

THE EFFECT OF TRACES OF ADDITIVES ON THE PROPERTIES OF
MOLTEN LITHIUM CHLORATE

A Thesis

Submitted to

the Committee on Postgraduate Studies
at The University of Manitoba



In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by

Digby Frederick Williams

September 1963

TO MY WIFE JUNE

ACKNOWLEDGEMENTS

I would like to thank Dr. A. N. Campbell and Dr. E. M. Kartzmark for their generous assistance and advice given during the course of this research.

Also I offer my sincere appreciation to Mr. M. K. Nagarajan for many stimulating discussions and helpful suggestions.

Many thanks to Mr. G. Epp, Mr. G. Trider, Mr. L. Wilkins, Mr. J. Gould, and Mr. E. Erickson for their assistance in the construction of much of the apparatus.

Finally I would like to thank The Consolidated Mining and Smelting Company of Canada for the financial assistance received.

ABSTRACT

The density ($2.088 \text{ gms. cc}^{-1}$), viscosity (0.35 poise), surface tension (85 dynes cm^{-1}) and electrical conductance ($0.115 \text{ ohm}^{-1} \text{ cm}$) and their temperature dependence have been determined for molten lithium chlorate. Similar results have been obtained for lithium chlorate melts containing small quantities of methyl alcohol, propyl alcohol, lithium nitrate, lithium hydroxide and water.

The results obtained for pure lithium chlorate all indicate the complexity of the melt constituents. It has been shown that there is probably considerable association. This is especially evident slightly above the melting point, for at these temperatures the temperature change of the properties of molten lithium chlorate is greatest.

A similar activation energy is found for the conductance of lithium chlorate and its lithium nitrate mixtures as for the activation energy of viscous flow for a pure lithium melt. This shows that the melt constituents are not primarily the simple ions, but that some form of cohesion exists between the simple melt constituents.

The addition of water to the lithium chlorate melt causes the melt properties to alter considerably, especially the transport properties (viscosity and conductance). These changes are in part due to a breakup of the structural entities in the pure melt though

the increase in electrical conduction cannot be completely explained by this. A cryoscopic investigation and a Raman spectrum of the effects of water additions both show that the water is not present as a simple unit in the melt: in fact the Raman spectrum shows the water has lost its identity.

TABLE OF CONTENTS

Chapter		Page
I	GENERAL AND THEORETICAL INTRODUCTION.	1
II	NATURE OF THE PROBLEM	14
III	SURVEY OF THE LITERATURE	16
IV	DENSITOMETRY	
	I. Introduction.	18
	II. Experimental.	19
	III. Results	29
	IV. Discussion.	35
V	VISCOMETRY	
	I. Introduction.	43
	II. Experimental.	46
	III. Results	52
	IV. Discussion.	58
VI	SURFACE TENSION	
	I. Introduction.	63
	II. Experimental.	67
	III. Results	70
	IV. Discussion.	77
VII	ELECTRICAL CONDUCTANCE	
	I. Introduction.	83
	II. Experimental.	96
	III. Results	102
	IV. Discussion.	139

Chapter	Page
VIII GENERAL DISCUSSION AND SUMMARY	153
BIBLIOGRAPHY.	170

LIST OF TABLES

TABLE		PAGE
4.1	Density and Molar Volume of Pure Lithium Chlorate and a Lithium Chlorate-Water Mixture Mole Fraction .046	30
4.2	Density and Molar Volume of Lithium Chlorate-Water Mixtures Containing 0.130 and 0.233 Mole Fractions of water	31
4.3	Molar Volume and Coefficient of Expansion of Lithium Chlorate-Water Mixtures	32
4.4	Analytical Representation of Density-Temperature Relationship for Lithium Chlorate-Water Mixtures..	33
4.5	Density, Molar Volume and Coefficient of Expansion for Some Typical Molten Salts	36
5.1	Water Flow Time at Different Temperature for Viscosity Determinations	49
5.2	Viscosity of Pure Lithium Chlorate	55
5.3	Viscosity of Lithium Chlorate-Water Mixture Mole Fraction Water .079	56
5.4	Viscosity of Lithium Chlorate-Water Mixture Containing .197 Mole Fraction Water	56
5.5	Viscosity of Lithium Chlorate-Water Mixture Containing .251 Mole Fraction Water	57
5.6	Analytical Representation of Viscosity	57
6.1	Surface Tension of Lithium Chlorate	71
6.2	Surface Tension of Lithium Chlorate-Water Mixtures	72
6.3	Surface Tension of Lithium Chlorate-Lithium Nitrate Mixtures	73
6.4	Analytical Representation of the Surface Tension Variation with Temperature for Lithium Chlorate and Lithium Chlorate-Water Lithium Chlorate-Lithium Nitrate Mixtures	75

TABLE	PAGE
6.5	Surface Tension and Surface Heat of Typical Group I Salts 78
6.6	Extrapolated Value of Surface Tension at the Melting Point of Several Alkali Salts 78
6.7	Parachor and Surface Heat of Lithium Chlorate 80
7.1	Conductances at 131.8°C. of Lithium Chlorate-Propyl Alcohol Mixtures 105
7.2	Conductance at 131.8°C. of Lithium Chlorate-Lithium Nitrate Mixtures 105
7.3	Conductances at 131.8°C. of Lithium Chlorate-Water Mixtures 106
7.4	Analytical Representation of the Change of Conductance with Mole Fraction of Additive at 131.8°C. 107
7.5	Variation of Specific and Equivalent Conductance of Pure Lithium Chlorate with Temperature 108
7.6	Temperature Dependence of Specific Conductance of a Lithium Chlorate-Methyl Alcohol Mixture 109
7.7	Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Water Mixture with Temperature 110
7.8	Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Water Mixture with Temperature 111
7.9	Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Water Mixture with Temperature 112
7.10	Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Lithium Nitrate Mixture with Temperature 113
7.11	Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Lithium Nitrate Mixture with Temperature 114

TABLE	PAGE
7.12	Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Lithium Nitrate Mixture with Temperature 115
7.13	Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Lithium Nitrate Mixture with Temperature 116
7.14	Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Lithium Nitrate Mixture with Temperature 117
7.15	Variation of Specific and Equivalent Conductance of Lithium Chlorate-Lithium Nitrate Mixture with Temperature 118
7.16	Arrhenius Representation of Conductances of Lithium Chlorate and its Water Mixtures 119
7.17	Arrhenius Representation of Conductances of Lithium Chlorate-Lithium Nitrate Mixtures 120
7.18	Temperature Variation of Specific and Equivalent Conductance for a Lithium Chlorate Mixture 122
7.19	Temperature Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Lithium Hydroxide-Water Mixture 123
7.20	Temperature Variation of Specific and Equivalent Conductance of a Lithium Chlorate-Lithium Hydroxide-Water Mixture 124
7.21	Analytical Representation of the Conductance of Lithium Chlorate-Lithium Hydroxide-Water Mixture ... 125
7.22	Viscosity and Conductance Parameters for Fused Salts 140
7.23	Degree of Ionization of Several Typical Salts 142
7.24	Theoretical and Experimental Activation Energy of Conductance 143
7.25	Equivalent Conductance of Lithium Chlorate Mixtures at Equal Viscosities 151

TABLE		PAGE
8.1	Fusion Parameters of Some Typical Substances	155
8.2	Raman Spectra of Molten Lithium Chlorate with Added Water	162
8.3	Composition of Lithium Chlorate-Water Mixtures for Raman Spectra	163
8.4	Previous Raman Studies in Molten Chlorates, Hydroxides and Liquid Water	164

LIST OF FIGURES

FIGURE		PAGE
4.1	Filling Apparatus and Dilatometer	22
4.2	Calibration Plots for Dilatometer	24
4.3	Density vs. Temperature of Lithium Chlorate-Water Mixtures	34
4.4	Variation of Molar Volume with Temperature for Lithium Chlorate and its Water Mixtures	39
4.5	Molar Volume at 130°C. vs. Mole Fraction Water	41
4.6	Coefficient of Expansion vs. Mole Fraction Water	41
5.1	Viscometer	47
5.2	Calibration Plot for Viscometer	50
5.3	Viscosity of Lithium Chlorate-Water Mixtures vs. Temperature	53
5.4	Log Viscosity vs. $\frac{1}{T^{\circ}K}$ of Lithium Chlorate-Water Mixtures	54
5.5	Isothermal Viscosity vs. Mole Fraction Water	61
5.6	Variation of Activation Energy with Mole Fraction Water	61
6.1	Surface Tension Apparatus	68
6.2	Plot of Surface Tension vs. Temperature for Lithium Chlorate and its Mixtures	74
6.3	Plot of Surface Tension vs. Mole Fraction Additive ...	76
7.1	Conductance Cell	98
7.2	Specific Conductance at 131.8°C. vs. Mole Fraction Additive	126
7.3	Equivalent Conductance of Lithium Chlorate Mixtures vs. Mole Fraction	127

FIGURE	PAGE
7.4 Plot of Specific Conductance of Lithium Chlorate Mixture vs. Temperature	128
7.5 Equivalent Conductance vs. Temperature of Lithium Chlorate-Water Mixtures	129
7.6 Equivalent Conductance vs. Temperature Lithium Chlorate-Lithium Nitrate Mixtures	130
7.7 Log Specific Conductance of Lithium Chlorate Mixture vs. $\frac{1}{T^{\circ}\text{K}}$	131
7.8 Log Equivalent Conductance Λ_1 of Lithium Chlorate Mixtures vs. $\frac{1}{T^{\circ}\text{K}}$	132
7.9 Log Equivalent Conductance Λ_2 of Lithium Chlorate Mixtures vs. $\frac{1}{T^{\circ}\text{K}}$	133
7.10 Specific Conductance of Lithium Chlorate-Lithium Hydroxide Mixtures vs. Temperature	134
7.11 Equivalent Conductance of Lithium Chlorate-Lithium Hydroxide Mixtures vs. Temperature	135
7.12 Log Specific Conductance of Lithium Chlorate-Lithium Hydroxide Mixtures vs. $\frac{1}{T^{\circ}\text{K}}$	136
7.13 Log Equivalent Conductance Λ_1 of Lithium Chlorate-Lithium Hydroxide Mixtures vs. $\frac{1}{T^{\circ}\text{K}}$	137
7.14 Log Equivalent Conductance Λ_2 of Lithium Chlorate-Lithium Hydroxide Mixtures vs. $\frac{1}{T^{\circ}\text{K}}$	138
7.15 Activation Energy of Specific Conductance vs. Mole Fraction Additive	148
7.16 Activation Energy of Equivalent Conductance vs. Mole Fraction Additive	149
8.1 Principal Raman Bands for Water	163

LIST OF SYMBOLS

α	Coefficient of expansion
γ	Surface tension
η	Viscosity
Θ	Einstein temperature
K	Specific conductance
λ	Individual ionic conductance
Λ_1, Λ_2	Equivalent conductance
μ_i	Mobility of an ion under a potential of 1 volt/cm.
μ_m	Molar conductance
ν	Raman frequency, cms^{-1}
ρ	Density gms. cc^{-1}
ϕ	Fluidity
a	Degree of dissociation
$a, b, \rho_0, \eta_0, A, \dots$	Theoretical constants
C_i	Volume concentration of ion i
ΔE_K	Activation energy for specific conductance
ΔE_Λ	Activation energy for equivalent conductance
ΔE_η	Activation energy for viscous flow
ϕ	Partition function
F	Faraday constant
h	Planck's constant
ΔH^\ddagger	Enthalpy of activation for conductance
ΔH_f	Latent heat of fusion per mole
H^s	Surface heat content

I	Moment of inertia
k	Boltzmann constant
L_0	Latent heat of fusion, per gram
K_i	Freezing point depression constant
m	Mass of the atom
M_1, M_2	Molecular weights
M_e	Mean equivalent weight
N	Avogadro's number
n_1, n_2	Mole fraction
R	Gas constant
ΔS_f	Entropy of fusion
ΔS^+	Entropy of activation for conductance
S^s	Surface entropy
T	Degrees absolute
t	Degrees centigrade
T_f	Temperature of fusion
V_s	Specific volume
V_m	Molar volume of a mixture of substances
Z_i	Charge on each ion

GENERAL AND THEORETICAL INTRODUCTION

CHAPTER I

GENERAL AND THEORETICAL INTRODUCTION

The liquid state is the most complex and least understood of the states of matter. Though the gaseous and solid states had been the subject of innumerable investigations, prior to the 1920's little interest was shown in the liquid state, it being considered as a condensed gas retaining complete disorder. Due to the results of many X-ray investigations and other observations on liquids at this time, interest became stimulated, and many papers were published in the following years on the general subject of liquids, notably those of Stewart.¹ Stewart explained the diffuse halos he obtained from X-ray investigations as caused by temporary crystalline aggregates called "Cytobatic Groups", which were present in the liquid structure. Stewart's hypothesis of the presence of these cytobatic groups was descriptive in nature, and many mathematical treatments of liquids followed which would correspond with this physical situation. For example, Bernal² considered that each liquid retained basically a crystal structure, such as face centred cubic, but that the position of each of the coordinating spheres surrounding the atom was altering continually. These surrounding positions were given by a gaussian distribution, the position of maximum probability being the normal equilibrium position of the atom in the crystal. Thus, if the lattice was viewed it would appear blurred. Bernal also assumed that

the normal equilibrium position of the coordinating spheres, and the number of spheres in the coordinating shell, were temperature and pressure dependent.

Other authors attempted to elucidate liquid structure by explaining why there is a definite melting point for a substance. Studies of alloys^{3,4} indicated that a solid is characterized by two kinds of order, long range order and short range order. Long range order in a crystal demands an orderly spatial arrangement of atoms at large distances with respect to the central lattice site, whereas short range order demands that atoms in the immediate vicinity of another atom be arranged in an orderly pattern with respect to that atom. As the temperature of the crystal is raised, the long range order at first decreases slowly, and then is suddenly lost completely, while the short range order persists over a temperature range, gradually decreasing to zero at a temperature much higher than that at which the long range order collapsed. This sudden loss of long range order is the melting process; the short range order becoming essentially zero at vaporization. Lindermann assumed that the melting process occurred when the amplitude of vibrations of the atoms in a crystal reached a certain fraction of the lattice energy, whereas Mott and Gurney⁵ associated the melting process with a breakup of the crystal into many polycrystalline species.

Lennard-Jones⁶ pictured the atoms of a liquid as being in cages, enclosed by their nearest neighbours, the size of the cage and the number of nearest neighbours being the same for all atoms present. The potential energy of the cage was considered to be symmetrical about the centre, varying in value from infinity at the edge of the cage to a minimum somewhere inside it. Using this basic model, the authors were able to predict the critical properties and boiling point for a few simple liquids. The primary advantage of this approach was that the configurational integral could be evaluated relatively easily. The configurational integral is the term in a partition function corresponding to the potential energy. If the partition function is known, then the other thermodynamic properties may be calculated in the manner of statistical mechanics. For the model proposed by Lennard-Jones the partition function takes the form

$$1.1(1) \dots \quad f = \frac{1}{N!} \left[\frac{(2\pi m k T)^{3/2}}{h^3} \right] C.I.$$

where C.I. is the configurational integral.

Other attempts have been made with similar models using various methods for evaluating the configurational integral, notably those of Kirkwood⁷ and Green.⁸ In general, the results have been poor. More satisfactory has been the approach of Eyring et al.⁹ From the concept of holes and also solid-like structures within liquids, Eyring developed a partition function based on these two significant

structures:-

$$1.2) \dots f = \underset{\text{like}}{f_{\text{solid}}} \cdot f_{\text{gaseous}}$$

From this composite partition function he obtained satisfactory correlation between many thermodynamic and transport properties of liquids. This function may be similarly developed for simple molten salts. For an alkali halide the partition function per mole has the form:-

$$1.3) \dots f = \left\{ \frac{e^{\frac{E_s}{2RT} \left(\frac{V}{V_0}\right)^{\frac{1}{3}}}}{\left(1 - e^{-\frac{\Theta}{T}}\right)^3} \left[1 + m_h e^{-\frac{aE_s \left(\frac{V}{V_s}\right)^{\frac{1}{3}}}}{2m_h RT} \right] \right\} \frac{2V_s}{V} N.$$

$$\times \left\{ \frac{(2\pi m k T)^{\frac{3}{2}} e V}{N h^3} \cdot \frac{8\pi^2 I k T}{h^2} \cdot \frac{1}{1 - e^{-\frac{h\nu}{RT}}} \right\} \left(1 - \frac{V_s}{V}\right) N$$

where $m_h = m \left(\frac{V}{V_s} - 1 \right)$

The concept of holes being present in a liquid, used by Eyring in the development of the partition function of equation (3), has much experimental support. Ubbelohde and his co-workers^{10, 11} have shown that a typical volume increase on fusion for an alkali halide is 20-30 per cent of the molar volume of the solid. From measurements of the velocity of ultrasonic vibrations, Bockris and Richards¹² calculated the compressibility and hence free volume of several molten salts including the halides investigated by Ubbelohde. They found the free volume increase on melting was 2 per cent of the molar volume compared to the total volume increase of 30 per cent. The logical explanation was the formation of holes.

Thus it can be seen that attention has been focused^s on the mathematical understanding of the structure of liquids. Liquids may rationally be subdivided into a number of different classes, the class being determined by the difference in type and symmetry of the intermolecular forces among the constituent particles, viz. nonpolar liquids, polar liquids, hydroxyl and hydrogen bonded liquids, metallic liquids and ionic liquids. Nonpolar liquids include those formed by the rare gases, and also the lower hydrocarbons such as methane. Polar liquids are formed from substances which have a direct electrostatic interaction between permanent dipole moments superimposed on a force field which is otherwise almost symmetrical. Also included in this class are liquids formed from molecules with quadrupole moments

such as carbon dioxide and the mercuric halides. The hydroxyl and hydrogen bonded class of liquids are self explanatory, and the metallic liquids are of course the molten metals. Ionic liquids include those formed from the simple salts, such as the alkali halides, and from other highly conducting fused salts possessing directional forces. In recent years the importance of these ionic liquids in many fields of science has increased rapidly. In addition to their use in the production of many of the rarer metals, ionic melts often have physical properties such as high temperature stability, low vapour pressure, and excellent solvent and conduction powers, which give them further technological advantages. For these reasons there has been a resurgence of research activity on the fundamental properties of molten salts. Moreover, they offer an opportunity to study that portion of the liquid state in which charged particles are in intimate contact, and coulombic forces predominate. General liquid properties, and the theoretical developments cited earlier apply equally to fused salt melts, though slight modifications of the theories may be necessary.

A comparative test of various proposed models for the liquid state has recently been made by Bockris. The models examined were:-

- (1) The quasi-lattice model
- (2) The hole model of Fürth
- (3) The crystallite model of Mott
- (4) The polyhedral hole theory of Bernal

(5) The liquid free volume model of Cohen

(6) The significant structure theory of Eyring.

The properties calculated were volume change on fusion, entropy change on fusion, compressibility, expansivity, and self-diffusion.

The results showed that the hole theory and the significant structure theory were most satisfactory in predicting the value of these experimental quantities.

The hole model for liquids regards the liquid as a quasi-crystalline lattice structure consisting of molecules and holes. The holes vary in size and shape with time due to the random movements within the liquid caused by thermal fluctuations and Brownian motion. Since the lifetime of a void of molecular dimensions is of the order of a few lattice vibration periods, the holes disappear and reappear again at a neighbouring lattice site continuously.

The static and transport properties of the liquid may be calculated using these structural foundations. The mechanism of molecular transport is envisaged as the jumping of a molecule from one lattice site to a neighbouring vacancy in the direction of flow. Often such motion has been treated successfully by the absolute rate theory.¹³

Thus the process of fusion of a crystalline lattice is thought to produce a melt consisting of holes and of melt units, which may be predominantly either molecules, polymeric units or ions, depending on the type of liquid formed. Often the electrical conductivity of a

molten salt is high (for sodium chloride the equivalent conductance is 143 mhos), indicating an ionic melt. Low electrical conductivity implies a high degree of covalency in the melt, but this does not necessarily mean the presence of molecular units in the crystal, since fusion may cause a fundamental change in bonding. The process of crystal fusion represents a transition between two stable states of matter, one with a high degree of order and low energy, the other with a lower degree of order but higher energy. The latent heat of fusion, ΔH_f , varies considerably, depending upon the substance under investigation, it being the energy required to overcome the attractive intermolecular forces of the crystal. The variation of the entropy of fusion, ΔS_f , is small, namely less than one order of magnitude for nearly all substances, indicating that the order-disorder process is the same for all fusion processes. The principal mechanisms contributing to this randomization in melting are classified as:-

(a) Increase in vibrational entropy due to looser packing, and a consequent decrease of characteristic frequencies in the melt ΔS_v .

(b) Increase of orientational randomization due to the marked reduction of repulsion barriers accompanying the expansion in volume on melting ΔS_o .

(c) Increase in positional disorder on melting ΔS_p .

(d) Randomization of the internal configurations of molecules or ions containing flexible groups ΔS_c .

(e) Changes of association or chemical bonding on melting ΔS_a .

Thus

$$1.4) \dots \Delta S_f = \Delta S_v + \Delta S_o + \Delta S_p + \Delta S_c + \Delta S_a$$

Ubbelohde¹⁴ postulates that low-melting salts containing ions such as ClO_3^- form melts in which appreciable concentrations of association complexes are present, and hence ΔS_a has an appreciable value.

A knowledge of the species present in a melt, whether formed from a pure salt or from a mixture, is of primary importance in the understanding of its liquid properties. The thermodynamic principles used for many years in classical chemistry apply also to molten salts, and often provide valuable information on the melt structure, for example, the use of cryoscopy. The freezing point depression exhibited by a solvent-solute system is a quantitative property depending on the nature of the solvent, and the activity of the solute particles, whether ions or molecules. Bloom and Richards¹⁵ have shown from e.m.f. measurements that the activity coefficients of molten salt systems are almost unity, and hence the slope of the freezing point depression curve is the constant of the Raoult-Van't Hoff law:-

$$1.5 \dots \Delta T_i = \frac{R T_0^2}{1000 L_0} m_i = K_i m_i$$

where ΔT_i is the freezing point depression, T_0 the freezing point of the solvent, and m_i the concentration of the solute in molality.

If the solute ionizes or dissociates, each particle formed acts independently of the others, and the equation corresponding to (5)

becomes

$$1.6 \dots \Delta T_i = v_i K_i m_i$$

where v_i is the number of particles formed per added molecule.

Janz et al^{16, 17, 18} illustrate the combined use of cryoscopic and conductometric investigations in their study of the behaviour of KF and K_2TiF_6 in a $KCl-LiCl$ eutectic melt. The combined results indicate the following ionization processes:-

<u>Solute</u>	<u>Ionization</u>	<u>Cryoscopic Depression</u>	
		<u>Theoretical</u>	<u>Observed</u>
KF	$KF = K^+ + F^-$	1	1
K_2TiF_6	$K_2TiF_6 = 2K^+ + 2F^- + TiF_4$	3	3

Tempkin¹⁹ studied the cryoscopic aspects of thermodynamics and interpreted them structurally. He showed that the freezing point depression equation is obeyed if the activity of a salt M_xA_y in a mixture is given by the relationship

$$1.7 \dots a_{M_xA_y} = \frac{n_{M_x^+}}{\sum n_{x^+}} \times \frac{n_{A_y^-}}{\sum n_{y^-}} = N_{M_x^+} \cdot N_{A_y^-}$$

where the ion fractions $N_{M_x^+}$ and $N_{A_y^-}$ are given by the ratio of the amount of a given ionic species to the total amount of ions of the same sign in the system. The Tempkin model, ideal for molten ionic salts, when statistically interpreted corresponds to the anions and cations being randomly distributed amongst themselves, such that each anion is surrounded by cations, and vice versa.

From these structural concepts, and the deviations of such systems from ideality, studies have been made of the relative degree of ionic or covalent bonding between nearest neighbours. Data on the heat of fusion and entropy of fusion, both calorimetric and cryoscopic in origin, have been used to interpret the structural changes of solids on melting.

It can be seen that both the classical and modern experimental techniques, which have been used to investigate aqueous solutions and other media, may be equally well suited for high temperature investigations of molten salts. Of the modern techniques, the application of Raman spectroscopy affords perhaps the most information relative to melt structure. From Raman absorption spectra it is possible to distinguish between several of the possible models of liquid structure. If the model was that of classical theory, compressed gas having complete disorder, then a continuous spectrum would be observed. If the liquid had a microcrystalline structure, that is, minute but perfectly crystalline aggregates floating within a medium of non-oriented molecules, then the Raman lines should decrease

in intensity on fusion of the solid, but their relative width and position should stay the same. If a quasi-crystalline model applies, in which a correlation exists between the mutual orientations and distances of neighbouring molecules, spreading over many molecules but getting weaker as distance increases, then the Raman lines should increase in breadth and suffer a slight displacement to a lower frequency.

The fact that Raman frequencies persist in a melt up to several hundred degrees above the melting point²⁰ is an indication that the observed frequencies are not due to vibrations in the crystal lattice, but rather are due to oscillations of molecular complexes having some degree of homopolar bonding. Substances with only heteropolar bonding show no Raman activity. In general, the pulsation frequency due to a complex in a melt lies below that of the pure compound if the complex is a single molecule, and lies above this frequency if the complex exists in either a highly polymeric or highly associated form, such as in zinc chloride.²¹

Thus, during the past thirty years the liquid state has received much attention. The mathematical treatments proposed initially for non-polar liquids have been adapted and applied in general to molten salts. No theoretical relationship has yet been advanced which will satisfactorily predict the properties of a melt, though considerable success has been achieved using the hole theory of Fürth and the significant structure theory of Eyring. This success

shows that the model of the melt upon which these theories are based is substantially correct--namely, a binary mixture of melt constituents and holes, throughout which short range order and long range disorder exists.

NATURE OF THE PROBLEM

CHAPTER II

NATURE OF THE PROBLEM

No satisfactory theory has yet been proposed which can predict the physical properties of concentrated aqueous solutions. The extreme of a concentrated aqueous solution is one in which water itself is by far the minor component, as is observed when a small amount of water is added to a melt. The tenacity with which water is retained by some molten salts has been noticed by many workers,^{12, 22, 23, 24} and the solubility of water vapour in several systems has been experimentally examined.^{25, 26} No attempt has been made to complete this investigation of the salt-water system in the region of the melt, nor have there been any theoretical publications on the conductance of fused salts to which a little inert "solvent" has been added. It was for this reason that the density, viscosity, surface tension and conductance of molten lithium chlorate and its mixtures containing small mole fractions of water were investigated. To correlate the changes in these properties with the melt constituents, organic compounds and inorganic salts were also chosen as additives. The organic compounds methyl alcohol and propyl alcohol were chosen so that the effect of the molecular size of the additive would then be apparent. Lithium nitrate was chosen as an inorganic salt additive, the thermodynamics of lithium nitrate mixtures being simultaneously investigated by Mr. Nagarajan,²⁷ in this laboratory. Lithium hydroxide

was chosen as the second inorganic substance, since after a preliminary survey of the conductance of water mixtures, it was of great interest to compare the property changes caused by an ionic hydroxide to those caused by the water additions.

The theoretical considerations applied to the results are those developed for molten salts.

SURVEY OF THE LITERATURE

CHAPTER III

SURVEY OF THE LITERATURE

Aqueous lithium chlorate solutions have been investigated throughout the complete range of concentration by Krauss and Burgess,²⁸ Kloschko and Grigorjew,²⁹ and Campbell et al.³⁰ The experimental standards employed by Krauss and Burgess²⁸ are no longer considered satisfactory. Kloschko and Grigorjew²⁹ compared their results with the phase diagram of the water-lithium chlorate system; however, the constituents of the solid phase need not necessarily be those of the liquid phase, and any correlation between specific conductance and the equilibrium diagram is arbitrary. The latest investigation of the lithium chlorate-water system was that of Campbell et al.³⁰ Though these workers studied the complete concentration range, the experimental techniques used restricted the results in the 90-100 per cent lithium chlorate range, so that only a single observation was made for these concentrations.

Conductance and viscosity isotherms of the complete concentration range for silver nitrate-water and ammonium nitrate-water systems³¹ have also been determined, though again no particular attention was paid to the 90-100 per cent salt region. Keenan³² studied the cryoscopic behaviour of small amounts of water in ammonium nitrate and showed that the water dissolved without ioniza-

tion or association.

A few surveys of the solubility of gases in a melt have been undertaken,^{25, 26} but no further properties of these melts have been determined. Duke and Doan²⁵ showed that water vapour has a strikingly greater solubility in melts containing Li^+ , the solubility in general varying as the square of the Li^+ concentration.

Even less work has been published on systems of molten salts plus a small mole fraction of an organic compound, though many studies have been made in organic solvent-salt systems in the dilute region of concentration.

This thesis is an extension of an earlier work by myself on the conductance of molten lithium chlorate and the effects of additives, and these results constitute the only known systematic study of salt-additive systems involving small amounts of an inert solute of an organic nature.

DENSITOMETRY

CHAPTER IV

DENSITOMETRY

I. INTRODUCTION

Density determinations were among the earliest experimental investigations of molten salts.

The knowledge of density or molar volume is fundamental in the understanding of complex transport processes occurring within a melt. The variation of density with temperature serves as a relationship from which the comparative size and type of intermolecular force existing within the melt may be estimated.

Experimentally the density-temperature variation has been found to be represented either by

$$4.1 \dots \rho = a - bt$$

where a and b are empirical constants, for example the work of Yaffe and Van Artsdalen,³⁴ or of the form³⁵

$$4.2 \dots \rho = \rho_0 \exp -\alpha T$$

where ρ_0 is a constant for the system, and α the expansivity defined as

$$4.3 \dots \alpha = -\frac{1}{\rho} \frac{d\rho}{dt}$$

Generalizations regarding the relationship of density or molar volume, and expansivity to the ionic character of the melt were initially proposed by Biltz and Klemm.³⁰ They suggested that, all other factors being equal, owing to weak intermolecular forces,

molten covalent compounds have larger molar volumes than those of ionic melts, which have in contrast a strong coulombic force field. Also, for the same reasons, the thermal expansivity of covalent melts is greater than that of ionic melts.

Of further importance is the accurate evaluation of the density of a molten salt for the possible substitution of density as a thermodynamic variable in the radial distribution function. It is possible to calculate almost all thermodynamic properties for a melt following an evaluation of the related radial distribution function.

Finally, knowledge of the change in volume on fusion provides a direct correlation between the usually known structure of the solid and that of the liquid. In addition, it may provide an estimate of the activation energy for lattice defect formation in the solid.

In conclusion, accurate density measurements and their temperature dependence are necessary for the evaluation of many of the basic properties of a melt, for example, equivalent conductance, and are in themselves an indication of the type of liquid structure present.

II. EXPERIMENTAL

The limiting factors encountered in high temperature densitometry are those typical of all accurate high temperature measurements. Maintaining a uniform temperature over the entire system becomes difficult at high temperatures, as is also the control of this temperature. The apparatus must be constructed of completely

inert material, and since many fused salts corrode glass, an optical method of density measurement is not then applicable. Lithium chlorate, however, does not attack pyrex glass, and the very low temperature of the melt allows the use of a simple oil-bath thermostat. For these reasons the density measurement of molten lithium chlorate may be undertaken using any of the well known procedures for low temperature non-corrosive liquids.

Apparatus

The dilatometric method was chosen for the determination of the densities of lithium chlorate and its water mixtures. This method affords both measurements of high precision, and the experimental control of the atmosphere needed because of the hygroscopic nature of the melts.

A thermostat was constructed in which density, viscosity, and surface tension experiments could be performed. It consisted of a rectangular pyrex glass jar, 15x15x30 cms., surrounded on the sides and base by 5mm. transite plates. This container was placed in a double walled wooden box, 30x30x30 cms., and the outside covered with a metal casing. The 25 cms. space between the container walls and the wooden box was filled with vermiculite. A 7.5 x 12.5 cms. glass window was installed in the front of the thermostat, and a 60 watt bulb in the rear between the double wall, so that it was possible to view directly any apparatus placed inside the thermostat. Since the experimental range of temperature, 120-170°C is so low, a

clear silicon oil was used as the bath liquid.

A 500 watt copper immersion heater connected in series with variable ohmite resistors was used to bring the temperature of the bath to within a few degrees of the experimental temperature required. The final temperature rise was obtained from a low wattage heating coil made of nichrome wire wound on glass tubing, and when used in conjunction with a mercury in glass regulator and a "thyatron" relay, temperature control was better than $\pm 0.1^{\circ}\text{C}$.

The temperature was measured using a copper-constantan thermocouple connected to a Tinsley vernier potentiometer, type 4363A, capable of measuring deflections caused by less than 1 microvolt. The thermocouple was initially calibrated at the boiling point of pure water, pressure corrected, and the freezing point of tin (231.85°C). An ice bath was used as the cold junction.

The temperature fluctuations of the thermostat were always less than 5 microvolts, or 0.1°C .

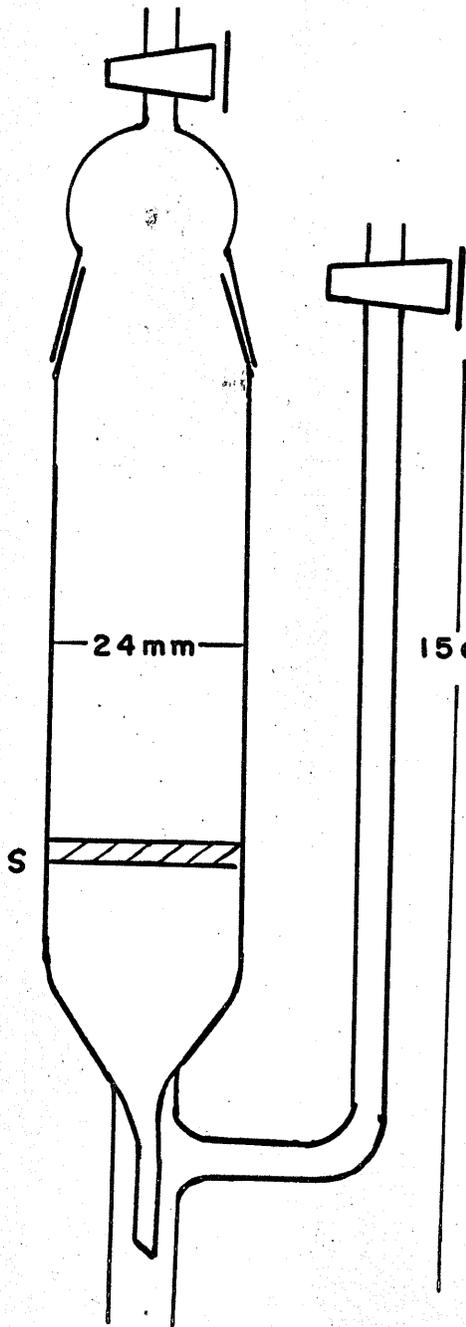
The dilatometers (Fig. 4.1) were made of pyrex glass, and consisted of a thin-walled bulb of about 10 mls capacity sealed to a stem of 1 mm. precision-bore capillary tubing, 10 cms. long. The tolerance in the capillary bore was $.0001\text{mm}$. A slanted side arm with a small bulb blown at its tip was attached to the top of the capillary, and served as a reservoir for any possible excess lithium chlorate added to the dilatometer when filling. Three calibration marks were made on the capillary using a lathe. The marks were

FIGURE 4.1

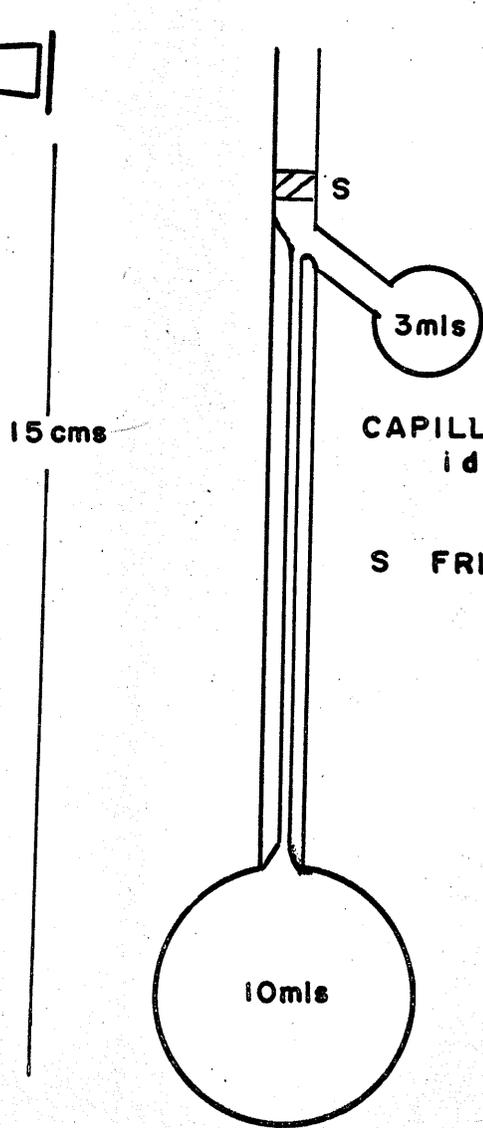
Filling Apparatus and Dilatometer

FIGURE 4-1

FILLING TUBE



DILATOMETER



CAPILLARY TUBING
id 1.0mm

S FRITTED GLASS
DISC

to dilatometer

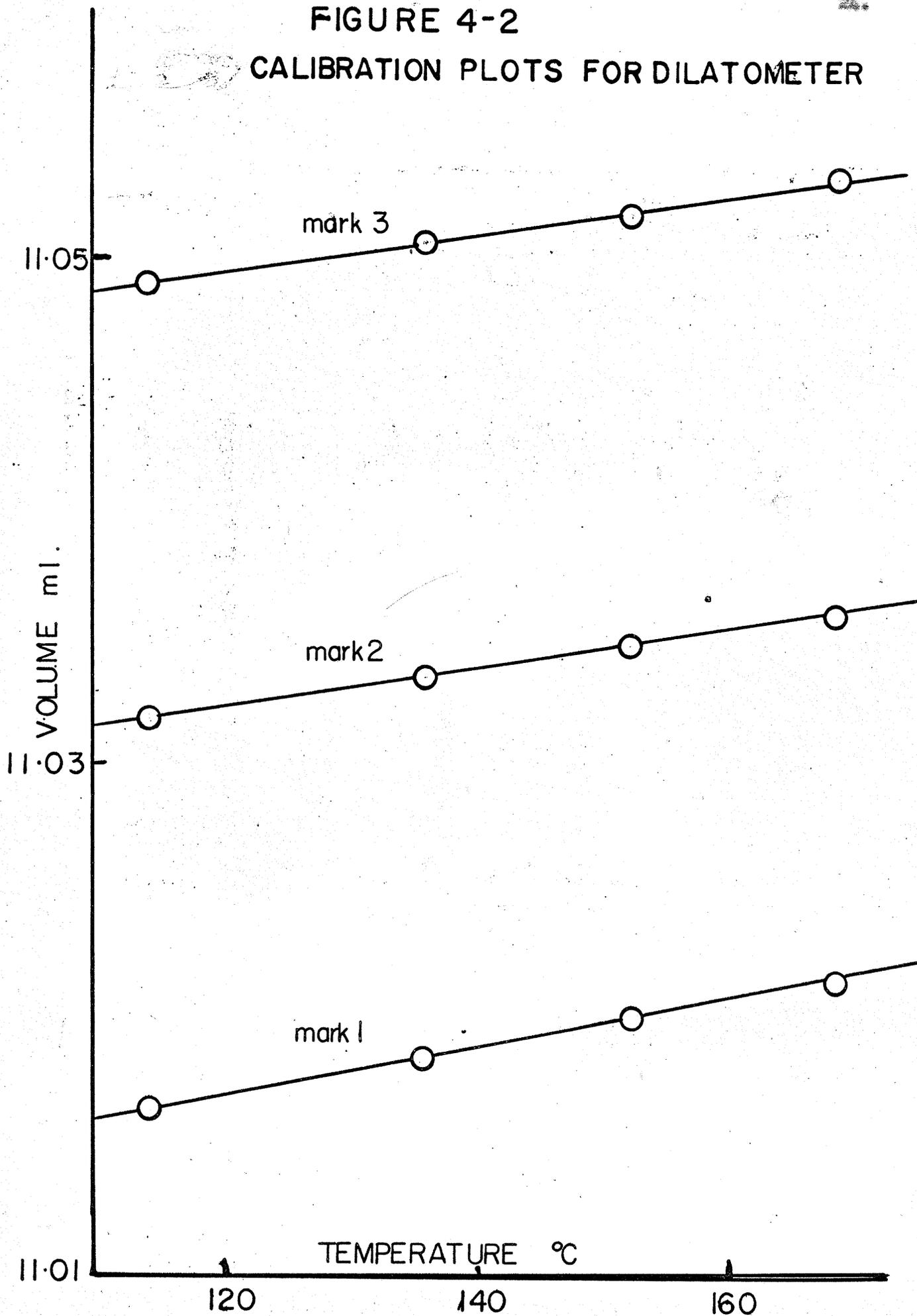
approximately 20 mm. apart, and served as reference lines in both the calibration and in the experiment.

