Transport numbers and ion mobilities in the fused salt KCl-PbCl2

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Transport numbers and ion mobilities in the fused salt KCl-PbCl₂

Abstract
Values of ionic transport numbers and ionic mobilities were determined for the fused system KCl-PbCl₂. Cation transport numbers of 0.24 (525°C) and 0.78 (850°C) were found for PbCl₂ and KCl, respectively. In each mixture studied t− deviated positively and both t+ and t++ deviated negatively from linearity when plotted against equivalent fraction. The initial very rapid depression of total equivalent conductance from that of pure KCl, caused by addition of small amounts of PbCl₂, was found to be due to the depression of the ionic conductance of K+ rather than complexing between Pb²⁺ and Cl⁻ as had been previously supposed. Values of 0 were compared with those in the system LiCl-PbCl₂, calculated from available literature data.
TRANSPORT NUMBERS AND ION MOBILITIES
IN THE FUSED SALT KCl–PbCl₂

By
Richard A. Fleming
F. R. Duke

December 1957

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Ames, Iowa

Technical Information Service Extension, Oak Ridge, Tenn.
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Transport Numbers and Ion Mobilities in the Fused Salt KCl-PbCl₂

Richard A. Fleming and F. R. Duke

ABSTRACT

Values of ionic transport numbers and ionic mobilities were determined for the fused system KCl-PbCl₂. Cation transport numbers of 0.24 (525°C) and 0.78 (850°C) were found for PbCl₂ and KCl, respectively. In each mixture studied \( t_- \) deviated positively and both \( t_+ \) and \( t_{++} \) deviated negatively from linearity when plotted against equivalent fraction. The initial very rapid depression of total equivalent conductance from that of pure KCl, caused by addition of small amounts of PbCl₂, was found to be due to the depression of the ionic conductance of K⁺ rather than complexing between Pb²⁺ and Cl⁻ as had been previously supposed. Values of \( \phi \) were compared with those in the system LiCl-PbCl₂, calculated from available literature data.

* This report is based on a Ph.D. thesis by Richard A. Fleming submitted December, 1957, to Iowa State College, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.
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INTRODUCTION AND LITERATURE SURVEY

Physical properties of molten or fused salts and fused salt systems are the subject of much interest, speculation and experimentation at the present time. The necessary development of a body of sound and varied data is gradually modifying and clarifying our knowledge of the ionic-liquid state of matter. Many techniques which in the past have been used in studies of solutions and molecular liquids and systems have been found to be useful in this quest for information.

The bulk of the earliest investigations of properties of fused salts was phase diagram determination and interpretation, done as early as 1900. This was closely followed by information on molar volumes, specific and equivalent electrical conductances and somewhat later by data on viscosities and surface tensions of melts.

A resurgence of interest in high temperature physical properties of fused salts began toward the end of the 1940's with voluminous phase diagram, viscosity, density and conductance data published by Bloom, Heymann and co-workers (1,2,3,4,5). Other recent investigative techniques include X-ray structure analysis (6,7,8,9,10,11,12), electromotive force measurements (13,14), calculations of degrees of dissociation of salts in melts (15), determination of an electromotive series of metals in molten salts (16), measurements of surface tensions (17), studies of optical properties
of molten systems (18,19), elucidation of diffusion coefficients (20,21) and measurement of transport numbers and ion mobilities. Janz (22) has authored a valuable review including some of the papers mentioned here.

Considering electrical conductance as an extensive property, the total equivalent conductance, $\Lambda$, of a system is equal to the sum of the ionic conductances, $\lambda_i$, of the ionic species present. Then $\lambda_i/\Lambda$ is the fraction of the total current carried by species $i$. This is known as the transport number (or transference number) of the species $i$ and may be denoted by $t_i$.

After carefully reviewing all available literature on transport numbers in fused salts, Laity and Duke (23,24,25) analyzed the experimental inconsistencies of previous papers and pointed out the basic problem. This was a lack of realization that $\lambda_i$ can be only a relative quantity. Noting that under normal conditions the actual number of ions carrying current is a small fraction of the total number of ions, they then proposed as a frame of reference the inert bulk liquid, i.e., the large group of ions of all species present which are at the moment non-conducting and at rest relative to one another. Following this they proposed an experimental arrangement for determination of transport numbers consistent with their definition. In order to prevent mass flow of their reference frame they suggested and justified the use of a porous membrane interposed between the anode and cathode.
compartments of a cell containing the melt. Their reported data on pure salts includes transport numbers in PbCl₂, PbBr₂ and TlCl; t for PbCl₂ at 565°C was reported as 0.758±0.014.

Bloom and Doull (26) have reported directly conflicting transport data for pure PbCl₂, t = 0.393±0.01 at 527°C, but Lorenz and Janz (27) have convincingly pointed out not only why the data of Bloom and Doull are incorrect but also a rather severe limitation on the "bubble-type" transport cell first used by Duke and Laity (25).

A few years earlier Aziz and Wetmore (28) published the first significant transport data on a fused salt system. They pointed out that there were only two independent transport numbers in the system they examined, AgNO₃-NaNO₃, since the sum of the transport numbers of the three ions was unity. Using a two compartment cell with a central porous membrane, they related transport numbers to concentration changes in the melt caused by the differing current-carrying capabilities of the ions. They embodied the concentration changes in the quantity $\phi$ which they related both to transport numbers and to measurable quantities. They then had one relationship between the two independent transport numbers but not having any second relationship, they could not report absolute ionic transport numbers.

Klemm, as part of a widespread investigation of properties of fused salts, has with Monse (29) published information on the relative current-carrying capabilities of the
cations in the system LiCl-PbCl₂ at 650°C. They report the mobilities of the cations with respect to the anions. It will be later shown that these relative mobilities may be equated to values of $\bar{o}$ through known values of the equivalent conducting, $\Lambda$, the faraday constant, $F$, and $E_{LiCl}$, a concentration term representing the "equivalent fraction" of LiCl.

Currently, Duke, Laity and Owens (30) have determined that the system NaN₃-AgNO₃ exhibits ideal transport numbers in the fused state; ionic mobilities are not functions of ionic concentration. Also, Owens (31) has found that the system KNO₃-AgNO₃ exhibits nearly ideal ionic transport numbers. Apparently $K^+$ does have a somewhat higher mobility when KNO₃ is slightly diluted with AgNO₃; the mobilities of $Ag^+$ and $NO_3^-$ are constant with composition.

It is the opinion of Sundheim (32) that the law of conservation of momentum predetermines transport numbers in pure fused salts. Also, he feels (33) that for systems of three types of ions, transport numbers can be calculated by combining this law with only one experimental relationship between transport numbers and measurable quantities.

The present investigation was begun with the object of delineating the transport numbers of all ions in a fused mixture, since no acceptable data of this type were available. The system KCl-PbCl₂ was chosen first because of its chemical stability at elevated temperatures and second because of the
available, previously referred to data on transport numbers in pure PbCl₂.

One of the earliest attempts to determine transport numbers in fused salts was that of Lorenz and Ruckstuhl (34) who examined the system KCl-PbCl₂ in 1907. Their cell utilized a porous clay membrane to separate anode and cathode compartments. Basically their approach was to determine the change in the number of equivalents of Pb⁺⁺ in the catholyte, or cathode sample, due to electrolysis. Corrections were made for absorption of Pb⁺⁺ into the membrane and electrode, loss of Pb⁺⁺ by evaporation and loss of Pb⁺⁺ by deposition on the cathode as Pb⁰. Their data include a tabulation, for various PbCl₂ weight percentages, of v/a where v is the decrease in Pb⁰ in the catholyte and a is the quantity of Pb⁰ deposited on the cathode. It can be easily shown that this determines t⁺⁺, the experimental transport number of Pb⁺⁺. Values are shown in Table 1.

Table 1. Transport data of Lorenz and Ruckstuhl for the system KCl-PbCl₂

<table>
<thead>
<tr>
<th>Weight % PbCl₂</th>
<th>v/a</th>
<th>t⁺⁺ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>95.72</td>
<td>0.7240</td>
<td>0.2760</td>
</tr>
<tr>
<td>88.04</td>
<td>0.8893</td>
<td>0.1107</td>
</tr>
<tr>
<td>78.89</td>
<td>1.0311</td>
<td>0.0311</td>
</tr>
<tr>
<td>78.64</td>
<td>1.0451</td>
<td>0.0451</td>
</tr>
<tr>
<td>64.83</td>
<td>1.1279</td>
<td>0.1279</td>
</tr>
<tr>
<td>47.83</td>
<td>1.5999</td>
<td>0.5999</td>
</tr>
</tbody>
</table>

ᵃValues calculated from data of Lorenz and Ruckstuhl.
At higher KCl concentrations, negative transport numbers were found for lead ions; in other words there was a net migration of lead ions toward the anode. Concluding that lead ions were to a large extent anionically complexed by Cl\(^{-}\) at these concentrations, Lorenz and Ruckstuhl presented their data as indicated, noting that exact concentrations and formulas for the complexes would have to be known before their transport numbers could be found. At any rate their data indicate that \(t_{++}\) is the algebraic sum of these undetermined transport numbers.

Transport studies on pure salts were first undertaken by Karpachev and Pal'guev (35) who reported values for \(t_{-}\) of 0.8 in PbCl\(_2\). They used a two compartment cell with a shredded-asbestos plug for separation of the catholyte and anolyte. They used the change-of-weight method of Lorenz and Ruckstuhl and checked this with independent measurement of \(t_{++}\); they measured the transfer of radioactive Pb\(^{++}\) from catholyte to anolyte as a function of faradays of electricity passed.

In 1938 the system KCl-PbCl\(_2\) was reexamined by Baimakov and Samusenko (36). They again used Lorenz and Ruckstuhl's change-of-weight technique but unfortunately failed to grasp the significance of the membrane separating anolyte from catholyte. They used a very porous asbestos plug in some experiments and eliminated the membrane completely in others. Their data must be considered meaningless.
Wirths (37) in 1937 used a radioactive isotope of lead, ThB, to investigate the system KCl-PbCl₂. His glass cell consisted of three vertical tubes; the center tube was connected to the outer ones with small diameter tubing. The 3-mm. connecting tubes were attached near the bottoms of the vertical tubes. He sintered powdered glass in the centers of the connecting tubes, producing fritted plugs about 6 mm. in thickness. Their porosity can be judged by the fact that a vacuum of 15 mm. Hg would cause passage of 0.5 ml. water in from one to three minutes. With the cell filled and the sample molten, radioactive lead was placed in the central compartment and electrolysis begun. Wirths's results show a tremendous amount of scatter; but he noted that in the four examined compositions, \( X_{KCl} = 0.00, 0.33, 0.50 \) and 0.67, for which the number of "successful" runs reported were 10, 6, 8, and 8, respectively, the average ratio of activity appearing in the anolyte to activity appearing in the catholyte showed a trend. The ratio was very high for pure PbCl₂, the value being 148. In order, the average values for the other three compositions were reported as 9.2, 4.7 and 3.6. This was interpreted as evidence for anionic complexing of lead by addition of KCl to PbCl₂.

