

THE UNIVERSITY OF MANITOBA

DENSITY MEASUREMENTS ON MOLTEN SALT MIXTURES:

THE SYSTEM $\text{LiClO}_3\text{-NaClO}_3$

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by

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TO HERMIONE

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ABSTRACT

Salts with unsymmetrical complex anions are generally low melting and are known to give rise to strongly covalent melts. Lithium chlorate belongs to this group of salts. Determinations of physical properties of lithium chlorate with additions of a salt containing a common cation were made before in this laboratory. It was therefore important to investigate next a system of salts which has a common anion. Chosen for this investigation was the system lithium chlorate-sodium chlorate.

In this system the densities of pure lithium chlorate and pure sodium chlorate were determined for the solid state from room temperature up to a few degrees below the melting point. The density of several lithium chlorate-sodium chlorate mixtures and of pure sodium chlorate was determined in the molten state. For the pure salts the increase in molar volume on melting was calculated. The dependence of molar volume on composition and temperature was calculated for the lithium chlorate-sodium chlorate mixtures and compared with the previous investigated common cation containing salt mixture.

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TABLE OF SYMBOLS

α	Coefficient of thermal expansion
β	Compressibility
C_p	Molar heat capacity
H	Hamiltonian
ϵ	Maximum energy of attraction
E	Potential energy
k	Boltzmann constant
m	Mass
p	Momentum coordinate
q	Position coordinate
Q	Configurational integral
R	Gas constant
r_+ r_-	Ionic radii of cation and anion respectively
σ	Distance between centres of two neighbouring ions
T	Temperature in absolute scale
T_f	Freezing point
U	Potential energy
V	Molar volume
V_f	Free volume
ΔV_f	Molar volume change at melting point
V_g	"Geometric contribution" to change in molar volume
V_m	Molar volume change due to temperature change
V_s	"Structural contribution" to change in molar volume

V_s	Molar volume of solid at melting point
V_T	Molar volume change due to composition changes
Z	Partition function

CHAPTER I

GENERAL INTRODUCTION

Apart from the general need to obtain data on molten salts for practical purposes, there are two main reasons for their investigation, namely:

(a) Molten salts form a class of liquids in which at least two different oppositely charged particles are present.

(b) Mixtures of molten salts often behave as if they contain new ionic species, such as complex ions, formed by interaction between simple ions.

Molten salts can be considered to consist mainly of ions and although they have the usual properties of liquids in general, there is the additional property of the existence of positively and negatively charged particles. Molten salts can therefore be called "ionic liquids".¹

Because in many respects the liquid state forms an intermediate mode between the solid and gaseous state, we can approach the liquid state either from the crystalline state or the gaseous state. There is no reason to regard one approach as better than the other. Therefore the two main models of the liquid state are:

1. The quasi gaseous model, which is most appropriate near the critical temperature, where the liquid closely resembles a gas.

2. The quasi crystalline model, which treats the liquid as a disordered crystal and is most appropriate near the melting point.

Because most of the experimental data on molten salts are near the melting point, the quasi crystalline model is for practical purposes the more important one.

LIQUID STATE MODELS

Three current models of the liquid state will illustrate the theoretical approach to the liquid state structure. Let us regard the liquid as being built up by uncharged particles.

1. The cell model or Lennard-Jones and Devonshire theory^{2,3} is one in which the liquid is essentially derived from a regular lattice structure. The lattice forms a large number of cells, each cell containing one molecule.

2. Eyring⁴ proposed a cell model for the liquid state in which not all cells contain a molecule. This model is generally known as the hole theory. There are unoccupied cells or "holes". Single occupancy is maintained as a maximum.

3. Barker in his tunnel theory^{5,6} imagined a lattice model which is one dimensionally disordered. Instead of one molecule in a cell as in previous models, he suggests there is a whole line of molecules in a tunnel.

Before treating these different liquid state models, it is necessary to describe a few principles on which these

theories are based. First of all the law of interaction, according to which the particles attract each other, must be known. Secondly, a few statistical mechanical principles must be reviewed shortly.

The Lennard-Jones Potential

A simple and widely used empirical law is the "Lennard-Jones 12-6 potential"⁷, which applies to spherical non-polar molecules. The potential energy $U(r)$ as a function of the distance r between the centers of the particles is given by:

$$U(r) = \lambda r^{-n} - \nu r^{-m} \quad (1)$$

Where $m > n$, usually 12 and 6 respectively. λ and ν are parameters characteristic of the interaction. The first term of equation (1) represents the repulsive effect and the second term the attractive effect.

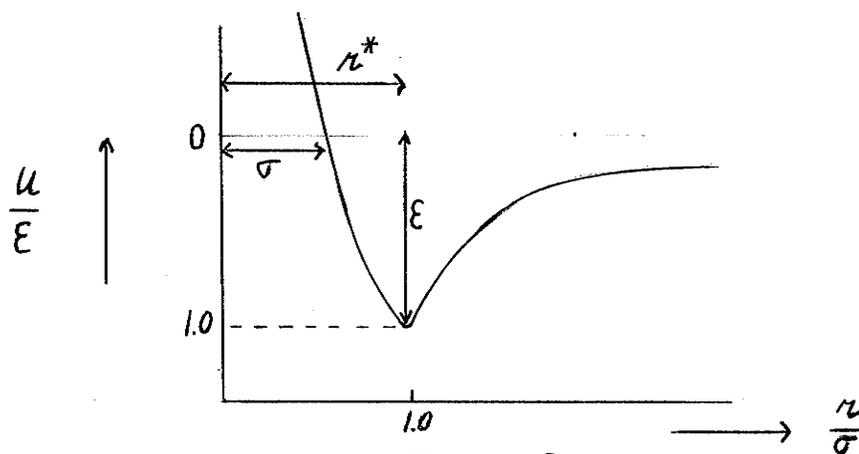


Figure 1

Equation (1) can be written in a form more appropriate for calculations:

$$U(r) = 4 \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where σ = value of r for which $U(r) = 0$

ϵ = max. energy of

attraction (or depth of potential well).

The maximum depth of the well occurs at a distance $r = 2^{1/6}\sigma$. This distance is found by differentiating $U(r)$ and equating to zero. At large separations ($r \gg \sigma$) the second term is dominant (Vander Waals forces). At the distance $r = \sigma$ the potential energy is zero. Finally at small separations ($r \ll \sigma$) the first term, i.e., the repulsive component is dominant.

The potentials are taken as additive⁸ which means that the potential energy of N molecules is the sum of the pair potentials between all of the $N(N-1)/2$ possible pairs. In other words, the potential energy is $\sum_{ij} E(R_{ij})$, where $E(R_{ij})$ is the potential energy of interaction of molecules i and j , depending on their separation R_{ij} .

Next a short explanation of the partition function and the configurational integral is necessary, to see the application of the 12-6 potential energy function.

STATISTICAL MECHANICAL PRINCIPLES

Consider states 1,2,3, ---- n with energies E_1, E_2, \dots, E_n . The partition function is then given by:

$$Z = \sum_{i=1}^n e^{-E_i/kT}$$

where k is the Boltzmann constant. If the temperature is high,

integrals may be used instead of sigma signs. The partition function for N particles in generalized coordinates

$q_1, \dots, q_{3N}, p_1, \dots, p_{3N}$ is:

$$Z_N = \frac{1}{N!} \iiint e^{-\beta H(p_1, \dots, p_{3N}, q_1, \dots, q_{3N})} dp_1 \dots dp_{3N}, dq_1 \dots dq_{3N} \quad (2)$$

where H is the Hamiltonian. The Hamiltonian is separable as a sum of terms and can therefore be written as a product of simpler integrals.

In the Hamiltonian the potential energy term depends on the coordinates only. This means that we can integrate immediately over the momentum part:

$$\int_{-\infty}^{\infty} \exp\left(-\frac{p^2}{2mkT}\right) dp = (2\pi mkT)^{1/2}$$

The partition function (2) now becomes:

$$Z_N = (2\pi m k T)^{\frac{3N}{2}} \frac{Q}{\lambda^{3N} N!} \quad \lambda^2 = \left(\frac{1}{2\pi m k T} \right)$$

where λ^{3N} is unit volume. Q is called the configurational integral and stands for:

$$Q = \iiint_{3N} e^{-U(q_1, \dots, q_{3N})} dq_1 \dots dq_{3N}$$

$U(q_1, \dots, q_{3N})$ is the potential energy of the system as a function of the coordinates, for which generally the Lennard-Jones 12-6 potential is taken.

The Helmholtz free energy A is related to the partition function by the equation:

$$A = -k T \ln Z$$

where Z and A are functions of the temperature and of any other variable necessary to specify the system. Statistical mechanics enable us to derive all thermodynamic properties of the system once the free energy is known as a function of the partition function.⁹

Partition functions of molten salts can be set up, but this goes beyond the scope of this introduction.

CELL THEORY OR FREE VOLUME THEORY

Of the cell theories the simplest possible one is described by Hirschfelder^{10,18}. In this theory specific volume and free volume are essential. The specific volume (V_S) is defined as the average amount of space available to each molecule, that is: total available space divided by number of particles ($\frac{V}{N}$). The free volume (V_f) is the space in which the center of the molecule can move and still not collide on the average with the neighbouring molecules.

Consider molecules numbered 1,2,3 and 4 as fixed, call molecule A the wanderer. Let the wanderer move in such a way, that it just does not collide with one of the other four molecules. The space described by the center of the wanderer is called the free volume (Black area in molecule A in Fig.2).

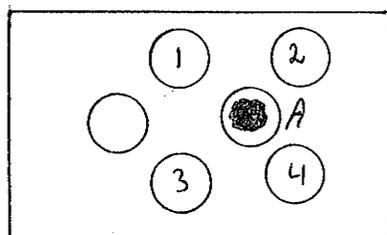


Figure 2

If the nearest neighbours lie on a sphere of radius "a" about the cell centers, then to a good approximation the free volume is the volume of a sphere of radius (a-D) from its cell center before colliding with another molecule:

$$V_f = \frac{4\pi}{3} (a-D)^3$$

This result underestimates the free volume because (a-D) is actually the minimum distance the central molecule can move from its cell center to collision; in most directions it can move further. The value above would be more accurate if the neighbours were "smeared" uniformly over the sphere of radius "a" (See Fig.3).

It is important to note that if the specific volume is greater than twice the cube of the molecular diameter the molecules are no longer confined to cages formed by neighbouring molecules. At these low densities the free volume concept is ambiguous.

When attractive forces between molecules are taken into consideration the assumption that molecules move independently in their cells implies that the potential energy is approximated by the expression:

$$E = E_0 + \sum_n \left\{ f(r_n) - f(0) \right\}$$

where E_0 is the energy when all molecules are at the centers of their cells; $\left\{ f(r_n) - f(0) \right\}$ is the change in potential energy, when the molecule n is displaced from the center of its cell over a distance r, while the other molecules remain

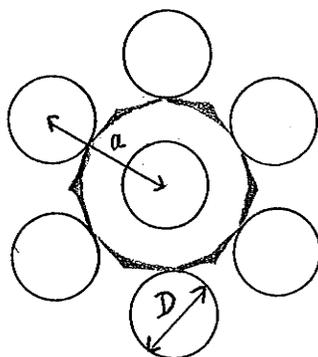


Figure 3

a is distance between the centers of molecules

D is diameter of molecule

Black area: is area neglected by free volume concept. A correction factor accounts for this neglected volume in the configurational integral.

at the centers of their cells. In this case the free volume is defined by the expression:

$$V_f = \int \left\{ \exp \left[- \left\{ f(r_n) - f(0) \right\} \right] \right\} (kT)^{-1} dr_n$$

The configurational integral is given by:

$$Q = V_f^N \left\{ \exp - E_0 \right\} (kT)^{-1}$$

The free volume concept neglects the cooperative motion of neighbouring molecules and multiple occupancy of the cells is disregarded.

The assumptions of the Lennard-Jones and Devonshire cell theory are:

- (i) Molecules move entirely independently of one another in their cells.
- (ii) All cages are identical and each contains just one molecule.
- (iii) Potential energy inside each cell is assumed to be spherically symmetrical.

The confinement of each molecule to a cell results in an error in the entropy of the system¹⁰ (too low). The correction term is usually called the communal entropy term. We will deal with this correction term in more detail later, (see communal entropy).

The Lennard-Jones and Devonshire theory fails to allow for vacant sites. This treatment in fact resembles a solid more than a liquid to allow for the existence of solid and

liquid phases within the framework of a lattice picture Lennard-Jones and Devonshire^{11,12} proposed a model in which N molecules are distributed on a lattice of $2N$ sites divided into two interpenetrating sub-lattices α and β each of N sites. In this model the solid corresponds to an ordered state in which almost all of the molecules lie on one of the two sub-lattices, while the liquid corresponds to a disordered state in which the molecules are distributed without long range order over the whole $2N$ lattice sites.

If we consider two interpenetrating face-centered cubic lattices α and β in which each α site has six neighbouring β sites and vice versa, the combined lattice is a simple cubic lattice. After setting up the configurational integral along the lines already outlined above, several thermodynamic properties can be calculated.

Instead of going into much theoretical detail let us look at the results obtained for argon by means of the Lennard-Jones and Devonshire theory. Because quantum effects influence the properties of helium and neon, argon is usually chosen for theoretical calculation.

We see that the values of molar volume change, entropy and pressure predicted by the theoretical treatment for the process of melting are in close accord with the experimental values.

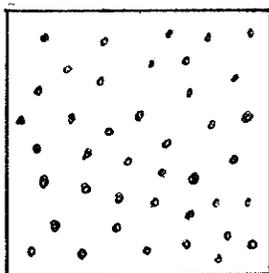
TABLE I
FUSION OF ARGON¹⁷

	Observed	Calculated
$\frac{\Delta V_f}{V_S}$ upon melting at zero pressure	12%	12.8-13.5%
S_f at zero pressure (83.8°K)	1.66k	1.70-1.74k
pressure of melting at 90.3°k (megadynes cm ⁻²)	291	286 - 294
coefficient of expansion of liquid in immediate neighborhood of melting point.	4.5×10^{-3}	$4-4.9 \times 10^{-3}$

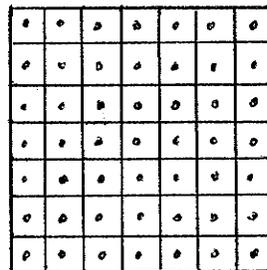
k is Boltzmann constant.

Communal Entropy

Consider a system of N non-interacting particles. Let us calculate the difference in entropy of the two states illustrated in Fig. 4.



State I. Perfect Gas of N Molecules in Volume V .



State II. N Molecules, Each One Confined to a Cell of Volume V/N

Figure 4

In State I the total volume V is shared by all the molecules. The partition function is then:

$$Z_N^{(I)} = \lambda^{-3N} \left(\frac{V^N}{N!} \right) \quad \text{where} \quad \lambda^2 = \frac{1}{2\pi m k T}$$

In State II, where each molecule is restricted to move within its own cell of volume $\frac{V}{N}$, the

$$Z_N^{(II)} = \lambda^{-3N} \left(\frac{V}{N} \right)^N$$

From statistical mechanics the entropy is given by the following equation:

$$S = k \ln Z_N + \frac{U}{T}$$

The entropy difference between the two states is:

$$S^{II} - S^{I} = k \ln \frac{Z_N^{II}}{Z_N^{I}} = k \ln \frac{N^N}{N!} = Nk$$

This result means that the cell model for a gas gives an entropy too low by Nk and a free energy too high by NkT . This defect may be corrected by inserting a factor of e^N in the expression for the partition function Z_N^{II} .

Hole Theory

In the hole theory Eyring proposed that in order to account for the many holes in the lattice (about 0.5% for normal liquids up to 50% near the critical point), allowance should be made for the presence of vacant lattice cells or "holes". The hole theory gives the correct value for the entropy of the perfect gas so that the communal entropy is included in the low density limit. At high densities the proportion of holes becomes very small and resembles more the cell theory. Transition from solid to liquid is regarded as an increase of the number of holes, but retention of short range order.

Tunnel Theory

Barker in his tunnel theory imagined a lattice model which is one dimensionally disordered. Instead of one molecule in a cell he suggests there is a whole line of molecules in a tunnel. The disorder in this model arises from the fact that the positions of the molecules in different tunnels are independent (see Fig.5).

In the tunnel theory the configurational integral is

the product of the configurational integrals for longitudinal and transversal motions. The configurational integral for the longitudinal motion is one dimensional and can be evaluated exactly. For the transverse motion the configurational integral can be evaluated in the same way as the free volume in the cell model. The most serious disadvantage of the tunnel model is its anisotropic character.

IONIC MELTS

The foregoing discussion has been restricted to liquids consisting of uncharged spherical particles. Obviously molten salts do not belong to this group. Extensions of the Lennard-Jones and Devonshire and hole theories to charged particles have been made.¹³ Essentially they consist of setting up the partition function for charged particles in the same way as was shown for uncharged particles.

It is advisable to start theoretical considerations of ionic melts from a regular ionic crystal. Ionic melts are formed from ionic crystals by introducing various kinds of disorder. Positional disorder is most important for spherical ions such as the halides. In this case there are isolated positional defects (Schottky defects⁵³) or atoms placed interstitially in the lattice, combined with holes (Frenkel defects⁵³). With ionic crystals, even when the ions are spherical and of the inert gas type positional disorder

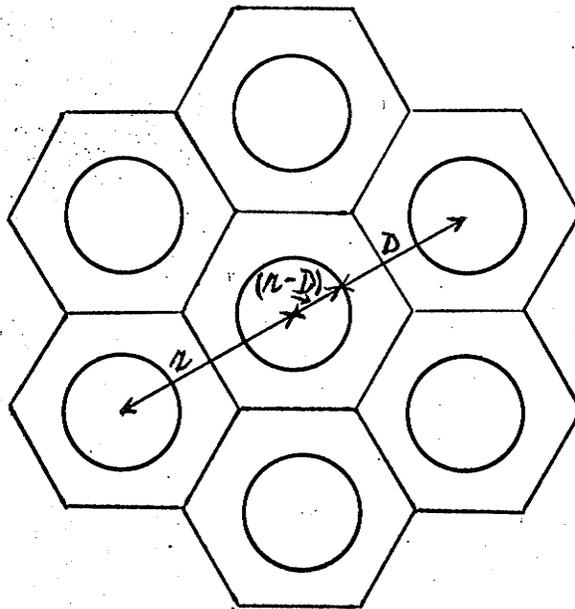


Fig. 5 Tunnel Model

includes processes other than simple randomization of position. For example when atoms are charged, paired positive or negative Schottky holes $\boxed{+ -}$ will require less energy of formation per ion than when isolated positive and negative holes are created. Positive and negative ions may form neutral pairs in the melt, with a minimum of potential energy lower than that in the completely ordered crystal.

