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THE ION EXCHANGE PROPERTIES OF
MONOCLINIC ZIRCONIA:
A STUDY WITH ION SELECTIVE ELECTRODES

Thesis submitted to the University of Glasgow for
the degree of Master of Science

by

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APRIL, 1990

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Special credit to my parents whose example of perseverance and quest for knowledge are a never ending source of inspiration.

Declaration

The work described in Chapter 6 has been submitted to *Journal of Colloid and Interface Science* for publication jointly with Dr. Ann Smith and Dr. Russell Paterson.

SUMMARY

The amphoteric ion exchange and sorptive properties of monoclinic zirconia are studied here in detail. Microcrystals of zirconia have been prepared and systematically characterized to give a full understanding of the method for crystal growth. A novel algorithm for calculation of ion exchange capacity employing a single pH electrode is utilized. Results are obtained which support the Donnan model for the exchange process. Anion and cation exchange capacities are shown to be a single valued function of the acid pA or base pB. Reversibility is demonstrated and enhancement of exchange capacity is accomplished through common ion addition.

A titration system is developed which incorporates additional ion selective electrodes and includes computer programs for calibration, ion exchange capacity calculations and graphic display of results. This system confirms previous work by showing chloride uptake to match proton uptake. Fluoride uptake by monoclinic crystals of zirconia is revealed to be ten times higher than typical capacities for exchangers of this kind. Again uptake is demonstrated to be reversible, and a single valued function of the acid pHF. Exchange properties of zirconia for fluoride ion are explained by ligand exchange and incorporation in the framework of the oxide.

CHAPTER 1

INTRODUCTION

Introduction

Zirconium, atomic number 40, and atomic weight 91.22, is abundant and widely distributed in the Earth's crust. It is very reactive and is predominantly found as the oxide, baddeleyite, and as zircon, ZrO_2-SiO_2 . The majority of uses for zirconium have been in the ceramics industry and recently as cladding uranium fuel elements in nuclear power plants(1). It is at oxidation level four in nearly all of its compounds and forms compounds which are anionic, cationic and non-ionic(2). The additions of base to acidic aqueous solutions of zirconium salts will cause polymerization and formation of hydrated oxides of zirconium which are amphoteric ion exchangers.

Ion exchange is the reversible exchange of ions of the same charge sign between a solution and an insoluble solid in contact with it(3). The effects of ion exchange were recognized by Aristotle and Moses but not until the late nineteenth century did scientists begin to understand the mechanisms involved. The first and most significant work was done with soils(4). Subsequently the clays, zeolites and humic acids, which acted as ion exchangers, were identified and used commercially to soften water(5).

In 1935 the first synthetic organic ion exchangers

were produced by Adams and Holmes(6). Soon D'Alelio(7) produced a resin made by copolymerizing styrene with the crosslinking agent, divinyl benzene. Nearly all current commercial resins are based on polystyrene beads which are either sulfonated to produce cation exchangers or treated with a tertiary amine for anion exchange. This revolutionized the science of ion exchange because it made it possible to vary the properties of ion exchangers for systematic experimentation(8).

The synthetic organic exchangers would seem to leave natural and synthetic inorganic exchangers no significant role in the ion exchange industry. However, there are two major limitations of organic exchangers; they are thermally unstable, at temperatures of greater than 50 °C, and they tend to breakdown in the presence of large doses of ionizing radiation.

In the mid 1950's a large number of inorganic insoluble oxides were studied for their ion exchange behavior. Of the oxides for potential practical interest, zirconia was one of the most important(9). A precipitate of hydrous zirconia is formed when excess base is added to a solution of a zirconyl salt. Kraus and Phillips(10) recognized the importance of hydrous zirconia as an ion exchanger for radioactive species and demonstrated that this was stoichiometric exchange and not a sorption process. Subsequent publications by Amphlett, McDonald and Redman(11) revealed zirconia's amphoteric behavior,

exchanging anions in acid and cations in alkali.

At this point research was limited by the random nature of hydrous gel materials and a crystalline supply of zirconia was needed. Knowledge of the crystal structure is fundamental for a deeper understanding of the ion exchange process, as well as the interpretation of thermodynamic measurements(12). Clearfield produced both monoclinic and cubic forms of zirconia by refluxing aqueous slurries of zirconia in 1955(13). A possible structure for zirconia was postulated later by Blumenthal(14) and Clearfield(15). Fryer, Hutchison and Paterson(16) studied samples drawn from solution at various times during the hydrolysis and crystallization process using electronmicroscopy. Their observations supported Clearfield's hypothesis on the steps involved in crystal growth.

Paterson and Rahman(17) used this preparation for monoclinic zirconia, systematically studied cation and anion exchange properties, and explained them with thermodynamic models. Their work demonstrated, through pH titrations, that anion exchange on the acid side of the zero point charge was due to the protonation of the crystalline material and that cation exchange in the alkaline range was attributed to hydroxylation. These experiments were reproducible, stoichiometric and verified by the fact that results could be represented as a single valued function of the acid or base.

A potentiometric system was developed specifically for this work. The system included a measuring cell capable of handling four ion-selective electrodes and allowing for the addition of reagents and standards. Computer programs were written for calibration, generating first and second order calibration equations. Previous programs for calculation of uptake using a pH electrode were updated and a new algorithm was written to calculate capacities including data from the multi-electrode system. All these programs were interfaced with a multi-color screen plotting program for fast graphic display of results.

Initially the new system was employed to confirm the previous work by Paterson and Rahman. Once again the addition of salt to suspensions of zirconia caused an increase in uptake by supplying the counter ions to preserve electroneutrality. Chloride, and sodium ion-selective electrodes were included in the pH titrations and the direct quantitative measurements dramatically verified previous findings.

The interaction between fluoride and zirconia is well documented(18)(19), and initial attempts to characterize the uptake of fluoride by hydrous gels of zirconia showed high capacities(20). The fluoride ion-selective electrode was introduced into the potentiometric system with some striking results. This study shows the capacity of fluoride by monoclinic

zirconia to be a decade larger than typical capacities for these types of exchangers. The uptake for fluoride is essentially equal to that for proton uptake, again a single valued function of the acid. Finally, the fluoride ion exchange is shown to be reversible over a large pH range. Calculations from surface area measurements prove that such large capacities for fluoride must include replacement of hydroxyl groups within the crystal lattice.

CHAPTER ONE REFERENCES

1. W. B. Blumenthal, *The Chemical Behavior of Zirconium*, (1958)
2. K. Dorfner, *Ion Exchangers: Properties and Applications*, 2nd ed., (1972)
3. H. S. Thompson, *J. Roy. Agr. Soc., Eng.* (1850) 11, 68.
4. J. T. Way, *J. Roy. Agr. Soc., Eng.* (1850) 11, 313.
5. J. Lemberg, *Z. Deut. Geol. Ges.*, (1870) 22, 335.
6. B. A. Adams and E. L. Homes, *J. Soc. Chem. Ind.*, (1935) T54, 1.
7. G. F. D'Alelio, *U.S. Patent*, (1944) 2, 336,007.
8. F. Helfferich, *Ion Exchange*, McGraw Hill, (1962)
9. C. B. Amphlett, *Inorganic Ion Exchangers*, Elsevier (1964)
10. K. A. Kraus, H. O. Phillips, et. al., *Proc. Int. Conf. Peaceful Uses of Atomic Energy*, Geneva, 28, 3, (1958).
11. C. B. Amphlett, L. A. McDonald and M. J. Redman, *J. Inorg. Nucl. Chem.*, 6, 236, (1958)
12. A. Clearfield, *Inorganic. Chem*, 3, 146, (1964)
13. A. Clearfield, *Rev. Pure Appl. Chem.*, 14, 9, (1964)
14. J. R. Fryer, J. L. Hutchison and R. Paterson, *J. Colloid Interface Sci.*, 34, 238, (1970)
15. R. P. Paterson, H. Rahman, *J. Coll. Interface Sci.*, Vol. 103, No. 1, (1985)

CHAPTER 2

PREPARATION OF MONOCLINIC ZIRCONIA

2.1 Introduction

The ion exchange properties of hydrous gels of multivalent metals has been studied for many years. These gels are produced by base precipitation and although a very effective ion exchange material they yield a great deal of variability in results. In the following chapter the preparation of monoclinic zirconia is outlined in detail. Zirconia is found naturally as the mineral baddelyite which has a monoclinic crystal structure. Not until Clearfield's work in 1964 was a method available to prepare monoclinic crystal zirconia from zirconyl chloride.(1) The continued refinement of that method by this laboratory has resulted in reproducibly high quality crystals. Also, through the efforts of several researches the mechanism for crystal development is understood and explained here in detail.

Electron micrographs, diffraction patterns, thermolysis curves and surface area measurements are provided in this chapter to verify the preparation of monoclinic zirconia.

2.2 Preparation

Monoclinic crystals of zirconia were prepared following the method of Clearfield(1) incorporating improvements made by Paterson and Raman(2) of this laboratory. Zirconyl chloride $ZrOCl_2 \cdot 8H_2O$ was used as a starting material. One mole per liter of this material was dissolved in distilled water and yielded a clear solution with an approximate pH of 0.4. To this 0.5 M NH_4OH was added as slowly and with as much stirring as possible. The pH was monitored and the solution was gradually brought up to pH 2.0. During the addition of base amorphous zirconia could be seen forming in the flask. This occurred more frequently above pH 1.5. When precipitates formed in the solution, time was allowed for dissolution to take place before subsequent additions of base were made. No permanent precipitation occurred.

After reaching pH 2 the solution was filtered, transferred to a round bottom three necked flask and refluxed at $100^\circ C$ for 24 hours. A milky white precipitate of zirconia was formed. The mixture was separated by centrifuging at 23000g. The supernatant was again adjusted to pH 2 using NH_4OH and refluxed at $100^\circ C$ for an additional 24 hours. Periodically small samples of solution were removed and tested for un-hydrolysed

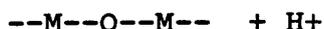
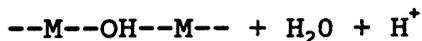
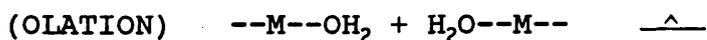
zirconia salts by addition of NH_4OH . At the point where addition of base no longer precipitated zirconia the reflux was discontinued. The monoclinic zirconia was removed washed with distilled water and centrifuged.

This step was repeated until the washings contained less than 10^{-5} M chloride ion. This chloride level was measured with an Orion model 94-17B Chloride electrode and a model no. 940 pH meter. Note: The use of added urea for homogenous generation of hydroxide as described by Skoog and West is an alternative method for addition of base. (3)

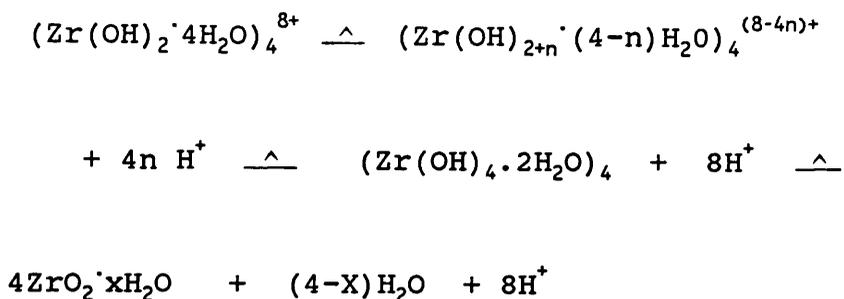
2.4 Results and Discussion

The electron micrographs and diffraction patterns show conclusively that the structure of our prepared material is monoclinic zirconia.

The precipitation of hydrous oxides and oxide hydroxides from metal salt solutions is more complex than most precipitation processes because nucleation and growth cannot be solely described by the deposition of ionic units upon a crystal nucleus. In this case chemical reactions, olation and oxolation, occur to form polymeric species. Olation is the formation of a hydroxyl bridge with the elimination of water. Oxolation is the formation of an oxo bridge at the expense of a hydroxyl bridge.



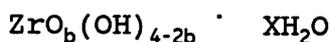
Using these reactions we can proceed to the overall mechanism for the preparation of monoclinic zirconia.



In step (1) the zirconyl chloride is dissolved in water and the hydrolysis begins. In step (2) the solution is refluxed, the olation reaction occurs between tetramer units and the two-dimensional layered polymers form. In step (3), continued refluxing causes oxolation. This condensation of water from two -ol bridges in adjacent layers yields the three dimensional structure. When the polymers attain a size of 12-24 unit cells, they precipitate. Initial crystals are poorly formed but continued refluxing causes crystal growth and crystal perfection with a transformation from the cubic to the monoclinic structure.(4)

Similar reactions take place in base precipitation, however the process occurs so rapidly that the resulting structure is much less orderly and little time is allowed for oxolation. Although the monoclinic zirconia has a composition close to (ZrO_2) it contains a significant number of hydroxyl groups.

Thus the crystalline hydrous zirconias are considered to be hydrated oxo-hydroxides, with the formula shown.



The value of b is variable and depends upon the conditions of the preparation. (5)

Of particular significance to the following fluoride ion exchange studies is the fact that monoclinic zirconia may be regarded as a distorted fluorite lattice. (6)

Thermogravimetric analysis with a thermobalance indicated 17% water in the monoclinic zirconia used in these studies. This was in agreement with the 16.4% weight loss measured after heating a sample at 1100°C for eight hours. No conclusive information is revealed in the thermolysis curve to predict the the relative distribution of moisture, hydroxide, and combined water. In similar work Duval reported a $\text{ZrO}_2 \cdot \text{H}_2\text{O}$ which corresponded to a distinct break at 120°C. He points out that continued loss of water above 100°C indicates a great likelihood that the water makes up part of the constitution of the material and also that water will be produced at the expense of hydroxyl groups concealed in the compound. (8) The lack of a significant weight loss at higher temperatures, which

would be due to the volatilization of contaminating salts, indicates the purity of the material.

The BET surface area was calculated to be $197.7 \text{ m}^2/\text{g}$ from the isotherms generated with N_2 and H_2 . Hutchison calculated a surface area from the dimension of the crystals and the density of monoclinic zirconia to be in the $10\text{-}40 \text{ m}^2/\text{g}$ range. He explained the large discrepancy between the measured and calculated areas as being attributed to a high porosity. As further evidence N.M.R. signals from aqueous solutions or suspensions showed a broadening consistent with highly porous structures. (8)

Plate 2.1 Electron micrograph of monoclinic zirconia used in this work.

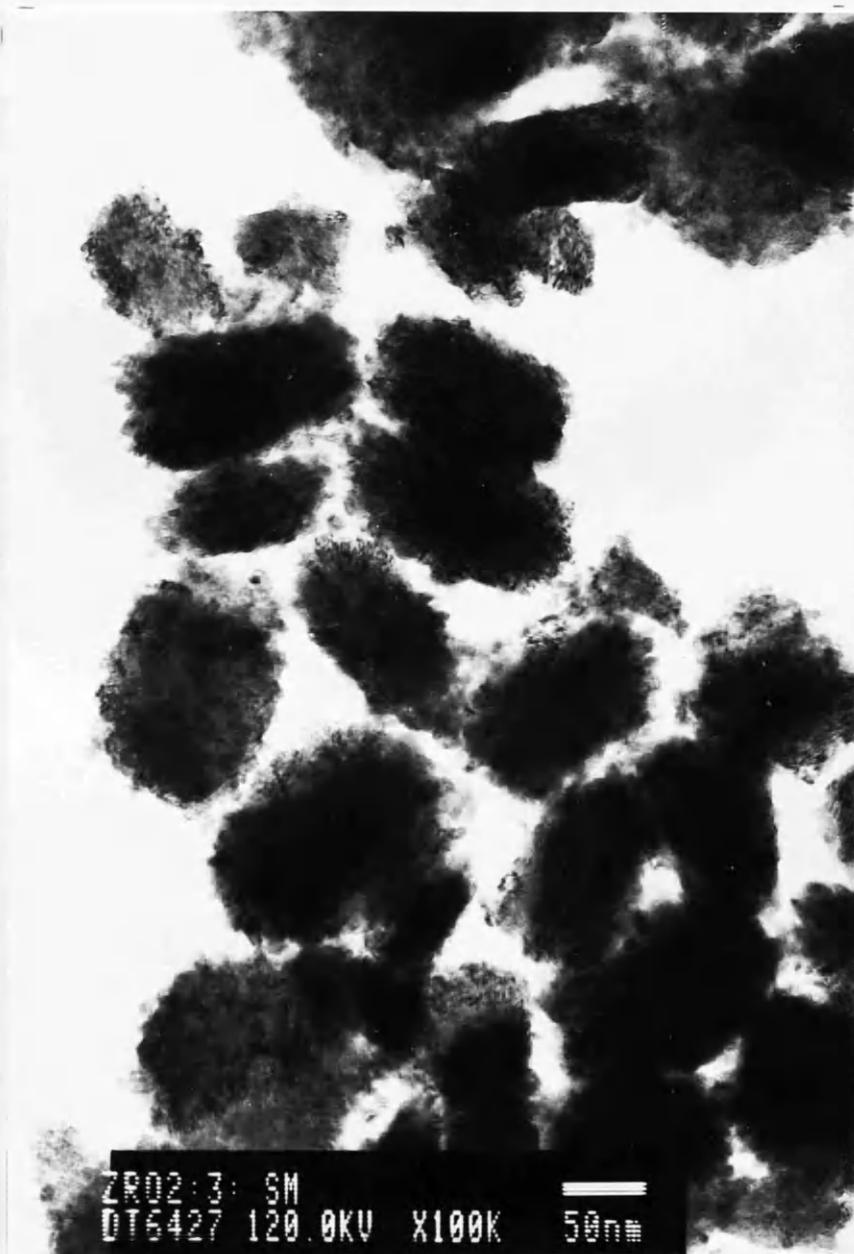


Plate 2.2 Electron micrograph of a second preparation of monoclinic zirconia showing the same morphology.

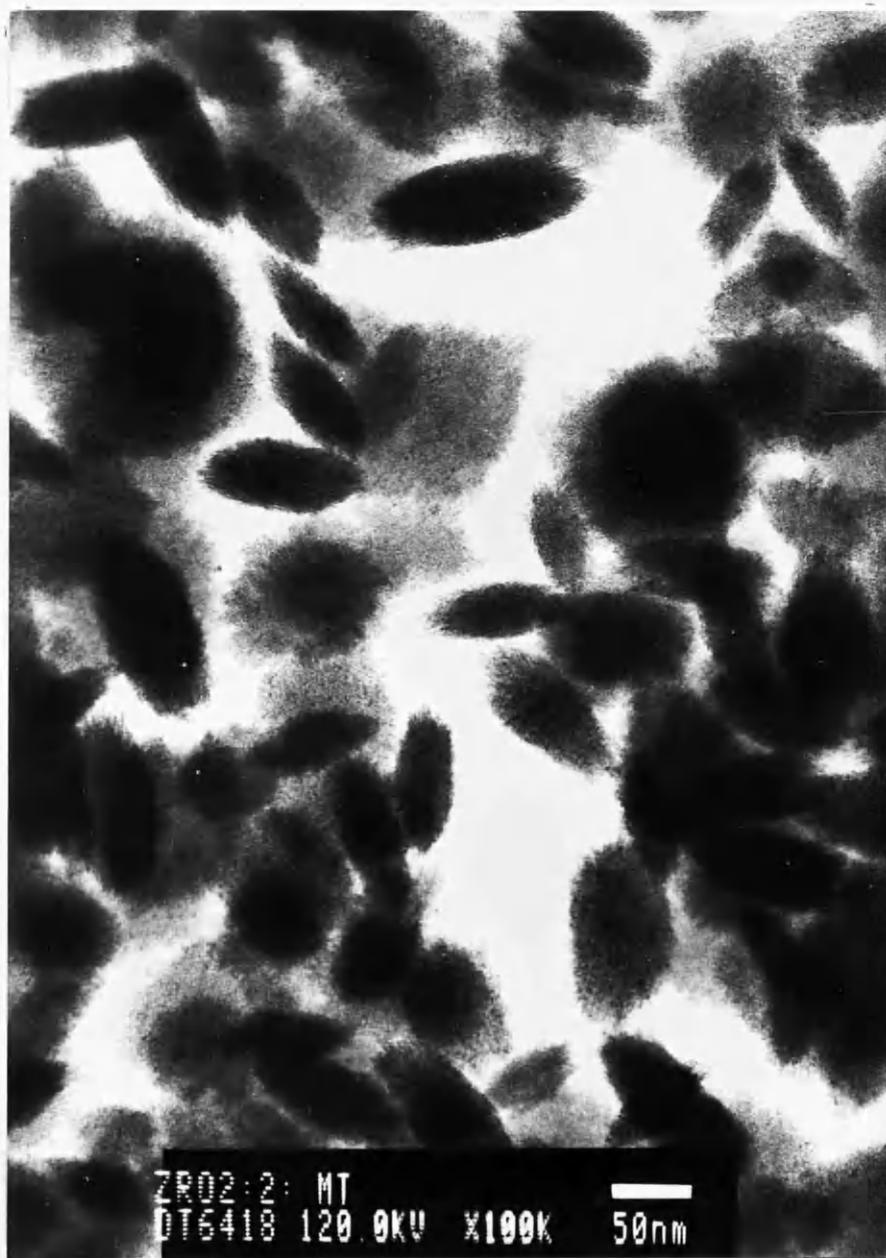


Plate 2.3 Electron micrograph of monoclinic zirconia after fluoride uptake.

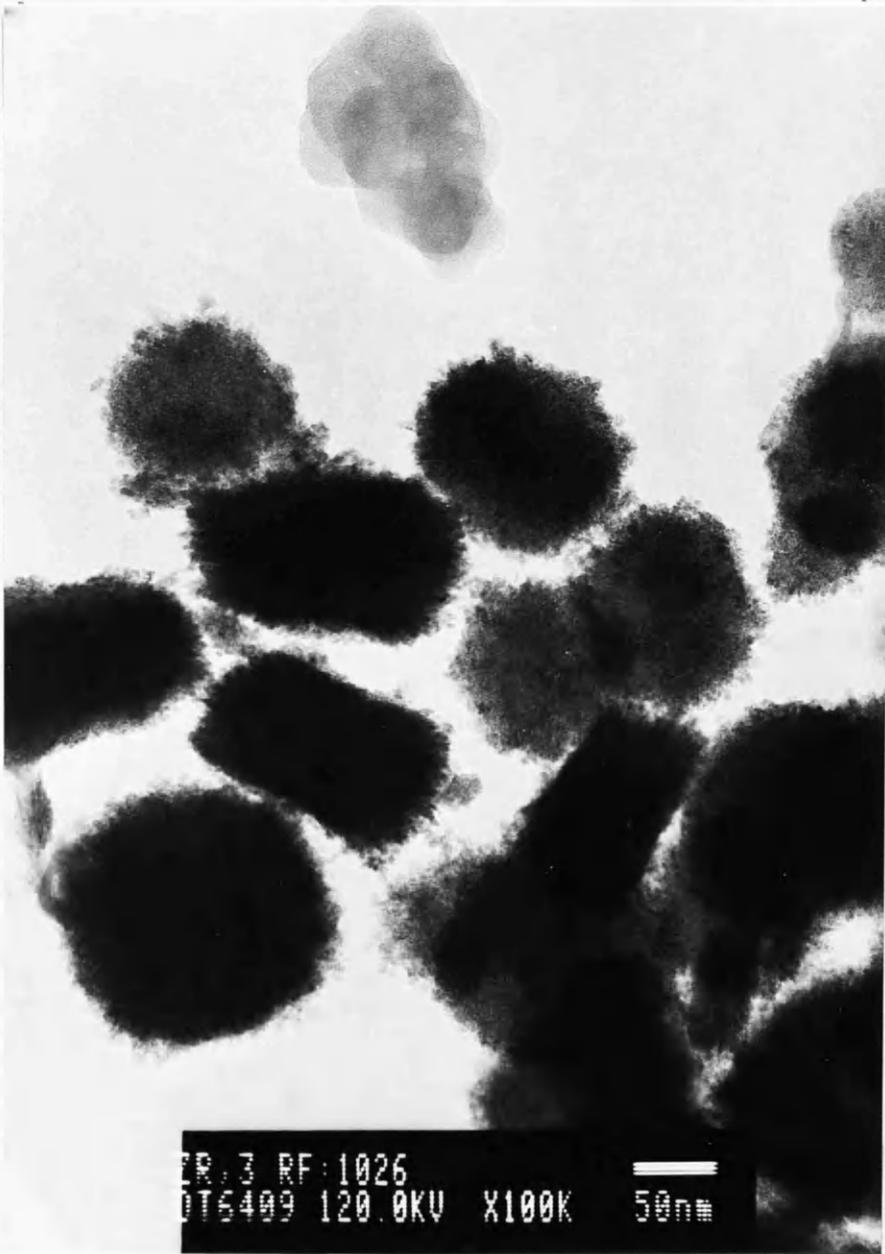


Plate 2.4 Diffraction pattern of monoclinic zirconia used in this work.

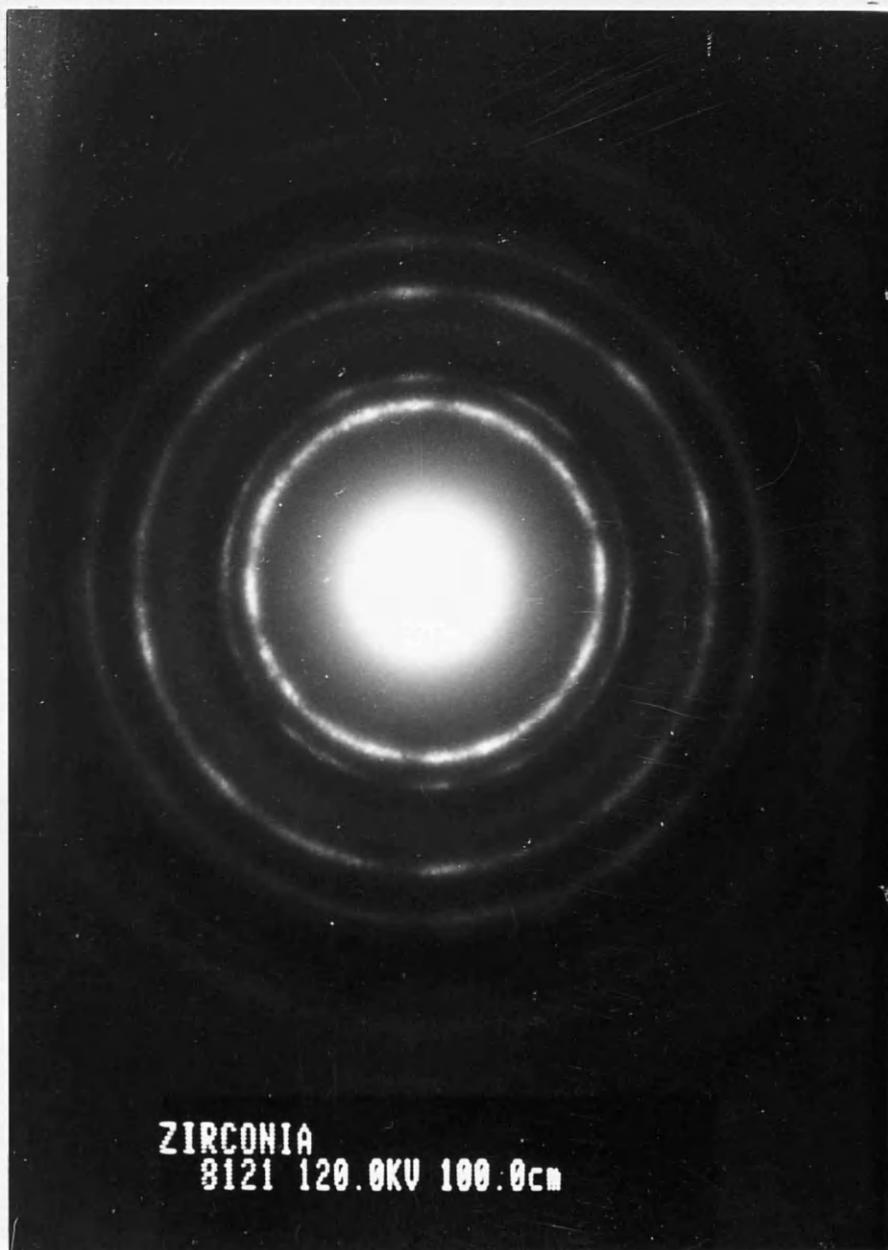
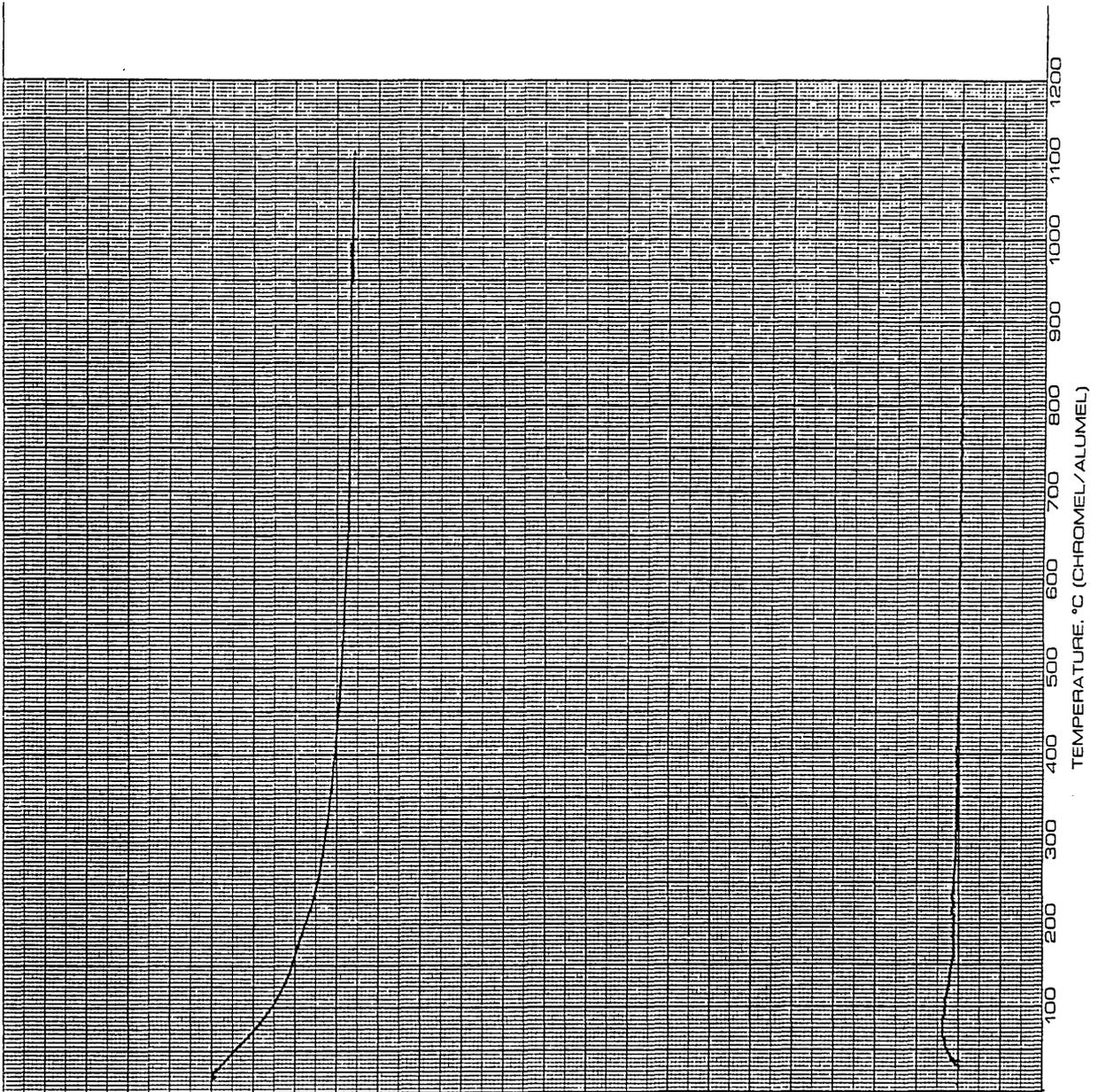


Plate 2.5 Thermolysis curve of monoclinic zirconia used in this work.



RUN NO. _____ DATE 27/12/85
 OPERATOR S. M. Colloff
 SAMPLE H/R Zr
 ATM SEA Ala ©
 FLOW RATE 50 ml/min

T-AXIS
 PROG. RATE: °C/min 2.0
 RANGE: °C/cm 50
 HEAT COOL ISO
 SHIFT: cm +10
 TIME: min/cm _____

TGA 50 µg/mV DTG 50 µg/(min mV)
 SUPPRESSION: mg 0
 RANGE: mV/cm 5
 WEIGHT: mg 6.95
 TIME CONST.: sec 1
 dY: 5 4/2

TMA 1 µm/mV DTM 0.1 µm/(min mV)
 MODE _____
 RANGE: mV/cm _____
 SAMPLE SIZE _____
 LOAD: g _____
 dY _____

Du Pont Instruments

MEASURED VARIABLE

CHAPTER TWO REFERENCES

1. A. Clearfield, *Inorg. Chem.* 3, 146, 1964
2. R. Paterson, H. Rahman, *J. Coll. Interface Sci.*, Vol. 103, No. 1, 1985
3. D.A. Skoog, D.M. West, pg 133, Holt, Reinhart and Winston, New York, 1976
4. J.L. Hutchison, Thesis, Glasgow University, 1970
5. A. Clearfield, Structural Aspects of Zirconium Chemistry *Rev. Pure and Appl. Chem.*, 14, 91, 1964
6. G. Lundgren, *Svensk Kem. Tidskr.*, 71, 200, 1959
7. C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier Publishing, New York, 1963, pg 446
8. J.R. Fryer, J.L. Hutchison and R. Paterson, An Electron Microscopic Study of the Hydrolysis Products of Zirconyl Chloride, *J. Coll. Interface Sci.*, 1970, Vol. 34, No. 2, pg 238

CHAPTER 3

POTENTIOMETRIC TITRATION

SYSTEMS

3.1 Introduction

The calculation of uptake based on the change in hydrogen ion activity, pH, has resulted in a greater understanding of the mechanisms involved in the ion exchange process. The recent developments with ion-selective electrodes make it possible to expand on the work with the pH electrode and include other species of interest.

Naturally, this presented the task of developing a system physically capable of handling the increased number of sensors and the new algorithms to process the data.

In this chapter there is a description of the new measuring cell with an explanation of the major considerations involved in the design. Also, the preparation of reagents and standards are discussed in detail. The general procedure followed for each titration and control titration is described and the specific equipment required is listed.

Last, computer programs were written to reduce the data to meaningful results. These programs are given in the Appendix. Calibration equations, first and second order are determined using Program(P.1), to create the data file, and Program(P.2) to calculate the results. The

uptake is calculated by interfacing Program(P.3), the experimental data file, with Program(P.4), the new algorithm for uptake calculation. All of these programs interface with a Program(P.5), a screen plotting program for immediate graphing results. The "screen dump" facility made it possible to have a hard copy at the completion of an experiment.

These tools provided a total system which was quick reliable, and performed perfectly when subjected to null and control testing.

3.2 Titration Cell

Initial work on the evaluation of zirconia ion-exchange crystals was done with a combination pH electrode. To further evaluate the selective properties of the crystals it became necessary to measure other species. For this reason it was decided to expand on the use of ion-selective electrodes, primarily chloride, fluoride and sodium.

A titration cell was designed with the following specifications:

First, it be capable of handling four electrodes in a volume of 20 ml.

Second, that the vessel containing the solution be made of polypropylene to avoid attack from hydrofluoric acid.

Third, the temperature be controllable using water from a constant temperature bath.

Fourth, provision be made for the introduction of nitrogen gas to maintain a carbon dioxide free atmosphere.