The experiment as performed by Wirths was well conceived, but if the data are subjected to careful statistical analysis, it quickly becomes apparent that little significance should be attached to the results. As will be pointed out
later, the success of an experiment of this general type is almost wholly dependent upon the quality of the porous membrane; in an experiment of this specific type a pair of membranes well matched as to degree of porosity is a necessity.

The general approach of this investigation was to determine $\phi$ for various compositions and then supply the necessary second independent relationship by direct determination of $t_\phi$, using the radioactive isotope $\text{Cl}^{36}$. 
APPARATUS AND INTRODUCTORY INVESTIGATION

Introduction

The furnace

A sixteen-inch Marshall Tube Furnace, Marshall Products Co., Columbus, Ohio, maintained temperature at the desired value for each run. Eight taps in the spiral furnace winding were connected to outside binding posts along the length of the furnace. This created, along the axis of the furnace, longitudinal zones whose temperature could be controlled to an extent by judicious use of shunts. Trial and error adjustment of shunts resulted in temperature uniformity of ±3°C at 525°C and ±10°C at 850°C attained over the center eight inches of the furnace.

The controller and thermocouples

In use, the furnace contained two chromel-alumel thermocouples sheathed with tubing of borosilicate glass or quartz. An indicating thermocouple mounted through a transite plug at one end of the furnace was on the axis of the furnace core and almost touched the transport cell. The thermocouple was connected to a Leeds and Northrup No. 8662 Potentiometer with reference junction compensator and was calibrated at the melting point of aluminum (38). A controlling thermocouple mounted through a transite plug at
the other end of the furnace was positioned so that the metal couple was near the midpoint of the furnace and almost touched the furnace wall. It then "anticipated" temperature fluctuations at the center of the furnace. This thermocouple was connected to a Brown Indicating Controller which operated a powerstat through a proportioning motor. The powerstat delivered up to 110 volts A. C. current to the furnace. The temperature of any given zone in the furnace could be indefinitely maintained within \( \pm 1^\circ C \) of any desired value by this control apparatus.

The current supply

Two current supplies were used during the course of this investigation. In each, selenium rectifiers together with a capacitor-inductor circuit converted line alternating current into full wave rectified direct current. The only essential difference between the two was that the first had a load limit of 100 milliamperes while the one constructed later (Figure 1) could handle currents of 300 milliamperes.

A variable transformer powered the current supply and current was manually regulated within \( \pm 1\% \) of any desired value. The number of faradays passed was obtained simply by multiplying the average current by the length of time of a run and dividing by the faraday constant.
A. AMMETER
B. SWITCH
C. 900 VOLT CENTER-TAP TRANSFORMER
D. 500 MILLIAMPERE, 150 VOLT SELENIUM RECTIFIERS
E. 300 MILLIAMPERE CHOKE
F. 4 MICROFARAD, 1000 VOLT OIL CAPACITOR
G. 8 MICROFARAD, 600 VOLT ELECTROLYTIC CAPACITOR
H. FUSE
L. SIGNAL LIGHT

Figure 1. Circuit diagram of the current supply
The Geiger-Muller Counter

A Tracerlab TGClCT standard end window Geiger-Muller tube with a 2.3 mg. cm.⁻² mica window mounted in Housing Model AL14A, Technical Associates, Glendale, California, was coupled to a Model 100 Berkeley Decimal Scaling Unit. Threshold and operating voltages were determined by standard procedures using PbCl₂ containing some Cl₃⁶ as a source. Counting data were taken using the same counter, scaler, housing, Lucite counter-mount and aluminum sample-holders for all samples.

Preliminary investigation

Effectiveness of sample analysis. Lead (II) chloride, Baker & Adamson Reagent Grade, was freed from water by fusing it at 550°C in a closed petri dish. It was yellowish when molten but perfectly transparent. After cooling it was pulverized to a white powder and stored in an oven at 110°C. Potassium chloride, Baker Analyzed Reagent, was dried at 600°C for two hours then stored in an oven at 110°C.

Samples were analyzed for Pb²⁺ content by the method of Loomis (39). All subsequently referred to water was singly-distilled water. The disodium salt of 1,2-diaminocyclohexanetetraacetic acid, Alrose Chemical Co., Providence, Rhode Island, was prepared; in solution it was standardized against ZnCl₂ prepared by reaction of Bunker Hill brand
electrolytic zinc, minimum purity 99.99%, and Baker and Adamson hydrochloric acid in which the maximum heavy metal impurity was 0.0008%. The direct titration is slow and so an excess of chelating agent was added. Back titration was then effected by a solution of Mg(NO₃)₂ whose disodium cyclohexanediaminetetraacetate equivalent had been determined. The titrations were done in the presence of an NH₄Cl-NH₄OH buffer using as the indicator Eriochromeblack T from the Hach Chemical Company, Ames, Iowa. Aliquots were titrated in quadruplicate.

For K⁺ two gravimetric methods using sodium tetraphenylboron are available (40,41). The method of Cluley (41) was used with a modification necessary because of the PbCl₂ present. An amount of solid disodium cyclohexanediaminetetraacetate sufficient to complex all the PbCl₂ in the aliquot analyzed was added to the solution prior to the sodium tetraphenylboron addition. Dilute sodium hydroxide solution was used with bromthymol blue indicator to adjust the pH of one aliquot to the correct value. No indicator was used in the other aliquots but the same amount of base was added. The sodium tetraphenylboron solution was prepared by dissolving the solid in water and then filtering the solution after it had been clarified by standing with some added Al(OH)₃ gel. This reagent was then added to the sample aliquot in slight excess. After waiting the required thirty minutes for precipitation to become complete, a vacuum
filtration was performed through fine-porosity borosilicate filtering crucibles which had been previously cleaned, dried at 110°C for two hours and weighed. The samples were then washed and the crucibles plus samples dried at 110°C for thirty minutes and reweighed. The wash water was saturated with potassium tetraphenylboron. Weights of potassium tetraphenylboron were converted to aliquot weights of KCl using the multiplicative factor 74.56/358.32.

Pure KCl and PbCl₂ samples with sizes approximating those to be encountered during analysis of actual transport runs were analyzed by the described method. Trial mixtures which were analyzed duplicated actual samples as closely as possible. The relatively large amount of PbCl₂ present necessitated one preliminary operation. The solid sample was transferred to a 250-ml. erlenmeyer flask and its weight determined in the process. It was leached for five minutes by boiling with 100 ml. distilled water. After cooling, the solution was decanted through a medium porosity borosilicate filtering crucible mounted in a clean and dry vacuum filtering flask. The crucible had been previously cleaned, dried at 110°C for one hour and weighed. The filtrations were aided by a water aspirator. The leaching was repeated with a second 100-ml. portion of water. Finally the remainder of the sample in the erlenmeyer was quantitatively transferred to the crucible. The material in the crucible was washed eight or ten times with 10-ml. portions of water.
The crucible was then dried at 110°C for one hour and weighed. The increase in weight was attributed entirely to PbCl₂. The filtrate was quantitatively transferred to a 500-ml volumetric flask and after coming to room temperature was diluted to the mark. The solution contained all of the KCl from the sample and the remainder of the PbCl₂. Analysis of the filtrate was completed volumetrically as previously described. Twenty-and fifty-milliliter aliquots were analyzed for K⁺ and Pb²⁺, respectively. All analyses were done at least in triplicate and usually in quadruplicate. The results of these preliminary analytical investigations appear in Table 2.

Table 2. Effectiveness of analysis of synthetic KCl-PbCl₂ samples

<table>
<thead>
<tr>
<th>Trials</th>
<th>gm. KCl taken</th>
<th>gm. PbCl₂ taken</th>
<th>gm. KCl found</th>
<th>gm. PbCl₂ found</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.6060⁺</td>
<td>-----</td>
<td>0.6110⁺</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>0.0004</td>
<td></td>
<td>0.0060</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-----</td>
<td>1.2000⁺</td>
<td>-----</td>
<td>1.1969⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0004</td>
<td></td>
<td>0.0038</td>
</tr>
<tr>
<td>3</td>
<td>0.6060⁺</td>
<td>1.2000⁺</td>
<td>0.6049⁺</td>
<td>1.1973⁺</td>
</tr>
<tr>
<td></td>
<td>0.0004</td>
<td>0.00</td>
<td>0.0015</td>
<td>0.0042</td>
</tr>
</tbody>
</table>

Transport cell design. Duke and Laity (24,25) showed that mass flow in any transport cell of reasonable geometry must be eliminated if reproducible and significant data are to be secured. They justified the use of a fritted glass disk interposed centrally between the cathode and
anode compartments. The necessity of such a barrier to mass flow was substantiated to the author's satisfaction by a preliminary experiment.

A cell without a disk was designed so that convection currents were minimized in the contained melt. The cell was formed from a 20-inch length of 4-mm. borosilicate tubing with the last four inches on either end being offset 1/4 inch. The offset portions were slightly tilted in the direction of the offset. The ends of the cell protruded from the horizontal tube furnace during a run. Filled by suction from a container of molten salt, the cell contained the sample between the offset portions on each end. Precautions were taken to prevent fractional crystallization of the sample on the cell walls during filling. Electrodes in the form of metal wire were inserted through the ends of the cell to complete the circuit. The cell was made accurately horizontal before a run was begun. Direct current was passed for the desired time and a blast of air at room temperature was then passed through the furnace causing the cell contents to solidify. The cell was removed and broken into a number of sections and each section analyzed chemically. In the absence of mass transport by other than electrical transport, the center portion of the cell would be expected to be unchanged in composition as in the Hittorf type experiment.

Trial runs were made at 245°C with silver wire electrodes and a sample of fused silver and potassium nitrates.
It became immediately apparent that in the time required to pass a number of faradays of electricity sufficient to cause measurable concentration changes in the anolyte and catholyte, mixing invariably occurred between them and ruined the run.

Although Laity (23) had shown that transport cells constructed with borosilicate disks of any porosity less than "medium" yielded essentially the same results, it was felt advisable to reexamine this also. In addition, borosilicate disks of "fine" porosity and 8 mm., instead of the standard 2 mm., thickness were obtained and investigation made to determine whether or not cells from these thicker disks gave the same data as cells made from disks of normal thickness. Finally, porous disks of quartz sealed in quartz tubing were also tested to see if the data were affected by this change in disk composition.

It was subsequently found that values of $\phi$ determined for a given composition and temperature in the system KCl-PbCl$_2$ agreed whether they were obtained from cells with "normal fine", "extra-thick fine" or "normal ultra-fine" borosilicate disks; quartz disks also yielded data in agreement with the above (Table 3). It was, however, also found that experimental values of $t_\tau$ were more sensitive to disk porosity than were values of $\phi$; closer disk inspection showed considerable differences in permeability exhibited by disks which nominally were of the same porosity. As will be
later discussed, it became apparent that repression of transport of ions across the disk by leakage and diffusion was necessary. A measure of the porosity of a disk was obtained by determining the time required for passage of 0.7 ml. of water when a vacuum was applied to the back side of the disk. Knowing this time, corrections could be applied to experimental data; the most satisfactory results were obtained for corrections less than 2% or, correspondingly, water times more than 700 seconds.

