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Allen Lee Bowman
Iowa State College

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TRANSPORT NUMBERS IN FUSED SILVER CHLORIDE-ALKALI METAL CHLORIDE SYSTEMS

by

Allen Lee Bowman

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Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1958

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INTRODUCTION

A knowledge of the transport numbers in fused salt systems should contribute toward a general understanding of the physical chemistry of the liquid state. The transport number data, especially when coupled with electrical conductivity data, should furnish evidence about the structure of fused salts, and about the mechanism of electrical conductivity.

Duke and Laity (1) have defined the transport number of an ionic species in a fused salt as "the fraction of the current carried by those ions which are moving measured with respect to that large group of ions of all species present which are at rest relative to each other." Experimentally, a quantity of salt is held in a thick, very fine porosity membrane, where its motion is restricted, and the movement of the ions through this membrane is measured. This is consistent with the definition, and the quantity measured will be a meaningful property of the salt if the salt in the membrane possesses the properties of the bulk salt. Duke and Laity justified the use of the membrane by showing that measured values of transport numbers are identical in glass, porcelain, and asbestos membranes, and that the activation energy of electrical conductivity of the salt is unchanged in the membrane.

Spiro (2) has pointed out that true ionic transport numbers can be measured only when a salt is completely dissociated. If an element is present in more than one ionic species, only one transport number can be determined for it. For example, if M is present as M^+ and MX_2^-, the individual transport numbers of these two species cannot be measured. One can define the total movement of M by a transport number for either M^+ or MX_2^-. In this paper all transport numbers will refer to the simple ionic species.

Laity (3), Laity and Duke (4), and Duke et al. (1, 5, 6) measured the transport numbers in single salts by measuring the volume change in electrode compartments separated by a membrane, and by following the movement of one of the ions of the salt by the use of a radioisotope. The latter method is particularly convenient for the measurement of the transport number of the chloride ion in any salt MCl. Earlier efforts, generally unsuccessful, to measure transport numbers in fused salts have been reviewed by Laity (3).

Aziz and Wetmore (7) studied the system $AgNO_3$-$NaNO_3$ prior to the work of Laity (3). Their experimental results were not valid, as shown, by Duke et al. (8), but they introduced a quantity, ϕ, which has been used in many subsequent discussions of transport numbers in binary fused salt mixtures with a common ion. For the general system AgX-MX, using silver electrodes, ϕ is defined by

$$\phi = (X_2^0 n_1 - X_1^0 n_2)/Z = 1 - t_1 - X_1^0 t_3 = t_2 + X_2^0 t_3$$

where X_i^0 is the mole fraction of species i in the original mixture, n_i is the number of equivalents of i in the anolyte after passage of Z faradays of charge, t_i is the transport number of the species i, and the subscripts are: $1 = Ag^+$, $2 = M^+$, $3 = X^-(NO_3^-$ or $Cl^-)$. Thus the quantity ϕ may be determined from a Hittorf-type experiment using a fine porosity membrane to separate anode and cathode compartments. A separate determination of t_3 (by any of the methods used for single salts) establishes the three transport numbers for the system. From the defining equation, the physical meaning of ϕ is obvious. It is the transport number of M^+ relative to the X^- ions.

Another quantity of interest in the study of fused salt mixtures is the ionic mobility μ, defined by

$$\mu_i = t_i \Lambda / X_i F$$

where Λ is the equivalent conductivity and F is the Faraday constant.

Duke _et al._ (8) have shown that the transport numbers are directly proportional to mole fraction in the system $AgNO_3$-$NaNO_3$, with $t_3 = 0.28$, and that the ionic mobilities are constant as a function of composition. Thus it is concluded that there are no complex species in $NaNO_3$ or $AgNO_3$ melts, and that all cations are in structurally equivalent positions. This requires complete dissociation in this system. Duke and Owens (9) have also determined the transport numbers and mobilities in the system $AgNO_3$-KNO_3. The mobility of the NO_3^- ion is again constant, while the mobilities of the Ag^+ and K^+ ions tend toward the mobility of the other ion as their concentration decreases.

Duke and Fleming (6) have determined the transport numbers and ionic mobilities for the system KCl-$PbCl_2$. Contrary to expectation, the mobility of the Pb^{++} ion seems to be constant, while the mobility of K^+ decreases and that of Cl^- increases when $PbCl_2$ is added to KCl. This result argues strongly against $PbCl_3^-$ ions playing a significant role in the electrical conductivity. No clear, unambiguous explanation is offered.

Frank and Foster (10) have determined the transport numbers of Na, O, and F in molten cryolite-alumina, using the three tracers in separate experiments. Their data indicate a Na^+ transport number of about .99. The movement of O and F is consistent with a $AlOF_2^-$ anion.

In this work t_3, the transport number of the Cl^- ion, will be determined directly by following the migration of Cl^{36} in the alkali metal chlorides, silver chloride, and mixtures of silver chloride with lithium, sodium, and potassium chloride. The transport numbers of the cations in the mixtures will be determined by measurement of ϕ or by following the migration of Ag^{110m}.

EXPERIMENTAL

Materials

Lithium chloride, sodium chloride, potassium chloride, and lead metal were "Baker Analyzed" reagent grade. Rubidium chloride was C. P. grade, obtained from Fairmount Chemical Company. Cesium chloride was Fisher purified. Silver wire (0.1 inch diameter) for electrodes was obtained from Engelhard Industries Inc. Silver chloride was precipitated from aqueous solutions of silver nitrate, "Baker Analyzed" reagent grade, and hydrochloric acid, E. I. du Pont de Nemours and Co., Inc.

The Cl^{36} isotope was obtained from Oak Ridge National Laboratory as an aqueous solution of hydrochloric acid. The alkali metal salts containing Cl^{36} were prepared by dissolving the salt in water, adding HCl^{36}, and evaporating the solution to dryness. The $AgCl^{36}$ was prepared by adding HCl^{36} prior to precipitation. The Ag^{110m} isotope was obtained from Oak Ridge National Laboratory as an aqueous solution of silver nitrate. The $Ag^{110m}Cl$ was prepared by adding $Ag^{110m}NO_3$ prior to precipitation.

All of the salts were used without further purification. The alkali metal chlorides were dried at 150°C. The silver chloride was dried in a vacuum desiccator, ground to a powder, and then dried at 150°C. Drying at higher temperatures seemed to have no effect on the results.

Apparatus

A Temco Electric Furnace, Model 1600, with Temcometer Controller, Model 530, Thermo Electric Mfg. Company, was used to provide the high temperature region for ϕ determinations. A sixteen inch Marshall Tube Furnace, Marshall Products Co., with a Brown Indicating Controller, Model 156R16PS-131, Minneapolis-Honeywell, Brown Instruments Division, was used for radiotracer experiments. The temperature was measured with a chromel-alumel thermocouple, connected to the meter circuit of the controller.

The power supply used to obtain direct current for electrolysis was a full-wave selenium rectifier circuit with a pi-section filter circuit, capable of delivering up to 350 ma. D. C. at 35 volts. The D. C. milliammeter was calibrated by comparison with a calibrated galvanometer. The electrolysis was timed with a "Time-It", Precision Scientific Co.

Counting of radioactive samples was done with a Tracerlab TGC1CT standard end window Geiger-Muller tube mounted in Housing Model AL14A, Technical Associates, and a Model 100 Berkeley Decimal Scaling Unit.

