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IONIC MOBILITIES IN

SELECTED FUSED SALT SYSTEMS

by

Boone Bailey Owens

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INTRODUCTION

This investigation of the mobilities of the ions in fused salts was undertaken in order to elucidate the structure of ionic melts. Because of the difficulties involved in the determination of the transport numbers of a fused salt, certain authors have questioned the justification of talking about transport numbers in pure fused salts (1), (2).

The transport number of an ion is commonly defined as the fraction of the current that is carried by a given ionic species in a solution (3, p. 107). When one considers electrical conductivity in a fused salt, one may assume that each ionic species carries a certain fraction of the current, depending upon the relative mobilities of the ions. The transport number of an ion in an aqueous solution is a property of both the salt and the solvent. In any discussion of the transport numbers of an ion in an aqueous solution, one must keep in mind the interactions of the solvent with the solute. A fused salt might at first appear to be a much simpler system because there is no solvent component to interact with the salt. However, it is the absence of this solvent reference frame that makes it difficult to go from the definition to the determination of the transport numbers in a fused salt.

Duke and Laity (4) defined the transport numbers in a fused salt in terms of current-carrying ions moving relative to the bulk of the liquid. By designing a cell in which the anode and cathode compartments were separated in such a manner that only current-carrying ions could move

between compartments, they were able to measure the transport numbers of fused $PbCl_2$. Their cell compartments were separated by a fritted glass disk of sufficiently fine porosity that flow of material through the disk due to a hydrostatic head was eliminated. In a system such as this one must consider the effects of the disk upon the liquid. The measured quantity was the motion of the ions relative to the disk. Thus, the disk took the place of a solvent reference frame. In so far as the liquid in the pores interacted with the disk material, the measured transport numbers were properties of both the salt and the disk.

A fairly comprehensive review of the literature on transport numbers in fused salts was carried out by R. W. Laity (5). Little of the early work served any purpose other than to stimulate interest in this field.

More recently Aziz and Wetmore (6) ran experiments on the system $AgNO_3$-$NaNO_3$, similar to a Hittorf experiment, in which concentration changes accompanying electrolysis were related to the transport numbers of the ions in the melts. As they pointed out, since there was no reference frame in this system, and there were three ionic species available for transporting current, the Hittorf experiment would only give relative values for the transport numbers.

Their equations relating the transport numbers to the concentration changes were developed in the following manner. Let Z equivalents of current be passed through a mixture of fused $AgNO_3$-$NaNO_3$ between silver electrodes. Let t_{Ag^+}, t_{Na^+}, and $t_{NO_3^-}$ represent the transport numbers of the Ag^+, Na^+, and NO_3^- respectively. Then the anolyte will gain $Z(1 - t_{Ag^+})$ equivalents of Ag^+, $- Zt_{Na^+}$ equivalents of Na^+, and $Zt_{NO_3^-}$ equivalents of

NO_3^-. The over-all effect will be that the anolyte has gained $Z(1 - t_{Ag^+})$ equivalents of $AgNO_3$ and lost Zt_{Na^+} equivalents of $NaNO_3$. If n_1^0 and n_2^0 represent the initial equivalents of $AgNO_3$ and $NaNO_3$ in the anolyte, respectively, and n_1 and n_2 represent the corresponding final equivalents, then

$$n_1 = n_1^0 + Z(1 - t_{Ag^+}) \tag{1}$$

$$n_2 = n_2^0 - Zt_{Na^+} \tag{2}$$

Letting the initial mole fraction of $AgNO_3$ be

$$N_1^0 = \frac{n_1^0}{n_1^0 + n_2^0} \tag{3}$$

then, from Equations 1 and 2,

$$N_1^0 = \frac{n_1 - Z(1 - t_{Ag^+})}{n_1 + n_2 - Z(1 - t_{Ag^+} - t_{Na^+})} \tag{4}$$

Utilizing the equation

$$t_{Ag^+} + t_{Na^+} + t_{NO_3^-} = 1 \tag{5}$$

to eliminate t_{Na^+}, and solving for t_{Ag^+}, it may be shown that

$$t_{Ag^+} = 1 - \phi - N_1^0 t_{NO_3^-} \tag{6}$$

where

$$\phi = \frac{N_2^o n_1 - N_1^o n_2}{Z} \tag{7}$$

By means of Equation 6 Aziz and Wetmore attempted to get relative values of the transport numbers in this system. However, as will be shown later, their experimental results were in error.

Hill and Wetmore (7) applied the same method to the system $AgNO_3$-$AgCl$ and claimed to obtain evidence for the complex ion Ag_2Cl^+. However, because the work of Aziz and Wetmore was in error, the accuracy of the work of Hill and Wetmore should be questioned.

Duke and Laity's work on the transport numbers of molten $PbCl_2$ (4), (8) led to the method of determining absolute transport numbers of pure fused salts. As pointed out earlier, they defined transport numbers as the fractions of current carried by the conducting ions moving relative to the bulk of the liquid. The character of the current carrying ions and the electrodes involved would determine the amount of mass flow accompanying electrolysis of the fused salt.

Consider the electrolysis of $PbCl_2$ between Pb electrodes. Upon the passage of Z equivalents of current the anolyte would gain $Z(1 - t_{Pb^{++}})$ equivalents of $PbCl_2$ and the catholyte would lose $Z(1 - t_{Pb^{++}})$ equivalents of $PbCl_2$ where $t_{Pb^{++}}$ was the transport number of Pb^{++}. The problem in this type of experiment would be to keep the anolyte separated from the catholyte. Duke and Laity overcame this problem by using various types of membranes to separate the two electrode compartments.

The volume change of the electrolyte during electrolysis was related to the transport numbers by the relation

$$\frac{\delta V_a}{Z} = -\frac{V_{Pb}}{2} + \frac{V_{PbCl_2}}{2}(1 - t_{Pb^{++}}) \qquad (8)$$

where

δV_a = volume change of the anolyte,

V_{Pb} = molar volume of Pb,

V_{PbCl_2} = molar volume of $PbCl_2$.

Since $t_{Pb^{++}} + t_{Cl^-} = 1$, Equation 8 allows one to determine the transport numbers by measuring the volume change of the liquid in the anode compartment and the densities of the salt and metal. In the cell of Duke and Laity the motion of an air bubble, trapped in a horizontal capillary tube connecting the anolyte to the catholyte was used to indicate the volume change of the anolyte due to electrolysis.

In this type of experiment one must consider any surface effects between the pores of the disk and the ions in the melt. Duke and Laity obtained identical results using three different membrane materials. The "ultrafine" porosity Pyrex fritted glass disk gave good results that agreed with the results obtained with an asbestos membrane and a porcelain disk. These Pyrex disks had a nominal maximum pore size of 0.9-1.4 microns (9). Thus, the pores of this type of membrane had a diameter of about 10^4 times the radius of the ions in the melt. Consequently, it seemed doubtful that surface effects would extend throughout the liquid in the pores. If there were any such effects, then one would expect a variation of the transport number with membrane material. Since this was

not observed, the use of "ultrafine" porosity fritted glass disks in transport cells was justified.

Bloom and Doull (10) determined the transport numbers of fused $PbCl_2$ and $CdCl_2$, obtaining results that were quite different from those of Duke and Laity. They felt that a hydrostatic head led to errors in the latter workers' experiment by causing leakage through the disk. Their apparatus consisted essentially of a horizontal capillary tube that was filled with $PbCl_2$, with molten Pb electrodes at each end. By following the movement of the $Pb-PbCl_2$ boundary they attempted to measure the volume change of the anolyte.

An analysis of these two methods of measuring the transport numbers of $PbCl_2$ was carried out by Lorenz and Janz (11). They studied the ease of motion of air bubbles through capillary tubes containing different melts. It was found that bubbles in AgCl melts had a very high resistance to motion under the influence of a hydrostatic head whereas $PbCl_2$ gave a much smaller resistance to bubble motion. Molten Pb was found to greatly hinder the movement of an air bubble. Furthermore, these workers noted that Bloom and Doull's results agreed with those of Duke and Laity when the latter used a coarse porosity fritted disk. In this case Duke and Laity obtained a volume change of zero. So, apparently the Pb electrodes of Bloom and Doull's experiment were sticking to the glass, and the movement of the boundary was due solely to the Pb dissolving at the anode.

Sundheim (1), (12) gave a theoretical treatment of transference numbers in molten salts. For a uni-univalent salt he calculated, from a

consideration of the momentum balance of the ions in the melt, that the transport number of the cation, t_C, is given by

$$t_C = \frac{M_A}{M_C + M_A} \qquad (9)$$

where M_A and M_C are the masses of the anion and cation respectively. He therefore concluded that the transport numbers in pure fused salts have little significance. Sundheim utilized, as a model for the conductivity process of a fused salt, an incompressible liquid that does not interact with the cell walls, but is restrained by them. As pointed out by Lorenz and Janz (11, p. 28) more information than was given in Sundheim's paper would be necessary in order to evaluate his considerations.

In the present work, equations were derived to relate the transport numbers of a pure nitrate salt, electrolyzed between Ag-$AgNO_3$ electrodes, to the volume change of the material in the cathode compartment. Letting MNO_3 represent the unspecified nitrate salt, it was assumed that the current was carried by the simple ionic species M^+ and NO_3^-. With the passage of Z equivalents of current through the cell the cathode compartment would gain Z equivalents of Ag, lose Z equivalents of $AgNO_3$ and gain Zt_{M^+} equivalents of MNO_3 where t_{M^+} is the transport number of M^+. Then,

$$\frac{\delta V_c}{Z} = V_{Ag} - V_{AgNO_3} + t_M^+ V_{MNO_3} \qquad (10)$$

where

δV_c = volume change of cathode material,

$$V_i = \text{molar volume of } i.$$

Since the sum of the transport numbers of MNO_3 must be one, both transport numbers may be determined by combining the volume change in the cathode compartment due to electrolysis with density data for the salts and the metal.

