A STUDY ON THE ADSORPTION OF ALKALINE ANIONS ON MANGANESE (IV) OXIDE USED IN DRY CELL

BY

ADAMU GABRIEL AFENE

(92/2395)

DECEMBER '98.

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A RESEARCH PROJECT REPORT SUBMITTED
TO THE DEPARTMENT OF CHEMICAL ENGINEERING
SCHOOL OF ENGINEERING AND ENGINEERING TECHNOLOGY ,
FEDERAL UNIVERSITY OF TECHNOLOGY,
MINNA, NIGER STATE.

IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF
BACHELOR OF ENGINEERING (B.ENG) DEGREE
IN CHEMICAL ENGINEERING.

DECEMBER '98.

DECLARATION

I hereby declare that this project is my original work and has never, to my knowledge be submitted elsewhere.

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ADAMU GABRIEL AFENE DATE

(92/2395)

CERTIFICATION

This is to certify that this project work "A study on the adsorption of alkaline anions on manganese (iv) oxide" which I have found adequate both in scope and quality, for the partial fulfilment of the requirement for the award of Bachelor of Engineering degree in chemical Engineering, was presented by Adamu Gabriel Afene (92/2395) of Chemical Engineering Department, Federal University of Technology Minna.

14-12-98

MR. DUNCAN ALOKO
(Project Supervisor)

DATE

DR. ODIGURE J.O
(HOD Chemical Engr. Dept.)

DATE

PROF. S.S. ADEFILA
(A.B.U., ZARIA)
External Examiner

DATE

DEDICATION

This project work is dedicated to the Most High God, His Son Jesus Christ and the Holy Spirit, and to my elder brother Mr. Joseph Adamu.

ACKNOWLEDGEMENT

I am indebted to my elder brother, **Mr. Joseph Adamu** who since my early youthful days has so consistently utilize every graceous potential at his disposal to the favor of my stability, and also to **Mr.David Adamu** and his wife, **Mrs Rose Ekojonwa David** whose continous prayers, support and encouragement I will not forget.

I can not but make mention of my late father **Mr Adamu Onye**, my mother **Mrs Achagba Adamu,** my aunts **Mrs Lare, Mrs Iyoma** and my elder sister **Mary Dajiba,** my brothers, **Amos Adamu** and wife, **Joshua Adamu** and wife, **Enukpeje Adamu** who also contributed in diverse ways to my success. Your labour and your unceasing travail in prayers has kept me.

How about my niece **Ladi David, Blessing, Deborah, Esther, Abigail, Ruth, Priscilla, Itamama, Ojochide, Benjamin, Job** and **Isreal**, of a truth they have been wonderfully sources of encouragement to me.

I will not forget to make mention of **Mr Roy Ilabija** whom God used as instrumental to my admission; **Mr Isa Omali** of the students affairs unit who made my stay on the campus less burdensome, **Mrs Akinbode** and **Mr Bala** of the chemistry laboratory, who greatly assisted during my project analysis. God bless you.

Also, I will not forget the enormous contributions of all the brethren-**Bro Mathew Negedu, Bro Monday Akogwu, Bro Emmanuel Akogwu, Bro Benson A. owofo, Bro Sunday A. Atawodi, Bro Monday Akor, Sister Mary Napoleon Sister Kemi Oyewole** (Mathematics Computer) and a host of others whose prayers, encouragement I will not forget.

I owe thanks to my able project surpervisor, **Mr Ducan Aloko** and **Bro. M. Olutoye** whose guidance and instructions have led me to the accomplishment of this work. Mrs Elizabeth E. is not exempted

And most of all, I will like to declare that I am most grateful to God, the lover of my soul, who by his immeasurable and unspeakable providence has brought me to this stage of my life and has made me what I am today by his grace. For in him I live and I have my being. Without him I am nothing . I'm, forever grateful.

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ABSTRACT

"A study on the Adsorption of alkaline anions on manganese (iv) oxide (MnO_2) used as cathode material in a leclanche dry cell" has been studied to improve the activity of MnO_2 in the same.

The alkaline anions on which this work was done are Nitrate v (NO^-_3), Sulphate vi (SO^{2-}_4), Chloride (Cl^-) and bromide (Br^-) ions.

An overall thirty two (32) successful titrations were conducted for four different concentrations of the interested anions in solution. Thirty two curves were plotted. On relating the change in volume of the titrants at a constant pH of 9.0 when MnO_2 is in the solution and when it is not, the amount of adsorption and the surface charges for each anion in their four different concentrations of solutioons were determined.

The surface area of MnO_2 was also determined to be 1719.3 m^2/g by "adsorption from solution". This showed that the MnO_2 used was of a gamma modification.

For all the anions, and from their different concentration there seems to be an order of decrease in surface charges from IM to 0.001M except for few concentrations (one of the four concentrations for each anion) which does not follow the order as a result of specific adsorption. However only SO^{2-}_4 ion maintained its consistency in its order. SO^{2-}_4 ion also gave the largest value of 1.91, 1.12, 1.0.0 and 0.95 μc for all its concentrations (i.e 1, 0.1, 0.01 and 0.001M respectively). The least of it is higher than the highest of any other anions.

The pattern of the curves for the adsorption of anions on MnO_2 were observed to follow Freundlich and Tomkin.

CHAPTER ONE

1.0 INTRODUCTION

This work on A study on the Adsorption of alkaline anions on manganese (iv) oxide in aqueous solution" is a project work based on Leclanches dry cell, the fore-runner of today's familiar dry cell ordinarily (commonly) known as battery.

Battery is a device that changes and transfer chemical energy into electrical energy. The term battery is usually applied to a group of two or more electric cells. A cell therefore, converts the energy of chemical reaction into an electrical current. This is known as electrochemical reaction. Battery, as it is generally known is used to power apparatus and equipment in which it supplies current to. There are two kinds of battery, primary and secondary batteries..

The attention of this work is towards the primary battery. The Leclanche dry cell upon which this work is centred, is a type of primary battery. Leclanches cell is an improved type of primary dry cell which has succeeded the first primary cells (Voltaic pile) in the line of invention to improve the first primary cell invented by Alesssandro volta.

A Laclanche's cell has a negative electrode of Zinc, an ammonium chloride electrolyte and, a positive electrode of finely divided carbon and manganese (iv) Oxide (MnO_2) packed around a carbon-rod terminal. Manganese (iv) Oxide is present to act as a depolarizer by absorbing the hydrogen gas that is formed at the positive electrode. The unlike electrodes are seperated by moistened paper, starch flour gel or some other porous non conductor. Generally the non conductor contains Zinc and mercuric chlorides. Mercuric chloride is used to amalgamate the Zinc in order to increase the storage life. When the cell is made in Cyliridrical from, the Zinc usually serves both as the negative electrode and as the container.

The reaction at the negative electrode is $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$ Where e^- denotes the electron and OH^- denotes the hydroxyl ion which comes from ionization of water: $H_2O \longrightarrow H^+ + OH^-$

The reaction at the positive electrode, if the discharge rate is slow is

$2MnO_2 + 2H^+ + 2e^- \longrightarrow MnO_3.H_2O$ ----------------------------------(1)

If the discharge rate is high, the reation at the positive is:

$2MnO_2 + NH^+_4 + 2e^- \longrightarrow MnO_3.H_2O + NH_3$

The ammonium ion (NH^+_4) comes from ion concentration of the ammonium chloride.

In each case the cell reation is the sum of the reactions at the two electrodes

$$Zn + H_2O + 2MnO_2 \longrightarrow MnO_3.H_2O + ZnO$$

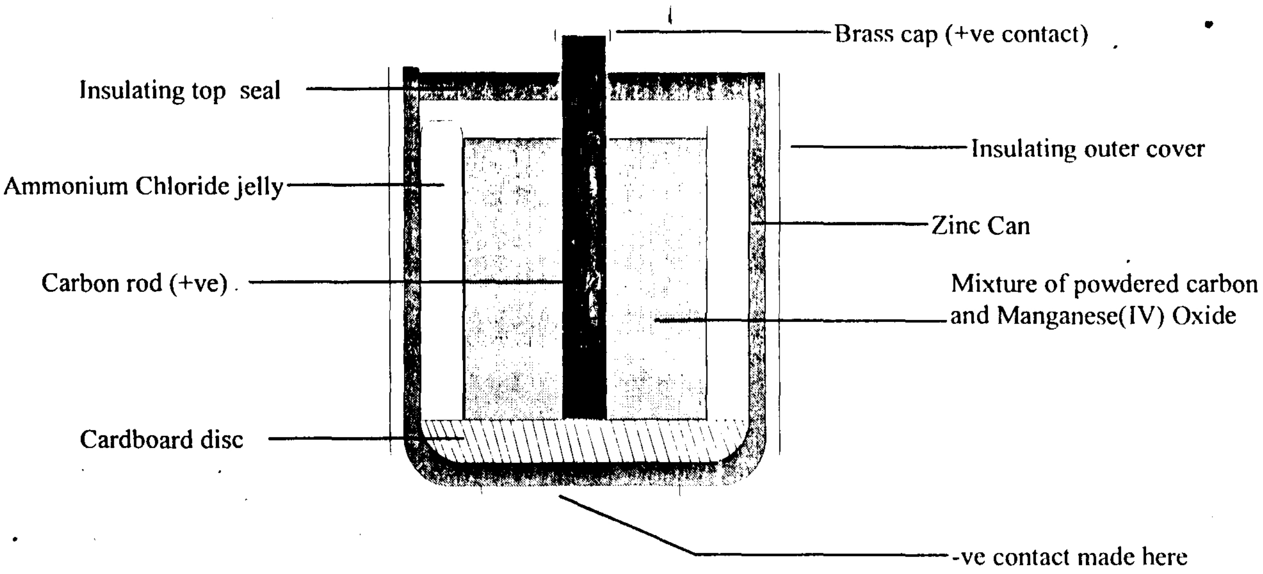


Fig. X Leclanche's dry cell

Though MnO_2 is present to act as a depolarizer (This depolarizer makes leclanches's cell better than the long time preceding volta cells) it does not totally eradicate the evolution of hydrogen gas. This is a serious defects which seems to limit leclanches cell in many ways; i.e. effective

voltage discharge is reduced by the hydrogen bubble that is formed at the possitive carbon electrode. The cell is thus easily run down and the storage life and the life span is shortened. This defect also, in this trend, makes it less economical. Therefore, there is a need for research in this area.

However, in recent discoveries, It was suggested that MnO_2 depolarising effectiveness could be enhanced when an alkaline or an alkaline earth anions are blended with it.

Hence, the objective of this research is to selectively impregnate alkaline anions on MnO_2 in order to study their effects on it by a way of increasing either its depolarizing effectiveness or its voltage output. If this is done, the questions to be answered will be which of these anions does it better, and if possible-how? does it prevent hydrogen from forming ?

It is in the mind of this research to adopt adsorption method by potentiometric titrations. By this potentiontric titration, a base (NaOH) will be titrated against the aqueous solution containing the anion. Additionally, the base will be titrated against the solution containing the anion into which some amount of MnO_2 is added. The difference in the change in volumes of titrant between this two titrations at a particular pH will be taken, and will be related to adsorption. Different concentrations of the anions in aqueous solution will likewise be used for the titrations. This will help us to know the better concentration suitable for adsorption from the analysis that will eventually involve.

Other methods which could also be used for this work are-Electrokinetic and Radio chemical methods of analysis. However, availabilty and accessibility to the apparatus needed for this methods is a limitation to their applications.

The effectiveness of MnO_2 among many factors is largely dependent on the surface area. This work will also try to determine the surface area of MnO_2 by a method of "adsorption from solution". This surface area will also tell us the nature or the modified form of the MnO_2 that will be used.

Finaly, the Isotherm upon which the adsorption anions relates to shsall be determined.

CHAPTER TWO

2.0.0 LITERATURE REVIEW

2.1 HISTORICAL BACKGROUND

The postulates that chemical and electrical phenomena were mutually related were put forward by M. L. Omonosov as early in the middle of 18th century. However, researcher drew their attention to a new field after L. Galvarn had published an article of which he outlined his investigation of the contractions of muscles in disected frogs when these muscles are connected to copper and iron wires.

This new discoveries led Alessandro Volta (1796) to make the first wet primary cells which consisted of Tin or Zinc and copper or silver seperated by pasteboard or hides soaked in water, vinegar, or salt solution. Thus, volta was credited with the discovery that a potential difference will be set up between two different metals in contact with an electrolyte. The cell so made was called voltaic pile.

The use of volta's invention quickly led to a number of important discoveries such that other scientists made volta's cell in various designs. One of special interest was introduced by William Wallaston (1816). Copper plates, doubled around Zinc plates with a space between the plates were submerged in dilute acid when the battery was in use and were withdrawn when it was not in use. This battery was a precursor of modern reserve cell.

A major step in the evolution of the battery was the Daniel cell, named for its inventor, the English Chemist John Fredric Daniel (1836). His cell was the first to include a depolariser, a modification that avoided the disadvantages of corosion and reduce the amount of hydrogen collected on the electrode which was exhibited by volta cells and gave the battery a longer life. Daniel in his invension immersed a Zinc electrode in a solution of $ZnS0_4$ (acidified with H_2S0_4) and a copper electrode in a solution of $CuS0_4$. He then placed a porous earthenware diaphram betweem the elctrodes. The Daniel cell voltage was 1.06 to 1.09 Volts In a modified form . called the gravity .cell the less dense $CuS0_4$ solution was placed over the more dense $CuS0_4$ solution. The gravity cell had a longer life than the Zn modified cell because there was less difusion of the electrolyte.

In 1866 the French Chemist George Leclanche invented the fore runner of today's Zinc- carbon dry cell. He used zinc negatives and MnO_2 (a depolariser) and carbon positive in ammonium chloride solution.

2.2 TYPES OF BATTERIES

There are generally two types or batteries : Primary batteries and secondary batteries (storage or acumulators). In primary batteries chemical reaction uses up the available electrode materials hence, the process cannot be reserved efficiently, as sthe electrode get deteriorated. The battery is then useless and must be thrown away. The storage battery, however, is constructed so that the electrode does not deteriorate. Upon discharge the battery can be recharged by an electrical generator.

2.2.1 **Primary Battery:** There are four types of primary battery: drycells, wet cells. reserve cells and fuel cells.

Dry cells: Dry primary batteries are non spillable and non-refillable. It is called a dry cell because the electrolyte is a moist paste, rather than a liquid. This makes the cell less likely to leak or spill. The electroyte usually is immobile (contained in an absorbent material). Because of this immobility, ion migration is slower in dry cells than in wet cells. Dry cells, therefore, substain lower current than wet cells. Because dry cells are non spillable, they can be used on a person, i.e in hearing aids.

Dry cells made in appreciable quantities are the Leclanches alkaline manganese (IV) oxide, and mercury cells. Silver chloride and silver oxide cells are made in lesser amounts, others in limited quantities.

2.2.2 **Leclanche's Dry Cells:** Leclanche cells are produced in various sizes and shapes. The cylindrical type is packaged as a unit cell, a well known example is the flashlight battery (commonly called a battery even though it has only one cell). A Leclanche cell has a zinc negative, an ammonium chloride electrolyte, and positives of finely divided carbon and manganese dioxide packed around a carbon - rod terminal. The unlike electrode are separated by moistened paper, starch-flour gel, or some other porous non conductor. Generally, the non-conductor contains zinc and mercuric chlorides. Mercuric chloride is used to amalgamte the zinc in order to increase the storage life.

2.3 SIZE

Batteries range in size and power from the tiny batteries used in, hearing (head phone), small electronic wrist watch to gingatic units that power submarines where a single cell has a weighed of 1 ton. They are used in flash cameras, flash lights, portable and non-portable radios, air conditioning, authomobiles and locomotives. They are also used as a standby source of emergency power. For example the telephone system in the event of power failure.

In application the cell must be constructed for its particular service, so that the best performance may be obtained consistent with cost, weight, space and operational requirement.

2.4 ELECTROCHEMISTRY OF BATTERIES

An electrochemical cell consists basically of two electrodes of unlike material placed in an electrolytic solutions. The electrodes may be placed in the same or in different electrolytic solutions. When the cell is operating, a reaction takes place between one of the electrodes and the electrolyte in which it is in contact, and thereby releasing electrons. This is an oxidation reaction, and the electrode at which this reaction occurs is called a negative electrode. The second electrode which is the positive takes on electron via external circuit. This reaction at the positive electrode is known as a reduction reaction. The negative electrode yields electrons to an external circuit, and the positive electrode accepts electron from this circuit. Thus, the electrons flow from the negative electrode to the positive electrode -a direction contrary to what is conventionally known as the direction of the current. This flow of excess electron is the electric current and can be used to power lights, motors, electronic circuits, or the other useful devices.

The overall reaction taking place within a battery is known as oxidation-reduction reaction. This reaction is driven by the chemical differences between the electrode materials. One material tends to give up electrons, the other to gain electrons. When these two half-reactions are combined, the resulting reaction proceeds automatically and current flows.

2.5 VOLTAGE

In any electrochemical cell the electrical pressure (voltage) depends upon the materials used to make up that cell, and not upon the size of the cell or the arrangement of the materials within it. All batteries having electrode of the same materials have the same voltage. The range of voltage produced by the various types of cell is not large, about 1.25V to 2V. For example the standard flshlight battery produces 1.5V. Higher voltages are obtained by connecting cells in series. A series is a string of battery connected to the negative electrode of the next. The two batteries usually found in a flash-light are connected in series to yeild 3V.

A battery can be thought of as a kind of pump used to move electrons, much,as a water pump moves water. Like water pumps batteries may be connected in series to obtain a higher "pressure". Batteries connected in parallel have higher capacity, that is they produced more current or water. Current in a battery is measured in ampere (A),and capacity amperes- hours.The ampere-hour is a measure of both how much current a battery gives and how long.

2.6 ADSORPTION

Adsorption involves the transfer of a constituent of a fluid (gas or liquid) to the surface of a liquid/solid phase. When a gas molecule is adsorbed on the surface of a solid. It settles on it very much like a condensing molecule, and is then held on the surface either by physical attractive forces (van der waals forces) or in certain cases depending on the chemical nature of the molecule and the surface by chemical forces (chemisorption). In a particular system both types of adsorption may occur as well as intermediate types.

2.6.1 **Physical Adsorption:** Physical adsorption is non specific and some what similar to the process of condensation. The forces attracting the fluid molecules to the solid surface are relatively weak, and the heat evolved during the exothermic adsorption process is of the same order of magnitude as the heat of condensation. Equilibrium between the solid surface and the gas molecules is usually rapidly attained and easily reversible, because the energy requirement are small. The energy of activation is usually no more than 4.12KJ/g mol, since the forces involved in physical adsorption decreases rapidly as the temperature is raised and is generally very small above the critical temperature of the adsorbed component.

Physical adsorption is not highly dependent on the irregularities in the nature of the surface, but is usually directly proportional to the amount of surface.

2.6.2 **Chemisorption:** The second type of adsorption is specific and involves forces much stronger than in physical adsorption. According to langmuir's pioneer work the adsorbed molecules are held to the surface by valence forces of the same type as those occuring between atoms in molecules.

Taylor suggested the name chemisorption for describing this second type of combination of gas molecules with solid surfaces.

Two kinds of chemisorption are encountered: activated and less frequently, nonactivated. Activated chemisorption means that the rate varies with temperature according to finite activation energy near zero. This is termed nonactivated chemisorption.

An important feature of chemisorption is that its magnitude will not exceed that corresponding to a monomolecular layer. This limitation is due to the fact that the valence forces holding the molecules on the surface diminish rapidly with distance.These forces become too small to form the adsorption compound when the distance from the surface is much greater than usual bond distances. The adsorption of gas on a solid takes place in several stages. The first is the movement of the gas molecules to the external surface of the solid. The second stage is the penetration of the molecules into the pores of the solid.
The third is the actual adsorption of the molecules on the site in the pore.

2.6.3 Adsorption Isotherm

A. Langmuir

I. Langmuir proposed simple formulations rates of adsorption and desorption of gases (applicable also to liquid) on solid surfaces. It is derived on the bases of several assumptions namely,

1. The adsorbed particles are associated with definite active sites on the surface of the adsorbent.
2. Only one adsorbate particle can attach itself to each site.
3. The energy of the adsorbed particle is the same at all sites on the surface and independent of the presence of other adsorbed particles at adjacent sites.

The Langmuir adsorption isotherm is deduced from the equality between the rates of adsorption and desorption at equilibrum .Let component A be the only adsorbate whose equilibrum pressure in gas phase is P_A. There is, on the surface, a definite total number N_{tot} of adsorption sites (or centres).Some of which, N_A, are occupied by the adsorbed molecules and the remainder, $N' = N_{tot} - N_A$, are left uncovered. the rate of desorption is assumed to be proportional to N_A and equal to $W_{des} = K_1 N_A$ ------------------------------------(1)

Where K_1 is the constant of desorption.

The rate of adsorption (condensation) is proportional to the number of uncovered site N^1 and the pressure of the gas:$W_{ads} = K_2 P_A \ N^1 = K_2 P_A \ (N_{tot} - N_A)$------------------------(2)

where K_2 is the rate constant of adsorption

At equilibrium $W_{ads} = W_{des}$ and $K_2P_A (N_{tot} - N_A) = K_1 N_A$.------------------------(3)

Let us introduce the adsorption factor b_A, defined as the ratio of the rates for adsorption and desorption $b_A = K_2/K_1$ --(4)

It follows from equation (3) that $N_A = N_{tot} \dfrac{b_A P_A}{1 + b_A P_A}$ ________________(5)

Let the ratio of the number of sites covered to the total number of adsorption sites (that is, the fraction of the surface covered) be designated as $\theta = N_A / N_{tot}$ -------------------(6)

Then langmuir isotherm can be written as $\theta = \dfrac{b_A P_A}{1 + b_A P_A}$ ________________(7)

Let $b_A = K$ therefore, $\theta = \dfrac{K P_A}{1 + K P_A}$ ________________(7b)

Analysis of equation (5) and (7) shows that at low pressure the quantity of adsorbed gas is proportion to its pressure $N_A = N_{tot} K P_A$---------------------(8)

and $\theta = K P_A$

At high pressures, the adsorbate tends to cover all the surface and θ tends to unity. For the adsorption of an ith compnent from a mixture of n gases, the above reasoning leads to the following equations.

$$N_i = N_{tot} \frac{b_i P_i}{1 + \sum_{j=1}^{n} b_j P_j} \quad \text{or} \quad \theta_i = \frac{b_i P_i}{1 + \sum_{j=1}^{n} b_j P_j}$$

where

k_j = adsorption factor for reactant J

N_j = Number of adsorption sites covered by the molecules reactants J.

P_j = partial pressure for reactant J

θ = fraction of surface covered by adsorbed reactant J.

The adsorption factor K_A is a function of temeprature and the heat of adsorption (the energy of interaction between the adsorption and the surface) which, within the framework of langmuir adsorption isotherm is taken to be constant and independent of the fraction of the surface covered: $K_A = K_{A,o} \exp (Q_A/RT)$

Where $K_{A,o}$ = frequency factor

Q_A = Heat of adsorption for component A.