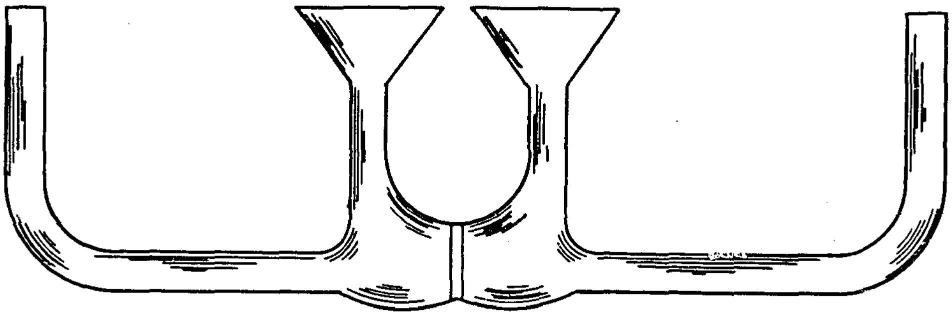
The cell used for determination of ϕ is shown in Figure 1 (a), and the cell used for radiotracer experiments in Figure 1 (b). The cells were made of quartz or Pyrex glass, with a 10 mm. diameter, 1.5 mm. thick membrane of fused quartz, porosity No. 4, Engelhard Industries, Amersil Quartz Division, or of fritted Pyrex glass, "ultrafine" porosity, Corning Glass Works. The porosity of the membrane was reduced by depositing silica within it. This was done by alternately running ethyl silicate and hydrochloric acid through the membrane, and dehydrating the resulting silica gel by baking at 600-800°C. This treatment was repeated until more than two hours was required for one milliliter of water to flow through the membrane under suction.

Determination of ϕ

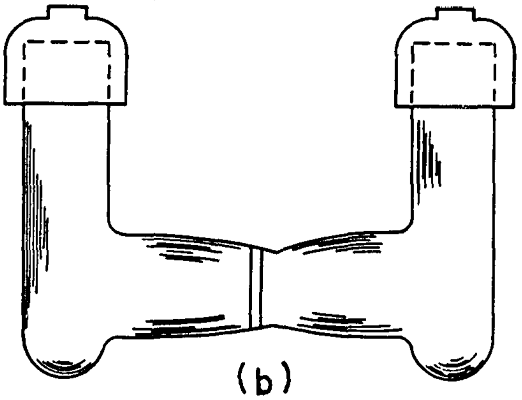
The equations relating transport numbers to measurable quantities can be developed by considering the changes occurring during the electrolysis of a mixture, AgCl-MCl, between silver electrodes. Consider the anolyte, and assume that it is separated from the catholyte by an ideal membrane which permits passage of current-carrying ions only. Also assume the net electrode reaction at the anode to be

$$Ag \longrightarrow Ag^{+} + e^{-} .$$

Figure 1. Cells for determination of transport numbers



(a)



(b)

Then, if Z equivalents of charge are passed through the cell, Z equivalents of Ag^+ will dissolve at the electrode, t_1Z equivalents of Ag^+ and t_2Z equivalents of M^+ will leave the anolyte through the membrane, and t_3Z equivalents of Cl^- will enter through the membrane. These changes can be expressed by the equations

$$n_1 = n_1^o + Z - t_1Z$$

$$n_2 = n_2^o - t_2Z$$

$$n_3 = n_3^o + t_3Z$$

where n_i^o and n_i are the number of equivalents of i before and after electrolysis, and t_i is the transport number of i. Since

$$X_1^o = n_1^o/(n_1^o + n_2^o) = n_1^o/n_3^o ,$$

$$X_2^o = n_2^o/(n_1^o + n_2^o) = n_2^o/n_3^o ,$$

and $\emptyset$ has been defined on page 3 as

$$\emptyset = (X_2^o n_1 - X_1^o n_2)/Z ,$$

these equations reduce to

$$t_1 = 1 - \phi - X_1^0 t_3$$

$$t_2 = \phi - X_2^0 t_3.$$

Thus ϕ can be determined by measuring the total AgCl and MCl in the anolyte after passage of a known quantity of charge through a salt mixture of known initial composition.

The cell, illustrated in Figure 1 (a), was placed in a muffle furnace at the temperature of the run, and filled with liquid salt. Silver electrodes were placed in each end, and the cell was allowed to stand for 30 minutes in order to come to thermal equilibrium. A metered D. C. current was passed for a measured time, and the cell was withdrawn and quickly frozen. The cell was then split at the membrane to separate anolyte and catholyte, which were analyzed.

The AgCl-MCl mixture was dissolved in aqueous ammonia and the solution was filtered to remove glass and electrodes. The silver chloride was precipitated with nitric acid, filtered, and weighed. The filtrate contained equal amounts of M^+ and Cl^-. Thus a determination of Cl^- should serve as a determination of M^+. This was done by precipitating and weighing as silver chloride. Both anolyte and catholyte were analyzed.

If w_1 and w_2 designate the first and second weights of silver chloride, K the number of aliquots, and the superscripts A and C the anolyte and catholyte analyses, then X_1^0 may be obtained from the equation

$$X_1^o = (w_1^A + w_1^C)/(w_1^A + w_2^A + w_1^C + w_2^C).$$

Let $Z^* = 1.485\ It \times 10^{-3}$. This converts Z into units of grams of silver chloride when I is the current in milliamperes and t the time in seconds. Then

$$\phi = K\left[w_1^A - X_1^o(w_1^A + w_2^A)\right]/Z^*$$

Determination of t_{Cl^-}

The determination of ϕ and t_3 (t_{Cl^-}) is sufficient to define the three transport numbers in the system AgCl-MCl. The determination of t_{Cl^-} defines the two transport numbers in pure AgCl or MCl. Again consider a cell whose anolyte and catholyte are separated by an ideal membrane which permits passage of current-carrying ions only. The number of current-carrying Cl^- ions which pass through the membrane, m_3, is equal to t_3Z. This is true for a salt MCl or for a mixture AgCl-MCl. Thus a determination of m_3 suffices to define t_3. One method of measuring m_3 is by the use of a radioisotope.

If the catholyte initially contains $(Cl^*)_C^o$ radioactive Cl^- ions and a total number of Cl^- ions $(Cl)_C^o$, then m_3 of the Cl^- ions will pass through the membrane during electrolysis. This will result in $(Cl^*)_m$ radioactive Cl^- ions being found in the anolyte at the end of the run. Then

$$m_3 = \left[(Cl^*)_m/(Cl^*)_C^o\right](Cl)_C^o = \left[(Cl^*)_m/(Cl^*)_C\right](Cl)_C .$$

The second identity must follow, since the initial and final ratio of Cl^*/Cl in the catholyte must be the same. If the amounts of radioactivity found in anolyte and catholyte at the end of the run, C_A and C_C, are expressed in (counts/minute)/ milligram, then

$$(Cl^*)_m = C_A W_A , \quad \text{and} \quad (Cl^*)_C = C_C W_C$$

where W_A and W_C are the total weights of anolyte and catholyte salt. This assumes that the samples used for counting are identical in size and composition. But $(Cl)_C = W_C/M$ where M is the equivalent weight of the salt. For a mixture $M = X_1M_1 + X_2M_2$. Then m_3 can be expressed by

$$m_3 = (C_A/C_C)(W_A/M) ,$$

and

$$t_3 = m_3/Z = (1/Z)(C_A/C_C)(W_A/M) .$$

The assumed condition that only current-carrying ions pass through the membrane can be realized in effect by carrying out a parallel blank run with no passage of charge, and subtracting the $(C_A)_{blank}$ from the observed value of C_A.

It was found experimentally that the blank correction was essentially zero if the membrane was sufficiently fine.

The cell, illustrated in Figure 1 (b), was filled with solid salt, with the Cl^* placed in the catholyte side. Silver electrodes were pushed into the salt, the ends of the cell were capped, and the cell was placed in a tube furnace at the temperature of the run. As soon as thermal equilibrium was attained, a metered D. C. current was passed for a measured time. The cell was then withdrawn, frozen, and split at the membrane to separate anolyte and catholyte. A molten lead cathode was used with the pure alkali metal chlorides. This was formed by placing granulated lead in the bottom of the cell, and pushing a nichrome wire into the lead (6).