In a similar fashion, if one considers a binary melt, $AgNO_3-MNO_3$, in a cell with Ag electrodes, one may show that

$$\frac{\delta V_c}{Z} = V_{Ag} + (t_{Ag^+} - 1)\overline{V}_{AgNO_3} + t_{M^+}\overline{V}_{MNO_3} \qquad (11)$$

where

$$\overline{V}_i = \text{partial molal volume of } i,$$

$$t_{Ag^+} = \text{transport number of } Ag^+.$$

The density data of Byrne, et al (13) and Bloom and Rhodes (14) show that the molar volume and partial molal volumes are equivalent for the systems $AgNO_3-NaNO_3$ and $AgNO_3-KNO_3$. Consequently, molar volumes may be used in Equation 11 with no loss of accuracy. Again one has the relation that the sum of the transport numbers is unity,

$$t_{Ag^+} + t_{M^+} + t_{NO_3^-} = 1 \qquad (12)$$

However, in order to determine the three transport numbers one needs another relationship. Applying Equation 6 to this system,

$$t_{Ag^+} - 1 = -\phi - N_1^0 t_{NO_3^-} \qquad (13)$$

and using Equation 12, one may write

$$t_{M^+} = \phi - N_2^o t_{NO_3^-} \tag{14}$$

Substituting from Equation 13 and 14 into Equation 11 and solving for $t_{NO_3^-}$, one finds that

$$t_{NO_3^-} = \frac{V_{Ag} + \phi(V_{MNO_3} - V_{AgNO_3}) - \delta V_c/Z}{N_1^o V_{AgNO_3} + N_2^o V_{MNO_3}} \tag{15}$$

Equations 6, 12, and 15 conveniently relate the transport numbers of the binary systems studied to quantities that may be experimentally determined.
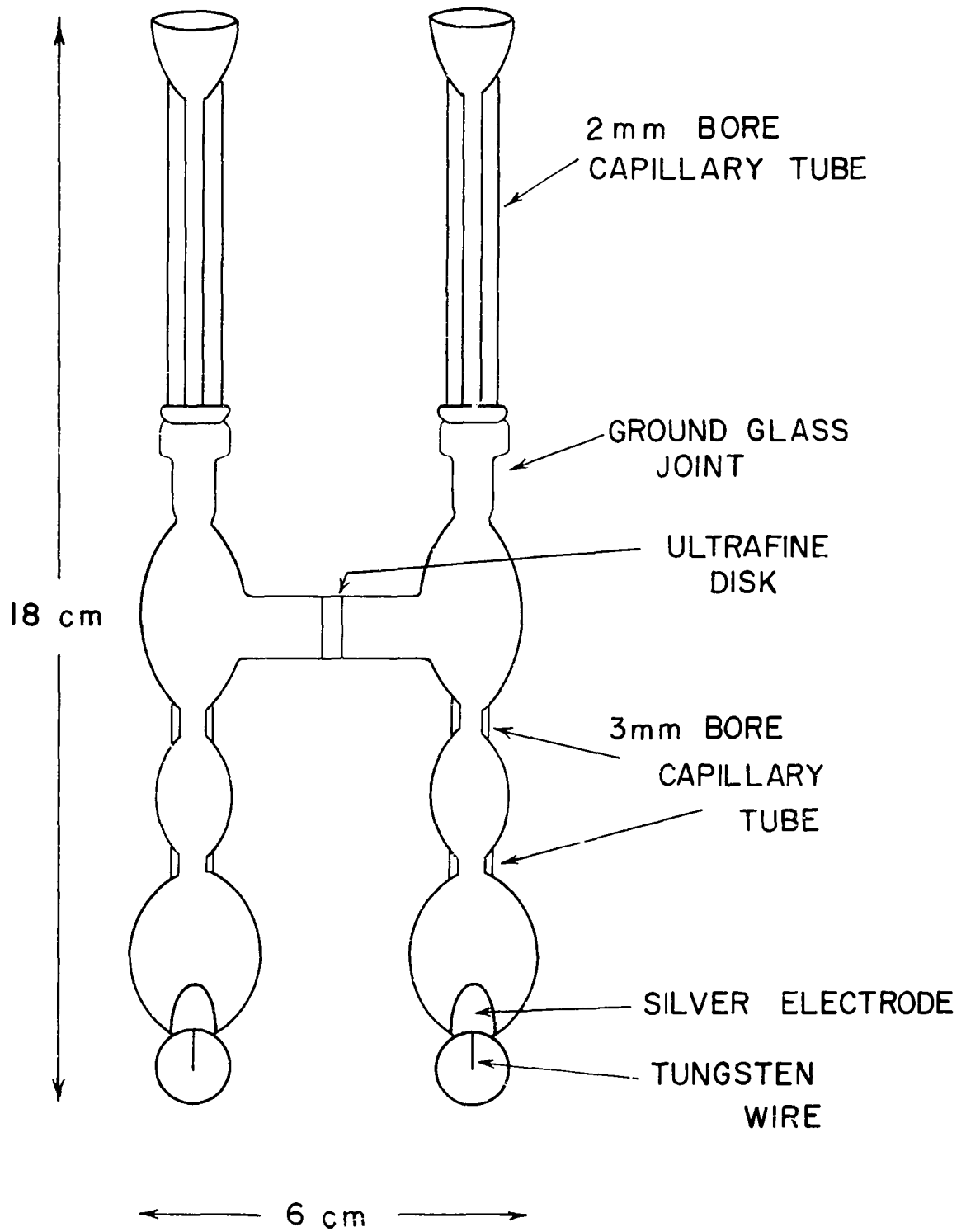
EXPERIMENTAL

Materials

'Baker Analyzed' Reagent grade salts were used in all of these experiments. The silver electrodes used in the volume change experiments were prepared by plating silver from a cyanide bath onto the tungsten lead wires in the cells. Silver wires (one mm diameter) were used as the electrodes for the concentration change experiments.

Apparatus

Three types of cells were used to measure the changes accompanying electrolysis of the fused salts. The first cell was used with the pure salts, and the other two cells were used with the mixtures. All of the cells were constructed of Pyrex glass.

In the measurement of the volume changes in the electrolyte due to electrolysis of the pure alkali nitrates, the cell shown in Figure 1 was used. The silver electrodes were located, as indicated, at the bottom of each electrode compartment, plated onto the tungsten wires that were sealed through the bottom of the cell. The tungsten wires were connected to more flexible nickel wires that led out of the furnace. The horizontal feet at the bottom of the cell were about ten cm long, extending perpendicularly from the plane of the cell, and the nickel wires were run

Figure 1.   Transport cell used for volume

change experiments of pure salts

2 mm BORE
CAPILLARY TUBE

GROUND GLASS
JOINT

ULTRAFINE
DISK

18 cm

3 mm BORE
CAPILLARY
TUBE

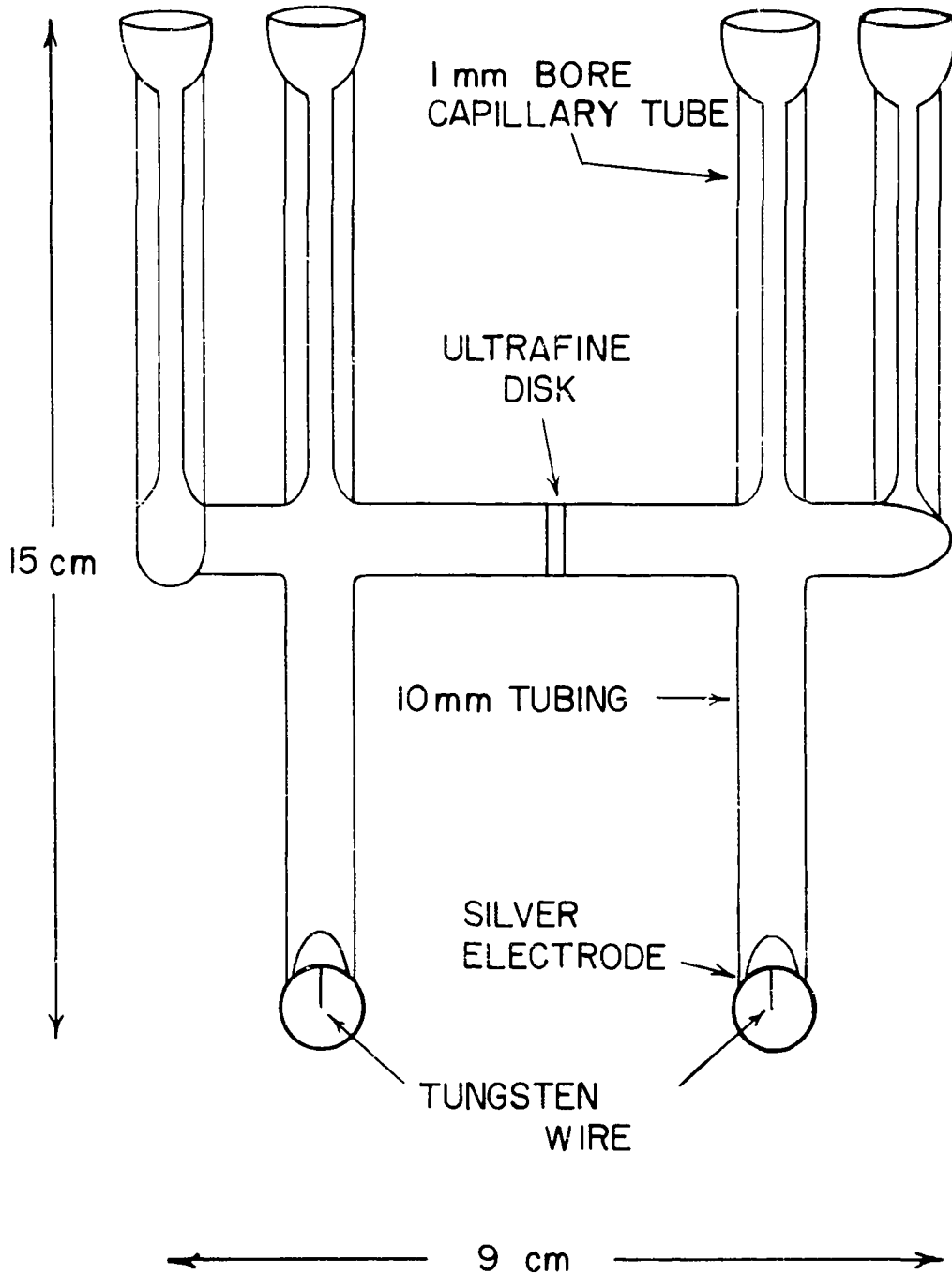SILVER ELECTRODE

TUNGSTEN
WIRE

6 cm

through these feet. The constrictions in the cell legs were to prevent mixing of the silver nitrate in the lower bulb with the less dense salt being studied. The vertical capillary arms, of two mm diameter, were connected to the cell by means of ground glass joints. The anode and cathode compartments were separated by a ten mm diameter "ultrafine" porosity fritted glass disk, obtained as a Buchner type funnel, Corning Code No. 400213.

