

THE CONDUCTANCE OF MOLTEN  
LITHIUM CHLORATE AND  
THE EFFECT OF ADDITION OF  
TRACES OF NONELECTROLYTES



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by

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TO MY PARENTS

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## ABSTRACT

The specific conductance of pure molten lithium chlorate between 130 - 145<sup>o</sup> C. was determined, and an activation energy of conduction calculated.

Conductance measurements upon molten lithium chlorate solutions containing 0 - 6 percent by weight water, 0 - 0.4 percent by weight nitrobenzene, and 0 - 1.25 percent by weight methyl alcohol have been completed.

A discussion of these effects has been included.

## TABLE OF CONTENTS

	Page
Acknowledgments	iii
Abstract	iv
List of Tables	vi
List of Figures	vii
List of Symbols	viii
GENERAL INTRODUCTION . . . . .	1
NATURE OF THE PROBLEM . . . . .	22
LITERATURE SURVEY . . . . .	24
EXPERIMENTAL PROCEDURE . . . . .	26
EXPERIMENTAL RESULTS . . . . .	39
DISCUSSION OF THE RESULTS . . . . .	46
Bibliography	51

## LIST OF TABLES

Table		Page
1	Table of equivalent conductance and cation radii	19
2	Temperature, resistance and specific conductance of pure molten lithium chlorate	39
3	Resistance, specific conductance and weight percent water of lithium chlorate water mixtures at 131.8°C.	40
4	Resistance, specific conductance and weight percent of nitrobenzene of lithium chlorate nitrobenzene mixtures at 131.8°C.	41
5	Resistance, specific conductance and percentage by weight of methyl alcohol in lithium chlorate methyl alcohol mixtures at 131.8°C.	42
6	Specific conductance and mole ratio of water, nitrobenzene or methyl alcohol in lithium chlorate at 131.8°C.	44

## LIST OF FIGURES

FIGURE		PAGE
1.	The drying tubes	28
2.	The dry box	29
3.	The conductance cell	30
4.	The thermostat	31
5.	Graphs of Temperature versus Resistance and Resistance versus $\frac{1}{\sqrt{\text{Frequency}}}$	36
6.	Graph of log specific conductance versus $\frac{1}{T^{\circ}\text{K}}$	39
7.	Graph of specific conductance versus mole ratio additive/lithium chlorate	43

## LIST OF SYMBOLS

$\alpha$	Coefficient of thermal expansion
$\gamma$	Surface tension in dynes/cm <sup>2</sup>
$\Lambda$	Equivalent conductance in mhos per equivalent
$\lambda$	Individual ionic conductance in mhos per equivalent
$\bar{\lambda}$	Average ionic mobility
$\bar{\lambda}_0$	Standard reference ionic mobility
$\eta$	Viscosity in poise
$\mu_i$	Mobility of each ion under a potential of 1 volt/cm.
$\mu_m$	Molar conductivity
$\rho$	Density
$A_1, A_2, A_3$	Theoretical constants
$\alpha$	Degree of dissociation
$C_i$	Volume concentration of ion i
$d$	Half distance between initial and final ion positions during conductance
$\Delta E_K$	Activation energy for specific conduction
$\Delta E_\Lambda$	Activation energy for equivalent conduction
$F$	Faraday's constant
$G$	Cell constant
$\Delta H^+$	Enthalpy of activation for conduction
$J$	Average ion velocity used by Sakai

- $K$  Specific conductance
- $k$  Boltzmann constant
- $l$  Mean free path of the ions
- $m$  Mass of the ion
- $n$  Numbers of free ions
- $R$  Gas constant
- $R_e$  Measured resistance
- $\Delta S^*$  Entropy of activation for conduction
- $T$  Temperature degrees Kelvin
- $U$  Potential energy barrier involved in ion migration
- $W$  Energy of formation of a lattice defect
- $X$  Effective potential gradient in a field of 1 volt/cm.
- $Z_i$  Charge on each ion  $i$

GENERAL AND THEORETICAL INTRODUCTION

## GENERAL INTRODUCTION

For the previous twelve years much research at the University of Manitoba has been directed towards a study of the electrical conductivity of concentrated electrolyte solutions. Recently Kay and Kraus<sup>1</sup> have stated, "It may be anticipated that any attempt to account for the conduction of electrolytic solutions at high concentrations on the basis of the current ion-atmosphere model will prove futile." Hence in this work the approach has been to consider the effect of dilution upon the conduction of a liquid melt, and to consider a concentrated solution as a solution of the "solvent" in the "solute". This implies that the dominating features are those of a liquid melt.

Interpretation of the electrochemical properties of a liquid melt is in no manner comparable to the modern theories developed for aqueous solutions by Onsager, Fuoss, Wishaw and Stokes, and others. In an aqueous solution the concepts of the Boltzmann distribution and electrostatic interaction of ions used by Debye-Hückel et al, introduce a model in which each ion is surrounded by an ion-atmosphere, this being a major feature involved in the application of theoretical thermodynamics to the transport properties of the system. The ion-atmosphere in a 0.1 Molar and 0.01

Molar Sodium Chloride solution are respectively 10 Å. and 30 Å. diameter, whereas the mean free cell-cell path is only 3 Å. This demonstrates the importance of this property in aqueous conduction. In contrast Oldekop<sup>2</sup> has shown that in a simple molten alkali halide this ion-atmosphere is only of the order of 0.2 Å. The transport properties of a melt are obviously governed by the coulomb forces between the nearest neighbour ions. The problem of electrical conduction in a melt has been most successfully approached by a consideration of the melt as a disordered solid, and applying mathematical relationships developed from a Solid State Defect Theory, and not from extended hydrodynamic theories.

#### THEORETICAL DEVELOPMENT OF CONDUCTIVITY EQUATIONS FOR A LIQUID MELT

For all systems the specific conductance K is given

by:-

$$K = \frac{G}{R_e}$$

where G is the cell constant, and  $R_e$  the measured resistance. The value of G is obtained experimentally using solutions of Potassium Chloride having precisely known values of specific conductance.<sup>3</sup> The specific conductance of a melt is determined by the volume concentration of each ion  $C_i$ , the charge on each ion  $Z_i$ , and

the mobility of each ion  $\mu_i$ , under a potential gradient of 1 volt/cm; the relationship being:-

$$2 \text{ ----- } K = \frac{F}{1000} \left( \sum C_i Z_i \mu_i \right)$$

If a binary electrolyte is considered which is completely dissociated, then the  $C_i Z_i$ s are equal for each conducting species, and thus:-

$$3 \text{ ----- } K = \frac{F}{1000} \cdot CZ \sum \mu_i$$

Including the Faraday constant in the mobility term:-

$$4 \text{ ----- } \Lambda = \lambda_{\text{anion}} + \lambda_{\text{cation}} = \frac{1000K}{CZ}$$

and if concentration is expressed as Moles/litre, as is usual:-

$$5 \text{ ----- } \frac{CZ}{1000} = \frac{\text{EQUIVALENTS}}{\text{LITRES}}$$

Bloom and Heymann<sup>4</sup> showed that:-

$$6 \text{ ----- } \frac{1000}{CZ} = \frac{\text{EQUIVALENT WEIGHT}}{\text{DENSITY}} = \frac{M_e}{\rho}$$

and thus from equation 3

$$7 \text{ ----- } \Lambda = KM_e \rho^{-1}$$

Differentiation of equation 7 with respect to  $\frac{1}{T}$ , and then taking logarithms of both sides converts the equation 7 to:-

$$8 \text{ ----- } \frac{\partial \ln \Lambda}{\partial \left(\frac{1}{T}\right)} = \frac{\partial \ln K}{\partial \left(\frac{1}{T}\right)} - \frac{\partial \ln \rho}{\partial \left(\frac{1}{T}\right)}$$

an equation which, in earlier work, has been used to compare theoretical and experimental values of specific and equivalent conduction at different temperatures. This derivation assumes that the molten salt is completely dissociated, a condition which is not always present, and the equation is found to be incorrect in many cases.

For nearly all fused salts it has been found experimentally that a graph of  $\ln k$  or  $\ln \Lambda$  against  $\frac{1}{T}$  is essentially linear, indicating that in these cases the mechanism of conductance is a rate process, and the simple Arrhenius expressions are applicable:-

$$9 \text{ ----- } K = A \exp. \frac{-\Delta E_K}{RT}$$

$$10 \text{ ----- } \Lambda = A \exp. \frac{-\Delta E_\Lambda}{RT}$$

$\Delta E_K$  and  $\Delta E_\Lambda$  are the empirical activation energies of conductance. In these equations, it can be seen that the elemental properties of the melt will be a primary factor in determining the conductance.

X Ray investigations<sup>5</sup> have led to the conclusion that the liquid state contains regions of relatively high

order over several atoms distance. The melt of a salt is thought to consist of a semi-lattice of large anions and small cations in positions comparable to those occupied in the solid state. This means a semi-lattice is added in an order-disorder transformation, and in a melt ions occupy both semi-lattice and lattice sites while in a solid only the lattice sites are occupied. Evidence of the similarity of Entropy of Fusion gives a further indication that even in substances of very diverse properties, the change within the lattices is similar:-

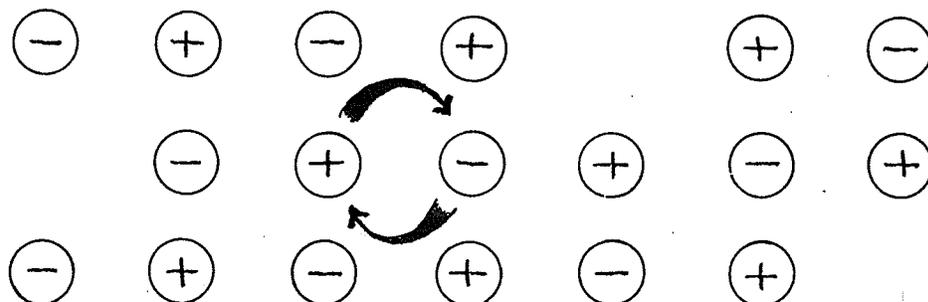
	<u>Melting Point</u>	<u>Heat of Fusion</u>	<u>Entropy of Fusion</u>
SOLID HYDROGEN	14.0°K	28.2 K.Cal/Mol	2.01
PLATINUM	2028.0°K	5310. K.Cal/Mol	2.6

Many models have been proposed to account for liquid properties in terms of position, interaction, and the constituents, the two most satisfactory models being the CELL MODEL and the HOLE THEORY. The ideal molten salt model, the Tempkin Model, has been interpreted statistically as one in which cations and anions are randomly distributed among themselves irrespective of valency, but each anion is surrounded by cations and vice versa.

