UNIVERSITY OF SOUTHAMPTON

Department of Chemistry

ELECTROCHEMICAL STUDIES OF MOLTEN SALT SYSTEMS

A Thesis submitted for the Degree of

Master of Philosophy

by

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ABSTRACT

The work consisted of three projects related by the theme of Electrochemistry in Molten Salt Systems.

1. The isothermal variation of electrical conductivity (κ) of sodium tetrachloroaluminate ($NaAlCl_4$) with pressure was investigated at various temperatures from 175°C-450°C. Ln(κ) vs. pressure plots showed linear behaviour and the volume of activation could be derived. Results obtained fit in well with values for ions of comparable size.

2. A rugged electrode was developed as an analytical probe for chloroaluminate melt compositions. The chlorobasicity of these melts varies greatly with composition over the range 49.8-50.2 mole % aluminium chloride. The potential between an aluminium wire and this electrode could be used as a measure of pCl^-, and hence, could be used to determine and monitor the composition of the melt.

3. The variation of electrical conductivity of molten sodium and potassium nitrate with temperature was investigated at pressures up to 1000 atmospheres, using nitrogen as the pressurising medium. Thermal decomposition to nitrite was suppressed by the pressure. In this way conductivity measurements on these melts could be extended to ca. 800°C from the previous limit of 500°C.

CONTENTS

ACKNOWLEDGEMENTS

I would like to acknowledge Merck Ltd, Poole Dorset for their assistance in this course of research, the staff at Southampton University for their technical support and my friends and colleagues for their moral support.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Molten salts as electrochemical solvents

The use of molten salts in chemistry is not a new development although their use has increased greatly in recent decades. The isolation of sodium and potassium from the molten hydroxides was demonstrated by Sir Humphrey Davy in 1807. However, problems with handling the materials such as the need for elevated temperatures, and also their hygroscopic and corrosive nature, have limited the amount of study undertaken on molten salt systems, water or organic solvents being the preferred media.

Molten salts can be considered as liquids consisting of distinct ions. They are normally categorised according to their anions eg. nitrates, halides etc. However, in general most commonly used molten salts have similar physical properties which are detailed in Table 1.

ADVANTAGEOUS	**DISADVANTAGEOUS**
Moderate viscosity	Sometimes hygroscopic
High thermal conductivity	Susceptible to hydrolysis
High electrical conductivity	Corrosive
High solvating effect	Problems and costs associated with high temperature experiments
Optical clarity	
Thermal stability	
Access to a wide temperature range (-75-1000°C)*	
Low vapour pressures	

* Trimethylphenylammonium chloride/aluminum chloride M.Pt. -75°C
Cryolite (Na_3AlF_6) M.Pt. 1003°C

Table 1

Molten salts are finding applications in a wide range of industries. Metal refining makes use of the high solvating effect to dissolve metals and their salts and also the high electrical conductivity and stability. The electrochemical processing of metals can be subdivided into four categories; electrowinning, electrorefining, electroplating and electroforming. The most commonly used salts for electrorefining are the molten alkali halides or alkaline earth halides. These have very negative Gibbs energy of formation which implies a high decomposition potential. This means that electrochemical processes that could not be done in aqueous systems can be achieved by using molten salt systems. The disadvantage of using molten salts for electrorefining is the cost of the energy required to keep the electrolyte molten. However the use of room temperature molten salts which have recently been discovered (1,2,3) could make the prospect more attractive.

1.2 Molten salts as battery electrolytes

Fuel cells and battery systems are other areas where molten salts are finding increased use. As concern increases about the depletion of fossil fuel reserves, and the pollution caused by fossil fuel consumption, development of batteries for electric vehicles and for load levelling has accelerated immensely over the last 10-15 years. Because of the good electrical stability of molten salts, batteries can be developed from very reactive materials producing high cell potentials and high specific energy. These factors are assisted by the high conductivity (which reduces Ohmic losses) and high temperature (which increases reaction rate). Two systems currently under development are the LAIS battery (Lithium Aluminium Iron Sulphide) (5,6) and the ZEBRA battery (sodium-nickel chloride) (7,8). The first of these comprises a lithium/aluminium alloy anode, an iron(II) sulphide cathode and utilises a LiCl-KCl eutectic molten salt electrolyte. The overall cell reaction for this is:

$$2\ LiAl_{(s)} + FeS_{(s)} \underset{charge}{\overset{discharge}{\rightleftharpoons}} Li_2S_{(s)} + 2\ Al_{(s)} + Fe_{(s)} \qquad 1.1$$

The cell has an emf of 1.33V and a theoretical energy density of 460Whkg^{-1} (6). The cell is operated at 500°C. Development of cell design and choice of electrolyte is aimed to improve these figures.

The ZEBRA cell utilises the reaction

$$2Na_{(l)} + NiCl_{2(s)} \underset{charge}{\overset{discharge}{\rightleftharpoons}} Ni_{(s)} + 2NaCl_{(s)} \qquad 1.2$$

Electrodes are assembled in the discharged state ie. Ni and NaCl solids and a molten sodium tetrachloroaluminate electrolyte is used in conjunction with β' alumina. This cell has an open circuit voltage of 2.57V and batteries built from these cells have achieved an energy density of 100Whkg^{-1} (9). The cell operates satisfactorily at a range of temperatures between 155°C (the melting point of $NaAlCl_4$) and 400°C.

1.3 **Molten salts as solvents for organic reactions**

Environmental concerns about the use of chlorinated hydrocarbons have made people consider the use of other solvents for organic reactions. The low temperature chloroaluminate molten salt systems are very useful for this since there is no thermal decomposition of the organic products. A reaction for which these molten salts are ideally suited is Friedel-Crafts alkylation.

$$ArH + RX \rightarrow ArR + HX \qquad 1.3$$

These reactions are catalysed by Lewis acids and normally $AlCl_3$ is used. A 2:1 mixture of $AlCl_3$ and methylethylimidazolium chloride (MEIC) provides a molten salt system which can not only act as a solvent for the reaction but can also provide the catalyst.

CHAPTER 2

CONDUCTIVITY MEASUREMENTS: THE EFFECT OF PRESSURE ON THE CONDUCTIVITY OF MOLTEN $NaAlCl_4$

2.1 Introduction

The electrical conductivity of a melt, κ, is defined as the proportionality constant between the current density and the applied electric field.

$$i = \kappa E = F(c_i z_i v_i + c_j z_j v_j) \tag{2.1}$$

where c is the concentration, z is the charge, v is the electrical mobility and i and j are the anion and cation respectively. Since the melt must remain neutral we have

$$c_i z_i + c_j z_j = 0$$

Hence

$$\kappa E = c_i z_i F(v_i - v_j) \tag{2.2}$$

The molar conductivity is defined as

$$\Lambda = \kappa V_m \tag{2.3}$$

where V_m is the volume of melt containing one mole of fully ionised salt. V_m obviously equals the molar mass divided by the density so we have

$$\Lambda = \frac{\kappa M}{\rho} \tag{2.4}$$

When measuring the effect of pressure on the electrical conductivity of a melt it is convenient to use the idea of "activation volumes" to present results. These activation volumes are defined as

$$\Delta V_\kappa = -RT\left(\frac{\partial \ln\kappa}{\partial P}\right)_T \tag{2.5}$$

and

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$$\Delta V_{\Lambda} = -RT\left(\frac{\partial \ln\Lambda}{\partial P}\right)_T \qquad 2.6$$

2.2 Conductivity in molten salts

Electrical conductivity in molten salts arises from the existence of discrete ions which are able to move freely through the melt. At constant temperature the application of an external pressure to a molten salt can affect its conductivity by three different processes. Firstly, since the molten salt is compressible, the pressure can cause a decrease in volume. If the salt is fully ionised then the number of ions per unit volume will increase. This would cause an increase in the melt conductivity; but would not change the molar conductivity. Secondly the increased density would restrict the movement of the ions which would reduce the conductivity. This applies only when the temperature is close to the melting point of the salt. At higher temperatures it has been seen that conductivity can increase with increasing pressure. An explanation for this is that the ions form clusters with larger areas of free space between them. As the pressure increases these clusters are pushed closer together and it becomes easier for ions to jump from one cluster to another. The third process which can affect the conductivity occurs when the melt contains neutral molecules or complex ions in equilibrium with simple ions. It has been shown (10) that increasing pressure tends to favour the formation of complex ions from molecules and of simple ions from complex ions. In both cases the conductivity of the melt would rise.

The pressure effect can sometimes reveal the relative extent to which these three processes occur in different melts. High pressure studies have led to a much fuller understanding of the behaviour of the halides of mercury and bismuth for which conductivity decreases with temperature when the compounds are held under their saturated vapour pressure (11,12).

2.3 Preparation and Purification of sodium tetrachloroaluminate

The purification procedure described here was developed by the author for commercial production of $NaAlCl_4$ at Merck Ltd., Poole.

Sodium tetrachloroaluminate was prepared in the following manner. Sodium chloride (BDH. Analar, 137.1 g) and anhydrous aluminium chloride (BDH. Analar, 318.2 g) were thoroughly mixed together, using a porcelain pestle and mortar, and placed in a 1 litre, 3-neck round bottomed flask. To this flask was attached a filtration tube, a flange neck collecting flask (to allow ease of recovery of the final product) and two electrodes. A diagram of the apparatus is shown in figure 2.1. The flask was placed in a heating mantle and the contents melted under a nitrogen atmosphere. Aluminium chloride tended to sublime out of the mix before it was completely molten. Any problem that this would cause was reduced by keeping the glassware thermally insulated to minimise deposition on the glassware. The sublimation losses meant that an excess of aluminium chloride was required. The melt was at first clear but turned yellowish brown and then black over a period of one hour. Hydrogen chloride gas was then passed through the melt via the sintered frit for half an hour; this gave no visible improvement to the melt. The HCl purge was replaced by a nitrogen purge to remove residual HCl. The purification was completed by carrying out pre-electrolysis.

A voltage of 0.76 V was applied between an aluminium anode

(Goodfellow 99.999%) and a reticulated vitreous carbon cathode (ERG Inc.). This gave rise to a current of c. 500 mA. The electrolysis was carried out overnight (or over a weekend). After this treatment the melt appeared as a fairly clear, colourless liquid. The preparations with extended electrolysis were water clear. The aluminium electrode appeared dark grey and sometimes had corroded. The material on the electrode could easily be washed off with distilled water and was insoluble in water. At this point a clean piece of aluminium could be inserted into the melt and would be untarnished when removed later. Some grey material was deposited on the carbon electrode. This too was insoluble in water. The melt was filtered by applying a vacuum to the collecting flask and drawing the melt through the sintered frit. The melt was then allowed to cool under a nitrogen blanket. The resulting solid was very crystalline and slightly grey in colour. The flask was transferred to the glove-box and the solid broken up and bottled. The solid is very easily broken up and can be formed into a fine powder if necessary. This was not done until the melt was needed to reduce the risk of moisture/oxygen pick up during storage. The solid material was left in large pieces, to reduce the surface area, and placed in an amber glass, screw cap bottle sealed with Parafilm. Experiments carried out at Merck previously showed that polypropylene bottles are attacked by chloroaluminates forming a brown colouring to the bottle.

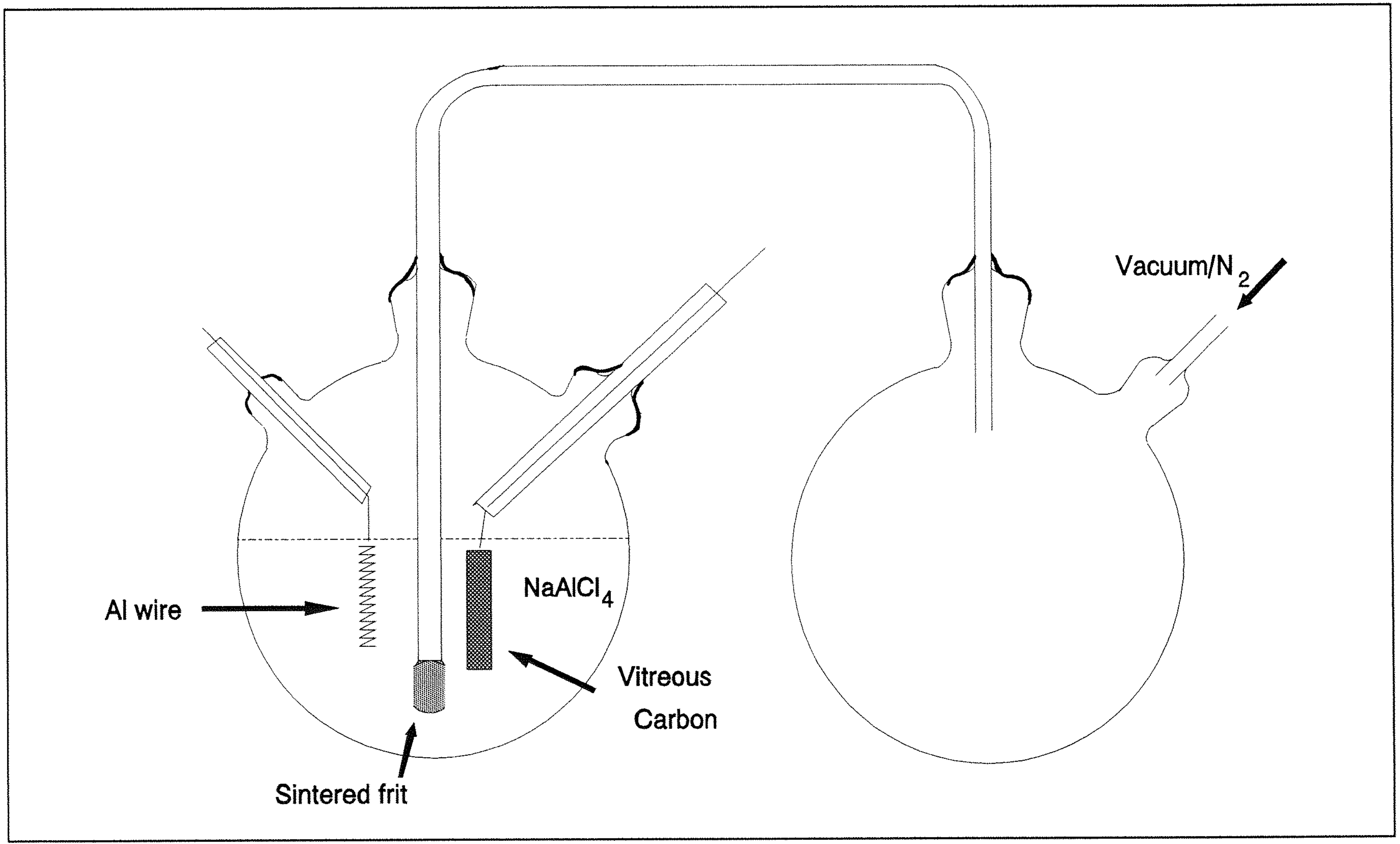

Figure 2.1   Apparatus for sodium chloroaluminate preparation

2.4 Experimental

Conductivity experiments were performed in an externally heated high pressure vessel constructed from Nimonic 105.(13) The base of the vessel was water cooled and fitted with six electrically insulated lead-throughs through which were passed the thermocouple and conductivity leads. Nitrogen was introduced into the furnace from a pressurised holding vessel. This vessel contained 3A molecular sieve to remove any residual moisture from the nitrogen. This was especially necessary in view of the hygroscopic nature of sodium tetrachloroaluminate. Pressures were measured with a Bourdon gauge to an accuracy of ±5 bar
The cell design and experimental set up for these experiments are shown in figures 2.2 and 2.3. The free surface area of the melt is kept to a minimum to reduce the rate of gas dissolution at high pressures. In this way the melt in the conduction path between the electrodes can be kept free from dissolved gas during the time of a typical experiment, approximately 2 hours. Having assembled the glassware and electrodes the solid $NaAlCl_4$ was added to the conductivity cell. The density of $NaAlCl_4$ over the temperature range 150-350°C is 1.6-1.8g/cm^3.(14) Given the volume of the cell, the amount of material, when molten, required to cover the electrodes could be calculated.

