Cation Transport Numbers in Molten AgNO₃-AgCl Mixtures
by Pressure-EMF Measurements

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ABSTRACT

The pressure-emf, or difference in electrode potential which results from a hydrostatic pressure difference, was measured in molten salt cells represented schematically as

\[
\text{Ag(s)/AgNO}_3, \text{AgCl(l) [P}_2\text{I]/AgNO}_3, \text{AgCl(l) [P}_2\text{I)/Ag(s)}
\]

containing 0-42.8 m/o AgCl, from 200° to 280°C. Measurements of this effect, which depends on the difference between anion and cation mobilities, indicate that the cation transport number increases with increasing AgCl content or with decreasing temperature. Because of the small differences between anion mobilities, the pressure-emf alone is shown to provide a good approximation to all three ion constituent transport numbers in this system.

It has been reported previously (1) that a pressure-emf can be measured in fused salts by applying a pressure difference between two electrode compartments separated by a porous diaphragm and by recording the changes in potential difference between two identical metallic electrodes in equilibrium with the same electrolyte. Equations have been derived (2)

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which show that this pressure-emf is a linear function of the mass transport numbers of the various components relative to an external reference frame such as the cell or the diaphragm. Although the theory in general applies to any electrolyte, the experiments have so far been limited to single fused salts, and only the results on silver nitrate have been reported in detail (3). The present paper describes a similar investigation which has been carried out with molten mixtures of silver nitrate and silver chloride.

In the general case of a cell, at uniform temperature and composition, containing a mixture of c elemental components (ion constituents), one of which (denoted
by subscript 1) is oxidized or reduced at either of the
two identical electrodes, it can be easily shown (2)
that as a consequence of Saxen's relation, the
pressure-emf is given by the following equation

$$\frac{\Delta E}{\Delta P} = -F \left[ \frac{\bar{V}_1}{z_1} + \sum_{k=2}^c \left( \frac{\bar{V}_k}{|z_k|} \right) \right]$$  \[1\]

where: $\Delta E$ is the electrical potential difference which is
caused by the hydrostatic pressure difference $\Delta P$; $F$
is the Faraday constant (96,487 coulombs); $\bar{V}_1$ and $z_1$
are the partial molar volume and the oxidation number of
the constituent of the electrolyte which reacts at the
electrode; $\bar{V}_k$ is the partial molar volume of the
same constituent in the electrode phase; $\bar{V}_k$ and $z_k$
are the partial molar volume and the oxidation number of
the remaining elemental components which constitute
the electrolyte and which can be determined by chemi-

cal analysis.

$\nu_k$ is the equivalent mass transport number of the
component $k$ relative to an external reference frame,
and it is defined as the number of equivalents of the
elemental component which would be transported
across the diaphragm per faraday of electricity during
an electrodiffusion of the experiment. The transport numbers
are algebraic numbers, positive for a transport toward
the cathode, and the sum of their arithmetic values
equals one.

As discussed previously (2), these definitions, which
lead to the above equation by a straightforward ther-

modynamic calculation, do not require any knowledge
or any assumption concerning the ionic species actu-
ally present in the melt. The transport numbers are
macroscopic quantities that describe the total fluxes
resulting from all possible transport mechanisms.

The pressure-emf equation has been derived by the
application of theories of thermodynamics of irrever-
sible processes and Onsager's reciprocal relation. It
requires only the assumption that the transport num-
bers and partial molar volumes remain constant within
the operating range and that no hydrostatic pressure
gradient across the fritted disk, and these conditions are
verified experimentally. It is also assumed
for the purpose of deriving the equation that the chemi-

cal composition and temperature remain uniform
throughout the system. These conditions are actually
fulfilled, even with a mixture as the electrolyte, be-
cause the pressure-emf can be measured very fast and
because, with a suitable measuring device, no appreci-
able current is drawn from the cell so that no transport
of matter occurs and no concentration gradient builds up.