#### CELL MODEL

The liquid state is essentially derived from an alloy structure of atomic or molecular structural units,

and lattice defects. The mechanism of conductance proposed for this model is that of place exchange involving a rotation of adjacent ions in the semi-lattice:-



Consider a pair of ions undergoing rotation in an ideal cell model. Both the final and transition positions involve the approach of pairs of like ions, and this would require a large heat of activation, which is not substantiated experimentally. Thus the emphasis has been placed upon the Hole Theory in recent studies of molten salt conduction.

#### HOLE THEORY

Initially proposed by Frenkel<sup>6</sup>, Altar<sup>7</sup>, and others, the liquid model consists of spherical ions, each behaving as a linear harmonic oscillator. A number of holes are fixed in random distribution among the ions. The liquid thus consists of a quasi-crystalline structure consisting of a binary mixture of holes and ions. The hole positions and sizes vary due to the random fluctuations in the melt caused by the thermal motions of the molecules. Bockris and Richards<sup>8</sup> have shown from compressibility measurements

that for certain alkali halides, the free volume increase per mole is only two percent of the solid molar volume. The logical explanation is the formation of holes within the melt since theoretical calculations based upon the Cell Model have shown that such a volume change necessitates a seven percent increase in the average interionic distance, while X-ray analyses have shown the actual increase to be much less.<sup>9</sup> Lark, Horowitz and Miller<sup>9</sup> have also shown by X-ray analysis of Lithium and Potassium Chlorides that the co-ordination number is less in the melt than in the solid while the distance between the first co-ordination sheaths remains essentially unchanged. Yaffe and Van Artsdalen<sup>10</sup> calculated that in molten Potassium Chloride, at a temperature 10% above its melting point, between one-fifth and one-sixth of the lattice sites are vacant. This has also been shown from the work of Bockris and Richards<sup>8</sup>. Further evidence of the importance of the formation of holes in a liquid melt for transport phenomena was offered by Borucka, Bockris and Kitchener<sup>11</sup> in a study of diffusion properties.

#### DEVELOPMENT OF CONDUCTIVITY EQUATIONS BASED UPON THE HOLE THEORY

Most work in this field has been carried out since 1945, as its importance in high temperature technology became apparent. Bloom and Heymann<sup>4</sup> treated the liquid

salt as a very disordered solid, using the relationships between ionic conductance in solid salts and the presence of imperfections in the crystal lattice. The high temperature conductance of a solid salt is proportional to the volume concentration of such defects and to their mobility. Both factors vary exponentially with the temperature resulting in the relationship:-

$$11 \text{ ----- } K = A \exp - \frac{\left(\frac{W}{2} + U\right)}{kT}$$

where W is the energy necessary for the formation of a lattice defect and U is the height of the potential barrier involved in the ion migration. This relationship applies only in the case where migration of a single ion alone is the cause of the conductance. These workers suggested that in the molten state the degree of disorder is such that the fraction of mobile ions is large. If no constitutional changes occur with change of temperature within the melt, then within limits the fraction of mobile ions could be assumed constant. For a purely ionic melt the equation obtained was:-

$$12 \text{ ----- } K = A_{\text{CATION}} \exp \frac{-\Delta E_{\text{CATION}}}{RT} + A_{\text{ANION}} \exp \frac{-\Delta E_{\text{ANION}}}{RT}$$

since the contribution of each ionic species to the total specific conductance would be

proportional to an exponential term involving only the energy barrier involved in the respective ion migrations. If the energy barriers are very different in value, then the ion having the smallest activation energy may be the predominant conducting species. Martin<sup>12</sup> was the first worker to obtain a correlation between the energy of activation for specific and equivalent conductance. By substitution of the definitions of the coefficient of thermal expansion,  $\alpha$ , and the energies of activation, he has shown:-

$$13 \text{ ----- } \Delta E_A = \Delta E_K + RT^2 \alpha.$$

Thus it can be seen that equality between these activation energies will only be observed in systems having a low coefficient of thermal expansion such as the silicates.

The Arrhenius equations had been found to be experimentally satisfactory in showing the relationship between conductivity and temperature and it seemed that an extension to these equations by means of the Absolute Reaction Rate Theory would give improved agreement between theoretical and practical values. This theory was initially applied by Baimakov and Samusenko<sup>13</sup>, the equation obtained being:-

14 -----

$$\Lambda = \frac{2}{3} \left( \frac{FZXd^2}{RT} \right) k \frac{T}{h} \exp. \frac{\Delta S^\ddagger}{R} \exp. - \frac{\Delta H}{RT}.$$

F = Faraday's Constant

Z = Charge on each ion

T = °K

k = Boltzmann constant

X = Effective potential gradient in a field of IV cm.

d = 1/2 distance between initial and final positions of  
the ion

$\Delta S^+$  = Entropy of activation

$\Delta H^+$  = Enthalpy of activation

R = Gas constant

A similar expression was obtained by Bockris, Kitchener, Iganovicz and Tomlinson<sup>14</sup>. The similarity to the Arrhenius equations 9 and 10 is immediately obvious if the first exponential term involving the entropy of activation is considered to be included in the constant A. It is possible to replace  $\Delta E$  by the enthalpy of activation since the restrictions of constant temperature and pressure are applied. The value of  $\Delta H^+$  may be regarded as a composite quantity consisting of the energy required to form a nearest neighbour hole, plus the energy required for the migrating ion to surmount the potential barrier imposed by the force fields of the nearest neighbour ions, and, if the melt is not completely ionic, the energy required for the formation of the ion is also included.

$$15 \text{ ----- } \Delta H^{\ddagger} = \Delta H_{\text{hole}} + \Delta H_{\text{JUMP}} + \Delta H_{\text{IONISATION}}$$

Recent measurements of the viscosity of molten salts at constant volume<sup>15</sup> tend to indicate that the heat of hole formation is the predominate term. The energy of viscosity has a value of between 0.3 to 0.4 K. cal per mole, and it may be considered that this activation energy is purely that required for the transport of mass, i.e.  $\Delta H_{\text{JUMP}}$ , since under constant volume conditions it may be assumed that the hole formation within the melt is zero. Similar measurements of viscosity at constant pressure give an activation energy of 3.0 to 4.0 K. cal per mole. In the absence of any constant volume conductivity data it is assumed that the ratio for  $\Delta H_{\text{JUMP}}$  and  $\Delta H_{\text{hole}} + \Delta H_{\text{JUMP}}$  are the same in conductivity as in viscosity.

Furth<sup>16</sup> has proposed the potential energy of a hole of radius  $r$  to be:-

$$16 \text{ ----- } \Delta F_{\text{hole}} = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 (p - p_0).$$

$\gamma$  = surface tension;  $p$  and  $p_0$  = external pressure and saturated vapour pressure of the liquid.

At ordinary pressures the second term is negligible and:-

$$17 \text{ ----- } \Delta F_{\text{hole}} \cong 4\pi r^2 \gamma$$

If the temperature coefficient for  $\gamma$ , the surface tension,

is known, then by the Gibbs-Helmholtz equation the heat of hole formation is:-

$$18 \text{ ----- } \Delta H_{\text{hole}} = 4\pi r^2 \left( \gamma - T \frac{\partial \gamma}{\partial T} \right)_P.$$

Though this theory is only of an empirical nature, since the macroscopic concepts of surface tension lose their significance when the hole radius is comparable to the intermolecular distances in the liquid, reasonable agreement between calculated and experimental values for the energy of hole formation may be obtained. Thus it can be reasoned that the chief cause of an increase in fluidity, diffusivity and electrical conductance as a molten salt is heated at constant pressure can be ascribed to an increase in the statistical number of cavities of molecular size within the melt, rather than to the smaller increase in the fractional number of mobile ions arising from the reduction in force fields due to expansion.

Equation 14, proposed by Bockris et al, assumes that the melt is composed only of ions and no molecular structure exists. This is an assumption which need not necessarily be correct. Greenwood and Martin<sup>17</sup> have proposed an approximate method for obtaining  $\alpha$ , the degree of dissociation of a melt, as:-

$$19 \text{ ----- } \Lambda = \frac{\mu_m}{Z} = \lambda_+ + \lambda_-$$

where  $\mu_m$  the molar conductivity, =  $\frac{1000K}{C}$

then by rearrangement of equation 4 the degree of dissociation is given by:

$$20 \text{ ----- } a = \frac{\mu_m}{Z(\lambda_+ + \lambda_-)}$$

For a uni-univalent electrolyte  $Z = 1$ , and assuming the remaining term in the denominator may be replaced by an average ionic conductance  $\bar{\lambda}$ , then:-

$$21 \text{ ----- } a = \frac{\mu_m}{2\bar{\lambda}}$$

If Walden's Rule is obeyed, i.e.

$$22 \text{ ----- } \Lambda \eta = \text{constant,}$$

where  $\eta$  = viscosity.