Also, note that for the concentration form of equation (7) can be derived in the same to obtain

$\theta = \dfrac{K_c C_g}{1 + K_c C_g}$ Where K_c = adsorption factor

C_g = concentration of the adsorbable constituent in the gas

2.6.4 B. Other isotherms

Two other well known isotherms may be classified in terms of

$\Delta H_A - \theta$ dependency

(i) The Tomkin isotherm may be derived from the langmuir isotherm by assuming that the heat of adsorption drops linearly with increasing θ. The result is $\theta = K_1 \ln K_2C$ where K_1 and K_2 are constants at a given temperatures. It has been shown that a straight line drawn through the plot of θ versus log C gives a positive intercept of K and a positive slope of n.

(ii) The Freundlich isotherm can be derived by assuming a logarithmic decrease in DHa with θ, that is $\Delta H_A = -\Delta H_0 \ln\theta$

The isotherm itself has the form $\theta = KC^n$: where n has value greater than unity

Owing to its flexibility, the Frerundlich isotherm usually fits experimnetal data over a reasonable range of concentrations.

In conclusion note two points. first the Freundlich isotherm can be reduced to either langmuir or the Tomkin form by proper simplification. It may be considered a general emprical form encompassing the other more specific types. Secondly a single isotherm of the langmiur or Tomkin type cannot be expected to fit over entire range of θ.

It has been shown that a straigt line drawn through a plot of log θ versus log C should give a positive intercept of K and a positve slope of n.

(iv) Also, from recent experimental work on adsorption in a journal titled oxide and oxide film it was shown that this relationship

$$\theta = \frac{\Delta V.C}{S.100} \quad \text{holds}$$

where θ = Adsorption gmole/cm², ΔV = change in volume of titrate cm³

S = surface area of the adsorbate cm²/g

2.7 PRACTICAL METHODS OF ADSORPTION

Generally, the adsorption analysis as it relates this research work could be achieved through three different broad method of anaysis namely:

1. Electro Kinetic method
2. Radio chemical method
3. Potentiometric titration method. The method of interest

2.7.1 **Electrokinetic Method:** The electrokinetic phenomena is that which is associated with the movement of a continous medium or with the movement of a continous medium a charged surface. The four principal electrokinetic phenomena are electrophoreis, electroosmosis, streaming potential and sedimentation potential or Dorn effect.

2.7.2 **Radio Chemical Method:** This method embraces the applications of radioactive isotopes. The wide spread use of isotopes (in chemistry) is based on two fundamental properties exhibited by all radio active substances. The first property is that the disintegration rate of an isotopic sample is directly proportional to the number of radio active atoms in the sample, thus, measurement of its disintegration rate (with a Gieger counter for example) serves to analyse a radio active compound with nearly all chemical elements (notable exception - nitrogen, and oxygen which have no suitable radioactive isotopes), an isotope may be incorporated in a chemical compund, and thereafter masses of these compunds as small as 10^{-6} to 10^{-10} grammes may be measured with a high precission. Because experimental chemisry depends largely upon analysis, isotopes may be employed in most chemical problems, especially those requiring high analytical sensitivity.

The second fundamental property is that the disintegration rate is completley unaffected by the chemical form of the isotope and conversely, the property of radioactivity does not affect the chemical properties of the isotopes. By substituting or labelling a particular atom within a molecule, isotopes can be used to trace the fate of that atom during a chemical reaction.

In a unique application of radio chemical studies (like in adsorption) an understanding of diffussion is of considerable importance because the rate of many chemical reactions are governed by the rate at which chemical reactions species can diffuse through a medium to the point of reaction/adsorption. For example, the rate of many electrode process depends upon the rate of oxidation of copper ions up to the metal surface.

If a layer or radioactive copper is sandwiched between two ordinary copper samples, it is found that at elevated temperature copper ions will diffuse considerable distance within the metal.

2.7.3 **Principles of Potentiometric (General Principle)**

The procedure involved measurement of the e.m.f. between two electrodes, an indicator electrode, the potential of which is a function of the concentration of the ion to be determined, and a reference electrode of constant potential: accurate determination of the e.m.f. is crucial. In potentiometric titrations absolute potentials or potentials with respect to a standard half-cell are not usually required, and measurement are made while the titrations is in progress. The equivalence point of the reaction will be revealed by a sudden change in potential in the plot of e.m.f. readings against the volume of the titrating solution, any method which will detect this abrupt change of potential may be used. One electrode must maintain a constant, but not necessarily known potential: the other electrode must serve as an indicator of the changes in ion concentration, and must respond rapidly. The solution must of course be stirred during the titrations. A simple arrangement for potentiometric titrations is given in the fig. 2 below. A is a reference electrode, B is the indicator electrode, and C is a mechanical stirrer (it may be replaced, with advantage, by a magnetic stirrer); the solution to be titrated is contained in the beaker. When basic or other solutions requiring the exclusion of atmospheric carbon dioxide or air are titrated it is advisable to use either a three or four necked flash or a tall lipless beaker equipped so that nitrogen may be bubbled through the solution before and if necessary during titration. The e.m.f. of the cell containing the initial solution is determined and relatively large increaments (1-5ml) of the titrant solution are added until the equivalence point is approached the of the e.m.p is determined after such addition. The approach of the e.p is indicated by a somewhat more rapid change of the e.m.f. In the vicinity of the equivalence point, equal increaments (e.g. 0.1 or 0.05ml) should be added; the equal additions in the region of the e.p are particulary important when the equivalence point is to be determined by the analytical method described below. Sufficient time should be allowed after each addition for the indicator electrode to reach a reasonably constant potential (to Ca - 1-2 Millivolts) before the next increament is introduced. Several points should be obtained well beyond e.p.

To measure e.m.f. the electrode system must be connected to a potentiometer or to an electronic voltmeter, if the indicator electrode is a membrane electrode (e.g. a glass electrode) then a simple potentiometer is unsuitable and either a PH meter readings may give directly the varying pH (pM) values as titration proceeds, or the meter may be used in the millivolt mode, so that e.m.f. values are recorded. Used as a millivoltmeter, such meters can be used with almost any electrode assembling to record the results of many different types of potentiometric titrations, and in many cases the instruments have provisions for connection to a recorder so that a continous record of the titrating result can be obtained, i.e. a titration curve is produced

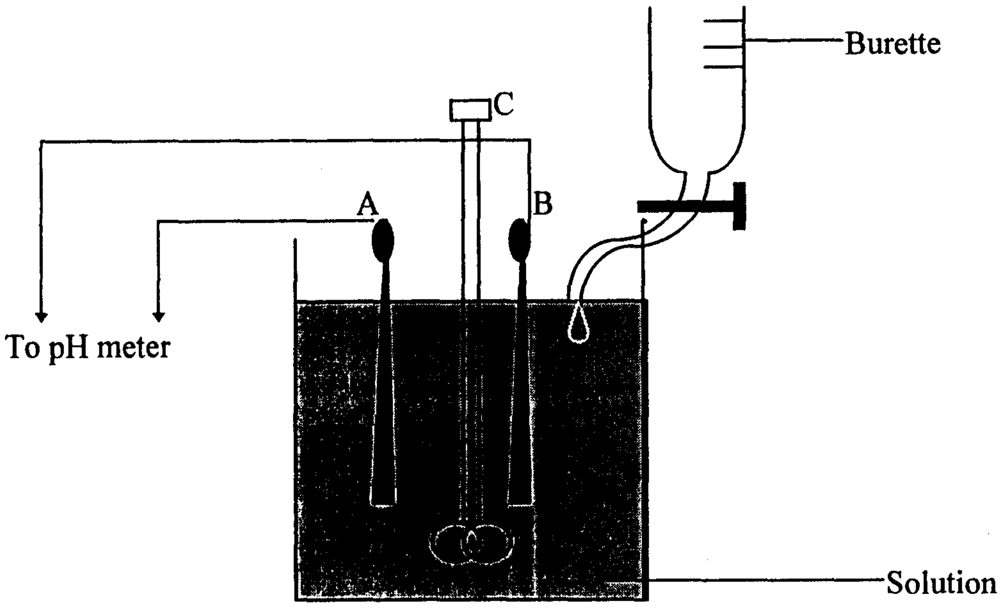


Fig. 2 Potentiometer Titration System

2.8 Manganese (IV) Oxide

Pyrolusite (MnO_2) was thought to be made of oxide of iron until the mid 18th century, when it began to be suspected that the substance contains not iron but an element unknown to science. In 1774 the Swedish chemist Carl Wilhelm Schede demonstrated that it contains a new element, and that same year his friend and compatriot Johnamn Gottlieb Gahn produced a small sample of this new metal by burning pyrolusite with charcoal.

2.8.1 Modifications of MnO_2

There are five existing modifications of MnO_2 - α(alpha), β(Beta), γ(gamma), δ(delta), ε(epsilon) and η(etha). The classification of MnO_2 is based on this modifications which differs in size of crystal, form and specific bond within the crystals. and all this play specific role to determine the quality of MnO_2 as an active material in a dry cell. Beta modification is usually used in a dry cell.

2.8.2 Properties of MnO_2

(i) Colour- MnO_2 which has a gray to gray-black clour is by far the most important oxide of manganese.

(ii) Solubility - It is insoluble in water and weak acids and bases.

(iii) Reactions- It reacts with concentrated H_2SO_4

$$2MnO_2 + 2H_2SO_4 \longrightarrow 2MnSO_4 + O_2 + 2H_2O$$

and with reducing acid such as concentrated HCl at room temperature

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

With ice-cold concentrated HCl it gives a red to brown solution which probably contains Manganese III chloride, and Manganese IV chloride

It also react with fused potassium hydroxide to form potassium manganate and hence potassium permanganate, $KMnO_4$

Other properties of MnO_2 which plays a great role in its usage in a dry cell are its

(a) Conductivity (it is an electrical semi-conductor)

(b) Void space

(c) density, bulk density, specific density

(d) surface area per unit mass

(e) Its modification β.– MnO_2 and

(f) Its depolarising ability (it absorbs hydrogen gas) usually β– MnO_2 is used for drycell production.. It has a surface area of between 10×10^4 - 1000×10^4 cm^2

Gamma has surface area of between 1000×10^4 - 2000×10^4 cm^2

2.8.3 Production of MnO_2

For Laclanche dry cells and other usage MnO_2 is manufactured by either of the following means

1. Chemically - chemical manganese dioxide (CMD)
2. Electrolytically - Electrolytic Managanse Dioxide (EMD)
3. Activatedly - Activated manganese Dioxide (AMD)

2.8.4 CMD Technological Processes of production

The following steps are the technological processes involved in the production of CMD. Pyroluisite (natural and impure MnO_2) is reacted with Nitrogen disoxide (NO_2) in the presence of water to yield an impure manganese nitrate $Mn(NO_3)_2$ This is further treated with hydrogen sulphide (H_2S) with the pH being regulated to produce pure $Mn(NO_3)_2$.

The pure $Mn(NO_3)_2$ is then treated with ammoniumm carbonate to yeild and impire precipitate of manganese carbonate $MnCO_3$, which is further made pure by washing and drying. The pure $MnCO_3$ moves to the next stage where it reacts with oxygen present in air to produce an indefinite variable oxide (MnO_x) of manganese.

Finally, MnO_x is treated with sodium chlorate ($NaClO_3$) and H_2SO_4 to yield MnO_2 which is then washed and the drying being regulated to yield a pure form of chemically produced MnO_2.

The following reactions summarizes this process.

1. $MnO_2 + 2NO_2 \xrightarrow{H_2O} \underset{\text{(impure)}}{Mn(NO_3)_2}$
2. $Mn(NO_3)_2 \xrightarrow{pH,\ H_2S} \underset{\text{(pure)}}{Mn(NO_3)_2}$
3. $Mn(NO_3)_2 + (NH_4)_2CO_3 \longrightarrow \underset{\text{(impure)}}{MnCO_3} + 2NH_4NO_3$
4. $MnCO_3 \xrightarrow[\text{drying,}]{\text{washing}} \underset{\text{(pure)}}{MnCO_3}$
5. $MnCO_3 \xrightarrow[O_2\text{ in air}]{} MnO_x\ (+MnCO_3)$
6. $MnO_x + NaClO_3 + H_2SO_4 \longrightarrow \underset{\text{(impure)}}{MnO_2} + NaCl + Na_2SO_4$
7. $MnO_2 \xrightarrow[\text{Regulating the drying}]{\text{washing}} MnO_2$

2.8.5 Laboratory Preparation of MnO_2

MnO_2 can be manufactured in the laboratory by heating $Mn(NO_3)_2$ at 180 - 200°C or by heating a mixture of manganese carbonate, $MnCO_3$ and potassium chlorate at 300°C. there is some questions about the purity of the product obtained; it has been stated that the purest product contains only 98% MnO_2 . This was attributed to the formation of a mixture of MnO_2 and MnO.

2.8.6 Adsorption from solution MnO_2 specific surface determination)

Adsorption of solutes from solution has frequently been recommended for the estimation of specific area S, of a solid. The method is simple and attractive. This involves shaking up some solid with known volume of solution at constant temp, until there is no further change in concentrate and then analyse the supernatant liquid, by a simple calculation of apparent adsorption per gramm of solid is readily found. The determination is repeated with solution varying over a wide range of concentrations so that the isotherm of concentrate change can be plotted.

The amount adsorbed per gram of solid depends on the specific area of the solid, the equilibrium solute concentration in solution, the temperature, and the nature of the molecule involved. From measurements at constant temperature, one can obtain a plot of N, the number of moles adsorbed per gram of solid, versus C, the equilibrium solute concentration.

Monolayer adsorption is distinguish by the fact that the amount adsorped reaches a maxiumm value at moderate concentrations (coresponding to complete coverage of the surface of the adsorbent by a layer one molecule thick) and remaining constant with further increase in concentration. The langmuir isotherm which can be derived from either kinetic or equilibrium arguments has a form appropriate to adsorption from solutions as

$$\theta = \frac{KC}{1+KC} \quad \text{-----------------------------------(1)}$$

Where θ is the fraction of the solid surface covered by adsorped molecules and K is a constant at constant temperature Now $\theta = N/N_m$ where N is the number of moles adsorped per gram of solid at an equilibrium solute concentration C and N_m is the number of moles per gram required to form a monolayer. Making this substitution and re-arranging eqn. (1) we obtain

$$\frac{C}{N} = \frac{C}{N_m} + \frac{1}{KN_m} \quad \text{---------------------------------(2)}$$

If the langmuir isotherm is an adequate description of the adsorption process, then a plot of C/N versus C will yield a sraight line with slope $1/N_m$. If the area occupied by an adsorbed molecule on the surface is known, then the specific area A (in square meters per gram) is given by $A = N_m N_o \sigma \times 10^{-20}$ -----------------------------------(3)

where N_o is avogadros number and σ is given in square angstroms.

2.9.0 Electric Charge

Electric charges are the quantity of electrcity that flow in elctric currents or that accumulate on the surface of dissimilar non metalic substances that are rubbed together vigorously. Electric charge, a basic property of matter, occurs in discrete natural units and is neither created nor destroyed. Electric charges are of two general types: positve and negative. Many fundamental or subatonic, particles of matter have the property of electric charge. For example electrons have negative charges and proton have positive charges but neutrons have zero charge. The negative charge of each electron is found by experiment to have the same magnitude to that of proton. Charges thus exists in natural units equal to the charge of an electron or a proton, a fundamental physical constant.

Electric charge is considered in any isolated system, in any chemical and nuclear reaction, the net electric charge is constant. The surface electric charge $E = nF\theta$ where

E = surface electric charge μc mole/cm^2

n = number of ionic charges of the substance

F = Faraday consttant 96500C

θ = adsorption mole/cm^2

was derived from Nerst equation $E^1 = E^o - \frac{RT}{nf} \frac{a_{product}}{a_{reactant}} = V$--------------------(1)

E^1 = energy

E^o = standard electrode

V = Volt

Hence, energy as it relates to charged particles considering Faraday constant could be expressed as $E = nFV$ --------------------(2)

Likewise, surface charge, E as a result of the presence of particles on an adsorbate could be expressed as $E = nF\theta$ ------------------(3)

CHAPTER THREE

3.0.0 EXPERIMENTAL WORK

3.1.0 Chemicals and Equipment

3.1.1 Chemicals

3.1.1.1 Chemicals (for the determination of density of MnO_2)

The following two chemicals were used

-Manganese (iv) oxide, MnO_2

-Water

3.1.1.2 Chemicals (used in the "adsorption from solution experinment to determine specific area of MnO_2)

* Pulverised MnO_2 10g

* 0.15M acetic acid, 500ml

* 0.1M Sodium hydroxide, 500ml

* Phenolpthalein indicator

3.1.1.3 Chemicals (used in potentiometic titration)

All these chemicals were produced in England by M & B chemical company

The chemicals that were used for this project work are as follows:

* Manganese (iv) oxide MnO_2

produced in England by M & B, chemical company

* Sodium hydroxide, NaOH

* Sodium chloride NaCl

* Sodium nitrate, $NaNO_3$

* Sodium sulphate Na_2SO_4

* Sodium Bromide NaBr

All these chemicals were produced in England by M & B chemical company.

Nitrogen gas.

Highly compressed at 250 Bar in $1m^3$ AIR LIQUIDE cylinder.

Nitrogen gas was necessarily used in the experiment in order to

(i) Provide an inert environment in the titrating vessles and thus inhibit side reaction

(ii) Drive off oxygen and carbondisoxide which might be present

(iii) Nitrogen takes the place of oxygen molecule present in the aqueos solution and perform its function by providing the necessary electrons that make up the quantity of oxygen needed in MnO_2 molecule.

3.1.2.0 **Equipment**

3.1.2.1 Equipment (for the determination of density of MnO_2)

* Density bottle

* Weighing balance

, Brain weighs B300 made in U.S.A. by OHAUS scal corporation

3.1.2.2 Equipment/Apparatus (for the determination of surface area of MnO_2)

* Seven 250ml Erlenmeyer flask with rubber stoppers
 - SIMAX Czechoslovakia

* Three funnels with funnel holder

* Fine porosity filter paper

* Three pyrex 250ml beakers, England

* Electric shaker - Gallenkamp flask shaker, made in England

* Analytical balance - AE160

* One 10ml and one 50ml burrette - Technico EX 20°C BS 846, U.K

* Burrette stand holders

* Several 100ml titration flasks - Pyrex, made in England

* 10-, 25-, 50-ml pipette - SCHOTT DURAN DIN B EX 20°C

* Spatula

* Wash glass

3.1.2.3 Equipment (for potentiometric titration)

The apparatus used were those of the potentiometric titrations

* pH meter EIL 7045/46 PH meter produced by Kent Industrial measurement Limted, England

* Magnetic stirrer - Migma stirrer

* Magnetic follower

* Weighing balance- Brainweigh B 300 made in U.S.A. by OHAUS scal corporation

* 50 ml Burrette- Jaytec EX 20°CBS 846 50 ml

* 25 ml pipette- SCHOTT DURA DIN B EX 20°C 25 ml pipetter

* 10 ml pipette- Technico BS EX 20o C ml made in England

* 10 ml beakers- Simax czechoslovia (csn) 10 ml

* Pyrex 250 ml beakers, England

- Technico class B 100 ml beakers, England
- 1000 cm³ volumetric flask
- 150 cm³ volumetric flask
- Nitrogen gas regulator (guage)
- Tripod stand and a clamp for clamping burrette
- A funnel

3.2 PREPARATIONS OF CHEMICALS USED IN THE POTENTIOMETRIC TITRATION

(a) Sodium hydroxide, NaOH

4g of NaOH was dissolved in some quantity of distil water, and was made up to 1000 cm³ in a cleaned volumetric flask to give 0.1 NaOH. The molar weight of NaOH being 40g.

Considering the molar weight of NaCL, $NaNO_3$, Na_2SO_4 and NaBr, appropriate mass of each of them were dissolved and then made up to 150 cm³ of distil water to first GET 1M of each of them. After the first round of experiment with the 1M solution, the remaining solutions was diluted with appropriate volume of distil water with a resulting solution of 0.1M

Subsequently, 0.01m and 0.001m of the solutions were made likewise.

3.3.0 METHODOLOGY

3.3.1 Density Determination

A dried clean density bottle was weighed empty. The weight was noted as m_1(g) it was then filled with some quantity of MnO_2 and the weight noted as m_2 (g). The remaining volume space was further filled with water and then weighed again. This was regarded as m_3(g). Finally the density bottle was empitied cleaned, dried, filled with water and then reweighed. This was noted as m_4(g). From this measured weight m_1 , m_2, m_3, and m_4, the density of MnO_2 was calculated see appendix A.

Surface area [illegible] determinant [illegible]

3.3.2 Adsorption from solution (methodology)

Seven 250-ml Erlenyar flask were thoroughly clean and dried.

Using analytical balance 1g of manganese iv oxide was weighed into six of the flask. 100 -ml of acetic acids of the following concentrations 0.15, 0.12, 0.09, 0.06, 0.03

and 0.015 m were then added to each of the flask. An additional 100 ml of 0.03M acid was also added to the seventh flask which does not have MnO_2. This was to serve as a control.

The flasks were further tight fitted with stopper and were then shaken periodically with a shaker for a period of 30 min after which they were left overnight in order to allow for equilibrium.

All the samples were further filtered through fine filter papers and the first 10 mls of the filtrate were discraded as a precaution against adsorption of the acid by the filter paper.

Two 25ml of the filtrate of each sample were titrated against 0.1M sodium hydroxide using phenolphathalein as indicator 10 ml burrette was used for the titration of the 0.03 and 0.015 samples of the filtrate.

From the values of the initial and final concentrations of acetic acid in 100 ml of solution the number of moles present before and after adsorption were calculated and the number of moles N adsorbed were obtained by difference.

The valuses of C/N versus C were plotted and the best lives through these points drawn. C is the equlibrium concentration. The number of moles per gram, Nm required to form a monolayer was then calculated from the slope.

On the assumption that adsorption area of acetic acid is 21 Å^2 the area per gram of MnO_2 was calculated from Eqn 3, section 2.8.4

3.3.3 Protentiometric Titration (methdology)

A clean 50 ml burrette was washed with distil water and was additionally rinsed with some little quantity of the prepared 0.1M NaOH. The burrette was then clamped on a tripod stand and the aqueous solution, 0.1M NaOH was poured into it to zero mark using a funnel. It was also ensured that there was no air bubble present.

A clean 100ml beaker was rinsed with water and 50 ml of 1M $NaNO_3$, solution was pipette into it.

A magnetic follower to provide a continous stirring was put into the solution and the beaker was then placed on a magnetic stirrer connected to a power source.

A reference electrode and an indicator electrode (built into one) connected to a PH meter was hanged into the solution in the beaker via an electrode holder.

A Nitrogen gas jet being regulated by the guage from a Nitrogen gas source was addionally directed into the solution in the beaker.

After bubbling the solution with the Nitrogen gas and a continous gas jetting being maintained, a contionous stirring was then initiated by switching on the magnetic stirrer. After a while, the pH meter counter gets stablizer and the initial pH when there was no drop of the titrant was read from the pH meter indicator counter.

Subsequently, 0.5 mls of the titraant (NaOH) were added from the burrette and the PH was noted for every 0.5 mls drops. Usually, sufficient time was allowed (mostly not more than two minute) after each addition for the indicator electrode to reach a reasonably constant value before taking the reading, and hence before the next increment was introduced. This 0.5 ml increament and their correspoonding pH were noted for the total 7.0 ml additions i.e 14 readings, and the increament is stopped.

The stirrer was then switched off and the solution was poured away after removing the magnetic follower. The beaker was made cleaned and was again rinse with distil water. The magnetic stirrer also being cleaned before using it for the next round.

