KINETIC STUDY OF ADSORPTION OF SOME CATIONS ON MANGANESE (IV) OXIDE

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ENGINEERING

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CERTIFICATION

This is to certify that this project titled Kinetic Study of adsorption of some cations (Zn^{2+} and Pb^{2+}) on manganese (iv) oxide was carried out by MUHAMMAD RABIU LAWAL of the department of Chemical Engineering, Federal University of Technology Minna under the supervision of Dr. Duncan F. Aloko.

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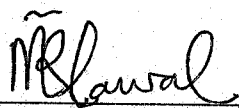Head of Department   Date

_____   _____
External Examiner   Date

DECLARATION

I here by declared that this work titled KINETIC STUDY OF ADSORPTION OF CATIONS (Zn^{2+} and Pb^{2+}) ON MANGANESE (IV) OXIDE is authentic and has not been presented elsewhere for the award of any degree or it equivalent.

MRLawal 20/10/03

MUHAMMAD RABIU LAWAL

97/ 6068 EH

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DEDICATION

I dedicate this work to the memories of my late father, in person of ALHAJI MUHAMMAD LAWAL MURSHID, for been a special father.

ACKNOWLEDGEMENT

My profound gratitude to Almighty Allah (S.W.) for the good health and opportunity given to me to study in this institution and finally graduating. God I thank you for all you have done to me right from birth to date.

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Rabiat you are wonderful and brought the best out me, thank you God bless you and promise you remain evergreen in my heart.

Lastly to my class mates, you guys are wonderful and the memories lingers on.

ABSTRACT

The kinetic study of adsorption of Zinc and Lead cations on manganese (iv) oxide was performed using the graphical and differential method of analyzing a rate-equation.

At a higher concentration of about $0.023mol/dm^3$ and cation concentration of $1.0mol/dm^3$ the rate of disappearance of manganese (iv) oxide is high with value of $5.750 \ mol/dm^3$ min but at same concentration of cations and lower concentration of the depolarizer the rate decreases rapidly.

The rate of disappearance of manganese iv oxide for both overall cell reaction without cations and with cations is derived to be $- r_A = 7.2464C_A^2$ and $-r_A = 10.869 \times 10^3 \ C_A^2 \ C_D$ with C_A and C_D as concentration of the depolarizer and cations respectively.

The order of overall cell reaction without the cation is second order and with the cations to be third order overall.

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CHAPTER ONE

1.0 INTRODUCTION

Dry cells are primary cells in which the electrolyte is absorbed in a porous medium or is otherwise restrained from flowing. Battery (cells) is the popularly known and are ingeniously engineered devices that operates through traditional electrochemical principles.

An electrochemical cell is a device designed to produce electrical energy as the primary output with the cell itself undergoing a chemical reaction. However, in an electrochemical cell some chemical reactions can be made to occur through ionic mechanism by passing electrical energy. The cell is classified into two forms namely, electrolytic and galvanic cell. This project work emphasised on the latter that is galvanic cell.

The galvanic cell can further be sub-divided into primary cells, secondary cells and fuel cells; area of study is centered around the primary cells also known as leclanche cells. The leclanche or dry cells consist of a positive electrode of finely divided carbon and manganese (IV) oxide (MnO_2) packed around carbon rod terminal which is placed in between the cell and the negative pole of Zinc (Zn) which makes up the case of the cell. The electrolyte consist of moist-mixture of Ammonium chloride (NH_4Cl), Manganese (IV) oxide (MnO_2), Zinc chloride ($ZnCl_2$) and a porous inert filter which occupied the space between the paper lined-zinc (Zn) container and the graphide rod.

Due to the property of the electrolytes or electrode used in the cell, for which they cannot be regenerated by reversing current flow through the cell, this has an adverse effect on the performance of the cell. Also as the chemicals in cell have been consumed further chemical action is impossible, this is due to the process of polarization which also gave the cell a least life span of about 300 minutes (five hours).

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The polarization effect is caused by the hydrogen gas evolved in the cell. The effect is corrected by the used of Manganese (IV) oxide (MnO_2). Experimental analysis revealed that the rate at which the depolariser (MnO_2) react with the hydrogen gas added to enhance or increase the rate at which the depolarization reaction occurs.

This project work is concerned with the Kinetic-study of adsorption of cations added to enhance the depolarization reactions by manganese (IV) oxide in dry cells. From the previous work the cations are added to the system and results are obtain. The cations used are Zn^{2+} and Pb^{2+} in their nitrate solution at different conditions.

1.1 SCOPE OF WORK

The data obtained from previous work on adsorption by potentiometric titration method were used for the purpose of the analysis of a cations in question, that is Zn^{2+} and Pb^{2+} to establish kinetic relationship between the various variable as a function of concentrations of depolariser and cations used.

1.2 AIMS AND OBJECTIVES

The main objective of this thesis is to undertake kinetic study of some selected cations notably Zn^{2+} and Pb^{2+} in their nitrate solutions ($Zn(No_3)_2$ and $Pb(No._3)_2$) in the presence of manganese (IV) oxide (MnO_2) in order to study the effectiveness of depolarization reaction.

1.3 APPROACH

The chemical reaction equation for reaction before adsorption and after adsorption will be derived and their various rate equations sorted out. The rate constant for reaction before and after adsorption are calculated and compared. And deduction from comparison made.

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The rate equation obtain are then used to ascertain the adsorption capacity or rate and also determine the extent of dependency of electrical charge in dry cell on specified variable(s) and suggest how to improve on the performance, this is achieved by comparing the results obtain in the potentiometric titration and the rate equation obtain through this research.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 HISTORICAL BACKGROUND

The first ever used cells are the wet cells made by Allessandro Volta in 1796, which consist of Zinc or tin and copper or silver, and was later modified by other scientist in various designs.

In 1836 John F. Daniel introduced another modification, in his design, he was able to avoid the occurrence or disadvantage of polarization and corrosion exhibited by the volta cells. The cell made by Daniel consist of Zinc electrode immersed in a zinc sulphate which is acidified by sulphuric acid and a copper electrode in a solution of copper sulphate. The cell voltage is in the range of 1.06 – 1.09 volts.

In the early 1800s, to be specific in 1811, Robert Bunsen and French chemist Georges leclanche in 1866 proposed some new primary cells. Leclanche used zinc negatives and manganese (IV) oxide as depolariser and carbon positives in ammonious sulphate solution, which is the widely used dry cell today. The cells are basically classified into two types, namely.

1. Primary cells

2. Secondary cells

In primary cells, chemical energy is converted to electrical energy and the process cannot be efficiently reversed. There are four types of primary cells, these include;

1. Wet primary cells

2. Dry primary cells

3. Reserve cells

4. Fuel cells

The Secondary cells involved inter-conversion of chemical energies which is achieved in repeated cycles.

The secondary cells are efficiently reversed as against the primary cells. The secondary cells include: lead acid batteries, Nickel-Iron batteries and Zinc-silver batteries with each of them for specific used.

2.2 CHEMICAL REACTION KINETICS

Chemical reactions are dynamic process in which matter and energy change continuously. A balanced equation is a convenient shorthand for the reaction and a qualitative tool for calculating product yield from reactant amounts. However the balanced equation tells or revealed nothing about three crucial aspects of the reaction which are,

1. How fast is the reaction proceeding at a given moment?
2. What will be the reactant and product concentrations be when it is completed?
3. Once the reaction begin, will it proceed by itself and release energy or will it required energy to continue?