The dilatometers were calibrated with Shawinigan redistilled mercury. After cleaning, each dilatometer was oven dried and weighed. The mercury was then introduced using a long thin capillary tube extending into the bottom bulb, care being taken to avoid trapped air. The dilatometers were then clamped in position inside the thermostat so that only the filling extension was above the thermostat liquid level. This extension was plugged with a small piece of cotton wool. After 3-4 hours, when thermal equilibrium had been established, mercury was removed from the dilatometers using a fine syringe, until the meniscus coincided with one of the reference marks on the capillary. A Gaertner microcathetometer was used to aid the visual coincidence of the mark and mercury level. Following this adjustment, which was completed in the thermostat, the dilatometers were removed, their outsides cleaned and dried thoroughly, allowed to cool and then weighed. Using the density of mercury at the calibration temperature,³⁷ the volume of the dilatometer corresponding to the reference mark was known. This complete process was repeated for each reference mark at four different temperatures. A typical calibration graph is shown in Fig. 4.2. Calibration in this manner obviated the necessity of a correction factor for the glass expansion.

Figure 4.2

Calibration Plots for Dilatometer

FIGURE 4-2
CALIBRATION PLOTS FOR DILATOMETER



A special filling technique had to be used for the lithium chlorate melts due to their hygroscopic nature. The dilatometer was connected to the apparatus shown in Fig. 4.1. It is primarily a series of glass filter discs set in glass tubing so that it is possible to evacuate any of the separate compartments by use of the side arm vacuum taps.

The top compartment of the transfer tube was filled with sufficient powdered anhydrous lithium chlorate to fill the dilatometer. This was done inside a drybox in a nitrogen atmosphere. The combined dilatometer-filter unit was then evacuated, removed from the drybox and placed in the thermostat. The charge of lithium chlorate melted, and slowly filtered through into the dilatometer bulb. When sufficient lithium chlorate had filtered, the level of the apparatus was adjusted inside the thermostat so that the bath fluid level was just above the lowest fritted disc of the filter tube. After the lithium chlorate above this level had solidified, and that below had drained completely into the bulb, the dilatometer was evacuated and sealed off just above this lower fritted disc, which then acted as a filter to retain any possible solid products formed by decomposition during sealing, from entering the dilatometer.

The sealed dilatometer was now completely immersed in the thermostat and clamped in a vertical position. After thermal equilibrium had been attained the height of the meniscus above one of the reference marks was measured accurately using the microcathetometer.

This cathetometer was mounted on a rigid concrete platform. From this measurement the volume of the charge of lithium chlorate at the known thermostat temperature was calculated by interpolation from the calibration graph. The measurements were repeated at at least six temperatures between 130-160°C. Several cathetometer readings were taken for each temperature, the variation limits being ± 0.01 mm. The cathetometer was calibrated to measure ± 0.001 mm.

After all cathetometer readings had been taken, the dilatometer was removed from the thermostat, cooled, the outside cleaned and dried, and then weighed. Next, the bulb was carefully cracked, the pieces of glass all being retained. The lithium chlorate was removed by washing with distilled water, and all of the dried cleaned glass was then weighed. From the weight of the dilatometer plus lithium chlorate and the separate weight of the glass only, the weight of the lithium chlorate present was obtained.

The reagents used in the density determinations were the same as used for the other investigations. The lithium chlorate was prepared by the method of Kraus and Burgess²⁸ as modified by Campbell and Griffiths,³⁸ which uses the metathetical reaction between lithium sulphate and barium chlorate. The lithium sulphate, supplied by Fisher Scientific Company, and the barium chlorate, obtained from the British Drug Houses Ltd., were of the highest purity and were used without further purification.

A molar solution of barium chlorate was heated to 90-100°C., and an equivalent solution of lithium sulphate slowly added. The mixture was digested for 3-4 hours before the barium sulphate was removed by filtration. The solution was then concentrated by evaporation until it had an oily appearance, and was then refiltered. The absence of sulphate or barium ion was demonstrated by titration of aliquot parts of this stock solution with solutions of barium chlorate and lithium sulphate. Where equivalence was not found, this was obtained by addition of the necessary solution, and the bulk then refiltered. The filtrate was heated to 80°C. under a pressure of 0-10 mms. mercury until, when cooled, crystals of lithium chlorate formed. These crystals were then rapidly filtered and placed in a vacuum desiccator over concentrated sulphuric acid for 10-12 weeks. To remove the final traces of water, the lithium chlorate crystals were powdered in a drybox, and then heated for 6-8 weeks under a high vacuum over anhydrous barium oxide.

The residual water was initially determined by gas-chromatography. A precision Chromofrac VP-7 unit was calibrated for water detection by injection of samples of 0.01 ml ethyl alcohol containing known amounts of water. The lower limit of detection was found to be 1 part of water in 500 parts of alcohol by volume. The dried powdered lithium chlorate was weighed, mixed with dry sand, and heated strongly. Under the catalytic action of the sand, the lithium chlorate rapidly decomposed evolving oxygen together with

any moisture it contained. These gases were trapped in a nitrogen cold trap. A test of the residue showed that decomposition was complete. The trapped gases were allowed to warm up slowly to 0°C., and a measured quantity of ethyl alcohol was then added. This solution was then allowed to warm up to room temperature and a portion passed through the chromatograph. The result showed that the lithium chlorate contained less than 0.006% water by weight. The specific conductivity at 131.8°C. of a sample of lithium chlorate known to be anhydrous was found to be $0.1150 \pm .0002$ mho. For all experiments following, the specific conductivity was used as the criterion of the anhydrous nature of the chlorate.

The additives used were water, methyl alcohol, propyl alcohol, lithium hydroxide and lithium nitrate. The lithium hydroxide supplied by the Foote Mineral Company, and the "analar" grade lithium nitrate supplied by the Fisher Scientific Company were each oven dried at 200°C. for 24 hours before use.

The methyl alcohol and propyl alcohol were obtained from the Eastman Distillation Products, and were of analytical quality. They were used with no further purification other than additional drying.

The water used was conductivity water, prepared by bubbling pure nitrogen through distilled water. The specific conductance of this water was found to be less than 1.5×10^{-7} mhos.

III. RESULTS

The density was determined for pure lithium chlorate, and for mixtures containing 0.046, 0.130 and 0.223 mole fractions of water. From a consideration of the length versus volume ratio of the capillary of the dilatometer used, there is a possible error of 8.0×10^{-5} mls. in the volume. This limits the density measurements to $\pm 2.0 \times 10^{-4}$ gms. cc⁻¹, all other errors being negligible. The results are shown in Tables 4.1, 4.2 and Fig. 4.3. The molar volume of the mixtures was obtained from the expression

$$4.4 \dots V_m = \frac{n_1 M_1 + n_2 M_2}{\rho}$$

The density in each case was found to be linear with respect to temperature, with the coefficient of expansion decreasing with water content. The coefficient of expansion was calculated from the simple expression

$$4.5 \dots V_t = V_0 (1 + \alpha t)$$

Together with the molar volume, the coefficient of expansion is shown in Table 4.3.

Equations of the forms which have been shown experimentally to represent the density-temperature relationship in fused salts have been calculated by a least square fit of the experimental results of Tables 4.1 and 4.2 using a computer. The equations are shown in Table 4.4.

TABLE 4.1

DENSITY AND MOLAR VOLUME OF PURE LITHIUM CHLORATE
AND A LITHIUM CHLORATE-WATER MIXTURE
MOLE FRACTION .046

Pure Lithium Chlorate			Lithium Chlorate-Water Mixture, Mole Fraction .046		
t°C.	Density gms cc ⁻¹	Molar Volume cc mole ⁻¹	t°C.	Density gms cc ⁻¹	Molar Volume cc mole ⁻¹
133.1	2.0858	43.34	130.3	2.0706	42.05
135.7	2.0838	43.38	131.0	2.0696	42.07
138.7	2.0818	43.42	132.0	2.0689	42.08
140.2	2.0809	43.44	132.4	2.0689	42.08
142.2	2.0794	43.47	135.6	2.0664	42.13
143.7	2.0783	43.49	137.1	2.0649	42.16
146.7	2.0763	43.54	139.8	2.0631	
149.0	2.0742	43.58	144.2	2.0595	42.27
150.5	2.0730	43.60	145.6	2.0583	42.30
152.8	2.0709	43.65	147.5	2.0568	42.33
153.4	2.0700	43.67			

TABLE 4.2

DENSITY AND MOLAR VOLUME OF LITHIUM CHLORATE-WATER MIXTURES
CONTAINING 0.130 AND 0.223 MOLE FRACTIONS OF WATER

Lithium Chlorate-Water Mixture, Mole Fraction Water 0.130			Lithium Chlorate-Water Mixture, Mole Fraction Water 0.223		
t°C.	Density gms cc ⁻¹	Molar Volume cc mole ⁻¹	t°C.	Density gms cc ⁻¹	Molar Volume cc mole ⁻¹
128.8	2.0300	39.89	131.0	1.9722	37.76
130.4	2.0287	39.91	133.0	1.9708	37.78
135.3	2.0251	40.00	135.6	1.9688	37.82
137.5	2.0237	40.02	139.8	1.9657	37.88
141.8	2.0204	40.08	142.2	1.9638	37.92
142.6	2.0188	40.11	145.7	1.9618	37.96
145.0	2.0178	40.14	146.2	1.9614	37.97
145.8	2.0172	40.15	147.0	1.9606	37.98
147.0	2.0162	40.17	148.1	1.9598	38.00
149.6	2.0145	40.20	150.6	1.9580	38.03

TABLE 4.3

MOLAR VOLUME AND COEFFICIENT OF EXPANSION
OF LITHIUM CHLORATE-WATER MIXTURES

Mole Fraction Water n_2	Molar Volume ccs, at 130°C.	Coefficient of Expansion deg. ⁻¹
0	43.26	4.12×10^{-4}
.046	42.04	4.09×10^{-4}
.130	39.91	3.87×10^{-4}
.223	37.75	3.77×10^{-4}

TABLE 4.4

ANALYTICAL REPRESENTATION OF DENSITY-TEMPERATURE RELATIONSHIP
FOR LITHIUM CHLORATE-WATER MIXTURES

Mole Fraction of Water	Equation Type		Standard Deviation
	(1) $\rho = \rho_0 \exp - \alpha T$	(2) $\rho = a - bt$	
0	(1) $\rho = 2.463 \exp - 4.12T \times 10^{-4}$		3.5×10^{-4}
	(2) $\rho = 2.188 - 7.672 \times 10^{-4}t$		3.5×10^{-4}
.046	(1) $\rho = 2.437 \exp - 4.09T \times 10^{-4}$		1.7×10^{-4}
	(2) $\rho = 2.172 - 7.798 \times 10^{-4}t$		1.7×10^{-4}
.130	(1) $\rho = 2.368 \exp - 3.87T \times 10^{-4}$		3.0×10^{-4}
	(2) $\rho = 2.125 - 7.429 \times 10^{-4}t$		3.0×10^{-4}
.223	(1) $\rho = 2.296 \exp - 3.77 \times 10^{-4}T$		1.5×10^{-4}
	(2) $\rho = 2.068 - 7.304 \times 10^{-4}t$		1.6×10^{-4}

Figure 4.3

Density vs. Temperature of Lithium Chlorate-Water Mixtures

DENSITY vs TEMPERATURE OF LITHIUM CHLORATE WATER MIXTURES

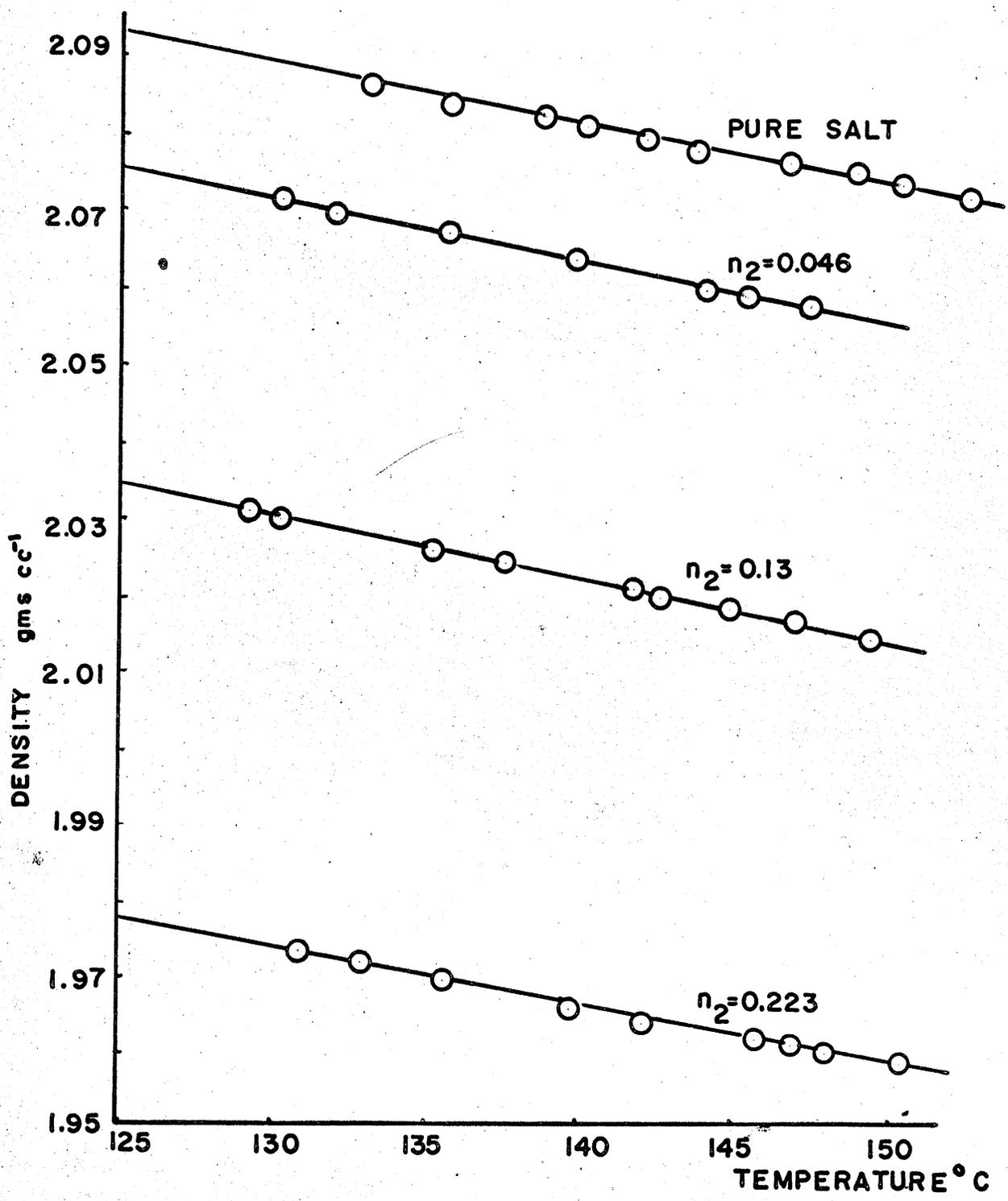


FIGURE 4-3

IV. DISCUSSION

The density of lithium chlorate at 131.8°C. , $2.0880 \text{ gms. cc}^{-1}$, is in agreement with the earlier result of Patterson.³⁰ The value of $1.998 \text{ gms. cc}^{-1}$ at 128°C. obtained by Klotschko²⁹ is probably low due to the presence of water in the very hygroscopic salt. Table 4.5 compares the density, molar volume and coefficient of expansion of several typical molten salts with those of lithium chlorate at corresponding temperatures.

The definition of a temperature at which the absolute magnitude of properties of molten salts may be compared is not obvious. Isothermal comparison is unsatisfactory due to the large differences in the temperatures of the stable liquid range for many molten salts. Moreover the temperature dependence curves of many properties for different salts intersect, and interpretation would depend on the temperature chosen. The thermodynamically sound comparison of properties at equal fractions of their respective critical temperature is not applicable, since the precise value of any of the critical constants is known for but a few simple molten salts. Similarly, though the comparison of properties at equal vapour pressures would be meaningful, this is not possible due to the lack of the necessary precise experimental data. Instead, an arbitrary definition of corresponding temperature has been adopted, as initially proposed by Bloom and Heymann.³⁹ The melting point is known accurately for most salts, and the temperatures chosen as corresponding are 10% above the

TABLE 4.5

DENSITY, MOLAR VOLUME AND COEFFICIENT OF EXPANSION
FOR SOME TYPICAL MOLTEN SALTS

Compound	Melting Point t ^o C.	Correspon- ding Temperature t ^o C.	Density gms. cc ⁻¹	Molar Volume cc mole ⁻¹	Coefficient of Expansion $\alpha \times 10^{-4}$ deg. ⁻¹	Refer- ence
LiClO ₃	127.9	168	2.059	43.90	4.12	
LiNO ₃	255	308	1.741	39.60	3.31	40
LiCl	613	701	1.463	28.98	2.96	34
KClO ₃	368	432	1.903	64.40	3.59	43
KNO ₃	334	395	1.828	55.31	3.99	42
KCl	776	880	1.464	50.93	3.98	34
AgNO ₃	212	260	3.909	43.46	2.78	41
AgCl	455	528	4.202	34.11	2.24	41
NaCl	808	916	1.494	39.12	3.63	34
NaNO ₃	307	365	1.877	45.29	3.76	42
HgCl ₂	279	334	4.202	64.62	6.81	44

respective melting points in degrees Kelvin. The melting point itself is not suitable because of the possibility of incipient lattice formation immediately above the melting point. The density of lithium chlorate is of the same order as the density of other Group 1 compounds formed with polyatomic anions. There is a linear relationship between the density of molten lithium chlorate and the temperature, which may be expressed as either

$$\rho = 2.463 \exp -4.12 \times 10^{-4} T \text{ or } \rho = 2.188 - 7.672 \times 10^{-4} T.$$

The general trend of increasing density for the chloride, nitrate and chlorate of both sodium and potassium is also present for the comparable lithium salts.

Biltz and Klemm³⁶ showed that: (i) other factors being equal, molten covalent compounds having weak intermolecular forces, have larger molar volumes than those of ionic melts which have in contrast a strong coulombic force field, (ii) for the same reasons the coefficient of expansion is greater for covalent melts, (iii) the molar volume of molten electrolytes increases as the molecular weight increases for covalent chlorides, and finally (iv) melts with varying stages of dissociation from ionic to covalent are possible. For compounds formed from non-spherical polyatomic anions (NO_3^- , ClO_3^- , ClO_4^-), some form of association is thought to exist between the melt constituents,⁴³ indicating a more covalent character than that of melts formed from compounds having spherical anions (Cl^- , Br^-). The

molar volume of lithium chlorate ($43.9\text{cm}^3\text{mole}^{-1}$), is found to be linearly temperature dependent (Fig. 4.4), and is in magnitude larger than that of either lithium chloride or lithium nitrate as shown in Table 4.3. The increase in the molar volume among the chlorides, nitrates and chlorates of both sodium and potassium is repeated for the lithium salts. The difference in the molar volume of lithium chloride and chlorate is $14.9\text{cm}^3\text{mole}^{-1}$, comparable to the difference between the molar volumes of potassium chloride and chlorate $13.5\text{cm}^3\text{mole}^{-1}$. This comparison is not valid when the molar volumes of the respective nitrates are considered. The molar volume of potassium nitrate is considerably smaller than that of potassium chlorate, and only $5\text{cm}^3\text{mole}^{-1}$ greater than that of potassium chloride. Sodium nitrate and sodium chloride also exhibit the same $5\text{cm}^3\text{mole}^{-1}$ difference in molar volume, whereas the increase in molar volume between lithium chloride and lithium nitrate is greater than $10\text{cm}^3\text{mole}^{-1}$. This indicates that lithium chlorate and lithium nitrate have a greater similarity of covalent character than the corresponding sodium and potassium salts.

Yaffe and Van Artsdalen³⁴ noted that the coefficient of expansion, α , for the chlorides, bromides and iodides of cesium, rubidium and potassium were almost equal, whereas α for the lithium halides were 30 per cent lower. The coefficient of expansion of lithium chlorate, $4.1 \times 10^{-4}\text{deg.}^{-1}$, is however larger than that of potassium chlorate, and also larger than that of the Group 1 halides.

VARIATION OF MOLAR VOLUME WITH TEMPERATURE

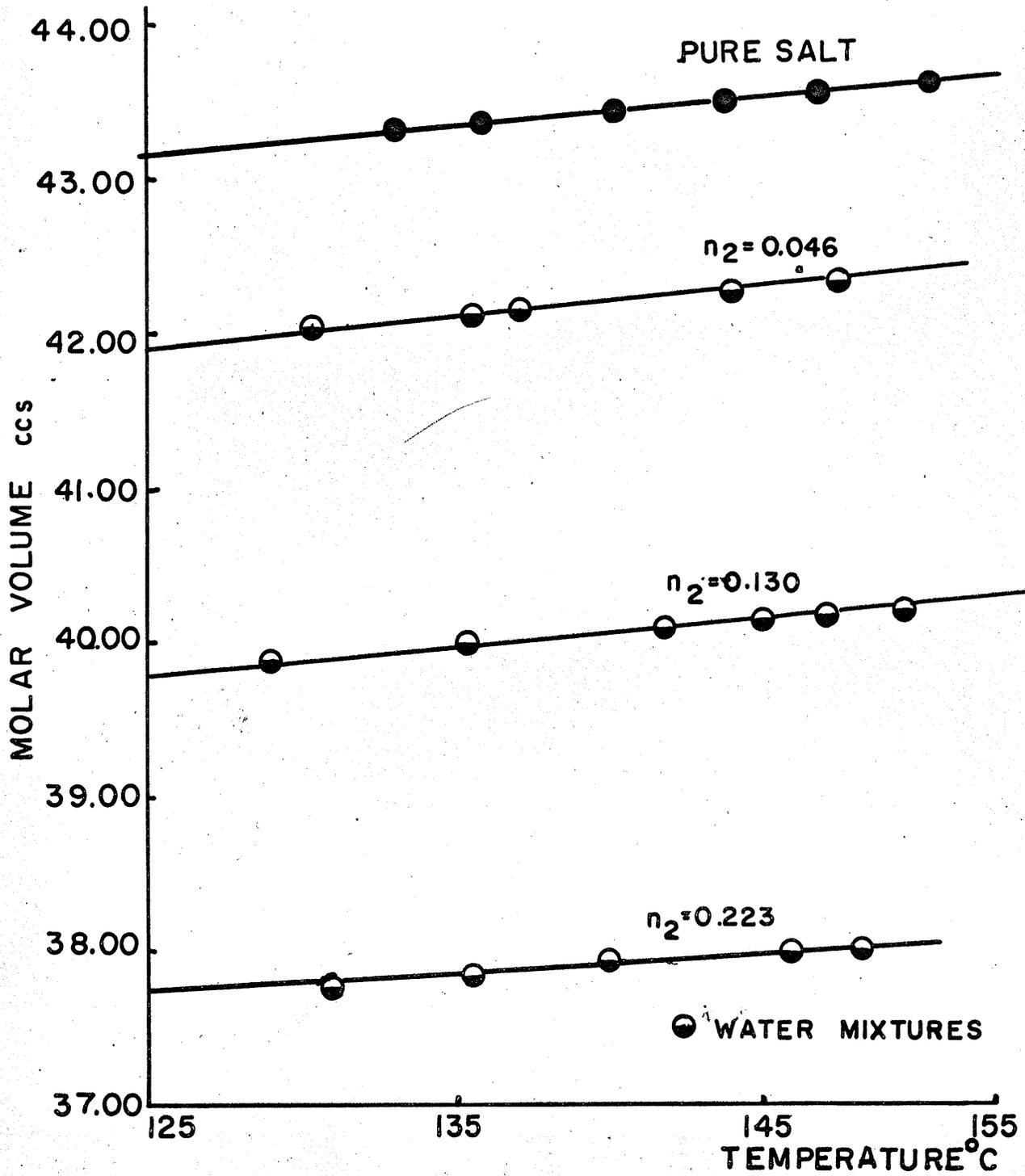


FIGURE 4-4

It does not compare in size with the coefficient of expansion of a purely non-polar liquid such as carbon tetrachloride,

$\alpha = 11.4 \times 10^{-4} \text{ deg.}^{-1}$, in which the London dispersion forces predominate, showing that coulombic forces determine the general properties of the lithium chlorate melt, though the melt may be more covalent in character than molten potassium chlorate.

Potassium chloride, nitrate and chlorate all have similar coefficients of expansion, and all are considered to form ionic melts. This is not true for comparable lithium salts, the chlorate having a much greater expansivity than the chloride or nitrate. Again this may indicate the lithium chlorate melt is comparatively less ionic in character.

The density of lithium chlorate-water mixtures decreases with increase of water content. The density-temperature variation of these mixtures may still be represented by the general equations

$$\rho = \rho_0 \exp -\alpha T \quad \text{or} \quad \rho = a - bt$$

The deviation from the ideal linear relationship between molar volume and mole fraction^{39,41,45} is negligible for the water mixtures studied (Fig. 4.5). Since large deviations have been found for systems in which complex formation occurs,^{42,46,47} probably there is little immediate association between the water and lithium chlorate. The decrease in coefficient of expansion α with the increase in water content may in part be due to an increase in the

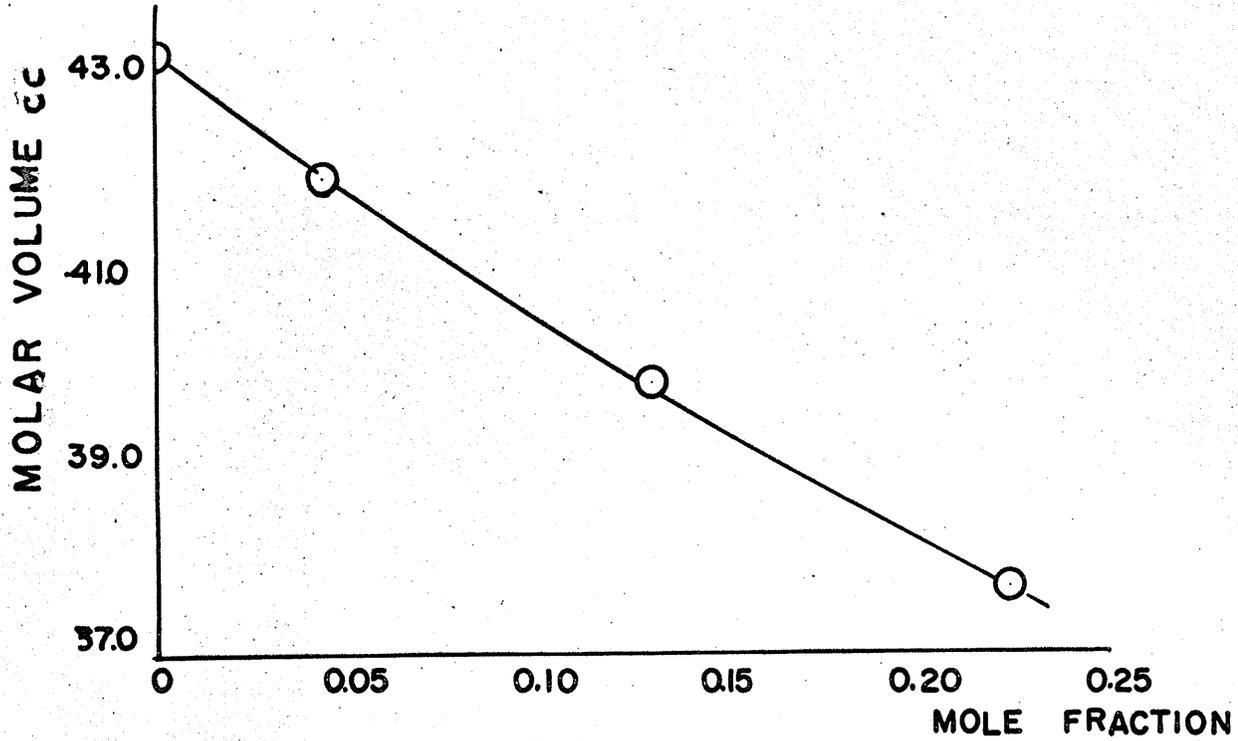
MOLAR VOLUME AT 130°C vs MOLE FRACTION
WATER

FIGURE 4-5

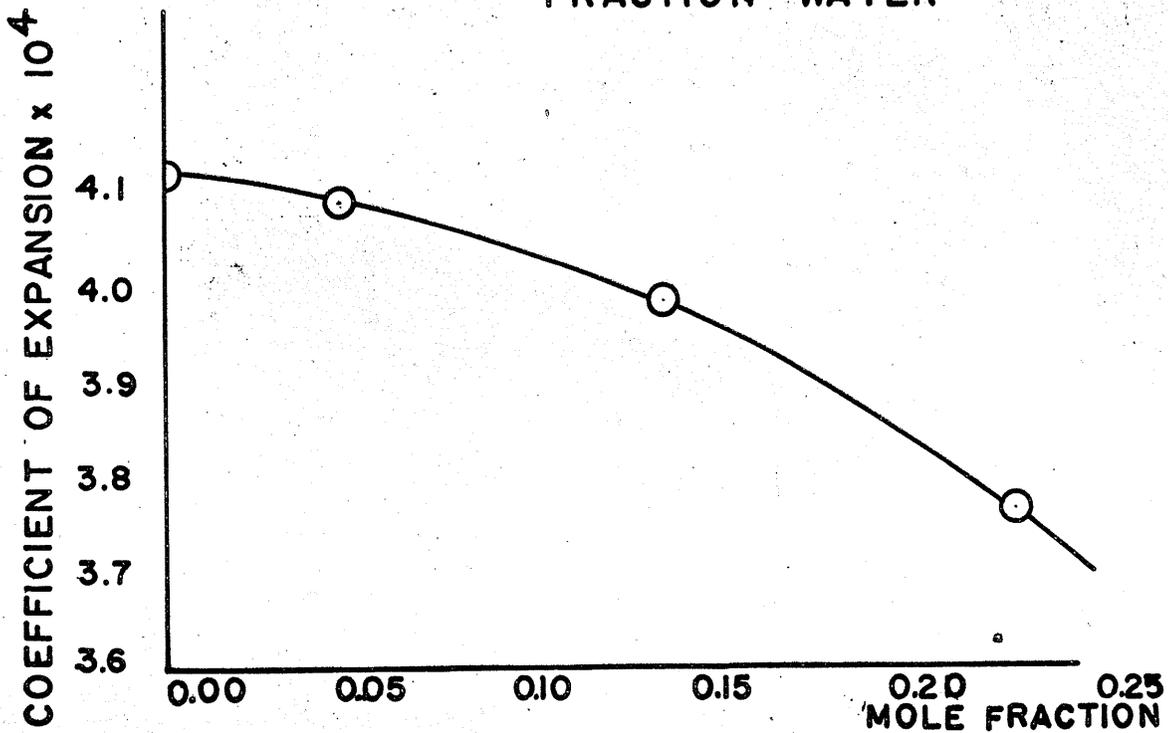
COEFFICIENT OF EXPANSION vs MOLE
FRACTION WATER

FIGURE 4-6



overall ionic character of the melt.

A graph of the coefficient of expansion against mole fraction of water (Fig. 4.6) curves, shows the slightly greater effect on melt structure caused by the initial water additions. This is also found in the viscosity changes as the water content of a lithium chlorate melt is increased. (See page 53).

VISCOMETRY

CHAPTER V

VISCOMETRY

I. INTRODUCTION

All liquids will flow under an infinitely small stress, and flow will continue until the stress is removed. The coefficient of viscosity, η , is defined as the force per unit area required to maintain unit difference in velocity between two parallel layers 1 cm. apart. The reciprocal of the coefficient of viscosity is called the fluidity, ϕ , and is a measure of the ease with which a liquid can flow.

The effect of temperature on the viscosity of gases and liquids is strikingly different. Whereas in the former case the coefficient increases with temperature, the viscosity of liquids invariably decreases markedly as temperature increases. A wide variety of liquids exhibit the exponential relationship between viscosity and temperature

$$5.1 \dots \eta = A \exp \frac{B}{RT}$$

first proposed independently by Arrhenius and de Guzman.⁴⁸

The realization that liquids possess a structure over a short range permitted the development of viscosity theories which do not involve molecular transfer in order to transfer the translational energy. Andrade⁴⁹ suggested that the contact between molecules at the extremes of their oscillations could lead to energy

transfer, and was able to derive an expression comparable to equation 5.1 using this model. Frenkel⁵⁰ developed a similar equation, though the pre-exponential term in his equation is temperature dependent. Eyring et al¹³ approached the problem as a reaction rate process, and derived the equation

$$5.2 \dots \eta = 1.09 \times 10^{-3} \frac{M^{\frac{1}{2}} T^{\frac{3}{2}}}{V^{\frac{2}{3}} \Delta H_{\text{vap}}} \exp \frac{E_{\text{vis}}}{RT}$$

where M is the molecular weight, V the molar volume and ΔH_{vap} the heat of vaporization.* The pre-exponential term in this case is again temperature independent. A linear relationship between $\ln \eta$ and $\frac{1}{T}$ has been found experimentally for many fused salt systems,^{51,52} and any theoretical equation proposed for viscosity must also predict this result.

In the absence of any satisfactory equation from which viscosities may be calculated, recourse must be made to equation 5.1. From its form, the equation suggests a rate process where B is the activation energy of viscosity, and A a constant of the system.

Since the bonds between neighbouring molecules which must be broken in order to form a hole, are the same as those broken in the process of vaporization, it follows that the energy required to form a hole is equal to the energy of vaporization ΔE_{vap} .

The free energy of activation should thus be proportional to the energy of vaporization. Empirically it is found that $\Delta E_{\eta} \approx \frac{\Delta E_{\text{vap}}}{2.5}$.⁵³

*

The change in T is compensated by changes in ΔH and V.