Fifth, it be possible to raise the level of the electrodes during the titration period.

Sixth, ports be available for the addition of titrants and other solutions.

Seventh, that the solution be well stirred.

The result can be seen in the drawings, Figure(3.1) and Figure(3.2) and the photograph Plate(3.1).

Temperature Control

To eliminate the possible effects of varying temperature all experiments were performed at 25°C. This temperature control was achieved with water from a constant temperature bath.

The temperature was maintained with a mercury-toluene regulator used as a switch to an infra-red light bulb. As the temperature decreased the toluene density decreased and the height of the mercury column in contact with the toluene decreased. Through the use of an electronic control system when the mercury contact was broken the light bulb was energized. The opposite effects occurred when the temperature increased. The temperature controlled water was then pumped through a double walled glass beaker. This arrangement maintained the temperature of the solution within beaker to 0.01°C.

3.3 Standards and Reagents

All chemicals used in the preparation of standards and reagents were of Analar grade and all glassware was grade "A". Distilled water was used exclusively throughout the experimental work.

Standard pH Buffer Solutions

The following solutions were prepared according to the method of Perrin and Dempsey(3). pH values are given at 25°C.

pH 1.50 : dissolve 1.864 grms of KCl in 200 ml H₂O, add 20.7 ml 1M HCl and dilute to 500 ml.

pH 3.00 : dissolve 5.1055 grms KHphthalate in 200 H₂O, add 11.15 ml of 1M HCl and dilute to 500 ml.

pH 4.00 : dissolve 5.1055 grms of KHphthalate in 200 ml H₂O, add 0.5 ml of 0.1 M HCl and dilute to 500 ml.

pH 7.00 : dissovle 3.0285 grms Tris in 200 ml H₂O, add 23.3 ml 1M HCl and dilute to 500ml.

pH 9.00 : dissolve 3.0285 grms of Tris in 200 ml H₂O, add 28.5 ml 0.1M HCl and dilute to 500 ml.

pH 10.00 : dissolve 2.384 grms of Na₂B₄O₇ · 10H₂O in 200 ml H₂O, add 91.5 ml 0.1M NaOH and dilute to 500 ml

pH 11.00 : dissolve 1.7745 grms Na₂HPO₄ in 200 ml H₂O, add 20.5 ml 0.1M NaOH and dilute to 500 ml.

pH 12.00 : dissolve 1.7745 grms of Na₂HPO₄ in 200 ml H₂O, add 134.5 ml 0.1M NaOH and dilute to 500 ml.

Preparation of 0.1M NaOH

A 100 ml VOLUCON, M & B Ltd, sealed container of CO_2 free 1M NaOH was added to approximately 800 ml of H_2O previously equilibrated with N_2 gas. This solution was contained in an automatic burette protected at the air openings with soda lime CO_2 adsorbant. Standardization against weighed samples of dry potassium hydrogen phthalate, using phenolphthalein as an indicator, gave precision within 0.1%.

Preparation of Sodium Chloride Solutions

Chloride solutions were prepared by dissolving NaCl salt in H_2O using volumetric glassware. These solutions were then analysed by potentiometric titration with a gravimetrically prepared standard silver nitrate solution. The titrant was contained in a specially prepared 10 ml buret with a silver wire sealed in below the stopcock. The tip of the burette was immersed in the analyte. This solution contained the second electrode, a chloridized silver wire, and was stirred with a magnetic stirrer. The two electrodes were connected to a "Solatron" model A210 voltmeter which measured the emf of the cell directly. After each addition from the buret the solution was first stirred and then allowed to stand. When a steady potential was achieved it was recorded along with the

buret reading. The precise endpoint was determined by a Gran Plot method(4).

Preparation of Sodium Fluoride Solutions

Fluoride solutions were prepared by dissolving NaF salt in H₂O using volumetric plasticware to allow for the fact that fluoride reacts with glass. These solutions were analyzed by ion exchange and by the alizarian red titration.(5,6) The polystyrene quaternary ammonium anion exchanger Amberlite IR-400 was prepared in the hydroxide form using 2M NaOH. These beads were then rinsed with CO₂ free H₂O and placed in columns 10 cm long and 1 cm in diameter. The rinsing with H₂O was continued until a neutral pH of 7 was found in the effluent. Approximately 0.5 meq of the fluoride solution to be analysed was added to the top of the column and this was washed through again until the the pH was neutral. The NaF now converted into NaOH was made acid with a known amount of analyzed HCl and back titrated with NaOH using phenolphthalian as an indicator. This was repeated several times and gave results within 0.2%. As a check on this method a sample was given to the micro-analysis group of the Chemistry Department. On a very diluted sample, using the alizarian red back titration with thorium nitrate, their results fell within 1% of the ion exchange method.

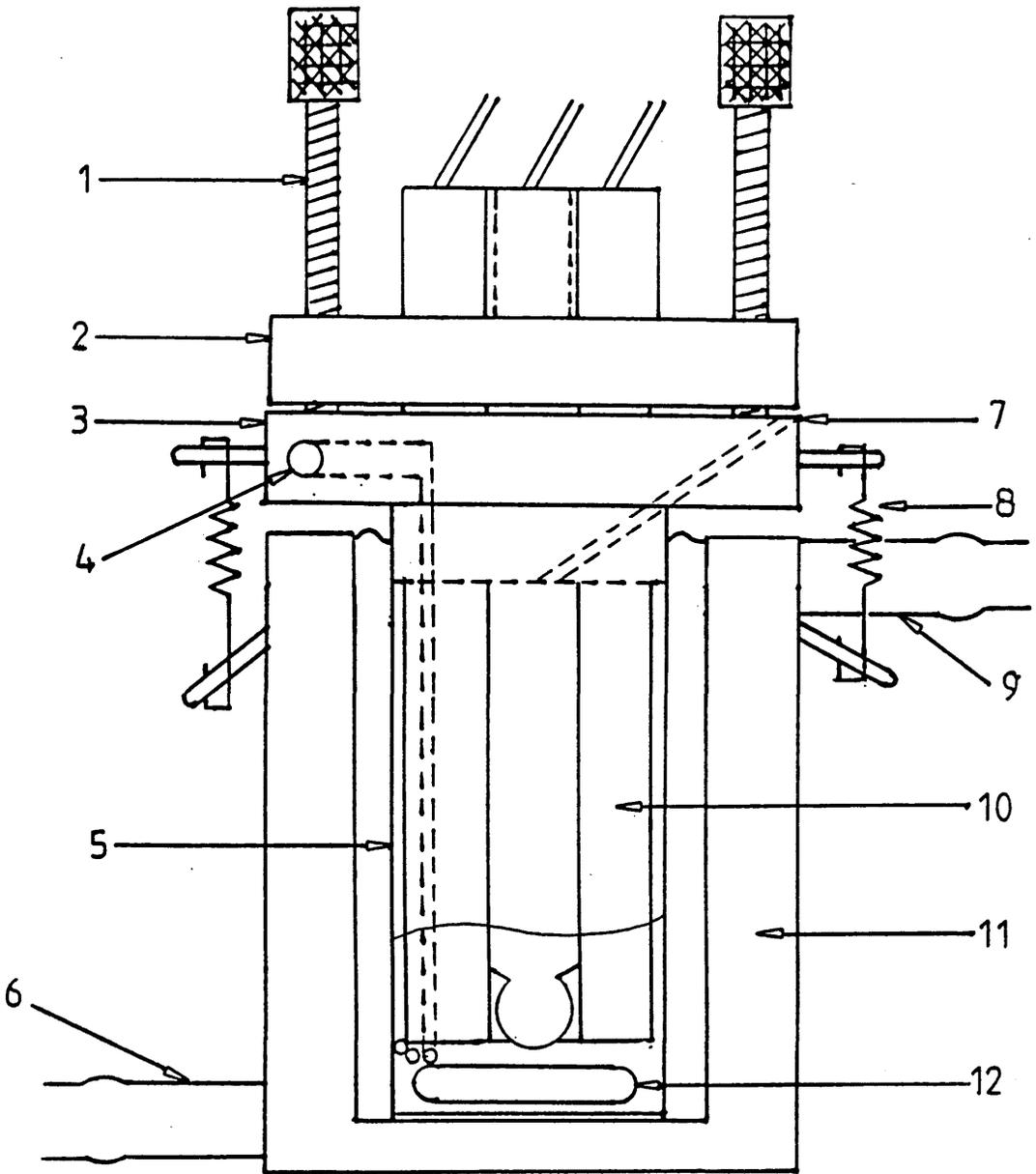
3.4 Experimental Procedure

The microcrystals of zirconium oxide are suited for titration due to their size and speed to reach equilibrium. Using the titration cell described, Ch.3.2, typically 0.3 + 0.05g of the oxyhydroxide was placed in 20 ml of distilled H₂O and stirred overnight to allow for complete hydration. Before the electrodes were introduced into the titration cell they were calibrated using the procedure given in Ch.4.4. Temperature was maintained at 25°C and N₂ gas was introduced to maintain a CO₂ free atmosphere. The colloidal suspension was made acid with HCl to allow for conversion and removal of any carbonate as CO₂. At this point experimental conditions were varied depending on the parameter to be investigated. One or more of NaCl, NaF, HCl, and NaOH were added using 10 ml micro burets with fine capillary tips. These capillaries were suspended directly in the titration solution. Previous work by Paterson and Raman(7) has shown that diffusion of titrants into the suspension is not significant.

The electrodes placed in this cell were connected to an Orion model 940 pH meter and model 607 electrode switch. This meter was used exclusively to take mV readings which were later used in computer programs to calculate concentrations and activities.

The electrodes, except those for pH, were manufactured by Orion Research: The model 94-17 B Chloride, the model 94-09 Fluoride, the model 94-11 Sodium electrode, and the model 90-02 double junction reference electrode. The pH electrodes, model SWL, were manufactured by Russell PH LTD.

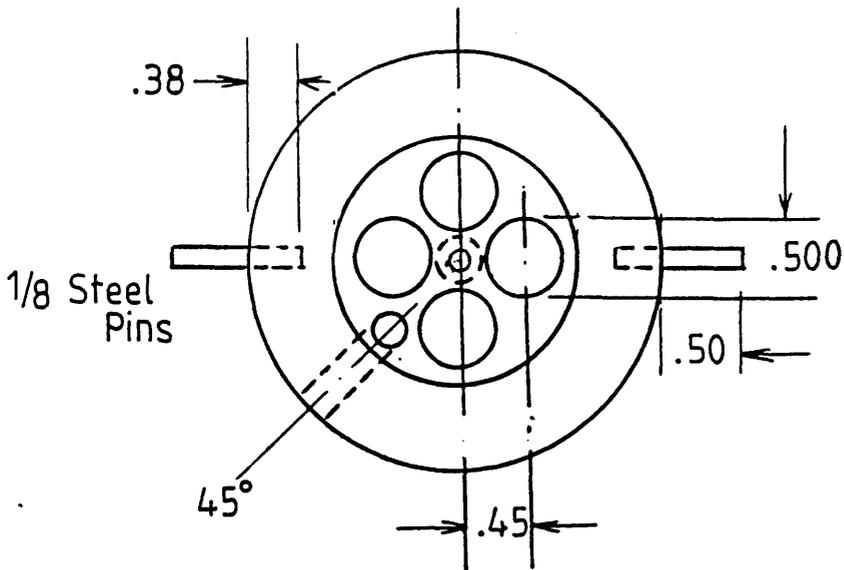
FIGURE 3.1



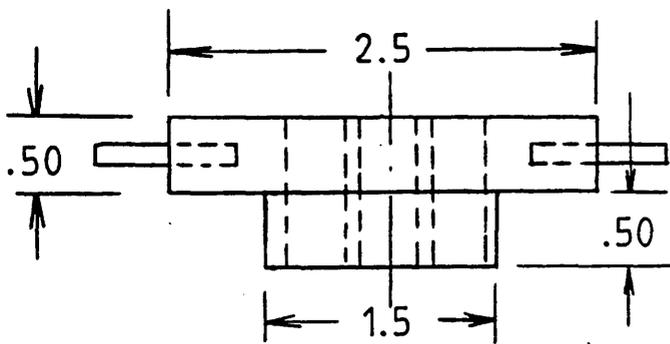
- | | | | |
|---|----------------------|----|--------------------------|
| 1 | Height Adjustment | 7 | Reagent Inlet Port |
| 2 | Electrode Holder | 8 | Spring |
| 3 | Cell Cap | 9 | Water Outlet |
| 4 | Nitrogen Inlet | 10 | Electrodes (Four) |
| 5 | Polypropylene Beaker | 11 | Double Wall Glass Beaker |
| 6 | Water Inlet | 12 | Stir Bar |

TITRATION CELL

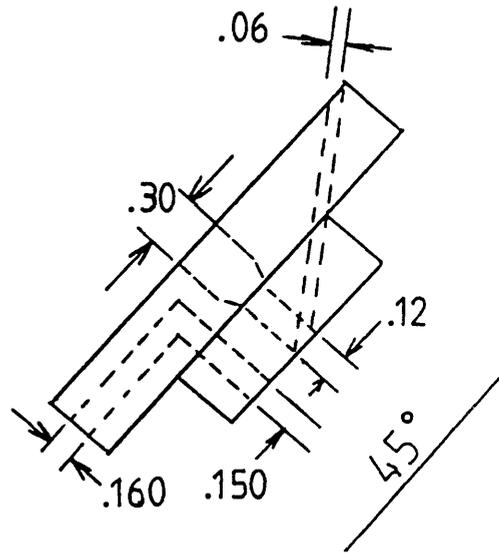
FIGURE 3.2



BOTTOM



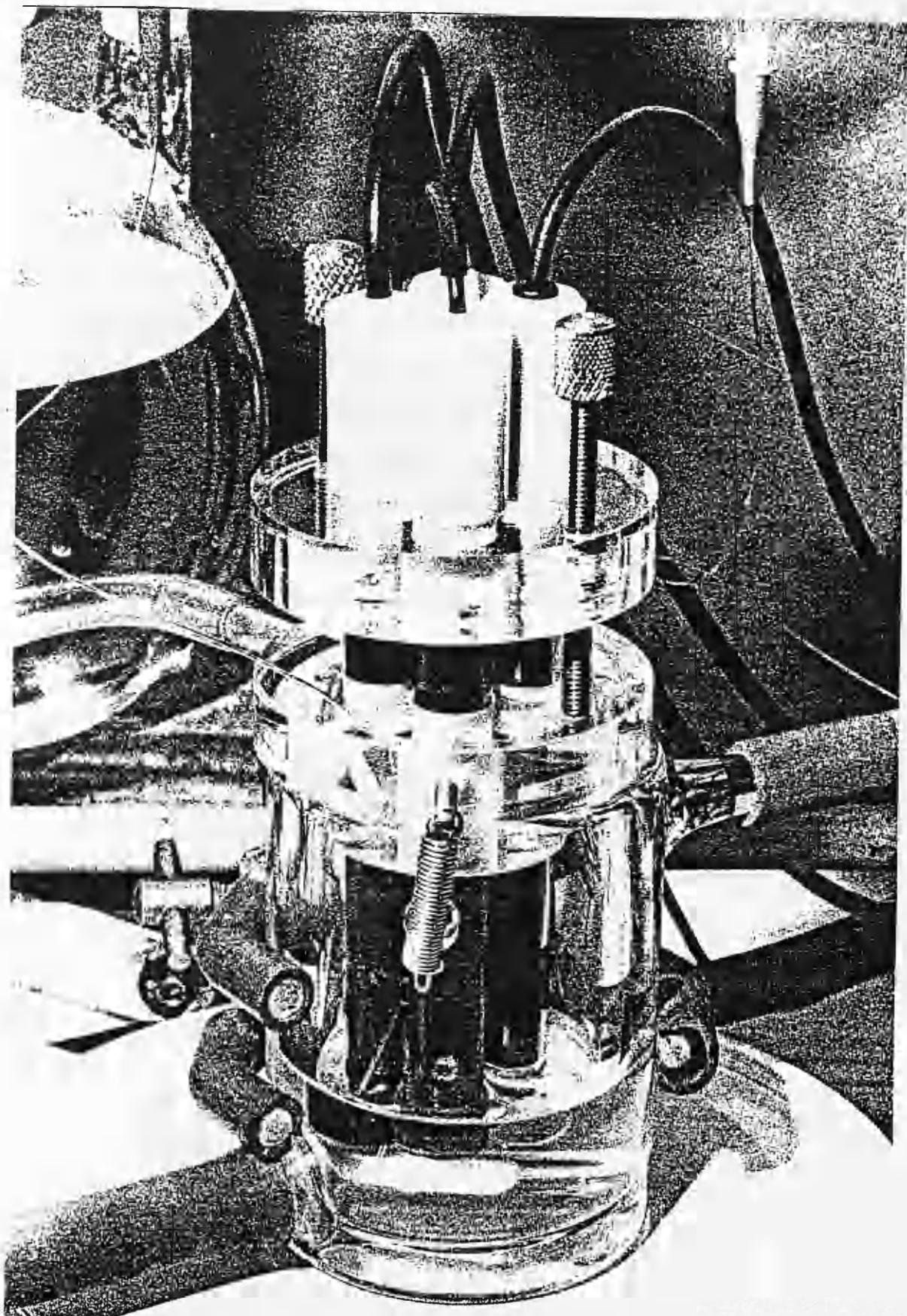
SIDE



Material:
Clear Acrylic

TITRATION CELL CAP

PLATE 3.1



CHAPTER THREE REFERENCES

1. C. J. Brooks, I.G. Betteley, *Fundamentals of Mathematics and Statistics for Chemistry*, John Wiley and Sons, Chinchester 1979
2. A.C. Norris, *Computational Chemistry*, John Wiley and Sons, New York, (1981).
3. D.D. Perrin and B. Dempsey, *Buffers for pH and Metal Ion Control*, Chapman and Hall Ltd, (1974).
4. G. Gram, *Analyst*, 77, 661, (1952)
5. W.J. Williams, *Handbook of Anion Determinations*, Butterworths London, (1979)
6. W. Wagner, C.J. Hull, *Inorganic Titremetric Analysis Contemporary Methods*, Marcel Dekker, (1971)
7. R. Paterson and H. Rahman, *J. Coll. Interface Sci.*, Vol. 94, No.1, (1983).

CHAPTER 4

ION SELECTIVE ELECTRODES

4.1 Introduction

In 1906 Cremer made the first observation that a hydrogen ion sensing glass electrode responded to hydrogen ions according to the Nernst equation(1). In the 1920s MacInnes and Dole developed a formula for pH glass which became the standard. During the late 1950s and early 1960s Eisenman(2) proposed theories to explain the origin of the glass electrode potential and developed an optimum formula for the composition of a glass to measure sodium ions. Also with the 1960s came the development of the fluoride electrode by Frant and Ross(3), along with the silver and halide electrodes made from pellets of the appropriate silver salt. Due to the recent discovery of these valuable analytical tools new applications are still being found. Their aid in the understanding of ion exchange mechanisms is an example.

In the following chapter the theory of operation, construction, calibration and interferences of the electrodes used in this experimental work will be discussed. Computer programs to store data, determine calibration equations, display results and print tables and graphs were written specifically for this work.

4.2 Theory

An ion selective electrode will develop an electrical potential proportional to the activity of a selected ion in solution. This potential, E , is described by the Nernst equation Eqn.(4.1). E_0 is the standard potential, z is the charge of the ion, x , being measured and

$$E = E_0 + \frac{RT}{z_x F} \ln a_x \quad (4.1)$$

a_x , is the activity of x . The activity is equal to the product of the concentration, C_x , and the activity coefficient, α . Eqn(4.2)

$$a_x = \alpha C_x \quad (4.2)$$

Substituting Eqn 4.2 into Eqn 4.1, including values for R , T and F the Nernst equation can be re-written in the form Eqn(4.3)

$$E = E_0 + \frac{\text{-----}}{z_x} \log C_x \quad @ 25^\circ\text{C} \quad (4.3)$$

The mean activity coefficient is given by the Debye-Huckel interionic attraction theory Eqn (4.4). Here, I , is the ionic strength, z_x, z_y , are the charges of the anions and

$$-\log \alpha = \frac{z_x z_y A \sqrt{I}}{1 + Ba \sqrt{I}} \quad (4.4)$$

the cations, a is the mean ionic diameter and at 25°C , A is 0.511 , and B is 3.29×10^7 . From this Davies(4) developed an empirical relationship Eqn (4.5) for the activity coefficient.

$$-\log \alpha = 0.51 z_x z_y \frac{B \sqrt{I}}{[1 + \sqrt{I}]} - 0.30 I \quad (4.5)$$

While the Debye-Huckel equation is limited to ionic strengths below $.02\text{M}$ the Davies equation accurately calculates α over a range from dilute solutions to ionic

strengths of 0.1 M. The ionic strength can be determined using Eqn(4.6) for the sum of all the ions, i.

$$I = 0.5 \sum_{\text{all ions}} C_i z_i^2 \quad (4.6)$$

4.3 Construction

pH Electrode

The pH electrode measures the activity of hydrogen ions in aqueous solutions. It consists of a thin walled glass bulb whose membrane potential, ideally, is developed solely by hydrogen ions. For many years the typical pH glass consisted of 22% Na₂O, 6% CaO, 72% SiO₂.(2) The most recent advances in the use of lithium based glass have eliminated problems at low hydrogen ion concentrations and reduced interferences of sodium and potassium ions. The potential at the glass solution interface is a consequence of exclusive exchange of hydrogen ions, between the solution and the hydrated surface layer of the glass membrane. As such, it is directly related to the ratio of hydrogen ion activities in the glass and solution.(5)

To complete the electrode an internal contact must be established. This is done with a chloridized silver wire which dips in a chloride containing pH buffer inside the glass bulb. In this way a stable potential is maintained at the internal glass /buffer interface and between the chloride in the buffer and the chloridized wire.

The electrical potential for the bulb assembly,

therefore contains only one variable; the pH of the external electrolyte. A typical pH electrode is shown in Figure(4.1).

Sodium Electrode

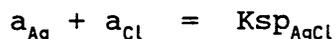
The sodium electrode differs from the pH electrode, in that the composition of the glass is designed such that it has a very high ion exchange selectivity for sodium ions.

Fluoride Electrode

The fluoride electrode employs a single crystal of lanthanum trifluoride. This crystal is doped with small percentages of EuF_3 to increase its conductivity.(6) It has been shown that the fluoride ions are mobile within the crystal lattice of LaF_3 and are rapid to establish an equilibrium potential with fluoride ions free in solution. The fluoride electrode has a Nernstian response to fluoride from 10^{-6}M to 1M and the only interference is from hydroxide ion. The internal contact is made with a chloridized silver wire(a silver/silver chloride electrode) in an internal solution of 1M KF , saturated KCl , and saturated AgCl . The Orion Research model 94-09 electrode used in these experiments has a LaF_3 crystal set in an epoxy resin tube.

Chloride Electrode

The chloride electrode is one of the series of silver halide based electrodes. The sensing pellet is pressed from a co-precipitated mixture of silver chloride and silver sulfide. The silver sulfide is added to increase conductivity. This electrode is referred to as an electrode of the second kind owing to the fact that although it exhibits Nernstian responses to changes in chloride ion activity, in actuality it is silver ions that are mobile in the membrane. The chloride ion activity affects the silver ion activity through the solubility equilibrium at the electrode surface.



Iodide and bromide electrodes work on the same principles. The internal electrical contact to this pellet can be made either with conductive epoxy resins or a standard Ag/AgCl reference electrode and a chloride solution saturated with AgCl. A diagram is given in Figure(4.2).

Reference Electrode

The reference electrode used in these experiments was a double junction, silver/silver chloride type. This

construction includes an inner chamber with a chloridized silver wire in contact with a chloride solution saturated with AgCl. This inner chamber is connected to an outer chamber containing 10% KNO₃ by a ceramic frit. Contact with the solution to be measured is made via a ground annular sleeve. The importance of the design of the reference electrode can not be over estimated. It must provide stable reproducible potentials free from large junction effects. The large area of contact with the measuring solution, through the ground annular sleeve, and the equal transport numbers of K⁺ and NO₃⁻ reduce junction potential and as a result this electrode was found to be particularly suitable. A diagram is given in Figure(4.3).

4.4 Calibration

The ion selective electrodes used to determine the ion exchange properties of these microcrystals were calibrated systematically to insure accurate results. A titration scheme was established which employed a large number of test points and provided an efficient calibration process.

Procedure:

Twenty milliliters of distilled water were brought to 25°C in a temperature controlled beaker. The pH of the water was checked to assure that it was in the proper range for the electrode being calibrated. A ten ml micro burette was filled with an analysed standard. This standard was then added to the beaker solution, first in 0.1 ml increments to 1 ml and then in 1 ml increments to 10 ml. This resulted in a nineteen point calibration in a measuring range similar to that of the ion exchange experiments that follow.

Calculations:

The data obtained from this calibration provided an emf vs concentration calibration curve. Activities were calculated from these concentrations with help of the Davies equation for ionic strength. Eqn.(4.5) To demon-

strate the effect of ionic strength the data points obtained from the calibration were plotted as emf versus, $-\log(C_x)$, and pX. pX is the accepted representation of $-\log(a_x)$. These plots for the chloride and sodium electrodes are shown in Figures(4.4) and (4.5) respectively. The effect of increasing concentration and the resulting increase in ionic strength can be seen as the non-linearity of the emf versus $-\log(C_x)$. In the subsequent analysis of the zirconia crystals ionic strengths will vary. As a result calibration equations based on the pX will be used. When concentration are required they will be calculated using the ionic strength, at that point in time. A typical calibration for the fluoride and pH electrodes, emf vs pF and pH are shown in Figures(4.6) and (4.7) respectively.

pH electrodes were calibrated with pH standards directly and as a result the above calculations were not necessary.

To obtain calibration equations for use in determining quantitative estimations of the electrode response the emf, and pX data was curve fitted by both first and second order curve fits. This resulted in two equations, Eqns.(4.7) and (4.8).

$$E = A_0 + A_1(pX) \quad (4.7)$$

$$E = B_0 + B_1(pX) + B_2(pX)^2 \quad (4.8)$$

A_i and B_i for $i=0,1,2$ are the constants of the curve fit polynomial. These equations were checked by calculating activity values given the emf readings.

Comparison of percent difference between the known activity values and the calculated activity values indicated the equation of choice. Tables(4.1), (4.2), (4.3), and (4.4) show typical data of this kind for chloride, sodium, fluoride, and pH electrodes respectively. In the majority of cases the difference was not sufficient to justify the use of the second order equation. This calibration system had three major advantages. Firstly, the additions from the buret caused small volume increases resulting in short temperature excursions, which would ape subsequent experimentation. Secondly, by using the same standard and the same buret during the the ion exchange experiments which followed accuracy was increased. Thirdly, the increased number of calibration points now made it possible to determine a meaningful first and second order best fit line equation using the least squares method.

Computer programs for these calculations are given in the program section of the appendix. Prog.(P.1) was used to store data from the calibration. Prog.(P.2) calculated concentrations, activities and determined first and second order equations.

FIGURE 4.1 DIAGRAM OF A pH ELECTRODE

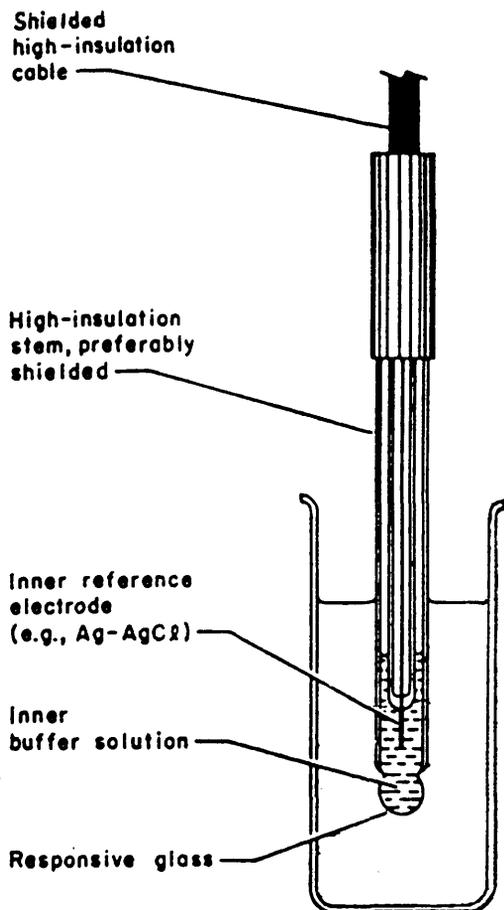


FIGURE 4.2 DIAGRAM OF A HALIDE ELECTRODE

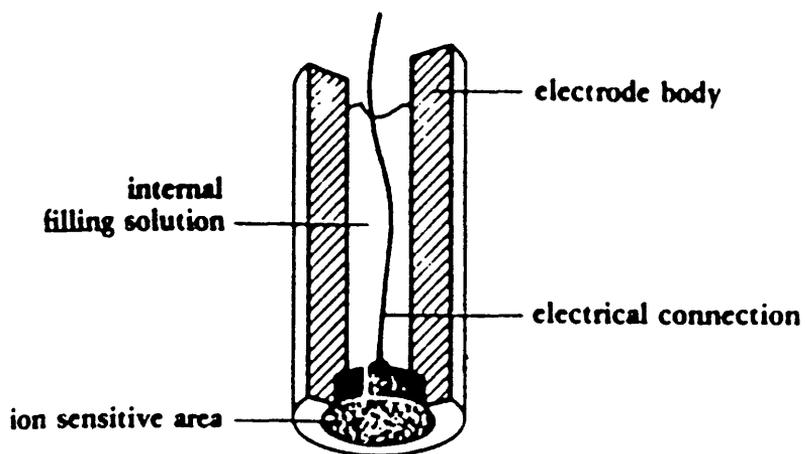
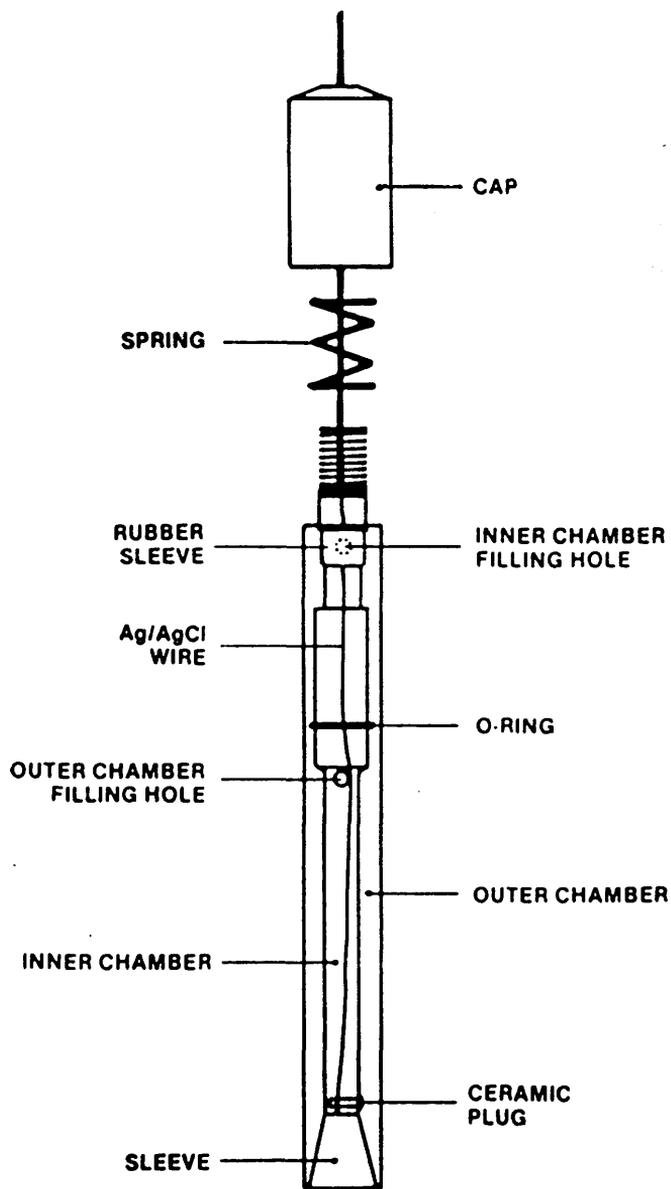


FIGURE 4.3 DIAGRAM OF A DOUBLE JUNCTION REFERENCE ELECTRODE



TABLE(4.1) TYPICAL CHLORIDE ELECTRODE CALIBRATION

FILE NAME = Cl_CAL

CONC OF STANDARD = .100 M

INITIAL VOLUME = 25 ml

FIRST ORDER EQUATION E = -9.206 + 60.424 pCl

SECOND ORDER EQUATION E = -13.027 + 63.713 pCl + -0.672(pCl)²

CURVE FITS

| N | E mV | * pCl (actual) | ** pCl 2ND ORDER | ** pCl 1ST ORDER | % error 2ND ORDER | % error 1ST ORDER |
|----|---------|-------------------|---------------------|---------------------|----------------------|----------------------|
| 1 | 196.2 | 3.409 | 3.406 | 3.399 | 0.7 | 2.3 |
| 2 | 179.0 | 3.114 | 3.116 | 3.115 | -0.5 | -0.2 |
| 3 | 168.6 | 2.942 | 2.942 | 2.943 | 0.1 | -0.0 |
| 4 | 161.6 | 2.822 | 2.825 | 2.827 | -0.8 | -1.2 |
| 5 | 155.9 | 2.728 | 2.730 | 2.732 | -0.3 | -0.9 |
| 6 | 151.2 | 2.653 | 2.652 | 2.655 | 0.2 | -0.4 |
| 7 | 147.4 | 2.589 | 2.589 | 2.592 | 0.1 | -0.6 |
| 8 | 143.9 | 2.534 | 2.531 | 2.534 | 0.9 | 0.1 |
| 9 | 141.0 | 2.486 | 2.482 | 2.486 | 0.9 | 0.1 |
| 10 | 138.2 | 2.444 | 2.436 | 2.440 | 1.7 | 0.9 |
| 11 | 121.9 | 2.169 | 2.167 | 2.170 | 0.4 | -0.2 |
| 12 | 112.9 | 2.015 | 2.019 | 2.021 | -1.0 | -1.3 |
| 13 | 106.7 | 1.911 | 1.918 | 1.918 | -1.7 | -1.7 |
| 14 | 101.9 | 1.833 | 1.840 | 1.839 | -1.6 | -1.4 |
| 15 | 97.9 | 1.771 | 1.774 | 1.773 | -0.7 | -0.3 |
| 16 | 94.7 | 1.721 | 1.722 | 1.720 | -0.2 | 0.4 |
| 17 | 91.9 | 1.679 | 1.677 | 1.673 | 0.6 | 1.3 |
| 18 | 89.6 | 1.643 | 1.639 | 1.635 | 0.9 | 1.8 |
| 19 | 87.9 | 1.612 | 1.611 | 1.607 | 0.1 | 1.1 |

% error = % difference between the actual chloride ion activity and the calculated activity