These three crucial and important questions outline above need to be put into account in other to give a well explanatory picture of the reaction , which lead to the kinetic study of the chemical reaction.

Kinetic study deals with the speed or rate of a reaction and it's Mechanism, the step wise changes reactant undergo in their conversion to product. An understanding of Kinetic provide us with the means to answer the first question earlier stated, that is how fast a reaction proceed at a given moment.

Knowing how fast a chemical change will occur can be extremely important, how quickly a medicine acts or blood clots could make difference between life and death. In general, the rates of this diverse processes depends on some variables which can be manipulated to maximize rate of product release in a given time or slow down an

unwanted reactions. It is very important to begin with general overview of some factors affecting the reaction or Kinetic rate

Kinetic rate could be express qualitatively in the form of a rate law and how concentration and temperature affect the rate. It is noteworthy, that under a given condition, each reaction has it's own characteristic rate which is ultimately determined by the chemical nature of the reactants. For example, at room temperature Hydrogen reacts immediately with fluorine but extremely slow with nitrogen as shown below.

$$H_{2(g)} + F_{2(g)} \longrightarrow 2HF_{(g)} \quad \text{very fast}$$

$$3H_{2(g)} + N_{2(g)} \longrightarrow 2NH_{3(g)} \quad \text{very slow}$$
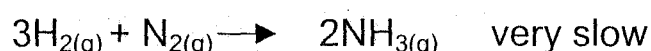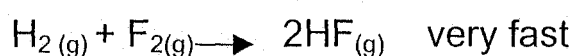
The reaction variation occurs in several situations and could be due to:

1. Bond in some compounds which breaks more quickly than those in others.

2. Some elements loose or gain elections more quickly than others and so on.

One key aspect of the diverse chemical behaviour of the elements is the variation is the rates of their reaction with another substance. For a given reaction, we can control three (3) factors that affect it's rate, namely:

1. The concentration of reactions

2. The physical state

3. The temperature at which the reaction occurs

Also worthy to mention is the use of catalyst for the reaction to proceed. Taking a look at the above stated factor give a clear state of the effect of the factors.

2.2.1 CONCENTRATION EFFECT ON RATE EQUATION

A major factor influencing the rte of a reaction is reactant concentration, this is mainly due to collision of the molecules which consequently lead them to react. For reaction to proceed, molecules must collide, therefore from this little explanation, we can say that temperature influence the reaction rate.

Taking an example of reaction between ozone and nitric oxide that occurs in stratosphere, when nitric oxide is released in the exhaust gases of aircraft, if the reactants are confined in a reaction vessels, the reactant are able to crashed into each other and the vessel walls. Usually the reaction will only proceed if the two molecules collide.

Generally, the more molecules that are present in a container or reaction vessels, the more frequent they collide and so, the more often a reaction occurs. Thus, reaction rate is proportional to the concentration of reactants:

Rate α Collision frequency α Concentration

In one step reactions and the complex reactions, the rate at all instances depends on the reactants concentration.

2.2.2 PHYSICAL STATE OF REACTION SPECIES ON RATE EQUATION

The rate or frequency of collisions between molecules also depends on the physical states of the reactants. When reactants are in same aqueous phase, occasionally stirring keeps them in contact, when they are in different phases, more vigorous mixing is needed. Also the degree to which the reactant material is divided can have a significant effect on rate: the more finely divided a solid or liquid reactant, the greater it's surface area per unit volume the more contact it makes with the other reactant, and the faster the reaction.

The mixing of molecules and collision and consequently the rate of reaction.

2.2.3 TEMPERATURE EFFECT ON RATE EQUATION

Temperature usually has a major influence on the speed of reaction. For instance molecules in a sample of gas have a range of speed, with the most probable speed dependant on the temperature. Thus, at higher temperature more collision occur in a given time. More important is the fact that the temperature affects the Kinetic energy of the molecules and the energy of collision. The molecules must collide with enough energy in other to react. If the molecules collide without enough energy, it result into the molecules recoiling with no reaction taking place. However, some collisions occur with such force that the molecule reacts. At higher temperature, more Collision occurs without enough energy to react. Thus, raising the temperature increase the reaction rate by increasing the number and especially the energy of the Collision.

The process of increasing or decreasing the temperature is usually employed in refrigerator and oven. In refrigerator the temperature is lowered in other to slow down chemical processes that spoil food, whereas the oven has high temperature to speed up some chemical processes.

2.3 EXPRESSION OF REACTION RATE

Before dealing qualitatively with the effects of concentration and temperature on reaction rate, we must be able to express the rate mathematically. Generally, reaction rate is define as rate of change of concentration of reactant per unit time.

The centerpiece of any Kinetic study is the rate law or rate equation, for many reactions, the rate is usually expressed as a function of reactant concentration, product concentration and temperature. Since rate law is based on experimental fact, any hypothesis to be made about how the reaction occurs on the Molecular level must confirm to it.

In our discussion, we will generally consider reactions for which the products are not involved in the rate law. In these cases, the reaction rate depends only on reactant concentration and temperature.

For general reaction:

aA + bB ………. cC = dD + ………….
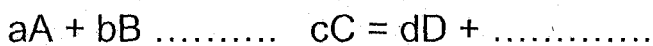
The rate law has the form

Rate = k $[A]^m [B]^n$ …………

The proportionality constant k, called rate constant is specific for a given reaction at a given temperature. The exponents m and n, called the reaction orders, define how the rate is affected by the concentration of each reactant. For example if the rate doubles when (A) doubles, the rate depends on (A), so m = 1; if the rate quadruples when (B) doubles, the rate depends on (B)2, so n=2, and so on.

In a chemical reaction, the position of a substance do not change over time as in motion of an object but their concentration do: reactant concentration decreases while product concentration increases considering a general reaction as shown below

A $\longrightarrow$ B

Measuring the staring reactant concentration as concentration of A_1 at time t_1, allow the reaction to proceed and then measure the reactant concentration again at time t_2 divided by the change in time gives the rate as

$$\text{Rate of reaction} = \frac{\text{change in concentration of A}}{\text{Change in time}}$$

$$= -\frac{\text{Conc } A_2 - \text{Conc } A_1}{t_2 - t_1}$$

$$= \frac{\Delta \text{ Conc A}}{\Delta t}$$

Note the introduction of minus sign. By convention, reaction rate is a positive number, but Conc A_2 will always be lower than conc A_1, so the change in concentration of A will be negative. The minus sign converts the negative change in reactant concentration to a positive value for the rate.

Square brackets is used to express concentration which is usually in moles per litre or any corresponding unit. Thus [A] is the concentration of A in mol/L so.

$$\text{Rate} = -\frac{\Delta [A]}{\Delta t}$$

At rate of reaction can also be determine for the product side of the reaction; in this case it's increase in concentration with respect to time is determine with rate is this case (product) carrying a positive sign.

Also worthy of mentioning are the average, instantaneous and initial reaction rates. For instance considering the reversible gas-phase reaction between ethylene and ozone, one of many possible reactions in the formation of photochemical smog, the reaction as follows

$$C_2H_{4(g)} + O_{3(g)} \rightleftharpoons C_2H_{4(g)} + O_{2(g)}$$
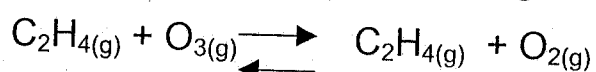
For this reaction above we can consider the reactants concentrations, from the equation coefficients it will be examine that every molecule of ethylene reacts with one mole of ozone. In other words, the concentration of both reactants decreases at same rate in this particular reaction. Thus:

$$\text{Rate} = -\frac{\Delta (C_2H_4)}{\Delta t} = -\frac{\Delta (O_3)}{\Delta t}$$

By monitoring the concentration of either of the reactants we can follow the rate of the reaction as it proceeds.