Equation [1] is readily applied to a mixture of silver
nitrate and silver chloride with two metallic silver
electrodes. Silver, chlorine, and the nitrate group are
the obvious choices as the elemental components, and
the oxidation numbers are +1 for the silver and −1
for the chlorine and nitrate. Thus, for the cell which
can be schematically represented as

$$\text{Ag(s)}/\text{AgNO}_3, \text{AgCl}(1) \quad [P_1]/\text{AgNO}_3,
\text{AgCl}(1) \quad [P_2]/\text{Ag(s)}$$

the pressure-emf for uniform temperature and com-
position is given by

$$-F \frac{\Delta E}{\Delta P} = V_\text{Ag} + \nu_{\text{NO}_3} \bar{V}_\text{AgNO}_3 + \nu_\text{Cl} \bar{V}_\text{AgCl}$$ \[2\]

Experimental

The pressure-emf, or difference in cell potential re-
sulting from a pressure difference between the elec-
trodes, has been measured by continuously recording
the voltage of the cell described above and noting the
changes that occur as the difference in hydrostatic

- pressure, $\Delta P = P_2 - P_1$, is alternately applied and re-
used. A glass frit separates the two electrode com-
partments and allows the pressure difference to be
maintained for finite times; 10-15 sec is usually allowed
to apply, measure, and release a given pressure differ-
ce. Voltage changes were recorded with a Keithley
150 microvoltmeter ($10^7$ ohms input resistance on
the 10 $\mu$V range) and a Bausch and Lomb VOM-5
recorder which were calibrated after a series of measure-
ments at a particular temperature by use of a Keithley
260 (better than $\pm 0.05 \mu$V for a 10 $\mu$V output)
nanovolt source. The technique employed was with some minor
changes identical to that previously described in detail
in connection with the measurement of pressure-emf in
pure molten salts (3). The modifications which were
made as a matter of experimental convenience and do
not appear to change the results include the use of
silver wire electrodes secured by Teflon seals, instead
of silver-plated tungsten wire electrodes sealed in
glass, and fine (4-5$\mu$) rather than medium ($10-15\mu$)
porosity fritted glass disks.

The pressure-emf has been studied in AgNO$_3$-AgCl
mixtures of five compositions (0.057, 0.117, 0.232, 0.345,
0.428 equivalent fraction AgCl) at temperatures ex-
tending from the liquidus (indicated by the left-hand
termini of the lines on Fig. 1) to the upper limit of the
Teflon seals, about 280°C. For each composition,
measurements were taken in a random sequence of
temperatures. At each temperature which was held
constant within $\pm 1^\circ$C by immersion of the cell in a
molten Pb-Sn bath, we performed 20-30 individual
measurements of the potential changes attending the
applied pressure differences which ranged from 5 to 70
cm Hg. The direction of flow was reversed on alternate
measurements. Plots of the potential changes, $\Delta E$
against the corresponding pressure differences, $\Delta P$,
typically result in straight lines, the slopes of which
are the pressure-emf, $\Delta E/\Delta P$. Standard deviations
of these slopes were generally within the range 0.05-0.15
$\mu$V/ATM. This scatter is related to changes in the slope
of the background drift (total background generally
less than 200 $\mu$V) which accompany the flow of salt
under the applied pressure difference. Typical record-
ings of the changes in cell potential as the pressure is
applied and released as well as additional experimental
details are given elsewhere (3, 11).

The minus sign on the $\Delta E/\Delta P$ values measured in
this investigation indicates that in all cases the elec-
trode at the higher pressure became more anodic
on application of the pressure difference.

The salt mixtures were prepared from Baker reagent-
grade salts, which were fused, mixed, and filtered
prior to placing within the cell.

Results and Discussion

The measurements of pressure-emf for mixtures of
AgNO$_3$-AgCl are summarized in Fig. 1. At each com-

![Fig. 1. $\Delta E/\Delta P$ vs. temperature for various compositions. Mole fractions of AgCl are respectively: \(\bigcirc\) 0.057, \(\bigcirc\) 0.117, \(\bigcirc\) 0.232, \(\bigcirc\) 0.345, \(\bigcirc\) 0.428.](image)
Fig. 2. $\Delta E/\Delta P$ vs. composition, $t = 230^\circ\mathrm{C}$. $\bigcirc$ pure salt value (ref. 3). $\blacklozenge$ this work, $\ldots$ calculated assuming $\tau^-$ remains constant with composition.

position (except at $N_{\text{AgCl}} = 0.428$, where only one temperature was studied) there appears to be a slight decrease in the absolute value of $\Delta E/\Delta P$ with increasing temperature. The lines drawn through the points at each composition were constructed by a least squares fit.