This result indicates that the hole size required for molecular motion is only a fraction of the specific volume of the molecule.⁵⁴

A further interesting relationship was proposed by Batschinski⁵⁵

$$5.3 \dots \eta = \frac{C}{V_s - V_o}$$

where V_s is the specific volume, and C and V_o are constants. This requires the fluidity $\frac{1}{\eta}$ to be a linear function of the specific volume, over a range of temperature. Davis, Rogers and Ubbelohde¹⁰ found such a linear relationship for molten silver nitrate. Harrap and Heymann⁵⁶ suggested the constant C is proportional to the geometric size of the unit of flow, but this has not been substantiated by further experimental evidence. An indication of the relative size of the unit of flow in viscosity compared to that involved in electrical conductance, is illustrated by the ratio of the respective activation energies.³⁹ The ratio $\frac{\Delta E_\eta}{\Delta E_\kappa}$ usually lies in the range 2-4 for molten salts, which suggests that viscous flow requires a much greater configurational change than occurs in conductance. Since viscous flow demands electrical neutrality, it will be governed by the slowest ion, whereas electrical conductivity may be primarily uni-ionic, the smaller or more mobile ion carrying the current. The approximate equality of ΔE_η and ΔE_κ observed for some melts, noticeably nitrates, has been considered as an indication that the structural units involved in electrical conductance are larger than the simple ion, and comparable in size to the units

involved in viscous flow.

Thus it can be seen that a knowledge of viscosity of the melt and its temperature dependence gives information regarding the melt structure, the intermolecular forces, and the mechanism and units involved in viscous flow.

II. EXPERIMENTAL

Liquid viscosities vary from 0.005-100,000 poise, the range of viscosity determining the basic experimental approach to measurement. Fused salts normally have viscosities lying between 0.005-0.5 poise. Numerous methods are available for the measurement of viscosities of this order at room temperature, though their successful application becomes progressively restricted as the temperature is increased. Lithium chlorate, because of its low melting point, lends itself to a flow method of viscosity determination, and a modified form of a capillary viscometer was constructed for this purpose.

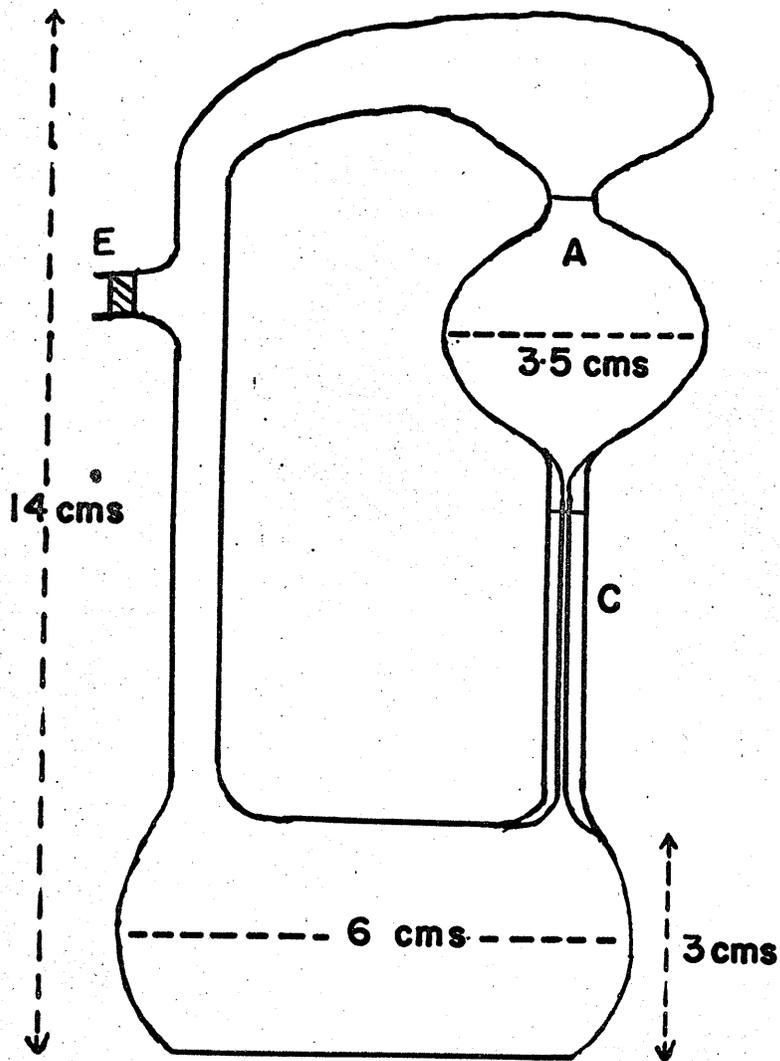
The viscometer is shown in Figure 5.1, being very similar to those used by Campbell and Debus.⁵⁷ The principal components are a small bulb of approximately 10 mls. capacity joined through a 6 cm. length of 1 Omm. bore capillary tubing to the main reservoir. The capillary entering this reservoir was made to have a trumpet shape; thus no Hagenbach kinetic energy correction is necessary. The reservoir was joined back to the top of the small bulb, completing the circuit. A side tube was joined to this return tube, to which a filling apparatus similar to that used in density measurements could

Figure 5.1

Viscometer

VISCOMETER

47.



- E fritted glass disc
- C 1 mm i.d. capillary

FIGURE 5-1

be attached. Since pyrex glass was used throughout, the viscometer was simple to construct.

Two marks were made above and below the small bulb to insure that the same volume of melt was timed in flow for each experiment.

The viscometers were calibrated with distilled water at temperatures between 110-170°C. First the viscometer was thoroughly cleaned. A quantity of distilled water was then added to the reservoir, sufficient to overflow the calibrated bulb. The reservoir was then immersed in a liquid nitrogen bath until the water had frozen. The viscometer was then evacuated, withdrawn from the nitrogen bath, and allowed to stand until the ice had melted. This process was repeated at least four times, to ensure the removal of all dissolved gases. The viscometer was finally vacuum sealed on the side filling tube and clamped into a device which would allow the viscometer to be rotated through 360° without removal from the thermostat. In this way the calibration bulb could be filled inside the thermostat. The viscometer was immersed completely in the thermostat until thermal equilibrium was established, rotated to fill the marked bulb, and then fixed in a vertical position. The time of flow of water between the two marks was recorded on an electric clock supplied by Labline Inc., Chicago., and was correct to 0.1 second. It was possible to time this flow since the water level could be seen through the illuminated glass window of the thermostat. During this time the temperature of the controlled

thermostat was measured. A series of flow times were observed at seven different temperatures between 110-170°C. and these are recorded in Table 5.1 for the viscometer used for the experiments. Using the literature values of viscosity (International Critical Tables, Vol. 5, pp. 10) and density (Handbook of Physics and Chemistry, 1961-62 ed., pp. 2156) of water at the experimental temperatures, a factor $C = \frac{\eta}{d t}$ was calculated, where η = viscosity of water in millipoise, d = density of water in gms/cc. and t = flow time in seconds. This factor was plotted against temperature and is shown in Fig. 5.2.

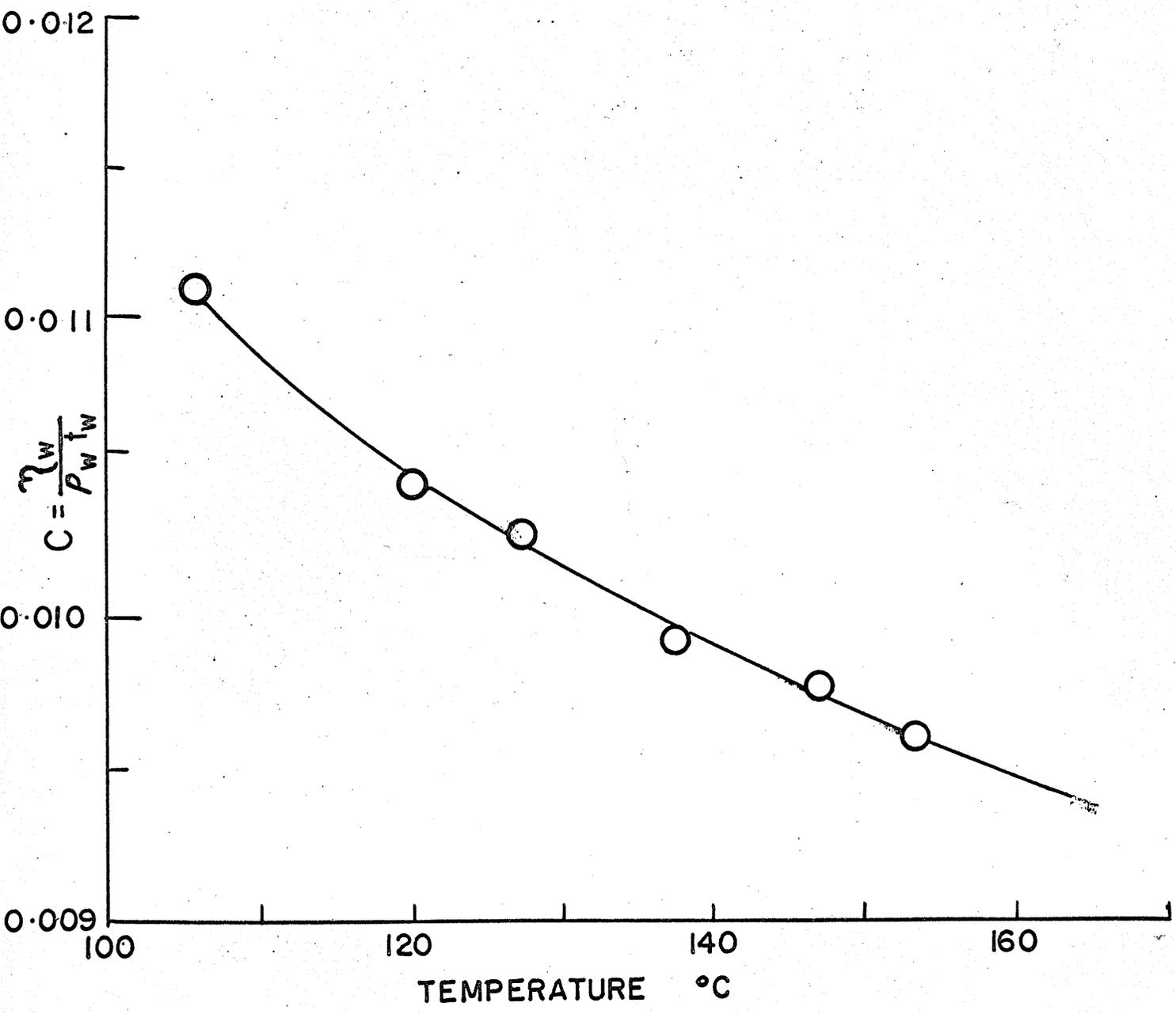
TABLE 5.1
WATER FLOW TIME AT DIFFERENT TEMPERATURES
FOR VISCOSITY DETERMINATIONS

t ° C.	Flow Time. Secs. t_w	Density of water gms/cc. d_w	Viscosity of water millipoise η_w	$\frac{\eta_w}{d_w t_w} = C$
98.45	266.2	0.9594	2.89	1.131×10^{-2}
105.75	248.3	0.9525	2.62	1.107×10^{-2}
119.85	231.8	0.9509	2.30	1.043×10^{-2}
127.35	222.2	0.9374	3.14	1.027×10^{-2}
137.70	212.8	0.9284	1.96	0.996×10^{-2}
146.95	204.8	0.9200	1.84	0.976×10^{-2}
153.10	199.6	0.9143	1.75	0.959×10^{-2}

Figure 5.2
Calibration Plot for Viscometer

FIGURE 5-2

CALIBRATION PLOT FOR VISCOMETER



The viscometer was filled with lithium chlorate using the technique and filling apparatus used for density measurements. It was finally sealed under a vacuum just above the small fritted disc to prevent the solid decomposition products from entering. The flow times of the pure salt and of three water mixtures were measured as in the calibration. The times were reproducible at the same temperature to ± 5 seconds on an average of 7,500 seconds.

The relative viscosity for each mixture was calculated for the different experimental temperatures using the relationship

$$5.4 \dots \frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

where η_1 , d_1 , t_1 are the viscosity in poise, the density in gms./cc. and the flow time in seconds for water, and η_2 , d_2 , t_2 are the equivalent values for the melt. Rearrangement of this equation, and substitution of the calculated experimental value C gives

$$5.5 \dots \eta_2 = C d_2 t_2$$

The appropriate density values were obtained by the standard interpolation techniques from the density-composition and density-temperature graphs.

The accuracy of the viscosity determinations was limited by the initial calibration of the viscometer, since the water viscosities are known only to $\pm 1.0\%$ in this temperature range. All other possible errors are negligible in comparison.

III. RESULTS

The relative viscosity was determined for lithium chlorate and its water mixtures containing 0.79, 0.197 and 0.251 mole fractions of water. The viscosity and its temperature dependence are shown in Tables 5.2 - 5.4, and illustrated in Figure 5.3.

To test the validity of the Arrhenius equation for the viscosity of lithium chlorate and its mixtures, $\log \eta$ was plotted against $\frac{1}{T}$. In each case a linear relationship was obtained (Figure 5.4). The activation energy of viscous flow was calculated from the slope of these graphs, since $\Delta E_{\eta} = -2.303RT \times \text{slope}$, and it is given in Table 5.6.

The Arrhenius equations which represent the viscosity-temperature variation of lithium chlorate and its water mixtures were determined by a least squares fit of the experimental results. These equations are given in Table 5.6.

Figure 5.3

Viscosity of Lithium Chlorate-Water Mixtures vs. Temperature

VISCOSITY vs TEMPERATURE

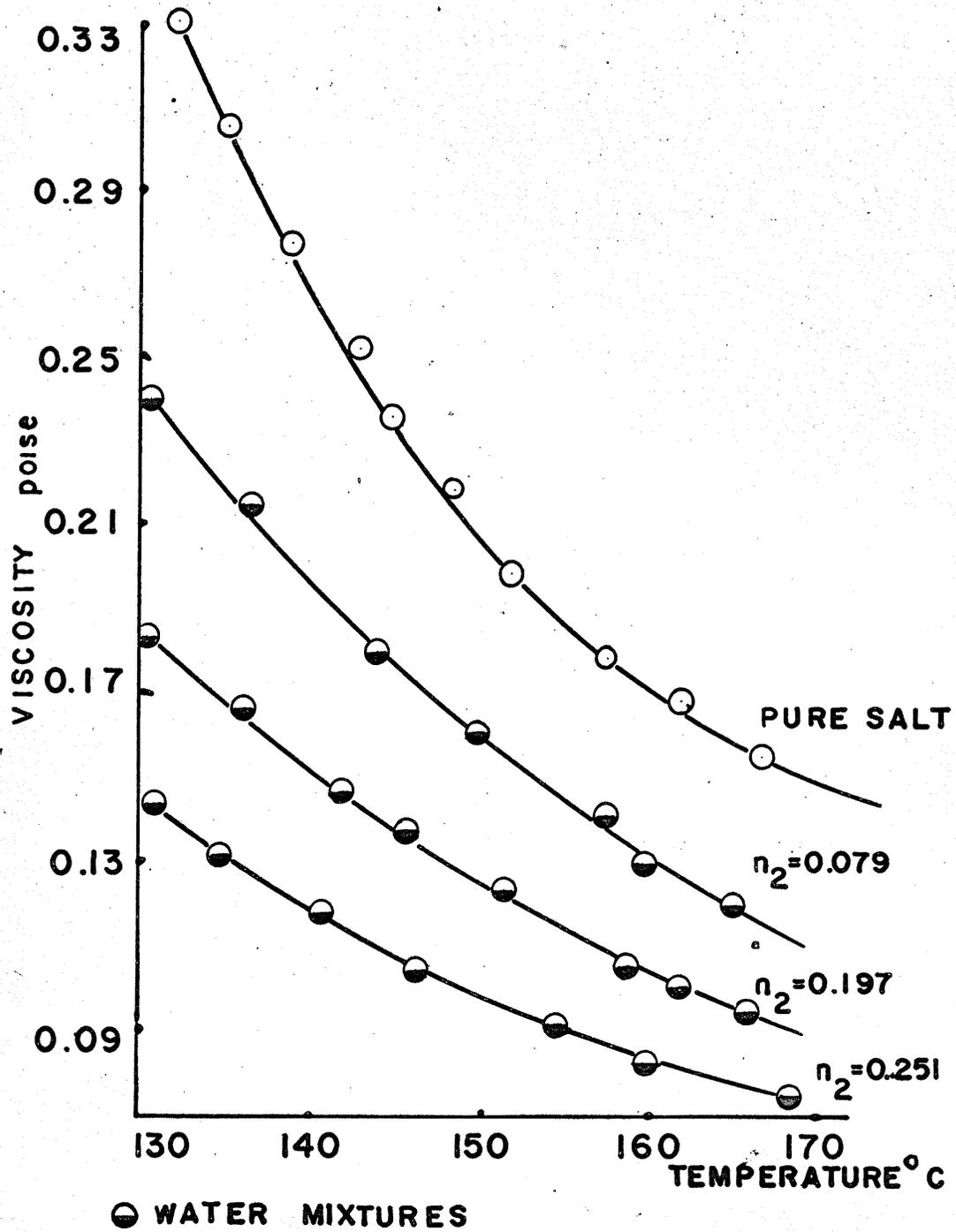


FIGURE 5-3

Figure 5.4

Log Viscosity vs. $\frac{1}{T^{\circ}K}$ of Lithium Chlorate-Water Mixtures

LOG VISCOSITY vs $\frac{1}{T^{\circ}K}$
OF LITHIUM CHLORATE WATER MIXTURES

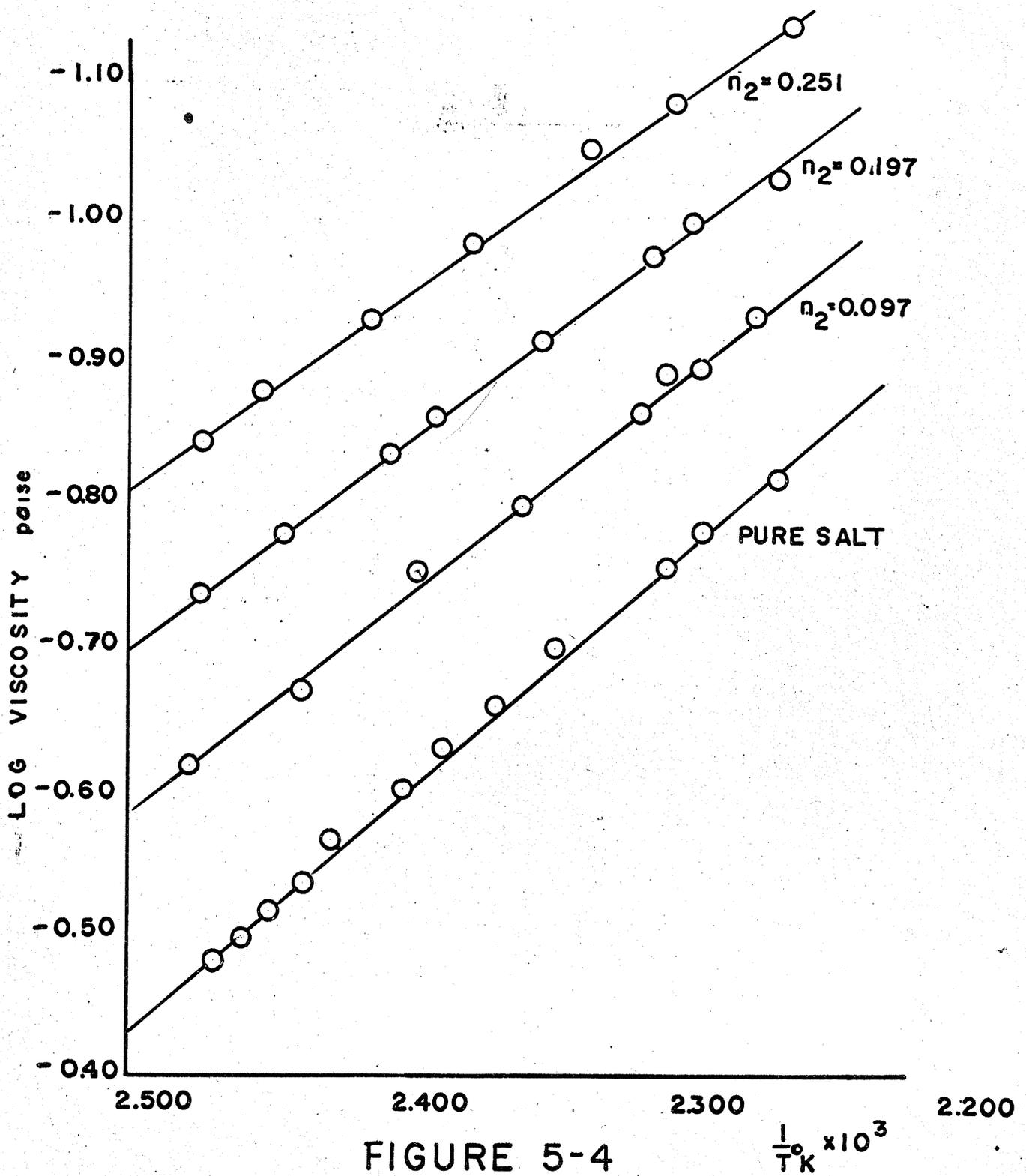


FIGURE 5-4

TABLE 5.2
 VISCOSITY OF PURE LITHIUM CHLORATE

$t^{\circ}\text{C.}$	$T^{\circ}\text{K.}$	$\frac{1}{T^{\circ}\text{K}} \times 10^{-3}$	(Poise) η	$-\log \eta$
131.8	404.9	2.4698	0.334	0.4763
133.3	406.4	2.4606	0.320	0.4949
135.0	408.1	2.4504	0.305	0.5157
137.5	410.6	2.4355	0.296	0.5287
138.7	411.8	2.4284	0.277	0.5575
142.7	415.8	2.4050	0.249	0.6038
144.7	417.8	2.3935	0.235	0.6289
148.4	421.5	2.3725	0.218	0.6615
152.4	425.5	2.3502	0.199	0.7011
156.3	429.4	2.3288	0.194	0.7122
158.6	431.7	2.3161	0.177	0.7520
162.1	435.2	2.2978	0.168	0.7747
166.9	440.0	2.2727	0.155	0.8097

Result of Mr. M. K. Nagarajan²⁷ of this department.

TABLE 5.3

VISCOSITY OF LITHIUM CHLORATE WATER MIXTURE
MOLE FRACTION WATER .079

$t^{\circ}\text{C.}$	$T^{\circ}\text{K.}$	$\frac{1}{T^{\circ}\text{K.}} \times 10^{-3}$	poise η	$-\log \eta$
130.5	403.6	2.4779	0.241	0.6180
136.5	409.6	2.4414	0.214	0.6696
143.7	416.8	2.3992	0.180	0.7447
150.0	423.1	2.3635	0.160	0.7959
157.6	430.7	2.3218	0.139	0.8570
160.0	433.1	2.3089	0.129	0.8894
162.0	435.1	2.2983	0.128	0.8928
164.8	437.9	2.2836	0.120	0.9208

TABLE 5.4

VISCOSITY OF LITHIUM CHLORATE WATER MIXTURE
CONTAINING .197 MOLE FRACTION WATER

$t^{\circ}\text{C.}$	$T^{\circ}\text{K.}$	$\frac{1}{T^{\circ}\text{K.}} \times 10^{-3}$	poise η	$-\log \eta$
130.5	403.6	2.4777	0.185	0.7328
136.0	409.1	2.4443	0.167	0.7773
142.0	415.1	2.4090	0.147	0.8327
145.5	418.6	2.3889	0.138	0.8570
151.5	424.6	2.3551	0.123	0.9101
159.0	432.1	2.3142	0.107	0.9706
162.0	435.1	2.2983	0.101	0.9957
166.0	439.1	2.2774	0.094	1.0269

TABLE 5.5

VISCOSITY OF LITHIUM CHLORATE WATER MIXTURE
CONTAINING .251 MOLE FRACTION WATER

$t^{\circ}\text{C.}$	$T^{\circ}\text{K.}$	$\frac{1}{T^{\circ}\text{K}} \times 10^{-3}$	η poise	$-\log \eta$
131.0	404.1	2.4746	0.144	0.8416
134.5	407.6	2.4534	0.132	0.8794
140.7	413.8	2.4166	0.118	0.9281
146.8	419.9	2.3815	0.104	0.9830
154.5	427.6	2.3386	0.090	1.0458
160.0	433.1	2.3089	0.083	1.0809
168.2	441.3	2.2660	0.073	1.1367

TABLE 5.6

ANALYTICAL REPRESENTATION OF VISCOSITY

Mole Fraction Water	Arrhenius Equation $\eta = A_0 \exp \frac{C}{RT}$	Standard Deviation $\times 10^3$	Activation Energy of Viscous Flow K. Cal mole^{-1}
0	$\eta = 1.979 \times 10^{-5} \exp \frac{7813}{RT}$	1.00	7.8
.079	$\eta = 3.314 \times 10^{-5} \exp \frac{7124}{RT}$	1.71	7.1
.197	$\eta = 4.144 \times 10^{-5} \exp \frac{6740}{RT}$	0.722	6.7
.251	$\eta = 4.573 \times 10^{-5} \exp \frac{6452}{RT}$	1.11	6.4

IV. DISCUSSION

The viscosity of pure lithium chlorate and its temperature variation may be analytically represented by the equation

$$\eta = 1.979 \times 10^{-5} \exp \frac{7113}{RT}$$

The value for the viscosity at 131.8°C., 33.0 centipoise, is larger than that proposed by Patterson,³⁰ the difference possibly being due to the improved viscometer technique used. Klotschko and Grigorjew²⁹ reported the viscosity of lithium chlorate as 52.2 centipoise at 136.0°C., almost twice the value obtained from this research. The density of lithium chlorate used by these workers for the calculation of the viscosity was low (as noted earlier, page 35), which will account in part for the high viscosity value. Also, Klotschko and Grigorjew did not take any precautions to exclude any possible insoluble decomposition products formed in sealing from entering the viscometer. These particles can interrupt the liquid flow through the controlling capillary, increasing the flow time, and hence increasing the apparent viscosity. This may completely account for the high viscosity of lithium chlorate which they reported, compared to the value obtained in this research using a viscometer to which a special glass filter disc had been attached.

The viscosity of lithium chlorate is much larger than that of simple ionic salts at corresponding temperatures. For example, we may compare the viscosity of silver nitrate, 2.3 centipoise at 450°C. to lithium chlorate, 15 centipoise at 168°C. Zinc chloride

also exhibits a high viscosity, 350 centipoise at 400°C ., which has recently been interpreted on the basis of a model for the zinc chloride liquid structure in which fragments of the original double layers of the crystalline ZnCl_2 , together with individual ZnCl_6^{-4} ions, are the predominant species.⁵⁸ A marked decrease in the activation energy for viscous flow is observed for such associated melts, which is not observed for lithium chlorate for which the activation energy is almost constant, $7.8\text{k.cal.mole}^{-1}$ between 130 - 170°C . This compares favourably with the activation energy for viscous flow, which is normally between 3 - 10k.cal.mole^{-1} for ionic melts.

Yaffe and Van Artsdalen³⁴ consider that the heat of activation for viscous flow is dependent upon two opposing factors. As a melt expands with rising temperature, the total coulombic forces among the constituent ions tend to decrease, and hence the activation energy for mass migration also decreases. Opposing this effect, due to the increase in the number of holes in the melt, the average number of nearest neighbour ions to any one particular ion may decrease, and thus increase the attractive force per nearest neighbour, and increase the activation energy. In melts in which there is a large disparity of ionic size, such as for lithium chlorate, the latter effect should predominate. For lithium chlorate, however, little change is noticed in the activation energy, which may be due to the association in the melt breaking down as temperature increases.

Thus fewer bonds need be broken in mass transfer at higher temperatures, which will compensate for the increase in ion neighbour attractive forces caused by the decrease in coordination number.

The addition of water to a lithium chlorate melt causes a considerable decrease in the viscosity of the melt. At temperatures slightly above the melting point, the decrease in viscosity following the initial addition of water is greater than that caused by subsequent additions. At higher temperatures this large difference is not noted, each addition causing a similar decrease, though the initial decrease is still slightly larger. This is shown in Figure 5.3.

Over the temperature range investigated, the viscosity isotherm for each mixture shows a negative deviation from linear dependence on molar composition, illustrated in Figure 5.5. Harrap and Heymann⁵² have found that this negative deviation is exhibited by molten salts regardless of the system.

The viscosity-temperature relationship for lithium chlorate-water mixtures is represented by the Arrhenius equations of Table 5.6. The activation energy of viscous flow becomes considerably smaller as the water content increases. The decrease of activation energy is not a linear function of the mole fraction of water, as seen in Figure 5.6, the initial rate of change decreasing as water content increases; however, the decrease itself indicates that the average size of the mass unit of viscous flow is lowered on the addition of water.

Figure 5.5

Isothermal Viscosity vs. Mole Fraction Water

Figure 5.6

Variation of Activation Energy with Mole Fraction Water

ISOTHERMAL VISCOSITY vs MOLE FRACTION WATER

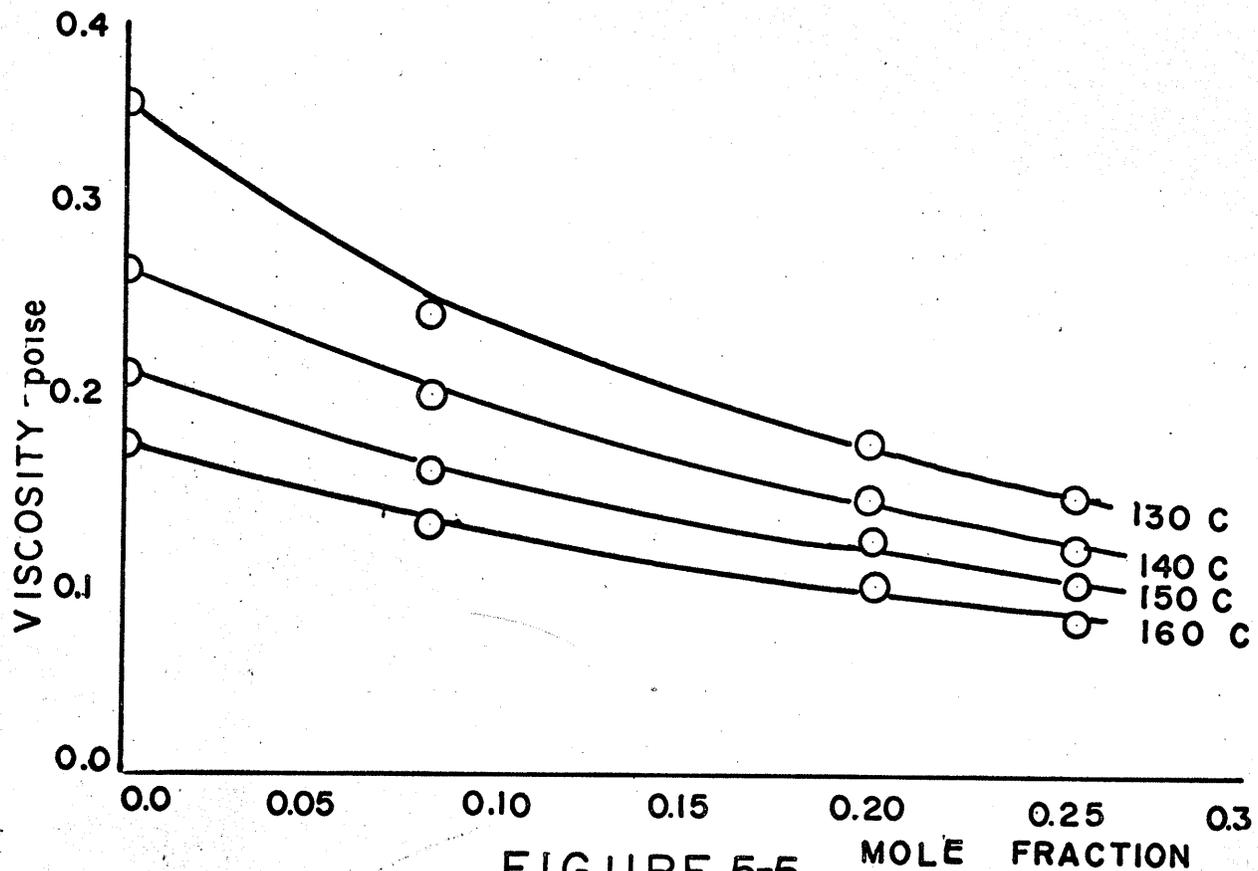


FIGURE 5-5

VARIATION OF ACTIVATION ENERGY WITH MOLE FRACTION WATER

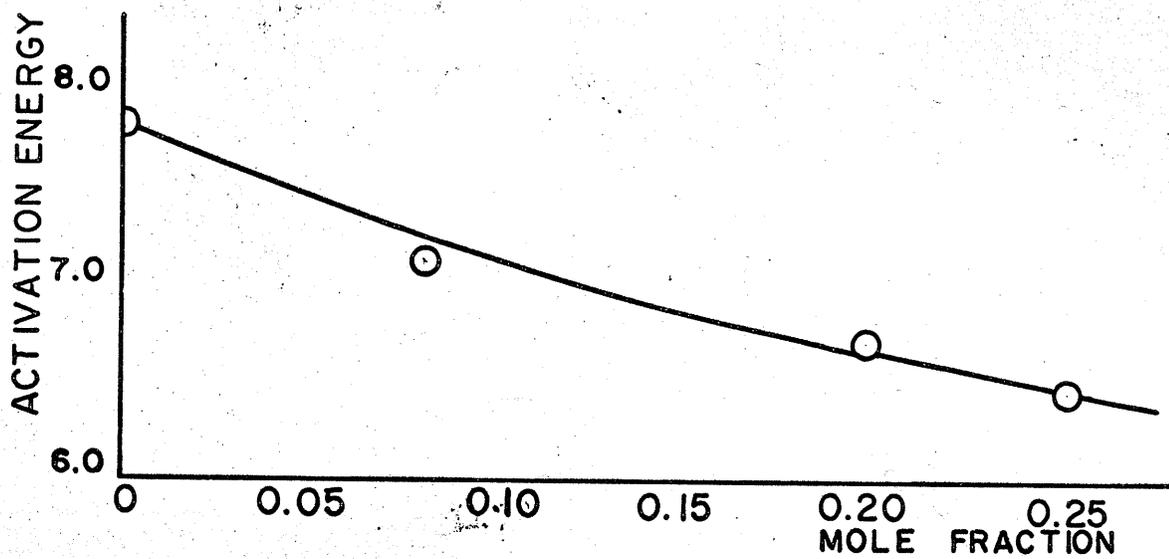


FIGURE 5-6

At temperatures slightly above the melting point, at which associated groups may be present in the lithium chlorate melt, the effect of water addition on viscosity is pronounced, probably owing to the immediate breakup of these groups. At higher temperatures at which the existence of these associated groups is improbable, the water additions lower the viscosity to a much smaller extent. The changes of the activation energy of viscous flow for these same mixtures may also be interpreted on the basis of these structural considerations.

SURFACE TENSION

CHAPTER VI

SURFACE TENSION

I. INTRODUCTION

The importance of surface tension measurements of molten electrolytes is considerable. Several empirical relationships have been proposed in which surface tension is connected with other physical properties of the melt. Surface tension has also been utilized in calculations of the mean radius of holes in molten electrolytes, in corroboration of other evidence for the proposed hole-ion nature of a melt.

The theoretical treatments, which provide a means of calculating surface tension from fundamental physical constants of the liquid, are many and varied with respect to the foundations upon which they are based. These include the free volume method of Lennard-Jones and Corner,⁵⁹ the radial distribution method of Kirkwood and Buff,⁶⁰ the partition function of normal liquids by Chang et al,⁶¹ the Lennard-Jones Devonshire theory of liquids,⁶² and an approach based on the Fowler partition function.⁶³ Each of these treatments is dependent upon an initial model for the liquid, from which a partition function may be derived using the well known principles of statistical mechanics. The equation for surface tension obtained by Eyring^{9,64} based on the significant structure theory has the form

$$6.1 \dots \gamma = \left[\Delta F_i \frac{0.9165}{V_i} \left(\frac{V_s}{N} \right)^{\frac{1}{3}} \right]$$

ΔF_i is the excess Gibbs free energy per area over that of the bulk liquid, and $\frac{0.9165}{V_i} \left(\frac{V_s}{N} \right)^{\frac{1}{3}}$ is the volume of a layer of surface lattice 1 cm.^2 in area.

Of the many other mathematical derivations proposed for surface tension, that of Guggenheim⁶³ has proved most useful in its application to molten salts. Guggenheim assumed that in a regular solution of two or more components, each and every constituent whether a molecule of type A or B, has the same number of nearest neighbours, and that the total intermolecular potential energy can be regarded as the sum of contributions from pairs of closest neighbours. From this model Guggenheim was able to show that for an equimolar solution in which the heat of mixing was zero, the surface tension is given by the expression

$$6.2 \dots \gamma = \bar{\gamma} - \frac{kT}{a} \log \cosh \frac{\Delta a}{2kT}$$

where $\bar{\gamma} = \frac{1}{2}(\gamma_A + \gamma_B)$ and $\Delta = \gamma_A - \gamma_B$.

For liquids which do not form perfect solutions, $\frac{\Delta}{\bar{\gamma}}$ will probably not exceed 0.1, and equation 6.2 will become

$$6.3 \dots \gamma = \bar{\gamma} - \Delta \frac{\Delta a}{8kT}$$

by the series expansion of $\log \cosh \frac{\Delta a}{2kT}$. Many workers^{35,65,66} have used deviations from equation 6.3 as a measure of the thermodynamic non-ideality of surface tension for molten salt mixtures, and postulated the presence of complex ions in cases where these deviations

are large.