In searching for a rate equation and mechanism to fit a set of experimental data, we have to answer the following questions:

1 have we the correct mechanism and corresponding type of rate equation?

2 Once we have the right form of rate equation, do we have the best values for the rate constants in the equation.

The difficult question to answer is the first of the proceeding two question. Let see why this is so

Suppose we have a set of data we wish to find out whether any of the families of curves-parabolas, cubic, hyperbolas, exponential and so on, each repressing a different rate family really fits these data better than any other. This question can not be answered simply; neither can high powered mathematical or statistical methods helps in deciding the rate of mechanism. The one exception to this conclusion occurs when one of the families being compared is a straight line. For this situation we can simply, consistently and fairly reliably tell whether the straight line does not reasonably fit the data.

2.3.1   RATE CONSTANT k

With rate equation at hands, the rate constant can be found for each experimental point by either the integral or differential method. The rate constant calculated this way are slopes of lines joining the individual points to the origin or initial starting point. Also to be noted is the scatter points usually associated with these kind of curves with rate constant calculated near the origin (low conversion) varying widely with those

calculated far away from the origin. Therefore it becomes difficult to decide whether rate constant. k, is constant and if so what is the best mean value. k values can also be calculated from successive pairs of experimental points.

The safest, soundest and most reliable method of evaluating a rate constant and consequently an effective rate equation is through the use of graphical method. With graphical method the data are plotted and then examined the deviations from linearity. The decision whether a straight line gives a satisfactory fit is usually made intuitively by using good judgement when looking at the data.

2.3.2 MOLECULARITY AND ORDER OF REACTION

The Molecularity of an elementary reaction is the number of Molecules involved in the reaction, and this has been found to have the values of one, two or occasionally three. It should be noted that the Molecularity refers only to an elementary reaction

Often, we find that the rate of progress of a reaction involving say, materials A, B, C ... D can be approximated by an expression of the following type.

$$- r_A = kc_A^a \, C_B^b \, ... \, C_Z^z$$

$$\text{for } a+b \, ...z = n$$

Where a,b ...z are not necessarily related to the stoichiometry coefficients. The power to which the concentrations, are raised, are refers to order of reaction.
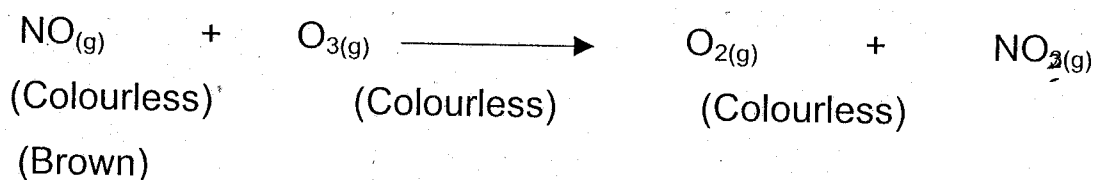
2.4 PRACTICAL MEASUREMENT OF REACTION RATES

Speculation about how a reaction occur at the molecular level must be based on measurement of reaction rates. From a practical standpoint, the experimental method should measure the concentration

of a single chemical species in the reaction quickly and reproducibly. Four general approaches are practice which are as follows

2.4.1 SPECTROMETRIC METHOD

These methods are used to measure the concentration of a reactant or product that absorbs (or emits) light of a marrow range of wavelengths. The reaction is typically performed in the sample compartment of a spectrometer set to measure a wavelength characteristic of one of the species.

For example is the $NO - O_3$ reaction only NO_2 has a colour.

$$NO_{(g)} \quad + \quad O_{3(g)} \longrightarrow \quad O_{2(g)} \quad + \quad NO_{2(g)}$$
(Colourless) (Colourless) (Colourless)
(Brown)

Known amounts of reactants are injected into a sample tube of known volume and the rate of NO_2 formation is measured by monitoring the colour over time. Reactant(s) is added to the sample tube and immediately places in the spectrometer. Rate data is then obtain from the plot of light absorbed versus time.

Reactions in aqueous solution can be studied similarly.

2.4.2 CONDUCTOMETRIC METHODS

When non-ionic reactions form ionic products, or vice-verse: the change in conductivity of the solution over time can be used to measure the rate. Electrodes are immersed in the reaction mixture and the increase (or decrease) in conductivity correlates with the formation of the product.

When a reactant mixture differs in conductivity from the product mixture, the change in conductivity is proportional to the reaction rate. It is usually easier to monitor a non-ionic reactant forming an ionic product.

2.4.3 MANOMETRIC METHOD

If a reaction involves a change in the number of moles of gas, the rate can be determined from change in pressure at constant volume and temperature over time.   In practice a manometer is attached to a reaction vessel of known volume that is immersed in a constant-temperature both.   As the reaction results in change in pressure with time corresponds to a change in reaction rate.

For example reaction of Zinc and acetic acid can be monitored by this method.   As Hydrogen (H_2) is form, the pressure increases in direct proportion to the reaction rate.

2.4.4 DIRECT CHEMICAL METHODS

Rates of slow reactions, or of those that can be easily slowed, are often studied by direct chemical method.   A small measured portion of the reaction mixture is removed by rapid cooling.   The concentration of reaction mixture continues to react and is sampled later.

For instance, the reaction between organic halide and water can be studied by titration.   The reaction rate is then measured, a portion is slowed by quickly transferring it to a chilled flask in an ice bath. HBr concentration in the measured portion is determined by titration with standardized NaOH solution.   To determine the change in HBr concentration with time; the procedure is repeated at regular intervals during the reactions.

2.5   ELECTROCHEMISTRY

The Science dealing with the chemical changes accompanying the passage of an electric current, or the reverse process in which a chemical reaction is used as source of energy to produce an electric current; as in the battery. Electric conduction occurs through the motion

of charge particles. The charge particles may be electrons or ions, which are electrically charge atoms, molecules or molecules aggregates.

A typical dry cell consist of an Zinc anode in the form of a can which houses a mixture of Manganese (IV) oxide (MnO_2) and an acidic electrolyte paste, consisting of NH_4Cl, $ZnCl_2.H_2O$ and starch. Powdered graphite improves conductivity and the inactive cathode is a graphite rod.

In the Anode Oxidation reaction occurs, as shown below.