Since reversible electrodes are the most convenient ones in a transport cell, potassium, lead or chlorine electrodes could have been tried. However, this was not done. Lead electrodes alone were used because of their convenience. Lead is molten at the temperatures required and, being more dense than the melt, forms a pool at the bottom of the cell.

The actual size of the cell is determined by the size of the sample needed. To determine the sample size, thought had to be given to three interrelated variables: concentration change during a run, analysis accuracy and faradays passed. Since in $\phi$ determinations it is change in concentration which is measured, it is desirable that this change be "large" so that good absolute accuracy can be obtained. On the other hand $\phi$ is a function of composition, albeit a slowly varying one, and for this reason it is desirable that the concentration change be "small". After considering
this problem for a time, it was decided that a 2% concentra-
tion change would not be undesirably high or undesirably
low. Since \( t_{++} \), the transport number of \( \text{Pb}^{++} \), was antici-
pated to be small and since the electrodes were to be lead,
a reasonable value of total faradays could be arrived at as
soon as the gross sample size was selected. The gross
sample size thus determined the size of the transport cell
and also the number of faradays required.

The design of the transport cell subsequently used was
perfected during the disk experiments just described. Major
requirements for the cell are as follows:

a. The cell must be closed. It was found that
preferential \( \text{PbCl}_2 \) loss by volatilization from a
cell open to the atmosphere caused an erratic and
ruinous concentration change with time.

b. The cell must be symmetrical with the disk centered.

c. Since the electrode reactions must be known and
metallic lead is the most convenient choice for
the electrodes, the dense lead at the far end of
the cell must be kept from the disk.

d. The cell should be easy to fill and lend itself to
convenient sample recovery after a run.

The final form of the cell (Figure 2) satisfies all of these
requirements.

In several runs, the initial and final weights of the
electrodes were recorded. From these, current efficiencies
Figure 2. Typical transport cell
of 0.983 ± 0.012 were calculated; it is felt that the current efficiency in the system is 100%.

Determination of φ

Derivation of an expression relating φ to measurable quantities (28)

Consider the previously described transport cell filled with a binary fused salt mixture with a common anion. Further consider the changes taking place in the anolyte, or material filling the anode compartment, during the passage of direct current through the cell. For the anolyte

\[ n_1 = n_1^0 + Z(1 - t_1) \]

In this derivation \( n_1 \) and \( n_1^0 \) are, respectively, the final and initial numbers of equivalents of salt 1, with 1 representing the salt to whose cation the anode is reversible. The number of faradays passed is represented by \( Z \) and \( t_1 \) indicates the transport number of cation 1.

Similarly for salt 2

\[ n_2 = n_2^0 - Zt_2 \]

Then if we let \( N_1^0 \) represent the overall (catholyte plus anolyte) equivalent fraction of salt 1,

\[ N_1^0 = \frac{n_1^0}{n_1^0 + n_2^0} = \frac{n_1 - Z(1 - t_1)}{n_1 - Z(1 - t_1) + n_2 + Zt_2} \]
Then since
\[ t_1 + t_2 + t_3 = 1 \]
we can rearrange to get
\[ t_1 = 1 - \frac{N_2^0n_1 - N_1^0n_2}{Z} - N_1^0t_3 \]
where
\[ \phi = \frac{N_2^0n_1 - N_1^0n_2}{Z} \]
This expression then relates the value of $\phi$ to measurable quantities.

**Preliminary investigation**

**Sample introduction.** Adding the sample to the cell as an intimate solid mixture was found to be a completely satisfactory procedure and was used for all runs. It will be detailed in a later section.

**Sample recovery.** Following the removal of the electrode-cap assemblies after a run, any adhering salt was transferred to marked weighing bottles. The cell was carefully cracked at the disk and each compartment treated separately. After continued tapping on the compartment with a wooden rod, the sample gradually cracked apart and was added to the appropriate weighing bottle. When as much sample as possible had been removed in this manner, the compartment and remaining adhering salt were placed in an
evaporating dish over a hot plate and leached with water. When the salt was dissolved, the hot solution was filtered, then boiled to dryness and the last of the sample placed in the weighing bottle.

The effectiveness of the recovery procedure was ascertained by making a blank $\phi$ determination. The run was normal in every respect save one; no current was passed through the cell. The total loss amounted to 0.0680 gm. almost equally divided between the two compartments; this was a recovery of 99.83%, a value comparable with that attained during actual runs.

The recovery is quite acceptable. One can also see that, as anticipated, sample loss by volatilization was negligible.

**Trial determinations and investigation of possible variables.** A complete series of experiments was carried out in order to examine the effect of disk porosity, thickness and composition on measured transport numbers (Table 3).

The precision of determination of $\phi$ at these compositions is $\pm 0.012$. It can be seen that within the limits of experimental accuracy of the technique, cells made from any of the different disks yielded values of $\phi$ falling within the range of $\phi_{\text{average}}$. It was decided to use ultra-fine porosity disks for all subsequent runs.

The effects on $\phi$ of total faradays and of total
Table 3. Effect of disk porosity, thickness and composition on $\phi$

<table>
<thead>
<tr>
<th>Run</th>
<th>$X_{KCl}$</th>
<th>Type of disk</th>
<th>Temperature ($^\circ$C)</th>
<th>$\phi$</th>
<th>$\phi - \phi_{\text{average}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>0.631</td>
<td>FET$^a$</td>
<td>525</td>
<td>0.592</td>
<td>-0.008</td>
</tr>
<tr>
<td>20</td>
<td>0.631</td>
<td>UF$^b$</td>
<td>525</td>
<td>0.616</td>
<td>+0.016</td>
</tr>
<tr>
<td>21</td>
<td>0.631</td>
<td>UF</td>
<td>525</td>
<td>0.588</td>
<td>-0.012</td>
</tr>
<tr>
<td>35</td>
<td>0.631</td>
<td>$Q^c$</td>
<td>525</td>
<td>0.604</td>
<td>+0.004</td>
</tr>
<tr>
<td>4</td>
<td>0.185</td>
<td>F</td>
<td>475</td>
<td>0.115</td>
<td>±0</td>
</tr>
<tr>
<td>5</td>
<td>0.185</td>
<td>F</td>
<td>475</td>
<td>0.123</td>
<td>+0.008</td>
</tr>
<tr>
<td>9</td>
<td>0.185</td>
<td>F</td>
<td>475</td>
<td>0.130</td>
<td>+0.015</td>
</tr>
<tr>
<td>10</td>
<td>0.185</td>
<td>UF</td>
<td>475</td>
<td>0.097</td>
<td>-0.018</td>
</tr>
<tr>
<td>12</td>
<td>0.185</td>
<td>UF</td>
<td>475</td>
<td>0.110</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

$^a$Extra-thick (8 mm.), fine porosity borosilicate disk.

$^b$Ultra-fine porosity borosilicate disk.

$^c$Quartz disk.

$^d$Fine-porosity, borosilicate disk.

current were also examined. In run number four, the current was 50 milliamperes and the determined value of $\phi$ deviated not at all from the average of the other four runs, all made at currents of 100 milliamperes. Runs 24, 27 and 28, with currents of 300 milliamperes for 0.001333 faradays, agreed with runs 22, 23 and 26 with currents of 100 milliamperes for 0.004000 faradays. It was concluded that currents and total faradays of the magnitudes used were not experimental
Experimental procedure

Cell construction. In the borosilicate cells used at 525°C the vertical tubes were initially constructed from the outer portion of 14/35 standard taper ground glass joints (Figure 2). Later some were constructed from regular tubing of the same size and these proved to be equally effective. The ultrafine fritted glass disks were obtained from Corning Glass Works, Corning, New York, as "Funnel, Buchner type, with fritted disk, 10 mm., ultrafine." The 8-mm. thick and 10-mm. diameter "fine" porosity disks were obtained by special order from Corning Glass Works. Nichrome lead wires were used and were welded to short pieces of tungsten that passed through the glass seal of the electrode-cap assembly. The exposed tungsten was completely immersed in molten lead during a run.

The runs at 850°C required cells made of quartz. The 10 mm. in diameter and 1.5-mm. thick quartz disks, Amersill Company, Hillside, New Jersey, were obtained sealed in the center of a six inch length of 10 mm. inside diameter quartz tubing. Since a lead wire could not be sealed to a quartz electrode-cap assembly, the short piece of tungsten was omitted for these assemblies. The nichrome wire was of such a size to almost completely fill, and hence block, the small diameter piece of quartz tubing of the electrode-cap
assembly. Borosilicate electrode-cap assemblies used for some high temperature runs also proved to be effective, although after the run they were often found to be distorted as a result of the high temperature.

The sample. As previously mentioned, the most satisfactory method of cell filling involved adding the salts as intimately mixed solids. Lead shot, Baker Analyzed Reagent, was first added to each electrode well of the cell. Predetermined approximate weights of KCl and PbCl₂ were transferred from weighing papers to a smooth surfaced mullite mortar. The exact weights were determined by difference. The contents of the mortar were carefully and thoroughly ground together and the mixture then quantitatively transferred first to weighing paper, then to the proper cell compartment. The exact amount added was determined by difference. Introduction of the electrode-cap assembly completed the filling procedure. The procedure was repeated to fill the other compartment.

Technique of run. The assembled cell was placed in the horizontal tube furnace and the furnace plugs with their thermocouples were attached. Wires from the current supply were attached to the cell's electrode leads projecting from small holes in the two furnace plugs. The furnace was brought up to temperature and the run commenced. When the passage of current was completed, one furnace plug was
removed and the cell quickly taken from the furnace. Working rapidly, the electrode-cap assemblies were removed before they could freeze in place and were replaced by small glass plugs. During freezing and contracting, the plugs prevented ejection of small bits of sample from the cell.

Sample recovery. The general recovery procedure previously described was employed.

Sample analysis. The sample analysis previously described was employed. For every run the weight of the gross sample was known. Consequently, although both components were determined directly for several compositions, when one component was present in small concentration, the determination of the major constituent by difference was considered more accurate than by analysis. The two calculated values of $\varnothing$ were then weighted accordingly to arrive at a best value.

Calculations

Values of $\varnothing$ were calculated in straightforward manner using the previously developed equation.

