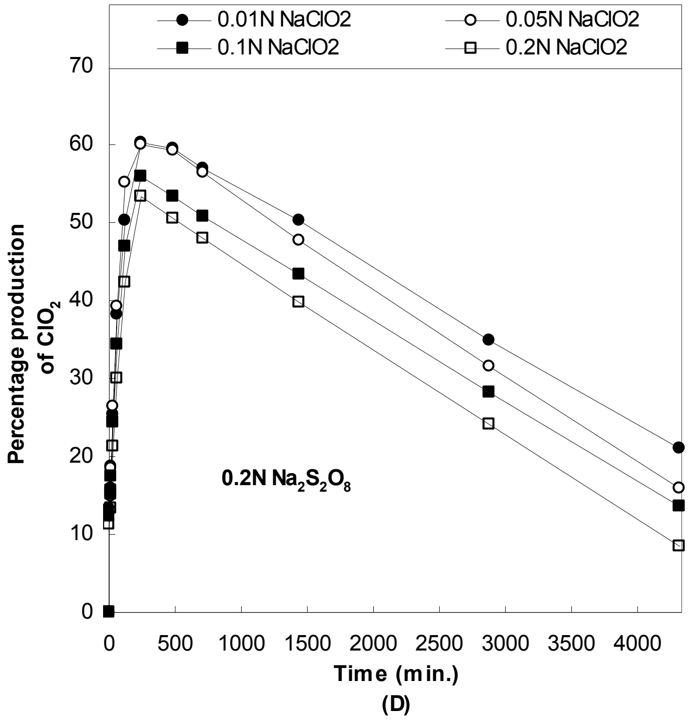
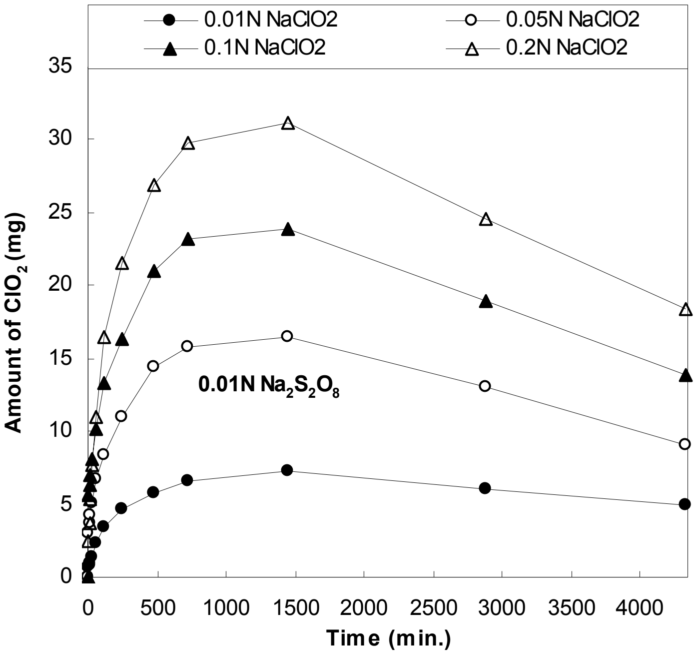


Fig. 5.29. The effect of time on the percentage productions of ClO_2
Reaction conditions: $Na_2S_2O_8$: $NaClO_2$ (v/v) 1: 1; temperature, 30 ± 1^0C
A = 0.02N $Na_2S_2O_8$; B = 0.1N $Na_2S_2O_8$; C = 0.2N $Na_2S_2O_8$; D = 0.4N $Na_2S_2O_8$
[APPENDIX, Table-5.15 for experimental data]

5.2.8. The effect of time on the amount of ClO_2 at various $NaClO_2$ concentrations

The effects of time on the amount of ClO_2 for a definite $Na_2S_2O_8$ and various $NaClO_2$ concentrations were shown in Fig. 5.30. The study observes that in the beginning, the amount of ClO_2 increased sharply with increasing time until reaching the maximum and then decreased with time (Figs. 5.30.A-30.D). The results also illustrate that for a definite $Na_2S_2O_8$ concentration, the amount of ClO_2 increased with increasing $NaClO_2$ concentration. The results show that the time to reach the peak (maximum percentage production) was reduced with increasing $Na_2S_2O_8$ concentration and the peak height was increased with $Na_2S_2O_8$ concentration. The overall observation of these figures illustrate that the amount of ClO_2 was largely dependent on time and reactants concentration. The figures (Figs. 5.30.A-30.D) also illustrate that the maximum amount of ClO_2 for various $NaClO_2$ concentrations was achieved to be between 240 and 1440 minutes and then the amount of ClO_2 decreased with time, this could be happened due to unstable nature of ClO_2 and moreover report showed that it was readily decomposed to chloride ions since it was formed. The highest amount of ClO_2 was found to be 146 mg in a reaction of 0.2N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes (Fig. 5.30.D).



(A)

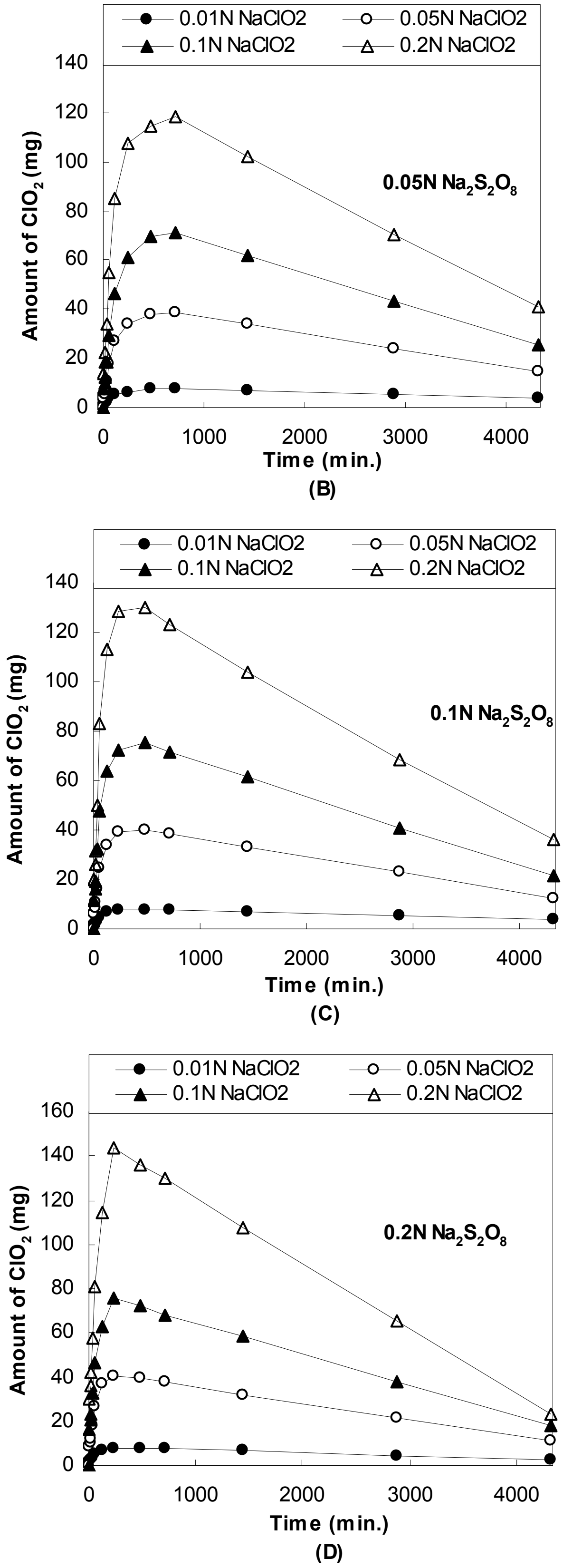


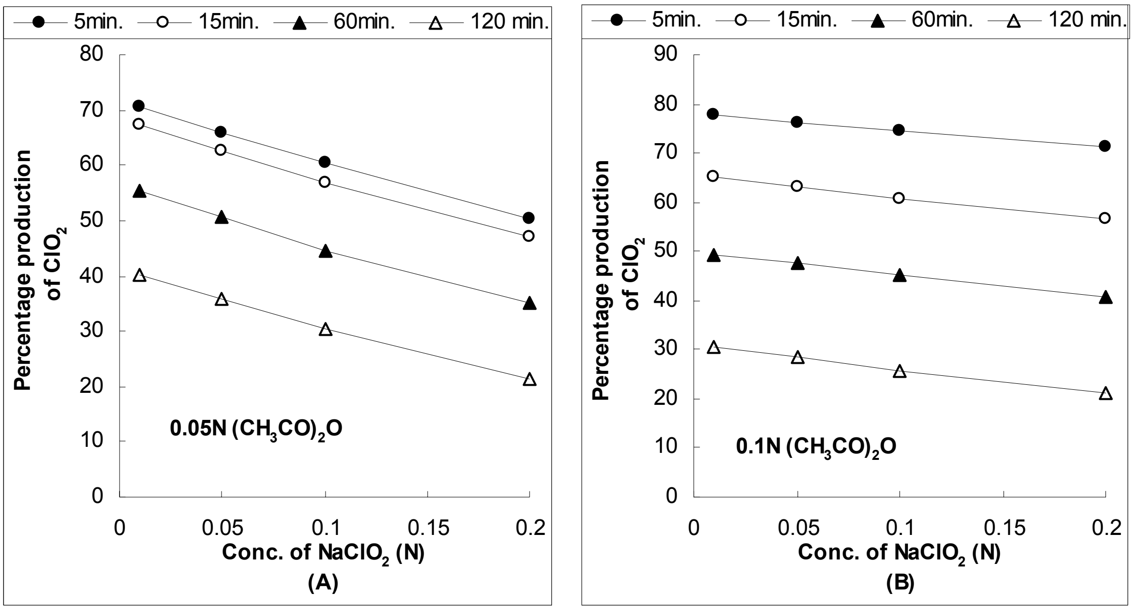
Fig. 5.30. The effect of time on the amount of ClO_2
Reaction conditions: $Na_2S_2O_8$: $NaClO_2$ (v/v) 1: 1; temperature, 30 ± 1^0C
A = 0.02N $Na_2S_2O_8$; B = 0.1N $Na_2S_2O_8$; C = 0.2N $Na_2S_2O_8$; D = 0.4N $Na_2S_2O_8$
[APPENDIX, Table-5.16 for experimental data]

5.3. Preparation of chlorine dioxide from sodium chlorite and acetic anhydride

This study was attempted to generate chlorine dioxide by a reaction of sodium chlorite and acetic anhydride. The effects of reactants concentration and reaction time on the production of chlorine dioxide are discussed here. The reaction was carried out at a temperature 30 ± 1^{0}C and the volume ratio of $(CH_3CO)_2O$ and $NaClO_2$ was 1:1(v/v).

5.3.1. The effect of $NaClO_2$ concentration on the percentage production of ClO_2

The study results show that the percentage production of ClO_2 decreased with increasing of $NaClO_2$ concentration (Fig. 5.31.). The results also illustrate that the percentage production of ClO_2 decreased with increasing reaction time and the highest percentage production was found in 5 minutes for all cases. The highest percentage production of ClO_2 was found to be 77% in a reaction of 0.01N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ in 5 minutes (Fig. 5.31.B). The study results illustrate that the percentage production of ClO_2 showed the maximum within a few minutes (Fig. 5.31.A-31.D), which indicating the rapid completion of the reaction process[146,149]. The figures illustrate that the percentage production of ClO_2 dependent on both the $NaClO_2$ concentration and the reaction time. As the percentage production of ClO_2 is a ratio of product (ClO_2) to initial $NaClO_2$ concentration, and $NaClO_2$ was the only source of chlorite species, thus it is obvious that the amount of ClO_2 was not proportional to $NaClO_2$ concentration for a definite $(CH_3CO)_2O$ concentration. Hence the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentration as expected.



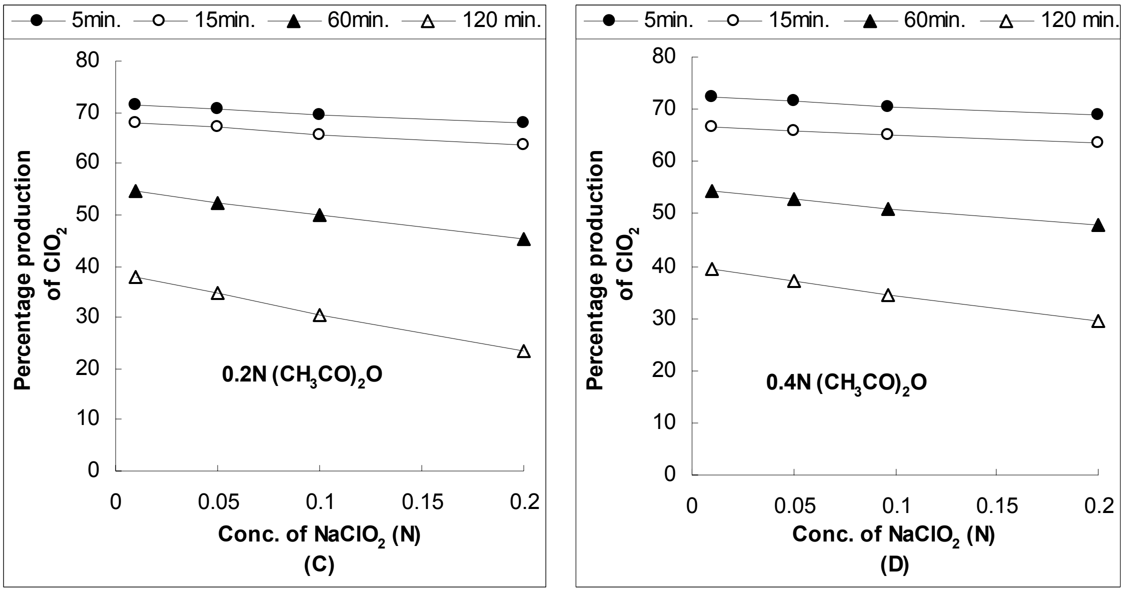


Fig. 5.31. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; temperature, 30 ± 1^0C
A = 0.05N $(CH_3CO)_2O$; B = 0.1N $(CH_3CO)_2O$;
C = 0.2 N $(CH_3CO)_2O$; D = 0.4N$(CH_3CO)_2O$
[APPENDIX, Table-5.17 for experimental data]

5.3.2. The effect of sodium chlorite concentration on the amount of ClO_2

The study results show that the amount of ClO_2 increased with increasing concentration of $NaClO_2$ (Fig. 5.32.). The results also illustrate that the amount of ClO_2 decreased with increasing reaction time and the highest amount of ClO_2 was obtained in 5 minutes for all cases. The highest amount of ClO_2 was found to be 191 mg in a reaction of 0.2N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ for 5 minutes (Fig. 5.32.B). $NaClO_2$ was the only source of chlorite ion hence; it is obvious that the concentration of $NaClO_2$ had a great effect on the production of ClO_2.

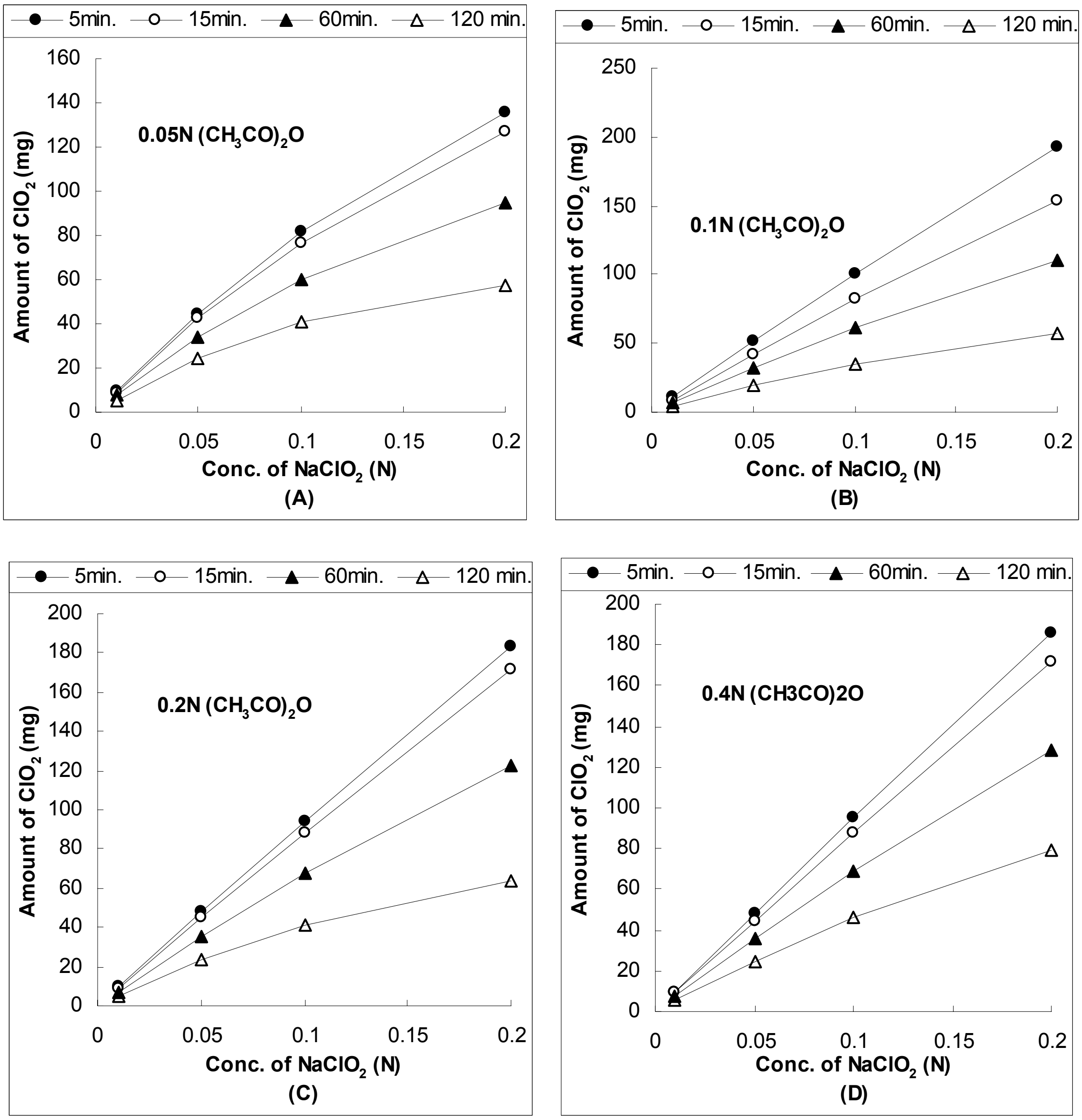


Fig. 5.32. The effect of $NaClO_2$ concentrations on the amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; temperature, 30 ± 1^0C.
A = 0.05N $(CH_3CO)_2O$; B = 0.1N $(CH_3CO)_2O$;
C = 0.2 N $(CH_3CO)_2O$; D = 0.4N$(CH_3CO)_2O$
[APPENDIX, Table-5.18 for experimental data]

5.3.3. The effect of $(CH_3CO)_2O$ concentration on the percentage production of ClO_2

The study results show that the percentage production of ClO_2 increased with increasing $(CH_3CO)_2O$ concentration up to 0.1N and then decreased with increasing $(CH_3CO)_2O$ concentrations (Fig. 5.33.). The highest percentage production of ClO_2 was found in 5 minutes for all cases. Similar observation was made for all figures (Figs. 5.33.A-33.D), where the percentage production of ClO_2 sharply increased with increasing $(CH_3CO)_2O$ concentration up to 0.1N and then decreased with $(CH_3CO)_2O$ concentration.. The experiment results illustrate that 0.1N $(CH_3CO)_2O$ was the optimum concentration for the production of ClO_2 from $NaClO_2$ solution. The highest percentage production of ClO_2 was found to be 77% in a reaction of 0.01N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ for 5 minutes (Fig. 5.33.A).

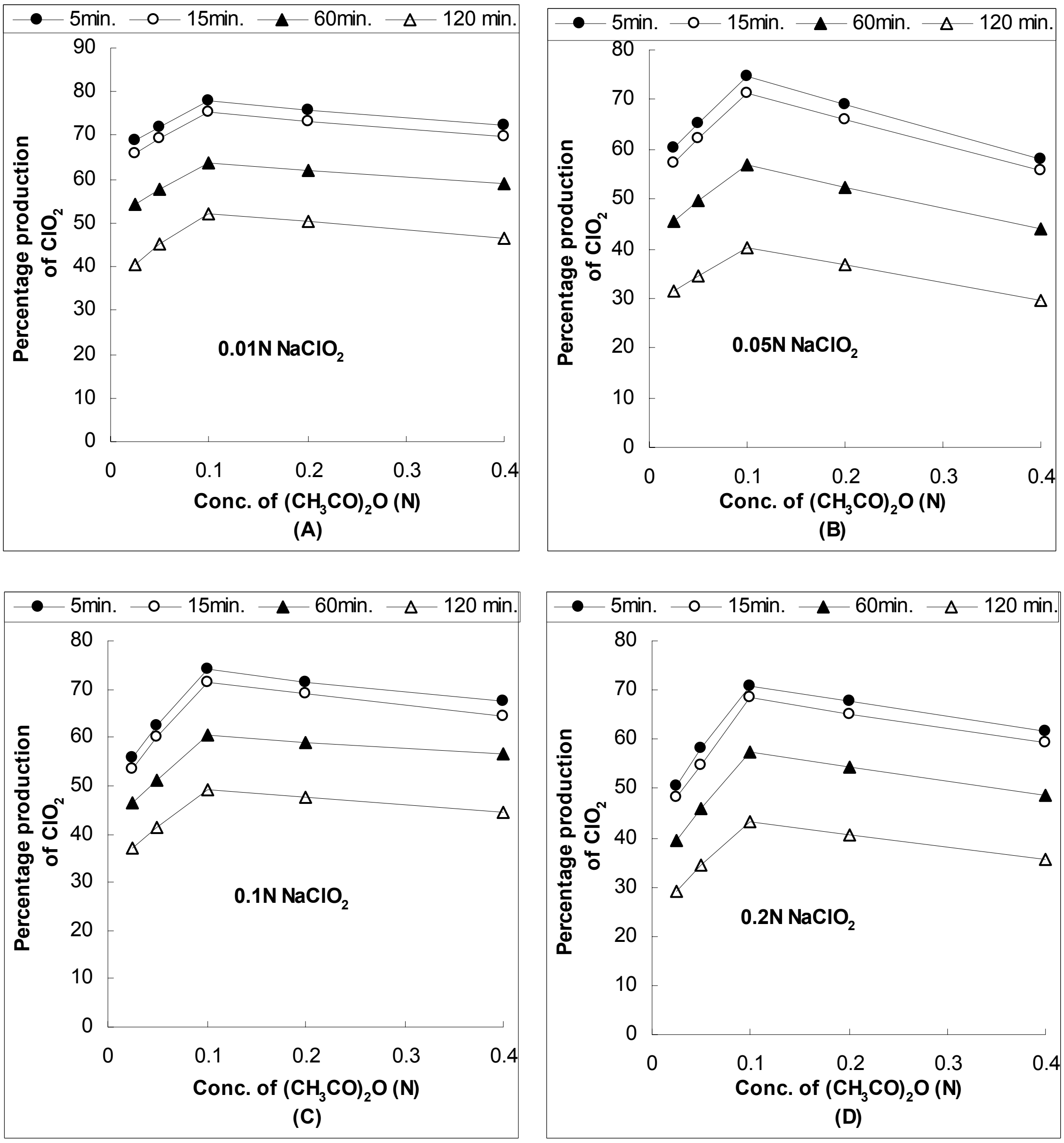


Fig. 5.33. The effect of $(CH_3CO)_2O$ concentrations on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; temperature, 30 ± 1^0C
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$
[APPENDIX, Table-5.19 for experimental data]

5.3.4. The effect of $(CH_3CO)_2O$ concentration on the amount of ClO_2

The study results show that the amount of ClO_2 increased with increasing $(CH_3CO)_2O$ concentration up to 0.1N and then decreased with $(CH_3CO)_2O$ concentration (Fig. 5.34.). The highest amount of ClO_2 was found in 5 minutes for all cases. Similar observation was made for all figures (Figs. 5.34.A-34.D), where the amount of ClO_2 sharply increased with increasing $(CH_3CO)_2O$ concentration up to 0.1N and then decreased with increasing $(CH_3CO)_2O$ concentration. The highest amount of ClO_2 was found to be 191 mg in a reaction of 0.2N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ for 5 minutes (Fig. 5.34.D). The experiment results illustrate that 0.1N $(CH_3CO)_2O$ was the optimum concentration for the production of ClO_2 from $NaClO_2$ solution.

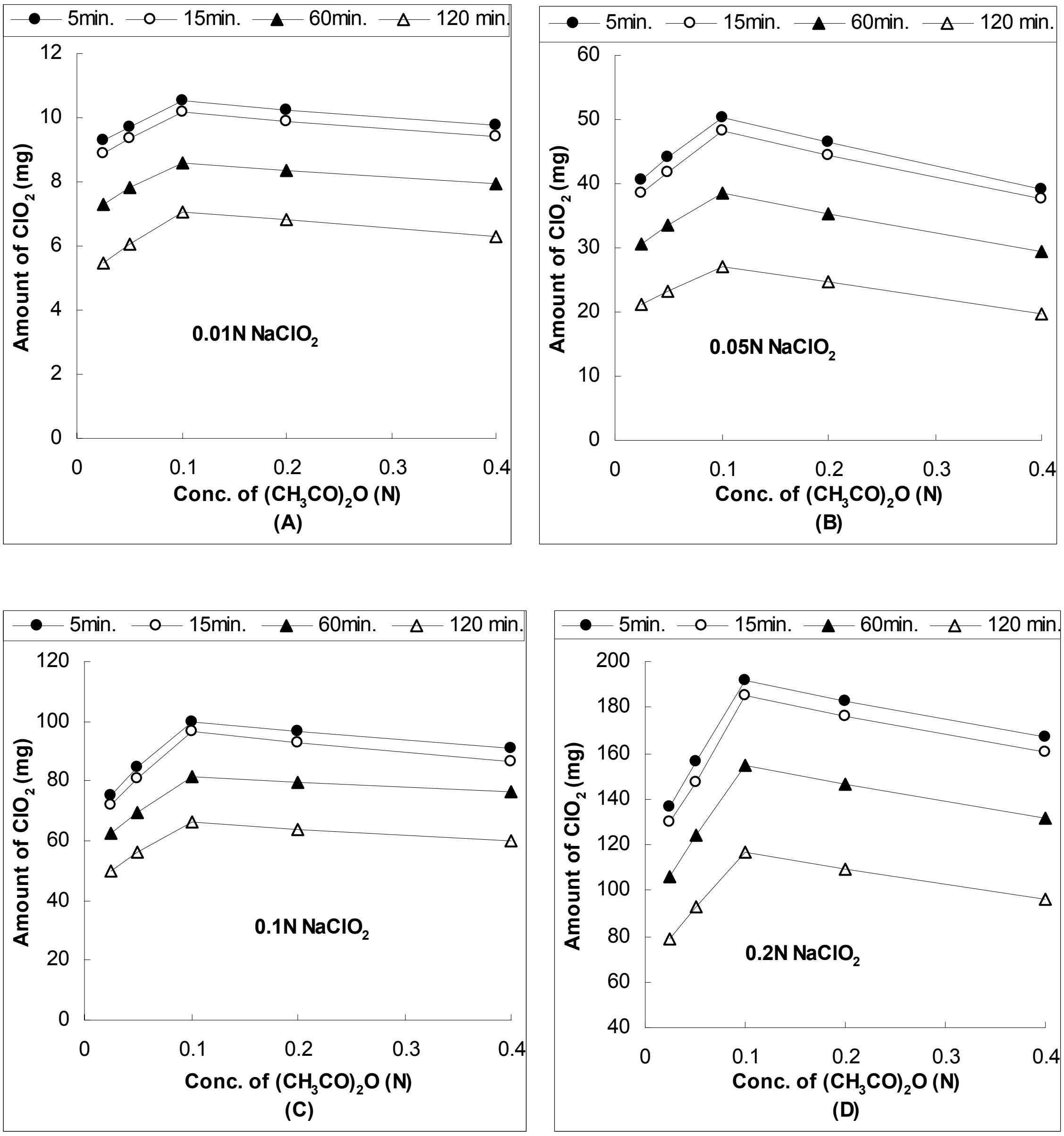


Fig. 5.34. The effect of $(CH_3CO)_2O$ concentrations on the amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; temperature, 30 ± 1^0C
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$
[APPENDIX, Table-5.20 for experimental data]

5.3.5. The effect of time on the percentage production of ClO_2 at various $CH_3CO)_2O$ concentrations

The effects of time on the percentage production of ClO_2 for a definite $NaClO_2$ and various $CH_3CO)_2O$ concentrations were shown in Figs. 5.35.-5.38. The study observes that from the beginning, the percentage production of ClO_2 decreased sharply with increasing time for all cases (Figs. 5.35.-5.38.), which indicating the rapid completion of the reaction process. The percentage production of ClO_2 was found for the reaction time in the order: 2 minutes >5 minutes > 15 minutes >30 minutes > 60 minutes > 120 minutes. The overall observation of these figures illustrate that the percentage production of ClO_2 was largely dependent on time and reactants concentration. The highest percentage production of ClO_2 was found to be 78% in a reaction of 0.01N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ within two minutes (Fig. 5.35.).