Electrostatic Compensation in Ionic Melts

If the distances between positive and negative ions, i.e. the contact radii $(r_+)_c$ and $(r_-)_c$ are compared in the crystal with the distance $(r_+)_g + (r_-)_g$ observed for the same ion pair in the gas, there is a shrinkage in the distance $(r_+) + (r_-)$ on passing from the crystal to the gas. The extent of the shrinkage is linearly dependent on the polarisability.¹⁴ This is shown in Table II. For the same anion an increase in shrinkage is found with increasing atomic weight of the alkali metals.

TABLE II

SHRINKAGE OF ION CONTACT DISTANCE ON PASSING
FROM CRYSTAL TO GASEOUS ION PAIR IN Å (14)

	Cl	Br	I
Na	0.30	0.34	0.33
K	0.35	0.35	0.30
Rb	0.38	0.37	0.40
Cs	0.50	0.57	0.54

This shrinkage follows from the fact that in the ideal crystal lattice the electrostatic forces acting between positively and negatively charged atoms are partly compensated by the crystal symmetry. Obviously this compensation does not occur for the ion pairs in the gas. This is a typical example where the melt shows an intermediate behaviour between the crystal and the gas.

Insofar as a quasi crystalline model applies, it can be seen that ionic melts contain microregions whose densities occur greatly below and above the density of the ideal crystal lattice. Such melts may be regarded as consisting of a highly disordered, but quasi crystalline arrangement, whose defects include holes, interstitially positioned ions, paired holes and paired ions, as well as dislocations extending over more than two ions.¹⁵

In a liquid the instantaneous structure changes continually, because of thermal motions of the particles. Liquids near their freezing points still possess short range order, but have lost long range order. In other words the first coordination shell still exists, while the second or third do not.

From thermodynamic studies of molten salt mixtures a model for an ideal molten salt has been developed, which may be interpreted as one in which the anions and cations are randomly distributed among themselves, irrespective of valency, but that each anion is surrounded by cations and vice versa.

○ Anion

○ Cation

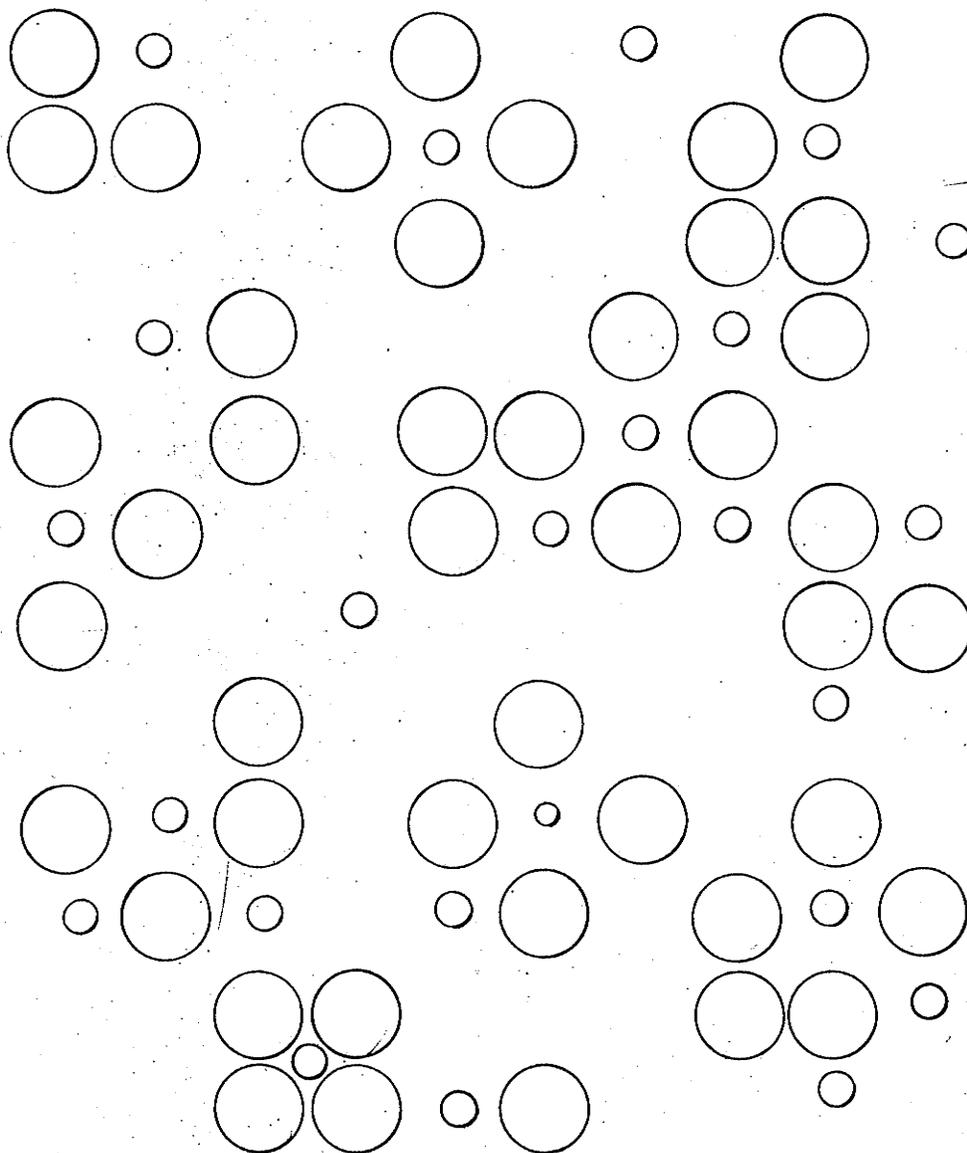


Fig. 6 Temken Model

This model, the Temken model¹⁶, is the generally accepted one.

Association Complexes in Ionic Melts

In spherical ions of groups IB or IIB in the periodic system, such as Ag^+ or Zn^{2+} , the formation of pairs and larger groups of atoms, in which bonding is actually covalent, may become important. Cations of groups IA and IIA are likely to form only σ bonds, whereas the B group can form additional π bonds. Another well known factor favouring covalent instead of ionic bonds arises from the smaller radii of the B than of the A cation. In some cases the tendency to form association complexes is so strong that it can be followed by the formation of complex ions even in dilute solution.

For example Cd halides may form covalently bonded species, such as $[\text{CdCl}]^+$ and $[\text{CdCl}_3]^-$ in dilute solution. If this complex ion formation happens in dilute solutions the tendency for anhydrous halides to form complex formation is correspondingly stronger.

Polyatomic Anions

With polyatomic anions the tendency to form ion pairs and association complexes in the melts tends to be favoured by the non-spherical shape of the ions. As with the small radius of the B group cations, the non-spherical shape of the anions favours strong local polarization. Melting points of salts with polyatomic anions tend to be much lower than

TABLE III

MELTING POINTS OF INORGANIC SALTS IN °C (14)

	Cl	I	CN	CNS	ClO ₄	ClO ₃	NO ₃	NO ₂
Li	613	446	-	237	236	127.9	255	100
Na	801	651	563	310	482	259.9	308	271
K	770	723	634	175	610	333	333	387
Rb	717	640	-	195	-	d	316	-
Cs	645	621	-	-	d	-	417	-
Ag	455	522d	320d	d	486d	210	212	140

those of salts where the anions are spherical (see Table III).

EXPERIMENTAL METHODS OF STUDYING MELTS

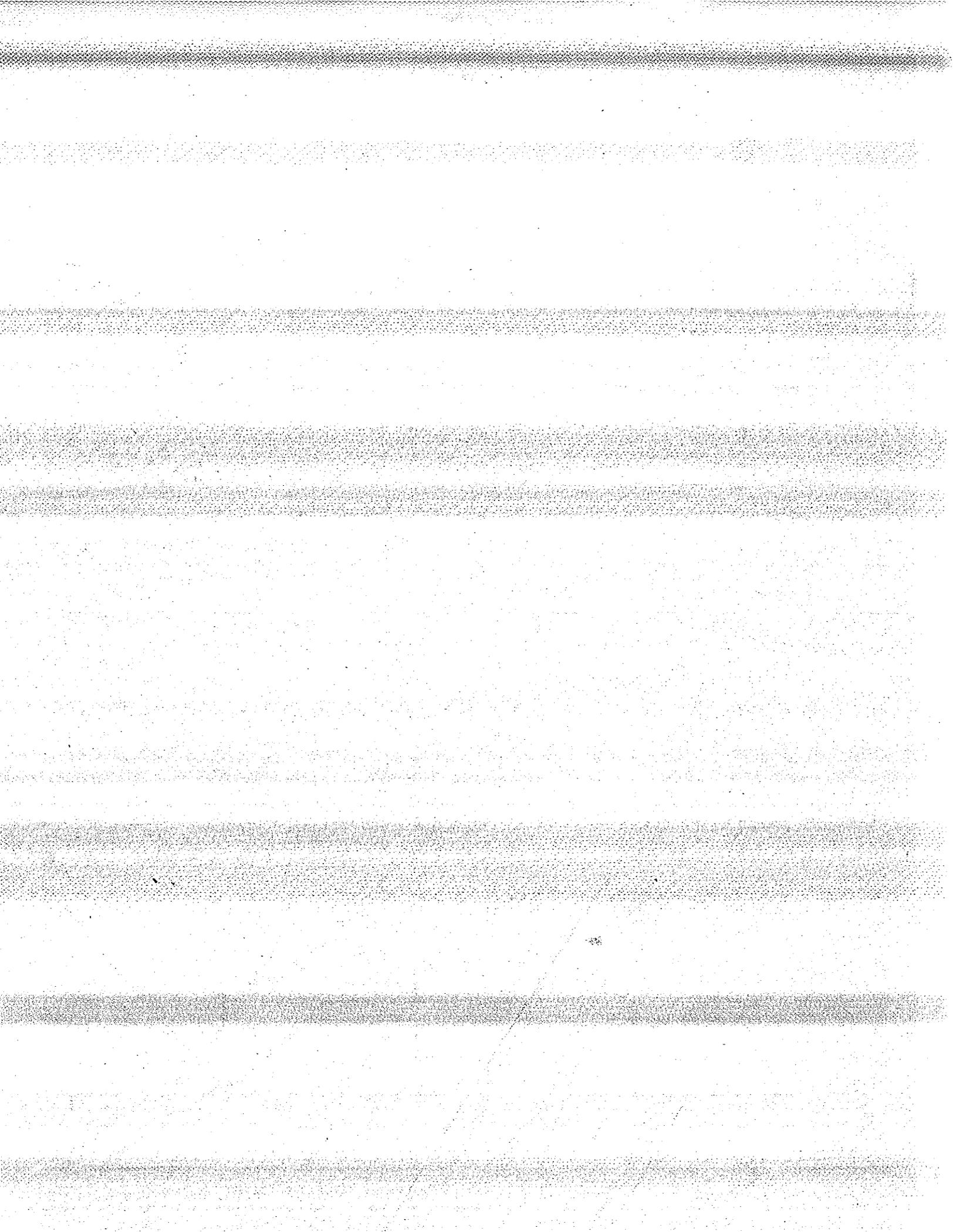
Since the melting point T_f is given by the ratio $T_f = \frac{H_f}{S_f}$, where H_f is the heat and S_f the entropy of fusion, factors such as multiple mechanism of melting that increase S_f without requiring too large an increase in H_f tend to give lower melting points.

The entropy of fusion¹⁹ is made up of contributions from various mechanisms for the increase in disorder on melting.

$$S_f = S(\text{position}) + S(\text{orientation}) + S(\text{association})$$

All ionic crystals undergo a marked increase of positional disorder on melting, hence $S(\text{position})$ always makes an important contribution to the total S_f ; for spherical ions of the inert gas type it is the major term.

$S(\text{orientation})$ is important only in non-spherical ions. Randomization of orientation may already exist in the crystal-line-state or alternatively, this randomization may occur at the melting point, as is the case in most ionic crystals. The factors that determine whether this randomization will or will not occur before the melting temperature, are still not clear. It may be expected that the more symmetrical ions such as SO_4^{2-} or NO_3^- would have lower potential barriers than the less symmetrical ions, such as SO_3^{2-} or NO_2^- but differences of



crystal structure make it difficult to predict a trend.

$S(\text{association})$. Salts with abnormally low melting points (with non-spherical anions such as ClO_3^- , NO_2^- , NO_3^- or SO_3^{2-} ¹⁴) make a large contribution to $S(\text{assoc.})$. The reason for an appreciable concentration of association complexes is usually not the same for all low melting salts but there must be a decrease in potential energy on passing from fairly random close packing of ions to the packing of microregions, called association complexes.

The positional entropy changes in low melting salts are much the same as in predominantly ionic melts, but the excess contributions to the entropy of fusion in low melting salts can be interpreted as due to the many reasons for crystal disorder or occurrence of short range low energy configurations.

CHANGE IN MOLAR VOLUME ON MELTING

Changes from one lattice type to another can account for volume changes on fusion.²⁰ If molecules rearrange themselves from a face-centered cubic to a body centered cubic lattice at constant intermolecular separations, there is an increase of 8.8 percent in molecular volume. This results is numerically sufficient to account for the increase in volume of methane and deuterio-methane on melting. But this argument is more adaptable to changes of state from one solid modification to another, than to the change of state from a solid to a liquid. In order to account for the change in

volume during fusion, Clusius and Weigand²¹ used the following argument: the arrangement of molecules in a liquid must be such as to allow a molecule to pass without great strain from one phase to another, while still being in contact with a number of neighbours. This theory accounts for volume increases on melting of the inert gas molecules.

For ionic melts the situation is considerably more complex than in argon; the model now consists of two interpenetrating lattices, namely one of anions and one of cations. X-ray²³ studies of some alkali halides show that the coordination number for the nearest neighbors is nearer to 4 or 5 than to 6 which was the case in the solid state.

The liquid structure thus contains regions of a relatively high order, ranging over several atoms in distance and as with the solid having two main kinds of positions, one for anions and one for cations.

A comparison of the entropies of fusion and volume changes of fusion for simple alkali chlorides with those for the rare gas solids shows an interesting correlation.¹⁷

TABLE IV (17)

	NaCl	KCl	Ne	Ar	Kr	Xe
S_f	3.35	3.08	3.26	3.35	3.36	3.4
T_f	1070	1074	24.6	83.6	115.9	161.3
$\Delta V_f/V_S\%$	25.6	20.2	15.3	14.4	15.2	15.1

A comparison of the entropies of fusion for potassium and sodium chlorides with solid rare gases show that the value is constant for these crystalline solids over a range of temperatures. A simple ionic model of the molten salt is thus one in which the anions and cations behave independently of each other, at least as far as entropy considerations are concerned.

Designating NaCl and KCl as normal simple ionic crystals, Ubbelohde²² proposed to take the entropy of fusion of 3.2 e.u. per gr. atom as due to positional melting. In ionic crystals the contribution of positional melting in a normal simple system (e.g. NaCl) is accompanied by an increase in the lattice defects from about 2-5 percent in the solid state to approximately 30 percent in the melt, leading to a comparatively large volume change (25 percent in NaCl).

Use of the ratio of the volumes before and after fusion also has been used as a criterion for association formation in ionic melts. If the cations and anions cluster or form chains that pack rather like in the crystalline state the ratio would be small. Where as the ratio is 20-30 percent for many halides (see Table V), for nitrates and chlorates it is in the order 1-12 percent (see Table VI). The small volume expansion on melting is usually accompanied by a low melting point for the salt. The many reasons for crystal disorder which result in lower melting points make theoretical interpretation difficult.

TABLE V
 MOLAR VOLUME EXPANSION (IN PERCENT)
 ON MELTING FOR ALKALI HALIDES²⁴

Salt	M.P., °C.	Vol. Exp.	Salt	M.P., °C.	Vol. Exp.
LiF	845	30.9	NaF	995	26
LiCl	610	24.8	NaCl	800	25.6
LiBr	550	22.7	NaBr	750	21.8
LiI	470	19.3	NaI	660	20.3
KF	856	19	RbF	775	18
KCl	772	20.2	RbCl	717	12.9
KBr	735	16.4	RbBr	680	12.8
KI	685	15.7	RbI	640	11.1

Salt	M.P., °C.	Vol. Exp.
CsF	703	14
CsCl	645	10
CsBr	636	26.8
CsI	621	28.5

TABLE VI

MOLAR VOLUME EXPANSION ON MELTING
(IN PERCENT) OF POLYATOMIC ANIONS

Salt	M.P., °C.	Vol. Exp.	Ref.
LiNO ₃	255	28.2	25, 26
NaNO ₃	308	11.0	27
KNO ₃	333	3.0	25, 26
RbNO ₃	316	- 0.23	28
Cs NO ₃	417	12	29
Ag NO ₃	212	0.7	27
LiClO ₃	127	6.41	
NaClO ₃	260	12.73	
KClO ₃	356	10	30, 31
KSCN	175.1	5.4	29
Na ₃ AlF ₆	1013	20.3	32, 33

CHAPTER II

NATURE OF THE PRESENT INVESTIGATION

The present project followed logically as a continuation of the work of Campbell and Nagarajan^{34,35} and Campbell and Williams.^{36,37} Previous work (which consisted of viz. density, viscosity measurements) was done on mixtures of lithium chlorate and lithium nitrate, in other words on mixtures with a common cation. The reason for the present investigation is to compare molar volume changes of lithium chlorate-lithium nitrate mixtures with lithium chlorate-sodium chlorate mixtures. The present work consisted in the addition of sodium chlorate instead of lithium nitrate to lithium chlorate, thus giving a mixture with a common anion. Mixtures of sodium chlorate with small additions of lithium chlorate were also investigated. Finally this investigation included a determination of the change of molar volume on melting of pure lithium chlorate and of pure sodium chlorate. The melting point of lithium chlorate is 127.9°C and of sodium chlorate 259.9°C , thus both belong to the relative low melting group of salts.