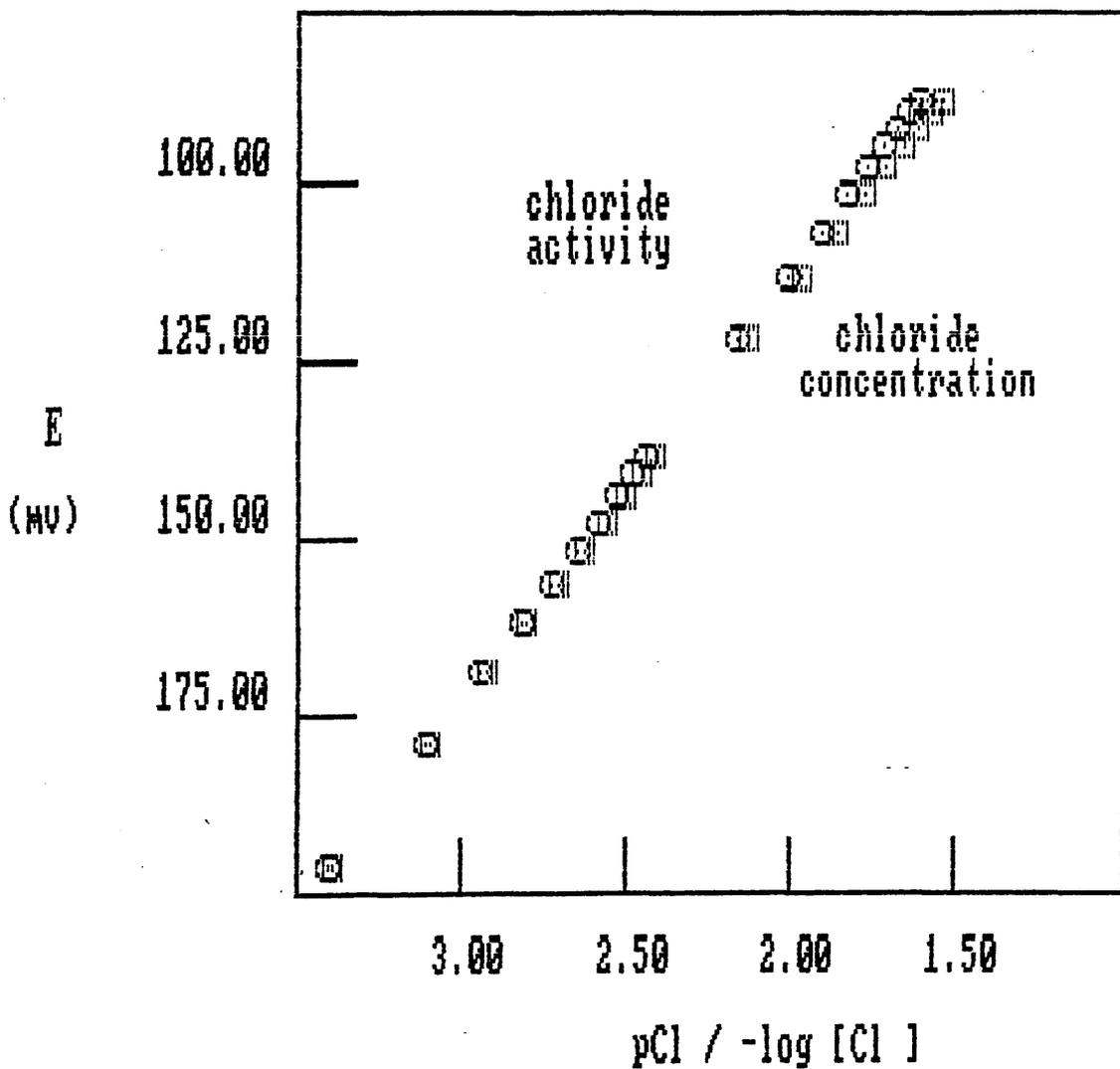
pCl = Negative log of the chloride ion activity

* Calculated from known concentration and ionic strength

** Calculated from curve fit equation

FIGURE(4.4) TYPICAL CHLORIDE ELECTRODE CALIBRATION

Emf vs negative log activity and Emf vs negative log concentration of chloride ion. TABLE(4.1)



TABLE(4.2) TYPICAL SODIUM ELECTRODE CALIBRATION

FILE NAME = Na_CAL

CONC OF STANDARD = .100 M

INITIAL VOLUME = 25 ml

FIRST ORDER EQUATION $E = 296.971 + -56.665 \text{ pNa}$ SECOND ORDER EQUATION $E = 300.466 + -59.638 \text{ pNa} + 0.602(\text{pNa})^2$

CURVE FITS

| N | E mV | * pNa (actual) | ** pNa | | % error | |
|----|---------|-------------------|-----------|-----------|-----------|-----------|
| | | | 2ND ORDER | 1ST ORDER | 2ND ORDER | 1ST ORDER |
| 1 | 104.4 | 3.409 | 3.405 | 3.398 | 1.1 | 2.5 |
| 2 | 120.6 | 3.114 | 3.114 | 3.113 | 0.0 | 0.3 |
| 3 | 130.5 | 2.942 | 2.937 | 2.938 | 1.2 | 1.1 |
| 4 | 137.0 | 2.822 | 2.821 | 2.823 | 0.1 | -0.3 |
| 5 | 142.1 | 2.728 | 2.731 | 2.733 | -0.5 | -1.1 |
| 6 | 146.4 | 2.653 | 2.654 | 2.657 | -0.4 | -1.0 |
| 7 | 149.9 | 2.589 | 2.593 | 2.595 | -0.8 | -1.4 |
| 8 | 153.0 | 2.534 | 2.538 | 2.541 | -0.8 | -1.5 |
| 9 | 155.7 | 2.486 | 2.490 | 2.493 | -0.8 | -1.6 |
| 10 | 158.0 | 2.444 | 2.449 | 2.452 | -1.4 | -2.1 |
| 11 | 174.1 | 2.169 | 2.166 | 2.168 | 0.6 | 0.1 |
| 12 | 183.1 | 2.015 | 2.009 | 2.010 | 1.5 | 1.3 |
| 13 | 189.3 | 1.911 | 1.900 | 1.900 | 2.4 | 2.4 |
| 14 | 193.6 | 1.833 | 1.826 | 1.824 | 1.7 | 2.0 |
| 15 | 196.8 | 1.771 | 1.770 | 1.768 | 0.3 | 0.8 |
| 16 | 199.6 | 1.721 | 1.721 | 1.718 | -0.0 | 0.7 |
| 17 | 201.8 | 1.679 | 1.683 | 1.680 | -0.9 | -0.1 |
| 18 | 203.7 | 1.643 | 1.650 | 1.646 | -1.6 | -0.6 |
| 19 | 205.2 | 1.612 | 1.624 | 1.620 | -2.8 | -1.7 |

% error = % difference between the actual sodium ion activity and the calculated activity

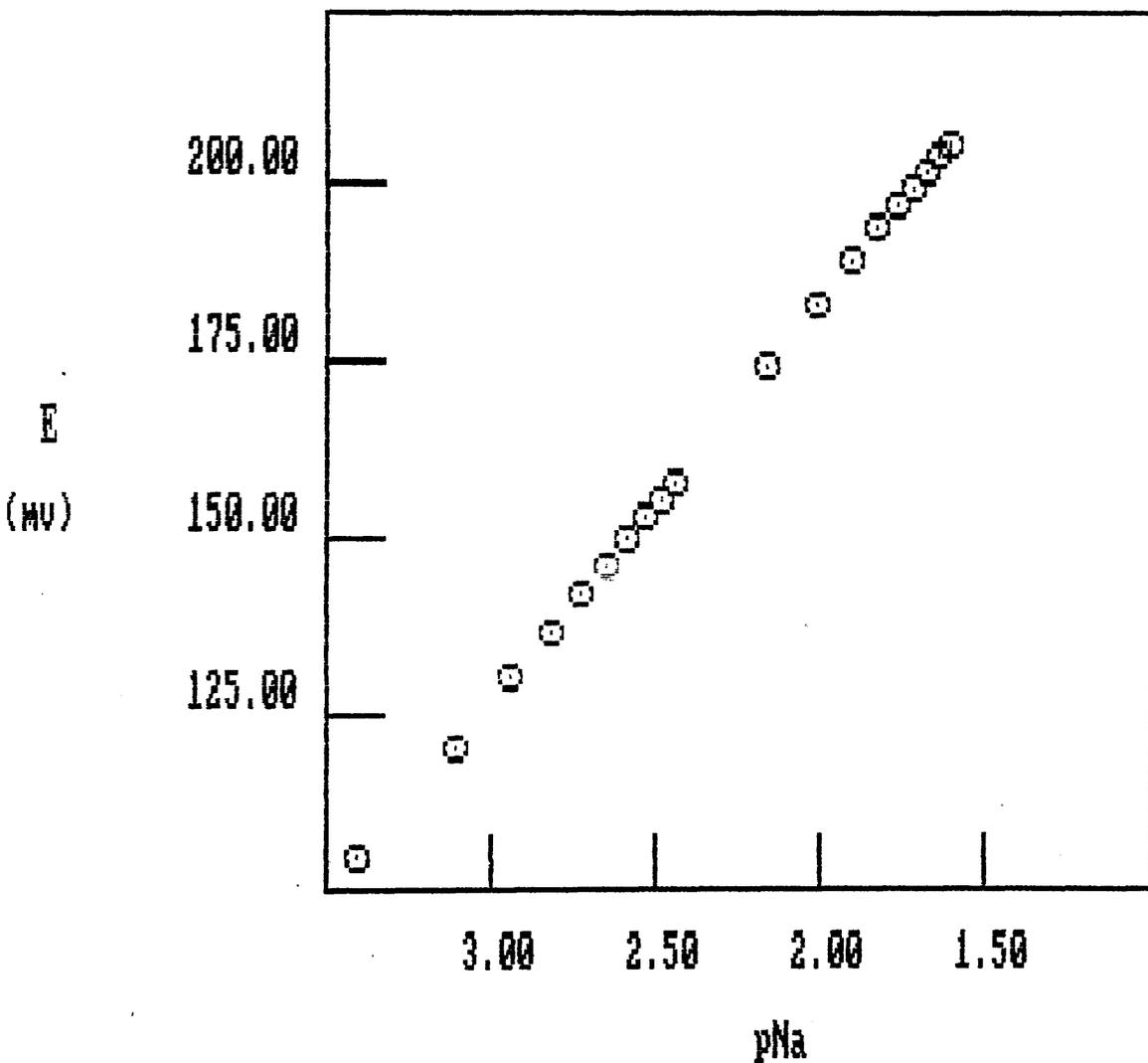
pNa = Negative log of the sodium ion activity

* Calculated from known concentration and ionic strength

** Calculated from curve fit equation

FIGURE(4.5) TYPICAL SODIUM ELECTRODE CALIBRATION

Emf vs negative log of sodium ion activity. TABLE(4.2)



TABLE(4.3) TYPICAL FLUORIDE ELECTRODE CALIBRATION

FILE NAME = F_CAL

CONC OF STANDARD = .467 M

INITIAL VOLUME = 24 ml

FIRST ORDER EQUATION $E = -285.223 + 58.484 \text{ pF}$ SECOND ORDER EQUATION $E = -285.232 + 58.498 \text{ pF} + -0.006(\text{pF})^2$

CURVE FITS

| N | E mV | * pF (actual) | ** pF 2ND ORDER | ** pF 1ST ORDER | % error 2ND ORDER | % error 1ST ORDER |
|----|---------|------------------|--------------------|--------------------|----------------------|----------------------|
| 1 | -123.3 | 2.770 | 2.769 | 2.769 | 0.2 | 0.3 |
| 2 | -140.5 | 2.473 | 2.475 | 2.475 | -0.4 | -0.3 |
| 3 | -150.6 | 2.301 | 2.302 | 2.302 | -0.2 | -0.2 |
| 4 | -157.6 | 2.180 | 2.182 | 2.182 | -0.6 | -0.5 |
| 5 | -163.4 | 2.087 | 2.083 | 2.083 | 0.8 | 0.8 |
| 6 | -167.6 | 2.011 | 2.011 | 2.011 | -0.1 | -0.0 |
| 7 | -171.2 | 1.948 | 1.950 | 1.950 | -0.5 | -0.5 |
| 8 | -174.6 | 1.893 | 1.892 | 1.892 | 0.3 | 0.3 |
| 9 | -177.3 | 1.845 | 1.845 | 1.845 | -0.1 | -0.1 |
| 10 | -179.9 | 1.802 | 1.801 | 1.801 | 0.4 | 0.4 |
| 11 | -195.8 | 1.530 | 1.529 | 1.529 | 0.2 | 0.2 |
| 12 | -204.6 | 1.378 | 1.379 | 1.379 | -0.0 | -0.0 |
| 13 | -210.6 | 1.275 | 1.276 | 1.276 | -0.1 | -0.1 |
| 14 | -215.1 | 1.198 | 1.199 | 1.199 | -0.1 | -0.1 |
| 15 | -218.6 | 1.138 | 1.139 | 1.139 | -0.3 | -0.3 |
| 16 | -221.6 | 1.088 | 1.088 | 1.088 | 0.1 | 0.1 |
| 17 | -224.0 | 1.047 | 1.047 | 1.047 | -0.1 | -0.1 |
| 18 | -226.1 | 1.011 | 1.011 | 1.011 | -0.0 | -0.0 |
| 19 | -228.0 | 0.980 | 0.978 | 0.978 | 0.4 | 0.4 |

% error = % difference between the actual fluoride ion activity and the calculated activity

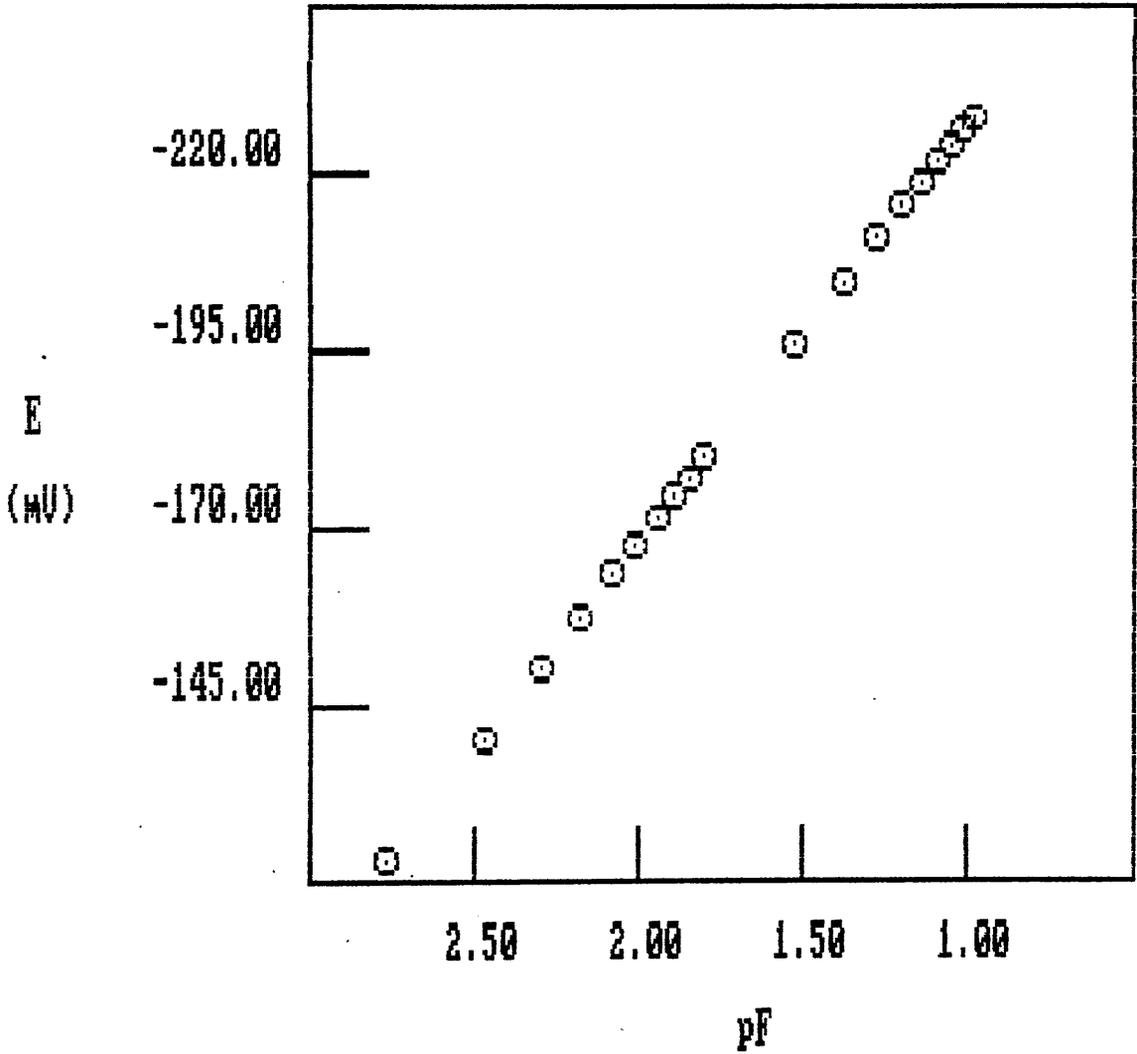
pF = Negative log of the fluoride ion activity

* Calculated from known concentration and ionic strength

** Calculated from curve fit equation

FIGURE(4.6) TYPICAL FLUORIDE ELECTRODE CALIBRATION

Emf vs negative log of fluoride ion activity. TABLE(4.3)



TABLE(4.4) TYPICAL pH ELECTRODE CALIBRATION

FILE NAME = pH_CAL

FIRST ORDER EQUATION E = 420.227 + -58.633 pH

SECOND ORDER EQUATION E = 417.645 + -57.534 pH + -0.081(pH)²

CURVE FITS

| N | E mV | * pH (actual) | ** pH 2ND ORDER | ** pH 1ST ORDER | % error 2ND ORDER | % error 1ST ORDER |
|---|---------|------------------|--------------------|--------------------|----------------------|----------------------|
| 1 | 332.4 | 1.500 | 1.479 | 1.498 | 4.8 | 0.5 |
| 2 | 244.3 | 3.000 | 3.000 | 3.000 | -0.0 | -0.1 |
| 3 | 183.6 | 4.000 | 4.045 | 4.036 | -10.9 | -8.6 |
| 4 | 11.7 | 7.000 | 6.987 | 6.967 | 3.0 | 7.2 |
| 5 | -106.8 | 9.000 | 9.001 | 8.989 | -0.2 | 2.6 |
| 6 | -162.7 | 10.000 | 9.947 | 9.942 | 11.5 | 12.5 |
| 7 | -227.4 | 11.000 | 11.039 | 11.045 | -9.4 | -11.0 |
| 8 | -284.7 | 12.000 | 12.003 | 12.023 | -0.8 | -5.4 |

% error = % difference between the actual hydrogen ion activity and the calculated activity

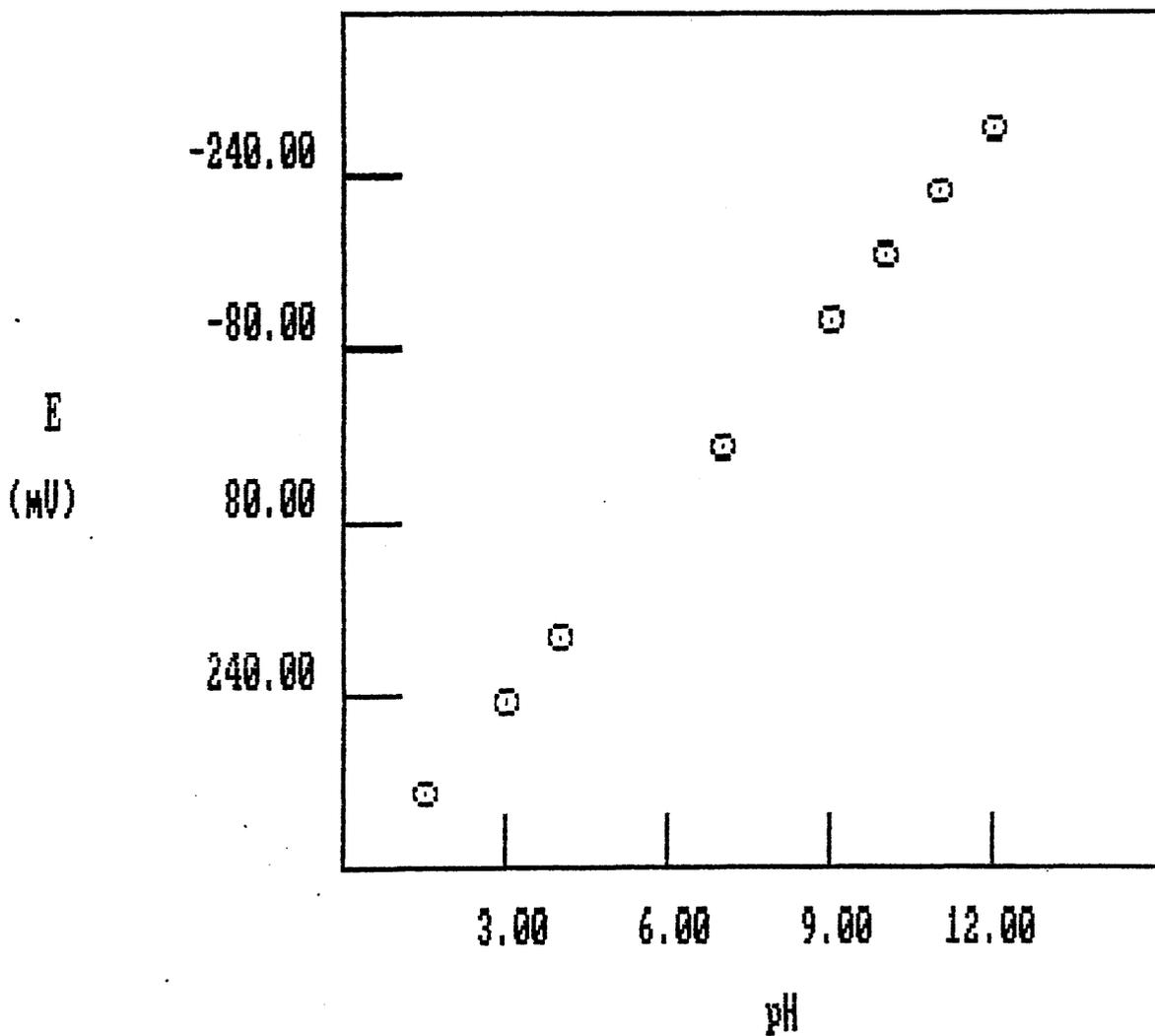
pH = Negative log of the hydrogen ion activity

* Prepared pH buffer standards per Perrin(7)

** Calculated from curve fit equation

FIGURE(4.7) TYPICAL pH ELECTRODE CALIBRATION

Emf vs negative log of hydrogen ion activity. TABLE(4.4)



CHAPTER FOUR REFERENCES

1. P.L. Bailey, Analysis with Ion-Selective Electrodes, Heyden, 2ndEd. (1980)
2. G. Eisenman, Glass Electrodes for Hydrogen and other Cations, Marcel Dekker, New York (1967)
3. M. Frant and J.W. Ross, Science, N.Y. 154, 3756 (1966)
4. C.W. Davies, Electrochemistry, William Clowes and Sons, London (1967)
5. A.K. Covington, Ion Selcetive Electrode Methodology, CRC, Florida (1979)
6. J. Koryta and K. Stulik, Ion-Selective Electrodes, Cambridge University Press, 2nd Ed. (1983)
7. D.D. Perrin and B. Dempsey, Buffers for pH and Metal Ion Control, Chapman and Hall Ltd, (1974)

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CHAPTER 5

CHLORIDE AND SODIUM UPTAKE BY MONOCLINIC ZIRCONIA

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5.1 Introduction

Hydrous oxides of zirconia have been known as ion exchangers for over fifty years.(1) The development in 1964 of a method for preparation of hydrated crystalline oxides of zirconia(2) has allowed for a more reproducible characterization of these ion exchange properties. The rapid kinetics of the exchange reactions combined with the use of ion selective electrodes for quantitative analysis has resulted in the generation of capacity or uptake isotherms over a wide pH range. Using a pH electrode alone uptake was calculated on the basis of mass balance. In this work the previous findings of Paterson and Rahman(3) are confirmed and further verification of the proposed mechanism is supplied by the use of the ion selective electrode for the species of interest.

Monoclinic zirconia is an amphoteric ion exchanger, exchanging anions in acid and cations in base. It has a zero point charge near pH 7. Hydrous oxides have been reported to have zpc between pH 4 and pH 11, this variability is attributed to the differences in gel preparations and composition. Amorphous material will give less reproducible results because the original salt, its concentration, the method of addition of base and the drying temperature(4)(5) all play a significant part in determining the properties of the hydrous zirconia.

Amphoteric exchange is the result of hydrogen ion uptake (protonation) in acid solutions causing an overall positively charged exchanger and an uptake of hydroxyl groups (hydroxylation) in base leaving a negative charge. This is demonstrated more dramatically by the addition of salt which, on the acid side, increases equally the uptake of both hydrogen ions and the anion of the salt added.

Computer programs for ion exchange calculations using curve fit calibration equations were used throughout the experimental work.

5.2 Experimental Theory

The uptake or release of ions from the oxide can be determined experimentally by considering solution mass balance. In this work, uptake by the exchanger will be expressed as negative due to the loss of ions from the solution. Release of ions to the solution by the exchanger will be represented as positive uptake. Dividing by the amount of dried exchanger the result is capacity, X , expressed in mmol/g. Initial investigations of this type were done with a pH electrode exclusively and therefore this mass balance was written as a H^+ ion balance Eqn.(5.1).

$$X = (B-A + H*V - OH*V - H_0*V_0)/G \quad (5.1)$$

B and A are the mmoles of NaOH and HCl added, H is the H^+ ion concentration, H_0 is the initial value of H^+ in the initial volume V_0 and OH is the hydroxide ion concentration. Using Eqn.(5.1) capacities were calculated from pH values. Hydrogen ion concentrations were determined using the ionic strength as discussed in Ch.(4.2). To determine the ionic strength the following assumptions were made. It was assumed that the solution volumes were additive,

$$V = V_0 + V_b + V_a + V_s \quad (5.2)$$

where V_b , V_a , and V_s represent volumes of base acid and salt added. Since monoclinic zirconia is an amphoteric exchanger with a zero point charge between pH 7 and pH 8 it was assumed that in the acid region there was no uptake of Na^+ and in the basic region Cl^- was excluded. Therefore, below pH 7 the concentration of Na^+ can be expressed as Eqn.(5.3) and above pH 7 the concentration of Cl^- can be expressed as Eqn.(5.4)

$$\text{Na}^+ = (\text{S} + \text{B})/\text{V} \quad (5.3)$$

$$\text{Cl}^- = (\text{S} + \text{A})/\text{V} \quad (5.4)$$

Taking advantage of the fact that these are all monovalent ions the ionic strength can be expressed as the sum of either the anions or the cations. At the same time employing the electroneutrality of the solution Eqn.(5.5) an expression for

$$\text{Na}^+ + \text{H}^+ = \text{Cl}^- + \text{OH}^- \quad (5.5)$$

the ionic strength can be obtained for acid Eqn.(5.6) and basic Eqn(5.7) solutions.

$$\text{I} = (\text{S} + \text{B})/\text{V} + \text{H}^+ \quad (5.6)$$

$$\text{I} = (\text{S} + \text{A})/\text{V} + \text{OH}^- \quad (5.7)$$

The sodium concentration above pH 7 Eqn.(5.8) and the chloride concentration below pH 7 Eqn.(5.9) were determined using Eqn.(5.5).

$$\text{Na}^+ = (\text{S} + \text{A})/\text{V} + \text{OH}^- + \text{H}^+ \quad (5.8)$$

$$\text{Cl}^- = (\text{S} + \text{B})/\text{V} + \text{OH}^- + \text{H}^+ \quad (5.9)$$

Having expressions for the ionic strength the concentration of H^+ ions could now be determined from pH. Using an iterative process the activity coefficient was first set to unity to estimate the hydrogen ion concentration and so to make a first approximation to the ionic strength. Using the Davies equation Eqn.(4.5) for activity coefficients an improved estimate of the hydrogen and hydroxyl ion concentration were made and a new ionic strength calculated. This cycle was repeated until the concentrations from these calculations varied by less than 0.1%. See Program(P.6).

The Davies equation for the activity coefficient was chosen on basis of two tests of solutions where the capacity was known. The first test was a solution of hydrochloric acid titrated with sodium hydroxide. In this case capacity should be zero at all pH values because both reagents are fully dissociated and there are no hidden "sources" or "sinks" for either acid or base.

These results are shown in the Appendix, Table(A.1) and Figure(A.1). Capacity was less than 0.005 mm/g over the entire pH range of the titration. In the second test of this system acetic acid was titrated with NaOH. Acetic acid provided undissociated H^+ ions which were released with the addition of base. Table(A.2) and Figure(A.2) show that capacity increased linearly to a maximum value equal to the amount of undissociated acid in the original solution.

Extending the work done with the pH electrode, sodium and chloride electrodes were incorporated into the analytical system. This made it possible to measure capacity directly by subtracting the amount of a species added to the titration cell from the amount measured in solution and dividing by the weight of dried exchanger. Ionic strength could also be determined more accurately because the concentration of more of the components of the solution could be measured directly. This algorithm is found in Program(P.4).

Control experiments, without exchanger present, over the pH range of interest were conducted with each of the ion selective electrodes used in this research. Table(A.3) and Figure(A.3) show the result of test of the sodium and chloride electrodes by titrating a boric acid solution from pH 7 to pH 11 with NaOH. The response of the pH electrode shows that X_{OH} , hydroxide ion capacity, decreased to a maximum value equal to the amount of

undissociated acid in the original solution. The sodium and chloride electrodes showed a null response, no uptake, as would be expected.

Table(A.4) and Figure(A.4) show the results of the titration of an acetic acid solution with NaOH while making measurements with pH, chloride and fluoride electrodes. NaCl and NaF were added and without the ion exchange medium present we would expect full recovery, no uptake, of these species with our electro-analytical technique. The expected proton release from the acetic acid was measured with the pH electrode while there was a null effect on the chloride electrode from pH 3 to pH 11 and a null effect on the fluoride electrode from pH 5 to pH 11. Further discussions of the work with the fluoride electrode are addressed in the following chapter.

The results with the chloride, fluoride and sodium electrodes proved they could be used with confidence over the pH ranges expected during the subsequent titrations with monoclinic zirconia.

5.3 Results and Discussion

Monoclinic zirconia prepared by the method of Clearfield was characterized by electron microscopy and electron diffraction. The particles are star and pod shaped and give single crystal diffraction patterns for monoclinic zirconia, Plate(2.4). Zirconia is extremely stable to both acid and alkali, although at both extremes the precision of pH measurements is difficult. Therefore, pH titrations were limited to the range of pH 3 to pH 11. In the standard titration 0.3 g of air dried zirconia was dispersed in twenty ml of distilled water. Since the sample was previously washed clear of chloride the suspension was near neutral pH. Hydrochloric acid was then added to reduce the pH to 3 and the suspension was titrated with sodium hydroxide. In the alkaline region 1 mmole of salt was added and the suspension backtitrated with hydrochloric acid.

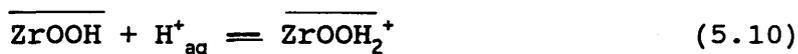
The results of these pH titrations are shown in Table(5.1) and Figure(5.2). There are two distinct curves, curve A-A' was obtained with no added salt present except that formed from the neutralization of acid released from the exchanger. Curve B-B' show the backtitration with acid after addition of 1 mmole of salt. The addition of salt causes an increase in pH in the acid region which is more pronounced than the corresponding decrease of pH in the alkaline region.

A second set of data were obtained using both a pH electrode and a chloride electrode. Calibration, selectivity, and pH information for this electrode is given in Chapter 3. In this experiment 1 mmole of acid was added to 0.25 g of crystals and the suspension was titrated with 0.1 M base to a pH of 11. Table(5.2), Figure(5.4) and Figure(5.5) show the results. The chloride ion uptake follows the hydrogen ion uptake in the acid region and remains at zero in the alkaline range.

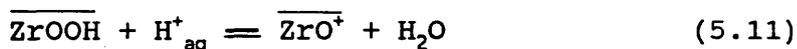
To verify the theory of exchange in the basic region experiments were conducted using a sodium electrode and a pH electrode. In these experiments 0.01 mmoles of acid was added to 0.3 g of crystals. The suspension was then titrated with base to pH 11 and then with acid to pH 7. The results from this indicated a lower uptake of sodium than expected. At present this anomaly remains unexplained.

5.3.1 Anion Capacity

The addition of acid to a suspension of monoclinic zirconia produces a pH higher than would be expected if there were no uptake of acid by the crystals. This uptake is verified by the high negative hydrogen ion capacity from the pH titrations, Figure(5.2). Hydrated oxides of multivalent metals are thought to exchange protons with the following mechanism, Eqn.(5.10). Barred species represent those bound to the exchanger.



This exchange could also be explained by Eqn(5.11)



Although pH titration would be unable to distinguish between these two mechanisms, for the purpose of this discussion we will consider the uptake to be protonation of a coordinated water molecule. Uptake of protons depends on a Donnan equilibrium between protons in solution and protons in the pore, Eqn.(5.12).

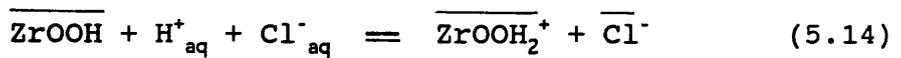


Neither of these processes could take place without concurrent uptake of chloride which would cancel the

Donnan potential caused by protonation and preserve electroneutrality, Eqn. (5.13).



The overall reaction is therefore a function of the whole acid where stoichiometric amounts of hydrochloric acid are taken up by the crystals, Eqn. (5.14).



From Eqn. (5.14) an increase in the amount of chloride in solution would shift the equilibrium in favor^U of uptake. In Figure(5.2) it can be see that added salt increased the uptake significantly. The pH versus capacity curves intersect between pH 7 and 8 at the isoelectric point (zero capacity). This is close to the zero point charge (zpc) quoted by several authors for amorphous zirconia. Also by reproducing the capacity data as a function of pA, Eqn. (5.15),

$$\text{pA} = \text{pH} + \text{pCl} \quad (5.15)$$

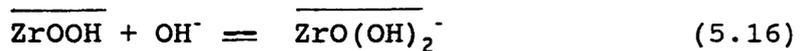
the capacities are shown, in Figure(5.3) and Table(5.1), to be single-valued function of pA in acidic solution. In basic solution a cation exchange mechanism would apply and as a result these curves diverge in the alkaline region.

This stoichiometric uptake is also dramatically shown in Table(5.2) and Figure(5.4) where hydrogen ion uptake, from the pH electrode and chloride ion uptake from an Orion chloride selective electrode are plotted together against pH. The overlap of these two curves in the acid region is further verification of the proposed mechanism. In Figure(5.5) the same values for hydrogen and chloride ion uptake are plotted against pHCl showing again the uptake to be a single valued function of the acid.

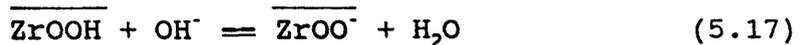
The absence of anion exchange in the basic region is clearly demonstrated by the zero uptake of chloride above the isoelectric point.

5.3.2 Cation Capacity

In an analogous fashion to the anion ion exchange mechanisms just described the addition of base to a suspension of monoclinic zirconia produces a pH which is lower than the pH that would be expected. Figure(5.2) shows the high positive hydrogen ion capacity, proton release, on the basic side of the pH titration. A mechanism for hydroxyl uptake is given where barred species represent those bound to the exchanger, Eqn(5.16).



Proton release would result in Eqn.(5.17).

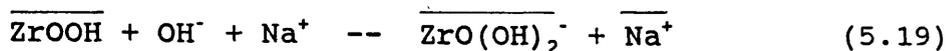


The pH electrode would not distinguish between these two mechanisms. In both cases there is a lowering of pH and the formation of a negatively charged exchanger. To preserve the electroneutrality of the solution positive counter ions will be removed from solution. Eqn(5.18)



The uptake of hydroxyl and sodium ions is therefore coupled electrically by the Donnan potential and this

results in the overall mechanism, Eqn(5.19)



The addition of Na^+ , in the form of added salt, to the above mechanism would move the equilibrium to the right with resulting removal of hydroxyl ions from solution and lowering of pH. This is seen quite clearly in Table(5.1) and Figure(5.2). The sodium capacity will therefore be a single-valued function of the activity of the base, a_{NaOH} , expressed on a logarithmic scale as $\text{pB} = \text{pNa} + \text{pOH}$. In Figure(5.6) it can be seen that plotting X against pB substantiates the proposed relationship.