The two halves of the cell were dissolved in aqueous ammonia. The Cl^* was precipitated from the ammoniacal solutions with excess silver nitrate, and counted as silver chloride. In order to obtain a smooth, fine-textured precipitate, it was necessary to keep the solution ammoniacal during the precipitation. A self-absorption curve was obtained, giving counting rate as a function of sample weight. All samples were then corrected to a common weight by the use of this curve. The weight of anolyte salt was obtained by weighing the anode portion of the cell before and after the salt was dissolved. The concentration of the mixtures was controlled by carefully weighing and mixing the solid salts prior to the run.

Determination of t_{Ag^+}

The determination of t_1 (t_{Ag^+}) in AgCl-MCl may be used in place of the determination of ϕ. For mixtures rich in AgCl this is the more precise method. This determination is carried out in the same manner as the determination of t_3, except that Ag^{110m} is placed in the anolyte, and the equation becomes

$$t_1 = (1/Z)(C_C/C_A)(X_1W_C/M) ,$$

where the symbols have the usual meaning. The procedure for the run was the same, except that the Ag^* was precipitated from solution with ammonium chloride.

RESULTS AND DISCUSSION

The values of t_{Cl^-} obtained in pure salts by following the migration of Cl^{36} are given in Table 1.

Although this is the first experimental determination of these quantities, several attempts have been made to predict them from conductivity data or from purely theoretical considerations. Mulcahy and Heymann (11) compared the equivalent conductivities of the alkali metal chlorides at a corresponding temperature defined as three-fourths of the boiling point. They found that the data could be approximated by the equation

Table 1. Transport numbers in pure fused salts

Salt	Temperature (°C)	t_{Cl^-}	δt^a
LiCl	660	.25	.03
NaCl	860	.38	.04
KCl	830	.38	.04
RbCl	765	.42	.04
CsCl	685	.36	.04
AgCl	550	.02	.02

[a] Standard deviation in t_{Cl^-}.

$$\Lambda = 105(1/r_A + 1/r_C)$$

where r_A and r_C are the crystal radii of the anion and cation, respectively, as given by Pauling (12). This equation implies that the transport numbers should be expressed by the relation

$$t_A = r_C/(r_A + r_C).$$

Duke and Owens (5) have derived the same equation by assuming that the restraining force on the ions is proportional to their radius and velocity (essentially Stokes' law), and have shown good agreement with experimental values for lithium, sodium, potassium, and silver nitrate, and thallous chloride. Karpachev *et al.* (13), however, found from a comparison of viscosity and conductivity data for fused potassium chloride-lithium chloride that Stokes' law could not be applied to the description of the movement of the ions in these melts.

Bloom and Heymann (14) concluded that the electrical conductance of the alkali halides is due primarily to the small cation. This was based on the fact that the equivalent conductivity changes strongly with change of cation but very little with change of anion. On the other hand, the situation is reversed with the alkaline earth halides. Thus it was concluded that these salts are primarily anion conductors.

The experimental results for barium chloride (15) and for lead chloride and lead bromide (4) support the latter conclusion.

Frenkel (16) suggested that only one of the ions in a molten salt should be responsible for electrical conductance, and that this would in general be the cation because of its smaller radius. He thus recognized the importance of the ionic size in determining the mobility of an ion, but faulty reasoning led him to the incorrect conclusion with respect to the relative mobilities of the two ions.

Sundheim (17) proposed that the transport numbers in a pure fused salt should be expressed by the equation

$$t_A = M_C/(M_A + M_C)$$

where t_A is the transport number of the anion, and M_A and M_C are the masses of the anion and cation respectively. Sundheim derived this equation by requiring a balance of momentum in a simplified model. He did not justify the extension of the result to such a complex system as an ionic liquid.

According to the results of Mulcahy and Heymann (11), the mobility of the chloride ion in the alkali metal chlorides should be constant at corresponding temperatures. Van Artsdalen and Yaffe (18) and Yaffe and Van Artsdalen (19) measured the equivalent conductivities of the alkali metal halides, and defined a corresponding temperature Θ by $\Theta = T/T_m$ where the actual temperature T and the melting point T_m are expressed in degrees Kelvin. The experimental values of t_{Cl^-} were obtained at $\Theta = 1.05$. Thus the chloride ion mobility at $\Theta = 1.05$ may be calculated directly. The chloride ion mobility at constant absolute temperature may also be calculated if the assumption is made that the transport numbers do not vary with temperature. Laity and Duke (4) found this to be essentially true in the pure salts lead chloride, lead bromide, thallous chloride, and silver nitrate.

The experimental values of t_{Cl^-} for the alkali metal chlorides are compared with the values calculated from the radius equation of Duke and Owens (5) and the mass equation of Sundheim (17), and the chloride ion mobilities at $\Theta = 1.05$ and $T = 1123^\circ K$ are tabulated in Table 2.

It is readily apparent that the transport numbers of the alkali metal chlorides do not agree with Sundheim's equation (17). With the exception of cesium chloride, the experimental values do agree, within experimental error, with the radius equation of Duke and Owens (5). Possibly the more polarizable rubidium and cesium ions are able to move with a smaller effective radius. It should be noted, however, that t_{Cl^-} may be considered as constant, within experimental error, for sodium, potassium, rubidium, and cesium chloride.

Table 2. Transport numbers and ion mobilities in the fused alkali metal chlorides

Salt	t_{Cl^-}			μ_{Cl^-}[a] x 10^4	
	Exp.	Calc.[b]	Calc.[c]	θ=1.05[d]	T=1123°K
LiCl	.25	.25	.16	4.4	5.4
NaCl	.38	.34	.41	5.6	5.6
KCl	.38	.42	.52	4.5	4.7
RbCl	.42	.45	.71	3.9	4.5
CsCl	.36	.48	.79	2.9	4.0

[a] $\mu_{Cl^-} = t_{Cl^-} \Lambda/F$ in units of cm^2/sec/volt. The conductivity data is from Yaffe and Van Artsdalen (19).

[b] $t_{Cl^-} = r_C/(r_A + r_C)$. Duke and Owens (5).

[c] $t_{Cl^-} = M_C/(M_A + M_C)$. Sundheim (17).

[d] Corresponding temperature scale of Yaffe and Van Artsdalen (19).

The chloride ion mobilities are not constant, either at constant corresponding temperature or at constant absolute temperature. In both cases, μ_{Cl^-} increases from lithium chloride to sodium chloride, then decreases with increasing molecular weight. This indicates that the free energy of activation for migration of chloride ion must increase with increasing size, or mass, of alkali metal cation. The behavior of lithium chloride is anomalous, as might be expected.

The almost complete immobility of the chloride ion in fused silver chloride indicates that the liquid contains a fairly rigid chloride lattice, with the silver ions moving freely through this lattice. Such a behavior has been noted in the high-temperature, or α, form of solid silver iodide (20). The mobility of the chloride ion is too low to permit an explanation in terms of complex $AgCl_2^-$ ions, although these could be present in small concentration. This explanation is consistent with the unusually high electrical conductivity and low activation energy for electrical conductivity observed in fused silver chloride (21).

The experimental values of ϕ and t_{Cl^-} obtained in mixtures of silver chloride and alkali metal chloride are presented for silver chloride-lithium chloride in Table 3, for silver chloride-sodium chloride in Table 4, and for silver chloride-potassium chloride in Table 5. These values are reproduced on triangular coordinate graphs in Figures 2, 3, and 4. Each ϕ value gives, with the corresponding t_{Cl^-} value, a parallelogram representing the limits of uncertainty. A smooth curve is drawn through the parallelograms. Each point on this curve then represents smoothed values of the three transport numbers at a given concentration. These smoothed values are then plotted against mole fraction of alkali metal chloride in Figures 5, 6, and 7, in order to display the variation of the transport numbers with concentration.