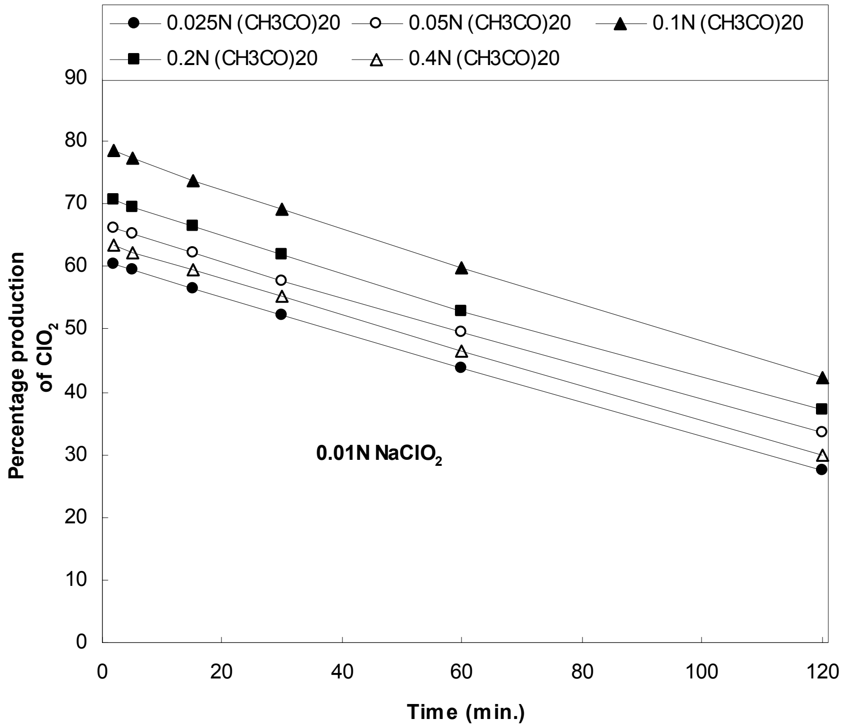


Fig. 5.35. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.21A for experimental data]

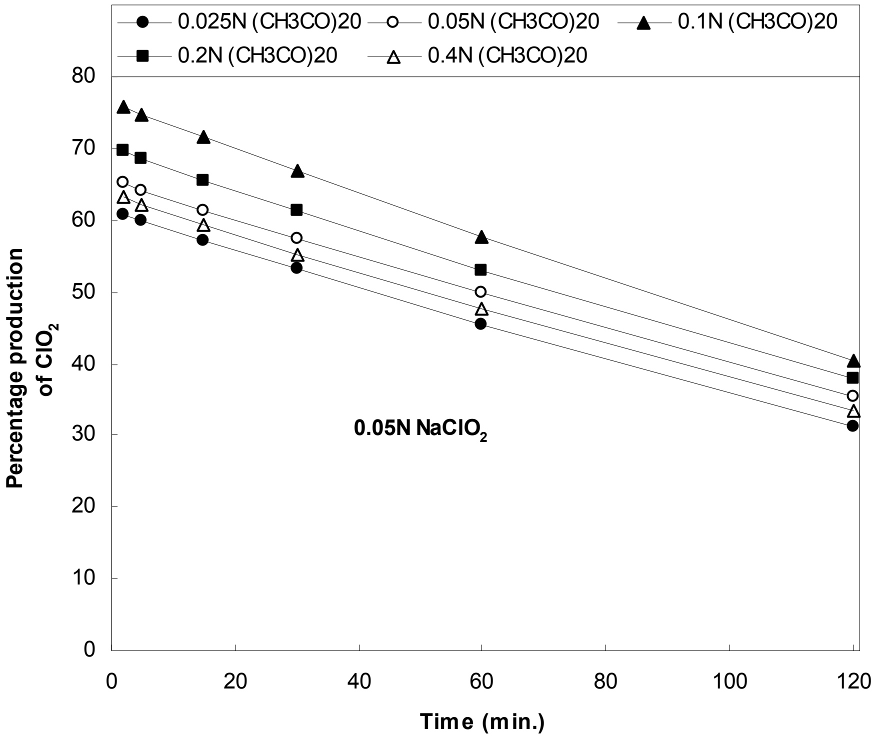


Fig. 5.36. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.21.B for experimental data]

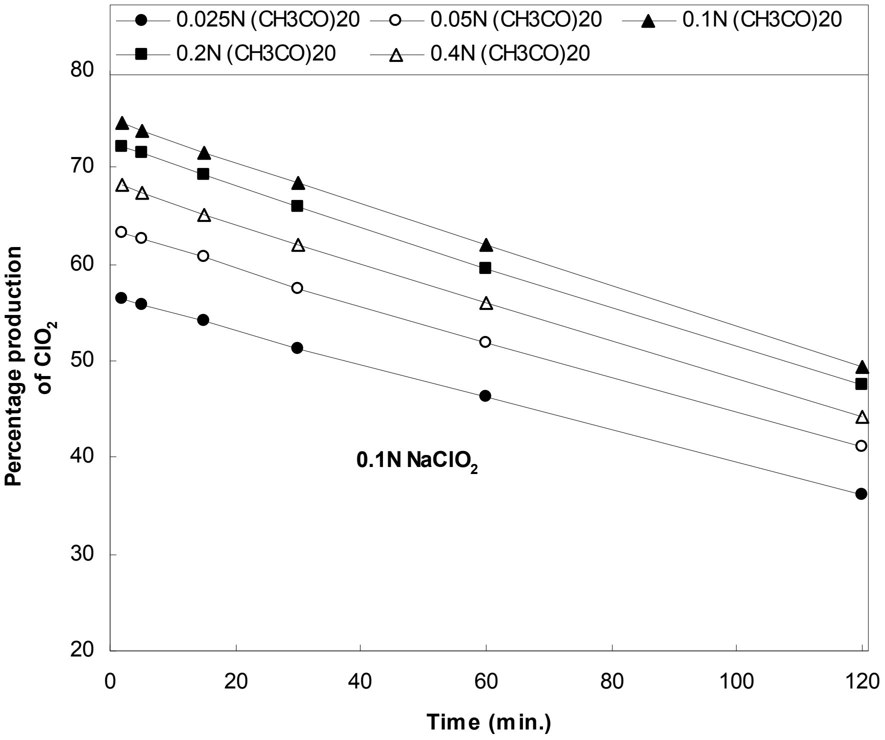


Fig. 5.37. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.21.C for experimental data]

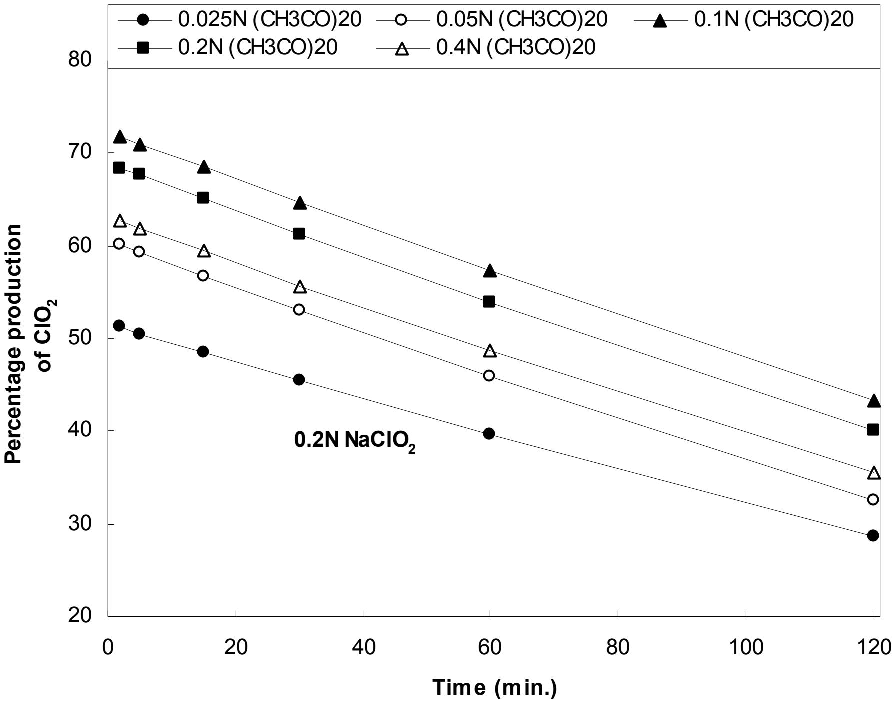


Fig. 5.38. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.21.D for experimental data]

5.3.6. The effect of time on the amount of ClO_2 at various $CH_3CO)_2O$ concentrations

The effects of time on the amount of ClO_2 for a fixed $NaClO_2$ and various $CH_3CO)_2O$ concentrations were shown in Figs. 5.39.-5.42. The study observes that from the beginning, the amount of ClO_2 decreased sharply with time for all cases (Figs. 5.39.-5.42.), which indicating the rapid completion of the reaction process. The amount of ClO_2 was found for the reaction time in the order: 2 minutes >5 minutes > 15 minutes >30 minutes > 60 minutes > 120 minutes. The overall observation of these figures illustrate that the amount of ClO_2 was largely depended on time and reactants concentration. The highest amount of ClO_2 was found to be 193 mg in a reaction of 0.2N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ within two minutes (Fig. 5.42.).

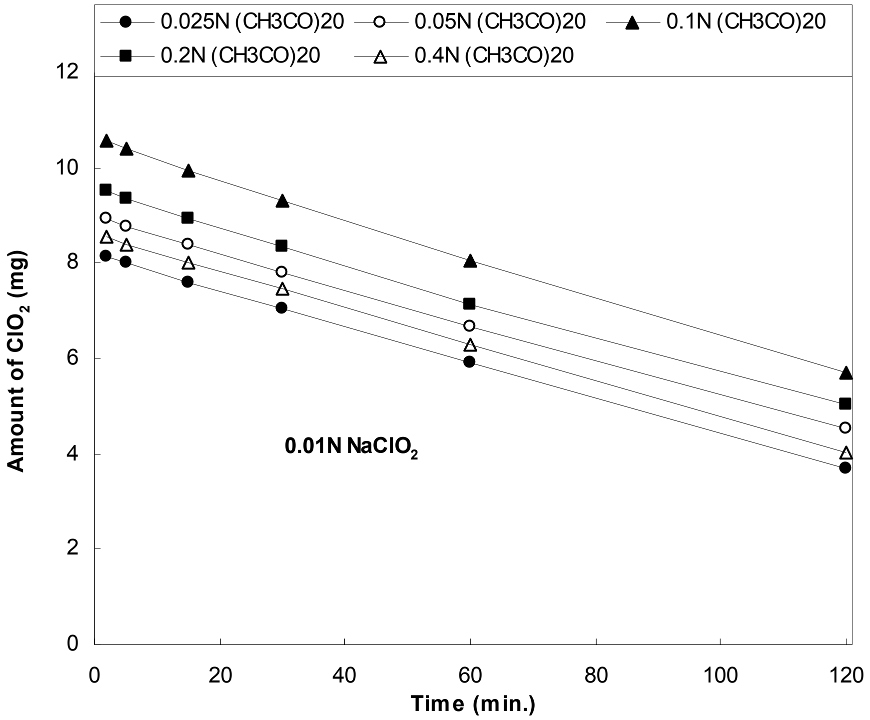


Fig. 5.39. The effect of reaction time on the amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.22.A for experimental data]

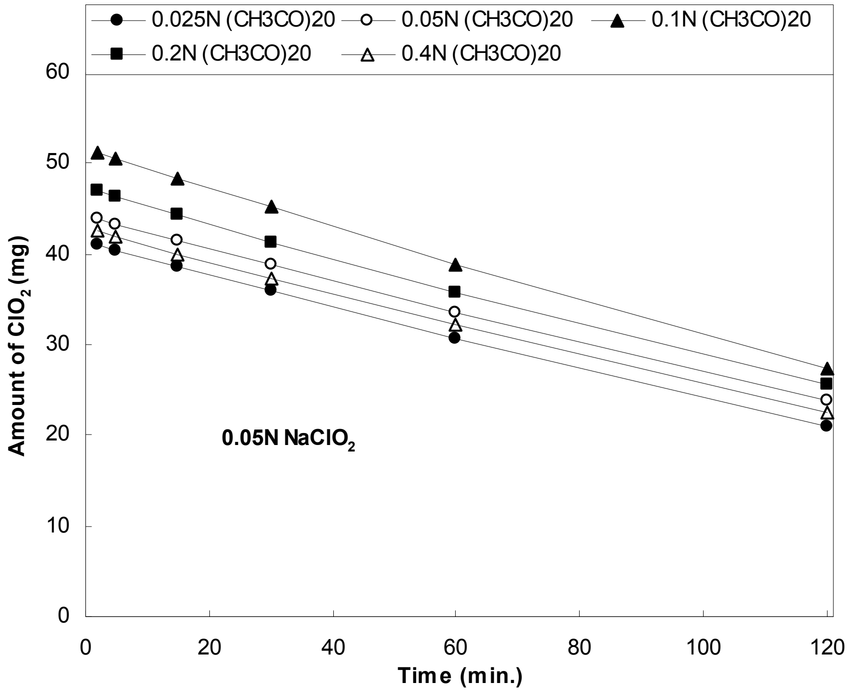


Fig. 5.40. The effect of reaction time on amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.22.B for experimental data]

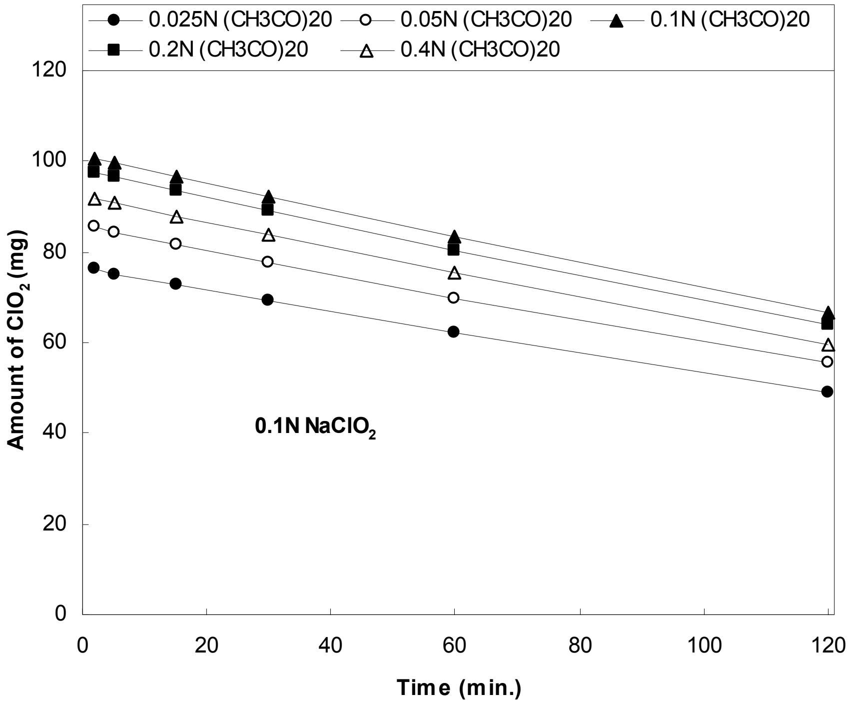


Fig. 5.41. The effect of reaction time on amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.22.C for experimental data]

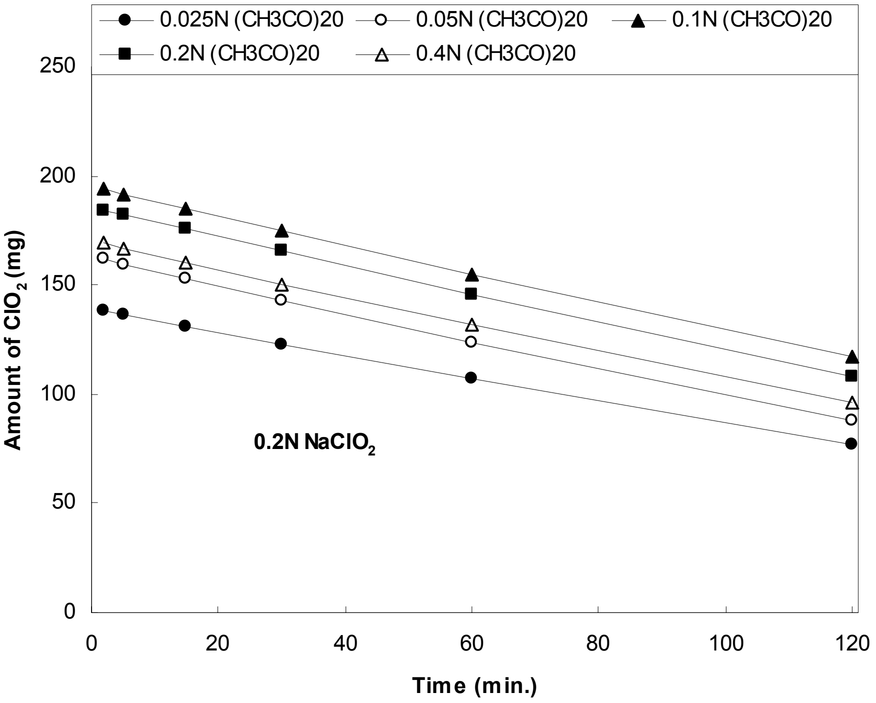


Fig. 5.42. The effect of reaction time on amount of ClO_2.
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.22.D for experimental data]

5.3.7. The effect of time on the percentage production of ClO_2 at various $NaClO_2$ concentrations

The effects of time on the percentage production of ClO_2 for a definite $CH_3CO)_2O$ and various $NaClO_2$ concentrations were shown in Figs. 5.43.-5.47. The results illustrate that from the beginning, the percentage production of ClO_2 decreased sharply with increasing time for all cases (Figs. 5.43.-5.47.), which indicating the rapid completion of the reaction process. The percentage production of ClO_2 was found for the reaction time in the order: 2 minutes >5 minutes > 15 minutes >30 minutes > 60 minutes > 120 minutes. The overall observation of these figures illustrate that the percentage production of ClO_2 was largely dependent on time and reactants concentration. The highest percentage production of ClO_2 was found to be 78% in a reaction of 0.01N $NaClO_2$ and 0.1N $CH_3CO)_2O$ within 2 minutes (Fig. 5.45.).

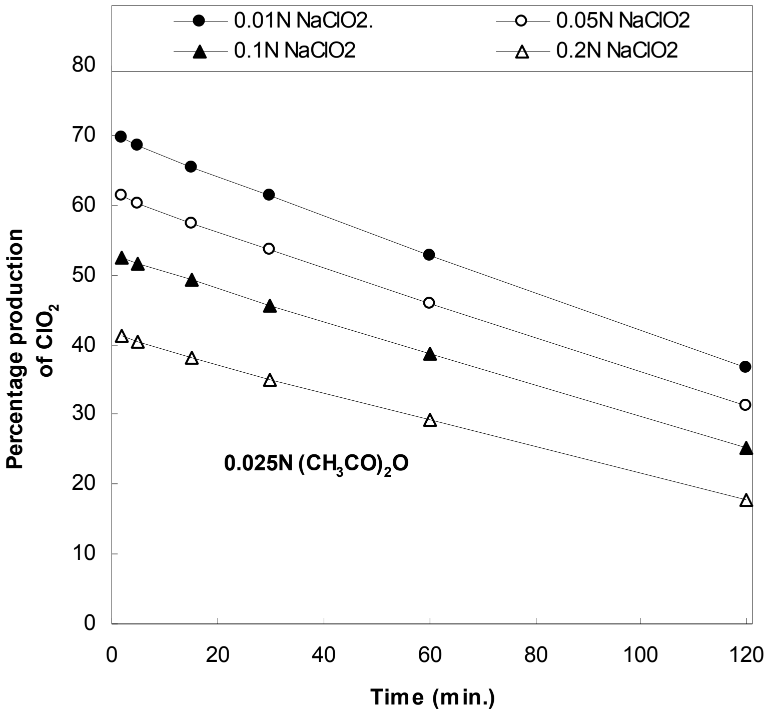


Fig. 5.43. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.23.A for experimental data]

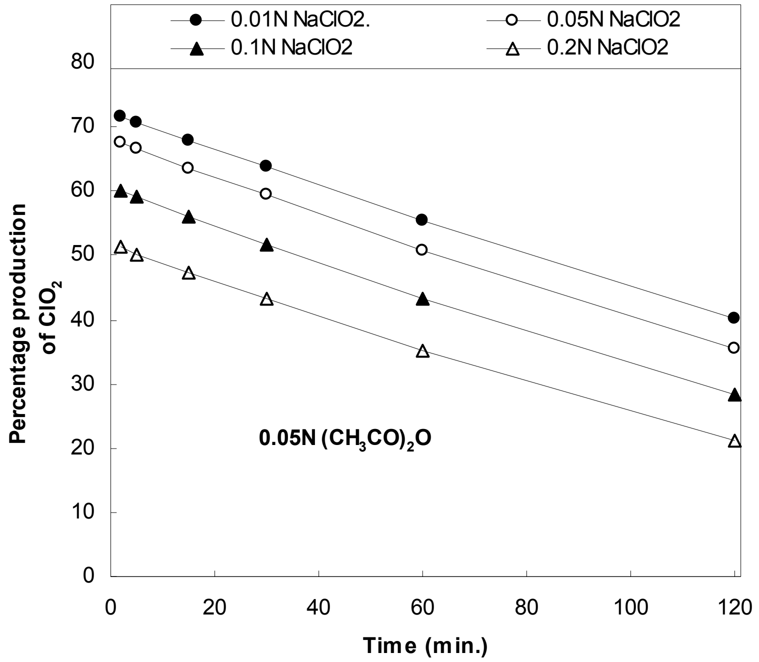


Fig. 5.44. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.23.B for experimental data]

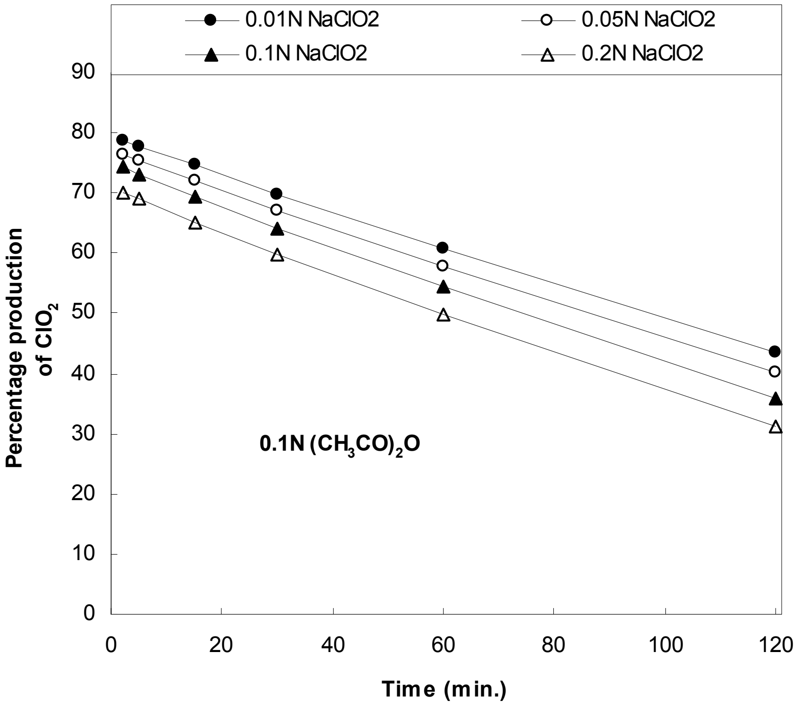


Fig. 5.45. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.23.C for experimental data]

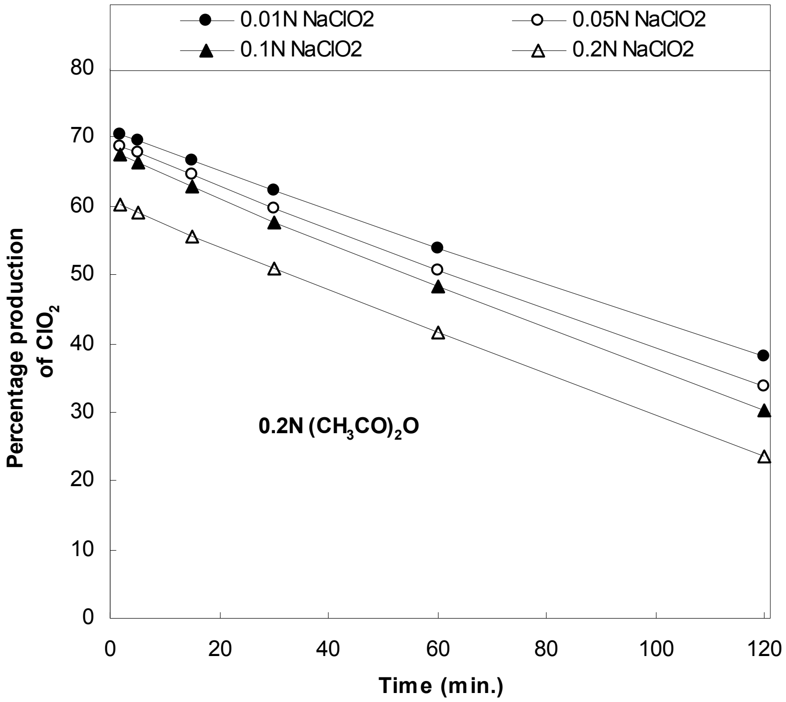


Fig. 5.46. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.23.D for experimental data]

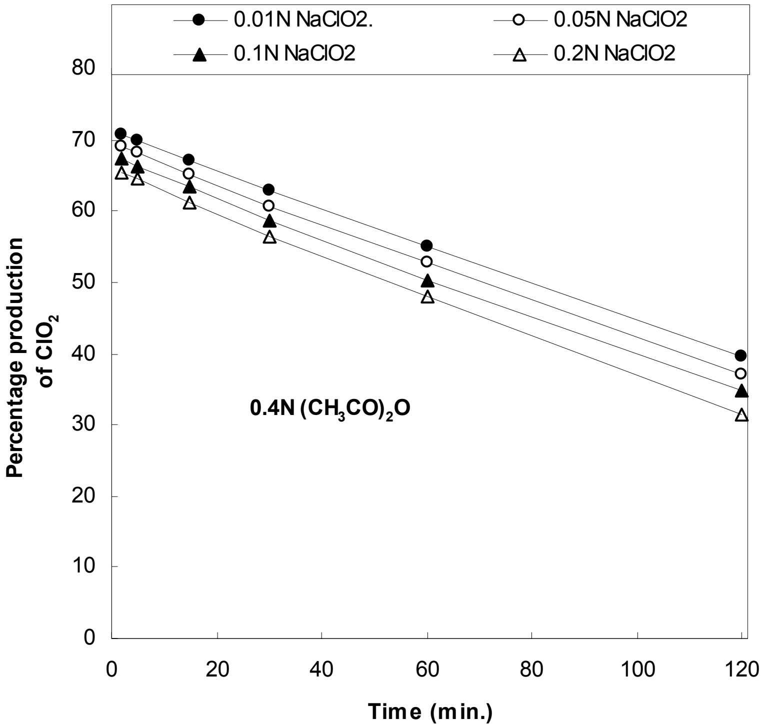


Fig. 5.47. The effect of reaction time on the percentage production of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.23.E for experimental data]

5.3.8. The effect of time on the amount of ClO_2 at various $NaClO_2$ concentrations

The effects of time on the amount of ClO_2 for a definite $(CH_3CO)_2O$ and various $NaClO_2$ concentrations were shown in Figs. 5.48-5.52. The results illustrate that from the beginning, the amount of ClO_2 decreased sharply with increasing time for all cases (Figs. 5.48-5.52.), which indicating the rapid completion of the reaction process. The amount of ClO_2 was found for the reaction time in the order: 2 minutes >5 minutes > 15 minutes >30 minutes > 60 minutes > 120 minutes. The overall observation of these figures illustrate that the amount of ClO_2 was largely depended on time and reactants concentration. The highest amount of ClO_2 was found to be 193 mg in a reaction of 0.2N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ within 2 minutes (Fig. 5.50.).

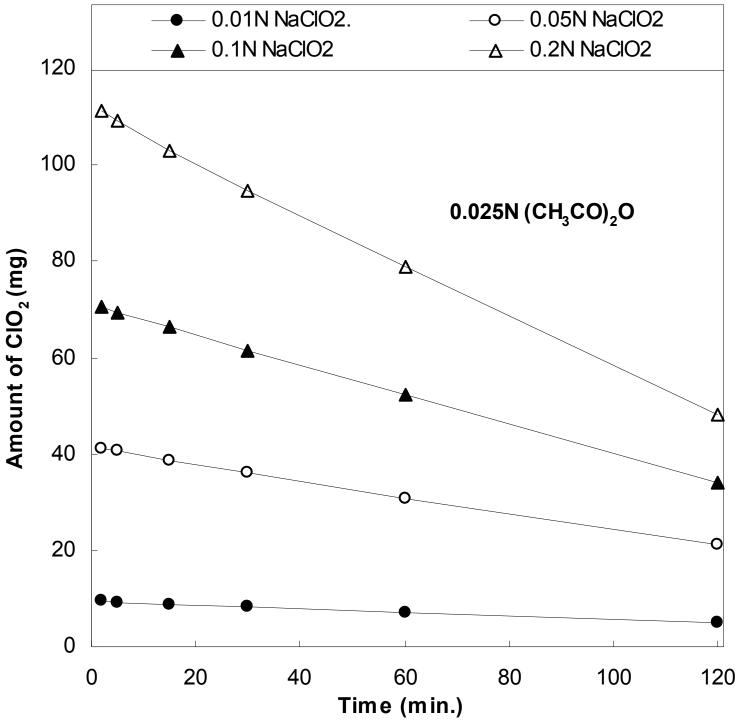


Fig. 5.48. The effect of reaction time on the amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.24.A for experimental data]

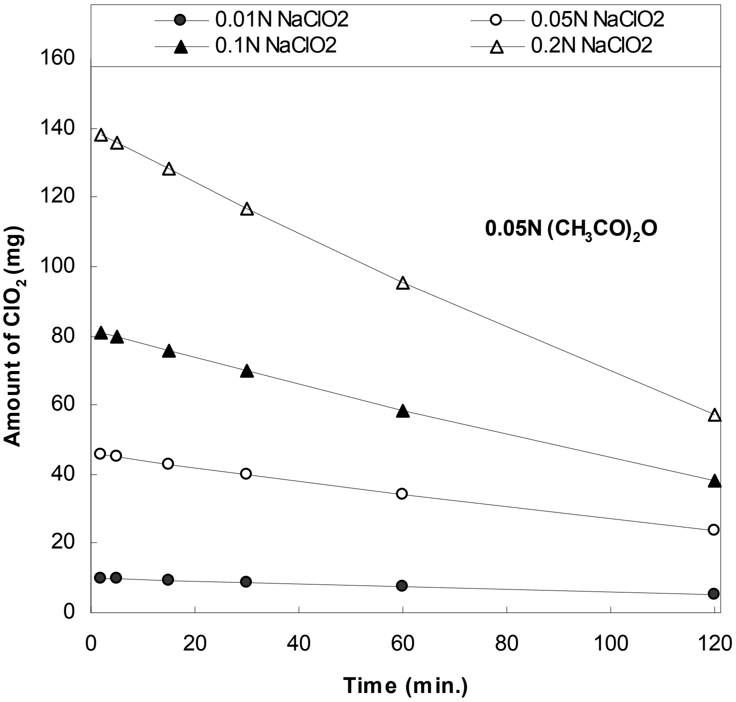


Fig. 5.49. The effect of reaction time on the amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.24.B for experimental data]

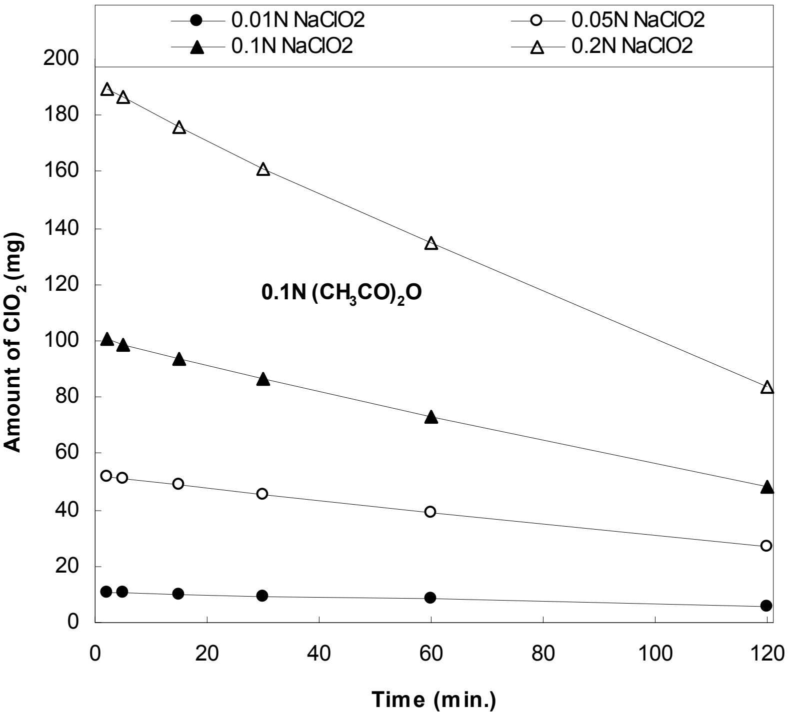


Fig. 5.50. The effect of reaction time on the amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.24.C for experimental data]

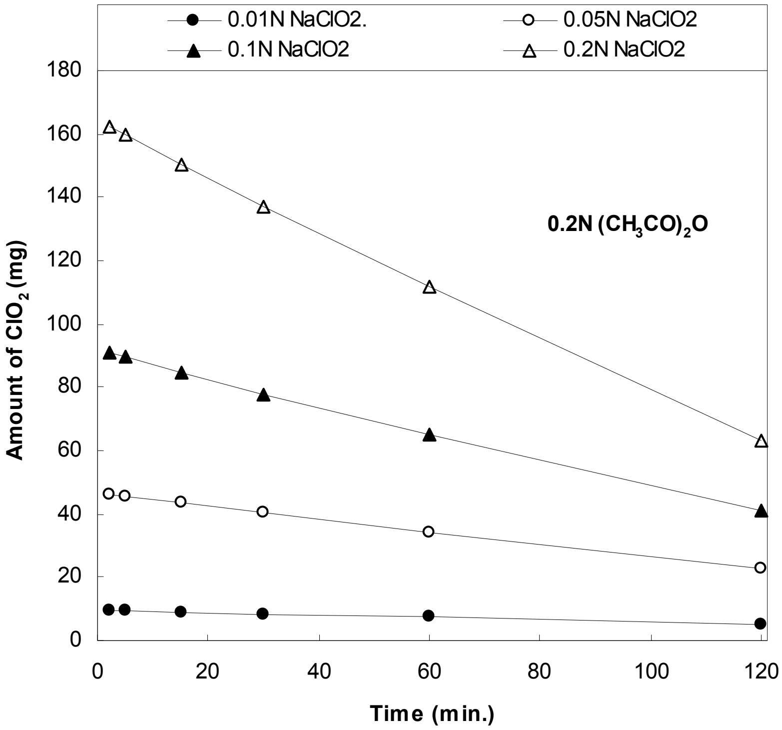


Fig. 5.51. The effect of reaction time on the amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.24.D for experimental data]

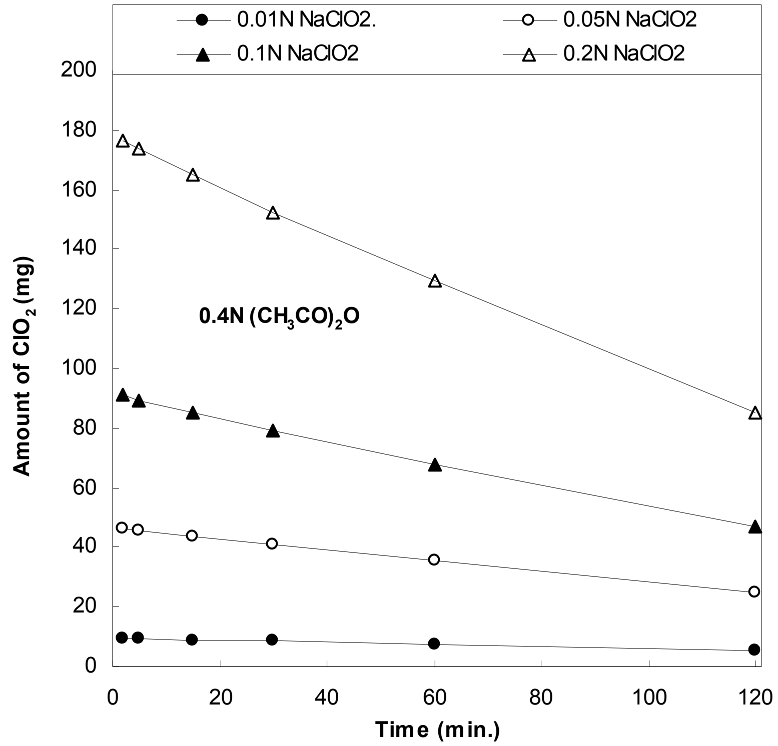


Fig. 5.52. The effect of reaction time on the amount of ClO_2
Reaction conditions: $(CH_3CO)_2O$: $NaClO_2$ (v/v) 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.24.E for experimental data]

5.4. Preparation of chlorine dioxide from sodium chlorite with a mixture of acetic anhydride and sulfuric acid.

Chloride dioxide produced by a reaction of sodium chlorite with a mixture of acetic anhydride and sulfuric acid. The effects of reactants concentration and reaction time on the production of chlorine dioxide are discussed here. The reaction was carried out at a temperature 30 ± 1^0C and the volume ratio of $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 was 1:1 (0.5:0.5).