The cell assembly was placed in an externally heated pressure vessel and left under a nitrogen blanket at 150 atm at room temperature overnight.
(1 atm =1.01625 x 10^5 Nm^{-2})
Silver leads were used to connect the electrodes to the conductivity bridge. The lead resistances were determined by connecting in series to a 100.0Ω resistor and measuring the total conductivity. The lead resistance was allowed for when calculating the conductivity of the melt. The temperature of the furnace was raised to melt the sample

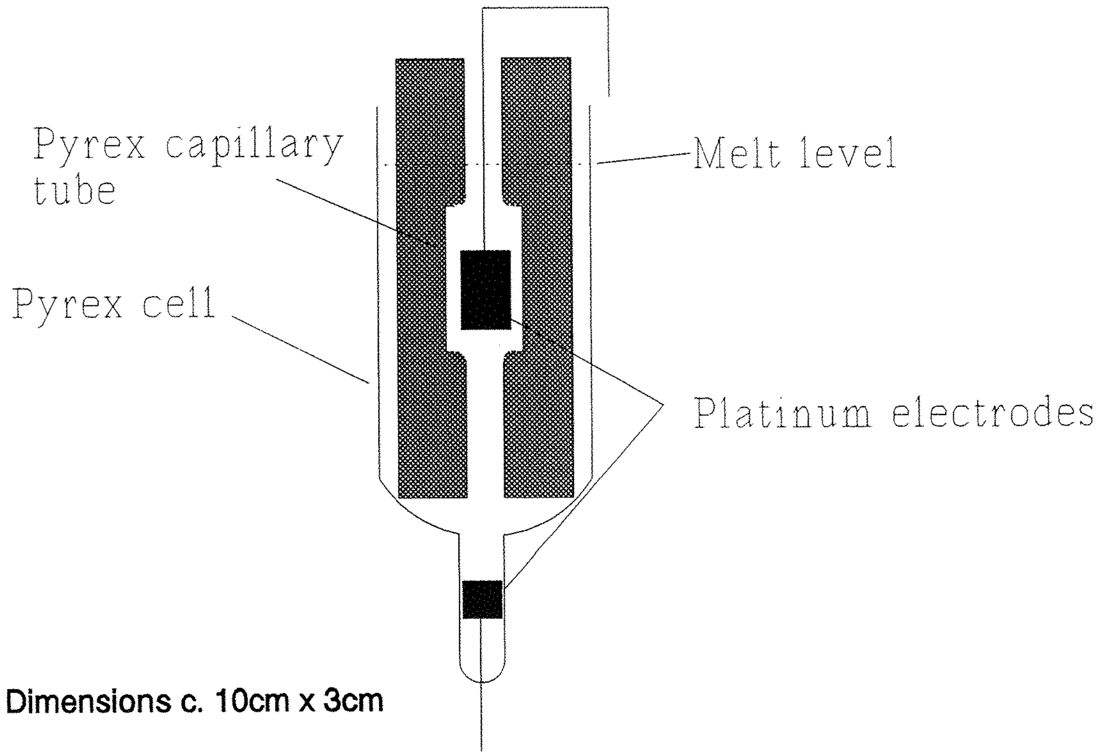

Figure 2.2 Cell design for sodium tetrachloroaluminate conductivity studies (Not to scale)

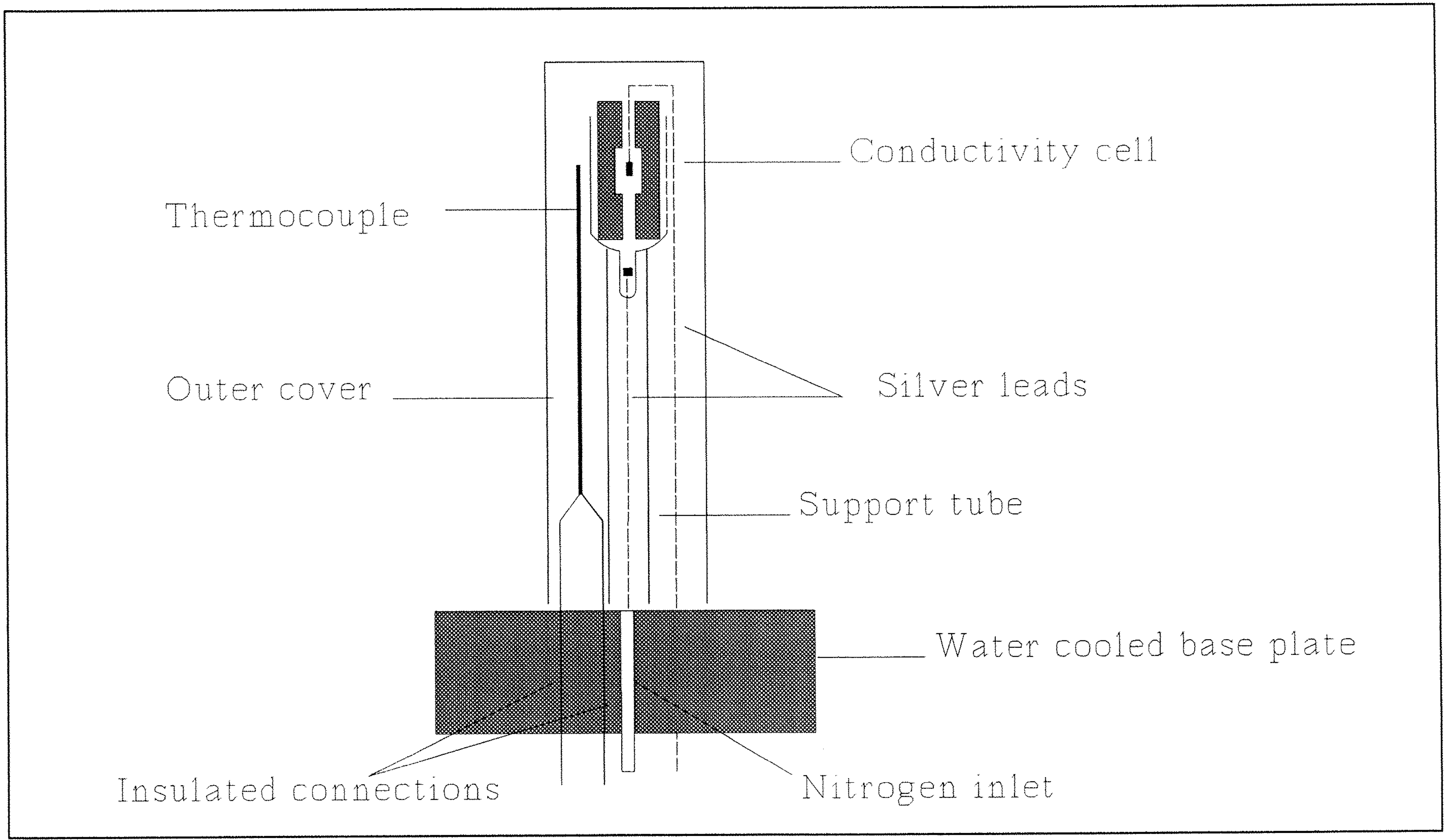

Figure 2.3 Furnace set up for conductivity studies (Not to scale)

and the conductivity measured using a Wayne Kerr Universal Bridge B221A over a pressure cycle 100-1000-100 atm. After each pressure change the temperature of the furnace was allowed to return to the original value. This normally took between 10 and 30 minutes. Cell constants were determined by extrapolating back to 1 atm and comparing with literature data.(15) These figures compared favourably with those determined experimentally by use of a standard KCl solution (see Chapter 4). This information was useful as it confirmed both the composition of the $NaAlCl_4$ melt and the similarity of different cells.

The experiment was repeated at temperatures from 175°C to 400°C and graphs were plotted of ln conductivity vs. pressure.

2.5 Results

Data obtained from the above experiments are shown in Appendix 1. Figures 2.4-2.11 show the plots of ln conductivity vs. pressure. For most of the graphs it can be seen that different values were obtained for ascending and descending pressure. However, all results lie on straight lines which indicate that the discrepancy is due to slight changes in the nature of the material itself. Possible changes that can occur in the melt are discussed later.