Radiochemical Determination of $t_-$

Derivation of an expression relating $t_-$ to measurable quantities

Of several possible experimental arrangements, the one
leading to highest accuracy for values of \( t_- \), the transport number of chloride ion, is that in which all of the radioactive anions are originally in the catholyte. Then

\[
t_- = \frac{\text{Equivalents of anion migrating from catholyte}}{Z} = \text{faradays of current passed}
\]

\[
t_- = \frac{(\text{Fraction of anions migrating}) \ (E_c = \text{eq. of anions initially in catholyte})}{Z}
\]

\[
t_- = \frac{\left[ \frac{\text{Cl}^{36} \text{in anolyte after run}}{\text{Cl}^{36} \text{in catholyte before run}} \right] E_c}{Z}
\]

\[
t_- = \frac{k_{\text{c}} a}{k_{\text{c}} c} E_c
\]

\[
t_- = \frac{E_c}{Z}
\]

where \( kC \) is the actual counting rate of the sample.

It is required that \( k \), the constant of proportionality between quantity of \( \text{Cl}^{36} \) and observed counting rate, must be the same for catholyte and anolyte if it is to cancel in the derivation.

**Preliminary investigation**

Preparation of stock KCl*. Radioactive chlorine
with a half life of $3.08 \times 10^5$ years (42), hereafter denoted by Cl*, was obtained as aqueous HCl$^{36}$ from Oak Ridge National Laboratory, Oak Ridge, Tennessee. The preparation of the stock was dictated by the desired final anolyte counting rate of 200-500 c/m for a 0.1000 gm. PbCl$_2$* sample. About two microcuries of activity were required in the catholyte for each run.

The HCl* was added to about 20 ml. H$_2$O in an evaporating dish and the solution made barely basic with dilute KOH solution. An appropriate amount of inert KCl was added as a diluent and the solution evaporated to dryness over a steam bath. The stock was thoroughly pulverized in a mortar and then placed in a weighing bottle and kept in an evacuated desiccator.

Preparation of stock PbCl$_2$*. In an evaporating dish, a slight excess of Pb($O_2CCH_3$)$_2$ was added to the aqueous HCl*; an additional predetermined amount of inert PbCl$_2$ as a diluent was also added. The solution was evaporated to dryness over a steam bath. This stock was also pulverized and stored in the vacuum desiccator.

Self-absorption. It was decided to count the activity as PbCl$_2$*. Under the existing experimental conditions self-absorption was found to be negligible for weights of PbCl$_2$* less than 150 milligrams (Figure 3). The weight of PbCl$_2$* selected for future inspection and comparison of activity was 0.1000 gm. From four to six sample aliquots
Figure 3. Self absorption in Pb(36Cl)_2
weighing less than 0.1300 gm. were counted and from the best straight line from the origin through these on a "counting rate vs. weight of PbCl₂*" graph, the counting rate of a 0.1000 gm. PbCl₂* sample was determined.

Blank runs and the leakage problem. Initial blank runs undertaken with the intent of determining the blank counting rate correction necessary showed an extreme lack of consistency as well as an unexpectedly high counting rate. The first nine blank runs had counting rates for 0.1000-gm. PbCl₂* samples from 17 c/m to 118 c/m with a clustered group of five having an average of 64±9 c/m. The wide spread was disconcerting in view of the expected counting rate due to ionic migration of only about 250 c/m and because of this a number of actual runs had to be discarded as meaningless. To reduce the leakage-diffusion correction, the second power supply was constructed and all subsequent radiochemical runs made with a direct current of 300 milliamperes. This allowed the desired number of faradays to be passed in one-third the time necessary at a current of 100 milliamperes. Also the furnace was brought to the temperature of the run before the transference cell was introduced. Following the introduction of the cell, the desired temperature was re-established in a minimum of time thus further reducing leakage-diffusion time. In addition to these changes, a closer look was taken at the fritted disks themselves.

A series of borosilicate disks, all nominally of
"ultrafine" porosity, were in turn attached to a water aspirator operating at maximum water pressure and a record was made of the time required for 0.7 cc. of water to pass through the disk. For the first ten disks examined the times varied from 46 to 384 seconds. It can be seen that this eightfold difference in porosity would result in very different diffusion-leakage magnitudes and would be hard to correct for when trying to determine the size of the blank correction to be made. Therefore, subsequently when the disks were made into cells, a moderate amount of sintering was purposely allowed with the hope of reducing disk porosity. In this manner cells were successfully constructed with water passage times of up to 3000 seconds; thereafter cells with times of less than 400 seconds were not used.

The quartz disks required different treatment. Their water passage times were initially on the order of three seconds, a completely unacceptable value. The disks were partially plugged by depositing silica within them. A gel was produced in the disk by saturating it with ethyl silicate, E. H. Sargent & Co., Chicago, Illinois, then adding concentrated hydrochloric acid. Heating to 850°C decomposed the gel to pure silica which remained in the pores of the disk. Each treatment roughly decreased the porosity by one-half and about a dozen treatments were given each disk; the better ones attained water passage times of more than
3000 seconds.

Finally, the furnace was given a very slight tilt (about a 1/4-inch rise in two linear feet) so that any leakage would always be from the anolyte to the catholyte. The significance of this modification will be discussed later. After these several changes, acceptable runs became possible.

Experimental procedure

Cell construction. The type of cell used for determination of $\bar{\phi}$ was also used for radiochemical determination of $t_\cdot$.

The sample. A somewhat smaller sample size was used. In every run the anolyte and catholyte samples were prepared so that not only was the composition as desired, but in addition, each compartment contained exactly 0.034 equivalents of Cl$^-$. Moreover, in each case 0.2270 gm. KCl on the catholyte side was replaced with an equal weight of KCl$^*$. The sample was prepared, introduced into the cell and the cell assembled in a manner analogous to that described for determination of $\phi$.

Technique of run. The run was conducted exactly as were $\phi$ runs.

Technique of analysis. The general recovery procedure previously described was employed. After removal from the weighing bottle, the weighed sample was pulverized and placed in a four-liter erlenmeyer flask and dissolved.
by boiling with as much as a liter of water for samples rich in PbCl$_2$. When solution had been effected, six 100-ml. beakers were filled with solution which was concentrated by boiling on a hot plate until 10-20 ml. were left. After quick cooling of the solution, the precipitated PbCl$_2$ was collected by vacuum filtration on a previously weighed filter paper disk. The disk was supported on a fritted glass filter and held in place with a glass chimney of 3-cm. diameter. Three washings with water followed by three with acetone removed all of the KCl$^+$ solution from the sample. The disk was then placed on a glass plate and covered with a glass ring which held the edges down and prevented "curling" during drying. After a final weighing the sample was mounted on a two-inch square manila cardboard backing using a cellophane cover held in place with tape.

The sample was then taped to an aluminum sample-holder and placed in the Lucite counter-mount which held it centered about one centimeter below the window of the Geiger-Muller tube. Radioactive decays were then recorded.

**Calculation of t**

For each run the weight and composition of the catholyte were known; hence, the total number of equivalents of Cl$^-$ initially in the catholyte was known. Then 0.1000 gm. PbCl$_2$ represented a known aliquot, $A_c$, of Cl$^-$ and $kC_c = (c/m$ for 0.1000 gm. PbCl$_2$)$ (A_c^{-1})$. From $\phi$ data the
concentration of the anolyte following the run is known. Knowing the anolyte sample weight, the total number of equivalents of Cl\(^-\) was found and the aliquot of Cl\(^-\) represented by 0.1000 gm. PbCl\(_2\)\(^*\) determined. Similarly, k\(_{C_a}'\) = (c/m for 0.1000 gm. PbCl\(_2\)\(^*\))(A\(_a^{-1}\)). Subtraction of the value of the blank from k\(_{C_a}'\) yielded k\(_C_a\). Then t\(_-\) was found by simple substitution in the derived equation.
RESULTS

Values of $\phi$

It is instructive to calculate how $\phi$ would vary with composition for a regular system—one in which the various ionic mobilities were, in general, different yet each was constant for all concentrations. The regular system AC-BC$_2$ is defined by

$$t_B = E_B t_B^0$$
$$t_C = \text{constant}.$$ 

Since, according to Aziz and Wetmore's derivation (28),

$$\phi = 1 - t_B - E_B t_C$$
we see that

$$\phi = 1 - E_B t_B^0 - E_B t_C$$
$$= 1 + (-t_B^0 - t_C) E_B$$

which is of the form

$$x = 1 + my.$$ 

Thus, in this regular system $\phi$ is proportional to $E_B$ and varies in a linear manner. The end points are zero at $E_B = 1$ and one at $E_B = 0$. Since this is true it can be seen that in this regular system $\phi$ is numerically identical to $E_A$.

Average values of $\phi$ and the standard deviations of the runs are summarized in Table 4. It will be noted that the
values deviate positively from the relationship described above.

Table 4. Summary of values of $\phi$ in the system $\text{KCl-PbCl}_2$

<table>
<thead>
<tr>
<th>$X_{\text{KCl}}$</th>
<th>$E_{\text{KCl}}$</th>
<th>Number of runs</th>
<th>Temperature ($^\circ$C)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>0</td>
<td>---</td>
<td>0.000</td>
</tr>
<tr>
<td>0.160</td>
<td>0.087</td>
<td>5</td>
<td>475</td>
<td>0.115 ± 0.011</td>
</tr>
<tr>
<td>0.312</td>
<td>0.185</td>
<td>3</td>
<td>525</td>
<td>0.257 ± 0.015</td>
</tr>
<tr>
<td>0.458</td>
<td>0.297</td>
<td>3</td>
<td>525</td>
<td>0.389 ± 0.012</td>
</tr>
<tr>
<td>0.631</td>
<td>0.461</td>
<td>3</td>
<td>525</td>
<td>0.599 ± 0.012</td>
</tr>
<tr>
<td>0.631</td>
<td>0.461</td>
<td>1</td>
<td>850</td>
<td>0.604</td>
</tr>
<tr>
<td>0.810</td>
<td>0.681</td>
<td>2</td>
<td>850</td>
<td>0.789 ± 0.012</td>
</tr>
<tr>
<td>1.000</td>
<td>1.000</td>
<td>0</td>
<td>---</td>
<td>1.000</td>
</tr>
</tbody>
</table>

These values of $\phi$ are presented in the customary manner in Figure 4.

There are advantages to be gained in representing these values of $\phi$ on a triangular coordinate graph. For our system we have three transport numbers, $t_+, t_+, t_-$, whose sum is unity. With proper coordinate labeling, the sum of the coordinates of a point on a triangular graph is also unity. Therefore, such a graph is admirably suited for the presentation of the variation of all three transport numbers with composition. On such a graph $\phi$ will necessarily be represented by a line since the system of two independent transport
Figure 4. Values of $\phi$ in the system KCl-PbCl$_2$
numbers still possesses one degree of freedom after $\phi$ has been determined. The data of Table 4 are thus also represented by Figure 5.

It might be noted that any line in Figure 5 can be positioned by assuming random values for $t_3$ (or $t_1$) in the previously developed relationship

$$t_1 = 1 - \phi - E_1 t_3$$

and solving for $t_1$ (or $t_3$). One soon finds that the line constructed is straight and simplifies matters thereafter by drawing straight lines through the two points determined by the assumption $t_1 = 0$ and the assumption $t_3 = 0$. Furthermore, it is true that the slope of the line is a function only of the overall composition of the sample. These two facts can be proved, and have been by Fleming (43, pages 36-56, page 75); the proof is tedious though not difficult.