Next, 50 mls of 1M $NaNO_3$ was again pipette into the beaker and 2g of MnO_2 was added. The titration was repeated and the pH were read for each 0.5 ml drop of NaOH as before.

The datas gotten from the experiment were used to plot two curves on a graph sheets curves, 1.pH of solution (without MnO_2) against change in volume of the titrant (NaOH) .

2. pH of solution (with MnO_2) against change in volume of the titrant

The change in volume, ΔV for the two curves at the pH of 9 was then determined and calculated from the graph. The adsorption and surface electric charge were determined by calculation.

Further, the above procedures were repeated for 0.1 M. 0.01M and 0.001M of the $NaNO_3$. Their adsorption and their surface electric charges were also determined in the same way.

Further more, all the above procedures were repeated for different concentrations (1M, 0.1M, 0.01M and 0.001M) of Na_2SO_4, NaCl and NaBr. Their results are presented in chapter four of this work. The calculations are shown in Appendix C.

CHAPTER FOUR

4.0.0 RESULTS

4.1.0 RESULTS/TABLES OF RESULTS

4.1.1 Result from MnO_2 density determination experiment.

The density of MnO_2 was determined to be equal to

1. Locally made MnO_2 - 2450Kg/m^3
2. Refined MnO_2 - 3580Kg/m^3

4.1.2 Tables of results from specific area of MnO_2 determination experiment

Initial conc. of acetic acid (M)	0.15	0.12	0.09	0.06	0.03	0.015
Volume of acetic acid (ml)	50	50	50	50	50	50
Volume of 0.1M NaOH (ml)	71	65	49.4	34.2	17.74	8.82

Table x: Datas from the Titration of 0.1M NaOH against various concentration of acetic acid.

C_1 (M)	C(M)	N	C/N
0.15	0.142	0.008	17.75
0.12	0.13	-0.01	-13.0
0.09	0.0988	-0.0088	-11.23
0.06	0.0684	-0.0084	-8.14
0.03	0.03548	-0.00548	-6.47
0.15	0.01764	-0.00264	-6.68

Table y: showing concentrations and the moles based on calculation from table x.

C_1 = Initial concentration of acetic acid, M

C = Equilibrium concentration of acetic acid, M

N = Number of moles

4.1.3 Tables of experimental datas from potentiometric titration experiment

The following datas shown in the tables below are the results from the potentiometrics adsorption titration experiment of 0.1M NaOH against different concentrations of aqueous solution containing the anions in question.

A. NaOH vs $NaNO_3$

To determine the adsorption of NO^-_3

1M $NaNO_3$

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	6.85	10.02	10.44	10.66	10.81	10.92	11.02	11.12
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.18	11.23	11.28	11.32	11.36	11.40	11.43	

1M $NaNO_3$ MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	2.62	4	4.89	6.90	9.21	10.00	10.40	10.61
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	10.77	10.85	10.95	11.03	11.10	11.17	11.21	

Table 1: Tables of datas for the titration of 0.1M NaOH against 1M$NaNO_3$

Vol of successive additions of titrant (ml)	0.0-0.50	0.50-1.00	1.00-1.50	---------	6.50-7.00
Diffeence in pH	3.17	0.42	0.22	---------	0.03

→

Decreasing differences in pH

Table 1a: Showing the decreasing differences in pH with successive additions of titrants in 1M $NaNO_3$ an extract from table 1

Corresponding volume of NaOH (with or without MnO_2) (ml)	0.00	2.0	4.0	7.0
Differences in pH	1.61	1.6	0.41	0.22

→

Decreasing differences in pH

Table 1b: Showing decreasing differences in pH for 1M $NaNO_3$ with and without MnO_2 considering equal volume of NaOH.

0.1M $NaNO_3$

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	8.56	10.02	10.39	10.59	10.72	10.83	10.92	10.99
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	0.1
pH	11.06	11.12	11.16	11.21	11.25	11.28	11.32	9.0

with MnO_2

V_{NaOH} (ml))	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.89	6.30	9.45	10.05	10.35	10.55	10.69	10.81
V_{NaOH} (ml))	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	10.89	10.97	11.03	11.08	11.14	11.18	11.22	

Table 2: Table of datas for the titration of 0.1M NaOH Vs 0.1M $NaNO_3$

0.01M $NaNO_3$ 8.9 12.9

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	8.92	12.34	12.71	12.94	13.04	13.16	13.24	13.31
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	13.37	13.47	13.55	13.58	13.62	13.64	13.67	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	2.03	5.80	8.96	9.86	10.20	10.38	10.52	10.61
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	10.71	10.77	10.83	10.88	10.92	10.96	11.00	

Table 3: Table of datas for the titration of 0.1M NaOH Vs 0.01M $NaNO_3$

0.001M $NaNO_3$

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	6.67	10.46	10.86	11.07	11.20	11.31	11.39	11.46
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.53	11.58	11.62	11.66	11.70	11.74	11.76	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.15	8.48	10.16	10.46	10.72	10.90	11.00	11.09
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.15	11.22	11.27	11.33	11.37	11.41	11.44	

Table 4: Table of datas for the titration of 0.1M NaOH Vs 0.001M $NaNO_3$

B. NaOH Vs Na_2SO_4

To determine the adsorption of SO^{2-}_4

1M $NaSO_4$

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	6.54	11.80	11.15	11.40	11.52	11.62	11.70	11.77
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.83	11.88	11.93	11.97	12.01	12.04	12.07	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.66	4.12	5.07	8.05	9.28	10.31	10.72	11.00
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.13	11.27	11.39	11.48	11.52	11.58	11.64	

Table 5: Table of datas for the titration of 0.1M NaOH Vs 1M Na_2SO_4

0.1M Na_2SO_4

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	6.74	10.80	11.22	11.43	11.57	11.66	11.78	11.84
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.91	11.96	12.00	12.05	12.09	12.13	12.16	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.55	4.85	8.35	10.45	11.02	11.28	11.46	11.57
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.67	11.74	11.80	11.85	11.90	11.94	11.98	

Table 6: Table of datas for the titration of 0.1M NaOH Vs 0.1M Na_2SO_4

0.01M Na_2SO_4

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	7.07	10.97	11.33	11.52	11.68	11.77	11.81	11.88
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.94	12.00	12.05	12.10	12.14	12.18	12.21	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.39	5.40	8.80	10.43	10.96	11.24	11.41	11.54
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.64	11.73	11.78	11.82	11.86	11.90	11.94	

Table 7: Table of datas for the titration of 0.1M NaOH Vs 0.01M Na_2SO_4

0.001M Na_2SO_4

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	9.38	11.22	11.56	11.76	11.90	12.00	12.09	12.15
V_{NaOH} (ml))	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	12.21	12.26	12.31	12.35	12.38	12.42	12.45	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.22	6.85	9.57	10.66	11.01	11.22	11.39	11.50
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.59	11.67	11.72	11.76	11.82	11.86	11.91	

Table 8: Table of datas for the titrations of 0.1M NaOH Vs 0.001M Na_2SO_4

C. NaOH Vs NaCl

To determine the adsorption of Cl^-

1M NaCl

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	6.78	11.13	11.49	11.73	11.85	11.98	12.08	12.16
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	12.23	12.28	12.34	12.39	12.44	12.48	12.51	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.03	4.17	6.35	9.10	10.42	10.66	11.21	11.37
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.46	11.65	11.77	11.87	11.96	12.03	12.08	

Table 9: Table of datas for the titrations of 0.1M NaOH Vs 1M NaCl

0.1M NaCl

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	7.77	11.47	11.80	12.03	12.14	12.25	12.33	12.41
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	12.46	12.52	12.56	12.61	12.65	12.68	12.72	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.36	4.17	6.94	8.14	9.92	11.25	11.57	11.79
V_{NaOH} (ml))	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.94	12.03	12.13	12.20	12.27	12.32	12.37	

Table 10: Table of datas for the tirations of 0.1M NaOH Vs 0.1M NaCl

0.01M NaCl

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	8.17	11.42	11.81	12.06	12.18	12.29	12.39	12.46
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	12.52	12.57	12.62	12.66	12.70	12.74	12.76	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.19	7.08	9.97	10.83	11.15	11.37	11.52	11.63
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.71	11.79	11.85	11.91	11.95	11.98	12.02	

Table 11: Table of datas for the titrations of 0.1M NaOH Vs 0.01M NaCl

0.001M NaCl

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	7.40	12.09	12.45	12.67	12.82	12.94	13.03	13.11
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	13.18	13.23	13.28	13.32	11.36	13.40	13.44	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	4.33	8.53	11.17	11.99	12.30	12.54	12.67	12.79
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	12.89	12.97	13.03					

Table 12: Table of datas for the titrations of 0.1M NaOH Vs 0.001M NaCl

D. NaOH Vs NaBr

To determine the adsorption of Br^-

1M NaBr

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	5.77	10.04	10.32	10.55	10.73	10.85	10.98	11.06
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.13	11.19	11.25	11.30	11.35	11.40	11.45	11.46

47

48

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	2.54	3.90	7.10	8.81	10.07	10.44	10.74	10.86
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	10.99	11.08	11.14	11.21	11.26	11.32	11.37	

49

Table 13: Table of datas for the titrations of 0.1M NaOH Vs 1M NaBr

0.1M NaBr

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	6.78	10.52	10.91	11.11	11.26	11.37	11.45	11.52
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.58	11.63	11.69	11.73	11.77	11.80	11.83	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	2.83	4.90	7.44	9.50	10.31	10.69	10.89	11.03
V_{NaOH} (ml))	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.17	11.27	11.34	11.40	11.46	11.50	11.55	

Table 14: Table of dats for the titrations of 0.1M NaOH Vs 0.1M NaBr

0.01M NaBr

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	6.57	10.72	11.04	11.23	11.37	11.49	11.57	11.64
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.70	11.75	11.80	11.85	11.88	11.92	11.94	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	2.95	6.23	9.04	10.18	10.60	10.88	11.05	11.22
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.31	11.42	11.48	11.54	11.59	11.64	11.69	

Table 15: Table of datas for the titrations of 0.1M NaOH Vs 0.01M NaBr

0.001M NaBr

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	6.54	11.21	11.56	11.78	11.92	12.02	12.10	12.16
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	12.23	12.28	12.33	12.36	12.40	12.44	12.48	

with MnO_2

V_{NaOH} (ml)	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
pH	3.17	5.91	8.32	9.73	10.61	11.05	11.28	11.44
V_{NaOH} (ml)	4.0	4.5	5.0	5.5	6.0	6.5	7.0	
pH	11.58	11.68	11.77	11.84	11.90	11.95	12.00	

Table 16: Table of datas for the titrations of 0.1M NaOH Vs 0.001M NaBr

Anions salt	Concentration solution (M)	change in volume ΔV at pH of 9 (cm^3)	Adsorption (mole/cm^2) θ	Log of conc.	Log θ
$NaNO_3$					
	1	1.4	8.143	0	-11.089
	0.1	0.75	4.362	-1	-11.36
	0.01	1.0	5.816	-2	-11.235
	0.001	0.4	2.327	-3	-11.877
Na_2SO_4					
	1	1.7	9.888	0	-11.00
	0.1	1.0	5.816	-1	-11.235
	0.01	0.9	5.235	-2	-11.28
	0.001	0.85	4.944	-3	-11.306
NaCl					
	1	1.2	6.980	0	-11.156
	0.1	1.6	9.306	-1	-11.031
	0.01	1.15	6.689	-2	-11.17
	0.001	0.4	2.326	-3	-11.63
NaBr					
	1	1.3	7.561	0	-11.12
	0.1	1.0	5.816	-1	-11.235
	0.01	0.65	3.781	-2	-11.42
	0.001	1.0	5.816	-3	-11.235

Table 17: Tables of results from potentiometric titrations

Concentration (M) / Anions/Surface charge	1M	0.1M	0.01M	0.001M
NO_3^-	0.79µc	0.42µc	0.56µc	0.225µc
SO_4^{2-}	1.91µc	1.12µc	1.01µc	0.95µc
Cl^-	0.67µc	0.89µc	0.65µc	0.225µc
Br^-	0.73µc	0.56µc	0.36µc	0.56µc

Table 18: Showing calculated surface charges for all the concentration of the anions

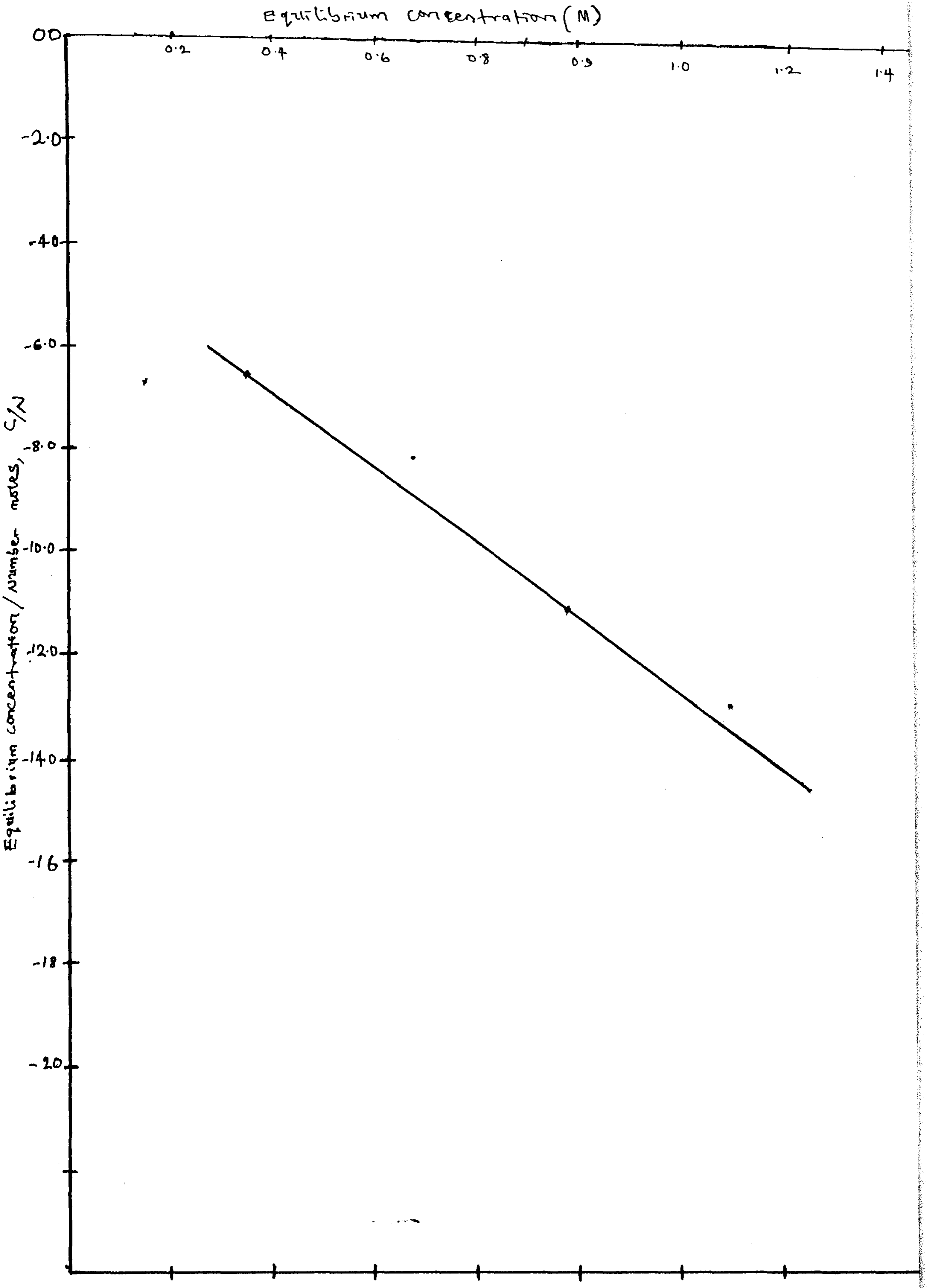


Fig y: MnO_2 Specific area determination.