Unfortunately, lithium chlorate-sodium chlorate mixtures decompose readily. Decomposition of pure sodium chlorate occurs at approximately 15°C above its melting point. By working rapidly and by limiting the range of temperature in which determinations were carried out, the decomposition

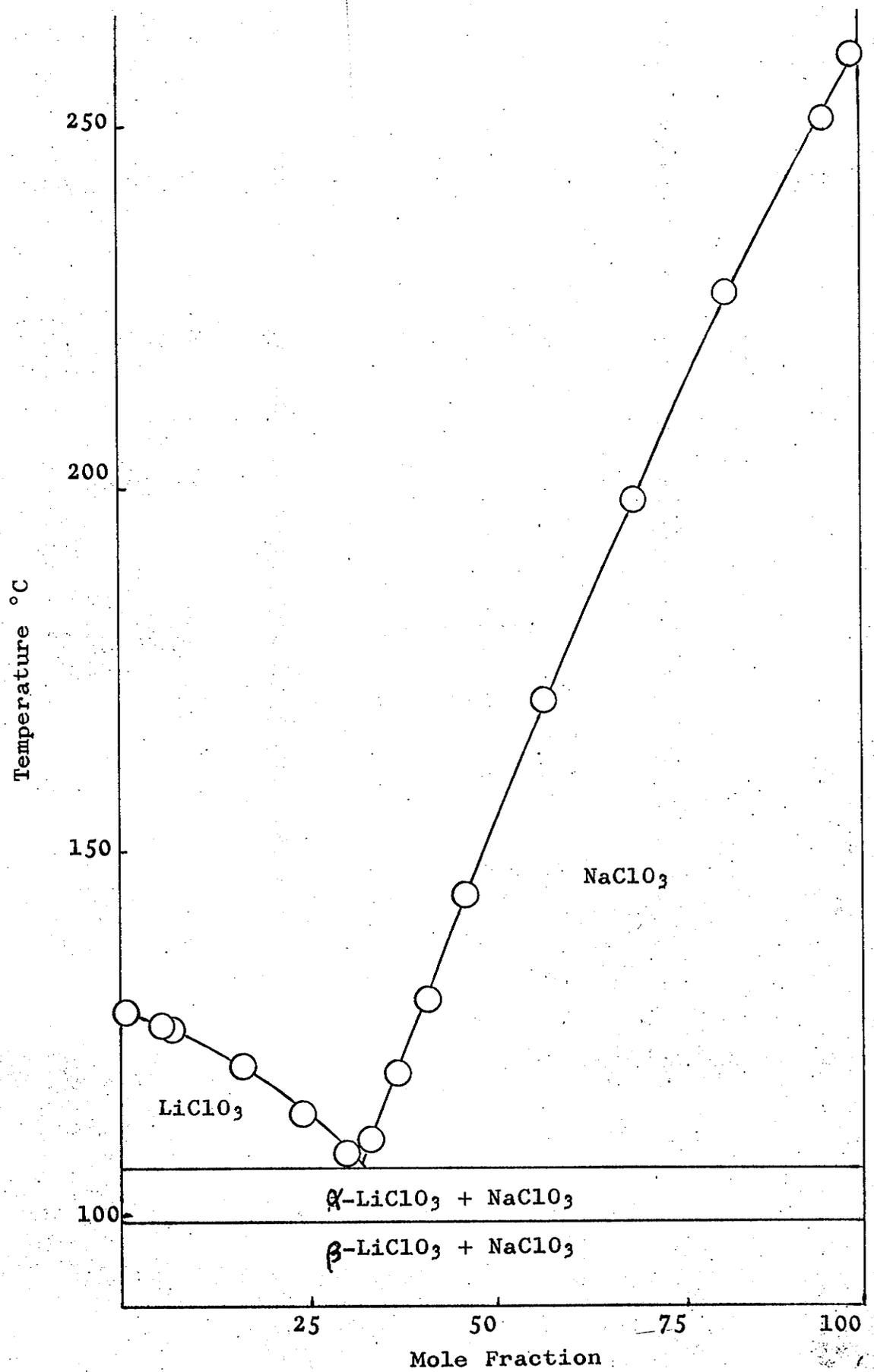
could be avoided, although measurements were still restricted either to mixtures near pure lithium chlorate or to mixtures near pure sodium chlorate.

The short range in which densities of molten lithium chlorate-sodium chlorate mixtures were measured decreased somewhat the accuracy of the determinations. Because of the above mentioned reasons, it was impossible to cover the complete range of density measurements from pure lithium chlorate to pure sodium chlorate.

In addition to the already mentioned determinations, densities of solid lithium chlorate and of solid sodium chlorate were determined in the range from room temperature up to near the melting point. By extrapolation to the melting point of the solid, the change in molar volume on melting could be calculated for both chlorates. The changes in molar volume on melting of the pure salts and of the mixtures may indicate changes in structure.

The system lithium chlorate-sodium chlorate is represented in Fig. 7³⁸. This system exhibits a simple eutectic at 107.1°C with an eutectic composition of 34.55 weight percent sodium chlorate (0.38 mole fraction lithium chlorate). Lithium chlorate has a transition point in contrast to sodium chlorate. The transition $\alpha\text{LiClO}_3 \rightleftharpoons \beta\text{LiClO}_3$ occurs at 99.1°C.⁴⁰

In some cases X-ray measurements of lattice spacings can be extrapolated to the melting point.³⁹ Pre-

Fig. 7 Phase Diagram for the System LiClO_3 - NaClO_3 

melting effects are however not considered and the volume changes calculated tend to be too large.¹⁴ X-ray measurements on lithium chlorate have been carried out only in the β -region.⁴⁰ For sodium chlorate⁴¹ and potassium chlorate³⁰ X-ray measurements at high temperatures have been made.

Fig. 8 shows the dimensions of the sodium chlorate molecule and its arrangement in the unit cell. Sodium chlorate crystallizes in the cubic tetrahedral class. X-ray crystal structure studies show⁴⁵ that this salt has four molecules per unit cell. A plot of resistance vs temperature showed that the crystal approaching its melting point becomes highly ionized.⁴² A thermodifferential analysis⁴³ showed no changes in crystal structure or decomposition of sodium chlorate below its melting point.

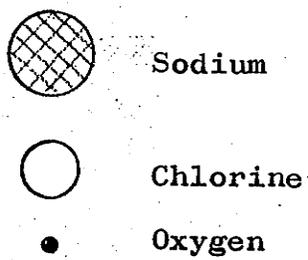
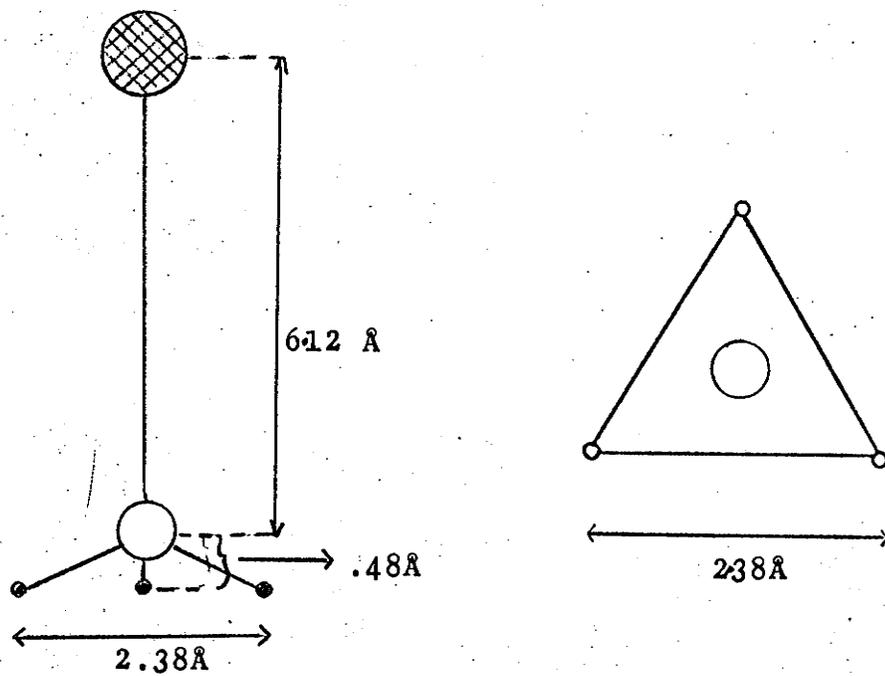


Fig. 8 Arrangement of Atoms in Sodium Chlorate Molecule

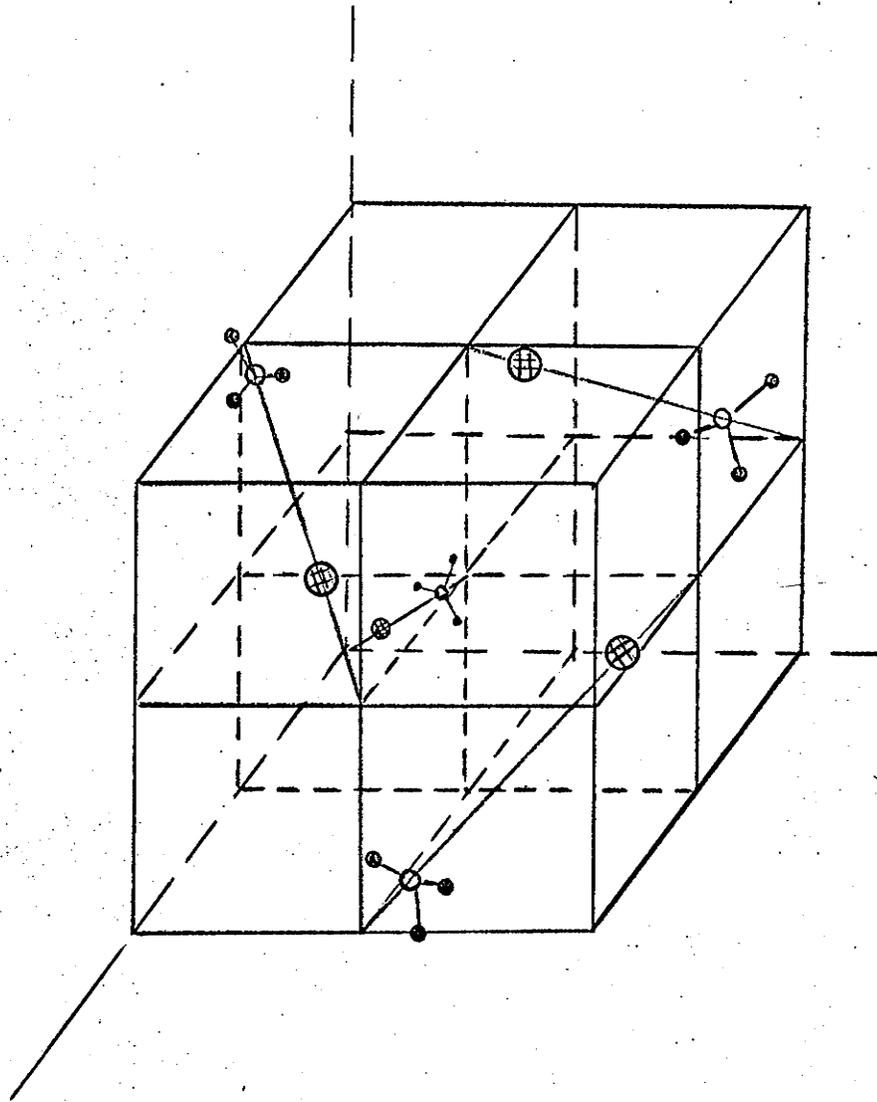


Fig. 8A Arrangement of Sodium Chlorate Molecules in Unit Cell

CHAPTER III

EXPERIMENTAL TECHNIQUES

A. PURITY OF MATERIALS

Lithium chlorate was prepared by the method used by Campbell and Griffiths.⁴⁰ It consisted of mixing equimolecular quantities of barium chlorate (Matheson, Coleman and Bell) and lithium sulphate (Fischer certified reagent). After precipitation the barium sulphate was filtered off. The solution of lithium chlorate was then titrated with lithium sulphate or barium chlorate until the solution was equimolar.

The solution was distilled under vacuum at $\pm 60^{\circ}\text{C}$ until a very viscous liquid was obtained. Next followed crystallization. After filtration of the mother liquid the lithium chlorate crystals were dried under vacuum. The lithium chlorate crystals were repeatedly pulverised in a dry box during the vacuum drying process. The melting point of lithium chlorate was found to be 127.9°C .⁴⁰ Griffiths reported 127.6°C . The sodium chlorate (Fischer certified reagent) was dried for at least forty-eight hours at 120°C before using.

B. THERMOSTAT

The relatively low temperature at which the present study was conducted made it possible to employ dilatometric techniques. For the same reason Dow Corning silicone oil fluid 500 was used as a bath liquid. A rectangular Pyrex glass

jar (ca. 1 gallon capacity) was used as a thermostat. The jar was surrounded by a double-walled wooden box and an outer metal casting. The space between the double walls was filled with Vermiculite. A glass window made it possible to look into the bath, which was illuminated from behind.

A copper constantan thermocouple (3 junctions) was used as temperature measuring device. The thermocouple was calibrated with pure boiling water (with necessary pressure correction) and the melting points of pure tin (231.9°C), pure bismuth (271.3°C) and pure cadmium (320.9°C) as fixed points. Thermocouple E.M.F.'s were measured with a Tinsley Potentiometer which is capable of measuring to 1 microvolt. Fluctuations in temperature did not exceed $\pm 0.2^{\circ}\text{C}$ at 260°C .

C. PYCNOMETER AND DILATOMETER

For the solid densities a weld-pycnometer with a volume of ca. 25 ml was used. It was approximately half filled with solid. Because of the large volume increase of the α -lithium chlorate smaller amounts (ca. 6 grms) were weighed for the range 100°C to 120°C . For the molten salts a special type dilatometer was used.

The dilatometers were made of pyrex glass and essentially consisted of bulbs of ca. 10 ml capacity sealed to stems of 1 mm capillary. This capillary was precision dis-

drilled capillary tube with a reported tolerance of ± 0.002 mm (Corning Glass). Four fine circular marks ca. 20 mm apart, were made on the stem to facilitate accurate measurement of the liquid level inside the capillary. A slanted side arm terminating in a bulb of ca. 3 ml capacity was attached very near the top and served as an overflow for excess melt. Fig. 10 is an illustration of the dilatometer used.

The volumes of the pycnometers and dilatometers were measured by calibration with redistilled mercury.⁴⁶ (Johnson, Matthey and Mallory). The volume of the pycnometer was plotted against temperature. In the case of the dilatometer the meniscus level of the mercury column inside the capillary was adjusted to coincide with one of the marks on the stem. This procedure was repeated for each of the four marks and at four different temperatures. The plots of volume vs temperature were essentially linear. With this method of calibration it was not necessary to apply corrections for expansion of the glass or nonuniformity of the bore.

The densities of silicone oil 550 (Dow Corning) used as inert liquid were determined over the whole temperature range from 25°C to 260°C. For a certain amount of solid salt the volume increase could be easily calculated from the known volume of the pycnometer and the density of the silicon oil.

Due to the extremely hygroscopic nature of anhydrous lithiumchlorate special precautions were necessary to handle

this salt. All manipulations such as filling dilatometers and pycnometers were carried out in a drybox. In the case of the solids, after the pycnometer had been filled, a small amount of oil was added and the pycnometer connected to a vacuum pump. Regular tapping was also necessary to eliminate air bubbles. Altogether the pycnometer was connected for at least ten hours to the vacuum pump. No signs were detectable of the oil attacking the solid or dissolving it. The pycnometer was kept in the oil bath for at least one hour to ensure proper temperature equilibrium with the bath. Special precautions were taken to make sure that the immersed height of the dilatometer in the bath was the same for all temperatures. After removal from the bath the pycnometer was allowed to cool and weighed. At every temperature at least two weighings were made.