Values of $t_{+\phi}$, $t_+$ and $t_-$

Blank runs were made first so that corrections due to leakage and diffusion could be applied to the data from actual runs. All radiochemical runs were made with currents of 300 milliamperes (except for blank runs made with no current) for times of 429 seconds. The data for blank runs are presented in Table 5. The blank data were placed on a graph of "time" vs. 

$$v(kC_a)^{-1}$$

and a best straight line drawn through the data points for each temperature. Then
Figure 5. Values of $\phi$ in the system KCl-PbCl$_2$. 

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$X_{KCl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.000</td>
</tr>
<tr>
<td>b</td>
<td>0.810</td>
</tr>
<tr>
<td>c</td>
<td>0.631</td>
</tr>
<tr>
<td>d</td>
<td>0.485</td>
</tr>
<tr>
<td>e</td>
<td>0.312</td>
</tr>
<tr>
<td>f</td>
<td>0.160</td>
</tr>
<tr>
<td>g</td>
<td>0.000</td>
</tr>
</tbody>
</table>
knowing the "time" for a cell used in an actual run, observed values of $kC_a$ for the run were corrected by simply subtracting the blank-diffusion correction found on the graph.

Table 5. Anolyte counting rates ($kC_a$) following blank runs

<table>
<thead>
<tr>
<th>Run</th>
<th>$X_{KCl}$</th>
<th>Disk</th>
<th>Time (sec)$^a$</th>
<th>Temperature ($^\circ$C)</th>
<th>$kC_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.631</td>
<td>UF$^b$</td>
<td>59</td>
<td>525</td>
<td>4460</td>
</tr>
<tr>
<td>27</td>
<td>0.631</td>
<td>UF</td>
<td>123</td>
<td>525</td>
<td>4120</td>
</tr>
<tr>
<td>32</td>
<td>0.631</td>
<td>UF</td>
<td>$&gt;2000$</td>
<td>525</td>
<td>146</td>
</tr>
<tr>
<td>33</td>
<td>0.631</td>
<td>UF</td>
<td>195</td>
<td>525</td>
<td>1750</td>
</tr>
<tr>
<td>41</td>
<td>0.631</td>
<td>UF</td>
<td>$&gt;2000$</td>
<td>525</td>
<td>140</td>
</tr>
<tr>
<td>53</td>
<td>0.631</td>
<td>FET$^c$</td>
<td>450</td>
<td>525</td>
<td>850</td>
</tr>
<tr>
<td>73</td>
<td>1.000</td>
<td>Q$^d$</td>
<td>600</td>
<td>850</td>
<td>2720</td>
</tr>
<tr>
<td>74</td>
<td>1.000</td>
<td>Q</td>
<td>900</td>
<td>850</td>
<td>760</td>
</tr>
<tr>
<td>75</td>
<td>1.000</td>
<td>Q</td>
<td>800</td>
<td>850</td>
<td>1160</td>
</tr>
</tbody>
</table>

$^a$Length of time required for 0.7 cm.$^3$ of water to be drawn through the disk by a vacuum of less than 5 cm. of mercury.

$^b$Ultrafine porosity borosilicate disk.

$^c$Fine porosity, 8 mm. thickness borosilicate disk.

$^d$Quartz disk.

Then the values of $t_-$ presented in Table 6 were calculated. These values are presented on Cartesian coordinates in Figure 6 and triangular coordinates in Figure 7. Duke and Laity's value for pure PbCl$_2$ (25) was used since it is felt
that the bubble-cell method is more accurate than the radio-tracer method of determination of $t_{-}$.

Table 6. Values of $t_{-}$ in the system KCl-PbCl$_2$

<table>
<thead>
<tr>
<th>Run</th>
<th>$X_{KCl}$</th>
<th>Disk</th>
<th>Temperature ($^\circ$C)</th>
<th>$t_{-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.458</td>
<td>UF</td>
<td>525</td>
<td>0.67</td>
</tr>
<tr>
<td>36</td>
<td>0.631</td>
<td>UF</td>
<td>525</td>
<td>0.61</td>
</tr>
<tr>
<td>38</td>
<td>0.631</td>
<td>UF</td>
<td>525</td>
<td>0.63</td>
</tr>
<tr>
<td>42</td>
<td>0.160</td>
<td>UF</td>
<td>525</td>
<td>0.73</td>
</tr>
<tr>
<td>43</td>
<td>0.160</td>
<td>UF</td>
<td>525</td>
<td>0.74</td>
</tr>
<tr>
<td>44</td>
<td>0.631</td>
<td>UF</td>
<td>525</td>
<td>0.57</td>
</tr>
<tr>
<td>45</td>
<td>0.312</td>
<td>UF</td>
<td>525</td>
<td>0.69</td>
</tr>
<tr>
<td>46</td>
<td>0.458</td>
<td>UF</td>
<td>525</td>
<td>0.69</td>
</tr>
<tr>
<td>47</td>
<td>0.312</td>
<td>UF</td>
<td>525</td>
<td>0.70</td>
</tr>
<tr>
<td>50</td>
<td>0.312</td>
<td>UF</td>
<td>525</td>
<td>0.80</td>
</tr>
<tr>
<td>51</td>
<td>0.000</td>
<td>UF</td>
<td>525</td>
<td>0.80</td>
</tr>
<tr>
<td>52</td>
<td>0.000</td>
<td>UF</td>
<td>525</td>
<td>0.75</td>
</tr>
<tr>
<td>55</td>
<td>0.160</td>
<td>FET</td>
<td>525</td>
<td>0.94</td>
</tr>
<tr>
<td>57</td>
<td>0.458</td>
<td>FET</td>
<td>525</td>
<td>0.51</td>
</tr>
<tr>
<td>58</td>
<td>0.631</td>
<td>FET</td>
<td>525</td>
<td>0.59</td>
</tr>
<tr>
<td>60</td>
<td>1.000</td>
<td>Q</td>
<td>850</td>
<td>0.23</td>
</tr>
<tr>
<td>62</td>
<td>1.000</td>
<td>Q</td>
<td>850</td>
<td>0.22</td>
</tr>
<tr>
<td>63</td>
<td>0.631</td>
<td>Q</td>
<td>850</td>
<td>0.56</td>
</tr>
<tr>
<td>64</td>
<td>0.631</td>
<td>Q</td>
<td>850</td>
<td>0.61</td>
</tr>
<tr>
<td>65</td>
<td>0.631</td>
<td>Q</td>
<td>850</td>
<td>0.55</td>
</tr>
<tr>
<td>67</td>
<td>0.810</td>
<td>Q</td>
<td>850</td>
<td>0.55</td>
</tr>
<tr>
<td>68</td>
<td>0.810</td>
<td>Q</td>
<td>850</td>
<td>0.44</td>
</tr>
<tr>
<td>70</td>
<td>1.000</td>
<td>Q</td>
<td>850</td>
<td>0.21</td>
</tr>
<tr>
<td>72</td>
<td>0.631</td>
<td>Q</td>
<td>525</td>
<td>0.60</td>
</tr>
</tbody>
</table>

The advantages of the triangular graph now become apparent. It is an easy matter to draw a best line through the data. This line then represents the smoothed values of all three transport numbers as functions of composition. These values are presented in Table 7 and Figure 8.
Figure 6. Chloride ion transport number in the system KCl-PbCl$_2$
Figure 7. Values of $t_i$ in the system KCl-PbCl$_2$
Table 7. Smoothed values of transport numbers in the system KCl-PbCl₂

<table>
<thead>
<tr>
<th>X_{KCl}</th>
<th>Temperature (°C)</th>
<th>t⁺</th>
<th>t++</th>
<th>t⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>525</td>
<td>0.00</td>
<td>0.024 ± 0.01</td>
<td>0.76 ± 0.01</td>
</tr>
<tr>
<td>0.160</td>
<td>525</td>
<td>0.05 ± 0.016</td>
<td>0.21 ± 0.023</td>
<td>0.74 ± 0.02</td>
</tr>
<tr>
<td>0.312</td>
<td>525</td>
<td>0.12 ± 0.023</td>
<td>0.17 ± 0.024</td>
<td>0.71 ± 0.02</td>
</tr>
<tr>
<td>0.458</td>
<td>525</td>
<td>0.19 ± 0.024</td>
<td>0.13 ± 0.025</td>
<td>0.68 ± 0.03</td>
</tr>
<tr>
<td>0.631</td>
<td>525</td>
<td>0.32 ± 0.032</td>
<td>0.08 ± 0.023</td>
<td>0.60 ± 0.03</td>
</tr>
<tr>
<td>0.631</td>
<td>850</td>
<td>0.32 ± 0.035</td>
<td>0.10 ± 0.023</td>
<td>0.58 ± 0.03</td>
</tr>
<tr>
<td>0.810</td>
<td>850</td>
<td>0.46 ± 0.037</td>
<td>0.04 ± 0.023</td>
<td>0.50 ± 0.04</td>
</tr>
<tr>
<td>1.000</td>
<td>850</td>
<td>0.78 ± 0.02</td>
<td>0.00</td>
<td>0.22 ± 0.03</td>
</tr>
</tbody>
</table>

Since the values of t⁺ and t++ were determined indirectly, they reflect errors in $\phi$ as well as errors in t⁻. Direct determination of t⁻ resulted in errors somewhat smaller than errors in t⁺ and t++. 