The average ionic mobility may be referred to a standard reference mobility  $\bar{\lambda}_0$ , in a medium of unit viscosity, that is:-

$$23 \text{ ----- } \bar{\lambda} = \frac{\lambda_0}{\eta}$$

Combining equations 22 and 23:-

$$24 \text{ ----- } a = \frac{\mu_m \eta}{2\lambda_0}$$

In any given solvent all ionic mobilities lie within a factor of ten of each other. In water at 20°C. and unit viscosity all mobilities are within a factor of 2 of

$\lambda_0 = 50 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ g. ion}^{-1}$  (other than the hydroxyl and hydroxonium ions), and if the melt viscosities are reduced to unity using this as the reference, from equation 24:-

25 -----

$$a = \frac{\mu_m \eta}{100} = \frac{K}{100}$$

Experimentally few molten salts are found to obey Walden's Rule, though it is found to have a wide range of validity when aqueous solutions of electrolytes are examined. This is because it is assumed in Walden's Rule that equivalent reactions occur in both charge transport and viscous flow. Frenkel, Bloom and other workers have found the ratio of the activation energies for equivalent conduction and viscosity for simple ionic salts to lie in the range 2 to 4. This has been interpreted as an indication that viscous flow involves a greater configurational change within the melt than does electrical conduction. Whereas electrical conduction can be primarily uni-ionic, the smaller ion carrying the current, electrical neutrality requires that both ions move in viscous flow, and therefore flow rate is governed by the larger ion.

Following Bockris in 1952, Sakai<sup>18, 19, 20</sup> proposed an equation for the electrical conductivity of a melt based upon an equation for ionic conductivity by Seitz<sup>21</sup> :-

26 -----

$$K = \frac{Z^2 J l n}{3 k T}$$

Z = charge on the ion

J = average velocity of the ions.

l = mean free path of the ions

n = number of free ions

The average velocity of an ion had previously been reported by Fowler<sup>22</sup> as:-

$$27 \text{ ----- } \bar{J} = 2 \left( \frac{2kT}{\pi m} \right)$$

Sakai assumes a Maxwell-Boltzmann distribution for the number of free ions available for conduction:-

$$28 \text{ ----- } n = A_1 \exp. - \frac{U}{kT}$$

$U$  = the energy required for the ion to migrate.

Since the semi-lattice and hence mean free path of the ion expands with an increase of temperature, then in general,

$$29 \text{ ----- } l = A_2 T^a$$

where 'a' is a positive constant and  $A_1$  and  $A_2$  are proportionality constants. Thus Sakai's final equation was:-

$$30 \text{ ----- } K = \frac{4 A_1 A_2 Z^2}{3 (2 \pi m k)^{1/2}} T^{a-1/2} \exp. - \frac{U}{kT}$$

Though this equation was developed from an essentially new approach, it is still of only a semi-quantitative value due to several assumptions used in its derivation. Yaffe and Van Artsdalen<sup>10</sup> have noted that "a", relating the free path of the ion to the temperature, is also temperature dependent and varies too widely to have any physical significance attached to its magnitude. Crook, Bockris et al<sup>23, 24</sup> also criticize the indefinite description

given to the free path, and are unable to correlate the average velocity of ideal gas molecules to their velocity in the liquid state as done by Sakai.

Further attempts to obtain equations which are able to predict the electrical conductance of fused salts based upon models for the liquid structure other than those mentioned, are numerous and varied in their approach and the assumptions made. These include equations developed by Oldekop<sup>25</sup>, Sundheim<sup>26</sup>, Markov and Delimarskii, etc.; all based upon molecular models of varying size and complexity. Duke and Victor<sup>27</sup> have obtained experimental results from transport number determinations which, they say, can only be explained if the ionic conductivity in the salts investigated, Potassium and Lithium Nitrates, is a poly-order process. This will mean that the ions move either in groups, or by means of some chain mechanism, such as a charged hole moving through many ionic diameters with a single activation step.

Bockris, Crook et al<sup>23</sup> applied the Absolute Reaction Rate Theory to a statistical model for the liquid state proposed by Stillinger et al<sup>28</sup>. By first considering an ideal situation in which every ion available for conduction was involved, and relating this to the free energy required, and secondly by mathematically correcting this rate of ion movement for the assumption (i) that some ions

are unsuccessful in crossing the potential barrier due to the coulomb forces, (ii) the effect of the application of a potential gradient upon this potential barrier, they finally obtained the equation:-

$$31 \text{ ----- } K_i = \frac{n_i Z_i^2 F^2 d_i^2 \nu_i}{3RTe} \exp. \frac{-\Delta H_j^+}{RT} \exp \frac{-\Delta F_h}{RT}$$

$\Delta H_j^+$  = enthalpy of activation to move an ion from one lattice site to another

$\Delta F_h$  = free energy of formation of a vacant lattice site

$\nu_i$  = vibrational frequency of the ion

Since  $\mathcal{L}_i = k_i V_i^{eq}$  (where  $\mathcal{L}_i$  is the ionic mobility, and

$V_i^{eq}$  is the equivalent volume of the ion i) and

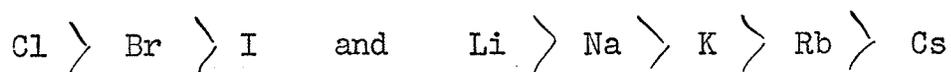
$V_i^{eq} Z_i n_i = 1$  then also:-

$$32 \text{ ----- } \mathcal{L}_i = \frac{Z_i F^2 d_i^2 \nu_i}{3RTe} \exp. \frac{-\Delta H_j^+}{RT} \exp \frac{-\Delta F_h}{RT}$$

Though this is a more elegant representation of the relationships between conductance and the energy and entropy of activation for ion movement in a melt, it has, at present, not been used sufficiently in comparison of calculated and experimental values to draw any conclusions.

It can be said that in studies involving the liquid state, at present no single theoretical relationship has been developed such that it may predict the physical properties of a melt. It is however possible to obtain a qualitative estimation of the conductivity of a simple fused

salt from a knowledge of its chemical constitution. Biltz and Klemm<sup>29</sup> observed, as did Yaffe and Van Artsdalen<sup>10, 30</sup> that the equivalent conductivity of the alkali metal chlorides increased with a decrease of cation radius, and a similar effect was noted for the variation of the anion size:-



As the ion radii are reduced, two opposing tendencies occur in the lattice. The larger the metal ion, the greater its co-ordination number and the lesser its mobility (see Table 1). Also if it is assumed that during migration there is a constant breaking-down and rebuilding of the lattice, then it will follow that the resistance to mobility will be an inverse function of the electrostatic forces between the ions, and the mobility will thus decrease with an increase in valency or with a decrease in average distance between the ions. The predominating effect is that of the change in atomic radii, as the conductivity of a lithium salt is normally greater than that of a corresponding cerium salt under the same conditions. The position of the metal ion involved may give a general indication of the conductance of a molten salt:-

Table 1

TABLE OF EQUIVALENT CONDUCTANCE AND CATION RADII

Taken from "Properties of Systems of Molten Salts"<sup>31</sup>

	<u>LiCl</u>	<u>BeCl<sub>2</sub></u>	<u>BCl<sub>3</sub></u>	<u>CCl<sub>4</sub></u>		
Equivalent Conductance	183.	0.088	0.	0.		
Cationic Radii	0.68	0.35	0.23	0.16		
	<u>NaCl</u>	<u>MgCl<sub>2</sub></u>	<u>AlCl<sub>3</sub></u>	<u>SiCl<sub>4</sub></u>	<u>PCl<sub>5</sub></u>	
Equivalent Conductance	150.	35.	15.1	0.	0.	
Cationic Radii	0.97	0.66	0.51	0.42	0.35	
	<u>KCl</u>	<u>CaCl<sub>2</sub></u>	<u>ScCl<sub>3</sub></u>	<u>TiCl<sub>4</sub></u>	<u>VCl<sub>5</sub></u>	
Equivalent Conductance	120.	64.	15.	0.	0.	
Cationic Radii	1.33	0.99	0.81	0.68	0.59	
	<u>CuCl</u>	<u>ZnCl<sub>2</sub></u>	<u>GaCl<sub>3</sub></u>	<u>GeCl<sub>4</sub></u>		
Equivalent Conductance	94.	0.02	-	0.		
Cationic Radii	0.96	0.74	-	0.53		
	<u>RbCl</u>	<u>SrCl<sub>2</sub></u>	<u>YCl<sub>3</sub></u>	<u>ZrCl<sub>4</sub></u>	<u>NbCl<sub>5</sub></u>	<u>MoCl<sub>6</sub></u>
Equivalent Conductance	94.	69.	9.5	0.85	2x10 <sup>-7</sup>	1.8x10 <sup>-6</sup>
Cationic Radii	1.47	1.12	0.92	0.79	0.69	0.62
	<u>AgCl</u>	<u>CdCl<sub>2</sub></u>	<u>InCl<sub>3</sub></u>	<u>SnCl<sub>4</sub></u>		
Equivalent Conductance	118.	58.5	14.7	0.		
Cationic Radii	1.26	0.97	0.81	0.71		
	<u>CsCl</u>	<u>BaCl<sub>2</sub></u>	<u>LaCl<sub>3</sub></u>	<u>HfCl<sub>4</sub></u>	<u>TaCl<sub>5</sub></u>	<u>WCl<sub>6</sub></u>
Equivalent Conductance	86.	77.	29.0	-	3x10 <sup>-7</sup>	2x10 <sup>-6</sup>
Cationic Radii	1.67	1.34	1.14	0.79	0.69	0.62
	<u>AmCl</u>	<u>HgCl<sub>2</sub></u>	<u>TlCl<sub>3</sub></u>	<u>PbCl<sub>4</sub></u>		
Equivalent Conductance	-	3x10 <sup>-2</sup>	3x10 <sup>-3</sup>	2x10 <sup>-5</sup>		
Cationic Radii	1.37	1.10	0.95	0.84		

CONCLUSION

No mathematical relationship is yet known which is able to predict accurate values for different physical constants in a fused salt system. The knowledge of the thermodynamic properties of fused salts is still in an elementary stage in its development.