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e$$
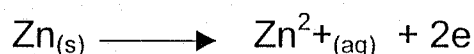
At the cathode, reduction reaction occurs. The cathode half reaction is complex even today is still being studied. Manganese (IV) oxide ($MnO_{2(s)}$ is reduced to $Mn_2O_{3(s)}$ through a series of steps that may involved the presence of Mn^{2+} and an acid-base reaction between NH^+_4 and OH. The reaction is as follows:

$$2MnO_{2(s)} + 2NH_4 + 2e \longrightarrow$$
$$Mn_2O_{3(s)} + 2NH_4 + H_2O_{(l)}$$
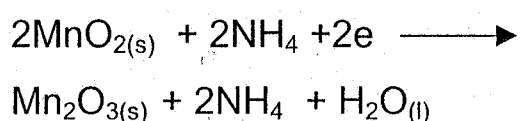
The ammonia, some of which may be gaseous, forms a complex ion with Zn^{2+} which crystallizes in contact with Cl^- ion.

$$Zn^{2+}_{(aq)} + 2NH_{3(aq)} + 2Cl^-_{(aq)} \longrightarrow Zn(NH_3)_2 Cl_{2(s)}$$
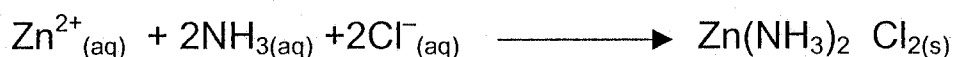
The overall cell reaction is given by the general equation:

$$2MnO_{2(s)} + 2NH_4 Cl_{(aq)} + Zn_{(s)} \longrightarrow$$
$$Zn(NH_3)_2 Cl_{2(s)} + H_2O_{(l)} + Mn_2O_3$$
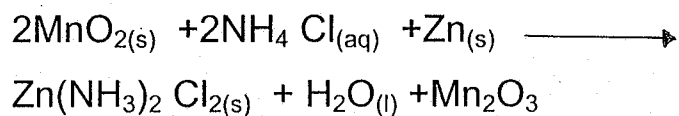
With E cell = 1.5V

At the anode, i.e oxidation of Zinc to Zinc ion with simultaneous liberation of electrons to the external circuit, at a rate proportional to the current for each ampere which flows. Approximately 1.2g of zinc per hour is converted to zinc ion. At the cathode the electrons from the external circuits reduces the Manganese (IV) oxide (MnO_2).

Studies have shown, however, that the total ampere-hour output of the cell can be accounted for by analyzing the cathode mix for the following substances.

(a) Solute manganese (Mn^{++}), each gram of which accounts for nearly 1A –hr of discharge.

(b) Insoluble manganite (Mn OOH) each gram of which accounts for about o.3A –hr of discharge.

(c) Insoluble hetaerolite (ZnO. Mn_2O_3) each gram of which accounts for about 0.22A –hr of discharge.

The electrochemical reduction of Manganese (IV) oxide (MnO_2) has been reported to occur as the reaction to form soluble manganese as examine in the cathode reaction. The service capacity of dry cell is not a fixed number of ampere- hours, but varies with current drain, operating schedule, cut off voltage, operating temperature and storage conduction prior to use.

The general; purpose dry cell operates at 2¼ ohms for 45 minutes period at 24 hour interval until the closed circuit voltage drops to 0.65V; 400 Minutes.

2.5.1 TEMPERATURE EFFECT ON CELL

The lower the temperature during discharge, the lower is the outputs. Conversely, the higher the temperature during discharge, the greater is the energy output. At –230C, the cell is virtually inoperative. However, shelf life is influenced in the reversed direction by environmental temperatures.

Better low- temperature can be obtained with special electrolytes and cell structure giving a high ratio of. Electrode area to maximum thickness and special type of Manganese (IV) oxide (MnO_2).

2.5.2 SHELF LIFE EFFECT ON CELL

This is the period of time that a cell (battery) can be stored before it drops to 90% of it's capacity when tested fresh at 210C and 50% relative humidity.

Deterioration is dry cells occurs in a score of ways, these includes:

(a) Zinc can Oxidizes by reacting with the electrolyte. This reaction produces hydrogen.

(b) Manganese (IV) oxide (MnO_2) can be reduced by carbon and by the organic material used in the cell.

(c) Water can be evaporates from the electrolyte: this increase the cell resistance and alters the composition of the electrolyte unfavorably.

CHAPTER THREE

3.0   METHODOLOGY

3.1   INTRODUCTION

Mechanism of reaction usually involves the measurement of reaction rate, which is possible through various experimental processes, with these various ways having different approach in which there rate equation sorted out. Before arriving at the final rate equation various steps are involved. The reaction is classified either to be a homogenous or heterogeneous system.

A reaction is said to be homogenous if it takes place in one phase alone and a heterogeneous reaction requires the presence of at least two phase.

The variable in which the rate or mechanism will be dependent upon is define and put into considerations. In homogenous systems, the temperature, pressure and composition are obvious variables.   In heterogeneous system due to presence of more than one phase, hence, the problem of defining the rate equation with a variable of interest becomes more complex. Material can move during reaction from one phase to another, hence the rate of mass transfer becomes important. Also rate of heat transfer can also be a limiting factor of rate equation when an endothermic or exothermic system considered. Presence of catalyst during chemical reaction also affect the final rate equation.

Also worthy of mentioning is the method to be used in the studying the mechanism of reaction, various method exist but the well accepted method is the use of rate equation to determine the path which a reaction follows. The rate constant which is a very important constant in defining the path of reaction is usually determine in other to have a rate equation which will be applicable to various dependable terms of rate equation.

3.2   ASSUMPTIONS IN KINETIC STUDY

A lot of assumptions are made in other to arrived at a final rate equation. These assumptions are usually based on theorems, law and postulations in natural sciences. Assumptions are made with careful consideration of the effect and consequently the importance and application of the assumption. It is important to note that there is limitation to freedom of assumption and postulations. Already there exist a lot of postulations in place to take care of problems to be encountered during the study of rate equation.

A reaction can be assumed to be elementary reaction in other to have a starting point of the study. Considering the reaction below.

$$A + B \longrightarrow R \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \qquad 3.2.1$$

It is postulated that the rate controlling mechanism of the above reaction involves the collision or interaction of a single molecule of A with single molecule of B, then the number of collision or interaction of molecules of A and B is proportional to the rate of reaction. But at a given temperature the number of collision is proportional to the concentration of the reactants in the mixture; hence, the rate of disappearance of A is given by

$$\frac{-dC_A}{dt} = -r_A = kC_AC_B \dots\dots\dots\dots\dots\dots\dots\dots \qquad 3.2.2$$

Such a reaction which the rate equation corresponds to the stoichiometric equation is known as ELEMENTARY REACTION.

When there is no direct correspondence between the stoichiometry and rate, then we have a NON ELEMENTARY REACTION. In non elementary reactions we assumed that what we observed as a single reaction is in reality the overall effect of a sequence of elementary reactions. The reason for observing only a single reaction rather then

two or more elementary reactions is that the amount of intermediates formed is negligibly small and therefore escape detection.

It is very important to note that the molecularity of a reaction apply only to the elementary reaction. It is defined as the number of molecules involved in the reaction and this has been found to have the values one, two and occasionally three.

Assumptions should be carefully made so that the rate equation that emerge is effective and deduction from it remain valid.
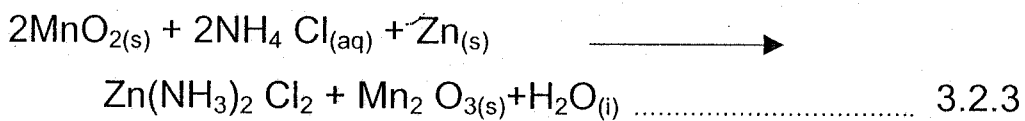
3.3 DERIVATION OF KINETIC RATE EQUATION

In deriving the rate equation for this analysis, two important chemical reaction equations are needed, they are as follows

1.   Chemical reaction equation before adsorption

2.   Chemical reaction equation after adsorption

The equations are both derived for each of the cations involved in the analysis, that is $Zn(NO_3)_2$ and $Pb(NO_3)_2$

The chemical equation before adsorption is the cell chemical reaction given earlier in chapter two which is written as

$$2MnO_{2(s)} + 2NH_4 Cl_{(aq)} + Zn_{(s)} \longrightarrow$$

$$Zn(NH_3)_2 Cl_2 + Mn_2 O_{3(s)} + H_2O_{(i)} \dots\dots\dots\dots\dots \text{ 3.2.3}$$

The reaction can be represented alphabetically as follows

$$2A + 2C + B \longrightarrow R + S + T \dots\dots\dots\dots \text{ 3.2.4}$$
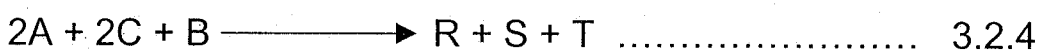
With A   representing the molecule of MnO_2

B   representing the molecule of Zn

C   representing the molecule of NH_4Cl

R   representing the molecule of $Zn(NH_3)_2Cl_2$

S   representing molecule of Mn_2O_3

T   representing molecule of H_2O

The above chemical reaction equation is applicable for both analysis of the cations, that is, for both $Zn(NO_3)$ aid $Pb(NO_3)_2$.