The volume changes of the binary systems were observed in the cell illustrated in Figure 2. This cell was basically the same as the preceeding cell. Since these systems contained silver nitrate as one component, it was unnecessary to have a bulb containing silver nitrate over the electrode. Therefore, no constrictions were necessary in the cell legs. The vertical capillary arms were sealed directly to the cell in order to prevent leakage that might otherwise occur at the ground glass joint. A second arm was sealed to each side of the cell so that air could escape when the cell was filled. The best results were obtained when one mm capillaries were used as vertical arms. The other features of the two cells were the same.

The concentration changes accompanying electrolysis of the binary systems were determined using the cell of Figure 3. The electrode compartments were designed to minimize mixing. Silver nitrate was formed at the anode, and since it was more dense than the bulk liquid it tended to remain in the cup on the anode side. The melt in the neighborhood of the cathode became less dense as silver came out of solution, and therefore tended to rise. The electrode compartments were again separated by ten

Figure 2. Transport cell used for volume

change experiments of mixtures

1 mm BORE CAPILLARY TUBE

ULTRAFINE DISK

10 mm TUBING

15 cm

SILVER ELECTRODE

TUNGSTEN WIRE

9 cm

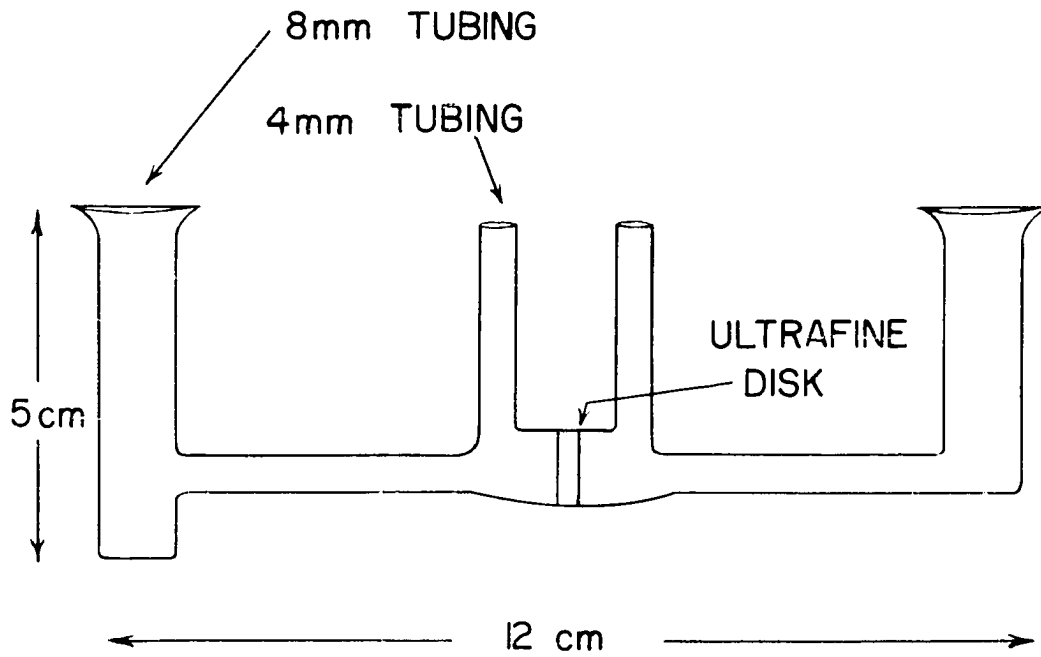8mm TUBING

4mm TUBING

ULTRAFINE
DISK

5 cm

12 cm

Figure 3. Transport cell used for concentration
change experiments of mixtures

mm "ultrafine" porosity glass disks. A transite rack was used to hold the cell upright in the furnace.

A Temco Electric Furnace, Model 1730, was used to maintain the cells at the desired temperature during a run. The volume change cells were observed through a two cm diameter hole in the front of the furnace by means of a cathetometer, while a light was shone upon the cell through a similar hole in the rear. An Eberbach Corporation cathetometer was used to measure the volume changes in the earlier experiments. A more accurate cathetometer, obtained from the Gaertner Scientific Corporation, was used with the mixtures.

Temperature variations during the volume change measurements, as determined with a chromel-alumel thermocouple and a Leeds and Northrup potentiometer, were always less than a degree Centigrade. During the concentration change measurements a Minneapolis-Honeywell Brown Electronic Controller was used to hold the furnace temperature constant within $\pm 5^{\circ}C$. Because of the large heat capacity of the furnace, the actual temperature variation during a run was less than $5^{\circ}C$. Since the concentration change due to electrolysis seemed to be temperature independent, this temperature control was satisfactory.

In the earlier measurements a six volt battery was used as the power supply, and the amount of electricity passed through the cell was determined by means of a Burlington milliammeter and a Precision Time-It second timer. In the later measurements a rectified current was used as the source of direct current. The anode of the concentration change cells served as a silver coulometer in order to determine the equivalents

of current passed through these cells.

Procedure

Volume change of pure salts

The cell of Figure 1 was packed with the calculated amounts of silver nitrate necessary to just fill the lower bulb of each leg. After slowly heating the cell up to the temperature of the experiment, any bubbles in the lower bulb were removed with a micropipette. Then molten alkali metal nitrate, which had been previously placed in the furnace in a 50 ml beaker, was poured into the cell, filling the center bulb and the cell compartments. The capillary arms were then placed in the cell, and the liquid levels were adjusted by adding or removing fused salt. The cell was then arranged so that both capillary arms could be seen through the hole in the furnace. The nickel wires that projected from the cell were connected to the power supply, and the system was allowed to come to thermal equilibrium.

A cathetometer was used to follow the level of the liquid in the capillary arms. The cessation of motion was used as the criterion for thermal equilibrium. A current of 100 milliamperes d.c. was passed through the cell, and the liquid levels were read every 1,000 seconds, an average run lasting 8,000 seconds. The polarity was reversed after three or four thousand seconds. In this manner, a number of successive runs were made with one cell.

Volume change of mixtures

In the experiments done on mixtures, the calculated amounts of salts were placed in a beaker and put in the furnace with the cell of Figure 2. After the salt had melted and was thoroughly stirred, the cell was filled in the furnace. The salt was poured in through the outermost cell arms as this seemed to remove most of the air bubbles that would get trapped in the cell. The liquid levels were adjusted so that they were about midway up the capillary arms. The cell was placed in the furnace with the horizontal cross arm running from front to rear so that all of the capillary arms could be seen through the hole in the furnace door. A glass arm was used to reach through the furnace hole and raise the front side of the cell, thus displacing the liquid in the cell until a one cm head was built up between the liquid in the two cell compartments. One hundred milliamperes a.c. was passed through the cell prior to the run in order to cancel out any volume changes due to heating at the disk. The rate of flow through the disk was found to be proportional to the difference in the levels of the liquid in the two cell compartments. By measuring the change of liquid levels both with and without electrolysis, the change in volume due to electrolysis was obtained. The cathetometer was used to follow the level of the liquid in both compartments of the cell prior to electrolysis, during electrolysis, and after electrolysis by recording the liquid level every 100 seconds for about 7,000 seconds. Electrolysis took place during a 1,000 second interval while 100 milliamperes d.c. was passed through the cell.

Concentration change of mixtures

The determination of ϕ was done for mixtures, using the cell shown in Figure 3. The cell was filled with molten salt, as described in the preceeding section, and silver electrodes were placed in the two ends of the cell. The anode was weighed before the run and after the run in order to determine the equivalents of current passed through the cell. A current of from 20 to 30 milliamperes d.c. was passed through the cell for about 6,000 seconds. At the same time a current of 150 milliamperes a.c. was passed through the cell in order to control the formation of Ag trees at the cathode.

To determine the concentration of the melt, a sample was withdrawn from the beaker for analysis at the same time that the cell was filled. Atlernatively, the entire cell was analyzed for total salt composition.

The amount of each component in the anolyte at the end of the experiment was obtained in the following manner. The anode compartment and its contents were weighed. Then all the salt was dissolved in H_2O, and the remaining glass and electrode weighed. The weight difference gave the total weight of salt in the anolyte. The solution containing the salt was then analyzed for Ag^+ by the Volhard procedure. At high $AgNO_3$ concentrations the K^+ was determined gravimetrically as the tetraphenylborate salt, using the pH 2 method of Cluley (15).

RESULTS AND CALCULATIONS

Pure Salts

Equation 10, derived in the Introduction, was used to calculate the transport numbers of the pure alkali metal nitrates. Using density data recorded in the literature (13), (16), (17), (18), (19) the necessary molar volumes were calculated, and the relationships shown in Table 1 were obtained.

Table 1. Transport number equations for pure salts

Salt	T ($^\circ$C)	$t_{NO_3^-} = 1 - t_{M^+}$
$LiNO_3$	273	$0.152 - .026(\delta V_c/Z)$
$NaNO_3$	337	$0.238 - .022(\delta V_c/Z)$
KNO_3	339	$0.380 - .0184(\delta V_c/Z)$
$AgNO_3$	260	$0.246 - .0232(\delta V_c/Z)$

The volume change of the catholyte due to electrolysis was calculated from the radius of the capillary arms of the cell and the height change of the liquid in the cathode compartment due to electrolysis, δh^c_{el}. It was necessary to consider the effects of temperature variations and decomposition upon the observed height change of the liquid, δh^c_{obs}.

Though the temperature during a run usually varied less than a degree, there was the possibility of a height change due to temperature variation, δh_T^c. Since the salts were not thermally stable, a height change due to decomposition, δh_d^c, could also take place. Thus, the observed height change was related to the height change due to electrolysis in the cathode compartment and the anode compartment by Equations 16 and 17, where superscript c refers to catholyte and superscript a refers to anolyte.

$$\delta h_{obs}^c = \delta h_{el}^c + \delta h_T^c + \delta h_d^c \tag{16}$$

$$\delta h_{obs}^a = \delta h_{el}^a + \delta h_T^a + \delta h_d^a \tag{17}$$

Because the cells used in these experiments were symmetrical, both electrode compartments held about the same quantity of salt. It was assumed that any height changes due to temperature variations and decomposition were the same in the two compartments since these two quantities would be proportional to the amount of salt.

$$\delta h_T^c = \delta h_T^a \tag{18}$$

$$\delta h_d^c = \delta h_d^a \tag{19}$$

Because of the electrode reactions the volume changes due to electrolysis must be equal in magnitude and opposite in sign,

$$\delta h_{el}^c = -\delta h_{el}^a \tag{20}$$

These equations led to the result that

$$\delta h^c_{el} = (1/2)(\delta^c_{obs} - \delta^a_{obs})$$ (21)

In some cases the two liquid levels were not quite equal initially, and there was a slow height change due to leakage. This rate was measured prior to the run and a correction was applied.