During recent years an increase in interest in high temperature work has initiated a similar interest in the broad field of liquid properties.

NATURE OF THE PROBLEM

## NATURE OF THE PROBLEM

The preparation of Lithium Chlorate in a high state of purity by Campbell and Griffiths<sup>32</sup> made available an inorganic salt which, due to certain of its physical properties is very convenient for use in the study of the thermodynamic properties of concentrated aqueous and fused salt systems. The latest work on this system was that of Campbell, Kartzmark and Patterson<sup>33</sup>, in which the electrical conductivities of solutions from the dilute aqueous to the pure molten salt were compared.

This research completes the study of the conductivity of 90-100% Lithium Chlorate solutions, and compares the effects of similar mole-ratios using other additives of different dielectric constant.

In all cases the thermodynamics of fused systems are used in the comparison of the results.

LITERATURE SURVEY

## LITERATURE SURVEY

Lithium chlorate solutions have been used by many workers in studies of electrical conductivity. These include Kraus and Burgess<sup>34</sup>, Scatchard<sup>35</sup>, Klotschko and Grigorjew<sup>36</sup>, and Campbell and Patterson<sup>33</sup>.

Scatchard was primarily interested in the dilute range of concentration. Kraus and Burgess studied the whole range of concentration, but the experimental techniques and standards employed are no longer considered satisfactory. Klotschko and Grigorjew compare their results to the phase diagram of the water/lithium chlorate system, and these results are often not comparable to those of Campbell, Kartzmark and Patterson. The latter workers have studied the system at all concentrations, though the experimental techniques used restricted the results obtained in the 90-100% lithium chlorate region to only one. Also the equations of conduction for aqueous solutions were applied.

No results are available in which lithium chlorate has been used in molten salt systems.

EXPERIMENTAL PROCEDURE

## EXPERIMENTAL PROCEDURE

### A. PREPARATION OF LITHIUM CHLORATE

The method used was essentially that of Kraus<sup>34</sup>, modified by Campbell and Griffiths<sup>32</sup>, utilizing the metathetical reaction between lithium sulphate and barium chlorate solutions. The lithium sulphate, supplied by Fisher Scientific Company, and the barium chlorate, obtained from the British Drug Houses Limited, were of the highest purity and were used without further purification.

A one molar solution of barium chlorate was heated to 90-100° C, and an equivalent solution of lithium sulphate added slowly. A large white precipitate of barium sulphate formed, and the mixture was digested for 3 - 4 hours, keeping the water level constant. After cooling, the solution of lithium chlorate was decanted from the bulk of the precipitate, and a further volume of distilled water added. This barium sulphate-water mixture was heated again for 3 - 4 hours, and the second volume of water added to the lithium chlorate solution following decantation. This process was repeated twice for each original litre of solution. The combined lithium chlorate solution and water washings were concentrated until a volume comparable to the initial water volume used was obtained. This solution was filtered through a sintered glass funnel to

remove the remaining barium sulphate. The absence of the sulphate and barium ions was shown by titration of aliquot parts of the filtrate against solutions of barium chlorate and lithium sulphate. Where equivalence was not found, this was obtained by addition of the necessary volume of either of the original solutions, followed by a second filtration. The filtrate was placed in a one litre round bottomed flask, and heated under a vacuum of - 0-10 mms. of mercury. The vacuum was obtained using a Welch Duo-seal Pump. The distillate was trapped in a liquid nitrogen cold trap. During this stage of the preparation the temperature was kept at  $80^{\circ}$  C, since concentrated solutions of lithium chlorate are found to decompose at temperatures above this. The dehydration was stopped when, on cooling, crystals of lithium chlorate were formed, leaving a mother liquor. It was assumed that any impurities present would remain in this mother liquor, which was discarded. The crystals were rapidly filtered through a coarse glass crucible, and placed in a vacuum desiccator over concentrated sulphuric acid for 10 - 12 weeks. The final traces of water were removed by a different technique. The crystals were removed from the desiccator, and crushed to a fine powder inside a dry box. The dry box was specially constructed to enable all operations involving the contact of the dry salt with the atmosphere to be carried out. The atmosphere within the

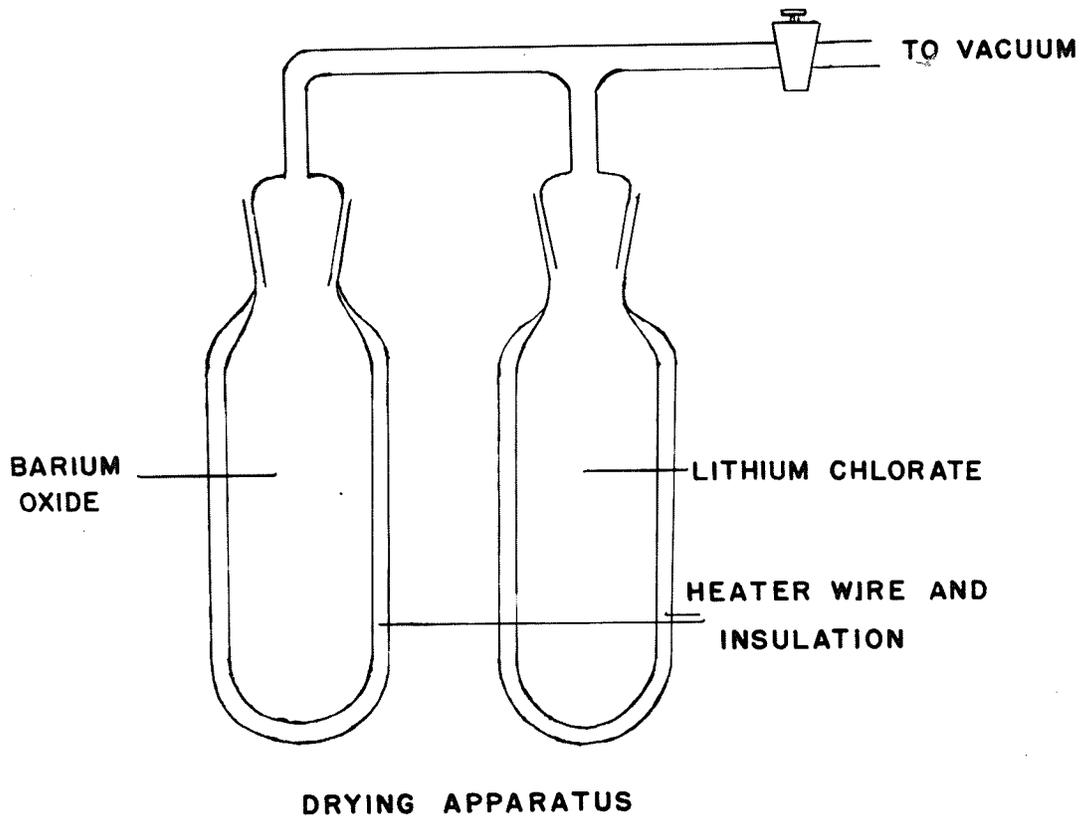
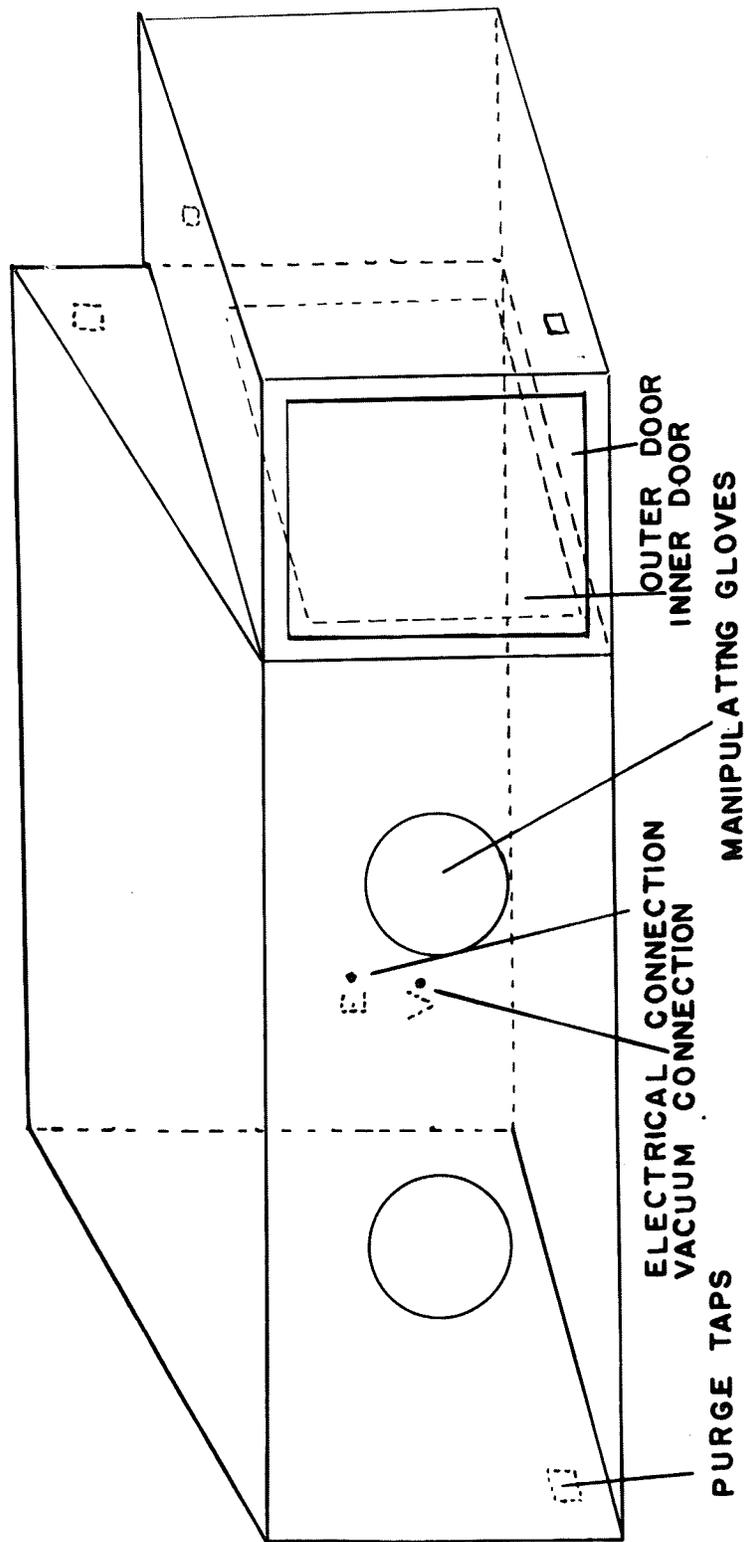