The second chemical reaction equation, which is define for each of the cations.
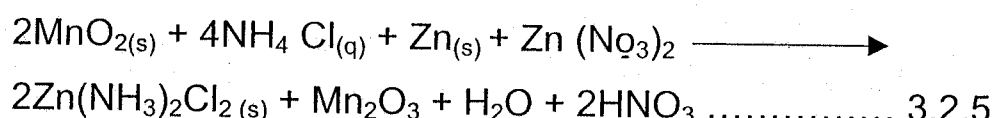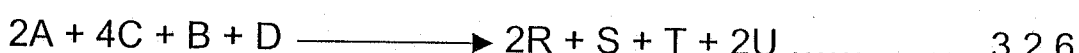
(a)   The reaction of $Zn(NO_3)_2$ after adsorption

$2MnO_{2(s)} + 4NH_4Cl_{(q)} + Zn_{(s)} + Zn(NO_3)_2 \longrightarrow$

$2Zn(NH_3)_2Cl_{2(s)} + Mn_2O_3 + H_2O + 2HNO_3$ 3.2.5

Representing alphabetically as follow

$2A + 4C + B + D \longrightarrow 2R + S + T + 2U$ 3.2.6

Where   D   represent the molecule of $Zn(NO_3)_2$

           U   represent the molecule of HNO_3

With other alphabet corresponding to earlier definition

(b)   The reaction of $Pb(NO_3)_2$

$2MnO_{2(s)} + 4NH_4Cl + Zn_{9s)} + Pb(NO_3)_2 \longrightarrow$

$Pb(NH_3)_2Cl_{2(s)} + Mn_2O_3 + H_2O + Zn(NO_3)_2$ 3.2.7

Represented alphabetically as follow

$2A + 2C + B + P \longrightarrow Q + S + T + X$ 3.2.8
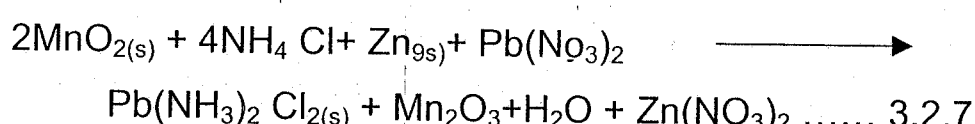
Where P represent molecule of $Pb(NO_3)_2$

         Q represent molecule of $Pb(NH_3)_2Cl_2$

         X represent molecule of $Zn(NO_3)_2$ formed.

3.3.1 ASSUPTONS IN RATE EQUATION DERIVATION

(a)   Assuming that all the reactions are elementary, this implies that the rate equations will correspond to their stoichiometric equations. Therefore the chemical reactions given earlier can have the following representation of rate equation.

Before adsorption, the rate equation is given as

$$-r_A = \frac{-dc_A}{dt} = k_1 C_A C_B C_C$$ 3.2.9

With C_A, C_B and C_C representing various concentrations of molecules represented alphabetically in the reaction.

(b) Since the subject under discussion or study deals with the effectiveness of manganese (iv) oxide and putting into consideration the complexity of cathode and electrolyte reaction which even today is still being study. Assumption is made that there concentration is negligible since MnO_2 react with the polarizer produce by above mention reaction. Because our rate equation is of an elementary system, therefore the molecularity of our rate equation is Two (2) from the chemical reaction equation. Therefore our rate equation before adsorption becomes.

$$-r_A = \frac{-dC_A}{dt} = = k_1 C_A^2 \dots\dots\dots\dots\dots\dots\dots\dots 3.3.0$$

All the assumptions made is applicable for both reactions before and after adsorption.

Rate equation after adsorption:

i. With $Zn(NO_3)_2$ cation, the rate equation is given as

$$-r_A = \frac{-dC_A}{dt} = k_2 C_A^2 C_D \dots\dots\dots\dots\dots 3.3.1$$

ii. With $Pb(NO_3)_2$ cation, the rate equation is given as

$$-r_A = \frac{-dC_A}{dt} = k_2 C_A^2 C_p \dots\dots\dots\dots\dots\dots 3.3.2$$

(c) The final concentration of manganese (iv) oxide is unknown, but from the chemical reactions, two molecules of manganese (iv) oxide react to give the product Mn_2O_3. Assuming that the final concentration of MnO_2 decreases by half it's initial concentration.

2g of MnO_2 was used during the practical, since the molecular mass of MnO_2 is 87g. That is one molecule of MnO_2 contain 87g of MnO_2.

Mathematically

1mole   -   Contain 87g in 1 dm^3 of MnO_2

Xmole   -   will contain 2g in 1 dm^3 of MnO_2

∴Xmole $\frac{1 \times 2}{87}$ =   0.023 mol/dm^3

Therefore the initial concentration of MnO_2 is 0.023 mol/dm^3 and our final concentration will be:

$\frac{0.023}{2}$ =   0.0115mol/dm^3

From the practical work, four different concentrations were used during the experiment. Readings are usually taken at an interval of sixty seconds (60secs), so with four different concentrations at constant temperature reaction time will be:

60secs x 4 =   240 secs

∴ $\frac{240}{60}$ =   4mins

CHAPTER FOUR

4.0   RESULTS

From equations 3.3.0 and 3.3.1 we have

$$-r_A \quad = \quad k_1 C_A^2 \quad\longrightarrow\quad 4.1.0$$

$$-r_A \quad = \quad k_2 C_A^2 C_D \quad\longrightarrow\quad 4.2.0$$

From equation 4.1.0 which involves the depolarizer, it's initial concentration is 0.023 mol/dm^3 with final concentration to be 0.0115 mol/dm^3 for time interval of four (4) minutes. Working towards having various concentration of depolarizer in other to match the time interval we assumed that the concentration decreases uniformly at rate of 0.002875mol/dm^3 for each minute of progressive reaction. This lead to the table below:

Table 4.1

S/No	Time (Minutes)	Concentration of $Mno_2(C_A)$ mol/dm^3	$1/C_A$ mol/dm^3
1.	0	0.023	43.4783
2.	1	0.020125	49.6894
3.	2	0.01725	57.9710
4.	3	0.014375	695652
5.	4	0.00115	86.9565