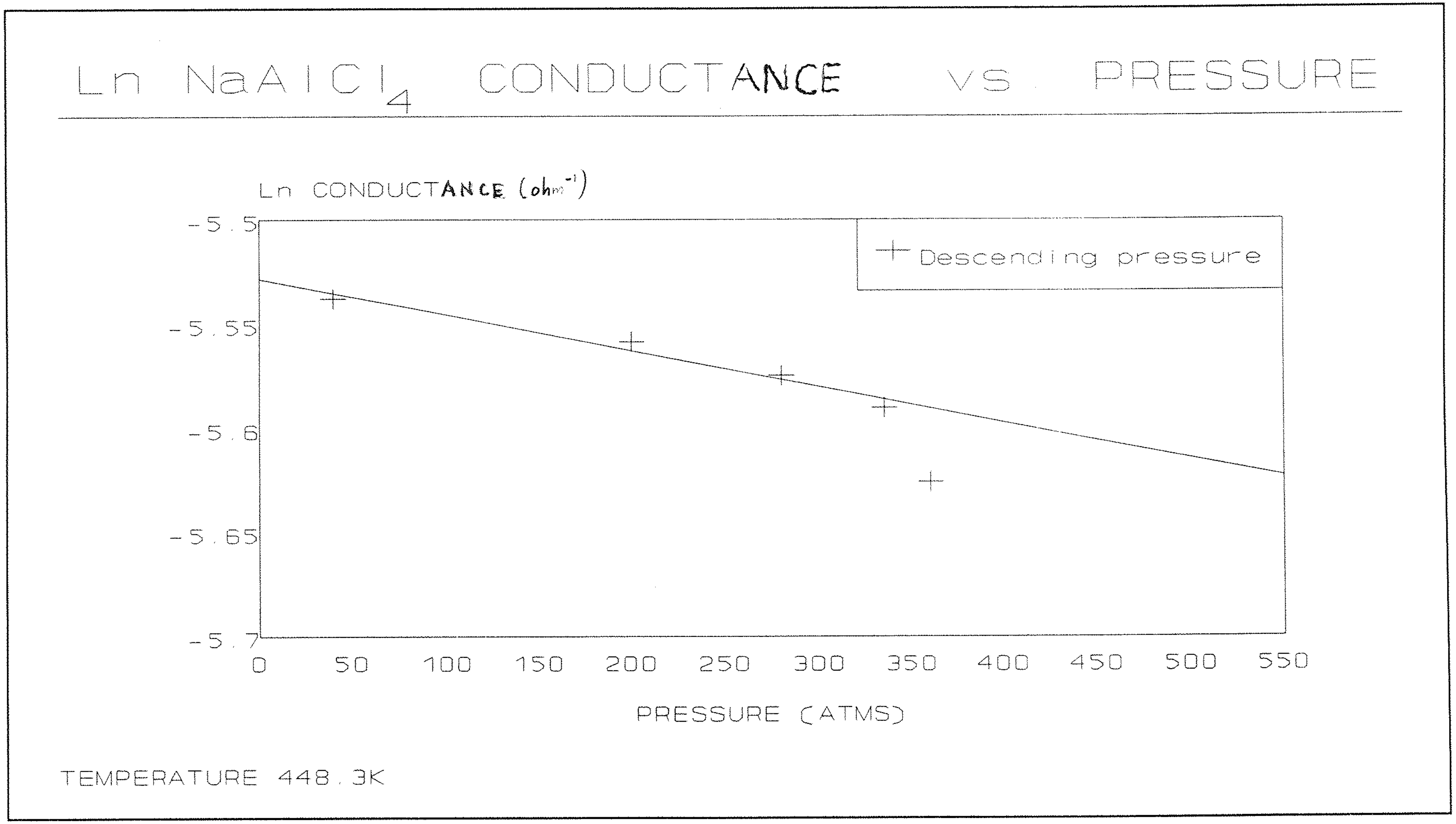

Figure 2.4 ln conduct**ance** vs. Pressure for $NaAlCl_4$ at 449K

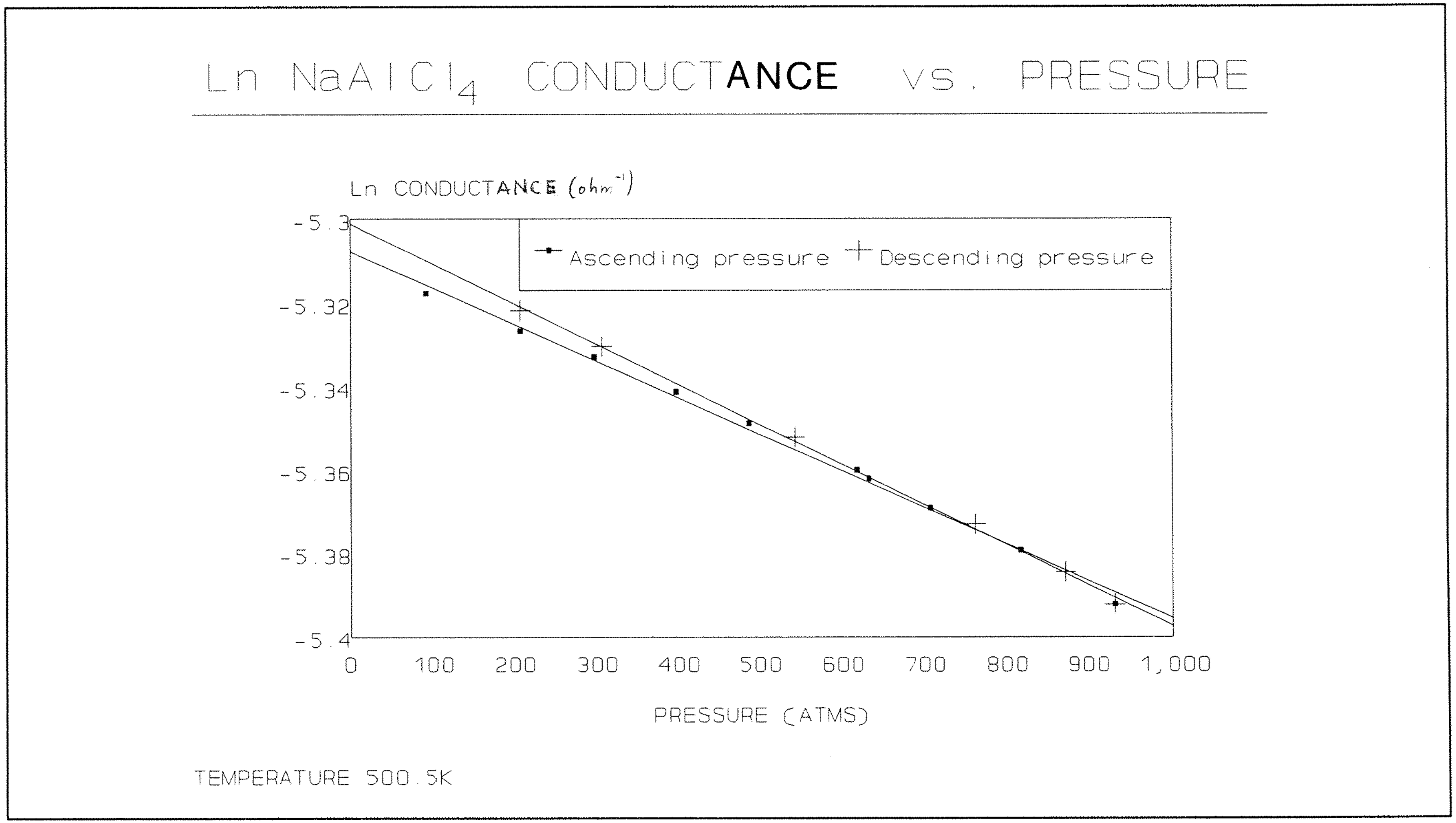

Figure 2.5 ln conductance vs. Pressure for $NaAlCl_4$ at 500K

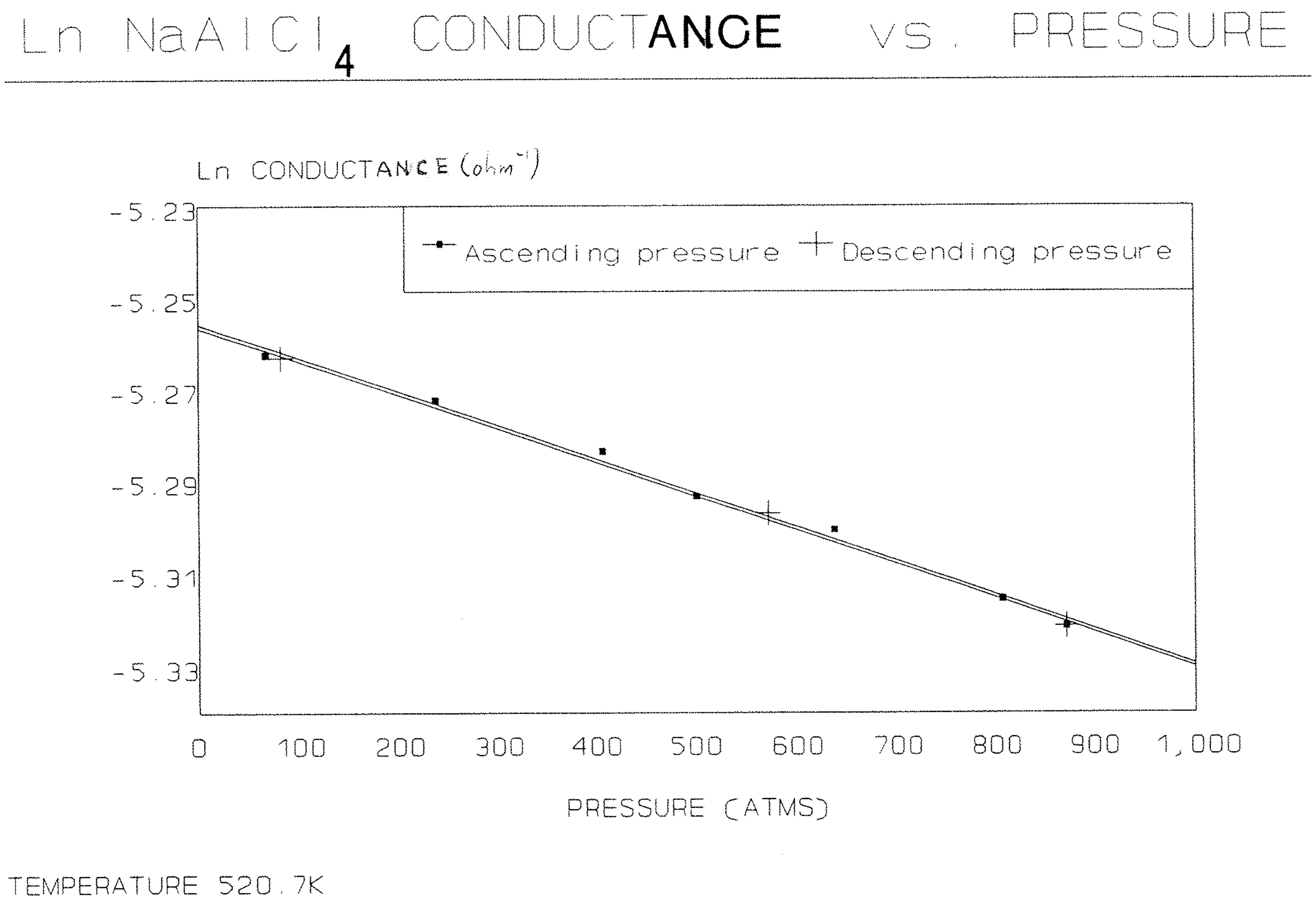

Figure 2.6 ln conduct**ance** vs. Pressure for $NaAlCl_4$ at 521K

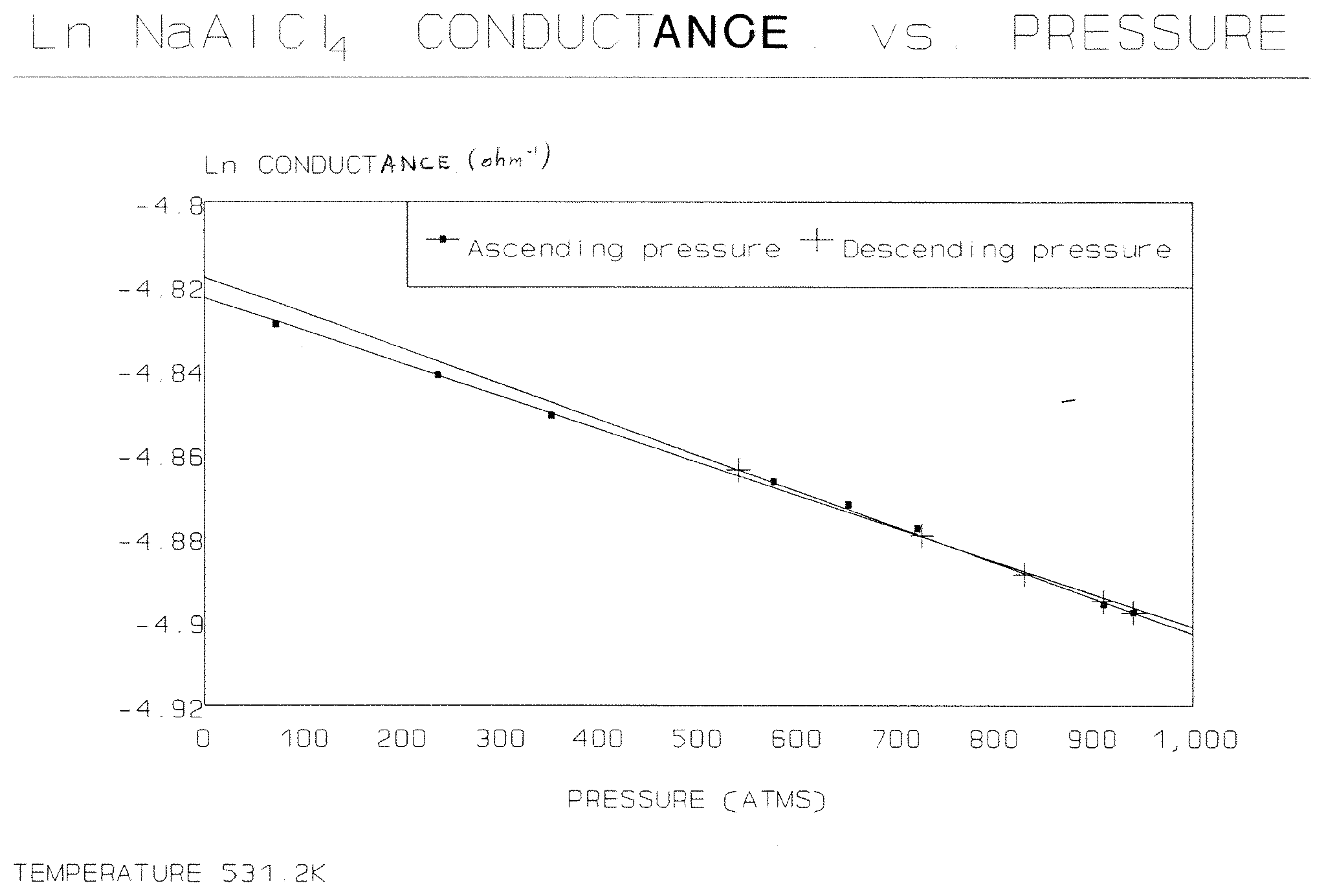

Figure 2.7 ln conduct**ance** vs. Pressure for $NaAlCl_4$ at 637K

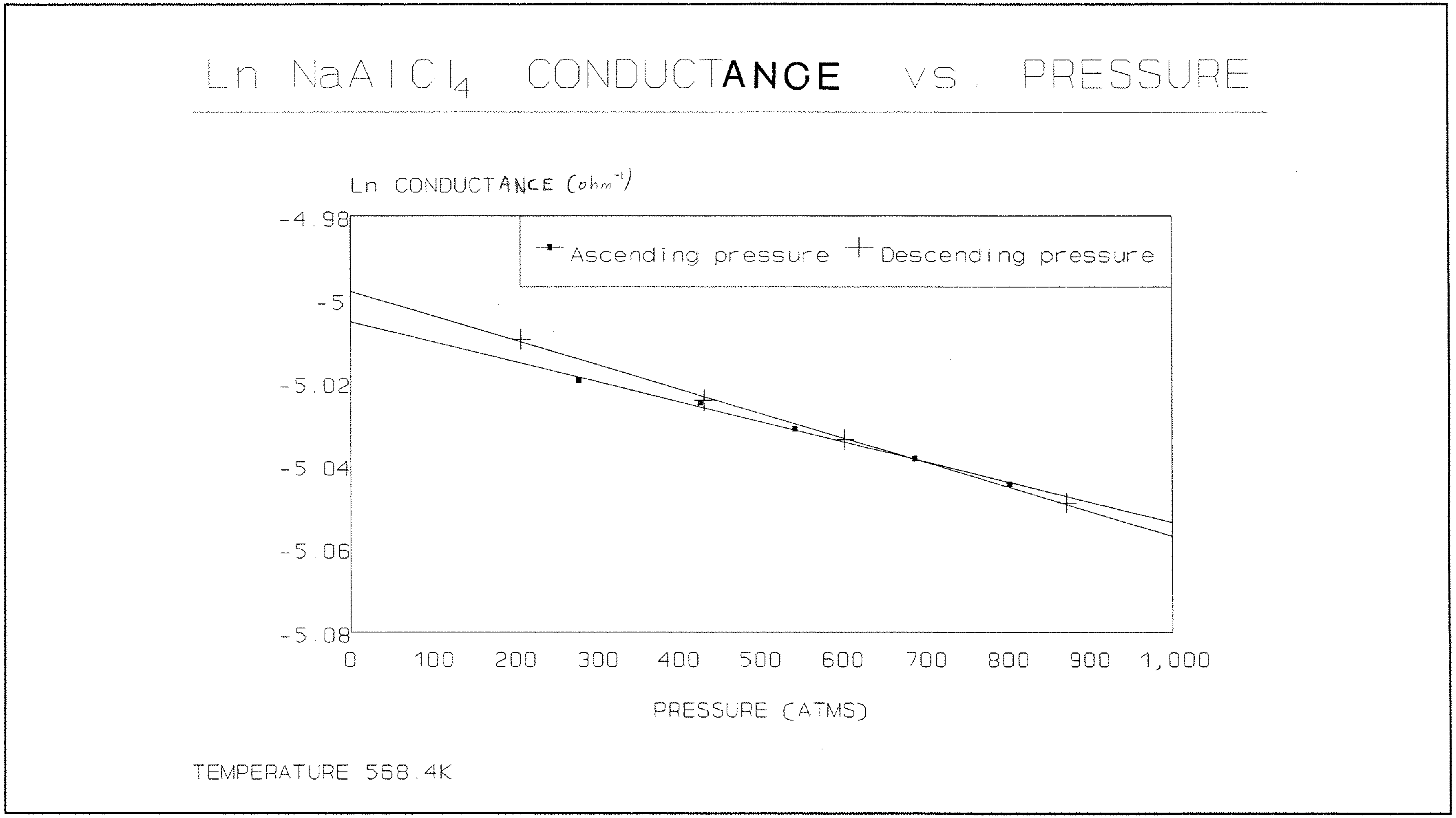

Figure 2.8 ln conduct**ance** vs. Pressure for $NaAlCl_4$ at 568K

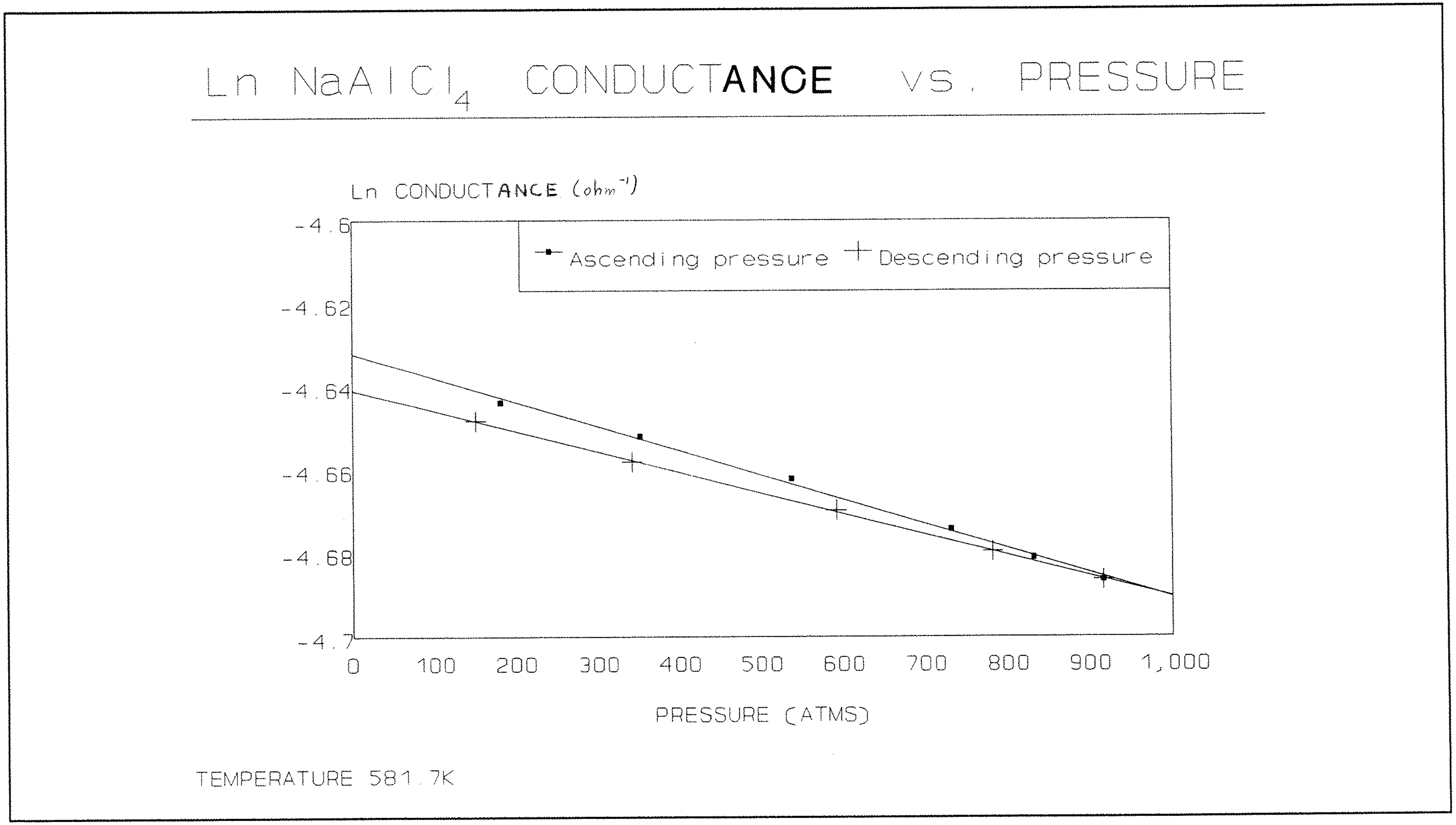

Figure 2.9 ln conduct**ance** vs. Pressure for $NaAlCl_4$ at 582K

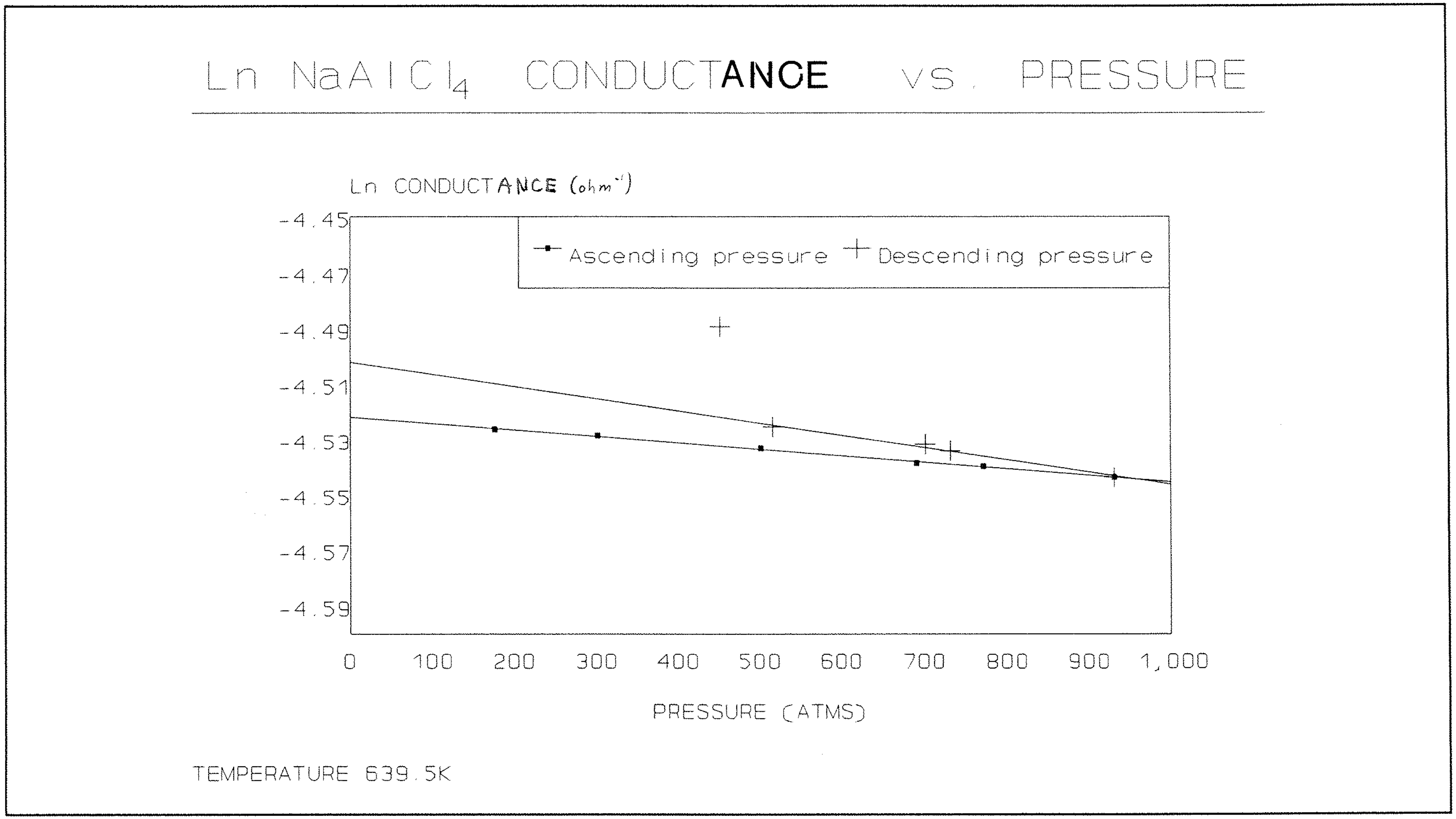

Figure 2.10 ln conduct**ance** vs. Pressure for $NaAlCl_4$ at 500K T

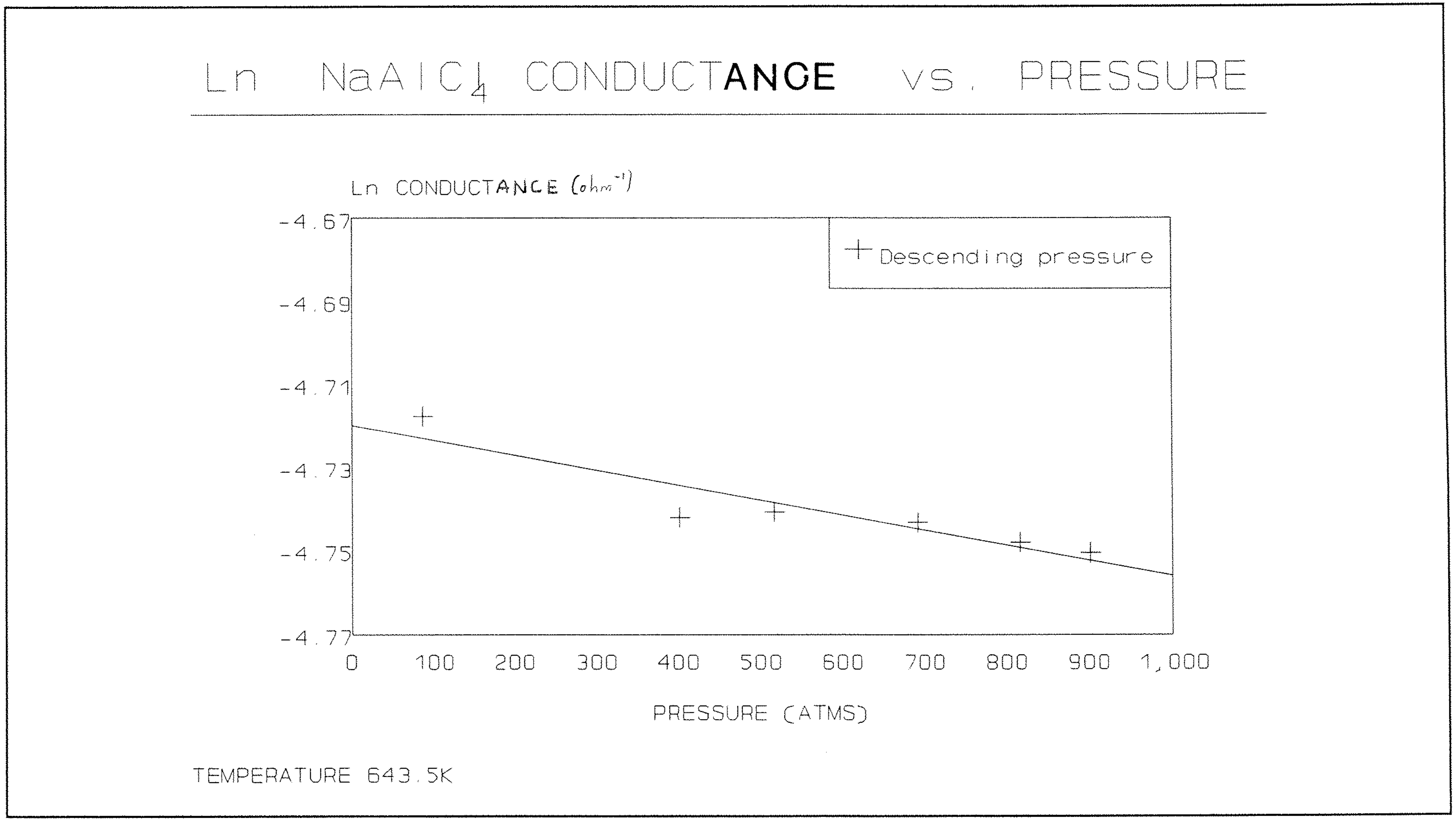

Figure 2.11 ln conduct**ance** vs. Pressure for $NaAlCl_4$ at 643K

Occasional results shown on the graph are obviously spurious. In figure 2.4 the melt began to freeze at a pressure of c. 350 atm. This caused a large decrease in the conductivity. Reducing the pressure allowed further measurements to be made. However, when the activation volume is calculated from these data the value obtained does not fit in with the other data. It is likely that the freezing of the melt affected the cell making the results obtained unreliable. In figure 2.10 the cell ruptured causing a sharp rise in the conductivity of the melt. These spurious values were omitted from the analysis of the data.

Linear regression by a least squares method of each set of results gave, where possible, two values for the activation volume at each of the temperatures studied. These are shown in Table 2.1. It is noteworthy that the uncertainty (expressed as 95% confidence limits) for individual runs with either ascending or descending pressure is smaller than the difference between these values. This must be attributed to changes in the melt composition, which is discussed more fully in section 2.6. By plotting these values against temperature it is possible to compare the data with that from other molten sodium salts such as nitrate, nitrite and perchlorate (16,17). This is shown in figure 2.12. It can be seen that the present results fit in well with the pattern obtained previously.