Table 3. Transport numbers for the fused system AgCl-LiCl

X_{LiCl}	Temperature (°C)	ϕ	$\delta\phi$[a]	t_{Cl^-}	δt[a]
0.00	550	---	---	.02	.02
0.25	600	.40[b]	.10	.03	.03
0.35	600	.60[b]	.10	.12	.03
0.50	600	.77	.07	.16	.03
0.75	600	.95	.08	.21	.03
1.00	660	---	---	.25	.03

[a] Standard deviation.

[b] Interpolated values.

Table 4. Transport numbers for the fused system AgCl-NaCl

X_{NaCl}	Temperature (°C)	ϕ	$\delta\phi$[a]	t_{Cl^-}	δt[a]
0.00	550	---	---	.02	.02
0.25	600	.28	.04	.03	.03
0.50	800	.60	.04	.23	.03
0.75	800	.95	.05	.35	.03
1.00	860	---	---	.38	.04

[a] Standard deviation.

Table 5. Transport numbers for the fused system AgCl-KCl

X_{KCl}	Temperature (°C)	ϕ	$\delta\phi$[a]	t_{Cl^-}	δt[a]
0.00	550	---	---	.02	.02
0.10	550	.10	.05	.02[b]	.02
0.25	550	.24	.03	.01	.02
0.32	550	.29	.05	.12[b]	.05
0.40	550	.45	.04	.23	.04
0.50	550	.59	.02	.26	.03
0.50	800	.60	.03	---	---
0.75	800	.85[c]	.04	.35	.03
1.00	830	---	---	.38	.04

[a] Standard deviation.

[b] Interpolated value.

[c] Calculated from measured value of $t_{Ag^+} = .06 \pm .03$.

The equivalent conductivity of potassium chloride-silver chloride at 800°C is plotted as a function of composition in Figure 8. The ionic conductivities λ_i, calculated from

$$\lambda_i = t_i \Lambda,$$

are also shown in Figure 8. The values of equivalent

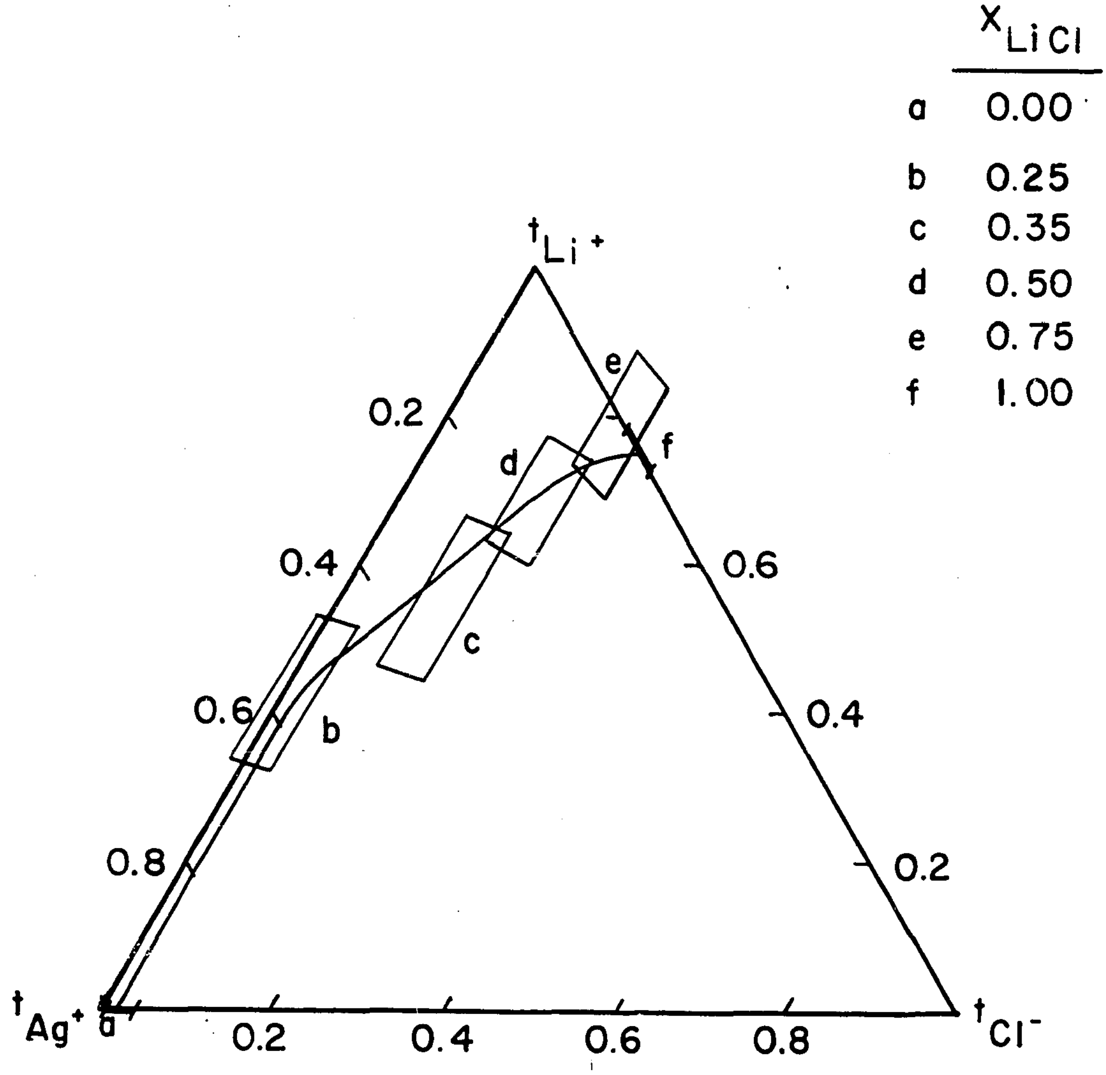
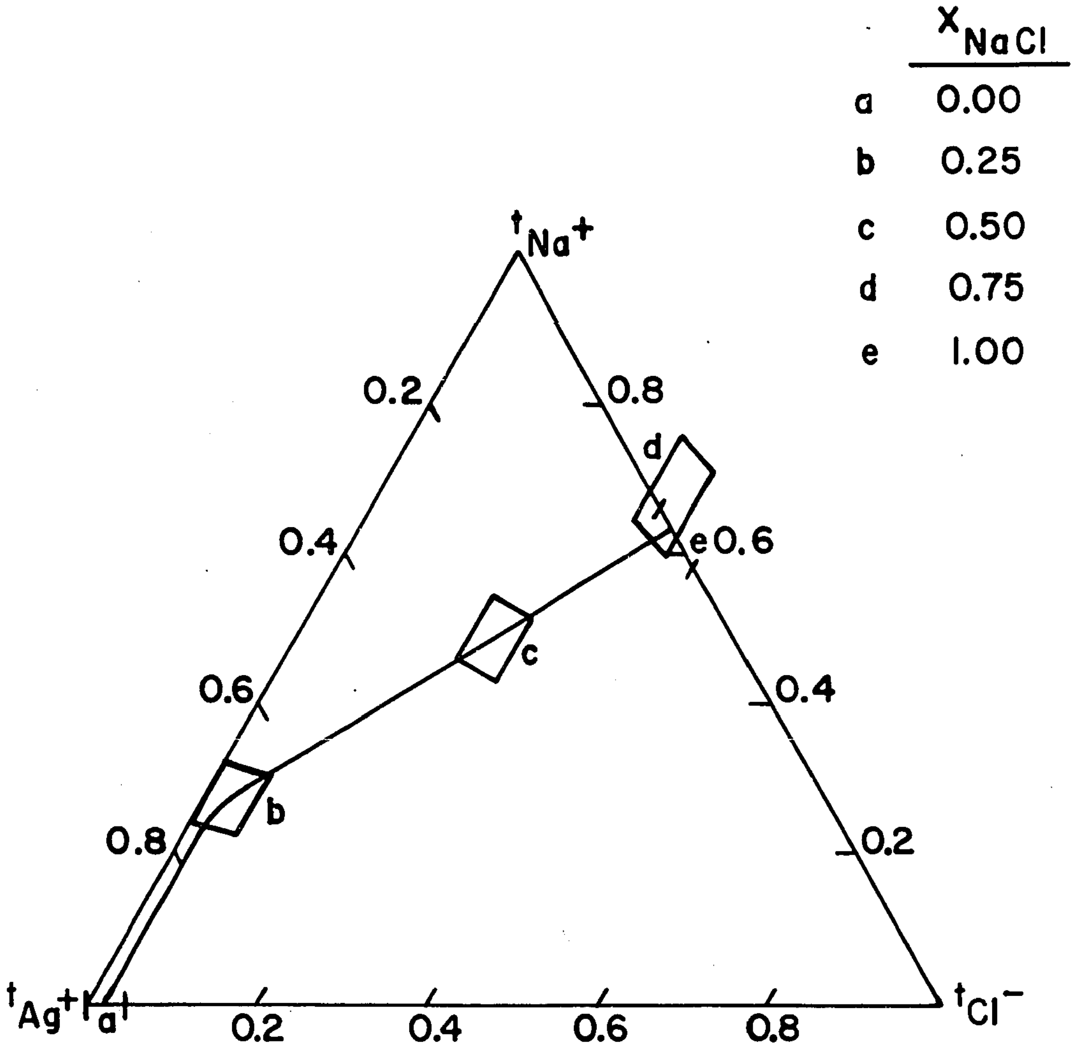