A plot of $1/C_A$ against time (t) yield a straight line graph with the origin at the initial concentration of the depolarizer. The slope of the plotted graph is the rate constant and calculated as

$$k_1 = \text{Slope} = \frac{5.7.9710 \quad - \quad 43.4783}{2-0} \quad = \quad 7.2464$$

$$-r_A \quad = \quad k_1 C_A^2 = \quad 7.2464 C_A^2$$

$$-r_A \quad = \quad 7.2464\ C_A^2$$

For the reaction that involves the additives (Cations) with rate equation as

$$-r_A = kC_A^2C_D$$

Using the differential method of analysis

$$-r_A = \frac{-dC_A}{dt} = k_2C_A^2C_D$$

$$\frac{-dC_A}{C_A^2} = k_2C_Ddt$$

$$\int_{C_{AO}}^{C_A} -C_A^{-2}dC_A = kC_D\int_0^t dt$$

$$-\frac{C_A^{-2+1}}{-2+1} \Big|_{C_{Ao}}^{C_A} = k_2C_Dt$$

$$C_A^{-1} \Big|_{C_{A0}}^{C_A} = k_2C_Dt$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = k_2C_Dt$$

But

$C_A = 0.0115\text{mol/dm}^3$

$C_{A0} = 0.023\text{mol/dm}^3$

$C_D = 0.001 \text{ mol/dm}^3$

$C_{DO} = 1\text{mol/dm}^3$

$t = 4\text{mins}$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = k_2 C_D t = \frac{1}{0.0115} - \frac{1}{0.023} = k_2(0.001)(4)$$

$$= 86.9565 - 43.4783 = k_2(0.004)$$

$$\therefore k_2 = \frac{43.4782}{0.004}$$

$$k_2 = 10869.55$$

$$k_2 = 10.8696 \times 10^3$$

$$\therefore -r_A = k_2 C_A^2 C_D = 10.8696 \times 10^3 C_A^2 C_D$$

$$\Rightarrow -r_A = 10.8696 \times 10^3 C_A^2 C_D$$

4.1 RATE AT VARIOUS CONCENTRATION

For the cell overall reaction with rate equation as

$$-r_A = 7.2464 C_A^2$$

The rates is calculated and tabulated below.

Table 4.2

Concentration of MnO_2 C_A, mol/dm^3	Rate of reaction of MnO_2 $(-r_A)$ mol/dm^3 min.
0.0230	3.83×10^{-3}
0.020125	2.93×10^{-3}
0.01725	2.16×10^{-3}
0.014375	1.050×10^{-3}
0.01150	9.58×10^{-4}

For the reaction with cations added.

(a)   if $C_A = 0.023$ Mol/dm^3 with rate $-r_A = 10.8696 \times 10^3 C_A^2 C_D$

Table 4.3

Concentration of Cation C_D Mol/dm^3	Rate of disappearance of Mno$_2$ ($-r_A$) mol/dm^3 min.
1.000	5.7500
0.100	0.5750
0.010	0.05750
0.001	0.005750

(b)   If $C_A = 0.0115$ Mol/dm^3

Table 4.4

Concentrations of cations C_D (Mol/dm^3)	Rate of disappearance of Mno$_2$ (mol/dm^3 min)
1.000	1.4376
0.100	0.14377
0.010	0.014376
0.001	0.0014376

4.2 ORDER OF REACTION

For the overall cell reaction with rate equation stated in equation 4.1.0 as

$$-r_A = k_1 C_A^2$$

The above rate equation is a bimolecular type rate equation which is proved by the graph drawn or plotted. Therefore the rate equation is a SECOND ORDER rate equation.

For the reaction involving the additives (cations), with the rate equation.

$$-r_A = k_2 C_A^2 C_D \text{ and } -r_A = k_2 C_A^2 C_D$$

The above rate equation is a trimolecular type equation. The order of the reaction is calculated as power of C_A plus power of C_D or C_P, this equal three, which suggest that the reaction order is a THIRD ORDER REACTION

CHAPTER FIVE

5.0   DISCUSSION OF RESULTS

It was observed that rate equation for the cations used, that is zinc and lead in their nitrate solution where assumed to be same after due consideration and comparing the two stoichiometry equation for each of the additives which are assumed to be an elementary reaction.

From the results obtain in chapter four, much consideration was given to the rate of disappearance of depolarizer because it is the factor we are working to improve upon.   It must be stated at this point that the target of this research is to see how the rate of disappearance of the depolarizer (manganese (iv) oxide) be able to cancelled the effect of the polarizer effectively.

5.1   ANALYSIS OF RESULT OBTAIN FROM OVERALL CELL REACTION WITHOUT THE CATIONS

From table 4.2, generally as the concentration of manganese (IV) oxide decreases, the rate of disappearance of the depolarizer decreases, this will lead to accumulation of the hydrogen gas deposited on the electrode and consequently lead to the stoppage of the reaction in the cell.

As time progress, the concentration decreases and consequently the rate of disappearance of manganese (IV) oxide and the effectiveness of the depolarization reaction or depolarizer decreases.

5.2   ANALYSIS OF RESULT OBTAIN WITH ADDITION OF CATIONS (Zn^{2+} and Pb^{2+})

The addition of cations is aimed at alleviating the problems stated above. The cations are expected to increase or decrease the

effectiveness of the manganese (IV) oxide. The question to be answered is what concentration of cations or depolarizer will be more favourable or unfavorable?

From Table 4.3 at concentration of 0.023mol/dm^3 with varying concentration of the cations, it was observed at cation concentration of 1.0 mol/dm^3 the rate of disappearance of the depolarizer is 5.750 mol/dm^3 min which is higher than that obtained with the cations as seen in table 4.2. The concentration of the cation decreases with time so also the rate of disappearance of Mno_2 and its effectiveness decreases with time in the cell.

From Table 4.4 As the concentration of manganese (IV) oxide decrease to a value of 0.0115 mol/dm^3 and varying the concentration of the cations used, it was observed that at concentration of 1.0mol/dm^3 for cation, the rate of disappearance of manganese (iv) oxide with time is recorded to be 1.4376 mol/dm^3 min which is low compared with that recorded when the concentration of Mno_2 was 0.023mol/dm^3.

Generally, it could be concluded that at higher concentration of cations and the depolarizer, the rate of disappearance of Mno_2 is high and decreases with time. At lower concentration of the depolarizer and higher concentration of the cations, the rate of disappearance of Mno_2 is low compared with the first case. Therefore the concentration of the depolarizer has much effect on the rate of disappearance.

5.3   COMPARISON WITH EXPERIMENTAL RESULTS

This thesis is based on previous research, title the adsorption of some cations (Zn^{2+} and Pb^{2+}) on manganese (IV) oxide in a dry cell through the used of potentiometric titration to ascertain the effect, at the end of the research adsorption capacity and electric charge were calculated at varying concentration, temperatures and P^H.

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As stated above, during the experimental analysis emphases were given to three variables viz P^H, concentration and temperature. Generally, from experiment at high concentration and P^H (alkaline) and lower temperature the adsorption capacity or electric charge increases which is associated with decrease in surface charge of manganese (IV) oxide and it effectiveness as a depolarizer.

The above statement shows that the kinetic study or result obtain is in line with the experimental result obtain from potentiometric titration. In the experimental result at high concentration of cations more electric charge are produce in the cell, while in kinetic study at higher concentration of cation there is high rate of disappearance of manganese (IV) oxide which also result in high electric charge from the cell.

One very important result provided by the kinetic study is the variation of the concentration of manganese (IV) oxide. During the experimental analysis manganese (IV) oxide is used at constant concentration.