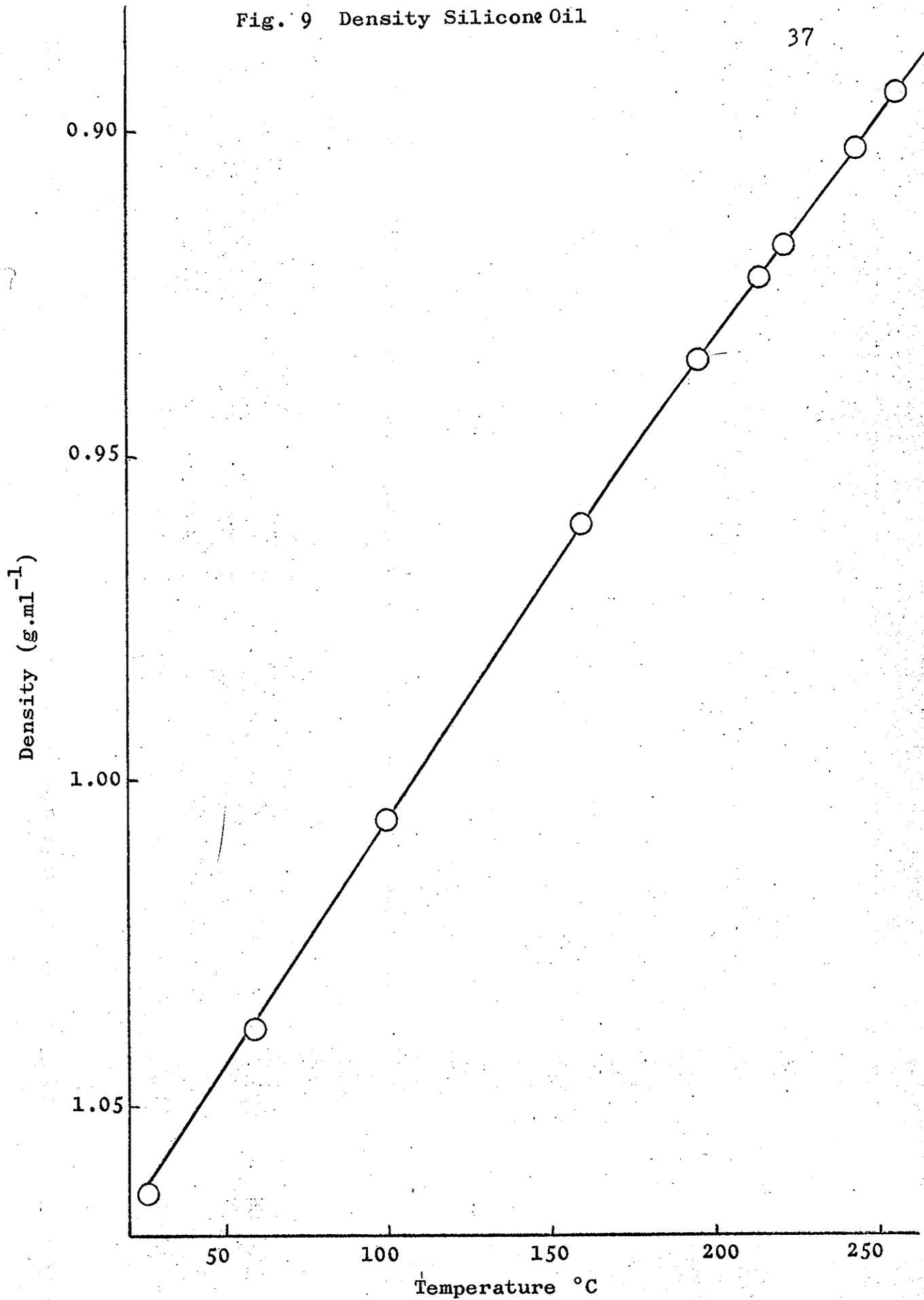
A specially designed transferring apparatus³⁹ was used in the case of molten salts (see Fig.11). It consisted of a pyrex glass tube separated into two compartments by a fitted glass disc of medium porosity. A side arm, carrying a stop-cock was attached to the tapering end of the tube to facilitate evacuation of the assembly. The transfer tube was sealed to the top of the dilatometer as indicated in Fig.11. The top compartment of the transfer tube was loaded with a sufficient amount of anhydrous lithium chlorate-sodium chlorate mixture (separately prepared), evacuated and placed in the oil bath. The bulb gradually filled itself with the

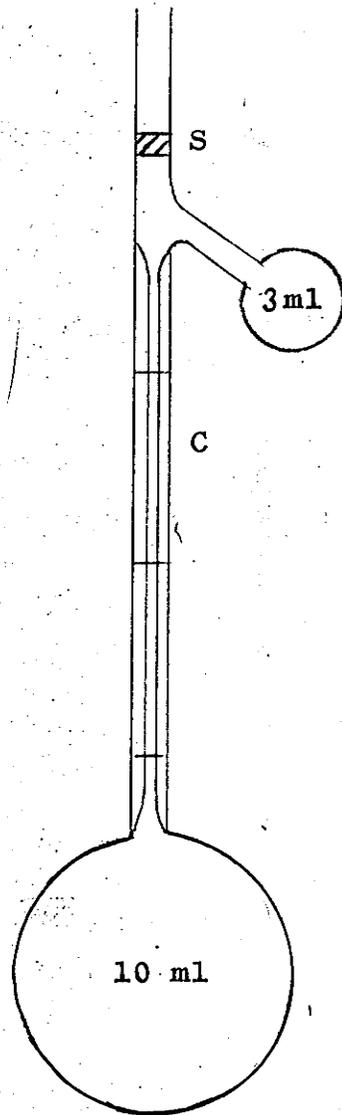
FIG. 9

Plot of density of silicone oil
vs. Temperature.

Fig. 9 Density Silicone Oil

37





C - 1 mm capillary
S - fritted glass disc

Fig. 10 Dilatometer

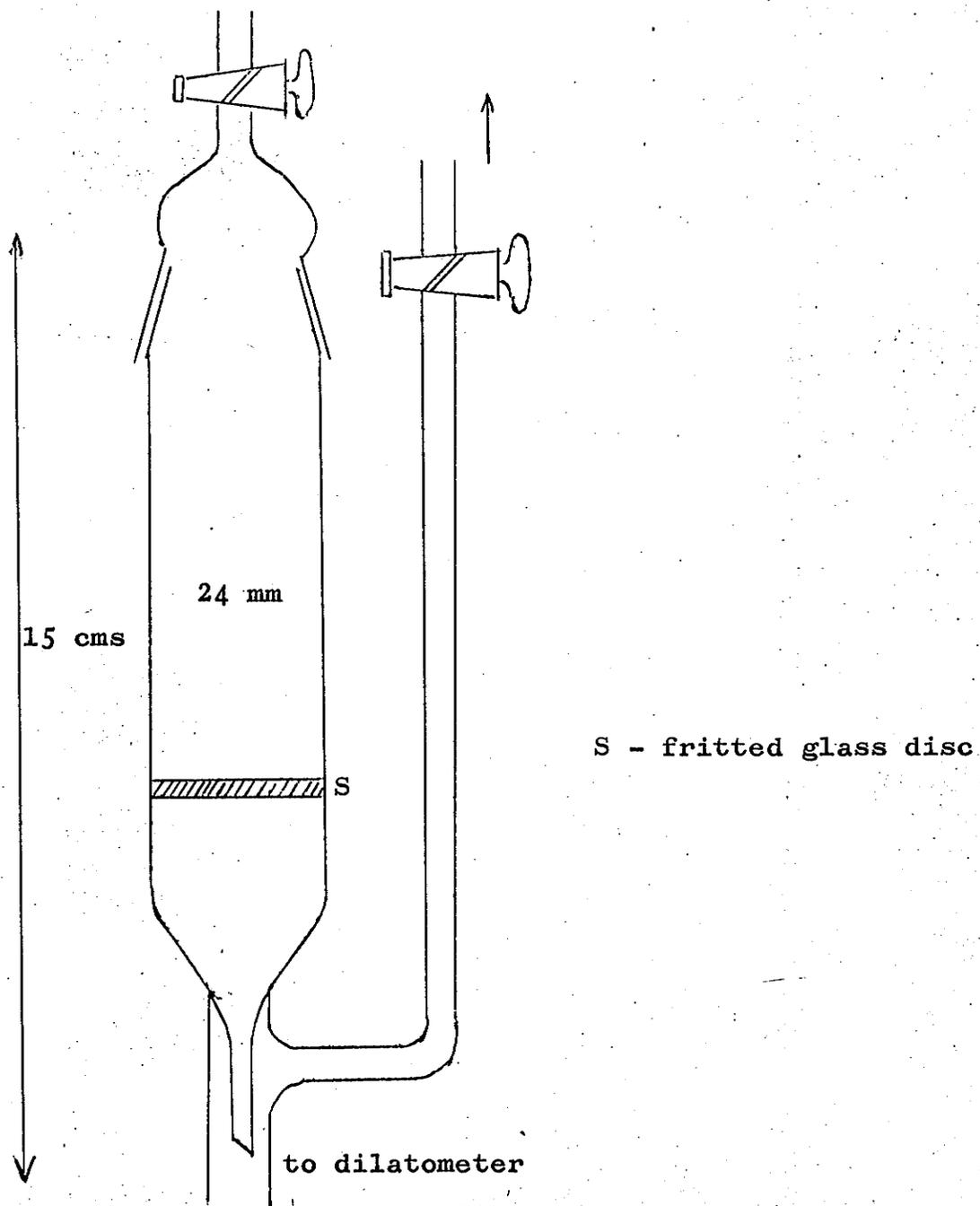


Fig. 11 Transfer Tube

molten salt. After the desired amount had melted the top part was sealed off and measurements of the salt levels in the capillary started.

By means of a cathetometer the heights of the molten salt levels could be measured at temperature intervals of approximately 3°C. Using the calibration graph, the distance between the marks and the height of the meniscus level above a certain mark on the stem, the volume of the liquid was calculated by an interpolation technique. The cathetometer was capable of measuring heights correct to 0.002 cm.

The weight of the specimen alone was obtained after cleaning the dilatometer, breaking it and weighing the cleaned broken pieces.

A careful estimate of the over-all precision of the method showed that the maximum possible error in the determination of density amounted to ± 0.0004 gr/ml or to 0.02 %.

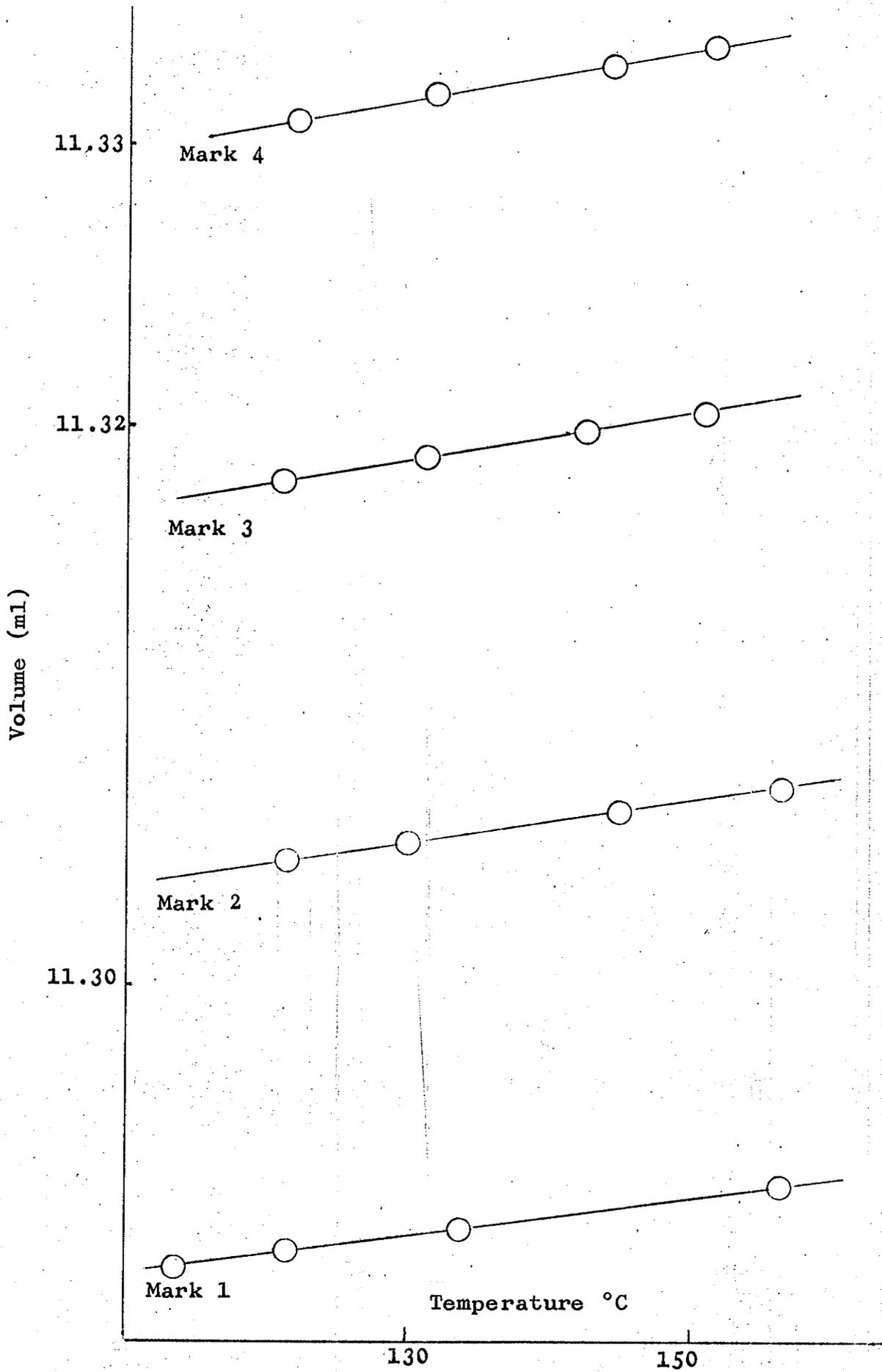
TABLE VII
DENSITY OF SILICONE OIL AT DIFFERENT TEMPERATURES

Temperature C	Density (gr/ml)
25.0	1.064
60.0	1.039
98.3	1.006
158.8	0.960
194.8	0.935
214.0	0.923
221.2	0.918
243.8	0.903
254.8	0.893

FIG. 12

Calibration plots for dilatometer.

Fig. 12 Calibration Plot for Dilatometer



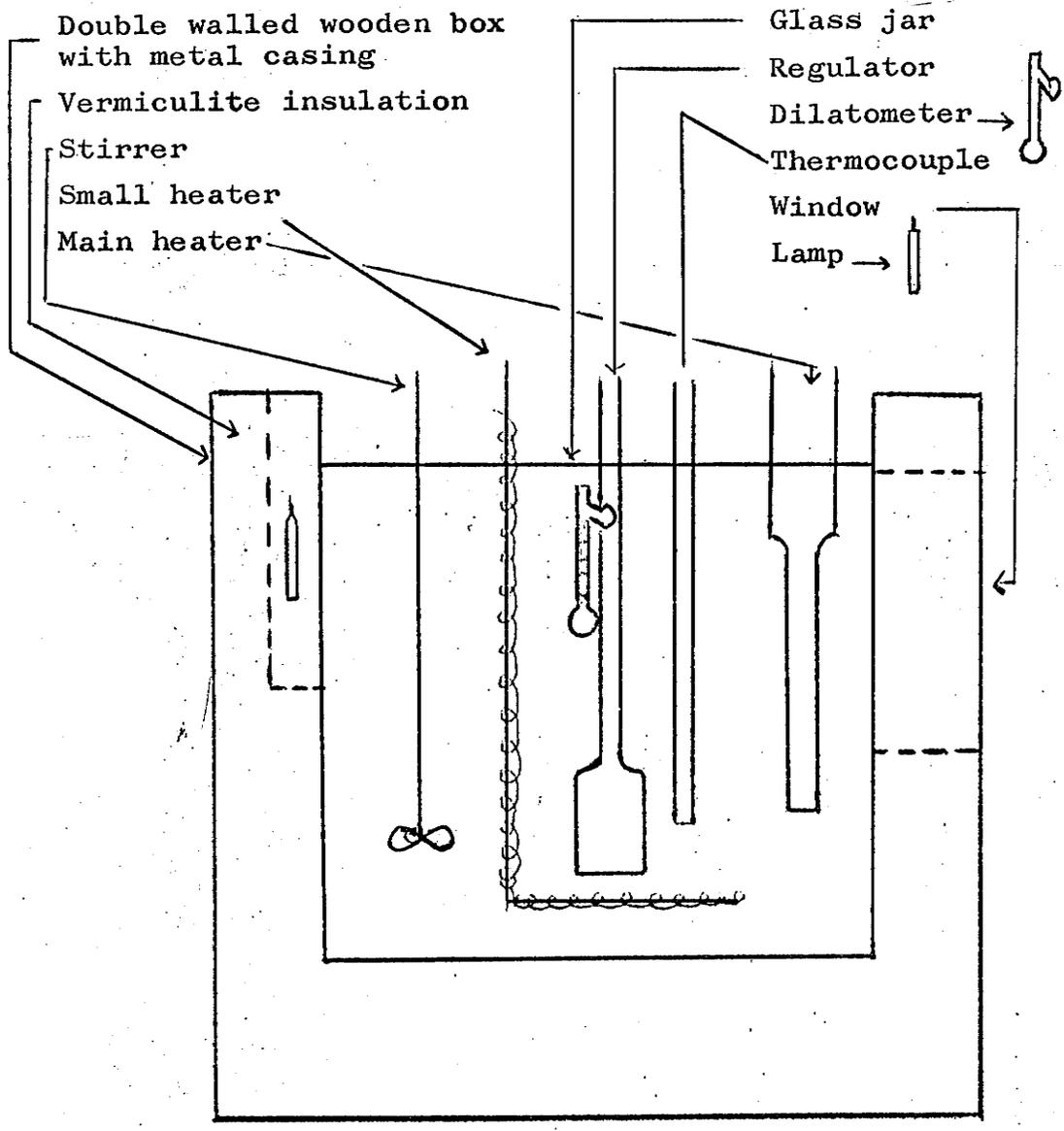


Fig. 12a Silicone Oil Thermostat

CHAPTER IV

RESULTS

No data were found in the literature for the density of either solid lithium chlorate or sodium chlorate up to the melting point. Tables VIII, IX and X give the densities and molar volumes of the two salts obtained in this research.

In the case of sodium chlorate and β -lithium chlorate the best straight line is calculated. In the case of α -lithium chlorate a plot of molar volume against temperature gave the solid volume at the melting point.

Figures 13 and 14 give respectively a plot of density vs. temperature, molar volume vs. temperature of sodium chlorate. Figure 15 gives a plot of molar volume vs. temperature of α - and β -lithium chlorate. Finally, Figure 16 gives the molar volume of α -lithium chlorate vs. temperature.

Because lithium chlorate can exist in two enantiotropic forms, hysteresis effects made density measurements below 108°C inaccurate hence measurements below 108°C are not recorded.

From X-ray measurements⁴¹ the lattice constant was calculated as a function of temperature. From these data the density of solid sodium chlorate can be calculated as a function of temperature. Sodium chlorate crystallizes in the cubic system. The density is related to the lattice parameter by the following relation⁴⁴:

$$d = \frac{\text{Mol. weight} \times \text{number of molecules per unit cell}}{\text{Avogadro number} \times \text{volume unit cell}}$$

The volume of the unit cell is taken to be the cube of the lattice parameter (a^3). The calculated and observed volumes are given in Table XI.

Figure 17 gives a plot of the density vs. temperature of sodium chlorate from X-ray data. Table XII gives the molar volumes of lithium chlorate and sodium chlorate at their melting point and the ratio $\Delta V_f/V_s$, where ΔV_f is the change in volume at the melting point and V_s the volume of the solid at the melting point.

Tables XIII to XVIII give the densities and molar volumes of five molten lithium chlorate and sodium chlorate mixtures and pure molten sodium chlorate.

The molar volumes of pure lithium chlorate and mixtures of 0.0859 and 0.2032 mole fractions sodium chlorate are plotted in Fig.18.

In the case of the pure salts the molar volume is given by $V = \frac{M}{d}$. The following relation was employed for the calculation of molar volumes of mixtures:

$$V = \frac{n_1 M_1 + n_2 M_2}{d}$$

where n_1 and n_2 are the mole fractions and M_1 and M_2 are the molecular weights of lithium chlorate and sodium chlorate.

The "Best" straight line was calculated by the method of least square analysis from the experimental data.

Isothermal sections from the basic molar volume data were obtained in order that the dependence of molar volume on composition might be interpreted. For the lithium chlorate side of the system temperature intervals of 10°C were chosen, the same temperature intervals were chosen for the sodium chlorate-lithium chlorate mixture on the high temperature side. Results are given in Tables XIX and XX. Illustrations of these isothermals are given in Figures 19 and 20.