Figure 2. Transport numbers in the system AgCl-LiCl



	X_{NaCl}
a	0.00
b	0.25
c	0.50
d	0.75
e	1.00

Figure 3. Transport numbers in the system AgCl-NaCl

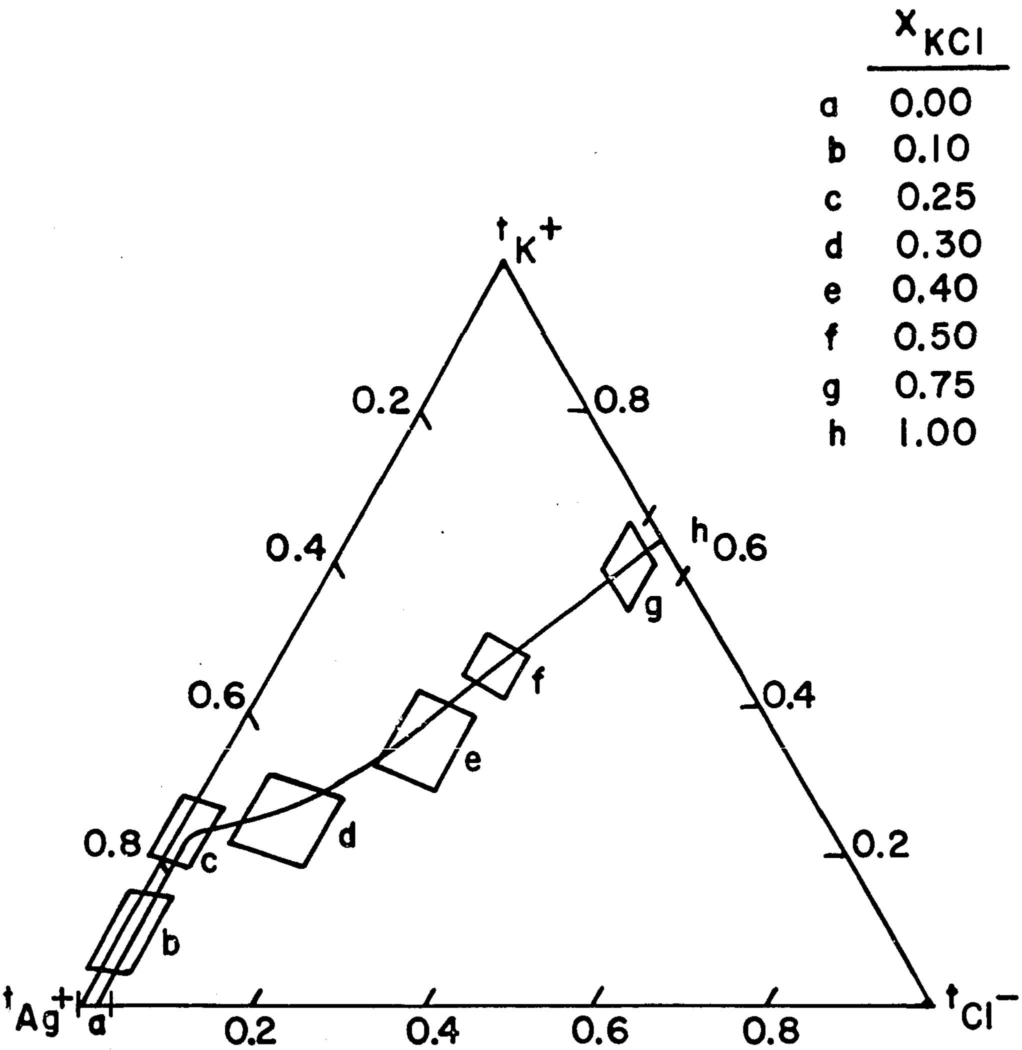


Figure 4. Transport numbers in the system AgCl-KCl