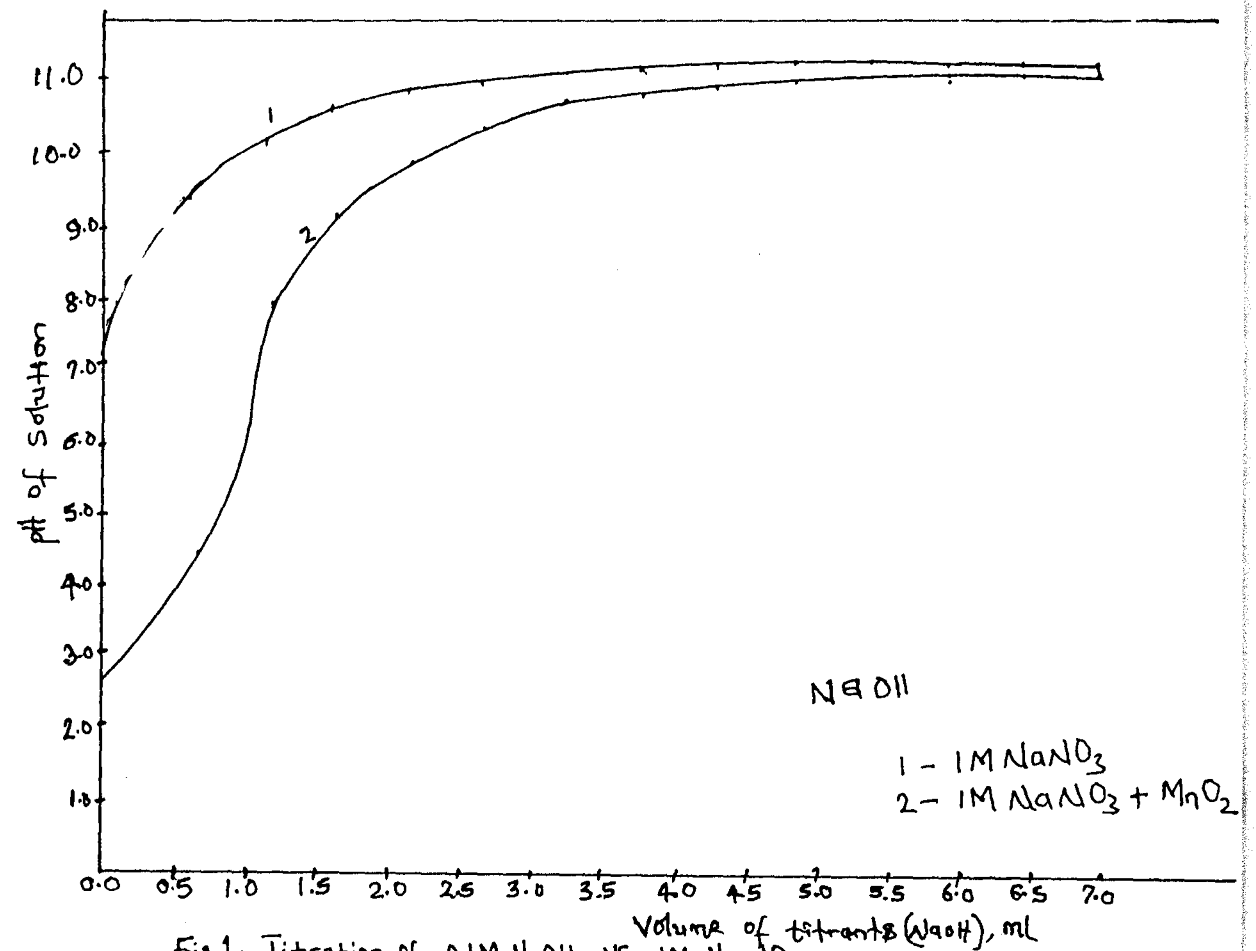


Fig 1. Titration of 0.1M NaOH VS 1M $NaNO_3$

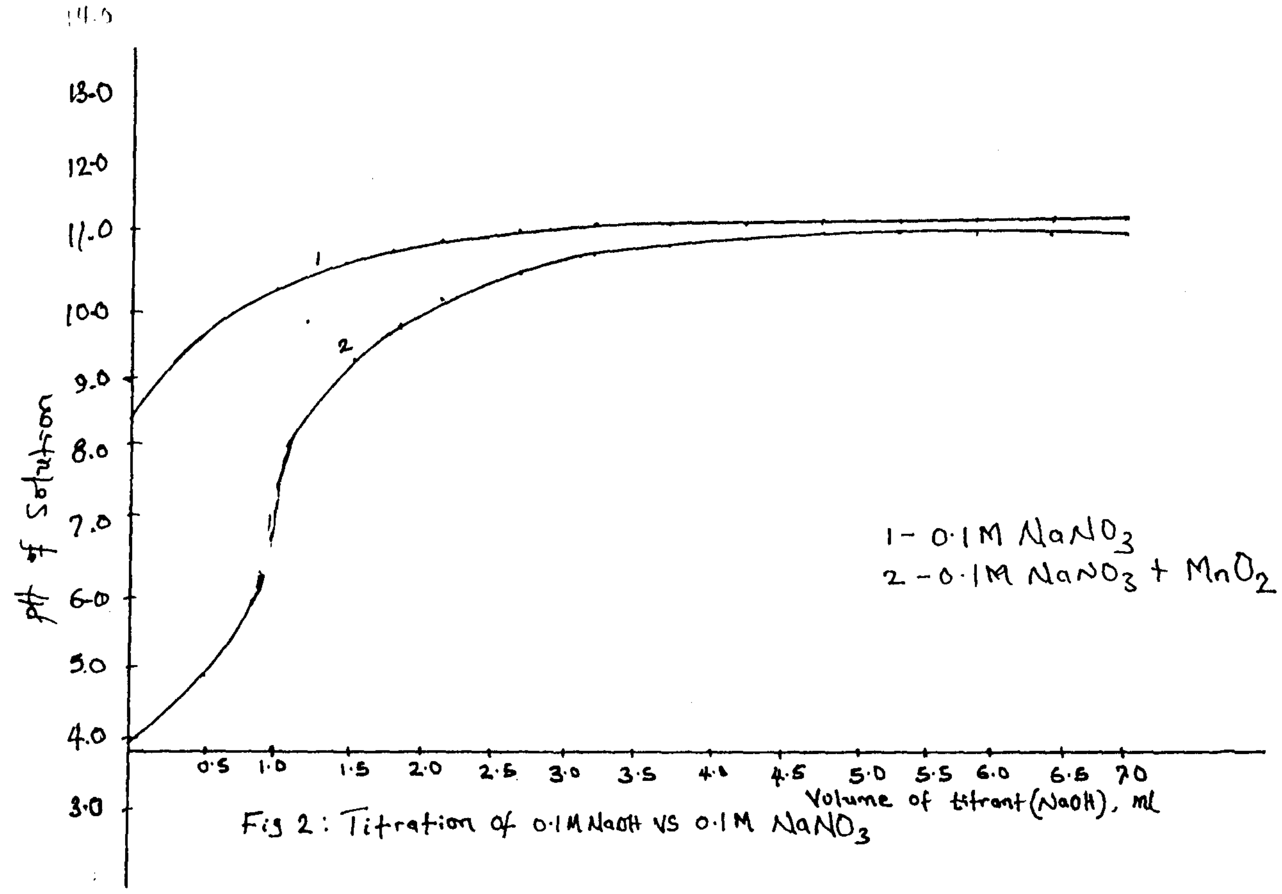
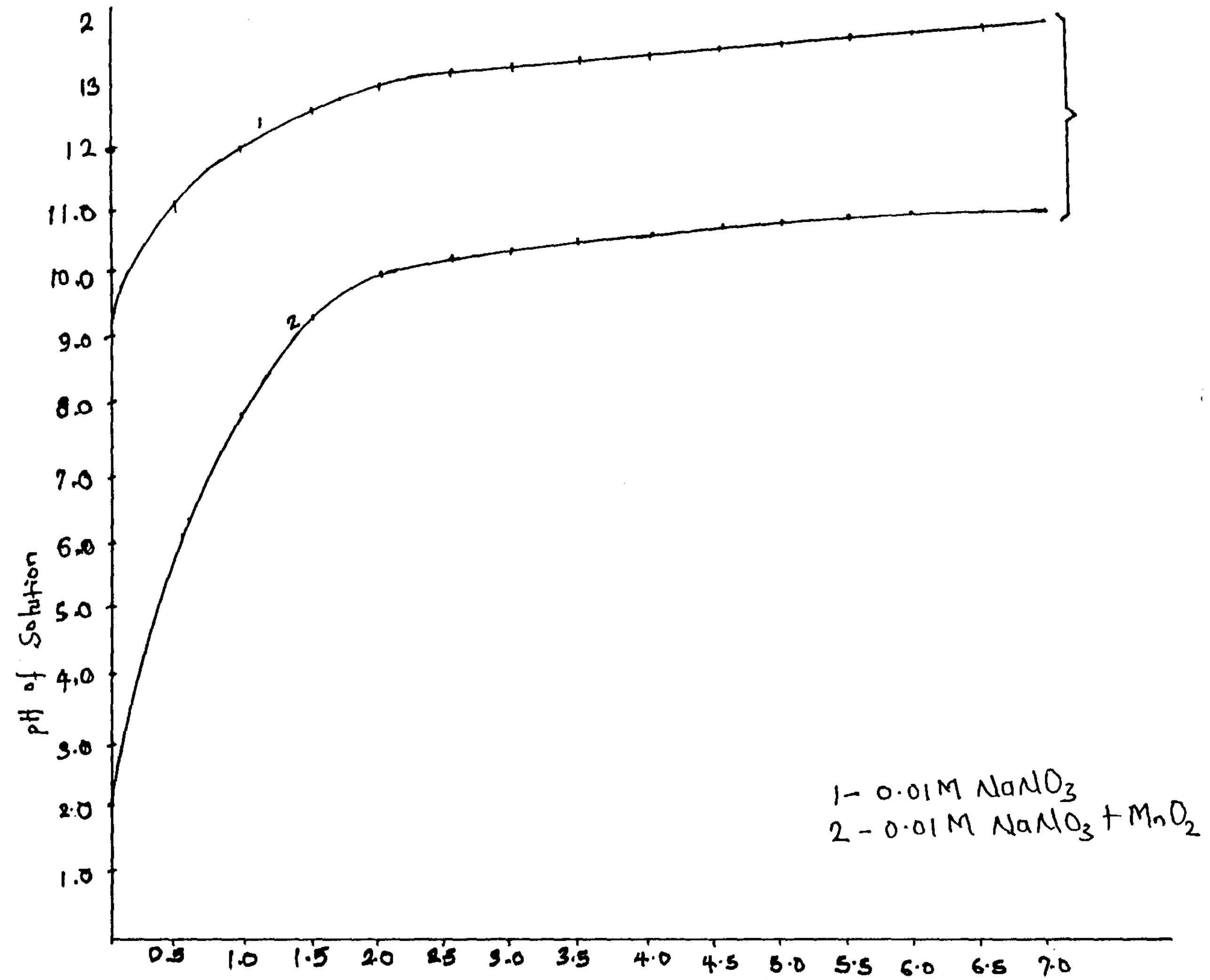


Fig 2: Titration of 0.1M NaOH VS 0.1M $NaNO_3$



Fis 3: Titration of 0.1M NaOH VS 0.01M $NaNO_3$

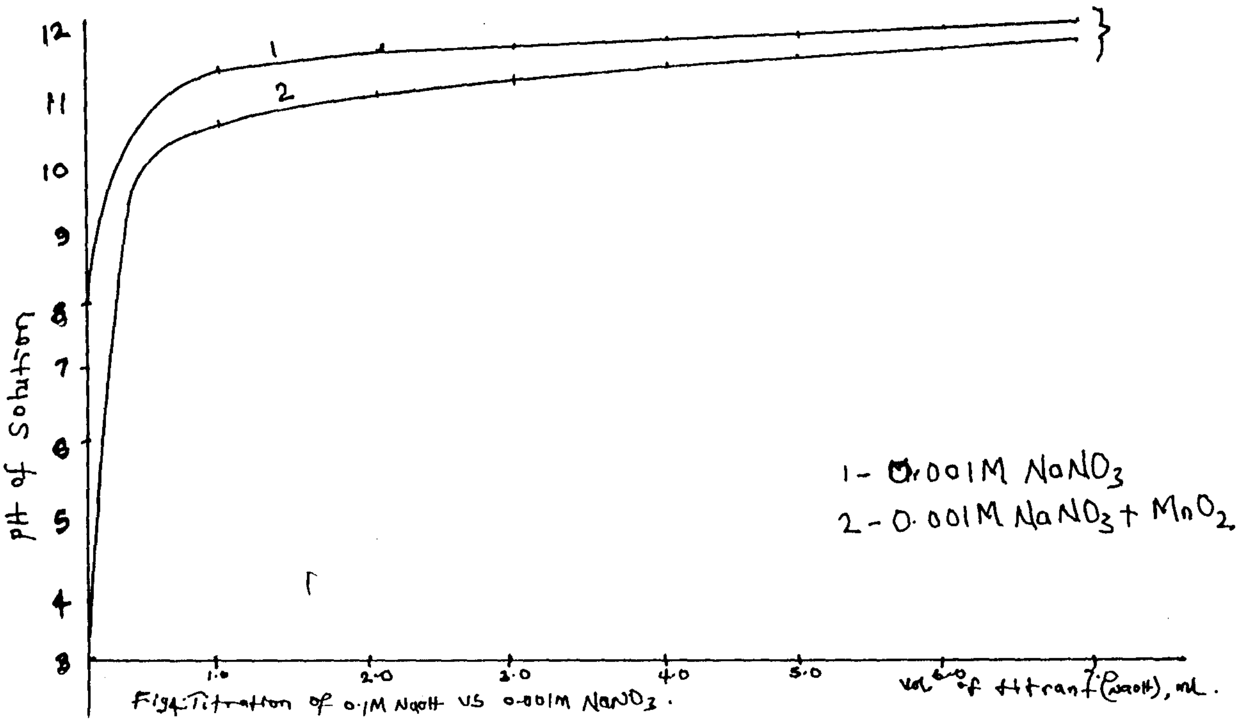


Fig4: Titration of 0.1M NaOH VS 0.001M $NaNO_3$.

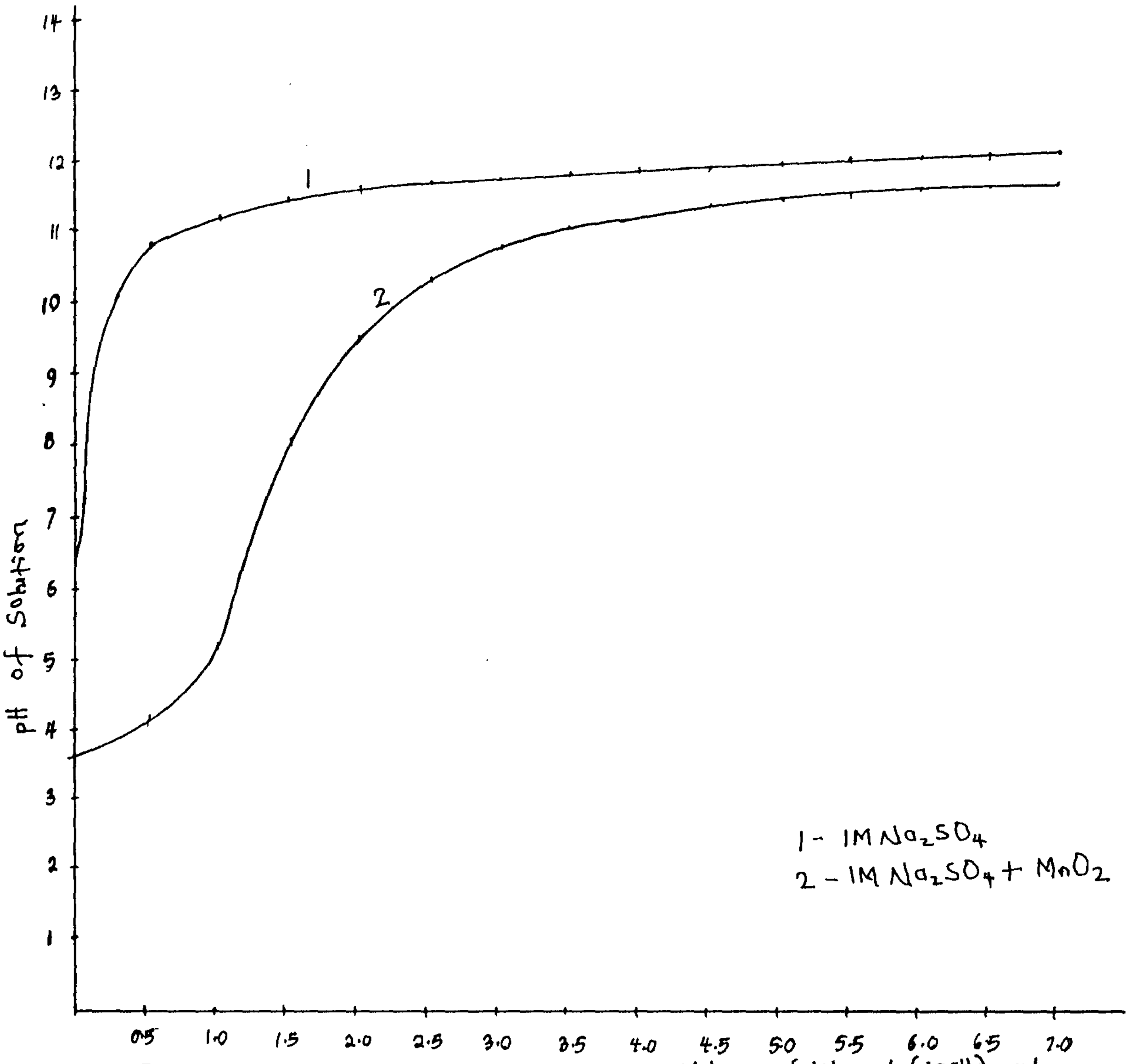


Fig 5: Titration of 0.1MNaOH vs 1M Na_2SO_4.