Temperature (°C)	Activation volume (cm^3 mol^{-1}) (Ascending pressure)	Activation volume (cm^3 mol^{-1}) (Descending pressure)
175		6.3 ± 1.2*
227	3.6 ± 0.16	3.9 ± 0.16
247	3.2 ± 0.16	3.2 ± 0.16
258	3.3 ± 0.26	3.7 ± 0.04
295	2.3 ± 0.15	2.8 ± 0.12
308	2.8 ± 0.14	2.4 ± 0.52
366	1.2 ± 0.06	2.3 ± 0.31
370		1.9 ± 0.70*

*Only one set of data obtained

Table 2.1

Activation volumes for sodium tetrachloroaluminate

2.6 Discussion

Changes in the melt can arise from a loss of aluminium chloride by sublimation, reaction with moisture in the blanketing gas or by the presence of dissolved gas in the melt. It is probably the last two of these factors that are most important since the application of pressure would reduce the rate of sublimation of $AlCl_3$. Despite being dried over a molecular sieve prior to use there would still be a small amount of moisture in the blanketing gas. Reaction between this moisture and the melt would be expected and would form an oxide species following the reaction

$$2\,AlCl_4^- + H_2O \rightarrow Al_2OCl_5^- + Cl^- + 2HCl$$

This would alter the physical properties of the melt quite considerably. This is discussed in more detail in the next chapter.

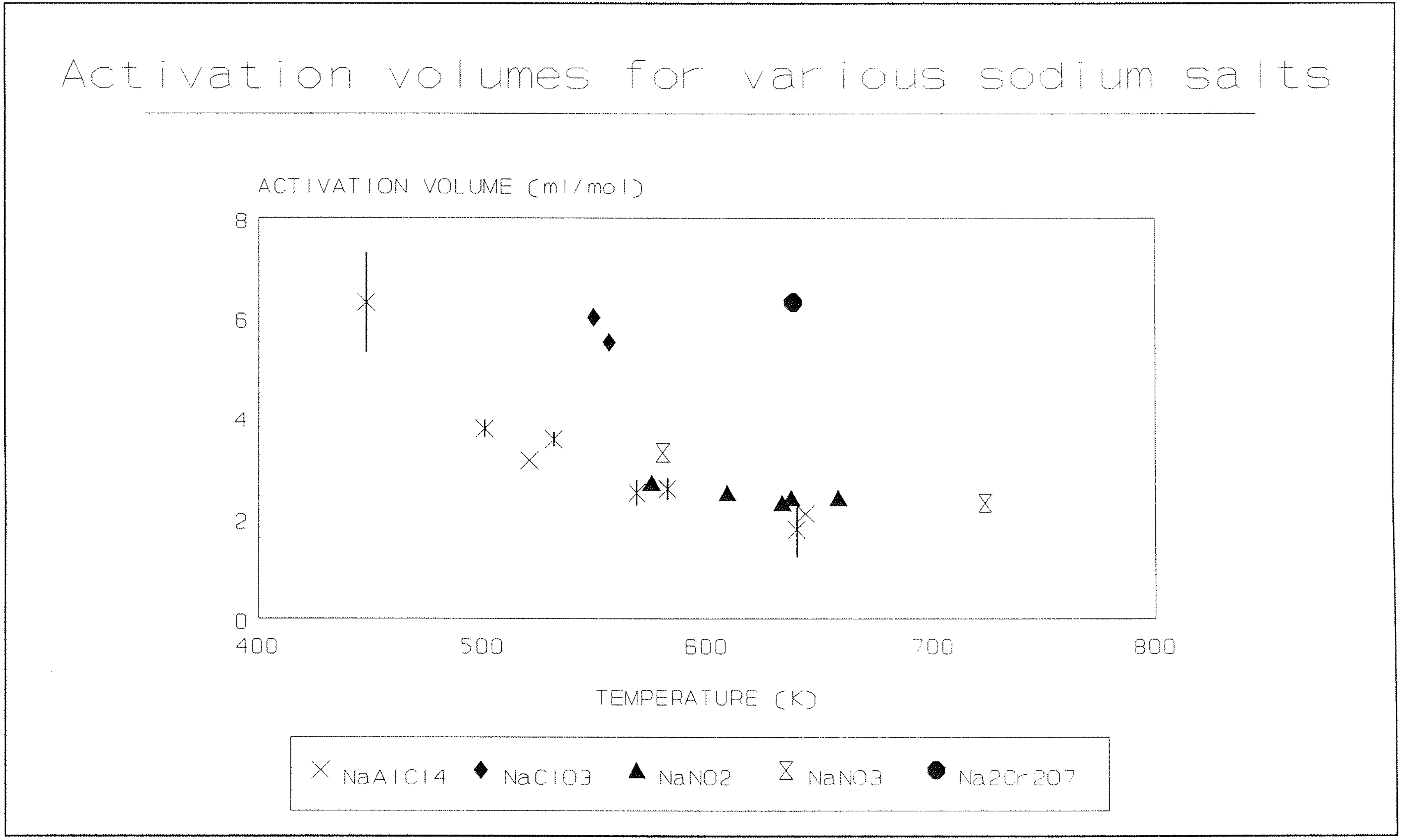

Figure 2.12 Activation volumes vs. Temperature

The effect of dissolved gas in melts is discussed briefly by Barton, Cleaver and Hills.(17) No firm predictions about the effect of dissolved gas can be made but, in the case of sodium nitrate, a small increase in apparent ΔV was noticed when nitrogen saturated samples were studied. It is likely that this would also occur in $NaAlCl_4$ melts but the effect would be fairly small; measurements made on stable salts using the cell design shown in figure 2.2 did not show hysteresis on pressure cycling, which indicates that contamination by dissolved gas should not occur in the time scale of the experiments.