Many theoretical relationships between surface tension and other physical constants of the liquid have been advanced. These include the Eötvös equation

$$6.4 \dots \frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt} = k$$

where v is the specific volume of the liquid, molecular weight M .

Integration of equation 6.4 gives

$$6.5 \dots \frac{-\gamma_1(Mv_1)^{\frac{2}{3}} - \gamma_2(Mv_2)^{\frac{2}{3}}}{t_1 - t_2} = k$$

For many organic substances it was shown that k was approximately 2.1, and if a lower value was obtained it was considered due to association. For molten salts k is often in the region of 0.5, but to assume association conflicts strongly with electrical conductance evidence. Bloom et al⁶⁵ do not consider any of the alternative suggestions for this low value to be satisfactory.

A further relationship often used in classical physical chemistry is given by equation

$$6.6 \dots P = \frac{M\gamma^{\frac{1}{4}}}{\rho}$$

where P is a constant called the molecular Parachor. For molten salts the Parachor has been shown to be frequently temperature dependent. This temperature variation, and the variation of calculated atomic Parachor,^{35,65} invalidates the use of the Parachor for molten salts.

The surface tension of a liquid is defined as its surface free energy per unit area

$$6.7 \dots \gamma = \frac{G}{a}$$

The surface entropy per unit area is given by

$$6.8 \dots \frac{S^s}{a} = - \frac{d\gamma}{dT}$$

and the surface heat content per unit area is thus

$$6.9 \dots \frac{H^s}{a} = \gamma - T \frac{d\gamma}{dT}$$

Since the temperature coefficient of surface tension for molten salts is constant the surface heat content is a constant independent of temperature, and thus provides a fundamental quantity which may be used to compare different molten salts, or other liquids. The comparison between the molecular character of the liquid, and its surface heat content per unit area is illustrated in the following values for this parameter:

<u>Compound</u>	Benzene	Magnesium Chloride	Sodium Nitrate	Sodium Chloride
Surface Heat Content ergs/cm. ⁻²	59.2	76.7	138.9	216.2

Bloom et al⁶⁵ and Janz³⁵ have used this parameter as an indication of the molecular character of the melt. Surface tension phenomena have been used in molten salt systems to substantiate the existence of complex ions.

Together with its temperature dependence, the surface tension of a melt provides an indication of the molecular character of melt, and is also a necessary experimental parameter for use in evaluating other properties of the melt, such as conductivity.

II. EXPERIMENTAL

The surface tension of a liquid may be measured using a wide variety of techniques. The maximum bubble pressure method has been used extensively for molten salts, though studies using the drop weight method, the dipping cylinder method, and the capillary rise method have been published. The capillary rise technique requires a large area of uniform temperature, the capillary must be made of an inert material, and an accurate method of determining the capillary rise must be available. These technical difficulties are absent in the present system, since a pyrex glass capillary and an oil thermostat are both satisfactory. Thus, since the capillary rise technique has been proven for measurements in the low temperature region, this was the method chosen.

The apparatus is shown in Figure 6.1. The inner tube is a precision bore capillary tube, internal diameter $0.5 \pm .001$ mm. The capillary tube was lightly marked in three places approximately 2.0, 4.0 and 6.0 centimeters from the tip, such that they could be easily seen through the cathetometer. These marks were of assistance in measuring the total capillary rise. An extension of 5.0 centimeter diameter at the foot of the outer tube provided a satisfactory reading

Figure 6.1

Surface Tension Apparatus

SURFACE TENSION APPARATUS

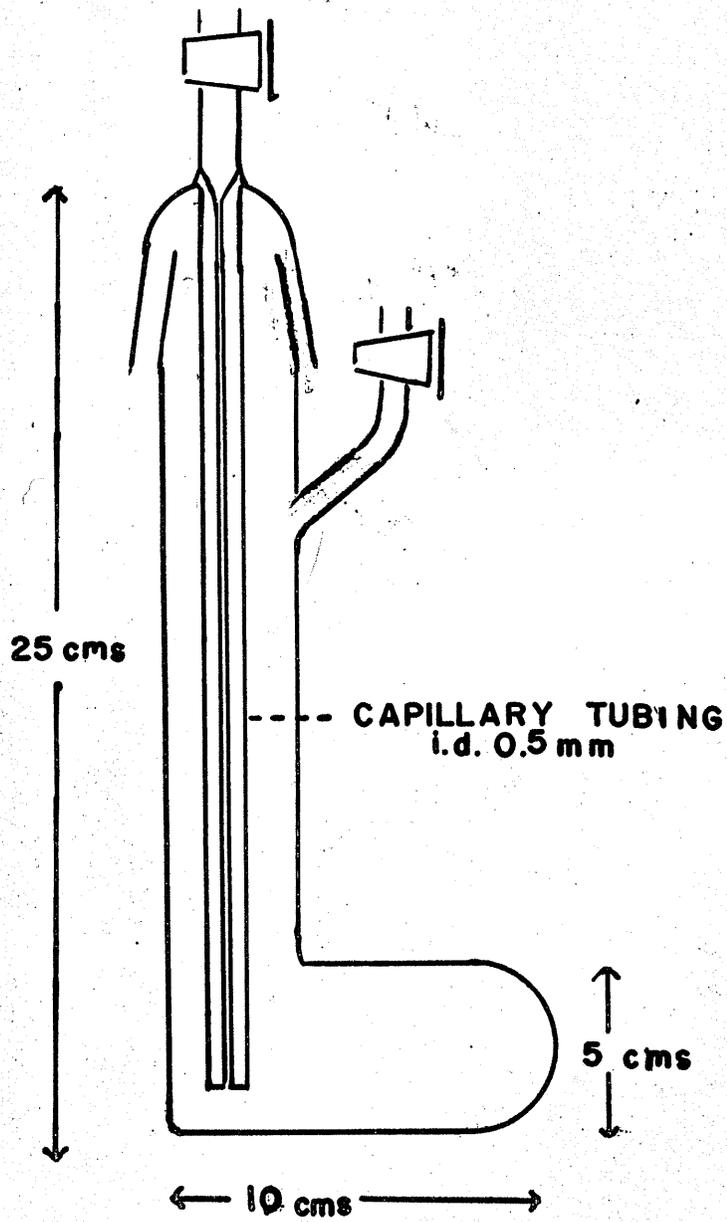


FIGURE 6-1

level for the lower meniscus. The position of the upper meniscus could be altered by application of a pressure gradient using either of the attached vacuum taps.

The thermostat used was that constructed for the previous density and viscosity determinations. A Gaertner microcathetometer capable of measuring to 0.01 mm. was used to measure the capillary rise.

The complete cell was carefully cleaned and oven dried. Enough powdered lithium chlorate was placed in the outer tube, so that when molten the liquid level corresponded to the maximum diameter of the bottom extension. The weight before and after filling was used to calculate the weight of lithium chlorate taken. During these manipulations the tube was covered with a B.24 standard cap. Additions were then made to the lithium chlorate if necessary, the cap replaced by the capillary, and the cell transferred from the drybox to the thermostat. At least four hours were allowed for thermal equilibrium to be established before readings were taken. The meniscus position was made to fall and rise several times in the capillary, and the average rise of several cathetometer readings considered as the absolute rise at that temperature. The total rise was always greater than the total range of the microcathetometer, and was calculated from the sum of the distances between the upper and lower meniscuses and a convenient mark.

Using this apparatus it was found possible to reproduce the surface tension of distilled water at 25°C. to ± 0.5 dynes. cm.⁻¹.

III. RESULTS

The surface tension and its temperature dependence has been determined for lithium chlorate and several lithium chlorate-water and lithium chlorate-lithium nitrate mixtures. The water mixtures contained 0.038, 0.090, 0.155 and 0.236 mole fractions of water, the lithium nitrate mixtures 0.032, 0.075, 0.172 and 0.213 mole fractions of lithium nitrate. The results are given in Tables 6.1, 6.2, 6.3, and the temperature dependence illustrated in Figure 6.2. The analytical representations of the temperature dependence of surface tension for pure lithium chlorate and the mixtures were obtained from a least squares fit of the experimental results of Tables 6.1, 2 and 3, using a computer, and are shown in Table 6.4.

A surface tension measurement of an equimolar lithium chlorate-water mixture was taken at 132.4°C. and was found to be 78.4 dynes. cm.⁻¹. The density of this mixture was calculated from

$$6.10 \dots \quad \rho_{\text{mixture}} = \frac{M_1 + M_2}{\frac{M_1}{\rho_1} + \frac{M_2}{\rho_2}}$$

where ρ_1 and ρ_2 are the densities of the pure components at this temperature. The surface tension for this mixture calculated from the ideal surface tension relationship proposed by Guggenheim is 67.6 dynes. cm.⁻¹.

TABLE 6.1
SURFACE TENSION OF LITHIUM CHLORATE

$t^{\circ}\text{C.}$	Density gms. cc.^{-1}	Surface Tension dynes cm.^{-1}
132.1	2.0878	87.41
138.2	2.0828	87.30
142.6	2.0794	86.91
150.6	2.0729	86.26
155.2	2.0691	86.02
162.0	2.0635	85.43

TABLE 6.2

SURFACE TENSION OF LITHIUM CHLORATE-WATER MIXTURES

Mole Fraction Water	t°C.	Density gms. cc ⁻¹	Surface Tension dynes cm. ⁻¹	Mole Fraction Water	t°C.	Density gms. cc ⁻¹	Surface Tension dynes cm. ⁻¹
.038	133.2	2.0715	86.20	.090	132.3	2.0488	85.97
	139.4	2.0666	85.52		139.7	2.0433	84.42
	145.7	2.0617	85.10		147.0	2.0378	83.11
	146.3	2.0614	83.93		153.3	2.0326	82.66
	153.7	2.0552	84.10		156.0	2.0306	82.69
	160.1	2.0502	84.07		161.6	2.0262	81.87
	164.8	2.0463	83.49				
.155	137.0	2.0103	83.79	.236	132.5	1.9617	83.44
	142.6	2.0062	82.79		141.7	1.9552	82.57
	147.7	2.0015	82.49		144.0	1.9536	82.87
	152.5	1.9990	81.79		149.0	1.9500	80.99
	158.7	1.9944	81.50		154.4	1.9465	80.90
	168.0	1.9876	79.39		155.3	1.9456	80.42
					159.0	1.9431	80.14

TABLE 6.3

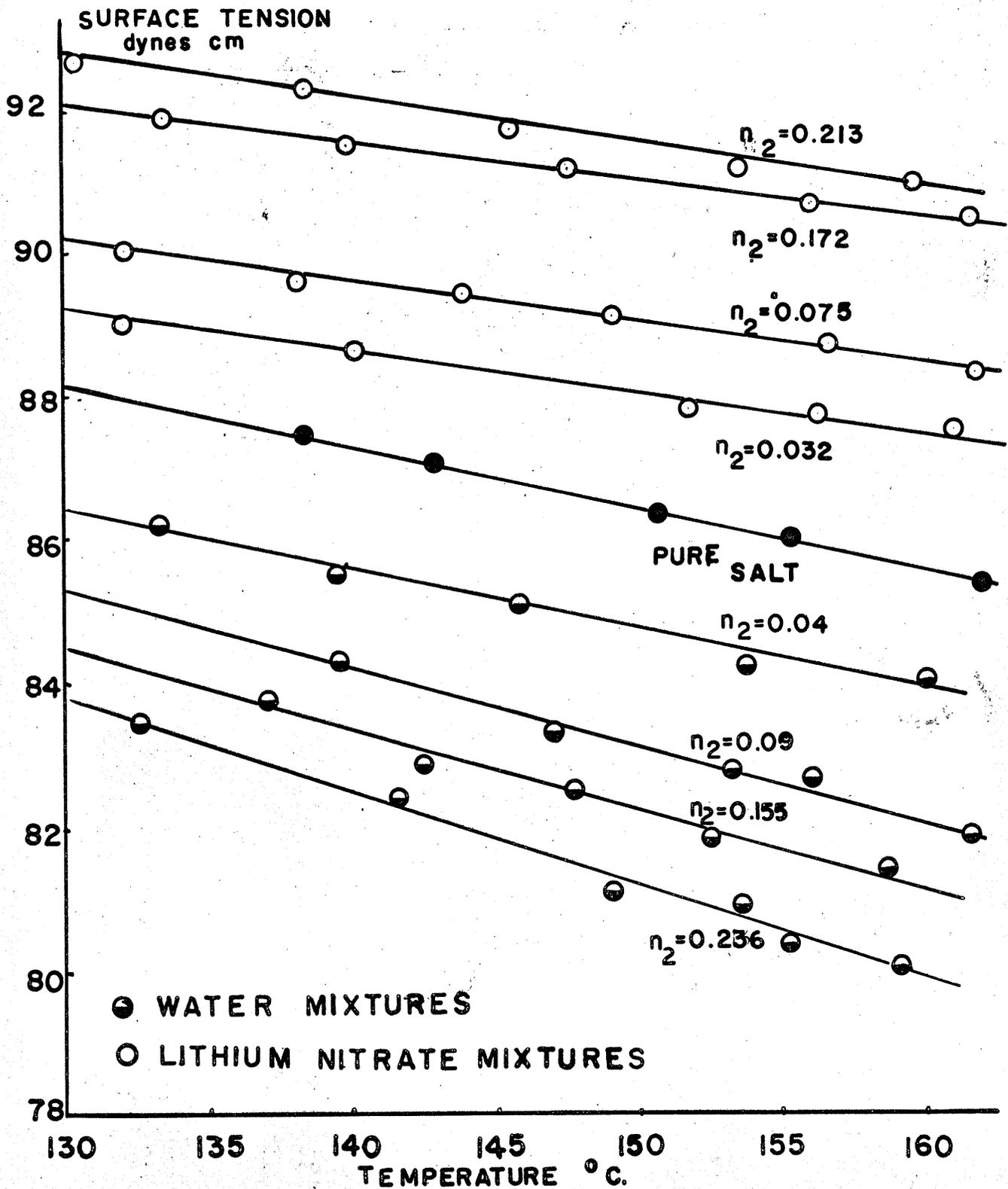
SURFACE TENSION OF LITHIUM CHLORATE-LITHIUM NITRATE MIXTURES

Mole Fraction Lithium Nitrate	t°C.	Density gms. cc ⁻¹	Surface Tension dynes cm ⁻¹	Mole Fraction Lithium Nitrate	t°C.	Density gms. cc ⁻¹	Surface Tension dynes cm ⁻¹
.032	132.0	2.0866	88.92	.075	132.0	2.0836	90.00
	136.5	2.0828	88.55		138.2	2.0790	89.51
	140.0	2.0799	88.60		143.6	2.0747	89.41
	145.8	2.0750	87.92		149.0	2.0705	89.02
	151.7	2.0700	87.78		156.0	2.0650	88.75
	156.1	2.0664	87.69		161.7	2.0606	88.21
	161.4	2.0619	87.60				
.172	133.0	2.0726	91.86	.213	130.5	2.0692	92.60
	139.7	2.0672	91.50		138.2	2.0632	92.27
	147.5	2.0615	91.34		145.6	2.0575	91.64
	156.0	2.0548	90.70		153.4	2.0513	91.11
	161.6	2.0506	90.66		159.4	2.0467	90.97
					166.7	2.0410	90.44

Figure 6.2

Plot of Surface Tension vs. Temperature for Lithium Chlorate
and its Mixtures

FIGURE 6-2
 PLOT OF SURFACE TENSION vs TEMPERATURE FOR
 LITHIUM CHLORATE AND ITS MIXTURES.



ANALYTICAL REPRESENTATION OF THE SURFACE TENSION VARIATION
WITH TEMPERATURE FOR LITHIUM CHLORATE
AND LITHIUM CHLORATE-WATER
LITHIUM CHLORATE-LITHIUM NITRATE MIXTURES

Additive	Mole Fraction	Equation of the General Type $\gamma = a - bt$	Standard Deviation
Pure salt		$\gamma = 96.7 - 6.3 \times 10^{-2}t$	0.11
Water	0.038	$\gamma = 96.2 - 7.7 \times 10^{-2}t$	0.44
Water	0.090	$\gamma = 103.2 - 13.3 \times 10^{-2}t$	0.33
Water	0.155	$\gamma = 101.6 - 13.0 \times 10^{-2}t$	0.31
Water	0.236	$\gamma = 101.7 - 13.6 \times 10^{-2}t$	0.38
Lithium nitrate	0.032	$\gamma = 94.9 - 4.6 \times 10^{-2}t$	0.17
Lithium nitrate	0.075	$\gamma = 97.4 - 5.6 \times 10^{-2}t$	0.09
Lithium nitrate	0.172	$\gamma = 97.7 - 4.4 \times 10^{-2}t$	0.10
Lithium nitrate	0.213	$\gamma = 100.5 - 6.0 \times 10^{-2}t$	0.09

Figure 6.3

Plot of Surface Tension vs. Mole Fraction Additive

PLOT OF SURFACE TENSION vs MOLE FRACTION
ADDITIVE

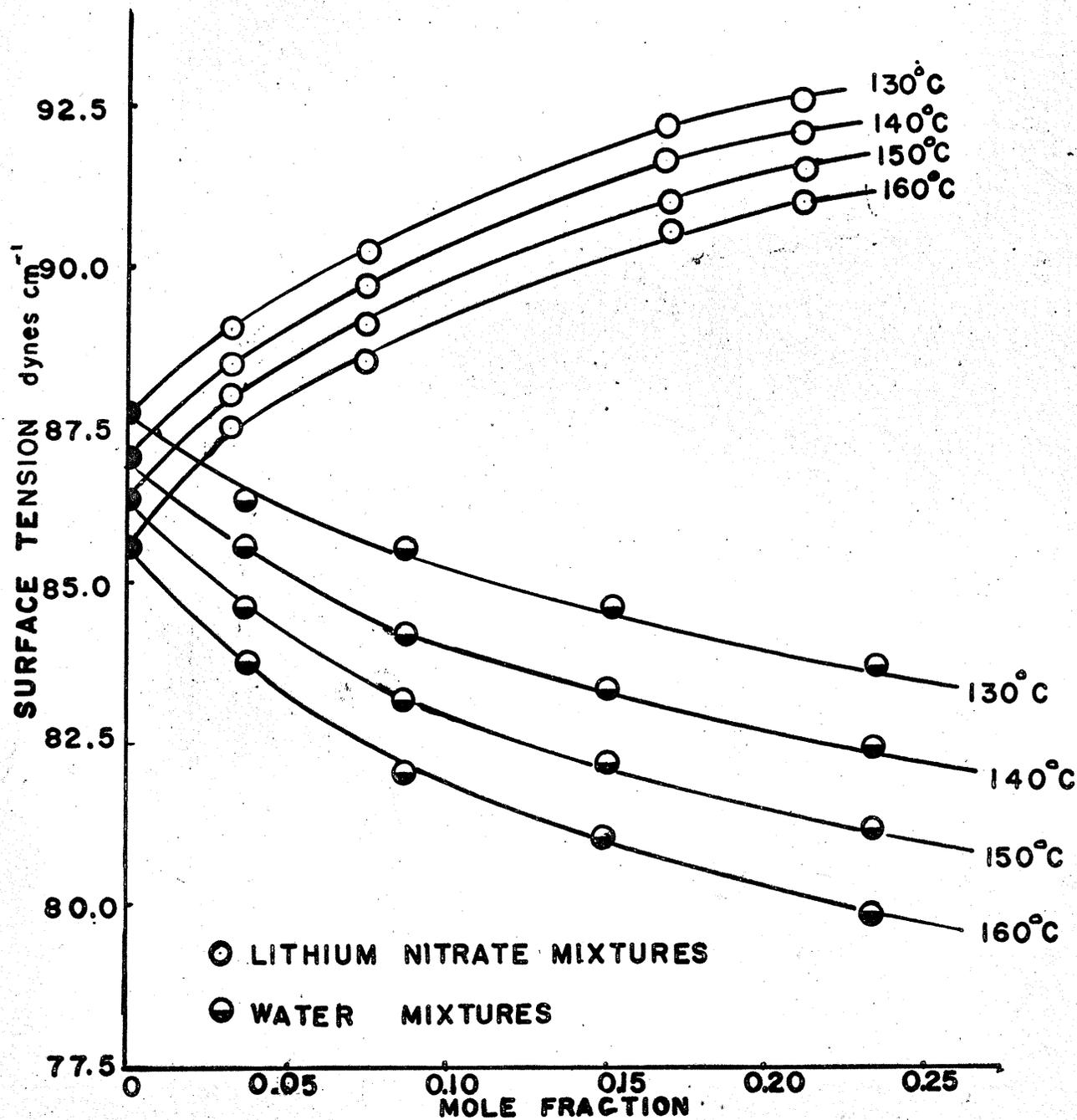


FIGURE 6-3

IV. DISCUSSION

The surface tension of lithium chlorate ($85.0 \text{ dynes cm.}^{-1}$) is typical of Group 1 salts of polyatomic anions when compared at corresponding temperatures as seen from Table 6.5. If association occurs within a melt it might be expected that these "associates" would affect the surface energy of the melt considerably. If these "associates" lower the surface energy they must be preferentially absorbed on the surface. Table 6.6 records the surface tension at the melting point for several alkali metal salts, obtained by extrapolation of the results of Jaeger.⁶⁷ For the simple spherical ions a marked trend is observed in the change of surface tension with the increase of cation radius only if the anion is small, e.g. the fluorides. For the nitrates this decrease of surface tension with cation radius does not occur, and the surface tension of all Group 1 nitrates are similar. The surface tension of lithium chlorate at its melting point, $88.6 \text{ dynes cm.}^{-1}$, is almost the same as that of potassium chlorate at its melting point, $81.0 \text{ dynes cm.}^{-1}$.⁴³ This indicates that the anion determines the surface energy in the Group 1 chlorates as in the Group 1 nitrates. Possibly in these melts the anions pack in contact, with the cations in crevices where their effect on the surface energy is limited. It is of interest to note that these concepts apply only to salts with polyatomic anions which have low melting points. The surface tensions of lithium, sodium and potassium carbonates were determined by Janz and Lorenz.³⁵ These salts

TABLE 6.5
SURFACE TENSION AND SURFACE HEAT (AT 1.10T)
OF TYPICAL GROUP 1 SALTS

Compound	Analytical Representation	Surface Tension dynes cm ⁻¹	Surface Heat ergs cm ⁻²	Reference
LiCl	= 181.8 - 7.1 x 10 ⁻² t	132	200	67
LiNO ₃	= 133.5 - 6.0 x 10 ⁻² t	115	149	67
LiClO ₃	= 96.7 - 6.3 x 10 ⁻² t	86.2	118	
KCl	= 155.2 - 7.3 x 10 ⁻² t	91.0	175	68
KNO ₃	= 128.9 - 5.78 x 10 ⁻² t	106	148	69
NaCl	= 190.8 - 9.3 x 10 ⁻² t	106	216	68
NaNO ₃	= 131.0 - 5.8 x 10 ⁻² t	110	139	69

TABLE 6.6
EXTRAPOLATED VALUE OF SURFACE TENSION
AT THE MELTING POINT OF SEVERAL ALKALI SALTS
dynes cm⁻¹[67]

	Li ⁺	Na ⁺	K ⁺	Rb ⁺
F ⁻	251	201	142	133
Cl ⁻	138	114	97	98
I ⁻		87	81	82
NO ₃ ⁻	117	120	113	109
ClO ₃ ⁻	88.6		81	

melt at 726°C., 858°C., and 899°C., and have surface tension values almost twice that of the corresponding chlorides, namely 240.0, 205.9 and 161.7 dynes cm.⁻¹ respectively. Thus for salts of simple spherical ions, or salts which have high melting points (and hence no association within the melt), the surface tension decreases as the number of ions per unit length and the polarizing power of the cation decrease. The surface tensions of the low melting salts lithium and potassium chlorate are similar, and this shows the possible presence of associated groups in these chlorate melts.

The parachor has been calculated from the surface tension results of Table 6.1, and is shown in Table 6.7. A small but definite increase in the value of the parachor with temperature is evident, approximately two per cent per 100°C. Due to this temperature dependence of the parachor for many molten salts,^{35,65} it is unsatisfactory as a comparative property of melts. The surface heat $H_s = \gamma - T \frac{d\gamma}{dT}$, of a molten salt is not temperature dependent, and is said to provide a measure of the covalent character of the melt.⁶⁵ For non-polar liquids the value of the surface heat lies usually between 40-65 erg.cm.⁻². Salts which are essentially ionic have the highest values, for example, sodium chloride, 216.7 ergs. cm.⁻², whereas molten salts which exist largely as covalent molecules have lower values approaching those of non-polar liquids, for example, magnesium chloride, 76.7 ergs. cm.⁻². The surface heat of several molten salts is shown in Table 6.5. The surface heat of lithium

chlorate is $118 \text{ ergs.cm.}^{-2}$, intermediate between that of ionic melts and that of covalent melts, showing that at least some covalent character exists within the lithium chlorate melt.

TABLE 6.7
PARACHOR AND SURFACE HEAT OF LITHIUM CHLORATE

$t^{\circ}\text{C.}$	Parachor	Surface Heat ergs.cm.^{-2}
130 $^{\circ}\text{C.}$	132.4	118
140 $^{\circ}\text{C.}$	132.6	118
150 $^{\circ}\text{C.}$	132.8	118
160 $^{\circ}\text{C.}$	133.1	118
170 $^{\circ}\text{C.}$	133.3	118

The surface tension of pure lithium chlorate and also that of the lithium nitrate and water mixtures decrease linearly with temperature (Figure 6.1). At any specific temperature the lithium chlorate-lithium nitrate mixtures have a surface tension greater than that of pure lithium chlorate, whereas the water mixtures exhibit surface tensions lower than that of pure lithium chlorate. This may be accounted for by comparing the surface tensions of pure lithium nitrate and pure water extrapolated to 130.0 $^{\circ}\text{C.}$ At 130.0 $^{\circ}\text{C.}$ the surface tension of water is $54.0 \text{ dynes cm.}^{-1}$, and that of lithium nitrate $126.0 \text{ dynes cm.}^{-1}$, and hence water additions should lower the surface tension of lithium chlorate from its value of $88.5 \text{ dynes cm.}^{-1}$

at 130°C ., and additions of lithium nitrate should cause an increase.

The relationship between the isothermal surface tension and the mole fraction of either lithium nitrate or water is not linear. The relationship is shown graphically in Figure 6.2. The initial additions up to 0.05 mole fraction tend to affect the surface tension of the melt to a greater extent than subsequent additions of either lithium nitrate or water. This greater effect of the first additions may be due to the breakup of any association present in the original melt.

The temperature coefficient of surface tension changes considerably as the water content in the lithium chlorate-water mixtures increases. The temperature coefficient of surface tension for water is much higher than that of molten salts, and must account for the increase in the temperature coefficient of surface tension of the lithium chlorate-water mixtures as the water content increases. This is substantiated by the fact that the surface tension temperature coefficient of the lithium nitrate mixtures remains constant, which is anticipated since the coefficients of pure lithium chlorate and pure lithium nitrate are substantially the same.

The surface tension of an ideal equimolar mixture of lithium chlorate-water calculated from the Guggenheim equation 6.3 does not compare with that determined experimentally. This indicates that the melt is not ideal in its surface tension behaviour at higher concentrations of water.

These surface tension results illustrate the partially covalent character of the lithium chlorate melt, and indicate the change in the melt constituents is greater for the initial addition of water than that for subsequent additions.

ELECTRICAL CONDUCTANCE

CHAPTER VII

ELECTRICAL CONDUCTANCE

I. INTRODUCTION

Measurement of the electrical conductivity and its temperature dependence in molten salt systems yields significant information regarding the ionic character of the system, the nature of the conducting species, and the structure and intermolecular forces present in the melt. When used in conjunction with the values of other transport properties it is possible to postulate the mechanism of these processes in terms of the lattice geometry, molecular force fields, and molecular motion.

Interpretation of the electrochemical properties of a molten salt or molten salt mixtures is in no manner comparable to the modern theories developed for aqueous solutions. If typical fused salt parameters are inserted into the equations by which the ion-atmosphere radius of aqueous ions may be calculated, the result shows a radius of the order of 0.2\AA , smaller than the radius of the ion alone. In view of the failure of the Poisson-Boltzmann equation on which the Debye-Huckel theories are based to take account of short range repulsive forces, this result is not surprising. These short range coulombic forces are of primary importance in a molten salt, and determine the transport properties.

The problem of electrical conduction in a molten salt has been most successfully approached by a consideration of the melt as a disordered solid, and applying the mathematical relationships developed from solid state defect theories.

For all systems the specific conductance is given by

$$7.1 \dots \quad \kappa = \frac{G_1}{R_e}$$

where G_1 is the cell constant, and R_e the measured resistance. The value of G_1 is obtained experimentally using solutions of potassium chloride having precisely known values of specific conductance.⁷⁰

From the simple electrodynamic theory for the transfer of charge through an electrolyte, the specific conductivity of an electrolyte which dissociates into ionic species is given by

$$7.2 \dots \quad \kappa = \frac{F}{1000} \left[c_i z_i \mu_i \right]$$

If a binary electrolyte is considered, of concentration C g.mole litre⁻¹, then

$$7.3 \dots \quad \kappa = \frac{C n_e}{1000} a F \left[\mu_i \right]$$

where a is the degree of dissociation, and n_e the electrochemical valency. From the principle of electrical neutrality, n_e for a binary electrolyte is given by

$$7.4 \dots \quad n_e = \nu_+ z_+ = \nu_- z_-$$

ν_+ and ν_- are the number of cations and anions formed as each electrolyte molecule dissociates, each having a charge Z_+e_0 and Z_-e_0 .

Introducing the Faraday constant into the mobility term

$$7.5 \dots \quad \Lambda = \lambda_{\text{anion}} + \lambda_{\text{cation}} = \frac{1000 K}{CZ}$$

If the concentration is expressed as moles.litre⁻¹, then

$$7.6 \dots \quad \frac{CZ}{1000} = \frac{\text{Equivalents}}{\text{litres.}}$$

For binary mixtures of molten salts Bloom and Heymann³⁹ replaced

M_e , the equivalent weight of the pure molten salt in the equation for equivalent conductance

$$7.7 \dots \quad \Lambda = K M_e \rho^{-1}$$

by the mean equivalent weight of the mixture, given by

$$7.8 \dots \quad M_M = M_e^{(1)} f^{(1)} + M_e^{(2)} f^{(2)}$$

$M_e^{(1)}$, $M_e^{(2)}$, $f^{(1)}$, $f^{(2)}$ being the equivalent weights and equivalent fractions of the components of the mixture.

Differentiation of equation 7.7 with respect to $\frac{1}{T}$, and then taking logarithms of both sides,

$$7.9 \dots \quad \frac{\partial \ln \Lambda}{\partial (\frac{1}{T})} = \frac{\partial \ln K}{\partial (\frac{1}{T})} - \frac{\partial \ln \rho}{\partial (\frac{1}{T})}$$

which may be used to compare either theoretical or experimental values of specific or equivalent conductance at different temperatures. This derivation does, however, assume complete dissociation in the molten salt, a condition not always present.

For nearly all fused salts it was experimentally shown that a graph of $\ln \kappa$ or $\ln \Lambda$ against $\frac{1}{T}$ is essentially linear, indicating that the mechanism of conductance is a rate process, and the simple Arrhenius expressions are applicable to both equivalent and specific conductance,

$$7.10 \dots \quad \kappa = A_{\kappa} \exp \frac{-\Delta E_{\kappa}}{RT}$$

$$7.11 \dots \quad \Lambda = A_{\Lambda} \exp \frac{-\Delta E_{\Lambda}}{RT}$$

ΔE_{κ} and ΔE_{Λ} are the empirical activation energies, and A_{κ}, A_{Λ} are constants for the system. Since electrical conductance occurs at constant pressure the empirical activation energies $\Delta E_{\kappa}, \Delta E_{\Lambda}$ may be identified with the empirical activation enthalpies $\Delta H_{\kappa}, \Delta H_{\Lambda}$.

A closer investigation over an extended temperature region has shown many of the experimental relationships between $\ln \kappa$ or $\ln \Lambda$ and $\frac{1}{T}$ are in fact slightly curved. Corroborating evidence must be available before structural changes are proposed which are based on the change of activation enthalpy with temperature, for from equation 7.11

$$7.12 \dots \quad \frac{d \ln \Lambda}{d(\frac{1}{RT})} = H_{\text{apparent}} = H_{\Lambda} - T \frac{dH_{\Lambda}}{dT} - \frac{d \ln A_{\Lambda}}{d(\frac{1}{RT})}$$

If A_{Λ} is independent of temperature, then the identification of H_{Λ} with the apparent heat of activation, H_{apparent} , at a certain temperature admits that $\frac{dH_{\Lambda}}{dT}$ is equal to zero at this temperature, regardless of the temperature dependence of H_{apparent} . Thus the

temperature dependence of H_u and H_{apparent} differ completely whenever

$$\frac{dH_{\text{apparent}}}{dT} \neq 0 \quad .71$$

Many equations have been proposed to predict the electrical conductivity of molten salts, often based on a model for the liquid similar to that of the solid state. Mention may be made of equations proposed by Sakai,^{72,73,74} Oldekop⁷⁵ and Sundheim.⁷⁶ Bockris⁷⁷ has critically examined the commonly proposed models of ionic liquids comparing the accuracy of the data predicted for volume and entropy change on fusion, compressibility, expansivity and self-diffusion. The models examined were: (a) a quasi-lattice model involving Schottky defects, (b) the hole model, (c) the crystallite model of Mott and Gurney,⁵ (d) the polyhedral hole theory of Bernal,⁷⁸ (e) the free volume model of Cohen and Turnbull,⁷⁹ and (f) the significant structure model of Eyring.⁹ (c) indicates that the crystallites would have to be molecularly sized, (a) gives good results for entropy of fusion if rotation is taken into account, and fair agreement for change of volume on fusion. Only two models considered satisfactory for all of the properties, the hole theory and Eyring's significant structure theory, though the latter required an empirical determination of its constants. In the hole theory, originally advanced by Frenkel,⁵⁰ Altar⁸⁰ and others, it was proposed that the liquid consisted of spherical ions each behaving as a linear harmonic oscillator. A number of holes are fixed in random distribution among

the ions. The liquid may be regarded as a quasi-crystalline structure consisting of a binary mixture of holes and ions. The position and size of the holes vary due to the random fluctuations in the melt caused by thermal motion of the molecules. X-ray evidence⁸¹ has substantiated the short range order and long range disorder which would be anticipated by this model. The short range order is similar to that of the crystalline state.

Indeed, Bloom and Heymann³⁹ treated the liquid as a very disordered solid, using the relationships between ionic conductance in solid salts, and the presence of imperfections in the 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 equation

$$7.13 \quad \dots \quad K = A \exp \frac{-\frac{W}{2} + U}{kT}$$

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 applies only if the migration of a single ion is the cause of the conductance. These workers suggested that the degree of disorder in a molten salt is so large that the fraction of mobile ions must also be large. For a purely ionic melt the equation 7.13 becomes

$$7.14 \dots \kappa = A_{\text{cation}} \exp \frac{-\Delta E_c}{RT} + A_{\text{anion}} \exp \frac{-\Delta E_a}{RT}$$

since the contribution of each ionic species to the total specific conductance is proportional to an exponential term involving only the energy barrier of the respective migrations. If these energy barriers are very different in value, then the ion having the smallest activation energy becomes the predominant conducting species, and equation 7.14 takes the form of the original Arrhenius equation. Martin⁸² first showed the relationship between the activation energies of specific and equivalent conductance. By substituting the definitions of the thermal expansion α , and of the energies of activation ΔE_c and ΔE_a into equation 7.9 he found

$$7.15 \dots \Delta E_a = \Delta E_c + RT^2 \alpha$$

Hence it can be seen that ΔE_a and ΔE_c may be equated only for systems having small temperature coefficients of expansion, or for systems at low temperatures.

From the successful application of the Arrhenius equation, it seemed probable that a more elegant equation could be developed for conductance from an application of the absolute reaction rate theory to ionic motion under a potential gradient. This was done by Baimakov and Samusenko⁸³ and Bockris *et al*⁸⁴ who found

$$7.16 \dots \Lambda = \frac{2}{3} \left(\frac{FZXd^2}{RT} \right) \frac{kT}{h} \exp \frac{\Delta S^\ddagger}{R} \exp \frac{-\Delta H^\ddagger}{RT}$$

where X is the effective potential gradient on the ion when a field of 1 volt. cm.⁻¹ is applied, d is the half distance between initial

and final positions of the ion along the coordinate of motion, and $\Delta S^\ddagger, \Delta H^\ddagger$ the activation entropy and enthalpy. This expression may be simplified to

$$7.17 \dots \Lambda = 5.18 \times 10^{18} (D+2) Z d^2 \exp \frac{\Delta S^\ddagger}{R} \exp \frac{-\Delta H^\ddagger}{RT}$$

where D is the dielectric constant of the medium.

Bockris, Crook et al⁸⁵ have recently applied the Absolute Reaction Rate theory to a statistical model for the liquid state proposed by Stillinger and Kirkwood and Wojowicz.⁸⁶ Their final equation took the form

$$7.18 \dots \Lambda_i = \frac{Z_i F^2 d_i^2 \nu_i}{3RTe} \exp \frac{-\Delta H_i}{RT} \exp \frac{-\Delta F_h}{RT}$$

where ν_i is the vibrational frequency of the ion, ΔH_i the activation enthalpy required to move an ion to the next "lattice" site, and ΔF_h the free energy of formation of a vacant "lattice" site. This is a more elegant representation of the relationships between conductance and the energy and entropy of activation for ionic movement in a melt.