5.4.1. The effect of sodium chlorite concentrations on the percentage production of ClO_2 at a definite concentration of $(CH_3CO)_2O$ and H_2SO_4 mixture

The study results show that the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentration for all reaction times (Fig. 5.53.). The results also illustrate that the percentage production of ClO_2 decreased with increasing reaction time and the highest percentage production was found in 5 minutes. Similar observation can be made for other figures (Figs. 5.54.-5.57.), where H_2SO_4 (0.02N) concentration remained fixed. The highest percentage production of ClO_2 was found to be 91% in a reaction of 0.01N $NaClO_2$ with a mixture of 0.1N $(CH_3CO)_2O$ and 0.02N H_2SO_4 in 5 minutes (Fig. 5.55.). The figures illustrate that the percentage production of ClO_2 reached the maximum within a few minutes, which indicating the rapid completion of the reaction process. The results illustrate that the percentage production of ClO_2 depended on both the $NaClO_2$ concentration and the reaction time. The percentage production is a ratio of the product (ClO_2) to initial reactant ($NaClO_2$) concentration, and was the only source of chlorite species, thus it is obvious that the amount of ClO_2 was not proportional to $NaClO_2$ concentration. Hence the percentage production of ClO_2 decreased with increasing $NaClO_2$ concentration as expected.

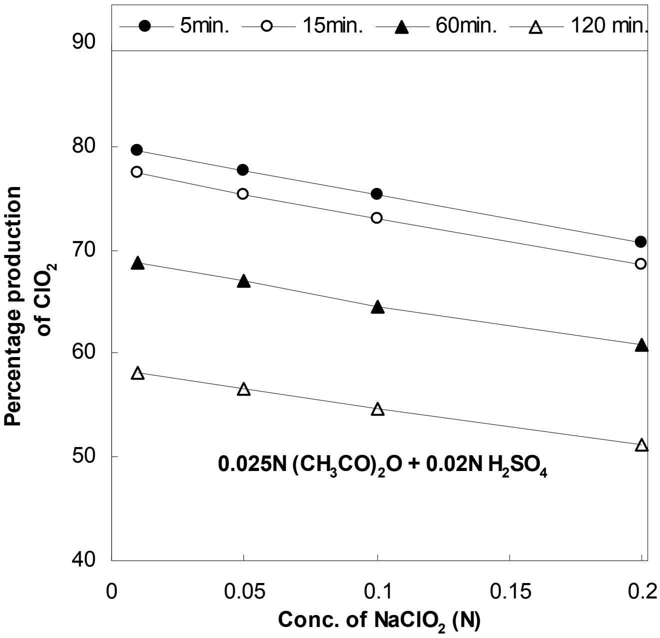


Fig. 5.53. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2 Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C [APPENDIX, Table-5.25.A for experimental data]

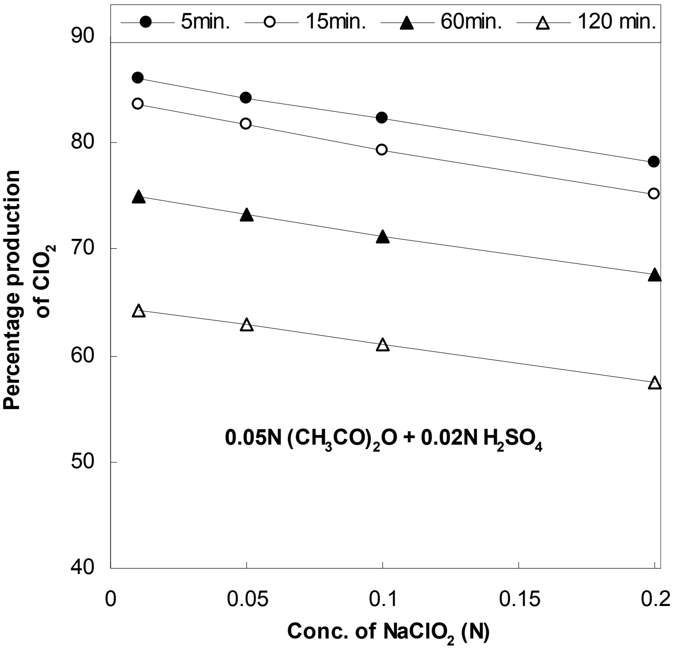


Fig. 5.54. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2 Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C [APPENDIX, Table-5.25.B for experimental data]

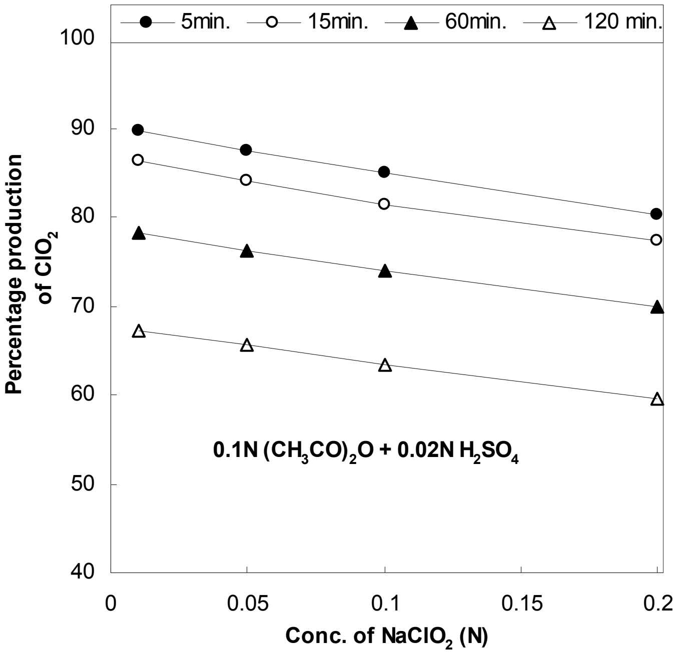


Fig. 5.55. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2 Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C [APPENDIX, Table-5.25.C for experimental data]

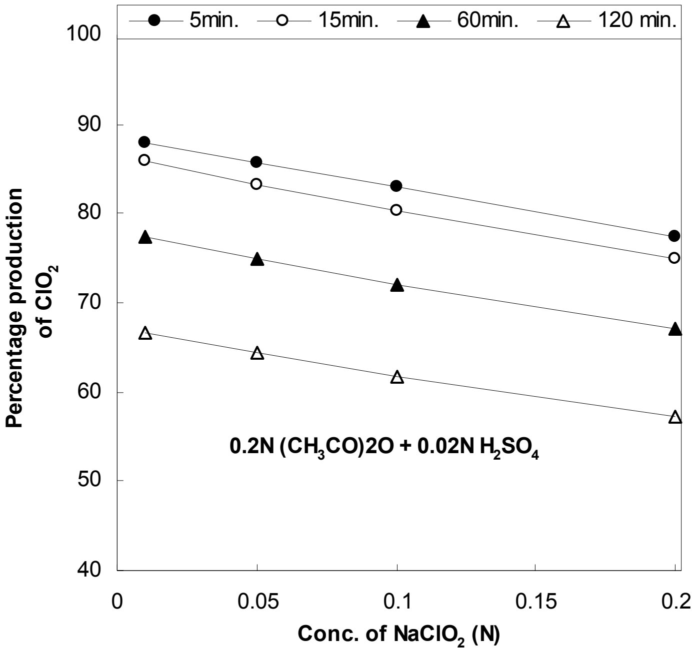


Fig. 5.56. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2 Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C [APPENDIX, Table-5.25.D for experimental data]

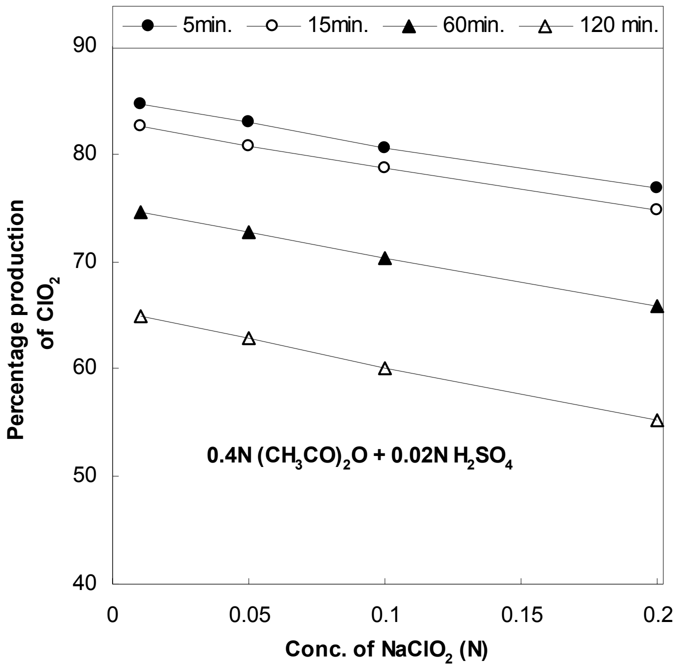


Fig. 5.57. The effect of $NaClO_2$ concentrations on the percentage production of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.25.E for experimental data]

5.4.2. The effect of sodium chlorite concentrations on the amount of ClO_2 at a definite concentration of $(CH_3CO)_2O$ and H_2SO_4 mixture

The study results show that the amount of ClO_2 increased with increasing $NaClO_2$ concentration for all reaction times (Fig. 5.58-5.62.). The results also illustrate that the amount of ClO_2 decreased with reaction time and the highest amount was shown within 5 minutes. Similar observation can be made for a fixed H_2SO_4 (0.02N) concentration for the Figs. 5.59-5.62. The highest conversion was achieved to be 216 mg in reaction of 0.2N $NaClO_2$ with a mixture of 0.1N $(CH_3CO)_2O$ and 0.02N H_2SO_4 within 5 minutes (Fig. 5.60.). The experiment results suggest that the amount of ClO_2 reached the maximum within a few minutes, which indicating the rapid completion of the reaction process. The results illustrate that the amount of ClO_2 depended on both the $NaClO_2$ concentration and reaction time, hence the amount of ClO_2 increased with increasing $NaClO_2$ concentration as expected.

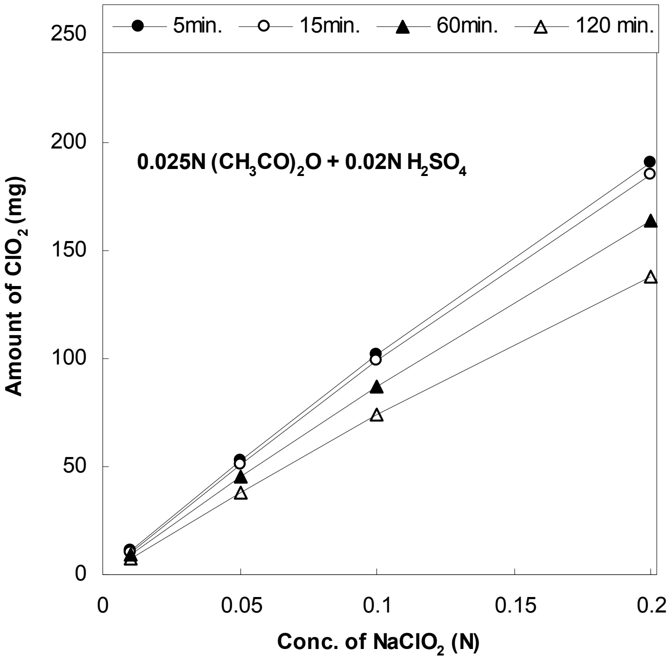


Fig. 5.58. The effect of $NaClO_2$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.26.A for experimental data]

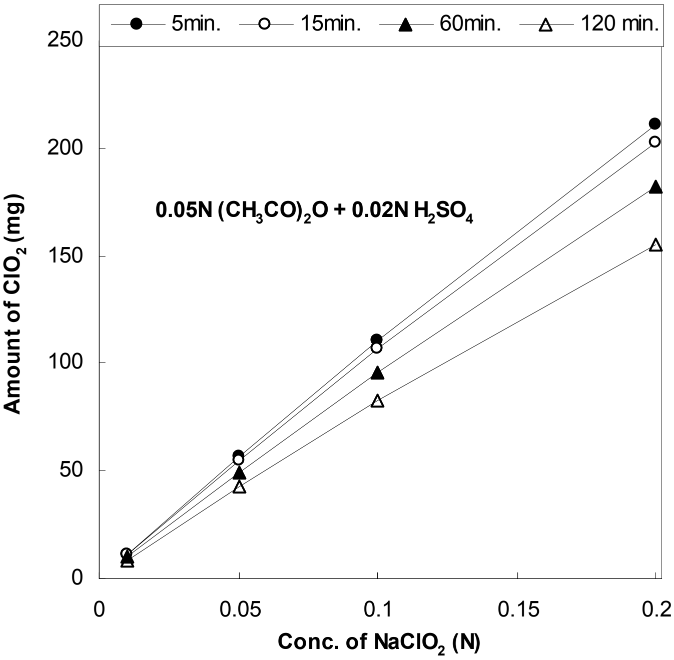


Fig. 5.59. The effect of $NaClO_2$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.26.B for experimental data]

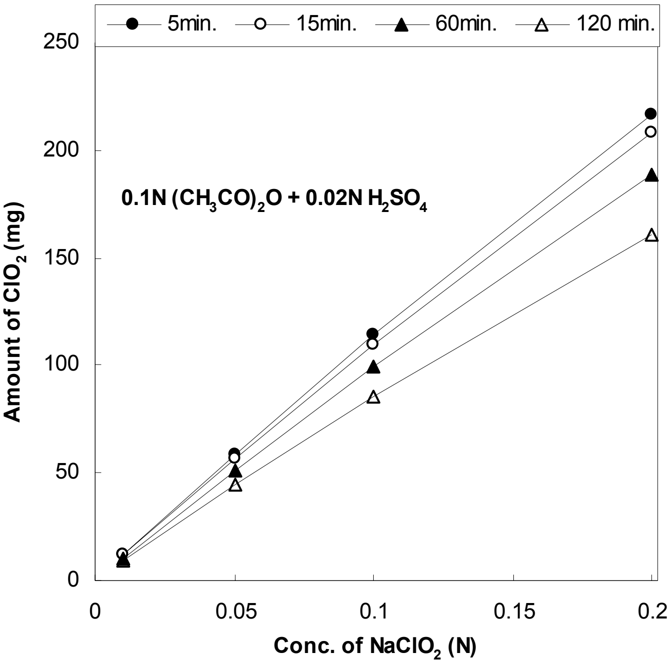


Fig. 5.60. The effect of $NaClO_2$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.26.C for experimental data]

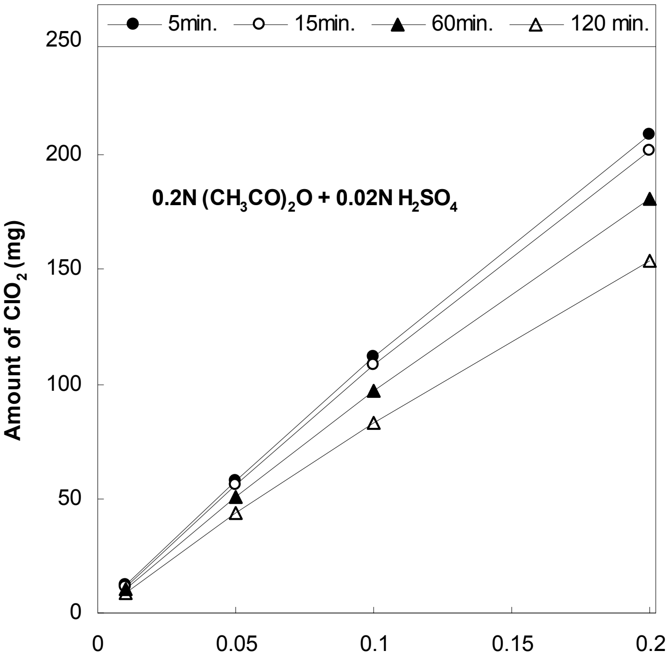


Fig. 5.61. The effect of $NaClO_2$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.26.D for experimental data]

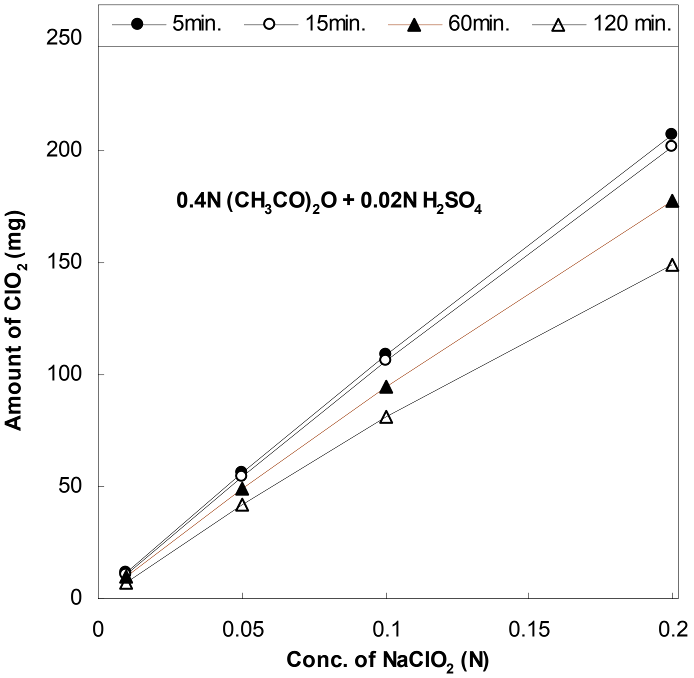


Fig. 5.62. The effect of $NaClO_2$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.26.E for experimental data]

5.4.3. The effect of acetic anhydride concentrations on the percentage production of ClO_2 at definite concentration of $NaClO_2$ and H_2SO_4

The study results show that the percentage production of ClO_2 increased sharply with $(CH_3CO)_2O$ concentration up to 0.1N and then decrease slowly with increasing $(CH_3CO)_2O$ concentration (Fig. 5.63.). The results also illustrate that the percentage production of ClO_2 decreased with reaction time and the highest percentage production was shown within 5 minutes. Similar observation can be made for a fixed H_2SO_4 (0.02N) concentration (Figs. 5.64.-5.66.). The highest conversion was achieved to be 91% in reaction of 0.01N $NaClO_2$ with a mixture (1:1) of 0.1N $(CH_3CO)_2O$ and 0.02N H_2SO_4 within 5 minutes (Fig. 5.63.). The experiment results suggest that the percentage production of ClO_2 reached the maximum within a few minutes, which indicating the rapid completion of the reaction process. It may be suggested that the percentage production of ClO_2 depended on both the $(CH_3CO)_2O$ concentration and the reaction time. As $NaClO_2$ was the only source of chlorite ion for the production of ClO_2, hence; it is obvious that the concentration of $NaClO_2$ had a great effect on the production of ClO_2. Thus the percentage production of ClO_2 increased sharply up to 0.1N and then decrease slowly with increasing $(CH_3CO)_2O$ concentration.

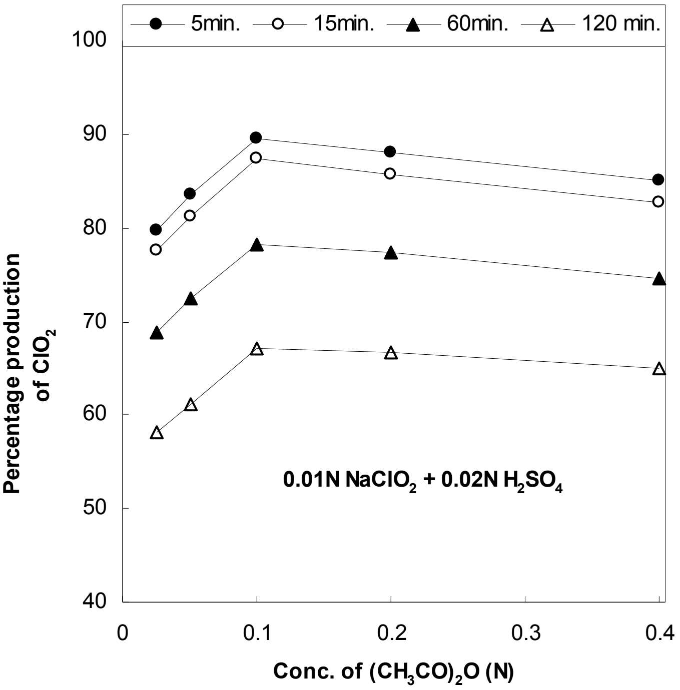


Fig. 5.63. The effect of $(CH_3CO)_2O$ concentrations on the percentage production of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.27.A for experimental data]

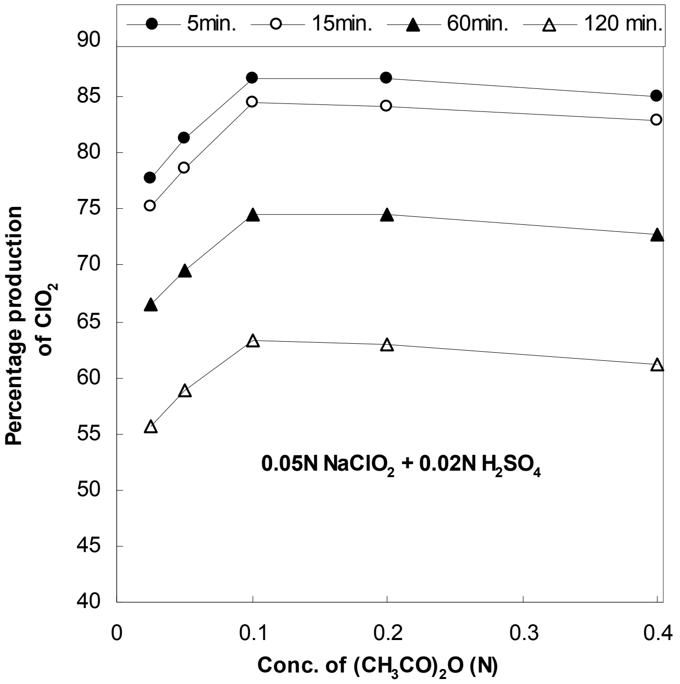


Fig. 5.64. The effect of $(CH_3CO)_2O$ concentrations on the percentage production of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.27.B for experimental data]

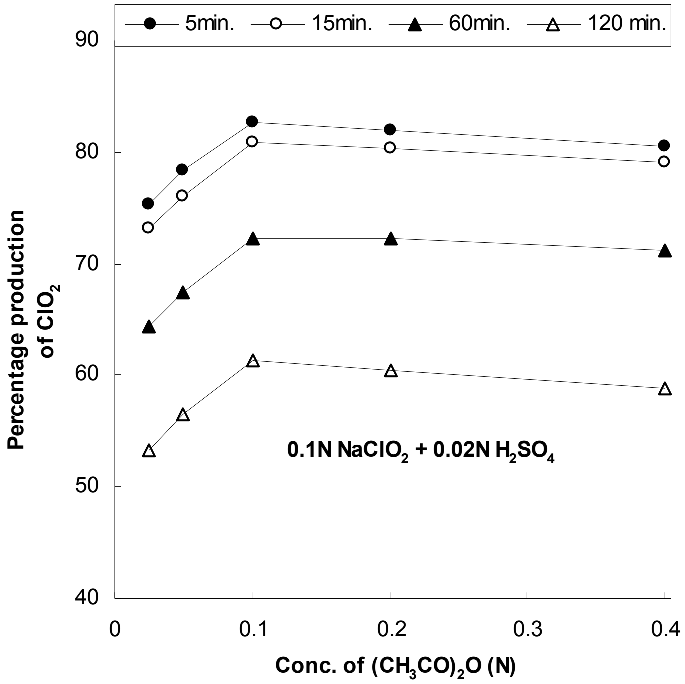


Fig. 5.65. The effect of $(CH_3CO)_2O$ concentrations on the percentage production of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.27.C for experimental data]

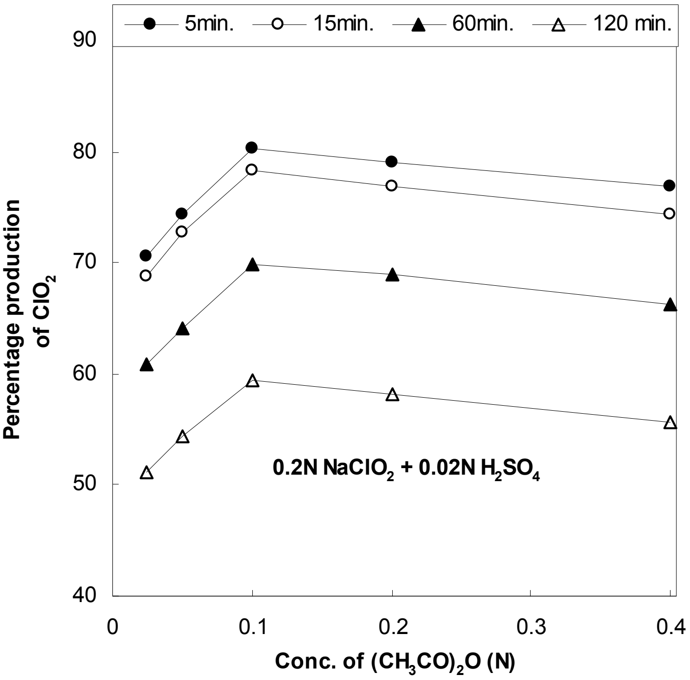


Fig. 5.66. The effect of $(CH_3CO)_2O$ concentrations on the percentage production of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.27.D for experimental data]

5.4.4. The effect of acetic anhydride concentrations on the amount of ClO_2 at definite concentration of $NaClO_2$ and H_2SO_4

The study results show that the amount of ClO_2 increased sharply with $(CH_3CO)_2O$ concentration up to 0.1N and then decrease slowly with increasing $(CH_3CO)_2O$ concentration (Fig. 5.67.-5.70.). The results also illustrate that the amount of ClO_2 decreased with reaction time and the highest amount was shown within 5 minutes in all cases. Similar observation can be made for a fixed H_2SO_4 (0.02N) concentration (Figs. 5.68.-5.70.). The highest conversion was achieved to be 216 mg in reaction of 0.2N $NaClO_2$ with a mixture (1:1) of 0.1N $(CH_3CO)_2O$ and 0.02N H_2SO_4 within 5 minutes (Fig. 5.70.). The experiment results suggest that the amount of ClO_2 reached the maximum within a few minutes, which indicating the rapid completion of the reaction process. It may be suggested that the amount of ClO_2 depended on both the $(CH_3CO)_2O$ concentration and the reaction time. Thus the amount of ClO_2 increased sharply up to 0.1N and then decrease slowly with increasing $(CH_3CO)_2O$ concentration .