An attempt to measure the sodium uptake directly with a sodium ion selective electrode is shown in Table(5.3) and Figures(5.7) and (5.8). In these plots sodium uptake, hydroxyl uptake and chloride uptake are plotted against pH and pB. In agreement with previous experiments there was no uptake of chloride. Hydroxyl uptake corresponds directly to work done with a pH electrode alone. However, the sodium uptake calculated in this manner was lower than would be predicted by the above mechanism and as of yet this is not explained.

TABLE(5.1) pH TITRATION OF MONOCLINIC ZIRCONIA WITH ADDED SALT

NAME OF FILE -ZR1A8

Concentration of NaCl = 1.00M

Concentration of NaOH = 0.11M

Concentration of HCl = 0.10M

Initial Volume = 25.00ml

Weight of ZrO₂ = 0.301gWeight of Dried ZrO₂ = 0.253g

N = Number of data set.

VB = Volume of base, ml.

VA = Volume of Acid, ml.

VS = Volume of Salt, ml.

pA = pH + pCl

pB = pNa + pOH

X = Capacity, mmoles/gram

| N | VB | VA | VS | pH | pA | pB | X |
|----|------|------|------|-------|--------|--------|-------|
| 1 | 0.00 | 0.00 | 0.00 | 6.06 | 12.120 | 15.877 | -.000 |
| 2 | 0.00 | 1.00 | 0.00 | 2.92 | 5.840 | 22.157 | -.267 |
| 3 | 0.10 | 1.00 | 0.00 | 3.05 | 5.940 | 14.350 | -.257 |
| 4 | 0.20 | 1.00 | 0.00 | 3.21 | 6.061 | 13.892 | -.244 |
| 5 | 0.30 | 1.00 | 0.00 | 3.44 | 6.252 | 13.488 | -.228 |
| 6 | 0.40 | 1.00 | 0.00 | 3.74 | 6.498 | 13.066 | -.205 |
| 7 | 0.50 | 1.00 | 0.00 | 4.18 | 6.877 | 12.532 | -.175 |
| 8 | 0.60 | 1.00 | 0.00 | 4.62 | 7.252 | 12.016 | -.137 |
| 9 | 0.65 | 1.00 | 0.00 | 4.90 | 7.501 | 11.703 | -.117 |
| 10 | 0.70 | 1.00 | 0.00 | 5.22 | 7.791 | 11.352 | -.096 |
| 11 | 0.75 | 1.00 | 0.00 | 5.61 | 8.154 | 10.934 | -.075 |
| 12 | 0.80 | 1.00 | 0.00 | 6.23 | 8.747 | 10.288 | -.054 |
| 13 | 0.85 | 1.00 | 0.00 | 7.44 | 9.897 | 9.017 | -.033 |
| 14 | 0.88 | 1.00 | 0.00 | 7.93 | 10.387 | 8.527 | -.020 |
| 15 | 0.94 | 1.00 | 0.00 | 8.53 | 10.988 | 7.928 | 0.006 |
| 16 | 0.98 | 1.00 | 0.00 | 8.79 | 11.249 | 7.668 | 0.022 |
| 17 | 1.02 | 1.00 | 0.00 | 8.97 | 11.429 | 7.488 | 0.039 |
| 18 | 1.10 | 1.00 | 0.00 | 9.29 | 11.751 | 7.168 | 0.072 |
| 19 | 1.20 | 1.00 | 0.00 | 9.58 | 12.042 | 6.878 | 0.113 |
| 20 | 1.30 | 1.00 | 0.00 | 9.79 | 12.254 | 6.666 | 0.153 |
| 21 | 1.44 | 1.00 | 0.00 | 10.07 | 12.536 | 6.382 | 0.206 |
| 22 | 1.60 | 1.00 | 0.00 | 10.25 | 12.719 | 6.197 | 0.267 |
| 23 | 1.80 | 1.00 | 0.00 | 10.47 | 12.942 | 5.966 | 0.338 |
| 24 | 2.10 | 1.00 | 0.00 | 10.73 | 13.208 | 5.683 | 0.437 |
| 25 | 2.40 | 1.00 | 0.00 | 10.95 | 13.434 | 5.429 | 0.522 |
| 26 | 2.40 | 1.00 | 1.50 | 10.40 | 11.757 | 4.955 | 0.593 |
| 27 | 2.40 | 1.30 | 1.50 | 10.18 | 11.534 | 5.172 | 0.489 |
| 28 | 2.40 | 1.60 | 1.50 | 9.90 | 11.250 | 5.450 | 0.381 |
| 29 | 2.44 | 1.90 | 1.50 | 9.54 | 10.888 | 5.807 | 0.286 |
| 30 | 2.44 | 2.06 | 1.50 | 9.29 | 10.636 | 6.056 | 0.225 |

TABLE(5.2) pH TITRATION WITH pH AND CHLORIDE ELECTRODES

NAME OF FILE =TZR1CL

Concentration of NaCl = 0.00M

Concentration of NaOH = 0.11M

Concentration of HCl = 0.10M

Initial Volume = 25.00ml

Weight of ZrO₂= 0.250g

Weight of Dried ZrO₂= 0.211g

N = Number of data set.

VB = Volume of base, ml.

VA = Volume of Acid, ml.

VS = Volume of Salt, ml.

pA = pH + pCl

XH = H⁺ Capacity in mmol/g

XCl = Cl⁻ Capacity in mmol/g

| N | VB | VA | VS | pH | pA | XCl | XH |
|----|------|------|------|-------|--------|--------|-------|
| 1 | 0.00 | 0.00 | 0.00 | 6.13 | 10.997 | 0.000 | -.000 |
| 2 | 0.00 | 1.00 | 0.00 | 2.80 | 5.588 | -0.265 | -.272 |
| 3 | 0.20 | 1.00 | 0.00 | 3.05 | 5.811 | -0.251 | -.256 |
| 4 | 0.40 | 1.00 | 0.00 | 3.47 | 6.177 | -0.216 | -.226 |
| 5 | 0.50 | 1.00 | 0.00 | 3.78 | 6.444 | -0.187 | -.197 |
| 6 | 0.60 | 1.00 | 0.00 | 4.22 | 6.829 | -0.145 | -.159 |
| 7 | 0.70 | 1.00 | 0.00 | 4.80 | 7.346 | -0.097 | -.114 |
| 8 | 0.74 | 1.00 | 0.00 | 5.02 | 7.552 | -0.079 | -.094 |
| 9 | 0.80 | 1.00 | 0.00 | 5.51 | 8.004 | -0.043 | -.064 |
| 10 | 0.84 | 1.00 | 0.00 | 5.94 | 8.414 | -0.021 | -.044 |
| 11 | 0.88 | 1.00 | 0.00 | 6.73 | 9.183 | 0.001 | -.024 |
| 12 | 0.92 | 1.00 | 0.00 | 7.61 | 10.066 | 0.006 | -.003 |
| 13 | 0.96 | 1.00 | 0.00 | 8.18 | 10.635 | 0.006 | 0.017 |
| 14 | 1.00 | 1.00 | 0.00 | 8.49 | 10.943 | 0.005 | 0.037 |
| 15 | 1.04 | 1.00 | 0.00 | 8.75 | 11.204 | 0.006 | 0.058 |
| 16 | 1.08 | 1.00 | 0.00 | 8.94 | 11.400 | 0.005 | 0.078 |
| 17 | 1.14 | 1.00 | 0.00 | 9.19 | 11.644 | 0.002 | 0.108 |
| 18 | 1.30 | 1.00 | 0.00 | 9.65 | 12.108 | 0.003 | 0.186 |
| 19 | 1.40 | 1.00 | 0.00 | 9.83 | 12.291 | -0.001 | 0.234 |
| 20 | 1.50 | 1.00 | 0.00 | 9.98 | 12.451 | 0.001 | 0.281 |
| 21 | 1.70 | 1.00 | 0.00 | 10.24 | 12.714 | -0.002 | 0.372 |
| 22 | 1.90 | 1.00 | 0.00 | 10.45 | 12.923 | -0.004 | 0.460 |

FILE NAME = ZR1AS CONTINUED FROM PREVIOUS PAGE

| N | VB | VA | VS | pH | pA | pB | X |
|----|------|------|------|------|--------|--------|-------|
| 31 | 2.44 | 2.20 | 1.50 | 9.02 | 10.364 | 6.324 | 0.170 |
| 32 | 2.44 | 2.30 | 1.50 | 8.84 | 10.183 | 6.503 | 0.131 |
| 33 | 2.44 | 2.40 | 1.50 | 8.57 | 9.912 | 6.772 | 0.092 |
| 34 | 2.44 | 2.50 | 1.50 | 8.23 | 9.571 | 7.111 | 0.053 |
| 35 | 2.44 | 2.60 | 1.50 | 7.81 | 9.150 | 7.530 | 0.014 |
| 36 | 2.44 | 2.70 | 1.50 | 7.33 | 8.669 | 8.009 | -.026 |
| 37 | 2.44 | 2.80 | 1.50 | 6.82 | 8.162 | 8.522 | -.065 |
| 38 | 2.44 | 2.95 | 1.50 | 5.90 | 7.244 | 9.444 | -.124 |
| 39 | 2.44 | 3.00 | 1.50 | 5.69 | 7.035 | 9.655 | -.144 |
| 40 | 2.44 | 3.10 | 1.50 | 5.30 | 6.646 | 10.046 | -.183 |
| 41 | 2.44 | 3.20 | 1.50 | 4.98 | 6.327 | 10.367 | -.222 |
| 42 | 2.44 | 3.30 | 1.50 | 4.69 | 6.038 | 10.658 | -.260 |
| 43 | 2.44 | 3.40 | 1.50 | 4.46 | 5.809 | 10.890 | -.297 |
| 44 | 2.44 | 3.50 | 1.50 | 4.28 | 5.630 | 11.071 | -.334 |
| 45 | 2.44 | 3.70 | 1.50 | 3.88 | 5.232 | 11.473 | -.401 |
| 46 | 2.44 | 3.90 | 1.50 | 3.63 | 4.984 | 11.726 | -.463 |
| 47 | 2.44 | 4.20 | 1.50 | 3.25 | 4.604 | 12.110 | -.529 |
| 48 | 2.44 | 4.50 | 1.50 | 3.02 | 4.374 | 12.344 | -.584 |

TABLE(5.3)

NAME OF FILE =ZRNA121

Concentration of NaCl = 0.10M

Concentration of NaOH = 0.11M

Concentration of HCl = 0.10M

Initial Volume = 25.00ml

Weight of ZrO₂ = 0.500gWeight of Dried ZrO₂ = 0.420g

N = Number of data set.

VB = Volume of base, ml.

VA = Volume of Acid, ml.

VS = Volume of Salt, ml.

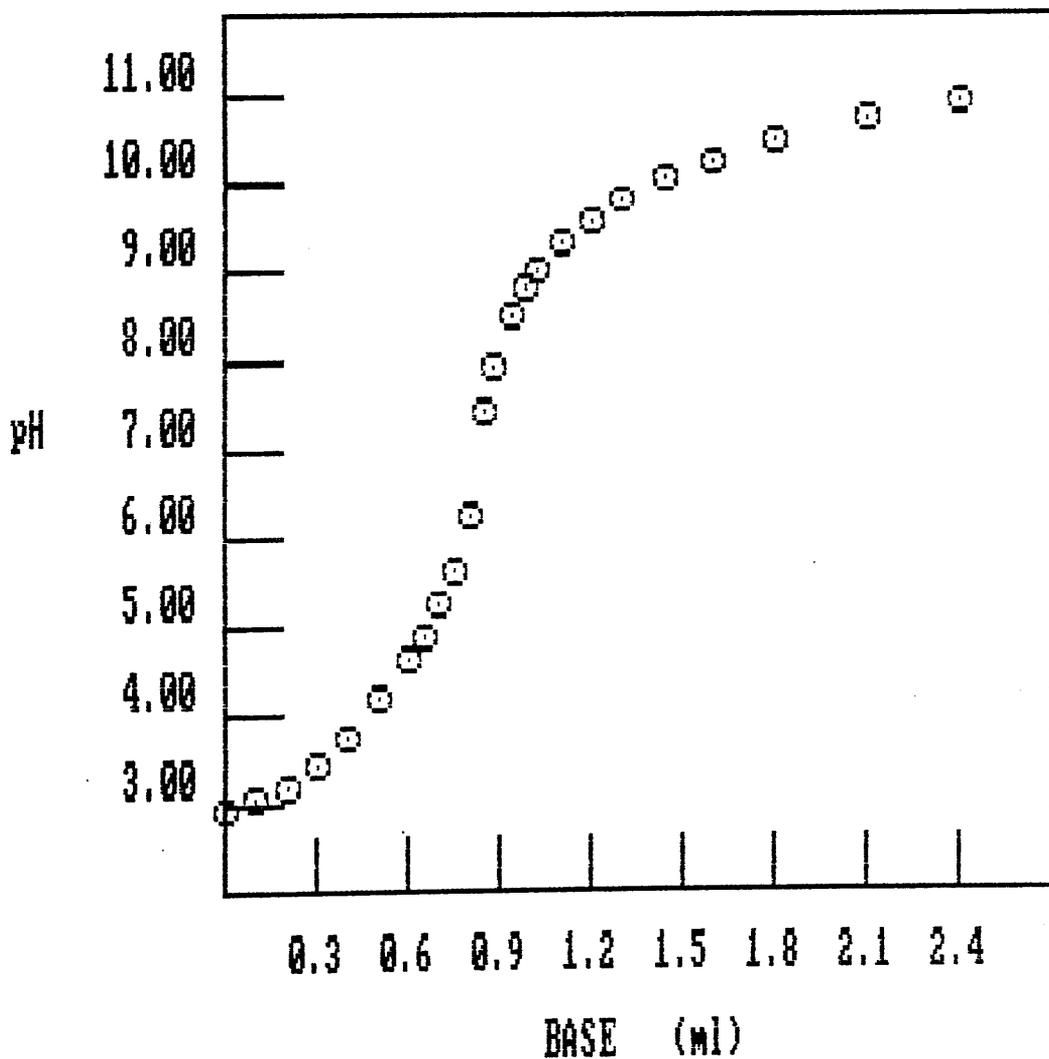
XNa = Na⁺ Capacity in mmol/gXOH = OH⁻ Capacity in mmol/gXCl = Cl⁻ Capacity in mmol/g

pNaOH = pNa + pOH

| N | VB | VA | pH | pNaOH | XNa | XCl | XOH |
|----|------|------|-------|-------|--------|--------|--------|
| 1 | 0.00 | 0.00 | 6.09 | 13.07 | 0.000 | 0.002 | 0.000 |
| 2 | 0.00 | 0.10 | 4.34 | 13.77 | 0.005 | -0.013 | 0.021 |
| 3 | 0.08 | 0.10 | 5.77 | 11.72 | -0.002 | 0.002 | 0.002 |
| 4 | 0.12 | 0.10 | 7.40 | 9.89 | -0.001 | 0.004 | -0.008 |
| 5 | 0.16 | 0.10 | 7.93 | 9.22 | -0.000 | 0.004 | -0.019 |
| 6 | 0.22 | 0.10 | 8.34 | 8.69 | -0.003 | 0.004 | -0.035 |
| 7 | 0.30 | 0.10 | 8.74 | 8.16 | -0.006 | 0.004 | -0.057 |
| 8 | 0.40 | 0.10 | 9.07 | 7.73 | -0.011 | 0.004 | -0.083 |
| 9 | 0.50 | 0.10 | 9.31 | 7.40 | -0.017 | 0.005 | -0.109 |
| 10 | 0.70 | 0.10 | 9.68 | 6.93 | -0.038 | 0.005 | -0.161 |
| 11 | 1.00 | 0.10 | 10.03 | 6.45 | -0.064 | 0.005 | -0.238 |
| 12 | 1.40 | 0.10 | 10.34 | 6.01 | -0.096 | 0.005 | -0.339 |
| 13 | 1.80 | 0.10 | 10.58 | 5.67 | -0.124 | 0.005 | -0.435 |
| 14 | 1.80 | 0.50 | 10.30 | 5.92 | -0.100 | 0.007 | -0.351 |
| 15 | 1.80 | 0.80 | 10.06 | 6.15 | -0.079 | 0.009 | -0.286 |
| 16 | 1.80 | 1.10 | 9.75 | 6.44 | -0.053 | 0.011 | -0.218 |
| 17 | 1.80 | 1.40 | 9.30 | 6.87 | -0.024 | 0.013 | -0.149 |
| 18 | 1.80 | 1.70 | 8.59 | 7.55 | 0.008 | 0.014 | -0.079 |
| 19 | 1.80 | 1.90 | 7.87 | 8.25 | 0.029 | 0.014 | -0.032 |
| 20 | 1.80 | 2.00 | 7.29 | 8.83 | 0.038 | 0.016 | -0.008 |

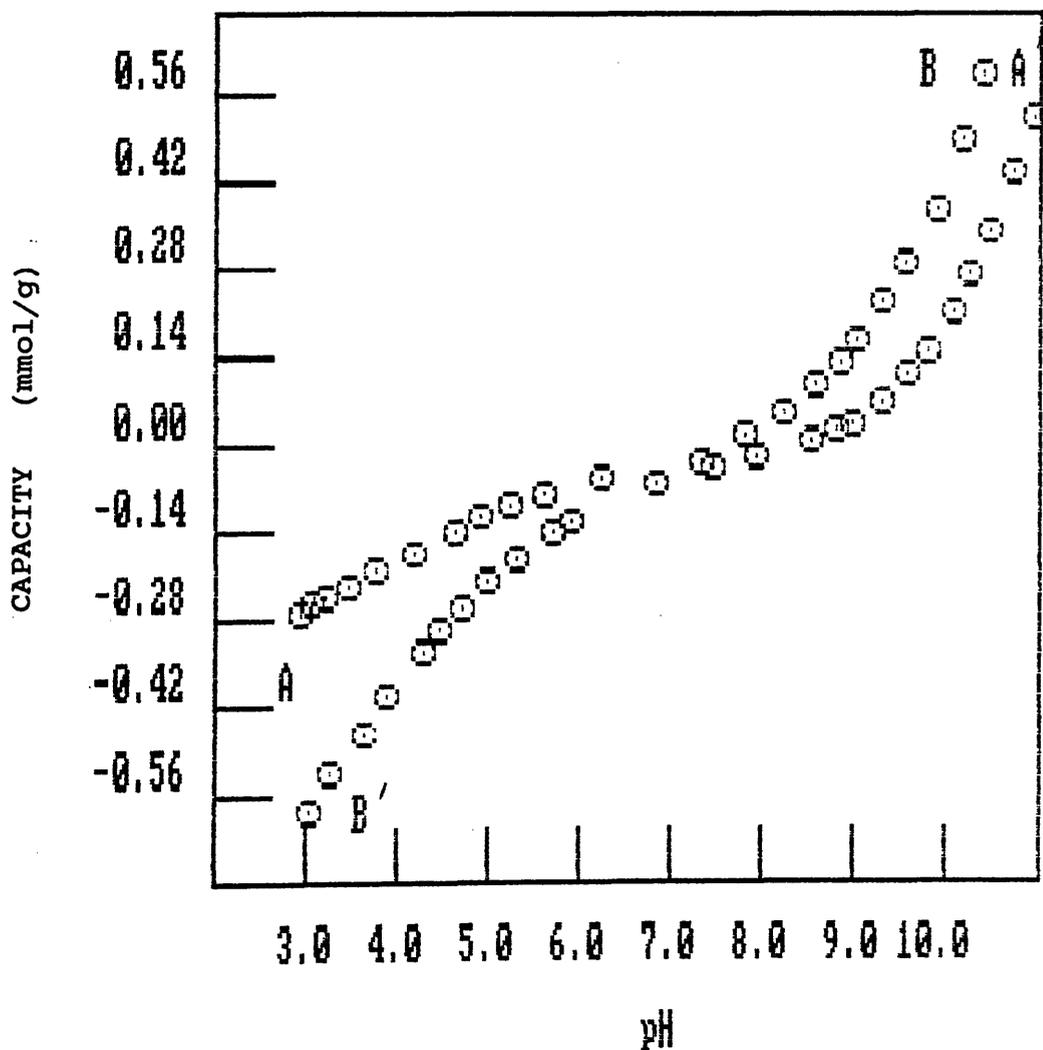
FIGURE(5.1) pH TITRATION OF MONOCLINIC ZIRCONIA

Addition of NaOH to an acidified suspension of monoclinic zirconia.



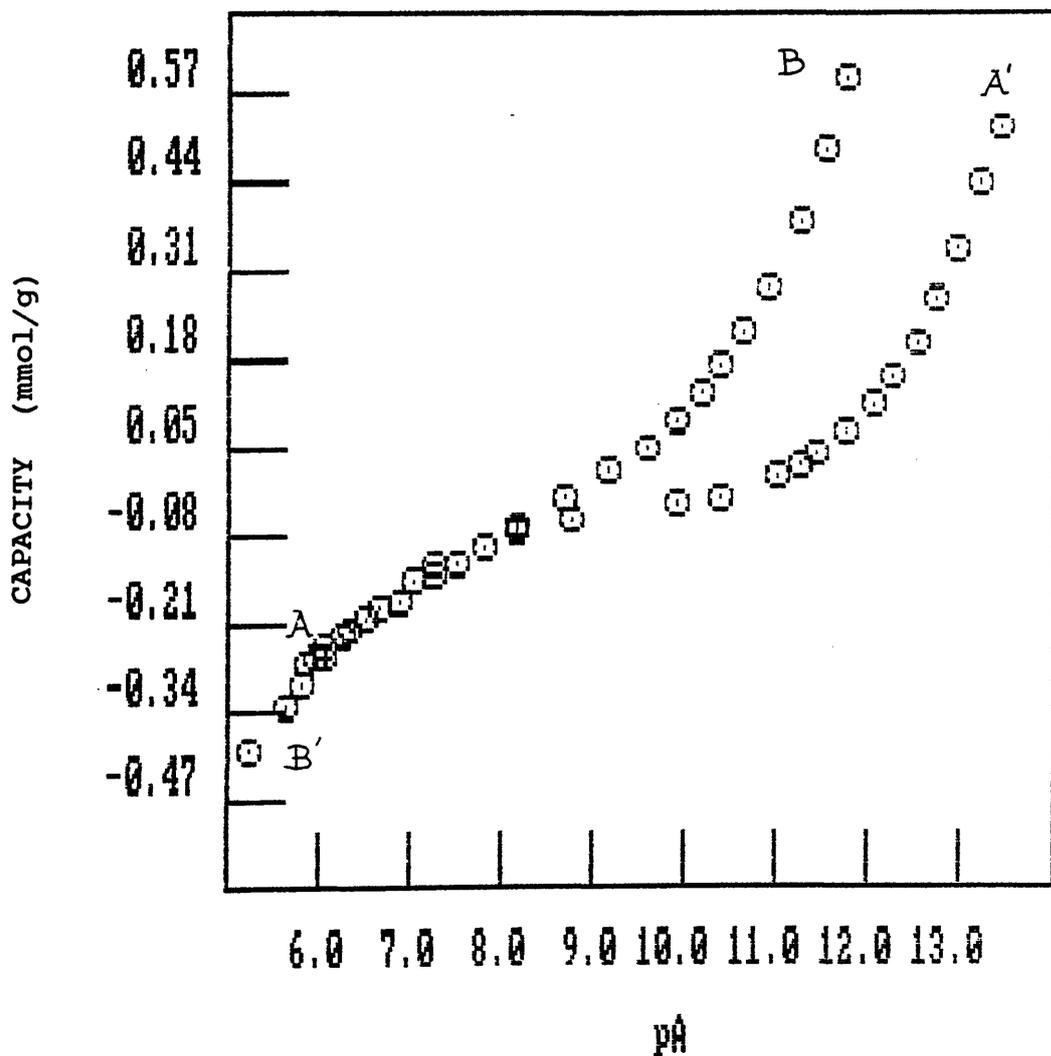
FIGURE(5.2) pH TITRATION OF MONOCLINIC ZIRCONIA WITH ADDED SALT.

A-A' 1 ml of 0.1 M HCl added to a suspension of 0.301g of ZrO_2 in 25 ml H_2O and titrated with 0.11M NaOH. B-B' 1.5 ml of 1M NaCl added and titrated with 0.10M HCl. TABLE(5.1)

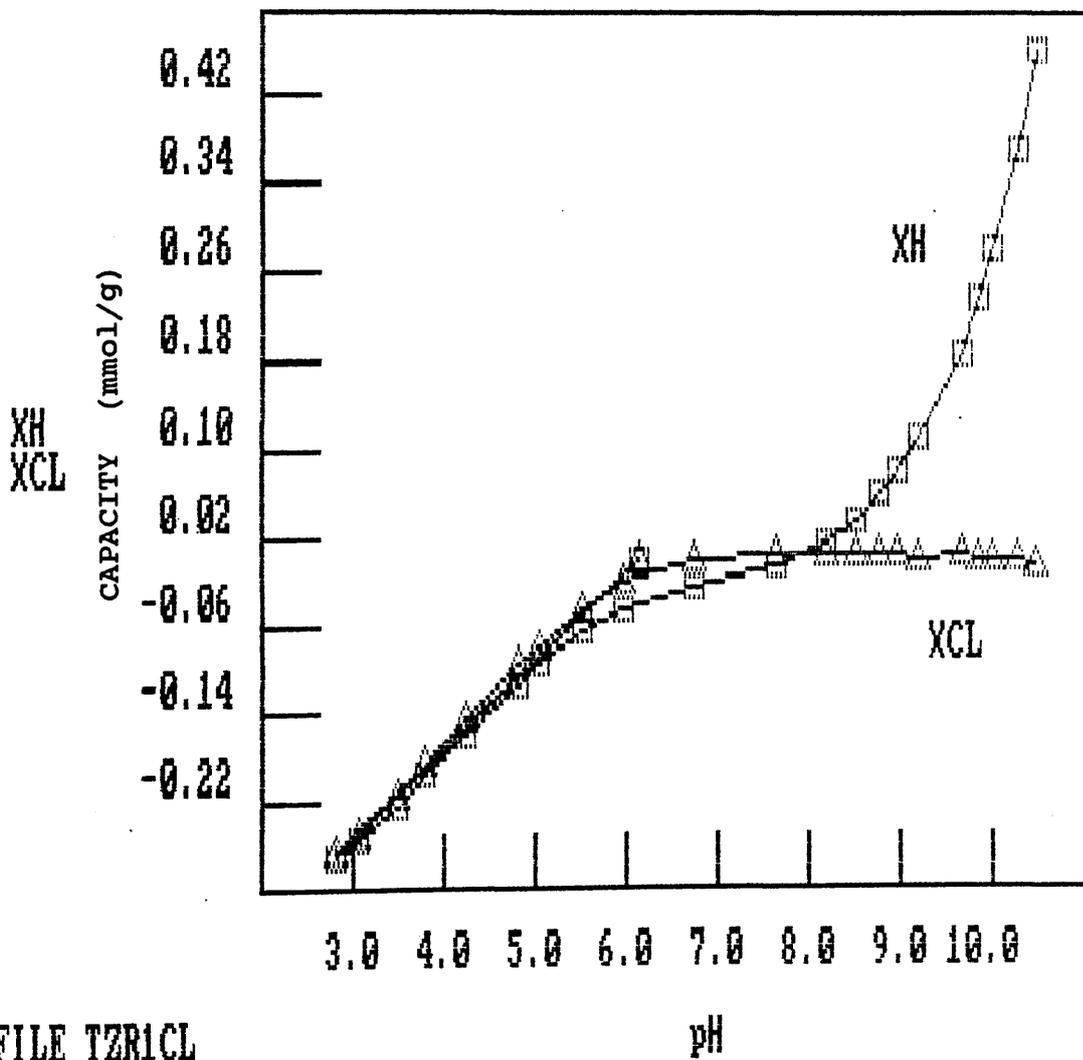


FIGURE(5.3) CAPACITY VS pA FOR MONOCLINIC ZIRCONIA

A-A' 1 ml of 0.1M HCl added to 0.250g ZrO_2 in 25 ml H_2O and titrated with 0.11M NaOH. B-B' 1.5 ml of 1 M NaCl added and titrated with 0.10M HCl. TABLE(5.1)



FIGURE(5.4) CHLORIDE UPTAKE BY MONOCLINIC ZIRCONIA VS pH
1 ml of 0.1M HCl added to 0.250g ZrO₂ in 25 ml H₂O and
titrated with 0.11 NaOH. TABLE(5.2)

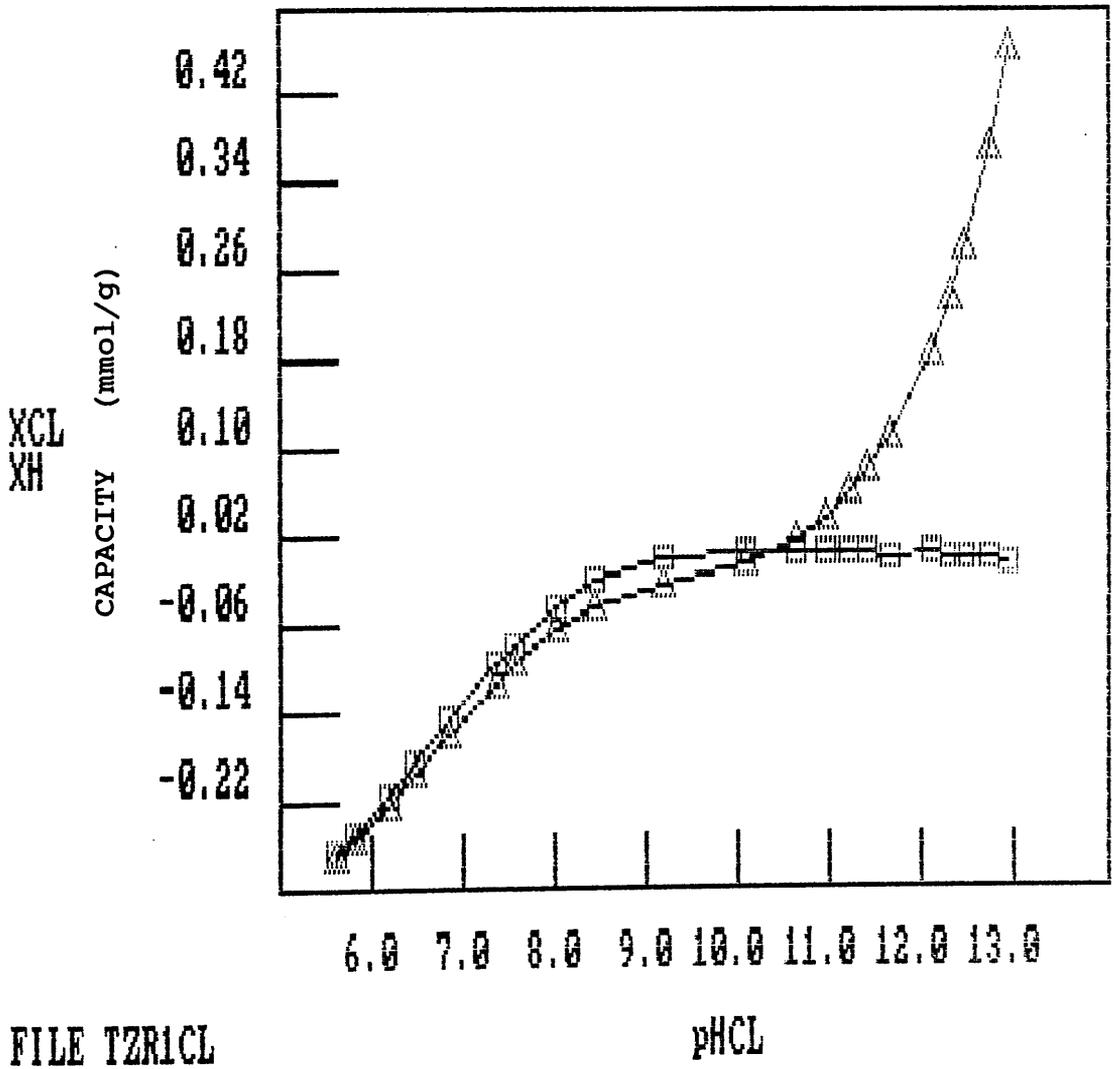


FILE TZR1CL

pH

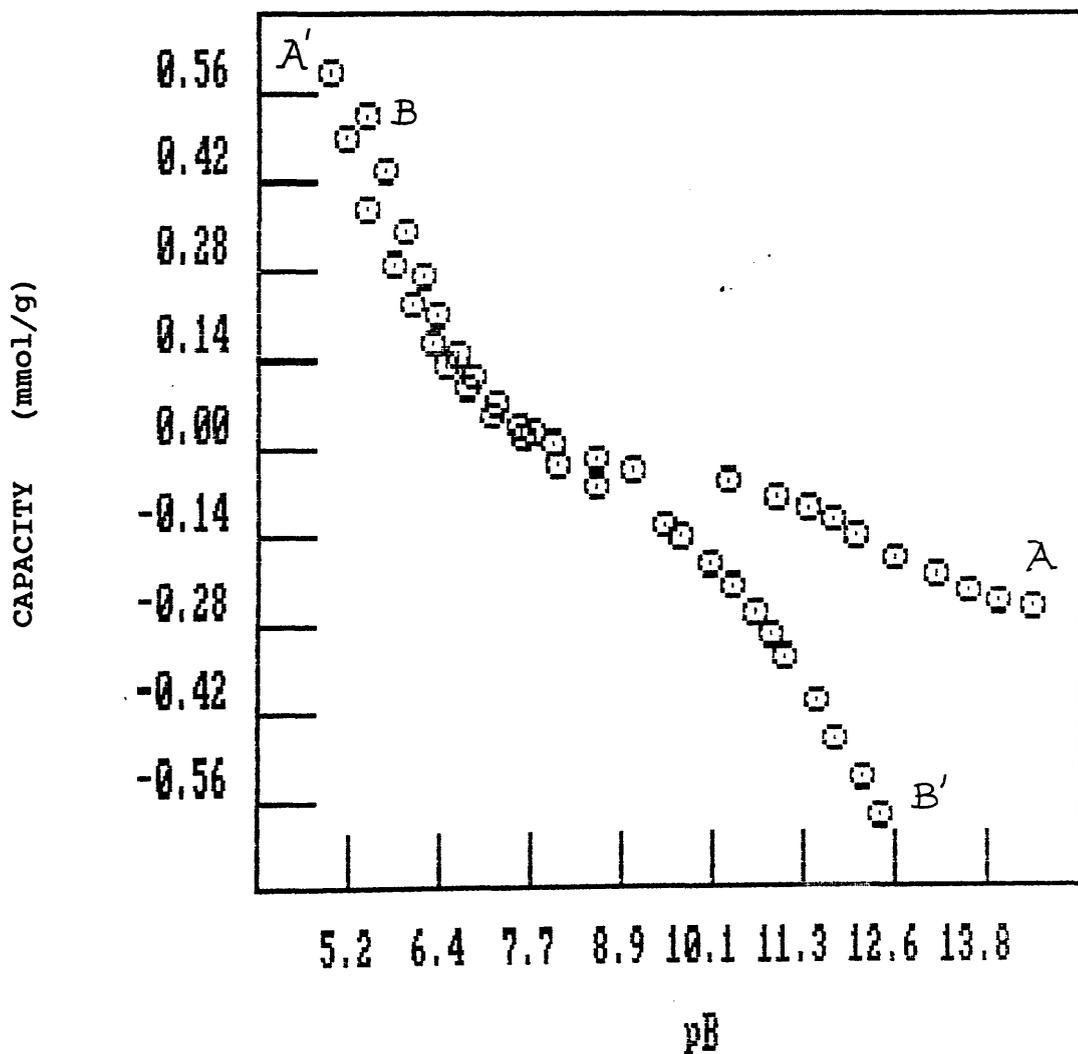
FIGURE(5.5) CHLORIDE UPTAKE BY ZIRCONIA VS pHCL