The results obtained for the volume change of the catholyte due to electrolysis, $\delta V_c/Z$, obtained for the pure salts are given in Table 2. All of the limits indicated in the tables and figures of this section are the standard deviations. The corresponding transport numbers, calculated using the equations of Table 1, are given in Table 3 where t_+ is the transport number of the cation.

Table 2. Volume change due to electrolysis
for pure nitrate salts

Salt	T (^{o}C)	$\delta V_c/Z$ ($\frac{cm^3}{Equiv.}$)	No. of runs
LiNO$_3$	273	- 0.5 $\pm$ 2.2	49
NaNO$_3$	337	- 2.2 $\pm$ 0.4	10
KNO$_3$	339	- 0.9 $\pm$ 1.3	11
AgNO$_3$	260	- 1.5 $\pm$ 2.6	4

The equivalent ionic conductivities, λ_+ and λ_-, of the cations and anions in the pure salts were calculated from the equivalent conductivities, $\bigwedge$, of the salts by use of the following equation.

$$\lambda_i = t_i \underline{\bigwedge} \qquad (22)$$

Table 3. Transport numbers of pure nitrate salts

Salt	t_+
$LiNO_3$	$0.84 \pm .06$
$NaNO_3$	$0.71 \pm .01$
KNO_3	$0.60 \pm .03$
$AgNO_3$	$0.72 \pm .06$

The ionic mobility is proportioned to the equivalent ionic conductivity as shown in Equation 23.

$$\mu_i = \frac{\lambda_i}{96,500} \qquad (23)$$

The equivalent ionic conductivities and ionic mobilities of the pure nitrate salts were calculated using the conductivity data of Goodwin and Mailey (16), and Byrne, Fleming and Wetmore (13). The results of these calculations are shown in Table 4. In these calculations it was assumed that the transport numbers are independent of temperature.

Binary Salt Systems

Equations 6, 12, and 15 related the transport numbers of the binary

Table 4. Equivalent ionic conductivities and ionic mobilities
of pure nitrate salts at 350° C.

Salt	Λ (ohms^{-1} cm^2)	λ_+ (ohms^{-1}cm^2)	λ_-	μ_+ x10^4 (cm^2 sec.$^{-1}$	μ_- x10^4 volt^{-1})
$LiNO_3$	53.55	45.0 ± 3.2	8.6 ± 3.2	4.66 ± .33	0.89 ± .33
$NaNO_3$	52.46	37.2 ± 0.5	15.3 ± 0.5	3.86 ± .05	1.58 ± .05
KNO_3	35.55	21.3 ± 1.1	14.2 ± 1.1	2.21 ± .11	1.47 ± .11
$AgNO_3$	55.82	40.2 ± 3.3	15.6 ± 3.3	4.16 ± .34	1.62 ± .34

salt system KNO_3-$AgNO_3$ to the molar volumes of the salts, the molar

volume of Ag metal, the volume change accompanying electrolysis, and the

concentration change accompanying electrolysis.

The necessary molar volumes were calculated using the density data

that was previously cited, and $t_{NO_3^-}$ was expressed in terms of $\delta V_c/Z$ and

ϕ as shown in Table 5.

The height change of the catholyte due to electrolysis, δh^c_{el}, was

determined by plotting log δh^c_{obs} vs time for the time prior to the run

and following the run, and then getting the rate of leakage through the

disk during the run by extrapolation. Correcting the observed height

changes for leakage, temperature variations and decomposition, the volume

changes due to electrolysis given in Table 6 were obtained.

The literature values of ϕ for the $AgNO_3$-$NaNO_3$ system are shown in

Figure 4, plotted against mole fraction of $AgNO_3$. As is quite evident

Table 5. Transport number equations for binary salt systems

System	N_1^o	T (°C)	$t_{NO_3^-}$
$AgNO_3-NaNO_3$	0.27	320	$0.236 - .022(\delta V_c/Z) + .018\ \phi$
	0.50	270	$0.239 - .023(\delta V_c/Z) + .011\ \phi$
	0.70	273	$0.240 - .023(\delta V_c/Z) + .011\ \phi$
$AgNO_3-KNO_3$	0.25	285	$0.206 - .020(\delta V_c/Z) + .187\ \phi$
	0.50	280	$0.216 - .021(\delta V_c/Z) + .195\ \phi$
	0.75	270	$0.229 - .022(\delta V_c/Z) + .206\ \phi$

Table 6. Volume change due to electrolysis for binary salt systems

System	N_1^o	T (°C)	$\delta V_c/Z\ (\frac{cm^3}{Equiv.})$	No. of runs
$AgNO_3-NaNO_3$	0.27	320	$- 1.5 \pm 3.8$	4
	0.50	270	$- 1.2 \pm 0.5$	4
	0.70	273	$- 1.2 \pm 0.7$	4
$AgNO_3-KNO_3$	0.25	285	$- 2.9 \pm 0.5$	7
	0.50	280	$- 1.2 \pm 2.0$	3
	0.75	270	$- 0.5 \pm 0.6$	4

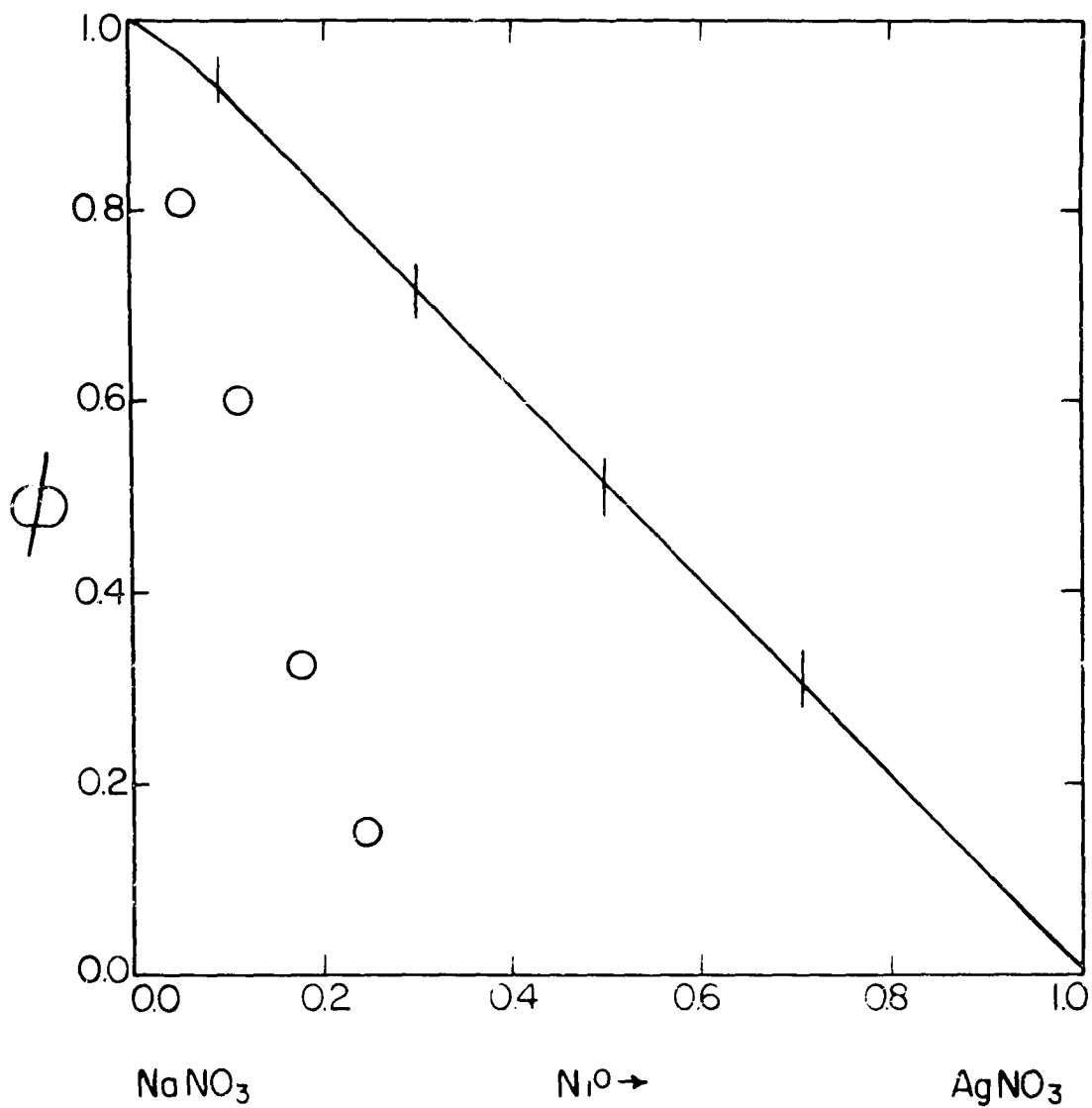there is a large discrepancy between the two sets of data. One of the

Figure 4. ϕ vs. composition in the system $AgNO_3-NaNO_3$: ╅ , Duke et al (20); ◯ , Aziz and Wetmore (6).

major sources of error in the determination of ϕ would be mixing of material between the anolyte and the catholyte. If complete mixing took place, there would be no change in the concentration of the melt between the anolyte and the catholyte. The numerator of the expression for ϕ, Equation 7, would become zero, so ϕ would become zero. If mixing did not take place, and the Ag^+ transport number was less than one, then ϕ would be positive.

In Aziz and Wetmore's cell (6), the electrode compartments were connected by a horizontal glass tube (1.8 mm internal diameter) containing two small glass bulbs. Because of concentration changes occuring in these two small bulbs, about two-thirds of their runs were rejected.

In the cell used by Duke et al (20) the electrode compartments were separated by an "ultrafine" porosity fritted glass disk. Any errors due to mixing would have made their ϕ values smaller than the true value of ϕ. Therefore, it seems quite probable that the results of Aziz and Wetmore were low because of mixing. Consequently, the results of Aziz and Wetmore were not used in the calculation of the transport numbers for the $AgNO_3-NaNO_3$ system.

The values of ϕ for the $AgNO_3-KNO_3$ system, determined in this work, are shown in Table 7. Figure 5 shows ϕ for this system as a function of concentration.