FIGURE I

dry box was obtained by controlled heating of liquid nitrogen, and in all cases it was purged for 2-3 hours before any operation was undertaken. Having crushed the salt, it was transferred to the final drying apparatus. This consisted of two inter-connected parallel tubes, 1" x 6", connected to a vacuum system. The lithium chlorate crystals were placed in one of these tubes (Figure 1) which could be heated to at least 150°C. The second of the parallel tubes contained barium oxide, supplied by Barium and Chemicals, Inc. This barium oxide is a drying agent with dehydrating powers comparable to those of phosphorus pentoxide, and much superior in its ease of manipulation. The lithium chlorate was heated to approximately 100°C. under a high vacuum for 6-8 weeks. Extension of this drying period gave no change in the melting point of the anhydrous lithium chlorate, viz. 127.8°C.

Figure 1



THE DRY BOX

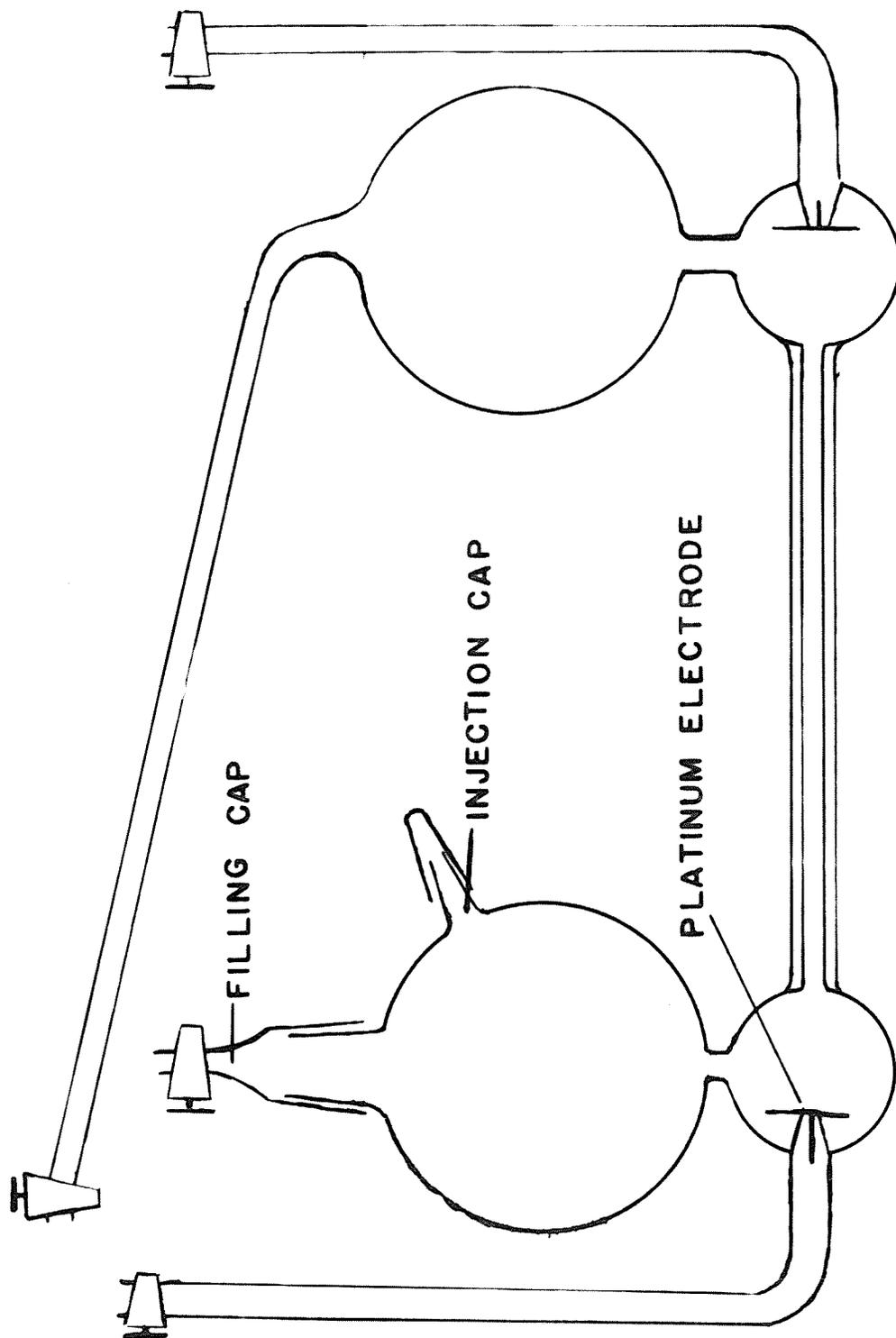
FIGURE 2

## B. THE DRY BOX

The dry box was constructed from angle brass, copper sheeting and  $\frac{1}{4}$ " perspex. A schematic diagram is shown in Figure 2.

### Figure 2

The entrance chamber was fitted with a perspex door, which was made to fit gas tight when closed by means of  $\frac{1}{2}$ " foam rubber. Two gas taps were also attached to enable this entrance chamber to be purged separately. The main chamber was entered via the smaller chamber through a large gas tight door. The top of the main chamber sloped towards the front, and was constructed of  $\frac{1}{4}$ " perspex to enable the operator to manipulate apparatus inside the chamber, using the sleeve-length rubber gloves attached to



THE CONDUCTANCE CELL

the front. Nitrogen purge taps were fitted to two opposite corners, and also provision for a vacuum connection and electrical connections were made to the main chamber.

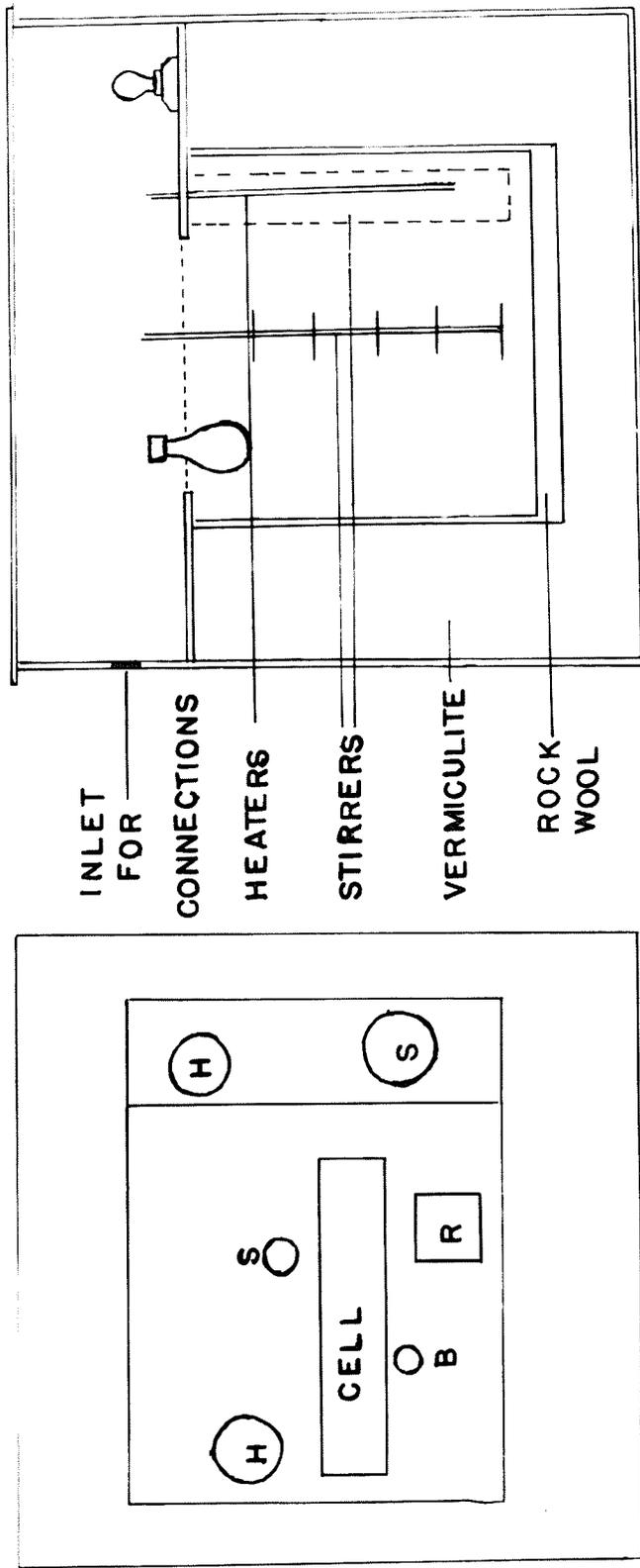
The atmosphere within the dry box was obtained by controlled heating of liquid nitrogen. A purge rate of 30-40 litres/hour for 3-4 hours was always used before any operation within the box was undertaken, and a slower purge rate continued while the dry box was in use, ensuring that a gas pressure greater than atmospheric was always present.

#### C. THE CONDUCTANCE CELL

For this work a capillary cell, with a large cell constant, of the type recommended by Jones and Bollinger<sup>37</sup> was used (Figure 3).