The dependence of molar volume on the mole fraction of sodium chlorate and the dependence of molar volume on the mole fraction of lithium chlorate were found to satisfy the quadratic equation $V = a_0 + a_1 n_2 + a_2 n_2^2$, where a_0 , a_1 and a_2 are constants³⁴. The data were fitted to a "best" curve by the method of least squares.

Table XXII gives the constants a_0 , a_1 and a_2 for lithium chlorate with sodium chlorate additions. Table XXIII gives the constants for sodium chlorate with additions of lithium chlorate. The values of the coefficients of thermal expansion (α) were calculated by suitably transforming the equation $V = a + bT$ into the more common form $V = V_0(1 + \alpha t)$ where "t" is in centigrade scale. These values are given in table XXI for pure lithium chlorate, all the mixtures and finally for pure sodium chlorate.

TABLE VIII
 DENSITIES AND MOLAR VOLUME OF NaClO_3 (SOLID)

Temperature °C	Density (gr/ml)	Molar Volume (ml)
25.0	2.487	42.809
60.0	2.472	43.065
84.8	2.461	43.254
96.1	2.455	43.358
96.8	2.454	43.381
121.0	2.445	43.539
124.5	2.441	43.610
132.0	2.440	43.617
138.4	2.436	43.701
144.8	2.434	43.728
190.1	2.414	44.092
208.5	2.405	44.265
214.0	2.402	44.311
235.1	2.393	44.492
248.3	2.388	44.571
249.4	2.386	44.610
252.0	2.385	44.625

Equation for "best straight line": $V = 42.592 + 0.008t$

TABLE IX
DENSITY AND MOLAR VOLUMES OF SOLID α -LiClO₃

Temperature °C	Density (gr/ml)	Molar Volume (ml)
108.0	2.303	39.260
112.0	2.302	39.272
114.0	2.301	39.295
117.0	2.296	39.378
117.3	2.298	39.337
119.1	2.296	39.377
121.0	2.284	39.575
122.0	2.275	39.730
124.0	2.256	40.071

TABLE X
DENSITIES AND MOLAR VOLUMES OF β -LiClO₃

Temperature °C	Density (gr/ml)	Molar Volume (ml)
25.0	2.596	34.822
35.0	2.592	34.882
81.5	2.576	35.098
85.5	2.571	35.160
95.0	2.567	35.222
110.0	2.563	35.265

Equation for the "best straight line": $V = 34.688 + 0.005t$

FIG. 13
Density of pure solid NaClO_3
as a function of Temperature.

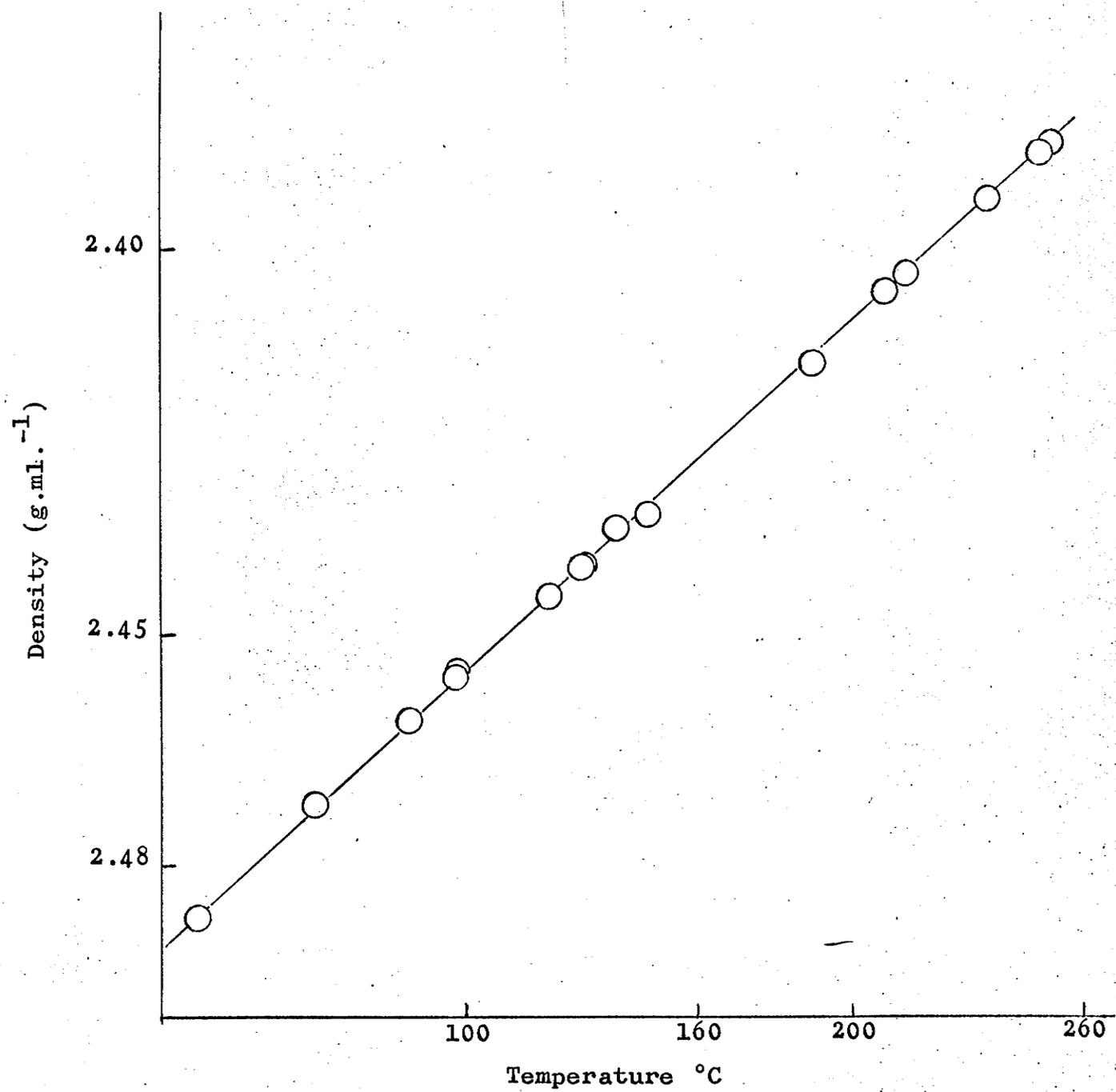
Fig. 13 Density of Pure NaClO_3 

FIG. 14

Plot of molar volume of NaClO_3
vs. Temperature.

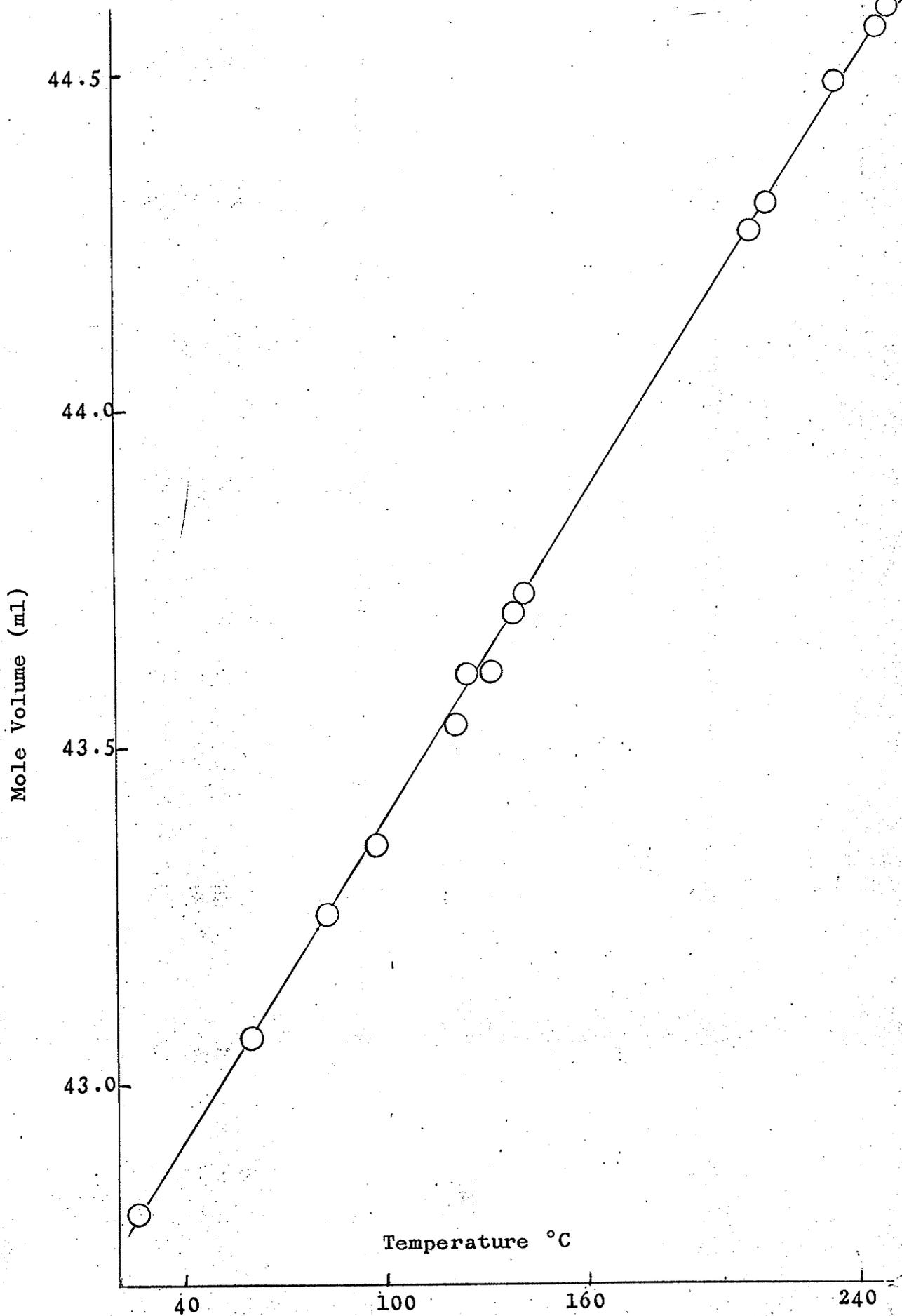
Fig. 14 Molar Volume of NaClO_3 

FIG.15

Molar volume of LiClO_3
vs. Temperature.

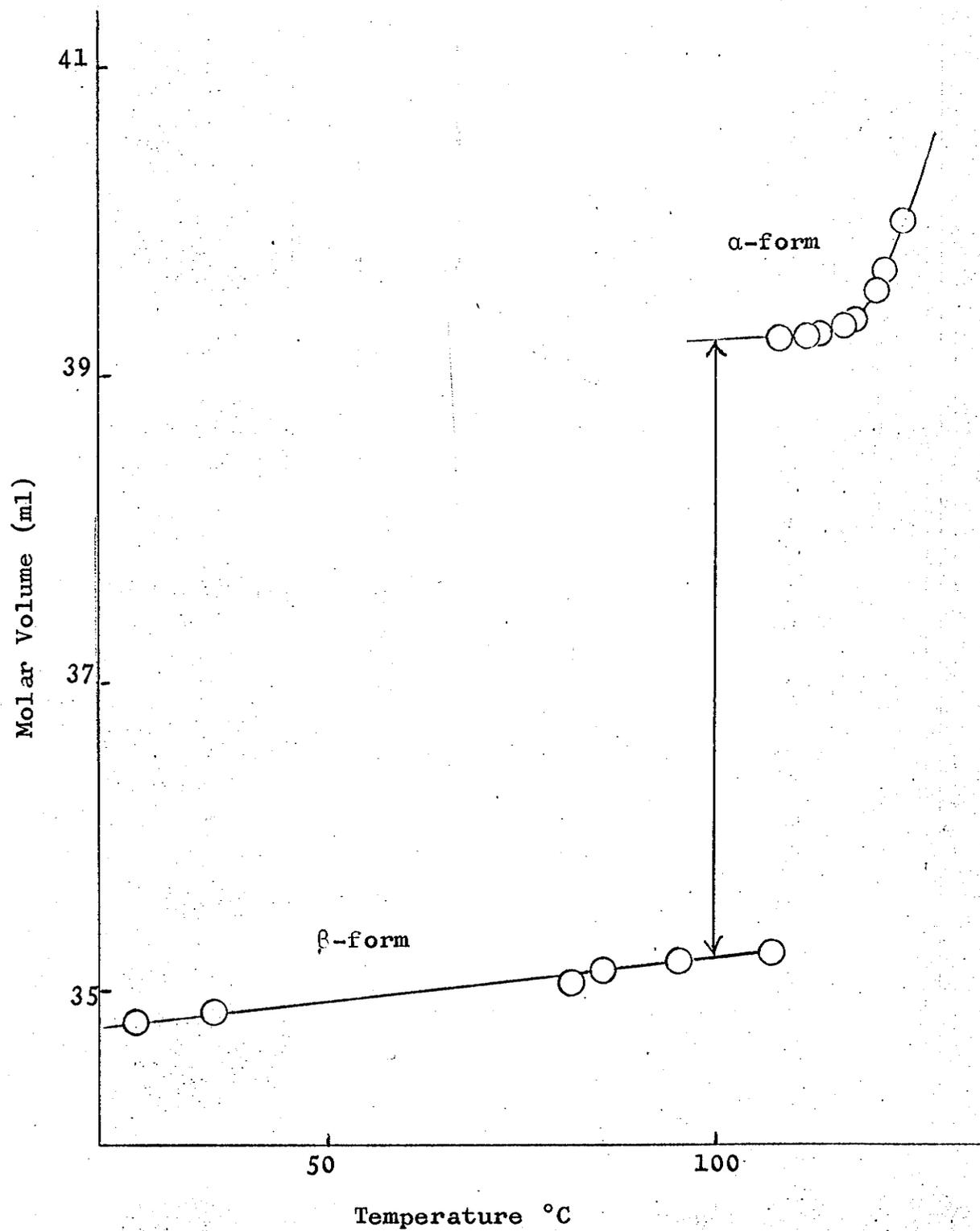


Fig. 15 Molar Volume of LiClO_3

FIG. 16

Molar volume of solid α -LiClO₃
vs. Temperature.

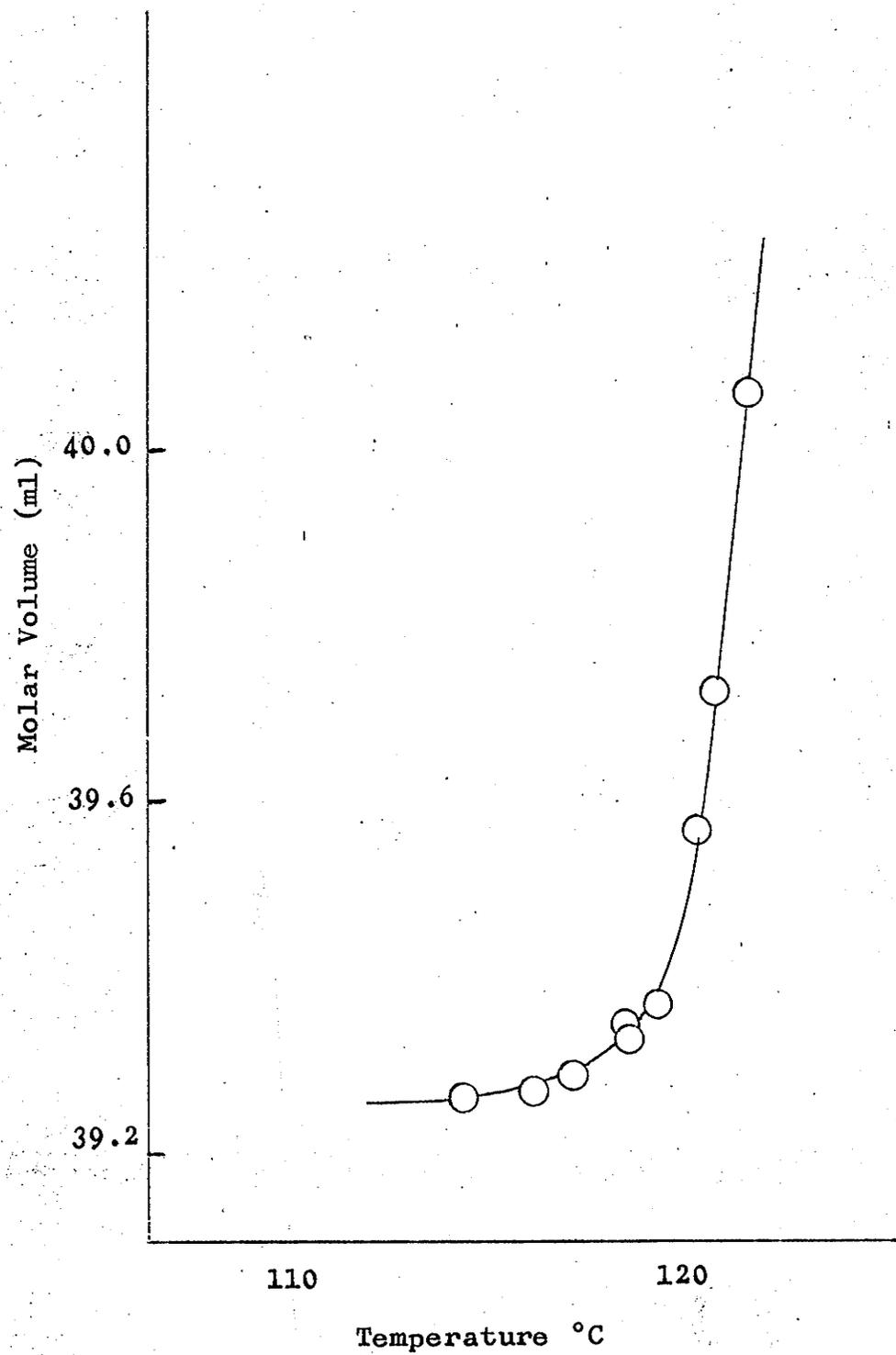
Fig. 16 Molar Volume of α -LiClO₃

TABLE XI

MOLAR VOLUMES OF SOLID SODIUM CHLORATE CALCULATED FROM
X-RAY DATA COMPARED WITH OBSERVED VALUES (41)

Temperature °C	Lattice constant (Å)	Molar Volume (calc.)	Molar Volume (obs.)
15	6.5726	42.759	42.712
31	6.5770	42.847	42.840
32	6.5774	42.852	42.848
82.5	6.5926	43.151	43.252
127.5	6.6060	43.415	43.612
180.0	6.6261	43.811	44.032
227	6.6475	44.237	44.408
232	6.6491	44.269	44.448

FIG.17

Plots of densities of NaClO_3 obtained
from dilatometric and X-ray measurements.