The ϕ data and volume change data were used, in conjunction with the equations of Table 5, to plot the transport numbers onto the triangular graphs of Figures 6 and 7. The transport numbers of these two systems are given in Tables 8 and 9.
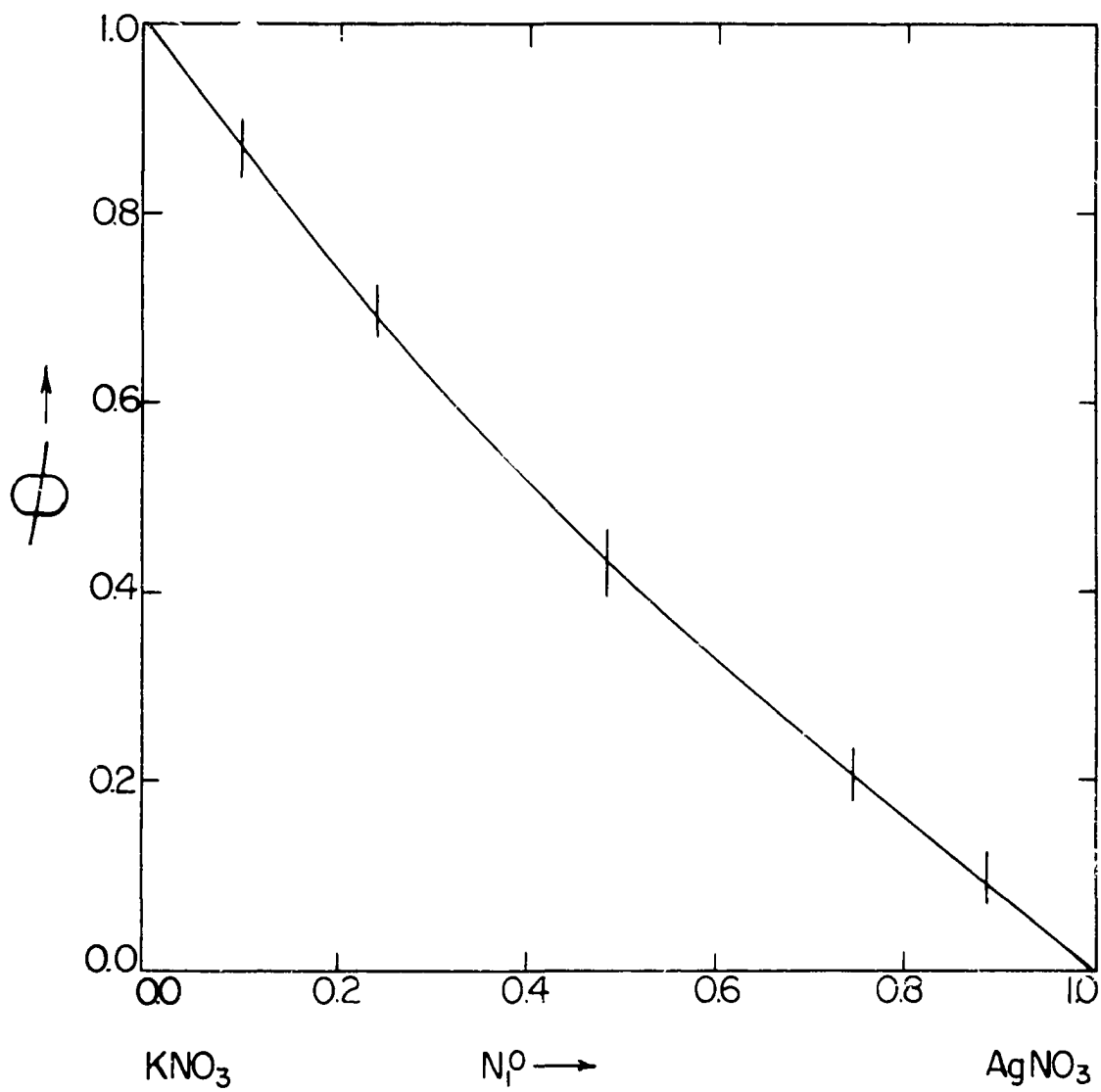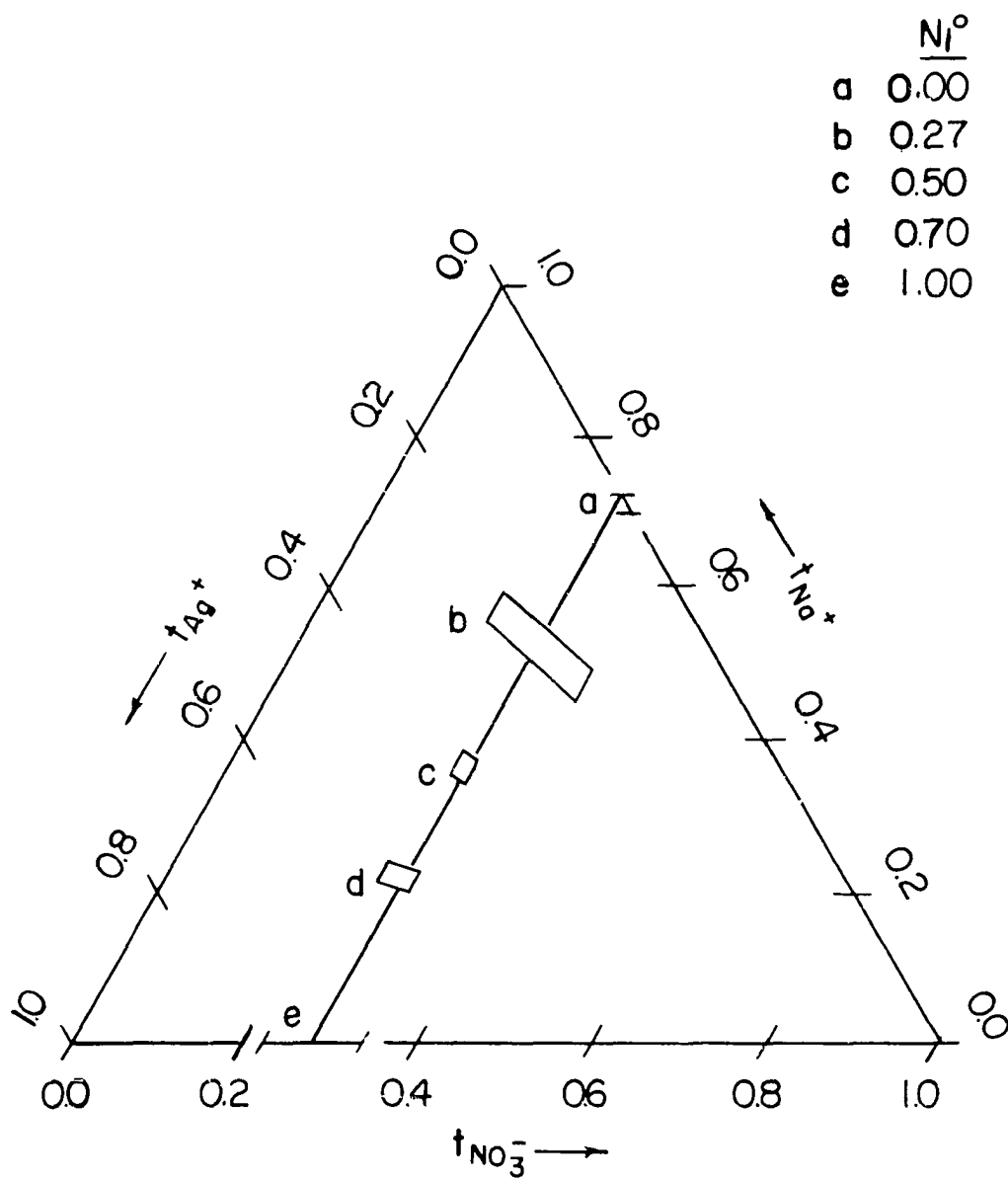
Figure 5. ϕ vs. composition in the system $AgNO_3$-KNO_3

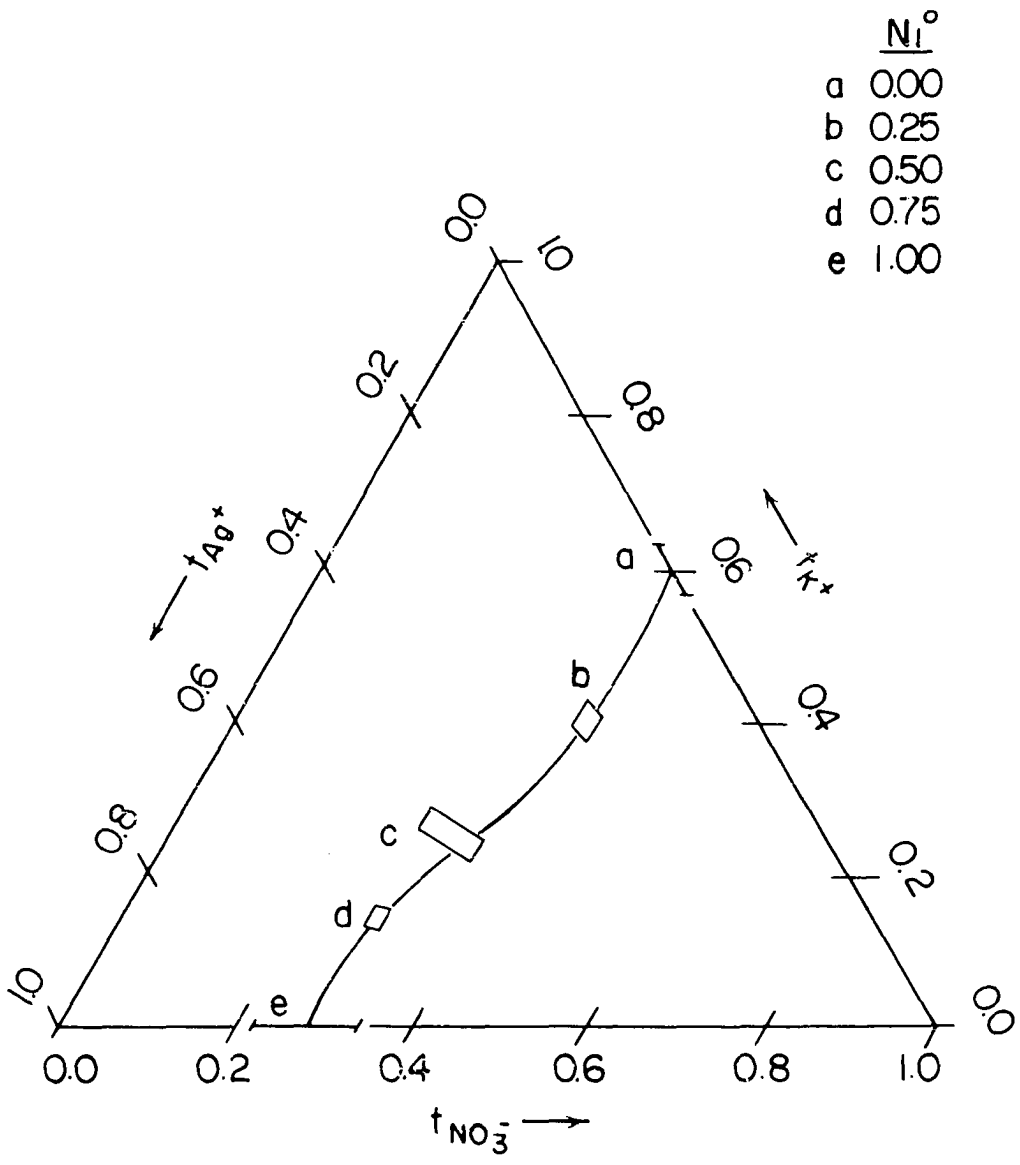Figure 6. Transport numbers in the system AgNO$_3$-NaNO$_3$