In all of these treatments based on the absolute rate theory, the enthalpy of activation ΔH^\ddagger is 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 itself must also be included, i.e.-

$$7.19 \dots \Delta H^+ = \Delta H_{\text{hole}} + \Delta H_{\text{jump}} + \Delta H_{\text{ionization}}$$

When comparison is made between the activation enthalpies of viscosity under constant volume and constant pressure conditions,⁸⁷ the activation enthalpy at constant volume is found to be approximately one tenth that of the corresponding activation enthalpy at constant pressure. Under constant volume conditions, ΔH_{jump} is the only enthalpy term present, since it may be assumed that there is no increase in the number of holes. Thus the ratio 1:10 is the ratio of $\Delta H_{\text{jump}} :: \Delta H_{\text{jump}} + \Delta H_{\text{hole}}$. From measurements of the velocity of sound in molten salts, Bockris and Richards¹² have also shown that the major part of the heat of activation of viscous flow consists of the energy of hole formation. In the absence of constant volume conductance measurements the ratio of $\Delta H_{\text{jump}} :: \Delta H_{\text{jump}} + \Delta H_{\text{hole}}$ is assumed to be the same in conductance as in viscosity. An approximate value for ΔH_{hole} may be calculated from considerations proposed by Fürth.⁸⁸ Fürth showed that the potential energy of a hole of radius r was

$$7.20 \dots \Delta F_{\text{hole}} = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 (p - p_0)$$

where p and p_0 are the external pressure and the saturated vapour pressure of the liquid respectively. At ordinary pressures the second term is negligible, and

$$7.21 \dots \Delta F_{\text{hole}} = 4\pi r^2 \gamma$$

If the temperature coefficient of surface tension is known, then the heat of hole formation is given by

$$7.22 \dots \Delta H_{\text{hole}} = 4\pi r^2 \left(\gamma - T \frac{d\gamma}{dT} \right)$$

Bockris and Richards¹² utilized Furth's theory, that the work required to form a hole is equal to that required to produce a surface area equal to the area of the hole, and showed that

$$7.23 \dots V_h = 0.68 \left(\frac{kT}{\gamma} \right)^{\frac{1}{2}}$$

where V_h is the mean volume of a hole. From the difference in volume, ΔV , between the molar volume of the liquid and that of the hypothetical solid at the same temperature, the total number of holes formed was shown to be

$$7.24 \dots N_h = \frac{\Delta V}{0.68} \left(\frac{\gamma}{kT} \right)^{\frac{1}{2}}$$

which suggests that 1/5 to 1/6 of the lattice sites in melts are not filled, which is in agreement with X-ray evidence.⁸⁹ From these correlations of theoretical and experimental values for the energy of hole formation, it seems that the macroscopic concepts of surface tension are applicable to the microscopic system.

Recent theoretical treatments of transport process in liquids^{85,90,91} indicate that the pre-exponential term of the Arrhenius-type equation may be temperature dependent to some extent. Bockris, Crook, Richards and Bloom⁸⁵ have recently developed a theoretical equation for conductance of the form

$$7.25 \dots \quad \mathcal{L} = \left[A_i T^{-1} \exp \frac{-\Delta H_i^+}{RT} \right]_{+-}$$

From this theory, in which the mechanism is again based on the hole model for molten salts, it follows that the experimental heat of activation for conductance, ΔH_{expt}^+ , is identified with the enthalpy of hole formation and ionic jump ΔH_{hole} and ΔH_{jump} , respectively, by the equation

$$7.26 \dots \quad \Delta H_{\text{hole}} + \Delta H_{\text{jump}} = \Delta H_{\text{expt}}^+ + RT$$

for any particular ionic species. Compensation between the pre-exponential factor and activation energy occurs such that plots of $\ln \mathcal{L}$ versus $\frac{1}{T}$ are rendered linear. This suggests that the activation energies defined by the simple Arrhenius equations are not true activation energies, and may include specific structural effects associated with the system studied.

It may be reasoned that the chief cause of an increase in diffusivity, fluidity, and electrical conductance as a molten salt is heated at constant pressure may 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 the force fields due to expansion. The total number of mobile ions does however also determine the conductivity of the melt. It is not necessary for an inorganic melt to be composed entirely of ions; the melt may be only partially ionized. Greenwood and Martin⁹² have proposed an approximate

method for obtaining a , the degree of dissociation of a melt. Since

$$7.27 \dots \quad \Lambda = \frac{\mu_m}{Z} = \lambda_+ + \lambda_-$$

where μ_m is the molar conductivity, $= \frac{1000\kappa}{C}$, then

$$7.28 \dots \quad a = \frac{\mu_m}{Z(\lambda_+ + \lambda_-)}$$

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

$$7.29 \dots \quad a = \frac{\mu_m}{2\bar{\lambda}}$$

If Walden's Rule is obeyed, that is

$$7.30 \dots \quad \Lambda\eta = \text{constant}$$

then the average ionic conductance may be referred to a standard reference conductance, λ° , in a medium of unit viscosity, and

$$7.31 \dots \quad \bar{\lambda} = \frac{\lambda^\circ}{\eta}$$

which when substituted into equation 7.29 shows

$$7.32 \dots \quad a = \frac{\mu_m \eta}{2\lambda^\circ}$$

Values of λ° are limited to a narrow range. Reference to ionic mobilities⁹³ indicates that in any given solvent, all mobilities lie within a factor of ten of each other. For example, in water, which has a viscosity of 1.00 centipoise at 20°C., the value $\lambda^\circ = 50 \text{ ohm}^{-1} \text{ cm}^2 \text{ g.ion}^{-1}$ represents an average value for all ions, bar the hydronium and hydroxyl ions, within a factor of two. This figure may be used as

a plausible standard when melt viscosities are reduced to zero, and substitution in equation 7.32 gives

$$7.33 \dots a = \frac{\mu_m \eta}{100}$$

The function $\mu \eta$ has been termed the "reduced conductivity". Though Walden's rule has been experimentally established for many systems, it implies a similar change in ionic migration and in viscous flow. Thus, if this were the case, the ratio of the activation energies for conductance and viscosity should be unity. The value of $\frac{\Delta E_\eta}{\Delta E_\mu}$ has been found to lie in the range 2 - 4 for most molten salts, indicating that Walden's rule is not satisfied. If the viscosity and molar conductance are represented by the equations

$$7.34 \dots \eta = \eta_0 \exp \frac{\Delta E_\eta}{RT}$$

$$7.35 \dots \mu = \mu_0 \exp \frac{-\Delta E_\mu}{RT}$$

then we see $\mu^m \eta$, or $\mu \eta^{\frac{1}{m}}$ is constant, where $m = \frac{\Delta E_\eta}{\Delta E_\mu}$. This value for the reduced conductance $\mu^m \eta$ affords an approximate value of a , the degree of dissociation, when substituted into equation 7.33 and applied to fused salt systems.

At the present time no single theoretical relationship has been developed which will successfully predict all of the transport properties of a molten salt. Quantitative estimations of the conductivity of a melt may be made following the principles developed by

Biltz and Klemm,³⁶ Yaffe and Van Artsdalen³⁴ and others. These workers showed that the equivalent conductivity of a melt increases with a decrease of cation radius and with a decrease of anion radius. Large or rapid decreases of the activation energy of conductance with rising temperature provide a definite indication of changes of structure or coordination within the melt; however, interpretation of the small variations in activation energy, often found over extended temperature ranges, must be treated with caution until more rigorous theories of transport properties are developed, unless supporting evidence is available. No theoretical investigations have been published in which the melt mixture has included water as one of the minor components, though the principles involved in the conductance of pure molten salts have often been applied successfully to mixtures of molten salts.

II. EXPERIMENTAL

The electrical conductance of molten salts may be determined by the conventional methods used in studies of aqueous solutions. The specific conductance is often high, and special capillary cells may have to be used.⁹⁴ In many cases much care must be taken in selecting the material for the cell, since fused salts are often corrosive, the capillaries, if necessary, being machined from single crystals. A different form of cell has been used by some workers,^{84,95} in which the cell has the form of a crucible, usually made of platinum,

which acts as one electrode and also the container for the melt. The second platinum electrode is then placed in the melt, its position and depth of immersion determining the cell constant. Lithium chlorate offers no such experimental difficulties, however, and typical pyrex glass cells in a liquid thermostat are satisfactory.

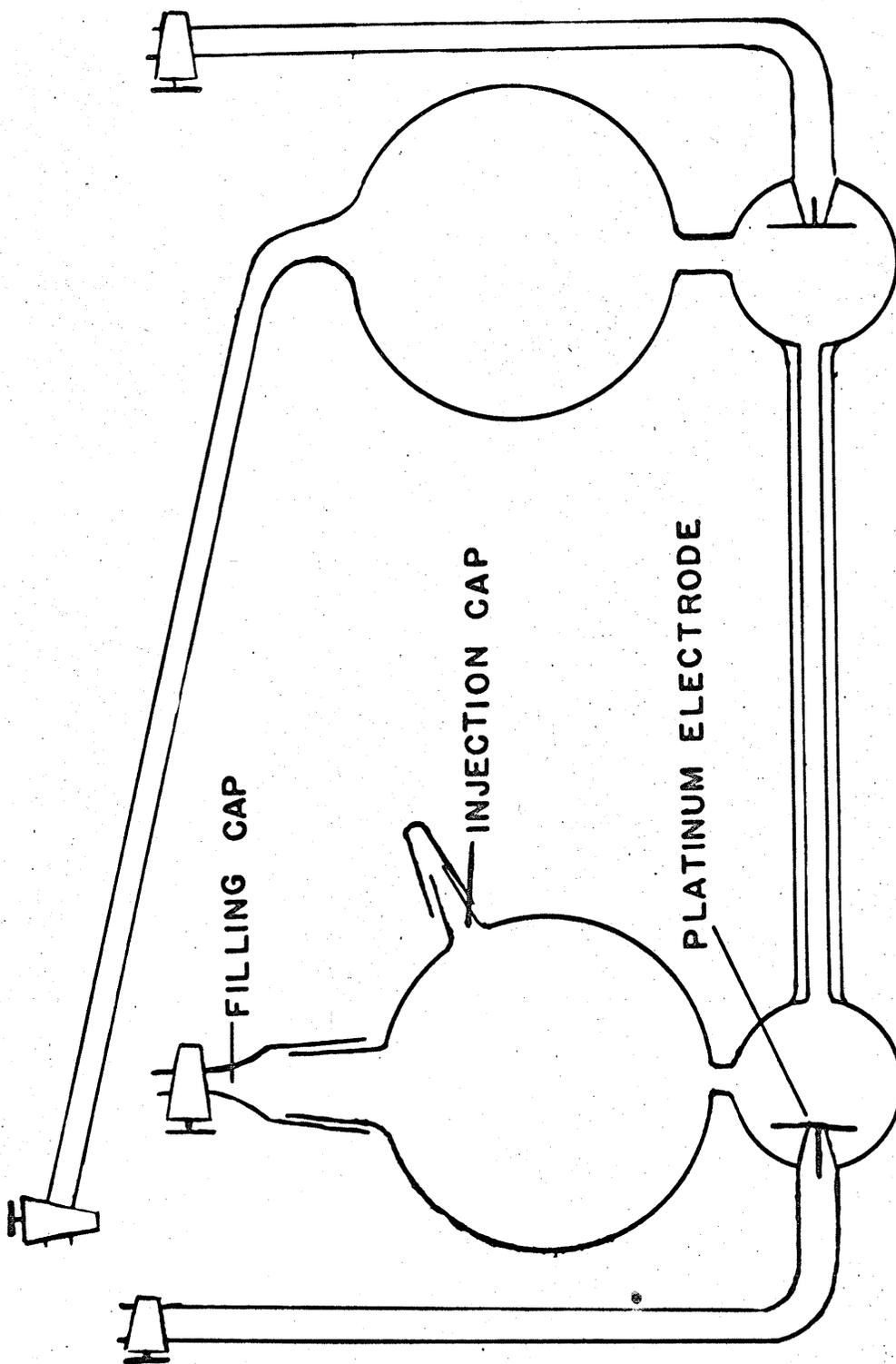
A conventional capillary cell (Figure 7.1) with a high cell constant of the type recommended by Jones and Bollinger⁹⁶ was used. The basic filling tubes and electrical connections were widely separated, thus eliminating possible errors due to the Parker effect.⁹⁷ The electrodes were not platinized, since even without conditioning with an electrodeposit of platinum black the detector showed sharp changes with small changes of resistance.⁹⁵ The variation of the measured resistance with the frequency of the input signal is about 0.5 per cent over the frequency range of 500 - 10,000 cycles. sec⁻¹ for many molten salts, the relationship being

$$R_e = R_{INF} + \frac{K}{\omega^2}$$

where R_e and R_{INF} are the measured resistances at the frequency ω , the polarization-free resistance at infinite frequency, and K a constant characteristic of the salt studied. A Jackson audio-oscillator capable of delivering a low wattage input with a selected frequency of between 0 - 100,000 cycles. sec⁻¹ was used for all of the conductance experiments. To measure the resistance a Leeds and Northrup Jones conductivity bridge was used in conjunction with a General Radio type 1231-B amplifier coupled to an oscilloscope.

Figure 7.1
Conductance Cell

FIGURE 7-1



THE CONDUCTANCE CELL

This system proved capable of detecting a resistance change of 1 ohm in 10,000 ohms on the bridge.

The conventional manner⁹⁸ of determining the cell constant of conductivity cells at high temperatures uses the data for molten KCl and KNO₃.^{34,42} No standard is available for the determination of cell constants at the temperature required for this research, 100-200°C. The method chosen was to determine the cell constant at 25°C., and to apply correction factors by the method of Washburn.⁹⁹ Potassium chloride solutions were madeⁱⁿ accordance with the specifications of Jones and Bradshaw,⁷⁰ and a series of resistance measurements at 25°C. taken. The cell constant was calculated from the resistance of each solution, and was found to be 416 ± 0.3 at 130°C. The correction factor is very small in each case. The thermostat designed by E. Bock¹⁰⁰ was used for these measurements, the temperature recorded being $25 \pm .0002^\circ\text{C}$.

Temperature variation during a conductance determination must always be at a minimum. The thermostat used for the measurements at 130°C. was that designed for the previous conductance investigation of lithium chlorate.³³ An inner rectangular copper tank, 30x60x60 cms., was covered by a primary insulation of rockwool, and placed inside a wooden case. This was then placed inside a second wooden case which allowed a further 25 cms. of vermiculite to surround the inner box. The thermostat fluid used was Marcol G.X. oil supplied by Imperial Oil Limited. A 450 watt immersion heater was used to heat the bath to

within 5°C . of the experimental temperature, the final heating being controlled from a 200 watt bulb connected through a large mercury regulator and a magnetic relay. Satisfactory stirring was provided by a large archimedean stirrer and a high speed centre drive electric stirrer. The temperature variation throughout the bath at 131.8°C . was no greater than 0.05°C . A Beckman thermometer calibrated against a platinum resistance thermometer was used for the temperature measurement at 131.8°C . For all other temperature measurements a single junction copper-constantan thermocouple calibrated at the boiling point of water and the freezing point of tin was used. When connected to a Tinsley vernier potentiometer temperature changes of less than $\pm 0.1^{\circ}\text{C}$. could be noted, and the temperatures measured were correct to $\pm 0.1^{\circ}\text{C}$.

The cell was filled with powdered anhydrous lithium chlorate inside the drybox, and then transferred to the thermostat at 131.8°C . From the cell weight before and after filling, the weight of lithium chlorate taken was known. After the salt had melted, the residual gas bubbles left along the capillary were removed by causing the melt to flow into either of the bulbous compartments. A special clamp was made such that this operation was possible without removing the cell from the thermostat. After 2 - 3 hours, when thermal equilibrium had been established, the resistance of the cell was measured using input frequencies of 1000, 2000, 5000, and 10,000 cycles. sec^{-1} . From a

graph of the measured resistance versus $\frac{1}{\sqrt{\text{frequency}}}$ the resistance at infinite frequency was found for pure lithium chlorate. The difference between the resistance at 1000 cycles sec^{-1} and at infinite frequency was -0.06 per cent indicating an absence of polarization effects. This correction of -0.06 per cent was applied to the resistance measured at 1000 cycles sec^{-1} for all other experiments.

The specific conductivity of a sample of lithium chlorate which had been analyzed for its water content and found anhydrous was determined at 131.8°C . The anhydrous nature of subsequent lithium chlorate samples was shown by a comparison of their respective specific conductivities with that of the anhydrous salt.

For experiments involving liquid additives, a calibrated syringe was filled with the necessary quantity, which was added to the melt through the cap. Solid lithium nitrate was added to the melt inside the drybox without removing the melt from the cell. A different technique was used to form the lithium hydroxide melts. In this case a separate mixture was made inside the drybox, filtered through a coarse filter disc, and this mixture then added to the re-cleaned conductivity cell. This was necessary since the lithium hydroxide melts prepared by the other technique left a slight suspension in the melt.

III. RESULTS

The specific conductance at 131.8°C. of lithium chlorate and its mixtures containing small quantities of propyl alcohol, lithium nitrate and water are shown in Tables 7.1, 7.2, 7.3. Figure 7.2 illustrates the changes in specific conductance with increasing mole fraction of additive. Also included in Figure 7.2 are the changes in specific conductance observed upon addition of methyl alcohol and nitrobenzene, results which were obtained in earlier investigations.³³

Using density values obtained by interpolation of the results of Chapter IV for the water mixtures and the density results of Mr. M. K. Nagarajan for the lithium nitrate mixtures,²⁷ the equivalent conductance of these mixtures were calculated from the expression

$$\Lambda = M \kappa \rho^{-1}$$

The equivalent conductance of an aqueous solution is the conductance of the volume of solution which contains one gram equivalent of the solute, and M is hence the weight of this volume of solution.

Λ_1 represents the equivalent conductance of the lithium chlorate-water mixtures calculated for one gram equivalent of lithium chlorate, i.e. as if they represent the extreme of concentration of an aqueous solution. The equivalent conductance, Λ_1 , has been calculated in the same manner for the lithium nitrate mixtures. Bloom and Heymann³⁹ determined the equivalent conductance of several molten salt mixtures, and considered M to be the mean equivalent weight (equation 7.8); Λ_2 represents the equivalent conductance of the lithium nitrate

and water mixtures calculated using this concept of Bloom and Heymann. Λ_1 and Λ_2 are given in Tables 7.2, 7.3 for the lithium chlorate-water and lithium chlorate-lithium nitrate mixtures. The changes of Λ_1 and Λ_2 at 131.8°C. with mole fraction of additive are illustrated in Figure 7.3. The analytical representation of the dependence of specific and equivalent conductance on mole fraction of lithium nitrate and water shown in Table 7.4 were obtained by a least squares fit of the results in Tables 7.2, 7.3.

The temperature dependence of the specific conductance of pure lithium chlorate and its mixtures with water, lithium nitrate and methyl alcohol have been determined and are given in Tables 7.5 to 7.15. Figure 7.4 illustrates graphically these results. The equivalent conductances Λ_1 and Λ_2 have been calculated for lithium chlorate and its water and lithium nitrate mixtures and are given in Tables 7.5, 7.7 to 7.15, and shown in Figures 7.5, 7.6, for the experimental temperatures.

Using these experimental results for K , Λ_1 , and Λ_2 at the equivalent temperatures, the Arrhenius conductance equations have been determined using a computer. They are given in Tables 7.16, 7.17, together with the standard deviation from the given equations, and the respective activation energies of conductance. The linear relationship between log conductance and $\frac{1}{T}$ for these mixtures is shown graphically in Figures 7.7, 7.8, 7.9.

The specific conductance of a lithium chlorate-lithium hydroxide mixture, and of two lithium chlorate-lithium hydroxide-water mixtures were determined over the temperature range 130-170°C. The results are given in Tables 7.18, 19, 20. The equivalent conductances Λ_1 and Λ_2 were also calculated for these mixtures, Tables 7.18, 19 and 20, using the density of lithium hydroxide reported by Klemm,¹⁰¹ and interpolating the results of Chapter IV to obtain the density of the water mixtures. Figures 7.10, 7.11 illustrate the change of specific and equivalent conductances of these mixtures with temperature, and Figures 7.12, 7.13 and 7.14 the Arrhenius relationship of log conductance against $\frac{1}{T}$. The analytical representation of the Arrhenius equations, the standard deviation and the activation energy of conductance for these lithium hydroxide mixtures are given in Table 7.20.

TABLE 7.1
 CONDUCTANCES AT 131.8°C. OF LITHIUM CHLORATE-
 PROPYL ALCOHOL MIXTURES

Series I	Mole Fraction Propyl Alcohol n_2	Specific Conduc- tance	Series II	Mole Fraction Propyl Alcohol	Specific Conduc- tance
	-	0.1150		-	0.1149
	0.004	0.1145		0.005	0.1140
	0.009	0.1132		0.011	0.1127
	0.013	0.1127		0.015	0.1125
	0.022	0.1113		0.020	0.1115
	0.026	0.1108			

TABLE 7.2
 CONDUCTANCES AT 131.8°C. OF LITHIUM CHLORATE-
 LITHIUM NITRATE MIXTURES

Mole Fraction $\text{LiNO}_3(n_2)$	Density gms cc^{-1}	Specific Conductance K	Equivalent Conductance	
			Λ_1	Λ_2
0	2.0881	0.1150	4.979	4.979
0.067	2.0841	0.1163	5.321	4.961
0.098	2.0824	0.1167	5.444	4.959
0.124	2.0803	0.1176	5.661	4.960
0.156	2.0767	0.1182	5.874	4.969
0.181	2.0727	0.1188	6.056	4.958
0.207	2.0690	0.1206	6.318	5.010

TABLE 7.3
 CONDUCTANCES AT 131.8°C. OF LITHIUM CHLORATE-WATER MIXTURES

Mole Fraction Water n_2	Density ρ	Specific Conductance K	Equivalent Conductance	
			Λ_1	Λ_2
0	2.0881	0.1150	4.979	4.979
0.013	2.0831	0.1171	5.079	5.029
0.025	2.0784	0.1202	5.253	5.121
0.038	2.0731	0.1227	5.393	5.188
0.043	2.0708	0.1243	5.474	5.237
0.061	2.0628	0.1268	5.629	5.282
0.072	2.0579	0.1302	5.804	5.386
0.084	2.0523	0.1326	5.945	5.445
0.116	2.0360	0.1368	6.231	5.504
0.126	2.0306	0.1397	6.393	5.590
0.175	2.0022	0.1492	7.019	5.785
0.216	1.9761	0.1594	7.693	6.029
0.240	1.9599	0.1631	7.997	6.077
0.256	1.9490	0.1662	8.236	6.131

TABLE 7.4

ANALYTICAL REPRESENTATION OF THE CHANGE OF CONDUCTANCE
WITH MOLE FRACTION OF ADDITIVE AT 131.8°C.

Additive	Analytical Representation conductance= $A + Bn_2 + Cn_2^2$ (n_2 = mole fraction additive)	Standard Deviation
Water	$K = 0.1152 + .194n_2 + .0238n_2^2$	6.9×10^{-4}
	$\Lambda_1 = 4.99 + 9.92n_2 + 10.87n_2^2$	3.4×10^{-2}
	$\Lambda_2 = 4.99 + 5.22n_2 + 28.2n_2^2$	2.8×10^{-2}
Lithium Nitrate	$K = .1151 + .0095n_2 + .0737n_2^2$	2.7×10^{-4}
	$\Lambda_1 = 4.98 + 3.73n_2 + 12.70n_2^2$	2.1×10^{-2}
	$\Lambda_2 = 4.98 - 0.57n_2 + 3.09n_2^2$	1.1×10^{-2}

TABLE 7.5

VARIATION OF SPECIFIC AND EQUIVALENT
CONDUCTANCE OF PURE LITHIUM CHLORATE
WITH TEMPERATURE

$t^{\circ}\text{C.}$	$\frac{1}{T^{\circ}\text{K}} \times 10^3$	Density	Specific Conductance	Equivalent Conductance	$-\log \kappa$	$\log \Lambda$
131.4	2.472	2.0883	0.1147	4.965	0.9404	0.6959
131.5	2.472	2.0883	0.1148	4.969	0.9404	0.6963
137.5	2.436	2.0834	0.1286	5.580	0.8908	0.7466
145.2	2.391	2.0772	0.1467	6.384	0.8336	0.8051
154.8	2.345	2.0692	0.1719	7.510	0.7676	0.8756
155.1	2.337	2.0690	0.1770	7.734	0.7510	0.8884
157.5	2.322	2.0672	0.1809	7.911	0.7425	0.8983
163.8	2.289	2.0621	0.1973	8.649	0.7049	0.9370
169.7	2.259	2.0574	0.2163	9.503	0.6650	0.9778
173.5	2.249	2.0544	0.2252	9.909	0.6474	0.9960

TABLE 7.6

TEMPERATURE DEPENDENCE OF SPECIFIC CONDUCTANCE
OF A LITHIUM CHLORATE-METHYL ALCOHOL MIXTURE

Mole fraction methyl alcohol = .03

$t^{\circ}\text{C.}$	$\frac{1}{T^{\circ}\text{K}} \times 10^3$	Specific Conductance κ	$-\log \kappa$
131.6	2.471	0.1139	0.9435
131.7	2.471	0.1141	0.9427
132.0	2.469	0.1147	0.9405
134.5	2.454	0.1197	0.9219
138.5	2.430	0.1284	0.8914

TABLE 7.7

VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A LITHIUM CHLORATE-
WATER MIXTURE WITH TEMPERATURE

t °C.	$\frac{1}{T^\circ K} \times 10^3$	Density ρ	Specific Conductance K	Mole fraction water .098		- log K	log Λ_1	log Λ_2
				Λ_1	Λ_2			
131.8	2.470	2.0457	0.1361	6.143	5.543	0.8661	0.7884	0.7437
143.1	2.403	2.0366	0.1653	7.413	6.689	0.7817	0.8770	0.8254
152.1	2.352	2.0299	0.1913	8.703	7.852	0.7183	0.9396	0.8950
158.7	2.316	2.0248	0.2069	9.436	8.514	0.6843	0.9748	0.9301
158.8	2.316	2.0248	0.2074	9.459	8.535	0.6832	0.9758	0.9312
162.7	2.295	2.0215	0.2181	9.963	8.989	0.6613	0.9984	0.9537
162.7	2.295	2.0215	0.2186	9.986	9.011	0.6603	0.9994	0.9547
170.1	2.254	2.0156	0.2407	11.030	9.951	0.6186	1.0425	0.9978
170.1	2.254	2.0156	0.2410	11.041	9.962	0.6180	1.0429	0.9984
174.3	2.235	2.0122	0.2470	11.335	10.228	0.6073	1.0542	1.0098

TABLE 7.8

VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A LITHIUM CHLORATE-
WATER MIXTURE WITH TEMPERATURE

Mole fraction water 0.175

t °C.	$\frac{1}{T^{\circ} K}$	Density ρ	Specific Conductance κ	Equivalent Conductance Λ_1	Λ_2	$-\log \kappa$	$\log \Lambda_1$	$\log \Lambda_2$
131.8	2.469	2.0022	0.1562	7.350	6.062	0.8062	0.8663	0.7826
139.1	2.426	1.9970	0.1704	8.042	6.632	0.7686	0.9054	0.8216
141.6	2.411	1.9951	0.1754	8.282	6.833	0.7560	0.9181	0.8346
149.3	2.367	1.9895	0.1949	9.229	7.614	0.7103	0.9651	0.8816
154.2	2.340	1.9859	0.2074	9.839	8.117	0.6832	0.9930	0.9094
158.0	2.319	1.9831	0.2204	10.471	8.638	0.6568	1.0199	0.9364
161.0	2.304	1.9809	0.2289	10.886	8.981	0.6405	1.0371	0.9533
165.3	2.281	1.9776	0.2404	11.452	9.448	0.6191	1.0588	0.9754
168.7	2.263	1.9752	0.2514	11.991	9.893	0.5996	1.0789	0.9953

TABLE 7.9

 VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A LITHIUM CHLORATE-
 WATER MIXTURE WITH TEMPERATURE

t °C.	$\frac{l}{T_0 K} \times 10^3$	Density ρ	Specific Conductance K	Mole fraction water 0.256				
				Equivalent Conductance Λ_1	Λ_2	$-\log K$	$\log \Lambda_1$	$\log \Lambda_2$
131.8	2.470	1.9490	0.1662	8.236	6.131	0.7794	0.9157	0.7867
139.0	2.425	1.9438	0.1855	9.217	6.831	0.7412	0.9646	0.8364
143.9	2.399	1.9402	0.1987	9.891	7.363	0.7018	0.9952	0.8671
150.1	2.363	1.9358	0.2135	10.652	7.929	0.6706	1.0274	0.8992
155.9	2.331	1.9314	0.2263	11.316	8.424	0.6453	1.0537	0.9255
160.5	2.306	1.9282	0.2413	12.086	8.997	0.6175	1.0820	0.9541
165.5	2.281	1.9246	0.2550	12.796	9.526	0.5926	1.1069	0.9789
169.8	2.258	1.9212	0.2675	13.447	10.010	0.5727	1.1285	1.0004
175.7	2.228	1.9170	0.2828	14.247	10.606	0.5485	1.1537	1.0259

TABLE 7.10

 VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A
 LITHIUM CHLORATE-LITHIUM NITRATE MIXTURE WITH TEMPERATURE

Mole fraction lithium nitrate 0.156

$t^{\circ}\text{C.}$	$\frac{1}{T^{\circ}\text{K}} \times 10^3$	Density ρ	Specific Conductance κ	Equivalent Conductance Λ_1	Λ_2	$-\log \kappa$	$\log \Lambda_1$	$\log \Lambda_2$
132.0	2.469	2.0763	0.1186	5.868	4.986	0.9255	0.7685	0.6977
136.4	2.442	2.0728	0.1343	6.656	5.656	0.8719	0.8232	0.7525
138.7	2.429	2.0716	0.1392	6.903	5.866	0.8564	0.8390	0.7683
142.6	2.406	2.0697	0.1494	7.422	6.307	0.8256	0.8705	0.7998
148.9	2.365	2.0629	0.1704	8.486	7.211	0.7686	0.9287	0.8580
154.9	2.337	2.0581	0.1833	9.150	7.774	0.7368	0.9614	0.8906
159.3	2.313	2.0547	0.1981	9.905	8.416	0.7031	0.9958	0.9251
162.4	2.297	2.0531	0.2090	10.458	8.886	0.6799	1.0195	0.9487
167.9	2.268	2.0481	0.2238	11.226	9.539	0.6502	1.0501	0.9795
170.9	2.252	2.0457	0.2332	11.712	9.951	0.6322	1.0686	0.9978

TABLE 7.11

VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A LITHIUM CHLORATE-LITHIUM NITRATE MIXTURE WITH TEMPERATURE

Mole fraction lithium nitrate 0.181

$t^{\circ} \text{C.}$	$\frac{1}{T_0 K} \times 10^3$	Density	Specific Conductance K	Equivalent Conductance Λ_1	Conductance Λ_2	$-\log K$	$\log \Lambda_1$	$\log \Lambda_2$
131.8	2.469	2.0727	0.1188	6.056	4.958	0.9251	0.7822	0.6952
135.9	2.445	2.0692	0.1290	6.588	5.393	0.8894	0.8187	0.7318
139.4	2.425	2.0666	0.1392	7.117	5.827	0.8564	0.8523	0.7654
146.4	2.384	2.0611	0.1585	8.126	6.652	0.7999	0.9099	0.8229
150.7	2.360	2.0577	0.1712	8.804	7.208	0.7665	0.9447	0.8578
154.7	2.338	2.0547	0.1826	9.391	7.688	0.7383	0.9727	0.8859
159.6	2.312	2.0508	0.1960	10.099	8.268	0.7077	1.0040	0.9174
159.9	2.310	2.0506	0.1977	10.187	8.340	0.7039	1.0076	0.9212
163.3	2.292	2.0477	0.2090	10.785	8.829	0.6799	1.0327	0.9459
169.8	2.258	2.0427	0.2295	11.872	9.719	0.6392	1.0745	0.9876
171.4	2.250	2.0413	0.2333	12.072	9.883	0.6322	1.0816	0.9949

TABLE 7.12

VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A LITHIUM CHLORATE-
LITHIUM NITRATE MIXTURE WITH TEMPERATURE

Mole fraction lithium nitrate 0.206

t °C.	$\frac{1}{T} \times 10^3$	Density ρ	Specific Conductance K	Equivalent Conductance Λ_1	Λ_2	- log K	log Λ_1	log Λ_2
131.8	2.470	2.0690	0.1205	6.313	5.006	0.9190	0.8002	0.6995
134.3	2.455	2.0667	0.1274	6.682	5.298	0.8948	0.8249	0.7242
137.6	2.435	2.0637	0.1360	7.143	5.664	0.8665	0.8539	0.7531
142.0	2.410	2.0606	0.1479	7.780	6.169	0.8300	0.8910	0.7902
146.0	2.387	2.0575	0.1591	8.382	6.646	0.7983	0.9233	0.8226
151.3	2.357	2.0532	0.1757	9.276	7.355	0.7553	0.9674	0.8666
156.3	2.329	2.0493	0.1908	10.092	8.002	0.7194	1.0037	0.9032
160.0	2.309	2.0464	0.2026	10.731	8.509	0.6933	1.0306	0.9299
166.6	2.275	2.0418	0.2228	11.828	9.379	0.6530	1.0729	0.9721
171.4	2.250	2.0376	0.2324	12.363	9.803	0.6338	1.0920	0.9913

TABLE 7.13

VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A LITHIUM CHLORATE-
LITHIUM NITRATE MIXTURE WITH TEMPERATURE

Mole fraction lithium nitrate 0.255

t°C.	$\frac{1}{T_0 K} \times 10^3$	Density ρ	Specific Conductance K	Equivalent Conductance $\Lambda_{.1}$	$\Lambda_{.2}$	- log K	log $\Lambda_{.1}$	log $\Lambda_{.2}$
137.7	2.435	2.0564	0.1378	7.693	5.727	0.8607	0.8861	0.7579
140.6	2.418	2.0542	0.1465	8.134	6.058	0.8341	0.9103	0.7824
143.2	2.403	2.0522	0.1539	8.553	6.368	0.8128	0.9322	0.8040
146.4	2.384	2.0496	0.1630	9.070	6.753	0.7878	0.9576	0.8295
149.4	2.367	2.0474	0.1721	9.587	7.138	0.7643	0.9817	0.8535
151.0	2.358	2.0458	0.1764	9.834	7.322	0.7535	0.9928	0.8646
153.1	2.347	2.0447	0.1829	10.202	7.595	0.7378	1.0086	0.8805
157.1	2.325	2.0415	0.1949	10.888	8.106	0.7102	1.0369	0.9088
159.4	2.313	2.0398	0.2021	11.299	8.413	0.6944	1.0531	0.9250
161.2	2.303	2.0386	0.2130	11.917	8.872	0.6696	1.0763	0.9480
165.2	2.282	2.0325	0.2203	12.361	9.203	0.6570	1.0920	0.9639
167.6	2.269	2.0336	0.2291	12.849	9.566	0.6400	1.1089	0.9808
169.5	2.260	2.0322	0.2358	13.233	9.852	0.6234	1.1216	0.9935
170.9	2.253	2.0308	0.2402	13.489	10.08	0.6194	1.1300	1.0033

TABLE 7.14

 VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A LITHIUM CHLORATE--
 LITHIUM NITRATE MIXTURE WITH TEMPERATURE

Mole fraction lithium nitrate 0.300

$t^{\circ} \text{C.}$	$\frac{l}{T^{\circ} K} \times 10^3$	Density ρ	Specific Conductance K	Equivalent Conductance Λ_1	Λ_2	$-\log K$	$\log \Lambda_1$	$\log \Lambda_2$
150.1	2.363	2.0405	0.1648	9.695	6.780	0.7416	0.9865	0.8312
151.1	2.358	2.0396	0.1805	10.623	7.430	0.7022	1.0261	0.8710
152.4	2.351	2.0386	0.1846	10.870	7.602	0.6923	1.0363	0.8809
155.7	2.333	2.0362	0.1959	11.548	8.077	0.6666	1.0622	0.9073
158.4	2.318	2.0343	0.2037	12.019	8.406	0.6498	1.0799	0.9246
163.4	2.291	2.0307	0.2201	13.010	9.099	0.6160	1.1142	0.9590
164.3	2.287	2.0301	0.2227	13.168	9.209	0.6108	1.1193	0.9642
166.6	2.275	2.0284	0.2298	13.599	9.511	0.5972	1.1335	0.9782
170.9	2.253	2.0252	0.2451	14.527	10.160	0.5692	1.1621	1.0068
173.0	2.242	2.0237	0.2545	15.096	10.558	0.5530	1.1786	1.0235

TABLE 7.15

VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE OF A LITHIUM CHLORATE--
LITHIUM NITRATE MIXTURE WITH TEMPERATURE

t° C.	$\frac{1}{T^{\circ}K} \times 10^3$	Density ρ	Specific Conductance K	Mole fraction lithium nitrate 0.319		Equivalent Conductance Λ_1	Equivalent Conductance Λ_2	- log K	log Λ_1	log Λ_2
				Specific Conductance K	Equivalent Conductance Λ_1					
158.0	2.320	2.0318	0.2080	12.567	8.552	0.6819	1.0991	0.9321		
160.3	2.308	2.0302	0.2169	13.114	8.925	0.6637	1.1177	0.9507		
163.1	2.293	2.0282	0.2256	13.654	9.293	0.6466	1.1351	0.9681		
165.3	2.282	2.0265	0.2332	14.126	9.614	0.6324	1.1499	0.9828		
166.2	2.277	2.0257	0.2357	14.283	9.721	0.6276	1.1547	0.9877		
168.7	2.264	2.0240	0.2428	14.726	10.02	0.6148	1.1682	1.0008		
169.2	2.262	2.0236	0.2467	14.966	10.185	0.6089	1.1750	1.0076		
170.9	2.253	2.0223	0.2508	15.224	10.361	0.6007	1.1825	1.0153		
172.9	2.243	2.0210	0.2582	15.684	10.674	0.5881	1.1953	1.0282		