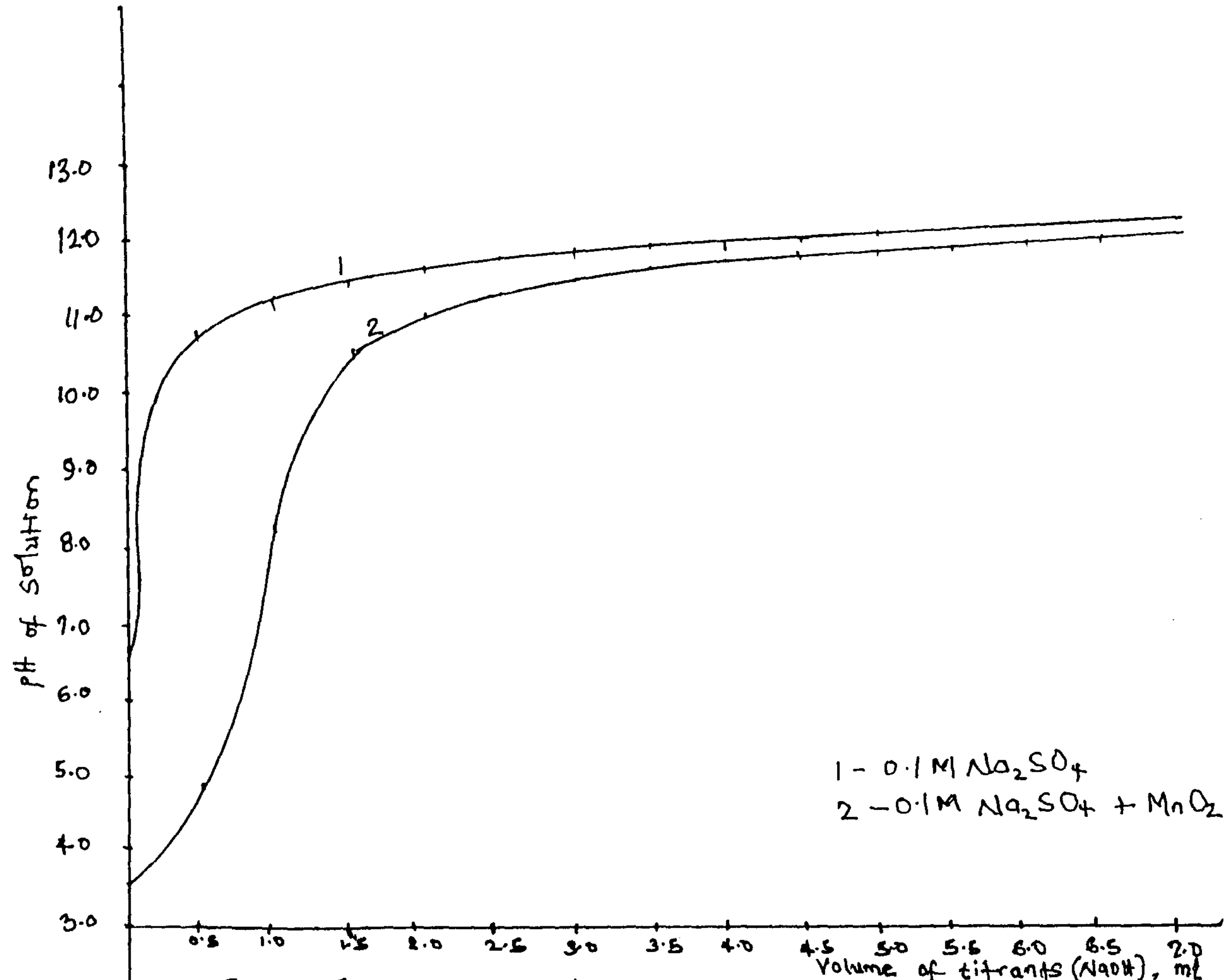


Fig 6: Titration of 0.1M NaOH vs 0.1M Na_2SO_4

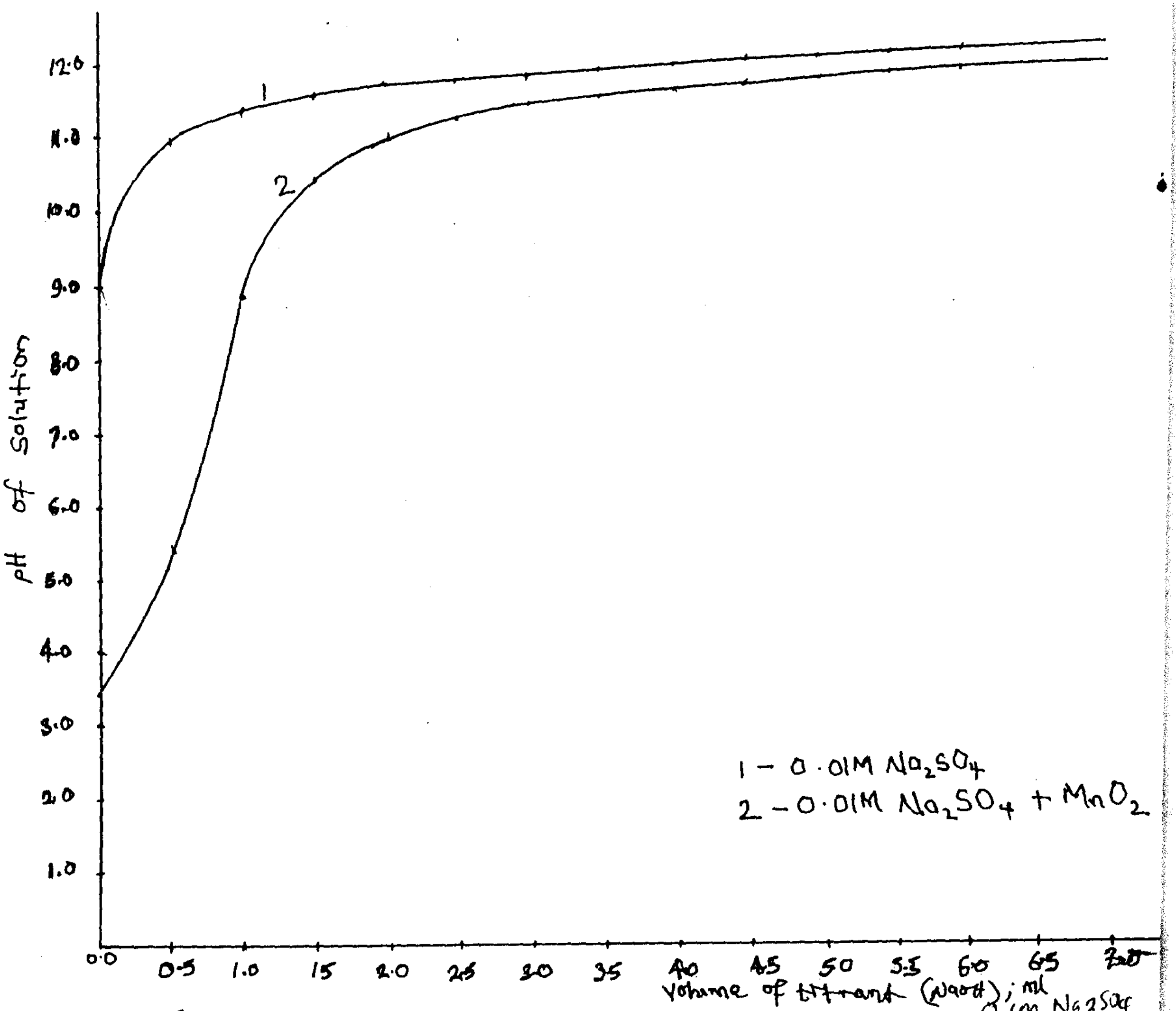


Fig 7: Titration of 0.1M NaOH VS 0.01M Na_2SO_4

0.1M Na_2SO_4
0.01M Na_2SO_4

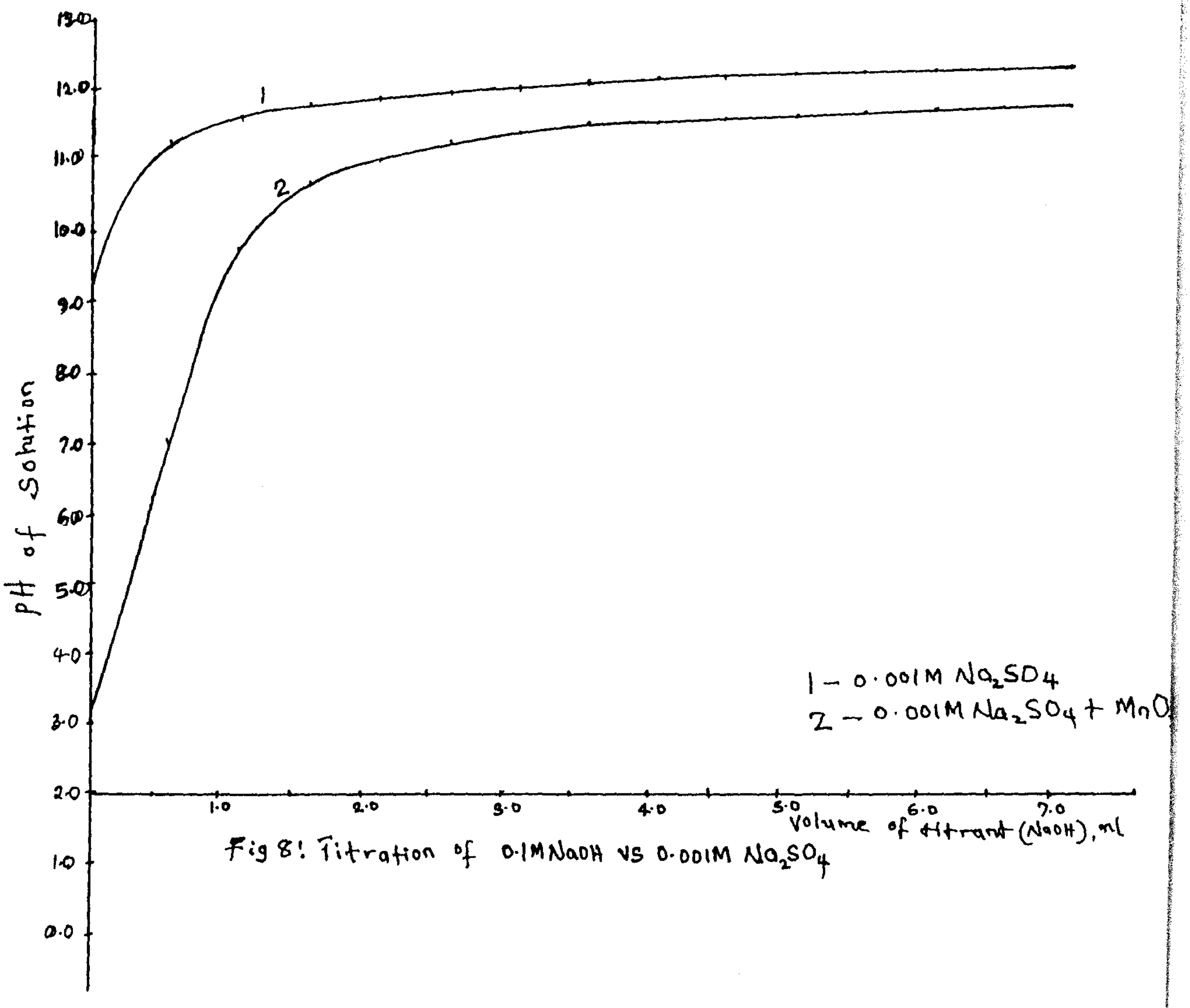


Fig 8: Titration of 0.1M NaOH VS 0.001M Na_2SO_4

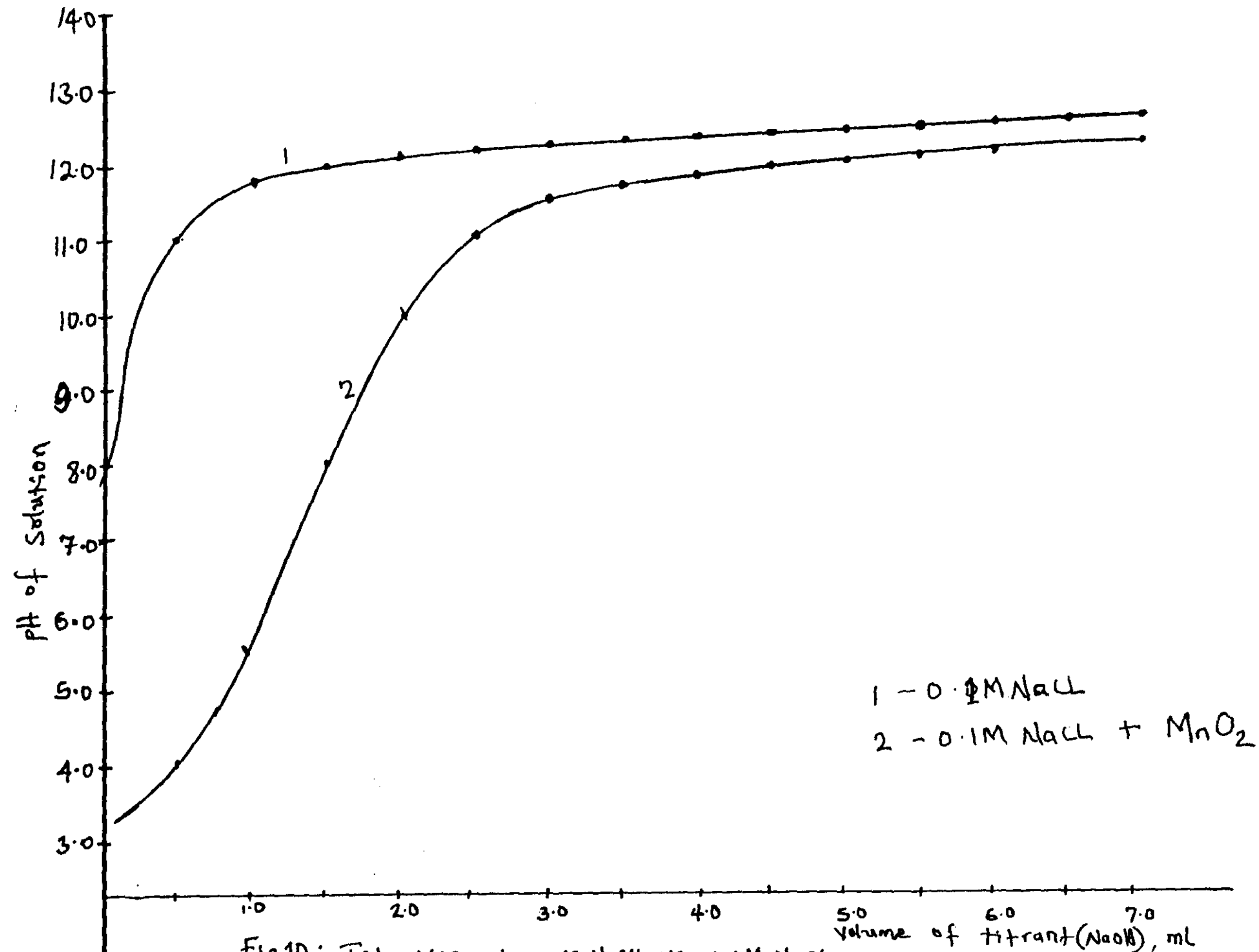


Fig10 : Titration of 0.1M NaOH VS 0.1M NaCL

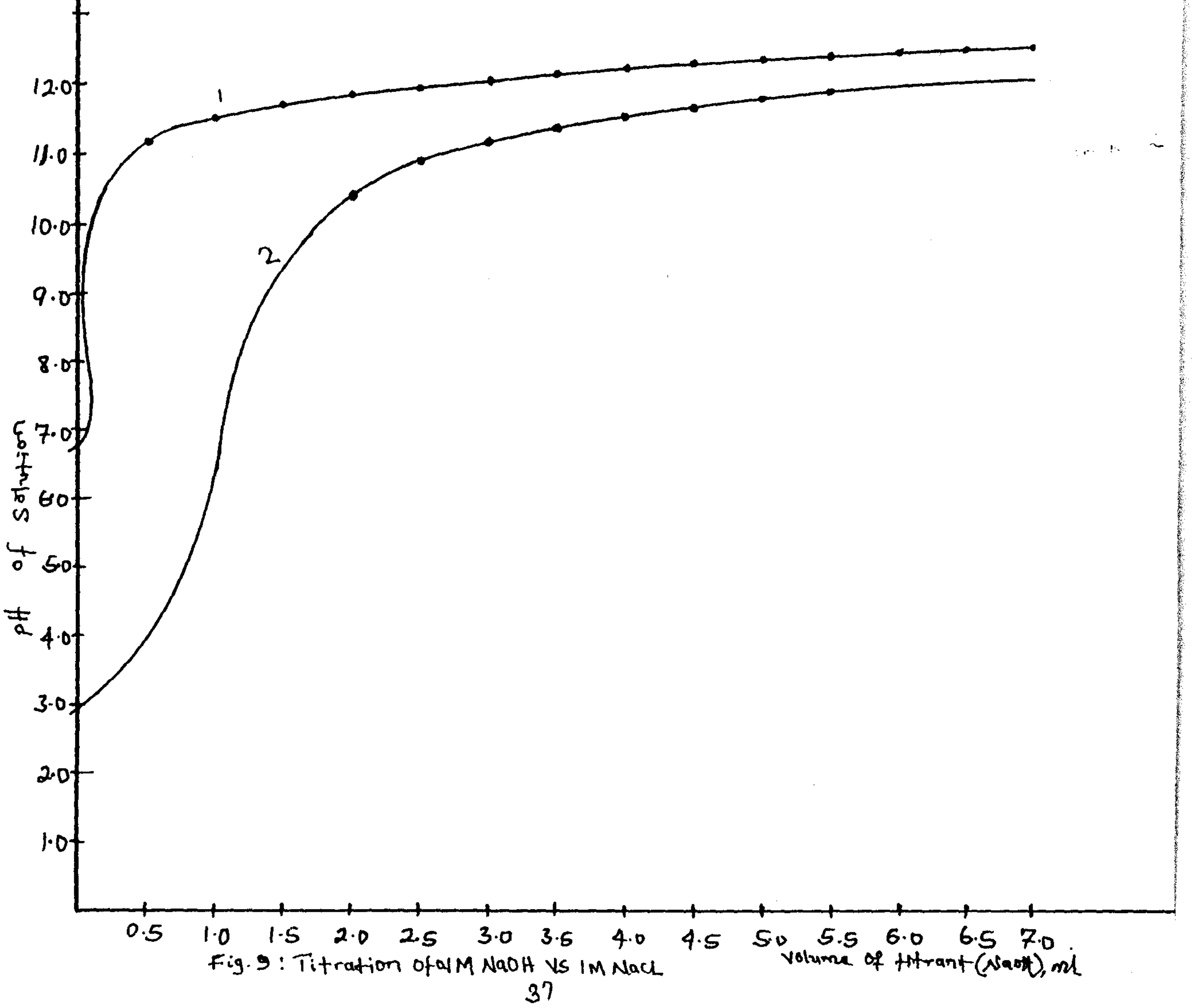


Fig. 9 : Titration of 1M NaOH VS 1M NaCL

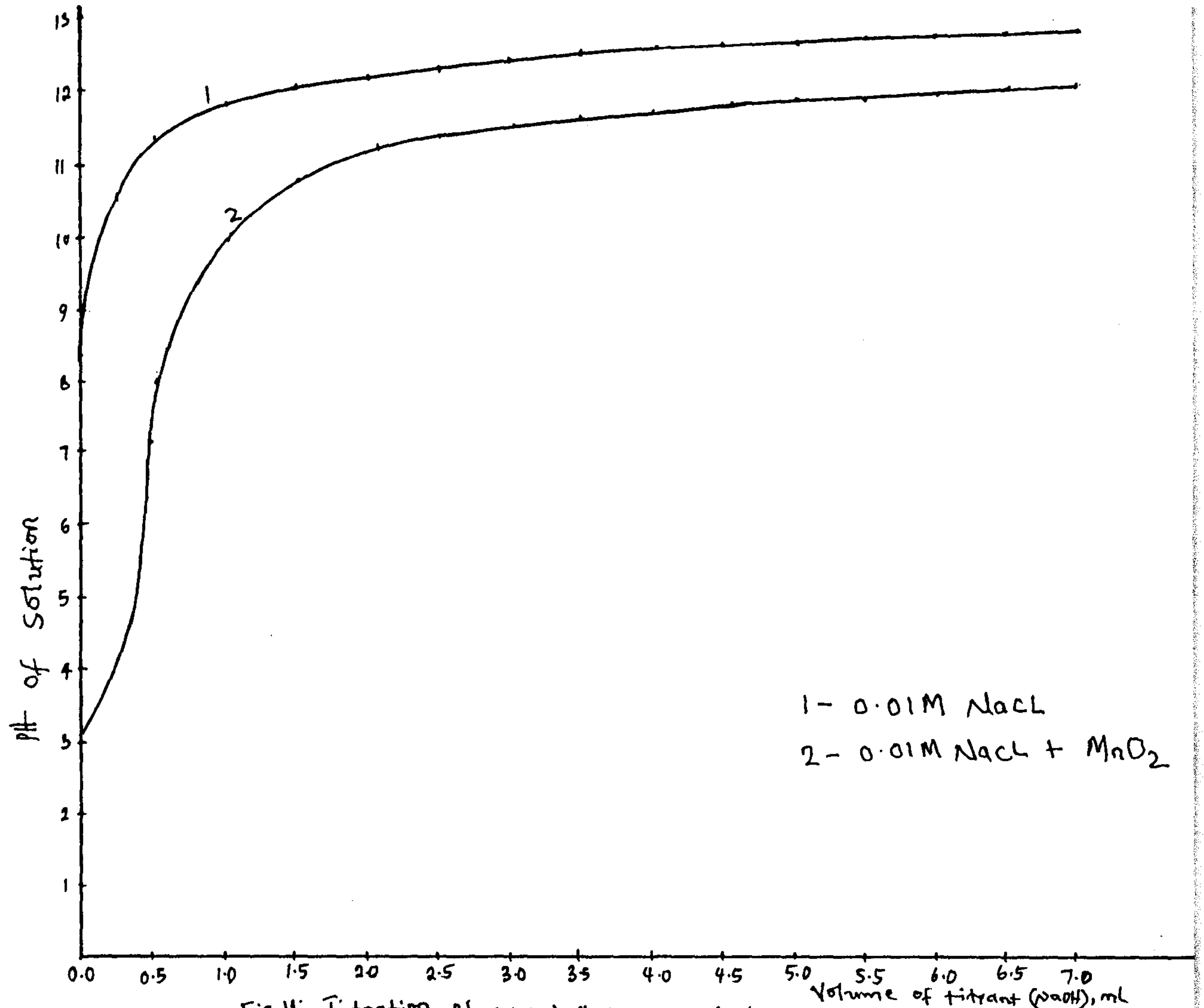


Fig 11: Titration of 0.1M NaoH vs 0.01M NaCL

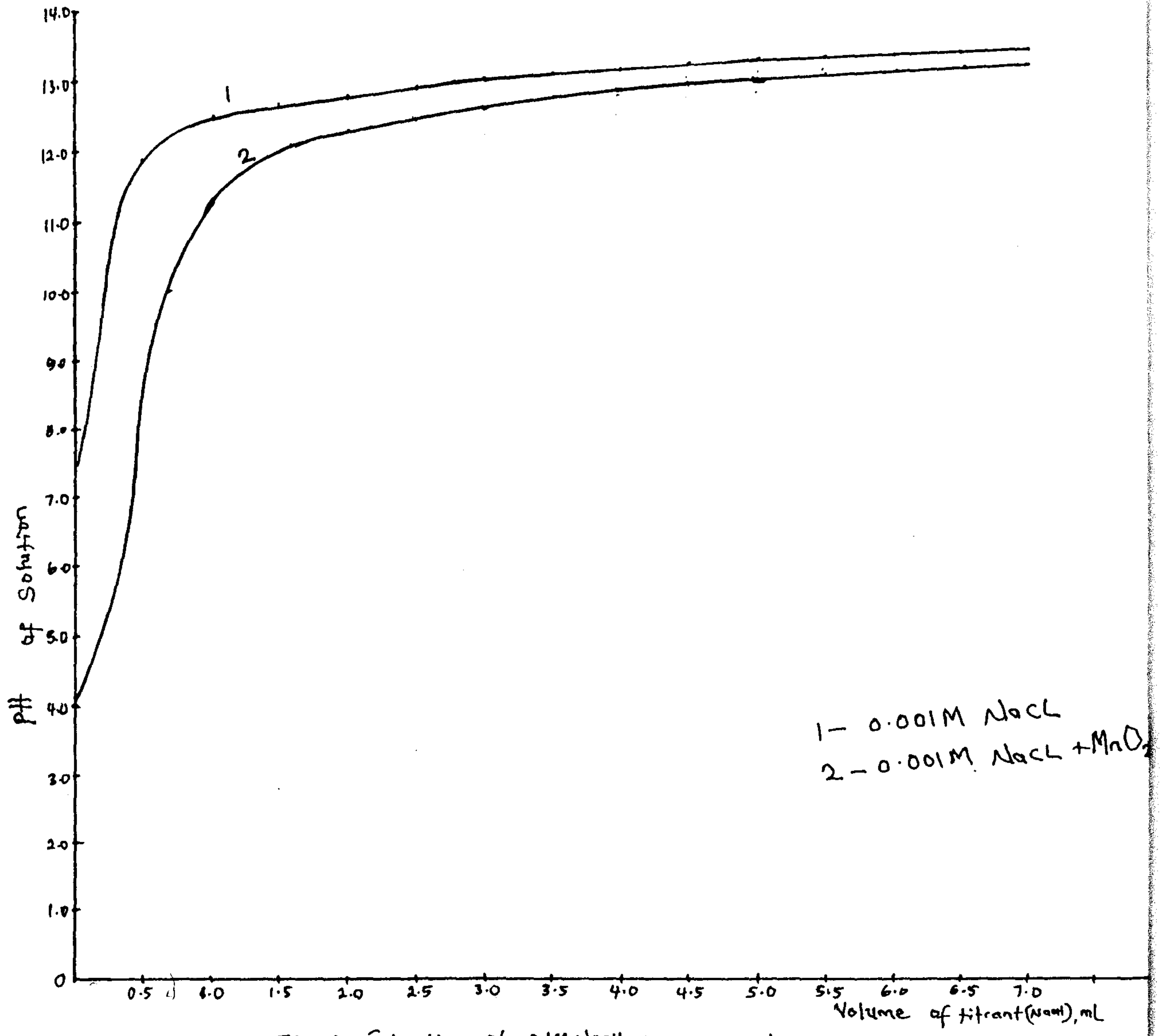


Fig 12: Titration of 0.1M NaoH vs 0.001M NaCL

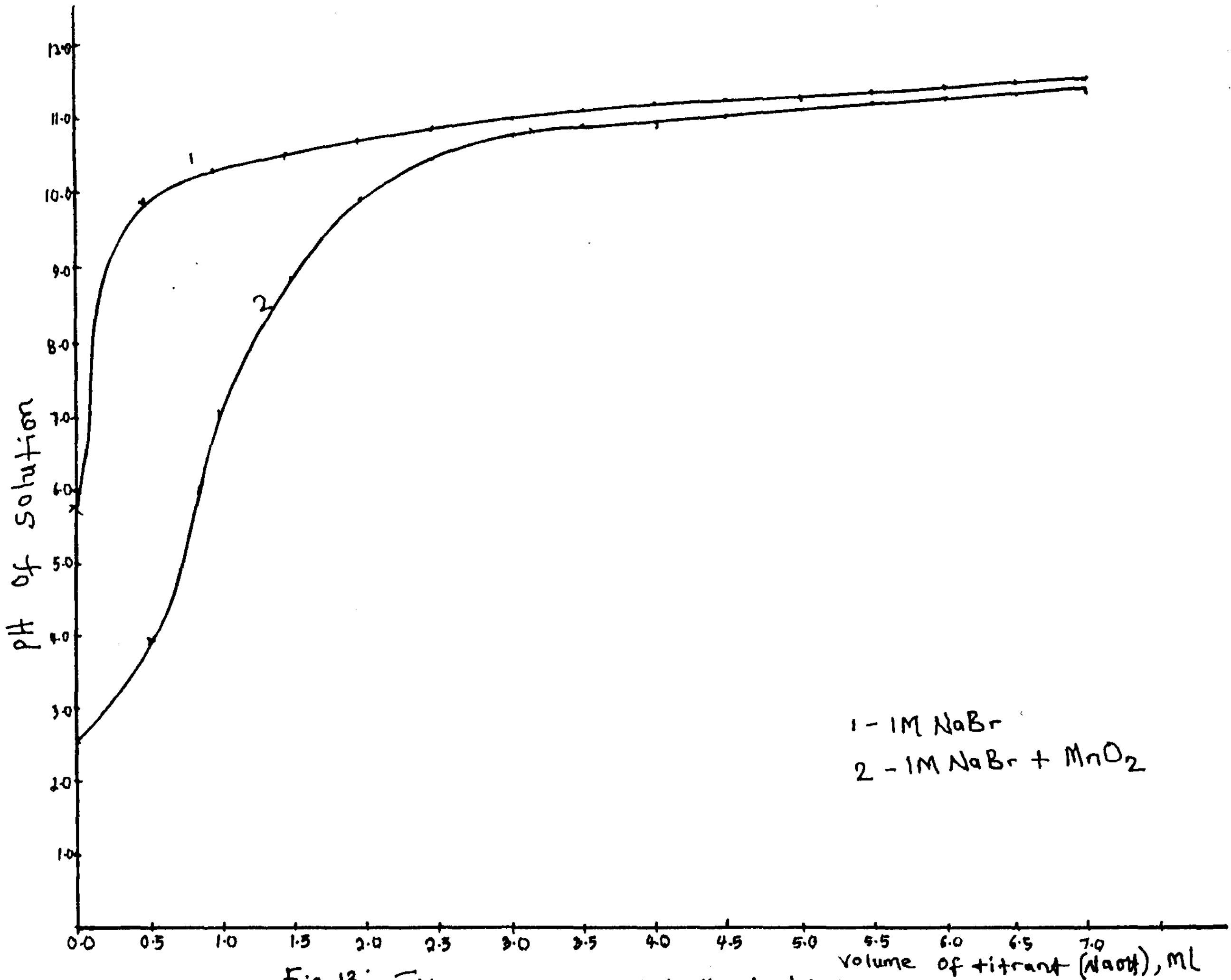


Fig 13: Titration of 0.1M NaOH vs 1M NaBr

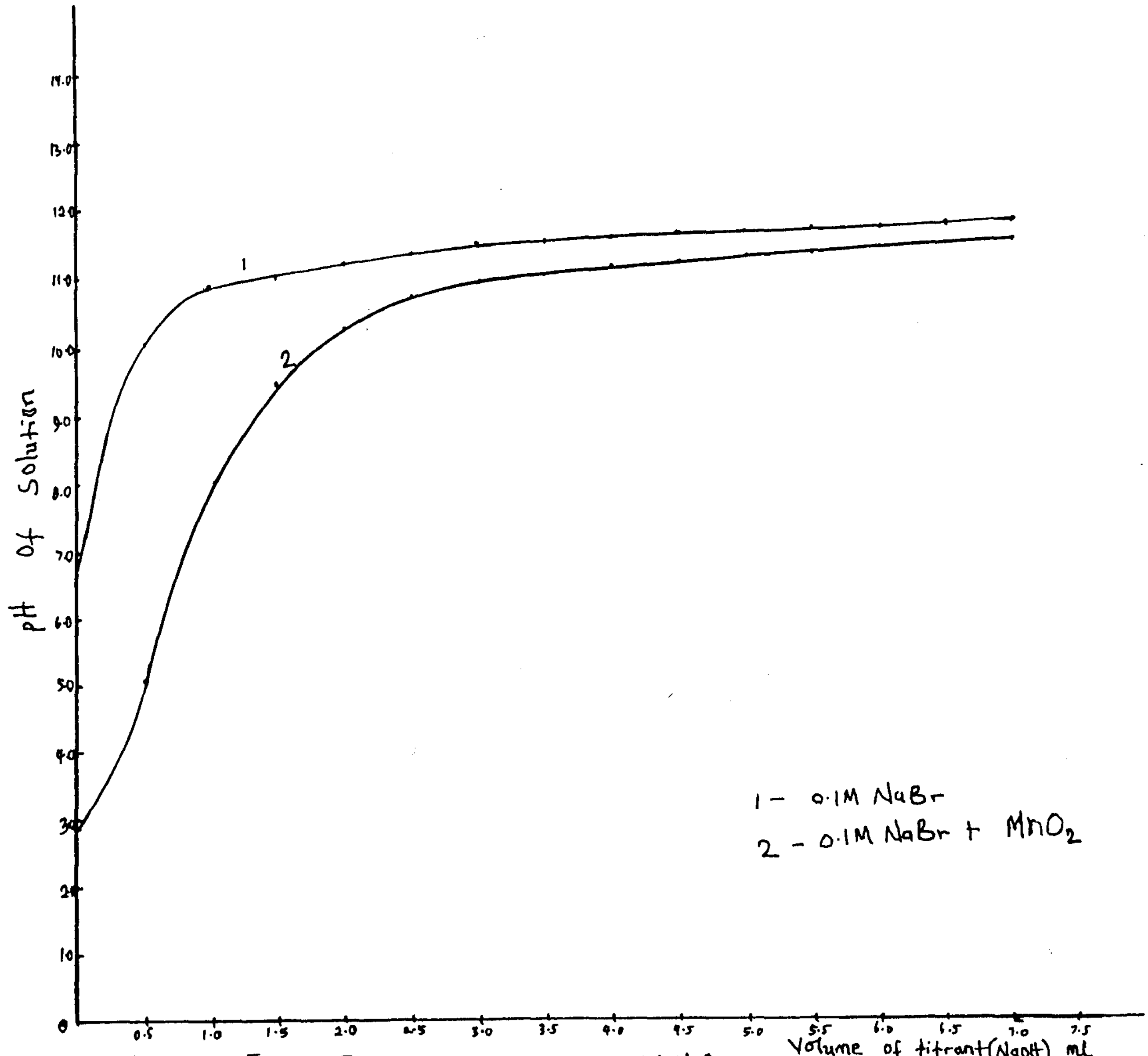


Fig 14: Titration of 0.1M NaOH vs 0.1M NaBr