Fig. 17 Density of NaClO_3 Obtained from Dilatometric (○) and X-ray (⊗) Measurements.

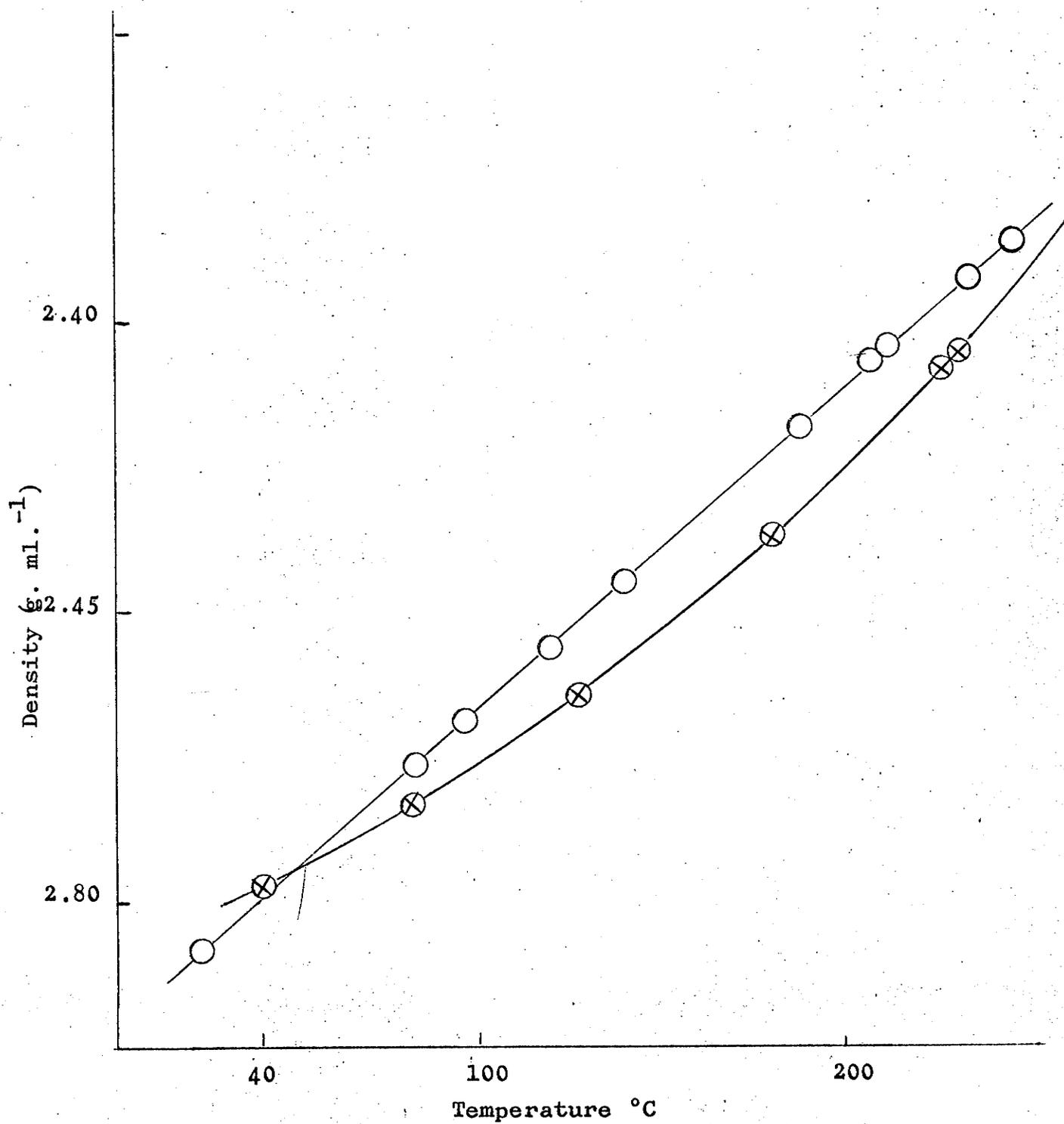


TABLE XII
MOLAR VOLUME CHANGE AT MELTING POINT

Substance	$\frac{\Delta V_f}{V_s} \%$	Method
LiClO ₃	6.41	Dilatometric
NaClO ₃	12.73	Dilatometric
	12.88	X-ray diffraction

Change in volume for LiClO₃ at transition point.

$$\frac{\Delta V_{tr}}{V} = 11.38$$

TABLE XIII

DENSITY AND MOLAR VOLUME OF $\text{NaClO}_3\text{-LiClO}_3$ MIXTURES $n_2 = \text{MOLE FRACTION NaClO}_3:0.0859$ Freezing point: 124.8°C

Temperature $^\circ\text{C}$	Density (gr/ml)	Molar Volume (ml)
132.2	2.102	43.655
133.3	2.102	43.667
135.4	2.099	43.715
136.5	2.099	43.728
138.4	2.097	43.763
139.5	2.096	43.786
141.3	2.095	43.813
143.4	2.093	43.849
144.8	2.092	43.872

Equation for "best straight line": $V = 41.345 + 0.017t$

TABLE XIV

DENSITY AND MOLAR VOLUME OF NaClO_3 - LiClO_3 MIXTURES N_2 = MOLE FRACTION NaClO_3 : 0.2032Freezing Point: 117.7°C

Temperature $^\circ\text{C}$	Density (gr/ml)	Molar Volume (ml)
126.3	2.121	44.149
127.5	2.120	44.170
129.1	2.119	44.204
130.4	2.118	44.224
132.1	2.116	44.258
133.6	2.115	44.291
134.8	2.114	44.310

Equation for "best straight line": $V = 41.728 + 0.019t$

TABLE XV

DENSITY AND MOLAR VOLUME OF NaClO_3 - LiClO_3 MIXTURES n_2 = Molar fraction NaClO_3 : 0.7034Freezing point : 198.1°C

Temperature $^\circ\text{C}$	Density (gr/ml)	Molar Volume (ml)
202.0	2.112	48.138
204.0	2.110	48.186
206.0	2.108	48.237
207.5	2.108	48.250
210.5	2.105	48.314
213.0	2.103	48.360

Equation for "best straight line": $V = 44.146 + 0.020t$

TABLE XVI

DENSITY AND MOLAR VOLUME OF NaClO_3 - LiClO_3 MIXTURES $n_2 =$ MOLE FRACTION NaClO_3 : 0.7569Freezing Point: 211.4°C

Temperature $^\circ\text{C}$	Density (gr/ml)	Molar Volume (ml)
216.5	2.113	48.527
218.1	2.112	48.559
220.0	2.111	48.582
222.0	2.109	48.632
223.5	2.108	48.653
225.5	2.106	48.692
227.5	2.104	48.734

Equation for "best straight line": $V = 44.468 + 0.019$

TABLE XVII

DENSITY AND MOLAR VOLUME OF NaClO_3 - LiClO_3 MIXTURES $n_2 =$ MOLE FRACTION NaClO_3 : 0.8641Freezing Point: 234.8°C

Temperature $^\circ\text{C}$	Density (gr/ml)	Molar Volume (ml)
243.5	2.110	49.425
245.7	2.108	49.472
247.8	2.106	49.507
249.0	2.105	49.542
250.5	2.104	49.568
252.5	2.102	49.613
254.5	2.100	49.646

Equation for "best straight line": $V = 44.471 + 0.020t$

TABLE XVIII

DENSITY AND MOLAR VOLUME OF PURE NaClO_3 Freezing Point: 259.9°C

Temperature $^\circ\text{C}$	Density (gr/ml)	Molar Volume (ml)
261.8	2.106	50.543
264.6	2.104	50.600
266.5	2.102	50.651
268.5	2.100	50.685
269.4	2.099	50.704

Equation for "best straight line": $V = 44.981 + 0.021t$

FIG. 18
Molar volume vs. Temperature for
 LiClO_3 - NaClO_3 mixtures.

Fig. 18 Molar Volume vs. Temperature for $\text{LiClO}_3\text{-NaClO}_3$ Mixtures

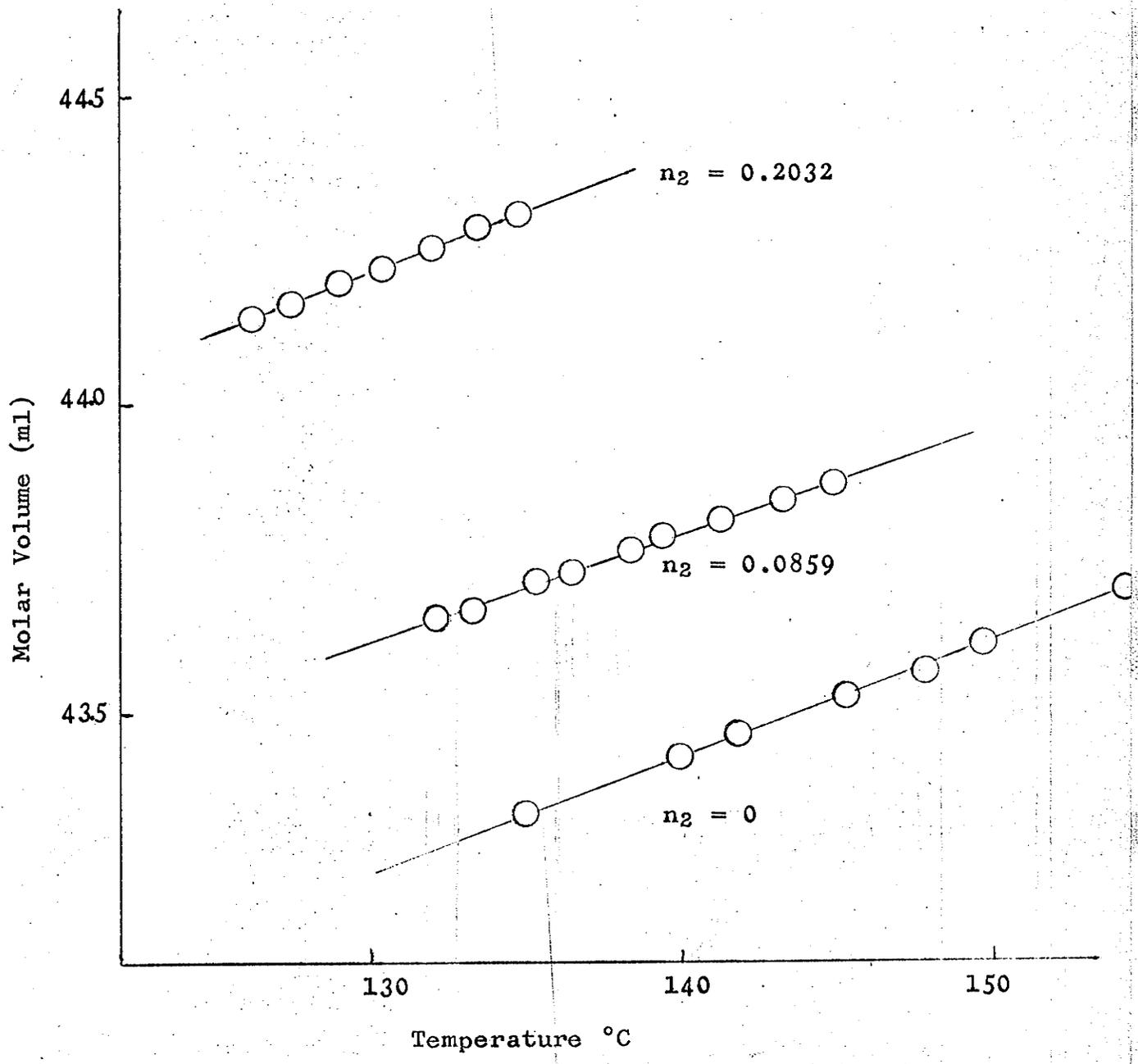


TABLE XIX
ISOTHERMAL MOLAR VOLUME AS A FUNCTION OF
MOLE FRACTION OF NaClO_3

Temperature °C	$n_2=0.0000$	$n_2=0.0859$	$n_2=0.2032$
116.9	42.985	43.379	43.952
126.9	43.177	43.553	44.164
136.9	43.369	43.727	44.356
146.9	43.561	43.901	44.548

TABLE XX
ISOTHERMAL MOLAR VOLUME AS A FUNCTION OF
MOLE FRACTION OF LiClO_3

Temperature C	$n_2=0.0000$	$n_2=0.1359$	$n_2=0.2431$	$n_2=0.2966$
270	50.651	49.871	49.598	49.546
260	50.441	49.671	49.408	49.346
250	50.231	49.471	49.218	49.146
240	50.021	49.271	49.028	48.946

TABLE XXI
COEFFICIENT OF THERMAL EXPANSION FOR
NaClO₃-LiClO₃ MIXTURES
 $V=V_0(1+\alpha t)$

Mole Fraction NaClO ₃	V ₀ (ml)	$\alpha \times 10^4$
0.0000	40.747	4.71
0.0859	41.345	4.21
0.2032	41.727	4.60
0.7034	44.145	4.46
0.7569	44.468	4.20
0.8641	44.470	4.49
1.0000	44.980	4.60

TABLE XXII

VALUES OF CONSTANTS IN THE EQUATION FOR THE "BEST"
CURVE BY THE METHOD OF LEAST SQUARES.

PURE $\text{LiClO}_3 + \text{NaClO}_3$

$$V = a_0 + a_1 n_2 + a_2 n_2^2$$

Temp. °C	a_0	a_1	a_2
126.9	43.178	3.973	4.347
136.9	43.370	3.589	6.231
146.9	43.561	3.282	7.753

TABLE XXIII

VALUES OF CONSTANTS IN THE EQUATION FOR THE "BEST"
CURVE BY THE METHOD OF LEAST SQUARES.

PURE $\text{NaClO}_3 - \text{LiClO}_3$

$$V = a_0 + a_1 n_2 + a_2 n_2^2$$

Temp. °C	a_0	a_1	a_2
270	50.656	-7.609	13.181
260	50.444	-7.444	12.776
250	50.234	-7.293	12.422
240	50.022	-7.133	12.038

FIG. 19

Molar volume isotherms of LiClO_3
with small additions of NaClO_3 .

Fig. 19 Molar Volume Isotherms for
 $\text{LiClO}_3 + \text{NaClO}_3$ Mixtures

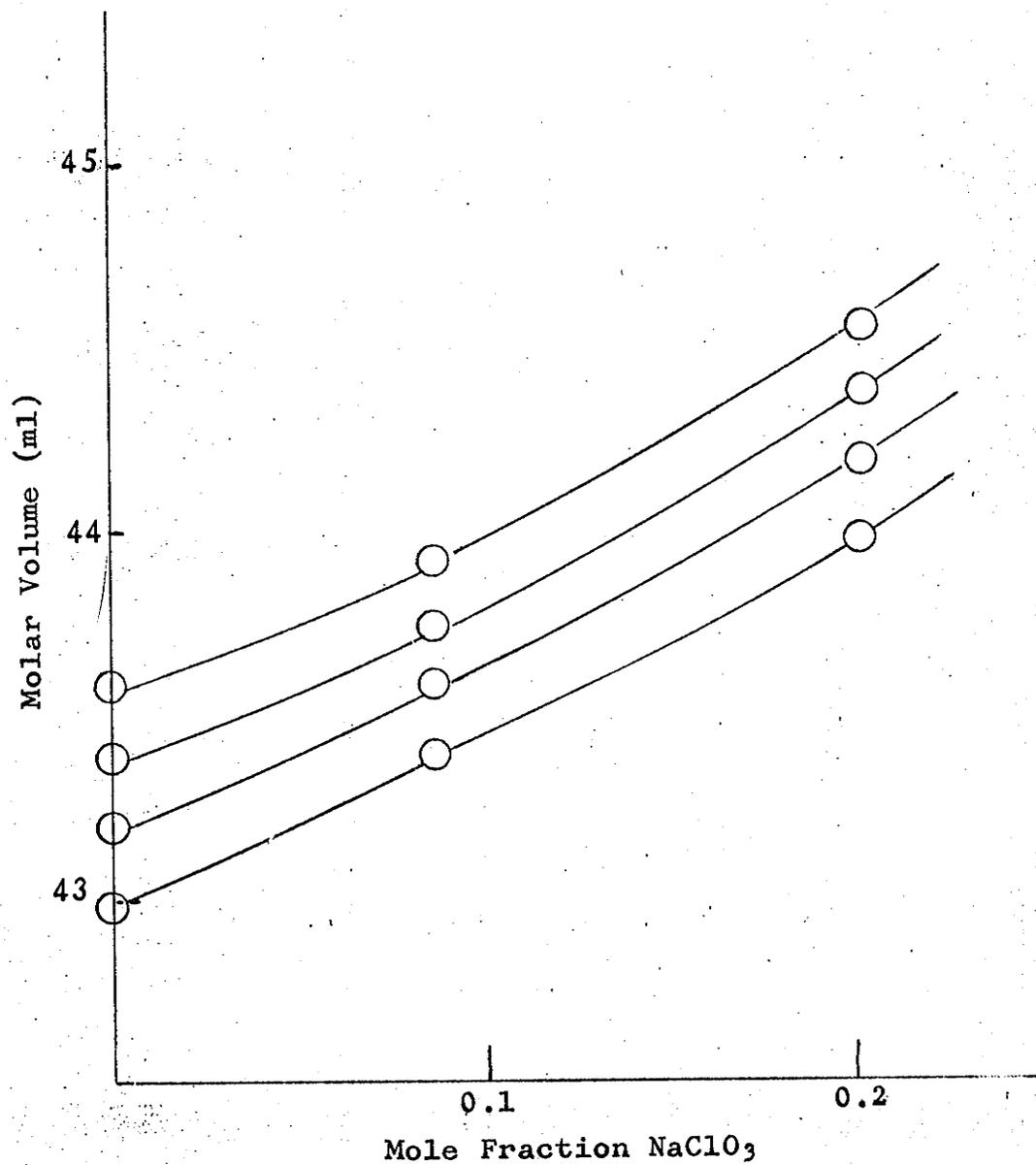
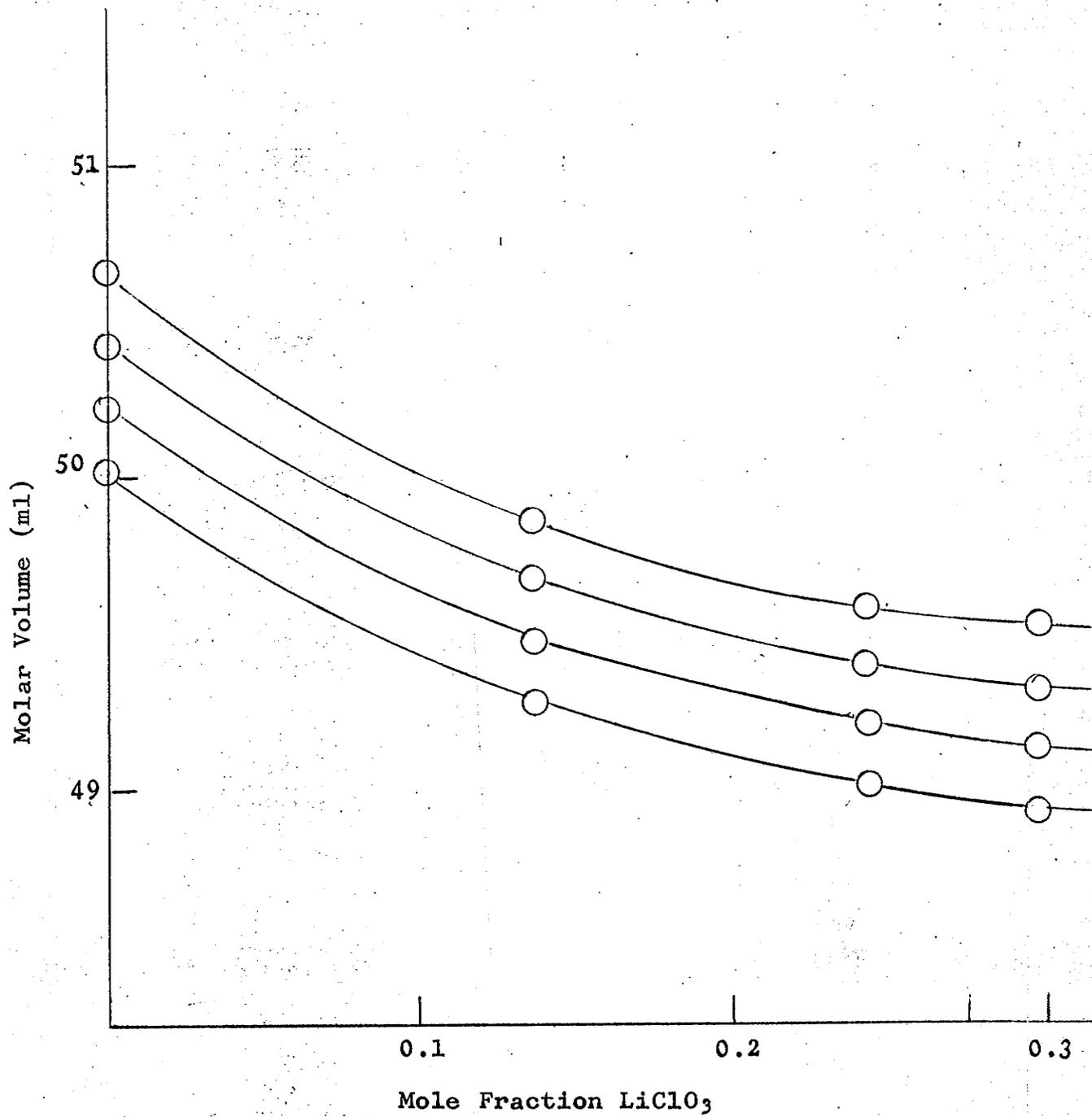