Figure 7. Transport numbers in the system $AgNO_3$-KNO_3

Table 7. ϕ for the system $AgNO_3\text{-}KNO_3$

N_1^o	T (°C)	ϕ	No. of runs
0.11	300	0.87 ± 0.01	2
0.25	300	0.70 ± 0.01	2
0.49	300	0.42 ± 0.04	2
0.49	200	0.41 ± 0.01	2
0.75	200	0.21 ± 0.01	2
0.90	200	0.10 ± 0.02	2

Table 8. Transport numbers for the system
$AgNO_3\text{-}NaNO_3$

N_1^o	t_{Ag^+}	t_{Na^+}	$t_{NO_3^-}$
.00	0.0	0.71 ± .01	0.29 ± .01
.27	0.20 ± .04	0.52 ± .08	0.28 ± .08
.50	0.37 ± .03	0.36 ± .03	0.27 ± .01
.70	0.51 ± .03	0.22 ± .02	0.27 ± .02
1.00	0.72 ± .06	0.0	0.28 ± .06

Table 9. Transport numbers for the system $AgNO_3-KNO_3$

N_1^o	t_{Ag^+}	t_{K^+}	$t_{NO_3^-}$
.00	0.0	0.60 ± .03	0.40 ± .03
.25	0.20 ± .03	0.40 ± .03	0.40 ± .02
.50	0.43 ± .04	0.25 ± .04	0.32 ± .04
.75	0.56 ± .03	0.15 ± .03	0.29 ± .02
1.00	0.72 ± .06	0.0	0.28 ± .06

The equivalent conductance of a salt at infinite dilution may be considered as equal to the sum of the equivalent ionic conductivities of the ionic species (3. p. 56). Thus,

$$\Lambda_o = \lambda_+^o + \lambda_-^o \tag{24}$$

The equivalent ionic conductivities of the ions in a pure salt, as defined by Equation 22, satisfies this relationship. For a pure fused salt,

$$\Lambda = \lambda_+ + \lambda_- \tag{25}$$

By analogy, for the fused salt system MNO_3-AgNO_3,

$$\Lambda = N_1^o(\lambda_{Ag^+} + \lambda_{NO_3^-}) + N_2^o(\lambda_{M^+} + \lambda_{NO_3^-}) \tag{26}$$

which simplifies to

$$\bigwedge = N_1^0 \lambda_{Ag^+} + N_2^0 \lambda_{M^+} + \lambda_{NO_3^-} \tag{27}$$

Then, the equivalent ionic conductivities of these ions would be given by

$$\lambda_{Ag^+} = t_{Ag^+} \bigwedge / N_1^0 \tag{28}$$

$$\lambda_{M^+} = t_{M^+} \bigwedge / N_2^c \tag{29}$$

$$\lambda_{NO_3^-} = t_{NO_3^-} \bigwedge \tag{30}$$

The ionic mobilities are related to the equivalent ionic conductivities by Equation 23. These quantities were calculated using literature data on conductivities (13), (21); the values of the equivalent ionic conductivities and the ionic mobilities are shown in Tables 10, 11, 12, and 13. The ionic mobility as a function of composition, is shown in Figures 8 and 9.

Table 10. Equivalent ionic conductivities for the system
$AgNO_3$-$NaNO_3$ at 350° C.

N_1^c	$\bigwedge$ (ohms^{-1}cm^2)	λ_{Ag^+}	λ_{Na^+}	$\lambda_{NO_3^-}$
0.00	52.46		37.2 ± 0.5	15.3 ± 0.5
0.27	54.0	40.0 ± 8.0	38.5 ± 5.9	15.1 ± 5.3
0.50	53.5	39.6 ± 3.2	38.5 ± 3.2	14.4 ± 0.5
0.70	53.6	39.1 ± 2.3	39.3 ± 3.5	14.5 ± 1.1
1.00	55.82	40.2 ± 3.3		15.6 ± 3.3

Table 11. Equivalent ionic conductivities for the system
$AgNO_3$-KNO_3 at $350°$ C.

N_1^o	Λ (ohms^{-1}cm^2)	λ_{Ag^+}	λ_{K^+}	$\lambda_{NO_3^-}$
0.00	35.55		21.3 ± 1.1	14.2 ± 1.1
0.25	40.7	32.6 ± 4.9	21.7 ± 1.6	16.3 ± 1.0
0.50	45.6	39.2 ± 3.6	22.8 ± 3.7	14.6 ± 1.8
0.75	50.3	37.6 ± 2.0	30.2 ± 6.0	14.6 ± 1.0
1.00	55.82	40.2 ± 3.5		15.6 ± 3.3

Table 12. Ionic mobilities for the system
$AgNO_3$-$NaNO_3$ at $350°$ C.

N_1^o	μ_{Ag^+}	μ_{Na^+}	$\mu_{NO_3^-}$
		(cm^2 sec.$^{-1}$ volt^{-1})x10^4	
0.00		$3.86 \pm .05$	$1.58 \pm .05$
0.27	$4.14 \pm .83$	$3.99 \pm .61$	$1.56 \pm .55$
0.50	$4.10 \pm .33$	$3.99 \pm .33$	$1.49 \pm .05$
0.70	$4.05 \pm .24$	$4.07 \pm .37$	$1.50 \pm .11$
1.00	$4.16 \pm .34$		$1.62 \pm .34$

Table 13. Ionic mobilities for the system
$AgNO_3-KNO_3$ at $350°$ C.

N_1^o	μ_{Ag^+}	μ_{K^+}	$\mu_{NO_3^-}$
		$(cm^2 sec.^{-1} volt^{-1}) \times 10^4$	
.00		$2.21 \pm .11$	$1.47 \pm .11$
.25	$3.38 \pm .51$	$2.25 \pm .17$	$1.69 \pm .08$
.50	$4.06 \pm .38$	$2.36 \pm .38$	$..51 \pm .19$
.75	$3.90 \pm .21$	$3.13 \pm .63$	$1.51 \pm .10$
1.00	$4.16 \pm .35$		$1.62 \pm .34$

Consideration of Errors

The transport number of the NO_3^- was calculated from Equation 15.

$$t_{NO_3^-} = \frac{V_{Ag} + \phi(V_{KNO_3} - V_{AgNO_3}) - \delta V_c/z}{N_1^o V_{AgNO_3} + N_2^o V_{KNO_3}}$$ (15)

The maximum error in $t_{NO_3^-}$ was given by

$$\Delta t_{NO_3^-} = \sum_i \frac{\partial t_{NO_3^-}}{\partial X_i} \Delta X_i$$ (31)

where X represents the quantities whose measurements were necessary to

determine $t_{NO_3^-}$.

The values of the molar volumes were taken from the literature. The

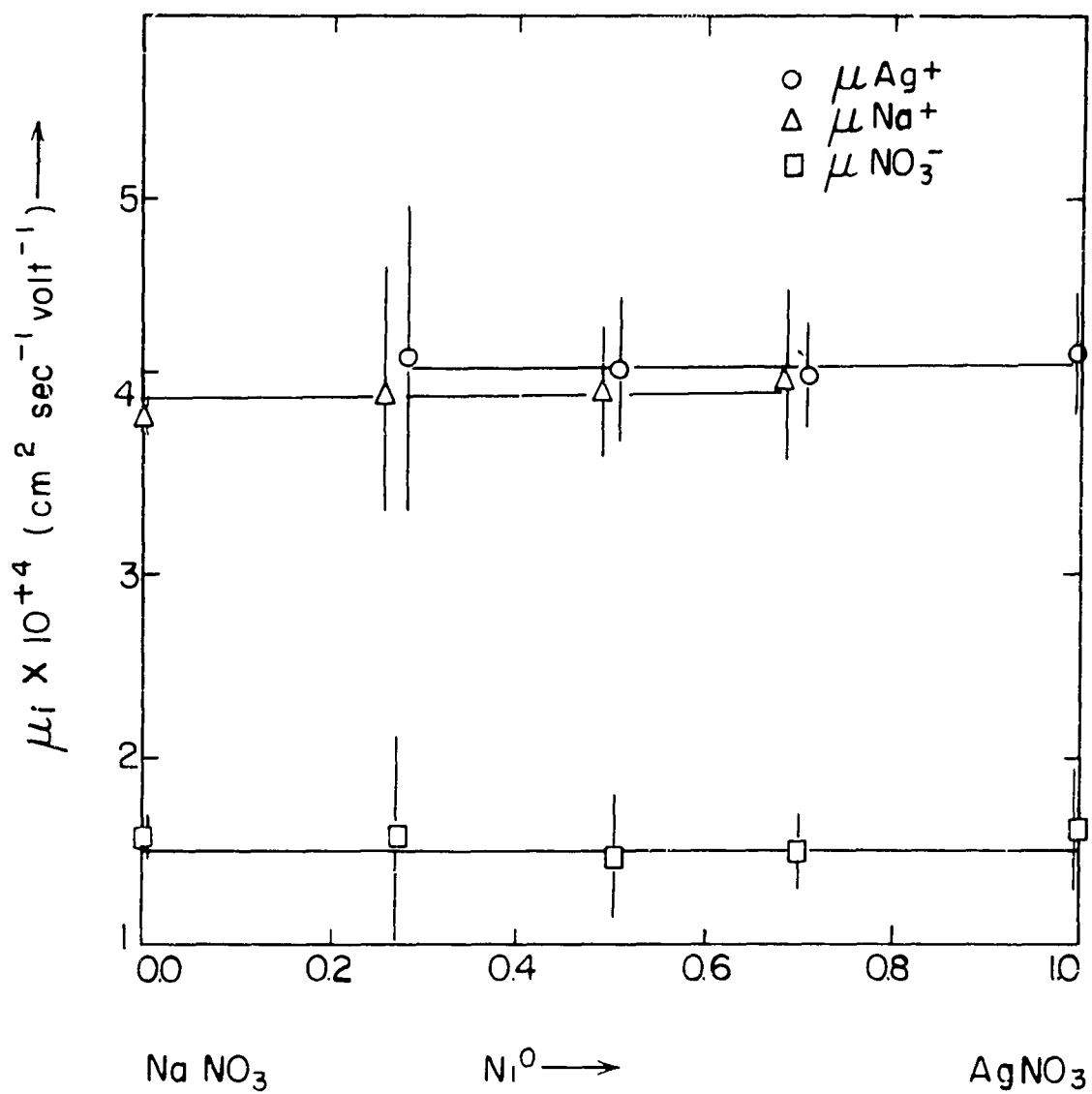Figure 8.   Ionic mobilities in the system $AgNO_3-NaNO_3$

at 350° C.