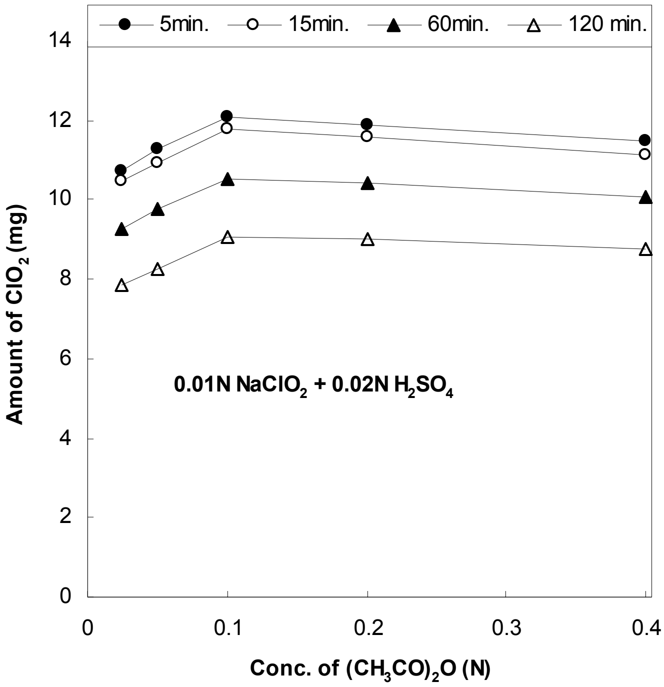


Fig. 5.67. The effect of $(CH_3CO)_2O$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.28.A for experimental data]

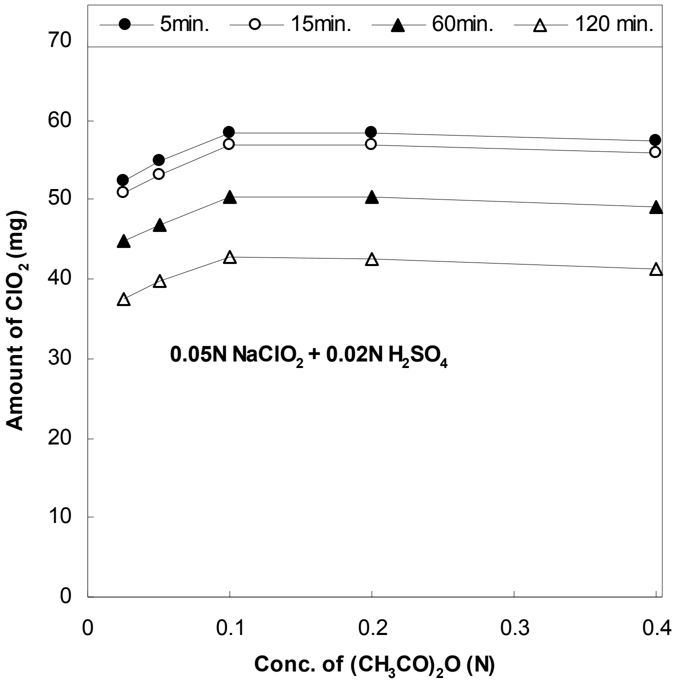


Fig. 5.68. The effect of $(CH_3CO)_2O$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.28.B for experimental data]

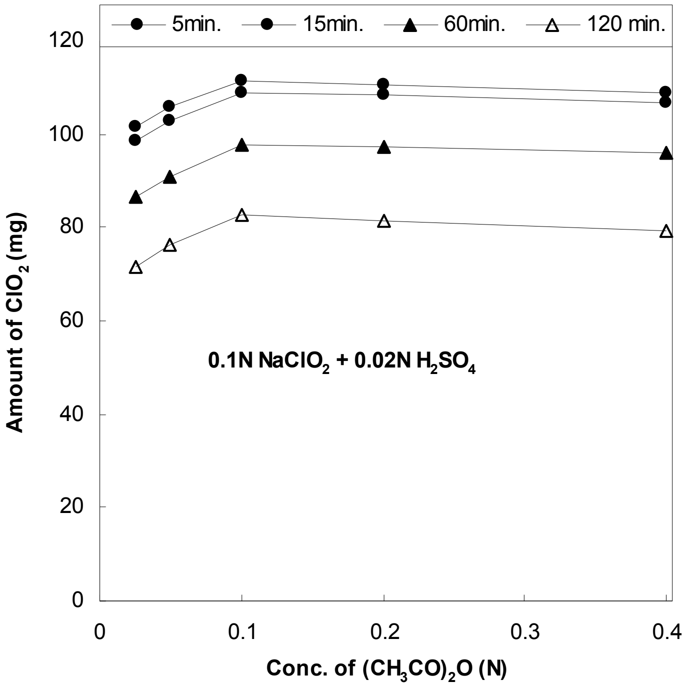


Fig. 5.69. The effect of $(CH_3CO)_2O$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.28.C for experimental data]

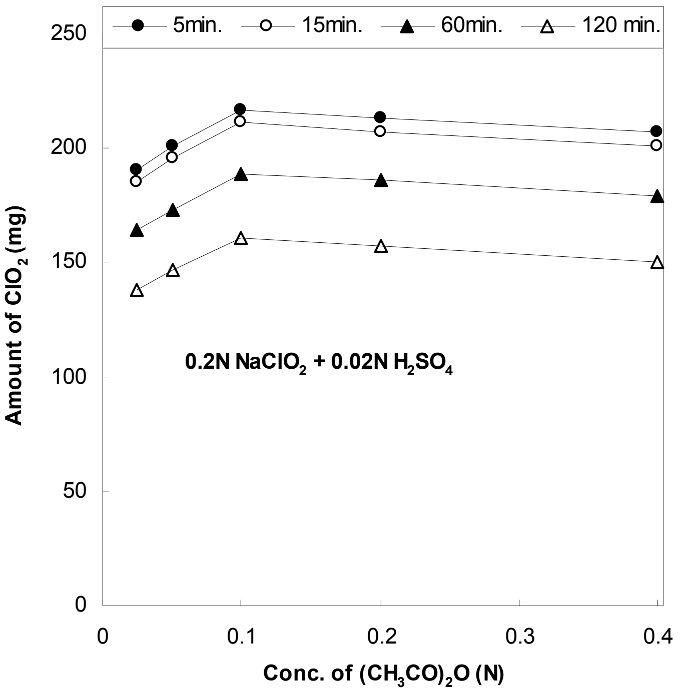


Fig. 5.70. The effect of $(CH_3CO)_2O$ concentrations on the amount of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.28.D for experimental data]

5.4.5. The effect of H_2SO_4 concentrations on the percentage production of ClO_2 at definite concentration of $NaClO_2$ and $(CH_3CO)_2O$

The study results show that the percentage production of ClO_2 increased sharply with H_2SO_4 concentration up to 0.02N and then decreased slowly with increasing H_2SO_4 concentration (Fig. 5.71.). The results also illustrate that the percentage production of ClO_2 decreased with increasing reaction time and the highest percentage production was found in 5 minutes. The highest percentage production of ClO_2 was achieved to be 91% in a reaction of 0.01N $NaClO_2$ with a mixture (1:1) of 0.1N $(CH_3CO)_2O$ and 0.02N H_2SO_4 (Fig. 5.71.). The experiment results suggest that the percentage production of ClO_2 reached the maximum within a few minutes, which indicating the rapid completion of the reaction process. It may be suggested that the percentage production of ClO_2 depended on both the H_2SO_4 concentration and the reaction time. As $NaClO_2$ was the only source of chlorite ion for the production of ClO_2, hence; it is obvious that the concentration of $NaClO_2$ had a great effect on the production of ClO_2. Thus the percentage production of ClO_2 increased sharply up to 0.02N and then decrease slowly with increasing H_2SO_4 concentration. Similar observation can be made for various concentrations of $NaClO_2$ and $CH_3CO)_2O$ (figures not shown).

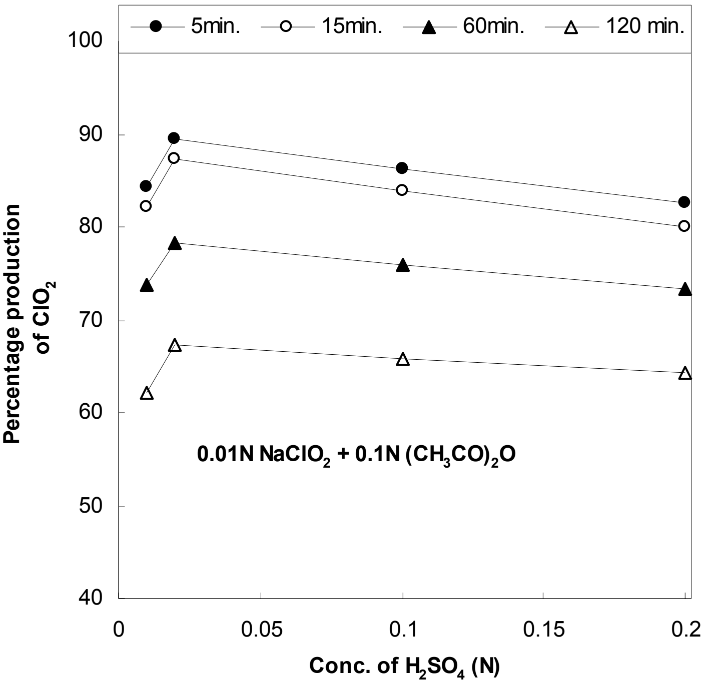


Fig. 5.71. The effect of H_2SO_4 concentrations on the percentage production of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.29 for experimental data]

5.4.6. The effect of time on the percentage production of ClO_2 at various concentrations of $NaClO_2$ and a definite concentration of $(CH_3CO)_2O$ and H_2SO_4

The effects of time on the percentage production of ClO_2 for a definite concentrations of $CH_3CO)_2O$ and H_2SO_4 and a various $NaClO_2$ concentrations were shown in Fig. 5.72. The results showed that from the beginning, the percentage production of ClO_2 decreased sharply with increasing time, which was indicating the rapid completion of the reaction process. The figure also showed that the percentage production of ClO_2 increased with decreasing $NaClO_2$ concentrations. The overall observation of the results illustrated that the percentage production of ClO_2 was largely depended on time and $NaClO_2$ concentration. The highest percentage production of ClO_2 was found to be 91% in a reaction of 0.01N $NaClO_2$ and a mixture of 0.1N $CH_3CO)_2O$ and 0.02N H_2SO_4 concentrations within 2 minutes (Fig. 5.72.). Similar observation can be made for various concentrations of $CH_3CO)_2O$ and H_2SO_4 (figures not shown).

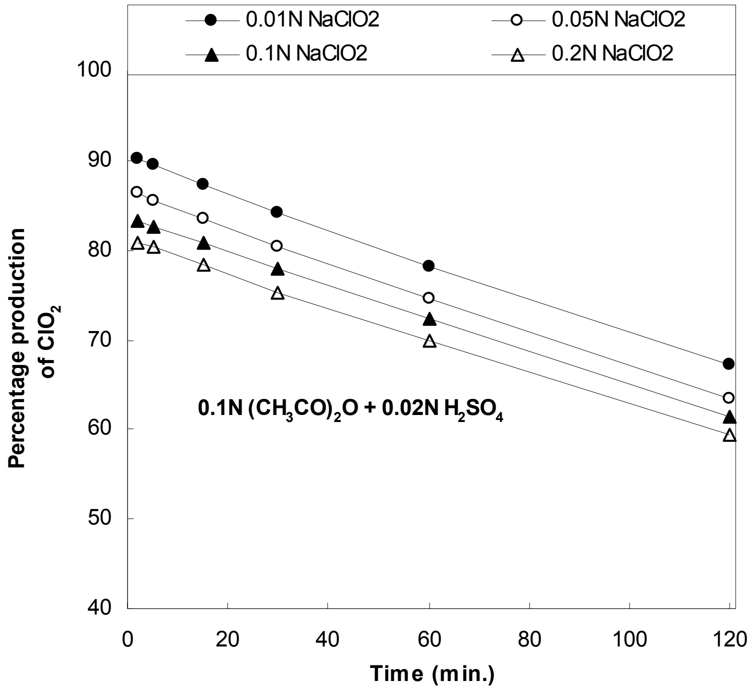


Fig. 5.72. The effect of time on the percentage production of ClO_2
Reaction conditions: $NaClO_2$: $(CH_3CO)_2O$ and H_2SO_4 1: 1; at temperature, 30 ± 1^0C
[APPENDIX, Table-5.30 for experimental data]

5.5. Synergistic Effect

About 91% of ClO_2 was produced by a reaction of 0.01N $NaClO_2$ with a mixture (1:1 v/v) of 0.1N $(CH_3CO)_2O$ and 0.02N H_2SO_4 within 2 minutes. But for the same reaction time, about 78% and 2% ClO_2 were produced, respectively from the reaction of $NaClO_2$ reacted separately with $(CH_3CO)_2O$ and H_2SO_4 and their sum was 80%, which is lower than that of the reaction of $NaClO_2$ with the mixture of $(CH_3CO)_2O$ and H_2SO_4 (91%). In the context of production behavior, it can be illustrated that the mixture [$(CH_3CO)_2O$ and H_2SO_4] was more reactive than the sum of its parts or reactant. A synergistic effect is the interaction of multiple reactants or elements in a system to produce an effect different from or greater than the sum of their individual effects[218-222].

Table 1

Comparative study for the conversion of ClO_2 from $NaClO_2$ solution and other reactants

Exp. No.	0.01N $NaClO_2$ + 0.02N H_2SO_4 (1)		0.01N $NaClO_2$ + 0.1N $(CH_3CO)_2O$ (2)		0.01N $NaClO_2$ + 0.02N H_2SO_4 + 0.1N $(CH_3CO)_2O$ (3)		sum of ClO_2 (1+2)
	Time (min.)	% ClO_2	Time (min.)	% ClO_2	Time (min.)	% ClO_2	
1	2	2	2	78	2	91	80
2	5	3	5	75	5	90	78
3	15	7	15	72	15	87	79
4	30	12	30	66	30	85	78

In other words, a synergistic effect is the ability of a mixture or group to outperform even its best individual reactant or member[223]. A catalyst is a substance, usually used in small amounts relative to the reactants, that modifies and increases the rate of a reaction without being consumed in the process[224]. Thus the reaction of $NaClO_2$ and a mixture (1:1 v/v) of $(CH_3CO)_2O$ and H_2SO_4 was not a catalytic reaction because the study results shows that H_2SO_4 or $(CH_3CO)_2O$ reacted separately with $NaClO_2$ to produce ClO_2. Hence, it may be concluded that the maximum percentage production of ClO_2 was achieved from the mixture of $(CH_3CO)_2O$ and H_2SO_4 indicating the synergistic effect rather than catalytic effect. The Table also shows the percentage production of ClO_2 from the mixture was found higher in 5, 15 and 30 minutes of reaction times than obtained in the reaction of $NaClO_2$ with the individual reactants [$(CH_3CO)_2O$ / H_2SO_4] (Table 1).

5.6. Proposed Reactions

5.6.1. Proposed reaction for the preparation of ClO_2 from ClO_2^- in the presence of sulfuric acid

Chlorine dioxide was produced by a reaction of $NaClO_2$ and H_2SO_4. The proposed reaction for the preparation of ClO_2 from ClO_2^- in the presence of sulfuric acid is discussed here. This attempt was made to analyze the decomposition of ClO_2^- into various chlorine species in the presence of H_2SO_4. Reports [40,225,226] illustrated that the disproportion reaction of ClO_2^- in the presence of acid to produce a various chlorine species such as chlorine dioxide, chlorate and chloride etc. Graphical representations of the decomposition of ClO_2^- are shown in Figs. 5.73.-5.75.

Fig. 5.73. shows the analysis results of the chemical reaction carried out at a definite concentration (0.01N) of $NaClO_2$ and various concentrations (0.02N, 0.1N and 0.2N) of H_2SO_4. The experimental results indicate that the ClO_2^- (●) concentration decreased sharply in the beginning and then slowly with time. The figure also illustrates that the concentration of ClO_2 (○) increased sharply in the beginning, then increased slowly until it reached the maximum and finally decreased with time. The analysis results show that both the concentration of ClO_3^- (■) and Cl^- (▲) increased sharply in the beginning and then increased slowly with time until 1440 minutes. In case of Cl^- graph line, the concentration rapidly increased after 1440 minutes of reaction time, but for the ClO_3^- graph line, it increased slowly with time. The figures show a good relation between the decomposition of ClO_2 and the formation of Cl^- indicated that majority of Cl^- was produced by the decomposition of ClO_2 (Figs. 5.73.A-73.C). Similar observations could be made for the figures (Figs. 5.74.-5.75.) constructed from the analysis results of the chemical reactions between various concentrations of $NaClO_2$ (0.05 and 0.1N) and H_2SO_4 (0.02N, 0.1N and 0.2N). The figures illustrate that ClO_2^- decomposed and produced ClO_2, ClO_3^- and Cl^- in the presence of H_2SO_4. The figures also express that the amount of ClO_2 decreased with increasing amount of Cl^- after certain reaction time.

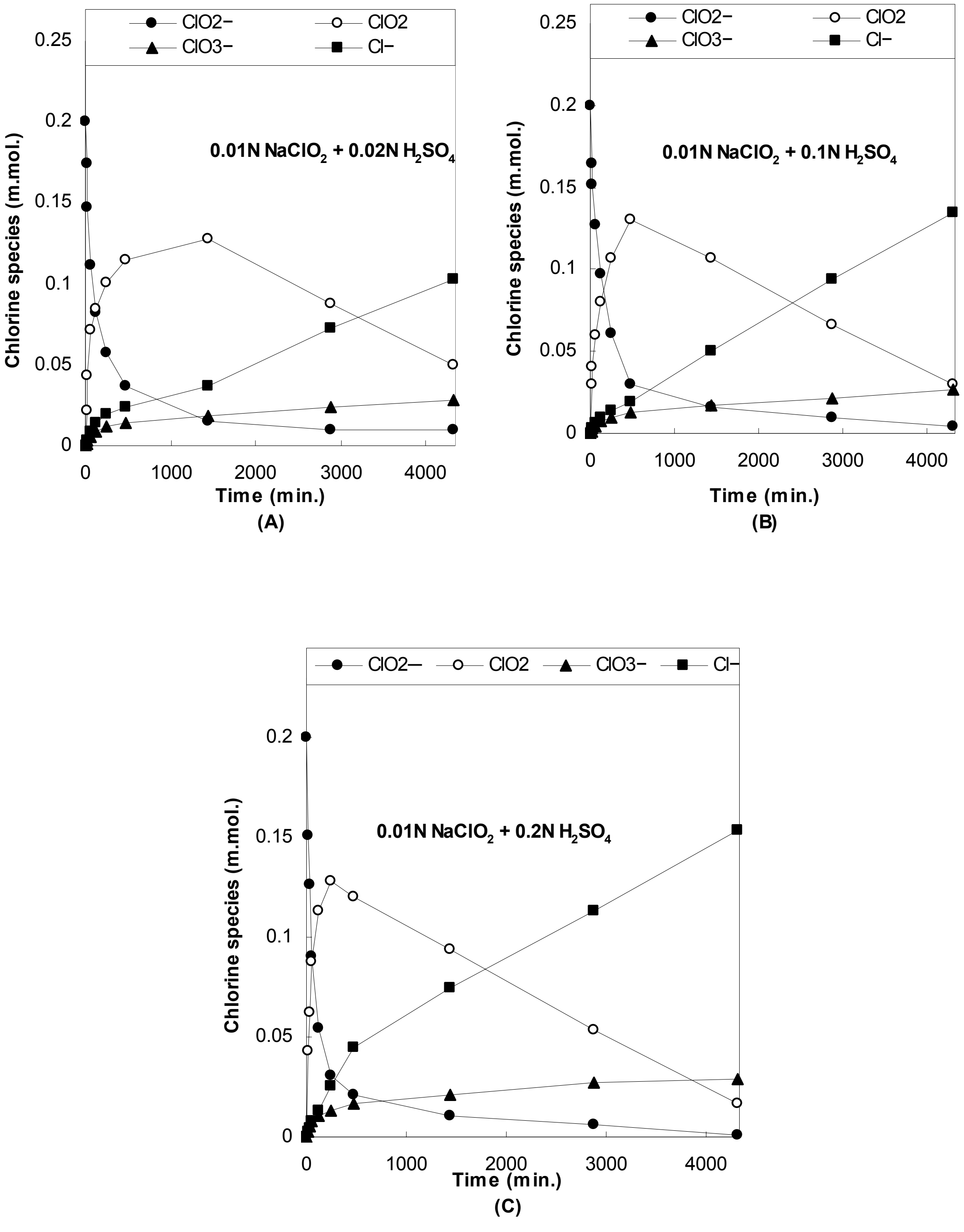


Fig. 5.73. The relation between different chlorine species (m.mol.) and time (min.)
Reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1: 1, at temperature, 30 ± 1^0C
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.31 for experimental data]

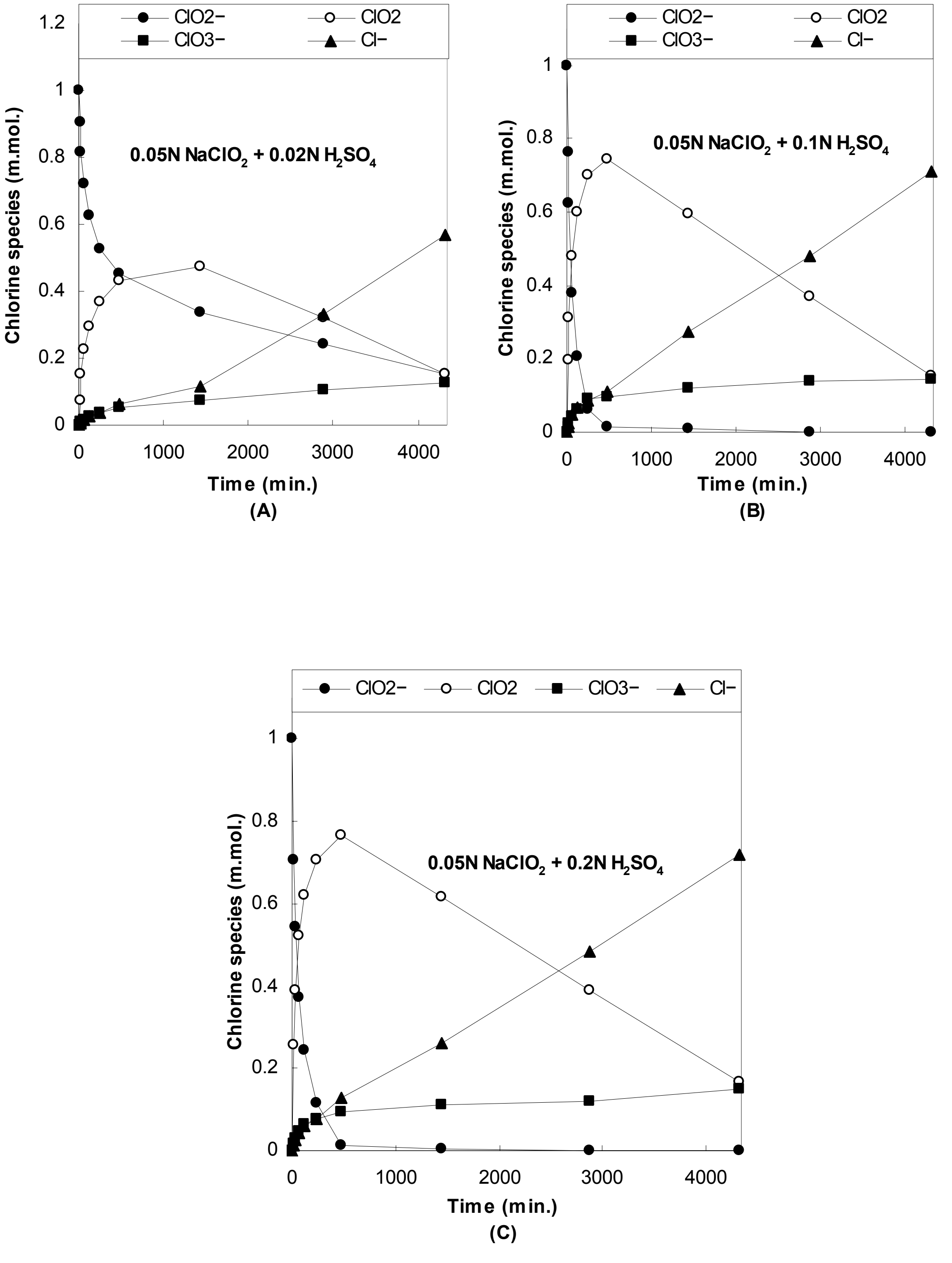
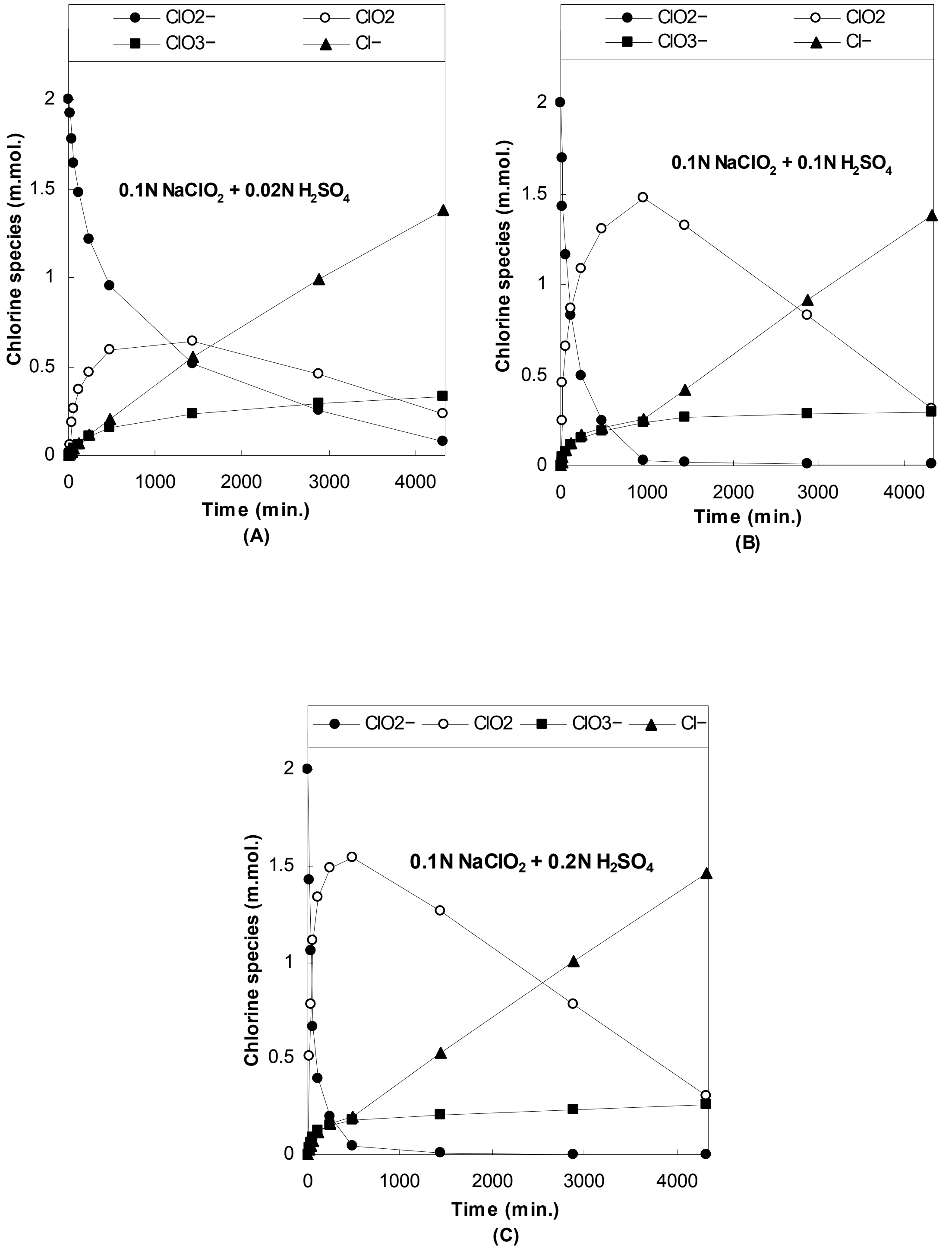


Fig. 5.74. The relation between different chlorine species (m.mol.) and time (min.)
Reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1: 1, at temperature, 30 ± 1^0C
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.32 for experimental data]



(A)

(B)

(C)

Fig. 5.75. The relation between different chlorine species (m.mol.) and time (min.)
Reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1: 1, at temperature, 30 ± 1^0C
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.33 for experimental data]

The analysis results of various chlorine species in different time intervals are shown in Table 2. In the table the mole fraction of the used ClO_2^- was converted into one mole and corresponding mole fractions of the other chlorine species were calculated as done by some workers[40]. Some earlier reports[40,225] showed that a number of stoichiometry reactions were found where ClO_2^- decomposed to ClO_2, ClO_3^- and Cl^- in acid medium. These stoichiometric reactions were supported by Aieta and Roberts[28]. They assumed that ClO_2, ClO_3^- and Cl^- were produced by the decomposition of sodium chlorite in the presence of H_2SO_4 and proposed decomposition reaction of ClO_2^- as stated in Eq. (A)

$$4ClO_2^- + 2H^+ \rightarrow 2ClO_2 + ClO_3^- + Cl^- + H_2O \text{ ------------- (A)}$$

Stoichiometrically the equation (A) can be written as

$$^{-} \longrightarrow \qquad ^{-} \quad ^{-} \text{-----}$$

Table 2

Composition of reactant and products in generation of ClO_2 from acid-chlorite system

Time (min.)	Used ClO_2^- (m.mol.)	Used ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)	Total (ClO_2 + ClO_3^- + Cl^-) (m.mol.)
15	0.025	1	0.832	0.053	0.063	0.950
30	0.052	1	0.827	0.064	0.070	0.962
60	0.095	1	0.747	0.073	0.098	0.919
120	0.113	1	0.745	0.078	0.125	0.949
240	0.142	1	0.720	0.088	0.145	0.954
480	0.163	1	0.723	0.093	0.165	0.983
1440	0.185	1	0.689	0.112	0.197	0.999
2880	0.185	1	0.54	0.136	0.328	1.005
4320	0.190	1	0.37	0.154	0.473	0.998

H^+

ClO_2

Reaction conditions: temperature: 30 ± 1^0C; reactants: 0.01N $NaClO_2$ and 0.02N H_2SO_4, 1:1(v/v).

The collecting terms and relating species to the conversion of one mole of ClO_2^- ion, analogous to the equation (B) gives the following equation, which is in approximate balance using the experimental results given in Table 2.

$ClO_2^- \rightarrow 0.82ClO_2 + 0.06ClO_3^- + 0.07\ Cl^-$ ----- (time 30 min.)

$ClO_2^- \rightarrow 0.71ClO_2 + 0.08\ ClO_3^- + 0.14\ Cl^-$ ----- (time 240 min.)

$ClO_2^- \rightarrow 0.37ClO_2 + 0.154\ ClO_3^- + 0.473\ Cl^-$ ---- (time 4320 min.)

Where, $x = 0.82$, 0.71 and 0.37 m.mol; $y = 0.06$, 0.08 and 0.186 m.mol.; $z = 0.07$, 0.14 and 0.47 m.mol., respectively, for 30, 240 and 4320 minutes of reaction time.

The Table 2 illustrates that the estimated value of total chlorine species was not equal to the amount of used ClO_2^- ion. The reaction time for 30 minutes, 0.962 m.mol. of total chlorine species were produced from 1 m.mol. of used ClO_2^- ion, and similarly it could be written for others reaction time that the total amount of chlorine species were not exactly the same as to the amount of used chlorite ion, considering experimental error and volatility behavior of ClO_2.