Previous studies(16) have indicated that the activation volumes for a range of salts with a common cation follow a sequence of the anion volumes. For a series of oxy anions this series is

$$NO_2^- < NO_3^- < ClO_3^- < Cr_2O_7^{2-}$$

$AlCl_4^-$ is tetrahedral and the Al-Cl bond length is 2.13Å(18), ClO_3^- is pyramidal with the Cl-O bond length of 1.57Å(19) but an electron lone pair occupies the fourth tetrahedral position. NO_3^- is planar with a N-O bond length of 1.24Å(20). According to the previous discussion the activation volume for $NaAlCl_4$ should be greater than for $NaNO_2$ or $NaNO_3$ (which is the case at lower temperatures) and also that for $NaClO_3$ (which is not the case). However, there is reason to believe that the result for $NaClO_3$ is anomalously high because of the proximity of the glass transition temperature(16).

CHAPTER 3

DEVELOPMENT OF A RUGGED REFERENCE ELECTRODE FOR USE IN CHLOROALUMINATE MELTS

3.1 Introduction

Development of alternative power sources has been extensive over the last two decades. The need to replace diminishing fossil fuels and, more recently, environmental concerns have led to the development of many secondary battery systems which have applications in load levelling and also for electric vehicle propulsion. Many of these systems use molten inorganic salts as electrolytes because of their high electrical conductivity. One such material is sodium tetrachloroaluminate ($NaAlCl_4$).

As can be seen from the phase diagram of the sodium chloride-aluminium chloride system (figure 3.1) the liquidus temperature of $NaCl-AlCl_3$ mixtures changes markedly on going through the 50-50 mol% region. Other properties, such as the solubility of $NiCl_2$ and other inorganic salts, also vary greatly around this region. It is therefore desirable to be able to determine the exact composition of a given melt. This does not pose a serious problem in small scale manufacture but for large industrial processes it is a major consideration. Small preparations can be done in closed containers with accurately weighed starting materials. However, these methods can not be used for large scale manufacture so it is necessary to monitor the composition continuously and be able to adjust it if necessary.

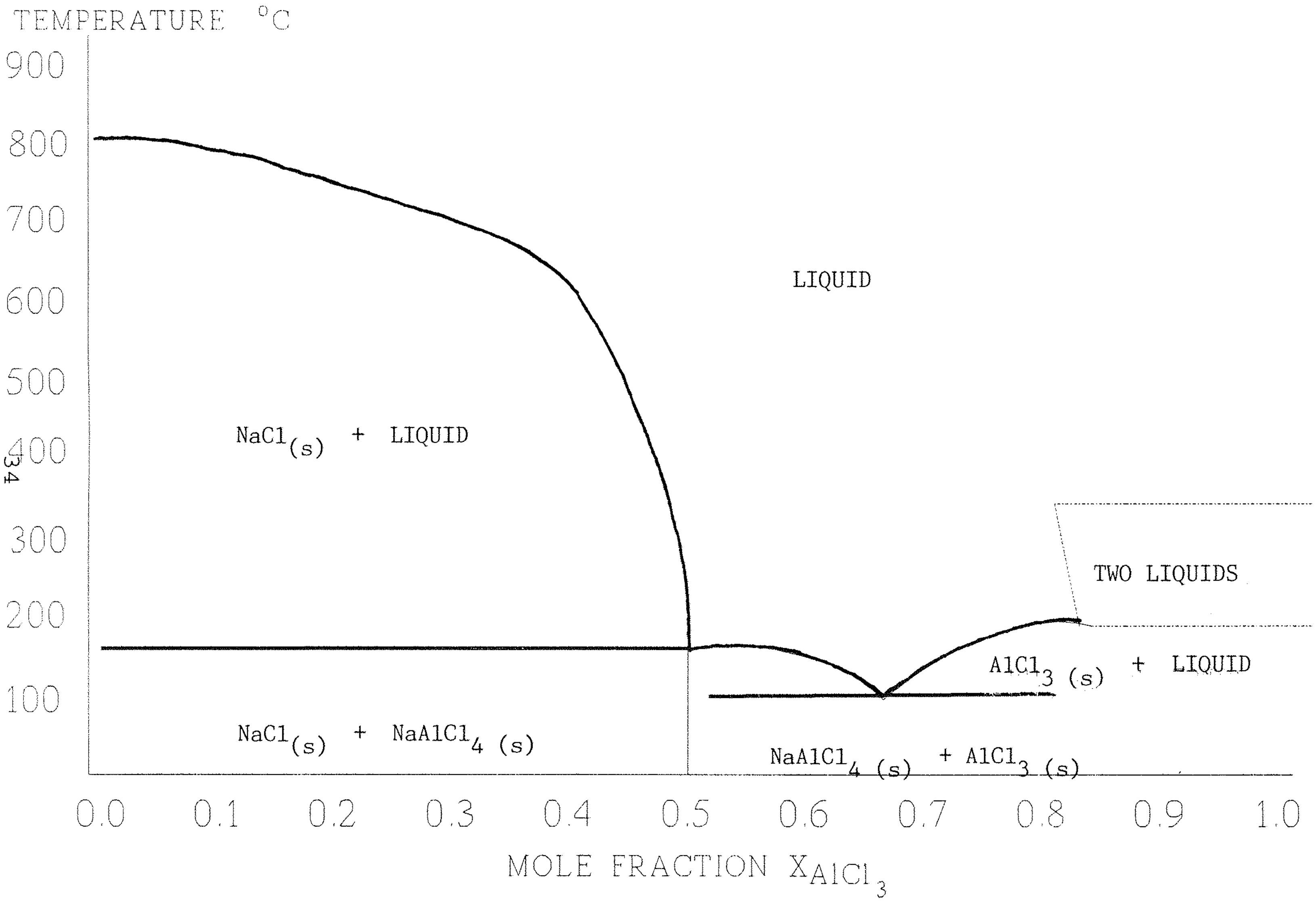

Figure 3.1 Phase diagram for the NaCl-$AlCl_3$ system

3.2 Acid base properties of $NaAlCl_4$

One physical property that can be measured fairly easily is the acidity of the melt. $NaAlCl_4$, in the molten state, consists of Na^+ cations and $AlCl_4^-$ anions. It has been demonstrated that these complex anions undergo dissociation according to

$$2AlCl_4^- \rightleftharpoons Cl^- + Al_2Cl_7^- \qquad 3.1$$

This is similar to the dissociation of water

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

In the same way as an equilibrium constant for water is obtained by assuming the activity of H_2O is unity it is possible to obtain an equilibrium constant for the chloroaluminate system by assuming the activity of $AlCl_4^-$ is unity. By replacing activities with concentrations this leads to

$$K_i = [Al_2Cl_7^-]\,[Cl^-] \qquad 3.2$$

Other equilibria have been reported involving species such as $Al_3Cl_{10}^-$ but calculations of equilibrium constants indicate that the concentration of these species is very low in the range of compositions near the equimolar region.(21)

The idea of acidity in chloroaluminate melts has been put forward by Tremillon *et al.*(17) They defined an acid as an acceptor of Cl^- (or donor of $Al_2Cl_7^-$) and a base as a donor of Cl^- (or acceptor of $Al_2Cl_7^-$). Addition of an acid to $NaAlCl_4$ causes the following equilibrium to be set up.

$$acid + 2\,AlCl_4^- \rightleftharpoons base + Al_2Cl_7^- \tag{3.3}$$

An acidity constant can then be defined by

$$K_A = \frac{[base]\,[Al_2Cl_7^-]}{[acid]} \tag{3.4}$$

(This again assumes the activity of $AlCl_4^-$ to be unity)

It is possible to measure the acidity of a melt by determining the concentration of Cl^- ions. The chloride potential is defined by

$$pCl^- = -\log a_{(Cl^-)} \tag{3.5}$$

(This is again analogous to the situation for water)

For a stoichiometric $NaAlCl_4$ melt, where the concentration of Cl^- is equal to the concentration of $Al_2Cl_7^-$, pCl^- would equal $\frac{1}{2}pK_i$. For a 1M solution of NaCl (which can not actually be attained due to the low solubility of NaCl in $NaAlCl_4$) pCl^- would be zero, and for a 1M solution of $AlCl_3$ $pCl^- = pK_i$.

Hence, any melts with $pCl^- > \frac{1}{2}pK_i$ are defined as acid solutions and melts with $pCl^- < \frac{1}{2}pK_i$ are defined as basic solutions. In particular melts with a ratio of $AlCl_3$:NaCl > 1:1 are acidic and melts with a ratio < 1 are basic.

The simplest method which can be used to determine the concentration of Cl^- utilises the fact that an electrochemical redox system will depend upon the concentration of Cl^-. The obvious choice for a redox system in chloroaluminate melts would be one which involves an aluminium electrode. The reaction at this electrode is in basic melts

$$AlCl_4^- + 3e^- = Al\downarrow + 4\ Cl^- \qquad 3.6$$

and in acidic melts

$$4Al_2Cl_7^- + 3e^- = Al\downarrow + 7AlCl_4^- \qquad 3.7$$

From the Nernst equation the equilibrium potential of this electrode can be given by

$$E = (E_o^O)_{Al} - \left(\frac{4RT}{3F}\right)\ln[Cl^-] \qquad 3.8$$

For any measurements made using this electrode system a suitable reference electrode needs to be developed. This work is detailed in the next section.

3.3 Experimental

The development of a reference electrode for this work has to take into account many factors. Amongst these are the stability of the potential, low cost, ease of use, long life and ease of storage.

Initial experimental work involved separation of an equimolar sodium tetrachloroaluminate melt reference electrode from the main body of melt using a sintered frit.(23) This allows good ionic conductivity but has the disadvantage of making the electrode only usable once, since on cooling the assembly the liquid in the sinter would freeze, expand and destroy the sinter. To overcome this problem a sealed unit had to be developed. The design for this is shown in figure 3.2. The glass bulb has to be made reasonably thin so as not to provide too much electrical resistance. The liquid junction potential across a Pyrex membrane is reported to be less than 1mV.(24)

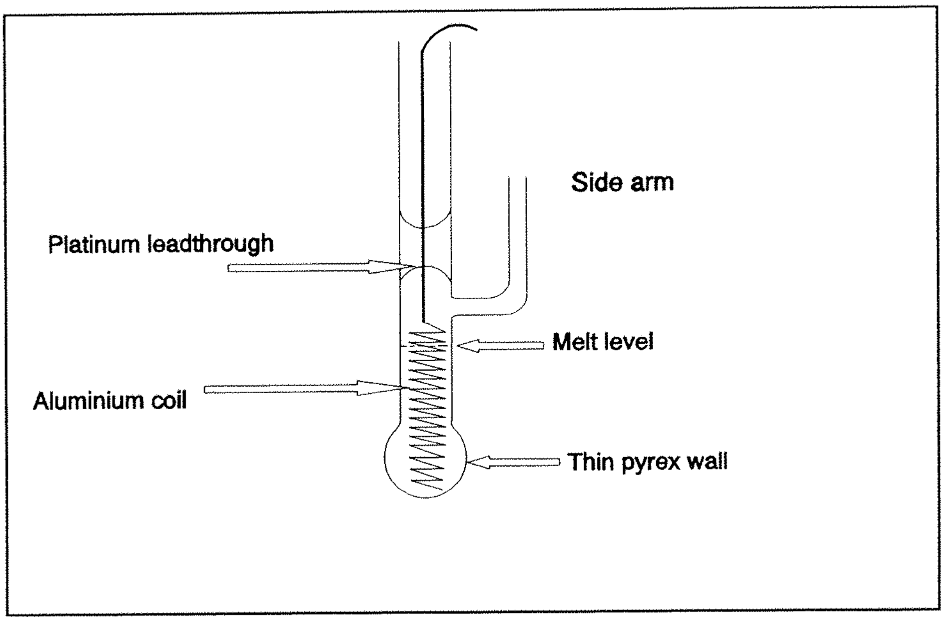

Figure 3.1 Initial electrode design.

The method of filling was as follows. After the glassware had been made, a prepared mix of aluminium chloride and sodium chloride (66.6 mol% $AlCl_3$) was added through the side arm. When the electrode was filled to the required level the side arm was sealed under vacuum. The solid material was then melted using a hot air blower. This caused a reduction in volume so that just the bulb was filled with melt. The side arm was then sealed nearer the main body of the electrode to enable easier manoeuvring. This secondary sealing proved difficult because of a build up of pressure during the melting phase; when the glass was hot the cell sometimes burst. This pressure build up could be due to aluminium chloride vapour which sublimed from the melt, or to hydrogen chloride which would be evolved if any residual moisture was in the system.

Having designed the cell, attention was then focused on the electrode reaction. Initial experiments utilised an aluminium wire in a 66 mol% $AlCl_3/NaCl$ melt. Reasons for choosing this system are that any breakage of the probe would cause minimal contamination by foreign ions to the melt being tested. The 2:1 composition was chosen on the grounds that a sodium chloride saturated melt, which would be an alternative possibility, is reported to be slow to achieve equilibrium. Additionally, as can be seen from the graphs of potential vs. composition shown in figures 3.3 and 3.4, the potential is less susceptible to small changes in composition at higher concentrations of $AlCl_3$.

Procedure

An electrode was constructed, as described above, from Pyrex. This was placed into a 100ml three-neck, round bottomed flask containing 81.46g of a sodium chloride saturated $AlCl_3/NaCl$ melt. The system was thermally insulated and held at a temperature of 195°C. An initial potential of 190mV was measured between the reference electrode and a pure aluminium wire in the bulk of the melt. This was far lower than the expected figure of c. 500mV. A tungsten counter electrode was placed in the melt and a coulometric addition of Al^{3+} attempted. A charge integrator was placed in the circuit and a potential of 2.0V was applied between the aluminium and tungsten