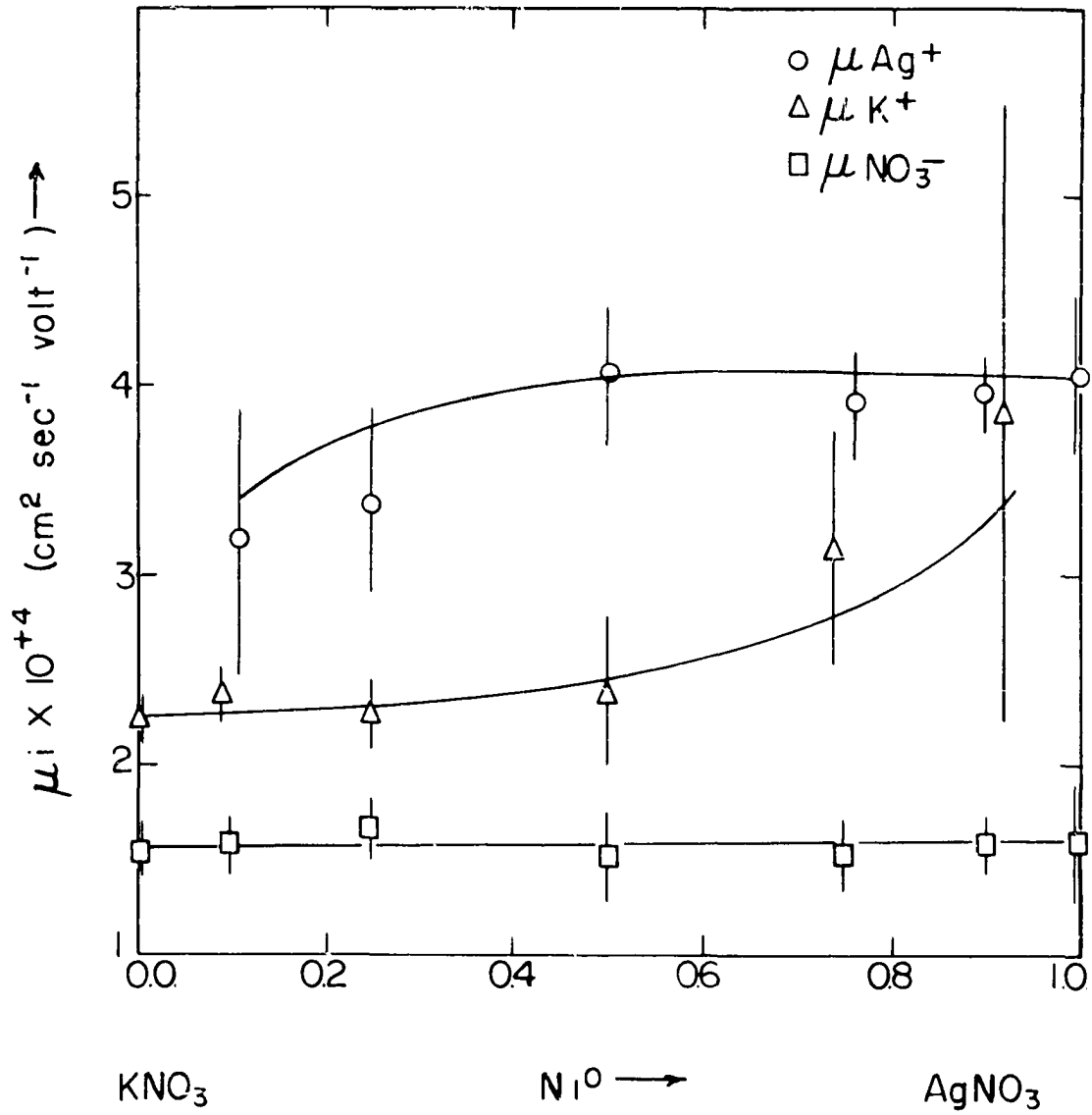Figure 9. Ionic mobilities in the system $AgNO_3 - KNO_3$
at 350° C.

error in $t_{NO_3^-}$ due to errors in the molar volumes was negligible compared to the total error in $t_{NO_3^-}$. The values of N_1^c and N_2^o were determined by the weights of the salts used in preparing the mixtures, and their contribution to the error in $t_{NO_3^-}$ was less than 0.001. The maximum error in ϕ was about 0.02, as determined by the differential method, and since ϕ was multiplied by a factor whose maximum value was 0.2, the error in $t_{NO_3^-}$ due to an error in ϕ was 0.004 or less.

The volume change accompanying electrolysis was calculated from the observation of the height change of the liquid in a capillary tube.

$$\delta V_c/Z = n \pi r^2 \delta h_c F/it \tag{32}$$

where,

n = number of capillary arms on cathode side

r = radius of capillary

δh_c = height change of liquid in cathode compartment

F = Faraday

i = current

t = time

The major source of the error in $t_{NO_3^-}$ was due to the error in the determination of the height change of the liquid. When the more accurate cathetometer was obtained, the error in $t_{NO_3^-}$ was reduced by a factor of about 3/4. The maximum probable error in $t_{NO_3^-}$ is given in Table 14.

The transport numbers of the cations in the mixtures were given by

$$t_{Ag^+} = 1 - \phi - N_1^o t_{NO_3^-} \qquad (6)$$

$$t_{M^+} = \phi - N_2^o t_{NO_3^-} \qquad (14)$$

Table 14. Maximum probable error in $t_{NO_3^-}$

System	$\delta t_{NO_3^-}$
Pure alkali nitrates	± 0.04
$AgNO_3\text{-}NaNO_3$, $N_1^o = 1.00$, 0.27	± 0.10
$AgNO_3\text{-}NaNO_3$, $N_1^o = 0.50$, 0.70	± 0.02 [a]
$AgNO_3\text{-}KNO_3$	± 0.02 [a]

[a] A second more accurate cathetometer was used in these experiments.

The error in the transport numbers of the cations was equal to the error in ϕ plus a fraction, N_1^o, of the error in $t_{NO_3^-}$; this error turned out to be about 0.03.

Because the ionic mobility is proportional to the transport number, the relative errors in these quantities are equal. When a cation was present as the minor constituent, its transport number was small, and the error in its mobility was large. For example, the transport number of the K^+ in the system $AgNO_3\text{-}KNO_3$, $N_1^o = 0.90$, was equal to 0.07 ± 0.03. The corresponding ionic mobility of the K^+ was $(3.86 \pm 1.66) \times 10^{-4}$ cm^2

sec.$^{-1}$ volt^{-1}.

It is seen that this method for determining ionic mobilities in binary systems is not satisfactory for low concentrations of an ion. Since the error in mobility becomes large as the concentration of the ion becomes small, one must use caution in interpreting the results at low concentration.

DISCUSSION

Below is given a summary of the results that were obtained in this work.

In the pure fused salts, except $LiNO_3$, the mobility of the NO_3^- was constant; in $LiNO_3$, its mobility was lower by about one third. The mobility of the cations in the alkali nitrates decreased as the size of the cation increased.

In the binary systems $AgNO_3-NaNO_3$ and $AgNO_3-KNO_3$, the mobility of the NO_3^- was constant with respect to a change in composition. In the former of these two systems, the mobilities of the Ag^+ and Na^+ did not vary with composition; these two cation mobilities were essentially equal. In the $AgNO_3-KNO_3$ system the mobility of the K^+ increased as its concentration was decreased, whereas the mobility of the Ag^+ decreased with decreasing concentration.

Early viewpoints on the structure of liquids were based on the idea that the liquid state was more closely related to the gaseous state than to the solid state. However, more recently the liquid state has been described as a highly disordered solid.

Frenkel (22, p. 112) suggested that liquids might be termed 'quasi-crystalline' because they appear to possess a local order that is similar to the order that is shown by the crystalline state. Lark-Horovitz and Miller (23), (24) used x-rays to investigate the structure of the molten alkali halides. Their work showed that over a short range the structure of the liquids is quite closely related to that of the solid state. An

x-ray investigation of fused KNO_3 and $NaNO_3$ was carried out by Danilov and Krasnitskii (25). They showed that the atomic distances were the same in the liquid state and the solid state; only the regularity of the lattice structure was lost.

Evidence for the presence of lattice defects in crystals has been obtained from conductivity studies of solids (26). Two types of defects are felt to be involved in conduction in crystals; Frenkel defects in which an ion moves from its lattice position to an interstitial position, and Schottky defects where equal numbers of oppositely charged ions move to the surface of the crystal, leaving holes in the lattice structure. The increase of the conductivity with temperature is attributed to an increase in the number of defects. The marked increase in the mobility of the ions upon fusion indicates a large increase in the number of defects in the liquid state, if the liquid state is described as 'quasi-crystalline'.

Mulcahy and Heymann (27), in studying the conductivity of a number of ionic melts, visualized the fused state as a distorted crystal lattice. Because the conductivities of the alkali metal chlorides were found to decrease with increasing size of the cation, they suggested that the ionic mobilities might be explained in terms of the radius ratios. These authors felt that with an increase in coordination, the mobility of the cation would decrease.

Mulcahy and Heymann considered the possibility of utilizing Stokes' law to describe the resistance against migration in an ionic melt. However, as they pointed out, it is very doubtful that this law would apply

to the case of an ion moving through an ionic melt. Mulcahy and Heymann did obtain an empirical equation that related the radii of the ions in the alkali halide melts to the equivalent conductivity of the melts. Defining corresponding temperatures to be three-fourths of the boiling point, Mulcahy and Heymann reported that the equivalent conductivity at corresponding temperatures is given by the equation

$$\Lambda = 105(^1/r_+ + {}^1/r_-) \tag{33}$$

where r_+ and r_- are the radii of the cation and anion respectively. Equation 33 represented the experimental results with an average deviation of 3%.