Therefore it could be stated that the kinetic study or rate equation obtain is in line with the experimental analysis.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS'

6.1 CONCLUSION

The results provided by graphical and differential method of analysis of the kinetics of the reaction which occur in a dry cell, that is the overall cell reaction and that of addition of cations aimed at enhancing the performance of the depolarizer using Zn^{2+} and Pb^{2+} in their nitrate solution gives a rate which suggest a high depolarizer concentration and high cation concentration which will result in high disappearance rate of the depolarizer, which is expected or aimed at enhancing the effectiveness of the cell. Therefore it is concluded that

1. Cations, like Zn^{2+} and Pb^{2+} be used as additives in dry cell in other to enhanced the performance of the cell and cell life span.

2. That the depolarizer and cations be used at high concentration in other to increase it effectiveness in the dry cell.

The reaction order of the adsorption of cations assuming an elementary reaction is a third order reaction with that of the overall cell reaction without the cations as second order reactions.

6.2 RECOMMENDATIONS

From thorough study of the Adsorption reaction to the kinetic study of the adsorption, the following are recommended.

1. A photo-type cell should be constructed in other to implement the research so as to ascertain the effectiveness of the research.

2. The used of organic depolarizer should be study, this is due to their low economic cost of production.

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3. Lastly it is recommended that the adsorption of cations on manganese (iv) oxide should be carried out with various cations at different temperature and concentrations to figure out the most effective cation to be inculcated in the modern dry cell.

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APPENDIX

From table 4.1

1. When $C_A = 0.023 \text{mol/dm}^3$

$$1/C_A = \frac{1}{0.023} = 43.4783 \ (\text{mol/dm}^3)^{-1}$$

2. When $C_A = 0.020125 \text{mol/dm}^3$

$$1/C_A = \frac{1}{0.020125} = 49.6894 \ (\text{mol/dm}^3)^{-1}$$

3. When $C_A = 0.01725 \text{mol/dm}^3$

$$1/C_A = \frac{1}{0.01725} = 57.9710 \ (\text{mol/dm}^3)^{-1}$$

4. When $C_A = 0.014375 \text{mol/dm}^3$

$$1/C_A = \frac{1}{0.014375} = 69.5652 \ (\text{mol/dm}^3)^{-1}$$

5. When $C_A = 0.0115 \text{mol/dm}^3$

$$1/C_A = \frac{1}{0.0115} = 86.9565 \ (\text{mol/dm}^3)^{-1}$$

From Table 4.2

Using $- r_A = 7.2464 C_A^2$

a. When $C_A = 0.0230 \text{mol/dm}^3$

    1. $-r_A = 7.2464(0.0230)^2$

        $-r_A = 3.83 \times 10^{-3} \text{ mol/dm}^3$. Min.

    2. When $C_A = 0.020125 \text{mol/dm}^3$

        $-r_A = 7.2464(0.020125)^2$

        $-r_A = 2.93 \times 10^{-3} \text{ mol/dm}^3$. Min.

    3. When $C_A = 0.01725 \text{mol/dm}^3$

        $-r_A = 7.2464(0.01725)^2$

        $-r_A = 2.16 \times 10^{-3} \text{ mol/dm}^3$. Min.

    4. When $C_A = 0.014375 \text{mol/dm}^3$

        $-r_A = 7.2464(0.014375)^2$

$$-r_A = 1.50 \times 10^{-3} \text{ mol/dm}^3 \cdot \text{min.}$$

5.   When $C_A = 0.0115 \text{ mol/dm}^3$

$$-r_A = 7.2464(0.0115)^2$$

$$-r_A = 9.58 \times 10^{-4} \text{ mol/dm}^3 \cdot \text{min.}$$

From Table 4.3

Using $-r_A = 10.8696 \times 10^3 \ C_A{}^2 \ C_D$

a.   If C_A is held constant at 0.023 mol/dm^3

1.   When $C_D = 1.00 \text{ mol/dm}^3$

$$-r_A = 10.8696 \times 10^3 \ (0.023)^2 \ (1.00)$$

$$-r_A = 5.7500 \text{ mol/dm}^3 \cdot \text{min.}$$

2.   When $C_D = 0.10 \text{ mol/dm}^3$

$$-r_A = 10.8696 \times 10^3 \ (0.023)^2 \ (0.10)$$

$$-r_A = 0.5750 \text{ mol/dm}^3 \cdot \text{min.}$$

3.   When $C_D = 0.01 \text{ mol/dm}^3$

$$-r_A = 10.8696 \times 10^3 \ (0.023)^2 \ (0.01)$$

$$-r_A = 0.05750 \text{ mol/dm}^3 \cdot \text{min.}$$

4.   When $C_D = 0.001 \text{ mol/dm}^3$

$$-r_A = 10.8696 \times 10^3 \ (0.023)^2 \ (0.001)$$

$$-r_A = 0.005750 \text{ mol/dm}^3 \cdot \text{min.}$$

b.   If C_A is held constant at $C_A = 0.0115 \text{ mol/dm}^3$

1.   When $C_D = 1.00 \text{ mol/dm}^3$

$$-r_A = 10.8696 \times 10^3 \ (0.0115)^2 \ (1.00)$$

$$-r_A = 1.4376 \text{ mol/dm}^3 \cdot \text{min.}$$

2.   When $C_D = 0.10 \text{ mol/dm}^3$

$$-r_A = 10.8696 \times 10^3 \ (0.0115)^2 \ (0.10)$$

$$-r_A = 0.14376 \text{ mol/dm}^3 \cdot \text{min.}$$

3.   When $C_D = 0.01 \text{ mol/dm}^3$
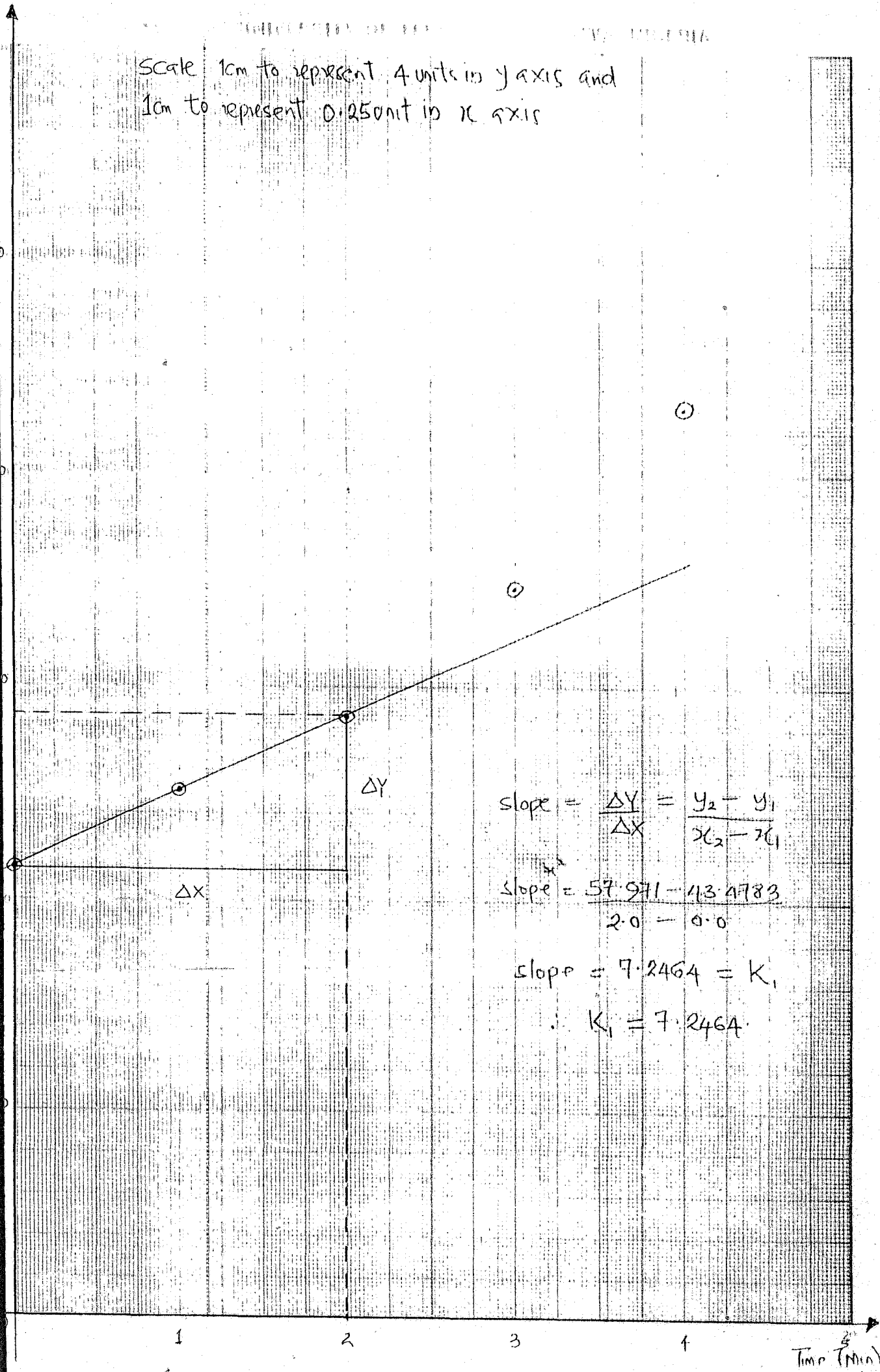
$$-r_A = 10.8696 \times 10^3 \ (0.0115)^2 \ (0.01)$$