FIG. 20

Molar volume isotherms of NaClO_3
with small additions of LiClO_3 .

Fig. 20 Molar Volume Isotherms
for $\text{NaClO}_3 + \text{LiClO}_3$ Mixtures



CHAPTER V
DISCUSSION

Disintegrating 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 polarisability of the atoms or ions present may become apparent on fusion. The constitution of a melt does not depend solely upon the crystal lattice structure of the solid salt.

The temperature of fusion, percentage volume increase on fusion, coefficient of expansion of the liquid, latent heat of fusion and entropy of fusion are given in Table XXIV for a number of salts. The magnitude of S_f , the change of entropy on fusion, is similar for almost all substances (5-12 e.u.).

The latent heat of fusion³⁴ of lithium chlorate was found to be 2.47 kcal mole⁻¹. From the freezing point 127.9° C the entropy of fusion results as 6.1 e.u. Similarly for sodium chlorate the latent heat of fusion⁴⁷ of 5.4 kcal mole⁻¹ results in an entropy of fusion of 9.9 e.u.

The percentage volume increase on fusion is found to be 6.41 and 12.7 for lithium chlorate and sodium chlorate respectively. A larger increase in volume on fusion is usually accompanied by a larger heat of fusion and a larger entropy of fusion (see Table XXIV). The same rule

TABLE XXIV

PHYSICAL PROPERTIES FOR SOME TYPICAL MOLTEN SALTS

Substance	Melting Point °C	$\frac{\Delta V_f}{V_s} \%$	$\alpha \times 10^{-4}$ deg. ⁻¹	H _f kcal mole ⁻¹	S _f e.u.	Molar Volume ml mole ⁻¹
LiClO ₃	127.9	6.41	4.71	2.47	6.1	43.90
LiNO ₃	255	21.4	3.31	6.06	12.1	39.60
LiCl	613	24.8	2.96	-	-	28.98
NaClO ₃	259.9	12.7	4.60	5.4	9.8	51.46
NaNO ₃	307	10.7	3.76	3.86	6.4	45.29
NaCl	808	25	3.63	7.22	6.7	39.12
KClO ₃	368	10	3.59	-	-	64.40
KNO ₃	334	3.2	3.99	4.0	4.0	55.31
KCl	776	20.2	3.98	6.41	6.2	50.93
HgCl ₂	279	-	6.81	-	-	-

applies to the nitrates. The fact that the volume change on fusion for lithium chlorate and sodium chlorate is so much less than in the case of sodium chlorate can be explained by the restricted orientation of the Li^+ and ClO_3^- ions in lithium chlorate and Na^+ and ClO_3^- ions in sodium chlorate. This means that ionic association occurs. Completely free rotation of the ClO_3^- ions would require an enormous volume increase. Similarly for free rotation of NO_3^- ions in sodium nitrate the volume increase would be at least 37% larger than the actual value⁴⁸.

From a knowledge of the density and thus the molar volume change with temperature information on the change in the structure of the melt is gained. Some approximate relations between the molar volume and the ionic character of a melt have been given by Drossbach:⁴⁹

(a) Other factors being equal, molten covalent compounds, owing to weak intermolecular forces, have larger molar volumes than those of ionic melts.

(b) For the same reason, the expansivity of covalent melts is greater than of ionic melts.

(c) Melts with different stages of dissociation from the ionic to the covalent state are possible. For ideal molten salt mixtures plots of molar volume vs. molar composition at constant temperature are linear. The "ideal" behaviour indicates that the free volume varies linearly

with composition. Systems with both positive and negative deviations from ideal behaviour are known, wherein the free volume is greater or smaller than that predicted by simple mixture theory. The changes of partial molar volume with varying composition may indicate whether any pronounced interaction is taking place or not. Molar volume isotherms for both pure sodium- and lithium chlorates and their respective mixtures show a negative deviation from ideal behaviour (Figs. 19 and 20).

It is generally accepted that salts with non-spherical polyatomic anions, such as nitrates and chlorates possess a more covalent character than salts with spherical anions (e.g. halides). Klemm's rule⁴⁹ states that in general covalent melts possess higher molar volume than ionic melts owing to weaker intermolecular forces prevalent among salts of the first type. An arbitrary reference temperature has been adopted for comparison of molar volumes of different salts. This arbitrary temperature is chosen as corresponding to a temperature 10% above the melting point in degrees Kelvin.⁵⁰ The melting point itself is not suitable because of the possibility of incipient lattice formation immediately above the melting point. The molar volumes of lithium chlorate, sodium chlorate and potassium chlorate increases steadily from 43.90, 51.46 to 64.40 cm³ mole⁻¹ (Table XXIV).

Jaffe and van Artsdalen⁵¹ noted that the coefficient of expansion, α , for the chlorides, bromides and iodides of Cs, Rb and K were almost equal, whereas for the lithium halides

were 30% lower, The coefficient of expansion for LiClO_3 , $4.71 \times 10^{-4} \text{ deg}^{-1}$, is larger than that of NaClO_3 ($4.60 \times 10^{-4} \text{ deg}^{-1}$) and KClO_3 ($3.59 \times \text{deg}^{-1}$) (Table XXIV), and also larger than that of group I halides. These values however do not compare 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; this shows that coulombic forces determine the general properties of the three alkali chlorates, though the melt of lithium chlorate may be more covalent in character than molten KClO_3 and NaClO_3 .

Papousek and Kucirek⁵² considered the compressibility (β_T), coefficient of volume expansion (α_T) and heat capacity (C_p or C_v) as being made up of two terms; one being the geometrical contribution and the other a structural contribution:

$$\begin{aligned} \beta_T &= \beta_S + \beta_g & C_p &= (C_p)_S + (C_p)_g \\ \alpha_T &= \alpha_S + \alpha_g & C_v &= (C_v)_S + (C_v)_g \end{aligned}$$

where the subscripts S and g stand for the structural and geometric contributions respectively. The geometric and part of each of the properties discussed is taken to arise solely from changes in the intermolecular (or inter-ionic) distances due to changes in pressure and volume and temperature.

The structural parts of the compressibility, heat capacity and coefficient of volume expansion can occur as second

derivatives of entropy (as functions of p , T) and therefore, represent the simultaneous increase or decrease in the molecular regularity of the liquid with changes in pressure, volume and temperature. In the case of unoriented liquids, Papousek and Kucirek found the structural contribution to be generally greater than the geometrical contribution. With an increase in the orientation (or orderliness) in the liquid, the value of the structural contribution is found to decrease and in the extreme case of an exceptionally densely packed, well ordered liquid (e.g. mercury) they found that the structural contribution is even lower than the geometric part. In the case of mixtures of liquids, these considerations lead to useful data on the structural changes taking place during the process of mixing.

This treatment may be applied to changes in molar volume with composition and temperature. When it is applied to the system molten lithium- and sodiumchlorate mixtures it is necessary to choose a reference state. The most appropriate one is the melting point of the pure salt. This assumption necessarily implies that the basic lattice of the reference state predominates over the entire range of temperature and composition involved. In other words no major breakdown of the basic reference state lattice may occur in the region of investigation.

Molar volumes of mixtures can be considered to be a function of two variables, temperature and composition, $V = f(T, n_2)$, where n_2 is the mole fraction of solute: in

the present investigation sodium chlorate and lithium chlorate, respectively. The change in molar volume dV from the volume in the reference state is then defined by the equation:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{n_2} dT + \left(\frac{\partial V}{\partial n_2}\right)_T dn_2$$

where $(\partial V/\partial T)_{n_2}$ is the rate of change in molar volume with temperature at fixed composition and $(\partial V/\partial n_2)_T$ is the rate of change in molar volume with composition at constant temperature. Let

$$V_{n_2} = \left(\frac{\partial V}{\partial T}\right)_{n_2}$$

$$V_T = \left(\frac{\partial V}{\partial n_2}\right)_T, \quad \text{then}$$

$$dV = V_{n_2} dT + V_T dn_2$$

The values of V_{n_2} at different compositions were obtained by differentiation of the equations of the "best" straight lines given in Table XIII to XVIII and are tabulated in Table XXV. With sodium chlorate as solute V_{n_2} remains almost constant, whereas with lithium chlorate as solute, V_{n_2} decreases slightly.

The isothermal molar volumes have been found to satisfy the equation

$$V = a_0 + a_1 n_2 + a_2 n_2^2$$

where n_2 is the mole fraction of sodium chlorate added to pure lithium chlorate. The same quadratic equation was used by Campbell³⁵ for lithium chlorate-sodium chlorate mixtures.

Partial differentiation of V gives:

$$\left(\frac{\partial V}{\partial n_2} \right) = V_T = a_1 + 2a_2 n_2$$

From the values of a_1 and a_2 in Table XXII the values of V_T have been calculated at temperatures selected at random and are shown in Fig. 21 as a function of composition. V_T is tabulated in Table XXVI and it is apparent that V_T values for isothermal additions of sodium chlorate to lithium chlorate increase steadily. Similarly the V_T values with lithium chlorates as solute are tabulated in Table XXVII and show the same trend, as in the case of sodium chlorate as solute.

In order to calculate dV (total molar volume change) the term $(\partial V/\partial T)_{n_2} dT$ or $V_{n_2} dT$ is obtained and given for both solutes in Table XXVIII. In order to calculate the second term in the expression for dV it is necessary to calculate the integral:

$\int_{T_{MP}}^T V_T dT$, where V_T is a function of n_2 . The values of the above integrals can be obtained by graphical integration of Fig. 21 and Fig. 22, using appropriate limits. The isotherms in Fig. 21 and Fig. 22 cross each other. This crossing might indicate a complete change in structure of the two original pure salts. It is significant that this crossover occurs more rapidly with sodium chlorate as solute, than with lithium chlorate as solute viz. about 0.1 mole fraction sodium chlorate in lithium chlorate as compared to about 0.21 mole fraction lithium chlorate in sodium chlorate. A possible explanation for this fact

may be that the bigger sodium ion (0.96\AA) disrupts the original lattice of the pure lithium chlorate more rapidly at smaller concentrations than the smaller Li^+ ion (0.60\AA) disrupts the sodium chlorate lattice.

Table XXIX shows the temperature and composition part of the total change in volume dV for sodium chlorate as solute. Table XXX shows the same contributions for lithium chlorate as solute. These values are plotted in Fig. 23 and Fig. 24 respectively as functions of the composition of the melt. Inspection of Fig. 23 shows:

(a) The temperature contribution ($V_n dT$) dominates in the entire region of temperature and composition studied. This contribution increases considerably with temperature increase, which probably reflects the process of breakdown of compact configurations.

(b) The composition contribution ($V_T dn_2$) shows small positive contributions for small additions of sodium chlorate, higher sodium chlorate concentrations however give rise to negative contributions.

(c) The total volume change in the studied region is mainly determined by the temperature contribution.

Inspection of Fig. 24 shows:

(a) The temperature contribution ($V_n dT$) is dominant and determines mainly the total volume change.

(b) The composition contribution ($V_T dn$) remains almost constant over the entire region studied.

The dV referred to in this discussion is the change in volume with respect to the reference state and not the excess volume.

TABLE XXV

VALUES OF V_{n_2} AT DIFFERENT COMPOSITIONS FOR
LITHIUM CHLORATE-SODIUM CHLORATE MIXTURES

n_2 is mole fraction of sodium chlorate

n_2	V_{n_2}
0.0000	0.019
0.0859	0.017
0.2032	0.019

n_2 is mole fraction of lithium chlorate

n_2	V_{n_2}
0.0000	0.021
0.1359	0.020
0.2431	0.019
0.2966	0.020

TABLE XXVI

VALUES OF V_T AT DIFFERENT TEMPERATURES FOR LITHIUM CHLORATE
SODIUM CHLORATE MIXTURES

n_2 = mole fraction of sodium chlorate

Temperature °C	$n_2=0.000$	$n_2=0.0859$	$n_2=0.2032$
126.9	3.973	4.719	5.739
136.9	3.589	4.659	6.121
146.9	3.282	4.613	6.432

TABLE XXVII

VALUES OF V_T AT DIFFERENT TEMPERATURES FOR SODIUM CHLORATE
LITHIUM CHLORATE MIXTURES

n_2 = mole fraction of lithium chlorate

Temperature °C	$n_2=0.000$	$n_2=0.1359$	$n_2=0.2431$	$n_2=0.2966$
270	-7.609	-4.027	-1.201	+ 0.209
260	-7.444	-3.972	-1.233	+ 0.134
250	-7.293	-3.917	-1.254	+ 0.075
240	-7.133	-3.862	-1.281	+ 0.007

TABLE XXVIII

 $V_{n_2} dT$ CONTRIBUTION TO THE TOTAL CHANGE IN MOLAR VOLUME

Mole Fraction NaClO ₃	t°C	$V_{n_2} dT$	Mole Fraction NaClO ₃	t°C	$V_{n_2} dT$
$n_2=0.0000$	126.9	-0.019	$n_2=0.0000$	240	+0.414
	136.9	+0.172		250	+0.207
	146.9	+0.364		270	-0.207
$n_2=0.0859$	126.9	-0.017	$n_2=0.1359$	240	+0.400
	136.9	+0.156		250	+0.200
	146.9	+0.331		270	-0.200
$n_2=0.2032$	126.9	-0.019	$n_2=0.2431$	240	+0.374
	136.9	+0.172		250	+0.187
	146.9	+0.364		270	-0.187
			$n_2=0.2966$	240	+0.394
				250	+0.197
				270	-0.197