1 ml of 0.1M HCl added to 0.250g ZrO₂ in 25 ml H₂O and titrated with 0.11 NaOH. TABLE(5.2)



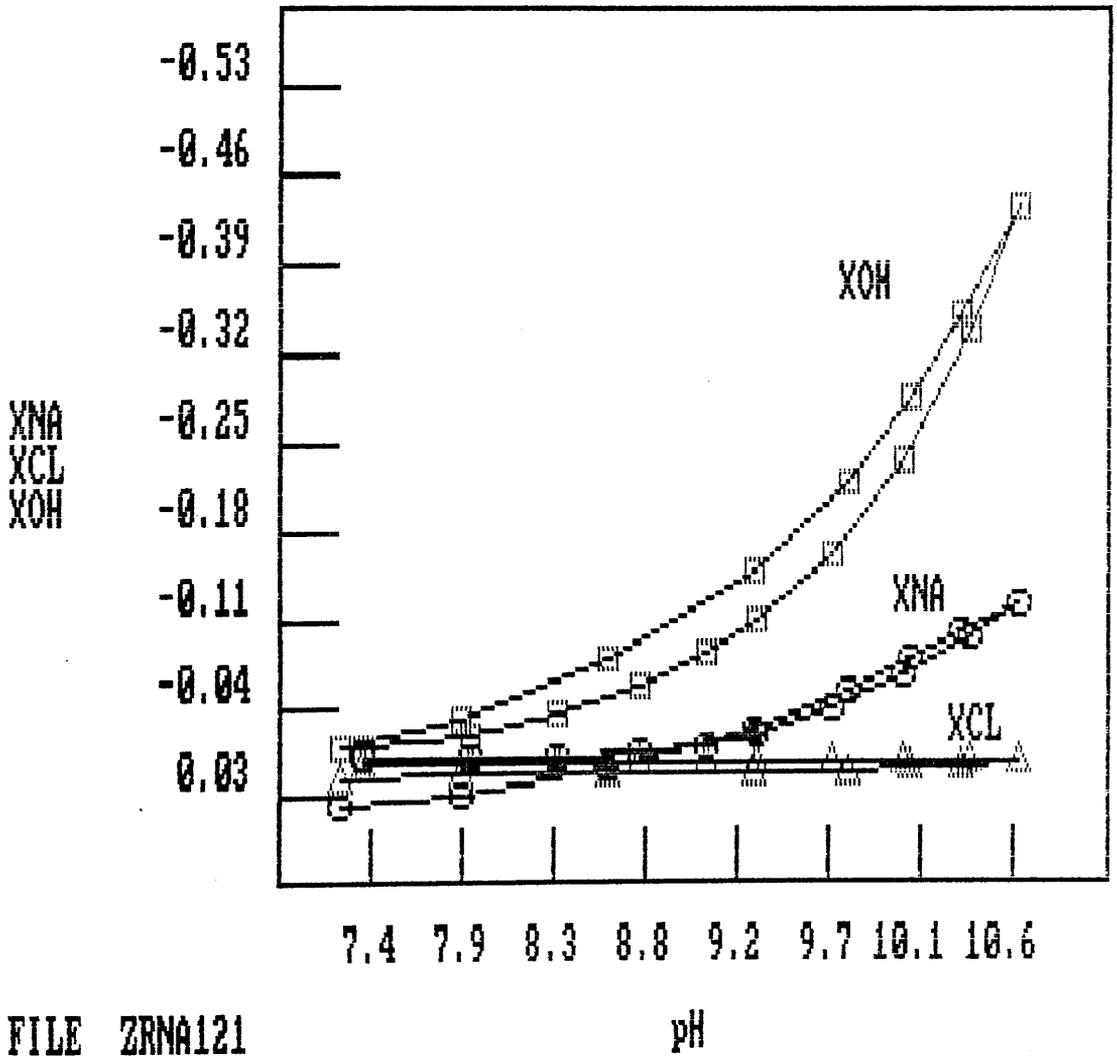
FIGURE(5.6) CAPACITY VS pB FOR MONOCLINIC ZIRCONIA

A-A' 1 ml of 0.1M HCl added to 0.250g ZrO_2 in 25 ml H_2O and titrated with 0.11M NaOH. B-B' 1.5 ml of 1 M NaCl added and titrated with 0.10M HCl. TABLE(5.1)



FIGURE(5.7) SODIUM, CHLORIDE AND HYDROXIDE CAPACITY VS pH FOR MONOCLINIC ZIRCONIA

1 ml of 0.1M HCl added to 0.250g ZrO_2 in 25 ml H_2O and titrated with 0.11M NaOH. 1.5 ml of 1 M NaCl added and titrated with 0.10M HCl. TABLE(5.3)

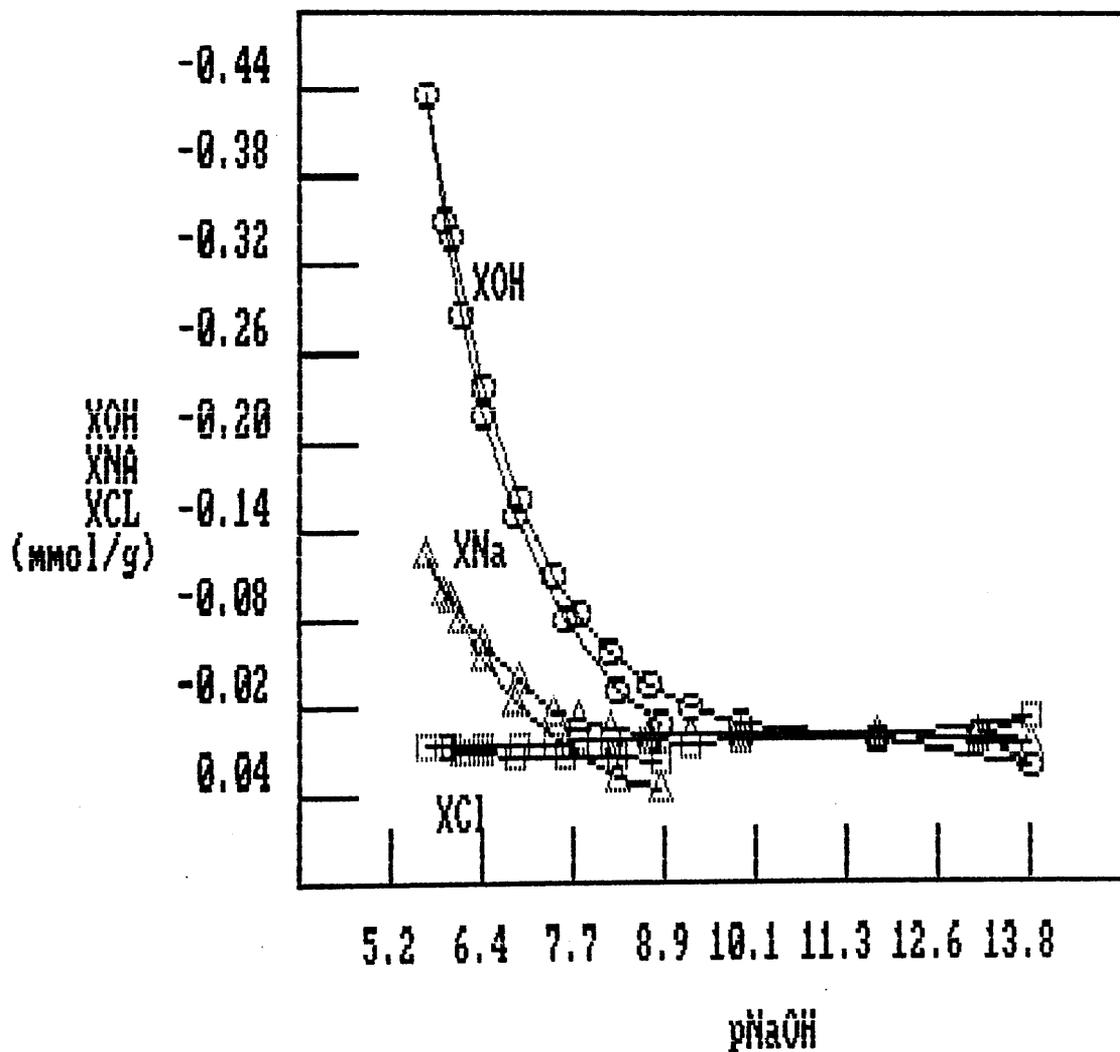


FILE ZRNA121

pH

FIGURE(5.8) SODIUM, CHLORIDE AND HYDROXIDE CAPACITY VS pNaOH FOR MONOCLINIC ZIRCONIA

1 ml of 0.1M HCl added to 0.250g ZrO₂ in 25 ml H₂O and titrated with 0.11M NaOH. 1.5 ml of 1 M NaCl added and titrated with 0.10M HCl. TABLE(5.3)



FILE ZRNA121

CHAPTER FIVE REFERENCES

1. A.W. Thomas, and H.S. Owens, J. Amer. Chem. Soc., 57,1825 (1935)
2. A. Clearfield, Inorg. Chem, 3, 146 (1964)
3. R. Paterson, and H. Rahman, J. Colloid and Interface Sci. 103, 106, (1985)
4. Amphlett, C.B., Inorganic Ion Exchangers, Elsevier, Amsterdam, 1964.
5. L.M. Sharygin, V.M. Galkin, Kinetika i Kataliz, Vol. 16, No. 6 pp. 1595-1601, 1975

CHAPTER 6

FLUORIDE UPTAKE BY MONOCLINIC ZIRCONIA

6.1 Introduction

In Chapter 5 the sodium and chloride ion exchange properties of monoclinic zirconia, as described by Paterson and Rahman, were reconfirmed by pH titration. Enhancement of the titration system to include the ion selective electrode of choice gave remarkable correlation. In order to take advantage of the techniques, equipment and computer programs available, it was logical to continue the study and fluoride was chosen as the next species of interest. The fluoride ion selective electrode is similar to the pH electrode in reliability and accuracy.

A series of control experiments were conducted to verify that the fluoride ion selective electrode would produce accurate and reproducible results in the pH range and sample matrix. Next the fluoride ion exchange properties of zirconia were studied, producing some striking results. Reversible fluoride ion capacities more than a decade greater in magnitude than other species were observed. An explanation is offered in the results and discussion section that follows in this chapter.

6.2 Experimental

The following ion exchange studies of the monoclinic zirconia crystals are enhanced by the capturing of real time data on the distribution of fluoride in a crystal suspension. This was accomplished using the fluoride electrode discussed in Chapter 4. It employs a membrane of lanthanum fluoride which is highly selective for fluoride ions and being a single crystal is quite robust in structural integrity. This electrode has a response time to changes in fluoride activity of less than one minute, and an accuracy comparable to the pH electrode. The second generation of computer programs for uptake calculations, as developed in Chapter Five, were used to process the data from the fluoride, chloride and pH electrodes. Millivolt potentials from each electrode were recorded during calibration and during the experimental work. Electrode calibration equations were determined and used to calculate fluoride ion concentration during the experiments with the crystalline zirconia.

To evaluate the analytical validity of the fluoride electrode system a null test was carried out. Acetic acid was added to distilled water and titrated with sodium hydroxide in the presence of pH, fluoride and chloride electrodes. Sodium chloride was added initially. Considering that the pK of hydrofluoric acid is 3.45, the sodium fluoride was added after pH 5 to minimize the

exposure of the crystals to the acid. At pH 5, 97.2 percent of the fluoride would be present as free fluoride and only 2.8 percent would be in the form of hydrofluoric acid. The data and results, file HAC912, can be found in the Appendix Table(A.4) and Figure(A.4). The pH electrode provided an ideal response to the hydrogen ion release from the acetic acid. After considering changes in volume and ionic strength, from the addition of reagents the response from the fluoride and chloride electrodes indicated that there was no release or uptake of either ion. This is as expected in this control situation where no ion exchanger is present. The pH excursion was terminated at pH 11 to prevent hydroxide interference on the fluoride and chloride electrodes.

Three experiments were conducted to examine the relationship between fluoride and the ion exchange characteristics of the monoclinic zirconia. First, the capacity for fluoride at constant pH was studied. 0.3 grms of the exchanger was suspended in twenty ml of distilled water and stirred overnight to allow for complete hydration. To release carbon dioxide the pH was adjusted to 3 using hydrochloric acid. Calibrated pH and chloride electrodes were placed in the suspension. The pH was adjusted to 5 with sodium hydroxide and the calibrated fluoride electrode was placed in the suspension. From this point onward 0.2 mmol additions of sodium fluoride were added and the pH re-established

using 0.10 M hydrochloric acid. This was continued until additions of fluoride no longer caused a significant change in the pH. The results from this experiment can be found in Table(6.1), and Figure(6.1) and Figure(6.2).

Capacity at a constant activity of fluoride from pH 5 to pH 10 was the second experiment in this series. The crystalline suspension was raised to pH 10 by additions of sodium fluoride and sodium hydroxide. This was back titrated to pH 5 using hydrochloric acid. Sodium fluoride was added at each point to maintain a constant amount of free fluoride. The results are displayed in Table(6.2) and Figure(6.3).

Finally, the reversibility of this fluoride ion exchange was studied. Sodium fluoride was added to a suspension of monoclinic zirconia and titrated from pH 10 to pH 5, with hydrochloric acid. The titration was continued back to pH 10 with sodium hydroxide and finally back to pH 5 with hydrochloric acid. In this way, observations could be made regarding the ability for zirconia to remove and release fluoride ions from solution over a wide pH range.

Chapter 6.3 Results and Discussion

The initial experiment of fluoride ion uptake on monoclinic zirconia was quite remarkable. Additions of sodium fluoride to a crystal suspension produced large pH excursions which corresponded to relatively large uptake of fluoride ion. While maintaining a constant pH, the final uptake calculated was 8 mmol/grm, over a decade higher than typical uptake figures for exchangers of this type. The results of this experiment are found in Table(6.1). Figure(6.1) shows the increasing uptake at pH 5 as the activity of fluoride ion is increased in the suspension. Figure(6.2) demonstrates that when this data is plotted as signal value function of the acid, pHF , it is nearly a smooth curve due to fact that each uptake of fluoride is apparently directly related to a proton uptake, or hydroxyl release.

Kraus, et al.(1) had previously encountered large capacities of amorphous hydrous zirconia for fluoride ions and attributed the effect to complexes formed between the Zr(IV) and F^- ion. It was suggested by Hingston , et al.(2) that fluoride adsorption on goethite was effected by forming a ligand exchange with water in the coordination layer of the exchanger surface. It has been observed repeatedly (1),(3), and in this laboratory that the percentage of water in the exchanger is directly related to capacity. Increased drying time or

drying at elevated temperatures has reduced uptake. Crystals titrated immediately after being added to water have lower capacities than crystals given twenty four hours for hydration equilibrium. This supports the theory that coordinated water molecules and hydroxyl groups play a significant role in the exchange mechanism.

The second experiment in this series see Table(6.2) and Figure(6.3) was a study of the hydroxyl release or proton uptake of the exchanger and its relation to the uptake of fluoride at a constant activity of fluoride. The results show a striking correlation between hydrogen ion uptake and fluoride uptake. It is more likely, in this case that the entering fluoride ion displaces hydroxyl ions from the zirconia matrix. The remarkable capacity of monoclinic zirconia must be attributed in some way to lattice uptake and replacement of bridging hydroxyls by fluoride. At the upper level of capacity, 8 mmol/grm there is a one to one fluoride to zirconia atom ratio. Calculations show that this could not entirely be surface adsorption. The fact that monoclinic zirconia is a distorted fluorite lattice(4) is further support for this theory.

To study the reversibility of this exchange the fluoride capacity was examined as the pH was cycled from pH 10 to pH 5 back to pH 10 and ending at pH 6. The results of these sodium hydroxide and hydrochloric acid titrations in the presence of sodium fluoride are found

in Table (6.3) and Figure(6.4). They demonstrate that the exchange is essentially reversible. The increasing background of sodium chloride concentration may contribute to the slight deviation from perfect reversibility. This result confirms that even though the capacities are large, and almost certainly include lattice replacement of hydroxide with fluoride, the mechanism does not include an irreversible complex between zirconium and fluoride. Similar reversibilities have been shown with goethite and gibbsite(5).

TABLE(6.1): UPTAKE OF FLUORIDE

NAME OF FILE =CONFPH5

Concentration of NaF = 0.50M

Concentration of NaOH = 0.11M

Concentration of HCl = 0.10M

Initial Volume = 20.00ml

Weight of ZrO₂ = 0.340gWeight of Dried ZrO₂ = 0.292g

N = Number of data set.

VB = Volume of base, ml.

VA = Volume of Acid, ml.

VS = Volume of Salt, ml.

XF = F⁻ Capacity in mmol/gXH = H⁺ Capacity in mmol/g

pHF = pF + pH

| N | VB | VA | VS | pHF | pH | XF | XH |
|----|------|-------|------|-------|-------|--------|--------|
| 1 | 0.00 | 0.00 | 0.00 | 12.55 | 6.254 | 0.000 | -0.000 |
| 2 | 0.00 | 0.50 | 0.00 | 12.20 | 3.296 | 0.000 | -0.134 |
| 3 | 0.00 | 1.00 | 0.00 | 11.91 | 2.790 | 0.000 | -0.220 |
| 4 | 0.00 | 1.50 | 0.00 | 11.74 | 2.511 | 0.000 | -0.272 |
| 5 | 0.00 | 2.00 | 0.00 | 11.65 | 2.337 | 0.000 | -0.311 |
| 6 | 0.50 | 2.00 | 0.00 | 11.77 | 2.685 | 0.000 | -0.325 |
| 7 | 1.00 | 2.00 | 0.00 | 13.68 | 5.109 | 0.000 | -0.307 |
| 8 | 1.50 | 2.00 | 0.00 | 12.62 | 5.074 | 0.000 | -0.119 |
| 9 | 2.00 | 2.00 | 0.00 | 12.95 | 5.021 | 0.000 | 0.069 |
| 10 | 2.00 | 2.00 | 0.40 | 11.29 | 9.014 | -0.188 | 0.067 |
| 11 | 2.00 | 3.82 | 0.40 | 9.60 | 5.039 | -0.681 | -0.553 |
| 12 | 2.00 | 3.82 | 0.80 | 9.86 | 7.549 | -0.854 | -0.554 |
| 13 | 2.00 | 5.60 | 0.80 | 8.79 | 5.021 | -1.349 | -1.162 |
| 14 | 2.00 | 5.60 | 1.20 | 9.02 | 6.700 | -1.496 | -1.163 |
| 15 | 2.00 | 7.40 | 1.20 | 8.34 | 5.021 | -1.993 | -1.777 |
| 16 | 2.00 | 7.40 | 1.60 | 8.61 | 6.329 | -2.080 | -1.778 |
| 17 | 2.00 | 8.90 | 1.60 | 7.86 | 5.011 | -2.549 | -2.290 |
| 18 | 2.00 | 8.90 | 2.00 | 8.09 | 5.848 | -2.660 | -2.291 |
| 19 | 2.00 | 10.00 | 2.00 | 7.62 | 5.021 | -3.070 | -2.666 |
| 20 | 2.00 | 10.00 | 2.40 | 7.84 | 5.654 | -3.189 | -2.667 |
| 21 | 2.00 | 11.00 | 2.40 | 7.50 | 5.039 | -3.602 | -3.008 |
| 22 | 2.00 | 11.00 | 2.80 | 7.70 | 5.564 | -3.707 | -3.009 |
| 23 | 2.00 | 12.06 | 2.80 | 7.44 | 5.056 | -4.164 | -3.371 |
| 24 | 2.00 | 12.06 | 3.20 | 7.62 | 5.510 | -4.271 | -3.372 |
| 25 | 2.00 | 13.00 | 3.20 | 7.29 | 4.987 | -4.685 | -3.692 |
| 26 | 2.00 | 13.00 | 3.60 | 7.50 | 5.442 | -4.754 | -3.693 |
| 27 | 2.00 | 13.90 | 3.60 | 7.25 | 5.039 | -5.155 | -4.000 |
| 28 | 2.00 | 13.90 | 4.00 | 7.40 | 5.388 | -5.227 | -4.001 |
| 29 | 2.00 | 14.50 | 4.00 | 7.14 | 5.039 | -5.502 | -4.205 |
| 30 | 2.00 | 14.50 | 4.40 | 7.29 | 5.353 | -5.558 | -4.206 |

| N | VB | VA | VS | pHF | pH | XF | XH |
|----|------|-------|------|------|-------|--------|--------|
| 31 | 2.00 | 15.10 | 4.40 | 7.03 | 5.021 | -5.833 | -4.410 |
| 32 | 2.00 | 15.10 | 4.80 | 7.17 | 5.300 | -5.869 | -4.411 |
| 33 | 2.00 | 15.70 | 4.80 | 6.96 | 5.021 | -6.153 | -4.615 |
| 34 | 2.00 | 15.70 | 5.20 | 7.09 | 5.266 | -6.195 | -4.616 |
| 35 | 2.00 | 16.20 | 5.20 | 6.89 | 5.021 | -6.426 | -4.786 |
| 36 | 2.00 | 16.20 | 6.00 | 7.06 | 5.372 | -6.465 | -4.787 |
| 37 | 2.00 | 17.00 | 6.00 | 6.75 | 5.004 | -6.837 | -5.060 |
| 38 | 2.00 | 17.00 | 7.00 | 6.94 | 5.353 | -6.878 | -5.061 |
| 39 | 2.00 | 17.80 | 7.00 | 6.61 | 4.987 | -7.236 | -5.333 |
| 40 | 2.00 | 17.80 | 8.00 | 6.81 | 5.300 | -7.274 | -5.334 |
| 41 | 2.00 | 18.80 | 8.00 | 6.60 | 5.056 | -7.775 | -5.675 |

TABLE(6.2): pH TITRATION AT CONSTANT ACTIVITY OF FLUORIDE

NAME OF FILE =TCONF918

Concentration of NaF = 0.46M

Concentration of NaOH = 0.11M

Concentration of HCl = 0.10M

Initial Volume = 20.00ml

Weight of ZrO₂ = 0.337g

Weight of Dried ZrO₂ = 0.300g

N = Number of data set.

VB = Volume of base, ml.

VA = Volume of Acid, ml.

VS = Volume of Salt, ml.

XF = F⁻ Capacity in mmol/g

XH = H⁺ Capacity in mmol/g

pHF = pF + pH

| N | VB | VA | VS | pHF | pH | XF | XH |
|----|------|-------|------|-------|-------|--------|--------|
| 1 | 0.00 | 0.00 | 0.00 | 12.98 | 6.017 | 0.000 | -0.000 |
| 2 | 0.00 | 0.50 | 0.00 | 10.19 | 3.232 | 0.000 | -0.125 |
| 3 | 0.34 | 0.50 | 0.00 | 11.78 | 4.821 | 0.000 | -0.041 |
| 4 | 0.34 | 0.50 | 1.00 | 11.10 | 9.311 | -0.181 | -0.044 |
| 5 | 1.00 | 0.50 | 1.00 | 11.74 | 9.976 | -0.045 | 0.192 |
| 6 | 1.00 | 0.80 | 1.06 | 11.47 | 9.698 | -0.126 | 0.096 |
| 7 | 1.00 | 1.20 | 1.14 | 11.12 | 9.357 | -0.204 | -0.035 |
| 8 | 1.00 | 1.60 | 1.24 | 10.80 | 9.037 | -0.311 | -0.168 |
| 9 | 1.00 | 2.00 | 1.32 | 10.52 | 8.749 | -0.420 | -0.301 |
| 10 | 1.00 | 2.30 | 1.40 | 10.31 | 8.541 | -0.494 | -0.400 |
| 11 | 1.00 | 2.70 | 1.52 | 10.04 | 8.275 | -0.631 | -0.534 |
| 12 | 1.00 | 3.10 | 1.64 | 9.79 | 8.026 | -0.767 | -0.667 |
| 13 | 1.00 | 3.50 | 1.76 | 9.56 | 7.787 | -0.932 | -0.800 |
| 14 | 1.00 | 3.90 | 1.88 | 9.37 | 7.604 | -1.047 | -0.933 |
| 15 | 1.00 | 4.30 | 1.98 | 9.18 | 7.416 | -1.177 | -1.067 |
| 16 | 1.00 | 4.80 | 2.10 | 9.02 | 7.246 | -1.351 | -1.233 |
| 17 | 1.00 | 5.30 | 2.24 | 8.91 | 7.143 | -1.494 | -1.400 |
| 18 | 1.00 | 6.00 | 2.40 | 8.77 | 7.000 | -1.657 | -1.633 |
| 19 | 1.00 | 7.00 | 2.66 | 8.48 | 6.718 | -1.959 | -1.967 |
| 20 | 1.00 | 8.00 | 2.94 | 8.27 | 6.502 | -2.292 | -2.300 |
| 21 | 1.00 | 9.00 | 3.24 | 8.09 | 6.314 | -2.690 | -2.633 |
| 22 | 1.00 | 10.00 | 3.60 | 7.95 | 6.183 | -3.114 | -2.967 |
| 23 | 1.00 | 11.00 | 3.96 | 7.84 | 6.075 | -3.573 | -3.300 |
| 24 | 1.00 | 12.00 | 4.30 | 7.72 | 5.947 | -3.996 | -3.633 |
| 25 | 1.00 | 13.20 | 4.74 | 7.62 | 5.852 | -4.550 | -4.033 |
| 26 | 1.00 | 15.00 | 5.38 | 7.34 | 5.572 | -5.352 | -4.633 |

TABLE(6.3): REVERSIBILITY STUDY FLUORIDE UPTAKE VS pH

NAME OF FILE =TRF1026

Concentration of NaF = 0.46M

Concentration of NaOH = 0.11M

Concentration of HCl = 0.10M

Initial Volume = 25.00ml

Weight of ZrO₂ = 0.314gWeight of Dried ZrO₂ = 0.260g

N = Number of data set.

VB = Volume of base, ml.

VA = Volume of Acid, ml.

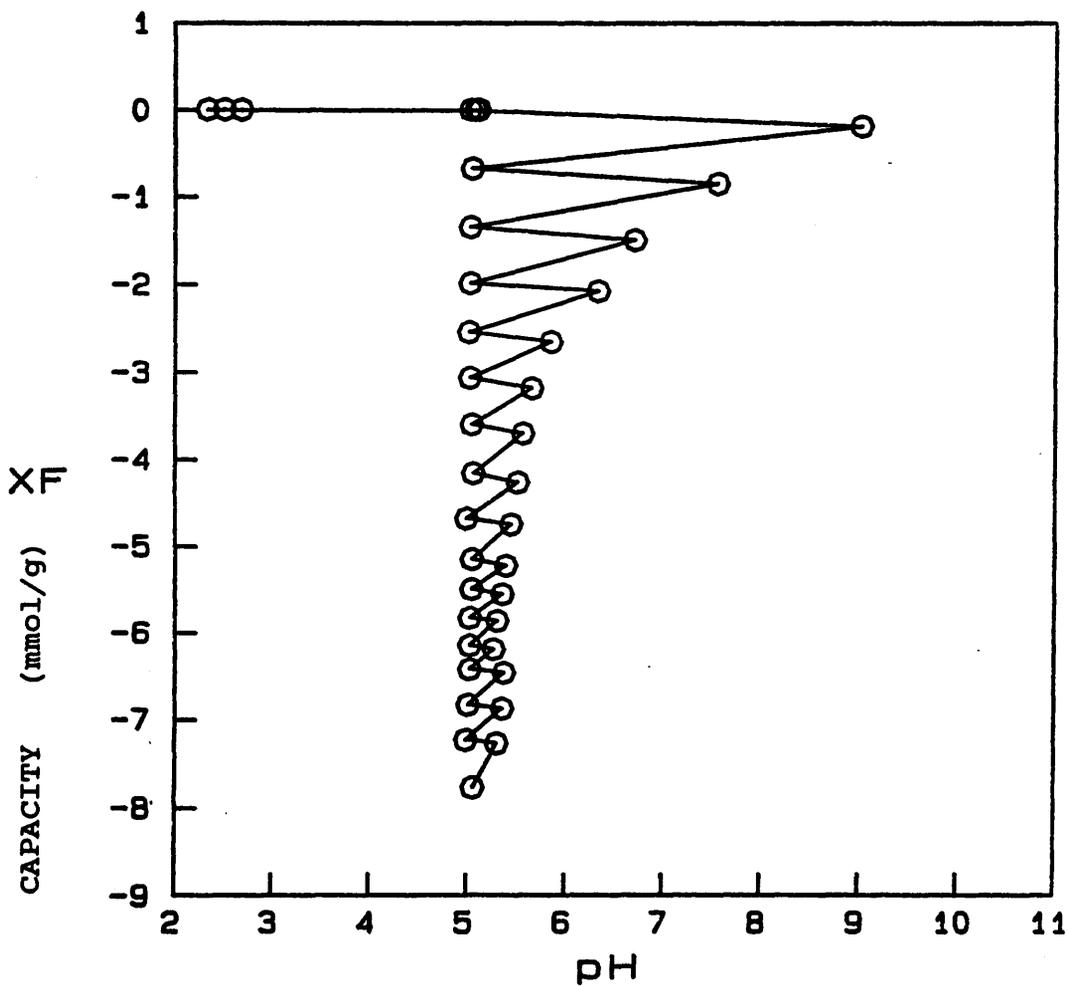
VS = Volume of Salt, ml.

XF = F⁻ Capacity in mmol/gXH = H⁺ Capacity in mmol/g

pHF = pF + pH

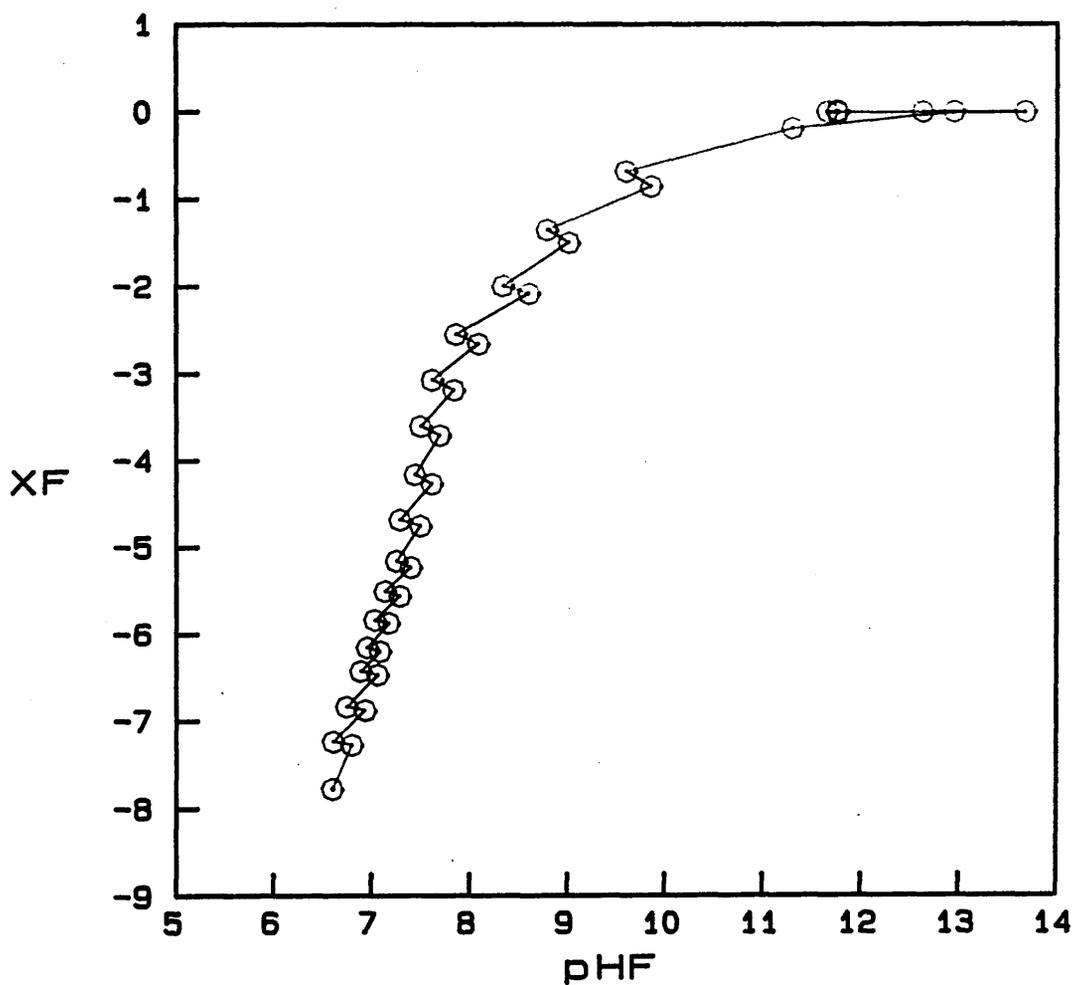
| N | VB | VA | VS | pHF | pH | XF | XH |
|----|-------|-------|------|-------|-------|--------|--------|
| 1 | 0.00 | 0.00 | 0.00 | 12.73 | 6.076 | 0.000 | -0.000 |
| 2 | 0.00 | 0.40 | 0.00 | 10.05 | 3.394 | 0.000 | -0.113 |
| 3 | 0.30 | 0.40 | 0.00 | 11.70 | 5.048 | 0.000 | -0.026 |
| 4 | 0.30 | 0.40 | 4.00 | 11.11 | 9.798 | -0.274 | -0.036 |
| 5 | 0.30 | 1.00 | 4.00 | 10.72 | 9.381 | -0.486 | -0.261 |
| 6 | 0.30 | 1.70 | 4.00 | 10.24 | 8.868 | -0.800 | -0.528 |
| 7 | 0.30 | 2.40 | 4.00 | 9.79 | 8.393 | -1.126 | -0.797 |
| 8 | 0.30 | 3.20 | 4.00 | 9.29 | 7.851 | -1.532 | -1.104 |
| 9 | 0.30 | 4.00 | 4.00 | 8.88 | 7.398 | -1.933 | -1.412 |
| 10 | 0.30 | 5.00 | 4.00 | 8.49 | 6.953 | -2.391 | -1.796 |
| 11 | 0.30 | 6.00 | 4.00 | 8.21 | 6.621 | -2.809 | -2.181 |
| 12 | 0.30 | 7.00 | 4.00 | 7.99 | 6.348 | -3.191 | -2.565 |
| 13 | 0.30 | 8.00 | 4.00 | 7.77 | 6.076 | -3.569 | -2.950 |
| 14 | 0.30 | 9.00 | 4.00 | 7.62 | 5.864 | -3.998 | -3.334 |
| 15 | 0.30 | 10.00 | 4.00 | 7.57 | 5.730 | -4.439 | -3.719 |
| 16 | 0.30 | 11.00 | 4.00 | 7.36 | 5.440 | -4.869 | -4.103 |
| 17 | 0.30 | 12.00 | 4.00 | 7.23 | 5.197 | -5.322 | -4.487 |
| 18 | 0.80 | 12.00 | 4.00 | 7.60 | 5.605 | -5.117 | -4.277 |
| 19 | 1.50 | 12.00 | 4.00 | 7.91 | 5.970 | -4.817 | -3.981 |
| 20 | 2.30 | 12.00 | 4.00 | 8.18 | 6.296 | -4.454 | -3.642 |
| 21 | 3.40 | 12.00 | 4.00 | 8.45 | 6.642 | -3.888 | -3.177 |
| 22 | 5.00 | 12.00 | 4.00 | 8.81 | 7.090 | -2.999 | -2.500 |
| 23 | 6.00 | 12.00 | 4.00 | 9.13 | 7.449 | -2.474 | -2.077 |
| 24 | 7.20 | 12.00 | 4.00 | 9.80 | 8.165 | -1.841 | -1.570 |
| 25 | 8.00 | 12.00 | 4.00 | 10.34 | 8.730 | -1.427 | -1.232 |
| 26 | 8.50 | 12.00 | 4.00 | 10.65 | 9.051 | -1.185 | -1.022 |
| 27 | 9.20 | 12.00 | 4.00 | 11.05 | 9.468 | -0.861 | -0.730 |
| 28 | 10.00 | 12.00 | 4.00 | 11.44 | 9.879 | -0.531 | -0.403 |
| 29 | 10.00 | 13.00 | 4.00 | 10.61 | 9.005 | -0.993 | -0.772 |
| 30 | 10.00 | 14.80 | 4.00 | 9.49 | 7.811 | -1.735 | -1.462 |
| 31 | 10.00 | 16.00 | 4.00 | 8.93 | 7.196 | -2.275 | -1.923 |
| 32 | 10.00 | 18.00 | 4.00 | 8.55 | 6.717 | -3.130 | -2.692 |
| 33 | 10.00 | 20.00 | 4.00 | 8.03 | 6.083 | -4.005 | -3.461 |