$$-r_A = 0.014376 \text{ mol/dm}^3 \cdot \text{min.}$$

4.   When $C_D = 0.001$mol/dm^3

$-r_A = 10.8696 \times 10^3 (0.0115)^2 (0.001)$

$-r_A = 0.0014376$mol/dm^3. min.

Scale 1cm to represent 4 units in y axis and
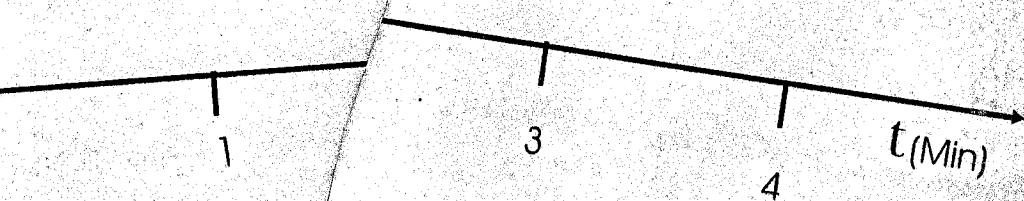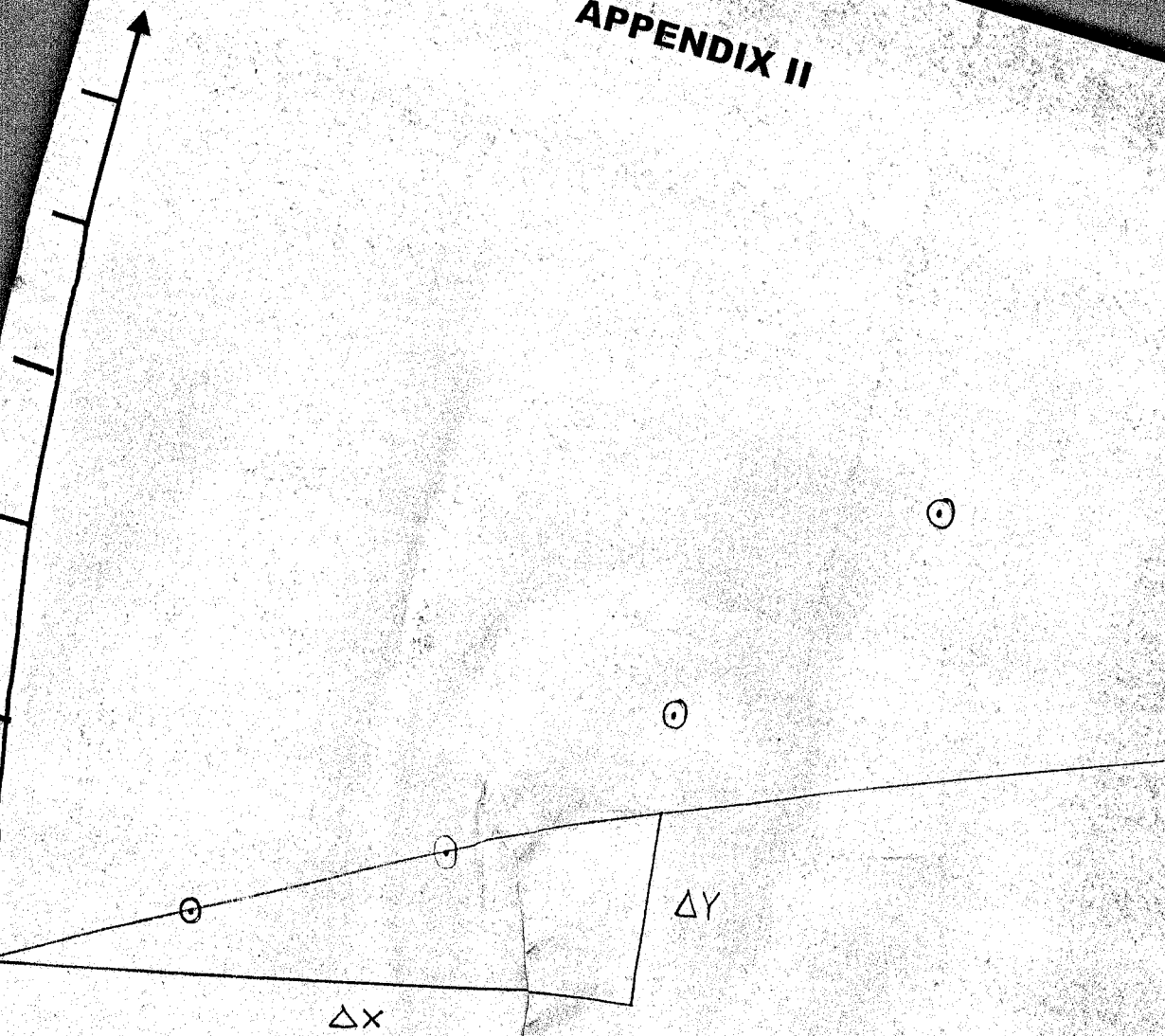1cm to represent 0.25 unit in x axis

$$\text{slope} = \frac{\Delta Y}{\Delta X} = \frac{y_2 - y_1}{x_2 - x_1}$$

$$\text{slope} = \frac{57.971 - 43.4783}{2.0 - 0.0}$$

$$\text{slope} = 7.2464 = K_1$$

$$\therefore K_1 = 7.2464$$

ΔY

ΔX

1   2   3   4   Time (Min)

ΔY

Δx

1

3

4

$t_{(Min)}$

A graph of $1/C_p$ ag

38.