Figure 3

THE THERMOSTAT



H HEATER

S STIRRER

B BECKMANN THERMOMETER

R RELAY

FIGURE 4

The basic filling tubes and electrical connections were widely separated, since this type of cell does not exhibit the Parker Effect.<sup>38</sup> It was found not necessary to platinize the electrodes as the detector gave a sharp change, either with or without the electrodes being covered with platinum black.

The cell was filled with powdered lithium chlorate inside the dry box, and then transferred to the thermostat. The weight of salt added was known from the change in cell weight before and after filling.

#### D. THE THERMOSTAT

Figure 4

A large thermostat was constructed which would enable a visible study of the cell to take place at the time of taking a conduction reading.

The inner copper bath, capacity 18 gallons, was rectangular in shape, 30 x 60 x 60 cm., and was covered by a primary insulation of 1" rock wool before being placed inside a first wooden case. An outer wooden box was then constructed, dimensions 85 x 75 x 65 cm., such that when the inner box was placed inside, it allowed a further ten inches of insulation. Vermiculite was used for this outer insulation. A glass panel was put in each of the concentric boxes to allow apparatus within the oil to be viewed directly.

The oil used was Marcol G X supplied by the Imperial Oil Company. Stirring was accomplished by a large Archimedian stirrer and a centre drive electrical stirrer. To heat the oil a 450 watt heater was used with a 100 watt bulb as the control heater. The temperature was measured on a Beckmann thermometer which had previously been calibrated against a standard Platinum thermometer using a Mueller bridge. A magnetic relay combined with a large mercury thermoregulator, to which the control heater was connected, gave a temperature variation of  $0.04^{\circ}\text{C}$ . at  $131.8^{\circ}\text{C}$ .

### E. THE CONDUCTANCE BRIDGE

The bridge used was a Leeds and Northrup Jones conductivity bridge. This is essentially a Wheatstone resistance bridge modified for use in alternating current measurements. A "Wagner Ground" is included in the bridge circuit, eliminating current leakage from the detector terminals. A three stage amplifier coupled to an Oscilloscope proved capable of detecting a resistance change of 1.0 ohm in 10,000 ohms on the bridge. The oscillating input was provided by a Jackson audio-oscillator, capable of delivering a low output voltage with a selected frequency of between 0-100,000 cycles per second.

### F. CELL CONSTANT

No standard is available for the determination of cell constants at a high temperature. The method used was to determine the constant at 25°C. and to apply correction factors obtained by the method of Washburn<sup>39</sup>.

Potassium chloride was used as the standard for the determination of the cell constant at 25°C. A thermostat designed by E. Bock<sup>40</sup>, of this University, was used in these determinations, and temperature fluctuations were of the order of 0.002°C. A sample of Analar potassium chloride supplied by May and Baker was fused in a platinum crucible and stored in a desiccator over anhydrous barium oxide.

The solutions used were made according to the specifications of Jones and Bradshaw<sup>41</sup>. The cell constant was calculated several times using freshly prepared solutions, and agreement to  $\pm 0.03\%$  was obtained. The mean value was taken to be the true cell constant at  $25^{\circ}\text{C}$ . The correction of the cell constant for a temperature of  $131.8^{\circ}\text{C}$ . is purely due to the geometrical changes in the cell. By definition:-

$$33 \text{ ----- } G = l/a$$

$l$  = distance between the electrodes

$a$  = effective area of solution between the electrodes

$G$  = cell constant

Differentiation with respect to temperature of equation 33 yields:-

$$34 \text{ ----- } \frac{dG}{dT} = \frac{1}{a} \frac{dl}{dT} - \frac{l}{a^2} \frac{da}{dT}$$

Now:-

$$35 \text{ ----- } \frac{dl}{dT} = B(l + s) - B^1 s$$

$B$  = coefficient of linear expansion of the glass

$B^1$  = coefficient of linear expansion of platinum

$s$  = length of the electrode posts

If the cell has a large capillary length, then equation 35 may be considered as:-

$$36 \text{ ----- } \frac{dl}{dT} = Bl$$

and similarly

$$37 \text{ ----- } \frac{da}{dT} = 2Ba$$

Substitution of equations 36 and 37 in equation 34 yields:-

$$38 \text{ ----- } \frac{dG}{dT} = \frac{1}{a} B_1 - \frac{1}{a^2} 2Ba = -BG. \quad \text{and}$$

$$39 \text{ ----- } \Delta G = -G \Delta T$$

Using equation 39, the final cell constant used in the calculations of the specific conductance at 131.8°C. was 270.3.

#### G. THE ADDITIVES

##### (1) Water

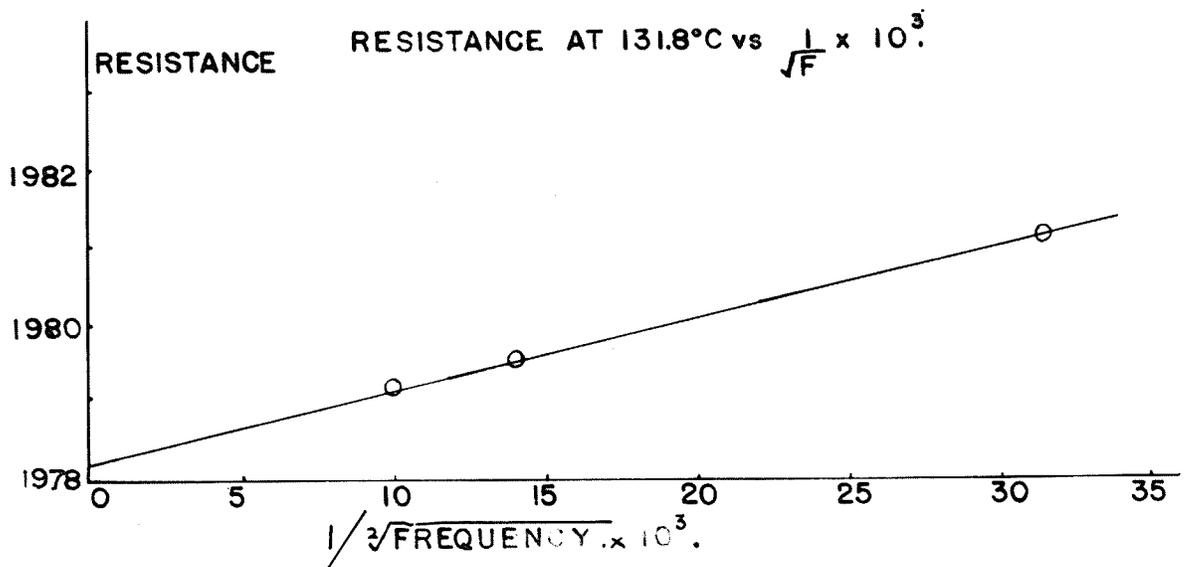
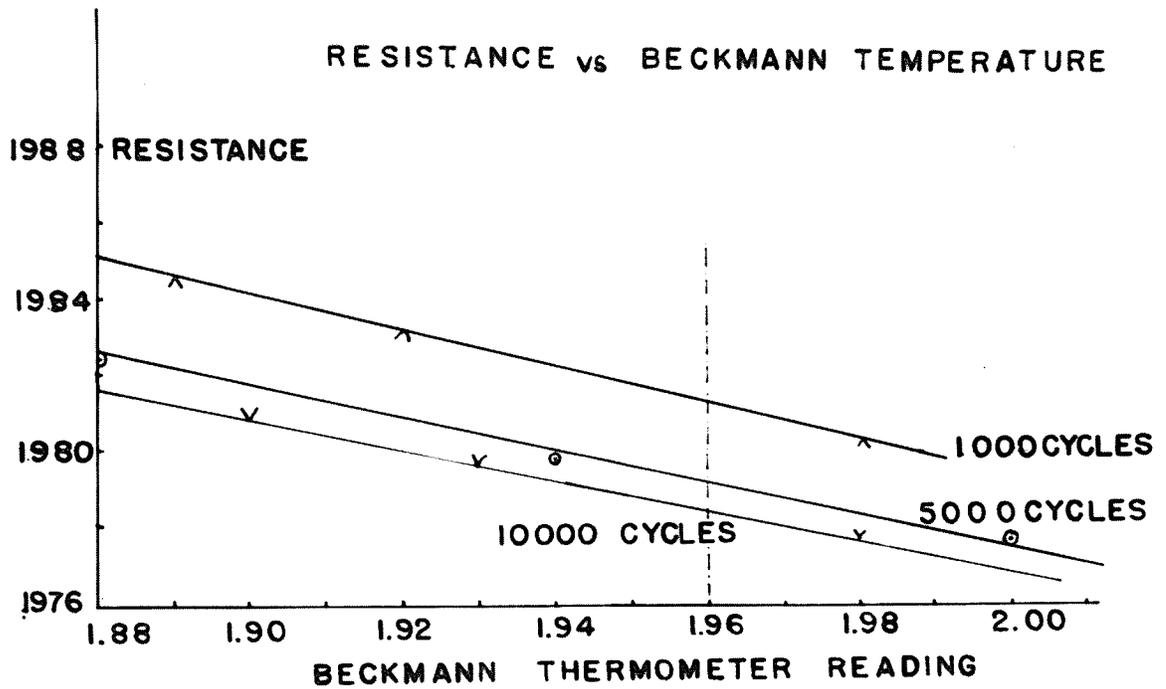
The water used was conductivity water prepared by passing pure nitrogen gas slowly through distilled water for a period of 8-10 hours to remove the dissolved carbon dioxide. In all cases the specific conductance of this water was, at the greatest,  $1.5 \times 10^{-7}$ .

##### (2) Methyl alcohol and nitrobenzene

These chemicals were obtained from Eastman Distillation Products, and both were of analytical quality. Each was used without further purification, other than drying over barium oxide and sodium metal respectively.