FIG. 2I

**Plot of V_T against Composition
for pure LiClO_3 - NaClO_3 mixtures.**

Fig. 21 Plot of V_T Against Composition of Pure LiClO_3 and NaClO_3 Mixtures

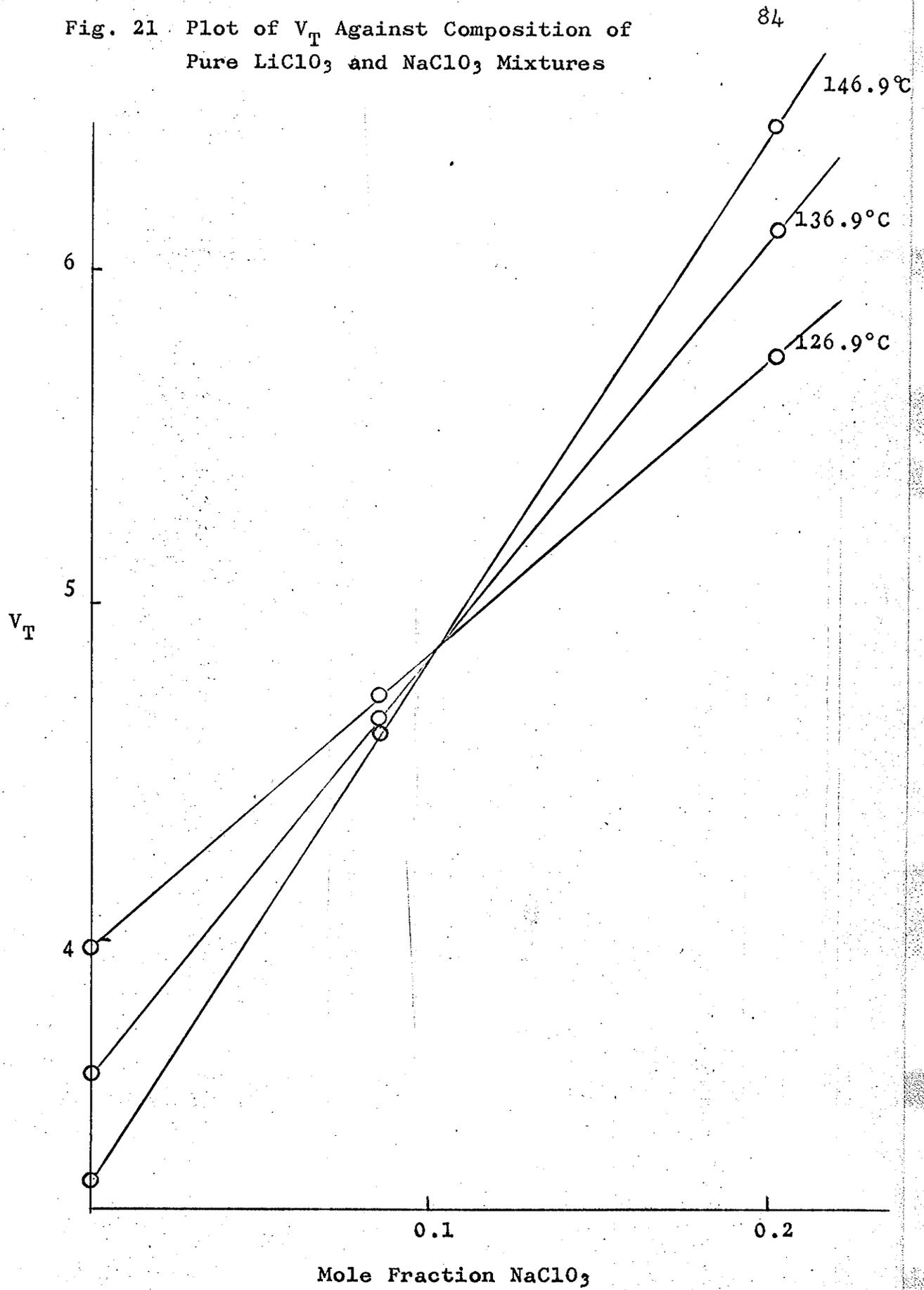


FIG.22
Plot of V_T against Composition
of pure NaClO_3 - LiClO_3 mixtures.

Fig. 22 Plot of V_T Against Composition of Pure LiClO_3 and NaClO_3 Mixtures.

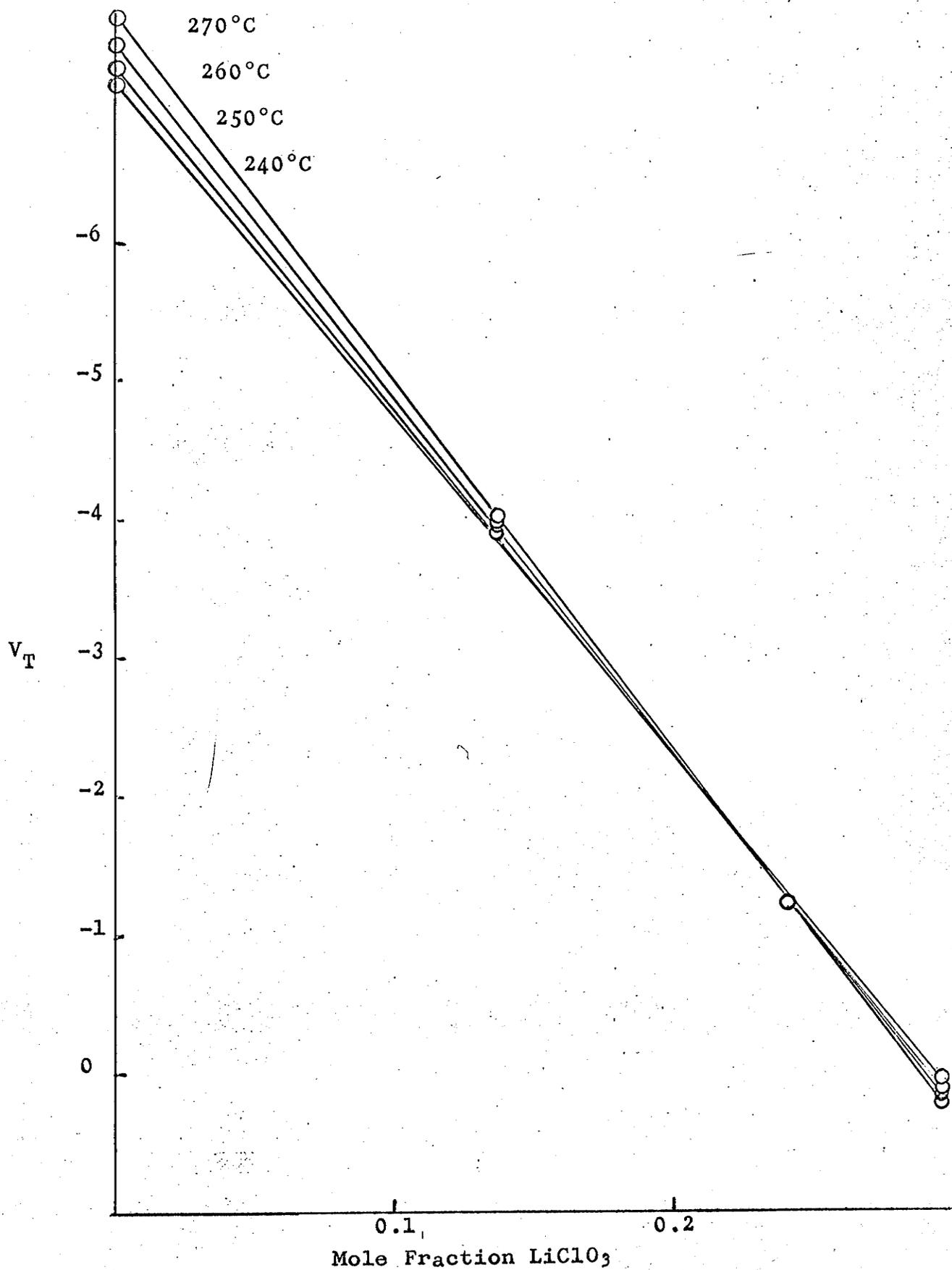


TABLE XXIX
 TEMPERATURE AND COMPOSITION CONTRIBUTIONS TO
 TOTAL VOLUME CHANGE FOR PURE $\text{LiClO}_3 + \text{NaClO}_3$

Mole Fraction NaClO_3	$t^\circ\text{C}$	$V_n dT$	$V_T dn_2$	dV
$n_2=0.0000$	126.9	-0.019	0	-0.019
	136.9	+0.172	0	+0.172
	146.9	+0.364	0	+0.364
$n_2=0.0859$	126.9	-0.017	-0.009	-0.026
	136.9	+0.156	+0.010	+0.166
	146.9	+0.331	+0.025	+0.356
$n_2=0.2032$	126.9	-0.017	-0.001	-0.018
	136.9	+0.157	-0.017	+0.140
	146.9	+0.331	-0.031	+0.300

TABLE XXX
 TEMPERATURE AND COMPOSITION CONTRIBUTIONS TO THE
 TOTAL VOLUME CHANGE FOR PURE $\text{NaClO}_3 + \text{LiClO}_3$

Mole Fraction LiClO_3	$t^\circ\text{C}$	V_{ndT}	V_{Tdn_2}	dN
$n_2 = 0.000$	240	+0.414	0	+0.414
	250	+0.207	0	+0.207
	270	-0.207	0	-0.207
$n_2 = 0.1359$	240	+0.400	+0.030	+0.430
	250	+0.200	+0.012	+0.212
	270	-0.200	-0.017	-0.217
$n_2 = 0.2431$	240	+0.374	+0.035	+0.409
	250	+0.187	+0.015	+0.202
	270	-0.187	-0.019	-0.206
$n_2 = 0.2966$	240	+0.394	+0.028	+0.422
	250	+0.197	+0.012	+0.209
	270	-0.197	+0.016	-0.213

FIG. 23

Temperature and Composition
Parts of change in volume for
pure NaClO_3 - LiClO_3 mixtures.

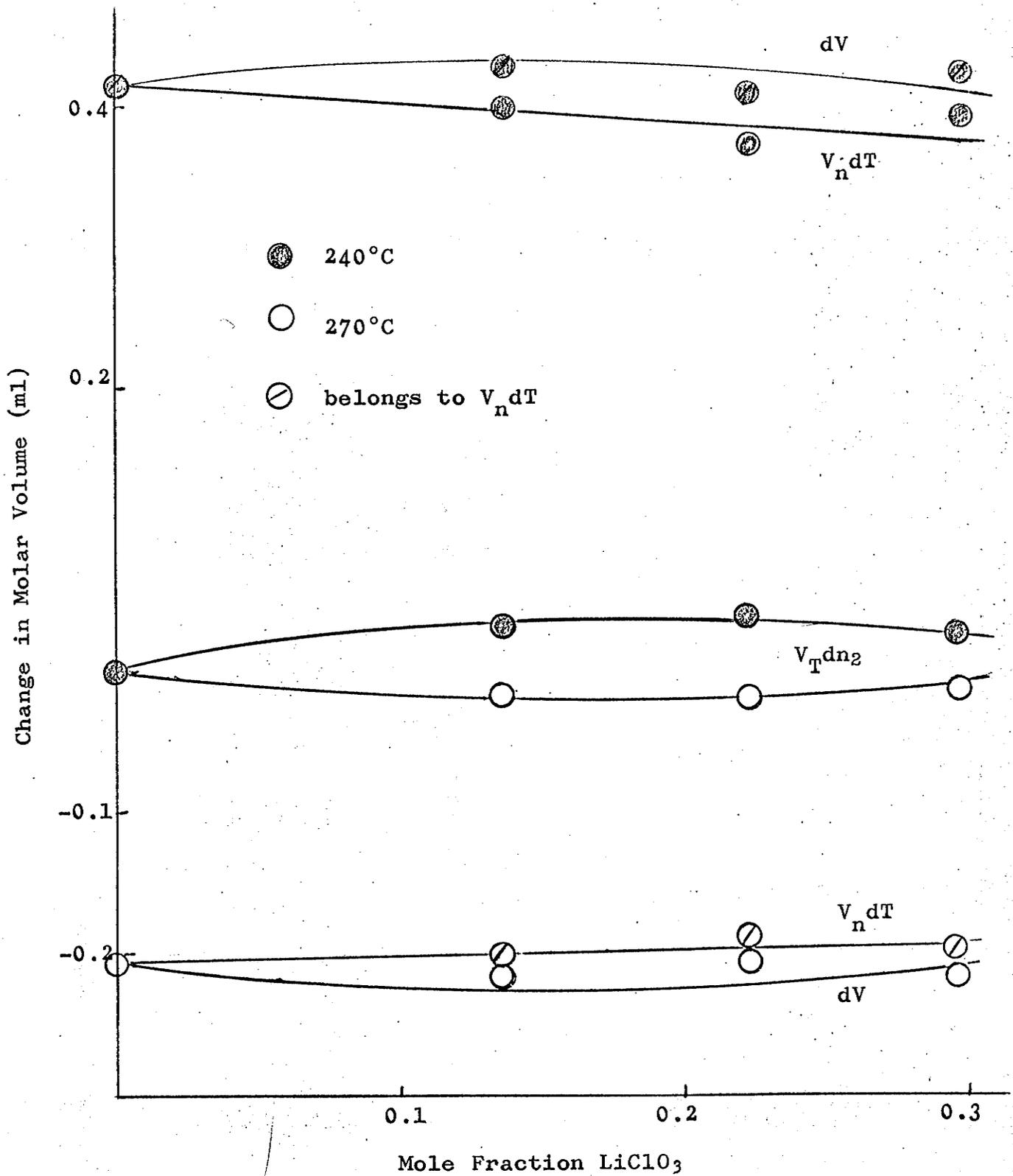
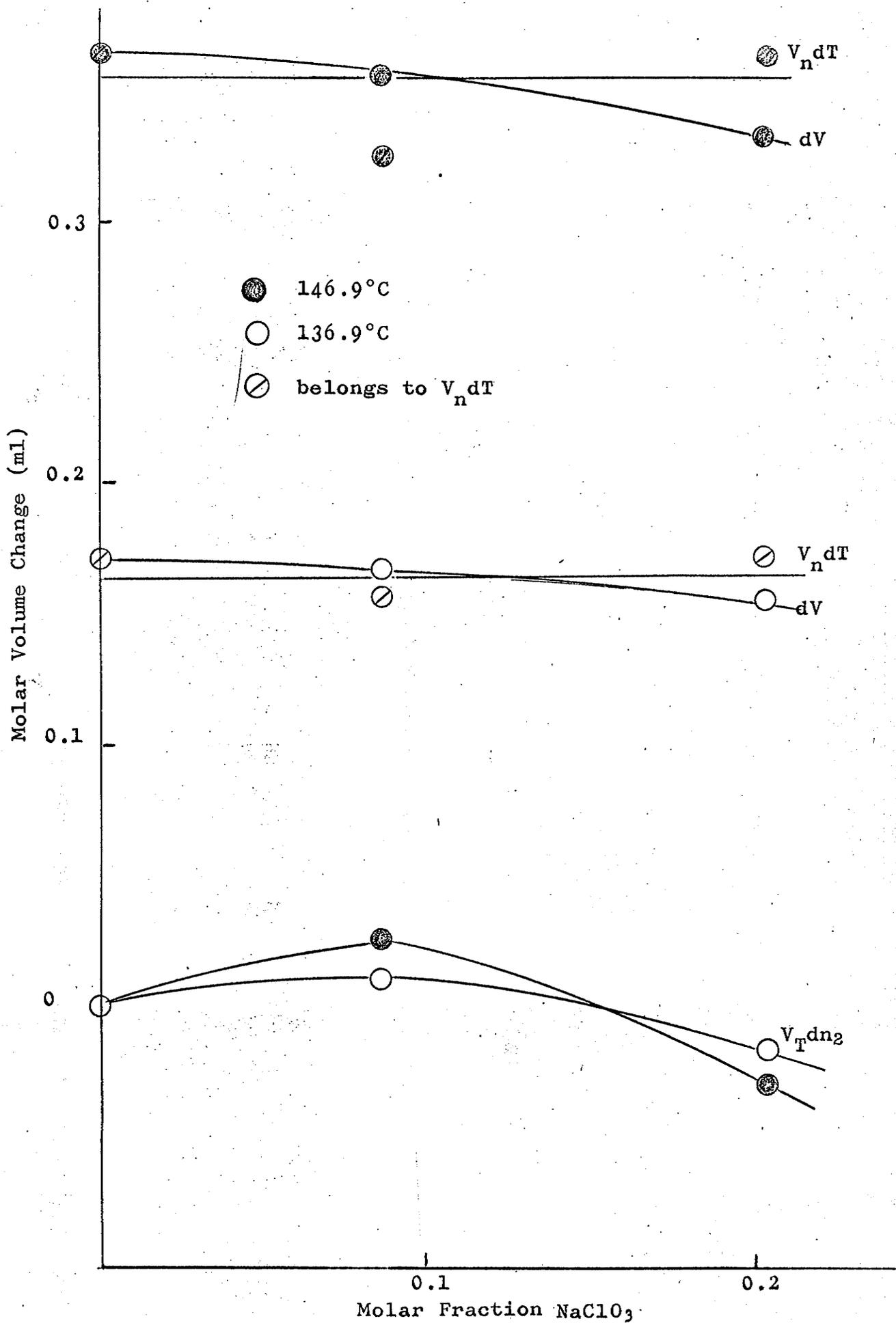


Fig. 23 Temperature and Composition
Parts of Change in Volume

FIG. 24

Temperature and Composition Parts
of change in volume for $\text{LiClO}_3\text{-NaClO}_3$
Mixtures.

Fig. 24 Temperature and Composition
 Parts of Change in Volume for $\text{LiClO}_3\text{-NaClO}_3$ Mixtures



CHAPTER VI

SUMMARY AND CONCLUSION

Densities of solid lithium chlorate and solid sodium chlorate were determined over the entire range from room temperature to melting point. Density measurements of molten sodium chlorate-lithium chlorate mixtures were limited to small additions to the pure components. The temperature range in which density measurements of the molten salts were made was about ten degrees centigrade.

The molar volume change on melting for pure lithium chlorate (6.41 %) is about half the increase for pure sodium chlorate (12.73 %). This small increase in volume is typical for all low melting salts.

The crossing of the isothermals in a plot of V_T (partial molar volume at constant temperature) vs. mole fraction may indicate a complete change in lattice structure. This cross-over occurs more rapidly where sodium chlorate is the solute. For sodium chlorate as solute the composition contribution ($V_T dn_2$) is more pronounced at lower concentrations than for the same concentration region, where lithium chlorate is the solute (see Figs. 23 and 24). For lithium chlorate additions to pure sodium chlorate the composition contributions remain almost constant over the entire region studied. These data may support the conclusion that the bigger sodium ion influences the lithium chlorate lattice more rapidly than the small ion of lithium the sodium chlorate lattice.

COMPARISON OF ADDITIONS OF SODIUM CHLORATE AND OF
LITHIUM NITRATE³⁵ TO LITHIUM CHLORATE.

Additions of lithium nitrate and sodium chlorate to lithium chlorate reduce the covalent character of lithium chlorate. Evidence is the decrease in the coefficient of expansion (α) which is, generally, higher in covalent than in ionic melts.

The total volume change (dV) for lithium chlorate lithium nitrate mixtures is mainly determined by the compositional contribution. For lithium chlorate-sodium chlorate mixtures the composition contribution is less dominant. Comparison of sodium chlorate-lithium chlorate mixtures show that the composition contribution is the smallest where lithium chlorate is the solute.

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