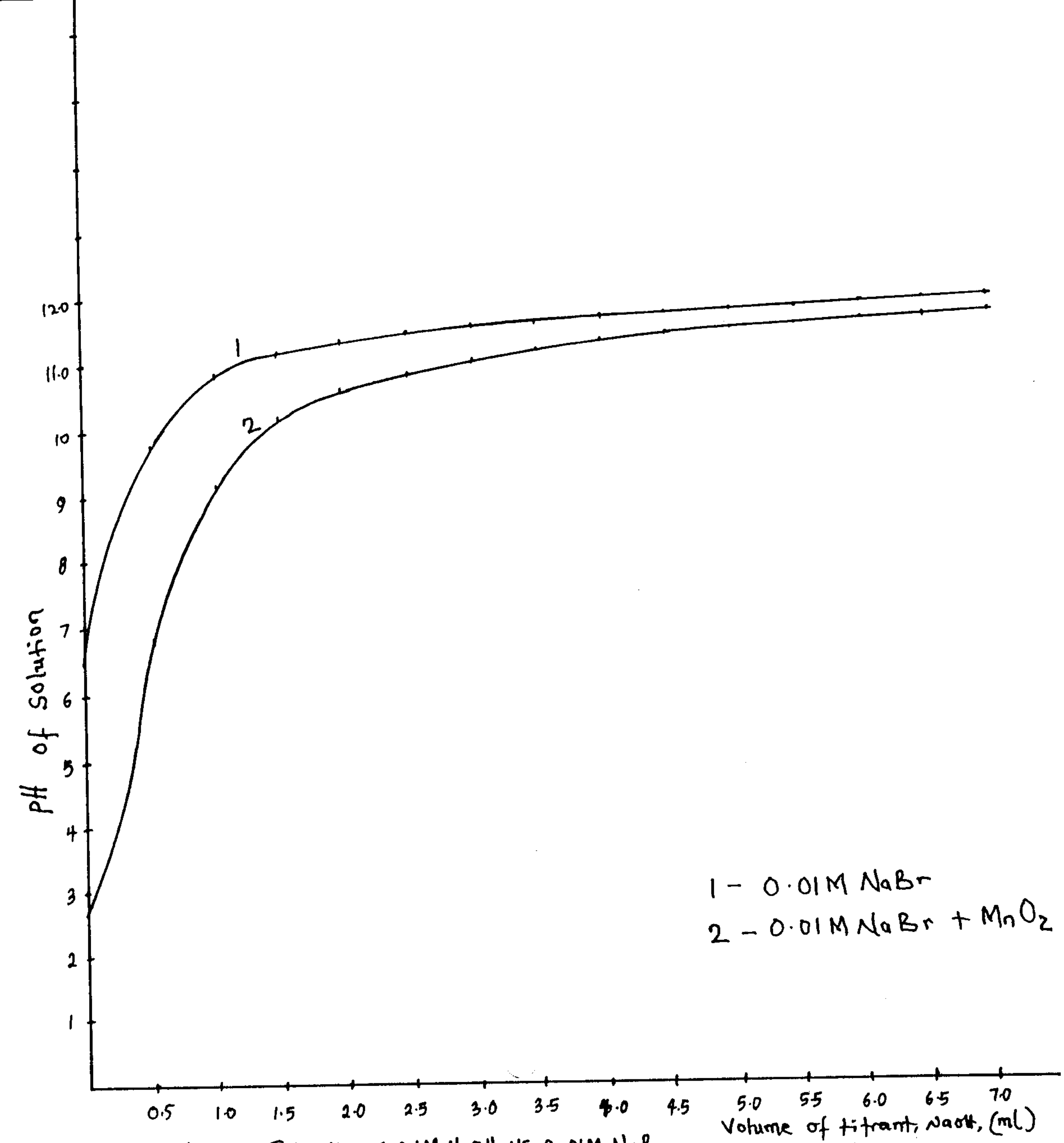


Fig 15: Titration of 0.1M NaOH VS 0.01M NaBr

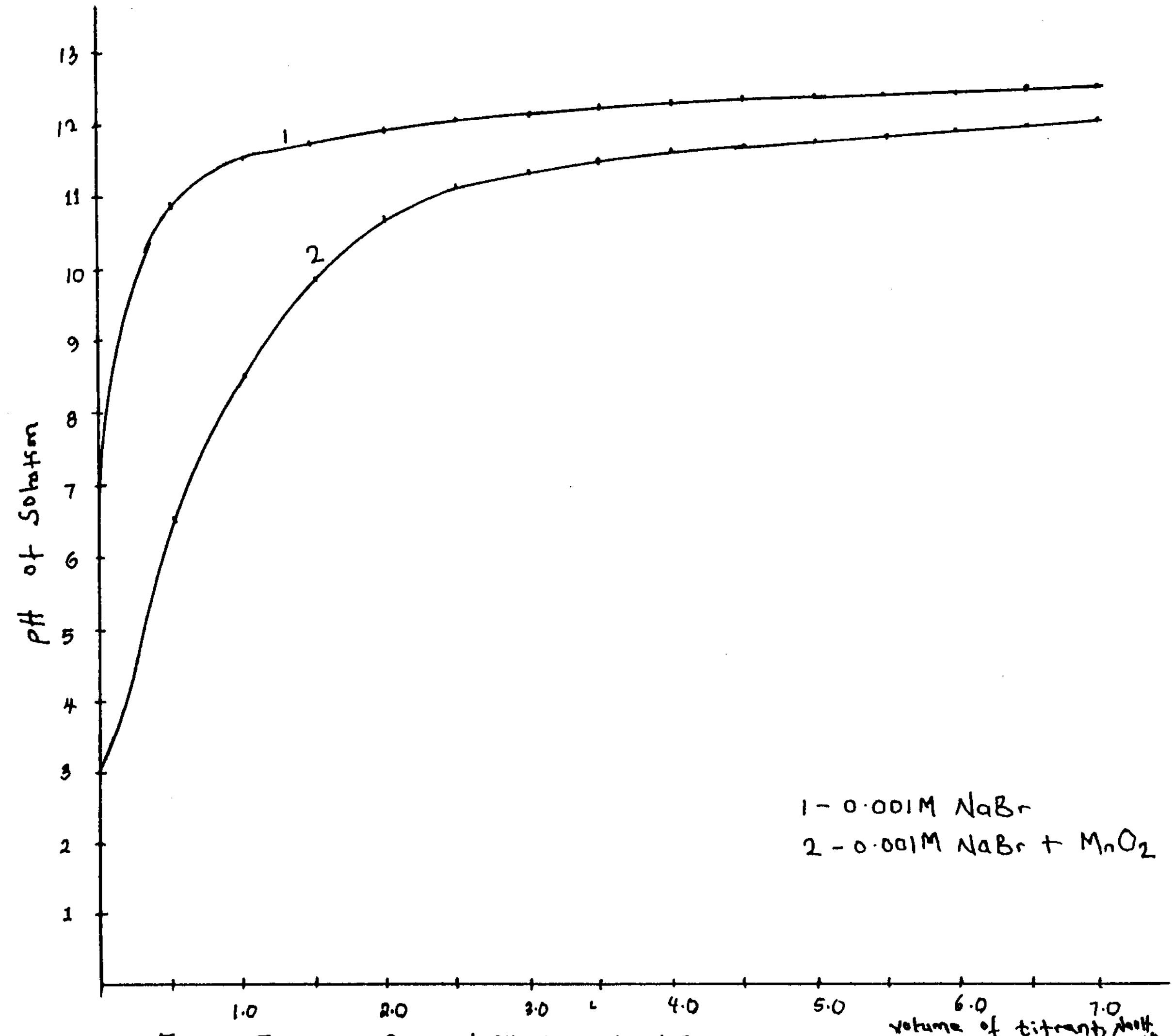
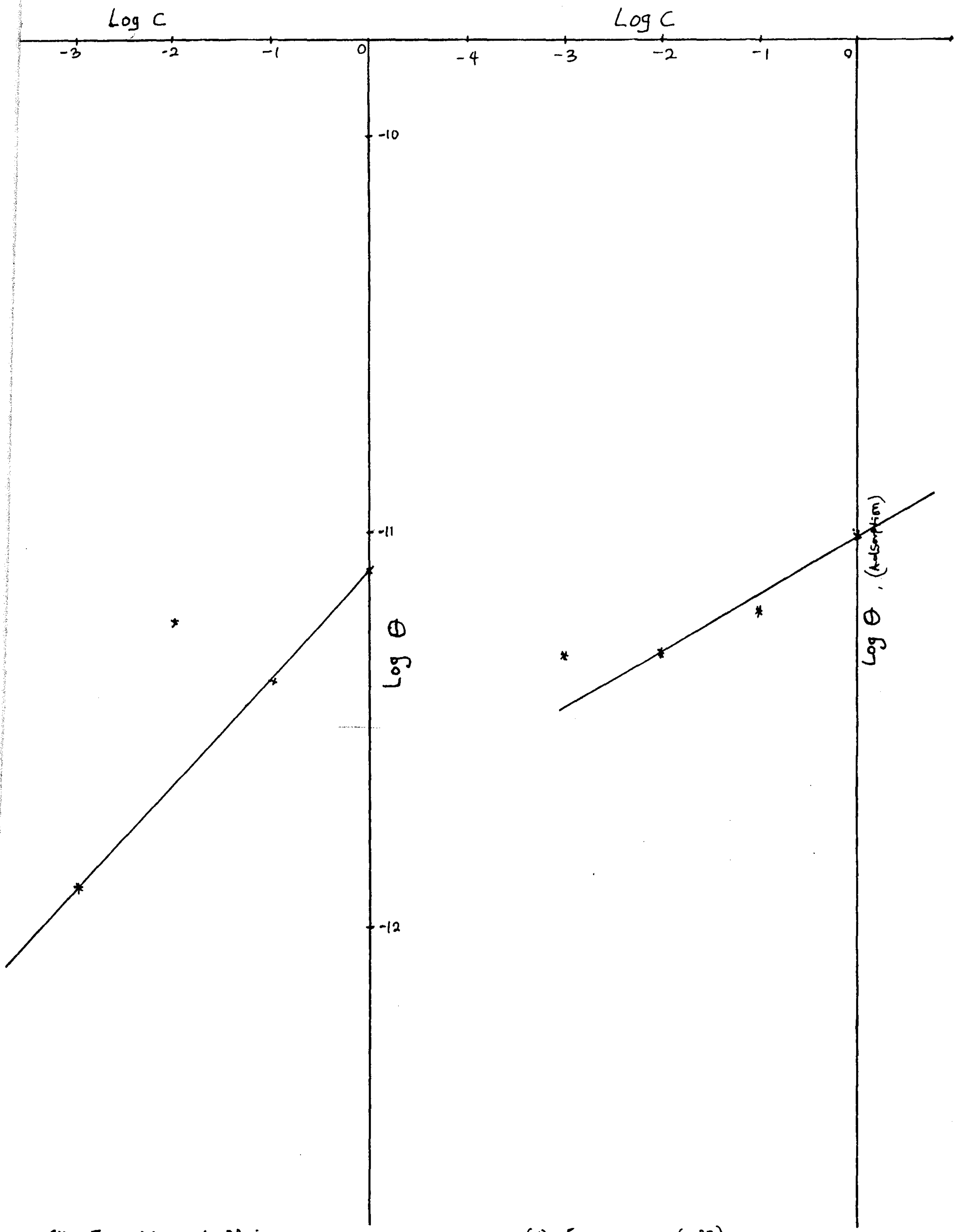


Fig 16: Titration of 0.1M NaOH VS 0.001M NaBr

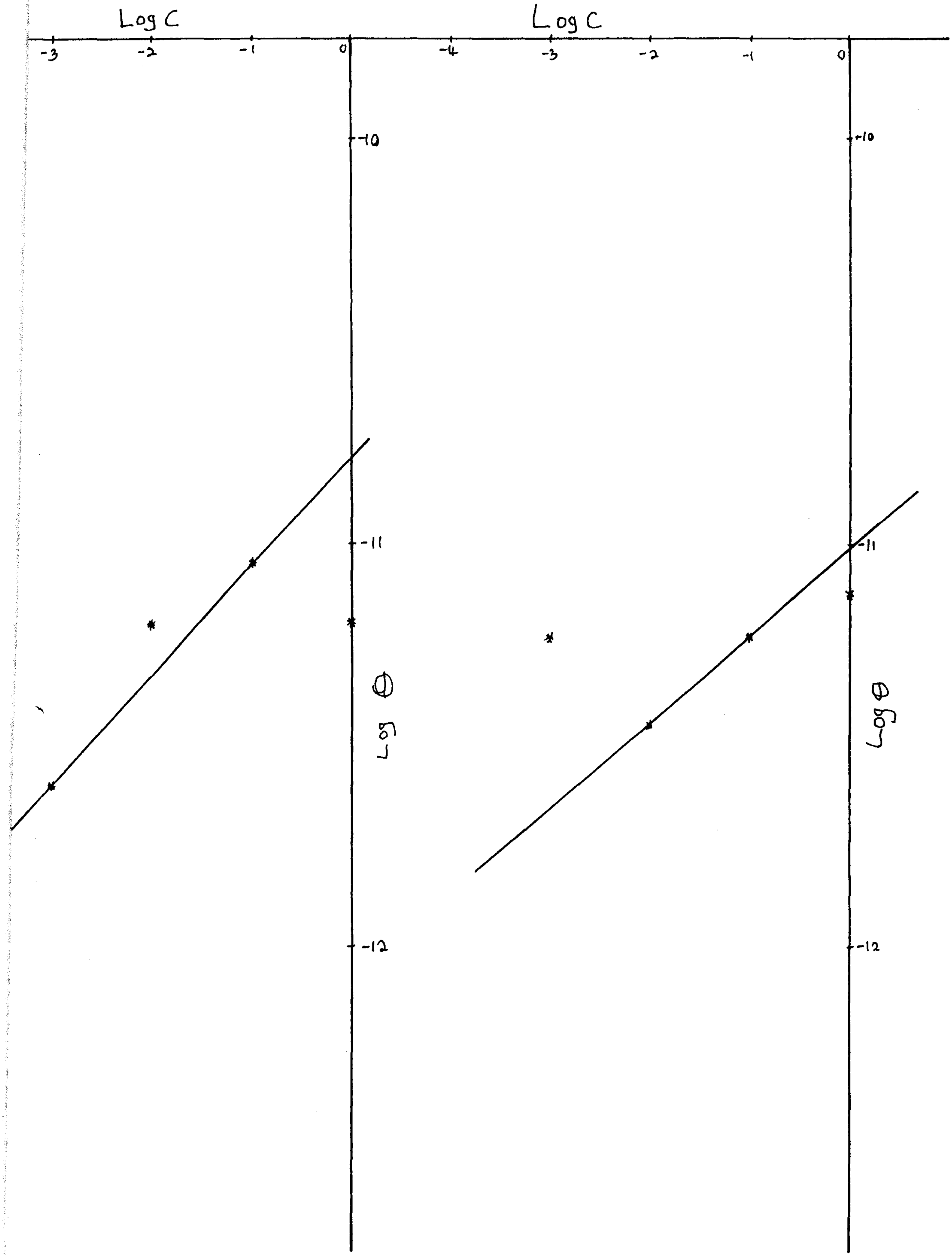


(i) For Nitrate (NO_3^-) ion

(ii) for sulphate (SO_4^{2-}) ion

Fig 17(a) freundlich Isotherm determination graphs for Nitrate and Sulphate ions

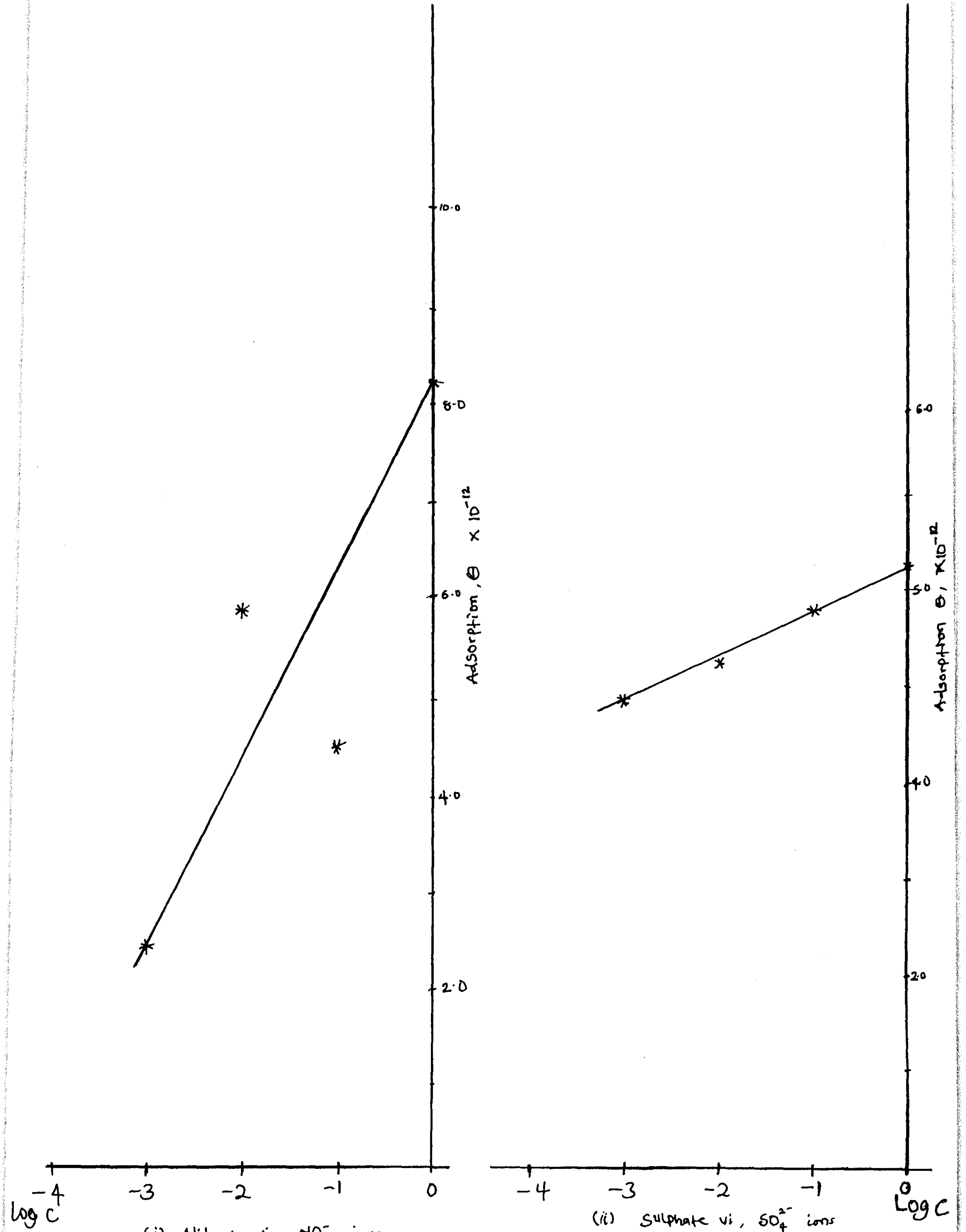
C – concentration
Θ – Adsorption



(iii) for chloride (CL$^-$) ions

(iv) For Bromide ions (CL$^-$).

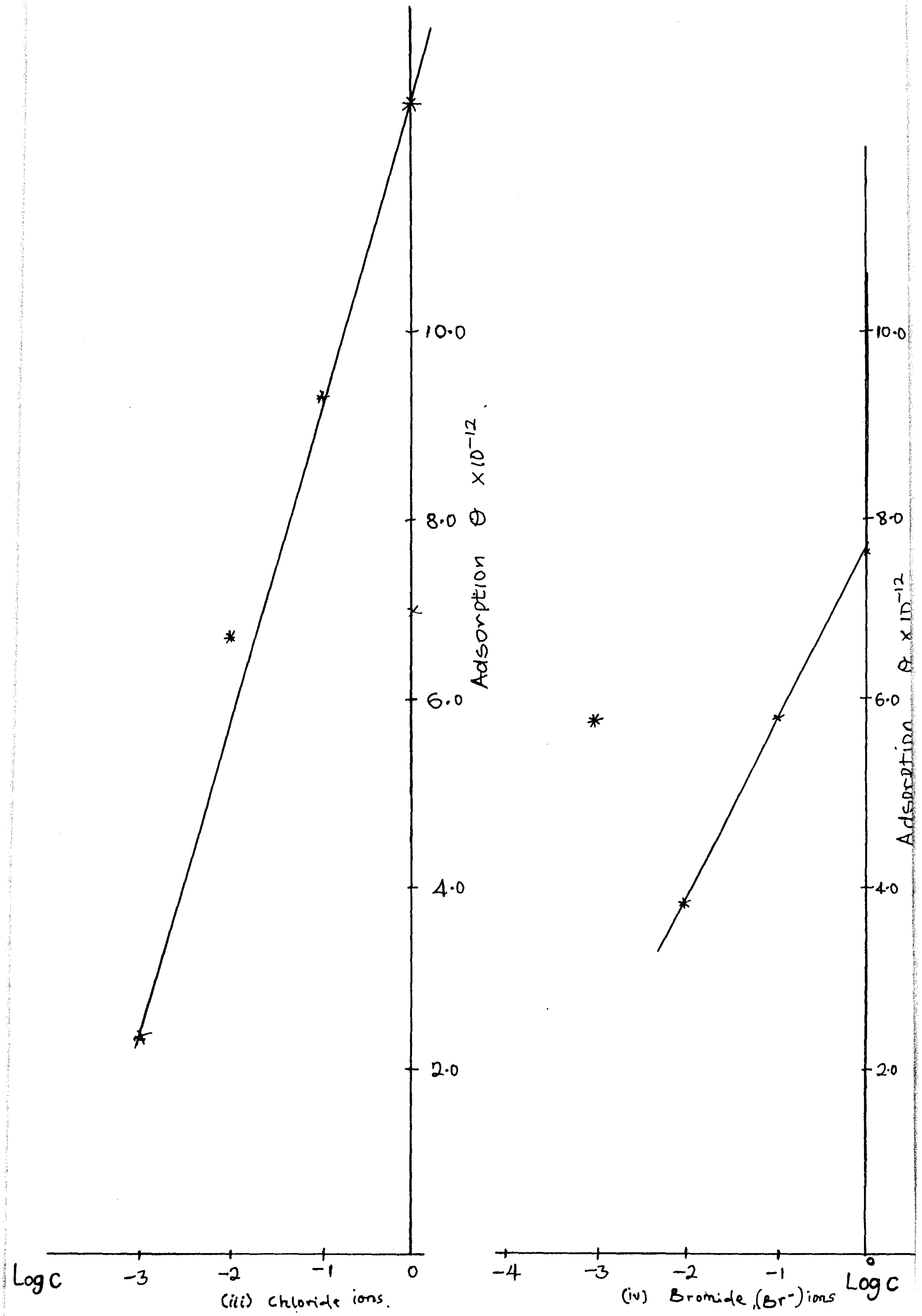
Fig 17(a) Freundlich Isotherm determination graphs for chlorite and Bromide ions



(i) Nitrate vi, NO_3^- ions

(ii) Sulphate vi, SO_4^{2-} ions

Fig 17(b) : Tomkin Isotherm determination graphs for Nitrate (NO_3^-) and sulphate ions.



(iii) Chloride ions.