#### H. EXPERIMENTAL TECHNIQUE USED IN THE DETERMINATION OF THE SPECIFIC CONDUCTANCE OF THE PURE SALT AND THE SALT PLUS ADDITIVE

The cell containing a known weight of powdered anhydrous lithium chlorate was placed in the thermostat at 131.8°C. The salt slowly melted leaving gas bubbles along



AN EXAMPLE SHOWING THE CALCULATION OF A  
RESISTANCE AT INFINITE FREQUENCY.

FIGURE 5

the capillary and attached to the electrodes. These were removed by causing the melt to flow into the bulbous compartments on either of the filling tubes, either by inverting the cell inside the thermostat, or by alternate application of a vacuum, and pressure of dry nitrogen. After thermal equilibrium had been reached, the resistance of the cell was measured at the maximum and minimum recorded temperature fluctuation of the thermostat, using signal frequencies of 1000, 5000 and 10,000 cycles per second. A graph of the temperature recorded against the resistance was then plotted for each of the used frequencies. The actual resistance for each frequency was then taken from these graphs and plotted against  $\frac{1}{\sqrt{\text{frequency}}}$  (Figure 5).

Figure 5

Extrapolation of this last graph to infinite frequency gave the resistance of the cell if no ionic polarization took place, and this was the resistance value used in the calculations.

The methyl alcohol, water, and nitrobenzene were all added using the same technique. A calibrated syringe was filled with the necessary quantity of the additive, and while the cell remained in the thermostat the injection cap was removed, the additive injected, and the cap replaced. This total operation took no longer than 1-2 seconds. Equilibrium in the salt was obtained by inverting the cell as before. Two to three hours was allowed to pass before any resistance measurements were taken.

A fresh cell constant was taken following each complete experiment, and agreement within 0.1 was obtained in each case.

## EXPERIMENTAL RESULTS

GRAPH OF LOG SPECIFIC CONDUCTANCE

AGAINST  $\frac{1}{T} \text{ } ^\circ\text{K} \times 10^4$ .

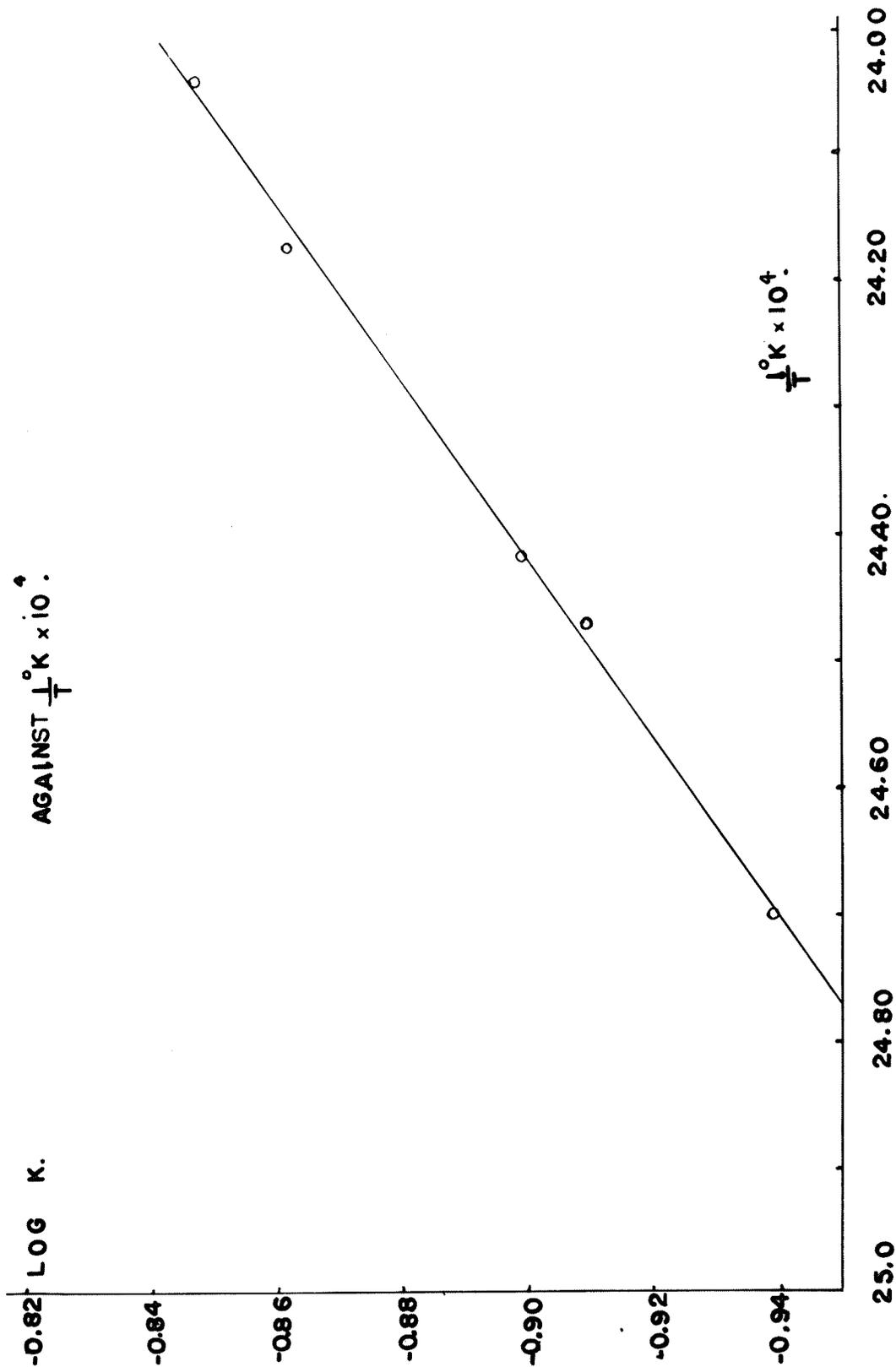


FIGURE 6

## EXPERIMENTAL RESULTS

### A. PURE LITHIUM CHLORATE

The activation energy of specific conductance for pure lithium chlorate was determined from measured conductance values in the temperature range 130 - 145°C.:-

Table 2

TEMPERATURE, RESISTANCE AND SPECIFIC CONDUCTANCE OF PURE MOLTEN LITHIUM CHLORATE

<u>Temperature</u> <u>°C.</u>	<u>Resistance at</u> <u>infinite frequency</u>	<u>Specific</u> <u>Conductance</u>	$\frac{1}{T} \times 10^4$ <u>°Kelvin</u>	$\log_{10} k$
131.80	2350.0 ohms	0.1150	24.70	-0.9389
143.01	1903.0	0.1420	24.04	-0.8477
140.78	1973.0	0.1370	24.17	-0.8623
136.49	2149.0	0.1258	24.42	-0.8993
135.69	2222.8	0.1231	24.47	-0.9098
131.80	2347.4	0.1152	24.70	-0.9385

From equation 9,

$$9 \text{ ----- } k = A \exp - \frac{\Delta E_k}{RT}$$

the activation energy was calculated from the slope of the graph of log. specific conductance versus

$\frac{1}{T}$  Kelvin, Fig. VI, the result being:-

that the activation energy of specific conductance for anhydrous lithium chlorate between 130-140°C. is 6.3 K. cal per mole.

### B. WATER ADDITIONS

A table of the measured values of resistance at infinite frequency, specific conductance and percentage by weight of water added in three completely separate experiments are shown below.

Table 3

RESISTANCE, SPECIFIC CONDUCTANCE AND WEIGHT  
PERCENT WATER OF LITHIUM CHLORATE  
WATER MIXTURES AT 131.8°C.

<u>Resistance at infinite frequency</u>	<u>Specific Conductance</u>	<u>Volume of water added</u>	<u>Percent by weight of water</u>
2350.0	0.1150	---	---
2308.2	0.1171	0.1 mls	0.261
2248.6	0.1202	0.2 mls	0.520
2202.1	0.1227	0.3 mls	0.779
2174.6	0.1243	0.4 mls	1.04
2132.4	0.1268	0.5 mls	1.29
2075.3	0.1302	0.6 mls	1.54
2038.3	0.1326	0.7 mls	1.80
1977.4	0.1368	1.00 mls	2.55
1935.5	0.1397	1.1 mls	2.80

<u>Resistance at infinite frequency</u>	<u>Specific Conductance</u>	<u>Volume of water added</u>	<u>Percent by weight of water</u>
1812.8	0.1491	1.6 mls	4.02
1695.3	0.1594	2.1 mls	5.21
1817.5	0.1487		3.87
1735.0	0.1559		4.70
1657.1	0.1631		5.92

If a linear relationship is presumed to exist between the results of Campbell and Patterson<sup>33</sup> for melts of 100 and 93.98 percent by weight lithium chlorate, then the above results do differ slightly for melts containing between 0-2 percent water. Melts containing a greater percentage of water however, compare throughout the range under investigation.

#### C. NITROBENZENE ADDITIONS

Nitrobenzene was found to have a very limited solubility in molten lithium chlorate. The maximum percentage by weight of nitrobenzene in a one phase system at 131.8°C. was only 0.4. The results are shown in Table 4.

Table 4

RESISTANCE, SPECIFIC CONDUCTANCE AND WEIGHT  
PERCENT OF NITROBENZENE OF LITHIUM CHLORATE  
NITROBENZENE MIXTURES AT 131.8°C.

<u>Resistance at infinite frequency</u>	<u>Specific Conductance</u>	<u>Volume nitrobenzene added</u>	<u>Weight percent of nitrobenzene (Density 1.19867)</u>
2353.8	0.1148	----	----
2359.2	0.1145	0.05 mls	0.1815
2367.5	0.1142	0.10 mls	0.362



D. METHYL ALCOHOL ADDITIONS

A one phase system is present with all methyl alcohol/lithium chlorate mixtures at room temperatures. A limit was present in this case due to the high temperature involved. Mixtures containing greater than five percent by weight of methyl alcohol were found to form gas bubbles, giving incorrect resistance readings. Results are recorded below for systems containing a maximum of 1.5 percent methyl alcohol by weight.