FIGURE(6.1) FLUORIDE UPTAKE VS pH FOR MONOCLINIC ZIRCONIA
 Alternate additions of 0.20 mmol fluoride and 0.1M HCl to
 0.340g of ZrO_2 suspended in 20 ml H_2O . TABLE(6.1)



FIGURE(6.2) FLUORIDE UPTAKE VS pHF FOR MONOCLINIC ZIRCONIA
Alternate additions of 0.20 mmol fluoride and 0.1M HCl to
0.340g of ZrO_2 suspended in 20 ml H_2O . TABLE(6.1)

F UPTAKE BY ZIRCONIA

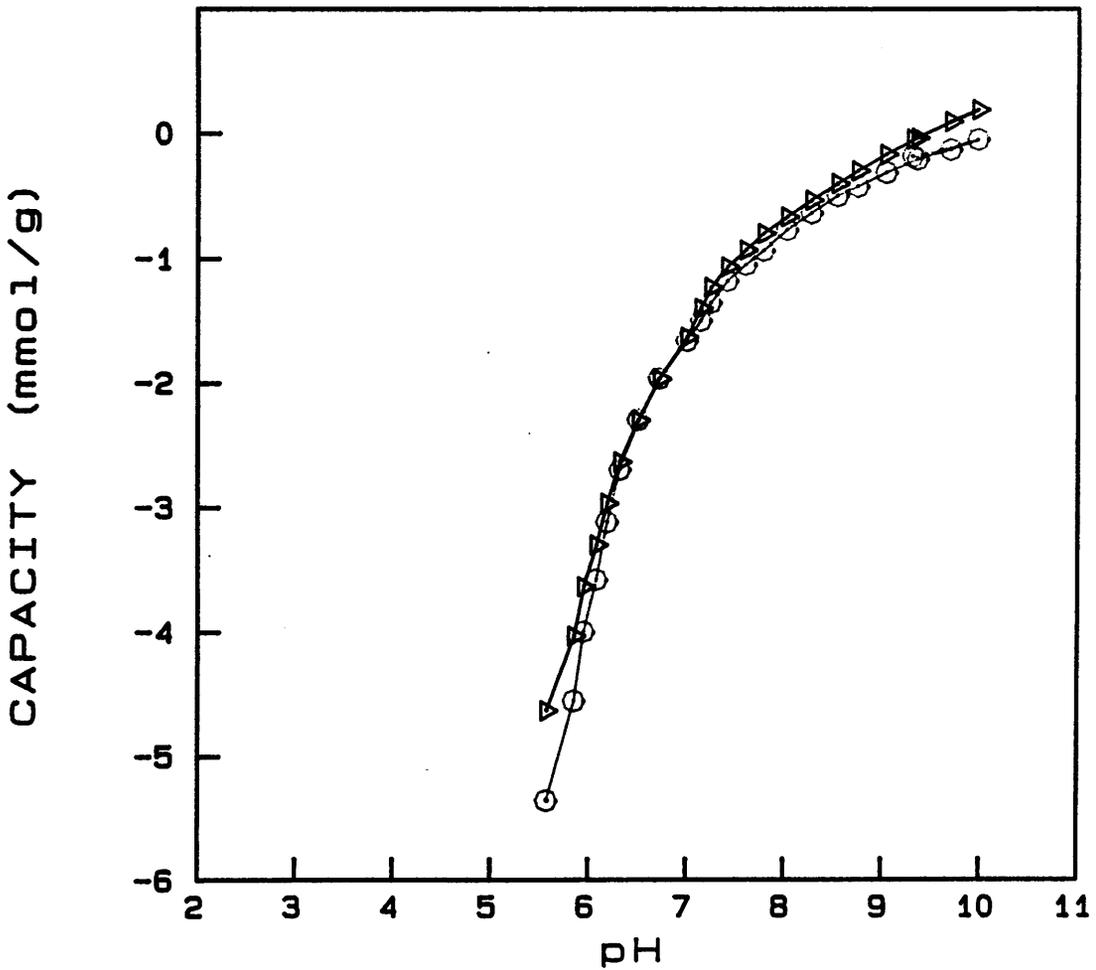


○ XF

FIGURE(6.3) FLUORIDE AND PROTON UPTAKE VS pH FOR MONOCLINIC ZIRCONIA

A constant activity of fluoride is maintained with alternate additions of 0.46M NaF and 0.10M HCl to 0.337g ZrO₂ in 20 ml H₂O. TABLE(6.2)

FLUORIDE CAPACITY



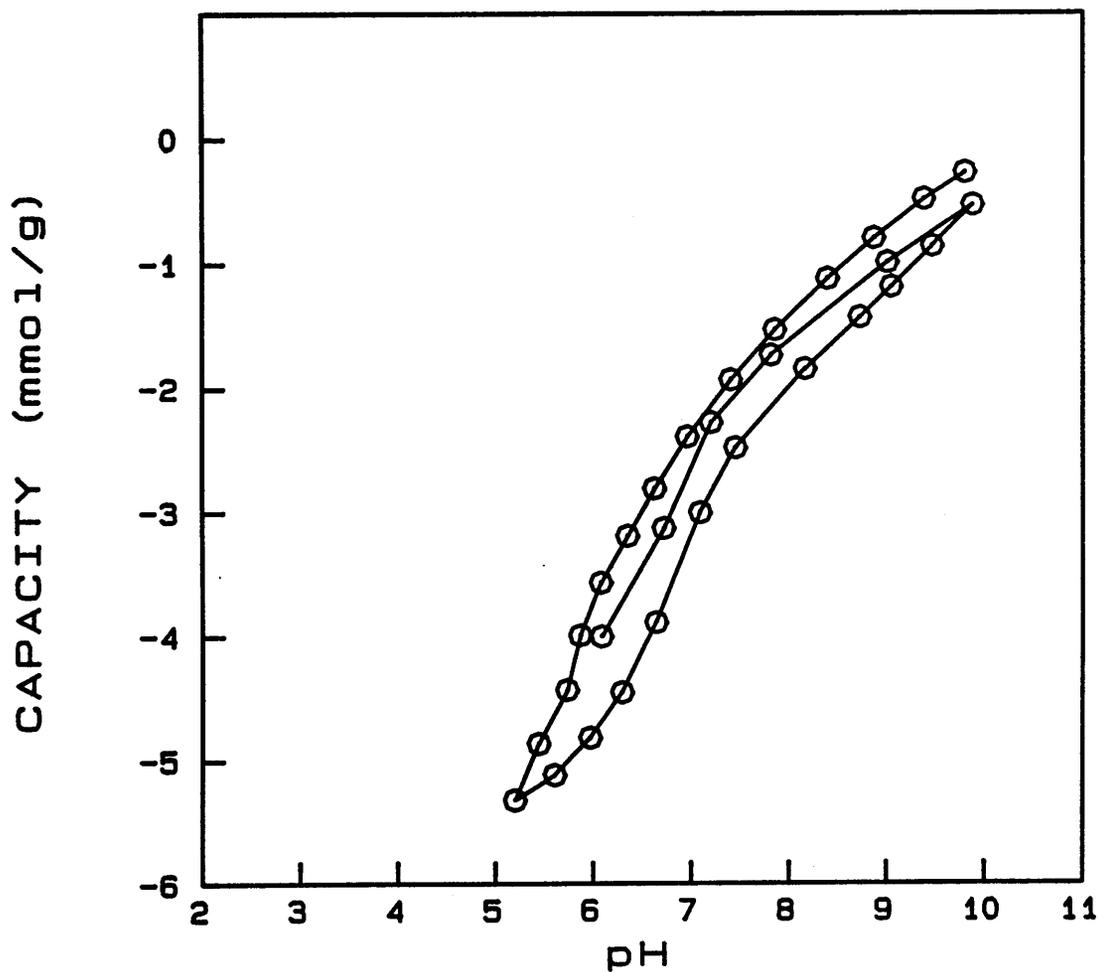
○ XF
△ XH

FIGURE(6.4) REVERSIBILITY OF FLUORIDE UPTAKE VS pH

0.46M NaF is added to 0.314g ZrO₂ (1) and the system is backtitrated with 0.10M HCl to pH 5 (2). Then titrated forward with 0.11M NaOH (3) and back again with HCl (4).

TABLE(6.3).

F UPTAKE BY ZIRCONIA



⊙ XF

CHAPTER SIX REFERENCES

1. K.A. Kraus, H.O. Phillips, T.A. Carlson and J.S. Johnson, Proc. Second Int. Conf. Peaceful Uses of Atomic Energy, Geneva, 28, 3, (1958)
2. F.J. Hingston, A.M. Posner and J.P. Quirk, J. Soil Sci., 23, 177, (1972)
3. C.B. Amphlett, L.A. McDonald, and M.J. Redman, J. Inorg. Nucl. Chem., 6, 236 (1958)
4. G.Lungren, Svensk. Kemisk. Tidskrift, 71, 200 (1959)
5. F.J. Hingston, A.M. Posner and J.P. Quirk, J. Soil Sci., 25, 16, (1974)

Appendix A

Null Test Experimentation

- A.1 Strong Acid pH Titration
- A.2 Weak Acid pH Titration
- A.3 Null Test of Sodium and Chloride Electrodes
Using Boric Acid
- A.4 Null Test of Fluoride and Chloride Electrodes
Using Acetic Acid

TABLE(A.1)

NAME OF FILE =HCL94

Concentration of HCl = 0.10M

Initial Volume = 20.00ml

Concentration of NaOH = 0.11

N = Number of data set.

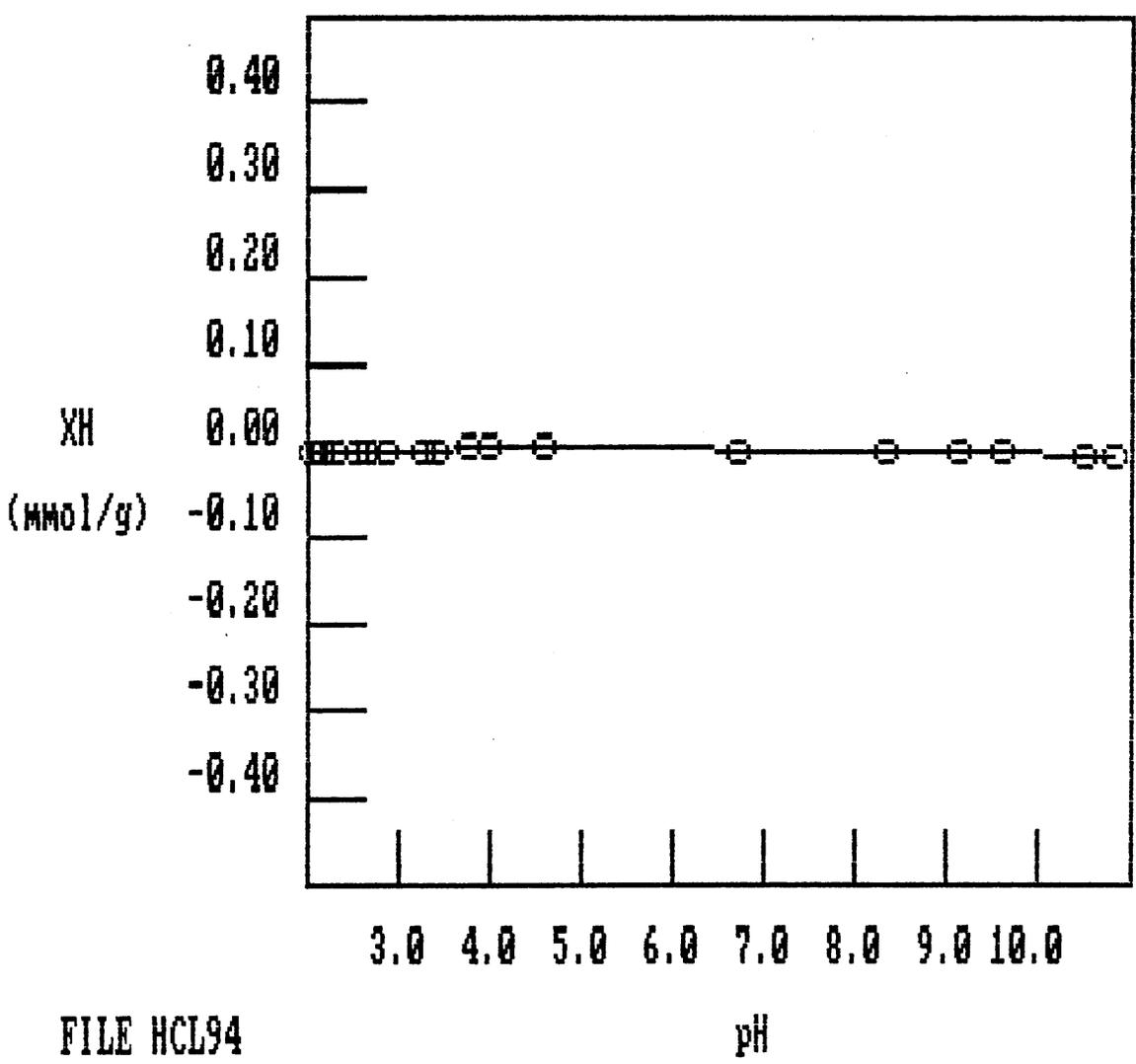
VB = Volume of base, ml.

VA = Volume of Acid, ml.

XH = H⁺ Capacity in mmol/g

| N | VB | VA | pH | XH |
|----|------|------|-------|--------|
| 1 | 0.00 | 0.00 | 6.70 | 0.000 |
| 2 | 0.00 | 3.00 | 1.94 | 0.004 |
| 3 | 0.50 | 3.00 | 2.03 | -0.001 |
| 4 | 1.00 | 3.00 | 2.14 | -0.001 |
| 5 | 1.50 | 3.00 | 2.30 | 0.001 |
| 6 | 2.00 | 3.00 | 2.53 | 0.001 |
| 7 | 2.20 | 3.00 | 2.66 | 0.001 |
| 8 | 2.40 | 3.00 | 2.86 | 0.002 |
| 9 | 2.60 | 3.00 | 3.24 | 0.003 |
| 10 | 2.65 | 3.00 | 3.41 | 0.003 |
| 11 | 2.70 | 3.00 | 3.75 | 0.003 |
| 12 | 2.72 | 3.00 | 3.98 | 0.003 |
| 13 | 2.74 | 3.00 | 4.58 | 0.003 |
| 14 | 2.76 | 3.00 | 8.32 | 0.002 |
| 15 | 2.78 | 3.00 | 9.13 | 0.000 |
| 16 | 2.80 | 3.00 | 9.61 | -0.001 |
| 17 | 2.90 | 3.00 | 10.50 | -0.004 |
| 18 | 3.00 | 3.00 | 10.84 | -0.004 |

FIGURE(A.1) NULL TEST OF CAPACITY VS pH FOR TITRATION SYSTEM
3.0 ml of 0.10M HCl added to 20 ml H₂O and titrated with
0.11 M NaOH. TABLE(A.1)



FILE HCL94

TABLE(A.2)

NAME OF FILE =HAC1

Concentration of NaCl = 0.00M

Concentration of NaOH = 0.11M

Concentration of HCl = 0.00M

Initial Volume = 25.00ml

N = Number of data set.

VB = Volume of base, ml.

VA = Volume of Acid, ml.

VS = Volume of Salt, ml.

pA = pH + pCl

pB = pNa + pOH

X = Capacity, mmoles/gram

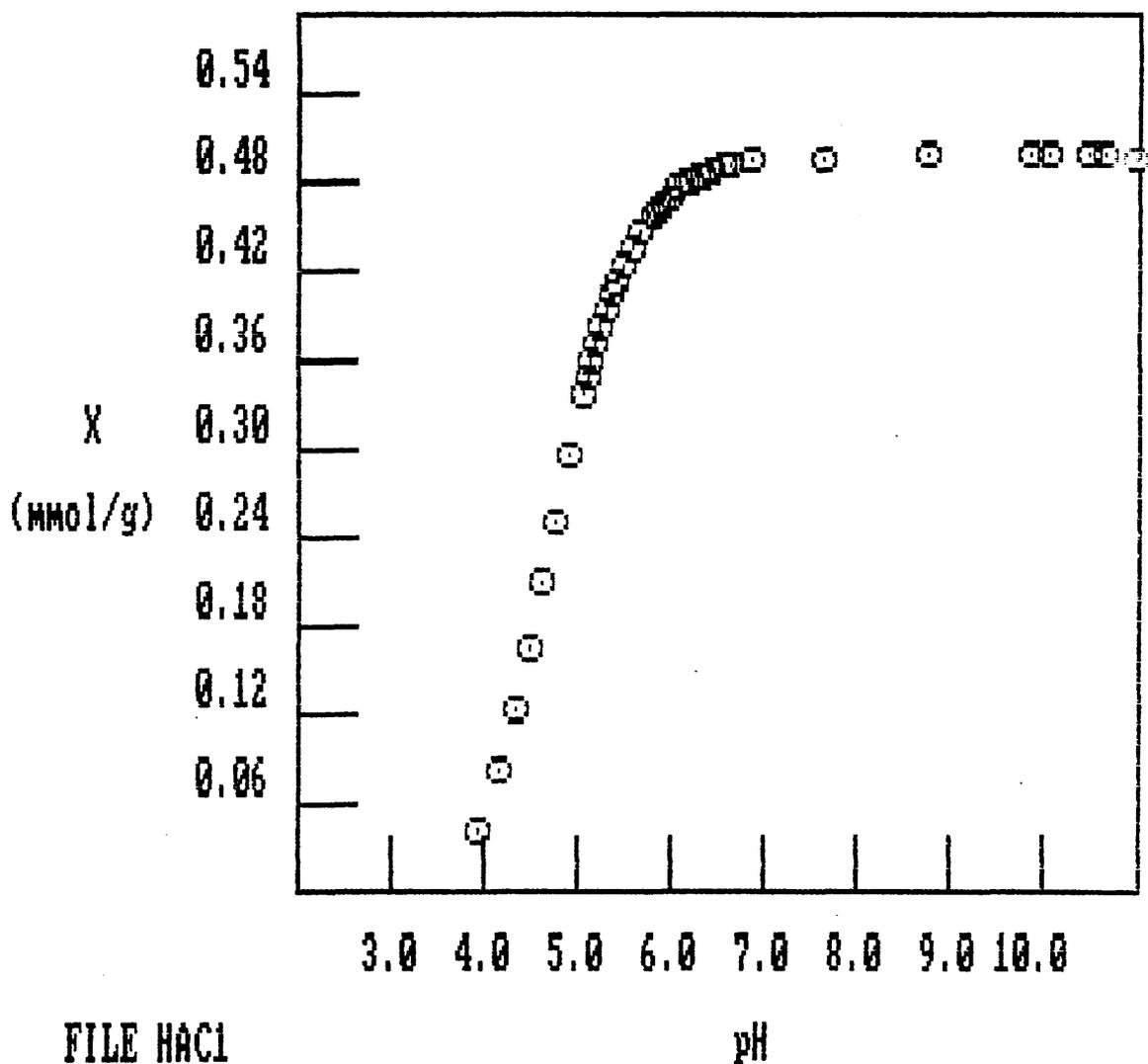
| N | VB | VA | VS | pH | pA | pB | X |
|----|------|------|------|------|-------|--------|-------|
| 1 | 0.00 | 0.00 | 0.00 | 3.56 | 7.120 | 20.877 | -.000 |
| 2 | 0.40 | 0.00 | 0.00 | 3.92 | 6.678 | 12.869 | 0.039 |
| 3 | 0.80 | 0.00 | 0.00 | 4.15 | 6.642 | 12.352 | 0.081 |
| 4 | 1.20 | 0.00 | 0.00 | 4.32 | 6.653 | 12.018 | 0.124 |
| 5 | 1.60 | 0.00 | 0.00 | 4.47 | 6.691 | 11.753 | 0.167 |
| 6 | 2.00 | 0.00 | 0.00 | 4.61 | 6.745 | 11.526 | 0.210 |
| 7 | 2.40 | 0.00 | 0.00 | 4.74 | 6.806 | 11.327 | 0.253 |
| 8 | 2.80 | 0.00 | 0.00 | 4.89 | 6.898 | 11.119 | 0.296 |
| 9 | 3.20 | 0.00 | 0.00 | 5.05 | 7.009 | 10.909 | 0.339 |
| 10 | 3.30 | 0.00 | 0.00 | 5.09 | 7.038 | 10.858 | 0.350 |
| 11 | 3.40 | 0.00 | 0.00 | 5.13 | 7.067 | 10.807 | 0.360 |
| 12 | 3.50 | 0.00 | 0.00 | 5.18 | 7.106 | 10.747 | 0.371 |
| 13 | 3.60 | 0.00 | 0.00 | 5.23 | 7.146 | 10.686 | 0.382 |
| 14 | 3.70 | 0.00 | 0.00 | 5.29 | 7.196 | 10.617 | 0.393 |
| 15 | 3.80 | 0.00 | 0.00 | 5.35 | 7.247 | 10.547 | 0.404 |
| 16 | 3.90 | 0.00 | 0.00 | 5.41 | 7.298 | 10.478 | 0.414 |
| 17 | 4.00 | 0.00 | 0.00 | 5.48 | 7.359 | 10.399 | 0.425 |
| 18 | 4.10 | 0.00 | 0.00 | 5.57 | 7.440 | 10.300 | 0.436 |
| 19 | 4.20 | 0.00 | 0.00 | 5.66 | 7.521 | 10.201 | 0.447 |
| 20 | 4.30 | 0.00 | 0.00 | 5.79 | 7.643 | 10.063 | 0.457 |
| 21 | 4.34 | 0.00 | 0.00 | 5.84 | 7.690 | 10.010 | 0.462 |
| 22 | 4.38 | 0.00 | 0.00 | 5.89 | 7.737 | 9.957 | 0.466 |
| 23 | 4.42 | 0.00 | 0.00 | 5.97 | 7.813 | 9.874 | 0.470 |
| 24 | 4.46 | 0.00 | 0.00 | 6.05 | 7.890 | 9.790 | 0.475 |
| 25 | 4.50 | 0.00 | 0.00 | 6.16 | 7.997 | 9.677 | 0.479 |
| 26 | 4.52 | 0.00 | 0.00 | 6.20 | 8.036 | 9.636 | 0.481 |
| 27 | 4.54 | 0.00 | 0.00 | 6.27 | 8.104 | 9.564 | 0.483 |
| 28 | 4.56 | 0.00 | 0.00 | 6.32 | 8.153 | 9.513 | 0.485 |
| 29 | 4.58 | 0.00 | 0.00 | 6.42 | 8.251 | 9.411 | 0.488 |
| 30 | 4.60 | 0.00 | 0.00 | 6.55 | 8.380 | 9.280 | 0.490 |

FILE NAME - HAC1 CONTINUED FROM PREVIOUS PAGE

| N | VB | VA | VS | pH | pA | pB | X |
|----|------|------|------|-------|--------|--------|-------|
| 31 | 4.62 | 0.00 | 0.00 | 6.63 | 8.458 | 9.198 | 0.492 |
| 32 | 4.64 | 0.00 | 0.00 | 6.85 | 8.677 | 8.977 | 0.494 |
| 33 | 4.66 | 0.00 | 0.00 | 7.63 | 15.260 | 12.737 | 0.496 |
| 34 | 4.68 | 0.00 | 0.00 | 8.74 | 17.480 | 10.517 | 0.498 |
| 35 | 4.70 | 0.00 | 0.00 | 9.86 | 19.720 | 8.277 | 0.498 |
| 36 | 4.72 | 0.00 | 0.00 | 10.04 | 20.080 | 7.917 | 0.499 |
| 37 | 4.76 | 0.00 | 0.00 | 10.47 | 20.940 | 7.057 | 0.498 |
| 38 | 4.80 | 0.00 | 0.00 | 10.65 | 21.300 | 6.697 | 0.498 |
| 39 | 4.90 | 0.00 | 0.00 | 10.97 | 21.940 | 6.057 | 0.493 |

FIGURE(A.2) TEST OF pH ELECTRODE UPTAKE SYSTEM USING ACETIC ACID.

0.5 mmol Acetic Acid titrated with 0.11M NaOH. TABLE(A.2)



TABLE(A.3)

NAME OF FILE =NAB125

Concentration of NaCl = 0.10M

Concentration of NaOH = 0.11M

Concentration of HCl = 0.10M

Initial Volume = 28.00ml

N = Number of data set.

VB = Volume of base, ml.

VA = Volume of Acid, ml.

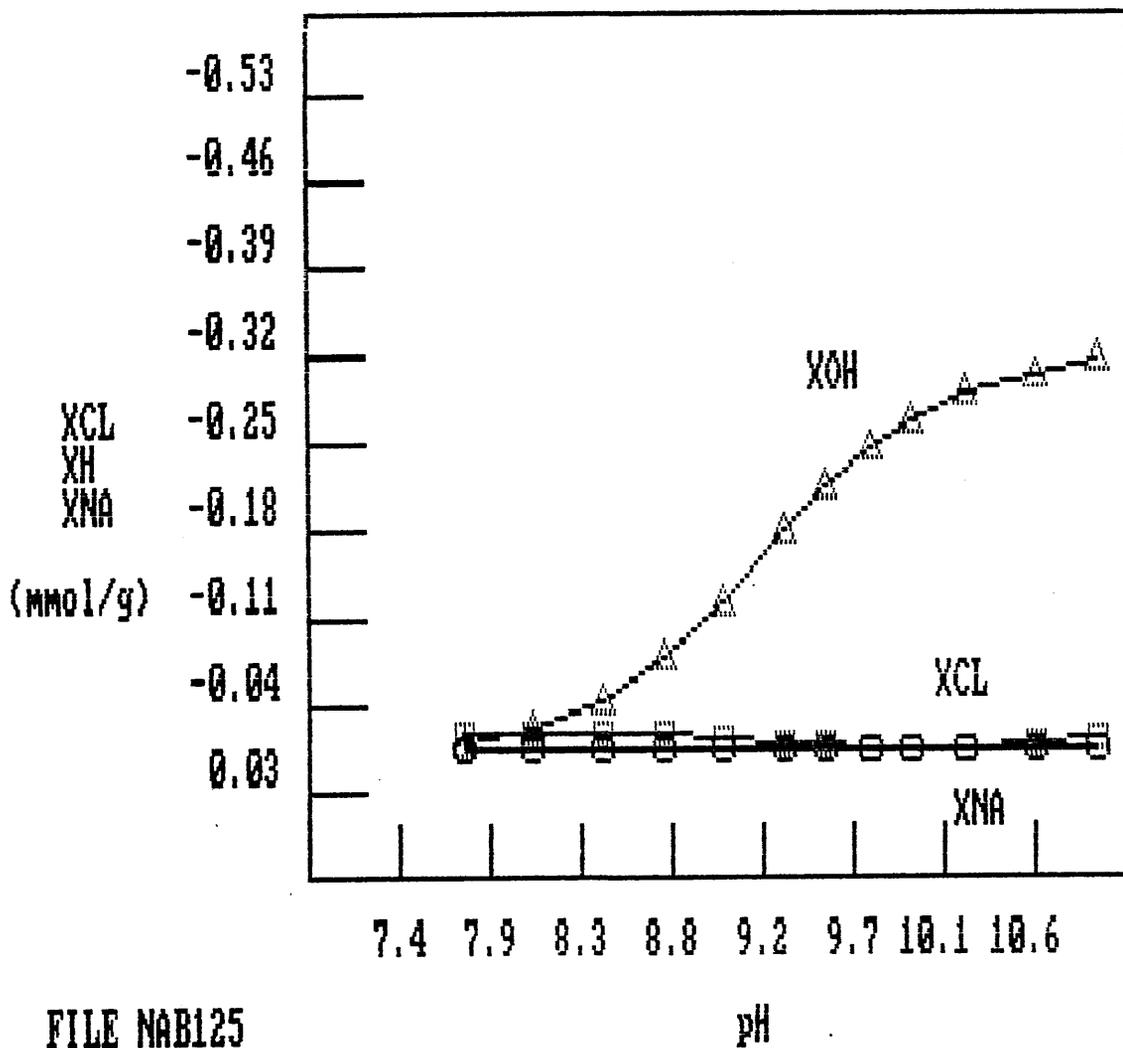
VS = Volume of Salt, ml.

XNa = Na⁺ Capacity in mmol/gXOH = OH⁻ Capacity in mmol/gXCl = Cl⁻ Capacity in mmol/g

| N | VB | VA | VS | pH | XNa | XCl | XOH |
|----|------|------|------|-------|-------|-------|-------|
| 1 | 0.00 | 0.00 | 0.00 | 5.87 | 0.001 | 0.001 | 0.000 |
| 2 | 0.00 | 0.00 | 0.20 | 5.84 | 0.019 | 0.005 | -.000 |
| 3 | 0.10 | 0.00 | 0.20 | 7.75 | 0.018 | 0.004 | -.011 |
| 4 | 0.20 | 0.00 | 0.20 | 8.08 | 0.019 | 0.004 | -.023 |
| 5 | 0.40 | 0.00 | 0.20 | 8.43 | 0.019 | 0.004 | -.045 |
| 6 | 0.70 | 0.00 | 0.20 | 8.74 | 0.018 | 0.004 | -.079 |
| 7 | 1.10 | 0.00 | 0.20 | 9.02 | 0.015 | 0.004 | -.124 |
| 8 | 1.60 | 0.00 | 0.20 | 9.33 | 0.010 | 0.004 | -.180 |
| 9 | 1.90 | 0.00 | 0.20 | 9.52 | 0.008 | 0.004 | -.214 |
| 10 | 2.20 | 0.00 | 0.20 | 9.75 | 0.004 | 0.004 | -.247 |
| 11 | 2.40 | 0.00 | 0.20 | 9.95 | 0.004 | 0.004 | -.268 |
| 12 | 2.60 | 0.00 | 0.20 | 10.22 | 0.005 | 0.004 | -.288 |
| 13 | 2.80 | 0.00 | 0.20 | 10.56 | 0.008 | 0.004 | -.304 |
| 14 | 3.00 | 0.00 | 0.20 | 10.86 | 0.014 | 0.003 | -.314 |

FIGURE(A.3) NULL TEST OF THE SODIUM AND CHLORIDE ELECTRODE SYSTEM USING BORIC ACID.

0.33 mmol Boric Acid titrated with 0.11M NaOH in a 0.02 mmol NaCl background. TABLE(A.3)



FILE NAB125

pH

TABLE(A.4)

NAME OF FILE =HAC912

Concentration of NaCl = 1.00M

Concentration of NaOH = 0.11M

Concentration of NaF = 0.46M

Initial Volume = 23.00ml

N = Number of data set.

VB = Volume of base, ml.

VS1 = Volume of Salt 1, ml.

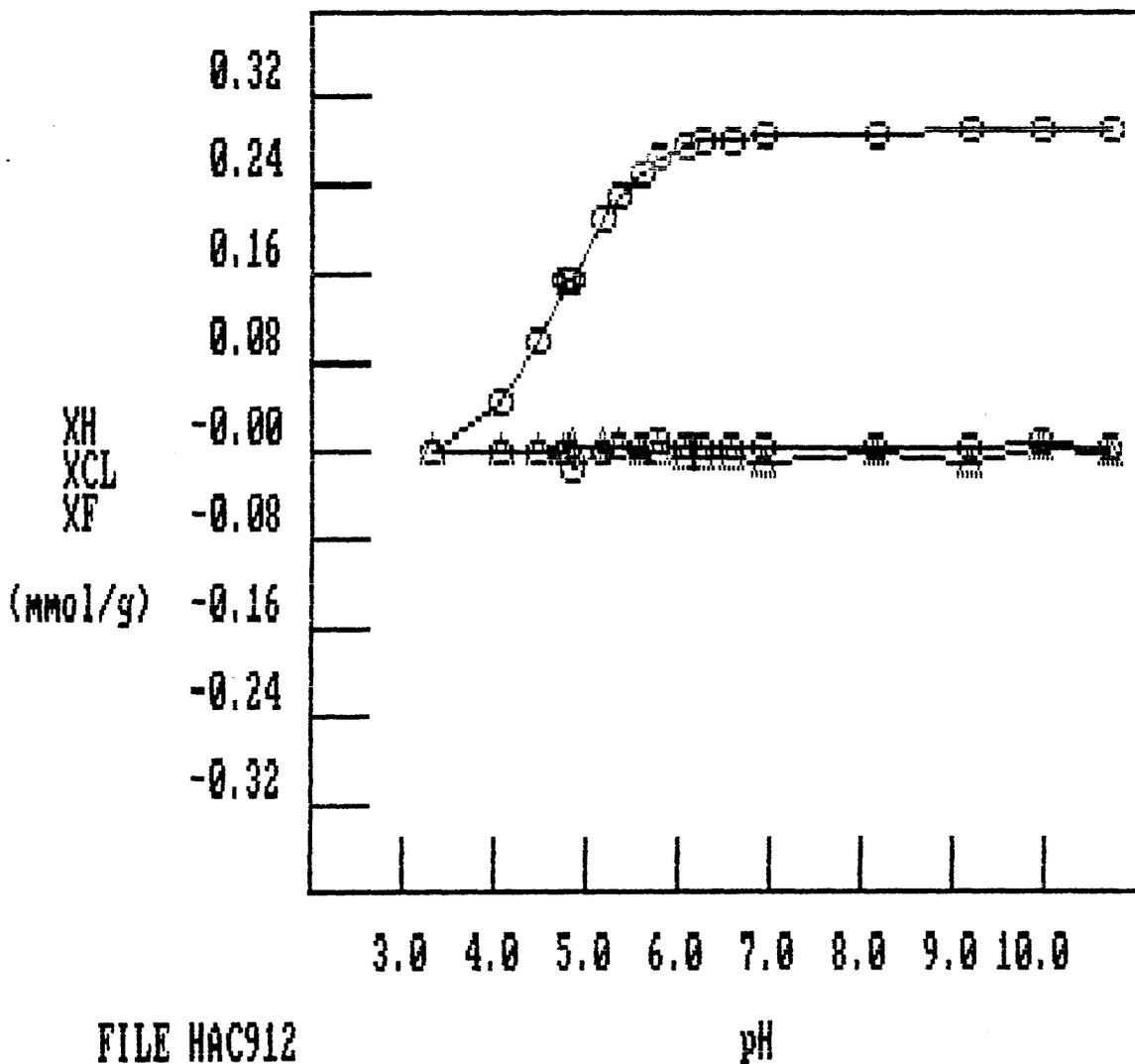
VS2 = Volume of Salt 2, ml.