(iv) Bromide (Br⁻) ions

Fig 17b: Tomkin Isotherm determination graphs for chloride and bromide ions

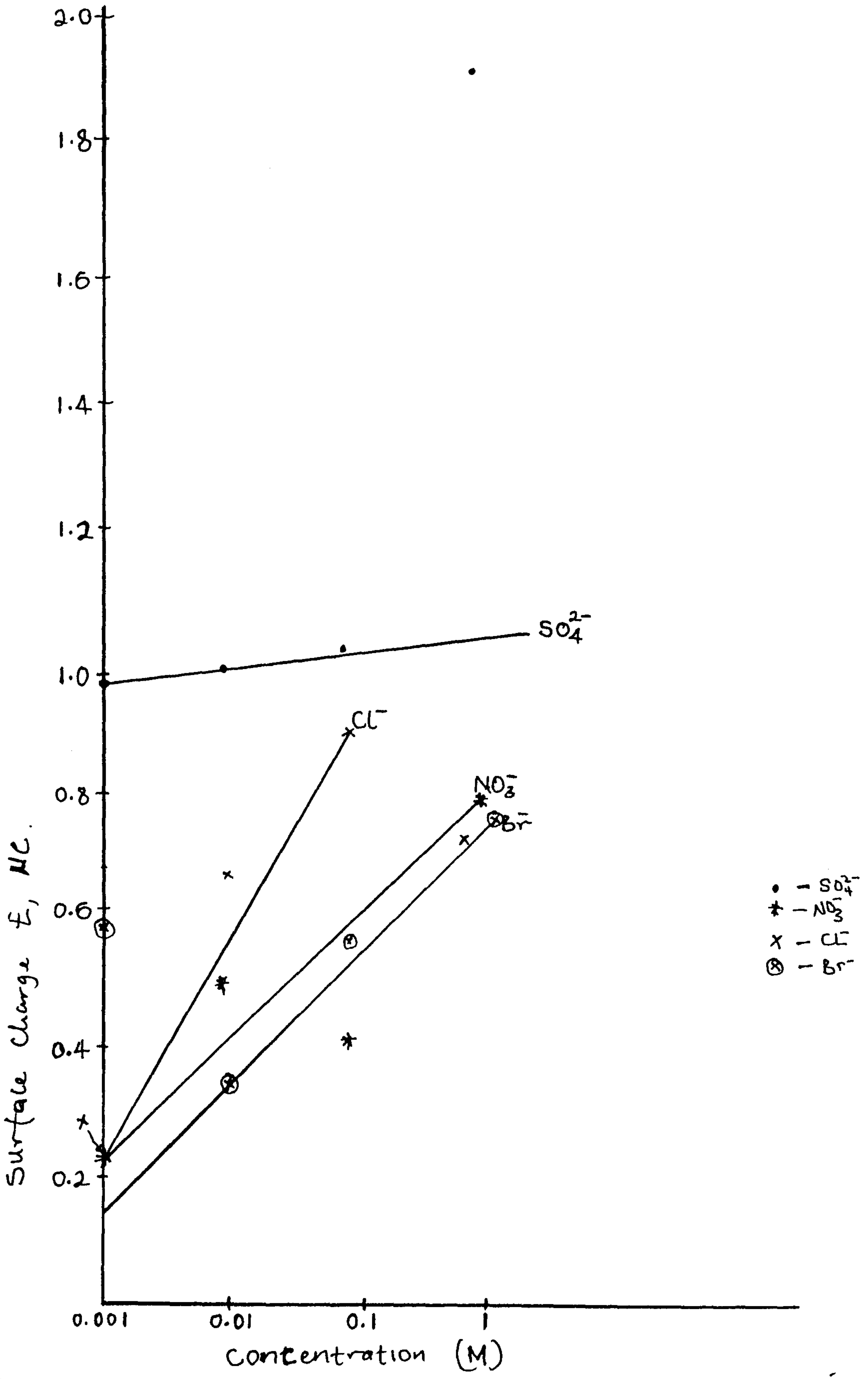


Fig 18. A graph of surface charge of anions against their various concentrations

CHAPTER FIVE

5.0.0 EQUIPMENT DESIGN

Design is a creative activity,as such can be one of the most rewarding and satifying activities undertaken by an engineer. It is the synthesis, the putting together, of ideas to achieve a desired purpose.

Design does not exist at the the commencement of the project. The designer starts with a specific objective in mind, a need, and by developing and evaluating and evaluating possible designs, arrives at what he considers the best way of achieving that objective; be it a better chair, a new bridge,or for the chemical engineer a new chemical product or a stage in the design of a production process.

Usually, so many constraints tends to set into the process of a design activities.Amongst the constraints which a designer should majorly give attention to is the economic consideration. Also, time available for completion of a design will usually limit the number of alternative design that can be considered.

Generally, design has the objective to fulfil a particular need of a manufacturing process, e.t.c.

5.1.0 PROBLEM STATEMENT

To design a Turbine mixer that will mix 6380Kg/hr cathode mix for bobbin making unit of a Dry cell producing plant.

5.1.1 RAW MATERIAL

Manganese(IV) Oxide (electrolytic MnO_2- 50% and natural MnO_2-38%)

Carbon (Acetylene black -5% and graphite powder- 9%)

5.1.2 CHARGING TIME - 20 minutes

5.1.3 ONSTREAM TIME-20 minutes

5.1.4 DISCHARGING TIME- 20 minutes

5.1.5 PRODUCT SPECIFICATION

A well and uniformly cathode mix ready to be made into bobbin for dry cell cathode elctrode.

5.2.0 PROCESS DESCRIPTION

The flow diagram shown below briefly describes the process involved in the production of dry cells.

This process starts from the cathode mixing unit where Electrolytic MnO_2, acetylene bleach and graphite powder are uniformly mixed in a mixer for 20 minutes to obtain the cathode mix. This cathode mix is further routed to a bobbin making unit where the bobbin machine moulds the cathode mix around the carbon rod.

Meanwhile Zinc ingot with 99.97% purity is smelted and rolled.The rolled Zinc is made into tablets and subsequently extruded by applying 250 ton pressure to make the plates.

At, the same time, the electrolyte is being made ion the elecrolyte making section. Here, Deionizing equipment removes ions from water to make pure paste. Maize flour is converted to maize starch and boiled to a gel.Water, and $ZnCl_2$ are added to form a millimg solution.This solution makes the electrolyte.

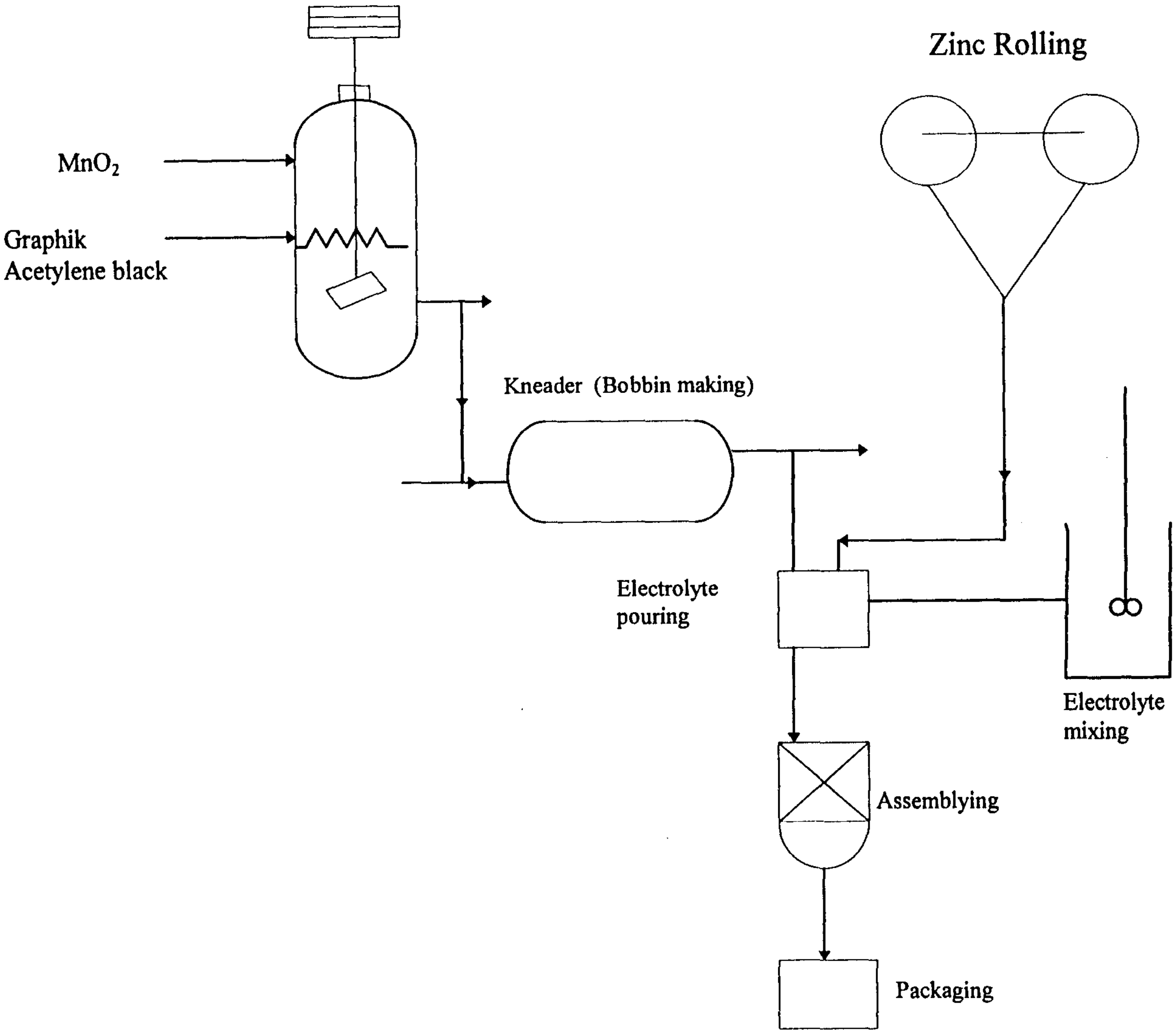
Further, the Zinc can, the bobbin so made and the electrolyte solution are being brought together in the elecroyte pouring unit.At this assemling unit the bobbin is placed in the zinc can and it is centralised. The electrolyte is also poured into the can. The Zinc can now containing the electrolyte and the bobbin is placed in boiled water bath to solidify the electrolyte in order toprevent positive and negative electrode to touch.

At this point the zinc can is routed to the paper washer fixing and the asphalt sealing units where insulating paper washer is placed on the bobbin and asphalt is poured on the paper washer to seal bobbin in order to disallow air from penetrating, otherwise battery life would be reduced.

Next, is the brass capping unit where brass cap is placed on the carbon rod to form the positive terminal cathode. It is then package to rest for 1-2 weeks before sending it to finishing.

At finishing, the zinc can bottom is cleaned for good electrical contact. Paper insulation is placed on the zinc can to cover it and it is inserted into paper tube. Placement of plastic cover on the dry cell, metal, jacketing fixing, bottom metal plate fixing transparent wrapping and packaging (in packets and cartons) are accomplished in this unit. The battery is ready for use by consumer.

5.3 PROCESS SCHEMATIC FLOW DIAGRAM



5.4 EQUIPMENT SELECTION

The equipment selected for design in this chapter is the turbines mixer for the belnding of MnO_2, acetylene black and graphite (solid mixing). The reason being that the project work itself was based on MnO_2. And, apart from electrolyte mixing unit, and the zinc can making unit paper jacket and metal jacket making units which majorly have Chemical Engineering equipment, every other unit in the plant as shown by the flow diagram are assemblage units.

Amongst the available types of mixers turbine mixer is chosen because of 1. avaliability of information 2. simplicity and 3. performance. It fits , MnO_2 graphite and acetylene black well.

Also, the material selected for construction is stainless steel. Stainless steel are the most frequently used corrosion resistant materials in the chemical industry. Usually, more than 12% of chromium content are added to impact corrossion resistance in oxidizing conditions. Nickel is also added to improve corrossion ristance in non-oxidizing environments. MnO_2 is an oxidizing agent.

5.5 DESIGN DATAS

Density of carbon = 2260Kg/m^3

Density of MnO_2 = 50Kg/m^3

Turbine power in horse power = 50 = 37.3KW given in perry .Table 21.3 section 21.9.

Approximate working capacity = 50ft^3 = 1.5m^3

Internal device shaft speed = 600ft/min = 3.0m/s = 0.72rev/s

Volume of a cylindrical vessel with one hemispherical end, $V=\pi^2 L + \frac{2}{3}\pi r^3$

Ratios:

1. Volume of a cylindrical vessel, $\frac{L}{D_T} = 1.3$
2. Diameter of agitator to diameter of tank, $= \frac{D_a}{D_T} = \frac{1}{3}$
3. Height of impeller above vessel flow to tank diameter, $= \frac{H}{D_T} = 1$
4. Height of impeller above vessel flow to tank diameter, $= \frac{E}{D_T} = \frac{1}{3}$
5. Impeller width to agitator diameter, $= \frac{W}{D_a} = \frac{1}{5}$
6. Length of impeller blade to agitator diameter, $= \frac{L}{D_T} = \frac{1}{4}$

Optimum diameter of pipe (using stainless steel)

$$d, \text{optimum} = 260\, G^{0.52}\, \rho^{-0.37}$$

where G = flow rate of substance, Kg/s

ρ = Density of substance, Kg/m^3

d = diameter of pipe, mm.

Formula for costing of equipment

$Ce = CS^n$

where Ce = purchased equipment cost (pounds)

S = characteristic size parameter

n = index for the type of equipment

Heat capacity, Cp of graphite = $2.673 + 0.002617T - 116900/T^2$

Heat capacity, Cp of MnO_2 = $1.92 + 0.0471T - 0.000297T^2$

5.6 MATERIALS BALANCE AROUND THE ELECTROLYTE POURING UNIT

Basic - 10 Kg

Equation of reaction in the battery after electrolyte pouring

$$5Zn + 10MnO_2 + ZnCl_2 + 2NH_4Cl + 8H_2O \longrightarrow Zn(NH_3)_2Cl_2 + ZnCl_2.4Zn(OH)_2 + 10MnOOH$$

INPUTS

5 Zn	-	5 x 65	=	325g
$10MnO_2$	-	10[55 + 2 x 16]	=	870g
$ZnCl_2$	-	65 + 2 x 35.5	=	136g
$2NH_4Cl$ 1	-	2[14 + 1 x 4 + 35.55]	=	107g
$8H_2O$	-	8[1 x 2 +16]	=	144g
		Total	=	1582g

OUTPUT

$Zn(NH_3)_2Cl_2$	-	65 +[14 +1x 3]2 + [35.5x 2]	=	170g
$ZnCl_2.4Zn(OH)_2$	-	65+[35.5 x 2] + 4[65+(16 +1)2]	=	532g
10MnOOH	-	10[55 + 16 +16 +1]	=	880g
		Total	=	1582g

Amount of Zn

1582g of reactant needed 325g of Zn for complete reaction, hence 10,000g of reactant will need Xg_{zn}

$$Xg_{zn} = \frac{10{,}000 \times 325}{1582}$$

= 2054.3616g

= 2.05Kg.

Amount of MnO_2

1582g of reactant needed 870g of MnO_2 for complete reaction, hence 10,000g of reactant will need Xg_{Zncl2}

$$Xg_{Zncl2} = \frac{10{,}000 \times 136}{1582}$$

= 859.67g

= 0.86Kg.

Amount of NH_4Cl

1582g of reactant needed 107g of NH_4Cl for complete reaction, hence 10,000g of reactant will need Xg_{NH_4Cl}

$$Xg_{NH_4Cl} = \frac{10{,}000 \times 107}{1582}$$

= 676.559g

= 0. 68Kg.

Amount of Water

1582g of reactant needed 144g of water for complete reaction, hence 10,000g of reactant will need Xg_{H_2O}

$$Xg_{H_2O} = \frac{10{,}000 \times 144}{1582}$$

= 910.24g

= 0. 91Kg.

Amount of $Zn(NH_3)_2Cl$

1582g of reactant needed 170g of $Zn(NH_3)_2Cl$ for complete reaction, hence 10,000g of reactant will need Xg_{NH_4Cl}

$$Xg = \frac{10,000 \times 107}{1582}$$

$= 1074.58$

$= 1.07Kg.$

Amount of $ZnCl_2.4Zn(OH_3)_2$

1582g of reactant needed 532g of $ZnCl_2.4Zn(OH_3)_2$ for complete reaction, hence 10,000g of reactant will need Xg_{NH_4Cl}

$$Xg = \frac{10,000 \times 532}{1582}$$

$= 3362.83g$

$= 3.36Kg.$

Amount of MnOOH

1582g of reactant needed 880g of MnOOH for complete reaction, hence 10,000g of reactant will need Xg_{NH_4Cl}

$$Xg = \frac{10,000 \times 880}{1582}$$

$= 5562.58g$

$= 5.56Kg.$

Summary of output/input

Input	Amount (Kg)
Zn	2.05
MnO_2	5.50
$ZnCl_2$	0.86
NH_4Cl	0.68
H_2O	0.91

Output	Amount (Kg)
$Zn(NH_3)_2Cl_2$	1.07
$ZnCl_2.4Zn(OH)$	3.36
MnOOH	5.56

PLEASE NOTE:

Material balance for this design was carried out around the electrolyte pouring unit. The reason is the amount of MnO_2 that is to be mixed with certain proportions of graphite and acetylene black is dependent upon the amount of MnO_2 needed for complete reaction at the electrolyte pouring unit. Hence, we need to know how much of MnO_2 is needed for complete reaction at electrolyte pouring unit.

5.7 ENERGY BALANCE

5.7.1 POWER TO DRIVE THE TURBINE

Usually, formulae are provided in literatures for the calculation of power to drive impellers or turbine of a mixer. Powers are usually calculated using the dimensionless (ie Reynolds, prantl, Nusselt etc) for liquid mixers.

But for solid mixers formulaes are not provided, instead the power that is needed to drive the impellers and turbine of solid mixers depending on the type and the capacities (volume) are given directly. See perry's handbook of Chemical Engineering section 21.9

For a turbine mixer of about $50ft^3$ (approximately $1.5m^3$) the power is given as 50 in horse powe. This is about 37.3 KW. Sec. chemical Engineering Handbook by Perry Table 21.3, section 21.9

5.7.2 ENERGY BALANCE

Heat capacities of graphite is negligible at room temperature

Heat capacity of MnO_2, Cp_{MnO_2} $= 1.92 + 0.0471T - 0.0000297T^2$

$= 1.92 +0.0471(25) - 0.0000297(25)^2$

$Cp_{MnO_2} = 3.08$

From H = Q = mcθ

Q = power impotu into the system via turbine, W

m = mass of cathode mix Kg

C = Heat capacity of substance

θ = change/rise in temperature

Hence from the given power of impeller

Q = mcθ

becomes 37312 = 6380 x 3.08 θ

$$\theta = \frac{37312}{6380 \times 3.08}$$

$= 1.5^\circ$ rise (Negligble)

Hence, final temperature at room temperature operation

$= 2.5^\circ C + 1.5^\circ$

$= 26.5^\circ C$

From this calculation it can be seen that changes in temperature is neglible, otherwise there would have been a need of a cooling system. This is because Dry cell producing plants are designed to operate at low temperature of about room temperatures.

The speed of internal device shaft (turbine) was given as 600ft/min

$$\text{conversion} = \frac{600\text{ft}}{\text{min}} \times \frac{0.3048\text{m}}{1\text{ft}} \times \frac{1\text{min}}{60\text{s}}$$

= 3.0m/s

Also converting to revolution per second

$$\text{Speed of shaft (rev/s)} = \frac{\text{velocity (m/s)}}{2\pi r}$$

$$\frac{3.0}{2\pi \times 0.66} = 0.72\text{rev/s}$$

where Diameter of vessels = 0.66(see sizing)

5.8 SIZING

To calculate the working capacity

mass of MnO_2 from material balance = 5.5Kg

Scaling up by 100 = 5500Kg

Using the ratio of 5:0.8 for MnO_2: carbon

mass of carbon (graphite and acetylene black)

$$\frac{0.8}{5} \times 5500 = 880\text{Kg}$$

Total mass of cathode mix (MnO_2 + graphite + acetylene black)

$$= 880 + 5500 = 6380\text{Kg}$$

Density of cathode mix, $\rho_{mix} = \frac{5026 \times 5500 + 2260 \times 880}{880 + 5500}$

$$= 46448\text{Kg/m}^3$$

$$= 4644.5$$

Volume of materials to be blended into a cathode mix = $\frac{\text{mass}}{\text{density}}$

$$\frac{6380}{4644.5} = 1.37\text{m}^3$$

Tolerance volume of 10% = $\frac{10}{100} \times 1.37 = 0.137\text{m}^3$

Design volume of the mixer = $1.37 + 0.137 = 1.5\text{m}^3$

Volume of a cylindrical vessels with a hemisphere

$$V = \pi \frac{D^2_T L}{4} + \frac{2}{3} \pi \frac{D^3_T}{8}$$

But $L = 1.3\, D_T$

$$V = \pi \frac{D^2_T (1.3D_T)}{4} + \frac{2}{24} \pi D^3_T$$

$$1.5 = 1.3\, \pi D^3_T + \frac{2\, \pi D^3_T}{6}$$

$$6 \times 1.5 = 6 \times 1.3\, \pi D^3_T + 2\pi D^3_T$$

$$9.0 = 7.8\, \pi D^3_T + 2\pi D^3_T$$

$$9.0 = 9.8\pi D^3_T$$

$$D^3_T = \frac{9.0}{9.8\pi}$$

$$D^3_T = 0.29$$

Diameter of vessel, $D_T = 0.66\text{m}$

Hence Length $L = 1.3 \times 0.66 = 0.86\text{m}$

5.9 DETAIL DESIGN

From the given relationships

Diameter of the impeller $D_a = \frac{D_T}{3} = \frac{0.66}{3} = 0.22m$

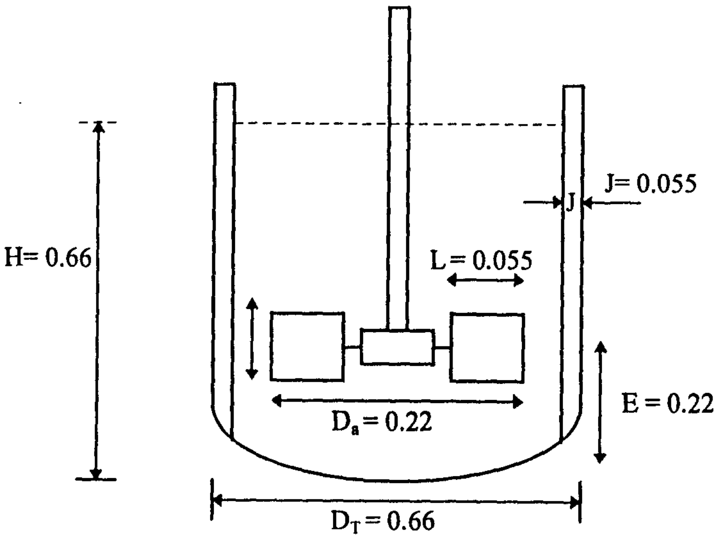
Height of material from base of vessel, $H = D_T \times 1 = 0.66 \times 1 = 0.66m$

Width of baffles, $J = \frac{D_T}{12} = \frac{0.66}{12} = 0.055m$

Height of the impeller above vessel wall, $E = \frac{D_T}{3} = \frac{0.66}{3} = 0.22m$

Impeller width, $w = \frac{D_a}{5} = \frac{0.66}{5} = 0.44m$

Length of impeller blade $Li = \frac{D_a}{4} = \frac{0.22}{4} = 0.055m$



All dimensions are in meters

5.10 PIPING

Charging time for MnO_2 = 20 mins

$$\text{flow rate} = \frac{5500Kg}{20 \times 60} = 4.58\ Kg/s$$

Charging pipe diameter for MnO_2

$d\ optimum = 260\ G^{0.52}\ \rho^{-0.37}$

G = flow rate of substance Kg/s

ρ = Density of substance

$d = 260 \times 4.58^{0.52} \times 5026^{-0.37} = 573.6 \times 0.0427$

= 24.49 mm

Flow rate of graphite and acetylene black

$\frac{880}{20 \times 60} = 0.73$Kg/s

Charging pipe diameter for graphite and acetylene black

$= 260\ G^{0.52}\ \rho^{-0.37}$

$= 260 \times 0.73^{0.52} \times 2260^{-0.37}$

$= 220.75 \times 0.057$

= 12.7mm

Discharging time (cathode mix) = 20 minutes

flow rate $= \frac{6380}{20 \times 60} = 5.3$Kg/s

Discharging pipe diameter $= 260 \times 5.3^{0.52} \times 4644.48^{-0.37}$

= 27.2mm

5.11 COSTING

Equipment

Using $Ce = CS^n$ (equation for costing)

where Ce = purchased equipment cost (pound)

S = characteristics size parameter

n = index for the type of equipment

(a) Turbine agitator

From literature, C = 3200, S = 37.3, n = 0.5,

Hence $Ce = 3200 \times 37.3^{0.5}$

£19464.8

(b) Vertical (cylindrical) tank

From literature, C = 1500, S = 1.5, n = 0.6,

Hence $Ce = 1500 \times 1.5^{0.5}$

£1837.1

Purchase cost estimation (PCE) = £19464.8 + £1837.1

=£21301.9

Now, total physical plant cost (ppc)

PPC = PCE (1 +0.5 + 0.2)

where 1 = fraction of the amount spent on PCE

0.5 = fraction of PCE spent to assemble the purchased equipment

0.2 = fraction of PCE spent on piping

Hence PPC = 21301.9(1+ 0.5 +0.2)

= £36213.23

= ₦(36213 x 125)

= ₦4526653.75

5.12 SAFETY

Any organisation has a legal and moral obligation to safeguard the health and welfare of its employees and the general public. Safety is also good business, the good management practices needed to ensure safe operation will also ensure efficient operation.