Upon comparing Equation 33 with Equation 25 which reads

$$\Lambda = \lambda_+ + \lambda_- \tag{25}$$

one observes that the equivalent ionic conductivities are inversely proportional to the ionic radii.

$$\lambda_+ = 105/r_+ \tag{34}$$

$$\lambda_- = 105/r_- \tag{35}$$

The transport number of the cation is related to λ_+ and λ_- by (3, p. 108)

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \tag{36}$$

By substituting for λ_+ and λ_- from Equations 34 and 35 into Equation 36, one obtains the equation

$$t_+ = \frac{105/r_+}{105/r_+ + 105/r_-} \tag{37}$$

which reduces to

$$t_+ = \frac{r_-}{r_+ + r_-} \tag{38}$$

It is interesting to note that one may derive Equation 38 by initially assuming that the restraining force felt by the migrating ion is proportional to the product of its velocity and radius.

$$\underline{F}_i = - C\underline{v}_i r_i \tag{39}$$

In the steady state this restraining force would be equal to the electrical driving force felt by the ion.

$$- C\underline{v}_i r_i = e\underline{E} \tag{40}$$

$\underline{E}$ is the electric field strength, e is the charge on the ion, and $\underline{v}_i$ is the velocity of the ion. Applying Equation 40 to a cation and an anion, one obtains the following.

$$- C\underline{v}_+ r_+ = e\underline{E} \tag{41}$$

$$- C\underline{v}_- r_- = -e\underline{E} \tag{42}$$

Adding Equations 41 and 42, and using absolute values of velocity, one finds that

$$Cv_+ r_+ - Cv_- r_- = 0 \tag{43}$$

or

$$\frac{v_+}{v_-} = \frac{r_-}{r_+} \tag{44}$$

Because the transport number is related to the ionic mobilities by

$$t_+ = \frac{v_+}{v_+ + v_-}$$ (45)

it follows from Equation 44 that

$$t_+ = \frac{r_-}{r_+ + r_-}$$ (38)

This is the same result that was obtained from the empirical equation of Mulcahy and Heymann.

A comparison of experimental values for the transport numbers with those calculated from Equation 38 and Equation 9 is given in Table 15. It is seen that the radius fraction gives somewhat better agreement with experimental values of the transport number than does the mass fraction. It therefore seems that the ion's size rather than its mass is one of the determining factors in the conductivity process. The analogous treatment for a di-univalent salt fails when applied to $PbCl_2$, and as seen, the transport number of the K^+ in KCl does not agree with the radius fraction or mass fraction. Undoubtedly, other factors must be considered before the conductivity process may be understood. Accordingly, the agreement between the radius fraction and the transport numbers is rather surprising.

Table 15. Comparison of measured transport numbers
with radius fraction and mass fraction

Salt	t_+	$\dfrac{r_-}{r_+ + r_-}$ [a]	$\dfrac{M_-}{M_+ + M_-}$
LiNO$_3$	0.84 ± .06	0.82 [b]	0.90
NaNO$_3$	0.71 ± .01	0.71 [b]	0.73
KNO$_3$	0.60 ± .03	0.63 [b]	0.61
AgNO$_3$	0.72 ± .06	0.65 [b]	0.36
TlCl [c]	0.51 ± .002	0.55 [d]	0.15
KCl [e]	0.73 ± .03	0.59	0.47

[a] Ionic radii reported by Pauling (28, p. 346)

[b] NO$_3^-$ radius reported by Wells (29, p. 138)

[c] Transport number reported by Laity (5, p. 72)

[d] Tl$^+$ radius, Goldschmidt's value reported by Moeller (30, p. 140)

[e] Transport number reported by Fleming (31) and Cook (32)

The observation that the mobility of the NO$_3^-$ was somewhat smaller in
LiNO$_3$ than it was in the other NO$_3^-$ melts may be attributed to the small
radius ratio of LiNO$_3$. Pauling (28, p. 352) shows that for the Li halide
salts the anions are in contact because of the difference in size between
the large anions and the Li$^+$. Yaffe and Van Artsdalen (33) proposed that
this accounts for the high mobility of the Li$^+$ in fused LiCl. A similar

situation in the $LiNO_3$ melt would account for the lowered mobility of the NO_3^-.

A qualitative explanation of the variation of the ionic mobilities with composition in binary salt systems may be given in terms of the following model discussed by Frenkel (22, p. 97). From a microscopic point of view, there may be certain ordered regions in the melt exhibiting a structure closely related to the order in the solid state; other regions would show a greater amount of disorder. The ordered and disordered regions would be constantly interchanging. The ions in the ordered 'crystalline' regions would have low mobilities compared to the ions in the disordered regions for the same reasons that the ions in a crystal have low mobilities compared to the ions in the liquid state. Most of the conduction through the melt would take place in the disordered regions.

Consider any pure fused salt such as $AgNO_3$. The region about any one Ag^+ would be ordered a certain fraction of the time, and disordered a certain fraction of the time. On the average all the Ag^+ would have the same mobility. If a small amount of a second salt MNO_3 is added to the melt, it would not disrupt the order in the melt if M^+ fit into the $AgNO_3$ lattices. However, if M^+ were too large to fit into the ordered regions of the melt, then these ions would create disordered regions in the liquid. This being the case, the mobility of the M^+ should be higher when it is a minor constituent than when it is a major constituent. Thus, if the larger K^+ disorders the $AgNO_3$ melt in the $AgNO_3-KNO_3$ system, this would explain the increase in the K^+ mobility with concentration as shown in

Figure 9. When $AgNO_3$ is the minor constituent, one might expect that the

smaller Ag^+ would fit loosely into the ordered KNO_3 regions and exhibit a

somewhat higher mobility. However, since conduction is taking place

primarily in the disordered regions, this effect might not show up. In

the disordered regions, the slower moving K^+ might hinder the motion of

the Ag^+.

In Figure 3 it is shown that the mobilities of the ions in the

$AgNO_3$-$NaNO_3$ system do not vary. It is probable that the Ag^+ and Na^+ fit

easily into each other's ordered regions, and consequently are present in

the disordered regions in proportion to their over-all composition in the

melt.

The present discussion of ionic mobilities is largely limited to

speculation because of the lack of sufficient information on various ionic

melts. Electrical conductivity studies of binary fused salt systems have

indicated the presence of complex ions in certain melts. However, as

shown by the work of Yaffe and Van Artsdalen (33) the interpretation of

conduction isotherms for fused salt mixtures is ambiguous. The variation

of the individual ionic mobilities with composition should give a better

indication of complex ion formation.

Although the work of Hill and Wetmore (7) on the fused $AgCl$-$AgNO_3$

system may very well be in error as was mentioned in the introduction,

it at least demonstrates a method for interpreting transport number data

in terms of ionic association. They reported a negative transport number

for the Cl^- when it was the minor constituent, and this meant that the

Cl^- was being transported towards the cathode in the form of a cationic

complex. They assumed the complex ion was Ag_2Cl^+, formed by the reaction

$$AgCl \; + \; Ag^+ \; = \; Ag_2Cl^+ \tag{46}$$

and recalculated transport numbers in terms of the constituents Ag^+, $AgCl$, Ag_2Cl^+, and NO_3^-. This time they obtained positive transport numbers which they felt were of reasonable magnitude from the standpoint of the size of the conducting species. However, before speculating too much about the structures in this system, it would be desirable to obtain better transport number data.

Suppose there is ionic association in $AgNO_3$ melts, and further that this association results only in the formation of $AgNO_3$ molecules according to the reaction

$$Ag^+ \; + \; NO_3^- \; = \; AgNO_3 \tag{47}$$

The equilibrium constant for this reaction is

$$K_1 \; = \; \frac{(AgNO_3)}{(Ag^+)(NO_3^-)} \tag{48}$$

where the equilibrium constant is expressed in terms of concentrations of the constituents in the melt, unit activity coefficients being assumed. Then the ratio of $AgNO_3$ to Ag^+ is given by

$$\frac{(AgNO_3)}{(Ag^+)} \; = \; K_1(NO_3^-) \tag{49}$$

From Figure 8 it is seen that the mobility of the NO_3^- was constant

throughout the $AgNO_3-NaNO_3$ system. This suggests that the concentration of the unassociated NO_3^- is constant throughout this system. If a considerable fraction of the NO_3^- were to become associated as the composition of the melt was varied, the NO_3^- mobility calculated on the basis of complete dissociation would decrease.

An expression similar to that of Equation 49 may be written for association in the $NaNO_3$ melt.

$$\frac{(NaNO_3)}{(Na^+)} = K_2(NO_3^-) \tag{50}$$

Because the unassociated NO_3^- concentration appears to be constant throughout the $AgNO_3-NaNO_3$ system, it follows that in the pure melts the degrees of association must be the same. Therefore $K_1 = K_2$.

In the $AgNO_3-KNO_3$ system the NO_3^- mobility is also constant. Applying the same arguments as above to this system one arrives at the conclusion that $K_1 = K_2 = K_3$. Since it is very doubtful that association would occur to the same extent in these melts it is more likely that these melts are completely dissociated. Doucet and LeDuc (34) carried out a cryoscopic study of the $AgNO_3-KNO_3$ system. Their results also indicated that there is complete dissociation in these melts. It is therefore concluded that the possibility of ionic association in these fused nitrate salts and their mixtures is very slight.

SUMMARY

Transport numbers were determined in the pure fused salts, $LiNO_3$, $NaNO_3$, KNO_3, and $AgNO_3$ by measuring the volume changes of the material in the electrode compartments which took place during electrolysis of the melt. Transport numbers in the two binary fused salt systems $AgNO_3-NaNO_3$ and $AgNO_3-KNO_3$ were determined by measuring the volume changes accompanying electrolysis and the concentration changes accompanying electrolysis.

The transport numbers of the pure fused salts were found to agree with a radius fraction expression which implied that the mobility of an ion moving through a melt is inversely proportional to its size. It was pointed out that this equation failed for other fused salts, so, factors other than the size must also affect the mobility of the ions in a fused salt.

The variation with composition of the cation mobilities in the binary systems studied was discussed in terms of ordered and disordered regions in the melt.

The constant mobility of the NO_3^- throughout the binary systems $AgNO_3-NaNO_3$ and $AgNO_3-KNO_3$ led to the conclusion that these salts are completely dissociated in the fused state.

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