5.6.2. Proposed decomposition reaction of ClO_2 in the presence of sulfuric acid

Chlorine dioxide is an unstable compound and it decomposes to produce various chlorine species. There are some intermediate products produced from the decomposition of ClO_2, which are more unstable at room temperature and no attempt has been made to identify or estimate them. Several reports have illustrated that many unsymmetrical intermediate product were produced during the formation of ClO_2 from chlorite solution. The kinetics of ClO_2 formation over a wide range of conditions and reaction lifetimes has not been yet available[53]. Cl_2O_2 is also an unsymmetrical intermediate, which leads to formation of chlorate and chloride ions[86] and unsymmetrical intermediate of Cl_2O_3 which is indefinitely stable at -78°C[226]. Gordon and Emmenegger[227] determined the composition of Cl_2O_4 that formed by the reaction of ClO_2 and chlorite. Deswal et al. (2004)[30,228-30] reported that ClO_2 decomposes to chloride ion in acid medium. The decomposition of ClO_2 was presented in figures (Figs. 5.75.-5.78.). Fig. 5.73. shows the experimental results of ClO_2 and Cl^- obtained from the reaction of 0.01N $NaClO_2$ and 0.02N H_2SO_4 [(v/v) 1: 1] in different reaction times. A comparison of the experimental and the projected results are also shown. The figure shows that in the beginning, the projected concentration of ClO_2 (○) increased sharply and then increased slowly with time. But, the experimental concentration of ClO_2 (●) increased sharply in the beginning, reached at a certain maximum level and then decreased with time. This could be happened due to the decomposition of ClO_2. Actually ClO_2 is very unstable compound and it decomposes soon after its formation [181,231,232]. This phenomena can be described as in the beginning of the reaction, the rate of formation of ClO_2 was higher than the rate of decomposition, thus the total amount increased with time and after certain time when the reactant concentration become low, then the decomposition rate was higher than the formation resulting decreased in ClO_2 concentration in the reaction vessel. The figure also illustrates that the time to get the maximum concentration of the experimental ClO_2 was reduced as the H_2SO_4 concentration increased, i.e., decreased in pH. The figure also demonstrates the projected and experimental Cl^- concentrations, where the projected chloride ion (Cl^-) (Δ) concentration increased sharply in the beginning and then increased slowly with time. But, the experimental results show that a good relation between ClO_2 and Cl^-, where the decomposition amount of ClO_2 was almost equal to the formation amount of Cl^- in the reaction. Thus the study proposes the decomposing reaction of ClO_2 in the presence of acid at the end of the reaction series could be stated as follows:

$$\longrightarrow \qquad \text{-----------}$$

Similar observations can be made for the Figs. 5.77.-5.78., where the projected and experimental results were illustrated for the reactions between a definite concentration of $NaClO_2$ (0.05N / 0.1N) and various concentrations of H_2SO_4 (0.02N, 0.1N and 0.2N).

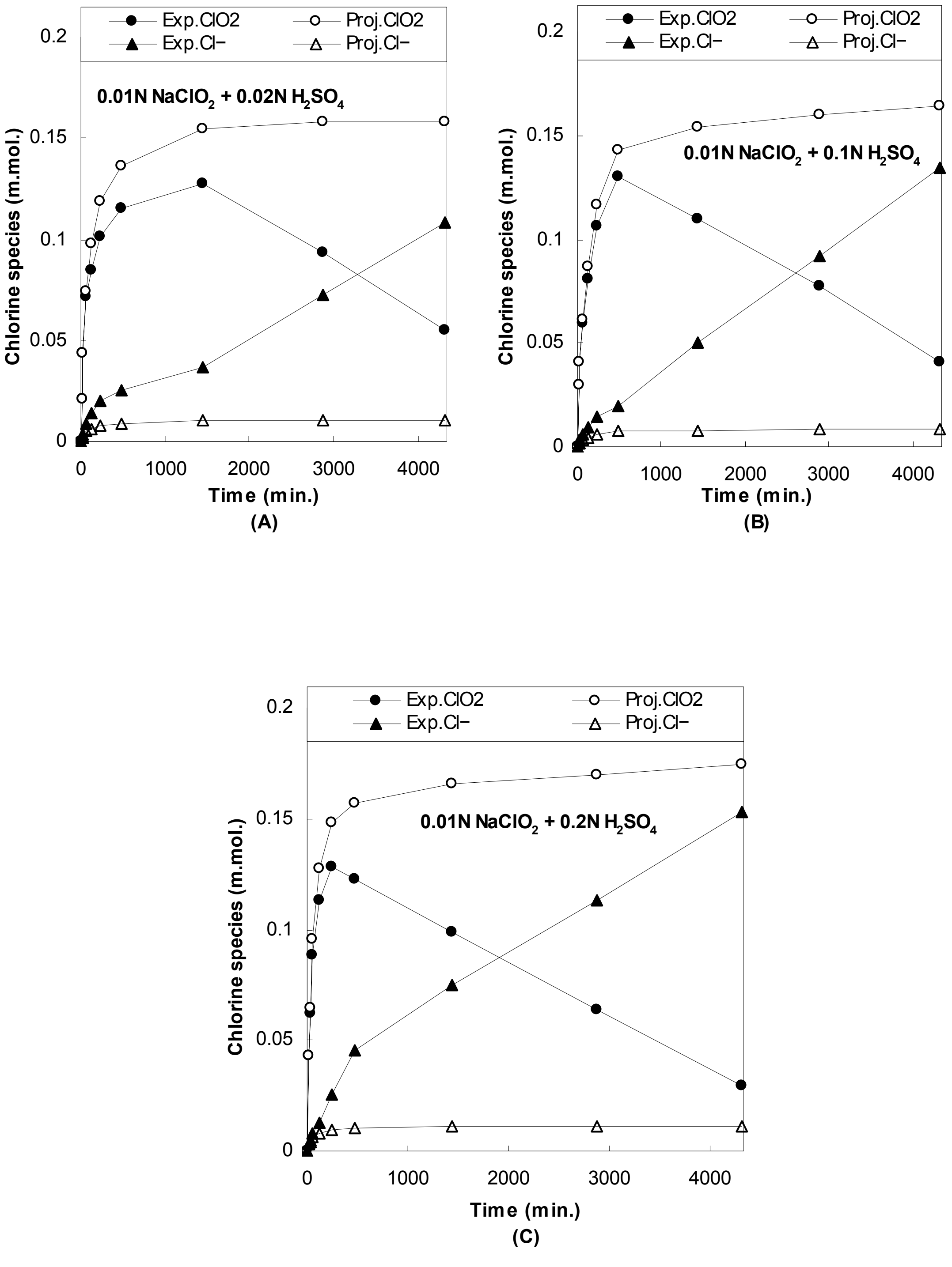


Fig. 5.76. The relation of concentrations of ClO_2 and Cl^- (m.mol.) with time (min.)
Reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1: 1, at temperature, 30 ± 1^0C
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.34 for experimental data]

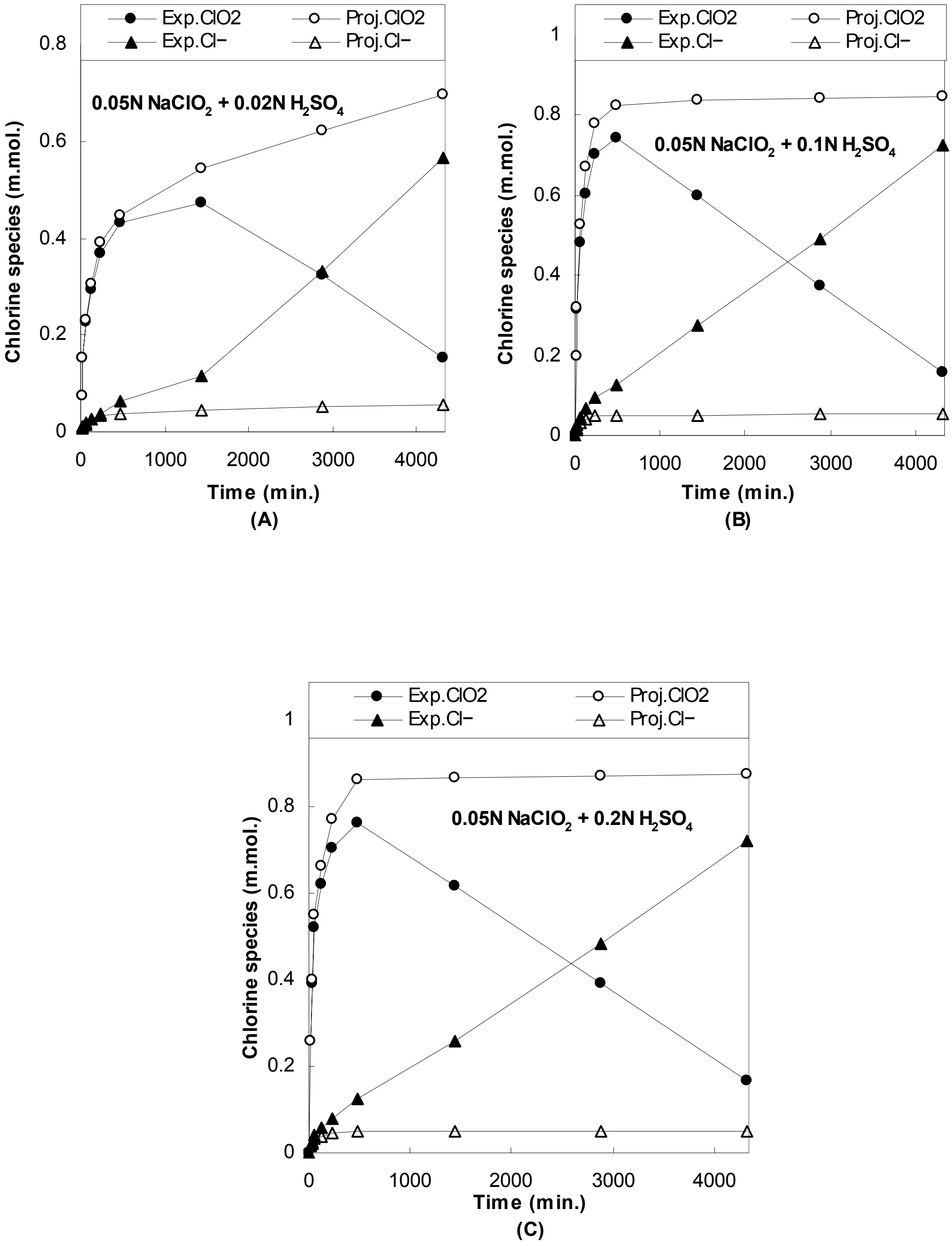


Fig. 5.77. The relation of concentrations of ClO_2 and Cl^- (m.mol.) with time (min.)
Reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1: 1, at temperature, 30 ± 1^0C
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.35 for experimental data]

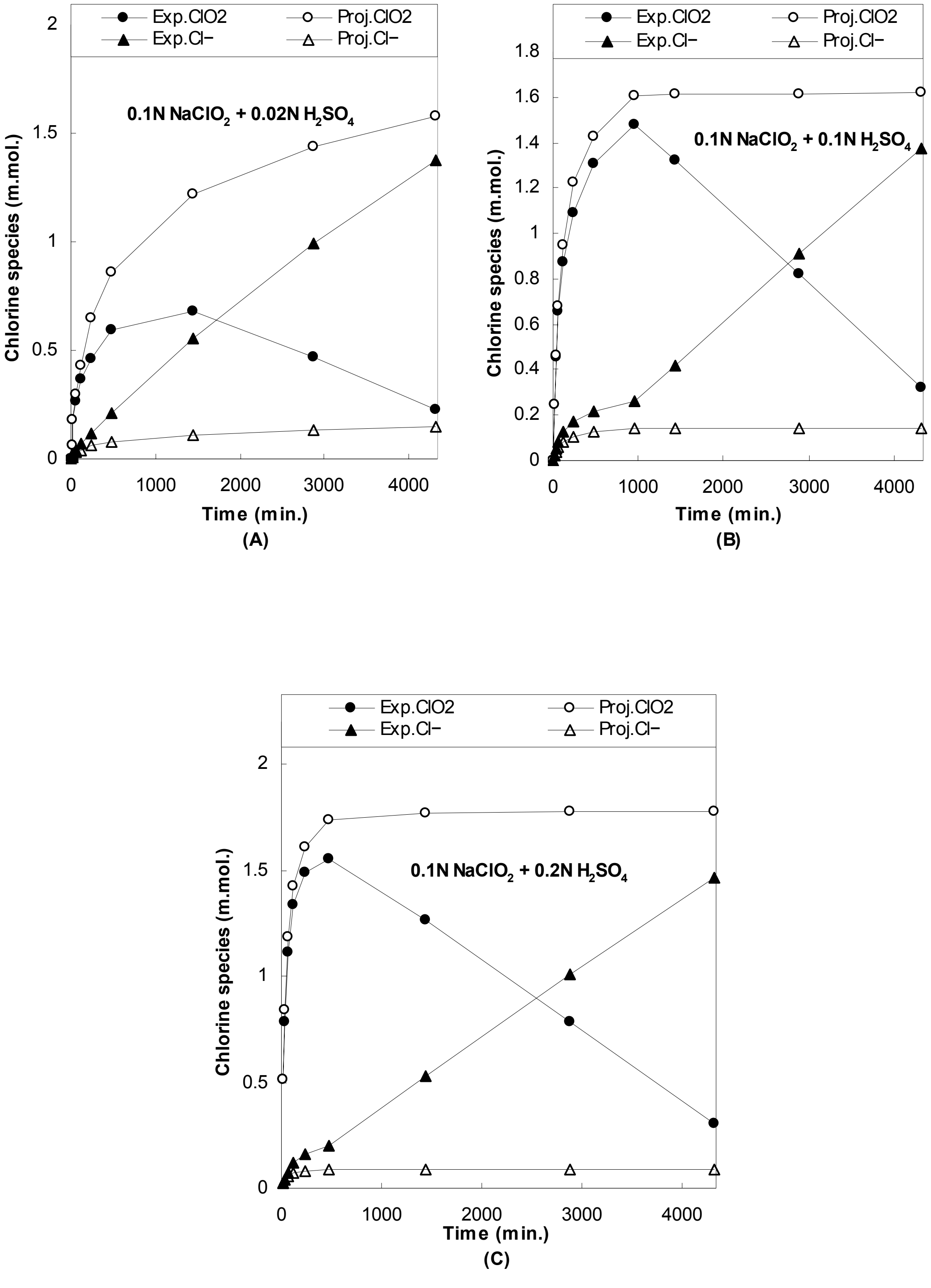


Fig. 5.78. The relation of concentrations of ClO_2 and Cl^- (m.mol.) with time (min.)
Reaction conditions: $NaClO_2$: H_2SO_4 (v/v) 1: 1, at temperature, 30 ± 1^{0}C
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.36 for experimental data]

5.7. Determination of reaction rate and order on the preparation of ClO_2 from $NaClO_2$

The reaction rate for a given chemical reaction is the measure of the change in concentration of the reactants or the change in concentration of the products per unit time Therefore the equation for rate of reaction can be written as follows:

$$\text{rete of reaction} = \frac{\text{change in concentration}}{\text{change in time}}$$

The rate of reaction tells as to what speed the reaction occurs. Let us consider a simple reaction: $A \rightarrow B$

The concentration of a reactant A decrease and that of B increase as time passes. For the given reaction rate of reaction may be equal to the rate of disappearances of A which is equal to the rate of appearances of B. Thus

$$\text{rate} = - d[A]/dt \ = +d[B]/dt$$

or,

$$\text{rate } (dx/dt) = k(a\text{-}x)$$

Where, a =initial concentration of reactant, x = product concentration at time t

A first-order reaction depends on the concentration of only one reactant (a unimolecular reaction). Other reactants can be present, but each will be zero-order. The rate law for a reaction that is first order with respect to a reactant A is

$$r = -\frac{d[A]}{dt} = k[A]$$

k is the first order rate constant, which has units of sec.$^{-1}$, min.$^{-1}$etc.

The integrated first-order rate law is

$$\ln[A] = -kt + \ln[A]o$$

or, $\ln(a\text{-}x) = -kt + \ln a$ ($y = -mx + c$)

A plot of $\ln(a\text{-}x)$ vs. time *t* gives a straight line with a slope of *-k*.

The goal of a kinetics experiment is to measure the concentration of a species at a particular time during a reaction so that a rate law can be determined.

The order of reaction is defined as the sum of the powers of concentration in the rate law. Let us consider the example of a reaction which has the rate law

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

The order of such a reaction is (m+n). The order of reaction can be determine from reactant concentration against time graph. It controls how the reactant concentration (or pressure) affects reaction rate. However, it can sometimes be difficult to decide if a reaction is first-order or second-order from the concentration against time graph. A rate against concentration graph quickly reveals the order with respect to a reactant concentration. In present study, ClO_2 was produced by the reaction of $NaClO_2$ with H_2SO_4. It is obvious that ClO_2 is generated from ClO_2^- ion ($NaClO_2$). Initial concentration (a) of the reactant ($NaClO_2$) and the concentration (*a-x*) after regular time interval were measured. The experimental values of $NaClO_2$ concentration and time (t) were placed into the integrated rate equation for the first order reaction.

Experiment No. 1

The graphical representations of generation of ClO_2 for a definite $NaClO_2$ concentration (0.01N) with various concentrations (0.02N, 0.1N and 0.2N) of H_2SO_4 are shown in Figs. 5.79.-5.80. The reaction was carried out at a constant temperature of 30 ± 1^0C and the volume ratio of $NaClO_2$ and H_2SO_4 was (v/v) 1:1. Initial concentration of $NaClO_2$ was estimated in 10, 15, 30 and 60 minutes time interval and then the value of log(*a-x*) was calculated and plotted against time, *t* (min.) gave a straight line with a slope of *–k* (Fig. 5.79.). Values of *dx/dt* were calculated using the above equation and rate constant (*k*). Then, *dx/dt* was plotted against (*a-x*) gave a straight line which passing through the origin (Fig. 5.80.), indicating the first-order reaction.

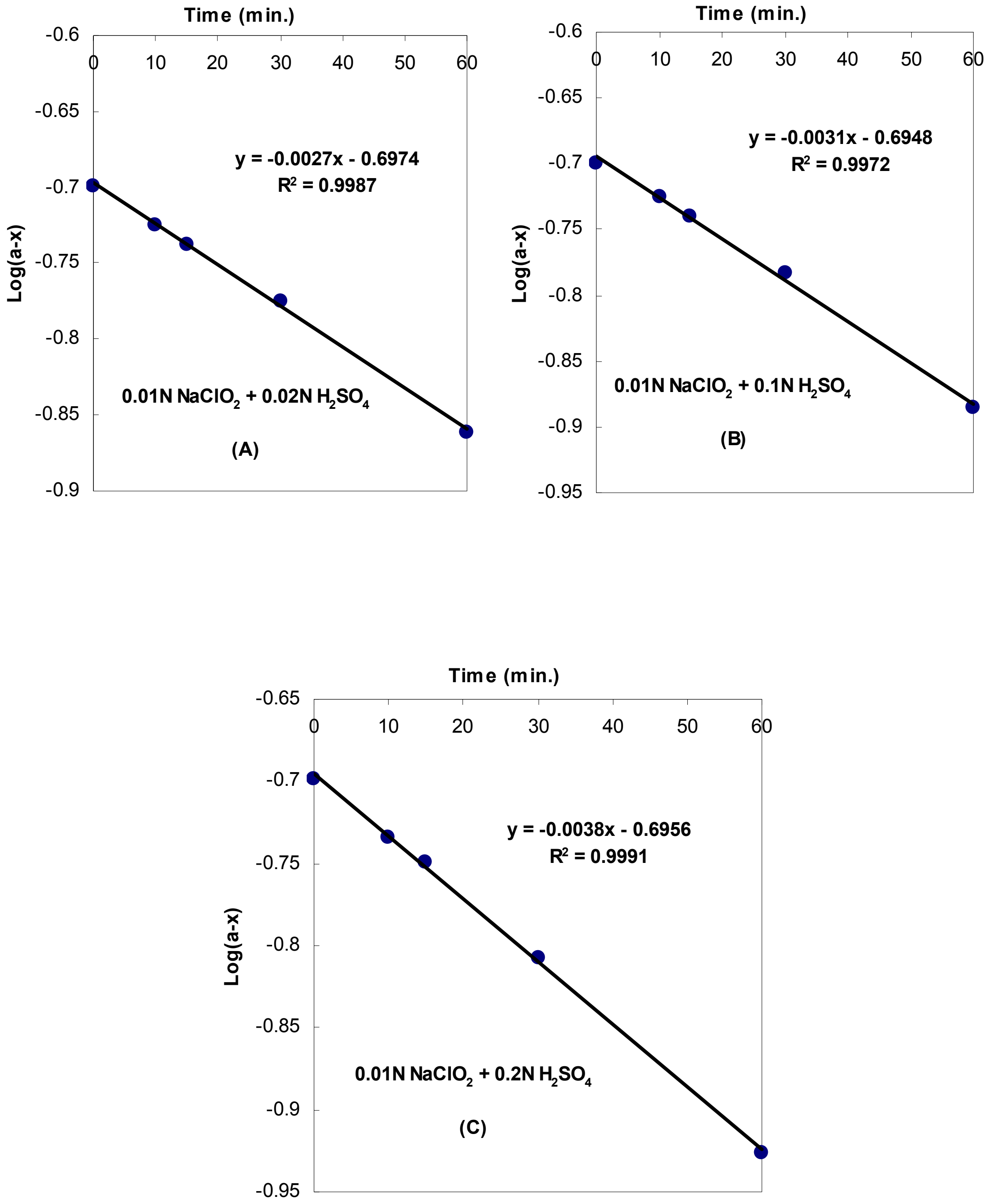
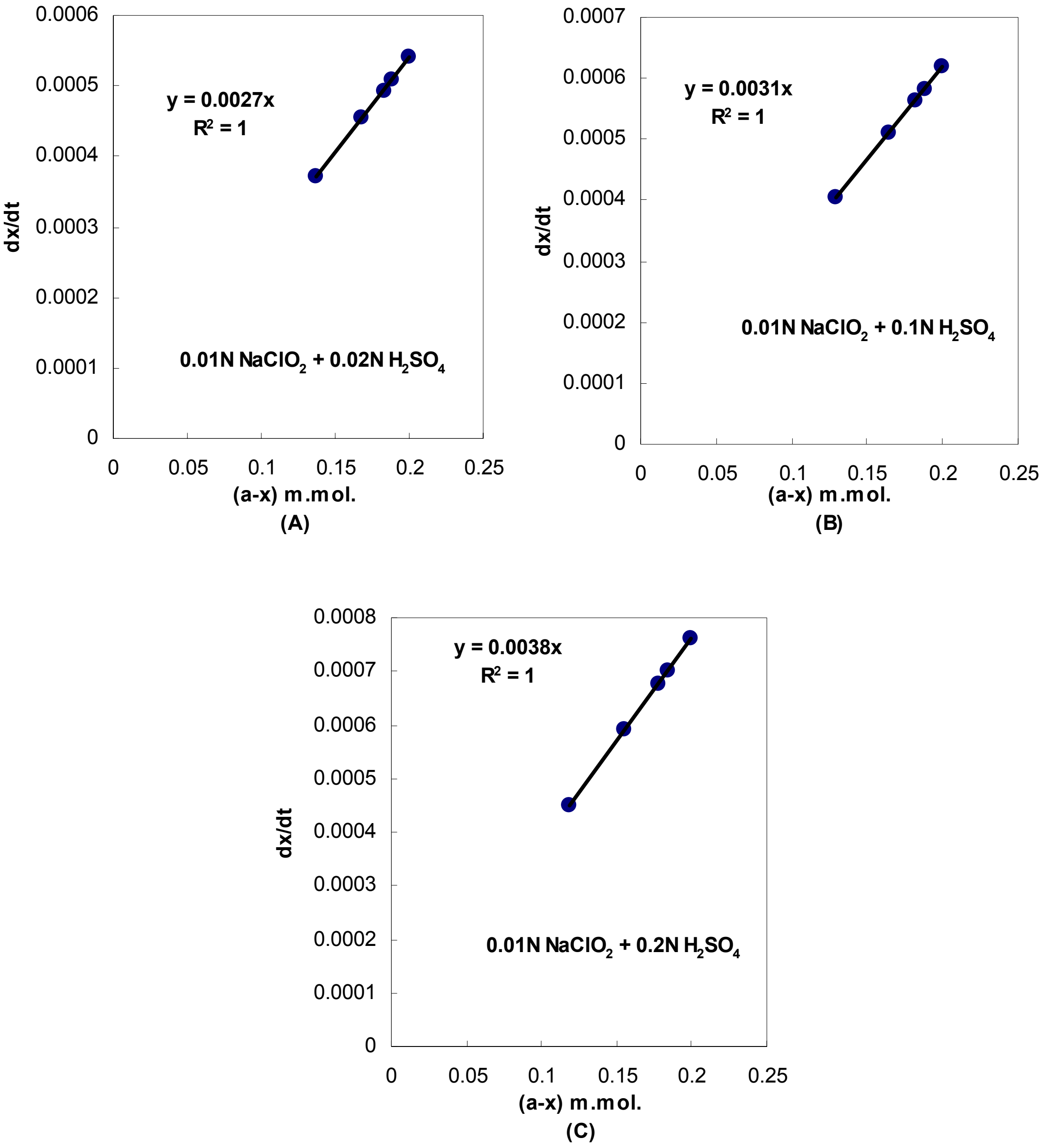


Fig. 5.79. The relation between log(*a*-*x*) and time (min.)
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.37 for experimental data]



(A)

(B)

(C)

Fig. 5.80. The relation between *dx/dt* (rate) and (*a-x*) (concentrations)
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.38 for experimental data]

Experiment No. 2

The graphical representations of generation of ClO_2 for a definite $NaClO_2$ concentration (0.05N) with various concentrations of H_2SO_4 are shown in Figs. 5.81.-5.82. The reaction was carried out at a constant temperature of 30 ± 1^0C and the volume ratio of $NaClO_2$ and H_2SO_4 was (v/v) 1:1. Initial concentration of $NaClO_2$ was estimated at 10, 15, 30 and 60 minutes time interval and then the value of log(*a-x*) was calculated and plotted against time, *t* (min.) gave a straight line with a slope of $-k$ (Fig. 5.81.). Values of *dx/dt* were calculated using the above equation and rate constant (*k*). Then, *dx/dt* was plotted against (*a-x*) gave a straight line which passing through the origin (Fig. 5.82.), indicating the first-order reaction.

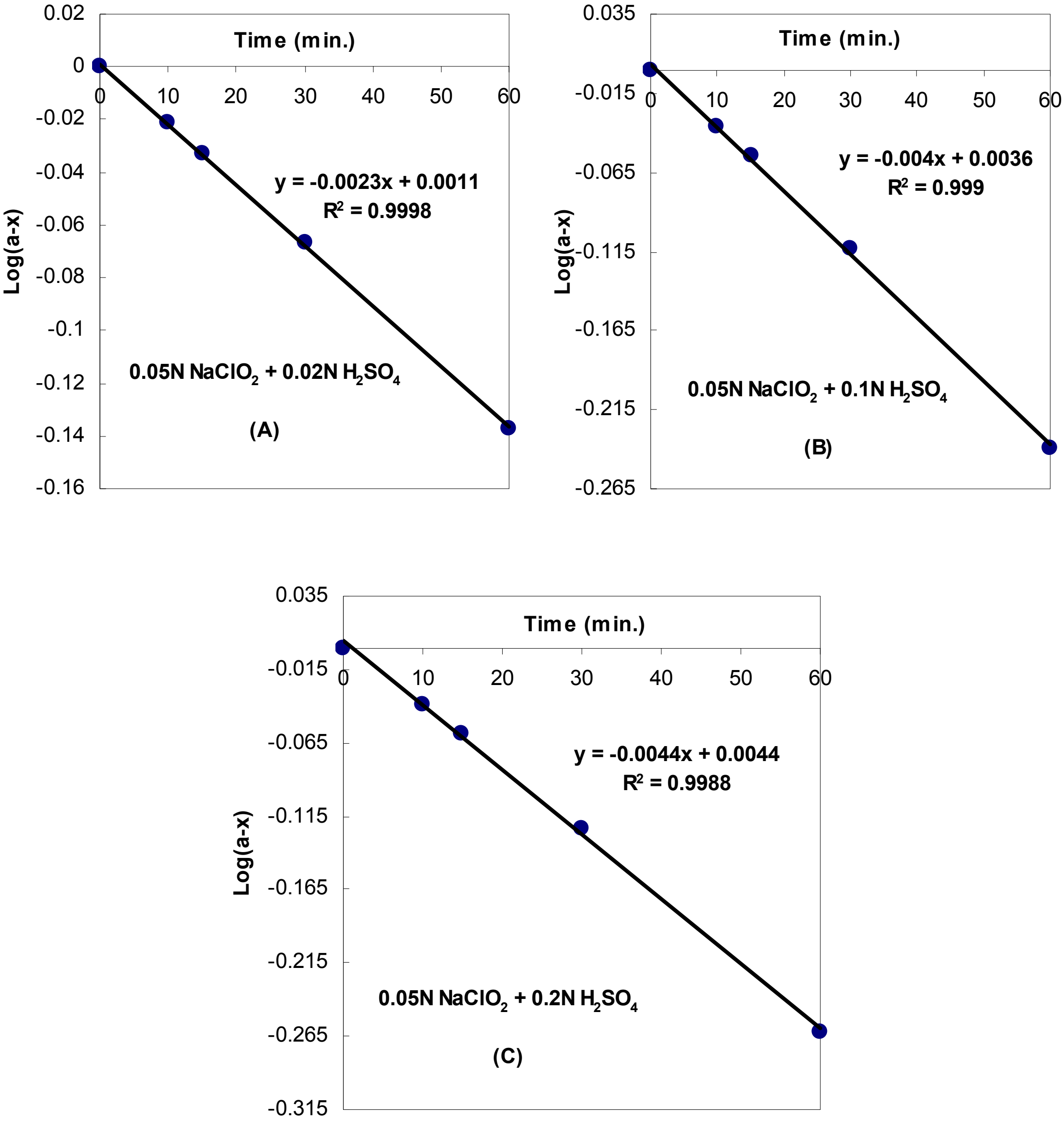


Fig. 5.81. The relation between log(*a-x*) and time (min.)
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.39 for experimental data]

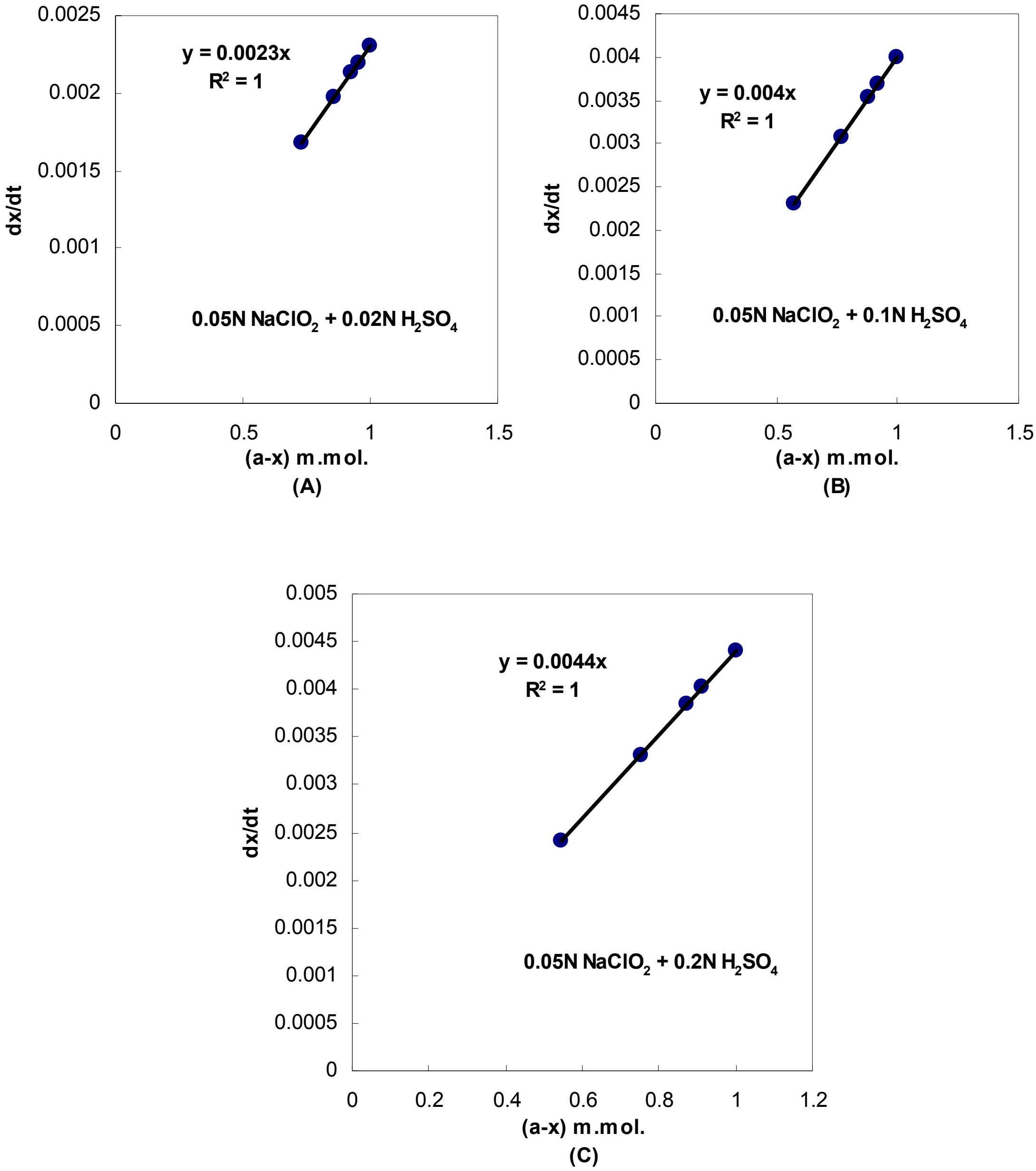


Fig. 5.82. The relation between *dx/dt* (rate) and (*a-x*) (concentrations)
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.40 for experimental data]

Experiment No. 3

The graphical representations of generation of ClO_2 for a definite $NaClO_2$ concentration (0.1N) with various concentrations of H_2SO_4 are shown in Figs. 5.83.-5.84. The reaction was carried out at a constant temperature of 30 ± 1^0C and the volume ratio of $NaClO_2$ and H_2SO_4 was (v/v) 1:1. Initial concentration of $NaClO_2$ was estimated at 10, 15, 30 and 60 minutes time interval and then the value of log(*a-x*) was calculated and plotted against time, *t* (min.) gave a straight line with a slope of –*k* (Fig. 5.83.). Values of *dx/dt* were calculated using the above equation and rate constant (*k*). Then, *dx/dt* was plotted against (*a-x*) gave a straight line which passing through the origin (Fig. 5.84.), indicating the 1st-order reaction.