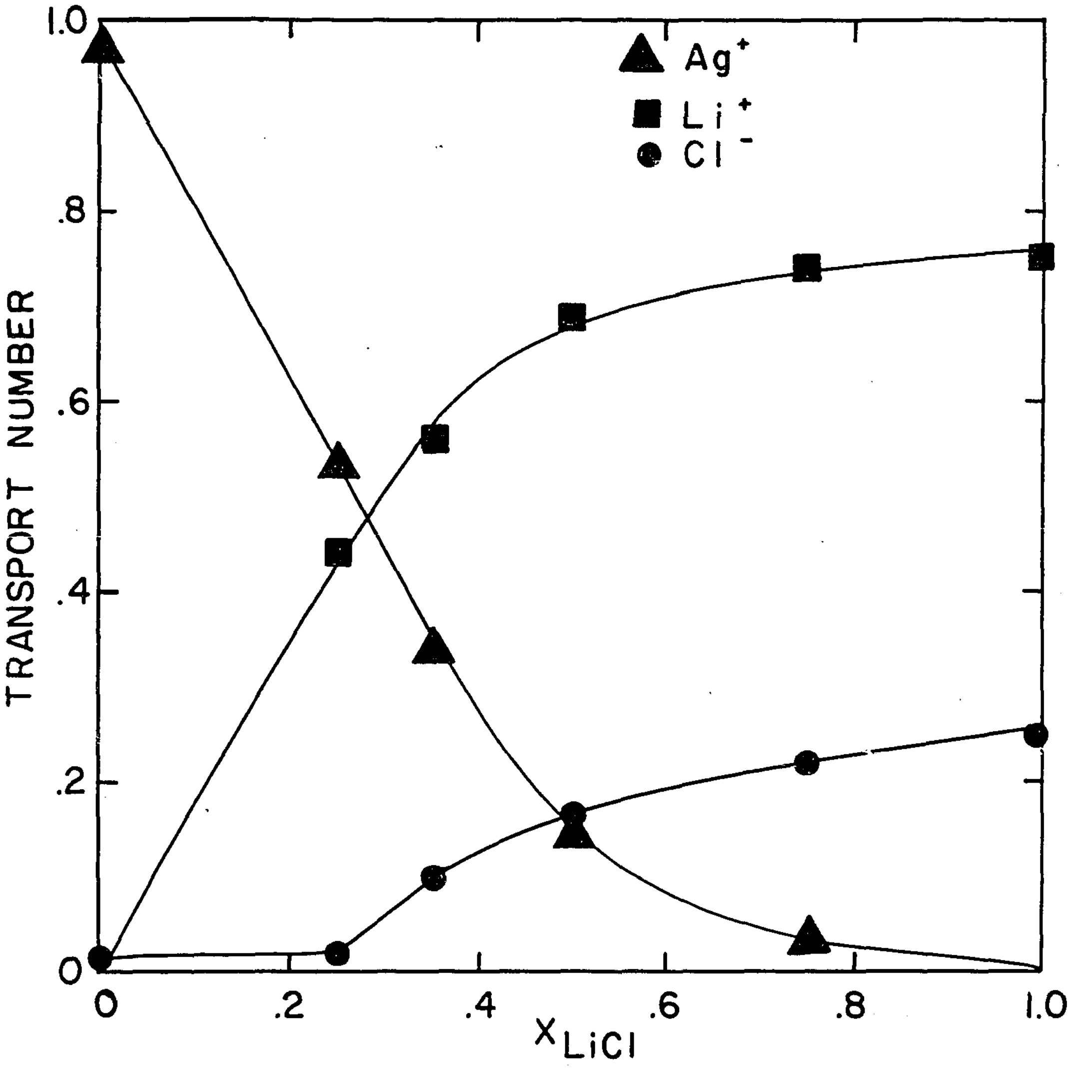


Figure 5. The variation of transport numbers with composition in the system AgCl-LiCl

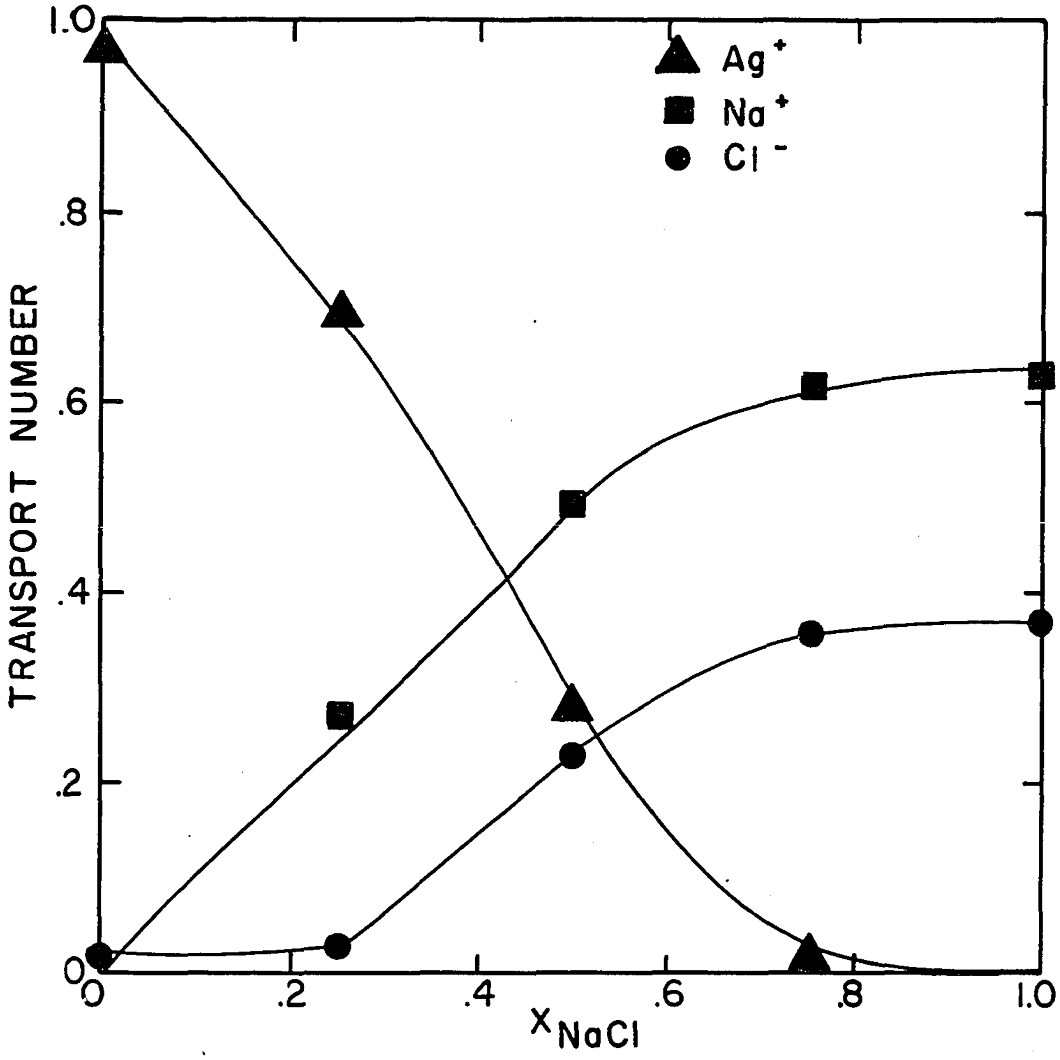


Figure 6. The variation of transport numbers with composition in the system AgCl-NaCl