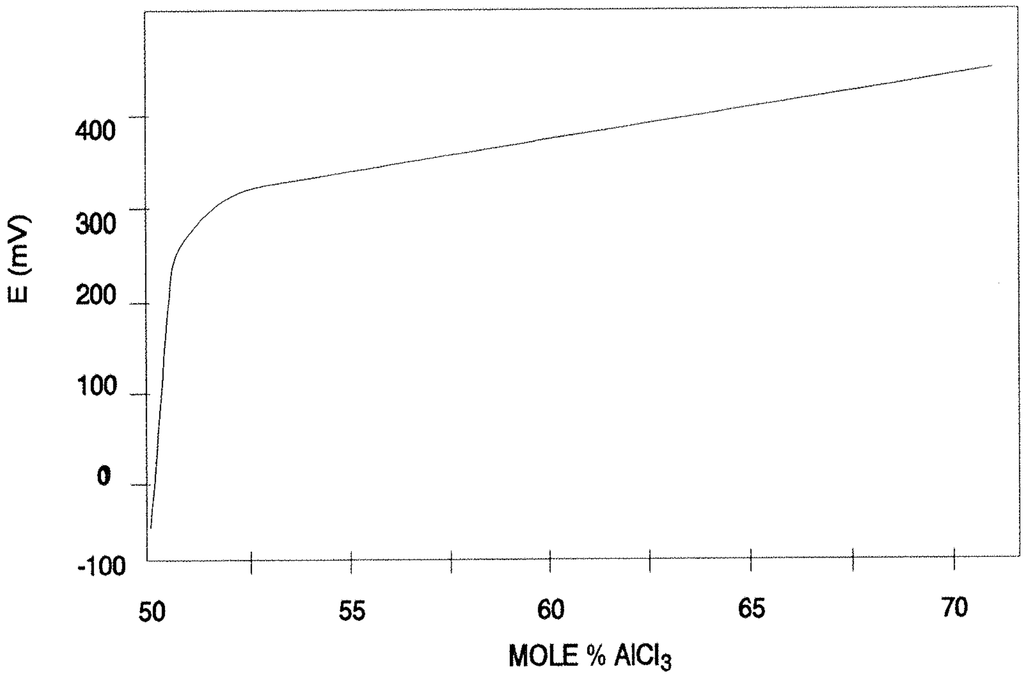

Figure 3.3 Potential of Al wire in sodium chloroaluminate melt

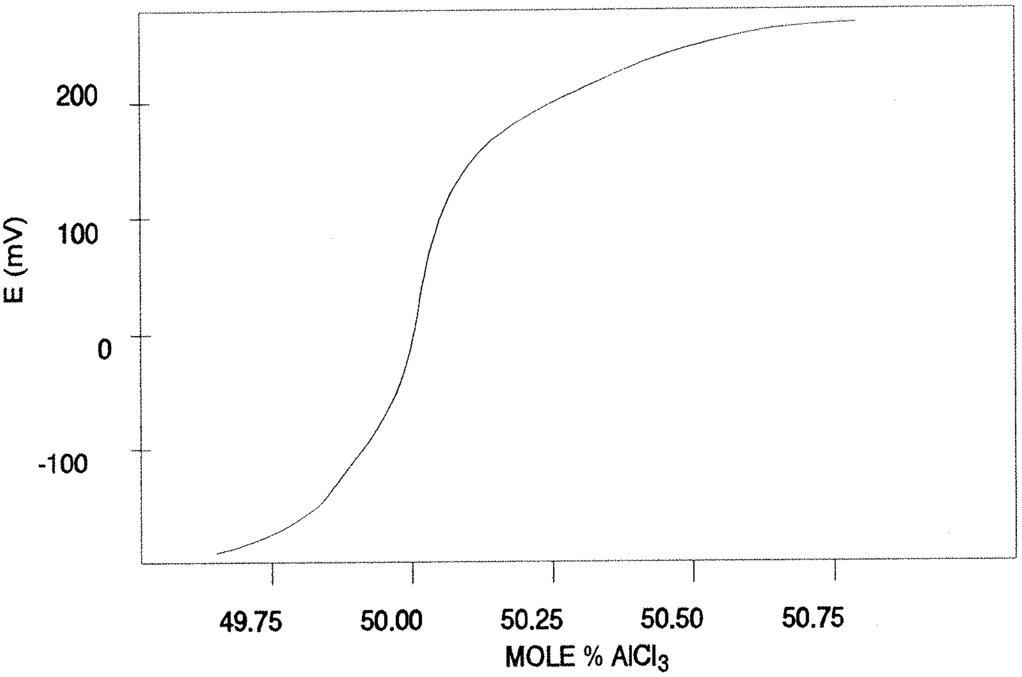

Figure 3.2 Potential of Al wire in sodium chloroaluminate melt

electrodes. The potential between the aluminium and reference electrode was measured periodically and seen to be fluctuating by ± 10mV, even after passing 500 coulombs through the melt. This experiment was repeated with a new reference electrode and similar results were obtained. In both these experiments the measured potential was expected to fall by several hundred mV, but did not do so. Another electrode was constructed in a similar fashion using soda glass (which has a greater conductivity). When this electrode was used as before an initial potential of 550mV was measured. An electrochemical method of changing the melt composition was again attempted, but no corresponding change in potential was observed. It was concluded that this method for changing the melt composition was ineffectual, so a different method was adopted. A gravimetric method was tried. Accurately weighed amounts of $AlCl_3$ were added to the bulk melt and the potential measured. This had the expected effect of reducing the potential but the reference electrode broke before many results were obtained. This failure in the reference electrode was noticed in all the previous experiments and was caused by failure of the platinum aluminium join. Additionally it was noticed that, when in use, appreciable amounts of $AlCl_3$ had sublimed into the top of the probe. This was undesirable since it would change the melt composition, and consequently the potential, quite considerably. This problem seemed to be progressive in that more $AlCl_3$ sublimed out each time the electrode was used. To overcome both these problems a new electrode system was tried. This comprised a $NaCl/NiCl_2$ saturated $NaAlCl_4$ melt and a nickel wire. The design is shown in figure 3.5. This system was an improvement inasmuch as the use of a NaCl saturated melt alleviated the $AlCl_3$ sublimation problems, and the nickel wire could be attached to the platinum leadthroughs much more strongly.

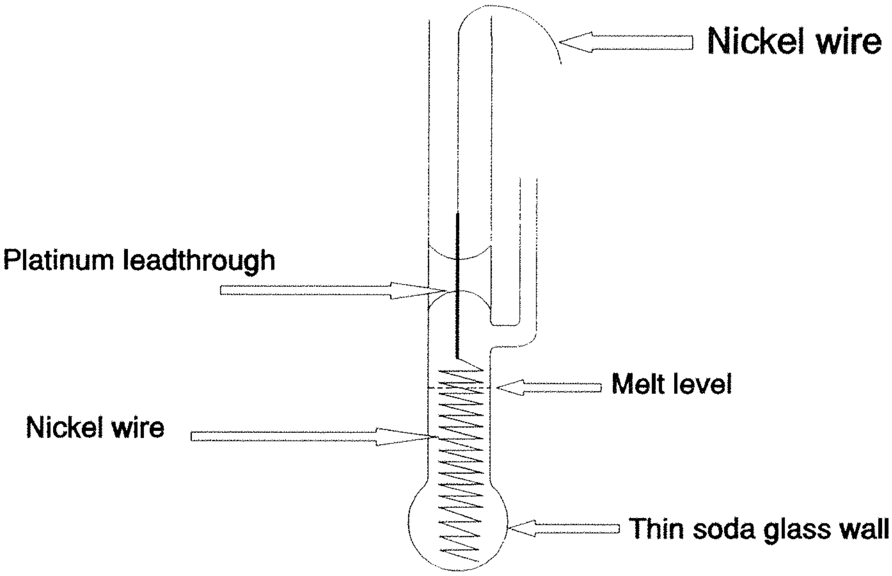

Figure 3.5 Nickel reference electrode

A reference electrode was constructed as shown in figure 3.5 from soda glass. A mix of purified $NaAlCl_4$ (4.57g), $NiCl_2$ (0.02g) and NaCl (0.05g) was prepared. This would be saturated in both NaCl and $NiCl_2$.(25) This electrode was placed in a sodium chloride saturated $NaAlCl_4$ melt along with an aluminium counter electrode. An initial potential of 1079mV was measured. Addition of $AlCl_3$ to the bulk melt was carried out gravimetrically and the potential measured. The expected S-shaped curve was obtained (see figure 3.5). Removal of the electrode and reinsertion into the melt showed that the measured potentials were reproducible within ±5mV.

3.4 Results

Use of Pyrex in the manufacture of the aluminium chloride rich electrode gave no meaningful results. However, use of Pyrex with the nickel based system was not tried. The liquid junction potential across a Pyrex membrane is reported to be negligible so it is possible that the nickel probe would work with Pyrex. This would be beneficial in both cost of material and ease of construction. However, for use near the melting point of $NaAlCl_4$ (156°C), the higher impedance of Pyrex would probably make its use impracticable. Experiments on the freeze-melting behaviour of the probe indicated that it would stand at least 15 cycles which would be suitable for industrial purposes.

Results obtained using the soda glass and aluminium electrode indicated that the electrochemical side of the probe would work sufficiently well if sublimation losses could be minimised. This could be done by raising the temperature of the whole probe which could not be done in the experimental set up described. However, the most important factor in this cell was the fragility of the platinum aluminium joint. The aluminium and platinum were spot welded together for this work which is highly unsatisfactory and it is virtually impossible to weld aluminium to platinum. Since aluminium will not seal into Pyrex or soda glass another metal had to be found. Nickel could be attached to platinum satisfactorily and could be used to obtain reproducible results. These results are shown in figure 3.5.

3.5 Discussion

It was stated earlier that NaCl takes a long time to reach equilibrium in $NaAlCl_4$, and recent studies(25) indicate that $NiCl_2$ behaves in a similar fashion. It may appear that the use of such a system would not be suitable. This may be true for obtaining very precise measurements, but the use of this electrode in industry would be to provide a quick indication of the melt composition. Conditions which are rigorously controlled in a small research laboratory, such as temperature and blanketing atmospheres, are difficult to maintain in large scale production. Thermal convection within a bulk melt would be considerable and temperatures are commonly measured to ±5°C. The effect of this temperature variation would probably outweigh the solubility effects within the reference electrode. Even so, it is the case that solid NaCl and $NiCl_2$ are present in the reference melt, and the potential determining process may involve the solid rather than solvated species. If this is so the question as to whether or not the melt is saturated with either $NiCl_2$ or NaCl becomes irrelevant. This point could be investigated by further experiments.

3.6 Conclusion

An electrode based on the reaction between Ni^{II} species and Ni metal has been constructed and successfully demonstrated as a suitable reference electrode for the potentiometric determination of composition in molten mixtures of NaCl and

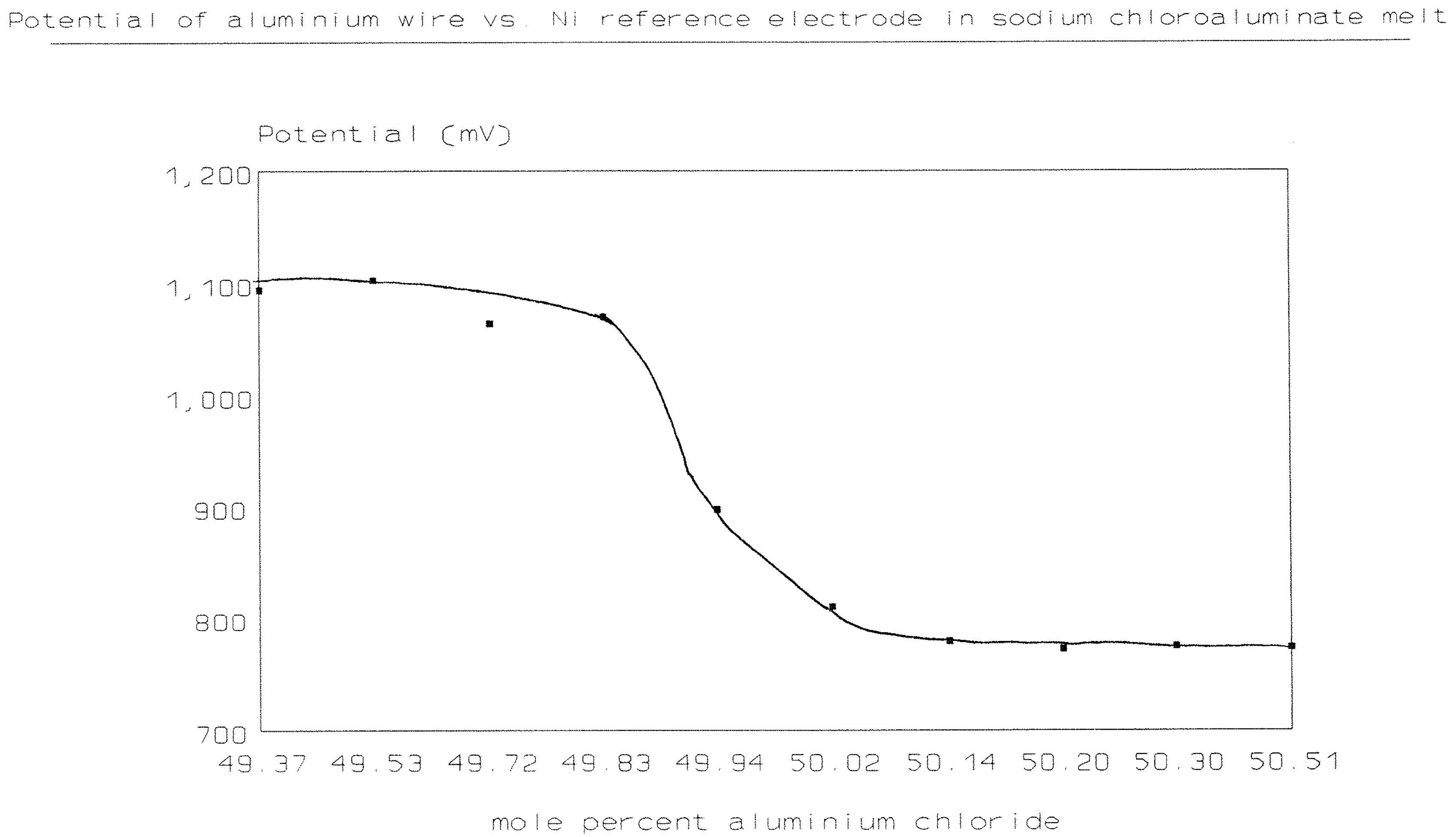

Figure 3.5 Potential of Al wire vs. a Ni wire in $NiCl_2$ saturated sodium chloroaluminate melt

$AlCl_3$. The durability of the electrode makes it useful as a method of quality control in the industrial preparation of chloroaluminates. Use of a similar electrode has since been reported(26) and gives similar results. This electrode has been taken to higher temperatures than were used in this study and has still performed well.

CHAPTER 4

EFFECT OF PRESSURE ON THE DECOMPOSITION EQUILIBRIUM IN MOLTEN NITRATE SYSTEMS

4.1 Theory of nitrate decomposition

When fused potassium nitrate is heated in air at atmospheric pressure, thermal decomposition to nitrite and oxygen begins at about 500°C, the rate increasing rapidly on further increases in temperature. Similar behaviour occurs for sodium nitrate, at temperatures some 50°C lower. If the reaction is carried out in a closed container, an oxygen pressure builds up due to the decomposition and the equilibrium shown below is established:(27)

$$MNO_3 \rightleftharpoons MNO_2 + \frac{1}{2}O_2 \qquad 4.1$$

It is reasonable to assume that the liquid mixture of nitrate and nitrite is ideal, so an equilibrium constant for 4.1 can be written as follows

$$K = \frac{x(MNO_2)\,(p(O_2)/p^\circ)^{\frac{1}{2}}}{x(MNO_3)} \qquad 4.2$$

where $x(MNO_3)$ and $x(MNO_2)$ are the mole fractions of nitrate and nitrite in the melt, $p(O_2)$ is the oxygen pressure and p° is the standard pressure (1 atm).

This equilibrium has been investigated by Bartholomew(27) and Sirotkin(28) and was confirmed by showing that the same melt composition is achieved, at a given temperature and oxygen pressure, whether the initial melt composition is pure nitrate or nitrite. The equilibrium constant K of equation 4.2 was determined by Sirotkin over a range of temperatures, and was found to vary according to

$$\ln K = A - \frac{B}{T} \qquad 4.3$$

Combining this with equation 4.2, and inserting the values of A and B quoted by Sirotkin for each salt, the relationship between equilibrium oxygen pressure, melt composition and temperature was found to be, for potassium nitrate

$$\log_{10}[\frac{p(O_2)}{p^o}] = 10.0 - \frac{11360}{T} - 2\log[\frac{x(KNO_2)}{x(KNO_3)}] \qquad 4.4$$

and for sodium nitrate

$$\log_{10}[\frac{p(O_2)}{p^o}] = 11.0 - \frac{11800}{T} - 2\log[\frac{x(NaNO_2)}{x(NaNO_3)}] \qquad 4.5$$

Using equations 4.4 and 4.5 it is possible to calculate the equilibrium oxygen pressure as a function of temperature for given values of $x(MNO_2)/x(MNO_3)$.

The thermal stability of nitrates can now be described in the following terms. A value for the nitrite/nitrate ratio, may be specified and the pressure of oxygen corresponding to this nitrite level may be calculated, as a function of temperature. If the melt is now confined under an applied gas pressure, p, equations 4.4 and 4.5 (or Figures 4.1 and 4.2) can be used to indicate the temperature at which the equilibrium oxygen pressure becomes equal to the applied pressure. Above this temperature oxygen would be evolved at a pressure greater than p, so would displace the blanket gas giving rise to rapid decomposition. At lower temperatures decomposition would be diffusion limited, and so would occur at a relatively slow rate depending upon the area of exposed melt surface and on the degree of mixing at the gas/melt interface. Since the function of the blanket gas is merely to prevent the free evolution of oxygen, not to force the equilibrium to the left, it is not essential that the blanket gas is oxygen, though obviously this would be the preferred choice. Equipment has been developed(30) which allows oxygen to be used but the equipment was not available for this investigation.