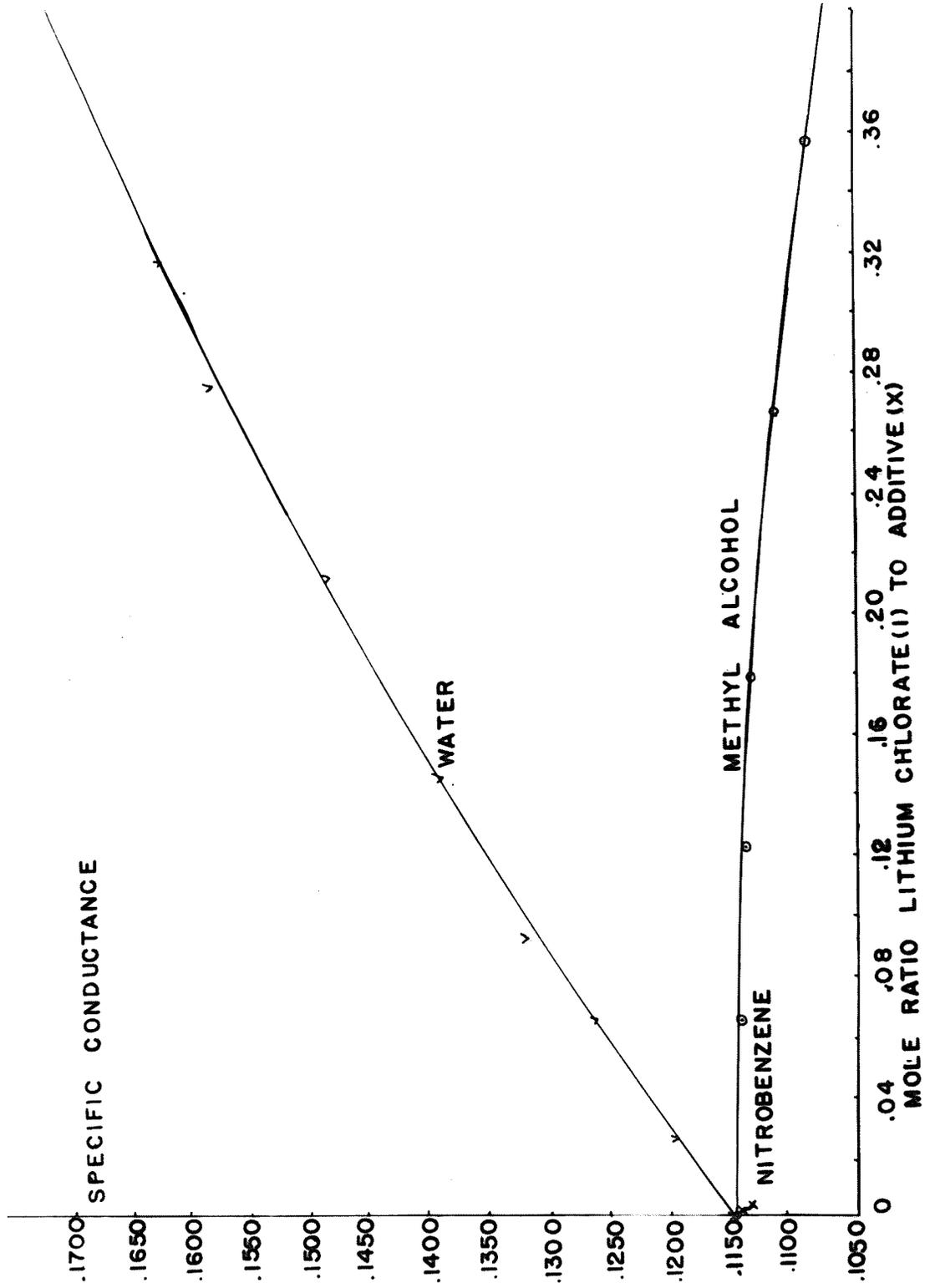
Table 5

RESISTANCE, SPECIFIC CONDUCTANCE AND PERCENTAGE  
BY WEIGHT OF METHYL ALCOHOL IN LITHIUM CHLORATE  
METHYL ALCOHOL MIXTURES AT 131.8°C.

<u>Resistance at infinite frequency</u>	<u>Specific Conductance</u>	<u>Volume methyl Alcohol added</u>	<u>Percentage by weight methyl alcohol (Density 0.7928)</u>
2351.5	0.1149	---	---
2358.2	0.1146	0.1 mls	0.223
2368.9	0.1141	0.2 mls	0.43
2353.8	0.1148	---	---
2373.0	0.1139	0.2 mls	0.63
2417.6	0.1118	0.3 mls	0.94
2474.7	0.1092	0.4 mls	1.25

For comparison with the known aqueous system,  
a value of the specific conductance of a lithium chlorate/

SPECIFIC CONDUCTANCE VS MOLE RATIO OF ADDITIVE



methyl alcohol mixture was taken at 25°C.

Percentage lithium chlorate (weight)	Percentage methyl alcohol (weight)	Resistance at infinite frequency	Specific Conductance
55.8	44.2	28,788.0	0.00939

The specific conductance related to the mole ratio of additive to lithium chlorate is shown in Table 6. This is also graphically represented in Figure 7.

Figure 7

Table 6

SPECIFIC CONDUCTANCE AND MOLE RATIO OF  
 WATER, NITROBENZENE OR METHYL  
 ALCOHOL IN LITHIUM CHLORATE AT 131.8°C.

Additive	Moles Additive	Moles lithium chlorate	Specific conductance
WATER	---	1.0	0.1150
	0.013	1.0	0.1171
	0.026	1.0	0.1202
	0.0394	1.0	0.1227
	0.0527	1.0	0.1243
	0.0656	1.0	0.1268
	0.0785	1.0	0.1302
	0.0922	1.0	0.1326
	0.1313	1.0	0.1368
	0.1445	1.0	0.1397
	0.2121	1.0	0.1492
0.2758	1.0	0.1594	
0.3157	1.0	0.1631	
NITROBENZENE	---	1.0	0.1148
	0.001335	1.0	0.1145
	0.002667	1.0	0.1142
METHYL ALCOHOL	---	1.0	0.1149
	0.06587	1.0	0.1146
	0.1218	1.0	0.1141
	---	1.0	0.1148
	0.1789	1.0	0.1139
	0.2686	1.0	0.1118
0.3580	1.0	0.1092	

DISCUSSION OF THE RESULTS

## DISCUSSION OF THE RESULTS

### A. THE ACTIVATION ENERGY OF CONDUCTANCE

The Arrhenius equation

$$9 \text{ ----- } K = A_k \exp - \frac{\Delta E_k}{RT}$$

was used to calculate the activation energy of conductance graphically. Over the small temperature range used, 130-145°C., the graph is essentially linear, giving an activation energy of 6.3 K. cal per mole. The relatively large value obtained seems to be excessive for a lithium salt, being comparable to that obtained for Mercuric bromide and chloride; 6.15 and 6.2 K. cal per mole<sup>42</sup>. Yaffe and Van Artsdalen<sup>30</sup> have shown that the value of  $\Delta E$  increases considerably as the melting point of the compound is approached, and thus the value of  $\Delta E$  between 130-145°C. for lithium chlorate may in no way be considered as the comparative activation energy. Further experiments are in progress to determine this activation energy at a temperature ten percent above the melting point of 127.8°C.

### B. THE EFFECTS OF ADDITIVES UPON THE CONDUCTANCE AT 131.8°C.

The addition of a small percentage by weight of water increased the specific conductance considerably as

was expected. Two separate experiments showed the specific conductance for the pure melt at  $131.8^{\circ}\text{C}$ . to be  $0.1150 \pm .0002$ , whereas following the addition of two percent of water the conductance had increased to  $0.1336$ . The initial rate of increase of conductance until two percent of water is present, is slightly greater than the rate of increase observed during the additions of between two to six percent. Measurements have not yet shown whether this final rate of increase remains constant, though Campbell, Kartzmark and Patterson<sup>33</sup> showed that there was a slight change at a concentration of approximately twenty percent water. This change of slope noted on a  $k$  versus percent water graph between the regions 0-2 and 2-6 percent water may indicate that the role played by the initial water molecules is not entirely that played by the molecules entering the system later. One may postulate that the effect of water addition will be twofold, causing an increase in the number of  $\text{Li}^+$  ions available for conduction, and also an increase in the size of the lithium ion caused by its association with the water molecules. The first effect will increase the conductivity, whereas the latter will cause the reverse.

It can be assumed that the role of the chlorate ion in conductance is negligible, due to its large size and hence small mobility compared to the lithium ion.

The second additive investigated was methyl alcohol. Little change in the conductivity is noticed until a mole ratio of 1:0.18 or 0.63 percent by weight of methyl alcohol is present. The tendency is towards a slow decrease in specific conductance. Thus a methyl alcohol/lithium chlorate solution of mole ratio 1:0.26 has a specific conductance of 0.1125 whereas a comparable water/lithium chlorate solution has a specific conductance of 0.1560. The difference is presumably due to the much greater ionizing power of water; a fact substantiated when the conductance of a 55.8% lithium chlorate solution in methyl alcohol, specific conductance at 25°C. 0.0094, is compared to an equivalent aqueous solution, specific conductance 0.115. Partial ionization of the lithium chlorate by the methyl alcohol present can be seen when the comparison is made to the effects of the third additive investigated, nitrobenzene. Though only a small addition is possible, the more rapid decrease in conductance for comparable mole ratios is immediately noticed.

These results have shown that in the case of lithium chlorate the predominating influence exerted by traces of non-electrolytes upon the conductance is that effecting the degree of ionization. Further experiments including density, viscosity, and conduction are in progress, which will enable a more complete study of the thermodynamic principles

involved in these transport properties, and comparative tests of the equations for the conductivity of fused salts.

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