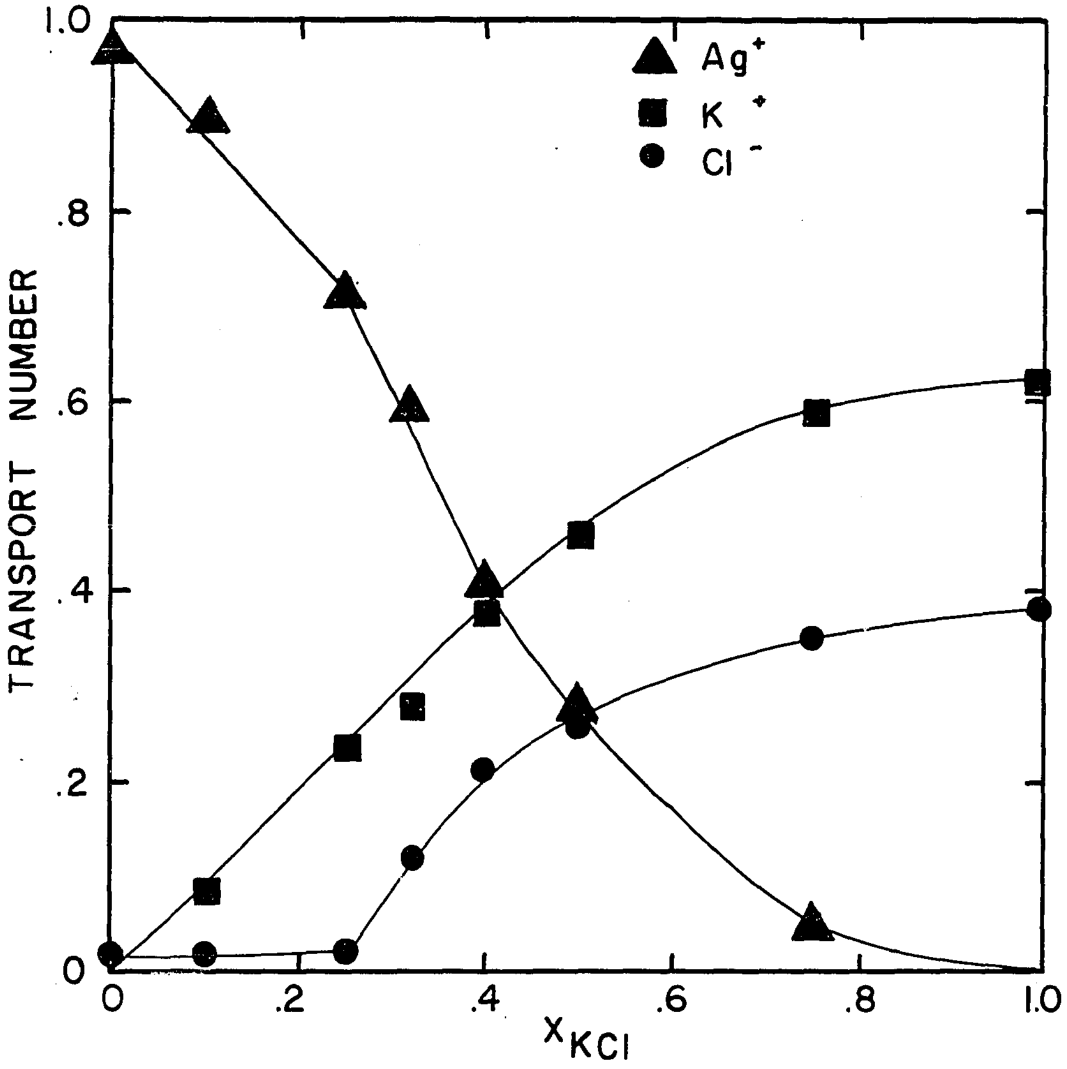


Figure 7. The variation of transport numbers with composition in the system AgCl-KCl

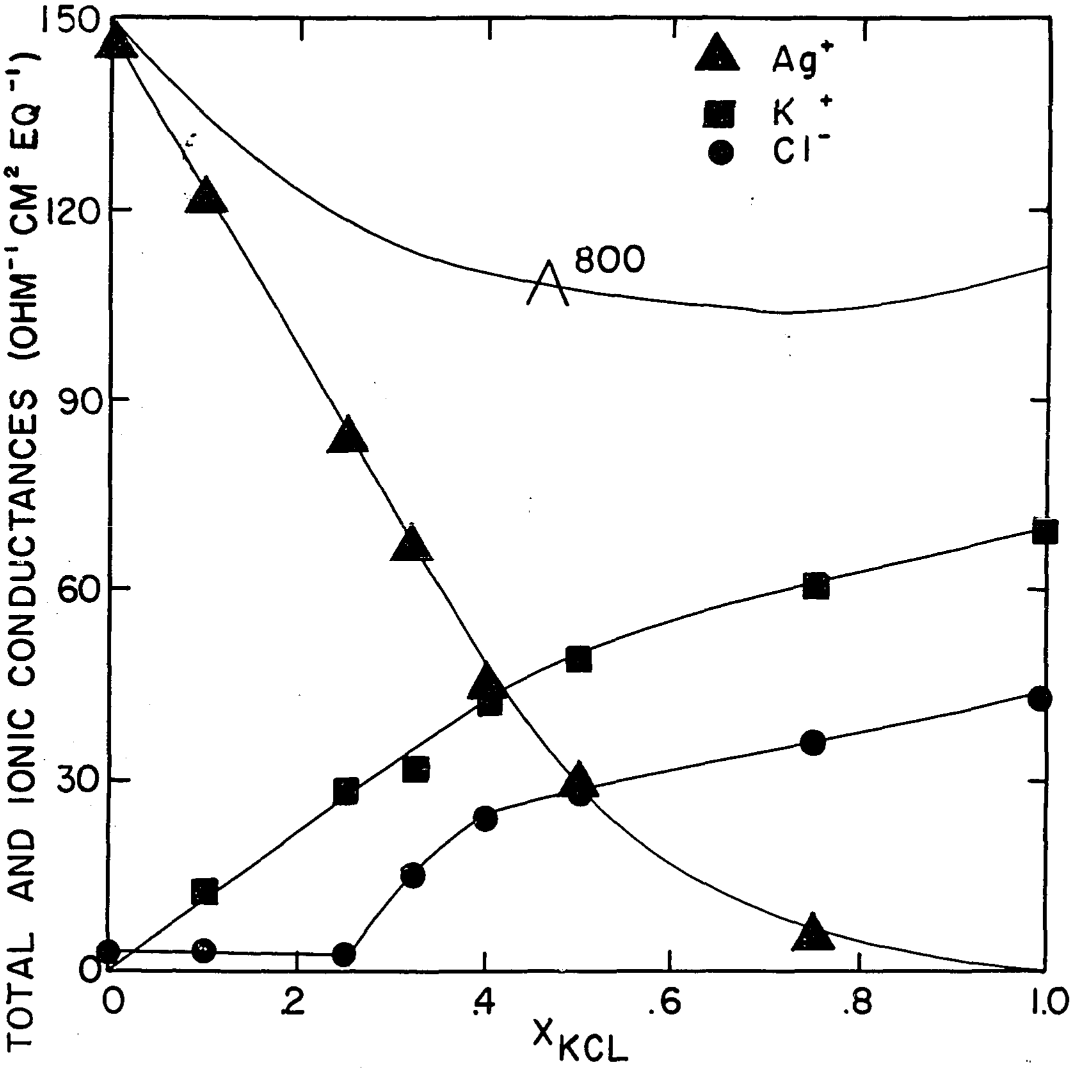


Figure 8. Total and ionic conductances in the system AgCl-KCl

conductivity for mixtures of less than 70 mole per cent potassium chloride were obtained by extrapolating the data of Harrap and Heymann (21) from lower temperatures. The value of equivalent conductivity for 80 mole per cent potassium chloride was obtained from Duke and Haas (22), and for pure potassium chloride from Van Artsdalen and Yaffe (18). The ionic mobilities μ_i are calculated from the conductivity curves by the equation

$$\mu_i = \lambda_i / X_i F$$

and plotted as a function of composition in Figure 9.

From Figure 7, it is apparent that the mobility of the chloride ion is not increased as potassium chloride is added to silver chloride until the concentration of potassium chloride is greater than 25 mole per cent. If it is true that the immobility of the chloride ion in pure silver chloride is due to the existence of a rigid chloride lattice, then it would appear that this lattice can contain up to 25 per cent potassium ions in place of silver. Above this concentration, it would appear that the lattice tends to break up rapidly, and the mixtures soon begin to take on the transport characteristics of potassium chloride. The change appears as an abrupt change of slope in both the chloride and silver transport number curves. Most probably, some of the silver