TABLE 7.16

ARRHENIUS REPRESENTATION OF CONDUCTANCES OF
LITHIUM CHLORATE AND ITS WATER MIXTURES

Mole Fraction Water	Arrhenius Equation Conductance = $B \exp \frac{-\Delta E}{RT}$	Standard Deviation	Activation Energy k.cal mole ⁻¹
0	$K = 197.0 \exp - \frac{6022}{RT}$	2.08×10^{-3}	6.02
	$\Lambda_{1, 2} = 10200 \exp - \frac{6168}{RT}$	9.2×10^{-2}	6.17
.098	$K = 76.64 \exp - \frac{5122}{RT}$	2.71×10^{-3}	5.12
	$\Lambda_1 = 4360 \exp - \frac{5318}{RT}$	1.2×10^{-1}	5.32
	$\Lambda_2 = 3934 \exp - \frac{5318}{RT}$	1.1×10^{-1}	5.32
.175	$K = 48.21 \exp - \frac{4546}{RT}$	3.1×10^{-3}	4.54
	$\Lambda_1 = 3086 \exp - \frac{4906}{RT}$	8.3×10^{-2}	4.90
	$\Lambda_2 = 2549 \exp - \frac{4910}{RT}$	9.4×10^{-2}	4.91
.256	$K = 37.0 \exp - \frac{4368}{RT}$	1.5×10^{-3}	4.37
	$\Lambda_1 = 2.73 \exp - \frac{4506}{RT}$	7.8×10^{-2}	4.50
	$\Lambda_2 = 1612 \exp - \frac{4502}{RT}$	5.8×10^{-2}	4.50

TABLE 7.17

ARRHENIUS REPRESENTATION OF CONDUCTANCES OF
LITHIUM CHLORATE-LITHIUM NITRATE MIXTURES

Mole Fraction Lithium Nitrate	Arrhenius Equation Conductance = $A \exp. - \frac{\Delta E}{RT}$	Standard Deviation	Activation Energy
0.156	$K = 231.1 \exp - \frac{6132}{RT}$	2.4×10^{-3}	6.1
	$\Lambda_1 = 13486 \exp - \frac{6246}{RT}$	1.2×10^{-1}	6.2
	$\Lambda_2 = 11437 \exp - \frac{6244}{RT}$	1.0×10^{-1}	6.2
0.181	$K = 249.7 \exp - \frac{6194}{RT}$	1.9×10^{-3}	6.2
	$\Lambda_1 = 15363 \exp - \frac{6338}{RT}$	1.0×10^{-1}	6.3
	$\Lambda_2 = 12445 \exp - \frac{6330}{RT}$	8.3×10^{-2}	6.3
0.206	$K = 231.6 \exp - \frac{6110}{RT}$	3.0×10^{-3}	6.1
	$\Lambda_1 = 14456 \exp - \frac{6252}{RT}$	1.5×10^{-1}	6.2
	$\Lambda_2 = 11462 \exp - \frac{6252}{RT}$	1.2×10^{-1}	6.2
0.255	$K = 219.4 \exp - \frac{6044}{RT}$	1.7×10^{-3}	6.0
	$\Lambda_1 = 16604 \exp - \frac{6302}{RT}$	9.2×10^{-2}	6.3
	$\Lambda_2 = 12682 \exp - \frac{6324}{RT}$	7.5×10^{-2}	6.3

TABLE 7.17 (continued)

Mole Fraction Lithium Nitrate	Arrhenius Equation Conductance = $A \exp -\frac{\Delta E}{RT}$	Standard Deviation	Activation Energy k.cal mole ⁻¹
0.300	$K = 3023 \exp -\frac{6310}{RT}$	4.0×10^{-3}	6.3
	$\Lambda_1 = 20668 \exp -\frac{6438}{RT}$	2.3×10^{-1}	6.4
	$\Lambda_2 = 14121 \exp -\frac{6418}{RT}$	1.6×10^{-1}	6.4

TABLE 7.18

TEMPERATURE VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE
FOR A LITHIUM CHLORATE MIXTURE

Mole fraction lithium hydroxide 0.076

$t^{\circ}\text{C.}$	$\frac{1}{T_0 K} \times 10^3$	Density ρ	Specific Conductance K	Equivalent Conductance Λ_1	Λ_2	$\log \Lambda_1$	$\log \Lambda_2$	$\log K$
131.9	2.470	2.041	0.1040	4.694	4.378	0.6716	0.6413	0.9830
133.4	2.460	2.040	0.1072	4.841	4.515	0.6849	0.6547	0.9698
135.0	2.452	2.039	0.1112	5.024	4.686	0.7010	0.6708	0.9539
135.2	2.450	2.039	0.1162	5.249	4.897	0.7200	0.6883	0.9347
137.4	2.436	2.037	0.1165	5.268	8.914	0.7216	0.6915	0.9336
139.8	2.422	2.035	0.1217	5.509	5.138	0.7411	0.7108	0.9148
144.8	2.393	2.031	0.1333	6.045	5.639	0.7814	0.7512	0.8751
154.0	2.342	2.024	0.1550	7.054	6.580	0.8484	0.8182	0.8097
157.3	2.324	2.021	0.1625	7.406	6.909	0.8696	0.8394	0.7892
159.5	2.312	2.019	0.1687	7.697	7.180	0.8853	0.8561	0.7729
162.0	2.299	2.017	0.1752	8.001	7.464	0.9032	0.8729	0.7565
167.3	2.271	2.013	0.1889	8.644	8.063	0.9367	0.9065	0.7231
171.7	2.249	2.009	0.2012	9.225	8.605	0.9649	0.9348	0.6964

TABLE 7.19

TEMPERATURE VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE
OF A LITHIUM CHLORATE-LITHIUM HYDROXIDE-WATER MIXTURE

Mole fraction lithium hydroxide .068; mole fraction water .072

$t^{\circ} \text{C.}$	$\frac{1}{T^{\circ} \text{K}} \times 10^3$	Density ρ	Specific Conductance κ	Equivalent Conductance Λ_1	Equivalent Conductance Λ_2	$-\log \kappa$	$\log \Lambda_1$	$\log \Lambda_2$
132.0	2.469	2.012	0.1123	5.234	4.507	0.9497	0.7188	0.6539
133.6	2.459	2.011	0.1154	5.381	4.633	0.9378	0.7309	0.6659
135.8	2.446	2.009	0.1199	5.596	4.819	0.9211	0.7479	0.6829
139.4	2.425	2.007	0.1266	5.915	5.093	0.8975	0.7720	0.7070
141.9	2.410	2.005	0.1332	6.229	5.364	0.8755	0.7944	0.7295
145.1	2.392	2.002	0.1402	6.567	5.655	0.8533	0.8174	0.7525
148.2	2.374	2.000	0.1479	6.934	5.971	0.8300	0.8409	0.7761
150.8	2.360	1.999	0.1543	7.238	6.233	0.8119	0.8596	0.7947
156.2	2.330	1.994	0.1677	7.840	6.750	0.7755	0.8943	0.8293
158.5	2.313	1.992	0.1737	8.176	7.041	0.7603	0.9125	0.8477
161.5	2.301	1.990	0.1818	8.567	7.377	0.7404	0.9329	0.8679
165.8	2.279	1.987	0.1932	9.145	7.875	0.7140	0.9611	0.8963
167.0	2.273	1.986	0.1963	9.264	7.981	0.7070	0.9668	0.9021
168.1	2.267	1.984	0.1989	9.434	8.124	0.7013	0.9747	0.9123
169.0	2.262	1.984	0.2016	9.528	8.205	0.6955	0.9789	0.9141

TABLE 7.20

TEMPERATURE VARIATION OF SPECIFIC AND EQUIVALENT CONDUCTANCE
OF A LITHIUM CHLORATE-LITHIUM HYDROXIDE-WATER MIXTURE

Mole fraction lithium hydroxide .069; mole fraction water .071

t° C.	$\frac{1}{T^{\circ}K} \times 10^3$	Density ρ	Specific Conductance K	Equivalent Conductance Λ_1	Equivalent Conductance Λ_2	- log K	log Λ_1	log Λ_2
131.8	2.471	2.012	0.1158	5.397	4.647	0.9363	0.7307	0.6672
132.0	2.469	2.012	0.1165	5.430	4.675	0.9336	0.7348	0.6698
136.3	2.443	2.009	0.1265	5.904	5.084	0.8979	0.7712	0.7062
140.4	2.419	2.007	0.1371	6.406	5.516	0.8360	0.8066	0.7417
144.4	2.396	2.002	0.1455	6.815	5.868	0.8371	0.8334	0.7685
147.6	2.377	2.000	0.1528	7.164	6.169	0.8160	0.8551	0.7902
154.1	2.341	1.995	0.1687	7.930	6.828	0.7728	0.8993	0.8343
159.9	2.310	1.990	0.1815	8.553	7.365	0.7411	0.9322	0.8672
165.0	2.283	1.987	0.1953	9.217	7.937	0.7093	0.9646	0.8997
166.8	2.274	1.986	0.2016	9.519	8.197	0.6955	0.9786	0.9137
171.2	2.251	1.983	0.2126	10.054	8.657	0.6625	1.0021	0.9374

TABLE 7.21

ANALYTICAL REPRESENTATION OF THE CONDUCTANCE OF LITHIUM CHLORATE-LITHIUM HYDROXIDE-WATER MIXTURES

Lithium Chlorate	Mole Fraction Lithium Hydroxide	Water	Arrhenius Equation Conductance = $A_0 \exp - \frac{\Delta E}{RT}$	Standard Deviation	Activation Energy E.k cal. mole ⁻¹
.924	.076		$K = 115.8 \exp - \frac{5866}{RT}$	4.8×10^{-3}	5.9
			$\Lambda_1 = 8182 \exp - \frac{6050}{RT}$	6.8×10^{-2}	6.1
			$\Lambda_2 = 7566 \exp - \frac{6050}{RT}$	6.2×10^{-2}	6.1
.860	.068	.072	$K = 126.5 \exp - \frac{5492}{RT}$	4.7×10^{-4}	5.5
			$\Lambda_1 = 6989 \exp - \frac{5848}{RT}$	3.0×10^{-2}	5.8
			$\Lambda_2 = 6039 \exp - \frac{5850}{RT}$	2.7×10^{-2}	5.8
.860	.069	.071	$K = 104.0 \exp - \frac{5494}{RT}$	1.3×10^{-4}	5.5
			$\Lambda_1 = 5667 \exp - \frac{5640}{RT}$	5.9×10^{-2}	5.6
			$\Lambda_2 = 4801 \exp - \frac{5628}{RT}$	5.2×10^{-2}	5.6

Figure 7.2 .

Specific Conductance at 131.8°C. vs. Mole Fraction Additive

SPECIFIC CONDUCTANCE AT 131.8° C vs MOLE FRACTION ADDITIVE

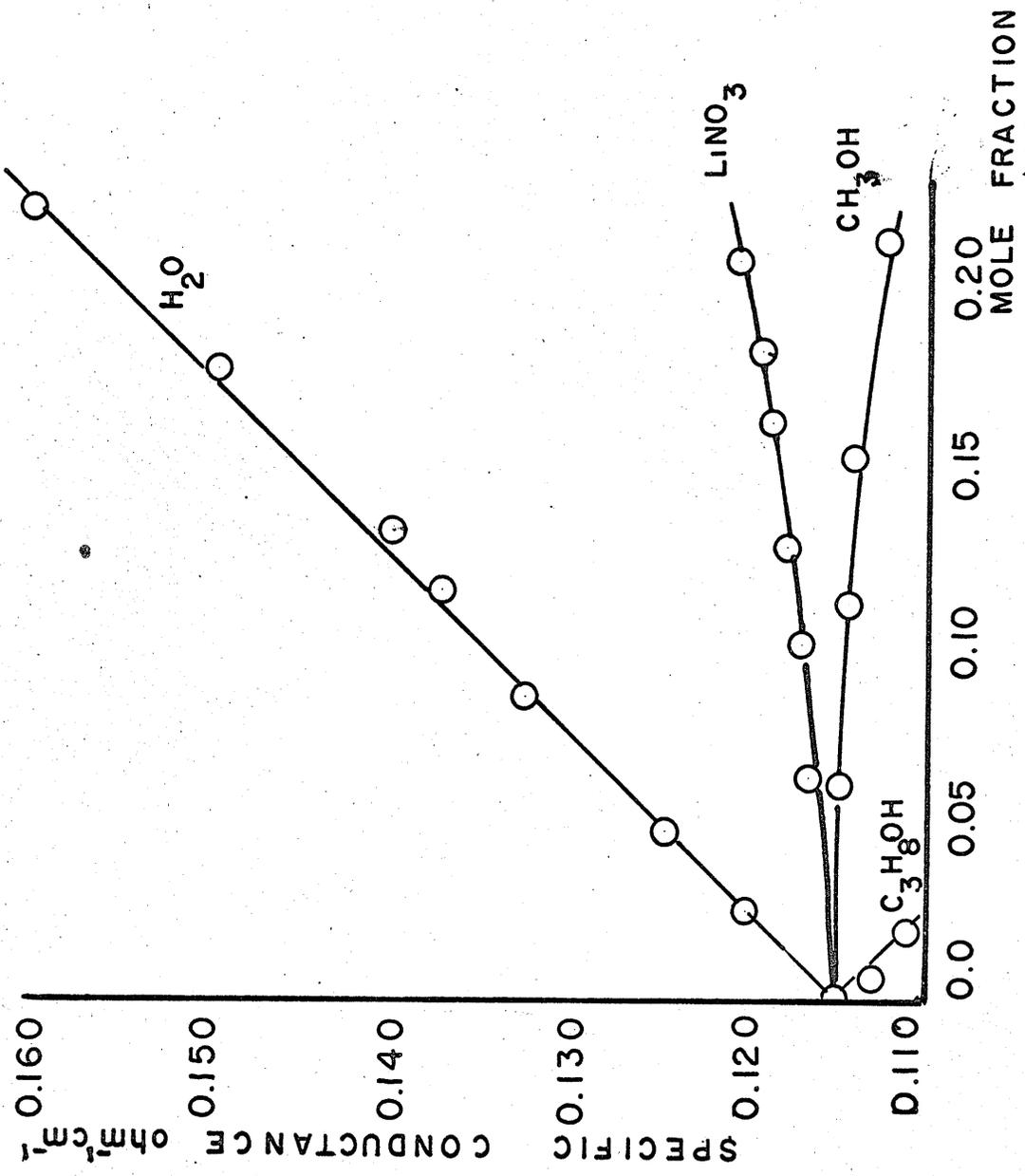


FIGURE 7-2

Figure 7.3

Equivalent Conductance of Lithium Chlorate Mixtures vs. Mole
Fraction

EQUIVALENT CONDUCTANCE vs MOLE FRACTION

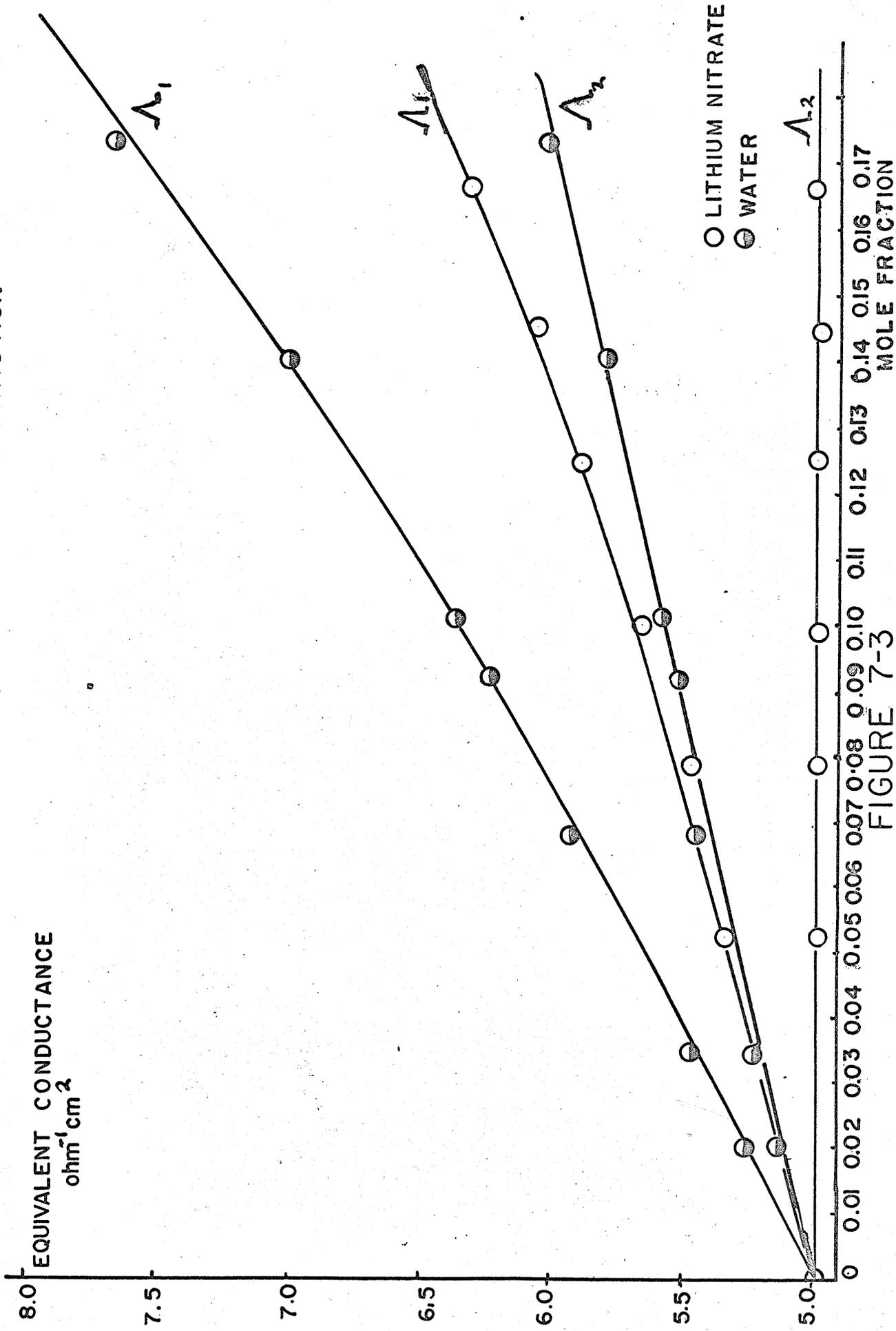


FIGURE 7-3

Figure 7.4

Plot of Specific Conductance of Lithium Chlorate Mixture vs.
Temperature

PLOT OF SPECIFIC CONDUCTANCE vs TEMPERATURE

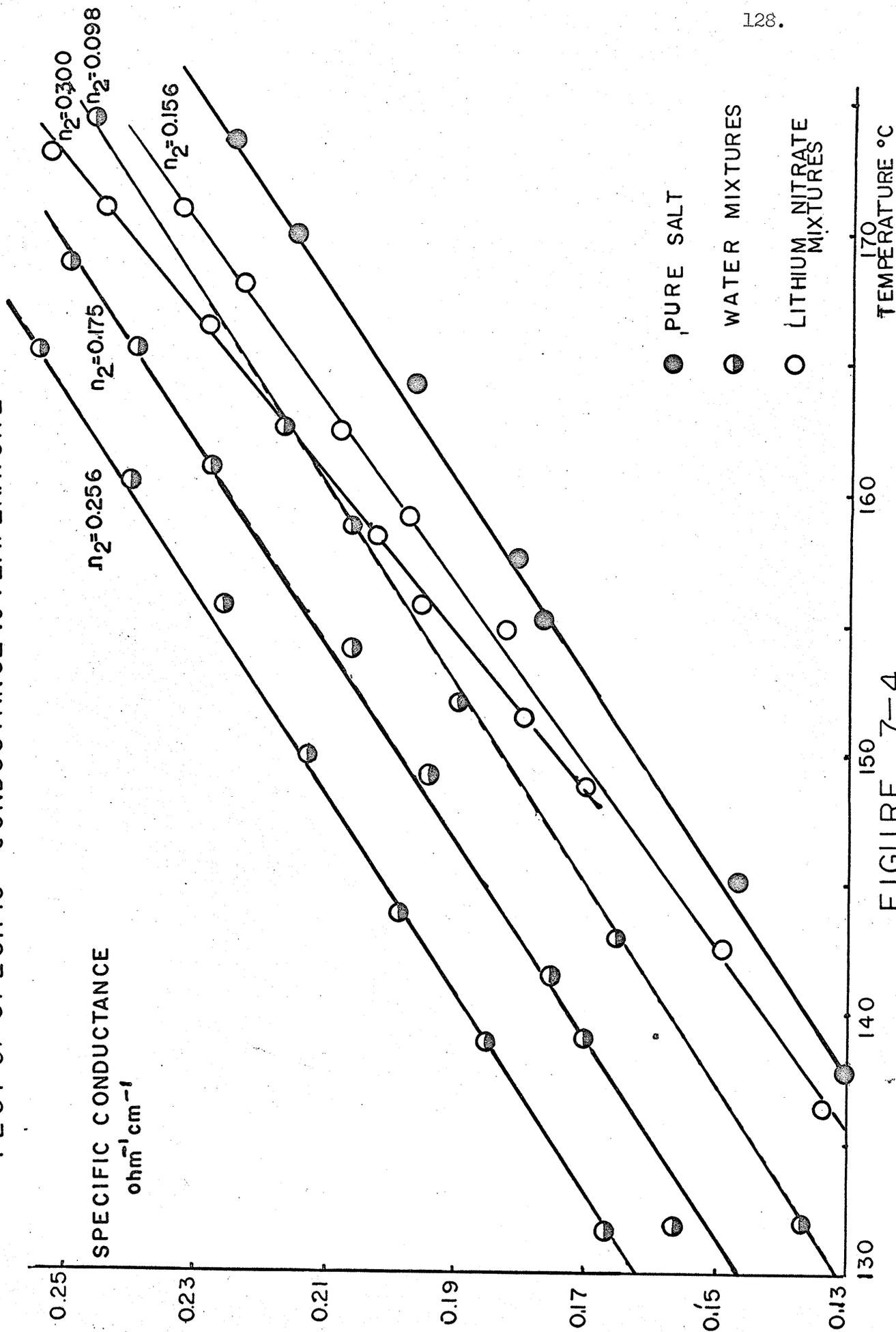


FIGURE 7-4

Figure 7.5

Equivalent Conductance vs. Temperature of Lithium Chlorate-
Water Mixtures

EQUIVALENT CONDUCTANCE vs TEMPERATURE OF LITHIUM CHLORATE - WATER MIXTURES

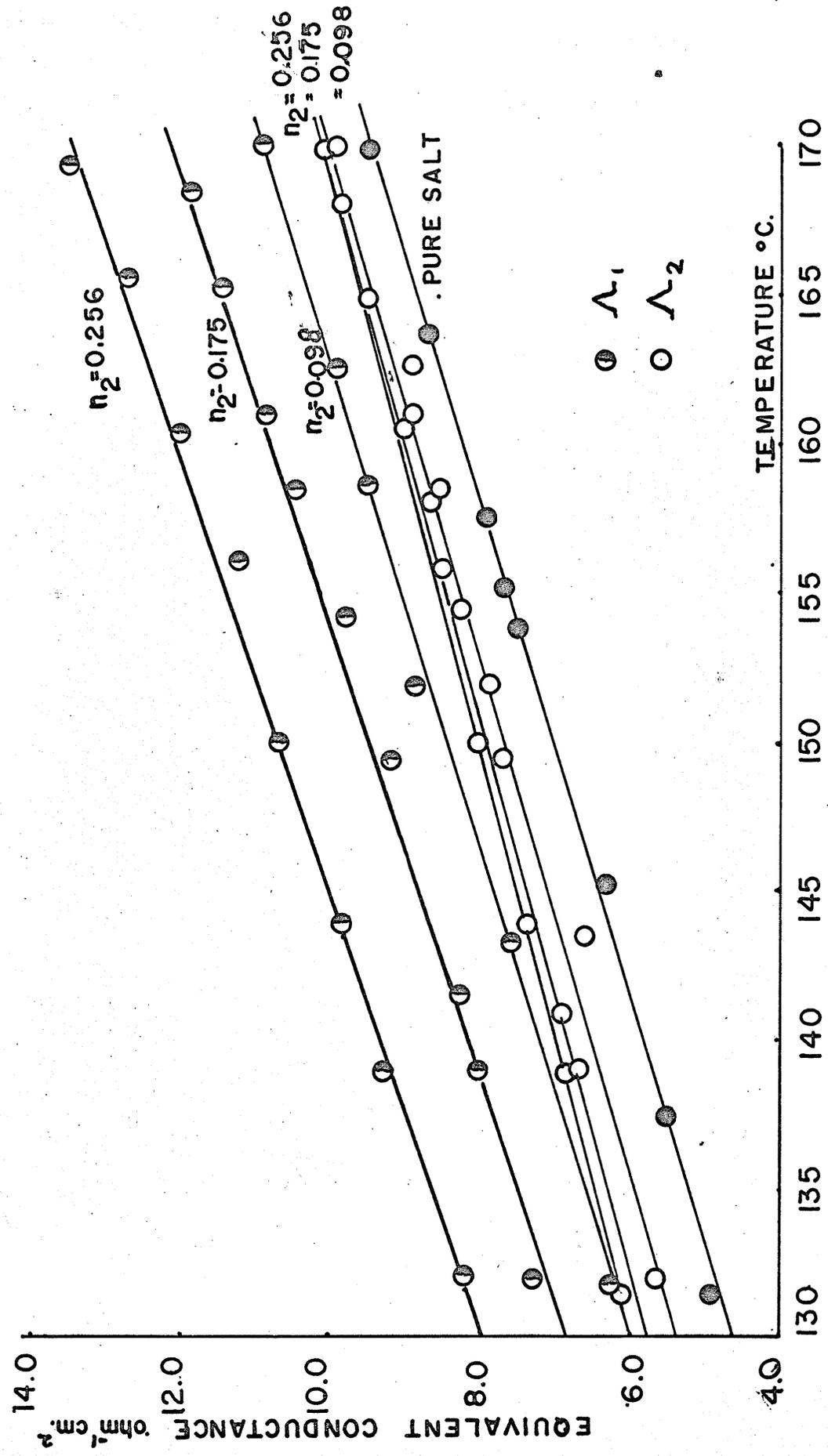
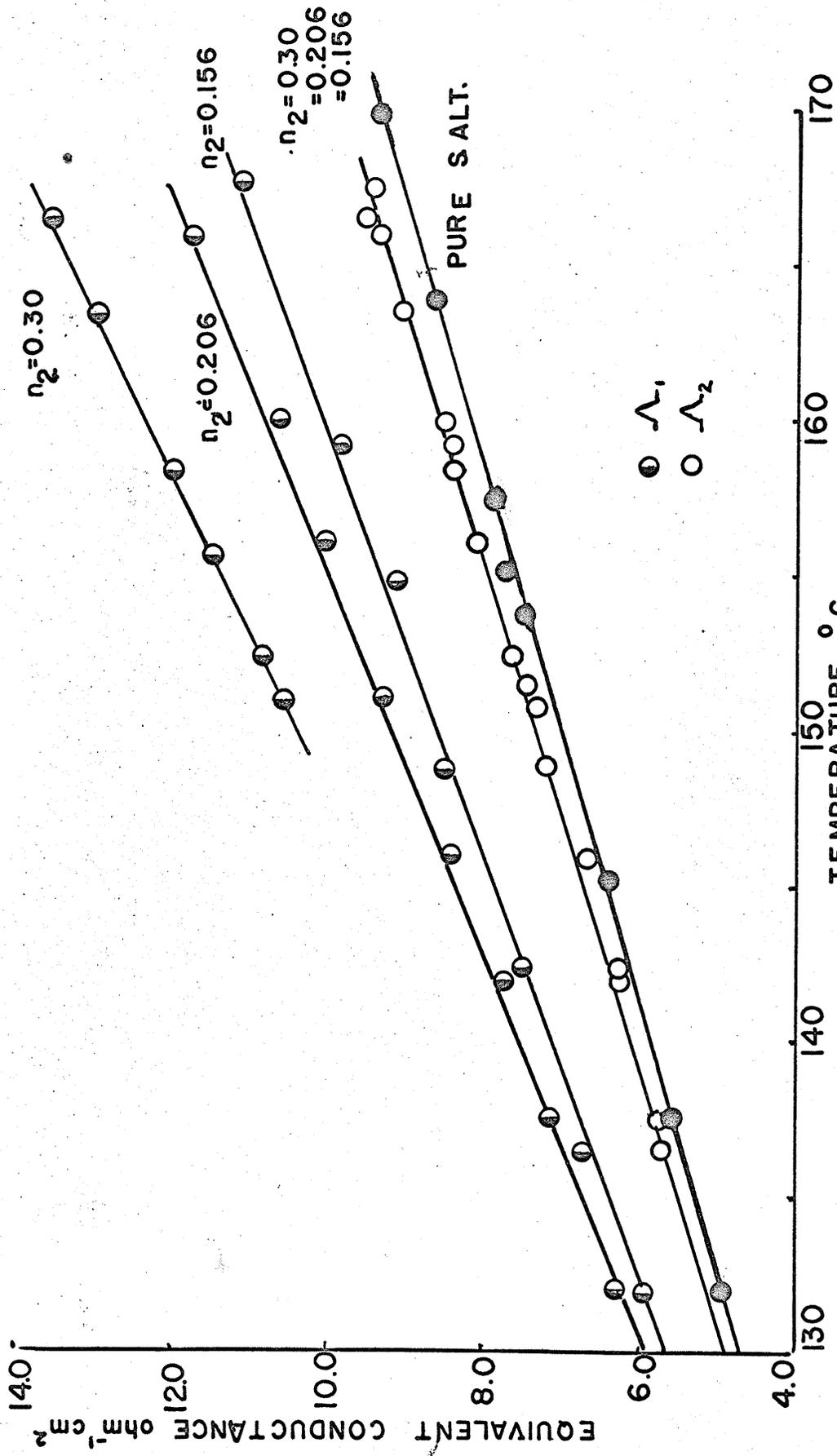


FIGURE 7-5

Figure 7.6

Equivalent Conductance vs. Temperature Lithium Chlorate-
Lithium Nitrate Mixtures

EQUIVALENT CONDUCTANCE vs TEMPERATURE
LITHIUM CHLORATE-LITHIUM NITRATE MIXTURES



TEMPERATURE °C.
FIGURE 7-6

Figure 7.7

Log Specific Conductance of Lithium Chlorate Mixture vs. $\frac{1}{T^{\circ}K}$

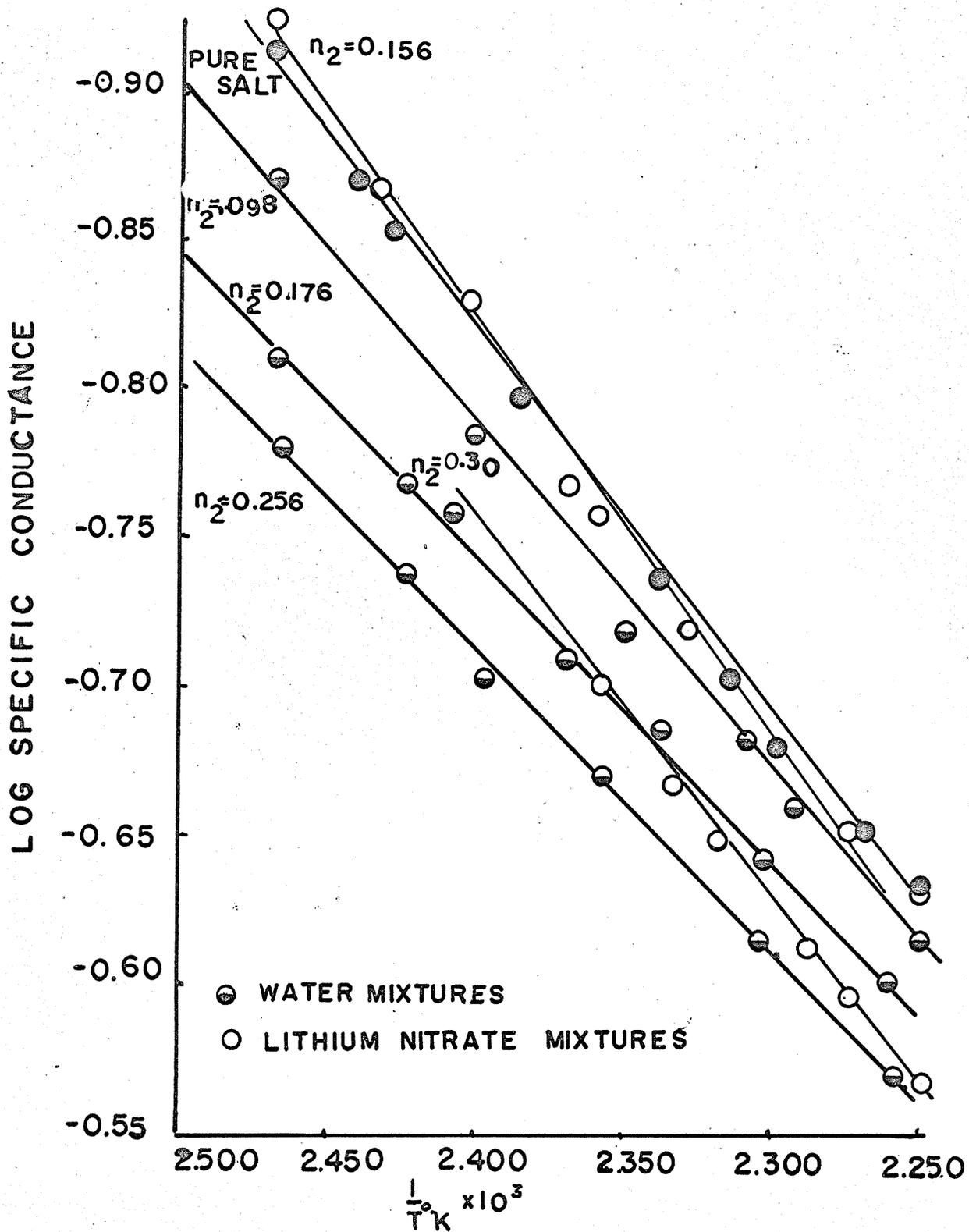
LOG SPECIFIC CONDUCTANCE vs $\frac{1}{T^{\circ}K}$ 