XF = F⁻ Capacity in mmol/gXH = H⁺ Capacity in mmol/gXCl = Cl⁻ Capacity in mmol/g

| N | VB | VS1 | VS2 | pH | XF | XCl | XH |
|----|------|------|------|-------|--------|--------|--------|
| 1 | 0.00 | 0.00 | 0.00 | 3.31 | 0.000 | 0.000 | -0.000 |
| 2 | 0.50 | 0.00 | 0.00 | 4.04 | 0.000 | 0.000 | 0.045 |
| 3 | 1.00 | 0.00 | 0.00 | 4.44 | 0.000 | 0.000 | 0.099 |
| 4 | 1.50 | 0.00 | 0.00 | 4.77 | 0.000 | 0.000 | 0.153 |
| 5 | 1.50 | 0.50 | 0.00 | 4.72 | 0.000 | -0.000 | 0.153 |
| 6 | 1.50 | 0.50 | 1.00 | 4.83 | -0.016 | 0.004 | 0.153 |
| 7 | 2.00 | 0.50 | 1.00 | 5.15 | -0.001 | 0.003 | 0.208 |
| 8 | 2.20 | 0.50 | 1.00 | 5.33 | 0.005 | 0.003 | 0.230 |
| 9 | 2.40 | 0.50 | 1.00 | 5.57 | 0.004 | -0.000 | 0.252 |
| 10 | 2.50 | 0.50 | 1.00 | 5.76 | 0.008 | 0.002 | 0.263 |
| 11 | 2.60 | 0.50 | 1.00 | 6.04 | 0.006 | -0.007 | 0.274 |
| 12 | 2.64 | 0.50 | 1.00 | 6.22 | 0.006 | -0.006 | 0.278 |
| 13 | 2.68 | 0.50 | 1.00 | 6.55 | 0.007 | -0.005 | 0.282 |
| 14 | 2.70 | 0.50 | 1.00 | 6.90 | 0.005 | -0.009 | 0.285 |
| 15 | 2.72 | 0.50 | 1.00 | 8.12 | 0.006 | -0.001 | 0.287 |
| 16 | 2.74 | 0.50 | 1.00 | 9.15 | 0.006 | -0.009 | 0.288 |
| 17 | 2.78 | 0.50 | 1.00 | 9.93 | 0.009 | 0.005 | 0.291 |
| 18 | 2.90 | 0.50 | 1.00 | 10.66 | 0.005 | -0.001 | 0.291 |

FIGURE(A.4) NULL TEST OF THE FLUORIDE AND CHLORIDE ELECTRODE SYTEM USING ACETIC ACID.

0.30 mmol Acetic Acid titrated with 0.11 M NaOH in a 0.5 mmol NaCl, 0.46 mmol NaF background. TABLE(A.4)



FILE HAC912

pH

Appendix P
Computer Programs

- P.1 Create Data File For Calibration Program**
- P.2 Calibration Equation Program**
- P.3 Create Data File For Uptake2 Program**
- P.4 Calculation of Uptake Program 2**
- P.5 Graphic Display of Results on CRT Monitor**
- P.6 Calculation of Uptake Program 1**

PROGRAM(P.1) CREATES DATA FILE FOR CALIBRATION PROGRAM

```
10 ' CALABRATION DATA FILE
20 ' FILE NAME CALDATA
30 '
40 DIM MV(50),ML(50),PH(50)
50 CLS
60 LOCATE 10,20: INPUT "pH Y/N";Q$
70 IF (Q$ = "Y") OR (Q$ = "y") THEN GOTO 280
80 IF (Q$ = "N") OR (Q$ = "n") THEN GOTO 100
90 GOTO 60
100 CLS :LOCATE 10,20 : INPUT " NUMBER OF CALIBRATION POIN
TS";N
110 PRINT : INPUT " INITIAL VOLUME ";VO
120 PRINT : INPUT " STANDARD CONCENTRATION";SC
130 PRINT : INPUT "INITIAL IONIC STRENGTH";IIO
140 FOR I = 1 TO N
150 PRINT : PRINT "ML","MV"
160 INPUT ML(I),MV(I)
170 NEXT
180 PRINT : INPUT " ENTER FILE NAME ";NM$
190 '
200 '
210 OPEN"O",1,"\\PROGRAMS\DATA\" + NM$
220 WRITE#1,N,VO,SC,IIO
230 FOR I = 1 TO N
240 WRITE#1, ML(I),MV(I)
250 NEXT
260 CLOSE#1
270 END
280 '
290 ' THIS SECTION HANDLES pH CALIBRATION DATA
300 ' FOR USE IN THE CALIBRATION EQUATION PROGRAM
310 '
320 CLS
330 PRINT : INPUT "NUMBER OF CALABRATION POINTS";N
340 FOR I = 1 TO N
```

```
350 PRINT : PRINT "PH      ,MV" : PRINT
360 INPUT PH(I),MV(I)
370 NEXT
380 INPUT " ENTER FILE NAME ";NM$
390 OPEN"O",1,"\\PROGRAMS\DATA\" + NM$
400 WRITE#1,N
410 FOR I = 1 TO N
420 WRITE#1, PH(I),MV(I)
430 NEXT
440 CLOSE#1
```

PROGRAM(P.2) CALIBRATION EQUATION PROGRAM

```
10 ' CALIBRATION EQUATION PROGRAM
20 ' FILENAME IS CALEQ
30 ' TO GENERATE A BEST FIT STRAIGHT LINE AND
40 ' CURVE FIT EQUATION FOR CALIBRATION
50 '
60 DIM PH(50),MV(50),C(50),F(50),A(50),Y(50),YY(50),LC(50)
70 DIM M(500),PHC(50),PHS(50),X(500),ML(50),ECF(50),ESL(50
)
80 DIM PES(50),PEC(50)
90 '
100 CLS : LOCATE 10,20 : INPUT " ENTER FILE NAME = "; NM
$
110 '
120 CLS : LOCATE 10,20 : INPUT " PH Y/N "; PH$
130 IF (PH$ = "Y") OR (PH$ = "y") THEN GOTO 190
140 IF (PH$ = "N") OR (PH$ = "n") THEN GOTO 310
150 GOTO 120
160 '
170 ' INPUT DATA FROM FILE
180 '
190 LA$ = "H"
200 OPEN "I",#1,"\\PROGRAMS\\DATA\\" + NM$
210 INPUT#1, N
220 FOR I = 1 TO N : INPUT#1,PH(I) : INPUT#1,MV(I) : NEXT
230 CLOSE
240 GOTO 690
250 '
260 '
270 ' THIS SECTION CHANGES CALIBRATION DATA TO p VALUES
280 '
290 '
300 CLS
310 CLS : LOCATE 10,20 : INPUT "LABEL OF ISE";LA$
320 OPEN "I",#1,"\\PROGRAMS\\DATA\\" + NM$
330 INPUT#1,N,VO,SC,IIO
340 FOR I = 1 TO N : INPUT#1,ML(I),MV(I) : NEXT
```

```

350 CLOSE #1
360 '
370 '
380 ' CALCULATE CONCENTRATIONS
390 '
400 FOR I = 1 TO N : C(I) = (ML (I) / ( VO + ML(I) ) ) * SC
   : NEXT
410 FOR I = 1 TO N : LC(I) = -LOG( C(I))/2.30285 : NEXT
420 '
430 '
440 '
450 ' CALCULATE ACTIVITY COEFFICIENTS
460 '
470 FOR I = 1 TO N
480 C(I) = C(I) + IIO
490 B = SQR(C(I))
500 F(I) = EXP( -1.1513 * ( B / ( 1 + B ) - .3 * C(I) )
   )
510 C(I) = C(I) - IIO
520 NEXT
530 '
540 ' CALCULATE ACTIVITIES
550 '
560 FOR I = 1 TO N : A(I) = F(I) * C(I) : NEXT
570 '
580 '
590 ' CHANGE ACTIVITY TO NEG LOG AVTIVITY
600 '
610 FOR I = 1 TO N : PH(I) = - LOG(A(I)) / 2.302585
620 NEXT
630 '
640 '
650 '
660 '
670 ' SUMS FOR SOLUTION OF DETERMINENTS
680 '
690 FOR I = 1 TO N : XA = XA + PH(I) : NEXT
700 FOR I = 1 TO N : YMV = YMV + MV(I) : NEXT
710 FOR I = 1 TO N : X2A = X2A + ( PH(I)^2 ) : NEXT
720 FOR I = 1 TO N : X3A = X3A + ( PH(I)^3 ) : NEXT

```

```

730 FOR I = 1 TO N : X4A = X4A + ( PH(I)^4 ) : NEXT
740 FOR I = 1 TO N : X2Y = X2Y + ( (PH(I)^2) * MV(I) ) :
NEXT
750 FOR I = 1 TO N : XY = XY + ( PH(I) * MV(I) ) : NEXT
760 '
770 '
780 ' SOLUTION OF DETERMINENTS FOR CURVE FIT
790 '
800 D1 = (-N)*( (-X2A)*(-X4A) - (-X3A)*(-X3A) )
810 D2 = (-XA)*( (-XA )*(-X4A) - (-X3A)*(-X2A) )
820 D3 = (-X2A)*( (-XA )*(-X3A) - (-X2A)*(-X2A) )
830 DD = (-1) * ( ( D1 )-( D2 )+( D3 )) :
840 '
850 '
860 A1 = (-XA)*( (-X3A)*(X2Y) - (XY)*(-X4A) )
870 A2 = (-X2A)*( (-X2A)*(X2Y) - (XY)*(-X3A) )
880 A3 = (YMV)*( (-X2A)*(-X4A)- (-X3A)*(-X3A) )
890 AA = ( ( A1 ) - ( A2 ) + ( A3 ) ) / ( DD )
900 '
910 '
920 B1 = (-N)*( (-X3A)*(X2Y) - ( XY )*(-X4A) )
930 B2 = (-X2A)*( (-XA )*(X2Y) - ( XY )*(-X2A) )
940 B3 = (YMV )*( (-XA )*(-X4A) - (-X3A)*(-X2A) )
950 BB = ( (-1) * ( ( B1 ) - ( B2 ) + ( B3 ) ) ) / ( DD )
960 '
970 '
980 C1 = (-N)*( (-X2A)*(X2Y) - ( XY )*(-X3A) )
990 C2 = (-XA)*( (-XA )*(X2Y) - ( XY )*(-X2A) )
1000 C3 = (YMV)*( (-XA )*(-X3A)- (-X2A)*(-X2A) )
1010 CC = ( ( C1 ) - ( C2 ) + ( C3 ) ) / ( DD )
1020 '
1030 '
1040 ' CALCULATIONS FOR BEST FIT STRAIGHT LINE
1050 '
1060 S1 = ( XY - ( ( 1 / N ) * ( XA * YMV ) ) )
1070 S2 = ( X2A - ( ( 1 / N ) * ( XA^2 ) ) )
1080 SS = S1 / S2
1090 YB = YMV / N
1100 XB = XA / N
1110 YYB = YB - SS*XB

```

```

1120 '
1130 '
1140 '
1150 ' CALCULATE pVALUE GIVEN MILLIVOLT READING AND
1160 ' EQUATION FOR STRAIGHT LINE
1170 '
1180 FOR I = 1 TO N
1190 PHS(I) = (MV(I) -YYB) /SS
1200 NEXT
1210 '
1220 '
1230 CLS : LOCATE 8,20 : PRINT "*****"
*"
1240 LOCATE 12,20 : PRINT "*****"
1250 '
1260 '
1270 ' SUBROUTINE FOR CALCULATING pVALUE GIVEN MILLIVOLT
1280 ' READING AND SECOND ORDER EQUATION FOR CURVE FIT
1290 ' USING SUCESSIVE APPROXIMATIONS
1300 '
1310 FOR I = 1 TO N
1320 LOCATE 10,20 : PRINT " CALCULATIONS IN PROGRESS"
1330 X(1) = PHS(I)
1340 T = 1 : TB = 0
1350 T = T + 1
1360 TB = TB + 1
1370 M(T) = AA + BB * X(TB) + CC * X(TB) ^ 2
1380 IF ABS(M(T) - MV(I)) < .001 THEN GOTO 1560
1390 '
1400 '
1410 IF M(T) > MV(I) THEN XH = X(TB) 'DEFINE HIGH VALUE F
OR X
1420 IF M(T) < MV(I) THEN XL = X(TB) 'DEFINE LOW VALUE FO
R X
1430 '
1440 '
1450 IF TB < 2.1 GOTO 1500
1460 IF X(TB) = XH THEN X(TB+1)=(XH + XL) /2 : GOTO 1350
1470 IF X(TB) = XL THEN X(TB+1)= (XH + XL) /2 : GOTO 1350
1480 '

```

```

1490 '
1500 IF X(TB) = XH THEN IF BB > 0 THEN X(TB+1) = .5*X(TB)
      : GOTO 1350
1510 IF X(TB) = XH THEN IF BB < 0 THEN X(TB+1) = 2*X(TB)
      : GOTO 1350
1520 IF X(TB) = XL THEN IF BB > 0 THEN X(TB+1) = 2*X(TB)
      : GOTO 1350
1530 IF X(TB) = XL THEN IF BB < 0 THEN X(TB+1) = .5*X(TB)
      : GOTO 1350
1540 '
1550 '
1560 PHC(I) = X(TB)
1570 NEXT
1580 FOR I = 1 TO N
1590 PES(I) = ( 1 - EXP((PHS(I)-PH(I))*2.30285))
1600 PEC(I) = ( 1 - EXP((PHC(I)-PH(I))*2.30285))
1610 NEXT
1620 '
1630 CLS
1640 PRINT "FILE NAME = ";NM$: PRINT : PRINT
1650 PRINT " Y = "YYB" + "SS"X"
1660 PRINT " Y = "AA " + " BB"* X + "CC" * X^2"
1670 PRINT : INPUT "HIT RETURN TO CONTINUE";CT$
1680 '
1690 '
1700 '
1710 CLS : LOCATE 10,30 : INPUT "WRITE TO FILE Y/N";WF$
1720 IF (WF$ = "Y") OR (WF$ = "y") THEN GOTO 1750
1730 IF (WF$ = "N") OR (WF$ = "n") THEN GOTO 1900
1740 GOTO 1710
1750 IF LA$ = "H" THEN GOTO 1820
1760 OPEN"O",#1,"\\PROGRAMS\DATA\RESULTS\" + NM$ + "_C"
1770 WRITE#1,N
1780 FOR I = 1 TO N : WRITE #1,LC(I),MV(I) : NEXT
1790 CLOSE #1
1800 '
1810 '
1820 OPEN"O",#2,"\\PROGRAMS\DATA\RESULTS\" + NM$ + "_A"
1830 WRITE #2,N
1840 FOR I = 1 TO N : WRITE #2,PH(I),MV(I) : NEXT

```

```

1850 CLOSE #2
1860 '
1870 '
1880 '
1890 '
1900 ' PRINT RESULTS ON PRINTER
1910 '
1920 CLS : LOCATE 10,30 : INPUT" PRINT RESULTS Y/N";PR$
1930 IF (PR$ = "Y") OR (PR$ = "y") THEN GOTO 1960
1940 IF (PR$ = "N") OR (PR$ = "n") THEN GOTO 2620
1950 GOTO 1700
1960 CLS
1970 LPRINT CHR$(27);"1";CHR$(12)
1980 LPRINT CHR$(27);"C";CHR$(70)
1990 LPRINT CHR$(27);"A";CHR$(18)
2000 LPRINT CHR$(27);CHR$(40)
2010 INPUT "TITLE OF TABLE";TITLE$
2020 LPRINT TITLE$ : LPRINT
2030 LPRINT "FILE NAME = ";NM$;
2040 IF (PH$ = "Y") OR (PH$ = "y") THEN GOTO 2100
2050 IF (PH$ = "N") OR (PH$ = "n") THEN GOTO 2060
2060 INPUT "CONCENTRATION OF STANDARD";CON$
2070 INPUT " INITIAL VOLUME";INV$
2080 LPRINT TAB(35)"CONC OF STANDARD = ";CON$
2090 LPRINT TAB(35)"INITIAL VOLUME = ";INV$ : LPRINT
2095 GOTO 2110
2100 LPRINT : LPRINT
2110 LPRINT "FIRST ORDER EQUATION      E = ";
2120 LPRINT USING "####.###";YB;
2130 LPRINT " + ";
2140 LPRINT USING "###.###";SS;
2150 LPRINT " p"LA$
2160 LPRINT "SECOND ORDER EQUATION      E = ";
2170 LPRINT USING "####.###";AA;
2180 LPRINT " + ";
2190 LPRINT USING "###.###";BB;
2200 LPRINT " p"LA$" + ";
2210 LPRINT USING "###.###";CC;
2220 LPRINT "p("LA$)";
2230 LPRINT CHR$(27);"S";CHR$(0);

```

```

2240 LPRINT "2";
2250 LPRINT CHR$(27);"T";
2260 LPRINT : LPRINT : LPRINT TAB(30)"CURVE FITS"
2270 LPRINT TAB(2)"N";TAB(8)"E";TAB(16)"* p"LA$;TAB(26)"*
* p"LA$;
2280 LPRINT TAB(38)"** p"LA$;TAB(47)"% error";TAB(57)"% er
ror";
2290 LPRINT CHR$(27);"-1";
2300 LPRINT TAB(1);TAB(7)"mV";TAB(14)"(actual)"TAB(24)"2ND
ORDER";
2310 LPRINT TAB(35)"1ST ORDER"TAB(46)"2ND ORDER"TAB(57)"1S
T ORDER"
2320 LPRINT TAB(1);TAB(66)
2330 LPRINT CHR$(27);"-0";
2340 LPRINT
2350 FOR I = 1 TO N
2360 LPRINT I TAB(5);
2370 LPRINT USING"####.#";MV(I);
2380 LPRINT TAB(15);
2390 LPRINT USING"##.###";PH(I);
2400 LPRINT TAB(24);
2410 LPRINT USING"##.###";PHC(I);
2420 LPRINT TAB(36);
2430 LPRINT USING"##.###";PHS(I);
2440 LPRINT TAB(47);
2450 LPRINT USING"####.#";(PEC(I) * 100);
2460 LPRINT TAB(57);
2470 LPRINT USING"####.#";(PES(I) * 100)
2480 NEXT
2490 CLS : INPUT "GIVE NAME OF ION BEING MEASURED";IA$
2500 LPRINT : LPRINT "% error = % difference between the a
ctual "IA$" ion"
2510 LPRINT TAB(11)"activity and the calculated activity"
2520 LPRINT "p"LA$" = Negative log of the "IA$" ion activi
ty
2530 LPRINT
2540 IF (PH$ = "Y") OR (PH$ = "y") THEN GOTO 2560
2550 IF (PH$ = "N") OR (PH$ = "n") THEN GOTO 2580
2560 LPRINT "** Prepared pH buffer standards per Perrin(33)"
2570 GOTO 2590

```

```
2580 LPRINT "** Calculated from known concentration and ion  
ic strength"  
2590 LPRINT "*** Calculated from curve fit equation"  
2600 CLS  
2610 LPRINT CHR$(12)  
2620 END
```

PROGRAM(P.3) CREATE DATA FILE FOR UPTAKE2 PROGRAM

```
10 REM CREATE DATA FILE WITH ISE RAW mV UPDATED 8/8/86
20 CLS
30 H = 80
40 DIM VB(H),VS1(H),VS2(H),VA(H),E1(H),E2(H),E3(H)
50 DIM A(H),B(H),AA(H),BB(H),CC(H)
60 PRINT: INPUT"ENTER NUMBER OF ISE'S RECORDED (1,2 OR 3)
";NI
70 PRINT"FIRST ELECTRODE MUST BE pH"
80 PRINT"SECOND ELECTRODE MUST BE CL"
90 PRINT"THREE ELECTRODES MAX."
100 PRINT: PRINT"ENTER CALIBRATION INFORMATION "
110 PRINT"IN THE FORM Y = A + BX"
120 PRINT"IN THE FORM Y = AA + BB(X) + CC(X^2)"
130 FOR I = 1 TO NI
140 PRINT
150 IF I = 1 THEN PRINT "PH DATA"
160 IF I = 2 THEN PRINT "CL DATA"
170 IF I = 3 THEN PRINT "ISE 3 DATA"
180 INPUT "A = ";A(I)
190 INPUT "B = ";B(I)
200 INPUT "AA = ";AA(I)
210 INPUT "BB = ";BB(I)
220 INPUT "CC = ";CC(I)
230 NEXT
240 PRINT
250 INPUT"NO. of DATA SETS ";N
260 INPUT"pH at the ISOELECTRIC POINT ";EO
270 INPUT "INITIAL VOLUME ";VO
280 INPUT "MOLARITY of BASE ";MB
290 INPUT "MOLARITY of SALT 1 ";MS1
300 INPUT "MOLARITY OF SALT 2 ";MS2
310 INPUT "MOLARITY of ACID ";MA
320 INPUT "GRAMS OF EXCHANGER ";GA
330 INPUT "GRAMS OF DRIED EXCHANGER ";GM
340 PRINT"ENTER RAW DATA. E1,E2, AND E3 CORRESPOND TO mV F
```

ROM PH, CL, AND ISE 3"

350 PRINT"VA IS VOLUME OF HYDROCHLORIC ACID ADDED"

360 PRINT"VS1 IS VOLUME OF CHLORIDE SALT ADDED"

370 FOR I= 1 TO N

380 PRINT: PRINT I

390 PRINT " VB, VS1, VS2, VA, E1, E2, E3"

400 INPUT " "; VB(I),VS1(I),VS2(I),VA(I),E1(I),E2(I),E3(I)
)

410 NEXT

420 PRINT: INPUT "FILENAME";NM\$

430 INFILE\$ = "\PROGRAMS\DATA\" + NM\$

440 OPEN INFILE\$ FOR OUTPUT AS #1

450 WRITE #1,N: WRITE #1,EO: WRITE #1,VO

460 WRITE #1,MB: WRITE #1,MS1: WRITE #1,MS2: WRITE #1,MA

470 WRITE #1,GA: WRITE #1,GM

480 WRITE #1,NI

490 WRITE #1,A(1): WRITE #1,B(1): WRITE #1,A(2)

500 WRITE #1,B(2): WRITE #1,A(3): WRITE #1,B(3)

510 WRITE #1,AA(1): WRITE #1,BB(1): WRITE #1,CC(1)

520 WRITE #1,AA(2): WRITE #1,BB(2): WRITE #1,CC(2)

530 WRITE #1,AA(3): WRITE #1,BB(3): WRITE #1,CC(3)

540 FOR I = 1 TO N

550 WRITE #1,VB(I),VS1(I),VS2(I),VA(I),E1(I),E2(I),E3(I)

560 NEXT

570 CLOSE #1

580 CLS

590 INPUT"DO YOU WANT A HARD COPY OF THIS DATA (Y/N) ";P\$

600 IF P\$ = "Y" GOTO 620

610 IF P\$ = "N" GOTO 630

620 RUN "PRINTCREATE"

630 END

PROGRAM(P.4) CALCULATION OF UPTAKE PROGRAM 2

Includes processing of data from multiple ion
selective electrodes.

```
10 ' UPTAKE CALCULATIONS PROGRAM
20 ' FILENAME UPTAKE 2
30 '
40 ' A PROGRAM TO CONVERT MV READINGS FROM TITRATIONS
50 ' TO ACTIVITIES AND CONCENTRATIONS AND CALCULATE
60 ' UPTAKE OF IONS BY CRYSTALS IN THE SOLUTION
70 '
80 CLS
90 H =80
100 DIM VB(H),VA(H),E1(H),E2(H),E3(H),G(H),PHCL(H),PHF(H),
H(H)
110 DIM PH(H),PCL(H),PF(H),XX(H),VS1(H),VS2(H),V(H),DF(H),
DCL(H)
120 DIM XCL(H),XF(H),XH(H),CB(H),OH(H),II(H),CL(H),F(H),FM
(H)
130 DIM A(5),B(5),AA(5),BB(5),CC(5),MV(H),M(500),X(500),CL
M(H)
140 '
150 ' EXPLANATION OF VARIABLES
160 '
170 ' A = E0 OF ELECTRODE
180 ' AA = FIRST TERM OF CURVE FIT
190 ' B = SLOPE OF ELECTRODE
200 ' BB = SECOND TERM OF CURVE FIT
210 ' CB = CHARGE BALANCE
220 ' CC = THIRD TERM OF BEST FIT
230 ' CL = CHLORIDE ION CONCENTRATION
240 ' CLM = MOLES OF CHLORIDE
250 ' DCL = CHORIDE DISTRIBUTION COEFFICIENT
260 ' DF = FLUORIDE DISTRIBUTION COEFFICIENT
270 ' E1 = MV READING PH ELECTRODE
280 ' E2 = MV READING CL ELECTRODE
290 ' E3 = MV READING ELECTRODE 3
300 ' F = FLUORIDE ION CONCENTRATION
```

```

310 ' FM - MOLES OF FLUORIDE IN SOLUTION
320 ' G = ACTIVITY COEFFICIENT
330 ' H = HYDROGEN ION CONCENTRATION
340 ' II = IONIC STRENGTH
350 ' M = MV ASSUMED FOR CALCULATION
360 ' MV = MILLIVOLT READING
370 ' OH = OH ION CONCENTRATION
380 ' PCL = NEG LOG CHLORIDE ACTIVITY
390 ' PH = NEG LOG OF HYDROGRN ION ACT
400 ' PHCL = PH + PCL
410 ' PHF = PH + PF
420 ' PF = NEG LOG OF FLUORIDE ACTIVITY
430 ' V = TOTAL VOLUME
440 ' VA = VOLUME OF ACID
450 ' VB = VOLUME OF BASE
460 ' VS1 = VOLUME OF SALT
470 ' VS2 = VOLUME OF SALT 2
480 ' XCL = CHORIDE UPTAKE
490 ' XH = HYDROGEN UPTAKE
500 ' XF = FLUORIDE UPTAKE
510 ' X = COUNTER
520 ' XX = SUM OF CL + F UPTAKE
530 '
540 '
550 PRINT: PRINT: PRINT
560 PRINT: PRINT"THE FIRST ISE RECORDED MUST BE A pH ELECT
RODE"
570 PRINT"THE SECOND ISE RECORDED MUST BE A Cl ELECTRODE"
580 PRINT"ALSO, THE ADDED ACID, VA, WILL BE HYDROCHLORIC A
CID"
590 PRINT: INPUT"ENTER FILE NAME ";NM$
600 PRINT : INPUT "ENTER INITIAL IONIC STRENGTH " ;II0
610 '
620 ' INPUT DATA FROM FILE
630 '
640 '
650 INFILE$ = "\PROGRAMS\DATA\" + NM$
660 OPEN INFILE$ FOR INPUT AS #1
670 INPUT#1,N: INPUT#1,EO: INPUT#1,VO
680 INPUT#1,MB: INPUT#1,MS1: INPUT#1,MS2 : INPUT#1,MA

```

```

690 INPUT#1,GA: INPUT#1,GM
700 INPUT#1,NI
710 INPUT#1,A(1): INPUT#1,B(1): INPUT#1,A(2)
720 INPUT#1,B(2): INPUT#1,A(3): INPUT#1,B(3)
730 INPUT#1,AA(1): INPUT#1,BB(1): INPUT#1,CC(1)
740 INPUT#1,AA(2): INPUT#1,BB(2): INPUT#1,CC(2)
750 INPUT#1,AA(3): INPUT#1,BB(3): INPUT#1,CC(3)
760 FOR I = 1 TO N
770 INPUT#1,VB(I): INPUT#1,VS1(I): INPUT#1,VS2(I): INPUT#1
,VA(I):
780 INPUT#1,E1(I): INPUT#1,E2(I): INPUT#1,E3(I)
790 NEXT
800 CLOSE #1
810 PRINT
820 GOTO 880 ' SKIP SUBROUTINE FOR ACT COEFF CALC
830 '
840 ' DAVIS EQUATION FOR CALCULATION OF ACTIVITY COEFFICIE
NT
850 ' FROM IONIC STRENGTH
860 '
870 F = EXP (-1.1513 * (SQR(F)/(1 + SQR(F)) - .3 * F )) :
RETURN
880 '
890 PRINT:CLS
900 PRINT"DO YOU PREFER STRAIGHT LINE OR CURVE FIT ";
910 PRINT "DATA FOR YOUR CALIBRATION"
920 LOCATE 10,10 : INPUT"ENTER SL OR CF ";D$
930 '
940 '
950 ' CALCULATE P VALUES USING ST LINE CALIBRATION DATA
960 '
970 '
980 FOR I = 1 TO N
990 ON NI GOTO 1020,1010,1000
1000 PF(I) = ( E3(I) - A(3) ) / B(3)
1010 PCL(I) = ( E2(I) - A(2) ) / B(2)
1020 PH(I) = ( E1(I) - A(1) ) / B(1)
1030 NEXT
1040 '
1050 '

```

```

1000 IF (D# - "EL") OR (D# - "e1") GOTO 1730
1070 IF (D$ = "CF") OR (D$ = "cf") GOTO 1140
1080 GOTO 1060
1090 '
1100 '
1110 ' MATCH EACH ELECTRODE WITH THE CONSTANTS FOR ITS
1120 ' CURVE FIT EQUATION
1130 '
1140 FOR K = 1 TO NI
1150 ON K GOTO 1160,1200,1240
1160 AA = AA(1): BB = BB(1): CC = CC(1):
1170 FOR I = 1 TO N : MV(I) = E1(I) : NEXT : GOSUB 1350
1180 GOTO 1260
1190 IF K = 2 GOTO 1200
1200 X = AC(I): AA = AA(2): BB = BB(2): CC = CC(2):
1210 FOR I = 1 TO N : MV(I) = E2(I) : NEXT : GOSUB 1350
1220 GOTO 1260
1230 IF K = 3 GOTO 1240
1240 X = AI(I): AA = AA(3): BB = BB(3): CC = CC(3):
1250 FOR I = 1 TO N : MV(I) = E3(I) : NEXT : GOSUB 1350
1260 NEXT
1270 GOTO 1790
1280 '
1290 ' SUBROUTINE FOR CALCULATING PH,PF,PCL USING CURVE F
IT
1300 ' FROM CALIBRATION DATA. A p VALUE IS ASSUMED AND A M
V VALUE
1310 ' IS CALCULATED. THIS IS REPEATED UNTIL THE CALCULAT
ED MV
1320 ' IS LESS THAN .01 MV DIFFERENT FROM THE MEASURED VA
LUE
1330 '
1340 '
1350 CLS : LOCATE 10,25 : PRINT "*****"
**"
1360 FOR I = 1 TO N
1370 LOCATE 9,25 : PRINT " CALCULATIONS IN PROGRESS"
1380 ON K GOTO 1390,1400,1410
1390 X(1) = PH(I) : GOTO 1420
1400 X(1) = PCL(I) : GOTO 1420

```

```

1410 X(1) = PF(I) : GOTO 1420
1420 T=1 : TB = 0
1430 T = T + 1
1440 TB = TB + 1
1450 M(T) = AA + BB * X(TB)+ CC * X(TB) ^ 2
1460 IF ABS(M(T) - MV(I) ) < .001 THEN GOTO 1650
1470 LOCATE 15,20 : PRINT "M(T)="M(T),"MV(I)="MV(I),I
1480 '
1490 '
1500 IF M(T) = > MV(I) THEN XH = X(TB)
1510 IF M(T) = < MV(I) THEN XL = X(TB)
1520 '
1530 '
1540 IF TB < 2.1 GOTO 1590
1550 IF X(TB) = XH THEN X(TB + 1) = (XH + XL ) / 2 : GOTO
1430
1560 IF X(TB) = XL THEN X(TB + 1) = (XH + XL ) / 2 : GOTO
1430
1570 '
1580 '
1590 IF X(TB) = XH THEN IF BB> 0 THEN X(TB + 1) = .5*X(TB)
: GOTO 1430
1600 IF X(TB) = XH THEN IF BB< 0 THEN X(TB + 1) = 2*X(TB)
: GOTO 1430
1610 IF X(TB) = XL THEN IF BB> 0 THEN X(TB + 1) = 2*X(TB)
: GOTO 1430
1620 IF X(TB) = XL THEN IF BB< 0 THEN X(TB + 1) = .5*X(TB)
: GOTO 1430
1630 '
1640 '
1650 ON K GOTO 1680,1670,1660
1660 PF(I) = X(TB) : GOTO 1690
1670 PCL(I) = X(TB) : GOTO 1690
1680 PH(I) = X(TB) : GOTO 1690
1690 NEXT
1700 RETURN
1710 '
1720 '
1730 CLS : LOCATE 10,10
1740 INPUT "DO YOU WANT SCREEN PRINT OF RESULTS Y/N ";SK$

```

```

1750 IF (SK# - "N") OR (SK# - "n") GOTO 1780
1760 IF (SK$ = "Y") OR (SK$ = "y") GOTO 1800
1770 GOTO 1740
1780 CLS
1790 LOCATE 15,30 : PRINT "CALCULATIONS IN PROGRESS"
1800 FOR I = 1 TO N
1810 '
1820 '
1830 'DISPLAYS NO. OF DATA POINT BEING PROCESSED
1840 '
1850 IF (SK$ = "y") OR (SK$ = "Y") GOTO 1920
1860 LOCATE 15,25 : PRINT I
1870 '
1880 '
1890 ' IONIC STRENGTH AND ACTIVITY COEFFICIENT CALCULATIONS
1900 '
1910 '
1920 ' MMOLLES OF SALTS ADDED
1930 '
1940 '
1950 ACID = VA(I) * MA
1960 BASE = VB(I) * MB
1970 S1 = VS1(I) * MS1
1980 S2 = VS2(I) * MS2
1990 '
2000 '
2010 '
2020 G(I) = 1
2030 V(I) = VO + VB(I) + VS1(I) + VS2(I) +VA(I)
2040 '
2050 '
2060 ' CHANGE P VALUES INTO CONCENTRATION USING
2070 ' CONCENTRATION = ACTIVITY / ACTIVITY COEFFICIENT
2080 '
2090 ON NI GOTO 2120,2110,2100
2100 F(I) = EXP (-PF(I) *2.302585) / G(I)
2110 CL(I) = EXP (-PCL(I) * 2.302585) / G(I)
2120 H(I) = EXP (-PH(I) * 2.302585) / G(I)
2130 '
2140 OH(I) = 1E-14 / (H(I) * G(I) ^ 2)

```

```

2150 IF NI = 1 THEN GOTO 2200
2160 '
2170 II(I) = CL(I) + F(I) + OH(I) + IIO : GOTO 2220
2180 ' USE OF ISOELECTRIC POINT TO CALCULATE IONIC STRENG
TH
2190 '
2200 IF PH(I) > EO THEN S = S1 + S2 + ACID ELSE S = S1 + S2
+ BASE
2210 II(I) = S / V(I) + OH(I) + H(I)
2220 F = II(I): GOSUB 870: Y = F
2230 IF G(I) / Y < 1.0001 THEN 2290
2240 G(I) = Y
2250 GOTO 2030
2260 '
2270 '
2280 '
2290 ' PA FOR EACH SALT
2300 '
2310 PHCL(I) = PCL(I) + PH(I)
2320 PHF(I) = PF(I) + PH(I)
2330 '
2340 '
2350 '
2360 ' MMOLES OF EACH SALT MEASURED
2370 '
2380 H(I) = H(I) * V(I)
2390 CLM(I) = CL(I) * V(I)
2400 FM(I) = F(I) * V(I)
2410 OH(I) = OH(I) * V(I)
2420 '
2430 '
2440 '
2450 ' UPTAKE OF EACH SALT
2460 '
2470 XCL(I) = ( CLM(I) - (ACID + CLM(1) + S1) ) / GM
2480 '
2490 ' XCL = ( MOLES OF CL MEASURED - ( INITIAL CL + HCL AD
DED
2500 ' + MOLES OF CL ADDED ) / GRMS OF EXCHANGER = CL / GM
2510 '