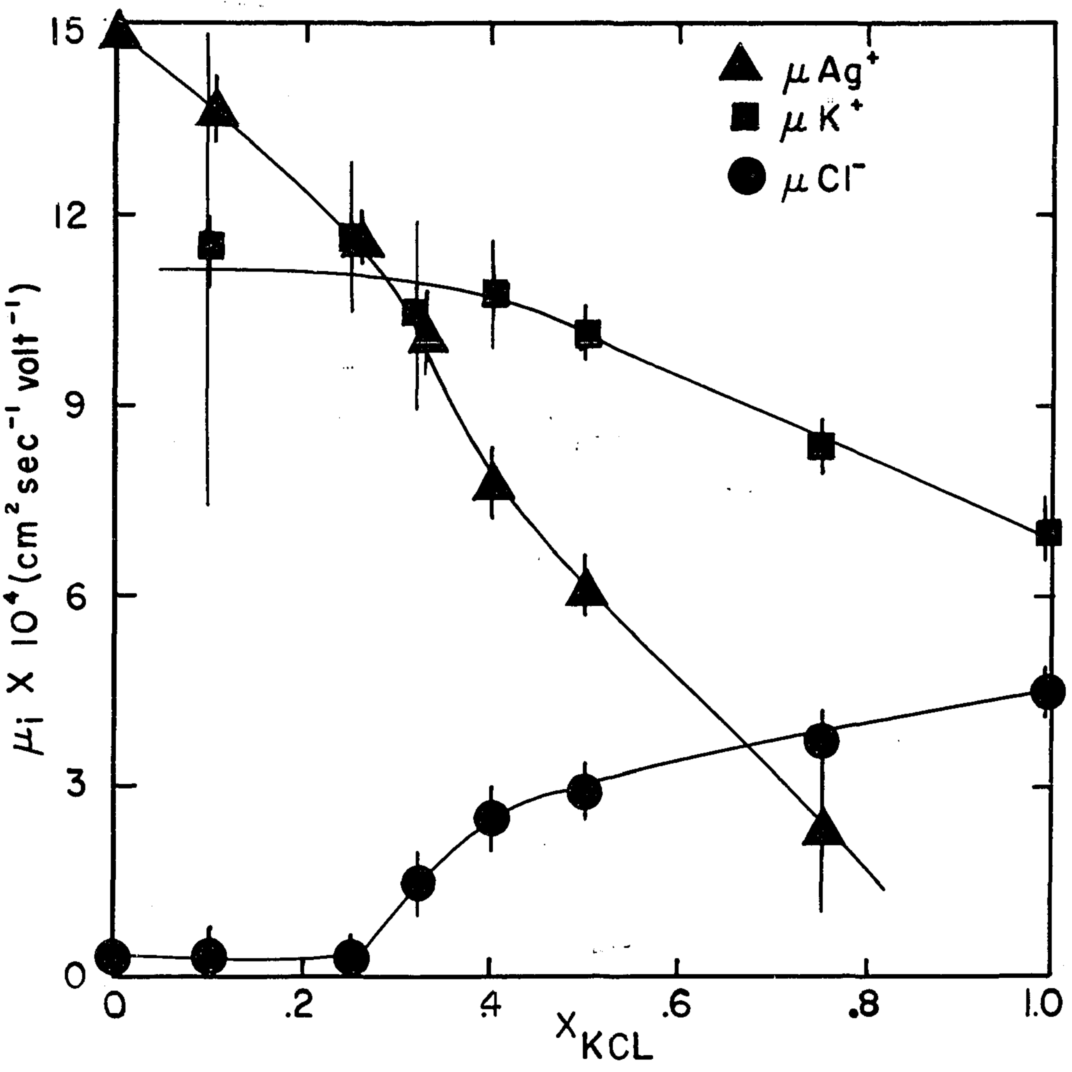


Figure 9. Ionic mobilities in the system AgCl-KCl

ions, perhaps 50 per cent, are required to hold the chloride lattice together. The other silver ions are replaced by potassium, up to about 50 per cent. Above this concentration, the potassium ions tend to knock out the silver ion "glue", and the lattice falls apart.

When silver chloride is added to potassium chloride, the transport numbers are essentially unchanged up to 25 per cent silver chloride. From Figure 9, however, it is seen that the mobility of the chloride ion decreases, while that of the potassium ion increases. This can be argued in terms of the formation of AgCl molecules and relatively immobile $AgCl_2^-$ complex ions, thus raising the effective concentration of potassium and lowering that of chloride. If it is assumed that the mobilities of potassium and chloride ions should remain constant as silver chloride is added, and that pure potassium chloride is completely dissociated, then the equilibrium constants for the formation of AgCl and $AgCl_2^-$ can be calculated from the slopes of the K^+ and Cl^- mobility curves. If μ_K^o and μ_{Cl}^o are the mobilities of potassium and chloride ions in pure KCl, and μ_K and μ_{Cl} the mobilities in a KCl-AgCl mixture, then the concentrations of the different species may be estimated from

$$(Ag\ ) = 1 - (\mu_K/\mu_K^o)X_{KCl}$$

$$(Cl^-) = (\mu_{Cl}/\mu_{Cl}^o)$$

$$(AgCl_2^-) = (Ag^+) + (K^+) - (Cl^-)$$

$$(AgCl) = (Ag_{Total}) - (Ag^+) - (AgCl_2^-).$$

The equilibrium constants are defined by

$$K_1 = \frac{(AgCl)}{(Ag^+)(Cl^-)} \quad \text{and} \quad K_2 = \frac{(AgCl_2^-)}{(AgCl)(Cl^-)} .$$

The constants obtained in this manner are

$$K_1 = 3 \pm 2$$

$$\log K_2 = -2 \pm 1 .$$

As an alternative argument, the change in mobility of the potassium and chloride ions could be attributed to a change in the structure of the melt as silver chloride is added. The rapid decrease in the mobility of the silver ion as potassium chloride is added to pure silver chloride, however, strongly indicates the existence of complex silver chloride species in these melts.

When sodium chloride is used in place of potassium chloride, the transport numbers of the mixtures remain essentially unchanged. With lithium chloride, the general character of the curves is the same, but at small concentrations of lithium chloride the silver transport number is less, the lithium number greater, than with sodium or potassium chloride. Since conductivity data are not available for the AgCl-LiCl and AgCl-NaCl systems, the mobilities of the ions in these systems cannot be calculated.

Modern theories of the liquid state consider it to be closely related to the solid state, and ascribe to it a degree of order, or "quasi-crystalline structure" (16). Thus the migration of a particle can be considered as the movement from one equilibrium position to another unoccupied one (hole). Glasstone *et al.* (23) have used this basic assumption to develop theories of viscosity, self-diffusion, and electrical conductivity in the liquid state. These theories require the same mechanism and activation energy for each process. The three processes may then be related by a single equation. These theories would appear to fail for fused salts, for the activation energies for electrical conductivity and viscous flow are different, the latter always being larger. This apparent failure can be overcome if three separate migration processes are assumed, the migration of cations, anions, and ion pairs, each with its own activation energy. The conductivity can depend only on the migration of the ions, while the viscosity probably depends only on the migration of the ion pairs, and the self-diffusion depends on both.

The following equations follow from the previous assumptions:

$$\Lambda = A_1e^{-E_1/RT} + A_2e^{-E_2/RT}$$

$$\phi = Be^{-E_3/RT}$$

$$D_+ = C_1Te^{-E_1/RT} + C_3Te^{-E_3/RT}$$

$$D_- = C_2Te^{-E_2/RT} + C_3Te^{-E_3/RT}$$

$$A_1 = (F^2/R)C_1 = 1.12 \times 10^9 C_1$$

$$B = (s/k)C_1 = 7.25 \times 10^{15} sC_1$$

$$t_1 = (A_1/\ \ )e^{-E_1/RT}.$$

The subscripts are: 1 = cation, 2 = anion, and 3 = ion pair. The E's are the activation energies, Λ is the equivalent conductivity, ϕ is the fluidity, or reciprocal of the viscosity, D_+ is the self-diffusion coefficient of cation plus ion pair, D_- is the self-diffusion coefficient of anion plus ion pair, s is the distance between equilibrium positions, t is the transport number, and A, B, and C are empirically determined pre-exponential terms.

In order to check this set of relations, the values of the self-diffusion coefficients are required. The only salts for which such data are available are sodium chloride (24) and sodium nitrate (25). For sodium nitrate, starting with the self-diffusion coefficients and the equivalent conductivity (26), the activation energies in kilocalories are: $E_1 = 3.4$, $E_2 = 3.4$, and $E_3 = 3.9$. The calculated anion transport number is .34, compared with the experimental value of .29 (5). In order to fit the viscosity data of Dantuma (27), a value for s of about 50 Angstrom units must be assumed. While the correlation is far from satisfactory, the difficulties may be due to the large experimental errors involved in some of the data. The temperature dependence of self-diffusion in sodium chloride was not described well enough to permit calculations on that salt.

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