FIGURE 7-7

Figure 7.8

Log Equivalent Conductance Λ , of Lithium Chlorate Mixtures

vs. $\frac{1}{T^{\circ} K}$

LOG EQUIVALENT CONDUCTANCE Λ_i vs $\frac{1}{T^{\circ}K}$

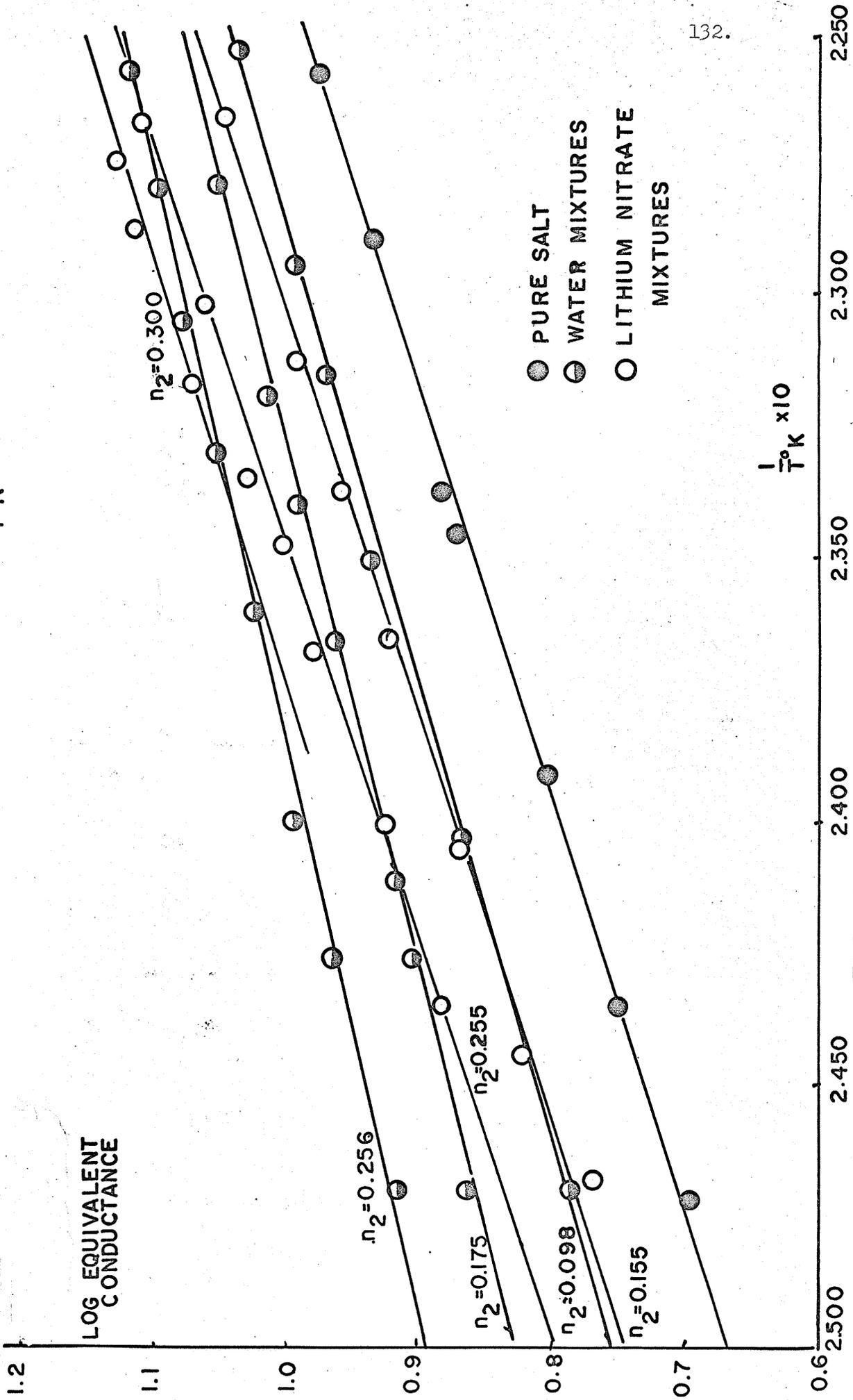


FIGURE 7-8

Figure 7.9

Log Equivalent Conductance Λ_2 of Lithium Chlorate Mixtures

vs. $\frac{1}{T^{\circ}\text{K}}$

LOG EQUIVALENT CONDUCTANCE Λ_2 vs $\frac{1}{T}^{\circ}\text{K}$

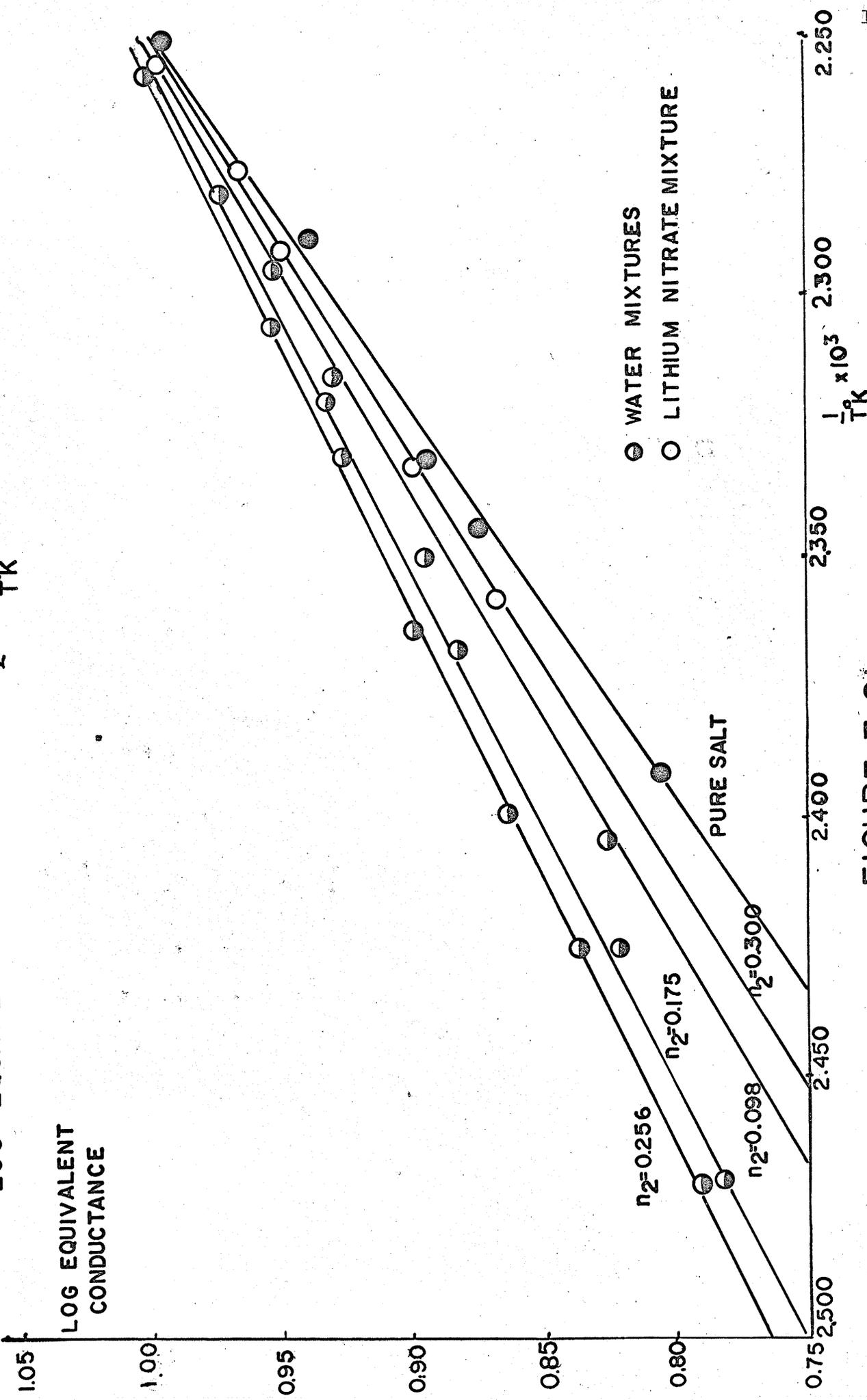


FIGURE 7-9

Figure 7.10

Specific Conductance of Lithium Chlorate-Lithium Hydroxide
Mixtures vs. Temperature

SPECIFIC CONDUCTANCE vs
TEMPERATURE

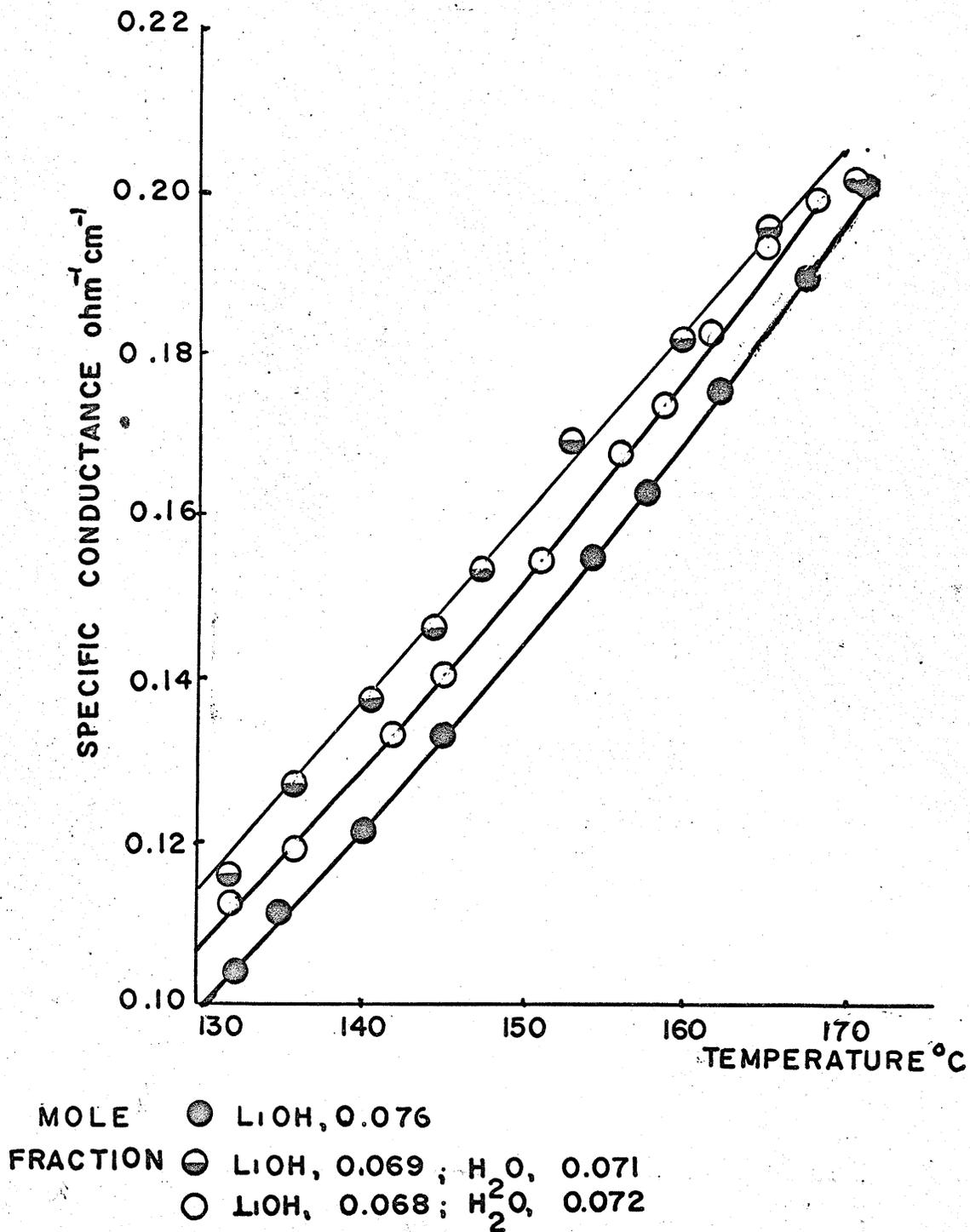


FIGURE 7-10

Figure 7.11

Equivalent Conductance of Lithium Chlorate-Lithium Hydroxide
Mixtures vs. Temperature

EQUIVALENT CONDUCTANCE vs TEMPERATURE

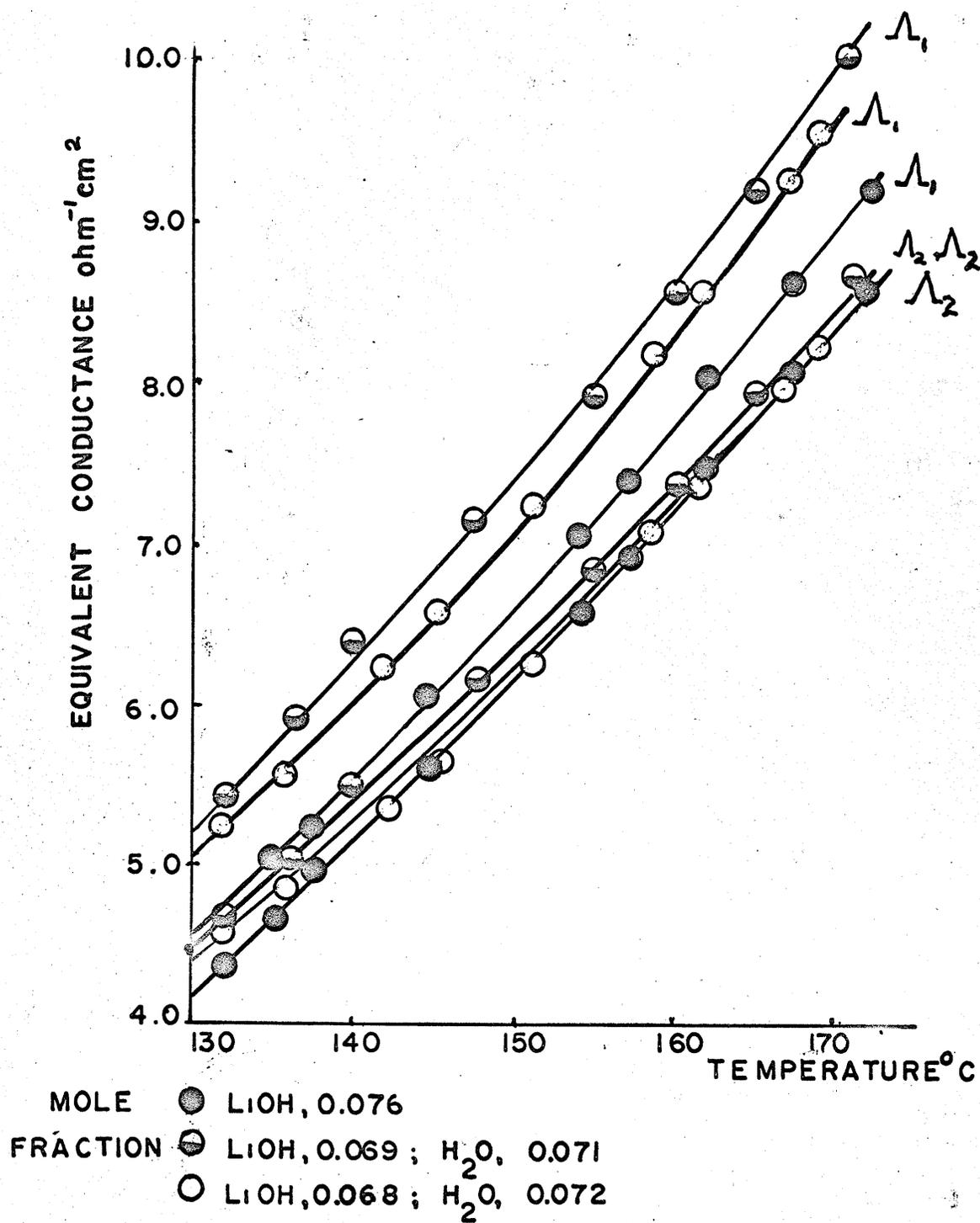


FIGURE 7-11

Figure 7.12

Log Specific Conductance of Lithium Chlorate-Lithium Hydroxide

Mixtures vs. $\frac{1}{T^{\circ}K}$

LOG SPECIFIC CONDUCTANCE vs $\frac{1}{T^{\circ}K}$

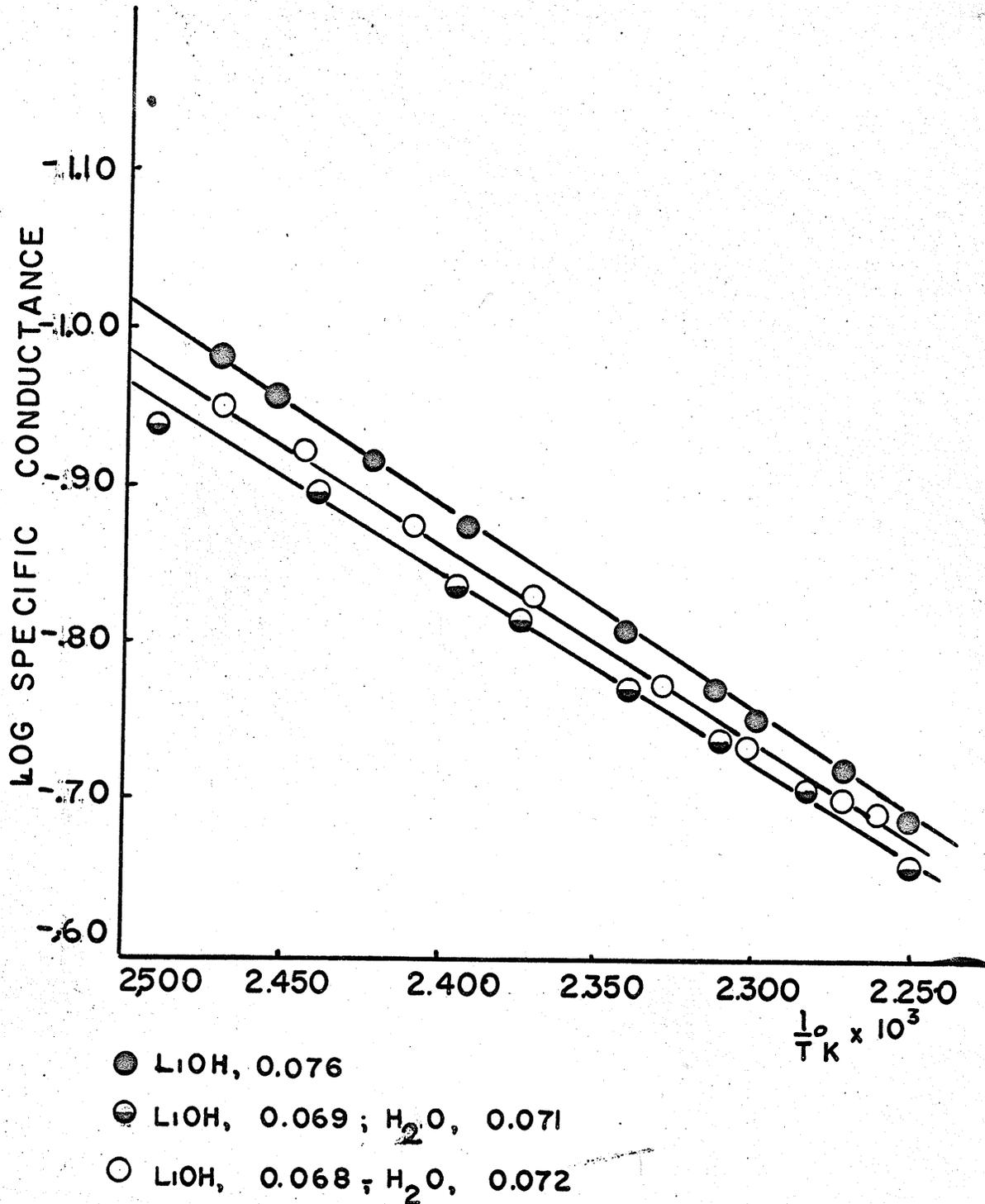


FIGURE 7-12

Figure 7.13

Log Equivalent Conductance Λ , of Lithium Chlorate-Lithium
Hydroxide Mixtures vs. $\frac{1}{T^{\circ}\text{K}}$

Figure 7.14

Log Equivalent Conductance Λ_2 of Lithium Chlorate-Lithium
Hydroxide Mixtures vs. $\frac{1}{T^{\circ}\text{K}}$

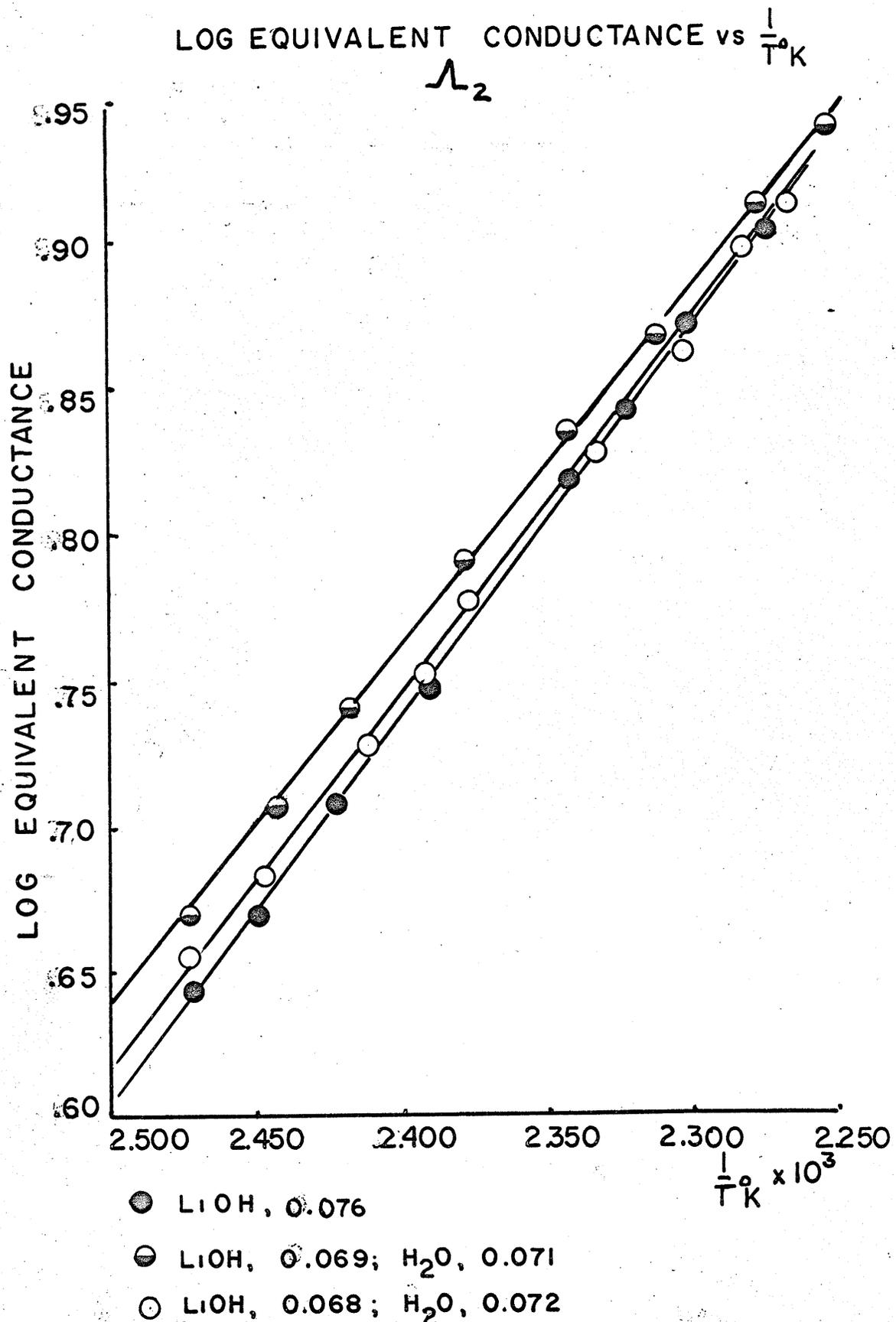


FIGURE 7-14

IV. DISCUSSION

The specific conductance of pure lithium chlorate, $0.1150 \text{ ohm}^{-1} \text{ cm.}^{-1}$ at 131.8°C . compares favourably with that of Patterson,³⁰ 0.1180 ohm^{-1} , but is lower than that proposed by Klotschko.²⁹ The higher specific conductance, $0.1252 \text{ ohm}^{-1} \text{ cm.}^{-1}$ and low density values of pure lithium chlorate obtained by Klotschko are both indicative of the presence of water in the sample.

The specific conductance and other transport parameters of lithium chlorate are compared to those of other molten salts in Table 7.22. For most fused salts in which the dissociation is large the values of these parameters¹⁰² are

$$K = 1 - 5 \text{ ohm}^{-1} \text{ cm.}^{-1}$$

$$\Lambda = 30 - 150 \text{ cm.}^2 \text{ ohm}^{-1} \text{ eqvt}^{-1}$$

$$\Delta E_K = 1 - 5 \text{ k. cal. mole}^{-1}$$

The values of K and Λ for lithium chlorate are slightly lower than those for other salts of polyatomic anions which have low melting points, but are considerably larger than those of salts which form covalent melts, such as HgCl_2 .

The ratio of the activation energies of viscosity and conductance normally has a value between 2 - 4 for ionic melts. This ratio is said to indicate that viscous flow in these salts involves a greater configurational change than does ionic migration caused by an electric field. If this activation energy ratio is found to be smaller than this range, this is indicative of association of some

TABLE 7.22

VISCOSITY AND CONDUCTANCE PARAMETERS FOR FUSED SALTS

Salt	t °C. M.P.	1.10T _f (° C.)	Specific Conductance K	Arrhenius Equations		$\frac{\Delta E \eta}{\Delta E \kappa}$				
				$\eta = \eta_0 \exp \frac{\Delta E \eta}{RT}$	$\kappa = \kappa_0 \exp \frac{-\Delta E \kappa}{RT}$					
			$\eta_0 \times 10^4$	$\Delta E \eta$	Refer- ence	κ_0	Refer- ence			
LiCl	613	701	6.32	-	8.8	39	11.5	1.15	39	7.6
LiNO ₃	255	308	1.16	11.9	4.23	103	55.4	4.49	104	0.9
LiClO ₃	127.9	168	0.197	19	7.81		197	6.02		1.26
KCl	776	881	2.99	3.55	7.8	39	6.5	2.30	39	3.4
KNO ₃	333.1	394	0.829	14.12	3.66	105	11.2	3.49	40	1.056
KCNs	173.2	218	0.50	0.15	8	102	100	5.2	102	1.38
KHSO ₄	207	255	.924	2.3x10 ⁻²	12.0	106	33	6.2	106	1.9418
NaCl	801	908	3.79	1.95	9.4	39	7.3	1.54	39	6.1
HgCl ₂	279	334			3.4	44		3.53	44	.9

kind within the melt. The equality of ΔE_{η} and ΔE_{Λ} noticed for many nitrates exists also for the lithium chlorate melt, and hence as in the nitrate melts the conducting species are not the simple ions themselves.

Using the viscosity data of Chapter V and the equivalent conductances given in Table 7.5, the degree of ionization of lithium chlorate has been calculated using the method of Greenwood and Martin,⁹² (see page 94) and is shown together with the degree of dissociation of other salts in Table 7.23. It appears as if the lithium chlorate melt is completely ionic, like the melts formed by the Group I nitrates. Though the degree of dissociation calculated (0.8) is lower than that calculated for the high melting ionic compounds, in view of the approximations involved this is still in satisfactory agreement for a degree of dissociation equal to one. Thus, though the lithium chlorate melt is completely ionic, the species involved in conductance are not the simple ions.

A recent theoretical equation⁸⁵

$$\Lambda = \left[AT^{-1} \exp \frac{-\Delta H^+}{RT} \right]_{+^-}$$

has been proposed (see page 93) and applied satisfactorily to the conductance process of the alkali halides, whose melts consist of simple symmetrical anions and cations. According to this theory the experimental heat of activation for conductance ΔH_{Λ}^+ is identified with the enthalpy of hole formation and that of the ionic jump so that

$$\Delta H_{\text{jump}} + \Delta H_{\text{hole}} = \Delta H_{\Lambda}^+ + RT$$

TABLE 7.23

DEGREE OF IONIZATION OF SEVERAL TYPICAL SALTS

Salt	t°C. M.P.	$\frac{1.101f}{(\text{° C.})}$	ΔE_{λ} k. cal. mole	$\frac{\Delta E_{\eta}}{\Delta E_{\lambda}}$	$\frac{\Delta E_{\eta}}{\Delta E_{\lambda}}$	Equivalent Conductance	η Viscosity (centipoise)	Degree of Ioniza- tion α	Reference
KBr	730	830	3.4	7.9	2.3	109	-	1.22	39
AgNO ₃	212	260	2.1	4.0	1.9	117	-	1.71	44
CdCl ₂	568	652	3.1	3.1	1.0	38.2	-	1.36	44
AgI	552	614	0.9	5.8	6.4	-	-	1.21	44
HgCl ₂	-	302	6.2	3.4	-	1.95×10^{-3}	1.79	3.5×10^{-5}	44
KNO ₃	334	395	-	3.66	-	5.52	14.4	.79	40,105
LiClO ₃	128	168	6.17	7.8	1.26	9.2	15.2	.80	-

Using the enthalpy of hole formation calculated from Fürth's equation⁸⁸

$$\Delta H_h = 4\pi r^2 \left(\gamma - T \frac{d\gamma}{dT} \right)$$

and considering ΔH_j to be equal in value to $0.1 \Delta H_h$ (see page 91)

then the values obtained for lithium chlorate and lithium nitrate at corresponding temperatures are

Ion	Crystallographic Ionic Radius Å°	Free Energy of Hole Formation k.cal.mole ⁻¹	$\Delta H_j + \Delta H_h$ k.cal.mole ⁻¹	$\Delta H_a + RT$
Li ⁺	0.60	0.55	0.98	6.5
ClO ₃ ⁻	2.00	6.17	9.4	
Li ⁺	0.60	0.72	0.99	5.8
NO ₃ ⁻	2.3	10.6	13.3	

TABLE 7.24

The value for the calculated activation enthalpy of conduction for the lithium ion is much lower than the experimental enthalpy in both cases, whereas the calculated activation enthalpy for the anions are both larger than the experimental activation enthalpy. Duke and Owens¹⁰⁷ have determined the transport number of the lithium ion in the lithium nitrate melt to be $0.84 \pm .06$, which indicates the conductance is primarily uni-ionic, and it is possible that the conductance of lithium chlorate is also uni-ionic. Nevertheless, if the simple ions were the conducting species, the experimental activation enthalpy should be close to that calculated for the Li⁺ ion.

Since this is not so, as seen in Table 7.24, then the radius of the ionic species involved in ionic migration in the lithium chlorate melt is not equal to the crystallographic radius of the lithium ion, but is much larger, despite the fact that the cation is the principal conducting species. This evidence together with the similarity of the activation enthalpies of conductance and viscous flow for molten lithium chlorate indicates that the conducting species is probably associated in some manner.

The internal consistency of the results obtained for the lithium chlorate melt is evident when the experimental results are substituted in the equation proposed by Martin⁸² (see page 89)

$$\Delta E_{\Lambda} = \Delta E_{\kappa} + RT^2\alpha$$

$\Delta E_{\kappa}(6.02) + \alpha RT^2(0.16) = 6.18$ compared with the experimental value for ΔE_{Λ} of $6.12 \text{ k. cal. mole}^{-1}$

The specific conductance of a lithium chlorate melt increases rapidly with the addition of small quantities of water; increases slightly with the addition of small quantities of lithium nitrate; and decreases with the addition of propyl alcohol, methyl alcohol and nitrobenzene. The slight increase of conductance caused by the addition of lithium nitrate will presumably be due to the higher specific conductance of the latter, while the decrease in conductance due to the addition of organic compounds may be explained as a dilution effect. The smaller decrease in conductance due to the addition of methyl alcohol compared with that caused by an equimolar

addition of propyl alcohol may be due to both the larger size of the propyl alcohol, and due to a possible breakdown of the cluster effect in the presence of methyl alcohol, especially in view of the high dielectric constant of the latter. The rapid increase in conductance on the addition of water must in part be caused by the decrease in viscosity of the medium.

In the study of the conductance of aqueous solutions, the equivalent conductance is calculated from the volume of solution containing 1 gm. equivalent of the solute. This presumes that the water itself does not produce conducting ions, whereas the method proposed by Bloom and Heymann³⁹ for molten salt mixtures (see equation 7.8) utilizes the volume of the mixture containing the mean equivalent weight of the components, all of which are thus considered to be involved in ionic conduction. Several workers, e.g. Corbett et al., have postulated that if small amounts of water are present in lithium salt melts, the water may not be in a molecular form, and may in fact be present as ions and thus would play a direct role in the ionic conductance of the melt. Because of the uncertainty as to the nature of the species formed by the water in the melt, the equivalent conductance for the mixtures has been calculated using the methods of Bloom and the classical methods of aqueous conduction. The results of Table 7.2 show that the equivalent conduction of lithium chlorate-lithium nitrate mixtures at 131.8°C. are independent of the concentration of lithium nitrate when calculated by the method

Bloom, Λ_2 , but increases slightly when calculated with respect to the equivalent weight of lithium chlorate Λ_1 . This apparent consistency of equivalent conduction may be due to the lower conduction of the added lithium nitrate being counterbalanced by an increase in the overall conductance of the lithium chlorate present due to the decrease in the viscosity. Neither of these effects, however, are very large. Since the viscosity of the mixtures are still greater than that of a hypothetical lithium nitrate melt at this temperature, it is not possible to calculate the deviation from ideality of the equivalent conductance. The equivalent conductances of the lithium chlorate-water mixtures, Λ_1 , and Λ_2 increase considerably as the water content increases.

The temperature effect on the conductance of the lithium chlorate-water, lithium chlorate-lithium nitrate and lithium chlorate-propyl alcohol is considerable, the specific conductance being doubled over a 40°C. rise in temperature. The activation energy of specific conductance decreases as the water content of the mixture increases, whereas the lithium nitrate mixtures exhibit an activation energy comparable to that of pure lithium chlorate, though a slight increase is noted at mole fraction lithium nitrate 0.3. The addition of methyl alcohol causes a decrease of activation energy, probably due to a decrease in viscosity.

The linear relationship between the activation energy of specific conductance ΔE_k and mole fraction of additive is shown in

Figure 7.15, and is shown in Figure 7.16 in which the activation energy of equivalent conductance, ΔE_{κ_1} , and ΔE_{κ_2} are plotted against mole fraction for the water and lithium nitrate mixtures. The activation energies of conductance, ΔE_{κ} , ΔE_{κ_1} , ΔE_{κ_2} , for the lithium chlorate-lithium nitrate mixtures up to 0.3 mole fraction lithium nitrate remain constant at a value higher than that exhibited by either pure lithium chlorate or lithium nitrate. The reason for this increase of the activation energy over that of both pure salts is not evident from these conductance results, but Mr. M. K. Nagarajan²⁷ has shown that bridging of the chlorate anions by nitrate anions may occur in lithium chlorate-lithium nitrate mixtures. This would increase the association present in the chlorate melt and hence increase the activation energy for conductance, though the effect on the magnitude of the isothermal conductance of these mixtures will alter only slightly if the Li^+ ion is the ionic species carrying the charge.