Values of Other Derived Quantities

Ionic conductances

As discussed in the "Introduction", we are now able to calculate values of ionic conductances, $\lambda_1$, for the ions at various compositions. We have already determined $t_1$ and need only to find the total equivalent conductance, $\Lambda$, as a function of composition and at the appropriate temperatures.
Figure 8. Values of $t_1$ in the system KCl-PbCl$_2$. 
We may then calculate $\lambda_1$ by means of the relationship

$$\lambda_1 = t_1 \Lambda.$$  

Boardman, Dorman and Heymann (2) have reported values of density in the system KCl-PbCl₂ as analytic functions of temperature for the pure salts and for three mixtures. These data were of the form

$$d_t = a - b (t - 600)$$

where $t$ was the temperature in °C. Values of $a$ and $b$ at compositions for which $t_1$ are known were determined by interpolation on a graph of the quantity vs. $X_{KCl}$. Values of density were then calculated. The value for pure KCl reported by Yaffe and Van Artsdalen (44) is in agreement, being higher by only 0.3%. Bloom and Heymann (1) have reported specific conductances, $\kappa'$, of the system and from their data, values of $\kappa'$ were found at the desired compositions and temperatures. Equivalent conductances were calculated from the relationship

$$\Lambda = \kappa' v_e = \kappa' x \frac{w_e}{d}$$

where $w_e$ is the equivalent weight (or average equivalent weight) of the system. Ionic conductances calculated on the basis of smoothed values of $t_1$ and calculated values of $\Lambda$ are shown in Table 8 and Figure 9 together with values of total equivalent conductance.
Table 8. Values of equivalent conductance and smoothed values of ionic conductance (ohm\(^{-1}\) cm\(^2\) eq\(^{-1}\)) in the system KCl-PbCl\(_2\)

<table>
<thead>
<tr>
<th>(x_{KCl})</th>
<th>Temperature (°C)</th>
<th>(\Lambda)</th>
<th>(\lambda_+)</th>
<th>(\lambda_{++})</th>
<th>(\lambda_-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>525</td>
<td>45.28</td>
<td>---</td>
<td>10.9 (\pm) 0.5</td>
<td>34.4 (\pm) 0.5</td>
</tr>
<tr>
<td>0.160</td>
<td>525</td>
<td>42.64</td>
<td>2.13 (\pm) 0.68</td>
<td>8.95 (\pm) 0.98</td>
<td>31.6 (\pm) 0.8</td>
</tr>
<tr>
<td>0.312</td>
<td>525</td>
<td>39.65</td>
<td>4.77 (\pm) 0.91</td>
<td>6.74 (\pm) 0.95</td>
<td>28.2 (\pm) 0.8</td>
</tr>
<tr>
<td>0.458</td>
<td>525</td>
<td>36.23</td>
<td>6.88 (\pm) 0.86</td>
<td>4.72 (\pm) 0.91</td>
<td>24.7 (\pm) 0.9</td>
</tr>
<tr>
<td>0.631</td>
<td>525</td>
<td>35.14</td>
<td>11.2 (\pm) 1.12</td>
<td>2.81 (\pm) 0.81</td>
<td>21.1 (\pm) 1.1</td>
</tr>
<tr>
<td>0.631</td>
<td>850</td>
<td>72.99</td>
<td>23.4 (\pm) 2.6</td>
<td>7.30 (\pm) 1.68</td>
<td>42.3 (\pm) 1.5</td>
</tr>
<tr>
<td>0.810</td>
<td>850</td>
<td>79.97</td>
<td>36.8 (\pm) 3.0</td>
<td>3.20 (\pm) 1.84</td>
<td>40.0 (\pm) 3.2</td>
</tr>
<tr>
<td>1.000</td>
<td>850</td>
<td>118.75</td>
<td>92.6 (\pm) 2.4</td>
<td>---</td>
<td>26.2 (\pm) 3.6</td>
</tr>
</tbody>
</table>

**Ionic mobilities**

The equivalent ionic conductance is equal to \(\lambda_i/C_i\) where \(C_i\) is an equivalent concentration term. Since \(\lambda_i/C_i\) equals \(\lambda_i\) in a pure salt, it is clear that in the system KCl-PbCl\(_2\)

\[
\begin{align*}
    C_+ &= E_{KCl} \\
    C_{++} &= E_{PbCl_2} = 1 - E_{KCl} \\
    C_- &= \text{a constant} = 1.
\end{align*}
\]

We can then determine values of ionic mobility (45, page 59), \(\mu_i\), by means of the relationship

\[
\mu_i = \frac{t_1 \Lambda}{96,500 C_i}.
\]
Figure 9. Total and ionic conductances in the system KCl-PbCl₂
These values are recorded in Table 9 and presented graphically in Figure 10.

Table 9. Smoothed values of ionic mobility, $\mu_1$ (cm$^2$ sec$^{-1}$ volt$^{-1}$), in the system KCl-PbCl$_2$

<table>
<thead>
<tr>
<th>$X_{KCl}$</th>
<th>Temperature ($^\circ$C)</th>
<th>$\mu_+ \times 10^4$</th>
<th>$\mu_{++} \times 10^4$</th>
<th>$\mu_- \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>525</td>
<td>---</td>
<td>1.12±0.05</td>
<td>3.57±0.05</td>
</tr>
<tr>
<td>0.160</td>
<td>525</td>
<td>2.54±0.81</td>
<td>0.94±0.10</td>
<td>3.27±0.08</td>
</tr>
<tr>
<td>0.312</td>
<td>525</td>
<td>2.67±0.51</td>
<td>0.86±0.12</td>
<td>2.92±0.08</td>
</tr>
<tr>
<td>0.458</td>
<td>525</td>
<td>2.40±0.30</td>
<td>0.70±0.13</td>
<td>2.56±0.09</td>
</tr>
<tr>
<td>0.631</td>
<td>525</td>
<td>2.52±0.25</td>
<td>0.54±0.16</td>
<td>2.19±0.11</td>
</tr>
<tr>
<td>0.631</td>
<td>850</td>
<td>5.26±0.58</td>
<td>1.40±0.32</td>
<td>4.38±0.16</td>
</tr>
<tr>
<td>0.810</td>
<td>850</td>
<td>5.61±0.46</td>
<td>1.04±0.60</td>
<td>4.14±0.33</td>
</tr>
<tr>
<td>1.000</td>
<td>850</td>
<td>9.60±0.48</td>
<td>---</td>
<td>2.72±0.37</td>
</tr>
</tbody>
</table>
Figure 10. Ion mobilities in the system KCl-PbCl₂
DISCUSSION OF RESULTS

The following symbols appear in the discussion. They are collected below, together with their definitions, for easy reference.

- $t_i$: the experimentally measured transport number of species $i$; $t_{++}$ refers to Pb$^{++}$, $t_+$ refers to K$^+$ and $t_-$ refers to Cl$^-$. $t_i$: the actual transport number of species $i$. The above subscripts have the same meaning and in addition $t_c^+$ refers to a cationic complex while $t_c^-$ refers to an anionic complex.

- $t_i^o$: the value $t_i$ would have if no complexing of any type existed.

- $E_{KCl}$: equivalent fraction of KCl; the number of equivalents of KCl in a sample divided by the total number of equivalents of salt.

- $\mu_i$: the mobility ($\text{cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$) of ionic species $i$. The above subscripts have the same meaning.

- $\Lambda$: total equivalent conductance of the melt being discussed.

Before discussing the general significance of the results of this investigation into some physical properties of the fused system KCl-PbCl$_2$, it is worthwhile to examine the results in the light of previously available data.

From the review in the "Introduction" it is apparent
that the values of $t_{++}$ reported by Lorenz and Ruckstuhl (34) are directly contradicted by values reported in this investigation. In the chapter on "Results" it is, however, not apparent that the data necessary for calculation of $\phi$ yield, in addition, transport numbers of all the ions if treated exactly as Lorenz and Ruckstuhl treated their data. For the anolyte the required equations are:

$$t_1 = \frac{|eq_1^0 - (eq_1' - mZ)|}{Z}$$

where

- $t_1$ = transport number of ion $i$
- $eq_1$ = number of equivalents of ion $i$ in anolyte
- $Z$ = number of faradays of electricity passed
- $m = 1$ when $i = Pb^{++};$ $m = 0$ otherwise
- $^0$ designates initial conditions
- $'$ designates final conditions.

It is easily seen that a very small amount of leakage through the membrane noticeably affects the calculated value of $t_1$. For example, in a typical run for which $Z = 0.001334$ and for which the correct value of $t_+$ is 0.50,

$$|eq_+^0 - eq_+'| = Zt_+ = 0.000667.$$

This is equivalent to about 0.0500 gm. KCl. Consequently leakage of 1.0 mg. would cause a 2% error and a 10% error would be caused by as little as 5.0 mg. KCl leaking through
the membrane.

Owens (31) has examined the rate of leakage through an ultrafine disk using molten AgNO₃-NaNO₃ at 300°C. He has found a leakage rate of about $4 \times 10^{-4} \text{ cm}^3 \text{ min}^{-1}$ caused by a one cm. head. Translated into leakage during a 21 minute run, this is equivalent to about 0.0100 gm. KCl for a mixture of 30 weight percent KCl. For a realistic average head of 2 mm., caused by lack of symmetry in the cell and differing volume changes in the cathode and anode compartments during a run, the amount of KCl leakage estimated from these figures would be on the order of 0.0020 gm. Moreover, since a different disk must be used for every run, and since eightfold porosity differences have been found between disks, it is not surprising that the values of $t_1$ calculated in this way showed such poor agreement that the method was abandoned. Furthermore, it is undoubtedly true that despite all of the precautions of Lorenz and Ruckstuhl, their data also suffered seriously from this source of error. The surprising fact is that they were able to reproduce data sufficiently well so that they would submit it for publication. As a matter of interest, average values for $t_{+\phi}$ of 0.31, 0.12, 0.12, 0.14 and 0.03 at KCl mole fractions of 0.000, 0.160, 0.312, 0.458 and 0.631, respectively, were calculated by their method from data used in the present study for determination of $\phi$. These values
incidentally reflect much greater agreement with the final results of the present study than they do with the older results of Lorenz and Ruckstuhl.

The two values of 0.80 and 0.75 obtained for $t_-$ in pure PbCl$_2$ at 525°C agree well with the value of 0.76 at 565°C as determined by Duke and Laity (25). They incidentally serve to substantiate the previously mentioned position of Lorenz and Janz (27) who presented reasons why Bloom and Doull's (26) value for $t_-$ of 0.39 at 528°C was probably incorrect.

No literature data on transport numbers in pure KCl are available. Recent work by Duke and Cook (46) has yielded a preliminary value for $t_+$ of 0.76 at 850°C while the present work reports a value for $t_+$ of 0.78 at the same temperature.

The data of Wirths (37) have already been discussed in the "Introduction". In connection with his work it is interesting to note that Laity (47) also used the radioactive isotope ThB in a recent experiment designed to determine anionic complexing of Pb$^{++}$. His results indicated no complexing of this type in spite of the positive results obtained by Wirths. Laity then showed how considerations of the probable life times of such projected complexes and considerations of the time necessary for the complex to traverse the disk or membrane lead one to the conclusion that an experiment such as the one performed by Wirths and
later by himself is not likely to produce information of the desired kind. Laity's contention was that because of exchange reactions in the melt, it would be unlikely for radioactive lead to be anionic a sufficient amount of time to allow it to cross the membrane toward the anode from a region of high radioactivity toward a region of low radioactivity. This completes the discussion of the available literature which is of direct interest in this investigation.

The preliminary investigation reported here indicated that neither a change in disk composition from borosilicate to quartz nor an increase in the thickness of the disk by a factor of four had an effect on either $\phi$ or $t_-$. It also indicated that while $\phi$ is rather insensitive to melt leakage through the disks used, $t_-$ is quite sensitive to this effect. In other words, disk porosity needs to be closely examined in the second case. This is reasonable from a qualitative viewpoint. If the composition of the melt leaking through the membrane is the same as the overall composition of the melt, $\phi$ will be unchanged by leakage. This condition will be met if the concentration changes which initially appear at the electrodes do not reach the membrane before the run is terminated. However, even if this does happen one can suspect that the large diluting effect of the bulk material in the compartment may well cause the error in $\phi$ to be less than the normal experimental deviations. In the case of $t_-$, any Cl$^{36}$ reaching the anolyte, whether by leakage or
diffusion, must be corrected for and it is absolutely necessary that this correction be as small as possible. Since the possibility of return of Cl\textsuperscript{36} to the catholyte from the anolyte by diffusion or leakage is low, again because of the large diluting effect of the anolyte, it is apparent that while slight leakage from anolyte to catholyte will not be too harmful, leakage in the other direction must be prevented. This is very simply taken care of by slightly tilting the furnace in the proper direction, as was described previously. This diluting effect is the advantage that radiochemical determination of transport numbers has over chemical, or change-of-weight, methods as practiced by Lorenz and Ruckstuhl (34) and by Baimakov and Samusenko (36).