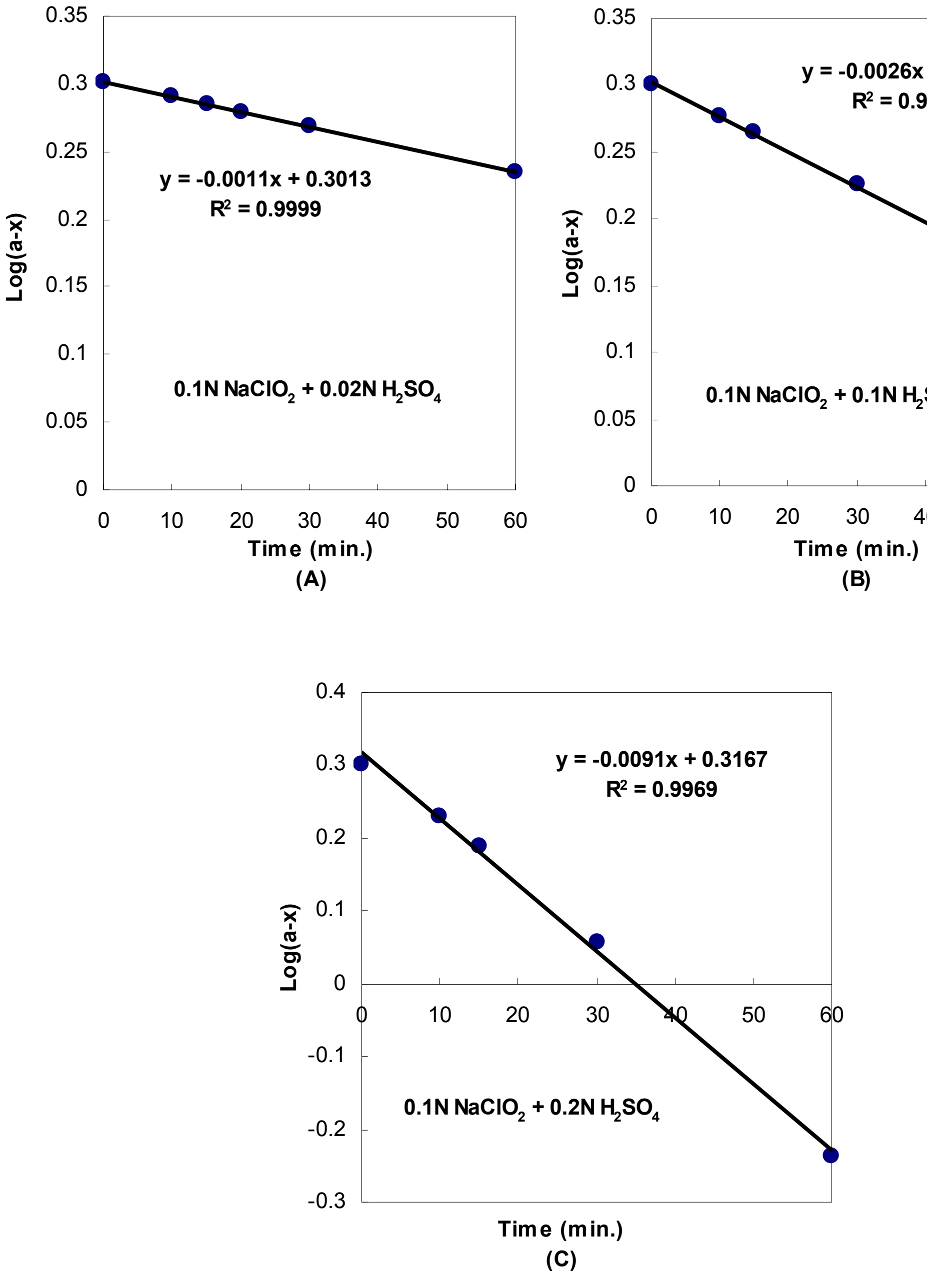


Fig. 5.83. The relation between log(*a*-*x*) and time (min.)
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.41 for experimental data]

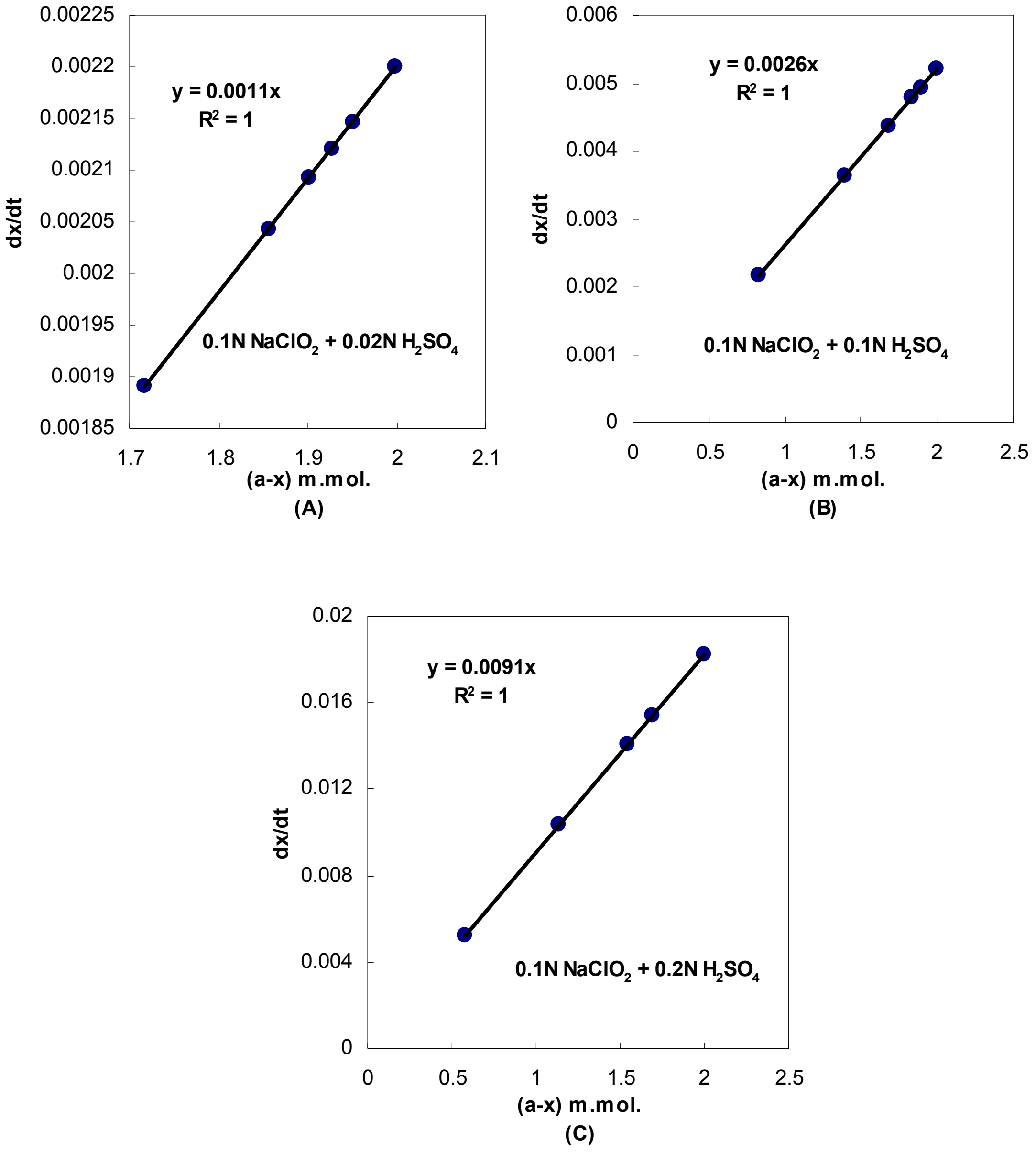
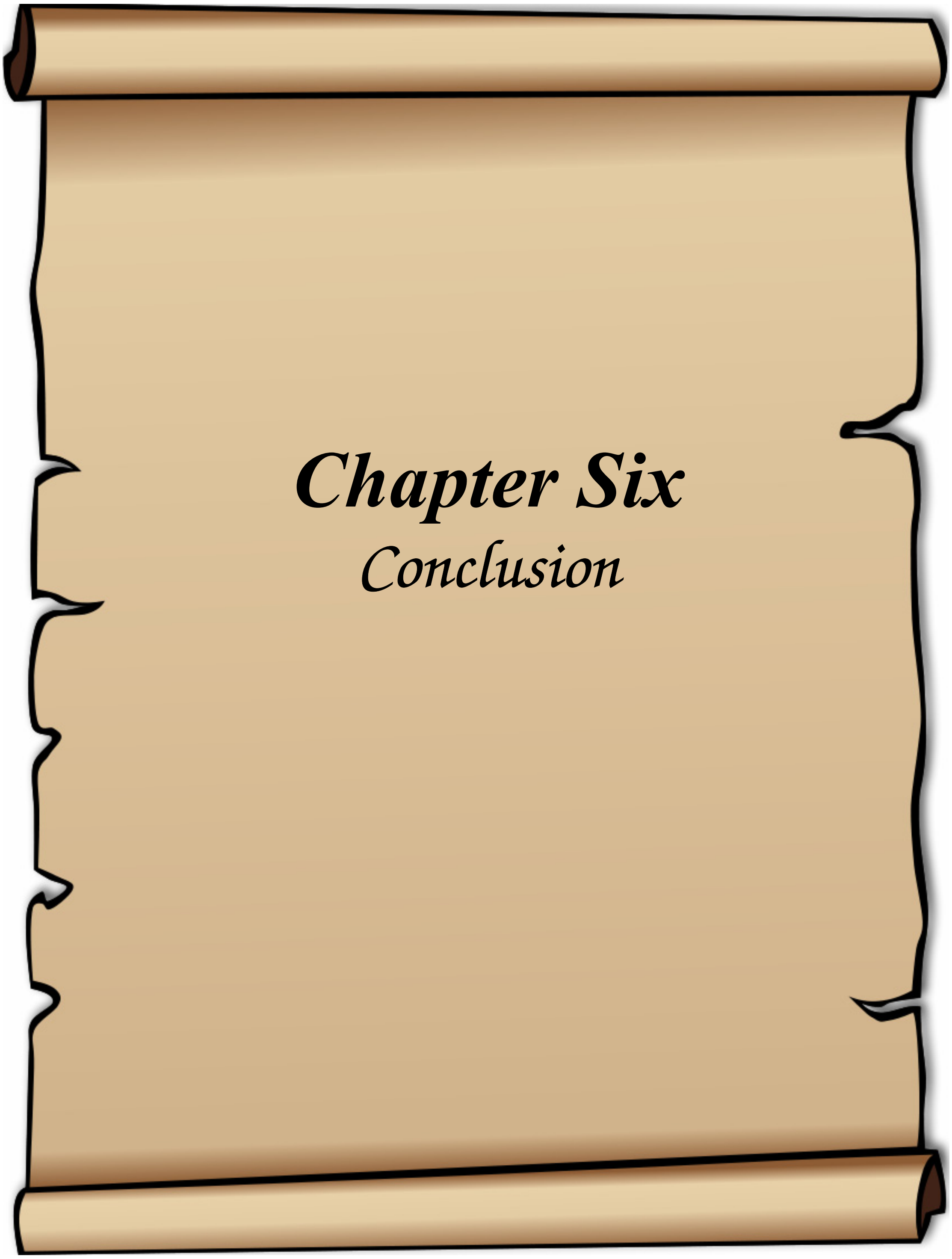


Fig. 5.84. The relation between dx/dt (rate) and (*a*-*x*) (concentrations)
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2N H_2SO_4
[APPENDIX, Table-5.42 for experimental data]

The above experimental results suggested that the generation of ClO_2 from ClO_2^- ion in the presence of H_2SO_4 was followed the first-order kinetics. A similar observation was made by Ionnalagadda et al.[160] and Chinake et al.[233] reported that the decomposition reaction of ClO_2^- ion in the presence of acid was the 1st-order reaction. It may be mentioned that, the above experimental data did not fit for the second-order or third-order equation (figure not shown). A set of best-fit and literature-derived parameters is presented for the complete mechanism as a first-order.



Chapter Six

Conclusion

CONCLUSION

Several methods have been practiced for the generation of chlorine dioxide (ClO_2), but the method of preparation by mixing acid and chlorite is widely used because of its simplicity.

The study was attempted to generate ClO_2 from H_2SO_4, $Na_2S_2O_8$, $(CH_3CO)_2O$ and a mixture [H_2SO_4 and $(CH_3CO)_2O$] reacted individually with $NaClO_2$. The effects of reactants concentration and reaction time were studied to get the maximum production of ClO_2 from an individual reaction. The study also determined the reaction order and proposed chemical reactions for the formation and decomposition of ClO_2 by a reaction of $NaClO_2$ and H_2SO_4.

The effect of $NaClO_2$ on the generation of ClO_2 was determined in the reaction between $NaClO_2$ and a definite concentration of H_2SO_4. The results showed that the percentage production of ClO_2 increased with decreasing concentration of $NaClO_2$ but the amount of ClO_2 production increased with increasing $NaClO_2$ concentration. The percentage production of ClO_2 is the ratio of the product (ClO_2) to the initial $NaClO_2$ concentration and $NaClO_2$ was the only source of chlorite species, it is obvious that the production of ClO_2 was not proportionally increased with increasing of $NaClO_2$ concentration.

The study also evaluated the effect of H_2SO_4 (the other reactant) on the production of ClO_2 in the reactions of various H_2SO_4 concentrations and a definite concentration of $NaClO_2$. The results showed that the percentage production and amount of ClO_2 increased rapidly with increasing H_2SO_4 concentration up to 0.4N and then increased very slowly or remained almost constant. Thus 0.4N H_2SO_4 was the most favorable concentrations for the production of ClO_2. The results suggested that the percentage production and amount of ClO_2 was greatly dependent on both the reactant concentrations and the reaction time. A similar observation was made for the reactions between $NaClO_2$ and other reactants ($Na_2S_2O_8$, $(CH_3CO)_2O$, and a mixture of $(CH_3CO)_2O$ and H_2SO_4 to generate ClO_2.

The maximum percentage production of ClO_2 was estimated from an individual reaction of chlorite solution with a specific reactant and they are stated below:

(i) About 75% ClO_2 was produced from chlorite ion in a reaction of 0.01N $NaClO_2$ and 1.0N H_2SO_4 in 240 minutes, 195 mg of ClO_2 was produced from chlorite ion in the reaction of 0.2N $NaClO_2$ and 1.0N H_2SO_4 for 240 minutes,

(ii) About 60% ClO_2 was produced from chlorite ion in a reaction of 0.01N $NaClO_2$ and 0.2N $Na_2S_2O_8$ in 240 minutes, 146 mg of ClO_2 was produced from chlorite ion in the reaction of 0.2N $NaClO_2$ and 0.2N $Na_2S_2O_8$ for 240 minutes,

(iii) About 78% ClO_2 was produced from chlorite ion in a reaction of 0.01N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ within two minute, 193 mg of ClO_2 was produced from chlorite ion in the reaction of 0.2N $NaClO_2$ and 0.1N $(CH_3CO)_2O$ within two minutes; and

(iv) About 91% ClO_2 was produced from chlorite ion in a reaction of 0.01N $NaClO_2$ with a mixture of 0.1N $CH_3CO)_2O$ and 0.02N H_2SO_4 within two minutes, 216 mg of ClO_2 was produced from chlorite ion in a reaction of 0.2N $NaClO_2$ with a mixture of 0.1N $(CH_3CO)_2O$ and 0.02N H_2SO_4 within two minutes.

Above results showed that 0.01N $NaClO_2$ was the most suitable concentration for the production of ClO_2 from chlorite solution.

The study results also revealed that above 91% ClO_2 was produced by a reaction of $NaClO_2$ with a mixture [1:1 (v/v); $(CH_3CO)_2O$ and H_2SO_4] within 2 minutes. But for the same reaction time, about 78% and 2% ClO_2 were produced, respectively from $(CH_3CO)_2O$ and H_2SO_4 reacted individually with $NaClO_2$ and their sum was 80%, which was lower than that of the percent production (91%) of the above reaction. In the context of production behavior, it was observed that the mixture [$(CH_3CO)_2O$ and H_2SO_4] was more reactive to $NaClO_2$ than their individual effect. Thus the reaction between $NaClO_2$ and the mixture of $(CH_3CO)_2O$ and H_2SO_4 was not considered to be a catalytic reaction as the results showed that H_2SO_4 or $(CH_3CO)_2O$ reacted individually with $NaClO_2$ to produce ClO_2. Since the percent of production (91%) was obtained in the reaction between $NaClO_2$ and a mixture [1:1 (v/v); $(CH_3CO)_2O$ and H_2SO_4], it was concluded that the mixture of $(CH_3CO)_2O$ and H_2SO_4 might have a synergistic effect on the production of ClO_2. A synergistic effect is the interaction of multiple reactants or elements in a system to produce an effect different from or greater than the sum of their individual effects.

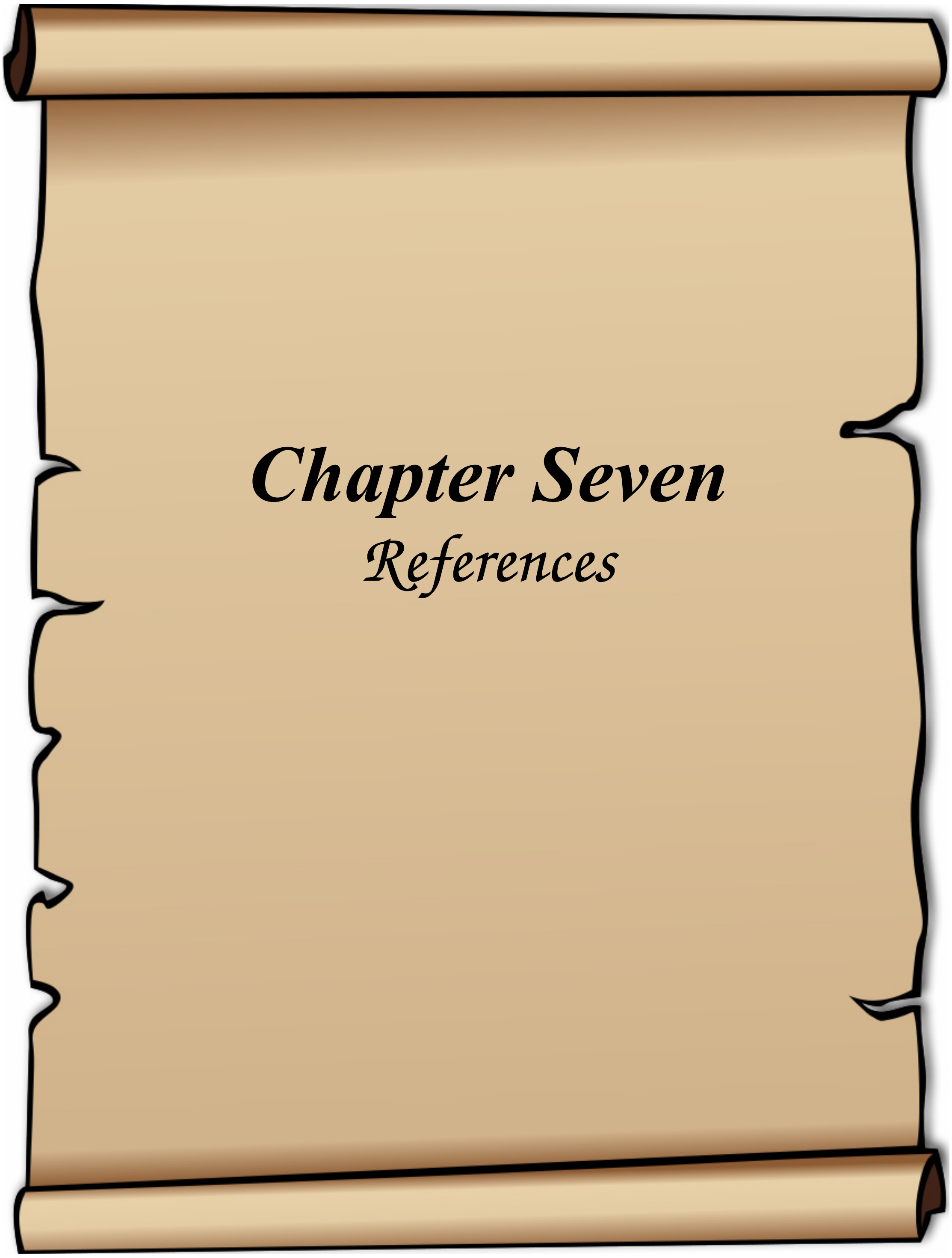
This study also proposed chemical reactions for the generation and decomposition of ClO_2 in the reaction of $NaClO_2$ and H_2SO_4. The decomposition of ClO_2^- produced various chlorine species such as ClO_2, ClO_3^-, Cl^- etc. in presence of H_2SO_4. The proposed reaction for the generation of ClO_2 from chlorite solution in an acidic media can be stated as:

$$ClO_2^- \xrightarrow{H^+} xClO_2 + yClO_3^- + zCl^-$$

At the same time, ClO_2 decomposed into various chlorine species due to its unstable behavior. The experimental results showed that at the end of the ClO_2^- decomposition reaction, the amount of ClO_2 decomposition was almost equal to the formation amount of chloride ion. The proposed reaction for ClO_2 decomposition in an acidic media could be written as:

$$ClO_2 \xrightarrow{H^+} Cl^- + 2H_2O$$

On the basis of the rate law, the initial concentration of $NaClO_2$ was estimated at a regular time interval and then the value of *log(a-x)* was calculated and plotted against time, *t* (minute) gave a straight line with a slope of $-k$. The estimated first-order reaction rate constant (*k*) for the decomposition of chlorite ion with H_2SO_4 was in the range from 0.002 to 0.006 min^{-1}. The values of *dx/dt* were calculated using the rate equation and rate constant (*k*). Then, *dx/dt* was plotted against *(a-x)* which gave a straight line indicating that the reaction is of the first order. The experimental data, however, did not fit to the zero-, second- or third-order equations. Hence, it was concluded that the decomposition reaction of ClO_2^- ion for the generation of ClO_2 followed the first-order kinetics.



Chapter Seven

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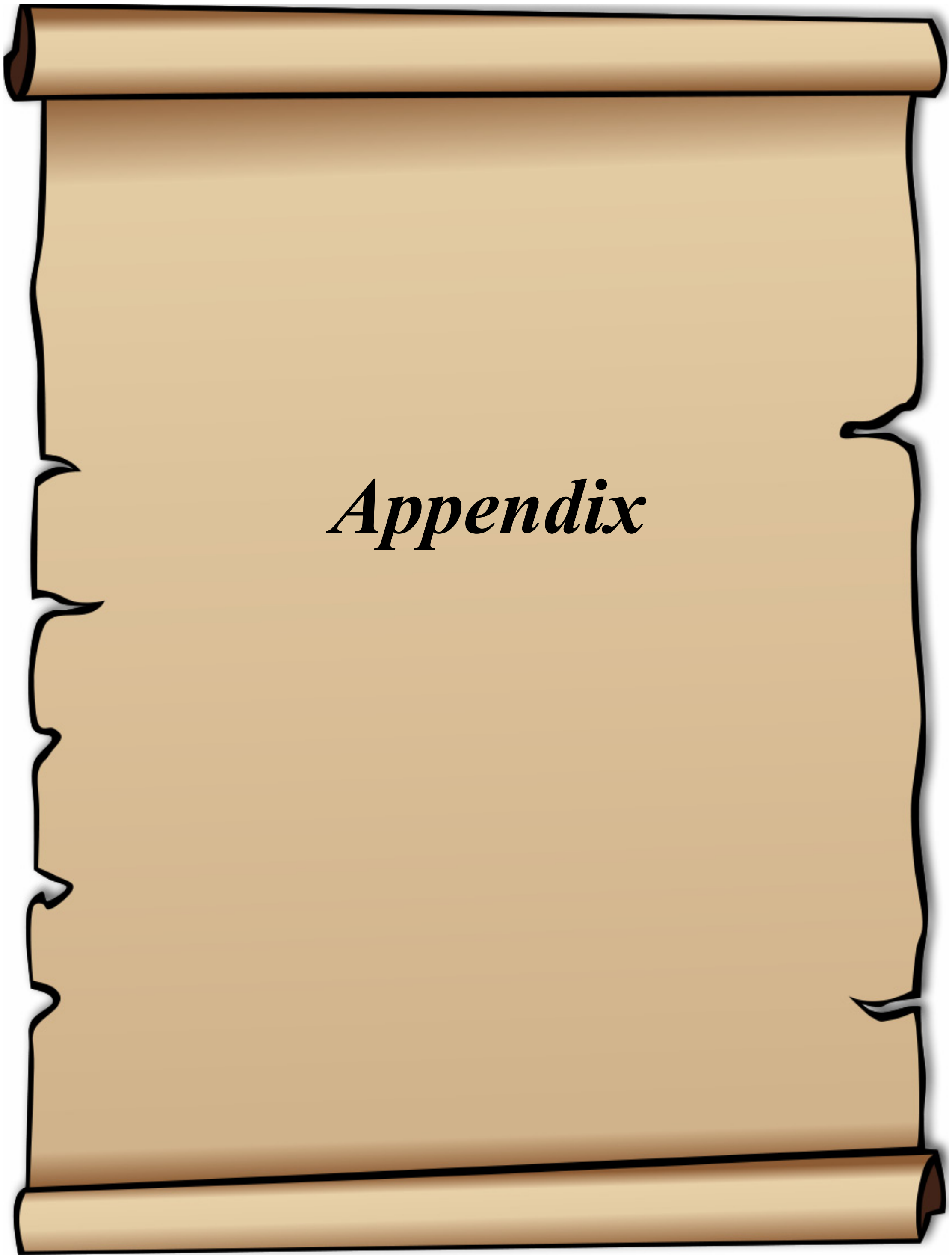

Appendix

Table-5.1

The effect of $NaClO_2$ concentrations on the percentage production of ClO_2

A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2 N H_2SO_4; D = 0.4N H_2SO_4; E = 1.0N H_2SO_4

(A)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	2.981	7.058	20.444	41.911
0.05	2.511	6.051	17	33.9
0.1	1.97	5	12.78	24.111
0.2	1.023	3.129	4.612	6.378

(B)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	4.10	10.27	36.71	68.35
0.05	3.8	9.32	33.11	64.00
0.1	3.48	8.32	28.88	58.82
0.2	2.88	6.22	21.26	48.47

(C)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	6.75	17.04	51.35	74.12
0.05	6.32	15.55	48.44	71.55
0.1	5.76	13.88	44.88	68.55
0.2	4.77	10.94	38.44	63

(D)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	8.77	20.66	61.53	73.84
0.05	8.31	19.67	58.66	73
0.1	7.77	18.53	55.25	71.91
0.2	6.76	16.11	48.70	69.52

(E)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	9.58	21.41	62.55	74.87
0.05	8.9	20.5	60.26	73.30
0.1	8.23	19.4	57.50	71.87
0.2	7.11	17.42	52.72	69.23

Table-5.2

The effect of $NaClO_2$ concentration on the amount of ClO_2

A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2 N H_2SO_4; D = 0.4N H_2SO_4; E = 1.0N H_2SO_4

(A)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	0.40	0.95	2.75	7.22
0.05	1.45	4	10.5	19.11
0.1	2.38	6.88	14.5	25.53
0.2	2.76	7.91	15.4	26.82

(B)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	0.55	1.38	4.95	9.22
0.05	2.52	5.913	18.33	37.62
0.1	4.80	9.592	33.22	69.7
0.2	7.79	16.78	60.91	138.11

(C)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	0.91	2.29	6.92	9.99
0.05	4.19	10.35	29.8	46.46
0.1	7.34	16.94	55.03	89.7
0.2	12.88	29.52	104.41	173.01

(D)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	1.18	2.78	8.31	9.94
0.05	5.47	12.77	34.8	49.28
0.1	10.22	24.20	67.11	95.46
0.2	18.24	46.3	131.41	186.81

(E)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	1.29	2.88	8.43	10.05
0.05	5.72	14.10	34.5	52.11
0.1	10.94	26.41	68.41	99.66
0.2	20.61	52.11	135.44	195.45

Table -5.3

The effect of H_2SO_4 concentration on the percentage production of ClO_2

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.02	2.87	6.42	16.51	56.8
0.1	5.11	11.22	35.22	66.31
0.2	6.75	15.91	51.35	71.33
0.4	8.31	19.33	58.5	73.71
1.0	9.58	21.41	62.55	74.87

(B)

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.02	2.16	5.22	15.56	28.32
0.1	4	8.76	25.70	48.51
0.2	6.22	12.62	37.11	65.12
0.4	7.82	18.94	56.61	71.50
1.0	8.49	20.91	58.89	73.42

(C)

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.02	1.76	4.44	10.74	18.91
0.1	3.56	7.5	20.72	51.42
0.2	5.44	11.22	33.6	66.4
0.4	7.57	17.94	52.75	70.76
1.0	8.11	17.77	56.95	73.88

(D)

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.02	1.02	3.12	5.55	9.74
0.1	2.88	6.22	21.26	52.33
0.2	4.77	9.53	35.71	62.33
0.4	6.34	15.02	46.8	68
1.0	7.63	17.42	52.72	71.22