In order to confirm these conclusions, the conductivity of molten sodium and potassium nitrate was measured under an applied pressure of nitrogen, over a temperature range upwards from 350°C to 800°C. The onset of decomposition was indicated by deviation from Arrhenius behaviour, and by subsequent chemical analysis.

4.2 Design and testing of glassware

A silica cell was constructed to the design shown in figure 4.3. This differs from that used in the sodium tetrachloroaluminate studies in a few ways. Firstly since the object of the experiment is to reduce decomposition of the molten nitrate, sleeves have been put around the electrodes to reduce the nitrogen/melt interfacial area. By reducing the surface area the rate of decomposition is reduced. The two electrode housings are supported by a silica glass ridge on the outer cell wall. This is to keep the capillary tubes away from the bottom of the cell thus ensuring a good conductive path between the electrodes.

Before any measurements on the nitrates could be made the cell constant had to be determined. To do this a 0.1 demal KCl solution of KCl was prepared by dissolving 0.7419g of KCl in 100ml of distilled water at 25°C.(29) The cell was filled with this solution and placed in a thermostatted water bath at 25°C. The resistance of this solution was then measured using a Wayne Kerr Universal Bridge. The measured resistance could then be used to determine the cell constant.

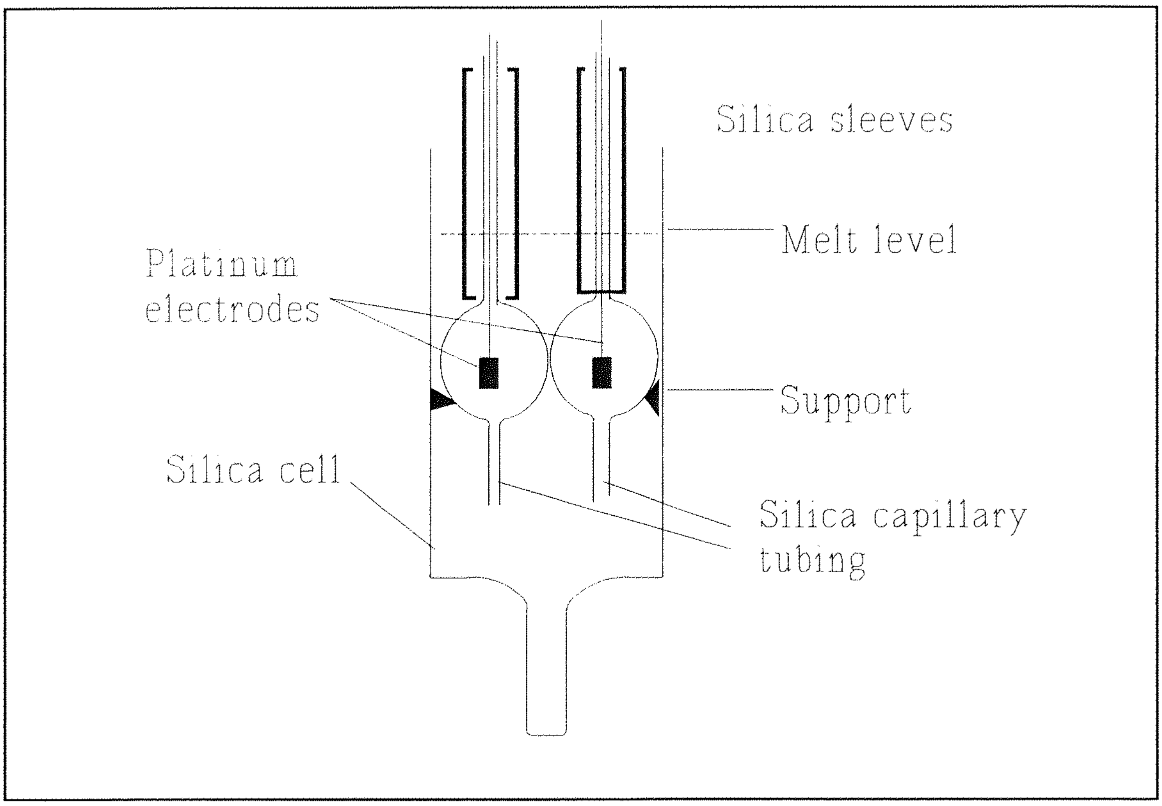

Figure 4.1 Conductivity cell for molten nitrate studies

$$K_{sp} = \frac{a}{R}$$

where a is the cell constant, R is the measured resistance of the cell and K_{sp} is the specific conductance of the solution in the cell. For 0.1D KCl solution K_{sp} = 0.012856 $\Omega^{-1}cm^{-1}$. For the cells used this gave a cell constant of approximately 200 cm^{-1}.

4.3 Experimental

The silica cell was assembled and filled with the nitrate to be studied. The amount of nitrate added was calculated to be sufficient to cover the electrodes when molten. The cell was then placed in the pressure vessel, in the same way as described in chapter 2 of this thesis, and heated under nitrogen at ca. 700 atm until the salt was molten. The electrical conductivity of the melts was measured, using a Wayne Kerr Universal Bridge B221A, as the samples were heated. Pressure changes due to increasing temperature were prevented by bleeding nitrogen out of the pressure vessel. The samples were then cooled to room temperature, still under gas pressure.

The solids obtained after the experiments were analysed for nitrite content. This was done by dissolving the solid in water and then titrating with acidified potassium permanganate solution. The pH of the aqueous solutions was also measured and found to be close to 7 in all experiments. From the titrations the degree of decomposition could be calculated and was found to be about 2 mol% in both cases. This demonstrates that equilibrium 4.1 is maintained up to the temperature and pressure limits indicated.

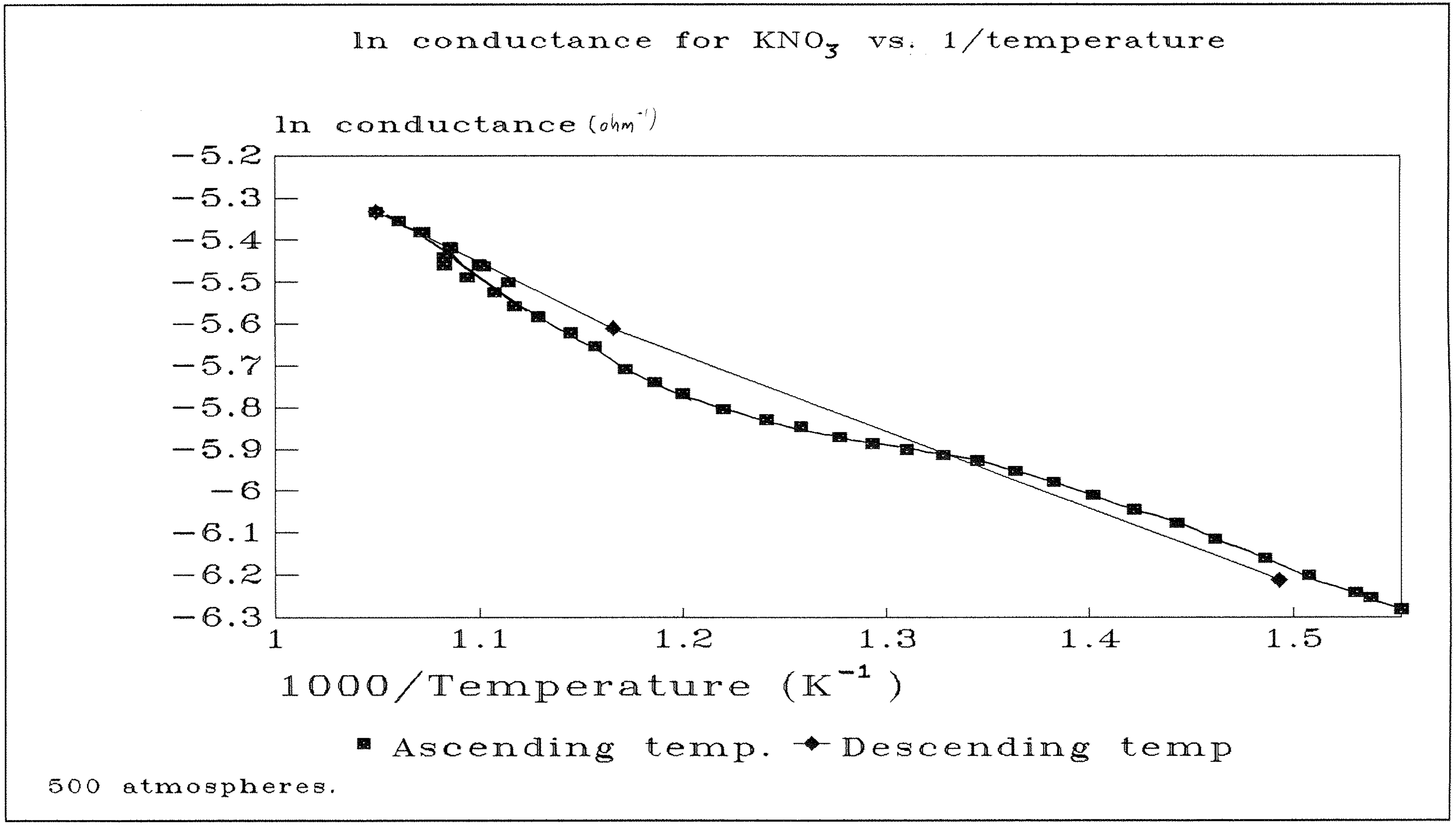

Figure 4.2 Ln conductance vs. reciprocal temperature for KNO$_3$ at 500 atm.

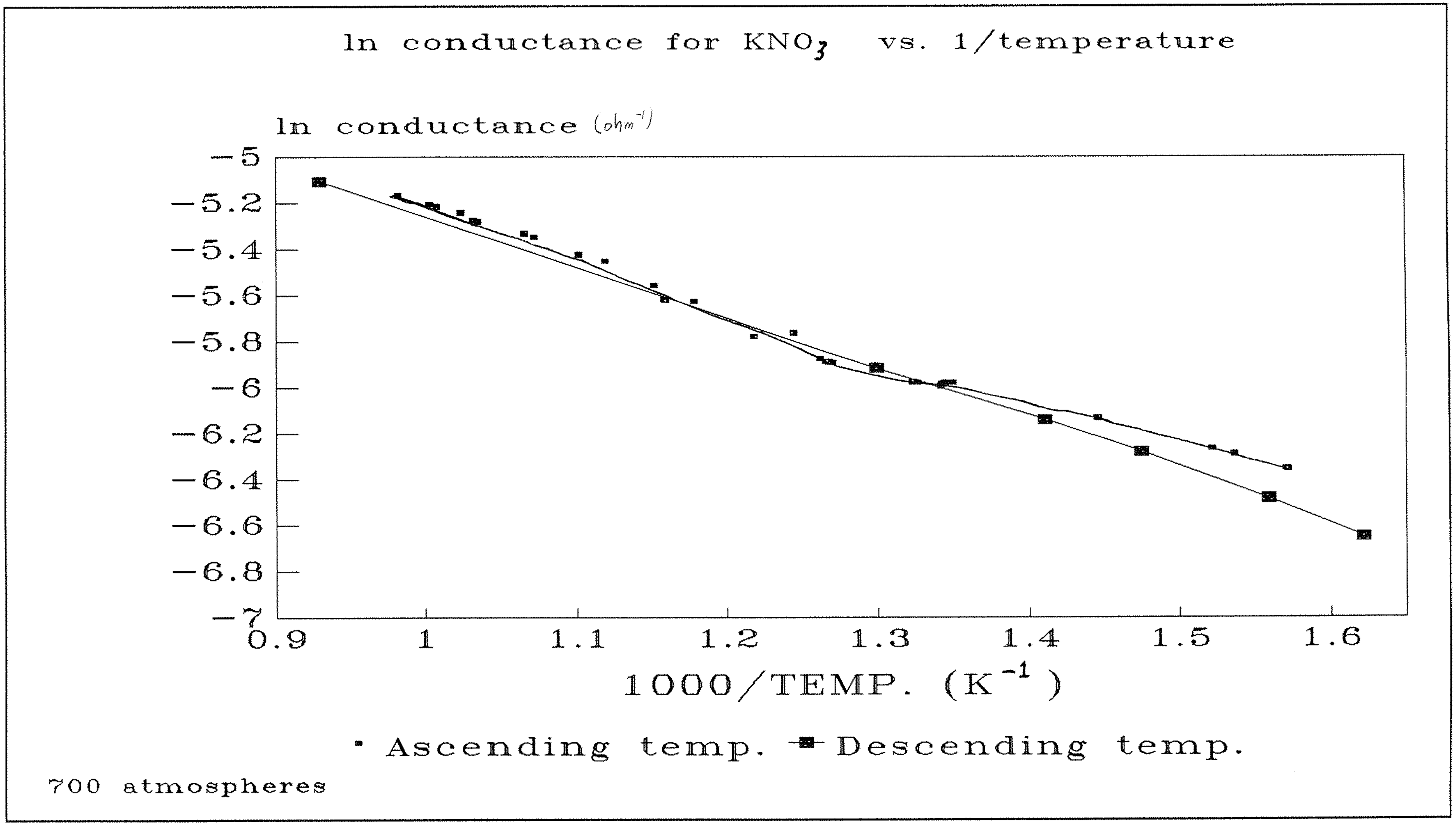

Figure 4.3 Ln conductance vs. reciprocal temperature for KNO_3 at 700 atm.