```

```

2520 XF(I) = ( FM(I) - S2 ) / GM
2530 '
2540 'XF = ( MOLES OF F MEASURED - MOLES OF F ADDED ) /
2550 ' GRMS OF EXCHANGER = UPTAKE F / GM
2560 '
2570 XH(I) = ( BASE - ACID + H(I) - OH(I) - H(1) ) / GM
2580 '
2590 ' XH = ( MOLES OF BASE ADDED - MOLES OF ACID ADDED
2600 ' + (H+) MEASURED - OH MEASURED - INITIAL (H+) ) / G
RMS OF EXCHANGER
2610 ' = CHANGE IN (H+) UPTAKE / GM
2620 '
2630 CB(I) = ( XCL(I) + XF(I) - XH(I) )
2640 XX(I) = ( XCL(I) + XF(I) )
2650 '
2660 '
2670 ' DITRIBUTION COEFFIECIENT
2680 '
2685 ON NI GOTO 2710,2700,2690
2690 DF(I) = XF(I) / F(I)
2700 DCL(I) = XCL(I) / CL(I)
2710 '
2720 IF (SK$ = "N") OR (SK$ = "n") GOTO 2930
2730 PRINT: PRINT: PRINT
2740 PRINT " N = "; I : PRINT
2750 PRINT " PH = "; PH(I)
2760 PRINT "ACTIVITY COEFFICIENT = "; G(I)
2770 PRINT "IONIC STRENGTH = "; II(I)
2780 PRINT "MMOLES CHLORIDE = "; CLM(I)
2790 PRINT "MMOLES ISE NO.3 = "; FM(I)
2800 PRINT "MMOLES H = "; H(I)
2810 PRINT "MMOLES OH = "; OH(I)
2820 PRINT "MMOLES A = "; ACID
2830 PRINT "MMOLES B = "; BASE
2840 PRINT "PCL = "; PCL(I)
2850 PRINT "PHCL = "; PHCL(I)
2860 PRINT "PF = "; PF(I)
2870 PRINT "PHF = "; PHF(I)
2880 PRINT "UPTAKE CHLORIDE ="; XCL(I)
2890 PRINT "UPTAKE ION NO.3 ="; XF(I)

```

```
2900 PRINT "UPTAKE H           = ";XH(I)
2910 PRINT "ANION BALANCE     =";XX(I)
2920 PRINT "CHARGE BALANCE    =";CB(I)
2930 NEXT
2940 PRINT
2950 '
2960 '
2970 ' WRITE RESULTS TO FILE
2980 '
2990 '
3000 INFILE$ = "\\PROGRAMS\DATA\RESULTS\" + NM$
3010 OPEN INFILE$ FOR OUTPUT AS #1
3020 WRITE#1,N: WRITE#1,EO: WRITE#1,VO
3030 WRITE#1,MB: WRITE#1,MS1: WRITE#1,MS2: WRITE#1,MA
3040 WRITE#1,GA: WRITE#1,GM: WRITE#1,NI
3050 FOR I = 1 TO N: WRITE#1,VB(I): NEXT
3060 FOR I = 1 TO N: WRITE#1,VS1(I): NEXT
3070 FOR I = 1 TO N: WRITE#1,VS2(I): NEXT
3080 FOR I = 1 TO N: WRITE#1,VA(I): NEXT
3090 FOR I = 1 TO N: WRITE#1,PH(I): NEXT
3100 FOR I = 1 TO N: WRITE#1,CLM(I): NEXT
3110 FOR I = 1 TO N: WRITE#1,FM(I): NEXT
3120 FOR I = 1 TO N: WRITE#1,XH(I): NEXT
3130 FOR I = 1 TO N: WRITE#1,XCL(I): NEXT
3140 FOR I = 1 TO N: WRITE#1,XF(I): NEXT
3150 FOR I = 1 TO N: WRITE#1,CB(I): NEXT
3160 FOR I = 1 TO N: WRITE#1,PHCL(I): NEXT
3170 FOR I = 1 TO N: WRITE#1,PHF(I): NEXT
3180 FOR I = 1 TO N: WRITE#1,XX(I): NEXT
3190 FOR I = 1 TO N: WRITE#1,II(I): NEXT
3200 FOR I = 1 TO N: WRITE#1,G(I): NEXT
3210 FOR I = 1 TO N: WRITE#1,DCL(I): NEXT
3220 FOR I = 1 TO N: WRITE#1,DF(I): NEXT
3230 FOR I = 1 TO N: WRITE#1,CL(I): NEXT
3240 FOR I = 1 TO N: WRITE#1,F(I): NEXT
3250 CLOSE #1
3260 CLS
3270 END
```

PROGRAM(P.5) GRAPHIC DISPLAY OF RESULTS ON CRT MONITOR

```

10 'SCREEN MULTILOT FOR UPTAKE 2      SEPTEMBER 1986
20 'FILENAME PLT4.BAS
30 H = 80
40 CLS
50 DIM PH(H),XX(H),ML(H),PA(H),PB(H),MA(H),C(H),YT(H),XT(H)
),CB(H),II(H)
60 DIM VB(H),VA(H),VS1(H),VS2(H),CLM(H),C3M(H),XCL(H),X3(H)
),CL(H),C3(H),XF(H)
70 DIM XH(H),XOH(H),PHCL(H),PHF(H),XAP(H),YAP(H),G(H),DCL(
H),D3(H),BT(H)
80 LOCATE 10,30 : PRINT " WELCOME TO MULTILOT "
100 LOCATE 19,1 : INPUT "NUMBER OF FILES ";NF
110 FOR I = 1 TO NF
120 PRINT:PRINT:PRINT "FILE";I;SPC(10)
130 INPUT "NAME OF FILE ";D$(I)
140 NEXT
150 '
160 CLS
170 PRINT: PRINT TAB(10) "THIS FILE CONTAINS THE FOLLOWING
PARAMETERS"
180 PRINT : PRINT TAB(5) "VOLUME OF BASE                VB"
190 PRINT TAB(5) "VOLUME OF SALT 1                VS1"
200 PRINT TAB(5) "VOLUME OF SALT 2                VS2"
210 PRINT TAB(5) "VOLUME OF ACID                VA"
220 PRINT TAB(5) "PH                PH"
230 PRINT TAB(5) "PCL                PCL"
240 PRINT TAB(5) "PF                PF"
250 PRINT TAB(5) "PHCL                PHCL"
260 PRINT TAB(5) "PHF                PHF"
270 PRINT TAB(5) "MOLES OF CHLORIDE                CLM"
280 PRINT TAB(5) "MOLES OF FLUORIDE                FM"
290 PRINT TAB(5) "PROTON UPTAKE                XH"
300 PRINT TAB(5) "CHLORIDE UPTAKE                XCL"
310 PRINT TAB(5) "FLUORIDE UPTAKE                XF"
320 PRINT TAB(5) "DISTRIBUTION COEFFICIENT CL    DCL"

```

```

330 PRINT TAB(5) "DISTRIBUTION COEFFICIENT F      DF"
340 PRINT TAB(5) "CHARGE BALANCE                  CB"
350 '
360 '
370 PRINT : INPUT "X AXIS = ";XT$
380 PRINT : INPUT "Y AXIS = ";YT$
390 '
400 PRINT : INPUT "CONNECT POINTS Y/N ";LN$
410 CLS
420 LOCATE 10,30 : INPUT "CALCULATE MAX MIN  Y/N ";CMM$
422 IF (CMM$ = "Y") OR (CMM$ = "y") THEN GOTO 650
424 IF (CMM$ = "N") OR (CMM$ = "n") THEN GOTO 500
426 GOTO 420
430 '
440 '
460 '
470 '
480 '      SUBROUTINE FOR INPUTTING MAX AND MIN VALUES
490 '
500 PRINT:PRINT:PRINT "TITLE OF X AXIS IS  ";XT$
510 PRINT : PRINT SPC(25) XT$ ;
520 INPUT " MIN  ";XMIN
530 PRINT: PRINT SPC(25) XT$ ;
540 INPUT " MAX  ";XMAX
550 PRINT:PRINT:PRINT "TITLE OF Y AXIS IS  ";YT$
560 PRINT: PRINT SPC(25) YT$ ;
570 INPUT " MIN  ";YMIN
580 PRINT: PRINT SPC(25) YT$ ;
590 INPUT " MAX  ";YMAX
600 GOTO 1240
610 '
620 '
630 '      SUBROUTINE TO DETERMINE MAX AND MIN VALUES  THR
U LINE 1100
640 '
650 CLS : LOCATE 10,10 : PRINT "CALCULATING MAX AND MIN VA
LUES"
660 FOR T = 1 TO NF
670 GOSUB 2970
680 BT$ = XT$ : GOSUB 3230 : FOR I = 1 TO N : XT(I) = BT(I)

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```

) : NEXT
690 BT$= YT$ : GOSUB 3230 : FOR I = 1 TO N : YT(I) = BT(I)
  : NEXT
700 '
710 '
720 '
730 '
740 '   XMIN
750 '
760 IF T = 1 THEN XMIN = XT(1) : GOTO 780
770 IF T > 1 THEN IF XMIN < XT(1) THEN GOTO 780 ELSE XM
IN = XT(1)
780 FOR K = 2 TO N
790 IF XMIN < XT(K) GOTO 810
800 LET XMIN = XT(K)
810 NEXT K
820 '
830 '   XMAX
840 '
850 IF T = 1 THEN XMAX = XT(1) : GOTO 870
860 IF T > 1 THEN IF XMAX > XT(1) THEN GOTO 870 ELSE XMAX
= XT(1)
870 FOR K = 2 TO N
880 IF XMAX > XT(K) GOTO 900
890 XMAX = XT(K)
900 NEXT K
910 '
920 '   YMIN
930 '
940 IF T = 1 THEN YMIN = YT(1) : GOTO 960
950 IF T > 1 THEN IF YMIN < YT(1) GOTO 960 ELSE YMIN = YT(
1)
960 FOR K = 2 TO N
970 IF YMIN < YT(K) GOTO 990
980 LET YMIN = YT(K)
990 NEXT K
1000 '
1010 '   YMAX
1020 '
1030 IF T = 1 THEN YMAX = YT(1) : GOTO 1050

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```

1040 IF T > 1 THEN IF YMAX > YT(1) GOTO 1050 ELSE YMAX = Y
T(1)
1050 FOR K = 2 TO N
1060 IF YMAX > YT(K) GOTO 1080
1070 YMAX = YT(K)
1080 NEXT K
1090 NEXT T
1100 CLS
1110 '
1120 PRINT "XMIN = "XMIN
1130 PRINT "XMAX = "XMAX
1140 PRINT "YMIN = "YMIN
1150 PRINT "YMAX = "YMAX
1160 '
1170 PRINT : PRINT : INPUT "USE CALCULATED MAX MIN Y/N";
MN$
1180 IF (MN$ = "Y") OR (MN$ = "y") THEN GOTO 1220
1190 IF (MN$ = "N") OR (MN$ = "n") THEN GOTO 480
1200 GOTO 1170
1210 '
1220 '          SUBROUTINE TO DRAW BOX
1230 '
1240 GX = 9 : GY = 10
1250 CLS
1260 LINE (220,1)-(580,160),,B          'DRAWS BOX
1270 LINE (219,1)-(219,160)          'FILLS IN VERTICAL LI
NES
1280 LINE (581,1)-(581,160)          'FILLS IN VERTICAL LI
NES
1290 '
1300 '
1310 ' SUBROUTINE FOR X GRATICES
1320 '
1330 B = 360 / GX                      'DEFINES SPACE BETWE
EN EACH X GRATICES
1340 FOR I = 1 TO GX-1
1350 BX = 220 + (B * I)                'DEFINES X POSITION
OF EACH X GRATICES
1360 LINE (BX,160)-(BX,160-10)        'DRAWS A LINE FOR EA
CH X GRATICES

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1370 LINE (BX-1,160)-(BX-1,160-10)      'FILLS IN THE X GRAT
ICES
1380 NEXT
1390 '
1400 '
1410 ' SUBROUTINE FOR VALUES OF X GRATICES
1420 '
1430 D = (XMAX -XMIN) / GX                'DEFINES DELTA VALUE
FOR EACH X GRATICES
1440 BNX = 45 / GX                        'DEFINES NUMBER OF C
HARACTER LINES BETWEEN
EACH X GRATICES
1450 FOR I = 1 TO GX - 1
1460 X = 26 + ( BNX * I )                'DEFINES X CHARATER
POSTION OF X VALUES
1470 Y = 22                              'DEFINES Y POSITION
OF X GRATICES VALUES
1480 C = XMIN + ( D * I )                'DEFINES VALUE OF
EACH X GRATICES
1490 IF OA = 2 GOTO 1520
1500 LOCATE Y,X : PRINT USING "##.#";C
1510 GOTO 1530
1520 LOCATE Y,X : PRINT USING "#.##";C
1530 NEXT
1540 LOCATE 24,52 : PRINT XT$            'LABELS X AXIS
1550 '
1560 '
1570 ' SUBROUTINE FOR Y GRATICES
1580 '
1590 E = 160 / GY                          'DEFINES SPACE BETW
EEN EACH Y GRATICES
1600 FOR I = 1 TO GY-1
1610 EY = 160 - ( E * I )                'DEFINES Y POSTION
OF EACH Y GRATICES
1620 '
1630 LINE (220,EY)-(220+25,EY)          'DRAWS A LINE FOR E
ACH Y GRATICES
1640 NEXT
1650 '
1660 '

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1670 ' SUBROUTINE FOR VALUES OF Y GRATICES
1680 H = (YMAX-YMIN) / GY           'DEFINES DELTA VAL
UE FOR EACH Y GRATICES
1690 ENY = 20/GY                     'DEFINES NUMBER OF CH
ARACTER LINES BETWEEN
                                     EACH Y GRATICES
1700 FOR I = 1 TO GY - 1
1710 Y = 20 - (ENY * I)             'DEFINES Y CHARACTE
R POSITION OF EACH Y
                                     GRATICES
1720 X = 22                           'DEFINES X CHARACTER
   POSITON OF Y GRATICES
1730 F = YMIN + (H * I)              'DEFINES ABSOLUTE
   VALUE OF Y GRATICES
1740 LOCATE Y,X : PRINT USING "##.##";F
1750 NEXT
1760 LOCATE 10,17 : PRINT.YT$       'LABELS Y AXIS
1770 LOCATE 24,1
1780 '
1790 ' SUBROUTINE FOR INPUTTNG DATA FROM FILE
1800 '
1810 FOR T = 1 TO NF
1820 GOSUB 2970
1830 BT$ = XT$ : GOSUB 3230 : FOR I = 1 TO N : XT(I) = BT(
I) : NEXT
1840 BT$ = YT$ : GOSUB 3230 : FOR I = 1 TO N : YT(I) = BT(
I) : NEXT
1850 FOR J = 1 TO N
1861 XQ = (XT(J) - XMIN) / (XMAX - XMIN) 'PROPORTIONAL DIS
TANCE OF X ON X AXIS
1870 YQ = (YT(J) - YMIN) / (YMAX - YMIN) 'PROPORTIONAL DIS
TANCE OF Y ON Y AXIS
1880 DX = 360 : DY = 160             'LENGTH OF X AND Y AX
IS IN PIXELS
1890 XP = XQ * DX                     'ABSOLUTE DISTANCE O
F X ON X AXIS
1900 YP = YQ * DY                     'ABSOLUTE DISTANCE O
F Y ON Y AXIS
1910 NC = T
1920 XAP(J) = 220 + XP               'ABSOLUTE LOCATI

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ON OF X ON THE SCREEN
1930 YAP(J) = 160 - YP                                'ABSOLUTE LOCATI
ON OF Y ON THE SCREEN
1935 IF (XAP(J) > 580) OR (XAP(J) < 220) OR (YAP(J) > 160)
    THEN GOTO 2050
1940 IF (AO$ = "Y") OR (AO$ = "y") THEN IF W = 1 THEN IF
T = 1 THEN GOTO 2040
1950 IF (AO$ = "Y") OR (AO$ = "y") THEN IF W = 1 THEN IF
T = 2 THEN GOTO 2020
1960 IF (AO$ = "Y") OR (AO$ = "y") THEN IF W = 2 THEN IF
T = 1 THEN GOTO 2020
1970 IF (AO$ = "Y") OR (AO$ = "y") THEN IF W = 2 THEN IF
T = 2 THEN GOTO 2040
1980 ON T GOTO 1990,2000,2010,2020,2030,2040
1990 GOSUB 2280 : GOTO 2050
2000 GOSUB 2280 : GOTO 2050
2010 GOSUB 2420 : GOTO 2050
2020 NC = 3 : GOSUB 2120 : GOTO 2050
2030 NC = 1 : GOSUB 2280 : GOTO 2050
2040 NC = 2 : GOSUB 2420 : GOTO 2050
2050 NEXT J
2060 GOSUB 2520
2070 NEXT T
2080 GOTO 2690
2090 '
2100 'SUBROUTINE FOR DRAWING CIRCLES
2110 '
2120 PRESET(XAP(J),YAP(J)),NC                            'DISPLAYS PIXE
L OF X,Y COORDINATES                                     ON THE SCREEN
, COLOR 1
2130 CIRCLE(XAP(J),YAP(J)),5,NC                          'DRAWS CIRCLE
OF 5 PIXEL RADIUS                                       ON THE SCREEN
, COLOR 1
2140 '
2150 IF (LN$ = "Y") OR (LN$ = "y") THEN GOSUB 2210
2160 RETURN
2170 '
2180 '

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```

2190 ' SUBROUTINE TO CONNECT THE POINTS
2200 '
2210 IF (J = 1) OR (LNS = 1) THEN RETURN
2211 IF (XAP(J - 1) > 585) OR (XAP(J - 1) < 218) THEN RET
URN
2212 IF (YAP(J - 1) > 165) OR (YAP(J - 1) < -1) THEN RETURN
2220 LINE(XAP(J-1),YAP(J-1))-(XAP(J),YAP(J)),NC
2230 RETURN
2240 '
2250 '
2260 ' SUBROUTINE FOR DRAWING SQUARE
2270 '
2280 PRESET(XAP(J),YAP(J)),NC 'DISPLAYS PIXE
L OF X,Y COORDINATES
ON THE SCREEN
,COLOR 1
2290 LINE (XAP(J)-4,YAP(J)-2)-(XAP(J)-4,YAP(J)+2),NC
2300 LINE (XAP(J)+4,YAP(J)-2)-(XAP(J)+4,YAP(J)+2),NC
2310 FOR PX = -4 TO 4
2320 PRESET (XAP(J)+PX,YAP(J)+2),NC
2330 PRESET (XAP(J)+PX,YAP(J)-2),NC
2340 PX = PX + 1
2350 NEXT PX
2360 IF (LN$ = "Y") OR (LN$ = "y") THEN GOSUB 2210
2370 RETURN
2380 '
2390 '
2400 ' SUBROUTINE FOR DRAWING TRIANGLE
2410 '
2420 PRESET(XAP(J),YAP(J)),NC 'DISPLAYS PIXE
L OF X,Y COORDINATES
ON THE SCREEN
,COLOR 1
2430 FOR PX = -5 TO 5
2440 PRESET(XAP(J)-PX,YAP(J)+2),NC
2450 PX = PX + 1
2460 NEXT PX
2470 LINE (XAP(J)-5,YAP(J)+2)-(XAP(J),YAP(J)-3),NC
2480 LINE (XAP(J)+5,YAP(J)+2)-(XAP(J),YAP(J)-3),NC
2490 IF (LN$ = "Y") OR (LN$ = "y") THEN GOSUB 2210

```

```

2500 RETURN
2510 '
2520 TX = 1
2530 COLOR NC
2540 YF = 17 + T
2550 LOCATE YF,3 :PRINT "FILE";T;D$(T)
2560 LNS = 1
2570 ON T GOTO 2580,2590,2600,2610,2620,2630
2580 XAP(J) = 140 : YAP(J) = 140 : GOSUB 2120 :GOTO 2640
2590 XAP(J) = 140 : YAP(J) = 148 : GOSUB 2280 :GOTO 2640
2600 XAP(J) = 140 : YAP(J) = 156 : GOSUB 2420 :GOTO 2640
2610 XAP(J) = 140 : YAP(J) = 164 : GOSUB 2120 :GOTO 2640
2620 XAP(J) = 140 : YAP(J) = 172 : GOSUB 2280 :GOTO 2640
2630 XAP(J) = 140 : YAP(J) = 180 : GOSUB 2420 :GOTO 2640
2640 LNS = 0
2650 RETURN
2660 '
2670 '
2680 '
2690 COLOR 3
2700 LOCATE 23,1 : PRINT " "
2710 LOCATE 23,1 : INPUT " ADD OPTIONS Y/N ";AO$
2720 IF (AO$ = "Y") OR (AO$ = "y") GOTO 2750
2730 IF (AO$ = "N") OR (AO$ = "n") GOTO 2870
2740 GOTO 2710
2750 W = W + 1
2760 LOCATE 23,1 : PRINT " "
2770 LOCATE 23,1 : INPUT " CHANGE X OR Y AXIS X/Y";CA$
2780 IF (CA$ = "X") OR (CA$ = "x") GOTO 2830
2790 LOCATE 23,1 : PRINT " "
2800 LOCATE 23,1 : INPUT " Y AXIS NOW = ";YT$
2810 LOCATE (10 + W),17 : PRINT YT$
2820 GOTO 1810
2830 LOCATE 23,1 : PRINT " "
2840 LOCATE 23,1 : INPUT " X AXIS NOW = ";XT$
2850 LOCATE 24,(52 + (4*W)) : PRINT XT$
2860 GOTO 1810
2870 W = 0 : LOCATE 23,1 : PRINT "
"
2880 LOCATE 23,1 : INPUT "CONTINUE Y/N";CT$

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```

2890 IF (CT# - "Y") OR (CT# - "y") GOTO 160
2900 IF (CT# - "N") OR (CT# - "n") GOTO 2920
2910 GOTO 2880
2920 END
2930 '
2940 '
2950 GOTO 1810
2960 '
2970 OPEN"I",#1,"\\PROGRAMS\DATA\RESULTS\" + D$(T)
2980 INPUT#1,N : INPUT#1,EO : INPUT#1,VO
2990 INPUT#1,MB: INPUT#1,MS1: INPUT#1,MS2 : INPUT#1,MA
3000 INPUT#1,GA: INPUT#1,GM : INPUT#1,NI
3010 FOR J = 1 TO N : INPUT#1,VB(J) : NEXT J
3020 FOR J = 1 TO N : INPUT#1,VS1(J) : NEXT J
3030 FOR J = 1 TO N : INPUT#1,VS2(J) : NEXT J
3040 FOR J = 1 TO N : INPUT#1,VA(J) : NEXT J
3050 FOR J = 1 TO N : INPUT#1,PH(J) : NEXT J
3060 FOR J = 1 TO N : INPUT#1,CLM(J) : NEXT J
3070 FOR J = 1 TO N : INPUT#1,C3M(J) : NEXT J
3080 FOR J = 1 TO N : INPUT#1,XH(J) : NEXT J
3090 FOR J = 1 TO N : INPUT#1,XCL(J) : NEXT J
3100 FOR J = 1 TO N : INPUT#1,X3(J) : NEXT J
3110 FOR J = 1 TO N : INPUT#1,CB(J) : NEXT J
3120 FOR J = 1 TO N : INPUT#1,PHCL(J) : NEXT J
3130 FOR J = 1 TO N : INPUT#1,PHF(J) : NEXT J
3140 FOR J = 1 TO N : INPUT#1,XX(J) : NEXT J
3150 FOR J = 1 TO N : INPUT#1,II(J) : NEXT J
3160 FOR J = 1 TO N : INPUT#1,G(J) : NEXT J
3170 FOR J = 1 TO N : INPUT#1,DCL(J) : NEXT J
3180 FOR J = 1 TO N : INPUT#1,D3(J) : NEXT J
3190 FOR J = 1 TO N : INPUT#1,CL(J) : NEXT J
3200 FOR J = 1 TO N : INPUT#1,C3(J) : NEXT J
3210 CLOSE#1
3220 RETURN
3230 ' SUBROUTINE TO SPECIFY PARAMETERS
3240 '
3250 IF BT$ = "VB" THEN GOSUB 3440
3260 IF BT$ = "VS1" THEN GOSUB 3450
3270 IF BT$ = "VS2" THEN GOSUB 3460
3280 IF BT$ = "VA" THEN GOSUB 3470

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```

3290 IF BT$ = "PH" THEN GOSUB 3480
3300 IF BT$ = "CLM" THEN GOSUB 3490
3310 IF BT$ = "C3M" THEN GOSUB 3500
3320 IF BT$ = "XH" THEN GOSUB 3510
3330 IF BT$ = "XCL" THEN GOSUB 3520
3340 IF BT$ = "XF" THEN GOSUB 3530
3350 IF BT$ = "CB" THEN GOSUB 3540
3360 IF BT$ = "PHCL" THEN GOSUB 3550
3370 IF BT$ = "PHF" THEN GOSUB 3560
3380 IF BT$ = "DCL" THEN GOSUB 3570
3390 IF BT$ = "DF" THEN GOSUB 3580
3400 IF BT$ = "PCL" THEN GOSUB 3590
3410 IF BT$ = "PF" THEN GOSUB 3600
3420 '
3430 RETURN
3440 FOR I = 1 TO N : BT(I) = VB(I) : NEXT : RETURN
3450 FOR I = 1 TO N : BT(I) = VS1(I) : NEXT : RETURN
3460 FOR I = 1 TO N : BT(I) = VS2(I) : NEXT : RETURN
3470 FOR I = 1 TO N : BT(I) = VA(I) : NEXT : RETURN
3480 FOR I = 1 TO N : BT(I) = PH(I) : NEXT : RETURN
3490 FOR I = 1 TO N : BT(I) = CLM(I) : NEXT : RETURN
3500 FOR I = 1 TO N : BT(I) = C3M(I) : NEXT : RETURN
3510 FOR I = 1 TO N : BT(I) = XH(I) : NEXT : RETURN
3520 FOR I = 1 TO N : BT(I) = XCL(I) : NEXT : RETURN
3530 FOR I = 1 TO N : BT(I) = X3(I) : NEXT : RETURN
3540 FOR I = 1 TO N : BT(I) = CB(I) : NEXT : RETURN
3550 FOR I = 1 TO N : BT(I) = PHCL(I) : NEXT : RETURN
3560 FOR I = 1 TO N : BT(I) = PHF(I) : NEXT : RETURN
3570 FOR I = 1 TO N : BT(I) = LOG(ABS(DCL(I))) / 2.302585
: NEXT : RETURN
3580 FOR I = 1 TO N : BT(I) = LOG(ABS(D3(I))) / 2.302585 :
NEXT : RETURN
3590 FOR I = 1 TO N : BT(I) = -LOG(CL(I) * G(I)) / 2.30258
5 : NEXT : RETURN
3600 FOR I = 1 TO N : BT(I) = -LOG(C3(I) * G(I)) / 2.30258
5 : NEXT : RETURN

```

PROGRAM(P.6) CALCULATION OF UPTAKE PROGRAM 1

```
10 ' " UPTAKE 1"   EDITED APRIL 3,1986
20 H=80
30 DIM ML(H),MS(H),MA(H),PH(H),XX(H),PA(H),PB(H),B(H)
40 DIM C(H),V(H),A(H)
50 CLS
60 PRINT: PRINT: PRINT:
70 INPUT "FILE NAME ";NM$
80 OPEN"I",#1,"\\PROGRAMS\\DATA\\" + NM$
90 INPUT#1,N,EO,VO,MB,MS,MA,GM,GA
100 FOR I= 1 TO N
110 INPUT#1,ML(I),MS(I),MA(I),PH(I)
120 NEXT I
130 CLOSE#1
140 PRINT:PRINT:INPUT"DO YOU WANT SCREEN PRINT OF RESULTS"
;SK$
150 IF (SK$ = "Y") OR (SK$ = "y") THEN GOTO 180
160 IF (SK$ = "N") OR (SK$ = "n") THEN GOTO 330
170 GOTO 140
180 PRINT:PRINT "NAME OF FILE ="; NM$: PRINT:
190 PRINT:PRINT "Concentration of NaCl =";SPC(2);MS;SPC(2)
;"M";
200 PRINT TAB(36)"Concentration of NaOH =";SPC(2)MB;SPC(2)
;"M"
210 PRINT "Concentration of HCl =";SPC(2)MA;SPC(2);"M";
220 PRINT TAB(36)"Initial Volume = ";SPC(2)VO;SPC(2);"m
1"
230 PRINT "Weight of ZrO  = ";SPC(2)GA;SPC(2)"g";
240 PRINT TAB(36) "Weight of Dried ZRO = ";SPC(2)GM;SPC(2)
);"g"
250 PRINT:PRINT "N = Number of Data Set";
260 PRINT TAB(36)"MLB = Volume of Base"
270 PRINT "MLA = Volume of Acid";
280 PRINT TAB(36)"MLS = Volume of Salt"
290 PRINT "PA = pH + pCl";
300 PRINT TAB(36)"PB = pNa + pOH"
310 PRINT: PRINT "N" TAB(8) "MLB" TAB(17) "MLA"TAB(25);
```

```

320 PRINT "MLB"TAB(33)"PH"TAB(41)"PA"TAB(50)"PB"TAB(60)"X"
330 B0 =1: CO=.3
340 GOTO 360
350 Z = EXP(-1.1513 * (SQR (Z) / (1 +B0 * SQR (Z))-CO * Z))
:RETURN
360 FOR I = 1 TO N
370 B(I) = ML(I) * MB
380 S = MS(I) * MS
390 A(I) = MA(I) * MA
400 V(I) = VO + ML(I) + MS(I) + MA(I)
410 IF PH(I) > =EO THEN S= S + A(I): GOTO 430
420 S = S + B(I)
430 LET G= 1
440 H = EXP ( -2.303 * PH(I))
450 H = H / G:
460 OH = 1E-14 / (H * G ^ 2)
470 II = S / V(I) + H + OH
480 Z = II: GOSUB 350:Y = Z
490 IF G / Y < 1.0001 THEN 520
500 G = Y
510 GOTO 440
520 IF I = 1 THEN HO = H
530 NA = ( S/ V(I) + OH ) * G
540 PN = - LOG (NA) / 2.303
550 PB = 14 - PH(I) + PN
560 CL = S / V(I) + H
570 CL = CL * G
580 PC = - LOG (CL) / 2.303
590 PA = PH(I) + PC
600 XX = ((B(I)-A(I)) + H * V(I) - OH * V(I) - HO * V(1))/
GM
605 C(I)= B(I)-A(I)
610 PA(I) = PA: PB(I) = PB: XX(I) = XX
620 IF (SK$ = "Y") OR (SK$ = "y") THEN GOTO 640
630 IF (SK$ = "N") OR (SK$ = "n") THEN GOTO 780
640 PRINT I TAB(8);
650 PRINT USING"###";ML(I);
660 PRINT TAB(16);
670 PRINT USING"###";MA(I);
680 PRINT TAB(24);

```

```

690 PRINT USING"#.##";MS(I);
700 PRINT TAB(32);
710 PRINT USING"##.##";PH(I);
720 PRINT TAB(40);
730 PRINT USING"##.###";PA(I);
740 PRINT TAB(48);
750 PRINT USING"##.###";PB(I);
760 PRINT TAB(58);
770 PRINT USING"#.###";XX(I)
780 NEXT I
790 OPEN"O",#2,"\\PROGRAMS\\DATA\\results\" + NM$
800 WRITE#2,N
810 FOR I = 1 TO N : WRITE#2,C(I) : NEXT I
820 FOR I = 1 TO N : WRITE#2,ML(I) : NEXT I
830 FOR I = 1 TO N : WRITE#2,MA(I) : NEXT I
840 FOR I = 1 TO N : WRITE#2,PH(I) : NEXT I
850 FOR I = 1 TO N : WRITE#2,PA(I) : NEXT I
860 FOR I = 1 TO N : WRITE#2,PB(I) : NEXT I
870 FOR I = 1 TO N : WRITE#2,XX(I) : NEXT I
880 CLOSE#2
890 CLS
900 PRINT: PRINT: PRINT:
910 INPUT "PRINT RESULTS Y/N";YN$
920 IF (YN$ = "Y") OR (YN$ = "y") THEN GOTO 950
930 IF (YN$ = "N") OR (YN$ = "n") THEN GOTO 1620
940 GOTO 910
950 LPRINT CHR$(27);"C";CHR$(70)
960 LPRINT CHR$(27);CHR$(40)
970 LPRINT CHR$(27);"1";CHR$(12)
980 INPUT "TITLE OF TABLE";TITLE$
990 LPRINT TITLE$: LPRINT : LPRINT
1000 LPRINT:LPRINT "NAME OF FILE ="; NM$,:LPRINT
1010 LPRINT:LPRINT "Concentration of NaCl =";
1020 LPRINT USING "##.##";MS;
1030 LPRINT "M";
1040 LPRINT TAB(34)"Concentration of NaOH =";
1050 LPRINT USING "##.##";MB;
1060 LPRINT "M":LPRINT
1070 LPRINT "Concentration of HCl =";
1080 LPRINT USING "##.##";MA;

```

```

1090 LPRINT "M";
1100 LPRINT TAB(34)"Initial Volume -";
1110 LPRINT USING "###.##";VO;
1120 LPRINT "ml":LPRINT
1130 LPRINT "Weight of ZrO";CHR$(27);"S1";
1140 LPRINT "2";CHR$(27);"T";
1150 LPRINT "=";
1160 LPRINT USING "##.###";GA;
1170 LPRINT "g";
1180 LPRINT TAB(37) "Weight of Dried ZrO";CHR$(27);"S1";
1190 LPRINT "2";CHR$(27);"T";
1200 LPRINT "=";
1210 LPRINT USING "##.###";GM;
1220 LPRINT "g":LPRINT
1230 LPRINT:LPRINT "N = Number of data set.";
1240 LPRINT TAB(34)"VB = Volume of base, ml." : LPRINT
1250 LPRINT "VA = Volume of Acid, ml.";
1260 LPRINT TAB(34)"VS = Volume of Salt, ml." : LPRINT
1270 LPRINT "pA = pH + pCl";
1280 LPRINT TAB(34)"pB = pNa + pOH" : LPRINT
1290 LPRINT "X = Capacity, mmoles/gram
1300 LPRINT : LPRINT : LPRINT CHR$(27);"-1";
1310 LPRINT "N" TAB(11) "VB" TAB(18) "VA" TAB(26) "VS" TAB
(34);
1320 LPRINT "pH"TAB(42)"pA"TAB(50)"pB"TAB(60)"X"SPC(5):
1330 LPRINT : LPRINT CHR$(27);"-0";
1340 LPRINT
1350 PA(I) = PA: PB(I) = PB: XX(I) = XX
1360 FOR I = 1 TO N
1370 LPRINT I TAB(8);
1380 LPRINT USING"##.##";ML(I);
1390 LPRINT TAB(16);
1400 LPRINT USING"##.##";MA(I);
1410 LPRINT TAB(24);
1420 LPRINT USING"##.##";MS(I);
1430 LPRINT TAB(32);
1440 LPRINT USING"##.##";PH(I);
1450 LPRINT TAB(40);
1460 LPRINT USING"##.###";PA(I);
1470 LPRINT TAB(48);

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```
1480 LPRINT USING"##.###";PB(I);
1490 LPRINT TAB(58);
1500 LPRINT USING"#.###";XX(I)
1510 IF I = 30 THEN GOTO 1520 ELSE GOTO 1600
1520 LPRINT CHR$(12)
1530 LPRINT : LPRINT : LPRINT : LPRINT
1540 LPRINT "FILE NAME = ";NM$;
1550 LPRINT "    CONTINUED FROM PREVIOUS PAGE"
1560 LPRINT : LPRINT CHR$(27);"-1";
1570 LPRINT "N" TAB(11) "VB" TAB(18) "VA" TAB(26);
1580 LPRINT "VS"TAB(34)"pH"TAB(42)"pA"TAB(50)"pB"TAB(60)"X
"SPC(5):
1590 LPRINT CHR$(27);"-0": LPRINT
1600 NEXT I
1610 LPRINT CHR$(12)
1620 END
```