Table-5.4

The effect of H_2SO_4 concentration on the amount of ClO_2

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.02	0.40	0.95	2.75	7.22
0.1	0.69	1.66	4.95	9.03
0.2	0.91	2.29	6.92	9.72
0.4	1.18	2.78	8.30	9.94
1.0	1.29	2.88	8.43	10.05

(B)

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.02	1.45	3.52	12.13	21.22
0.1	3.11	7.60	21.42	41.22
0.2	4.19	10.35	32.12	46.46
0.4	5.47	12.77	37.97	49.28
1.0	5.72	14.10	39.72	49.52

(C)

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.02	2.38	6.02	18.51	30.44
0.1	4.80	11	34.11	71.6
0.2	7.34	16.94	55.02	92.25
0.4	10.22	24.20	71.16	95.46
1.0	10.94	23.98	76.82	99.66

(D)

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.02	2.76	8.44	12.44	16.61
0.1	7.79	18	57.37	105
0.2	12.88	29.52	104.41	173.01
0.4	18.24	43.47	131.40	186.80
1.0	20.61	47.01	142.26	195.45

Table-5.5

The effect of time on the percentage production of ClO_2 at various H_2SO_4 concentrations
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Time (min.)	0.02N H_2SO_4	0.1N H_2SO_4	0.2N H_2SO_4	0.4N H_2SO_4	1.0N H_2SO_4
0	0	0	0	0	0
2	1.76	2.24	3.88	4.93	5.27
5	2.98	4.10	6.75	8.77	9.58
10	4.98	7.18	11.77	14.74	15.76
15	7.05	10.27	17.04	20.66	21.41
30	13.11	19.61	29.73	37.53	38.41
60	20.44	36.71	51.35	61.53	62.55
120	35.11	55.30	70.12	75.12	75.22
240	53.59	68.35	74.12	73.71	74.55
480	65.71	73.41	71.34	71.11	72.11
960	70.11	67.51	65.45	65.76	66.66
1440	71.24	60.41	59.76	60.34	61.78
2880	45.34	41.35	42.86	44.41	47.11
4320	21.22	23.62	26.70	29.17	33.12

(B)

Time (min.)	0.02N H_2SO_4	0.1N H_2SO_4	0.2N H_2SO_4	0.4N H_2SO_4	1.0N H_2SO_4
0	0	0	0	0	0
2	1.20	2.12	3.44	4.42	5.11
5	2.16	3.74	6.22	8.11	8.49
10	3.77	6.20	10.88	13.56	14.35
15	5.22	8.76	15.35	18.94	20.91
30	9.65	15.74	27.66	35.93	37.36
60	17.98	29.55	47.62	56.30	58.89
120	25.36	50.27	61.30	67.89	70.33
240	31.46	64.40	68.89	73.07	73.42
480	36.74	70.78	72.43	70.10	70.97
960	41.19	64.44	65.77	64.53	65.55
1440	42.83	57.88	59.35	59.11	60.33
2880	30.39	39.33	41.23	43.10	45.42
4320	18.44	21.11	24.11	27.12	30.21

(C)

Time (min.)	0.02N H_2SO_4	0.1N H_2SO_4	0.2N H_2SO_4	0.4N H_2SO_4	1.0N H_2SO_4
0	0	0	0	0	0
2	1.01	2.01	3.22	4.22	5.00
5	1.76	3.56	5.44	7.57	8.11
10	3.10	5.23	9.11	12.86	13.11
15	4.44	7.11	12.56	17.94	17.77
30	8.11	12.21	23.12	32.65	32.12
60	13.72	22.12	40.78	52.75	56.95
120	18.64	39.83	56.87	63.53	69.64
240	22.56	57.48	68.38	70.76	73.88
480	25.85	68.10	70.25	72.25	70.44
960	28.77	69.65	64.01	65.74	64.86
1440	29.65	61.88	57.67	59.41	59.11
2880	22.66	39.78	39.32	41.22	42.33
4320	15.44	18.14	21.42	24.22	26.66

(D)

Time (min.)	0.02N H_2SO_4	0.1N H_2SO_4	0.2N H_2SO_4	0.4N H_2SO_4	1.0N H_2SO_4
0	0	0	0	0	0
2	0.88	1.82	2.65	4.00	4.61
5	1.41	2.88	4.77	6.76	7.63
10	2.26	4.66	7.74	11.33	12.62
15	3.05	6.22	10.94	16.11	17.42
30	4.71	11.36	20.15	29.33	31.89
60	7.16	21.26	38.69	48.70	52.72
120	10.06	35.80	55.38	61.50	68.72
240	12.19	48.47	64.12	69.23	72.44
480	15.11	53.53	65.39	71.28	69.42
960	17.41	54.69	59.55	64.64	63.74
1440	18.11	48.44	53.33	58.22	57.67
2880	14.51	31.42	35.75	39.55	40.21
4320	10.48	14.60	18.10	21	23.82

Table-5.6
The effect of time on the amount of ClO_2 at various H_2SO_4 concentrations
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Time (min.)	0.02N H_2SO_4	0.1N H_2SO_4	0.2N H_2SO_4	0.4N H_2SO_4	1.0N H_2SO_4
0	0	0	0	0	0
2	2	0.238	0.302	0.524	0.666
5	5	0.403	0.553	0.911	1.183
10	10	0.672	0.969	1.588	1.989
15	15	0.952	1.385	2.299	2.787
30	30	1.769	2.646	4.011	5.063
60	60	2.757	4.952	6.927	8.301
120	120	4.736	7.459	9.459	10.13
240	240	7.229	9.221	9.999	9.944
480	480	8.864	9.904	9.624	9.592
960	960	9.458	9.107	8.830	8.871
1440	1440	9.610	8.149	8.062	8.140
2880	2880	6.116	5.579	5.781	5.991
4320	4320	2.863	3.186	3.602	3.935

(B)

Time (min.)	0.02N H_2SO_4	0.1N H_2SO_4	0.2N H_2SO_4	0.4N H_2SO_4	1.0N H_2SO_4
0	0	0	0	0	0
2	2	0.811	1.433	2.320	2.983
5	5	1.458	2.526	4.198	5.470
10	10	2.542	4.183	7.343	9.150
15	15	3.522	5.913	10.35	12.77
30	30	6.514	10.61	18.66	24.23
60	60	12.13	19.93	32.12	37.97
120	120	17.11	33.90	41.34	45.79
240	240	21.22	43.44	46.46	49.28
480	480	24.78	47.74	48.85	47.28
960	960	27.78	43.46	44.36	43.53
1440	1440	28.88	39.04	40.03	39.87
2880	2880	20.49	26.52	27.81	29.07
4320	4320	12.43	14.24	16.26	18.29

(C)

Time (min.)	0.02N H_2SO_4	0.1N H_2SO_4	0.2N H_2SO_4	0.4N H_2SO_4	1.0N H_2SO_4
0	0	0	0	0	0
2	1.363	2.712	4.346	5.695	6.745
5	2.382	4.807	7.347	10.22	10.94
10	4.188	7.067	12.29	17.35	17.68
15	6.002	9.592	16.94	24.20	23.98
30	10.94	16.47	31.19	44.05	43.32
60	18.51	29.84	55.02	71.16	76.82
120	25.15	53.73	76.71	85.71	93.94
240	30.44	77.54	92.25	95.46	99.66
480	34.88	91.86	94.76	97.47	95.02
960	38.81	93.96	86.35	88.68	87.50
1440	40.00	83.48	77.79	80.14	79.74
2880	30.57	53.66	53.04	55.60	57.10
4320	20.82	24.47	28.90	32.67	35.96

(D)

Time (min.)	0.02N H_2SO_4	0.1N H_2SO_4	0.2N H_2SO_4	0.4N H_2SO_4	1.0N H_2SO_4
0	0	0	0	0	0
2	2.395	4.913	7.171	10.798	12.44
5	3.777	7.793	12.88	18.24	20.61
10	6.097	12.58	20.89	30.57	34.13
15	8.228	16.78	29.52	43.47	47.01
30	12.70	30.67	54.38	79.15	86.06
60	19.31	57.37	104.41	131.40	142.26
120	27.14	96.59	149.42	165.93	185.41
240	32.88	130.75	173.01	186.80	195.45
480	40.73	144.44	176.44	192.31	187.29
960	46.94	147.55	160.67	174.41	171.97
1440	48.86	130.69	143.89	157.08	155.59
2880	39.14	84.77	96.45	106.71	108.48
4320	28.29	39.39	48.83	56.65	64.266

Table-5.7

The effect of time on the percentage production of ClO_2 at various $NaClO_2$ concentrations
A= 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2 N H_2SO_4; D = 0.4N H_2SO_4; E = 1.0N H_2SO_4

(A)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	1.766	1.203	1.011	0.888
5	2.986	2.162	1.766	1.4
10	4.988	3.77	3.105	2.26
15	7.058	5.223	4.449	3.05
30	13.11	9.659	8.111	4.71
60	20.44	17.98	13.72	7.16
120	35.11	25.36	18.64	10.06
240	53.59	31.46	22.56	12.19
480	65.71	36.74	25.85	15.1
960	70.11	41.19	28.77	17.4
1440	71.24	42.83	29.65	18.11
2880	45.34	30.39	22.66	14.51
4320	21.22	18.44	16.11	10.48

(B)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	2.244	2.125	2.011	1.821
5	4.101	3.746	3.564	2.888
10	7.186	6.202	5.239	4.663
15	10.27	8.767	7.111	6.222
30	19.61	15.74	12.21	11.36
60	36.71	29.55	22.12	21.26
120	55.30	50.27	39.83	35.80
240	68.35	64.40	57.48	48.47
480	73.41	70.78	68.10	53.53
960	67.51	64.44	69.65	54.69
1440	60.41	57.88	61.88	48.44
2880	41.35	39.33	39.78	31.42
4320	23.62	21.11	18.14	14.60

(C)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	3.889	3.441	3.222	2.658
5	6.759	6.224	5.446	4.776
10	11.77	10.88	9.111	7.744
15	17.04	15.35	12.56	10.94
30	29.73	27.66	23.12	20.15
60	51.35	47.62	40.78	38.69
120	70.12	61.30	56.87	55.38
240	74.12	68.89	68.38	64.12
480	71.34	72.43	70.25	65.39
960	65.45	65.77	64.01	59.55
1440	59.76	59.35	57.67	53.33
2880	42.86	41.23	39.32	35.75
4320	26.70	23.28	21.42	18.81

(D)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	4.936	4.424	4.222	4.000
5	8.772	8.111	7.577	6.761
10	14.74	13.56	12.86	11.33
15	20.66	18.94	17.94	16.11
30	37.53	35.93	32.65	29.33
60	61.53	56.30	52.75	48.70
120	75.12	67.89	63.53	61.50
240	73.71	73.07	70.76	69.23
480	71.11	70.10	72.25	71.28
960	65.76	64.53	65.74	64.64
1440	60.34	59.11	59.41	58.22
2880	44.41	43.10	41.22	39.55
4320	29.17	27.12	24.43	21.31

(E)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	5.275	5.114	5.000	4.614
5	9.585	8.495	8.111	7.639
10	15.76	14.35	13.11	12.65
15	21.41	20.91	17.77	17.42
30	38.41	37.36	32.12	31.89
60	62.55	58.89	56.95	52.72
120	75.22	70.33	69.64	68.72
240	74.35	73.42	73.88	72.44
480	72.11	70.97	70.44	69.42
960	66.66	65.55	64.86	63.74
1440	61.78	60.33	59.11	57.67
2880	47.11	45.42	42.33	40.21
4320	33.12	30.21	26.33	23.28

Table-5.8

The effect of time on the amount of ClO_2 at various $NaClO_2$ concentrations

A = 0.02N H_2SO_4; B = 0.1N H_2SO_4; C = 0.2 N H_2SO_4; D = 0.4N H_2SO_4; E = 1.0N H_2SO_4

(A)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	0.238	0.811	1.363	2.395
5	0.403	1.458	2.382	3.777
10	0.672	2.542	4.188	6.097
15	0.952	3.522	6.002	8.228
30	1.769	6.515	10.94	12.70
60	2.757	12.13	18.51	19.31
120	4.736	17.11	25.15	27.14
240	7.229	21.22	30.44	32.88
480	8.864	24.78	34.88	40.73
960	9.458	27.78	38.81	46.94
1440	9.610	28.88	40.00	48.86
2880	6.116	20.49	30.57	39.14
4320	2.863	12.43	21.73	28.29

(B)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	0.302	1.433	2.712	4.913
5	0.553	2.526	4.807	7.793
10	0.969	4.183	7.067	12.58
15	1.385	5.913	9.592	16.78
30	2.646	10.61	16.47	30.67
60	4.952	19.93	29.84	57.37
120	7.459	33.90	53.73	96.59
240	9.221	43.44	77.54	130.79
480	9.904	47.74	91.86	144.44
960	9.107	43.46	93.96	147.55
1440	8.149	39.04	83.48	130.69
2880	5.579	26.52	53.66	84.77
4320	3.186	14.24	24.47	39.39

(C)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	0.524	2.320	4.346	7.171
5	0.911	4.198	7.347	12.88
10	1.588	7.343	12.29	20.89
15	2.299	10.35	16.94	29.52
30	4.011	18.66	31.19	54.38
60	6.927	32.12	55.02	104.41
120	9.459	41.34	76.71	149.42
240	9.999	46.46	92.25	173.01
480	9.624	48.85	94.76	176.44
960	8.830	44.36	86.35	160.67
1440	8.062	40.03	77.79	143.89
2880	5.781	27.81	53.04	96.45
4320	3.602	15.70	28.90	50.74

(D)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	0.666	2.983	5.695	10.79
5	1.183	5.470	10.22	18.24
10	1.989	9.150	17.35	30.57
15	2.787	12.77	24.20	43.47
30	5.063	24.23	44.05	79.15
60	8.301	37.97	71.16	131.40
120	10.13	45.79	85.71	165.93
240	9.944	49.28	95.46	186.80
480	9.592	47.28	97.47	192.31
960	8.871	43.53	88.68	174.41
1440	8.140	39.87	80.14	157.08
2880	5.991	29.07	55.60	106.79
4320	3.935	18.29	32.96	57.51

(E)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
2	0.711	3.449	6.745	12.44
5	1.293	5.729	10.94	20.61
10	2.126	9.682	17.68	34.13
15	2.888	14.10	23.98	47.01
30	5.182	25.19	43.32	86.06
60	8.438	39.72	76.82	142.26
120	10.24	47.43	93.94	185.41
240	10.05	49.52	99.66	195.45
480	9.727	47.87	95.02	187.29
960	8.992	44.21	87.50	171.97
1440	8.335	40.69	79.74	155.59
2880	6.355	30.63	57.10	108.49
4320	4.468	20.38	35.52	62.814

Table-5.9

The effect of sodium chlorite concentration on the percentage production of ClO_2

A = 0.01N $Na_2S_2O_8$; B = 0.05N $Na_2S_2O_8$; C = 0.1N $Na_2S_2O_8$; D = 0.2N $Na_2S_2O_8$

(A)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	4.76	7.31	19.61	37.71
0.05	3.96	6.14	16.13	30.22
0.1	2.95	4.76	12.00	21.72
0.2	1.55	2.88	4.44	6.00

(B)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	6.32	12.63	32.44	55.13
0.05	6.08	11.64	29.88	51.77
0.1	5.79	10.43	26.52	47.8
0.2	5.27	8.00	20.29	39.84

(C)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	9.88	16.22	37.42	58.88
0.05	9.33	15.28	35.91	57.77
0.1	8.61	14.13	34.00	56.00
0.2	7.33	11.75	30.41	53.09

(D)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	13.11	19.922	40.37	60.27
0.05	12.65	18.92	38.33	58.83
0.1	12.17	17.79	35.62	57.18
0.2	11.23	15.62	30.81	54.22

Table-5.10

The effect of sodium chlorite concentration on the amount of ClO_2

A = 0.01N $Na_2S_2O_8$; B = 0.05N $Na_2S_2O_8$; C = 0.1N $Na_2S_2O_8$; D = 0.2N $Na_2S_2O_8$

(A)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	0.51	1.62	2.75	3.85
0.05	2.14	4.14	9.91	17.40
0.1	3.54	6.42	15.63	29.27
0.2	4.18	8.14	17.22	31.81

(B)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	0.852	1.703	4.377	7.438
0.05	4.102	7.851	19.96	34.93
0.1	7.816	14.07	35.74	64.48
0.2	14.21	23.58	57.75	107.50

(C)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	1.33	2.188	5.048	7.986
0.05	5.28	10.30	24.21	36.60
0.1	10.30	19.06	45.86	68.91
0.2	19.78	34.71	84.01	129.50

(D)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	1.769	2.687	5.446	8.130
0.05	8.537	12.76	25.83	39.66
0.1	16.41	23.99	48.02	77.13
0.2	30.30	42.14	83.09	146.28

Table-5.11

The effect of $Na_2S_2O_8$ concentration on the percentage production of ClO_2

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Conc. of $Na_2S_2O_8$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	4.76	7.31	19.61	37.7
0.05	7.28	12.63	31.6	55.13
0.1	9.88	16.22	37.42	58.82
0.2	12.11	18.22	40.37	59.22

(B)

Conc. of $Na_2S_2O_8$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	3.44	6.14	15.78	30.22
0.05	6.34	11.64	29.61	51.80
0.1	9.3	15.28	35.91	56.71
0.2	12.65	18.92	38.33	57.49

(C)

Conc. of $Na_2S_2O_8$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	2.55	5.47	11.59	21.70
0.05	5.79	10.43	26.51	47.81
0.1	8.61	14.13	34	53.81
0.2	12.17	17.79	35.62	56.00

(D)

Conc. of $Na_2S_2O_8$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	1.05	2.08	3.65	6.00
0.05	5.27	8	20.29	39.84
0.1	7.33	11.75	30.41	48.11
0.2	11.23	15.62	30.80	49.72

Table-5.12

The effect of sodium per sulfate concentration on the amount of ClO_2

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Conc. of $Na_2S_2O_8$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	0.642	0.986	2.645	5.085
0.05	0.982	1.703	4.262	7.438
0.1	1.333	2.188	5.048	7.934
0.2	1.634	2.458	5.446	7.986

(B)

Conc. of $Na_2S_2O_8$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	2.324	4.141	10.64	20.36
0.05	4.276	7.851	19.96	34.93
0.1	6.272	10.30	24.21	38.24
0.2	8.537	12.76	25.83	38.77

(C)

Conc. of $Na_2S_2O_8$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	3.446	7.387	15.63	29.27
0.05	7.816	14.07	35.74	64.48
0.1	11.61	19.06	45.86	72.57
0.2	16.41	23.99	48.02	75.54

(D)

Conc. of $Na_2S_2O_8$ (N)	5 (min.)	15 (min.)	60 (min.)	240 (min.)
0.01	2.832	5.611	9.847	16.18
0.05	14.21	21.58	54.75	107.50
0.1	19.78	31.71	82.01	129.50
0.2	30.30	42.14	83.09	134.09

Table-5.13

The effect of time on the percentage production of ClO_2 at various $Na_2S_2O_8$ concentrations

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Time(min)	0.01N $Na_2S_2O_8$	0.05N $Na_2S_2O_8$	0.1N $Na_2S_2O_8$	0.2N $Na_2S_2O_8$
0	0	0	0	0
5	4.76	6.32	9.88	13.33
10	5.92	8.73	12.89	16.00
15	7.11	11.33	16.22	18.62
30	10.59	16.11	24.22	25.55
60	17.42	27.00	35.72	38.22
120	25.22	38.61	49.44	50.33
240	34.22	47.81	58.33	60.22
480	43.00	57.11	59.61	59.51
720	48.53	58.25	58.44	57.11
1440	53.89	53.77	51.71	50.22
2880	45.2	42.00	38.66	34.90
4320	36.53	31.31	26.12	20.92

(B)

Time (min)	0.01N $Na_2S_2O_8$	0.05N $Na_2S_2O_8$	0.1N $Na_2S_2O_8$	0.2N $Na_2S_2O_8$
0	0	0	0	0
5	4.321	6.118	9.126	12.68
10	5.285	8.123	12.22	14.94
15	6.227	10.11	15.41	18.41
30	9.124	15.76	24.11	26.34
60	14.62	26.59	36.37	39.13
120	21.49	40.33	49.74	55.14
240	29.11	49.97	57.88	59.88
480	35.82	55.88	58.88	59.32
720	39.55	57.31	57.41	56.33
1440	41.41	49.33	49.40	47.81
2880	33.61	35.61	34.00	31.51
4320	25.44	21.35	18.72	15.96

(C)

Time (min)	0.01N $Na_2S_2O_8$	0.05N $Na_2S_2O_8$	0.1N $Na_2S_2O_8$	0.2N $Na_2S_2O_8$
0	0	0	0	0
5	4.222	5.994	8.651	12.20
10	4.678	7.692	12.07	15.13
15	5.123	9.134	14.50	17.53
30	6.538	13.48	23.88	24.47
60	9.171	21.73	35.31	34.37
120	10.96	34.20	47.11	46.82
240	12.97	44.11	53.48	56.87
480	15.97	51.45	55.11	54.43
720	17.71	52.97	53.11	51.72
1440	18.71	48.12	45.72	44.11
2880	15.25	36.00	30.41	28.53
4320	10.90	24.72	16.17	13.85

(D)

Time (min)	0.01N $Na_2S_2O_8$	0.05N $Na_2S_2O_8$	0.1N $Na_2S_2O_8$	0.2N $Na_2S_2O_8$
0	0	0	0	0
5	0.922	7.332	7.332	11.23
10	1.218	9.566	9.566	13.35
15	1.844	11.75	11.75	15.62
30	2.635	18.49	18.49	21.26
60	3.162	30.65	30.65	30.11
120	3.651	41.89	41.89	42.33
240	4.262	47.70	47.70	53.35
480	5.00	48.10	50.10	50.50
720	5.383	45.61	47.72	47.99
1440	5.534	38.61	39.91	39.73
2880	4.668	25.42	25.11	24.1
4320	3.821	13.49	11.09	8.45

Table-5.14

The effect of time on the amount of ClO_2 at various $Na_2S_2O_8$ concentrations
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Time (min.)	0.01N $Na_2S_2O_8$	0.05N $Na_2S_2O_8$	0.1N $Na_2S_2O_8$	0.2N $Na_2S_2O_8$
0	0	0	0	0
5	0.642	0.852	1.333	1.798
10	0.798	1.173	1.738	2.158
15	0.957	1.524	2.188	2.509
30	1.428	2.158	3.267	3.439
60	2.347	3.642	4.815	5.153
120	3.399	5.207	6.664	6.785
240	4.613	6.448	7.864	8.123
480	5.800	7.702	8.042	8.026
709	6.542	7.858	7.878	7.689
1340	7.269	7.254	6.974	6.774
2880	6.097	5.665	5.215	4.708
4320	4.928	4.224	3.523	2.819

(B)

Time (min.)	0.01N $Na_2S_2O_8$	0.05N $Na_2S_2O_8$	0.1N $Na_2S_2O_8$	0.2N $Na_2S_2O_8$
0	0	0	0	0
5	2.915	4.126	6.155	8.558
10	3.565	5.478	8.246	10.07
15	4.200	6.820	10.39	12.41
30	6.154	10.63	16.26	17.77
60	9.862	17.93	24.53	26.39
120	14.49	27.20	33.55	37.19
240	19.62	33.70	39.04	40.38
480	24.14	37.69	39.71	39.99
720	26.68	38.65	38.71	37.97
1440	27.93	33.25	33.32	32.24
2880	22.66	24.01	22.93	21.24
4320	17.13	14.40	12.62	10.76

(C)

Time (min.)	0.01N $Na_2S_2O_8$	0.05N $Na_2S_2O_8$	0.1N $Na_2S_2O_8$	0.2N $Na_2S_2O_8$
0	0	0	0	0
5	5.695	8.085	11.67	16.46
10	6.310	10.37	16.29	20.41
15	6.910	12.32	19.56	23.64
30	8.819	18.18	32.21	33.01
60	12.37	29.32	47.64	46.37
120	14.78	46.14	63.55	63.16
240	17.49	59.35	72.15	76.72
480	21.55	69.40	74.34	73.38
720	23.87	71.46	71.63	69.74
1440	25.24	64.91	61.64	59.36
2880	20.58	48.56	41.00	38.49
4320	14.71	33.34	21.81	18.68

(D)

Time (min.)	0.01N $Na_2S_2O_8$	0.05N $Na_2S_2O_8$	0.1N $Na_2S_2O_8$	0.2N $Na_2S_2O_8$
0	0	0	0	0
5	2.487	19.78	19.78	30.30
10	3.286	25.80	25.80	36.03
15	4.975	31.71	31.71	42.14
30	7.109	49.89	49.89	57.38
60	8.531	82.69	82.69	81.25
120	9.847	113.04	113.04	114.22
240	11.49	128.71	128.71	143.94
480	13.49	129.77	135.17	136.24
720	14.51	123.02	128.69	129.47
1440	14.93	104.14	107.65	107.11
2880	12.59	68.52	67.71	65.04
4320	10.30	36.40	29.92	22.81

Table-5.15

The effect of time on the percentage production of ClO_2 at various $NaClO_2$ concentrations

A = 0.02N $Na_2S_2O_8$; B = 0.1N $Na_2S_2O_8$; C = 0.2N $Na_2S_2O_8$; D = 0.4N $Na_2S_2O_8$

(A)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
5	4.766	4.542	4.222	0.922
10	5.922	5.411	4.678	1.363
15	7.111	6.227	5.191	2.00
30	10.59	7.633	6.055	2.871
60	17.41	9.871	7.561	4.091
120	25.22	12.48	9.833	6.122
240	34.22	16.33	12.11	8.111
480	43.00	21.34	15.52	9.951
720	48.51	23.43	17.17	11.05
1440	53.89	24.41	17.71	11.53
2880	45.22	19.42	14.11	9.111
4320	36.53	13.44	10.22	6.821

(B)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
5	6.321	6.118	5.994	5.182
10	8.722	8.123	7.692	6.811
15	11.33	10.11	9.134	8.255
30	16.00	15.76	13.48	12.51
60	27.00	26.59	21.73	20.29
120	38.62	40.33	34.20	31.41
240	47.81	49.97	45.54	39.84
480	57.11	55.88	51.45	42.36
720	58.25	57.31	52.97	43.75
1440	53.77	50.00	45.81	37.82
2880	42.11	35.72	32.00	26.11
4320	30.31	21.35	18.72	15.12

(C)

Time (min.)	0.0N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
5	9.886	9.126	8.651	7.332
10	12.89	12.22	12.07	9.566
15	16.22	15.41	14.50	11.75
30	24.22	24.11	23.88	18.49
60	35.71	36.37	35.31	30.65
120	49.44	49.74	47.11	41.89
240	58.33	57.88	53.48	47.70
480	59.61	58.88	55.61	48.10
720	58.44	57.42	53.11	45.61
1440	51.71	49.42	45.71	38.62
2880	38.66	34.11	30.44	25.41
4320	26.12	18.72	16.17	13.49

(D)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
5	13.33	12.68	12.20	11.23
10	16.11	14.94	15.13	13.35
15	18.62	18.41	17.53	15.62
30	25.51	26.34	24.47	21.26
60	38.22	39.13	34.37	30.11
120	50.33	55.14	46.82	42.33
240	60.22	59.88	55.87	53.35
480	59.51	59.33	53.42	50.53
720	57.00	56.33	50.66	47.99
1440	50.22	47.82	43.21	39.72
2880	34.91	31.52	28.15	24.11
4320	20.92	15.96	13.60	8.457

Table-5.16

The effect of time on the amount of ClO_2 at various $NaClO_2$ concentrations

A = 0.02N $Na_2S_2O_8$; B = 0.1N $Na_2S_2O_8$; C = 0.2N $Na_2S_2O_8$; D = 0.4N $Na_2S_2O_8$

(A)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
5	0.642	3.062	5.695	2.487
10	0.798	3.642	6.310	3.669
15	0.957	4.200	7.001	5.396
30	1.428	5.146	8.161	7.743
60	2.347	6.657	10.19	11.03
120	3.399	8.417	13.26	16.45
240	4.613	10.99	16.33	21.58
480	5.800	14.39	20.93	26.84
720	6.542	15.80	23.16	29.81
1440	7.269	16.46	23.89	31.11
2880	6.097	13.08	18.88	24.55
4320	4.928	9.038	13.79	18.40

(B)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
5	0.852	4.126	8.085	13.98
10	1.173	5.478	10.37	18.37
15	1.524	6.820	12.32	22.27
30	2.158	10.63	18.18	33.77
60	3.642	17.93	29.32	54.75
120	5.207	27.20	46.14	84.74
240	6.448	33.70	61.43	107.50
480	7.702	37.69	69.40	114.30
720	7.858	38.65	71.46	118.04
1440	7.254	33.72	61.78	101.98
2880	5.665	24.07	43.16	70.14
4320	4.089	14.40	25.25	40.80

(C)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
5	1.333	6.155	11.67	19.78
10	1.738	8.246	16.29	25.80
15	2.188	10.39	19.56	31.71
30	3.267	16.26	32.21	49.89
60	4.815	24.53	47.64	82.69
120	6.664	33.55	63.55	113.04
240	7.864	39.04	72.15	128.71
480	8.042	39.71	75.02	129.77
720	7.878	38.71	71.63	123.02
1440	6.974	33.32	61.64	104.18
2880	5.215	22.93	41.00	68.52
4320	3.523	12.62	21.81	36.40

(D)

Time(min)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
0	0	0	0	0
5	1.798	8.558	16.46	30.30
10	2.158	10.07	20.41	36.03
15	2.509	12.41	23.64	42.14
30	3.439	17.77	33.01	57.38
60	5.153	26.39	46.37	81.25
120	6.785	37.19	63.16	114.22
240	8.123	40.38	75.37	143.94
480	8.026	39.99	72.06	136.24
720	7.689	37.97	68.34	129.47
1440	6.774	32.24	58.29	107.16
2880	4.708	21.24	37.97	65.04
4320	2.819	10.76	18.34	22.81

Table-5.17

The effect of $NaClO_2$ concentration on the percentage production of ClO_2

A = 0.05N $(CH_3CO)_2O$; B = 0.1N $(CH_3CO)_2O$; C = 0.2 N $(CH_3CO)_2O$; D = 0.4N$(CH_3CO)_2O$

(A)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	70.45	67.33	55.22	40.22
0.05	65.82	62.71	50.52	35.62
0.1	60.33	57.01	44.61	30.44
0.2	50.22	47.22	35.00	21.22

(B)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	77.22	65	49.444	30.6
0.05	76.18	63.03	47.36	28.449
0.1	74.37	60.8	45.07	25.77
0.2	71.33	56.7	40.8	21.11

(C)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	71.42	68	54.5	38
0.05	70.55	66.93	52.32	34.63
0.1	69.56	65.67	49.84	30.58
0.2	67.885	63.666	45.4	23.5

(D)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	72.22	66.66	54.50	39.51
0.05	71.42	65.94	52.92	37.02
0.097	70.56	65.13	51.04	34.33
0.2	68.89	63.71	47.66	29.33

Table-5.18

The effect of sodium chlorite concentration on the amount of ClO_2

A = 0.05N $(CH_3CO)_2O$; B = 0.1N $(CH_3CO)_2O$; C = 0.2 N $(CH_3CO)_2O$; D = 0.4N$(CH_3CO)_2O$

(A)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	9.503	9.078	7.449	5.425
0.05	44.38	42.29	34.06	24.01
0.1	81.34	76.89	60.16	41.00
0.2	135.49	127.34	94.43	57.19

(B)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	10.50	8.768	6.669	4.127
0.05	51.38	42.51	31.94	19.18
0.1	100.32	82.01	60.79	34.76
0.2	192.44	152.97	110.07	56.95