A discussion of the implications of the results of this method of investigating the fused system KCl-PbCl\textsubscript{2} should take into account other types of data on the same system. Molar volume isotherms deviate positively from additivity when plotted against mole fraction (2); viscosity isotherms show a distinct negative deviation (5) and isotherms of equivalent conductivity show deep minima (1). The phase diagram of the system (48) reproduced in Figure 11 indicates a congruently melting solid state compound KCl\cdot2 PbCl\textsubscript{2} and incongruently melting compounds 2 KCl\cdotPbCl\textsubscript{2} and 4 KCl\cdotPbCl\textsubscript{2}. Conductivity minima in systems whose phase diagrams indicate solid state compound formation have long been explained on the basis of the existence of discrete complex ions persisting
Figure 11. Phase diagram of the system KCl-PbCl₂
in the liquid state. For example, Bloom and Heymann (1) predicted existence in the KCl-PbCl₂ melt of PbCl₃⁻ and PbCl₆⁴⁻, either as discrete ions or polymeric complex structures of the same composition, on the basis of such evidence. Addition of PbCl₂ causes an initially rapid depression of equivalent conductivity from the value of pure KCl. They saw this as evidence for removal from the melt of Cl⁻ in the form of the above mentioned complexes whose mobility would be expected to be low. Further addition of Pb^{++} would result in additional complexing until at a certain favorable concentration, corresponding to the minimum (or the maximum negative deviation from ideality) of the equivalent conductivity and also corresponding closely to the composition of a solid state compound, the complexing would be at a maximum. Further addition of Pb^{++}, or removal of K⁺, would result in a melt with fewer complexes and the equivalent conductivity would then rise from the minimum to that of pure PbCl₂. Since the magnitude of the maximum negative deviation of \( \Lambda \) from ideality decreased with increasing temperature, Bloom and Heymann felt that the extent of the complexing decreased with increasing temperature. They cited the work of Lorenz and Ruckstuhl (34) as confirmatory evidence for the existence of a large amount of lead in anionic complexes. This picture, although not without critics, has been so plausible that it has been applied over and over again to situations of this sort.
An example quickly indicates how anionic complexing is reflected in the experimentally determined values, \( t_{++} \) and \( t_- \). Consider the species \( \text{PbCl}_3^- \). For every unit of electricity transported by \( \text{PbCl}_3^- \), three \( \text{Cl}^- \) must migrate while for every unit of electricity transported by \( \text{Cl}^- \), one \( \text{Cl}^- \) must migrate. On the basis of such an example, anionic complexing has been said to increase observed chloride ion transport for a given number of faradays of current and hence increase the experimental value \( t_- \) relative to the expected value, \( t_-^0 \), if there were no complexing. The chloride ion itself contributes \( \Upsilon_- \) and the anionic complex contributes \( \Upsilon_c^- \). Note that \( t_- = \Upsilon_- + 3 \Upsilon_c^- \). Similar reasoning indicates a reduction in the experimental value \( t_{++} \) due to anionic complexing. However, this argument fails to consider relative ionic mobilities.

If the mobility of the complex is zero, then \( \Upsilon_c^- = 0 \) and \( \Upsilon_- = t_- t_-^0 \) since the complex would remove \( \text{Cl}^- \) from the melt and contribute nothing to the transport of \( \text{Cl}^- \). If the mobility of the complex is large, then by the previous argument we would expect \( t_- t_-^0 \). At some definite intermediate \( \text{PbCl}_3^- \) mobility, which is a function of the relative mobilities and concentrations of \( \text{Cl}^- \) and \( \text{PbCl}_3^- \), the complexing would not affect experimental values of \( t_- \) and we would have \( t_- = t_-^0 \). The values of mobility and composition would result in \( 3 \Upsilon_c^- = t_-^0 - \Upsilon_- = t_- - \Upsilon_- \). A corresponding
argument leads one to the conclusion that \( \tau_{++} = t_{++}t_{++}^0 \) if the complex has zero mobility. The inequality becomes greater for larger values of the mobility of the complex. Incidentally, it is also true that existence of an anionic complex would cause \( t_+t_+^0 \) with the inequality being less for larger values of \( \mu_\text{c}^- \).

The effect of cationic complexing such as PbCl\(^{+}\) can be discussed in the same manner. For a cationic complex of zero mobility, \( t_- = \tau_-t_-^0 \); also \( \tau_{++} = t_{++}t_{++}^0 \). To the extent that the complex is increasingly mobile, \( t_{++} \) becomes larger and \( t_- \) smaller still. In this case \( t_+t_+^0 \) if a cationic complex exists and the inequality is less for larger values of \( \mu_\text{c}^- \). It is important to note that cationic complexing alone results in \( t_-t_-^0 \) while anionic complexing alone results in \( t_{++}t_{++}^0 \).

Consider now the most important aspects of the previously reported data:

1. None of the experimentally observed transport numbers varied linearly with \( E_{\text{KCl}} \). In each mixture studied, \( t_- \) varied positively and both \( t_+ \) and \( t_{++} \) varied negatively from linearity. In the cases of \( t_- \) and \( t_{++} \) the maximum relative deviations increased monotonically with increasing \( E_{\text{KCl}} \); at \( E_{\text{KCl}} = 0.681 \) these values were \( +28\% \) and \( -50\% \), respectively.

2. One composition was examined at two temperatures.
Increasing the temperature from 525°C to 850°C caused a reduction in \( t_- \) of 0.02 and an increase in \( t_{++} \) of 0.02. There was no change in \( t_+ \).

3. When KCl is added to PbCl\(_2\), although \( \mu_+ \) remains unchanged between \( X_{\text{KCl}} = 0.000 \) and 0.631, a monotonic decrease from the value at \( X_{\text{KCl}} = 0.000 \) is seen in both \( \mu_{++} \) and \( \mu_- \). An examination of the mobilities and ionic conductances reveals that the depression of total equivalent conductance in this range, caused by addition of PbCl\(_2\), is due to apparent decreased current-carrying capabilities of Pb\(^{2+}\) and Cl\(^-\).

4. As KCl is diluted by the gradual addition of PbCl\(_2\), although \( \mu_{++} \) and \( \mu_- \) exhibit a gradual increase, the effect having the greatest consequence is the rapid reduction in \( \mu_+ \). The consequent rapid reduction in the ionic conductance of K\(^+\) is responsible for the depression of total conductance below the ideal or additive values when PbCl\(_2\) is added to KCl.

5. The value of \( \mu_- \) at a given temperature is roughly twice as large in PbCl\(_2\) as it is in KCl.

From the above discussion it is first of all apparent that the behavior of the transport number and the mobility isotherms of Cl\(^-\) and Pb\(^{2+}\) do not contradict the concept of complexing as proposed for this system by Bloom and Heymann (1) and a number of other authors (13,14,17). If one were to carry through this type of reasoning the conclusion
arrived at would be that the complexing is predominantly anionic. The decrease of $t_-$ and increase of $t_{+++}$ with increasing temperature would also be in accord with the concept of complexing since the degree of complexing would be expected to decrease with increasing temperature.

Although this method of reasoning nicely explains data for $\text{Cl}^-$ and $\text{Pb}^{++}$, an explanation of the behavior of $t_+$ and $\mu_+$ is more difficult. After all, $\text{KCl}$ added to $\text{PbCl}_2$ causes a reduction in both $t_{+++}$ and $\mu_{+++}$ but addition of $\text{PbCl}_2$ to $\text{KCl}$ also causes a reduction in $t_+$ and $\mu_+$. Because of purely chemical considerations one is loath to interpret this as evidence for complexing of $\text{KCl}$, yet there is no a priori reason to avoid examining $\mu_+$ and $t_+$ in the same manner that $\mu_{+++}$ and $t_{+++}$ were examined.

Furthermore, if one were to take the position that $K^+$ is not complexed in this system, then another explanation must exist for the unexpected behavior of $t_+$ and $\mu_+$. Also this other explanation might serve to equally well explain the behavior of all $t_+$ and $\mu_+$. It might be noted here that both the relative and the absolute variation of $\mu_+$ isotherms with composition are in fact larger that the corresponding variations of either $\mu_{+++}$ or $\mu_-$. Thus while Bloom and Heymann are not contradicted by the data presented here, their concept of complexing does not receive unambiguous support.
Examination of the law of mass action as applied to complexing yields interesting results. For any complex, e.g. $\text{PbCl}_3^-$, we may write

$$K_e = \frac{a_c^-}{a^{++} \times a_3^-}$$

or

$$\frac{a_c^-}{a^{++}} = K_e a_3^-.$$

From molar volume data it is known that the ratio of the analytical concentration of $\text{Cl}^-$ in pure KCl to that in pure $\text{PbCl}_2$ is about 1.4. With an assumption of unit activity coefficients we may conclude that addition of KCl to PbCl$_2$ increases the degree of complexing very slowly. As a matter of fact, the degree of complexing in the above example would, for $X_{\text{KCl}} \to 1.000$, approach only $1.4^3$ or 2.7 times the degree of complexing in pure PbCl$_2$. These considerations also lead one to suspect that complexing alone may well not account for the observed variations in $t_{++}$ and $t_-$. A second conclusion of Bloom and Heymann (1) is incorrect. The rapid reduction in total equivalent conductance from that of pure KCl caused by addition of small amounts of PbCl$_2$ is not due to mere removal of Cl$^-$ by complexing with Pb$^{++}$. While this apparently does occur and to some extent causes a reduction in $\Lambda$, by far the greatest contribution to the reduction in $\Lambda$ is the large initial reduction in
It can now be seen that while the experimental results presented here answer some old questions and raise some new ones, little new data are presented which can yield information on the extent of complexing in the system KCl-PbCl₂. Upon reflection one can see why this must be so. The system is in some ways analogous to a water solution containing two solutes. The corresponding solvent is Cl⁻ and the two solutes are Pb²⁺ and K⁺. Of course, for a given amount of Cl⁻, Pb²⁺ and K⁺ cannot be varied independently. Examination of complexing of one component, e.g., Pb²⁺, with the solvent Cl⁻ is in many ways similar to the examination of degree of hydration in water. Thus just as one would prefer to use a neutral solvent and avoid the large and almost constant excess of water in the second case, one would obtain more information on complexing of Pb²⁺ and Cl⁻ by turning to a neutral solvent in which both a⁺ and a⁻ could be varied independently.