At those compositions for which measurements were performed at the greatest number of temperatures, it was observed that measurements (those which deviate most from the least-squares lines of Fig. 1) at the first few temperatures differed by several standard deviations from the least-squares lines. After the initial measurements, however, the results which followed seemed to fit more closely to the downward sloping line. Accordingly, one might be justified in rejecting the initial data on the basis of a possible systematic error. We have chosen not to do this because (a) only a few measurements were performed for two of the compositions and (b) the salient results of this study, namely, the composition dependence at constant temperature, are largely unaffected.

At a given temperature, the value of pressure-emf increases markedly with increasing concentration of AgCl. Figure 2 clearly shows the increase of $\Delta E/\Delta P$ relative to the pure salt value (3) as AgCl concentration is increased at $230^\circ\mathrm{C}$. The error limits associated with each point are based on the standard deviation calculated from the distribution of the data about the least-squares lines of Fig. 1.

The composition dependence of $\Delta E/\Delta P$ can now be considered in relation to mass transport in this system. An average anion mass transport number, $\tau^-$, can be defined as

$$\tau^- = \frac{1}{V_m} \left( \frac{\tau_{\text{NO}_3} V_{\text{AgNO}_3} + \tau_{\text{Cl}^-} V_{\text{AgCl}}} {V_m} \right)$$

where $V_m = N_{\text{AgNO}_3} V_{\text{AgNO}_3} + N_{\text{AgCl}} V_{\text{AgCl}}$ is the equivalent volume of the mixture and $N_{\text{AgNO}_3}$ and $N_{\text{AgCl}}$ are the equivalent fractions of those components. This allows Eq. (2) to be written as

$$-F \frac{\Delta E}{\Delta P} = V_{\text{Ag}} + \tau^- - V_m$$

The broken line shown in Fig. 2 is a plot of Eq. (4) where the assumption has been made that $\tau^-$ remains unchanged as AgCl is added to pure AgNO$_3$. The slight upward slope reflects the decrease in $V_m$ (4) with increasing $N_{\text{AgCl}}$. The measured values occur significantly above this line, thus indicating that the average anion mass transport number decreases with increasing concentration of AgCl.

$^*$Since similar behavior was not observed in experiments with pure AgNO$_3$ (3), we suspect that incomplete mixing in the case of the initial measurements with mixtures may be a possible source of error.

Fig. 3. Mass transport numbers vs. composition, $t = 230^\circ\mathrm{C}$. $\bullet$ pure salt values calculated from Eq. (4); $\ldots$ calculated from Eq. (4); $\triangle$ Ag$^+$ and NO$_3^-$, respectively; $\bigcirc$ $\tau_{\text{Ag}}$; $\bigcirc$ $\tau_{\text{NO}_3}$; $\bigcirc$ $\tau_{\text{Cl}^-}$; $\bigcirc$ $\tau^-$ $N_{\text{AgNO}_3}$ (negative slope) and $\tau^+$ $N_{\text{AgCl}}$ (positive slope).

The decrease in $\tau^-$ with increasing AgCl is shown explicitly in Fig. 3, where the solid line has been drawn through values computed from Eq. (4). Correspondingly, there is an increase in the average cation mass transport number, $\tau^+$, defined by

$$\tau^+ = 1 + \tau^-$$

shown at the top of Fig. 3.

The average anion mass transport number can be related to those of the elemental components by

$$\tau_{\text{NO}_3} = \tau^- - N_{\text{AgNO}_3} - \frac{V_{\text{AgCl}}}{V_m}$$

$$\tau_{\text{Cl}^-} = \tau^- - N_{\text{AgCl}} + \frac{V_{\text{AgNO}_3}}{V_m}$$

where

$$\phi = \tau_{\text{Cl}^-} N_{\text{AgNO}_3} - \tau_{\text{NO}_3} N_{\text{AgCl}}$$

The function $\phi$ is a measure of the difference between the mobilities of the two unlike elemental components with the same oxidation number in a binary common mixture. It is often used to summarize results such as those of a Hittorf experiment (5, 6), a measurement of liquid junction potential (7, 8), or a measurement of the potential of a gravity cell (4), which all depend on that difference and are related to the function $\phi$.