(C)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	9.634	9.173	7.352	5.126
0.05	47.58	45.14	35.28	23.35
0.1	93.83	88.58	67.23	41.25
0.2	183.15	171.77	122.48	63.40

(D)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	9.742	8.992	7.352	5.328
0.05	48.15	44.47	35.68	24.95
0.1	95.18	87.86	68.85	46.27
0.2	185.86	171.86	128.58	79.05

Table-5.19

The effect of $(CH_3CO)_2O$ concentration on the percentage production of ClO_2

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	68.71	65.91	54.22	40.66
0.05	72.22	69.44	57.81	45.11
0.1	77.22	75.31	63.65	52.31
0.2	76.11	73.41	62.07	50.37
0.4	72.4	69.55	58.88	46.67

(B)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	60.26	57.27	45.54	31.33
0.05	65.22	62.11	49.54	34.46
0.1	74.75	71.38	57.11	40.24
0.2	68.91	66.22	52.22	36.63
0.4	58.02	55.71	43.82	29.41

(C)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	55.73	53.55	46.31	37.14
0.05	62.62	60.33	51.31	41.44
0.1	73.98	71.54	60.54	49.13
0.2	71.53	68.91	59.11	47.47
0.4	67.32	64.32	56.66	44.55

(D)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	50.51	48.23	39.43	29.22
0.05	58.11	54.72	45.91	34.51
0.1	71.22	68.54	57.42	43.33
0.2	67.77	65.14	54.29	40.44
0.4	61.81	59.41	48.81	35.55

Table-5.20

The effect of sodium per sulfate concentration on the amount of ClO_2

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	9.267	8.889	7.311	5.485
0.05	9.712	9.362	7.797	6.070
0.1	10.50	10.16	8.586	7.056
0.2	10.25	9.901	8.373	6.794
0.4	9.766	9.382	7.943	6.295

(B)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	40.64	38.62	30.71	21.13
0.05	43.97	41.88	33.41	23.24
0.1	50.42	48.14	38.44	27.14
0.2	46.47	44.51	35.22	24.68
0.4	39.12	37.56	29.54	19.83

(C)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	75.17	72.24	62.45	50.10
0.05	84.44	81.34	69.20	55.90
0.1	99.81	96.51	81.67	66.28
0.2	96.49	92.95	79.73	64.03
0.4	90.82	86.76	76.44	60.10

(D)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	136.27	130.12	106.38	78.78
0.05	156.48	147.58	123.83	93.08
0.1	191.55	184.81	154.86	116.82
0.2	182.84	175.74	146.47	108.92
0.4	166.73	160.26	131.66	95.92

Table-5.21

The effect of time on the percentage production of ClO_2 at various $(CH_3CO)_2O$ concentrations
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Time (min.)	0.025N $(CH_3CO)_2O$	0.05N $(CH_3CO)_2O$	0.1N $(CH_3CO)_2O$	0.2N $(CH_3CO)_2O$	0.4N $(CH_3CO)_2O$
2	60.24	66.22	78.11	70.66	63.44
5	59.41	65.11	77.22	69.44	62.22
15	56.41	62.11	73.83	66.33	59.45
30	52.22	57.71	68.91	61.81	55.22
60	43.71	49.54	59.44	53.01	46.55
120	27.33	33.51	42.24	37.21	29.77

(B)

Time (min.)	0.025N $(CH_3CO)_2O$	0.05N $(CH_3CO)_2O$	0.1N $(CH_3CO)_2O$	0.2N $(CH_3CO)_2O$	0.4N $(CH_3CO)_2O$
0	0	0	0	0	0
2	61.24	65.22	75.92	68.66	63.22
5	60.26	64.23	74.75	67.77	61.88
15	57.27	61.43	71.38	65.22	59.11
30	53.33	57.44	66.41	61.11	55.12
60	45.54	49.54	57.03	52.88	47.63
120	31.33	35.33	40.24	37.81	33.33

(C)

Time (min.)	0.025N $(CH_3CO)_2O$	0.05N $(CH_3CO)_2O$	0.1N $(CH_3CO)_2O$	0.2N $(CH_3CO)_2O$	0.4N $(CH_3CO)_2O$
0	0	0	0	0	0
2	56.46	63.33	74.44	72.22	68.11
5	55.73	62.61	73.78	71.53	67.32
15	53.88	60.41	71.54	69.33	65.22
30	51.33	57.41	68.42	65.91	62.00
60	46.22	51.82	61.72	59.22	55.82
120	37.14	41.44	49.13	47.47	44.55

(D)

Time (min.)	0.025N $(CH_3CO)_2O$	0.05N $(CH_3CO)_2O$	0.1N $(CH_3CO)_2O$	0.2N $(CH_3CO)_2O$	0.4N $(CH_3CO)_2O$
0	0	0	0	0	0
2	51.23	60.07	71.76	68.37	62.48
5	50.51	59.22	71.11	67.63	61.82
15	48.54	56.72	68.52	65.14	59.43
30	45.33	53.11	64.72	61.33	55.71
60	39.43	45.91	57.41	54.21	48.81
120	29.22	32.44	43.33	40.13	35.55

Table-5.22
The effect of time on the amount of ClO_2 at various $CH_3CO)_2O$ concentrations
A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Time (min.)	0.025N $(CH_3CO)_2O$	0.05N $(CH_3CO)_2O$	0.1N $(CH_3CO)_2O$	0.2N $(CH_3CO)_2O$	0.4N $(CH_3CO)_2O$
0	0	0	0	0	0
2	8.126	8.933	10.53	9.532	8.558
5	8.013	8.781	10.41	9.367	8.394
15	7.608	8.377	9.955	8.943	8.020
30	7.041	7.783	9.294	8.336	7.449
60	5.895	6.683	8.013	7.149	6.279
120	3.687	4.519	5.698	5.020	4.016

(B)

Time (min.)	0.025N $(CH_3CO)_2O$	0.05N $(CH_3CO)_2O$	0.1N $(CH_3CO)_2O$	0.2N $(CH_3CO)_2O$	0.4N $(CH_3CO)_2O$
0	0	0	0	0	0
2	41.30	43.99	51.20	46.31	42.64
5	40.64	43.32	50.42	45.71	41.73
15	38.62	41.43	48.14	43.99	39.79
30	35.95	38.74	44.78	41.21	37.16
60	30.71	33.41	38.44	35.66	32.10
120	21.13	23.83	27.14	25.50	22.48

(C)

Time (min.)	0.025N $(CH_3CO)_2O$	0.05N $(CH_3CO)_2O$	0.1N $(CH_3CO)_2O$	0.2N $(CH_3CO)_2O$	0.4N $(CH_3CO)_2O$
0	0	0	0	0	0
2	76.17	85.43	100.41	97.42	91.88
5	75.17	84.44	99.54	96.49	90.82
15	72.68	81.47	96.51	93.48	87.95
30	69.20	77.43	92.27	88.89	83.63
60	62.32	69.87	83.23	79.88	75.27
120	50.10	55.90	66.28	64.03	60.10

(D)

Time (min.)	0.025N $(CH_3CO)_2O$	0.05N $(CH_3CO)_2O$	0.1N $(CH_3CO)_2O$	0.2N $(CH_3CO)_2O$	0.4N $(CH_3CO)_2O$
0	0	0	0	0	0
2	138.21	162.08	193.60	184.46	168.59
5	136.27	159.79	191.55	182.46	166.73
15	130.97	152.97	184.81	175.74	160.26
30	122.30	142.99	174.56	165.38	150.27
60	106.38	123.83	154.86	146.26	131.66
120	78.78	87.53	116.82	108.29	95.92

Table-5.23

The effect of time on the percentage production of ClO_2 at various $NaClO_2$ concentrations
A = 0.025 N $(CH_3CO)_2O$; B = 0.05N $(CH_3CO)_2O$; C = 0.1N $(CH_3CO)_2O$;
D = 0.2 N $(CH_3CO)_2O$; E = 0.4N$(CH_3CO)_2O$

(A)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	69.66	61.24	52.33	41.23
5	68.44	60.26	51.51	40.53
15	65.51	57.27	49.22	38.22
30	61.11	53.11	45.53	35.22
60	52.44	45.33	38.81	29.33
120	36.66	31.14	25.33	17.82

(B)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	71.56	67.55	60.11	51.21
5	70.45	66.66	59.02	50.22
15	67.33	63.66	55.76	47.22
30	63.01	59.43	51.33	42.91
60	55.22	50.81	43.41	35.01
120	40.22	35.33	28.44	21.21

(C)

Time	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	78.22	76.33	74.45	70.88
5	77.11	75.22	73.22	69.66
15	73.61	71.63	69.22	66.33
30	68.91	66.81	63.71	60.82
60	60.11	57.70	53.71	50.22
120	43.53	40.22	35.77	31.11

(D)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	70.51	68.66	67.44	60.11
5	69.55	67.66	66.34	59.11
15	66.33	64.11	62.75	55.74
30	62.00	59.11	57.66	50.83
60	53.33	50.22	48.22	41.33
120	38.11	33.11	30.22	23.51

(E)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	70.75	69.11	67.44	66.18
5	69.76	68.11	66.35	65.11
15	66.76	65.11	63.13	61.55
30	62.61	61.22	58.46	56.61
60	54.52	52.71	50.33	48.01
120	39.54	37.33	34.77	30.88

Table-5.24

The effect of time on the amount of ClO_2 at various $NaClO_2$ concentrations

A = 0.025 N $(CH_3CO)_2O$; B = 0.05N $(CH_3CO)_2O$; C = 0.1N $(CH_3CO)_2O$;
D = 0.2 N $(CH_3CO)_2O$; E = 0.4N$(CH_3CO)_2O$

(A)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	9.397	41.30	70.59	111.23
5	9.233	40.64	69.47	109.34
15	8.835	38.62	66.37	103.13
30	8.228	35.81	61.37	94.96
60	7.068	30.55	52.34	79.05
120	4.946	21.00	34.17	48.02

(B)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	9.653	45.56	81.09	138.17
5	9.503	44.96	79.61	135.49
15	9.078	42.94	75.22	127.34
30	8.498	40.08	69.20	115.72
60	7.449	34.26	58.54	94.43
120	5.425	23.83	38.37	57.19

(C)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	10.58	51.48	100.43	191.23
5	10.40	50.72	98.74	187.78
15	9.928	48.29	93.35	178.87
30	9.294	45.05	85.93	164.03
60	8.094	38.91	72.44	135.43
120	5.868	27.12	48.25	83.93

(D)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	9.510	46.31	90.97	162.17
5	9.382	45.64	89.49	159.48
15	8.947	43.16	84.64	150.27
30	8.363	39.86	77.79	137.05
60	7.190	33.85	65.02	111.424
120	5.126	22.32	40.73	63.40

(E)

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	9.544	46.61	90.97	178.55
5	9.410	45.93	89.51	175.66
15	9.006	43.90	85.16	166.07
30	8.444	41.14	78.87	152.70
60	7.352	35.54	67.90	129.50
120	5.328	24.95	46.91	83.33

Table-5.25

The effect of sodium chlorite concentrations on the percentage production of ClO_2 at a definite concentration of $(CH_3CO)_2O$ and H_2SO_4 mixture

A = 0.025 N $(CH_3CO)_2O$; B = 0.05N $(CH_3CO)_2O$; C = 0.1N $(CH_3CO)_2O$;
D = 0.2 N $(CH_3CO)_2O$; E = 0.4N$(CH_3CO)_2O$

(A)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	79.66	77.44	68.81	58.11
0.05	77.71	75.42	66.95	56.62
0.1	75.33	73.11	64.62	54.72
0.2	70.61	68.66	60.81	51.22

(B)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	86.00	83.65	75.01	64.33
0.05	84.44	81.44	73.22	62.88
0.1	82.22	79.22	71.11	61.00
0.2	78.11	75.11	67.62	57.44

(C)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	89.56	86.33	78.21	67.21
0.05	87.31	84.06	76.16	65.55
0.1	84.86	81.44	73.91	63.31
0.2	80.32	77.31	69.91	59.51

(D)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	88.11	85.82	77.33	66.66
0.05	85.61	83.33	74.91	64.42
0.1	82.91	80.44	72.22	61.72
0.2	77.43	75.11	66.98	57.13

(E)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	84.66	82.62	74.52	64.91
0.05	82.87	80.71	72.63	62.77
0.1	80.55	78.61	70.28	60.00
0.2	76.88	74.77	65.88	55.33

Table-5.26

The effect of sodium chlorite concentrations on the amount of ClO_2 at a definite concentration of $(CH_3CO)_2O$ and H_2SO_4 mixture

A = 0.025 N $(CH_3CO)_2O$; B = 0.05N $(CH_3CO)_2O$; C = 0.1N $(CH_3CO)_2O$;
D = 0.2 N $(CH_3CO)_2O$; E = 0.4N$(CH_3CO)_2O$

(A)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	10.74	10.44	9.281	7.839
0.05	52.40	50.85	45.15	38.17
0.1	101.57	98.61	87.14	73.81
0.2	190.47	185.24	164.03	138.13

(B)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	11.60	11.28	10.11	8.674
0.05	56.95	54.93	49.38	42.41
0.1	110.91	106.86	95.92	82.28
0.2	210.71	202.61	182.38	154.98

(C)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	12.08	11.64	10.54	9.067
0.05	58.89	56.69	51.36	44.21
0.1	114.47	109.86	99.70	85.40
0.2	216.70	208.55	188.59	160.53

(D)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	11.87	11.57	10.42	8.992
0.05	57.73	56.18	50.52	43.45
0.1	111.83	108.45	97.12	83.26
0.2	208.90	202.35	180.71	154.15

(E)

Conc. of $NaClO_2$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	11.42	11.14	10.05	7.459
0.05	55.89	54.43	48.98	42.33
0.1	108.62	106.04	94.80	80.94
0.2	207.42	201.72	177.75	149.19

Table-5.27

The effect of acetic anhydride concentrations on the percentage production of ClO_2 at definite concentration of $NaClO_2$ and H_2SO_4

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	79.66	77.62	68.81	58.11
0.05	83.64	81.11	72.41	61.11
0.1	89.56	87.33	78.22	67.21
0.2	88.11	85.82	77.33	66.66
0.4	85.11	82.62	74.52	64.91

(B)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	77.71	75.33	66.62	55.73
0.05	81.22	78.66	69.62	58.82
0.1	86.71	84.44	74.51	63.36
0.2	86.71	84.22	74.51	63.11
0.4	85.02	82.91	72.77	61.22

(C)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	75.31	73.11	64.33	53.21
0.05	78.33	76.11	67.51	56.51
0.1	82.71	80.82	72.33	61.43
0.2	82.22	80.33	72.22	60.51
0.4	80.55	79.01	71.11	58.91

(D)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	70.62	68.82	60.82	51.22
0.05	74.44	72.66	64.11	54.44
0.1	80.32	78.33	69.91	59.51
0.2	79.11	76.82	69.11	58.22
0.4	76.88	74.41	66.33	55.72

Table-5.28

The effect of acetic anhydride concentrations on the amount of ClO_2 at definite concentration of $NaClO_2$ and H_2SO_4

A = 0.01N $NaClO_2$; B = 0.05N $NaClO_2$; C = 0.1N $NaClO_2$; D = 0.2N $NaClO_2$

(A)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	10.74	10.46	9.281	7.839
0.05	11.28	10.94	9.766	8.242
0.1	12.08	11.77	10.54	9.067
0.2	11.87	11.57	10.42	8.992
0.4	11.47	11.14	10.05	8.755

(B)

Conc. of $(CH_3CO)_2O$(N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	52.40	50.78	44.92	37.58
0.05	54.78	53.05	46.94	39.66
0.1	58.47	56.92	50.25	42.73
0.2	58.47	56.79	50.25	42.49
0.4	57.33	55.91	49.08	41.27

(C)

Conc. of $(CH_3CO)_2O$(N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	101.57	98.61	86.74	71.78
0.05	105.66	102.67	91.05	76.21
0.1	111.56	108.99	97.53	82.82
0.2	110.61	108.32	97.39	81.61
0.4	108.66	106.57	95.91	79.45

(D)

Conc. of $(CH_3CO)_2O$ (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.025	190.47	185.62	164.03	138.13
0.05	200.84	196.05	172.96	146.87
0.1	216.70	211.25	188.59	160.53
0.2	213.41	207.20	186.16	157.02
0.4	207.42	200.73	178.87	150.27

Table-5.29

The effect of H_2SO_4 concentrations on the percentage production of ClO_2 at definite concentration of $NaClO_2$ and $(CH_3CO)_2O$

0.1N $(CH_3CO)_2O$ + 0.01N $NaClO_2$

Conc. of H_2SO_4 (N)	5 (min.)	15 (min.)	60 (min.)	120 (min.)
0.01	84.41	82.11	73.71	62.21
0.02	89.56	87.33	78.22	67.21
0.1	86.34	83.88	75.88	65.87
0.2	82.61	79.97	73.23	64.21

Table-5.30

The effect of time on the percentage production of ClO_2 at various concentrations of $NaClO_2$ and a definite concentration of $(CH_3CO)_2O$ and H_2SO_4

0.1N $(CH_3CO)_2O$ + 0.02N H_2SO_4

Time (min.)	0.01N $NaClO_2$	0.05N $NaClO_2$	0.1N $NaClO_2$	0.2N $NaClO_2$
2	90.77	86.33	83.28	80.76
5	89.66	85.43	82.72	80.32
15	87.33	83.51	80.81	78.33
30	84.22	80.43	77.88	75.33
60	78.22	74.51	72.33	69.91
120	67.21	63.36	61.43	59.51

Table-5.31

The relation between different chlorine species (m.mol.) and time (min.) at 0.01N $NaClO_2$

A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and C = 0.2N H_2SO_4

(A)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	0.2	0	0	0
15	0.174366	0.021349	0.001366	0.001408
30	0.147681	0.043291	0.003379	0.003693
60	0.111342	0.071609	0.005512	0.008451
120	0.082135	0.084804	0.008388	0.014085
240	0.057715	0.101112	0.011384	0.019944
480	0.036737	0.115196	0.01402	0.023662
1440	0.014861	0.127666	0.018574	0.03662
2880	0.010082	0.088065	0.024086	0.072394
4320	0.009708	0.049414	0.027921	0.103099

(B)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	0.2	0	0	0
15	0.164715	0.029652	0.001449	0.001521
30	0.151386	0.040474	0.002898	0.003239
60	0.126761	0.059303	0.004311	0.006085
120	0.097109	0.080652	0.007425	0.009296
240	0.060934	0.106746	0.00982	0.014366
480	0.029503	0.130467	0.012335	0.019718
1440	0.016457	0.106746	0.016886	0.050056
2880	0.009785	0.066716	0.021796	0.093718
4320	0.004744	0.029652	0.026347	0.134366

(C)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	0.2	0	0	0
15	0.150778	0.043143	0.002683	0.002817
30	0.126019	0.062268	0.00503	0.00462
60	0.090586	0.088213	0.007784	0.007803
120	0.054262	0.113121	0.010539	0.012958
240	0.031134	0.128391	0.013293	0.0251
480	0.021349	0.120237	0.01685	0.04507
1440	0.010896	0.093551	0.02109	0.07493
2880	0.006393	0.053521	0.027425	0.1134
4320	0.000789	0.016753	0.029102	0.153239

Table-5.32

The relation between different chlorine species (m.mol.) and time (min.) at 0.05N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and C = 0.2N H_2SO_4

(A)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	1	0	0	0
15	0.907635	0.07576	0.006679	0.006172
30	0.815419	0.15315	0.010646	0.010873
60	0.720534	0.225352	0.016054	0.016563
120	0.627131	0.293551	0.026263	0.024789
240	0.524833	0.369162	0.038888	0.037746
480	0.454574	0.431431	0.05229	0.061972
1440	0.337583	0.47278	0.073174	0.115775
2880	0.240178	0.323202	0.104477	0.331577
4320	0.15152	0.151223	0.125749	0.566507

(B)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	1	0	0	0
15	0.76608	0.197677	0.014141	0.012148
30	0.622683	0.314307	0.025269	0.024817
60	0.377168	0.48052	0.044431	0.046761
120	0.205515	0.60275	0.064144	0.068845
240	0.060934	0.701918	0.088982	0.087606
480	0.016457	0.742937	0.097126	0.112676
1440	0.010695	0.59748	0.121078	0.275324
2880	0.001692	0.372128	0.139665	0.481972
4320	0.000381	0.154781	0.146347	0.710423

(C)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	1	0	0	0
15	0.7061	0.256961	0.0187	0.014625
30	0.542758	0.3904	0.0317	0.025
60	0.370645	0.5222	0.046467	0.041408
120	0.243752	0.622683	0.062515	0.06
240	0.116474	0.705708	0.077126	0.078873
480	0.013062	0.7644	0.094371	0.126761
1440	0.006394	0.615271	0.110419	0.259718
2880	0.0017	0.391401	0.121078	0.484507
4320	0.001	0.168003	0.148503	0.719718

Table-5.33

The relation between different chlorine species (m.mol.) and time (min.) at 0.1N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and C = 0.2N H_2SO_4

(A)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	2	0	0	0
15	1.925574	0.060934	0.005269	0.005634
30	1.776488	0.180875	0.015928	0.02169
60	1.63812	0.263558	0.035928	0.040563
120	1.474037	0.364715	0.061198	0.068732
240	1.21275	0.464047	0.104192	0.11831
480	0.948851	0.595997	0.152994	0.208451
1440	0.512973	0.637509	0.237126	0.552113
2880	0.247927	0.452187	0.292216	0.994366
4320	0.07576	0.2298	0.331737	1.376901

(B)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	2	0	0	0
15	1.696219	0.247262	0.022515	0.02169
30	1.431727	0.453011	0.046467	0.049859
60	1.166612	0.6553	0.073174	0.08169
120	0.831772	0.870274	0.110443	0.126479
240	0.493165	1.089696	0.155689	0.168569
480	0.247976	1.30467	0.19521	0.212958
960	0.027872	1.475167	0.238323	0.259718
1440	0.018814	1.325426	0.263473	0.419155
2880	0.013973	0.824314	0.288623	0.909859
4320	0.006514	0.31793	0.294611	1.376408

(C)

Time (min.)	ClO_2^- (m.mol.)	ClO_2 (m.mol.)	ClO_3^- (m.mol.)	Cl^- (m.mol.)
0	2	0	0	0
15	1.425457	0.51066	0.032359	0.024789
30	1.058033	0.782461	0.058443	0.040625
60	0.665678	1.111935	0.087784	0.069448
120	0.398814	1.334322	0.121475	0.120682
240	0.194218	1.48851	0.148503	0.161466
480	0.048925	1.548466	0.182275	0.200282
1440	0.007623	1.263158	0.20491	0.526761
2880	0.004	0.784285	0.231138	1.008451
4320	0.001457	0.304744	0.256287	1.467887

Table-5.34

The relation of concentrations of ClO_2 and Cl^- (m.mol.) with time (min.) at 0.01N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and C = 0.2N H_2SO_4

(A)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0	0		0	
15	0.021349	0.021349	0.001408	0.001408
30	0.043291	0.043574	0.003693	0.002875
60	0.071609	0.073839	0.008451	0.004871
120	0.084804	0.098164	0.014085	0.006476
240	0.101112	0.118502	0.019944	0.007818
480	0.115196	0.135974	0.0252	0.008971
1440	0.127666	0.154193	0.03662	0.010172
2880	0.0936	0.158174	0.072394	0.010435
4320	0.0554	0.158485	0.1087	0.010456

(B)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0	0	0	0	0
15	0.029652	0.029652	0.001521	0.001521
30	0.040474	0.040852	0.003239	0.002096
60	0.059303	0.061546	0.006085	0.003157
120	0.080652	0.086463	0.009296	0.004436
240	0.106746	0.116862	0.014366	0.005995
480	0.130467	0.143275	0.019718	0.00735
1440	0.1098	0.154238	0.050056	0.007912
2880	0.0772	0.159845	0.091718	0.0082
4320	0.0411	0.16408	0.134366	0.008417

(C)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0	0	0	0	0
15	0.043143	0.043143	0.002817	0.002817
30	0.062268	0.064845	0.00462	0.004234
60	0.088213	0.095902	0.007803	0.006262
120	0.113121	0.12774	0.012958	0.00834
240	0.128391	0.148012	0.0251	0.009664
480	0.1229	0.156589	0.04507	0.010224
1440	0.0987	0.165751	0.07493	0.010822
2880	0.064	0.169698	0.1134	0.01108
4320	0.0294	0.17461	0.153239	0.011401

Table-5.35

The relation of concentrations of ClO_2 and Cl^- (m.mol.) with time (min.) at 0.05N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and C = 0.2N H_2SO_4

(A)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0	0	0	0	0
15	0.07576	0.07576	0.006172	0.006172
30	0.15315	0.151398	0.010873	0.012334
60	0.225352	0.229225	0.016563	0.018674
120	0.293551	0.305836	0.024789	0.024915
240	0.369162	0.389744	0.037746	0.031751
480	0.431431	0.447372	0.061972	0.036446
1440	0.47278	0.54333	0.115775	0.044263
2880	0.323202	0.623225	0.331577	0.050771
4320	0.151223	0.695945	0.566507	0.056696

(B)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0	0		0	
15	0.197677	0.197677	0.012148	0.012148
30	0.314307	0.318856	0.024817	0.019595
60	0.48052	0.526331	0.046761	0.032345
120	0.60275	0.671389	0.068845	0.041259
240	0.701918	0.779126	0.093803	0.04788
480	0.742937	0.82231	0.12507	0.050534
1440	0.59748	0.836024	0.275324	0.051376
2880	0.372128	0.843632	0.492958	0.051844
4320	0.158043	0.84474	0.726315	0.051912

(C)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0	0	0	0	0
15	0.256961	0.256961	0.014625	0.014625
30	0.3904	0.399773	0.025	0.022752
60	0.5222	0.550254	0.041408	0.031317
120	0.622683	0.661197	0.06	0.037631
240	0.705708	0.772478	0.078873	0.043964
480	0.7644	0.862894	0.126761	0.04911
1440	0.615271	0.868723	0.259718	0.049442
2880	0.391401	0.872827	0.484507	0.049676
4320	0.168003	0.873439	0.719718	0.04971

Table-5.36

The relation of concentrations of ClO_2 and Cl^- (m.mol.) with time (min.) at 0.1N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and C = 0.2N H_2SO_4

(A)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0	0		0	
15	0.060934	0.060934	0.005634	0.005634
30	0.180875	0.182995	0.02169	0.016919
60	0.263558	0.29628	0.040563	0.027393
120	0.364715	0.430619	0.068732	0.039814
240	0.464047	0.644541	0.11831	0.059593
480	0.595997	0.860602	0.208451	0.079569
1440	0.677509	1.217467	0.552113	0.112564
2880	0.472187	1.434466	0.994366	0.132627
4320	0.2298	1.575424	1.376901	0.14566

(B)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0	0	0	0	0
15	0.247262	0.247262	0.02169	0.02169
30	0.453011	0.462545	0.049859	0.040575
60	0.6553	0.678334	0.08169	0.059504
120	0.870274	0.950877	0.126479	0.083412
240	1.089696	1.226485	0.168569	0.107589
480	1.30467	1.426057	0.212958	0.125096
960	1.475167	1.60521	0.259718	0.140811
1440	1.325426	1.612583	0.419155	0.141458
2880	0.824314	1.616523	0.909859	0.141804
4320	0.31793	1.622594	1.376408	0.142336

(C)

Time (min.)	Exp. ClO_2 (m.mol.)	Proj. ClO_2 (m.mol.)	Exp. Cl^- (m.mol.)	Proj. Cl^- (m.mol.)
0				
15	0.51066	0.51066	0.024789	0.024789
30	0.782461	0.837231	0.040625	0.040641
60	1.111935	1.18596	0.069448	0.05757
120	1.334322	1.423152	0.120682	0.069083
240	1.48851	1.604999	0.161466	0.077911
480	1.548466	1.734137	0.200282	0.084179
1440	1.263158	1.770846	0.526761	0.085961
2880	0.784285	1.774067	1.008451	0.086118
4320	0.304744	1.776326	1.467887	0.086227

Table-5.37

Determination of reaction rate and order on the preparation of ClO_2 from 0.01N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and
C = 0.2N H_2SO_4

(A)

Time(min.)	log(a-x)
0	-0.69897
10	-0.72484
15	-0.73802
30	-0.77475
60	-0.86143

(B)

Time(min.)	log(a-x)
0	-0.69897
10	-0.72586
15	-0.74014
30	-0.78327
60	-0.88598

(C)

Time (min.)	log(a-x)
0	-0.69897
10	-0.73364
15	-0.7498
30	-0.80738
60	-0.92589

Table-5.38

Determination of reaction rate and order on the preparation of ClO_2 from 0.01N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and
C = 0.2N H_2SO_4

(A)

(a-x) (m.mol.)	dx/dt
0.2	0.00054
0.188436	0.000509
0.182802	0.000494
0.167976	0.000454
0.137583	0.000371

(B)

(a-x) (m.mol.)	dx/dt
0.2	0.00062
0.187991	0.000583
0.181913	0.000564
0.164715	0.000511
0.130022	0.000403

(C)

(a-x) (m.mol.)	dx/dt
0.2	0.00076
0.184655	0.000702
0.17791	0.000676
0.155819	0.000592
0.118606	0.000451

Table-5.39

Determination of reaction rate and order on the preparation of ClO_2 from 0.05N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and
C = 0.2N H_2SO_4

(A)

Time (min.)	log(a-x)
0	0
10	-0.02131
15	-0.03282
30	-0.06705
60	-0.13702

(B)

Time(min.)	log(a-x)
0	0
10	-0.03582
15	-0.0549
30	-0.11298
60	-0.23926

(C)

Time (min.)	log(a-x)
0	0
10	-0.03898
15	-0.05901
30	-0.12337
60	-0.26219

Table-5.40

Determination of reaction rate and order on the preparation of ClO_2 from 0.05N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and
C = 0.2N H_2SO_4

(A)

(a-x) (m.mol.)	dx/dt
1	0.0023
0.952113	0.00219
0.927205	0.002133
0.856931	0.001971
0.729429	0.001678

(B)

(a-x) (m.mol.)	dx/dt
1	0.004
0.92083	0.003683
0.881245	0.003525
0.770941	0.003084
0.576427	0.002306

(C)

(a-x) (m.mol.)	dx/dt
1	0.0044
0.914159	0.004022
0.872943	0.003841
0.752706	0.003312
0.546775	0.002406

Table-5.41

Determination of reaction rate and order on the preparation of ClO_2 from 0.1N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and
C = 0.2N H_2SO_4

(A)

Time (min.)	log(a-x)
0	0.30103
10	0.290274
15	0.284961
20	0.279346
30	0.268692
60	0.235043

(B)

Time(min.)	log(a-x)
0	0.30103
10	0.277447
15	0.264035
30	0.226014
60	0.144608

(C)

Time (min.)	log(a-x)
0	0.30103
10	0.229401
15	0.188969
30	0.055813
60	-0.23792

Table-5.42

Determination of reaction rate and order on the preparation of ClO_2 from 0.1N $NaClO_2$
A = 0.02N H_2SO_4; B = 0.1N H_2SO_4 and
C = 0.2N H_2SO_4

(A)

(a-x) (m.mol.)	dx/dt
2	0.0022
1.951075	0.002146
1.927354	0.00212
1.902595	0.002093
1.856486	0.002042
1.718079	0.00189

(B)

(a-x) (m.mol.)	dx/dt
2	0.0052
1.894292	0.004925
1.836685	0.004775
1.682728	0.004375
1.395107	0.003627
0.831772	0.002163

(C)

(a-x) (m.mol.)	dx/dt
2	0.0182
1.695902	0.015433
1.545145	0.014061
1.137139	0.010348
0.578206	0.005262