Wilmshurst¹⁰⁸ has determined the infrared reflection spectra of molten lithium, potassium and sodium hydroxides. The absorption spectra are consistent with some lattice-like structure in the liquid state (showing that some cation-anion forces are present), with the degree of order virtually the same in each hydroxide melt. The hydroxide ion itself was shown to be probably unassociated and freely rotating. It was thought that the addition of lithium hydroxide to a lithium chlorate melt would increase the concentration

Figure 7.15

Activation Energy of Specific Conductance vs. Mole Fraction

Additive

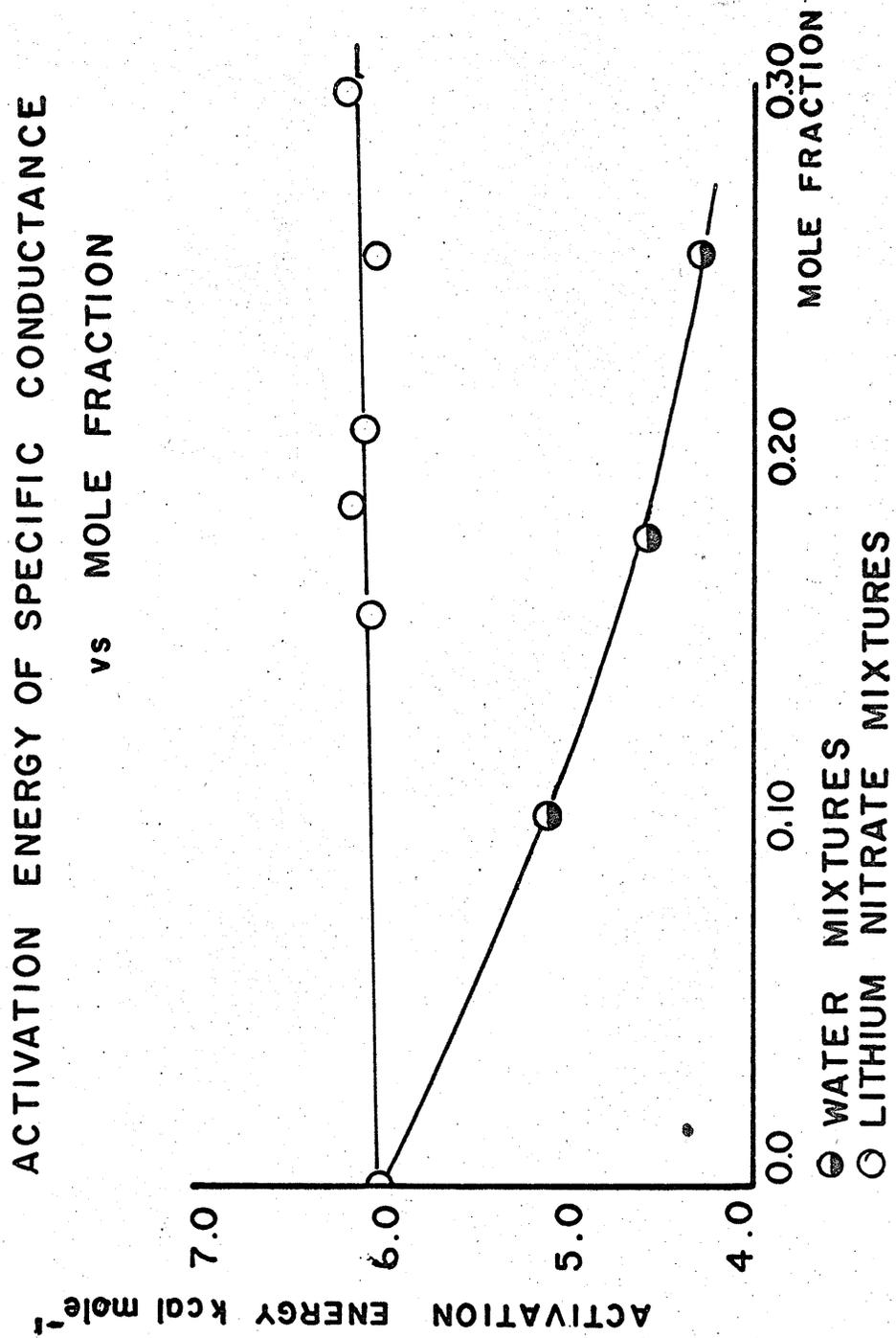
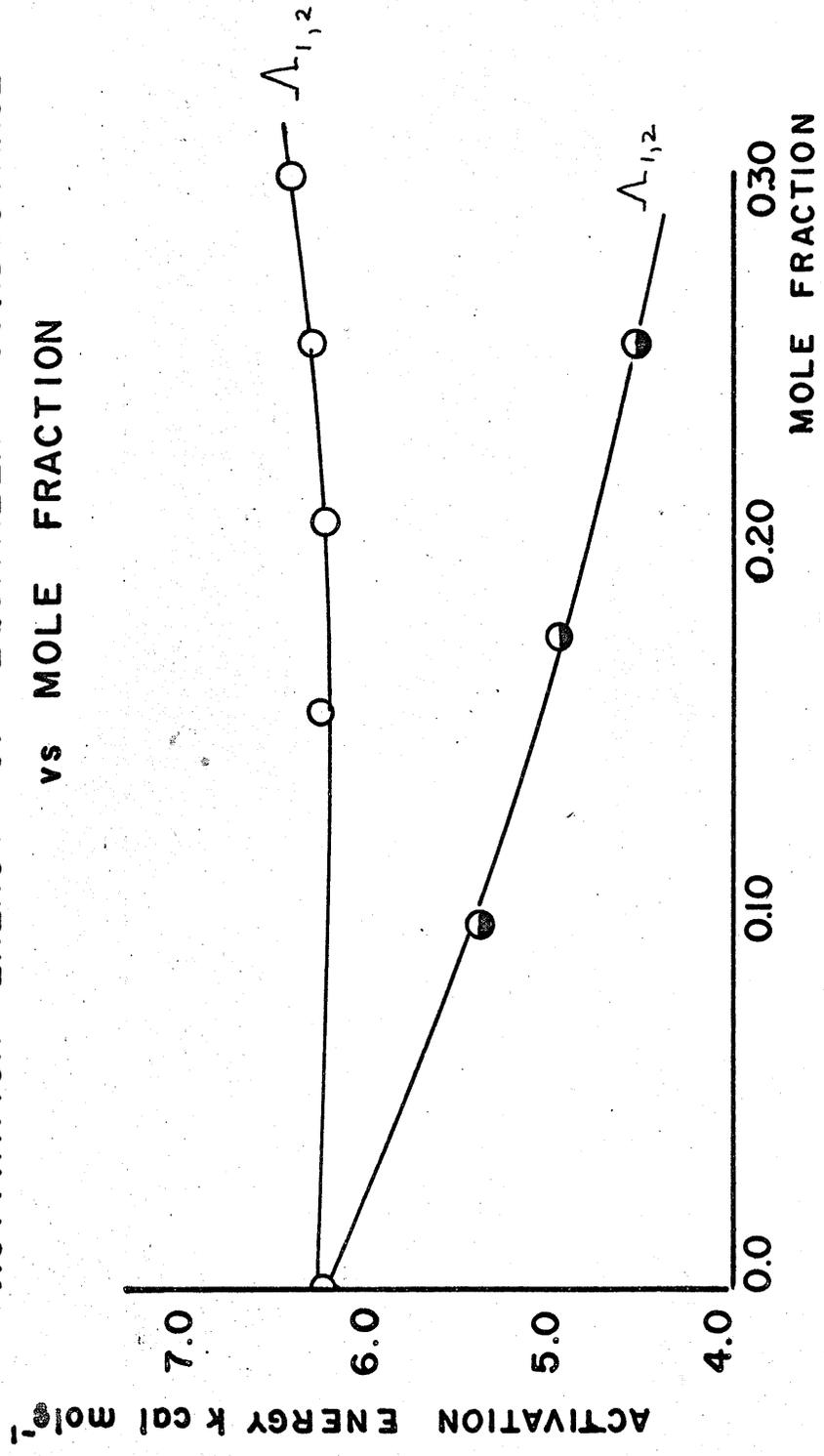


FIGURE 7-15

Figure 7.16

Activation Energy of Equivalent Conductance vs. Mole Fraction
Additive

ACTIVATION ENERGY OF EQUIVALENT CONDUCTANCE
vs MOLE FRACTION



● WATER MIXTURES

○ LITHIUM NITRATE MIXTURES

FIGURE 7-16

of Li^+ available for conductance, and would also add free OH^- ions to the melt, which may themselves participate in ionic migration. The conductance of a lithium chlorate-lithium hydroxide (mole fraction .076) is in fact less than that of the pure lithium chlorate (Table 7.18), though the activation energy of conductance remains the same (Table 7.21). This indicates that lithium hydroxide is more associated than lithium chlorate under these conditions. The similarity of the activation energy of ionic migration in the lithium hydroxide mixture and the pure lithium chlorate melt shows the average energy required for ionic migration is almost the same, and probably the OH^- ion plays a small part in the conductance process which is thus dependent on the Li^+ ion. If the changes in conductance of lithium chlorate-water melts compared to the conductance of a pure lithium chlorate melt were only due to the viscosity reduction, then the equivalent conductance of 1 gram equivalent of lithium chlorate should always be almost the same, whether the viscosity change was caused by either the addition of water or a temperature effect. Table 7.25 shows the equivalent conductance of lithium chlorate, lithium chlorate-water and lithium chlorate-lithium hydroxide melts at equal viscosities:

TABLE 7.25

EQUIVALENT CONDUCTANCE AT EQUAL VISCOSITIES

Viscosity 0.235 poise			Viscosity 0.21 poise	
Melt	t°C.	Equivalent Conductance $\Lambda_1 = \text{ohm}^{-1} \text{cm}^2$ equivt^{-1}	t°C.	Equivalent Conductance $\Lambda_1 = \text{ohm}^{-1} \text{cm}^2$ equivt^{-1}
LiClO ₃	145	6.4	150	6.9
LiClO ₃ + .07 H ₂ O	132	5.9	137	6.5
LiClO ₃ + .07 LiOH	145	5.9	150	6.5

The equivalent conductance of the lithium chlorate melt is the largest, possibly because of the increased mobility of the ions in the melt at the higher temperature. However, this effect is evidently not large, for the equivalent conductance of a lithium chlorate-lithium hydroxide mixture at the same temperature is much smaller than that of the pure melt. The equivalent conductance Λ_1 of this lithium chlorate-lithium hydroxide mixture has been calculated for the conductance of 1 gram equivalent of lithium chlorate, which presumes the lithium hydroxide acts only as a solvent, and plays no part in the conductance. This cannot be true, and hence the equivalent conductance Λ_2 would probably offer a better comparison. The values for Λ_2 for this mixture at these temperatures are 5.5 and 6.1 $\text{ohm}^{-1} \text{cm}^2 \text{equivt}^{-1}$ respectively, even lower than the values of

Λ_1 , and much lower than the equivalent conductance of a lithium chlorate-water mixture of equal viscosity.

Thus the addition of water causes a far greater increase in conductance than the addition of an equal mole fraction of lithium hydroxide under these circumstances. This may be due to an increase in the concentration of free ions available for conductance in the lithium chlorate-water system, in which case the water will not only act as a diluent, but may also play an active part in the conduction process.

GENERAL DISCUSSION AND SUMMARY

CHAPTER VIII

GENERAL DISCUSSION

Disintegration by fusion of a crystalline lattice produces a melt consisting of simple molecules, polymeric units and ions in varying proportions. Although the lattice types of several salts may be alike, differences between the polarity and polarizability of the atoms or ions present may become apparent on fusion.

Whether simple ions, complex ions, molecules, or polymeric units predominate in the melt depends upon the relative solvation energy, the polarizing power and the shielding coefficients of the metal ions and the polarizability of the anions. The constitution of a melt thus does not depend solely upon the crystal lattice structure of the solid salt.

The process of crystal fusion represents a transition between two stable states of matter, the solid and liquid states, of which the liquid state is characterized by a statistical short range order. The latent heat of fusion, ΔH_f , is the energy required to overcome the overall order which exists in a crystal. The magnitude of ΔH_f depends upon the type of intermolecular forces which exist within the melt, and is related to the temperature of fusion T_f by the equation $T_f = \frac{\Delta H_f}{\Delta S_f}$ since the free energy of the system remains constant. The magnitude of ΔS_f , the change of entropy on fusion, is similar for almost all substances (2 - 9 entropy units), showing

that the increase of randomization on melting is similar for all substances. The entropy of fusion, latent heat of fusion and temperature of fusion are shown in Table 8.1 for several different substances, including lithium chlorate.

The latent heat of fusion of lithium chlorate was found to be 2.47 k. cal mole⁻¹[27]. From the freezing point, 127.9°C. the entropy of fusion results as 6.1 e.u. This is similar to that of most inorganic salts, which normally have values between 5 - 9 e.u. whether they form molecular or ionic melts. Ubbelohde¹⁵ ascribes a large part of the entropy change on fusion for low melting salts containing polyanionic units such as ClO₃⁻ to the formation of "association" complexes within the melt. The low value of ΔH_f shows that the energy necessary to overcome the interionic forces present in the crystalline salt is less than in most inorganic substances, and this may indicate that the general crystalline lattice of lithium chlorate persists to a considerable extent in the molten state, possibly in the form of these "associated" complexes.

The surface tension of lithium chlorate, 88 dynes cm.⁻¹ at its melting point, is similar in value to that of potassium chlorate, 81 dynes cm.⁻¹, whereas there is a large difference between the surface tension of the respective fluorides (251 and 142 dynes cm.⁻¹). It is typical of low melting salts of polyatomic anions that a change of cation has little effect upon the surface energy of the melt. This is thought to be due to the anions packing closely and touching each

TABLE 8.1
FUSION PARAMETERS OF SOME TYPICAL SUBSTANCES

Type	Compound	T_f °K.	ΔH_f k.cal mole ⁻¹	ΔS_f e.u.
Molecular	HCl	159	0.506	3.20
	H ₂ O	273	1.43	5.25
Metal	Ag	1234	2.60	2.19
	Hg	234	0.58	2.48
Salt	NaCl	1073	7.22	6.7
	KCl	1043	6.41	6.2
	ZnCl ₂	548	5.5	10.0
	NaNO ₃	581	3.86	6.6
	AgNO ₃	483	2.76	5.7
	LiClO ₃	401	2.47	6.1

other, with the cations set in the crevices between these anion groups. If this view is correct, the properties of the lithium chlorate melt will in part be determined by the anionic association, as with molten lithium and potassium nitrates.

The molar volumes of potassium chlorate and of potassium nitrate differ by approximately 25 per cent, compared to a 10 per cent difference between the molar volumes of the corresponding lithium salts. This shows that the larger potassium ion (radius=1.3A^o)

has a greater structural effect upon the melt than has the lithium ion (radius = 0.6\AA), and thus it is probable that the association of the anions in lithium chlorate is more evident in determining the liquid properties.

The surface heat of lithium chlorate (see page 66), $118 \text{ ergs cm.}^{-2}$, is intermediate between that of covalent melts, $50\text{--}70 \text{ erg cm.}^{-2}$, and of predominantly ionic melts, $150\text{--}200 \text{ erg.cm.}^{-2}$, and illustrates the observed partially covalent character of molten lithium chlorate (due to the chlorate group).

Though the Greenwood-Martin calculation shows that lithium chlorate is completely ionised in its liquid state, the electrical conductivity is much lower than that of many melts formed from either salts having simple symmetrical anions and cations or salts having a high melting point. There has been considerable controversy over the experimental determination of transport numbers in a pure melt due to the lack of a reference substance¹⁰⁹ but it is generally agreed that the results of Duke¹⁰⁷ for lithium nitrate ($t_{\text{Li}^+} = 0.9$, $t_{\text{NO}_3^-} = 0.1$) is of the correct order. Because of the similarity in size of the nitrate and chlorate ions, it may be assumed that lithium chlorate will also be primarily a uni-ionic conductor, the charge being carried by the lithium ion. The experimental activation energy of lithium chlorate, $6.1 \text{ k. cal. mole}^{-1}$, is not however in agreement with that calculated for a lithium ion having its crystallographic radius, $0.98 \text{ k. cal. mole}^{-1}$, and hence it is improbable that the

simple Li^+ ion is the charge-carrying unit; it is probably a much larger species. Indeed, the ratio of the activation energy for viscous flow to that of electrical conductance is almost unity, which indicates that the structural changes involved in viscous flow, which are dependent upon the largest species present in the melt, are similar to those involved in electrical conduction, and hence the simple Li^+ ion cannot be the principal conductor.

The viscosity of lithium chlorate is very high compared to that of other simple salts, and this also indicates that the constituents of the melt are complex. Zinc chloride also has a high viscosity, due to the formation of large complex ions, but this type of association does not occur within the lithium chlorate melt since the activation energy for viscous flow is independent of the temperature, whereas for zinc chloride a considerable temperature dependence is found.

Thus it appears that the density, surface tension, viscosity and electrical conductance of lithium chlorate all indicate that the melt has a considerable covalent character. It is probable that the association which has been postulated to exist in a lithium nitrate melt is also present in molten lithium chlorate. From the properties I have investigated, it is not possible to determine the actual constituents of the melt, nor the nature of the forces causing the presumed association, though it is probable that the molten salt retains a considerable "liquid lattice" structure

formed by large entities having a structure similar to that of the crystalline salt.

The effect of adding lithium nitrate to the lithium chlorate melt has been studied thermodynamically by Mr. M. K. Nagarajan.²⁷ The detailed interpretation of the change of entropy on fusion, the specific heat of the solid and liquid mixtures, and the heat of mixing with increasing mole fraction of lithium nitrate indicate that an interaction occurs between the added nitrate ions and the chlorate lattice of the melt. This interaction is probably in the form of bridging between the anion clusters of the lithium chlorate melt by the nitrate ions. The large positive deviation from the ideal change of entropy of mixing ΔS^m shows that the melt has a lower energy and hence more stable configuration resulting from the nitrate addition. This anionic interaction is evident in the increase of the activation energy of viscous flow with increasing lithium nitrate content, whereas the activation energy of electrical conductance remains constant. The ratio of these activation energies thus increases, but it is always lower than that found in the simple ionic melts. Thus the addition of lithium nitrate to molten lithium chlorate increases the partially covalent character of the melt because of the interaction of the NO_3^- ion with the ClO_3^- ion, that is, the addition of a dissimilar ion strengthens the covalent character. Kleppa has found a similar effect in silver nitrate-silver halide mixtures.¹¹⁰

The addition of propyl alcohol or nitrobenzene to a lithium chlorate melt causes a decrease in the specific conductivity, probably due to a dilution effect. The smaller decrease of specific conductance due to the addition of comparable mole fractions of methyl alcohol may be due to the partial breakup of the association in the chlorate melt compensating in part for the dilution. This breakup may be accentuated in this case by the high dielectric constant of methyl alcohol (32.63 at 25°C.), which is in fact known to be a solvent with considerable ionizing power. Thus, though the addition of a dissimilar ion increases the covalent character of the melt, e.g. NO_3^- , methyl alcohol may interact in the opposite manner causing a decrease in the association present, and hence an increase in the ionic character of the melt.

The large decrease in the viscosity of lithium chlorate slightly above its melting point, produced by the addition of a small quantity of water, compared to the smaller decrease produced by the same addition at a higher temperature, shows the strong interaction between water and the residual crystalline lattice which is thought to exist in the melt just above its melting point. The addition of lithium hydroxide caused a slight decrease in the specific conductivity and no change in the activation energy of conductance, whereas the addition of water caused a rapid increase in conductance and a decrease in the activation energy. This indicates that the overall energy required for ionic conductance is

unchanged by the addition of OH^- ion from the lithium hydroxide, and that consequent on the addition of water there is a general increase in the ionic character of the melt. The decrease in the coefficient of expansion of these water mixtures is also characteristic of this increase in ionic character. To understand further the nature of this water interaction a cryoscopic investigation using lithium chlorate as the solvent and water and lithium nitrate as solutes was undertaken. The freezing point depression produced by the addition of lithium nitrate can only be due to the addition of one foreign species to the melt, either molecular lithium nitrate or the NO_3^- ion. Presumably the addition of water should cause an equal depression per mole. Equilibrium studies of the lithium chlorate-water³⁸ and lithium chlorate-lithium nitrate¹¹¹ systems had indicated that these freezing point depression constants of the two systems were not the same. A cryostat similar to that developed by Keenan³² and Janz¹¹² was used, but the very high viscosity of the medium caused considerable experimental difficulty. The freezing point depression constants were found to be 6.9°C . per mole for lithium nitrate additions and 12.4°C . per mole for water additions. The latent heat of fusion of lithium chlorate calculated from the depression constant of the lithium nitrate additions is $2.2 \text{ k. cal. mole}^{-1}$, compared to the thermodynamic value $2.47 \text{ k. cal. mole}^{-1}$. The results indicate that the addition of one molecule of water forms more than one particle foreign to the lithium chlorate

system. Thus the water added cannot retain its simple molecular character after its strong interaction with the lithium chlorate melt.

A nuclear magnetic resonance spectrum was taken of the proton resonance in a 0.15 mole fraction water mixture at 131°C ., but only a single absorption peak was obtained. This may indicate that each proton of the water molecule was in the same environment within the melt, but it is more likely that the rate of exchange of protons at this temperature is so great that the environment is averaged out on an N.M.R. spectrum.

It was thought that the Raman spectrum of a lithium chlorate-water mixture would provide further insight into the nature of the water present in the melt. The author is indebted to Dr. G.J. Janz and Dr. C.B. Baddiel who kindly obtained the high temperature Raman spectra given in Table 8.2,¹¹³ no Raman spectrometer being available at this University. The high temperature assembly has been described in the literature,¹¹⁴ and uses a Toronto type mercury arc to provide the exciting radiation. Polarization ratios were determined by the use of polarized sleeves. The spectra were recorded at approximately 150°C .

TABLE 8.2

RAMAN SPECTRA OF MOLTEN LITHIUM CHLORATE WITH ADDED WATER

$\Delta \text{ cm}^{-1}$	Assignment
474.5	$\text{ClO}_3^- (\nu_4, e)$
607.3	$\text{ClO}_3^- (\nu_2, a_1)$
934.4	$\text{ClO}_3^- (p) (\nu_3, a_1)$
996	$\text{ClO}_3^- (\nu_3, e)$
1487.0	$\text{ClO}_3^- (\nu_3 + \nu_4)$
2231.6	
2496.4	
2783.0	
2827.6	
2870	
2912	
3348.2	(p)
3419.0	(dp)
3455.0	$\text{OH}^- (\text{symm str.})$
3478.0	
3737.0	

The mixtures examined were the following:

Weight of Lithium Chlorate (1% H ₂ O initially present) grams	Weight of Water		Mole Percent Water
	In Sample grams	Added grams	
14.23	0.144	-	4.9
13.4	0.135	0.6	21.
14.8	0.149	0.8	25.

TABLE 8.3

The resulting spectra were found to be independent of the water content of the sample, and are given in Table 8.2. The errors in determining the position of the Raman lines were estimated as ± 4 cms.⁻¹

The Raman spectrum of liquid water has received considerable attention. Typical are the studies by Hibben¹¹⁵ and the later work by Walrafen.¹¹⁶ Figure 8.1 shows the Raman spectrum of water recorded by Hibben.

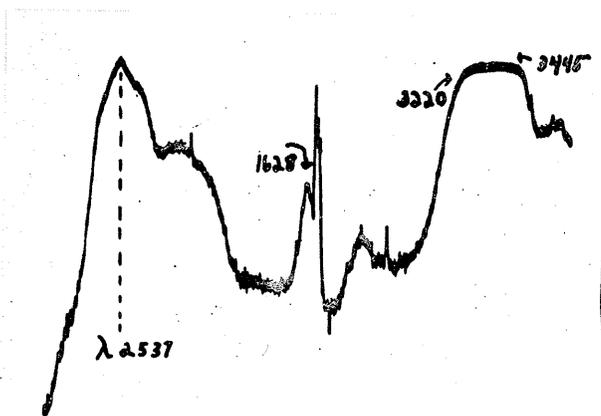


FIG 8.1(a) The principal Raman bands for water excited by the 2537A mercury line, namely, $\Delta\bar{\nu}$ 150, 445, 1628, 2170, 3220, 3445, which are, from left to right, indicated by arrows.

The spectrum obtained by Walrafen is similar but shows greater detail. Of note is the sharp band at 1645 cm^{-1} which has been assigned to the bending frequency of the water molecule. Wilmschurst has determined the spectra of several molten chlorates,¹¹⁷ including lithium chlorate. The spectra obtained by Wilmschurst (lithium chlorate) and Walrafen (liquid water) are given in Table 8.4 together with the infrared reflection spectrum of fused lithium hydroxide which has also been determined by Wilmschurst.¹⁰⁸

TABLE 8.4
PREVIOUS STUDIES IN MOLTEN CHLORATES,
HYDROXIDES AND LIQUID WATER

Wilmschurst Molten Lithium Chlorate ($\Delta \text{ cm}^{-1}$)	Walrafen Liquid Water ($\Delta \text{ cm}^{-1}$)	Wilmschurst Fused Lithium Hydroxide ($\Delta \text{ cm}^{-1}$)
478 $\nu_4(e)$	450 ν_{Li} Libration from H Bonding	441 Lattice mode
620 $\nu_2(a_1)$	780 ν_{L_2} Libration from H Bonding	
938 $\nu_1(a_1)$	1645 $\nu_2 a_1$, Bending	
977 split $\nu_3(e)$	2115 $\nu_{L_1} + \nu_2 a_1$ combination	
1018	3225 Fermi Resonance	
1490 $\nu_3 + \nu_4$	3450 $\nu_1 a_1$, Symmetric OH Stretch	3490
1900 1960 $\nu_1 + \nu_2$	3630 ν_3 Asymmetric OH Stretch	OH vibration
	3990 $2\nu_2 a_1 + \nu_{L_2}$ Combination	

It is immediately apparent that the spectra obtained from the lithium chlorate-water mixtures contain all of the lines for the ClO_3^- as present in a pure one component melt. The 1650 cm.^{-1} water mode, due to the transverse oscillations or bending motion of the hydrogen atoms of the water molecule, is missing. The OH^- stretching frequency is present at approximately 3500 cms.^{-1} just as in the molten hydroxides (see Table 8.4). The absence of the water bending mode indicates that in all probability the interaction between the added water and the lithium chlorate melt is such that no water molecules as such exist within the melt. The appearance of the spectral lines at $2231, 2496, 2783, 2827$ and 2912 cms.^{-1} however, shows that this interaction does not produce the simple H^+ and OH^- ions.

The effects of dissolved salts on the structure of water have been summarized by Frank and Evans¹¹⁸ and the applications of the methods of vibrational spectroscopy to the structure of aqueous electrolytic solutions described by Young,¹¹⁹ but in neither case is an effect evident which could cause a shift of the bending mode of vibration of water into the 2000 cm.^{-1} range. Indeed, Busing and Hornig¹²⁰ have found that the intensity of this bending is in fact increased by the addition of KOH , HCl or KBr , and is very easily discerned in solutions of concentrations up to 15M . This increase in intensity is also produced by an increase in temperature of an aqueous solution. Thus it is evident that the water

bending mode is indeed absent in the lithium chlorate-water mixtures investigated.

It is not possible to assign the lines found between 2200-2900 cms.^{-1} to any particular vibration within the melt. They were not mentioned in an earlier investigation of 10M sodium chlorate,¹²¹ nor was any mention made of the 1650 cms.^{-1} band at all. It is possible, however, that these lines are due to a form of hydrogen bonding between the water hydrogen atoms and the lithium chlorate melt, though the nature of this bonding is uncertain.

Ion pair formation may also occur within the lithium chlorate melt, but it is not possible to prove ion pair formation from Raman spectra. The intensity of a vibrational line depends upon the change of polarizability with the change of internuclear distance. The polarizability of an ion pair is dependent on the distance between the ions due to their mutual effect on each other, and so a Raman effect associated with the vibration of the ion pair does exist. Woodward¹²² has analyzed this system theoretically, and found that the intensity of such an effect for an electrostatic ion pair in water is at least 100 times weaker than for a covalent bond, and is unlikely to be observed. Thus it is not possible to determine completely the constituents of a lithium chlorate-water melt. The interaction of the added water does however cause large changes in the physical properties of the pure melt.

II. SUMMARY

The densities, viscosities, surface tensions and electrical conductances have been determined for molten lithium chlorate and its aqueous solutions, containing 95-100 per cent lithium chlorate. Several binary mixtures of lithium chlorate have also been investigated, in which propyl alcohol, methyl alcohol, lithium nitrate or lithium hydroxide has been minor component, with respect to these same properties.

The low melting point of pure lithium chlorate has made it possible to determine the values of these properties with a high degree of accuracy over a range of temperature. Due to their hygroscopic nature, lithium chlorate melts require careful control throughout. The experimental techniques and the apparatus used for the determination of each property are given in detail. The results obtained are discussed in relation to present theories concerning molten salts.

The general nature of the lithium chlorate melt is of a partially covalent character, caused primarily by the association of chlorate groups. This is evident in the low electrical conductance and high viscosity. The melt constituents are not primarily the simple ions.

The changes in the properties of the lithium chlorate melt vary in degree and nature when a second component is added. The addition of lithium nitrate enhances the covalent characteristics

of the melt, whereas the addition of water decreases the viscosity and increases the electrical conductance, changes which indicate an increase in ionic character. The interaction of water with the lithium chlorate melt is not simple, as is shown by the electrical conductance, cryoscopic behaviour and Raman spectra of these lithium chlorate-water melts. Indeed, a Raman spectrum shows that the water added has lost its identity as such.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. G. W. Stewart. Rev. Mod. Phys. 2, 116 (1930).
2. J. D. Bernal. Trans. Farad. Soc. 33, 27 (1937).
3. W. L. Bragg and E. W. Williams. Proc. Roy. Soc. A145, 669 (1934).
4. H. A. Bethe. Proc. Roy. Soc. A150, 552 (1935).
5. N. F. Mott and R. W. Gurney. Rep. Progs. Phys. 5, 46 (1939).
6. J. E. Lennard-Jones and A. F. Devonshire. Proc. Roy. Soc. A169, 317 (1937).
7. J. G. Kirkwood. J. Chem. Phys. 3, 300 (1935).
8. M. Born and H. S. Green. Proc. Roy. Soc. A188, 100 (1946).
9. H. Eyring, T. Ree and N. Hirai. Proc. Nat. Acad. Sci. 44, 683 (1958).
10. W. J. Davies, S. E. Rogers, and A. R. Ubbelohde. Proc. Roy. Soc. A220, 14 (1953).
11. G. J. Landon and A. R. Ubbelohde. Trans. Farad. Soc. 52, 647 (1956).
12. J. O'M. Bockris and N. E. Richards. Proc. Roy. Soc. A241, 44, (1957).
13. S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes". New York: McGraw-Hill, 1941.
14. A. R. Ubbelohde. Disc. Farad. Soc. 32 (1961).
15. H. Bloom and N. E. Richards, quoted p. 175 "Electrochemistry", No. 2. Edited J. O'M. Bockris; Butterworth Scientific Publications, London, 1959.
16. G. J. Janz, C. Solomons, H. J. Gardner, J. Goodkin, and C. T. Brown. J. Phys. Chem. 62, 823 (1958).
17. G. J. Janz, C. T. Brown, H. J. Gardner, and C. Solomons. J. Phys. Chem. 62, 1479 (1958).
18. B. R. Sundheim and G. Greenberg. J. Chem. Phys. 28, 439 (1958).

19. M. Tempkin. Acta. Phys. Chem., USSR. 20, 411 (1945).
20. W. Bues. Z. anorg. u. allgem. Chem. 279, 104 (1955).
21. E. J. Salstrom and L. Harris. J. Chem. Phys. 3, 241 (1935).
22. C. Jennings. J. Electrochem. Soc. 103, 531 (1956).
23. S. Senderoff and A. Brenner. J. Electrochem. Soc. 101, 16 (1954).
24. R. S. Dantuma. Z. anorg. u. allgem. Chem. 175, 37, (1928).
25. F. R. Duke and A. S. Doan. Iowa State College Journal of Science. 32, No. 3, 451 (1957).
26. J. P. Frame, E. Rhodes and A. R. Ubbelohde. Trans. Farad. Soc. 57, 1075 (1961).
27. M. K. Nagarajan, Private communication.
28. C. A. Krauss and W. M. Burgess. J. Am. Chem. Soc. 49, 1226 (1927).
29. M. A. Klotschko and J. C. Grigorjew. English translation of a Paper in Akad. Wiss (USSR). Nachr. Abt. Physik-Chem. Analyse. 21, 288 (1950).
30. A. N. Campbell, E. M. Kartzmark and W. G. Patterson. Can. J. Chem. 36, 1004 (1958).
31. A. N. Campbell, E. M. Kartzmark, M. E. Bednas and J. T. Herron. Can. J. Chem. 32, 1051 (1954).
32. A. G. Keenan. J. Phys. Chem. 61, 780 (1958).
33. A. N. Campbell, E. M. Kartzmark and D. F. Williams. Can. J. Chem. 40, 890 (1960).
34. I. S. Yaffe and E. R. Van Artsdalen. J. Phys. Chem. 60, 1125 (1956).
35. G. J. Janz and M. R. Lorenz. J. Electrochem. Soc. 108, No. 11, 1961.
36. W. Biltz and W. Klemm. Z. anorg. Chem. 152, 267 (1926).

37. Selected from the Smithsonian Tables, Handbook of Chemistry and Physics, Chemical Publishing Co. 43d ed. 1961-62. p. 2157.
38. A. N. Campbell and J. E. Griffiths. Can. J. Chem. 34, 1647 (1956).
39. H. Bloom and E. Heymann. Proc. Roy. Soc. A188, 392 (1946).
40. H. M. Goodwin and R. D. Mailey. Physical Reviews. 25, 469 (1907).
41. N. K. Boardman, F. H. Dorman and E. Heymann. J. Phys. Chem. 53, 375 (1949).
42. H. Bloom, I. W. Knaggs, J. J. Molloy and D. Welch. Trans. Farad. Soc. 49, 1458 (1953).
43. J. D. Frame, E. Rhodes and A. R. Ubbelohde. Trans. Farad. Soc. 55, 2042 (1959).
44. G. J. Janz and J.D.E. McIntyre. Ann. N.Y. Acad. Sci. 79, 790 (1960).
45. E. R. Van Artsdalen and I.S. Yaffe. J. Phys. Chem. 58, 259 (1955).
46. E. W. Dewing. J. Am. Chem. Soc. 77, 2639 (1955).
47. K. A. Sense, M. J. Snyder and J. W. Clegg. J. Phys. Chem. 58, 223 (1954).
48. J. de Guzman. Anal. Fis. Quim. 9, 353 (1913).
49. E. N. da C. Andrade. Nature. 125, 309 (1930).
50. J. Frenkel. "The Kinetic Theory of Liquids". Oxford, 1946.
51. H. Bloom, B. S. Harrap and E. Heymann. Proc. Roy. Soc. A194, 237 (1948).
52. B. S. Harrap and E. Heymann. Trans. Farad. Soc. 51, 259 (1955).
53. J. Hirshfelder, C. F. Curtiss and R. B. Bird. "Molecular Theory of Liquids and Gases". New York: Wiley, 1954.
54. J. Hirshfelder, D. Stevenson and H. Eyring. J. Chem. Phys. 5, 896 (1937).
55. A. J. Batschinski. Z. Physik Chem. 84, 643 (1913).

56. B. S. Harrap and E. Heymann. Chem. Reviews. 48, 45 (1951).
57. A. N. Campbell, G. H. Debus and E. M. Kartzmark. Can. J. Chem. 33, 1508 (1955).
58. J. D. MacKenzie and W. K. Murphy. J. Chem. Phys. 33, 366 (1960).
59. J. E. Lennard-Jones and J. Corner. Trans. Farad. Soc. 36, 1156 (1940).
60. J. G. Kirkwood and F. P. Buff. J. Chem. Phys. 17, 338 (1949).
61. S. Chang, T. Ree, H. Eyring and I. Matzner. 2nd Symposium on Thermophysical Properties, Princeton University, 1962.
62. D. A. McQuarrie. J. Phys. Chem. 67, 518 (1963).
63. E. A. Guggenheim. Trans. Farad. Soc. 41, 150 (1945).
64. J. Walter and H. Eyring. J. Phys. Chem. 9, 393 (1941).
65. H. Bloom, F. G. Davies and D. W. James. Trans. Farad. Soc. 56, 1179 (1960).
66. N. K. Boardman, A. R. Palmer and E. Heymann. Trans. Farad. Soc. 51, 277 (1955).
67. F. M. Jaeger. Z. anorg. Chem. 101, 1 (1917).
68. H. Bloom and F. G. Davies. Quote p. 198 Modern Aspects of Electrochemistry, No. 2. London: Butterworth, 1959.
69. H. Bloom and Jamieson, p. 198, Modern Aspects of Electrochemistry, No. 2. London: Butterworth, 1959.
70. G. Jones and B. C. Bradshaw. J. Am. Chem. Soc. 55, 1780 (1933).
71. A. Klemm. 18th I.U.P.A.C. Congress, Montreal, 1961.
72. K. Sakai. J. Chem. Soc. Japan. 75, 186 (1954).
73. K. Sakai. J. Chem. Soc. Japan. 76, 101 (1955).
74. K. Sakai. J. Chem. Soc. Japan. 77, 1169 (1956).
75. W. Oldekop. Z. Physik. 140, 181 (1955).
76. B. R. Sundheim. J. Phys. Chem. 61, 116 (1957).

77. J. O'M. Bockris. Disc. Farad. Soc. No. 32, p. 266, 1961.
78. J. D. Bernal. Nature. 183, 141 (1959).
79. M. H. Cohen and D. Turnbull. J. Chem. Phys. 31, 1164 (1959).
80. W. Altar. J. Chem. Phys. 5, 577 (1937).
81. R. L. Harris, R. E. Wood and H. E. Ritter. J. Am. Chem. Soc. 73, 3151 (1951).
82. R. L. Martin. J. Chem. Soc. 3246, 1954.
83. Yu. V. Baimakov and S. P. Samusenko. Quoted in "Modern Aspects of Electrochemistry, No. 2." London: Butterworth, 1959.
84. J. O'M. Bockris, J. A. Kitchener, S. Ignatowicz and J. Tomlinson. Trans. Farad. Soc. 48, 76 (1952).
85. J. O'M. Bockris, E. H. Crook, H. Bloom and N. E. Richards. Proc. Roy. Soc. A255, 588 (1960).
86. F. H. Stillinger, J. G. Kirkwood and P. J. Wojtowicz. J. Chem. Phys. 32, 1837 (1960).
87. P. W. Bridgeman. "The Physics of High Pressures". London: Bell, 1931.
88. R. Fürth. Proc. Camb. Phil. Soc. 37, 352 (1941).
89. J. W. Johnson, P. A. Agron and M. A. Bredid. J. Am. Chem. Soc. 77, 2734 (1955).
90. E. McLaughlin and A. R. Ubbelohde. Trans. Farad. Soc. 54, 1804 (1958).
91. E. McLaughlin. Quat. Rev. London. 14, 236 (1960).
92. N. N. Greenwood and R. L. Martin. J. Chem. Soc. 1427 (1953).
93. H. S. Harned and B. B. Owen. "The Physical Chemistry of Electrolytic Solutions". 3d ed. New York: Reinhold, 1957.
94. H. C. Cowen and H. J. Axon. Trans. Farad. Soc. 52, 242 (1956).
95. J. D. Edwards, C. S. Taylor, A. S. Russell and L. F. Maranville. J. Electrochem. Soc. 99, 527 (1952).

96. G. Jones and G. M. Bollinger. J. Am. Chem. Soc. 53, 411 (1931).
97. H. C. Parker, J. Am. Chem. Soc. 45, 1366 (1923).
98. G. J. Janz and M. R. Lorenz. Rev. Sci. Instr. 1960.
99. E. W. Washburn. J. Am. Chem. Soc. 38, 2431, (1916).
100. E. Bock. Ph.D. Thesis, University of Manitoba, 1959.
101. W. Klemm, W. Tilk and S. V. Mullenheim. Z. anorg. allgem. Chem. 176, 1 (1928).
102. D. W. Plester, S. E. Rogers and A. R. Ubbelohde. Proc. Roy. Soc. A235, 469 (1956).
103. R. S. Dantuma. Z. anorg. Chem. 175, 1 (1928).
104. F. M. Jaeger and B. Kampa. Z. anorg. Chem. 113, 27 (1920).
105. R. Lorenz and H. T. Kalmus. Z. Physik. Chem. 59, 17 (1907).
106. S. E. Rogers and A. R. Ubbelohde. Trans. Farad. Soc. 46, 1051 1950.
107. F. R. Duke and B. Owens. J. Electrochem. Soc. 105, 548 (1958).
108. J. K. Wilmshurst. J. Chem. Phys. 35, 1800 (1961).
109. C. Sinistri. J. Phys. Chem. 66, 1600 (1962).
110. O. J. Kleppa and S. V. Meschel. J. Phys. Chem. 67, 668 (1963).
111. A. N. Campbell, E. M. Kartzmark and M.K. Nagarajan. Can. J. Chem. 40, 1258 (1962).
112. C. Solomons and G. J. Janz. Rev. Sci. Instr. 29, 302 (1958).
113. G. J. Janz and C. B. Baddiel. Private communication, 1963.
114. G. J. Janz, Y. Mikawa and D. W. James. Appl. Spectroscopy. 15, 000 (1961).
115. J. H. Hibben. J. Chem. Phys. 5, 166 (1937).
116. G. E. Walrafen, quoted. G.J. Janz and C.B. Baddiel, Private communication.

117. J. K. Wilmshurst. J. Chem. Phys. 36, 2415 (1962).
118. H. S. Frank and N. W. Evans. J. Chem. Phys. 13, 507 (1945).
119. T. F. Young, L. F. Maranville and H. Smith. "The Structure of Electrolytic Solutions" (W.J. Hamer, Ed.) New York: John Wiley, 1959.
120. W. R. Busing and D. F. Horning. J. Phys. Chem. 65, 284 (1961).
121. S. T. Shen, Y. T. Yao and Ta-You Wu. Physical Reviews. 51, 235 (1937).
122. J. H. B. George, J. A. Rolfe and L. A. Woodward. Trans. Farad. Soc. 49, 375 (1953).