For the system AgNO$_3$-AgCl, it has been previously shown that $\phi$ is quite small (4) (less than 0.03), which indicates that the values of the mobilities of the two anionic elemental components are nearly equal in these ranges of composition and temperature. Thus, the last term in Eq. (6) may be neglected as a first approximation, allowing computation, within a reasonable degree of precision, of $\tau_{\text{NO}_3}$ and $\tau_{\text{Cl}^-}$, as well as $\tau_{\text{Ag}}$ from

$$\tau_{\text{Ag}} = 1 + \tau^-$$

Values of $\tau_{\text{NO}_3}$ and $\tau_{\text{Cl}^-}$ that result from neglecting the last terms in Eq. (6) are plotted as the two lowermost dashed lines in Fig. 3. Exact values of elemental component mass transport numbers, $\tau_{\text{Ag}}$, $\tau_{\text{NO}_3}$, and $\tau_{\text{Cl}^-}$, which have been computed without approximation using Eq. (4) and (6), with the experimental values of $\phi$ (4), are also shown on Fig. 3 with the associated uncertainties. Within the cumulative uncertainty, the exact values are coincident with the approximate quantities which have been inferred from the pressure-emf measurements alone, assuming equal anion mobilities. Thus, the approximations

$$\tau_{\text{Ag}} = 1 + \tau^-$$

$$\tau_{\text{NO}_3} = \tau^- - N_{\text{AgNO}_3}$$

$$\tau_{\text{Cl}^-} = \tau^- - N_{\text{AgCl}}$$
are quite satisfactory; and this system as well as others (8, 9), for which $\phi$ has been determined to be small relative to the precision with which it can be measured, are amenable to description in terms of a single mass transport number, $\tau^+$, determined by the relatively simple experimental technique of pressure-emf.

Without necessarily invoking any microscopic model one can define electrical mobilities which correspond to the quantities $\tau^-$ and $\tau^+$ as

$$U^* = \tau^*/F$$

where $\Lambda$ is the equivalent conductance. These mobilities have been calculated at 10-degree intervals by use of available conductivity data (10) and are shown in Fig. 4 for each of the compositions studied. Although the slope $dU^*/dT$ is greater than $dU^*/dT$, the fractional rate of increase is greater for $U^-$, a fact which is significant for two reasons. First, it indicates that the average cation mass transport number

$$\tau^+ = \frac{U^+}{U^+ - U^-}$$

is decreasing with temperature. Second, it indicates that the activation energies for electrical transport, which can be deduced from an Arrhenius plot of these mobilities, are larger for anion transport. A trend of decreasing anion mobility and hence increasing activation energy with increasing concentration of AgCl is also evident in Fig. 4.

At all temperatures the values calculated for $U^+$ are identical up to 0.232 AgCl as shown on Fig. 4. However, within experimental uncertainty (about 5%, cf. Fig. 3), it would be possible to assume that, with increasing concentration of AgCl, a linear increase in $U^+$ occurs simultaneously with the decrease in $U^-$. On the basis of the relative anion mobilities as well as the concentration dependence of conductivity and the thermodynamic properties of these mixtures, it has been previously suggested (4) that the process of mixing molten AgNO$_3$ and AgCl could be described in terms of the formation of relatively low-mobility mixed anionic complexes, the simplest example of which is ClAgNO$_3^-$. The results of this investigation, notably (a) the decrease in combined anion mobility (as shown in Fig. 3 and 4), and (b) the larger (absolute) value of activation energy for anion mobilities, may be consistent with that point of view.

The relationship of item (a) above to a model of mixed anionic complexes is obvious enough, particularly when one notes that the values of $N_{\text{NO}_3}$ and $N_{\text{Cl}}$ seem to approach the same value at $N_{\text{AgCl}} = N_{\text{AgNO}_3}$. Item (b) could be related to the same phenomenon in that an additional activation energy is required for thermal dissociation of the complex species as they are formed to an increasing extent with increasing $N_{\text{AgCl}}$. However, any models of complex ion formation based solely on macroscopic transport and thermodynamic information will admittedly remain quite speculative until further information such as self-diffusion, x-ray, and spectroscopic data become available.

One might also inquire as to the generality of the phenomenon of decreased average mobility for the noncommon elemental components in common-ion binary mixtures exhibiting negative heats of mixing. Additional transport measurements in other systems would be useful in this regard.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1971 JOURNAL.

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