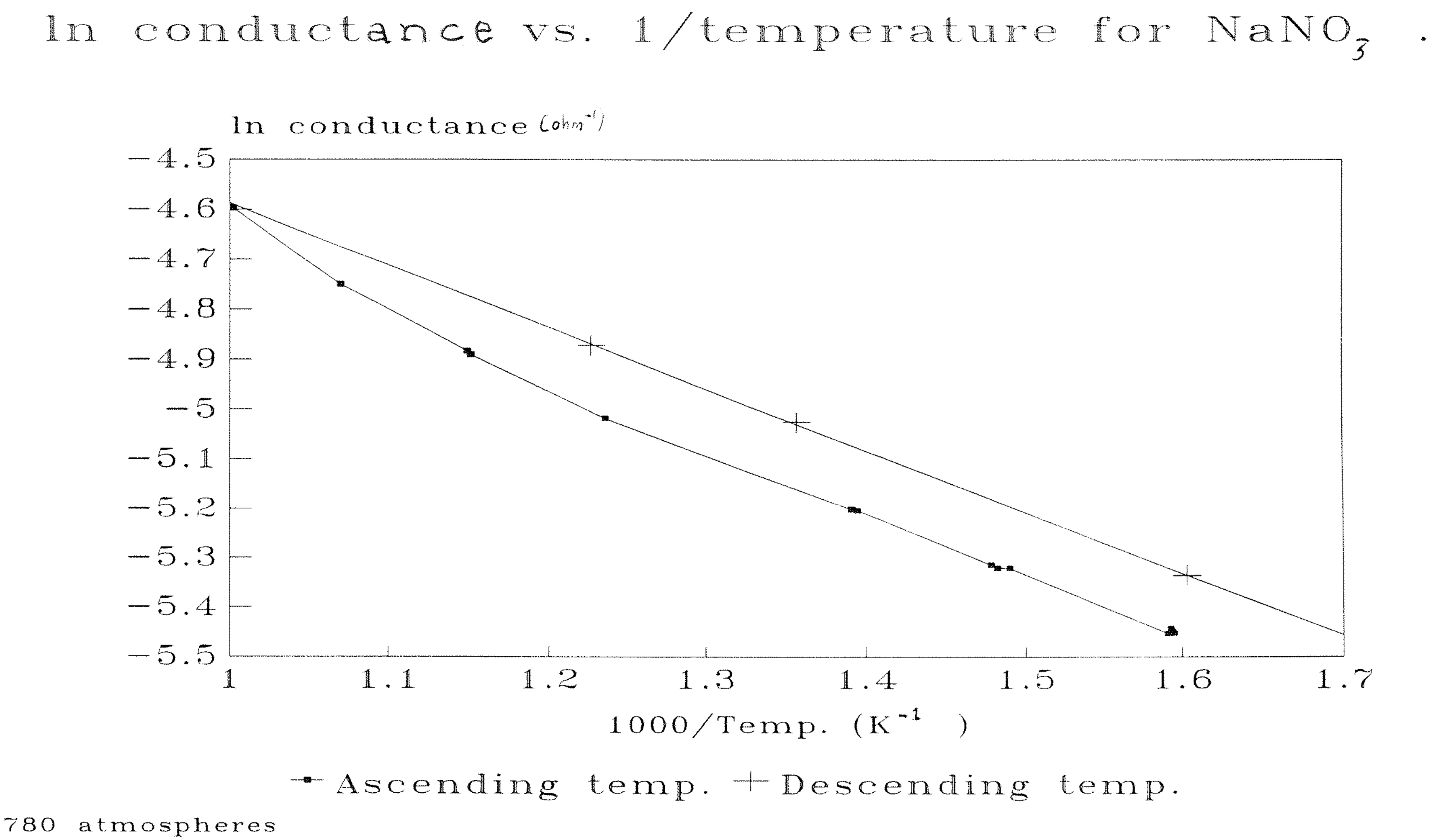

Figure 4.4 Ln conductance vs. reciprocal temperature for $NaNO_3$ at 780 atm.

This study reveals the possibility for carrying out a variety of studies in molten nitrates over the extended temperature range indicated. Some further suggestions along these lines are described in Chapter 5 of this thesis.

CHAPTER 5

SUMMARY

The three projects undertaken and reported in this thesis have all been successful and have produced some useful information and technical advances.

The conductivity studies on molten sodium tetrachloroaluminate have yielded new physical data for this system and calculations of activation volumes correspond closely with other inorganic sodium salts. Since $NaAlCl_4$ is used in high temperature batteries at temperatures of up to 450°C it would be useful to extend these studies to higher temperatures.

The analytical probe which is described could have industrial applications in the large scale manufacture of chloroaluminate melts. The electrode is relatively easy to construct and use, can go through many freeze-thaw cycles and provides a stable reference potential. Since the melt is saturated in both $NiCl_2$ and NaCl the melt composition is invariant and different probes should produce comparable results. This would alleviate the problem of having to calibrate each individual probe before use. Extensions to the work reported here could be to develop reference electrodes for room temperature chloroaluminate systems and for more acidic chloroaluminate melts. Before a reference electrode of this type can be designed for use in room temperature chloroaluminates the solubility of transition metal chlorides in these melts must be determined. If a suitable salt can be found the problem of ionic conductivity through the pyrex or soda glass membrane at the lower temperatures would become an important factor. It has been suggested(21) that the Cu/Cu^{2+} couple could be used as a reference electrode for acidic melts.

The conductivity studies on sodium and potassium nitrates have shown that nitrate decomposition can be suppressed by the application of a gas pressure, this gas not necessarily being oxygen. From this study the conductivity of molten potassium and sodium nitrates has been measured up to 1000K. At these temperatures no indication of a negative temperature coefficient was noticed. Further work which could be done includes a study of the decomposition of nitrates when under an oxygen blanket. Furthermore, at a recent conference on molten salts it was postulated that the reaction between nitrate melts and certain transition metal chlorides actually proceeds via reaction with a nitrite species formed by thermal decomposition. To check if this is indeed the case the reaction between these metal halides and molten nitrates could be performed under pressure thus avoiding the extensive formation of nitrite species.

APPENDIX

DATA FOR FIGURE 2.4

TEMPERATURE (°C)	CONDUCTANCE (mMho)	Ln CONDUCTANCE	PRESSURE (atm)
175.1	3.780	-5.5780	165
175.1	3.689	-5.6024	350
175.1	3.157	-5.7580	430
175.0	3.604	-5.6257	360
175.0	3.735	-5.5900	335
175.0	3.793	-5.5746	280
175.0	3.855	-5.5584	200
175.0	3.936	-5.5376	40

DATA FOR FIGURE 2.5

TEMPERATURE (°C)	CONDUCTANCE (mMho)	Ln CONDUCTANCE	PRESSURE (atm)
227.3	4.904	-5.3177	90
227.3	4.860	-5.3267	205
227.3	4.830	-5.3329	295
227.3	4.790	-5.3412	395
227.4	4.754	-5.3488	485
227.5	4.701	-5.3600	615
227.3	4.691	-5.3621	630
227.3	4.658	-5.3692	705
227.3	4.611	-5.3793	815
227.3	4.552	-5.3922	930
227.4	4.587	-5.3845	870
227.4	4.640	-5.3730	760
227.3	4.738	-5.3521	540
227.3	4.842	-5.3304	305
227.3	4.884	-5.3218	205

DATA FOR FIGURE 2.6

TEMPERATURE (°C)	CONDUCTANCE (mMho)	Ln CONDUCTANCE	PRESSURE (atm)
247.4	5.182	-5.2626	65
247.3	5.131	-5.2725	235
246.6	5.024	-5.2836	405
247.3	5.074	-5.2935	500
246.6	4.968	-5.3007	635
247.3	4.914	-5.3157	805
247.3	4.885	-5.3216	870
247.4	5.006	-5.2971	570
247.2	5.179	-5.2631	80

DATA FOR FIGURE 2.7

TEMPERATURE (°C)	CONDUCTANCE (mMho)	Ln CONDUCTANCE	PRESSURE (atm)
258	7.992	-4.8293	70
258	7.882	-4.8414	235
258	7.807	-4.8510	350
258	7.686	-4.8667	575
258	7.601	-4.8778	720
258	7.644	-4.8722	650
258	7.465	-4.8959	910
258	7.450	-4.8979	940
258	7.470	-4.8952	910
258	7.518	-4.8888	830
258	7.588	-4.8795	725
258	7.707	-4.8639	540

DATA FOR FIGURE 2.8

TEMPERATURE (°C)	CONDUCTANCE (mMho)	Ln CONDUCTANCE	PRESSURE (atm)
295.3	6.608	-5.0195	275
295.2	6.572	-5.0249	425
295.2	6.531	-5.0312	540
295.3	6.484	-5.0384	685
295.3	6.445	-5.0445	800
295.3	6.416	-5.0490	870
295.2	6.519	-5.0338	600
295.3	6.576	-5.0243	430
295.2	6.714	-5.0096	205

DATA FOR FIGURE 2.9

TEMPERATURE (°C)	CONDUCTANCE (mMho)	Ln CONDUCTANCE	PRESSURE (atm)
308	9.600	-4.6439	180
309	9.522	-4.6521	350
309	9.426	-4.6622	535
309	9.313	-4.6743	730
309	9.251	-4.6811	830
309	9.200	-4.6865	915
309	9.263	-4.6797	780
308	9.356	-4.6697	590
308	9.465	-4.6582	340
309	9.558	-4.6483	150

DATA FOR FIGURE 2.10

TEMPERATURE (°C)	CONDUCTANCE (mMho)	Ln CONDUCTANCE	PRESSURE (atm)
366	10.793	-4.5265	175
365.7	10.769	-4.5287	300
366.3	10.720	-4.5333	500
366.3	10.662	-4.5387	690
366.4	10.649	-4.5399	770
366.4	10.608	-4.5438	930
366.3	10.710	-4.5342	730
366.4	10.735	-4.5319	700
366.3	10.802	-4.5256	515
366.5	11.200	-4.4894	450

DATA FOR FIGURE 2.11

TEMPERATURE (°C)	CONDUCTANCE (mMho)	Ln CONDUCTANCE	PRESSURE (atm)
369.9	8.288	-4.7929	80
369.4	8.358	-4.7845	175
369.4	8.347	-4.7859	340
371.3	8.694	-4.7451	395
370.8	8.697	-4.7448	575
370.5	8.647	-4.7505	900
370.3	8.669	-4.7480	815
370.3	8.710	-4.7433	690
370.3	8.733	-4.7407	515
370.3	8.720	-4.7421	400
370.4	8.935	-4.7178	85

DATA FOR FIGURE 3.5

MOL% $AlCl_3$	MOL% NaCl	WEIGHT NaCl (g)	WEIGHT $AlCl_3$ (g)	TOTAL WEIGHT (g)	POTENTIAL (mV)
49.37	50.63	25.4296	56.5704	82.0000	1093.9
49.44	50.56	25.4296	56.7225	82.1521	887.6
49.53	50.47	25.4296	56.9358	82.3654	1102.8
49.72	50.28	25.4296	57.3699	82.7995	1064.0
49.83	50.17	25.4296	57.6231	83.0527	1069.9
49.94	50.06	25.4296	57.8858	83.3154	897.4
50.02	49.98	25.4296	58.0673	83.4969	810.2
50.14	49.86	25.4296	58.3423	83.7719	779.4
50.20	49.80	25.4296	58.4908	83.9204	772.5
50.30	49.70	25.4296	58.7042	84.1338	774.8
50.51	49.49	25.4296	59.2016	84.6312	773.7

DATA FOR FIGURE 4.2

PRESSURE (atm)	TEMPERATURE (K)	RECIPROCAL TEMPERATURE (1000 x K^{-1})	CONDUCTANCE (mMho)	ln CONDUCTANCE (ohm^{-1})
500	643.9	1.553	1.872	-6.2807
500	650.2	1.538	1.924	-6.2533
500	653.2	1.531	1.945	-6.2425
490	663.1	1.508	2.029	-6.2002
490	672.9	1.486	2.113	-6.1597
490	684.5	1.461	2.208	-6.1157
490	693.0	1.443	2.294	-6.0775
490	703.2	1.422	2.371	-6.0444
495	713.3	1.402	2.456	-6.0092
495	723.1	1.383	2.533	-5.9784
495	733.1	1.364	2.601	-5.9519
500	743.5	1.345	2.665	-5.9276
500	753.0	1.328	2.700	-5.9145
500	763.4	1.31	2.736	-5.9013
500	773.4	1.293	2.776	-5.8867
500	783.1	1.277	2.818	-5.8717
500	794.9	1.258	2.891	-5.8462
500	805.8	1.241	2.941	-5.8290
500	819.7	1.220	3.015	-5.8042
500	833.3	1.200	3.129	-5.7670
500	843.1	1.186	3.216	-5.7396
500	853.2	1.172	3.318	-5.7084
500	864.3	1.157	3.508	-5.6527
500	873.4	1.145	3.621	-5.6210
500	885.7	1.129	3.621	-5.5828
500	895.3	1.117	3.858	-5.5576
500	897.7	1.114	4.086	-5.5002
500	903.3	1.107	3.989	-5.5242
500	907.4	1.102	4.247	-5.4615

PRESSURE (atm)	TEMPERATURE (K)	RECIPROCAL TEMPERATURE (1000 x K^{-1})	CONDUCTANCE (mMho)	ln CONDUCTANCE (ohm^{-1})
500	909.1	1.100	4.260	-5.4585
500	914.1	1.094	4.132	-5.4890
500	920.8	1.086	4.437	-5.4178
500	923.4	1.083	4.334	-5.4413
500	932.0	1.073	4.606	-5.3804
500	932.8	1.072	4.600	-5.3816
500	942.5	1.061	4.728	-5.3543
500	952.4	1.050	4.827	-5.3335
500	857.6	1.166	3.656	-5.611
500	669.8	1.493	2.005	-6.212

DATA FOR FIGURE 4.3

PRESSURE (atm)	TEMPERATURE (K)	RECIPROCAL TEMPERATURE (1000 x K^{-1})	CONDUCTANCE (mMho)	ln CONDUCTANCE (ohm^{-1})
700	636.1	1.572	1.739	-6.3544
700	636.5	1.571	1.741	-6.3533
700	651.0	1.536	1.853	-6.2909
700	657.5	1.521	1.900	-6.2659
700	691.6	1.446	2.169	-6.1335
700	692.0	1.445	2.174	-6.1312
700	741.3	1.349	2.531	-5.9791
700	744.0	1.344	2.528	-5.9803
700	745.2	1.342	2.514	-5.9859
700	745.7	1.341	2.494	-5,9939
700	754.1	1.326	2.534	-5.9780
700	755.3	1.324	2.537	-5.9768
700	755.9	1.323	2.538	-5.9764
700	753.0	1.328	2.535	-5.9776
700	787.4	1.270	2.761	-5.8920
700	788.6	1.268	2.767	-5.8900
700	789.9	1.266	2.775	-5.8871
700	792.4	1.262	2.811	-5.8742
700	803.9	1.244	3.139	-5.7639
700	821.0	1.218	3.091	-5.7793
700	848.9	1.178	3.600	-5.6268
700	862.8	1.159	3.621	-5.6210
700	863.6	1.158	3.630	-5.6185
700	868.8	1.151	3.862	-5.5566
700	893.7	1.119	4.283	-5.4530
700	908.3	1.101	4.400	-5.4262
700	933.7	1.071	4.757	-5.3481
700	939.0	1.065	4.826	-5.3337
700	967.1	1.034	5.080	-5.2820

PRESSURE (atm)	TEMPERATURE (K)	RECIPROCAL TEMPERATURE (1000 x K^{-1})	CONDUCTANCE (mMho)	ln CONDUCTANCE (ohm^{-1})
700	969.9	1.031	5.123	-5.2740
700	977.5	1.023	5.285	-5.2429
700	992.0	1.008	5.436	-5.2147
700	997.0	1.003	5.490	-5.2048
700	1018.3	0.982	5.704	-5.1666
700	1076.4	0.929	6.061	-5.1059
700	769.8	1.299	2.695	-5.9164
700	708.7	1.411	2.151	-6.1418
700	678.0	1.475	1.871	-6.2813
700	629.7	1.588	1.529	-6.4831
700	616.5	1.622	1.294	-6.6500

DATA FOR FIGURE 4.4

PRESSURE (atm)	TEMPERATURE (K)	RECIPROCAL TEMPERATURE (1000 x K^{-1})	CONDUCTANCE (mMho)	ln CONDUCTANCE (ohm^{-1})
780	626.96	1.595	4.287	-5.4522
780	627.35	1.594	4.299	-5.4494
780	627.75	1.593	4.324	-5.4436
780	628.54	1.591	4.284	-5.4529
780	671.14	1.490	4.888	-5.3210
780	674.76	1.482	4.890	-5.3206
780	676.59	1.478	4.920	-5.3145
780	716.85	1.395	5.498	-5.2034
780	718.39	1.392	5.508	-5.2016
780	718.91	1.391	5.511	-5.2010
780	809.06	1.236	6.618	-5.0180
780	868.81	1.151	7.520	-4.8902
780	870.32	1.149	7.574	-4.88830
780	933.71	1.071	8.650	-4.7502
780	998.00	1.002	10.082	-4.5970
780	815.00	1.227	7.657	-4.872
780	736.92	1.357	6.569	-5.025
780	623.83	1.603	4.818	-5.335

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