Most of the materials used in the manufacture of chemicals are poisonous/harzardous to some extent. The safe opearation of such processes depends on the design and provision of engineering safety devices, and in good operating practices to prevent adangerous sistuation developing, and to minimise the consequences of any incident that arises from the failure of these safeguards.

The unit that is so designed under this chapter is relatively simple and does not pose too a serious danger, though harzard can not be totally ruled out. Several safety precaution listed below are thus to be enforced in other to reduce harzrads and procure safety.

A harzard and operability study, a procedure for a systematic, critical examination of the operability of a process should also applied to a process design or an operating plant. These will indicates potential harzards that may arise from deviation from the intended design conditions.

The basic and fire protective measures that should be included in all chemical process design are

1. Adequate and secure, water supplies for fire fighting
2. Correct structure design of vessels, piping steel work.
3. Earthing of electrical equipment
4. Safe location of auxillary electrical equipment, transformer switch gears
5. Provision of back up utility supplies and services
6. Compliance with national codes and standards
7. Provision of access of emergency vehicles and the evacuation of personnel.
8. Adequate drainage for spills and fire fighting water.
9. Safe design and location of control rooms.

5.13 ECONOMIC EVALUATION

As the purpose of investing money in chemical plant is to earn money, some means of comparing the economic performance of project is needed.

For small projects, and for simple choices between alternative processing schemes and equipment, the decision can usually be made by comparing the capital and operation costs.

The mixer so designed in this chapter for solid mixing is simple and it is economically viable. The use of stainless steel as the construction material is more economical than the carbon steel, though carbon steel is cheaper. This is so because the cost value which carbon still pose as a result of its inability to resist corrosion will not be comparable with the cost saving ability of stainless steel through its corrosion resisting ability.

Also, apart from the power supplied to the turbine via the shaft no heat is required, and hence the steam and other form of heat supply cost is eliminated. Acetylene black and graphite can be gotten locally. MnO2 though it is imported it is readily made avaliable.

The other economic implication of the cathode mix blending unit is that at least six personnels are needed to operate the plant with take away pay as follows:

1 Supervisor (an engineer) ₦18,000

1 Chemical analyst ₦12,000

2 operators = ₦8,000 x 2

2 maintenance men = ₦8,000 x 2

However, the revenue generated from the final sales of produced batteries should compensate thses implications. A thorough survey has shown that over 160 million units of batteries are being consumed every month. The current rampant failure from NEPA will certainly increase this figure.

On the whole, dry cells making business is profiting.

CHAPTER SIX

6.0.0 DISCUSSIONS OF RESULTS

pH Responses during titrations

The following pH reponses were noticed during the titrations.

1. As titration proceeds and more more volume of titrants are being added to the titrate the pH of the solution tends towards greater alkalinity. This was expected since the titrant itself is alkaline.
2. Considering any given molarity of any of the anions salt (i.e 1M $NaNO_3$), with two of its normal titrations (i.e(i) without MnO_2 (ii) with MnO_2). At any given equal total volume of added titrants to the solutions and comparing the pH of the solution with MnO_2 and that which contains no MnO_2, the pH value of the solution with MnO_2 is always lower, hence, its curve always falls below the curve of the solution without MnO_2. The reason being that whenever MnO_2 is introduced into the solution some of the anions gets adsorbed unto it, thereby decreasing the anions concentration from the solution. This leaves less anions in solution, hence less alkalinity, and a lower pH value for solution with MnO_2.
3. Also, from experinmental datas it was observed that the difference in the change in pH value between a preceeding and a succeeding pH values in a titration progressively decrease with successive additions of titrants to the solution. This observation is true for either of the solutions containing (i) no MnO_2 and (ii) that which contains it. See table 1a.

   Likewise, on comparing the titrations of 1M $NaNO_2$ i.e the titration of (i) 1M $NaNO_3$ only no MnO_2 and the titration of (ii) 1M $NaNO_3$ with MnO_2: The difference in pH between (i) and (ii) at any given but equal added volume of titrant to the solutions decreases progressively. This is also shown in table 1b. These changes in pH is appilcable to all the anions and their different concentrations.

Reasons for this decrease could be traced to the fact that as the adsorption of the anions progesses the number of site left for further adsorption decreases, so that less and less number of anions goes for adsorption with time. Hence the rate of change of the pH values decreases. As seen from the literature and this experiment it can be inferred that a point will be reached when all the sites would have been covered by the adsorbed anions i.e a complete mono adsorption. Further additions of the titrant from this point will yield no changes in either the pH or the differencesin the change in pH between (i) and (ii).

Effects of Concentration on Adsorption

From the calculation of adsorption from different concentrations it can be clearly seen that the higher the concentration the higher the amount of adsorption per time, except for cases where there are specific adsorption. The reason for this is that higher concentrations contains more of the adsorbate (concentration gradient is higher) and more of it tends to be adsorbed the less concentrated ones contains less of the adsorbate and the concentration gradient between the solid and the adsorbate is less, hence less of it tends to be adsorbed.

Effects of Concentration on Surface charges

With the same reason as stated above the higher the concentration of the anions the higher the surface charge they pose on MnO_2. Calculations of surface charges of MnO_2 from different concentrations of $NaNO_3$ shows that 1, 0.1, 0.01 and 0.001M gave the following respective surface charges - 0.79, 0.42, 0.56 and 0.225ml. Also in the same order of concentration SO^{2-}_4 gave 1.91, 1.12. 1.01 and 0.95 μc.

for Cl^- it was 0.67, 0.89, 0.645 and 0.225μc and Br^{--} gave 0.73, 0.56, 0.36, 0.56 μc.

Now comparing these claculated surface charges (also see table 18 and fig 18) of these anions based on

1. different concentration for each of the anions, we have

NO^{-}_3: 1M >0.01M >0.1M >0.001M

SO^{-}_4 : 1M >0.1M >0.01M >0.001M

Cl^- : 0.1M >1M >0.01M >0.001M

Br^- : 1M >0.1M >0.001M >0.01M

This implies that the surface charges as calculated from 1M of NO^{-}_3 is greater than that calculated from 0.01M of NO^{-}_3 and that of 0.1M NO^{-}_3 of and hence greater than that of 0.001M etc

2. same concentration for different anion

1M: $SO^{2-}_4 > NO^{-}_3 > Br^- > Cl^-$

0.1M: $SO^{2-}_4 > Cl^- > Br^- > NO^{-}_3$

0.01M: $So^{2-}_4 > Cl^- > NO^{-}_3 > Br^-$

0.001M: $So^{2-}_4 > Br^- \geq NO^{-}_3 > Cl^-$

From comaprison 1.

There seems to be an order of decrease of the surface charges from 1M to. 001M except that; for NO^-_3, 0.01M was greater than 0.1M, for Cl^- 0.1M was greater than 1M; and for Br^- 0.1M equals 0.001M and were both greater than 0.01M. The explanation to this difference could be traced to what is referred to as selective or specific adsorption. This is the adsorption of an adsorbate at a particular condition (at a particular concentration in this case) which most at times does not follow a known trend as indicated above. Only SO^{2-}_4 was noticed to follow this order without any specific adsorption.

From comparison 2,

The order of higher surface charges obtained from the experiment for four concentration is shown on comparison number 2 above.

Considering 1M solutions of these anions SO^{2-}_4 takes the lead with the highest surface charge both of high and at low concentration. It is then followed by NO^-_3, Br^- and Cl^- respectively.

The order for 0.1M. 0.01M and 0.001M are also clearly shown in the comparison table.

From the curves of the surface charges E versus concentration C, (fig. 18) $SO2^-_4$ took a distinct lead. This is respectively followed by Cl^-, $NO3^-$ and Br^- the plots for Cl^-, NO_3^- and Br- takes a more slopy form than SO_4^-. This is an indication that small changes in concentration of these anions leads to a more rapid change in the surface charges. Br- and NO_3^- looks more or less paralle to each other.

The isotherm determining curves (fig. 17a and 17b) shows that n and k constants to be all positives. This confirms Tomkin and Freundlich isotherms. See appendix D for calculation

CHAPTER SEVEN

7.0.0 CONCLUSION AND RECOMMENDATION

7.1.0 CONCLUSION

Based on this project and other major work related work carried out on this subject the following conclusions are made-

1. That if MnO_2 is blended with alkaine anions the voltage output will be enhanced. This is because their presence carries some charges which in turn increases the voltage output.
2. That 1M of the anions in solutions will yield a greater surface charge output
3. That SO^{2-}_4 ion is preferable when compared with NO_3^-, Cl^- and Br^-
4. Only SO^{2-}_4 ion has a consistent order of decreaseing surface charges from 1M to 0.001M of solution.
5. That the adsorption of alkaline anion on MnO_2 follows Freundlich and Tomkin isotherms as both isotherms drawn from the result gave the constants n and k, corresponding to the slope and the intercept to be positive all through.

7.2.0 RECOMMENDATION

On viewing the project work and what it involves the following recommendations are made.

1. That in the production of a dry cell alkaline anions most preferably sulphate ion should be blended with MnO_2 in order to enhance its activities.
2. That 1M of the anion in solution should be used . Greater surface charges are obtained from it than that of any less concentration.
3. Any interested person could use Breneaur-Emmet-Teller (BET) method of gas adsorption to determine the surface area of MnO_2 and compare the result with the one obtained by determination by adsorption from water solution as contained in this work.
4. Being the first to work on this subject in the department lots of frustrating difficulties were encountered in the search for chemicals, equipment to use, and books to consult including journals. The department should see to it that all these materials necssary for such an interesting research be made available for interested students and lecturers.

5. BET apparatus should be made available for this work and other works on catalysis requiring the measurement of surface area.

APPENDIX A

MnO_2 DENSITY CALCULATION

$$\text{Relative Density, R.D} = \frac{\text{mass of substance}}{\text{mass of equal volume of water}}$$

mass of substance = $m_2 - m_1$

mass of equla volume = $(m_4 - m_1) - (m_3 - m_2)$

$$\text{R.D} = \frac{m_2 - m_1}{(m_4 - m_1) - (m_3 - m_2)} \text{ ---------------------------------(1)}$$

$$\text{Also, R.D.} = \frac{\text{Density of substance}}{\text{Density of water}}$$

Density of substance = R.D x Density of water--------------------------(2)

From experiment

Locally made MnO_2

mass of density bottle m_1 = 4.45g

mass of density bottle + MnO_2 , m_2 = 18.71g

mass of density bottle + MnO_2 + water, m_3 = 38.704.45g

mass of water m_4 = 30.26

From (1)

$$\text{R.D} = \frac{18.71 - 4.45}{(30.26 - 4.45) - (38.70 - 18.71)}$$

$$\frac{14.46}{25.81 - 19.99} = 2.45$$

From (2)

Density of Locally made MnO_2 = 2.45 x 1000Kg/m^3

= 2450Kg/m^3

Refined MnO_2

m_1 = 4.45g

m_2 = 14.87g

m_3 = 37.77g

m_4 = 30.26g

From (1)

$$R.D = \frac{10.42}{25.81 - 22.9} = 3.58$$

From (2)

Density Refined MnO_2 = $3.58 \times 1000 Kg/m^3$

$= 3580 Kg/m^3$

APPENDIX B

CALCULATIONS INVOLVED IN THE DERTMINATION OF SURFACE AREA OF MnO_2 BY ADSORPTION FROM SOLUTION METHOD

(i) To calculate the concentration C of acetic acid Given

percentage purity (%P) - 99%

Specific gravity S.G. - 1.048

Molar mass (.m) = 60.05

Hencce from

$$C = \frac{\%P \times S.G \times 100}{m.m \times 100}$$

$$\frac{99 \times 1.048 \times 1000}{60.05 \times 100}$$

$$= 17.276002M$$
$$= 17.28M$$

(ii) To calculate the volume of acid needed for $500cm^3$ of 0.15 M

Let $M_1 = 0.15M$

$V_1 = 500cm^3$

$M_2 = 17.28M$

$V_2 = ?$

And from

$$M_1V_1 = M_2V_2$$

$$V_2 = \frac{M_1\ V_1}{M_2}$$

$$= \frac{0.15 \times 500}{17.24} = 4.34cm^3$$

80, 60, 40, 20 and $10cm^3$ of 0.15M were made up to 100 cm^3 with distil water in order to get 0.12, 0.09, 0.06, 0.03 and 0.15M respectively

To calculate the concentration left after adsorption (final conc.)

(iii) Let final concentration of acetic acid = $M_1 = C$

Let final volume of acetic acid $V_1 =$

Let final concentration ofNaOH $M_2 = 0.1M$

Let final volume of NaOH $V_2 =$

$$M_1 = \frac{M_2 V_2}{V_1}$$

Hence using the values from table 1

final conc. for the initial 0.15M sample

$$M_1 = \frac{71 \times 0.1}{50.0} = 0.142M$$

Final conc. for initial sample of 0.12M

$$M_1 = \frac{65 \times 0.1}{50.0} = 0.13M$$

For 0.09M

$$M_1 = \frac{49 \times 0.1}{50.0} = 0.0988M$$

For 0.06M

$$M_1 = \frac{34.2 \times 0.1}{50.0} = 0.0684M$$

For 0.03M

$$M_1 = \frac{17.74 \times 0.1}{50.0} = 0.03548M$$

For 0.015M

$$M_1 = \frac{8.82 \times 0.1}{50.0} = 0.0176M$$

(v) Calculation of slope from graph of fig. y.

$$\text{Slope} = \frac{Dy}{Dx} = \frac{14.2 - 7.0}{(1.4 - 0.42) \times 10^{-1}} = 73.47 = \frac{1}{N_m}$$

Hence $N_m = 0.0136$

(vi) Calculation of specific area

From equation

$A = N_m N_o \times 10^{-20}$

$= 0.0136 \times 6.02 \times 10^{23} \times 10^{-20}$

$= 1719.321\ m^2/g$
or $= 17193120\ cm^2/g$

APPENDIX C

CALCULATIONS OF ADSORPTION AND SURFACE ELETRIC CHARGES.

From last equation in section 2.6.4

Adsorption, $\theta = \frac{\Delta V.\ c}{S.1000}$ --------------------------------(1)

where c and s are constants

$C = 0.1M$ of NaOH

$S = 17193120\ cm^2/g$ (surface area of MnO_2)

Also from equation 3 page 17surface charge $E = nF\theta$ ---------------------(2)

where n = number of charges on anion

F= Faraday's constant 96500C

noow substituting values into (1) $\theta = \frac{\Delta V \times 0.1}{1719312 \times 1000}$?

$\theta = 5.81628 \times 10^{-12}\ \Delta V$---------------------(3)

From table and equation (1) above

1. 1M NO^-_3

Substituting values of ΔV determined from fig 1 into equation (3)

$\theta = 5.81628 \times 10^{-12} \times 1.4$

$= 8.143 \times 10^{-12}$ mole/cm^3

and from (2) $E = 1 \times 96500 \times 8.143 \times 10^{-12}$

$= 7.76 \times 10^{-7}$ C

$= 0.79\mu c$

2. 0.1M NO^-_3

substituting value of ΔV determined from fig 2

$\theta = 5.816 \times 10^{-12} \times 0.75$

$= 4.362 \times 10^{-12}$ mole/cm^3

Hence from equation (2)

$E = 1 \times 96500 \times 4.362 \times 10^{-12}$

$= 0.42\mu c$

3. 0.01M NO^-_3

ΔV from fig. 3

$\theta = 5.816 \times 10^{-12} \times 1$

$= 5.816 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 5.816 \times 10^{-12}$

= 0.56μc

4. 0.001M NO^-_3

ΔV from fi. 4

$\theta = 5.816 \times 10^{-12} \times 0.4$

$=2.327 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 2.327 \times 10^{-12}$

= 0.225μc

5. 1M SO^{2-}_4

ΔV from fig. 5

$\theta = 5.816 \times 10^{-12} \times 1.7$

$= 9.8876 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 9.88 \times 10^{-12}$

= 0.42μc

6. 0.1M SO^{2-}_4

ΔV from fig 6

$\theta = 5.816 \times 10^{-12} \times 1.0$

$= 5.816 \times 10^{-12}$ mole/cm^3

$E = 2 \times 96500 \times 9.88 \times 10^{-12}$

= 1.12μc

7. 0.01M SO^{2-}_4

ΔV from fig. 7

$\theta = 5.816 \times 10^{-12} \times 0.9$

$= 5.23 \times 10^{-12}$ mole/cm^3

$E = 2 \times 96500 \times 5.23 \times 10^{-12}$ μc

8. 0.001M SO^{2-}_4

ΔV from fig. 8

$\theta = 5.816 \times 10^{-12} \times 0.85$

$= 4.944 \times 10^{-12}$ mole/cm^3

$E = 2 \times 96500 \times 4.944 \times 10^{-12}$ μc

9. 1M Cl^-

ΔV from fig. 9

$\theta = 5.816 \times 10^{-12} \times 1.2$

$= 6.98 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 6.98 \times 10^{-12}$

$= 0.674$μc

10. 0.1M Cl^-

ΔV from fig. 10

$\theta = 5.816 \times 10^{-12} \times 1.6$

$= 9.306 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 9.306 \times 10^{-12}$

$= 0.8984$μc

11. 0.01M Cl^-

ΔV from fig. 11

$\theta = 5.816 \times 10^{-12} \times 1.15$

$= 6.98\ 9\times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 6.989 \times 10^{-12}$

$= 0.645$μc

12. 0.001M Cl^-

ΔV from fig. 12

$\theta = 5.816 \times 10^{-12} \times 0.4$

$= 2.33 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 2.33 \times 10^{-12}$

$= 0.225$μc

13. 1M Br^-

ΔV from fig. 13

$\theta = 5.816 \times 10^{-12} \times 1.3$

$= 7.561 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 7.561 \times 10^{-12}$

$= 0.730$μc

14. 0.1M Br^-

ΔV from fig. 14

$\theta = 5.816 \times 10^{-12} \times 1$

$= 5.816 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 5.816 \times 10^{-12}$

$= 0.56$μc

15. 0.01M Br^-

ΔV from fig. 15

$\theta = 5.816 \times 10^{-12} \times 0.65$

$= 3.78 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 3.78 \times 10^{-12}$

$= 0.36$μc

16. 0.001M Br^-

ΔV from fig 16

$\theta = 5.816 \times 10^{-12} \times 1$

$= 5.816 \times 10^{-12}$ mole/cm^3

$E = 1 \times 96500 \times 5.816 \times 10^{-12}$

$= 0.56$μc

APPENDIX D

CACULATION OF CONSTANTS n AND k IN ISOTHERM DETERMINATION

From fig 17(a)

$\frac{\Delta y}{\Delta x}$ = slope = n

(i) n= $\frac{-11.1 - (-11.9)}{0-(-3)} = \frac{0.8}{3} = 0.267$

Also at intercept Logk = -11.1

k = log-(-11.1) = 7.9×10^{-12}

(ii) n = $\frac{-11.1 + 11.4}{-1 + 1.43} = \frac{0.3}{3.3} = 0.09$

logk = -11.1, k= 7.9×10^{-12}

(iii) $\frac{-10.7 + 11.5}{0 + 2.7} = \frac{0.8}{2.7} = 0.296$

logk = -10.7, k = 1.99×10^{-11}

(iv) $\frac{-11.1 + 11.4}{3} = \frac{0.3}{3} = 0.1$

logk = 11.1, k= 7.9×10^{-12}

From 17(b)

(i) n = $\frac{(7-2.3)10^{-12}}{-0.6 + 3}$ $\frac{47 \times 10-12}{2.4} = 1.96 \times 10^{-12}$

k= 8.1×10^{-12}

(ii) n = $\frac{(6.2 - 4.9)}{-0.1 + 2.9} \times 10^{-12}$

$\frac{1.3 \times 10-12}{2.8} = 4.6 \times 10^{-12}$

k = 6.25×10^{-12}

(iii) $n = \frac{(11.1 - 6.0)}{-0.4 + 1.9} 10^{-12}$

$\frac{5.1 \times 10^{-12}}{1.5} = 3.4 \times 10^{-12}$

$k = 12.4 \times 10^{-12}$

(iv) $n = \frac{(7.6 - 3.5)}{2.2} \times 10^{-12}$

$= 1.90 \times 10^{-12}$

$k = 7.7 \times 10^{-12}$

NOMECLATURE

A	adsorbate substance, g
AMD	activated manganese dioxide, g
b_A	adsorption factor of A
$b_{A,O}$	frequency factor
C	concentration, M, g/cm^3, mole/cm^3 mol/g
C_g	concnetration of adsorbable constitutent in the gas, mole/cm^3
CMD	chemical manganese dioxide, g
E	Surface electric charge, μc mole/cm^2
EMD	electrolytic manganese dioxide, g
F	Faraday constant 96500C
ΔH_a	Enthalpy change KJ/gmol
K	adsorption of factor cm/g mole
K_1	constant of adsorption
K_2	constant factor of gas
$N^1{}_A$	The number of sites occupied by the adsorbed molecules of substance A
N^1	The number of sites left uncovered
N_{tot}	Total number of adsorption sites
n	number of charge on ion
P_A	equilibrium presssure of A, mmHg, Atmosphere
Q_A	heat of adsorption for component KJ/gmol
R	gas constant 8.134J/K-mol
S	Surface area cm^2/g
T	temperature °C
V	Volt
V_{NaOH}	Volume of sodium hydroxide titrated m1 or cm
W_{des}	rate of desorption

W_{ad}	rate of adsorption
θ	ratio of the number of sites covered to the total number of adsorption sites (adsorption)mole/cm2
α	alpha
β	beta
γ	gamma
δ	delta
ε	epsilon
η	etha
subscript	
i	ith molecule or substance
j	substance j
D_a	Diameter of impeller, m
D_T	Diameter of cylindrical tank, m
E	Height of impeller above vessel wall, m
L	length of cylindrical vessel, m
L_i	Length of impeller blade, m
H	Height of material from base of vessel m
m	mass of substance g, Kg
J	Width of baffles m
C, Cp	Heat capacity J/Kg K
G	Flow rate of substance Kg/s
d	diameter of pipe, mm
Ce	purchased equipment cost (pound)
S	characteristic size parameter
n	index for the type of equipment
V	volume of vessel m^3
ρ	Density.

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