Iverson (49) has recently obtained complexing constants for a fused mixture of Pb²⁺ and Cl⁻ in a KNO₃-NaNO₃ binary eutectic solvent. The obvious extension of his work would be to determine \( t_+ \) and \( t_- \) in these melts. Since one would then know both the formulae and analytical concentrations of each complex species in addition to the experimental transport numbers \( t_- \) and \( t_+ \), one could calculate
the actual transport numbers, $\tau_i$, for each species. The required equations are:

$$t_{++} = \left[ \sum_r v_r \mu_r E_r \right]^{-1} \left[ v_{++} \mu_{++} E_{++} + \sum_i v_i \mu_{c_1} E_{c_1}^+ - \sum_j v_j \mu_{c_j} E_{c_j}^- \right]$$

$$t_- = \left[ \sum_r v_r \mu_r E_r \right]^{-1} \left[ v_- \mu_- E_- - \sum_i v_i \mu_{c_1} E_{c_1}^+ + \sum_j v_j \mu_{c_j} E_{c_j}^- \right]$$

where it will be recalled that $c^-$ refers to an anionic complex and $c^+$ refers to a cationic complex. The first summation includes all ionic species $r$. The symbol $v_1$ is equal to the number of equivalents of $Cl^-$ (when using the first equation) or $Pb^{++}$ (when using the second equation) transferred per equivalent of complex. Knowing $t_{++}$, $t_-$ and all $v_r$ and $E_r$, the only unknowns are $\mu'_r$. These can all be evaluated by simultaneous solution of the set of $r$ equations, each representing data at a different $Pb^{++}$ and $Cl^-$ concentration. Iverson has actually found that his data may be interpreted on the basis of the existence of some undissociated $PbCl_2$ as well as four ionic species, these being $Pb^{++}$, $Cl^-$, $PbCl^+$ and $PbCl_3^-$. Thus transport data need to be taken at four different combinations of $Cl^-$ and $Pb^{++}$ concentrations.

The above mobilities are only relative since each $\mu'_r$
may be multiplied by a constant, \( k \) without changing \( t_1 \). To determine absolute mobilities one must evaluate \( k \). This may be done if one knows the equivalent conductivity. Since

\[
\Lambda = F \sum_r \frac{k\mu'_r I_r}{t_r}
\]

proper choice of \( k \) will balance the equation. Then \( \mu'_r \) is determined by

\[
\mu'_r = k\mu'_r.
\]

A second interesting and valuable experiment was performed recently by Klemm and Monse (29). With an ingeniously devised moving boundary type of experiment, they have determined relative mobilities of cations in the system LiCl-PbCl\(_2\). In essence they have determined \( \phi \) for these systems. One can, for example, relate \( \phi \) to \( b_{13} \) (Klemm and Monse’s notation for the mobility of 1, or Li\(^+\), with respect to 3, or Cl\(^-\)) in the following way. Since \( b_{13} \) is the mobility of 1 with respect to 3 then,

\[
b_{13} = \mu_1 + \mu_3
\]

which upon expansion gives

\[
b_{13} = \frac{t_1 \Lambda}{E_1 F} + \frac{t_3 \Lambda}{E_3 F}.
\]

This can be rearranged to

\[
b_{13} = \frac{\Lambda}{F} \left[ \frac{t_1}{E_1} + t_3 \right]
\]
by recalling that $E_3 = 1.000$. Then

$$b_{13} = \frac{\Lambda}{PE_1} \left[ t_1 + E_1 t_3 \right]$$

which finally is equivalent to

$$b_{13} = \frac{\Lambda}{PE_1} \left[ \phi \right].$$

Similarly

$$b_{23} = \frac{\Lambda}{PE_2} \left[ 1 - \phi \right].$$

If one then eliminates $\Lambda$ between the last two equations and solves for $\phi$, the result is

$$\phi = \frac{b_{13} E_1}{b_{13} E_1 + b_{23} E_2}.\]$$

The data of Klemm and Monse have made it possible to complete the determination of absolute experimental transport numbers and ion mobilities in this system by application of the radiochemical technique for determination of $t_-$ which is presented in this dissertation. The similarities and dissimilarities of the two alkali chloride-lead chloride systems result in the data in the system LiCl-PbCl$_2$ being of great and obvious interest. Values of $\phi$ in this system are reported in Table 10 together with values of $\phi - \phi_{\text{ideal}}$, a measure of the deviation of $\phi$ from ideality. Since $\phi_{\text{ideal}}$ is the same for corresponding concentrations in both systems, values of $\phi$ in the two systems are most easily compared by looking at
the sensitive functions $\phi - \phi_{\text{ideal}}$. Values of the deviation of $\phi$ from ideality for the two systems are presented in Figure 12. It is certainly interesting to note the close similarity in the behavior of the functions in the two systems. Nothing can be said regarding absolute values of $t_1$ and $\mu_1$ in the system LiCl-PbCl$_2$ however until an independent set of determinations relating them to measurable quantities is available.

Table 10. Values of $\phi$ in the system LiCl-PbCl$_2$ $^a$

<table>
<thead>
<tr>
<th>$E_{\text{KCl}}$</th>
<th>$\phi$</th>
<th>$\phi - \phi_{\text{ideal}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.051</td>
<td>0.116</td>
<td>0.065</td>
</tr>
<tr>
<td>0.129</td>
<td>0.219</td>
<td>0.090</td>
</tr>
<tr>
<td>0.151</td>
<td>0.237</td>
<td>0.086</td>
</tr>
<tr>
<td>0.254</td>
<td>0.382</td>
<td>0.128</td>
</tr>
<tr>
<td>0.527</td>
<td>0.639</td>
<td>0.112</td>
</tr>
<tr>
<td>0.755</td>
<td>0.841</td>
<td>0.086</td>
</tr>
<tr>
<td>0.900</td>
<td>0.939</td>
<td>0.039</td>
</tr>
<tr>
<td>0.945</td>
<td>0.964</td>
<td>0.019</td>
</tr>
<tr>
<td>0.975</td>
<td>0.983</td>
<td>0.008</td>
</tr>
<tr>
<td>0.989</td>
<td>0.993</td>
<td>0.004</td>
</tr>
</tbody>
</table>

$^a$Calculated from data reported by Klemm and Monse (29).

Sundheim’s (32) method of calculating transport numbers for KCl results in $t_1 = 35.5 / (35.5 + 39.1) = 0.48$ for all temperatures at which the salt is molten. Since the present study’s value of 0.78 for pure KCl is in wide disagreement, poor agreement must necessarily exist between reported values of $t_1$ at various compositions and values calculated by means of his equations (33). Research in
Figure 12. Deviations of $\Phi$ from ideality in the systems LiCl-PbCl$_2$ and KCl-PbCl$_2$.
progress (50) will yield transport numbers of other alkali and alkaline earth chlorides. When these results are available, they may make possible a more sound judgment as to the validity of Sundheim's proposals.
SUMMARY

Values of ionic transport numbers and ionic mobilities were determined for the fused system KCl-PbCl₂. A series of preliminary investigations indicated that the nature of the membrane used to separate the anode and cathode compartments in a Hittorf type transport cell did not measurably affect the results as long as the membrane porosity was sufficiently low. In addition, variation in current density and in total faradays of current had no measurable effect within the range examined.

A transport cell adapted to the present system was designed and values of \( \phi \) were determined. Following the determination of \( \phi \), direct determination of \( t_- \), the experimental transport number of chloride ion, using the radioisotope Cl\(^{36} \) was accomplished. During the course of the determination of \( t_- \), the importance of severely limiting the migration of ions across the membrane by leakage and diffusion was discovered. Conditions under which the leakage-diffusion correction would be acceptably low were outlined. A recommended experimental procedure for the radiochemical determination of \( t_- \) was presented and an equation was developed which relates \( t_- \) to measurable quantities.

Values of \( \phi \) and \( t_- \) were presented in tabular and graphical form. It was recommended that a triangular coordinate system be used to simultaneously present the
variation of all \( t_1 \) with composition. From measured values of \( \varphi \) and \( t_\varphi \), smoothed values of \( t_+, t_++ \) and \( t_- \) were obtained. From these data and the known equivalent conductance of the system, values of ionic conductance and ionic mobility were obtained.

The most important aspects of the results are as follows:

1. None of the experimentally observed transport numbers varied linearly with \( E_{KCl} \), the equivalent fraction of KCl. In each mixture studied, \( t_- \) deviated positively and both \( t_+ \) and \( t_++ \) deviated negatively from linearity. In the cases of \( t_- \) and \( t_+ \) these deviations increased monotonically with increasing \( E_{KCl} \); at \( E_{KCl} = 0.681 \) the relative values were \(+28\%\) and \(-50\%\), respectively.

2. The composition \( E_{KCl} = 0.461 \) was examined at two temperatures. Increasing the temperature from 525\( ^\circ \)C to 850\( ^\circ \)C caused a reduction in \( t_- \) of 0.02 and an increase in \( t_+ \) of 0.02. There was no change in \( t_++ \).

3. When KCl was added to PbCl\(_2\), although \( \mu_+ \), the experimental ionic mobility of K\(^+\), remained unchanged between \( E_{KCl} = 0.000 \) and 0.461, a monotonic decrease from the value in pure PbCl\(_2\) was seen in both \( \mu_++ \) and \( \mu_- \). An examination of the mobilities and ionic conductances revealed that the depression of total equivalent conductance in this range, caused by addition of PbCl\(_2\), was due to apparent decreased current-carrying capabilities of Pb\(^{++}\) and Cl\(^-\).
4. As KCl was diluted by the gradual addition of PbCl$_2$, although $\mu_{++}$ and $\mu^-$ exhibited a gradual increase, the effect having the greatest consequence was the rapid reduction in $\mu^+$. The consequent rapid reduction in the ionic conductance of K$^+$ was responsible for the depression of total conductance below the ideal or additive values when PbCl$_2$ was added to KCl.

5. The value of $\mu^-$ at a given temperature was determined to be roughly twice as large in PbCl$_2$ as it was in KCl.

The major conclusions arrived at are as follows:
1. Duke and Laity's experimental value for $t_-$ in pure PbCl$_2$ (25) is substantiated.
2. Sundheim's (32) predicted value for pure KCl is not substantiated.
3. The concept of complex ions in the system is not contradicted, nor does it receive unambiguous support.
4. The initial very rapid depression of $\Lambda$ from that of pure KCl, caused by addition of small amounts of PbCl$_2$, is due to the depression of $\lambda_+$ rather than to the effect of complexing of Pb$^{++}$ and Cl$^-$. 
5. Unambiguous information on complexing is not likely to be obtained when the activity of Cl$^-$ is relatively constant for all compositions.

It was shown how $\phi$ could be calculated for the system LiCl-PbCl$_2$ from cation mobility data presented by Klemm and
Monse (29). Interestingly enough, values of $\phi$ at the same $E_{PbCl_2}$, in the two systems LiCl-PbCl$_2$ and KCl-PbCl$_2$ are practically identical.


